OPTIMIZATION OF PYROCHLORE CATALYSTS FOR THE DRY REFORMING OF METHANE

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OPTIMIZATION OF PYROCHLORE CATALYSTS FOR THE DRY REFORMING OF METHANE

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Chemical Engineering

by
Felipe Polo Garzón
December 2015

Accepted by:
Dr. David A. Bruce, Committee Chair
Dr. Rachel B. Getman
Dr. Mark E. Roberts
Dr. Steven J. Stuart
ABSTRACT

The conversion of methane into syngas (a mixture of CO and H₂), which can be further converted into a variety of chemicals and particularly liquid fuels, is of growing importance given recent increases in methane production world-wide. Furthermore, since using CO₂ as the co-feed offers many environmental advantages, dry reforming of methane (DRM, CH₄ + CO₂ ⇌ 2CO + 2H₂) has received renewed attention.

In recent years, experimentalists have shown that the Rh-substituted lanthanum zirconate pyrochlore (LRhZ) material is catalytically active for DRM, exhibits long-term thermal stability and resists deactivation; however, previous to this doctoral work, a detailed understanding of the reaction mechanism on pyrochlore catalyst surfaces was still scarce, making it difficult to optimize this material.

In this work, initial computational efforts employing density functional theory (DFT) showed the plane (111) of the LRhZ crystal structure as the one catalytically active for DRM. In addition, the primary reaction pathway was identified, along with two rate determining steps (RDSs), the CH₂ oxygenation step and the CHO dehydrogenation step, which lie on the CH₄ dehydrogenation/oxygenation path.

The mechanistic understanding of DRM over LRhZ was further developed using steady-state isotopic transient kinetic analysis (SSITKA). Reversible adsorption of CO₂ on the surface was observed, along with short surface residence times (< 0.6 s) at 650 and 800 °C, and increasing turnover frequencies with temperature. Comparisons between isotopic responses supported the DFT-derived reaction mechanism. Furthermore, isotopic
transient kinetics confirmed that all metal atoms (Rh, Zr and La) on the surface are involved in the reaction mechanism, as previously pointed by DFT calculations.

A DFT-based microkinetic model that predicts the reaction performance at different conditions was built. The model was validated against experimental data, showing remarkable agreement, which further confirmed the reliability of the DFT data.

Computational analysis of one of the RDSs (the CHO dehydrogenation step) suggested Pd as an effective co-dopant to reduce the activation barrier of this step. This bimetallic Rh-Pd-substituted lanthanum zirconate pyrochlore (Rh-Pd-LZ) was synthesized, characterized and tested. The Rh-Pd-LZ catalyst successfully increased conversions at high temperatures while providing H₂ to CO ratios close to unity; thus fostering DRM and inhibiting the competing reaction, the reverse water gas shift reaction (RWGS, \( \text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O} \)). The Rh-Pd-LZ catalyst outperformed the initial catalyst, the LRhZ, at high temperatures.
DEDICATION

To God, to my mom, to my dad and to my amazing sisters.
ACKNOWLEDGMENTS

First, I want to thank God for giving me this beautiful life and filling it with loving family and friends.

I thank my adviser, Dr. David Bruce. I admire him as a person and as a scientist. His advice and guidance were very important to find the meaning of what I do.

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Thanks to Dr. Bob Lippert and the Graduate School Recruiting Program in Latin America. This program made me decide to get a PhD at Clemson University.

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Thanks mom, standing extremely close to me since day 1. I love you.
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<td>a) Activation energy for CHO dehydrogenation (CHO* → CO* + H*) over the Rh-doped pyrochlore and a series of co-doped pyrochlores; b) adsorption energy for the combined CO* and H* species in close proximity; and c) adsorption energy for carbon on the 3-fold site Rh-M-Zr, where M is Zr for a single-doped pyrochlore, or (M = \text{Ru}, \text{Pd}, \text{Os}, \text{Ir} ) or Pt for the co-doped pyrochlores. The asterisc (*) next to species means ‘adsorbed’.</td>
<td>153</td>
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<tr>
<td>5.10</td>
<td>Reactant conversion and molar H(<em>2) to CO product ratio for DRM reaction studies using LRhZ, Rh-LZ and Rh-Pd-LZ catalysts at 1.1 atm and GHSV = 58,800 cm(^3)/g(</em>{\text{cat}})/h.</td>
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CHAPTER ONE
INTRODUCTION AND LITERATURE REVIEW

Petroleum is a leading source of energy for transportation, home and business heating, and power generation, and is the primary feedstock to produce a variety of chemicals consumed everywhere every day. Nevertheless, petroleum is a non-renewable resource and a decay in its production is to be expected after a peak production (called peak oil) is reached. Even, some geologists say peak oil has already passed or is currently happening. [1]

Synthesis gas (syngas), which can be derived from renewable as well as fossil fuel sources, is a mixture of carbon monoxide and hydrogen and is an alternative to replace petroleum as a source of chemicals, electricity, heat and fuels. [2] Although syngas-related chemistry has been studied since the beginning of the 20th century [3], its suitability to replace petroleum-related chemistry has been considered in recent years due to the projected increase in natural gas production, a readily available reactant for syngas production.

**Methane sources**

Methane, the main component of natural gas, can also be produced from different biomass anaerobic digestion processes that can make use of food and crop wastes as well as cellulosic plants as feedstocks [4, 5]. However, anaerobic methane production facilities often require costly purification processes. The cost of these technologies will over time
reduce as new separation technologies become commercialized, which will in turn make biogas a more economical fuel source. In the meantime, shale gas, a non-renewable source of methane, arises as a reliable source with increasing production throughout the next decades (see Fig. 1.1) [6].

Fig. 1.1. U.S. dry natural gas production over the past and prediction. Source: U.S. Energy Information Administration, Annual Energy Outlook 2013 Early Release. “Tight gas” is natural gas produced from reservoir rocks with such low permeability that massive hydraulic fracturing is necessary to produce the well at economic rates, "associated" refers to natural gas found in oil fields, "non-associated" refers to natural gas isolated in natural gas fields, and “coalbed” refers to natural gas adsorbed into the solid matrix of coal.

Shale gas refers to natural gas found in shale formations. Shale is sedimentary rock composed of clay and other minerals, especially quartz and calcite. Over time, decaying biomass became trapped in these sedimentary layers and was converted into methane via anaerobic biological and chemical processes. Some of the methane formed
from this deposited biomass became encapsulated within the sedimentary rock layers, while portions of the methane escaped to more superficial rock layers, ultimately yielding what is now known as conventional natural gas resources. However, a considerable amount of methane remained trapped in the low permeability shale layers, and it is only with recent advances in drilling technology that it has become economical to recover methane from these shale gas deposits. [7, 8]

Innovative advances in horizontal drilling, hydraulic fracturing and other well stimulation technologies have made much of the shale gas recoverable, as depicted in Fig. 1.1. U.S. government estimates predict that domestic shale gas production is expected to rise from 5 trillion cubic feet per year in 2010 (23 % of total U.S. dry gas production) to 13.6 trillion cubic feet per year in 2035 (49 % of total U.S. dry gas production) [9, 10]

Despite the tremendous increases in U.S. shale gas production expected for the upcoming years, the U.S. is not the country with the highest natural gas proven reserves. According to data published in January 2014, the largest proven reserves of natural gas in the world reside in Russia, with a reserve 5 times bigger (in m$^3$) than the US’, followed by Iran, Qatar and then the U.S. [11]

The growth in shale gas production not only provides an alternative for petroleum, but also guarantees continuity of existing methane-dependent technologies, which is especially important given that natural gas currently provides a quarter of the overall U.S. energy demand and is used to generate a quarter (and growing percentage) of the nation’s electricity, besides providing heat for 56 million residences and businesses.
Despite the positive advances with methane production, costs associated with the shipment of natural gas from production facilities or wells to potential end users is still costly and in some cases prohibitive. A promising alternative to these high gas shipping costs is to convert natural gas into a higher energy density liquid chemical and fuel, which is more readily shipped via pipeline. Moreover, emission of methane, the second most emitted greenhouse gas after carbon dioxide, during processing, storage, transmission and distribution could be greatly reduced. [12]

**Methane to Syngas**

Synthesis gas (syngas) constitutes the bridge between methane and the clean production of fuels and chemicals widely used around the world. Syngas is a mixture of carbon monoxide and hydrogen and is used in the manufacture of hydrogen (great amounts of which are consumed in the synthesis of ammonia), the generation of electricity, the production of methanol, the synthesis of Fischer-Tropsch fuel products, the hydroformylation of olefins, and carbonylation of organics. [3]

Steam Reforming of Methane (SRM) is currently the main route to produce hydrogen. This reaction is highly endothermic, and therefore is carried out at very high temperatures.

\[
\text{SMR: } \text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2 \quad \Delta H^\circ = +206.2 \text{ kJ/mol}
\]

Nickel catalysts are the most suitable for this reaction due to the high turnover rates, low cost and long term stability. The advantage of SRM is that carbon deposition on the catalyst surface can be substantially reduced by the use of excess water and
temperatures around 1073 K. However, the generation of super-heated steam is very expensive, and the H₂ to CO ratios are too high for optimum subsequent syngas conversion to other chemicals. [13] Further, significant amounts of carbon dioxide can be produced via the reverse water gas shift (RWGS) reaction.

\[
\text{RWGS: } \text{CO}_2 + \text{H}_2 \leftrightharpoons \text{CO} + \text{H}_2\text{O} \quad \Delta H^\circ = +41.2 \text{ kJ/mol}
\]

Methane partial oxidation (POX) is an alternative route for syngas production.

\[
\text{POX: } \text{CH}_4 + \frac{1}{2}\text{O}_2 \leftrightharpoons \text{CO} + 2\text{H}_2 \quad \Delta H^\circ = -35.6 \text{ kJ/mol}
\]

As advantages, one can list that the reaction is exothermic, the H₂ to CO ratio is ideal for methanol synthesis and the CO₂ concentration in the product gases is low (which otherwise must be removed before further use of synthesis gas). Since POX produces very high yields of synthesis gas, oxygen is often added to the SMR process to keep the temperature high and promote methane oxidation. This combined methane reforming route is called Autothermal Reforming (ATR). [13]

\[
\text{ATR: } \text{CH}_4 + \frac{1}{4}\text{O}_2 + \frac{1}{2}\text{H}_2\text{O} \leftrightharpoons \text{CO} + \frac{5}{2}\text{H}_2 \quad \Delta H^\circ = +85.3 \text{ kJ/mol}
\]

Another alternative for syngas production is the Dry Reforming of Methane (DRM), which provides key advantages such as the independence from water supplies and no requirement of an oxygen source; furthermore, the reactants needed for this methane reforming route are two greenhouse gases, methane and carbon dioxide. Although DRM appears as the path to follow keeping in mind environmental concerns and also liquid-to-gas conversion at distant locations, the high temperatures required to carry out this highly endothermic reaction makes it difficult to find materials that show
long-term stable catalytic activity. In addition, the absence of H$_2$O and O$_2$ in the feed mixture promotes carbon deposition on the catalyst surface, and thus, deactivation of the catalytic sites is a problem to overcome. Therefore, the present doctoral work focuses on optimizing catalyst materials (more specifically, pyrochlores) for DRM from a fundamental understanding of the reaction mechanism.

\[
\text{DRM: } \quad \text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{CO} + 2\text{H}_2 \quad \Delta H^\circ = +247.4 \text{ kJ/mol}
\]

**Dry Reforming of Methane (DRM)**

As mentioned before, DRM is of interest due to the independence from H$_2$O and O$_2$ supplies, the conversion of two inexpensive naturally abundant (see Fig. 1. 2) greenhouse gases into higher-value compounds and the lower H$_2$ to CO ratios (compared to other routes for syngas production), which makes syngas a preferable feedstock for long-chain hydrocarbon production, such as liquid fuels. [14]

Additionally, the use of dry reforming technologies offers additional advantages for methane deposits that contain significant amounts of CO$_2$, which if not removed, lowers the heating value of the produced natural gas and becomes corrosive to pipelines and equipment in the presence of moisture. Current approaches for dealing with this problem use energy intensive processes to separate CO$_2$ from the desired methane product, but DRM technologies could significantly reduce these costs and enable syngas-to-liquids processes to be efficiently deployed near the production well. Such technologies could enable the economical production of fuels from gas fields previously ignored, particularly at locations like the Natuna field in the Greater Sarawak Basin in
Indonesia, the largest gas field in south Asia (approximately 46 trillion cubic feet recoverable reserves), which has not been explored due to high CO₂ content (71%). Furthermore, DRM could prove vital to other production sites, such as the Platong and Erawan fields in Thailand that have 90% CO₂ content, or in Malaysia, where the CO₂ content in natural gas fields ranges from 28% to 87%. [15, 16]


DRM typically coexists with the RWGS reaction (CO₂+H₂ ⇌ CO+H₂O), and thus, water formation can lead to H₂ to CO ratios lower than unity, which is detrimental for the energetic value of the syngas mixture.

Data from multiple experiments and simulations have been used to understand the DRM reaction mechanism on different heterogeneous catalysts. Nevertheless, there is not
a general accepted mechanism for DRM on metal catalysts because the intermediates involved in the reaction pathway depend upon the geometry of the surface, the metal catalyst used, and the interactions with the support. The deactivation mechanisms have also been studied and different factors often lead to the deactivation of these catalysts, such as, sintering of active metals, the structural rearrangement of atoms in the support and carbon deposition on the active metal sites. To date, a wide variety of catalysts have been studied for this reaction, including zeolites, unsupported metals, supported group VIII metals, transition metal carbides and sulfides, bimetallic catalysts, and more recently, perovskites and pyrochlores have received attention. The pyrochlore materials are of particular interest in the present work because of their exceptional long-term thermal stability and high selectivity to desired products. [14, 17]

Some insights into the DRM reaction mechanism on pyrochlores can be discerned from prior experimental and computational kinetic studies that examined the CO₂ and CH₄ dissociation mechanisms on catalysts somewhat related to the materials studied in this work, the metal-substituted lanthanum zirconate pyrochlores. For instance, experimental work performed by others concluded that La activates CO₂ decomposition [18-20], that methane cracking is a slow reaction step over multiple transition metals (e.g., Pt, Ni, and Rh) [21-24], and that the reaction of surface carbon species with the oxycarbonates present on the working catalyst (Rh/La₂O₃) is another slow step [19]. As methane dehydrogenation is achieved by multiple, rapid elementary steps, computational methods are the only way to fully discern the rates and importance of each of these mechanistic steps. Therefore, \textit{ab initio} methods have been used to understand the surface
chemistry and quantify the energetics associated to methane dehydrogenation on different pure and substituted metal surfaces. The metals studied include Fe, Ni, Co, Au, Cu, Pd, Rh, Pt, Os, Ru, Ir and Ag, as summarized in [25], although to our knowledge, there are no *ab initio* studies on how this occurs on pyrochlore structures and even less how the whole reaction mechanism for DRM proceeds on transition metal substituted pyrochlores, which is the matter of this doctoral work.

Computational studies to understand the reaction mechanism for DRM on different catalytic surfaces have generally focused on nickel-based catalysts, since they have been the preferred choice due to the low cost of nickel. However, deactivation due to carbon deposition remains as an issue.

For instance, the work reported in [26] uses density functional theory (DFT) to study DRM on Ni(111). The computed activation barriers pointed at the CH₄ dehydrogenation into CH₃ and H as the rate determining step, also, carbon deposition was attributed to very strong CO adsorption. Zhu et al. [27] studied the reaction pathway for DRM on Ni(111) starting from a complex reaction network and identified the oxidation step of the C-atom provided by CH₄ as the rate determining step under the investigated conditions, while CH₄ dehydrogenation is the rate determining step at low temperatures. In another work [28], activity and coke formation on both flat and stepped nickel catalysts as well as nickel carbide catalysts were also studied using DFT.

Despite the existence of several computational studies, no work was found where computational findings have guided the successful synthesis and testing of an improved catalyst for DRM, which is matter of this doctoral work. Nevertheless, multiple
computational studies have been done on the optimization of catalysts for reactive systems other than DRM. [29-36].

An experimental approach to obtain insight into reaction mechanisms and estimate kinetic parameters is the use of advanced isotopic labelling techniques. Amongst the few authors who have used isotopic tracing techniques to study DRM over catalyst materials, one can count Tsipouriari and Verykios (Ni/La$_2$O$_3$ and Ni/Al$_2$O$_3$) [37]. They confirmed that CH$_4$ reversibly adsorbs on the nickel surface and further concluded that the activation of CH$_4$ is a slow step over the Ni/La$_2$O$_3$ catalyst. They also found that the dissociation of the CO$_2$ molecule over Ni/La$_2$O$_3$ is a fast step in comparison to CH$_4$ activation, but the opposite trend was observed for the Ni/Al$_2$O$_3$ catalyst. In their experiments, the La$_2$O$_3$ support behaved as a dynamic oxygen pool, and the presence of oxycarbonates provided a route for C-O association to form CO. Bobin et al. [38] studied DRM on metal-supported (Pt, Ru, Ni and Ni-Ru) ceria-zirconia catalysts, stating that the rate-limiting step is the irreversible dehydrogenation of CH$_4$, CO$_2$ reduction is a reversible process, and that the concentration of C-containing intermediates was negligible. In another study [39] on DRM using a Rh/Al$_2$O$_3$ catalyst, steady-state isotopic tracing and transient techniques, as well as in situ FTIR spectroscopy were used to enlighten aspects of the reaction mechanism, such as the surface coverage of active carbon-containing species, the surface coverage of active oxygen-containing species, and the fact that most of the carbon accumulated on the catalyst surface comes from CO$_2$ molecules, not CH$_4$ molecules.
In this dissertation, surface kinetic parameters are calculated for the first time for DRM on pyrochlore catalysts using Steady-State Isotropic Transient Kinetic Analysis (SSITKA) [40, 41]. The SSITKA results back up quantum computational results and microkinetic modeling results described herein and provide further information about the turnover frequencies (TOF) and surface concentrations of reaction intermediates. The combination of these experimental and modeling results enable us to provide a full explanation of the reaction mechanism for DRM on the Rh-substituted lanthanum zirconate pyrochlore (LRhZ) and to achieve a microkinetic model of the reaction mechanism that enabled further optimization of the catalyst.

DFT data have been used by multiple authors to build microkinetic models (MKMs) [42-50] that estimate the relative concentration of intermediates on the catalyst surface and show how product distributions vary with changes in reaction conditions (i.e., T, P, and concentrations of reactants). These DFT-based MKMs describe the overall reaction from a fundamental perspective without relying on parameter-fitting, which may englobe mechanistic steps into fewer pseudo-steps. To the best of our knowledge, there is only one published report on DFT-based microkinetic modelling of DRM [51], and the catalysts modeled in that study were comprised of nickel and nickel carbide. That work considered 8 elementary steps, used the steady-state approximation, and considered adsorption of products to be equilibrated. The MKM developed as part of this doctoral work constitutes the first DFT-based MKM for DRM on a highly heterogeneous catalytic surface such as the pyrochlore surface; furthermore, the doping percentage, temperature, pressure and amount of reactants are tunable. Additionally, this new model differentiates
between two kinds of surface reaction sites, and includes 62 elementary reaction steps, 19 surface species and 6 gas phase species.

After achieving a complete description of the reaction mechanism for DRM on the LRhZ pyrochlore, this understanding was brought to the level of computationally guided catalyst optimization. In the literature, experimental work driven by computational findings is rather scarce, and amongst the few cases, bimetallic catalysts have been proposed and tested as improved versions to existent catalysts for steam reforming of methane (STM) [29, 30] but such a work has not been done for DRM.

The final part of this dissertation deals with the successful targeting of one of the rate-determining steps on Rh-doped pyrochlores, CHO dehydrogenation, identified by computational methods, and supported by isotopic tracing studies. The reduction of this key activation barrier was achieved with the inclusion of a co-dopant, Pd, which was purely suggested from DFT calculations. Furthermore, as part of the optimization stage of this project, an alternative synthesis method (slightly different from the synthesis method previously used by collaborators [24, 52]) was used to synthesize the Rh-substituted and Rh-Pd-substituted pyrochlores. The bimetallic-substituted (Rh and Pd) pyrochlore successfully reduced the activation energy of the rate-determining step for DRM, providing greater reactant conversions while inhibiting the competing RWGS reaction.

What are Pyrochlores? Why use them as catalysts for DRM?

An alternative to conventional supported catalysts are crystalline oxide catalysts. As advantages, some of these materials exhibit enhanced oxygen mobility, which helps
catalyze the reaction and reduce carbon deposition. A further advantage of crystalline oxide catalysts is that they often inhibit the deleterious sintering of active metals isolated in the lattice and in some cases require a lower overall concentration of active metals (which reduces overall catalyst cost). Crystalline oxides studied for reforming reactions are perovskites, pyrochlores, fluorites and hexaaluminates. However, pyrochlores for DRM have only been studied by two research groups, as reported in a recent review (2014). [53]

Pyrochlores are crystalline oxides having high thermal stability and a general formula of $A_2B_2O_7$, where $A$ represents a rare-earth metal and $B$ represents a transition metal. Metals located in the $A$ lattice position are 8-coordinate, while $B$ metals are 6-coordinate (see Fig. 1.3 and Fig. 1.4). Early experimental efforts indicated that pyrochlores are active for DRM, but the tested catalysts exhibited poor long term stability [54, 55]; whereas, more recent data suggests that this trend in deactivation may not be applicable to all pyrochlores. For example, $La_2Zr_2O_7$ (LZ) is a pyrochlore catalyst that has shown good long term stability [56-58], and it exhibits a propensity to accept a wide variety of metal substitutions into the lattice. In the past, others have sought to optimize the performance of pyrochlore catalysts towards DRM by adding substitutions into the lattice [24, 52, 59, 60], and all of these efforts that were driven by experimental trial-and-error techniques. Before the beginning of this doctoral work, collaborators at the DOE National Energy Technology Laboratory (NETL) and Louisiana State University (LSU) [52] showed that Rh-substituted lanthanum zirconate (LRhZ) pyrochlore catalysts showed stable performance with low carbon deposition for DRM; however, these groups
were unable to clearly define the DRM mechanism nor had they identified an obvious path for further optimization of the catalyst.

**Fig. 1.3.** (001) plane of the LZ pyrochlore. Green spheres represent La-atoms, blue spheres represent Zr-atoms and red spheres represent O-atoms.

**Fig. 1.4.** Coordination of atoms in the LZ pyrochlore. Green spheres represent La-atoms, blue spheres represent Zr-atoms and red spheres represent O-atoms.
This doctoral work explains the mechanism for DRM on Rh-substituted pyrochlores using DFT methods, completes this explanation by finding information about the reaction kinetics using advanced isotopic labelling techniques and successfully optimizes the LRhZ pyrochlore by using a co-dopant. It is a unique combined computational and experimental work on the dry reforming of methane.
References

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CHAPTER TWO

AB INITIO DERIVED REACTION MECHANISM FOR THE DRY REFORMING OF METHANE ON Rh DOPED PYROCHLORE CATALYSTS

Abstract

The conversion of methane into syngas is of growing importance given recent increases in methane production world-wide. Furthermore, using CO$_2$ as the co-feed offers many environmental advantages. To this end, experimentalists have shown that Rh-substituted lanthanum zirconate pyrochlore (LRhZ) catalysts are active and stable at the high temperatures needed for the dry reforming of methane (DRM). To enable further improvements to these catalysts, the reaction mechanism for DRM on LRhZ catalysts was attained using density functional theory (DFT). Following the identification of favored reaction sites for all elementary reactions, reaction and activation energies were calculated and used to discern the primary reaction pathway. Simulations show that inclusion of Rh decreases activation barriers, including the barrier for the two rate limiting steps (CH$_2$ oxygenation and CHO dehydrogenation), which makes the plane (111) catalytically active for DRM. The slow steps are on the CH$_4$ dehydrogenation/oxygenation path, which agrees with experimental observations.
1. **Introduction**

Syngas is a mixture of H\(_2\) and CO, which has proven to be a versatile feedstock for the production of a variety of chemicals and fuels, including methanol and diesel fuel. This energy rich mixture is widely used for electricity and heat generation and is a key intermediate for many methane gas-to-liquid processes that yield products more easily shipped via pipeline. [1] In recent years, considerable effort has been put toward the development of organic waste to syngas processes, but with the advent of low-cost shale gas, traditional syngas production from methane is also receiving renewed attention. There are several technologies available for syngas production from methane, such as Steam Methane Reforming (SMR), Partial Oxidation (POX), Autothermal Reforming (ATR) and Dry Reforming of Methane (DRM).

\[
\begin{align*}
\text{SMR:} & \quad \text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2 \quad \Delta H^\circ = +206.2 \text{ kJ/mol} \\
\text{POX:} & \quad \text{CH}_4 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{CO} + 2\text{H}_2 \quad \Delta H^\circ = -35.6 \text{ kJ/mol} \\
\text{ATR:} & \quad \text{CH}_4 + \frac{1}{4}\text{O}_2 + \frac{1}{2}\text{H}_2\text{O} \rightleftharpoons \text{CO} + \frac{5}{2}\text{H}_2 \quad \Delta H^\circ = +85.3 \text{ kJ/mol} \\
\text{DRM:} & \quad \text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2 \quad \Delta H^\circ = +247.4 \text{ kJ/mol}
\end{align*}
\]

Steam methane reforming is currently the main route to produce hydrogen from natural gas. This reaction is highly endothermic, and therefore is carried out at very high temperatures. Nickel catalysts are often the most suitable for this reaction due to their observed high turnover rates, low cost and long term stability. The advantage of SRM is that carbon deposition on the catalyst surface can be substantially reduced by the use of
However, the generation of the required super-heated steam is very expensive, significant amounts of carbon dioxide are produced via the reverse water gas shift (RWGS) reaction, and the H₃ to CO ratio is in excess of what is required for most downstream syngas conversion processes to other chemicals. Alternative strategies for syngas production, such as partial oxidation, offer several advantages, including the reaction being exothermic, the resulting syngas H₃ to CO ratio being ideal for methanol synthesis and the CO₂ concentration in the product gases being low (which otherwise CO₂ must be removed before further use of synthesis gas). Since POX produces very high yields of synthesis gas, oxygen is often added to the SMR process to keep the temperature high and promote methane oxidation. This combined methane reforming route is known as Autothermal Reforming.

The work described herein, focuses on the Dry Reforming of Methane, as the reactants involved are two greenhouse gases, and unlike other syngas production methods, there is neither a significant water supply dependence nor is a purified oxygen supply required. Although DRM using CO₂ has long been considered a viable method for converting methane from geologic or biological sources into syngas, the high temperatures required for the reaction (~ 1000 K) have made it very difficult to find catalysts that exhibit high activity for extended periods. Several factors often lead to the deactivation of these catalysts, including the sintering of active metals, the structural rearrangement of the catalyst support causing a reduction in surface area, and the accumulation of carbon on the catalyst surface. To-date, many catalyst materials have been investigated for this reaction, for example, zeolites, supported group VIII metals,
transition metal carbides and sulfides, bimetallics, and more recently, perovskites and pyrochlores have received attention. The pyrochlore materials are of particular interest because of their exceptional thermal stability and high selectivity to desired products.[3]

Pyrochlores are crystalline oxides having high thermal stability and a general formula of \( \text{A}_2\text{B}_2\text{O}_7 \), where \( \text{A} \) represents a rare-earth metal and \( \text{B} \) represents a transition metal. Early experimental efforts indicated that pyrochlores are active for DRM, but the tested catalysts exhibited poor long term stability [4, 5]; whereas, more recent data suggests that this trend in deactivation may not be applicable to all pyrochlores. For example, \( \text{La}_2\text{Zr}_2\text{O}_7 \) (LZ) is a pyrochlore catalyst that has shown good long term stability [6-8], and it exhibits a propensity to accept a wide variety of metal substitutions into the lattice. Thus, efforts have been made to tailor its catalytic properties by incorporating select transition metals into the lattice. Specifically, the use of Rh as a dopant has been shown to enhance catalytic performance for DRM [9]. When tested for DRM activity, a 2% Rh-doped LZ catalyst (LRhZ) showed conversions of 95% and 98% for \( \text{CH}_4 \) and \( \text{CO}_2 \), respectively; whereas, a similar Ni-based pyrochlore catalyst deactivated rapidly due to coke deposition on the catalyst [3]. Despite the high conversions and enhanced catalyst stability of the Rh-based pyrochlore, the required reaction temperature remains high (~1000 K), and the reaction mechanism is not well understood.

Some insight into the DRM reaction on LRhZ pyrochlores can be discerned from prior kinetic studies that examined the \( \text{CO}_2 \) and \( \text{CH}_4 \) dissociation mechanisms of catalysts somewhat related to the LRhZ pyrochlores. For instance, Gronchi et al. [10] compared the catalytic performance of Rh and Ni metals supported on \( \text{SiO}_2 \) and \( \text{La}_2\text{O}_3 \),
concluding that there is considerable influence of the support on the reaction performance. Most notably, increased CO production is obtained with the use of a lanthana support, which is presumed to activate CO$_2$ decomposition. Múnera et al. [11] also performed kinetic studies on Rh/La$_2$O$_3$ and concluded that lanthanum plays an important role in CO$_2$ adsorption, in contrast to the data reported by Wei and Iglesia [12] for Rh supported on Al$_2$O$_3$, which showed that CO$_2$ is only weakly bound to the alumina. Matsui et al. [13] also observed CO$_2$ activation on the support for Ru/La$_2$O$_3$ and only CO$_2$ physisorption on Al$_2$O$_3$. Research examining the DRM activity of multiple transition metals (e.g., Pt, Ni, and Rh) showed that methane cracking is the slow reaction step [14-17]. This was also observed by Munera et al. [11], due to the constancy of $\Gamma_{\text{CH}_4}$ with increasing hydrogen pressure, but they also identified the reaction of surface carbon species with the oxycarbonates present in the working catalyst (Rh/La$_2$O$_3$) as another slow step.

Considerable effort has been put towards understanding the reactivity of CH$_x$ species on metals, and it is well known that the high activation barrier associated with C-H cleavage is believed to directly influence the rate of transformation of natural gas into syngas. In addition to experimental efforts, several theoretical studies employing \textit{ab initio} methods have also sought to understand the surface chemistry and quantify the activation energy required for methane dehydrogenation on different transition metals, as summarized in [18], but to our knowledge, there are no \textit{ab initio} studies on how this occurs on pyrochlore structures and even less how the whole reaction mechanism for DRM proceeds on transition metal substituted pyrochlores.
Thus, this work seeks to describe the overall DRM reaction mechanism on Rh doped pyrochlore catalysts and more specifically, the role played by Rh in the formation of syngas. To understand and quantify reaction energetics, density functional theory (DFT) methods were used to calculate the structural stability of the LRhZ pyrochlores, identify minimum energy surface structures and favored adsorption sites for reactants and products, as well as quantify activation barriers for all DRM possible elementary reaction steps. Though a number of DFT simulations are reported for pyrochlore structures, these studies were not focused on catalytic uses for pyrochlores, but instead dealt with the structural stability, mechanical and electronic properties of the oxide [19-25]. To our knowledge, the work done by Mantz [26] is the only DFT-based work that deals with the interactions of adsorbed species with pyrochlore surfaces, where O$_2$ adsorption on selected La$_2$Zr$_2$O$_7$ pyrochlore surfaces is studied.

To validate the computational results obtained in this work, our findings are compared to experimental reaction and surface characterization data from collaborators [9, 17] as well as experimental data by others for non-pyrochlore rhodium-based oxide catalysts [10, 11, 13].

2. **Computational methods**

First principles calculations were performed employing the Vienna *ab initio* simulation package (VASP) [27-30], which is based on a plane-wave DFT code. Previously, it was shown [31] that the lattice parameter calculations as well as the trends in surface stability and reactivity for Rh$_2$O$_3$ surfaces were very similar using DFT or
DFT+U methods. Therefore, in the present study it was decided to only use DFT methods. To describe the interaction between the core and valence electrons, the projector augmented wave (PAW) pseudopotentials were used [32, 33]. Three different exchange correlation functionals were tested to find the optimum lattice parameters for both LZ and LRhZ. For these studies, predicted crystal structure parameters, including bulk density, were compared with experimental observations. The functionals tested were: the local density approximation (LDA) [34], the generalized gradient approximation using the implementation of Perdew, Burke and Ernzerhof (GGA-PBE) [35], and the GGA implementation of Perdew and Wang (GGA-PW91) [36]. The lattice parameters predicted by the GGA-PBE exchange-correlation functional were found to accurately match experimental data, and thus, GGA-PBE was employed in all further calculations. A plane wave cutoff of 500 eV is used in all calculations, and all geometries are optimized until the forces on the atoms are less than 0.001 eV/Å for bulk catalyst optimization and 0.03 eV/Å for all further calculations. During electronic optimization, the energy is converged to within $1 \times 10^{-6}$ eV/atom for the bulk catalyst optimization and $1 \times 10^{-4}$ eV/atom for all further calculations. For some special cases where force convergence was difficult to obtain, the electronic iterations were further converged to within $1 \times 10^{-9}$ eV. A Monkhorst-Pack k-point sampling scheme [37] (2x2x2 for bulk, 2x2x1 for surfaces and 1x1x1 for isolated species) is used and electronic occupancies are determined using the Methfessel-Paxton scheme [38], with an energy smearing ($\sigma$) of 0.1 eV. All calculations are spin-polarized.
Activation energies were calculated for selected elementary reactions using the climbing image nudged elastic band method (CI-NEB) via scripts developed previously in the Henkelman Research Group at UT Austin [39, 40]. A test using five and three structural images between reactants and products for a select reaction step was performed. This test showed that three structural images are sufficient to describe the energetics of the reaction barrier (see Appendix A for further details); therefore, for computational efficiency three images were used for all CI-NEB calculations. A 5.0 eV/Å² spring constant was used in all CI-NEB calculations. The force and energy convergence criteria were 0.03 eV/Å and 10⁻⁷ eV, respectively, during the electronic optimization. To reduce computational effort and increase simulation convergence when employing CI-NEB, only the adsorbed atoms involved in the respective chemical reaction were allowed to move while fixing the atoms in the catalyst surface. Initial simulation studies and subsequent BEP analysis (see later discussion) indicated that the transition state structure for reaction intermediates more closely resembled the combined product species from addition reactions or the reactant from a dissociation reaction. Therefore, the slab structure used in all final CI-NEB calculations was for the product slab of the respective association reaction. To correct for this simplification, the energy values obtained from single species adsorption were used to address the influence of surface relaxation (see later discussion). Prior to performing CI-NEB calculations for an elementary reaction step, the intermediates were placed in their most favorable adsorption site and structure optimization was performed to allow for readjustments of the species on the surface when being nearby other surface species.
The complete set of elementary steps considered in the reaction network consists of 130 reactions, counting both forward and reverse reactions. Some activation energies were derived from rigorous DFT calculations (CI-NEB method), while others were estimated by a Bronsted-Evans-Polanyi (BEP) relation derived from our DFT data.

Due to the heterogeneity of the surface, studies of optimum vacuum height and slab thickness were carefully performed, so as to yield systems that accurately represent experimental catalyst samples and at the same time reduce computational expenses, so that the scope of the work can be covered in a time-effective manner.

2.1 Bulk catalyst model

LZ and LRhZ are cubic oxide pyrochlores of space group $Fd-3m$. Within this work, origin choice 2 [41] is used. The ideal stoichiometric pyrochlore has eight formula units (88 atoms) per unit cell and within it there are four crystallographically nonequivalent atom types: the cations La and Zr (or Rh) and the oxygen ions O and O’. The La atoms are eight coordinate, whereas the Zr (or Rh) atoms are six coordinate. The dimensions of the pyrochlore unit cell are described by the lattice parameter ($a$), and the location of lattice oxygens (O) are specified by the oxygen positional parameter ($x$).

DFT calculated energy versus lattice parameter ($a$) data for the bulk catalyst were fit to the Murnaghan equation of state [42] to obtain optimum lattice parameters that yield the lowest energy structure. These optimum parameters were cross-checked with experimental pyrochlore characterization data [9, 43] to further validate the optimized simulation parameters. The results obtained using different exchange correlation
functionals and the available experimental data for comparison can be found in Appendix A.

The computational results are in good agreement with the available experimental data for both the LZ and LRhZ pyrochlores, and there is only a moderate difference between the computational results obtained using the tested functionals. However, careful inspection of the data shows that the LDA functional underestimates the lattice parameter, as has been previously reported [20]. Based on these data, both GGA-PBE and GGA-PW91 accurately describe the pyrochlore structure. The GGA-PBE functional is used for all further calculations involving the LRhZ pyrochlore, and the lattice parameter is set to 10.88 Å, which corresponds to an error of 0.2% in the lattice parameter and an error of 0.6% in the crystal density.

2.2 Optimization of slab dimensions

To create a catalytically active surface, the bulk pyrochlore structure must first be cleaved through a specific crystallographic plane. Using experimental XRD data [9], the pyrochlore structure was cleaved along the (111) plane, leaving one Rh atom at the surface. Further corroboration of the likelihood of appearance of the plane (111) on the pyrochlore catalyst surface is provided in section 2.3.

The catalyst surface is modeled using the periodic slab technique, in which a slab model with a vacuum region is periodically replicated in three dimensions to obtain a 2D infinite surface. The presence of adjacent replica slabs parallel to the catalyst surface can diminish the accuracy of the calculations if these surface replicas interact significantly with each other. Due to this fact, the adsorption energy for CH₄ on the same active site
on the surface (111) is tested for different heights of the vacuum region. A stoichiometric slab model is employed, which contained 4 formula units (44 atoms) and has lateral dimensions of $a/\sqrt{2} \times a/\sqrt{2}$. Additionally, the metal and oxygen layers are intercalated in the slab and the two bottom layers are kept fixed.

Since the top of the slab is metal terminated and the bottom of the slab is oxygen terminated, a strong dipole moment is to be expected. The value of this dipole moment depends both on the termination of the slab and on the proximity of the slab replicas above and below. Calculations showed that having a vacuum region of 12 Å yields a methane adsorption energy that differs by less than 0.001 eV from the calculated most accurate value (at 18 Å of vacuum); furthermore, it was found that beyond a vacuum region of 11 Å the value of the adsorption energy is unaffected by the inter-slab distance. The data corresponding to the adsorption energy of methane on the plane (111) and the dipole moment of this pyrochlore slab with respect to the vacuum space between slabs is shown in Appendix A.

Though extending the vacuum space between adjacent pyrochlore slabs reduces the overall slab dipole moment, the inherent asymmetry caused by terminations of the slab layer ensures that some residual dipole will continue to exist. To further address this issue, an extra metal layer is added to the bottom of the pyrochlore slab and full relaxation is allowed, reducing the slab dipole moment from -15.9 to -1.6 Debye (without embedded dipole moment correction as implemented in VASP 5.2). Independent of the inclusion of this extra metal layer, the adsorption energy of CH$_4$ is unaffected due to its lack of a molecular dipole. Nevertheless, reducing the dipole moment in the system
decreases the overall computational effort considerably and thus, an extra metal layer was added to the non-reacting surface of all simulated pyrochlore slabs.

To ascertain the optimum pyrochlore slab thickness that most accurately mimics real systems and yet is computationally achievable, simulations of CH$_4$ adsorption on the (011) surface of metal terminated pyrochlore slabs (both ends) of varying thickness were compared. These simulations indicated that a 9-layer fully relaxed pyrochlore slab (48 atoms) is sufficiently thick, as the adsorption energy for CH$_4$ differed by only 0.02 eV for slabs containing 9 layers and a much thicker system containing 13 layers (70 atoms). For all subsequent simulations, parallel slabs are separated by 12 Å of vacuum and the slab thickness is maintained at a value equal to or greater than 7.50 Å (approximately a 48-atom slab).

2.3 Surface energy

Specific species adsorption and the overall reaction mechanism for a given catalyst are strongly dependent on the prevalence and spacing of surface atoms, which themselves are a function of the crystallographic planes exposed on the catalyst surface. To determine what planes are most likely to appear on the pyrochlore surface, the surface energy is calculated for multiple low index planes that were suggested by experimental X-ray diffraction studies. The surface energy for smooth crystallographic planes can be defined as the energy needed to cleave the bulk crystal along that specific plane. The lower the surface energy, the more thermodynamically stable is the plane.

As mentioned in the previous section, to reduce the dipole moment in the slab, nonstoichiometric slabs were created so that the terminations at the top and bottom of the
slab are equivalent and the dipole moment is reduced. To calculate the surface energy independently of the termination used to adsorb the species, both metal terminated and oxygen terminated slabs (fully relaxed) are created, and their energies are used to calculate the surface energy as follows:

$$E_s = \frac{(E_{\text{slab}1} + E_{\text{slab}2} - nE_{\text{bulk}})}{(4S)}$$  \hspace{1cm} (3.1)

When calculating the surface energy ($E_s$), $S$ is the surface area of the 2D unit cell, $E_{\text{slab}1}$ is the total energy of the metal terminated slab, $E_{\text{slab}2}$ is the total energy of the oxygen terminated slab, $n$ is the stoichiometric factor describing the fraction of bulk unit cells that are equivalent to the atoms contained in the two slabs (1 and 2), and $E_{\text{bulk}}$ is the total energy of a crystallographic or bulk unit cell. Mastrivok et al. [44] used the software VASP and the GGA-PW91 correlation functional to calculate surface energies of the LaMnO$_3$ perovskite structure (structure similar to pyrochlore). The surface energy calculations using stoichiometric and non-stoichiometric slabs gave similar results. In addition, Evarestov et al. [45] used hybrid HF-DFT LCAO simulations to calculate surface energies of SrTiO$_3$ and SrZrO$_3$ cubic perovskites using stoichiometric and non-stoichiometric slabs and surface energy values did not show any significant difference. These previous studies indicated that significant improvements in overall computational efficiency with minimal loss in accuracy are obtained by modeling non-stoichiometric oxide slabs, which is even more important for simulating systems with species in dilute concentration (such as Rh in the LRhZ pyrochlore). Thus, non-stoichiometric slabs were used to perform all surface energy calculations for the LRhZ pyrochlore in the present work.
To calculate the surface energy at a moderate computational effort and to reduce future computational expenses, a fraction of the plane after cutting the bulk structure was used as representation of the whole plane for the planes showing slow convergence. This means that the dimensions of the planes used for the surface energy calculations were $a \times a$ for the plane (001), $a \times a/\sqrt{2}$ for the plane (011) and $a/\sqrt{2} \times a/\sqrt{2}$ for the plane (111), where $a$ equals the length of a side of the pyrochlore cubic unit cell. Fig. 2.1 shows the top and the side view (one of them) for both metal terminated and oxygen terminated slabs of the planes (001), (011) and (111).

<table>
<thead>
<tr>
<th>Plane</th>
<th>Oxygen terminated slab</th>
<th>Metal terminated slab</th>
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<tr>
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<td>Top view</td>
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**Fig. 2.1** Top view and the side view (one of them) for both metal terminated and oxygen terminated slabs of the planes (001), (011) and (111) of the LRhZ pyrochlore. The color code is as follows: La – green, Zr – light blue, Rh – dark blue, O – red.
The surface energy simulation results indicated that the planes (111) and (011) are the most thermodynamically stable ($E_{s(111)} = 0.09$ eV/Å² and $E_{s(011)} = 0.14$ eV/Å²). In contrast, the plane (001) was found to have the highest surface energy ($E_s = 0.19$ eV/Å²), suggesting that it is the least thermodynamically stable.

Computational results from Mantz [26] also showed the planes (011) and (111) are the most thermodynamically stable for the LZ pyrochlore, which is in good agreement with our results for the LRhZ pyrochlore. For the present work, all catalytically relevant simulations are performed using metal terminations of both the (011) and (111) pyrochlore planes, enabling us to evaluate the extent to which DRM proceeds on each plane.

3. Results and Discussion

3.1 Species adsorption

To achieve an accurate description of the DRM reaction mechanism on the pyrochlore surface, multiple pathways for the reaction are considered based on experimental observations [9, 12, 17, 46-48] and prior computational results [49]. This network of elementary reaction steps is shown in Fig. 2.2. Methanol formation was not detected in the experiments but is included in the reaction network as a way to cross-check the model, because inhibition of alcohol production should be predicted by calculated activation energy values. Additionally, water formation was observed experimentally due to the Reverse Water Gas Shift Reaction (RWGS, $\text{CO}_2 + \text{H}_2$ ⇌...
CO+H₂O) but in low amounts. All reactions involved in the RWGS mechanism are shown implicitly in Fig. 2.2, and a separate figure showing the detailed mechanism for RWGS on LRhZ catalysts is shown in Appendix A. Finally, CHₓOH (where x = 0, 1, 2, 3) dehydration was ruled out from the reaction network because no stable configuration for CHₓ and H₂O was found using DFT methods when these species were placed close to each other on the same pyrochlore slab.

![Fig. 2.2. Proposed reaction network for the dry reforming of methane on a pyrochlore catalyst.](image)

The preferred adsorption sites of the species on both planes and the corresponding adsorption energies (ΔE_ads) are calculated as follows,

\[ \Delta E_{ads} = E_{ads+surf} - E_{surf} - E_{ads} \]  

(3.2)

where \( E_{ads+surf} \) is the calculated energy of the combined slab and adsorbate; \( E_{surf} \) is the energy of the clean slab without any adsorbate, and \( E_{ads} \) is the energy of the isolated adsorbing species, which was simulated in a 20.0 x 20.5 x 21 Å box, including as well spin-polarized considerations. According to this definition of adsorption energy, the more negative the value of \( \Delta E_{ads} \), the stronger the binding between the adsorbate and the
surface. Analogously, as the value of $\Delta E_{\text{ads}}$ approaches zero, the weaker the adsorption of the molecule on the surface.

Planes (011) and (111) of the LRhZ pyrochlore present a variety of possible active sites for adsorption and conversion of the different species. After carrying out structure optimization simulations for all of the reactants and intermediates shown in Fig. 2.2, certain sites provided stronger adsorption for specific species and on some sites no stable adsorbate structure was found. Specifically, no stable structure for COH was found on any site on the (111) plane. Thus, all reactions involving this intermediate are not considered for this plane. The specific reactions excluded from studies of the (111) surface are:

$$\text{CHOH}^* + ^* \rightleftharpoons \text{COH}^* + \text{H}^*$$
$$\text{C}^* + \text{OH}^* \rightleftharpoons \text{COH}^* + ^*$$
$$\text{COH}^* + ^* \rightleftharpoons \text{CO}^* + \text{H}^*$$

Further insight into the chemisorption behavior of CO$_2$ and CO on pyrochlores can be garnered from prior experimental studies examining related metal oxides. For example, Múnera et al. [11] working with Rh/La$_2$O$_3$ catalysts and Matsui et al. [13] working with Ru/La$_2$O$_3$ and Ru/ZrO$_2$ catalysts arrived at similar conclusions, namely, that La facilitates CO$_2$ adsorption. Additionally, Gronchi et al. [10] concluded from experiments with Rh/La$_2$O$_3$ that La activates CO$_2$ decomposition. This is in very good agreement with our computational results, since all sites where CO$_2$ adsorbs both on planes (011) and (111) involve at least one La atom, see Fig. 2.3.
Fig. 2.3. Favored adsorption sites and energies predicted by DFT simulations for CO$_2$ and CO on the (011) and (111) LRhZ pyrochlore planes.

Validation of Simulation Results

In an effort to verify the predicted adsorption behavior of CO$_2$ and CO, our simulation results were compared to available experimental data. In previous IR spectroscopy studies of tightly bound CO$_2$ on LRhZ pyrochlores [17], two relatively sharp absorption bands were observed at frequencies of 1509 and 1367 cm$^{-1}$ (see Fig. 2.4) after flowing CO$_2$/He for 15 min followed by 15 min of He flush, removing then any weakly bound species. The difference between the frequencies of the two CO$_2$ absorption bands ($\Delta\nu = 142$ cm$^{-1}$) agrees remarkably well with the calculated (via DFT) difference between the highest frequencies for the two most stable configurations of adsorbed CO$_2$ on the (011) plane ($\Delta\nu = 152$ cm$^{-1}$), namely, at the bridge Zr-La and 3-fold Zr-La-La sites. When computing the difference between the highest frequencies for the two most stable configurations of adsorbed CO$_2$ on the (111) plane, at the 3-fold Zr-Zr-La and Rh-
Zr-La sites, this difference is considerably less ($\Delta \nu = 53$ cm$^{-1}$). Considering the computational results presented in Fig. 2.3 for CO$_2$ adsorption energy, it is expected that the experimental IR data for strongly bound CO$_2$ [17] would more closely match that of the (011) LRhZ pyrochlore surface because CO$_2$ binds more strongly to the (011) surface and is only weakly bound to the (111) LRhZ surface.

Furthermore, our DFT results show that the most favorable CO$_2$ adsorption sites for LRhZ planes (011) and (111) involve La species, which is congruent with Pakhare et al. [17], who concluded that oxycarbonates form on the LRhZ surface at La sites.

![FTIR spectra](image.png)

**Fig. 2.4.** FTIR spectra after 15 min of CO$_2$/He flow → 15 min of He flush over reduced LRhZ. Reprinted from J. Catal., 316, Devendra Pakhare, Viviane Schwartz, Victor Abdelsayed, Daniel Haynes, Dushyant Shekhawat, James Poston, James Spivey, Kinetic and mechanistic study of dry (CO$_2$) reforming of methane over Rh-substituted La$_2$Zr$_2$O$_7$ pyrochlores, 78-92, Copyright (2014), with permission from Elsevier. [17]

Separate DRIFTS studies of Rh supported on different oxides (Al$_2$O$_3$ and SiO$_2$) [50, 51] indicated that the dominant surface species under reaction conditions is CO bound in linear and bridge schemes to metallic Rh. A similar adsorption behavior was
observed in our simulations of Rh doped pyrochlores. Specifically, stable, linear atop binding of CO on Rh sites was observed on the (011) and (111) pyrochlore planes, but as expected, no bridge adsorption of CO on Rh sites was observed due to the high dispersion and low concentration of Rh surface sites.

As the limited experimental observations for species adsorption on LRhZ pyrochlores are in reasonable agreement with the computational results, it is assumed that the DFT simulation scheme used in this study is adequate to describe the energetics for the overall reaction process.

**Adsorption behavior for DRM reactants, intermediates and products**

DFT simulations were used to quantify the energetics of adsorption for all DRM reactants, intermediates and products on multiple LRhZ pyrochlore surface sites. The sites for species adsorption on one or both of the studied LRhZ surfaces included atop (on Rh, Zr, and La), bridge (on Rh-Zr, Zr-La, Rh-La, and La-La), and three fold sites (on Rh-Zr-Zr, Rh-La-La, Zr-La-La, and Zr-Zr-La). A summary of the strongest adsorption energies for all relevant species on the (011) and (111) surfaces are shown in Fig. 2.5. In general, a low adsorption energy (negative but close to zero) suggests that the tested site is not preferred for that intermediate or that it only physisorbs to the catalyst surface. In contrast, a very high adsorption energy (negative value far from zero) suggests that the surface site may become poisoned by that particular intermediate. Species having moderate adsorption energies on a given site are those most likely to actively participate for multiple turnovers in the mechanism to convert methane and CO₂ into syngas. A detailed list of the adsorption behavior for all species on all tested sites along with a
summary of the most important adsorption sites for the dry reforming of methane is provided in the Appendix A.

From the DFT simulations, it is observed that the DRM reactants (CH\textsubscript{4} and CO\textsubscript{2}) can adsorb on both the (011) and (111) LRhZ pyrochlore planes, and thus, DRM reactions are possible on both surfaces. It is also observed that neither pyrochlore plane considerably favors the adsorption of any intermediate.

For physisorbed molecular species, such as CH\textsubscript{4} and H\textsubscript{2}, the favored adsorption sites identified in this study can only be interpreted as the approximate region where these molecules associate because DFT methods are insufficient to accurately describe van der Waals forces. Along these lines, multiple adsorption sites are expected for physisorbed species such as CH\textsubscript{4} and H\textsubscript{2}. Likewise, H\textsubscript{2}O presents multiple adsorption sites since it is weakly bound (E\textsubscript{ads} \sim -1eV). In contrast, the majority of reaction

**Fig. 2.5.** Predicted adsorption energies (\(\Delta E_{\text{ads}}\)) of species involved in the dry reforming of methane for the (011) and (111) LRhZ pyrochlore planes.
intermediates are chemisorbed to the pyrochlore surface; thus, it was possible to clearly identify favored adsorption sites for these species via DFT minimization methods. It should also be noted that hydrogen and other possible reaction products, such as methanol, are more readily adsorbed on the pyrochlore surface via a dissociative pathway, yielding molecular fragments that chemisorb to select sites on the LRhZ pyrochlore surface.

On the plane (011), an adsorbed structure for C in the bulk was found after structure optimization ($\Delta E_{\text{ads}} = -7.11 \text{ eV}$) and it exhibits stronger adsorption than the surface C adsorbed in the 3-fold Zr-La-La position. The C adsorbed in the bulk was however not considered as a reactive species for further analysis, due to steric interactions that would limit its reaction with other surface adsorbed species.

3.2 Reaction and activation energies

3.2.1 Reaction energy

A greater understanding of the overall DRM reaction pathway can be discerned by examining the reaction enthalpy ($\Delta H_{\text{rxn}}$) for each possible mechanistic step. These values can also prove useful in calculating the corresponding activation barrier associated with each of these mechanistic steps. Therefore, the heats of reaction were calculated for all possible reaction processes using the optimized system energies for reactants and products, which were calculated using DFT. For the example, for the surface catalyzed dissociation reaction, $AB^* + ^* \rightarrow A^* + B^*$ (‘*’ denotes a surface site or surface bound species), the heat of reaction was calculated as follows:

$$\Delta H_{\text{rxn}} = E_{\text{slab-A}} + E_{\text{slab-B}} - E_{\text{slab-AB}} - E_{\text{slab-empty}}$$  \hspace{1cm} (3.3)
where $E_{\text{slab-}A}$, $E_{\text{slab-}B}$, and $E_{\text{slab-}AB}$ equal the energy of a pyrochlore slab with A, B or AB adsorbed, respectively, and $E_{\text{slab-empty}}$ is the energy of a pyrochlore slab without adsorbates. Full atom relaxation (slab and adsorbates) is allowed in all these calculations.

To calculate activation energies using the CI-NEB method, all DFT simulations of multiple reactants/products involved in a given reaction were placed upon the same pyrochlore slab. More specifically, the species were placed at the preferred adsorption site identified from earlier DFT all-atom energy minimization simulations involving each individual species adsorbed on a pyrochlore slab. In some cases, the final minimized energy structure for systems with two adsorbants indicated that there were lateral interactions between adsorbed species but that no chemical bond existed between them. To account for pyrochlore surface relaxation effects, the enthalpy of reaction for every elementary reaction step was calculated as in eq. (3.3), and the value of the activation energy calculated via CI-NEB (see later discussion) was adjusted to the value of $\Delta H_{\text{rxn}}$ considering surface relaxation effects. Further explanation on how the enthalpies of reaction and the corresponding activation barriers are calculated can be found in the Appendix A.

Using the calculated activation barriers for all reactions, it was possible to identify the favored reaction pathway for the dry reforming of methane on LRhZ pyrochlore catalysts. The change in reaction energy for each mechanistic step along this favored reaction pathway is shown in Fig. 2.6 (a full list of reaction energies used in the making of Fig. 2.6 can be found in Appendix A).
It is observed that the dehydrogenation and subsequent oxidation of methane, shown in the top of Fig. 2.6, involves several endothermic and exothermic reaction steps along the entire pathway. As methane undergoes dehydrogenation, the surface hydride species formed via these reactions can recombine to form molecular hydrogen and desorb from the catalyst surface. The hydrogen-hydrogen addition and desorption processes are endothermic.

To complete the DRM catalytic cycle, methane oxidation processes are complemented by CO₂ reduction reactions to yield CO. The DFT derived energetics
associated with the reduction of CO₂ are shown in the lower part of Fig. 2.6. Ab initio calculations suggest that two reaction pathways are possible, an indirect route involving hydrogen addition to adsorbed CO₂ and a direct route since both routes present similar energetic barriers.

Inspection of the energy of reaction data in Fig. 2.6 shows the reaction of O* with CH₂* is the most endothermic step (2.08 eV), suggesting it as a slow step. As discussed later, the assignment of the rate limiting step to the CH₄ dehydrogenation segment of the overall reaction mechanism was confirmed by activation energy calculations as well as experimental observations [17]. Additionally, the overall reaction energy for DRM calculated by DFT methods is 374.4 kJ/mol, whereas the theoretical value calculated from the heats of formation of reactants and products is 247.4 kJ/mol.

3.2.2 Activation energies and the Brønsted-Evans-Polanyi relationship

The proposed reaction network for DRM on pyrochlore surfaces (Fig. 2.2) includes 130 reactions, considering all forward and reverse reactions occurring on multiple site types on two different catalytic planes. To solve this computationally intensive problem, the coupling of rigorous DFT calculations with proven scaling methods was critical. For activation energies calculated using rigorous DFT methods, the climbing image – nudged elastic band approach was used to identify the minimum energy pathway between reactants and products. It was attempted to verify few transition state structures via the vibrational mode analysis. However, this verification was not successful, most probably due to the low number of images used between reactants and products (3 images); therefore, the found transition state structure is an approximation to
the real one. This approximation was taken to cover the scope of this doctoral work in a
time-effective manner.

For activation energies not explicitly calculated using DFT, the Brønsted-Evans-
Polanyi (BEP) scaling method was used to estimate reaction energy barriers. The BEP
relationship ($\Delta E_{\text{act}}' = \beta \Delta H_{\text{rxn}}' + \alpha$) linearly correlates the activation energy of an
elementary reaction to the reaction enthalpy for that process, and it has been successfully
applied to many catalytic systems for efficiently locating activation barriers.[52-59]
However, use of this approach requires that all reactions be defined such that the
reactants are non-associated gases adsorbing on pristine catalyst surface sites, see Fig.
2.7. For a certain set of elementary reactions, e.g., dissociation reactions, the BEP
correlation is independent of the adsorbate (reactant) and the metal on the catalytic
surface, which enables the development of a universal reaction correlation for a given
metal surface geometry. This universality is based on the fact that the transition state
structures are independent of the adsorbate and the metal on the surface.

Fig. 2.7. Potential energy diagram for the dissociative adsorption of a representative
diatomic gas. For the BEP relationship, the activation and reaction energies reference the
gas phase reactant.
On the pyrochlore catalyst surface, metal adsorption sites are separated by bridging oxygen atoms. As the preferred adsorption sites for species involved in a given reaction step are not necessarily adjacent to each other on the catalyst surface, calculated activation energies implicitly include all necessary energy barriers associated with close proximity diffusion upon the surface. Fig. 2.8 shows a select case of a reaction path found using the CI-NEB method, the CHO dehydrogenation on the plane (011) of LRhZ, where major displacement of the H-atom is required to reach the preferred adsorption site (bridge Rh-La), which leads to a high activation barrier (3.08 eV). All the reaction barriers calculated by rigorous DFT methods are shown in Fig. 2.9 for reactions occurring on both the (011) and (111) LRhZ pyrochlore surfaces. Additional structures for reaction paths calculated using the CI-NEB method can be found in the Appendix A.
Fig. 2.8 Reaction path for CHO*++ ⇌ CO*++H* on the plane (011) of LRhZ. Energetics and structures calculated using CI-NEB. The Rxn coordinate ‘0’ refers to CHO*++*. The Rxn coordinate ‘4’ refers to CO*++H*. The Rxn coordinates ‘1’, ‘2’ and ‘3’ refer to the three intermediate images considered. The color code for the spheres is as follows: La – green, Zr – light blue, Rh – dark blue, O – red, C – grey, H – white.
Fig. 2.9. DFT calculated activation energies for selected reactions, as well as the combined BEP correlation for the (011) and (111) LRhZ pyrochlore surfaces.

Despite the heterogeneity of the adsorption sites found on the LRhZ surfaces, the reaction and activation energies for most DRM reactions showed an evident linear correlation. Furthermore, the reactions used to construct the correlation involved the breaking of multiple types of bonds, including C-O, H-H, C-H and O-H, confirming that
the linear BEP relationship $\Delta E_{\text{act}} = 0.8253 \cdot \Delta H_{\text{rxn}} + 0.6216 \ (R^2=0.88)$ could be applied to all elementary reaction steps occurring on the LRhZ surface. Subsequently, the BEP relationship was used to quantify all activation energies not explicitly calculated by CI-NEB/DFT methods using previously calculated heats of reaction data derived using rigorous DFT methods.

3.3 Reaction mechanism

The first steps of the DRM reaction mechanism are by necessity the adsorption of reactants on to the catalyst surface. From prior simulation and experimental data, it is expected that the methane adsorption process is energetically unfavorable because of the low affinity that methane has for metal and oxide surfaces. To elucidate the exact mechanism for the adsorption of DRM reactants on LRhZ catalysts, DFT simulations were used to develop the potential energy diagrams for CH$_4$ and H$_2$ adsorption and dissociation that are shown in Fig. 2.10. Though it is possible for the molecular reactants to adsorb intact on the catalyst surface, these adsorption processes are found to only yield physisorbed species. Recognizing from simulations that low activation barriers exist for dissociation of the physisorbed species, it is more likely that methane and hydrogen undergo dissociative adsorption, compacting then the physisorption and later dissociation into a single step (see Fig. 2.10).
Fig. 2.10. Potential energy diagram for CH$_4$ and H$_2$ physisorption and subsequent dissociation. Solid lines indicate the dissociation path over the physisorbed species. Dashed lines indicate the dissociative adsorption path.

The activation energies for the forward and reverse reactions of all considered elementary steps are presented in Fig. 2.11 for the (011) and (111) pyrochlore planes. Based upon the magnitude of the barriers for these reactions, some elementary steps were considered irreversible reactions, and those reactions are represented by single-ended arrows in the diagram. In contrast, reactions indicated by two-sided arrows are considered reversible.
Fig. 2.11. Full reaction network for DRM on planes (011) and (111) of LRhZ. The values above, below and next to the arrows are the activation energies in eV, and the small arrows next to these values indicate what direction each activation energy corresponds to.

On both LRhZ planes, the dissociation of CH₃OH into CH₃ and OH, as well as the dissociation of CH₂OH into CH₂ and OH are nearly barrierless reaction steps, inhibiting then methanol formation, as observed experimentally. Water dissociation is also a barrierless reaction in both planes, for this reason, water formation is not expected in significant amounts. Experimentally, RWGS takes place over LRhZ up to approximately 700 °C [9], and therefore, negligible amounts of water are observed at higher reaction temperatures.
CH dissociation into atomic C and atomic H is practically unfeasible with this catalyst according to our simulation results. This observation helps to explain the resistance LRhZ pyrochlore catalysts have to coke formation during reaction. Further, many experimentalists [14-17] have proposed methane cracking to be the rate limiting step for the DRM. These observations corroborate the findings of this work; where the two rate limiting steps for DRM are found in the CH$_4$ dehydrogenation process. However, the reaction network proposed in this work provides an alternative route for C from CH$_4$ to oxidize and produce CO, different from what has been reported experimentally on Rh [11, 17, 48, 60, 61] and Ni supported catalysts [47], where full dehydrogenation of CH$_4$ is a necessary part of the reaction mechanism, and also different from computational findings using Ni surfaces, where CH and C species are generated [49, 62]. Specifically, the formation and subsequent dissociation of a CHO intermediate provides an alternative (minimum energy) pathway for CO generation from methane. By analyzing the activation energies for all possible reaction steps it is possible to discern a most favored reaction pathway for the DRM reactions. This preferred pathway for methane conversion to CO is illustrated in Fig. 2.12 for both the (011) and (111) LRhZ pyrochlore planes, identified by means of the activation energies presented in the complete reaction network (Fig. 2.11).
Fig. 2.12. Main reaction pathway for DRM on planes (011) and (111) of LRhZ. The values above, below and next to the arrows are the activation energies in eV, and the small arrows next to these values indicate what direction each activation energy corresponds to. The stars (★) represent active sites where Rh is present.

The calculated activation barriers for the (011) plane suggest that it is less active for DRM. More specifically, it is energetically unfavorable for reactive carbon species proceeding from CH₄ to fully dehydrogenate and undergo subsequent oxidation to form adsorbed CO. The oxidant feed gas CO₂ is however able to readily dissociate into CO and O via direct decomposition. These results suggest that the (011) LRhZ plane is partially poisoned by unreacted carbon species resulting from adsorbed CH₄, which severely limits overall H₂ and CO production.

In contrast, the (111) LRhZ pyrochlore plane provides a moderate activation energy route for CH₂ oxygenation ($\Delta E_{\text{act}} = 2.88$ eV) and later CHO dehydrogenation ($\Delta E_{\text{act}} = 2.40$ eV) to produce CO, compared to the higher energy barrier on the (011)
plane for the same reaction steps ($\Delta E_{act} = 3.49$ eV and $\Delta E_{act} = 3.08$ eV, respectively). Along with this barrier reduction, most of the elementary reactions occurring on (111) plane possess lower activation barriers compared to the (011) plane, and more species (CH$_4$, CH$_2$, CH$_2$O, CHO, CH, C, CO, COOH, H, O) present their most stable configurations on Rh-containing active sites (see Fig. 2.12) compared to the (011) plane. Additionally, surface energy calculations described in Section 2.3 suggest that the (111) plane is the most thermodynamically stable, which helps to support the conclusion that the (111) plane exhibits greater catalytic activity towards DRM. Finally, rhodium facilitates the indirect decomposition of CO$_2$ via hydrogenation to form carboxylic species on the plane (111). Yet, both direct and indirect decomposition are of consideration for this plane. The structures of absorbed species involved in the reaction pathway on the (111) LRhZ pyrochlore plane can be found in the Appendix A.

From Fig. 2.12, a simplified main reaction pathway can be discerned, since CH dehydrogenation encounters high activation barriers (3.37 eV or 4.01 eV) and later on, C oxygenation possesses a high activation barrier (3.31 eV) as well. Therefore, the main reaction pathway can be narrowed down to the one shown in Fig. 2.13. Where CH$_2$ oxygenation ($\Delta E_{act} = 2.88$ eV) and CHO dehydrogenation ($\Delta E_{act} = 2.40$ eV) appear as rate determining steps, taking into account the inherent limitations associated with DFT calculations and the simplifications assumed in this work.
Fig. 2.13 Simplified main reaction pathway for DRM on the plane (111) of LRhZ. The values above, below and next to the arrows are the activation energies in eV, and the small arrows next to these values indicate what direction each activation energy corresponds to. The stars (☆) represent active sites where Rh is present.

The identified main reaction pathway occurring on the (111) LRhZ pyrochlore surface shows remarkable agreement with experimental results. The absence of Rh in the most favorable adsorption sites for the key species on plane (011) goes along with the fact that no catalytic activity for DRM was observed for undoped LZ pyrochlores; whereas, the (111) LRhZ surface readily adsorbs intermediates at Rh containing sites and shows activity for DRM. The reported CH₄ and CO₂ conversions after 200 min at 550 °C, 1 atm and a GHSV = 48,000 mL/g_cat/h are 12.3% and 19.7%, respectively. This difference in conversion occurs despite there being a stoichiometric feed to the reactor and results from reverse water gas shift (RWGS, CO₂ + H₂ ⇌ CO + H₂O) reactions, which also consume CO₂, occurring simultaneously with the dry reforming of methane. Specifically, the lower conversion for methane (as compared to CO₂) results from the high number of dehydrogenation/oxidation steps and relatively high activation barriers (e.g., ΔEₐ = 2.88 eV and 2.40 eV for CH₄ versus 1.26 eV for CO₂) that must be overcome for methane to convert to CO; whereas CO₂ is readily converted to CO via two
reactions pathways, DRM and RWGS. The relative rates of the DRM and RWGS reactions are also reflected in the H₂ to CO ratio 44:100 found experimentally [9], which indicate that CO₂ molecules on the surface react with methane derived hydrogen through RWGS reactions.

Apparent activation energies calculated from experimental data for CH₄ and CO₂ conversion using LRhZ catalysts are 1.50 and 1.17 eV, respectively.[17] This difference in activation energies is explained by the DFT simulation results, which show that the RWGS reaction has lower barriers to reaction than the DRM reaction on LRhZ catalysts. Specifically, the highest activation barrier calculated using DFT methods for CH₄ and CO₂ consumption via DRM reactions is 2.88 eV (for CO formation from methane), whereas the highest barrier for CO₂ consumption from RWGS was 2.08 eV (for OH* +H* → H₂O*, see reaction energetics reported in Appendix A). These data clearly show that the RWGS reaction has lower activation barriers to conversion than DRM reactions. Thus, the RWGS reaction is likely limited by the DRM reaction, which produces surface bound hydrogen species essential for the RWGS reaction. This qualitative comparison of experimental and DFT derived simulation results further indicates that the reaction mechanism, energetics, and general methodology for computations reported here provide an accurate description of the DRM and RWGS reactions occurring on LRhZ pyrochlore catalysts.
4. Conclusions

Plane wave DFT methods proved effective at modeling the reaction mechanisms for the dry reforming of methane and reverse water gas shift reactions on Rh-substituted lanthanum zirconate pyrochlore catalysts. DFT simulation results were found to accurately describe the bulk crystal properties of LRhZ pyrochlore catalysts as well as the energetics for species adsorption, diffusion and reaction on the catalyst surface. The activation barriers calculated for all elementary steps of the proposed DRM reaction network on the (111) and (011) pyrochlore planes yielded reaction energetics that were consistent with reported experimental data for this system. Further, the computed LRhZ lattice parameters match experimental X-ray diffraction results, and the predicted adsorption behavior for CO and CO₂ agree with infrared absorption data for these species adsorbed on LRhZ pyrochlores and related metal oxide surfaces.

From the computed activation barriers, the (111) plane of LRhZ pyrochlore catalysts was identified as the most reactive surface for DRM, and surface Rh atoms incorporated into the lattice are integral to many of the active sites along the main reaction pathway. This pathway consists of the dehydrogenation of adsorbed CH₄ to form CH₂, which then is oxygenated by atomic oxygen generated from CO₂ dissociation. CH₂O dehydrogenates to create CHO, which undergoes dissociation to release a hydrogen atom and an adsorbed CO that later desorbs to yield product gas. These adsorbed hydrogens can also interact with surface bound species derived from CO₂ to yield additional CO product and water via the reverse water gas shift reaction. The CH₂ oxygenation and CHO dehydrogenation processes exhibit the highest activation energies.
(2.88 eV and 2.40 eV, respectively) in the proposed DRM reaction mechanism, thus placing the rate limiting step along the CH$_4$ dehydrogenation segment of the reaction pathway. The highly endothermic reaction of CH$_2$ with O corroborates that the CH$_4$ dehydrogenation/oxidation is the rate limiting pathway in the mechanism, whereas CO$_2$ dissociation presented lower activation barriers and can occur either directly or via a hydrogen-induced route involving COOH species. Finally, experimental results of L RhZ catalyst performance show great agreement with the findings in this work. For example, activation energies calculated in this work indicate that CO$_2$ undergoes both RWGS and DRM reactions, with CH$_4$ conversion to yield hydrogen and CO being the rate limiting step for both processes. This observation explains why feeding a stoichiometric ratio of CO$_2$ and CH$_4$ to a DRM reactor yields higher CO$_2$ conversions than observed for CH$_4$ and why H$_2$ to CO product ratios obtained experimentally are always less than unity.

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References


CHAPTER THREE

DRY REFORMING OF METHANE ON Rh DOPED PYROCHLORIDE CATALYSTS: A STEADY-STATE ISOTOPIIC TRANSIENT KINETIC STUDY

Abstract

Dry reforming of methane (DRM) to produce syngas has recently received significant attention due to increase in world-wide methane production. Experimental efforts have shown that select pyrochlore materials, such as the Rh-substituted lanthanum zirconate pyrochlore (LRhZ), are catalytically active for DRM, exhibit long-term thermal stability and resist deactivation; however, to-date a detailed understanding of the reaction mechanism on pyrochlore catalyst surfaces is incomplete. The present work adds to the mechanistic understanding of DRM over pyrochlores by using steady-state isotopic transient kinetic analysis (SSITKA) to examine dry reforming over the LRhZ pyrochlore. Isotopically labeled CH₄ and CO₂ were used in multiple SSITKA experiments to elucidate the migration of carbon atoms to product species. Short surface residence times at 650 and 800 °C (< 0.6 s) and increasing turnover frequencies with temperature were observed. Isotopic responses support the mechanistic steps found in our earlier work via DFT and the participation of all surface metal atoms as active sites for DRM, not only Rh.
1. Introduction

The advent of new oil and gas drilling technologies and the resulting availability of natural gas from unconventional deposits has led to a renewed interest in methane conversion processes, especially those that offer the possibility of efficiently converting methane into higher value liquid-phase products that are easily transported. To further advance this idea, promising new catalyst materials have been identified that may enable traditional methods for converting methane into liquid fuels to be partially supplanted by alternative technologies that yield syngas with an H₂ to CO ratio near unity [1]. One such technology involves the dry reforming of methane (DRM):

\[ \text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2 \quad (\Delta H^\circ = +247.4 \text{ kJ/mol}) \]

This syngas production method combines CO₂, a greenhouse gas and low-cost feedstock material, with methane from fossil or anaerobic biomass conversion sources. Furthermore, the product gas mixture from DRM, syngas (H₂ + CO), is a versatile starting material for the production of chemicals, fuels, heat and electricity, and the possibility of converting syngas into liquid hydrocarbons through Fischer-Tropsch or related processes could yield a fuel mixture more easily shipped over long distances. [2]

Use of dry reforming technologies offers additional advantages for methane deposits that contain significant amounts of CO₂, which if not removed, lowers the heating value of the produced natural gas and becomes corrosive to pipelines and equipment in the presence of moisture. Current approaches for dealing with this problem use energy intensive processes to separate CO₂ from the desired methane product, but DRM technologies could significantly reduce these costs and enable syngas-to-liquids
processes to be efficiently deployed near the production well. Such technologies could enable the economical production of fuels from gas fields previously ignored, particularly at locations like the Natuna field in the Greater Sarawak Basin in Indonesia, the largest gas field in south Asia (approximately 46 trillion cubic feet recoverable reserves), which has not been explored due to high CO₂ content (71%). Furthermore, DRM could prove vital to other production sites, such as the Platong and Erawan fields in Thailand that have 90% CO₂ content, or in Malaysia, where the CO₂ content in natural gas fields ranges from 28% to 87%. [3]

Although DRM has long been considered a viable method for converting methane from geologic or biological sources into syngas, the high temperature required for the reaction (~1000 K) has made it very difficult to find catalysts that exhibit the desired thermal stability and catalytic activity for extended periods of time. However, in recent work done by collaborators, it was found that the 2 wt% Rh-substituted lanthanum zirconate pyrochlore (LRhZ) material is catalytically active for DRM and possesses exceptional thermal stability and high selectivity towards syngas. [4]

Pyrochlores are crystalline oxides having high thermal stability and a general formula of A₂B₂O₇, where the A-site is occupied by a rare-earth metal and the B-site by a transition metal. Pyrochlore materials with a lattice framework composed of La and Zr in the A and B sites, respectively, (La₂Zr₂O₇ or LZ) have shown significant stability over a wide range of reaction conditions for fuel conversion processes [5-7]. These materials also exhibit a propensity to allow isomorphic substitution of a wide variety of metals into the lattice. Using Rh as a dopant yielded a catalyst with enhanced performance for DRM
In our earlier computational work with these materials (Chapter 2), we used DFT methods to discern the main reaction pathway for DRM as well as the most active catalyst surface, namely the (111) plane. Although the main reaction pathway was identified via these models, validation of this work and direct measurement of certain mechanistic kinetic parameters is best obtained from reaction studies, such as steady-state isotopic transient kinetic analysis (SSITKA). SSITKA is a surface analysis technique which provides resolution to study active site reaction kinetics that are otherwise inaccessible under solely steady state conditions. SSITKA has been used extensively in carbon monoxide hydrogenation studies for both supported metal and promoted metal oxide catalysts [8-15], but very few of these studies have examined other C\textsubscript{1} reactions, such as reverse water gas shift (RWGS) [16] or the dry reforming of methane.

Although steady-state isotopic tracing techniques have not previously been used to study the dry reforming of methane on Rh-substituted pyrochlores, related work by Tsipouriari and Verykios did make use of SSITKA to study DRM reaction kinetics on catalysts comprised of nickel on two different supports, namely, La\textsubscript{2}O\textsubscript{3} and Al\textsubscript{2}O\textsubscript{3} [17]. They concluded that the activation of CH\textsubscript{4} is a slow step over the Ni/La\textsubscript{2}O\textsubscript{3} catalyst due to the detection of reversibly adsorbed CH\textsubscript{4}. Further, the dissociation of CO\textsubscript{2} over Ni/La\textsubscript{2}O\textsubscript{3} is a fast step in comparison to CH\textsubscript{4} activation, but the opposite trend is observed in the Ni/Al\textsubscript{2}O\textsubscript{3} catalyst. Additionally, they found that the La\textsubscript{2}O\textsubscript{3} support behaves as a dynamic oxygen pool, and the presence of oxycarbonates provides a fast step in the oxidation of carbon species, produced by dissociation of CH\textsubscript{4}, to form CO. Bobin et al. [18] also studied the dry reforming of methane on metal-supported (Pt, Ru,
Ni and Ni-Ru) ceria-zirconia catalysts. They identified the rate-limiting reaction as the irreversible transformation of CH$_4$ on metal sites, and concluded that CO$_2$ transformation occurs much faster and is reversible at steady-state conditions. They also observed that the surface concentration of C-containing intermediates was negligible and that the $^{13}$C-atom from $^{13}$CH$_4$ in the feed migrated to form $^{13}$CO$_2$, under conditions where unlabeled CO$_2$ was fed to the reactor.

In 2003, Verykios [19] also published a study on the mechanistic aspects of dry reforming of methane over the Rh/Al$_2$O$_3$ catalyst. Steady-state tracing and transient techniques, as well as in situ FTIR spectroscopy were used to enlighten aspects of the reaction mechanism. For instance, the surface coverage of active carbon-containing species is 0.2, for an equimolar reactant feed at 650 °C, while the surface coverage of active oxygen-containing species is very small. They also concluded that most of the carbon accumulated on the catalyst surface comes from the CO$_2$ molecule, not the CH$_4$ molecule.

In the present work, surface kinetic parameters are calculated for the first time for DRM on a pyrochlore catalyst using SSITKA; moreover, isotopic tracing is used to track the migration of carbon atoms amongst reactants and products. The results of this work are compared to computational findings described in Chapter 2, so that a more complete description of the reaction kinetics is achieved.
2. Experimental methods

2.1 Catalyst synthesis

The catalyst used in this work, the 2 wt% Rh-substituted lanthanum zirconate (LRhZ), was provided by collaborators [20]. This catalyst was synthesized by the modified Pechini Method [21] using the corresponding La, Zr and Rh nitrates as metal precursors. The synthesis procedure has been reported earlier [20].

2.2 Catalyst characterization

Previous work performed extensive characterization of the LRhZ catalyst [4] by means of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and temperature programmed reduction (TPR); concluding that the Rh dopant was located within the lattice of the pyrochlore crystal phase. In the present work, Scanning Transmission Electron Microscopy (STEM) and Energy Dispersive X-ray spectroscopy (EDX) were performed to ascertain catalyst morphology and the dispersion of Rh on the surface. SEM and EDX were performed using the Hitachi Scanning Transmission Electron Microscope – HD2000, with a field emission source and a resolution of 0.24 nm at 200 kV.

The BET (Brunauer–Emmett–Teller) surface area of the catalyst was analyzed by N₂ physisorption using a Micromeritics ASAP 2020 system. 0.2943 g of LRhZ were degassed under a vacuum of 10⁻³ mmHg at 90°C for 10 h; after this, the temperature was ramped to 300 °C at a rate of 10°C/min and held for 1 h before N₂ physisorption data were collected at 77 K.
2.3 Kinetic measurements

Reactor set-up and catalyst reduction

Catalytic measurements were carried out in a straight tube quartz microreactor (4 mm i.d., 6.35 mm o.d.). An 9 mg catalyst sample was added to the reactor and held in place using quartz wool above and below the catalyst. The lower portion of the reactor tube was filled with quartz beads (2 mm diameter) so as to maintain the vertical position of the catalyst bed at a fixed height. Reactor heating was provided by a furnace (Applied Test Systems, Inc.) controlled by a programmable temperature controller, and the temperature in the catalytic bed was appropriately calibrated with respect to the set point value in the temperature controller for the furnace. Before catalyst testing, the sample was first reduced at 800 °C and 1.1 atm using 73.9 cm³/min of 26.9 % (v/v) H₂ (UHP) in Helium (industrial grade) for 1 hour (after heating to that temperature at a rate of approximately 35 °C/min). Then, 65 cm³/min of He was used to purge the reactor system for 15-20 min before DRM experiments at 800 °C and 1.1 atm were carried out. The total flow rate of gaseous feed to the reactor was kept constant at 74.6 cm³/min and contained 64.8 cm³/min of 95.1% He + 4.9% Ar (Airgas), 4.9 cm³/min of CH₄ (instrument grade, Airgas) and 4.9 cm³/min of CO₂ (instrument grade, Airgas). Note that all listed gas flow rates in this text are at standard temperature and pressure conditions, i.e., not reactions conditions. Initial DRM reactions were always at 800 °C just after the reduction with H₂ because the species created during reaction further reduced the surface of the catalyst. After steady-state was reached at 800 °C, the catalyst temperature was then changed (if needed) to the desired reaction temperature.
The product gases exiting the reactor were sent to the mass spectrometer (MS) (Pfeiffer Vacuum) for analysis via 1/16-inch stainless steel capillary tubing. The MS was connected to a computer for high-speed continuous data acquisition using the software Balzers Quadstar 422 version 6.0. The tubing connecting the reactor and MS analysis system were maintained at 120 °C, and the inlet assembly to the mass spectrometer was held at 70 °C to avoid water condensation.

**Steady-state isotopic transient kinetic analysis (SSITKA) set-up**

The masses followed with respect to time in the mass spectrometer were 44 (CO₂), 28 (CO), 15 (CH₄), 2 (H₂), 45 (¹³CO₂), 29 (¹³CO), 17 (¹³CH₄) and 40 (Ar). The MS signal used for masses 28 (CO) and 29 (¹³CO) were adjusted so that the contribution from CO₂ and ¹³CO₂ ionization, respectively, are appropriately subtracted. Although water is produced, its mass (18) was not followed in order to optimize the recording speed of the mass spectrometer, and in work reported by Pakhare et al. [4] on the same catalyst it is shown that the quantity of water produced from the Reverse Water Gas Shift (RWGS) reaction is small, and RWGS takes place up to approximately 700 °C.

SSITKA measurements were performed using two different labeled gases. First, labeled methane (¹³CH₄, 99 atom % ¹³C, Aldrich) was used. Therefore, a switch between 64.8 cm³/min Ar/He (95.1 % He+ 4.9 % Ar (Airgas)) with 4.9 cm³/min ¹²CH₄ and 64.8 cm³/min He with 4.9 cm³/min ¹³CH₄ was made, while holding the ¹²CO₂ flow constant at 4.9 cm³/min. Second, labeled carbon dioxide (¹³CO₂, 99 atom % ¹³C, <3 atom % ¹⁸O, Aldrich) was used. Therefore, a switch between 64.8 cm³/min Ar/He (95.1 % He+ 4.9 % Ar (Airgas)) with 4.9 cm³/min ¹²CO₂ and 64.8 cm³/min He with 4.9 cm³/min ¹³CO₂ was
made, while holding the $^{12}$CH$_4$ flow constant at 4.9 cm$^3$/min. The switch was made using a Valco 2-position valve with an electric actuator without disturbing any reaction condition (i.e., the total gas flow rate and reaction pressure were kept constant at 74.6 cm$^3$/min and 1.1 atm during the switch). In addition, two back pressure regulators in the system were used to keep the pressure of the flow going through the reactor constant at 1.1 atm before and after the switch. The gas-phase holdup for the reaction system was measured using the dilute Ar tracer in the He carrier gas.

The SSITKA apparatus used in this study (see Fig. 3.1) readily enabled the effects of switching between labeled and unlabeled gases to be quantized, which in turn provided information about the rate of carbon migration through different species on the catalyst surface at steady-state reaction conditions. Surface kinetic parameters, such as the average surface residence time, surface concentration of intermediates and turnover frequency were determined following the SSITKA formalism [22].
Normalized transient responses

SSITKA is an experimental technique that provides information about surface kinetic parameters, such as, surface residence time, surface concentration of intermediates and turnover frequencies during steady-state reaction conditions; information which is practically inaccessible computationally or using any other surface analysis technique.

After reaching steady-state reaction conditions, the switch from an unlabeled reactant to a labeled one leads to the replacement of unlabeled surface intermediates by the labeled ones, without altering the steady-state conditions of the reaction (assuming...
the molecular mass and vibrational characteristics of the labeled and unlabeled species are similar). The speed with which the surface intermediates are replaced gives information about the surface residence time and the concentration of intermediates on the surface.

As the switch from unlabeled to labeled reactants provokes a transient decay of the unlabeled product species and a transient rise of the labeled ones, the normalized step decay transient response for a product P is defined as:

\[ F^P(t) = \frac{r^P(t)}{r_{ss}} \]  

(1)

Where, the normalized step decay \( F^P(t) \) is the ratio between the transient reaction rate during the switch \( r^P(t) \) and the reaction rate at steady-state conditions \( r_{ss} \).

Therefore, it can be calculated as,

\[ F^P(t) = \frac{|y(t) - y_{ss}|}{|y_{\infty} - y_{ss}|} \]

where \( y(t) \) is the mole fraction of a reactor effluent species as a function of time \( t \), \( y_{ss} \) is the mole fraction at steady-state, which is just before the switch at \( t = 0 \), and \( y_{\infty} \) is the mole fraction long after the switch, when the concentration of labeled species completely replaces that of the unlabeled species. The responses recorded by the MS detector must be corrected for the contribution of gas-phase hold up in the system. This correction is achieved by measuring the outlet concentration profile of a dilute inert gas (argon). In this work, the system gas-phase hold up is measured using an argon tracer that is included with the unlabeled reactant streams. [19, 22]
3. Results and discussion

3.1 SEM and EDX analysis of catalysts

SEM and EDX imaging of a representative catalyst particle are shown in Fig. 3.2 and 3, respectively. The catalyst particle exhibits an amorphous morphology and the Rh dopant appears to have some segregation (see Fig. 3.3). EDX results indicate that Rh surface concentration is 3.67 wt%, considerably above data reported previously by Pakhare et al. [4] of 1.7 wt% for the bulk (via inductively couple plasma-optical emission spectroscopy) and 0.78 wt% for the surface (via X-ray photoelectron spectroscopy). This discrepancy confirms the relative heterogeneity of the substitution in the pyrochlore particles, which is supported by some non-isotropicity of Rh observed in Fig. 3.3; however, there is no evidence for the formation of Rh clusters on the surface despite the possibly uneven distribution of Rh amongst catalyst particles.

![Fig. 3.2 SEM image of the LRhZ pyrochlore catalyst.](HD-2000_200kV_x200k_SE_150nm)
3.2 Isotopic tracing

3.2.1 $^{13}$C-atom migration between reactants

Density Functional Theory (DFT) based simulation results described in Chapter 2 indicate that there are a greater number of elementary reaction steps involved in CH$_4$ dehydrogenation and oxidation, when compared to CO$_2$ reduction (see Fig. 3.4), to yield CO gas production. Those DFT results also indicated that each of the reverse mechanistic steps required to convert adsorbed CO into CH$_4$ or CO$_2$ were energetically feasible at the high temperatures commonly used for DRM. Despite this fact, the collective effect of multiple reactions being required to convert CO to CH$_4$ made that overall pathway inaccessible, but the pathway for CO conversion to CO$_2$ was accessible. Furthermore, CO adsorbs the strongest to the surface ($E_{\text{adsorption}} = -1.63$ eV) when compared with the other gas phase species: CO$_2$ (-1.46 eV), H$_2$ (-0.38 eV) and CH$_4$ (-
0.07 eV). Thus, it is much more likely that CO oxidation to CO₂ will occur, as it can occur through O or OH addition. Therefore, a goal of the SSITKA experiments was to ascertain the validity of this DFT prediction and determine the extent to which a ¹²CO₂/¹³CH₄ reactant mixture would yield ¹³CO₂ product and likewise from separate experiments whether a ¹³CO₂/¹²CH₄ reactant mixture would yield any ¹³CH₄ product from the migration of carbon species between reactants and products via an adsorbed CO intermediate.
Fig. 3.4 Reaction energies for elementary steps in the main reaction pathway for DRM on the LRhZ pyrochlore surface as identified by DFT methods. A* means that species A is adsorbed on the catalyst surface. DFT data depicted in this figure are provided in Appendix A.

CH$_4$ dehydrogenation and oxidation to CO involves 7 elementary steps (including adsorption, reaction and desorption processes); whereas, CO$_2$ reduction to CO involves 3 reaction steps (via a direct pathway) or 5 steps (via an H-induced decomposition pathway). As shown in Fig. 3.4, the magnitude of the greatest reaction energy changes...
are comparable on the CH$_4$ dehydrogenation/oxygenation and CO$_2$ decomposition pathways to form CO product, but the oxidation of CO to CO$_2$ is clearly more favorable as it involves fewer steps.

To experimentally corroborate the DFT derived mechanism, steady state DRM was performed over LRhZ at 1.1 atm and 800 °C using the unlabeled CH$_4$ and CO$_2$. Later, the unlabeled reactant gas mixture was rapidly switched to a partially labeled mixture, $^{13}$CO$_2$/$^{12}$CH$_4$. In another steady-state reaction experiment, the unlabeled reactant mixture was switched to $^{12}$CO$_2$/$^{13}$CH$_4$. The transient responses to these changes in reactant composition at otherwise steady-state reaction conditions at 1.1 atm and 800 °C are shown in Fig. 3.5. When the labeled reactant introduced was $^{13}$CO$_2$ (Fig. 3.5a), no labeled CH$_4$ was observed, which indicates that the labeled carbon atom ($^{13}$C) from $^{13}$CO$_2$ did not migrate and desorb as $^{13}$CH$_4$. In contrast, when $^{13}$CH$_4$ (Fig. 3.5b) was introduced in the reactive mixture, some $^{13}$CO$_2$ was observed as product, confirming that once labeled $^{13}$CO is formed, it can be readily oxidized to form $^{13}$CO$_2$. Thus, the isotopic switch successfully confirmed the C-atom migration from CH$_4$ to CO$_2$ as was predicted qualitatively by DFT calculations; and also observed by Bobin et al. [18] for DRM over metal-supported ceria-zirconia catalysts.
Fig. 3.5 DRM products transient response following a reactants switch from a) $^{12}$CO$_2$ to $^{13}$CO$_2$; and b) $^{12}$CH$_4$ to $^{13}$CH$_4$. The LRhZ pyrochlore catalyst was used at 800°C and 1.1 atm for all data shown. GSHV = 65,333 cm$^3$/g-cat/h.

At moderate DRM reaction temperatures (650 °C), it was similarly observed that no C-atom migration from $^{13}$CO$_2$ to $^{13}$CH$_4$ existed (Fig. 3.6). The following SSITKA studies are performed using $^{13}$CO$_2$, since the re-adsorption processes are more prominent, which increases the average surface residence time and makes it measurable at high temperatures.
Fig. 3.6 DRM products transient response following a reactant switch from $^{12}$CO$_2$ to $^{13}$CO$_2$ using the LRhZ pyrochlore catalyst at 650 °C and 1.1 atm. GSHV = 65,333 cm$^3$/g cat/h.

### 3.2.2 SSITKA (Steady-state isotopic transient kinetic analysis)

**Average surface residence time ($\tau_{\text{avg}}$)**

The average surface residence time ($\tau_{\text{avg}}$) is calculated as the area between the normalized transient responses of the product, $F^{\text{CO}}(t)$, and that of the inert gas tracer, $F^{\text{Ar}}(t)$.

$$\tau_{\text{avg}}^{\text{CO}} = \int_0^\infty \left[ F^{\text{CO}}(t) - F^{\text{Ar}}(t) \right] dt$$
This area corresponds to the average time that carbon-containing species (since $^{13}$C labeled gases were used), which are in the reactive pathway to form CO, spend on the surface.

A representative set of normalized transient responses of DRM reaction products at different temperatures for a switch from $^{12}$CO$_2$ to $^{13}$CO$_2$ are shown in Figure 7. The area between the transient response for CO and Ar decreases as the temperature increases because the reaction proceeds significantly faster at the higher reaction temperature; therefore, intermediates spend less time on the catalyst surface. At temperatures relevant for significant DRM activity (650 and 800 °C), the CO response almost overlaps the Ar response, which corresponds to enhanced rates of diffusion and reaction on the surface and in turn gives high conversion of CO$_2$ and CH$_4$. Fast transients were also observed by Verykios [19] analyzing DRM over a Rh/Al$_2$O$_3$ catalysts and by Bobin et al. [18] using a Pt/PrCeZr catalysts.

As expected, the time required for the labeled reactant to reach steady-state following a switch in reactant gases increases as the catalyst bed temperature decreases, which means that the replacement of surface intermediates is slower and diffusion processes are not as effective at low temperatures ($\tau_{\text{avg}} = 2.29$ s at 450 °C and $\tau_{\text{avg}} = 1.19$ s at 500 °C). From Fig. 3.7, one can also observe that at moderate (650 °C) and high (800 °C) temperatures the reaction has extremely short residence times (0.57 s at 650 °C and 0.35 s at 800 °C) since the $^{12}$CO signal almost overlaps the Ar signal, meaning that the last carbon monoxide produced from the exiting $^{12}$CO$_2$ in the system is generated fractions of a second after the flow of the unlabeled reactant ($^{12}$CO$_2$) is cut-off. In
addition, $^{13}$CO$_2$ and $^{13}$CO practically exit the reactor at the same time, suggesting that DRM proceeds almost instantaneously.

As seen from Fig. 3.7d, at 450 °C there is some noticeable loss in signal to noise for the DRM product concentrations measured by MS, which is a result of very low catalytic activity at this temperature, and thus, low product concentrations. In this work, SSITKA experiments were performed at low temperatures (450 °C and 500 °C) with the purpose of extending the analysis of surface kinetic parameters, since the surface residence times at moderate and high temperatures (>650°C) are very short. However, DRM is not thermodynamically favorable at low temperatures ($\Delta G_{\text{Rxn}}^* \gg 0$), as shown in Fig. 3.8, and rather RWGS reaction becomes important, as evidenced by the low H$_2$ to CO ratios. Kinetically speaking, increases in surface residence time at lower temperatures enable provide additional time for H$_2$, produced from the dry reforming of methane, to
react with the CO₂ fed to the reactor, which leads to water formation through the reverse water gas shift reaction (CO₂ + H₂ ⇌ CO + H₂O).

![Graph showing standard Gibbs free energy of DRM](image)

**Fig. 3.8** Standard Gibbs free energy of DRM (Top plot). Reactants conversion and H₂ to CO ratio (bottom plot) for DRM as a function of temperature at specified reactor conditions: 1.1 atm, equimolar feed (CO₂ and CH₄) and GHSV = 65,333 cm³/gcat/h.

Equilibrium conversions at 1 bar for the stoichiometric mixture of CO₂ and CH₄ were calculated at different temperatures by Jafarbegloo et al. [23] considering multiple reactions: dry reforming, steam reforming, RWGS and coke formation reactions (CH₄ ⇌ C +2H₂, 2CO ⇌ C+CO₂, 2CO+H₂ ⇌ C +H₂O). The calculated equilibrium conversions are higher than the conversions shown in Fig. 3.8 at all temperatures.
**Concentration of surface intermediates**

The concentration of surface intermediates \(N^{CO}\) is the another parameter that can be calculated as follows [22],

\[
N^{CO} = r_{ss}^{CO} \tau_{avg}
\]

From \(N^{CO}\), the coverage of surface intermediates (intermediates per active site) can be obtained as follows,

Coverage = \([\text{Surface concentration of intermediates, } N^{CO}][\text{Avogadro’s Number}][\text{BET surface area}]^{-1}[\text{area per metal atom}]\]

Coverage \((\theta) = [\text{mol/g_cat}][\text{molecules/mol}][\text{g_cat/m}^2][\text{m}^2/\text{metal-atom}]\]

The BET surface area was 8.72 m\(^2\)/g, and the area per metal atom (including Rh, Zr and La) for the plane (111) is 1.28 x10\(^{-19}\) m\(^2\)/atom.

The calculated surface coverage of intermediates when the labeled gas used was \(^{13}\)CO\(_2\) exceeded unity at all temperatures \((\theta = 1.7, 1.2, 1.1 \text{ and } 2.1, \text{ at } T = 800, 650, 500 \text{ and } 450 \, ^\circ\text{C}, \text{ respectively})\), which means that either the obtained surface residence time from SSITKA is higher than the true value due to readsorption of CO\(_2\), or, that a metal atom can adsorb multiple intermediates at the same time, which is somewhat less likely given the size of some of the surface species (e.g., CH\(_x\)) and the nature of available metal orbitals for binding adsorbates. Nonetheless, when the labeled gas used was \(^{13}\)CH\(_4\), the coverage was 0.5 (at 800 \, ^\circ\text{C}), which supports the hypothesis that CO\(_2\) readsorption may have increased the value of \(\tau_{avg}\) and in turn provided higher values of \(N^{CO}\) (and therefore coverages greater than unity). CO\(_2\) readsorption is enhanced by the basicity of the catalyst due to the presence of La on the surface.[24-26]
**Turnover frequency (TOF)**

In general, TOF represents the number of product molecules produced per catalytic site per unit time. The turnover frequency (TOF) can be calculated from $\tau_{avg}$ as follows,

$$\text{TOF}_{\text{ITK}} = \frac{1}{\tau_{avg}}$$

As defined in [22], there are three variations for the definition of TOF, and the relationships between these definitions are generally described as,

$$\frac{\text{Rate}}{\text{[surface metal atoms]}} \leq \frac{\text{Rate}}{\text{[active sites]}} \leq \frac{\text{Rate}}{\text{[active intermediates]}}$$

Or

$$\text{TOF}_{\text{Chem}} \leq \text{TOF}_{\text{true}} \leq \text{TOF}_{\text{ITK}}$$

TOF$_{\text{Chem}}$, the rate per surface metal atoms, can be calculated as follows,

$$\text{TOF}_{\text{Chem}} = \left[\text{Rate of CO production per mass of catalyst}\right]\left[\frac{\text{Avogadro’s Number}}{\text{BET surface area}}\right]^{-1}\left[\text{area per metal atom}\right]$$

$$\text{TOF}_{\text{Chem}} = \left[\frac{\text{mol/gcat/s}}{\text{molecules/mol}}\right]\left[\frac{\text{g_cat/m}^2}{\text{m}^2/\text{metal-atom}}\right]$$

TOF$_{\text{Chem}}$ is calculated taking into account all metal atoms in the surface (Rh, Zr, La), not only the Rh atoms, since previous DFT calculations (Chapter 2) showed that even though Rh atoms are present in the main reaction pathway, many of the identified active sites are a combination of Rh with the other two metals, Zr and La.

Fig. 3.9 shows the values for TOF$_{\text{Chem}}$ and TOF$_{\text{ITK}}$ and the proximity of these values provides good agreement with theory [22]. However, the fact that TOF$_{\text{Chem}}$ is slightly higher than TOF$_{\text{ITK}}$ at high temperatures (800 °C), contradicting what stated
before \((\text{TOF}_{\text{Chem}} \leq \text{TOF}_{\text{true}} \leq \text{TOF}_{\text{ITK}})\), suggests that the values of \(\tau_{\text{avg}}\) are greater than the actual surface residence time, which is due to readsoption of reactants or products, and this was previously concluded from the few mechanistic steps between \(\text{CO}_{(g)}\) and \(\text{CO}_2(g)\), and vice versa (see Fig. 3.4). To confirm this hypothesis, a labeled switch from \(^{12}\text{CH}_4\) to \(^{13}\text{CH}_4\) was done at \(800^\circ\text{C}\) and the value for \(\tau_{\text{avg}}\) was \(0.10\) s; whereas, the switch from \(^{12}\text{CO}_2\) to \(^{13}\text{CO}_2\) had a \(\tau_{\text{avg}}\) of \(0.35\) s. This supports that \(\text{CO}_2\) readsorbs during reaction as shown in the section \(^{13}\text{C}\)-atom migration between reactants’.

![Fig. 3.9 TOF\(_{\text{Chem}}\) and TOF\(_{\text{ITK}}\) as a function of temperature for DRM over LRhZ catalyst at 1.1 atm and GHSV = 65,333 cm\(^3\)/g\(_{\text{cat}}\)/h.](image)

The lower value for TOF\(_{\text{ITK}}\) when compared to TOF\(_{\text{Chem}}\) at \(800^\circ\text{C}\) also suggests an increase in the number and type of active surface intermediates, which is explained by the overcoming of activation barriers that lead to the formation of intermediates that do not necessarily take part in the main reaction pathway for DRM, called spectators, such as \(\text{CH}^*\), as shown in Chapter 2. Table 3.1 summarizes the surface reaction kinetic parameters for DRM on LRhZ found in this study.
Table 3.1 Surface reaction kinetic parameters for DRM on LRhZ.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Temperature ((^\circ)C)</th>
<th>Labeled gas</th>
<th>Rate\textsuperscript{b} (mmol CO/g\textsubscript{cat}/s)</th>
<th>(\tau\text{avg})\textsuperscript{c} (s)</th>
<th>TOF\textsubscript{ITK}\textsuperscript{d} (s\textsuperscript{-1})</th>
<th>N\textsuperscript{e} (mmol/g\textsubscript{cat})</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>(^{13})CO(_2)</td>
<td>0.555</td>
<td>0.35\textsuperscript{f}</td>
<td>2.84</td>
<td>0.195</td>
</tr>
<tr>
<td>800</td>
<td>(^{13})CH(_4)</td>
<td>0.555</td>
<td>0.10\textsuperscript{f}</td>
<td>10.14</td>
<td>0.055</td>
</tr>
<tr>
<td>650</td>
<td>(^{13})CO(_2)</td>
<td>0.227</td>
<td>0.57\textsuperscript{f}</td>
<td>1.74</td>
<td>0.130</td>
</tr>
<tr>
<td>500</td>
<td>(^{13})CO(_2)</td>
<td>0.107</td>
<td>1.19\textsuperscript{g}</td>
<td>0.84</td>
<td>0.128</td>
</tr>
<tr>
<td>450</td>
<td>(^{13})CO(_2)</td>
<td>0.103</td>
<td>2.29\textsuperscript{g}</td>
<td>0.44</td>
<td>0.237</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction was carried out at 1.1 atm, GSHV = 65,333 cm\(^3\)/g\textsubscript{cat}/h/.
\textsuperscript{b} Steady-state rate. The steady-state MS signal was averaged over at least 1 min to reduce eliminate the noise effect.
\textsuperscript{c} Surface residence time of intermediates.
\textsuperscript{d} TOF\textsubscript{ITK} = 1/ \(\tau\text{avg}\).
\textsuperscript{e} N = Rate \(\times\) \(\tau\text{avg}\).
\textsuperscript{f} Experimental errors are \(\pm 0.1\) s.
\textsuperscript{g} no replicas were done at these conditions, since they are not relevant for real DRM applications.

4. Conclusions

Isotopic labeling studies validated findings from DFT calculations about the main reaction pathway for the dry reforming of methane on the Rh-substituted lanthanum zirconate pyrochlore catalyst, in which the CH\(_4\) dehydrogenation/oxygenation to CO proceeds as follows: \(\text{CH}_4(g) \rightleftharpoons \text{CH}_4^* \rightleftharpoons \text{CH}_3^* \rightleftharpoons \text{CH}_2^* \rightleftharpoons \text{CH}_2\text{O}^* \rightleftharpoons \text{CHO}^* \rightleftharpoons \text{CO}^* \rightleftharpoons \text{CO}_2(g)\); whereas CO\(_2\) can dissociate directly and indirectly (through COOH formation) to CO.

The observed migration of C-atom from CH\(_4\) to CO\(_2\) but not from CO\(_2\) to CH\(_4\) confirms that CH\(_4\) dehydrogenation/oxygenation to form CO involves more elementary steps than the decomposition of CO\(_2\) to CO, as predicted by DFT simulations. A Steady-State Isotopic Transient Kinetic Analysis (SSITKA) allowed for the calculation of
average surface residence times, surface species concentrations and turnover frequencies at different temperatures. The residence time increased at lower temperatures which allows time for the reaction of H\(_2\) produced from the dry reforming of methane with the CO\(_2\) fed to the reactor, promoting the competing reaction, the reverse water gas shift reaction: \(\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}\).

Extremely short residence times (< 0.6 s) were observed at temperatures relevant for the dry reforming of methane (> 650 °C) since activation barriers are more easily overcome and the diffusion of intermediates on the surface is favored. The observed short residence times have an associated error estimated from the replicas taken in this study. It is difficult to draw definitive conclusions about the exact value of the kinetic parameters due to the extremely fast rate of the reactions involved. Despite this fact, this work helps provide an understanding of the reaction kinetics from the comparison of kinetic parameters at several conditions so that systematic errors due to the arrangement of the experimental apparatus and the recording capabilities of the mass spectrometer are appropriately compensated for in all calculations.

The calculated values of turnover frequencies corroborated two hypotheses: that the estimated average surface residence times are slightly increased when compared to the real values due to the reversible adsorption of CO\(_2\) on the surface, and that all surface metal atoms (Rh, Zr and La) take part as active sites for at least some DRM reactions on the LRhZ pyrochlore material, as previously seen from DFT results. Despite all metals being catalytically active, it is the presence of Rh that makes the LRhZ catalyst active for DRM when compared to the non-substituted lanthanum zirconate (LZ) pyrochlore;
specifically, prior DFT results indicated that Rh metal sites promote the adsorption and dehydrogenation of methane, see Chapter 2.

The DFT data used in this work along with the estimated surface residence times can be employed to predict overall catalyst performance by means of a microkinetic model, which will be presented in one of our upcoming publications.

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References


Abstract

Dry reforming of methane (DRM) is a promising gateway technology for energy and fuels production that utilizes methane and CO$_2$, a common contaminant in natural gas deposits, as feed. Previous experimental work has shown that Rh-substituted lanthanum zirconate pyrochlores (LRhZ) are catalytically active and stable at the high temperatures needed for DRM. Although experimental and ab initio computational approaches have been used to study aspects of the DRM reaction mechanism on pyrochlores, this work is the first to describe a tunable microkinetic model with parameters derived from DFT simulations for DRM over the (111) plane of an LRhZ pyrochlore catalyst. This model was used to gain insight into the favored reaction pathway for DRM and evaluate the time evolution of key intermediates (e.g., CH$_3$, CH$_2$, CH, OH, O) within the reactor as a function of reactor operating conditions and catalyst metal loading. Model predictions of reactant conversion and H$_2$/CO product ratio were compared to experimental reaction data, and predicted yields compared well with experimental results.
1. Introduction

The availability of shale-gas has granted CH\textsubscript{4}-related chemistry renewed attention. One efficient pathway for converting methane into useful chemicals and fuels involves the formation of syngas, a mixture of CO and H\textsubscript{2}. [1] Multiple routes to produce syngas are currently available: Steam Methane Reforming (SMR), Partial Oxidation (POX), Autothermal Reforming (ATR) and the Dry Reforming of Methane (DRM). Though steam reforming and autothermal reforming are currently the most widely used methods, the dry reforming of methane (CH\textsubscript{4}+CO\textsubscript{2} \rightleftharpoons 2CO+2H\textsubscript{2}, \Delta H^\circ = +247.4 \text{ kJ/mol}) offers several advantages. Specifically, DRM yields syngas with a favorable H\textsubscript{2} to CO ratio, and it offers the possibility of efficiently using methane from natural deposits that are rich with CO\textsubscript{2}. Current approaches for dealing with this latter problem use energy intensive processes to separate CO\textsubscript{2} from the desired methane product, but DRM technologies could significantly reduce these costs and enable syngas-to-liquids processes to be efficiently deployed on-site near the production well, enabling the economical production of fuels from gas fields previously ignored, such as the Natuna field in the Greater Sarawak Basin in Indonesia, the largest gas field in south Asia (approximately 46 trillion cubic feet recoverable reserves), which has not been explored due to high CO\textsubscript{2} content (71%). [2, 3]

Despite these advantages, dry reforming has not been widely adopted due to the absence of long-term, thermally stable catalysts for the reaction, which occurs at approximately 1000 K. In recent years, however, Rh-substituted lanthanum zirconate
pyrochlores (La$_2$Zr$_{2-x}$Rh$_x$O$_7$) have been found to be catalytically active and stable for DRM. To further develop and improve these materials research efforts have sought to understand the reaction mechanism, both computationally (Chapter 2) and experimentally (Chapter 3) [4, 5], but these efforts failed to yield a detailed kinetic model for the overall reaction that accounted for the effects of catalyst composition and reaction conditions. Building upon this prior work, we herein present a microkinetic model (MKM) based on DFT data (Chapter 2) that quantitatively describes reaction performance for DRM over Rh-doped pyrochlores and accounts for the effects of varying Rh loading in the catalyst.

In studies of other catalyst systems [6-11], DFT data have been used to build microkinetic models (MKMs) that in-turn were used to predict reaction performance. Such tools aim to reduce trial-and-error experimental efforts focused on catalyst optimization. In general, DFT-based MKMs enable a more fundamental approach to system optimization than purely parameter-fit models, as DFT-based MKMs consider a wide network of possible reaction steps, for which activation barriers are available, and do not overlook possible branching of the reaction network due to limitations in experimental data for parameter estimation. Furthermore, calculated activation energies by DFT rely on first principles calculations and consider interaction among intermediates at an atomic level.

Medford et al. [12] used DFT data to construct a mean-field MKM for the formation of ethanol via CH$_x$-CO coupling to illustrate why it is difficult to find transition-metal higher alcohol catalysts. They numerically solved the coupled differential equations with the steady state approximation and included four different
adsorption sites to account for the complex stepped surface. This model suggested that there is a small window of carbon and oxygen binding energies that promotes ethanol formation over methane and methanol. Although no pure metal lies in the required region, alloying and doping of materials can be used to create materials that favor ethanol production. Syngas conversion to ethanol (and higher alcohols) was experimentally and computationally approached by Prieto et al. [13], who used a DFT-based MKM to conclude that a specific Co-Cu alloy was favorable for the production of ethanol and higher alcohols, which was then validated experimentally. This model solved the material balance for surface species following the steady state assumption and considered diffusion steps between different catalyst sites. Methanol production from syngas has also been studied employing a combined DFT-MKM approach. [14] In this study, the kinetic rate equations are solved to steady-state and the results showed qualitative agreement with experiment and provided information about optimum operating conditions for the reactor containing ZnO catalysts.

To our knowledge, the only reported work on DFT-based microkinetic modelling of DRM was the recently published study by Wang et al. [15] that employed nickel and nickel carbide catalysts. In that work, the steady-state approximation was used to solve the reaction rate equations for 8 elementary steps and two equilibrium processes, which included the adsorption of CO and the dissociative adsorption of hydrogen. Though this study offers useful insight into the DRM reaction mechanism, the present work is much more comprehensive in nature and constitutes the first DFT-based MKM for DRM on pyrochlore catalysts.
In our DFT based computational work (Chapter 2), the main reaction pathway for DRM on LRhZ catalysts was discerned from the activation barriers of a proposed reaction network. This qualitative approach to the main reaction pathway is taken to a further level in the present work; specifically, an MKM is developed to obtain quantitative information about DRM product yields at different reaction conditions and with catalysts of varying Rh metal loading. The predictions of the model are compared to experimental data for LRhZ catalyst activity (reported in Chapter 3) and used to explain overall catalyst activity and resistance to fouling as well as the role (active intermediate or spectator) played by different surface species.

2. Theory

2.1 Density functional theory (DFT)

The activation energies for reactions used in the present MKM were previously calculated (Chapter 2) by first principles techniques using the Vienna \textit{ab initio} simulation package (VASP) [16-19], which is based on a plane-wave DFT code. The projector augmented wave (PAW) pseudopotentials were used [20, 21]. The exchange-correlation functional employed was the generalized gradient approximation using the implementation of Perdew, Burke and Ernzerhof (GGA-PBE) [22]. Further details can be found in Chapter 2.

The complete set of elementary steps considered in the reaction network on the (111) plane of the LRhZ catalyst consists of 62 reactions, counting both forward and reverse reactions. Some activation energies were derived from rigorous DFT calculations.
(CI-NEB method), while others were estimated by a Bronsted-Evans-Polanyi (BEP) relation derived from DFT data. A detailed description of the procedure used to calculate individual activation barriers in the reaction network can be found in Chapter 2.

2.2 Microkinetic model (MKM)

To quantitatively describe the extent of reaction and the concentration of intermediate species on the catalyst surface, an MKM for DRM on the (111) plane of the LRhZ pyrochlore catalyst was developed. A batch reactor was modeled and all elementary reaction steps shown in Fig. 4.1 were considered. This reaction network, which accounts for adsorption, desorption and surface reactions, includes a total of 62 reactions. The model was implemented in the package SUNDIALS (SUite of Nonlinear and DIfferential/ ALgebraic equation Solvers), more specifically the CVODE code, that solves initial value problems for ordinary differential equation (ODE) systems [23, 24]. The relative tolerance and absolute tolerance for solved variables were set to $1 \times 10^{-20}$ and $1 \times 10^{-8}$, respectively. Additionally, the material balances for C, H and O atoms inside the reactor allowed for a direct cross-checking of the solver results. Following the time evolution of the variables allowed us to follow the reaction progression as it approached steady-state. This helped verify the meaning of the coverages obtained, which can be an issue when solving for static variables at steady-state conditions.
Fig. 4.1 DRM reaction network on the (111) plane of the LRhZ pyrochlore catalyst.

The pyrochlore MKM for DRM consists of a set of ordinary differential equations (ODEs) corresponding to the net change of surface coverage of particular species with respect to time and a second set of ODEs corresponding to the change of gas phase species with respect to time, also known as the design equation of the batch reactor. It should also be noted that the equations describing adsorption rates differ from those used to describe surface reaction and desorption rates. This is because the driving force and physical nature of these processes are inherently of a different nature; namely, the partial pressure and kinetic energy of the gas phase species combined with the availability of vacant surface sites controls rates of adsorption, while surface concentrations combined with vibrational and electronic states control the rates of surface reaction and desorption processes. In the model, the initial coverage of surface species is set to zero.
Adsorption and desorption processes

Collision theory may be used to estimate rate constants for adsorption processes. In the work reported by Cortright and Dumesic [25], it is shown that for these processes, the rate of adsorption is given by:

\[ r_{f,\text{ads}} = \frac{\omega}{\sqrt{2\pi m_A k_B T}} \exp \left[ -\frac{E_{f,\text{ads}}}{k_B T} \right] \sigma^o(T, \theta) P_{A(g)} \]  

(4.1)

where \( r_{f,\text{ads}} \) is the rate of adsorption with units of coverage (molecules/active site) per time, \( m_A \) is the molecular weight of the adsorbing species \( A \), \( k_B \) is the Boltzmann constant, \( E_{f, \text{ads}} \) is the activation energy for adsorption, \( \omega \) is the area per active site (\( \omega = 1.28 \times 10^{-19} \) m\(^2\) per active site, for the (111) LRhZ plane), \( P_{A(g)} \) is the partial pressure of the adsorbant \( A \), and \( \sigma^o(T, \theta) \) is the sticking probability of \( A \) on the catalyst surface, which is a function of temperature \( T \) and coverage \( \theta \) and represents the probability that a collision with the surface leads to adsorption. In this work, the adsorption processes are assumed to be nearly barrierless and the energy term \( E_{f, \text{ads}} \) was therefore set equal to zero. Furthermore, the sticking probability can be approximated as the coverage of empty sites (\( \theta^{R_h} \) or \( \theta^* \) depending on whether the molecule preferably adsorbs to Rh-containing or non-Rh-containing sites, respectively); this assumption implies setting the value of the rate constant for adsorption as an upper limit. In our study on steady-state isotopic tracing (Chapter 3), it was confirmed that \( CO_2 \) adsorbs and desorbs from the surface; thus, the present model considers the reversible adsorption of reactants. The rate of adsorption for the reactants is expressed as,

\[ r_{1,f} = k_{1,f} \theta^{R_h} P_{CH_4(g)} \]  

(4.2)

\[ k_{1,f} = \frac{\omega}{\sqrt{2\pi m_{CH_4} k_B T}} \]
and desorption rates are assumed to be first order processes with rate constants calculated using an Arrhenius Law expression:

\[ r_{1,r} = k_{1,r} \theta_{CH_4}, \quad k_{1,r} = A \exp \left[ \frac{-E_{des,CH_4}}{k_B T} \right] \]  \hspace{1cm} (4.4)  \\

\[ r_{6,r} = k_{6,r} \theta_{CO_2}, \quad k_{6,r} = A \exp \left[ \frac{-E_{des,CO_2}}{k_B T} \right] \]  \hspace{1cm} (4.5)  

R1 and R6 are steps corresponding to the reversible adsorption of the two reactants CH\(_4\) and CO\(_2\), respectively (see Appendix D). In a similar manner, the reversible desorption of products was also considered. And so, the equilibrium constants for adsorption are defined as,

\[ K_{1,eq} = k_{1,f} / k_{1,r}, \text{ for CH}_4(\text{g}) \text{ physisorption} \]

\[ K_{6,eq} = k_{6,f} / k_{6,r}, \text{ for CO}_2(\text{g}) \text{ adsorption} \]

Analogous definitions of the equilibrium constant were used for the reversible desorption of products.

**Surface reactions**

In the DFT based computational work (Chapter 2), the activation energies were calculated for each of the elementary reaction steps shown in Fig. 4.1. In both works, it was chosen to combine the energetics associated with the diffusion of reactants to neighboring surface sites and reaction processes involving those species into a single ‘full’ reaction as explained in Fig. 4.2. This was done to reduce the number of variables
and equations considered in the model, so as to guarantee its robustness and speed the rate of system convergence.

\[
\begin{align*}
&\text{Surface reaction, } \Delta H_{\text{rxn, surf}}, \Delta E_{\text{act, surf}} \\
&AB^* + * \rightleftharpoons A^* + B^* \rightleftharpoons A^* + B^* \\
&\text{slab 1} \quad \text{slab 2 & 3}
\end{align*}
\]

\[
\begin{align*}
&\text{Surface diffusion, } \Delta H_{\text{diff}}, \Delta E_{\text{act, diff}} \\
&AB^* + * \rightleftharpoons A^* + B^*
\end{align*}
\]

\[
\begin{align*}
&\text{Full reaction, } \Delta H_{\text{rxn}}, \Delta E_{\text{act}} \\
&\text{AB}^* + * \rightleftharpoons A^* + B^*
\end{align*}
\]

Fig. 4.2 Definition of reaction and activation energy based on surface reaction and surface diffusion. ‘A* + B*/slab 1’ means that A and B are placed on the same slab (close to each other but as separate species), the slab is allowed to relax. ‘A* + B*/slab 2 & 3’ means that A and B are placed far from each other, or, in other words, placed in separate slabs and full relaxation is allowed. Further explanation to this approach can be found in Appendix A. The diffusion of two species apart from each other is assumed to be a nearly barrierless process. In the implementation of the model, all \( \Delta E_{\text{act}} \) values were scaled by 0.66 which is the ratio between the reaction energy for DRM from enthalpies of formation and the value calculated from DFT.
Due to similar values for forward and reverse activation energies for some reactions, both forward and reverse reactions are considered in the model. The surface reaction rate constants for forward ($k_f$) and reverse ($k_r$) reactions are calculated as,

$$k_f = A \exp \left[ \frac{-E_{a,f}}{k_B T} \right]$$  \hspace{1cm} (4.6)

$$k_r = A \exp \left[ \frac{-E_{a,r}}{k_B T} \right]$$  \hspace{1cm} (4.7)

where $E_{a,f}$ and $E_{a,r}$ are the activation energies of the forward and reverse reactions, respectively, $A$ is the pre-exponential factor, which is estimated as $k_B T/h$, $k_B$ is the Boltzmann constant, $T$ is absolute temperature, and $h$ is Planck’s constant. For simplicity in the calculation of $A$, entropy contributions were not included. The reaction rate constants for desorption processes are calculated using the Arrhenius expression as in eq. (6).

In the LRhZ pyrochlore MKM, the desorption barriers used for CH$_4$, CO$_2$, H$_2$O, CH$_3$OH, CO and H$_2$ were assumed to be equivalent to the energy needed to desorb from the weakest adsorption site (see Table 4.1) because the adsorbates readily diffuse on the catalyst surface at the high temperatures at which DRM is carried out ($\sim$ 1000 K). For similar reasons, each species in the model is considered to be adsorbed to the site with strongest adsorption energy. CH$_4$ and H$_2$ are considered in the model as species that occupy Rh sites; although strictly speaking, they do not have a formal bond with any surface metal atom due to the lack of dipole on the molecules. A list of the strongest adsorption sites and the corresponding adsorption energies for the species considered in
the model can be found in the Appendix A. Table 4.1 summarizes the species considered in the model and the identified most favorable active sites. The present model distinguishes between two types of sites: the Rh-sites and the non-Rh-sites. The Rh-sites refer to active sites where at least one Rh-atom is involved; whereas, the non-Rh-sites refer to active sites where no Rh-atoms are involved.

**Table 4.1** List of species considered in the microkinetic model.

<table>
<thead>
<tr>
<th>Adsorbed species</th>
<th>On Rh-sites</th>
<th>On non-Rh-sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 CH(_4)(^{\text{Rh}})</td>
<td>12 H(_2)O*</td>
<td></td>
</tr>
<tr>
<td>2 H(_2)(^{\text{Rh}})</td>
<td>13 CH(_3)OH*</td>
<td></td>
</tr>
<tr>
<td>3 CO(^{\text{Rh}})</td>
<td>14 CO(_2)*</td>
<td></td>
</tr>
<tr>
<td>4 CH(_2)O(^{\text{Rh}})</td>
<td>15 CHO(_{\text{H}})*</td>
<td></td>
</tr>
<tr>
<td>5 H(^{\text{Rh}})</td>
<td>16 CH(_3)*</td>
<td></td>
</tr>
<tr>
<td>6 COOH(^{\text{Rh}})</td>
<td>17 CH(_2)OH*</td>
<td></td>
</tr>
<tr>
<td>7 CHO(^{\text{Rh}})</td>
<td>18 CH(_3)O*</td>
<td></td>
</tr>
<tr>
<td>8 CH(_2)(^{\text{Rh}})</td>
<td>19 OH*</td>
<td></td>
</tr>
<tr>
<td>9 CH(^{\text{Rh}})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 O(^{\text{Rh}})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11 C(^{\text{Rh}})</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Gas phase species</th>
<th>Lowest desorption barrier (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 CH(_4)(g)</td>
<td>0.03</td>
</tr>
<tr>
<td>21 CO(_2)(g)</td>
<td>1.02</td>
</tr>
<tr>
<td>22 H(<em>2)O(</em>(g))</td>
<td>0.50</td>
</tr>
<tr>
<td>23 H(_2)(g)</td>
<td>0.02</td>
</tr>
<tr>
<td>24 CO(_(g))</td>
<td>1.62</td>
</tr>
<tr>
<td>25 CH(<em>3)OH(</em>(g))</td>
<td>0.52</td>
</tr>
</tbody>
</table>

**Explicit forms of the rate equations for each intermediate**

The ODEs corresponding to the net change of surface coverage with respect to time have the general form:
\[
\frac{d\theta_i}{dt} = r_{formation \ of \ i} - r_{consumption \ of \ i} = 0 \tag{4.8}
\]

50 surface reactions are considered (counting forward and reverse reactions). A full list of reaction formulas, reaction energies and activation energies can be found in the Appendix D.

The rate of consumption/formation for reactants/products in the gas phase can be calculated as follows,

**Water:**
\[
r_{H_2O(g)} = \frac{d\theta_{H_2O(g)}}{dt} = -k_{30r}\left(\frac{P_{H_2O(g)}\theta^*}{K_{30,eq}\theta_{H_2O}}\right) \tag{4.9}
\]

**Methanol:**
\[
r_{CH_3OH} = \frac{d\theta_{CH_3OH}}{dt} = -k_{34r}\left(\frac{P_{CH_3OH(g)}\theta^*}{K_{34,eq}\theta_{CH_3OH}}\right) \tag{4.10}
\]

**Carbon monoxide:**
\[
r_{CO} = \frac{d\theta_{CO}}{dt} = -k_{33r}\left(\frac{P_{CO(g)}\theta^*}{K_{33,eq}\theta_{CO}}\right) \tag{4.11}
\]

**Hydrogen:**
\[
r_{H_2} = \frac{d\theta_{H_2}}{dt} = -k_{32r}\left(\frac{P_{H_2(g)}\theta^*}{K_{32,eq}\theta_{H_2}}\right) \tag{4.12}
\]

**Methane:**
\[
r_{CH_4} = \frac{d\theta_{CH_4}}{dt} = -k_{1f}\left(\frac{P_{CH_4(g)}\theta^*}{K_{1,eq}} - \frac{\theta_{CH_4}}{K_{1,eq}}\right) \tag{4.13}
\]

**Carbon dioxide:**
\[
r_{CO_2} = \frac{d\theta_{CO_2}}{dt} = -k_{6f}\left(\frac{P_{CO_2(g)}\theta^*}{K_{6,eq}} - \frac{\theta_{CO_2}}{K_{6,eq}}\right) \tag{4.14}
\]

**Reactor design equations**

A batch reactor model was assumed for these calculations, but the same system of equations approximates the reaction behavior of a pocket of fluid traversing a plug flow reactor (PFR) system, where the batch reactor time would be somewhat equivalent to the
plug flow reactor residence time. Throughout the simulated operation of the reactor the moles and therefore the partial pressure of gaseous species vary, and this phenomenon is addressed through the balance of gas phase species inside the reactor using the batch reactor design equation.

The design equation for any batch reactor containing heterogeneous catalysts is:

\[
\frac{dC_A}{dt} = r_{A(g)}
\]

(4.15)

where \( C_A \) is the concentration of gas phase species \( A \) relative to the weight of heterogeneous catalyst present in the reactor (mol A/g-cat), \( t \) is time, and \( r_{A(g)} \) is the molar rate of production of species \( A \) (mol A/g-cat).

In eq. (15), \( r_{A(g)} \) has units of concentration (mol A/g-cat) per time; however, \( r_{A(g)} \) is calculated from the solution of the set of differential equations corresponding to the rate expressions for the surface intermediates (eq. (9)-(14)) that have units of coverage (molecules/active site) per time. Thus,

\[
\frac{dC_A}{dt} = r_{A(g)} \left( \frac{s}{N_A \omega} \right)
\]

(4.16)

where \( s \) is the catalyst surface area per weight of catalyst (8720 m\(^2\)/kg as measured by BET analysis), \( \omega \) is the approximate surface area per active site on the (111) plane (1.28x10\(^{-10}\) m\(^2\)/active site) and \( N_A \) is the Avogadro’s number. \( C_A(g) \) can be expressed as \( n_{A(g)}/m_{cat} \), where \( n_{A(g)} \) is the moles of gas phase species \( A \) and \( m_{cat} \) is the mass of catalyst in the reactor (9 mg, matching data from experiments), see Chapter 3. Given that all of
the catalyst is contained within the simulated batch reactor, one can then express eq. (16) as:

\[
\frac{dn_{A(g)}}{dt} = r_{A(g)} \left( \frac{m_{\text{cat},s}}{N_a,0} \right)
\] (4.17)

A set of 19 ODEs of the form of eq. (8) and a set of 6 ODEs of the form of eq. (17) are solved simultaneously to obtain the time evolution of both surface and gas phase species in the reactor for a specified set of conditions. A full list of the equations used in the model can be found in Appendix D.

**Model assumptions**

The doping percentage (wt\% Rh) of a Rh-substituted pyrochlore can be related to its molecular formula (La\(_2\)Zr\(_{2-x}\)Rh\(_x\)O\(_7\)) as follows:

\[
x = \frac{(\text{wt}\% \text{ Rh})(2M_{\text{La}} + 2M_{\text{Zr}} + 7M_{\text{O}})}{(100M_{\text{Rh}} - (\text{wt}\% \text{ Rh})(M_{\text{Rh}} - M_{\text{Zr}}))}
\] (4.18)

where \(x\) is the subscript in the formula La\(_2\)Zr\(_{2-x}\)Rh\(_x\)O\(_7\), and \(M_{\text{Rh}}, M_{\text{Zr}}, M_{\text{La}}\) and \(M_{\text{O}}\) are the atomic masses for Rh, Zr, La and O, respectively. Derivation of eq. (18) can be found in Appendix D.

Assuming each metal atom is an active site and there is perfect dispersion of metal atoms between the bulk and the surface of the catalyst, the fraction of Rh-sites (\(\theta^{\text{Rh}}\)) on the surface of the pyrochlore is calculated as follows,

\[
\text{Fraction of Rh-sites} \equiv \theta^{\text{Rh}} = \frac{x}{2 + (2 - x) + x}
\] (4.19)

and for the non-Rh-sites,

\[
\text{Fraction of non-Rh-sites} \equiv \theta^{\text{non-Rh}} = 1 - \theta^{\text{Rh}}
\] (4.20)
Therefore, for a 2 wt% substituted lanthanum zirconate pyrochlore catalyst (La$_{2}$Zr$_{1.888}$Rh$_{0.112}$O$_{7}$): x = 0.112 and $\theta^{\text{Rh}} = 0.028$.

Based on Table 4.1, the coverage of vacant Rh-sites can be calculated as:

$$\theta^{\text{Rh}} = \theta^{\text{Rh}} - \left( \theta_{\text{CH}_4} + \theta_{\text{H}_2} + \theta_{\text{CO}} + \theta_{\text{CH}_3} + \theta_{\text{H}} + \theta_{\text{COOH}} + \theta_{\text{CHO}} + \theta_{\text{CH}_2} + \theta_{\text{CH}} + \theta_{\text{O}} + \theta_{\text{C}} \right)$$

and the coverage of vacant non-Rh-sites as,

$$\theta^{\text{non-Rh}} = \theta^{\text{non-Rh}} - (\theta_{\text{H}_2\text{O}} + \theta_{\text{CH}_3\text{OH}} + \theta_{\text{CO}_2} + \theta_{\text{CHOH}} + \theta_{\text{CH}_3} + \theta_{\text{CH}_2\text{OH}} + \theta_{\text{CH}_4\text{OH}} + \theta_{\text{OH}})$$

**Transition from plug-flow reactor used in experiments to the modeled batch reactor**

The herein described batch reactor model with a perfectly mixed gas phase provides the opportunity to consider a broad set of surface intermediates and reactions and still achieve a robust model without having to account for the fluid mixing and diffusion phenomena that are essential to the performance of flow reactor systems.

The initial moles of reactants inside the modeled batch reactor were calculated as follows,

$$n_{\text{CH}_4,0} = n_{\text{CO}_2,0} = \nu_{\text{PFR}} \tau P_{\text{line}} / RT_{\text{room}}$$

where $n_{\text{CH}_4,0}$ and $n_{\text{CO}_2,0}$ are the initial moles of CH$_4$ or CO$_2$ in the reactor, respectively. $n_{\text{CH}_4,0}$ equals $n_{\text{CO}_2,0}$ because the reactive system used was fed with an equimolar mixture of CH$_4$ and CO$_2$. $\nu_{\text{PFR}}$ is the volumetric flow of CH$_4$ (or CO$_2$) fed to the PFR in the experiments, $\tau$ is the surface residence time at the reaction temperature found through Steady-State Isotopic Transient Kinetic Analysis (SSITKA), see Chapter 3, $P_{\text{line}}$ is the
pressure in the line feeding the reactant, $R$ is the gas constant and $T_{room}$ is the room temperature since the flowmeters were placed far from the furnace surrounding the reactor. For a more detailed description of the reactive system set-up refer to Chapter 3.

The volume of the modeled batch reactor ($V_{batch}$) was calculated as follows,

$$V_{batch} = (n_{CH_4,0} + n_{CO_2,0} + n_{\text{Inert},0}) \cdot \frac{RT_{\text{reactor}}}{P_{\text{reactor}}},$$  \hspace{1cm} (4.24)

and

$$n_{\text{Inert},0} = \frac{\upsilon_{\text{PFR,Inert}} \cdot \tau \cdot P_{\text{line}}}{RT_{\text{room}}}$$  \hspace{1cm} (4.25)

where $n_{\text{Inert},0}$ is the moles of the inert carrier gas, $T_{\text{reactor}}$ is the temperature inside the reactor and $P_{\text{reactor}}$ is the pressure inside the reactor. $P_{\text{line}}$ equals $P_{\text{reactor}}$ for the reactive system since the back-pressure regulator in the experimental set-up was placed after the reactor.

3. **Results and Discussion**

3.1 **Validation of the model**

The LRhZ pyrochlore MKM was able to reproduce experimental trends remarkably well. In the reaction network, methanol and water were included as possible byproducts, despite methanol never being observed experimentally and water only being observed in small amounts. Analysis of predicted outcomes shows that the MKM model also does not favor the generation of these two byproducts, which corroborates the validity of the employed DFT data. As seen in Fig. 4.3, the trends in CO$_2$ and CH$_4$ conversion are properly described by the LRhZ pyrochlore MKM; furthermore, CO$_2$ conversion is higher than CH$_4$ conversion at each temperature, which suggests that the model correctly describes the propensity of the catalyst to activate the reverse water gas-
shift reaction (RWGS), which has been shown to be a competing reaction at low temperatures [4] (see Chapter 3).

The product concentrations predicted by the MKM model generally agreed with the experimental data after steady state had been achieved within the reactor. To ensure that steady state was achieved, species concentrations in the batch reactor were modeled for at least $1 \times 10^7$ s; therefore, all data from the MKM reported in this work are at a reaction time of $1 \times 10^7$ s. At many of the system conditions studied, steady state was reached at reaction times approaching 1,000 s (see later discussion), which is significantly longer than is required experimentally (normally less than 50 s). This long time required to achieve steady state suggests that all of the reported rate constants are systematically too low (i.e., activation energies are too high), but that the error is equal amongst all rate constants. These somewhat high activation barriers arise from the merging of reaction and diffusion processes as explained in Fig. 4.2. Greater activation energies make the reaction more difficult to occur and therefore delay its development; in addition, in a closed batch reactor with a clean surface catalyst (as modeled), the species must populate the surface and the driving force for development of DRM, the partial pressure of reactants, is reduced; hence increasing the required residence time.
Fig. 4.3 Conversion of reactants for DRM over 2 wt% LRhZ at 1.1 atm. Comparison between MKM results and experimental data (from Chapter 3) at different temperatures (450, 500, 650 and 800 °C). Equimolar feed (CO₂ and CH₄) and GHSV = 65,333 cm³/gcat/h.

The H₂ to CO molar ratio is a key parameter to evaluate reaction performance, as the closer this ratio is to unity, the higher energetic power has the syngas mixture. This product ratio was well described by the microkinetic model (see Fig. 4.4), and the decrease in this ratio at lower temperatures is consistent with the coexistence of the RWGS reaction that the model addresses.

Fig. 4.4 H₂ to CO molar ratio for DRM over 2 wt% LRhZ at 1.1 atm. Comparison between MKM results and experimental data (from Chapter 3) at different temperatures (450, 500, 650 and 800 °C). Equimolar feed (CO₂ and CH₄) and GHSV = 65,333 cm³/gcat/h.
3.2 Pressure influence on reaction performance

Predictions from our model show how an increase in the reactor pressure has little impact on the obtained H₂ to CO ratio, but is detrimental to the overall conversion of reactants (see Fig. 4.5). Jafarbegloo et al. [26] reported in their thermodynamic equilibrium analysis of dry reforming of methane that equilibrium conversions for CH₄ and CO₂ decrease monotonically when increasing pressure from 1 to 9.9 atm, at 800 °C using a stoichiometric feed, which is the same trend obtained from the MKM as shown in Fig. 4.5. However, their studies indicated that the H₂ to CO ratio decreases from 0.94 to 0.77 with increasing pressure (from 1 to 9.9 atm) at 800 °C and equimolar feed, suggesting an increase in the extent of RWGS occurring, whereas the MKM data presented here show a somewhat increasing H₂ to CO ratio over a similar range of pressures, see Fig. 4.5.

![Fig. 4.5](image_url)  
*Fig. 4.5 Pressure influence on conversion of reactants and H₂ to CO ratio for DRM over 2 wt% LRhZ at 800 °C.*
DRM is a reaction where there is a positive change in the total number of moles with reaction \((\text{CH}_4+\text{CO}_2 \rightleftharpoons 2\text{CO}+2\text{H}_2)\), whereas the competing reaction, RWGS \((\text{H}_2+\text{CO}_2 \rightleftharpoons \text{CO}+\text{H}_2\text{O})\), is net neutral in terms of a change in the number of total moles with reaction. At relatively high pressures and temperatures, it is more favorable for the \(\text{H}_2\) generated through DRM to undergo the reverse DRM reaction yielding \(\text{CH}_4\) and \(\text{CO}_2\) as compared to hydrogen being consumed by the RWGS reaction, due to there being a decrease in the total number of moles with DRM. This leads to a reduction in RWGS rates and is why the present MKM predicts a slight increase in the \(\text{H}_2\) to CO ratio with increasing pressure, as shown in Fig. 4.5. The predicted increase in the \(\text{H}_2/\text{CO}\) ratio is slight because the total change in system pressure is also relatively small. Calculations by Jafarbegloo et al. [26] use a thermodynamic analysis of DRM and RWGS that explicitly accounts for equilibrium system pressure effects, but their model does not include pressure effects on the reaction kinetics, specifically related to adsorption and desorption rates.

### 3.3 Rh-doping percentage influence on reaction performance

At high temperatures (800 °C), the doping percentage of Rh in the pyrochlore catalyst has only a minor influence on the reaction performance, as high temperatures favor surface diffusion of intermediates and thus available Rh atoms on the surface are easily accessed. At moderate temperatures (650 °C), however, the quantity of Rh atoms at the catalyst surface has a greater impact on catalyst performance due to the decreased mobility of surface intermediates, see Fig. 4.6. Thus, at surface Rh loadings below a specific value the reaction performance drops precipitously. From our calculations, the
DRM performance at 650°C and 1.1 atm drops significantly with Rh doping levels less than approximately 0.35 wt%; nevertheless, further experimental data are required to verify the accuracy of the model as it relates to predictions of the minimum required Rh doping percentage.

**Fig. 4.6** Influence of Rh-doping percentage on the conversion of CO₂ and CH₄ reactants and H₂ to CO ratio for DRM over LRhZ pyrochlore catalysts at 1.1 atm and 800 °C (upper graph) and 650 °C (lower graph).

### 3.4 Reaction mechanism with respect to time

The MKM presented in this work describes the reaction network presented in Fig. 4.7.
When the reaction mechanism is qualitatively described by effective activation energies for combined surface diffusion and reaction processes, the resulting main reaction pathway has two possible routes for CH\textsubscript{4} dehydrogenation/oxygenation to form CO as shown in Fig. 4.8. The branch that leads to CH formation has a slightly lower activation energy (ΔE\textsubscript{act,f} = 2.53 eV) than the branch that leads to CH\textsubscript{2}O formation (ΔE\textsubscript{act,f} = 2.88 eV), nonetheless, once CH is formed, it encounters very high activation barriers to form CO\textsubscript{(g)} (either 3.37 eV → 3.31 eV → 1.62 eV through one route, or 4.01 eV → 2.40 eV → 1.62 eV through an alternate route). On the other hand, if CH\textsubscript{2}O is formed the activation barriers encountered to form CO\textsubscript{(g)} are considerably lower (1.37 eV → 2.40 eV → 1.62 eV). Thus, CH\textsubscript{4} dehydrogenation/oxygenation is proposed to mainly proceed as: CH\textsubscript{4(g)} → CH\textsubscript{4}* → CH\textsubscript{3}* → CH\textsubscript{2}* → CH\textsubscript{2}O* → CHO* → CO* → CO\textsubscript{(g)}.
CO₂ dissociation proceeds mainly through direct dissociation into adsorbed CO and atomic oxygen, with a dissociation barrier of 1.26 eV. Nonetheless, H-induced CO₂ decomposition may coexist since the barriers involved in this processes are also low.

**Fig. 4.8** Main reaction routes for DRM on the (111) plane of the LRhZ pyrochlore. The values above, below and next to the arrows are the activation energies in eV, and the small arrows next to these values indicate what direction each activation energy corresponds to. Reprinted from Chapter 2.

From this qualitative analysis of the CH₄ dehydrogenation, one can conclude that CH is formed on the surface but acts rather as a spectator, especially on Rh containing sites, since further dehydrogenation and later oxygenation involves high activation barriers. Results from the LRhZ pyrochlore MKM support the existence of CH on the catalyst surface as a spectator as shown in Fig. 4.9. In fact, CH possesses the greatest surface coverage on Rh-sites and remains adsorbed on the surface even after steady state is reached even though it does not belong to the main reaction pathway. Similarly, some atomic carbon is deposited on the catalyst surface, where it acts as a spectator. However, the observed rate of carbon deposition is significantly slower than the rate of DRM product formation, which helps explain why LRhZ pyrochlore catalysts shows very low carbon deposition when used for DRM.
In a previous work by Pakhare et al. [5], FTIR studies were performed over LRhZ pyrochlores to distinguish between the reactive oxycarbonate species from the spectator ones. In their experiment, a pretreated pyrochlore catalyst was initially dosed with CO₂, then the catalyst was exposed to 10 CH₄/He pulses. After the 10ᵗʰ pulse, CO₂ was re-adsorbed to study the regrowth of any oxycarbonate species. When comparing the FTIR spectra after CO₂ adsorption, after the 10ᵗʰ CH₄ pulse and after readsorbing CO₂, no C-H stretching bands were observed at about 2800 cm⁻¹ for the 2 and 5 wt% LRhZ pyrochlores, suggesting the dissociative adsorption of CH₄. In the present model, however, CH is suggested as a spectator. The difference between the present findings and the observation in the experiments by Pakhare et al. [5] can be explained through DFT-data reported in Chapter 2. The preferred adsorption site for CH on the plane (111), which is the LRhZ pyrochlore surface most catalytically active for DRM, is a Rh-containing site, more specifically, the 3-fold Rh-Zr-Zr site. Due to the low Rh substitution (2 and 5 wt%) in the LRhZ pyrochlore used in the experiments by Pakhare et al. [5], the CH coverage on the overall catalyst surface is expected to be very low, so that the intensity of the IR mode for C-H bond stretching is negligible when compared to bands associated with species adsorbed on non-Rh sites, such as adsorbed CO₂ (see Chapter 2). For instance, in our model, at 800 °C and 1.1 atm, the surface coverage of CH on the 2 wt% LRhZ pyrochlore is no greater than 2.6 % (see Fig. 4.9). Additionally, the predicted surface coverage for select carbonate species observed in the FTIR studies by Pakhare et al. [5], where CO₂ rich feed gas was present, are not appreciable in our MKM studies of DRM because the model included a stoichiometric feed containing CH₄ and
CO₂, and the experimentally observed carbonate species that are involved in the DRM reaction are quickly consumed when methane is also present. Other spectator carbonate species observed by FTIR are not predicted by the present MKM model as a result of only lowest energy pathway reactions being included in the model.

In Fig. 4.9, a maximum in CH coverage corresponds to a minimum in O coverage, since high CH coverage indicates that the reaction is favored through the CH₂O intermediate and thus more oxygen is consumed to oxygenate CH₂. In addition, the disappearance of CH₃ and CH₂ towards the steady-state conditions inside the modeled reactor suggests that these two species belong to the low surface residence time CH₄ dehydrogenation pathway shown in Fig. 4.8.

The time evolution of surface and gas phase (see Appendix D) species supports the main reaction pathway deduced from the activation energies of the elementary reaction steps and clearly shows the role played by intermediates along the DRM pathway. Results from the MKM model clearly show that the existence of specific surface intermediates does not necessarily mean that those intermediates belong to the main reaction pathway. Thus, the present work evidences the importance of advanced experimental surface techniques that look at the time evolution of intermediates on the surface, such as combined FTIR/SSITKA approaches.
The presented DFT-based microkinetic model (MKM) accurately accounts for the collective behavior of a complex set of reactions (62 reactions), provides the time evolution of both gas phase species and surface intermediates and has multiple tunable reaction conditions. The model provides a generally accurate description of the trends in reactant (CO\textsubscript{2} and CH\textsubscript{4}) conversion with temperature, as well the change in H\textsubscript{2} to CO ratio with temperature. This shows that the MKM can successfully account for the partial...
inhibition of the dry reforming reaction due to the coexistence of the competing reverse water gas shift reaction, which produces water. Furthermore, the model did not suggest production of methanol, as observed experimentally, even though the reaction network, upon which the model equations were laid out, provided a theoretical route for methanol formation. This allowed cross-checking of the reliability of the model and validates the DFT data found in Chapter 2 against experimental data (Chapter 3).

Trends in reactant conversion with increases in pressure were well described by the model when compared to thermodynamic data [26], and the analysis of the influence of the Rh-doping percentage on the reaction performance suggests a critical value, which sets the ground for future experimental research on the optimal surface loading of the Rh dopant.

The main pathway for CH₄ dehydrogenation/oxygenation is explained in a time scale by the MKM: CH₄(g) → CH₄* → CH₃* → CH₂* → CH₂O* → CHO* → CO* → CO(g); as well as the CO₂ decomposition pathway: CO₂(g) → CO₂* → CO* → CO(g) or CO₂(g) → CO₂* → COOH* → CO* → CO(g). CH* is identified as the primary reaction spectator, followed by atomic carbon, but in considerably less quantities, which explains the low rates of carbon deposition observed experimentally with this catalyst. This detailed understanding of species evolution on the surface is as yet inaccessible through experimental techniques and therefore emphasizes the significance of the present work in educating future pyrochlore catalyst optimization efforts.
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References


CHAPTER FIVE
OPTIMIZATION OF PYROCHLORE CATALYSTS FOR DRY REFORMING OF METHANE: A COMPUTATIONALLY GUIDED EXPERIMENTAL WORK

Abstract

The advent of advanced drilling technologies has significantly increased methane production rates world-wide, and further increases are possible if cost effective technologies can be developed to remove or make use of CO$_2$ species present in many untapped natural gas deposits. Therefore, the dry reforming of methane (DRM) has received special attention as it provides a route for the production of fuels and chemicals via syngas, by employing methane and CO$_2$ as feedstocks. The trial and error optimization of catalysts for DRM has thus far yielded a modicum of promising catalysts. For example, Rhodium-substituted lanthanum zirconate pyrochlores (LRhZ) have been shown to exhibit high catalytic activity and long-term thermal stability for DRM. To further develop lower cost DRM pyrochlore catalysts with even greater catalyst lifetimes an \textit{in silico} optimization study was undertaken that build upon our density functional theory and microkinetic modeling studies of the Rh-doped pyrochlore materials. Computational analysis of one of the rate determining steps (the CHO dehydrogenation reaction, which lies on the favored CH$_4$ dehydrogenation pathway) suggested Pd as an effective co-dopant to reduce the activation barrier of this step. Thus, a bimetallic Rh-Pd co-doped lanthanum zirconate pyrochlore (Rh-Pd-LZ) was synthesized, characterized and
tested for DRM activity. The Rh-Pd-LZ catalyst exhibited high conversions for DRM and H₂ to CO product ratios close to unity at high temperatures, which evidences the fostering of DRM through reduced surface residence times.

1. **Introduction**

The production of liquid fuels from methane and the energy efficient use of natural or biogas gas feedstocks that are rich in CO₂ have been driving forces for increased efforts to develop improved dry reforming processes, which reacts methane and CO₂ to produce syngas. Syngas is a mixture of H₂ and CO, which has been used for electricity and heat generation, and has proven to be a versatile feedstock for many methane gas-to-liquid processes that yield chemicals and fuels more easily shipped via pipeline. [1]

In recent years, the low-cost shale gas has brought renewed attention to traditional syngas production from methane. There are currently several technologies available for syngas production from methane, including Steam Methane Reforming (SMR), Partial Oxidation (POX), Autothermal Reforming (ATR) and Dry Reforming of Methane (DRM). Dry reforming of methane is the only route that has neither significant water supply nor purified oxygen supply dependence, and the reactants involved are two greenhouse gases. The overall DRM reaction (CH₄ + CO₂ ⇌ 2CO + 2H₂) is endothermic with a heat of reaction (ΔH°) equal to +247.4 kJ/mol.

Although DRM using CO₂ has long been considered a viable method for converting methane from geologic or biological sources into syngas, the high
temperatures required for the reaction (~ 1000 K) have made it very difficult to find catalysts that exhibit high activity for extended periods. However, recent efforts by experimentalists have shown that pyrochlore materials are of particular interest because of their exceptional thermal stability and high selectivity to desired methane conversion products [2-4].

Pyrochlores are crystalline oxides have a general formula of $A_2B_2O_7$, where $A$ and $B$ represent rare-earth and transition metals, respectively. Early experiments indicated that pyrochlores were active for DRM, but the tested catalysts exhibited poor long term stability [5, 6]; whereas, more recent data have shown that the $La_2Zr_2O_7$ (LZ) is a pyrochlore catalyst with good long term stability [7-9], and it can accept a wide variety of metal substitutions into the lattice. Thus, efforts have been made to tailor its catalytic properties by incorporating select transition metals into the lattice [2, 3, 10]. Specifically, the use of Rh as a dopant has shown to enhance pyrochlore catalytic performance for DRM [3], while inhibiting deactivation processes caused by carbon deposition [2]. Most of the initial improvements to this catalyst were guided by experimental trial and error, but more recent ab initio computational work (see Chapter 2), which included a detailed analysis of the DRM reaction mechanism on Rh doped pyrochlore surfaces, has provided a computationally guided approach for optimizing these materials.

Similar to our previous pyrochlore DRM work, others have used computational efforts to describe the reaction mechanism for methane reforming but on non-pyrochlore catalyst surfaces. For example, Wang et al. [11] studied the CO$_2$ reforming of CH$_4$ on Ni (111) and concluded that CH dissociation was not a part of the main reaction pathway; in
addition, they attributed carbon deposition to the Boudouard back reaction \(2\text{CO} = \text{C}_{\text{ads}} + \text{CO}_2\) and concluded that the \(\text{CH}_4\) dissociation to \(\text{CH}_3\) and \(\text{H}\) was the rate-limiting step and that strong \(\text{CO}\) adsorption hinders subsequent reactions and promotes carbon deposition. In other work [12], DFT methods were used to analyze the activity of flat and stepped Ni surfaces for dry reforming, finding that flat surfaces are more active; furthermore, it was concluded that metallic nickel catalysts are more active than nickel carbide catalysts; thus, the \textit{in-situ} formation of Ni-carbide phases during reaction will reduce overall catalyst activity. Wang et al. [13] concluded that the bimetallic Ni-Cu catalyst is an active carbon-tolerant catalyst for steam reforming of methane for solid-oxide fuel cells. Nonetheless, the transition to use these computational findings on the successful synthesis and testing of a better catalyst is scarce.

The work by Nikolla et al. [14] describes the use of DFT calculations to study carbon deposition on Ni surfaces during steam reforming. This effort also helped to identify a Sn/Ni alloy as a catalyst with enhanced resistance to carbon poisoning as compared to pure Ni in the steam reforming of methane, propane and isooctane at moderate steam-to-carbon ratios. Additionally, Mei et al. [15] presented a combined experimental and theoretical work on MgAl\(_2\)O\(_4\)-supported Rh and Ir catalysts for methane steam reforming in which DFT calculations were used to probe the relationship between structure and reactivity and brought deeper insight into the reaction mechanism and the role of Rh and Ir.

The catalyst synthesized by collaborators, a 2 wt\% rhodium-substituted lanthanum zirconate pyrochlore (LRhZ) [3, 4], showed catalytic activity towards DRM
and long term thermal stability. For these reasons, a computational effort by our group sought to ascertain the reaction mechanism for DRM on this surface using a quantum mechanical approach (see Chapter 2). This computational work elucidated the plane (111) of the LRhZ as the most catalytically active for DRM, and also pointed out the CHO dehydrogenation ($\text{CHO}^* \rightleftharpoons \text{CO}^* + \text{H}^*$) as one of the two rate limiting steps. In the past, other authors using DFT methods have also reported the formyl species (CHO) as one of the key intermediates for CO$_2$ reforming of methane on Ni [11] and also for steam methane reforming on Rh [16].

To our knowledge, the work presented in Chapter 2 is the first to describe the reaction mechanism for DRM on pyrochlore surfaces. As a consequence, the present work is the first to optimize DRM catalysts based on these DFT calculations. This work describes the synthesis procedure followed to obtain the optimized catalyst suggested by 

*ab initio* calculations and presents the testing of this catalyst against a related catalyst provided by collaborators, a LRhZ pyrochlore [3, 4].

2. Experimental and computational methods

2.1 Catalyst synthesis

Computational results (discussed later) suggested the synthesis of two catalysts: the 1.94 wt% Rh-doped lanthanum zirconate ($\text{La}_2\text{Zr}_{1.89}\text{Rh}_{0.11}\text{O}_7$ or Rh-LZ) and the bimetal doped 2 wt% Rh, 0.5 wt% Pd lanthanum zirconate ($\text{La}_2\text{Zr}_{1.86}\text{Rh}_{0.11}\text{Pd}_{0.03}\text{O}_7$ or Rh-Pd-LZ). These two catalysts correspond to two optimization stages of the 2 wt% Rh-doped lanthanum zirconate synthesized by collaborators (LRhZ) [3, 4]. The
pyrochlore catalysts were prepared by the glycine-nitrate combustion method (GNC) [17-19], where glycine was used as the ignition promoter [20-23]. All chemicals, including ZrO(NO$_3$)$_2$·6H$_2$O (99%, Aldrich), La(NO$_3$)$_3$·6H$_2$O (99.99 %, Aldrich), Rh(NO$_3$)$_3$·xH$_2$O (36% Rh, Aldrich), Pd(NO$_3$)$_2$·xH$_2$O (39.89 % Pd, 99.9 % metal basis, Alfa Aesar) and glycine (H$_2$NCH$_2$CO$_2$H, crystalline/certified, Fisher), were used as received.

Initially, separate aqueous solutions of each of the required metal nitrates were prepared using deionized water, with the final metal concentration of each solution being approximately one molar (cation basis). After the separate solutions were mixed and stirred, glycine was added to the combined aqueous solution, so that the final molar ratio of nitrate anion to glycine molar ratio (NO$_3$ to RNH$_2$ molar ratio) was one [17]. The solution was then heated to 130 °C and the temperature was maintained at that value until excess water evaporated and a viscous gel was obtained. The resulting gel was then heated to approximately 270 °C, which is the temperature at which the gel self-ignites, producing a voluminous powder. To contain the powder inside the columnar glass reactor, a stainless steel mesh (SST 316, 250x250) was used.

The powder was calcined at 700 °C for 10 h in air to oxidatively remove all remaining carbon deposits. Afterwards, the material was heat-treated under argon at 1000 °C for 10 h, which allowed for the mixture to reorganize into a pyrochlore crystal structure.

The overall Rh-LZ synthesis reaction is given by:
0.11Rh(NO_3)_3+1.89ZrO(NO_3)_2+2La(NO_3)_3+YNH_2CH_2COOH+ZO_2 \rightarrow \\
La_{2}Zr_{1.89}Rh_{0.11}O_{7}+\left(\frac{Y+10.11}{2}\right)N_2+(2Y)CO_2+\left(\frac{5Y}{2}\right)H_2O

where, Y = (25.22+2Z)/4.5

For stoichiometric combustion (Z = 0), Y = 5.60; and thus, the NO_3 to NH_2 ratio used in the synthesis provides for a fuel-rich combustion.

The overall synthesis reaction for Rh-Pd-LZ materials is given by:

0.03Pd(NO_3)_2+0.11Rh(NO_3)_3+1.86ZrO(NO_3)_2+2La(NO_3)_3+YNH_2CH_2COOH+ZO_2 \rightarrow \\
La_{2}Zr_{1.86}Rh_{0.11}Pd_{0.03}O_{7}+\left(\frac{Y+10.11}{2}\right)N_2+(2Y)CO_2+\left(\frac{5Y}{2}\right)H_2O

where, Y = (25.19+2Z)/4.5. Again, the NO_3 to NH_2 ratio used in this synthesis provides for a fuel-rich combustion.

The catalysts synthesized in this work (Rh-LZ and Rh-Pd-LZ) were compared to a similar catalyst provided by collaborators, the 2 wt% Rh substituted lanthanum zirconate (LRhZ). The LRhZ pyrochlore was synthesized by the modified Pechini Method [18] using La, Zr and Rh nitrates as metal precursors. The detailed synthesis procedure has been reported earlier [4].

### 2.2 Catalyst characterization

**Powder X-ray Diffraction (PXD)**

The crystal structure of the pyrochlore catalyst was confirmed by means of PXD. Spectra were obtained on a Rigaku Ultima IV X-ray diffractometer. The Cu Kα radiation (λ = 1.5418 Å) used for analysis was generated using power settings of 40 kV and 40 mA. The spectra were recorded at 2θ between 20° and 80° with a scan speed of 1 °/min. The step width was 0.02 °. The incident and receiving slits were both set to 2/3 °. PXD
spectra were collected of the catalyst materials before and after the heat treatment step described in the synthesis procedure.

**Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDX)**

Catalyst morphology and the local dispersion of Rh and Pd on the surface were analyzed by SEM and EDX techniques, respectively. Images were collected on a Hitachi HD2000 Scanning Transmission Electron Microscope equipped with a field emission source and resolution of 0.24 nm at 200 kV.

**Temperature Programmed Reduction (TPR)**

Temperature Programmed Reduction measurements were completed by collaborators at the Pyrochem Catalyst Company.

**Brunauer–Emmett–Teller (BET) method**

The BET surface area of the catalyst was analyzed by N\textsubscript{2} physisorption using a Micromeritics ASAP 2020 system. Prior to analysis, all catalyst samples (0.2943 g of LRhZ, 0.1208 g of Rh-LZ and 0.2974 g of Rh-Pd-LZ) were dried and degassed under vacuum (10^{-3} mmHg) at 90 °C for 10 h. Additionally, samples were heated at a rate of 10°C/min to 300 °C and the temperature maintained at that value for 1 h before N\textsubscript{2} physisorption experiments were conducted at 77 K.

**Thermogravimetric Analysis (TGA)**

Carbon deposition for all catalysts was analyzed after 4 h time-on-stream at 800 °C, 1.1 atm and GHSV = 58800 cm\textsuperscript{3}/g\textsubscript{cat}/h. Measurements were performed in the
instrument TGA Q5000. All experiments were run under air atmosphere and the temperature was increased from room temperature to 1000 °C at a rate of 2 °C/min.

2.3 Activity measurements

Reactor set-up

DRM catalytic measurements were carried out in a straight tube quartz microreactor (4 mm i.d., 6.35 mm o.d.). A 10 mg catalyst sample was introduced in the reactor and held in place using quartz wool above and below the catalyst bed. The quartz wool supporting the catalyst powder was held in place by quartz beads (2 mm diameter x 2 mm long) that filled the lower portions of the reactor tube. The beads also helped to reduce gas holdup in the reactor tube, which is important for transient kinetic experiments. Quartz wool was also placed around the reactor tube at the top of the furnace to limit the formation of thermal gradients within the reactor tube. Reactor heating was provided by an external furnace (Applied Test Systems, Inc.) equipped with a programmable temperature controller. The temperature in the catalyst bed was appropriately calibrated with respect to the set point value in the temperature controller of the furnace, but no thermocouple was mounted inside the reactor during catalyst testing, so as to avoid undesired catalytic activity by the thermocouple sheath material. The catalyst inside the reactor was placed at the same height with respect to the bottom of the furnace for each run, so that the conclusions drawn from measurements are not biased by any small thermal gradients inside the furnace.
Catalyst reduction

All catalyst samples were first reduced at 800 °C and 1.1 atm using a 26.9 % (v/v) H₂ (UHP) in Helium (industrial grade) gas mixture flowing at a rate of 73.9 cm³/min for 1 hour (after heating to that temperature at a rate of approximately 35°C/min). Then, the reactor and catalyst were purged for 15-20 min with He at 800 °C, 1.1 atm and a flow rate of 64.8 cm³/min of He. Immediately after the He flush, the DRM reaction is conducted at 800°C and 1.1 atm. Steady state is reached before recording any data concerning the activity of the catalyst, since the reaction has a mild reducing effect on the surface. The total flow rate of the feed to the reactor was kept constant in all experiments at 74.6 cm³/min (measured at 1.1 atm and 25 °C). The component feed gas flow rates were 64.8 cm³/min of He (industrial grade, Airgas), 4.9 cm³/min of CH₄ (instrument grade, Airgas) and 4.9 cm³/min of CO₂ (instrument grade, National Specialty Gases), all measured at 1.1 atm and 25 °C, to give a total gas hourly space velocity (GHSV) of 58,800 cm³/gcat/h.

Catalyst performance

The exit gases from the reactor were fed through a 1/16-inch (316 SS) capillary tube to the mass spectrometer (MS) (Pfeiffer Vacuum) for analysis. The MS was connected to a computer for high-speed continuous data acquisition using Balzers Quadstar 422 software (v. 6.0). To avoid water condensation downstream of the reactor, the tubing between the reactor and MS analyzer were maintained at 120 °C and the inlet to the mass spectrometer was held at 70 °C. A precision back pressure regulator (Tescom) was used to maintain pressure in the reactor at 1.1 atm.
The product ions masses \( m/z \) followed with respect to time in the mass spectrometer were 44 (CO\(_2\)), 28 (CO), 18 (H\(_2\)O), 15 (CH\(_4\)) and 2 (H\(_2\)). For the measurement of CO \( m/z=28 \) in the presence of CO\(_2\) \( m/z=44 \), the contribution of CO\(_2\) to the mass \( m/z \) 28 signal was determined from calibration studies using test gases containing known concentrations of CO\(_2\) in He. The reported performance data in this study are at steady state conditions, and the recorded data at steady state were averaged over a 5 min time interval to reduce the influence of noise in the reported signal.

2.4 Computational details

First principles calculations were performed employing the Vienna \textit{ab initio} simulation package (VASP) [24-27], which is based on a plane-wave density functional theory (DFT) code. The projector augmented wave (PAW) pseudopotentials were used to describe the interaction between the core and valence electrons [28, 29]. The exchange correlation functional employed for all calculations was the generalized gradient approximation using the implementation of Perdew, Burke and Ernzerhof (GGA-PBE) [30]. A plane wave cutoff of 500 eV was used for all calculations, and all geometries were optimized until the forces on the atoms were less than 0.03 eV/Å. During electronic optimization, the energy was converged to within \( 1 \times 10^{-7} \) eV/atom; however, for some special cases where force convergence was difficult to obtain, the electronic iterations were further converged to within \( 1 \times 10^{-9} \) eV. A Monkhorst-Pack k-point sampling scheme [31] (2x2x2 for bulk, 2x2x1 for surfaces and 1x1x1 for isolated species) was used and electronic occupancies were determined using the Methfessel-Paxton scheme [32],

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with an energy smearing (σ) of 0.1 eV. All calculations were spin-polarized. Finally, the lattice parameter was set to 10.88 Å.

In Chapter 2, a Brønsted-Evans-Polanyi (BEP) relationship was developed to relate the reaction and activation energies of elementary steps occurring on the pyrochlore surface. To build that relationship, activation energies were calculated for selected elementary reactions using the climbing image nudged elastic band method (CI-NEB) via scripts developed previously in the Henkelman Research Group at the University of Texas at Austin [33, 34]. Further details can be found in Chapter 2. Due to the heterogeneity of the surface, studies of optimum vacuum height and slab thickness were also carefully performed and are reported in Chapter 2.

In Chapter 2, CH₂* oxygenation to CH₂O* and CHO* dehydrogenation to CO* were identified as the two rate-determining steps for DRM on the LRhZ pyrochlore, since they presented the two highest activation barriers in the main reaction pathway, 2.88 and 2.40 eV, respectively. In the present chapter, DFT simulations were used to evaluate the energetics of one of the two rate-limiting reaction steps for DRM (CHO* → CO* + H*) on multiple pyrochlore surfaces containing different metals in the lattice. In Chapter 2, full relaxation of CHO* on a (111) pyrochlore slab was performed and the most stable adsorbate structure was found (3-fold Rh-Zr-Zr). In this work, the Zr-atom adjacent to the Rh-atom was replaced by a series of co-dopants (Ru, Pd, Os, Ir and Pt) using criteria discuss later in this text. Structure optimization calculations were performed for the CHO* intermediate while holding fixed the catalyst atoms in the lowest energy positions found when only Rh was doping the surface. In a different set of simulations, the CHO*
was removed from the surface and replaced by CO* and H* (placed in their favored adsorption sites when only Rh doped the surface, see Chapter 2). Again, structure optimization calculations were performed for the CO* and H* intermediates while holding fixed the catalyst atoms. These calculations allowed calculating the reaction and activation energies for the studied RDS (CHO* → CO* + H*) when using different co-dopants, along with estimating the adsorption energy of CO* and H*.

In a similar way, in Chapter 2, full relaxation of C* on a (111) pyrochlore slab was performed and the most stable adsorbate structure was found (3-fold Rh-Zr-Zr). The same series of co-dopants (Ru, Pd, Os, Ir and Pt) were used to replace the Zr-atom adjacent to the Rh-atom using criteria discuss later in this text. Structure optimization calculations were performed for the C* intermediate while holding fixed the catalyst atoms in the lowest energy positions found when only Rh was doping the surface. These calculations allowed calculating adsorption energy of atomic carbon when using different co-dopants, and thus, gain insight into possible carbon deactivation of the catalyst. Holding fixed the surface atoms allowed for reduced computational efforts, and deviations arising from fixing the positions of the surface atoms are expected to cancel out in the type of calculations performed in this work.
3. Results and discussion

3.1 Catalyst characterization

*Powder X-ray Diffraction (PXD) of fresh catalyst*

The X-ray diffraction (PXD) patterns are shown in Fig. 5.1 for fresh Rh-LZ and Rh-Pd-LZ and compared to the reference diffraction pattern for a La\(_2\)Zr\(_2\)O\(_7\) (LZ) pyrochlore [35]. Pakhare et al. [3] reported the PXD pattern for LRhZ and LZ pyrochlores and they match the diffraction patterns for the catalyst synthesized in this study. The diffraction patterns for Rh-LZ and Rh-Pd-LZ pyrochlores show remarkable agreement with that of the undoped lanthanum zirconate, which confirms the formation of the pyrochlore crystal structure and furthermore suggests that metal clusters are not formed on the surface or if they do, then their size is small (less than 2 nm in diameter) or amorphous and thus, undetectable by the PXD techniques. Almost no shift can be observed in the diffraction patterns for Rh-LZ and Rh-Pd-LZ when compared to LZ, which is expected due to the low doping percentage (~ 2 wt% or less). PXD patterns for the as-synthesized pyrochlore materials (Rh-LZ and Rh-Pd-LZ) prior to the extended heat treatment step at 1000 °C were taken (see Appendix F) and presented broad diffraction peaks around 28.6, 33.2, 47.6 and 56.5 °, which confirmed that the extended heat treatment under Ar is crucial to the formation of the crystalline pyrochlore structure.
Pakhare et al. [3] reported the reduction profile (not reprinted in this document) for the non-doped lanthanum zirconate pyrochlore (LZ) and a separate Rh-doped lanthanum zirconate pyrochlore (LRhZ) prepared via a different synthesis process than the one used in the present work. LZ presented two reduction peaks at 490 and 580 °C, and LRhZ presented reduction peaks at 280, 380, 455 and 570 °C. Therefore, all peaks above 450 °C correspond to the reduction of the LZ structure and the peaks at 280 and 380 °C correspond to the reduction of the Rh atoms at the surface. In a previous work, Haynes et al. [8] also reported TPR profiles for LZ and LRhZ (see Fig. 5.2), where two distinct peaks at 527 °C and 549 °C, respectively, correspond to the reduction of the pyrochlore structure; whereas a peak at 280 °C appears for the LRhZ pyrochlore.
indicating the presence of Rh at the surface. The difference between the number the peaks detected by Pakhare et al. [3] and Haynes et al. [8] is due to the difference in the H₂ concentration in the two TPR procedures, as explained in [3]. Pakhare et al. [3] and Haynes et al. [8] used the same synthesis procedure.

Fig. 5.2 compares the TPR results reported by Haynes et al. [8] (LZ, LRhZ and supported Rh/γ-Al₂O₃), with the TPR results of the Rh-LZ catalyst synthesized in the present work. The peak observed in Fig. 5.2 for the Rh-LZ pyrochlore at 543 °C corresponds to the reduction of the lanthanum zirconate itself. The reduction peak for the Rh-LZ at 206 °C suggests that the Rh-atoms of the Rh-LZ pyrochlore bind less strongly than those in LRhZ (reduction peak at 280 °C), and hence, they are in more readily reducible surface positions. This can also imply that a fraction of the Rh-atoms is supported on the pyrochlore surface and another fraction is actually included into the lattice. The low-temperature reduction peak (136 °C) of the supported Rh/γ-Al₂O₃ is not observed in the Rh-LZ pyrochlore, which does not support considerable exo-lattice clustering of the dopant metals on the pyrochlore surface.
**Fig. 5.2** Temperature programmed reduction of fresh LZ pyrochlore [8], LRhZ pyrochlore [8], supported Rh/γ-Al₂O₃ [8] and Rh-LZ pyrochlore (this work). Adapted from Catal. Today, 136, Daniel J. Haynes, David A. Berry, Dushyant Shekhawat, James Spivey, Catalytic partial oxidation of n-tetradecane using pyroclores: Effect of Rh and Sr substitution, 206-213, Copyright (2008), with permission from Elsevier. [8]

**Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDX)**

SEM images of the Rh-LZ (Fig. 5.3) and Rh-Pd-LZ (Fig. 5.4) show amorphous shapes for the pyrochlore catalyst particles. The variations in catalyst particle size are a direct result of the aggressive and relatively uncontrolled nature of the self-combustion synthesis method used to prepare the pyrochlore precursor structures.
EDX images of Rh-LZ (Fig. 5.5) and Rh-Pd-LZ catalysts (Fig. 5.6) reveal that the dopant metals are well dispersed on the catalyst surface, and no segregation is observed. This dopant distribution was obtained from the post-calcination pyrochlore samples that
had previously undergone heat treatment at 1000 °C in argon for 10 h, suggesting that it is unlikely for there to be any thermally driven process that would lead to the clustering of the dopants during reaction conditions (up to 950 °C).

The EDX mapping of Rh-LZ (Fig. 5.5) gave a weight percent of 0.37 % for Rh, even though EDX imaging of two catalyst particles before the heat treatment under argon (see Appendix F) showed 2.08 and 1.79 % weight percent of Rh in the catalyst; therefore, this suggest that some of the surface Rh migrated into deeper lattice positions under the heat treatment at 1000 °C or that there is some heterogeneity in the composition of the catalyst particles.

![EDX mapping of the surface of Rh-LZ after heat treatment.](image)

**Fig. 5.5** EDX mapping of the surface of Rh-LZ after heat treatment.
Fig. 5.6 EDX mapping of the surface of Rh-Pd-LZ after heat treatment.

EDX imaging of the Rh-Pd-LZ pyrochlore shows great spread of the two dopants Rh and Pd. Elemental analysis showed a weight percentage of 1.91 % Rh and 0.77 % Pd, which is extremely close to the expected values, 2 wt% and 0.5 wt%, respectively. EDX analysis of another Rh-Pd-LZ particle but before the heat treatment (see Appendix F) shows 1.16 wt% Rh and 0.02 wt% Pd, which contradicts the hypothesis of dopant migrating deeper into the lattice during the heat treatment. In conclusion, the EDX data suggest that the dopant noble metals are well dispersed in the pyrochlore lattice and that there was no evidence for exo-lattice formation of dopant clusters on the pyrochlore surface, but the variation in dopant content amongst the particles remains as a topic of further research and may require further enhancements of the synthesis procedure. Further SEM and EDX images for the catalysts under considerations can be found in Appendix F.
Brunauer–Emmett–Teller (BET) method and Thermogravimetric Analysis (TGA)

The synthesis method used in the present work provided greater catalyst surface area compared to the method used by Pakhare et al. [4]. The BET surface for LRhZ (catalyst provided by collaborators [3, 4]), Rh-LZ and Rh-Pd-LZ were 8.72, 11.75 and 13.68 m$^2$/g, respectively. The Rh-containing lanthanum zirconate pyrochlores presented negligible carbon deposition (0.007 g$_{\text{carbon}}$/g$_{\text{catalyst}}$ for LRhZ and 0.014 g$_{\text{carbon}}$/g$_{\text{catalyst}}$ for Rh-LZ), whereas the Pd-Rh-LZ presented significant carbon deposition (0.237 g$_{\text{carbon}}$/g$_{\text{catalyst}}$) despite the low doping percentage of Pd (0.5 wt%); which suggests that there is a direct connection between carbon deposition rates and the presence of Pd on the pyrochlore surface. The effects of the induced carbon deposition will be discussed in the Catalyst optimization stage 2: Inclusion of a co-dopant section.

3.2 Catalyst optimization stage 1: Rearrangement of the Rh atoms

In the earlier DFT computational work on the LRhZ pyrochlore catalysts (Chapter 2), it was found that the pyrochlore crystalline plane most active for DRM is the (111) surface, and the most stable configurations for species involved in the main reaction pathway occur mainly on Rh-containing sites.

The GNC method used for catalyst synthesis in this work is a successful method to synthesize the doped lanthanum zirconate pyrochlores; however, contrary to the catalyst synthesized by collaborators (LRhZ) [4], the GNC method places the dopant atoms in a more readily reducible position of the Rh-LZ pyrochlore surface, suggesting that they will be more easily available for species adsorption and thus, the reaction performance is enhanced. However, it could also be the case that for longer reaction
times (days/months) than the ones used in this study (hours), the surface Rh-atoms on the surface of the Rh-LZ pyrochlore may tend to sinter. The Rh-doped lanthanum zirconate synthesized in the present work (Rh-LZ) constitutes then the first stage of catalyst optimization.

**Temperature programmed surface reaction (TPSR)**

The dry reforming of methane reaction was carried out at temperatures from 550 to 900 °C, and the concentration of product species were measured by mass spectrometry. Analysis of the calibrated MS signal enabled the calculation of reactant conversion and the molar H$_2$ to CO ratio as a function of temperature (see Fig. 5.7). Additional information about the analysis of the MS output can be found in the Appendix I.

Concurrent to the dry reforming of methane, some water is also formed from the competing Reverse Water Gas Shift reaction (RWGS, CO$_2$ + H$_2$ ⇌ CO + H$_2$O) at moderate temperatures. The concentration of water in the product gas goes through a maximum at a reaction temperature of approximately 700 °C when the Rh-LZ pyrochlore is used to catalyze DRM reactions, but the rate of reaction and overall conversion for DRM increase near monotonically with temperature until up to approximately 850 °C.
The H₂/CO molar ratio ascends monotonically with temperature, which is the result of the mildly endothermic RWGS reaction being less favored at elevated temperatures and the endothermic DRM reaction becoming more favored at these conditions. From Fig. 5.7, it is seen that as the temperature increases, the overall
conversion of CO$_2$ and CH$_4$ become more similar. This result also supports the idea that
the RWGS reaction is less favored, because the RWGS reaction causes the H$_2$/CO molar
ratio to decrease. The comparison between the performances of the optimization stage 1
catalyst (Rh-LZ) and the catalyst synthesized by collaborators (LRhZ) is presented in the
next section.

3.3 Cataly st optimization stage 2: Inclusion of a co-dopant

3.3.1 Computational predictions

Reduction of the activation energy of the rate determining step (RDS)

In Chapter 2, the complete set of elementary steps considered in the reaction
network for DRM consisted of 130 reactions, counting both forward and reverse
reactions. Some activation energies were derived from rigorous DFT calculations (CI-
NEB method), while others were estimated by a Bronsted-Evans-Polanyi (BEP) relation
derived from our DFT data. The CHO dehydrogenation step was identified as one of the
rate determining steps (RDS) and occurs in the minimum energy CH$_4$ dehydrogenation
pathway of the DRM reaction mechanism. In the present work, DFT methods are used to
calculate the change in this barrier when a co-dopant is added in an adjacent superficial
B-position in the pyrochlore crystal, which corresponds to the Zr sites in the LZ
pyrochlore crystal). The BEP correlation derived in Chapter 2 ($\Delta E_{act} =
0.8253\cdot \Delta H_{\text{Grx}'}+0.6216$) was used to estimate the activation energies for CHO
dehydrogenation in the presence of the different co-dopants. The BEP correlation
depends solely on the type of reaction (e.g., dissociation reaction in this case) and the
geometry of the surface; meaning that it is highly surface structure dependent, but only
marginally impacted by changes in the B position metal on the surface [36, 37]. Although, the calculations were made assuming full inclusion of the dopant inside the lattice, this is not necessarily the case as shown in the section *Temperature programmed reduction (TPR)*. However, the computations presented in this work aim to provide trends in reactivity and therefore assuming full inclusion of the dopant inside the lattice is deemed appropriate.

Although the co-dopant is computationally added in a position adjacent to the Rh-atom, this is not necessarily the case for all active sites, since the synthesis method used in this work does not provide atomic-level control over the placing of the dopant atoms. However, the idea behind the present computational prediction is to find a co-dopant that provides an active site where CHO dehydrogenation occurs more readily (lower $\Delta E_{\text{act}}$). This co-doped site is meant to appear on the catalyst surface less frequently than the sites provided by the Rh-LZ pyrochlore, since it is desired to conserve the general reaction mechanism for DRM provided by the Rh-LZ pyrochlore, but including few co-doped sites where CHO species can diffuse due to the high reaction temperatures ($> 650 \, ^\circ\text{C}$) and dissociate more easily into CO and H.

The set of possible co-dopants was chosen based upon noble metals used in previous catalyst systems investigated for DRM as summarized in [38] that also exhibit a stable (+4) oxidation state and possess an electronic configurations that favors octahedral coordination, which is required for substitution at the Zr site in LZ pyrochlore materials. Additionally, it is important that the ionic radius ratio between La and any of the possible
test atoms equal 1.4 to 1.8, which is ratio required to form a stable pyrochlore [39]. The computationally tested co-dopants selected were Ru, Pd, Os, Ir and Pt (see Fig. 5.8).

Fig. 5.8 Computational strategy for testing the effect of including different co-dopants into the LRhZ pyrochlore upon the activation energy of one of the RDS (CHO* dehydrogenation), the desorption of products and the adsorption energy of atomic carbon. The co-dopant replaces the Zr-atom (B-site of the pyrochlore) adjacent to the Rh-atom.

The DFT derived activation barriers for the CHO* dissociation reaction to form CO* and H* on pyrochlore surfaces with different co-dopants is shown in Fig. 5.9a. The data in Fig. 5.8a clearly show that the presence of the co-dopant reduces the activation barrier for the CHO dehydrogenation reaction, and the Rh-Pt, Rh-Ir and Rh-Pd combinations provide the lowest activation barriers for this rate limiting reaction.

**Products desorption**

The products of CHO dehydrogenation are adsorbed CO and adsorbed H, which constitute final stages of the DRM reaction mechanism. In other words, CO desorption leads to CO gas formation and the reaction of adsorbed H species leads to the desorption of H2 gas species. Therefore, the weaker the adsorption of CO and H to the surface, the
more favorable the formation of gas products. The adsorption energy of CO and H adsorbed on the same slab ($\Delta E_{\text{ads(CO}^*+\text{H}^*)}$) was calculated as follows:

$$\Delta E_{\text{ads(CO}^*+\text{H}^*)} = E_{\text{CO}^*+\text{H}^*+\text{surf}} - (E_{\text{surf}} + E_H + E_{\text{CO}})$$

where $E_{\text{CO}^*+\text{H}^*+\text{surf}}$ is the calculated energy of the combined slab and adsorbates (CO* and H*); $E_{\text{surf}}$ is the energy of the clean slab without any adsorbate, $E_H$ is the energy of the isolated H-atom and $E_{\text{CO}}$ is the energy of the isolated CO molecule. Therefore, the more negative $\Delta E_{\text{ads(CO}^*+\text{H}^*)}$, the stronger the adsorption. The values of $\Delta E_{\text{ads(CO}^*+\text{H}^*)}$ are shown in Fig. 5.9b. Pd and Pt as co-dopants provide the weaker adsorption for CO and H ($\Delta E_{\text{ads(CO}^*+\text{H}^*)} = -2.02$ and -1.82 eV, respectively). Therefore, Pd and/or Pt are suggested by DFT calculations as suitable co-dopant metals to enhance the DRM reaction and inhibit RWGS, since the rate for CH4 dehydrogenation would increase, causing more CO2 to be consumed via DRM and water production through RWGS would be less favored. Additionally, CO and H2 products can more easily leave the surface, also contributing to the inhibition of RWGS.

**Coke formation**

Since carbon deposition is an issue when using different dopants on pyrochlore catalysts [2], computational methods were also used to calculate the adsorption energy for atomic carbon on the different co-doped pyrochlores, see Fig. 5.9c. The adsorption energy of atomic carbon ($\Delta E_{\text{ads(C}^*)}$) was calculated as follows:

$$\Delta E_{\text{ads(C}^*)} = E_{C^*+\text{surf}} - (E_{\text{surf}} + E_C)$$
Where $E_{C^*+surf}$ is the calculated energy of the combined slab and adsorbate (C*); $E_{surf}$ is the energy of the clean slab without any adsorbate and $E_C$ is the energy of the isolated C-atom. Therefore, the more negative $\Delta E_{\text{ad}(C^*)}$, the stronger the atomic carbon adsorption.

Again, Pd and Pt stand out as the two best candidates for co-doping the Rh-doped lanthanum zirconate, as carbon adsorption is the weakest amongst all metal combinations when either Pd or Pt are co-located near a Rh atom. The co-doped Rh-Ru-LZ pyrochlore presents the strongest surface carbon adsorption, followed by the single doped pyrochlore (Rh-LZ). This suggests that the presence of Ru dopants may enhance coke formation and lead to a rapid loss in overall catalyst activity.
Fig. 5.9 a) Activation energy for CHO dehydrogenation (CHO* → CO* + H*) over the Rh-doped pyrochlore and a series of co-doped pyrochlores; b) adsorption energy for the combined CO* and H* species in close proximity; and c) adsorption energy for carbon on the 3-fold site Rh-M-Zr, where M is Zr for a single-doped pyrochlore, or M = Ru, Pd, Os, Ir or Pt for the co-doped pyrochlores. The asterisc (*) next to species means ‘adsorbed’.
Choosing the appropriate co-dopant and its concentration

Menegazzo et al. [40] concluded from their experimental work that the addition of Pt or Pd to Ni/ZrO₂ prevents coke formation when compared with the Ni/ZrO₂ sample, and they indicate that the Ni-Pd/ZrO₂ catalyst is the most promising for industrial application. In a different study by Nematollahi et al. [41], different noble metals supported on alumina-stabilized magnesia were tested for dry reforming combined with partial oxidation of methane to syngas. When tested for dry reforming, Pd showed better H₂ to CO ratios when compared to Pt for equimolar feed of CH₄ and CO₂, which indicates that DRM is favored over RWGS when Pd is used. Hence, based upon our computational findings with inputs from experimental observations made by others, we have chosen to synthesize the Rh-Pd co-doped lanthanum zirconate (Rh-Pd-LZ) for the present study. However, using Pt as a co-dopant is also being considered for investigation by our group.

The Rh dopant percentage on the Rh-Pd-LZ was chosen to be 2 wt%, which allows comparison to the performance of the catalyst provided by collaborators (LRhZ) and the catalyst synthesized in the first optimization stage (Rh-LZ). There were two reasons to hold the Rh-percentage constant. First, previous work [3, 4] studied 2 and 5 wt% Rh-doped lanthanum zirconate pyrochlore catalysts, but the activity at Rh-doping percentage less than 2 wt% is unknown, and therefore, synthesizing catalysts with Rh-doping percentage less than 2 wt% could potentially present a dramatic drop in activity due to the existence of a possible critical value of the Rh-doping percentage, which is still an unexplored area and is matter of future work. The second reason to hold the Rh-
percentage constant at 2 wt% was because the new catalyst, the Rh-Pd-LZ pyrochlore, is meant to provide generally the same reaction mechanism for DRM as the Rh-LZ pyrochlore (see Chapter 2), with the exception of providing few extra Rh-Pd sites (Pd-doping percentage was 0.5 wt%) where the CHO species can diffuse and dehydrogenate undergoing a lower activation energy ($\Delta E_{\text{act}} = 1.38$) than the one provided at Rh-only sites ($\Delta E_{\text{act}} = 2.40$), and thus promote DRM.

3.3.2 Experimental comparison amongst LRhZ, Rh-LZ and Rh-Pd-LZ

Comparison between LRhZ and Rh-LZ (optimization stage 1)

As shown in Fig. 5.10, at both moderate and high temperatures (650 and 800 °C, respectively), CO$_2$ conversion is significantly greater than CH$_4$ conversion for the LRhZ pyrochlore, due to the occurrence of the reverse water gas shift reaction (RWGS, CO$_2$ + H$_2$ $\rightleftharpoons$ CO + H$_2$O), which uses adsorbed CO$_2$ and adsorbed H$_2$ for water production, decreasing then the H$_2$/CO ratio (where this ratio is unity assuming only dry reforming takes place). As expected, it is also observed that the H$_2$/CO molar ratio increases with temperature, as a result of the RWGS reaction becoming less favored at higher temperatures.

The Rh-LZ catalyst showed greater H$_2$ to CO ratios than LRhZ due to the placing of the Rh-atoms in a more reducible position and the possible coexistence of supported Rh-atoms on the surface and Rh-atoms included in the lattice. The inclusion of Rh into the structure makes the LZ pyrochlore active for DRM [3] and is involved in the key steps of the main reaction pathway, as discerned computationally in Chapter 2. Therefore, the more exposure of Rh-atoms the more activity towards DRM is expected.
The Rh-LZ catalyst successfully increased the DRM reactant conversion at high temperatures (85.2 % for CO₂ and 81.5 % for CH₄) when compared to LRhZ (73.0 % for CO₂ and 62.0 % for CH₄). This is due to the fact that at high temperature (800 °C) DRM is thermodynamically (∆G° < 0) favorable, and so, the greater accessibility of surface Rh-atoms in the Rh-LZ catalyst ends up fostering DRM more than the LRhZ catalyst. When RWGS is suppressed, the surface residence times shortens and active sites are freed more quickly, which gives higher conversions.

**Reduction of the activation energy of the rate determining step (RDS)**

The H₂ to CO ratio was the greatest with the two catalysts synthesized in this work (Rh-LZ and Rh-Pd-LZ) at high temperatures (800 °C) and ~1.2 atm as shown in Fig. 5.10. The co-doped Rh-Pd-LZ catalyst showed the highest conversions at temperatures favorable for DRM (800 °C), this agrees well with the computationally designed goal of this catalyst: reduce the highest activation barrier for dry reforming (CHO dehydrogenation) so that surface residence time is reduced, and therefore, the conversion of reactants is increased. Further, H₂ to CO ratios close to unity mean that the RWGS is inhibited.
Fig. 5.10 Reactant conversion and molar H₂ to CO product ratio for DRM reaction studies using LRhZ, Rh-LZ and Rh-Pd-LZ catalysts at 1.1-1.3 atm and GHSV = 58,800 cm³/gcat/h.

In previous studies [10], a 2 wt% Ru-doped lanthanum zirconate (LRuZ) and a 3.78 wt% Pt-doped lanthanum zirconate (LPtZ), whose levels of substitution by weight correspond to identical atomic levels of substitution at the B-site, were tested for dry reforming of methane. TPR results for LRuZ suggested that Ru is not stable within the pyrochlore structure, and moves from the B-site of the pyrochlore (A₂B₂O₇) to the surface. The LPtZ catalyst, although stable, showed slightly higher apparent activation energies ($\Delta E_{appCH_4} = 36.5 \pm 0.4$ kcal/mol and $\Delta E_{appCO_2} = 27.9 \pm 0.2$ kcal/mol) [42] than the LRhZ ($\Delta E_{appCH_4} = 34.2 \pm 0.4$ kcal/mol and $\Delta E_{appCO_2} = 27 \pm 0.2$ kcal/mol) [4]. The present work explores for the first time the co-doping of the B-site of the La₂Zr₂O₇ pyrochlore for dry reforming, and shows a synergetic effect when two co-dopants are used. These
findings encourage further investigations on co-doping of the B-site in the pyrochlore structure.

**Coke formation**

The Rh-Pd-LZ showed moderate conversion of CH\(_4\) and CO\(_2\) at low and moderate temperatures (500 °C and 650 °C, respectively), see Fig. 5.10. This can be attributed to the reduction of active sites due to considerably greater carbon deposition (0.237 g\(_{\text{carbon}}\)/g\(_{\text{catalyst}}\) for Rh-Pd-LZ, 0.014 g\(_{\text{carbon}}\)/g\(_{\text{catalyst}}\) for Rh-LZ and 0.007 g\(_{\text{carbon}}\)/g\(_{\text{catalyst}}\) for LRhZ).

At high temperature (800 °C), however, the Rh-Pd-LZ catalyst showed the highest conversions for CO\(_2\) and CH\(_4\), despite the greater carbon deposition observed, and thus reduction of surface active sites. This is explained by the fact that at high temperatures, surface diffusion processes are enhanced and therefore intermediates can migrate more quickly through active sites, being the number of active sites not as critical as it is at low (500 °C) and moderate temperatures (650 °C).

Even though the Rh-Pd-LZ catalyst showed considerable carbon deposition (0.237 g\(_{\text{carbon}}\)/g\(_{\text{catalyst}}\)), the catalyst performance was stable once it reached steady-state (Rh-Pd-LZ underwent up to 4 h time-on-stream on a single run, without observing a decrease in catalyst activity). Further, the carbon deposited on the surface did not deactivate all of the Rh-Pd sites, which are of interest to reduce the activation barrier for the RDS, since greater conversions at high temperatures were achieved when compared to the Rh-LZ pyrochlore.
**Products desorption**

As presented in Fig. 5.9b, Pd favors CO and H₂ desorption, since these two species are not as strongly adsorbed to the surface as when using other co-dopants; nonetheless, if the adsorbed CO is thermodynamically less stable (easier desorption), this may simultaneously favor CO dissociation (CO∗ ⇌ C∗ + O∗), which directly leads to carbon deposition, as observed experimentally. Further computational insights to discern the propensity to carbon deposition will be matter of future work.

4. **Conclusion**

The performance of three catalysts, the LRhZ (provided by collaborators), the Rh-LZ and the Rh-Pd-LZ pyrochlore was compared in this work. The Rh-Pd-LZ catalyst was computationally suggested, as it was predicted to lower the activation energy for one the rate determining steps (RDS), the CHO dehydrogenation, for dry reforming of methane (DRM) on Rh-doped lanthanum zirconate pyrochlores; as well as favor products desorption and weaken carbon adsorption on the surface.

Increased surface concentrations of Rh atoms (Rh-LZ) on the pyrochlore catalyst surface increased DRM conversions at high temperatures when compared with the LRhZ pyrochlore catalyst prepared by others, again reinforcing the idea that the Rh sites are essential for DRM activity on pyrochlore surfaces. At moderate temperatures (650 °C), although CH₄ conversion was nearly the same for the three catalysts, CO₂ conversion was the highest for the LRhZ pyrochlore. This evidences more activity towards the RWGS on the LRhZ catalysts, and the existence of diffusion barriers that prevent species
from readily reaching Rh-Pd sites on the Rh-Pd-LZ pyrochlore. Rh-Pd sites lower the activation barrier of one of the RDS for DRM.

At low temperature (500 °C), the improved Rh-Pd-LZ catalyst presented low conversions and H₂ to CO ratio. This is due to the fact that: DRM is not thermodynamically favorable below 650 °C, there exist diffusion limitations to reach Rh-Pd active sites and that carbon deposition was observed on this catalyst, by visual inspection and then further corroborated though TGA measurements (0.237 g₉carbon/g₉catalyst). Although the presence of Pd on the surface induced carbon deposition, the catalyst performance was stable once it reached steady-state and the carbon deposited on the surface did not deactivate all of the Rh-Pd sites because conversions at high temperatures were greater than for Rh-LZ, showing how the activation energy for the RDS (CHO dehydrogenation) was successfully decreased. Despite our calculations showed weaker adsorption of atomic carbon on the surface of the Rh-Pd-LZ pyrochlore, the carbon deposition observed on this catalyst may be due to favored CO* dissociation in the Rh-Pd or Pd-only sites. The kinetics of atomic carbon generation on co-doped pyrochlore surfaces will be addressed in a future work.

The Pd-loading in the Rh-Pd-LZ catalyst was lower (0.5 wt%) than the Rh-loading (2 wt%), so that the catalyst provides comparatively less Pd-Rh sites than Rh-only sites, which aims to attain generally the same reaction pathway as for the Rh-doped pyrochlore, but when the high activation barrier for CHO* dehydrogenation is encountered on the Rh-only site (ΔE₉act = 2.40 eV) it is hypothesized that the surface bound CHO species can readily diffuse at the high reaction temperatures to other Pd-Rh
sites where the barrier to product formation is much less ($\Delta E_{\text{act}} = 1.38$ eV), leading to increases in DRM activity. Although the present work suggests improvement of the catalyst based on successful targeting of the RDS, work on the optimum concentration of dopants and the effect on carbon deposition is necessary to continue the optimization of this catalyst.

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References


CHAPTER SIX
CONCLUSIONS

The present doctoral work combines computational and experimental efforts so as to optimize pyrochlore catalysts for the dry reforming of methane (DRM). Density functional theory (DFT) computations allowed calculating the activation energies for select elementary steps of the proposed reaction network for DRM over the Rh-substituted lanthanum zirconate (LRhZ) pyrochlore catalyst. These DFT data were used to build a Brønsted-Evans-Polanyi correlation relating heats of reaction data (more easily calculated) to reaction activation energies (difficult to calculate) for DRM reactions on pyrochlore surfaces. This correlation was used to estimate the activation energies of all remaining DRM elementary steps that were not explicitly modeled via DFT and climbing image nudged elastic band (CI-NEB) methods. Calculations suggest that the plane (011) and (111) are the most thermodynamically stable pyrochlore surfaces, but activation energies of elementary reaction steps showed the plane (111) to be the most catalytically active for DRM. Thus, the activation energies for all likely surface reactions involved with DRM were modeled, which lead to the identification of the main reaction pathway for DRM on the LRhZ pyrochlore plane (111). Part of this pathway included CH₄ dehydrogenation/oxygenation to CO, which proceeds as follows: CH₄(g) ⇌ CH₄* ⇌ CH₃* ⇌ CH₂* ⇌ CH₂O* ⇌ CHO* ⇌ CO* ⇌ CO(g). Further, CO₂, the other DRM reactant, proceeds to products via a process where it dissociates directly or an alternative pathway where it indirectly dissociates (through COOH formation) to CO. The two rate
determining steps for the overall DRM reaction are CH$_2^*$ oxygenation and CHO$^*$ dehydrogenation.

Isotopic labeling experiments using the LRhZ pyrochlore catalyst distinctively showed reversible CO$_2$ adsorption, but the conversion of CO$_2$ to methane via a reverse hydrogenation pathway was not observed. This correlates with the considerably greater number of reaction steps (7 steps) involved in CH$_4$ dehydrogenation/oxygenation to CO, when compared to CO$_2$ dissociation to CO (3 steps). Steady state isotopic transient kinetic analysis (SSITKA) enabled the calculation of average surface residence times, turnover frequencies and surface concentration of intermediates at different temperatures. Reaction data also showed that surface residence times shorten with increasing temperature as expected. Thus, at lower temperatures, the competing reverse water gas shift reaction (RWGS, CO$_2$ + H$_2$ $\rightleftarrows$ CO + H$_2$O) is promoted. This is partially a result of adsorbed H$_2$ products from DRM remaining adsorbed long enough to react with adsorbed CO$_2$. Thermodynamic calculations showed that the DRM reaction is thermodynamically unfavorable ($\Delta G^\circ_{\text{Rxn}} > 0$) at temperatures below approximately 650 °C.

Comparison between turnover frequencies calculated as rate per active-intermediates (from SSITKA) and rate per surface-metal-atoms showed that all metals on the catalyst surface (Rh, Zr and La) are involved in the reaction mechanism (which corroborates DFT findings), even though, the absence of Rh makes the lanthanum zirconate pyrochlore non-catalytically active for DRM. Very short residence times (< 0.6 s) at temperatures relevant for DRM (> 650 °C) were observed, due to enhanced diffusion processes on the surface and the increased kinetic energy of adsorbates. Which readily
enabled species to overcome all reaction activation barriers leading to CO and H₂ formation.

A DFT-based microkinetic model (MKM) based on DFT derived kinetic parameters was able to reproduce DRM experimental data for CO₂ and CH₄ conversion with respect to temperature as well as the coexistence of a competing reaction (RWGS). This latter capability enabled the model to accurately predict trends in H₂ to CO ratio with respect to temperature. The MKM model also helped to validate the DFT data calculated in this doctoral work, and were used to optimize co-doped pyrochlore catalysts for DRM.

Computationally guided efforts to optimize Rh-doped pyrochlore catalysts focused on the calculation of the activation energy for one of the rate determining steps (CHO* dehydrogenation), the adsorption of adsorbed CO and H, and the strength of carbon deposition when using a series of co-dopants (Ru, Pd, Os, Ir and Pt) neighboring the Rh-atom. Results from these DFT calculations and work done by other authors on related systems indicated that Pd was a promising co-dopant that may reduce activation barriers for the rate determining step for DRM and inhibit the competing RWGS reaction. Therefore, a Rh and Pd substituted lanthanum zirconate (Rh-Pd-LZ) was synthesized and catalyst testing proved this novel catalyst reduced the activation energy for reactions associated with the dry reforming of methane and provided higher yields of desired products as compared to the Rh-substituted pyrochlore catalyst synthesized at Clemson University (Rh-LZ) and the Rh-substituted pyrochlore catalyst synthesized by collaborators (LRhZ) at NETL, West Virginia. The lower activation barriers DRM led to
greater conversion of reactants, while giving a product mixture where the H₂ to CO ratio was close to unity, suggesting that the DRM reaction was heavily favored while suppressing the RWGS reaction, which leads to water generation. However, Rh-Pd-LZ presented considerably more carbon deposition (0.237 g_{carbon}/g_{catalyst}) when compared to Rh-LZ (0.014 g_{carbon}/g_{catalyst}) and LRhZ (0.007 g_{carbon}/g_{catalyst}), most probably due to a reduction in the activation energy required for CO dissociation. Nonetheless, the presence of carbon on the surface did not inhibit the catalytic activity of the Rh-Pd-LZ, as it was able to reach significant steady state conversions of CH₄ and CO₂.
CHAPTER SEVEN
RECOMMENDATIONS

Laboratory safety

The MOST IMPORTANT thing to know before you engage in the type of experimental work presented in this dissertation is to be aware of the multiple safety hazards that exist and the deadly consequences that may occur if proper safety protocols are not followed. For future students working in the research area described herein that do not feel comfortable dealing with the associated safety hazards I am about to present, I strongly recommend you discuss the situation with your advisor (in my case Dr. Bruce) or departmental/university safety officer. They should be understanding and informative and help find a way for the needed research to be conducted in a safe and effective manner. And even if you do feel comfortable, DO NOT engage in any experimental activity until you have appropriate safety training about the specific hazards associated with this work.

Carbon monoxide

Although extended exposure to any gas may have fatal consequences, carbon monoxide (CO) represents a particular safety hazard. CO is a toxic odorless gas, exposure to CO causes sleepiness, which can be easily confused with being tired, followed by death. In the laboratory (e.g., Room 202 in Earle Hall as of September 2015) there are two portable CO detectors, I recommend you hang one to the neck of your shirt at all
times while working with CO, and place the other detector as close as possible to the valve of the CO cylinder in the lab or any other location that is highly suspect of leaking CO gas. These alarms must be tested before every work day and any required batteries replaced at regular intervals. There are two carbon monoxide sources in the laboratory: the products of the reforming reaction and the high pressure CO cylinder (used for calibration purposes). A detailed safety protocol for operating with CO can be found in Appendix G, it is recommended that any researcher working with this CO read this appendix and make sure he/she understands all of the presented material thoroughly; furthermore, the researcher must be judgmental of it, remember that your life and the lives of everybody else in the building may depend on the research working with this gas. If the CO alarms sound, evacuate nearby rooms and possibly the building depending on the severity of the leak, and notify the fire department of the incident as necessary.

Within this dissertation, there is a description of how to convert the signals from the mass spectrometer to gas concentrations in the mixture without calibrating the signal for CO, by only performing material balances on the other components. I strongly recommend to follow this procedure (see Appendix I), so that you eliminate a safety hazard, the CO cylinder in the laboratory. In general, the CO gas cylinder has the highest concentration of CO gas and thus poses the greatest health risk.

**Flammable and toxic gases**

CH$_4$ and H$_2$ are highly flammable gases and represent a tremendous safety hazard. The H$_2$ flame is colorless; therefore, you may have an H$_2$ leak in your system, without realizing it, which might lead to fire. You must leak-check all piping/tubing
connection in any experimental system using a leak indicating fluid (e.g., Snoop leak detector) with the system pressurized with N₂ or similar inert. In general, one should flow N₂ through all process lines and look for major leaks, “snooping” every fitting. Then isolate parts of the system, pressurize them and monitor the pressure decay with time using appropriate pressure gauges. If you observe a pressure decay, leak-check the system again, recognizing that some devices (e.g., pressure gauges, pressure regulators, etc.) may have leak at location other than plumbing connections to that device.

Gases like N₂, Ar and He can also be hazardous due to asphyxia; for that reason, you must make sure the room is properly ventilated. Ensure that the ventilation hood or snorkel hood and makeup air source are working properly, and keep the lab door closed to minimize the spread of hazardous gases to other parts in case of leak.

**Inherent hazards of the catalyst synthesis procedure**

The glycine nitrate combustion (GNC) method involves flammability issues, due to the nature of the procedure. Self-ignition of the gel mixture at around 270 °C is very aggressive and the voluminous ashes may land everywhere if they are not properly contained, which can cause fires in the laboratory. Make sure you perform this synthesis inside the hood and that no other combustible chemicals/materials are round your work space. The elevated temperatures required for this synthesis procedure can lead to burns if elements involved in the synthesis are not handled properly.

**High temperature reactor**

The high temperatures required for dry reforming of methane (DRM) (around 1000 K) imply extra precautions during the set-up and operation of the system. You must
keep in mind that many fittings/clamps/wires are made of materials whose melting point is below the reaction temperature; therefore, you must avoid using these fittings/clamps/wires close to the furnace. Additionally, the top of the shell furnace (as shown in Appendix B, Fig. B.2) must be insulated with QUARTZ wool (NOT glass wool) to reduce heat loss and also prevent burn hazards (note, glass wool melts below 1000 °C).

You should NEVER open the shell furnace when it is turned on, it may cause severe injuries due to heat exposure or electrical shock. Furthermore, wait for the furnace to cool down after turning it off, due to burn hazards and also because the temperature shock may crack the quartz reactor which may lead to quartz debris flying across the lab, which might cause minor/major injuries.

**Experimental work**

**Synthesis**

The synthesis set-up and procedure using the GNC method allows room for improvement and standardization. As explained in Appendix E, the homogeneous heating of the reacting mixture is quite a challenge. So far, the best procedure consisted of creating the gel mixture using a deep electrically heated mantel (bucket-like mantel) filled with sand and then promoting the self-combustion reaction using a small diameter heating mantel (zipper-mantel) on the outside of a tall cylindrical glass vessel (e.g., bubbler flask). To improve heat conduction from the walls of the bucket-like mantel to
the reactive mixture inside the glass container, I recommend surrounding the glass container with a conducting high-heat capacity ‘jacket’, such as one made of aluminium and also filling the space between the bucket-like mantel and the glass containing the reactive mixture with metal beads, so that all steps of the synthesis can be done in the bucket-like mantel.

When the synthesis procedure is achieved in only one heating device, I recommend you attempt to standardize every step, in other words, the change in temperature from 130 °C to 270 °C is currently done when a ‘gel is formed’, which can be a slightly subjective indicative. It would be better to have the total solution volume to a constant value (adjust with deionized water) and measure the time needed for gel formation, so that the procedure can become more reproducible.

**Plug flow reactor set-up**

After several runs, the catalyst held inside the quartz reactor in-between the two pieces of quartz wool tended to leak out of the space designated as the catalytic bed, this is due to the pressure plug generated by the reactants flow and also due to gravity. I suggest looking into the possibility of using a U-shaped plug flow reactor, so that the gravity effects can be eliminated; moreover, it might be worth looking into lower flowrates for the feed, although it is important to keep in mind that the flowrates and mass of catalyst must be chosen so that incomplete conversion (< 100%) of reactants are achieved at moderate temperatures (around 650°C). This facilitates the comparison between the performances of different catalysts over a wide range of temperatures (up to approximately 1000 K).
Further experiments

Future steady-state isotopic transient kinetic analysis (SSITKA) should ideally be done with an argon concentration in the feed less than what was used in the experiments presented in Chapter 3, reducing the concentration of Ar in the total feed helps maintain the identity of the flow alike when switching from the unlabeled feed to the labeled one. In addition, you must remember to keep the concentration of helium in the flow as high as possible. The determination of the desired fractional compositions in the feed comes from trial-and-error, since one must check if all species are still detectable by the mass spectrometer with a good signal-to-noise ratio.

Testing other concentrations of the dopant (Rh) and co-dopant (e.g., Pd or Pt) in LZ type pyrochlore catalysts will help elucidate the specific role of each metal in the reaction mechanism and also constitutes the first step towards the optimization of costs, looking forward to commercial applications of these catalysts. For each catalyst sample, conduct powder X-ray diffraction (PXD), energy-dispersive X-ray spectroscopy (EDX), temperature programmed reduction (TPR) and inductively couple plasma-optical emission spectroscopy (ICP-OES), in order to evaluate the crystallinity of the pyrochlore material, the dispersion of the dopant metals, the extent of substitution of the dopant in the lattice, and total percentage of dopant in the structure, respectively. Dynamic light scattering (DLS) was performed in the current doctoral work but the results were not consistent due to the poor solubility of the pyrochlore in water. I recommend looking into other solvents to perform DLS measurements, since information about particle sizes using different dopants may provide unexplored information about catalyst performance.
Testing other co-dopants (Ru, Pd, Os, Ir and Pt) and analyzing the trends in both catalyst performance as well as carbon deposition, while comparing to DFT results presented in Chapter 5 is an extremely vein of research. It is important to remember that moderate carbon deposition should not be considered a major problem, as long as the catalytic activity is maintained over time, which means that enough active sites to carry out the reaction are still exposed.

Previously, it has been seen that the use of excess water in steam reforming can substantially reduce carbon deposition [1]. In the present doctoral work, it was seen that inhibiting the competing reaction for DRM, the reverse water gas shift (RWGS) reaction, reduced water production, therefore increasing H$_2$ to CO ratios but also increasing carbon deposition. This doctoral work sets the ground to achieve a fundamental understanding of the relationship between water presence during the reforming reaction and carbon deposition, which can further be used for catalyst design.
Computational Work

I recommend calculating the activation barrier for CO dissociation in pyrochlore surfaces with different metal substitutions, which may be correlated to the amount of carbon deposition observed in different catalysts. This study can be done rigorously if barriers for CO dissociation are calculated for different adsorption sites of CO*, C* and O*, and also for different arrangement of neighboring atoms, for instance, Rh isolated, Rh and Pd adjacent, and Pd isolated on the surface. I recommend limiting this analysis to the plane (111). Activation barriers calculated using the climbing image nudge elastic band (CI-NEB) method can be used to improve the Brønsted-Evans-Polanyi correlation developed in Chapter 2, since this linear relationship is independent from the metals on the surface and relies heavily on the arrangement of the atoms [2-9].

The microkinetic model can be brought to a higher level by altering it to describe a packed bed reactor (PBR). In addition, I recommend setting the diffusion and reaction processes as separate elementary steps; however, to do that, it is necessary to use a smaller set of steps in the reaction mechanism than those used in Chapter 4, in order to guarantee the robustness of the model. Furthermore, the model can be expanded to include a total of 4 different types of sites; for instance, for the Rh-Pd lanthanum zirconate pyrochlore, the sites to be taken into account would be: Rh-sites, Pd-sites, Rh-Pd sites and dopant-free-sites. Hopefully, information from this improved microkinetic model could be correlated to experimental results for catalysts with different concentrations of dopants.
I also recommend looking into a similar analysis as the one described in Chapter 5 for the other identified rate determining step, CH₂* oxygenation.
References


Appendix A

Supplementary DFT Data

**Fig. A 1.** Reaction mechanism for Reverse Water Gas Shift Reaction (RWGS) on the (111) plane of the LRhZ Pyrochlore Catalyst.

**Fig. A 2.** Potential energy plot calculated using CI-NEB for the elementary reaction step O*+H* ⇌ OH*+* over the plane (011) of LRhZ pyrochlore. CI-NEB calculations were completed using 3 and 5 images. LRhZ surface atoms were held fixed for all calculations. The transition state structure and energy identified using both CI-NEB methods are nearly identical; thus for this system, using 3 CI-NEB images is sufficient to identify the transition state.
Definition of enthalpy of reaction

The CI-NEB calculations were performed by holding the pyrochlore substrate atoms fixed due to difficulties in convergence if done otherwise. The substrate structure corresponded to the relaxed minimum energy structure for the respective addition reaction product. From the preliminary analysis of the BEP correlation it was found that all of the transition states exhibited a structure most similar to that of the product species from addition reactions, which is why that support structure was selected for each of the respective CI-NEB calculations. Despite this simplification for CI-NEB calculations, all starting and final structures were fully relaxed; thus, restructuring of the pyrochlore surface atoms was taken into account in the calculation of the enthalpy of reaction (ΔH$_{\text{rxn}}$).

Fig. A 3 illustrates how the reaction energy and the reaction barrier for a particular elementary step were calculated. The procedure consisted of the following steps: 1) Adsorbate OH is allowed to relax on the surface, creating the slab1. 2) Adsorbate OH is removed from slab 1, and the adsorbates O* and H* are manually placed on this slab in best guess surface locations (fixing the substrate atoms). 3) Structure optimization is performed for slab 1 with O* and H*. 4) CI-NEB method is used to find the transition state structure for the addition reaction. 3) Adsorbates O* and H* are placed on separate slabs (slab 2 and slab 3) and the whole structures are allowed to relaxed. Using the energetics of these fully relaxed slabs (with or without surface adsorbents), the reaction energy is calculated as follows:
\[ \Delta H_{\text{rxn}} = E_{\text{OH}^*|\text{slab1}} - \left( E_{\text{O on slab2}} + E_{\text{H on slab3}} - E_{\text{empty slab}} \right) \]

where \( E_{\text{OH}^*|\text{slab1}} \) is the energy of a slab with OH adsorbed on it after full relaxation, \( E_{\text{O on slab2}} \) is the energy of a slab with O adsorbed on it after full relaxation, \( E_{\text{H on slab3}} \) is the energy of a slab with H adsorbed on it after full relaxation, and \( E_{\text{empty slab}} \) is the energy of a slab without adsorbates after full relaxation.

Although surface relaxation occurs parallel to the occurrence of the elementary reaction step, when CI-NEB calculations were performed allowing substrate atoms to relax, the majority of simulations did not converge under the stipulated tolerances.

The energies of adsorbates placed by themselves in separate slabs were already available from adsorption studies (also presented in this paper) and allowed performing the rest of the calculations presented in this document in a timely manner.
Fig. A 3 Potential energy plot for the reaction $\text{O}^*+\text{H}^* \rightleftharpoons \text{OH}^*+^*$ over the plane (011) of LRhZ pyrochlore. CI-NEB calculations were done using 3 images. Surface atoms in slabs 1, 2 and 3 are in slightly different positions. $\Delta E_{\text{act}}^{\text{CI-NEB}}$ is the activation energy obtained from CI-NEB calculations, $\Delta H_{\text{rxn}}^{\text{CI-NEB}}$ is the energy difference between the starting and final structures used in the CI-NEB calculation. $\Delta E_{\text{act}}$ and $\Delta H_{\text{rxn}}$ are the activation energy and enthalpy of reaction, respectively, used for analysis in the present work.
**Table A 1.** Predicted (via DFT simulation) and experimental crystal structure lattice parameters for LZ and LRhZ pyrochlore materials.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>LZ</th>
<th>LRhZ</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Computational</strong></td>
<td><strong>Experimental</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Parameter</strong></td>
<td><strong>Functional</strong></td>
<td><strong>Value</strong></td>
</tr>
<tr>
<td>Lattice parameter, (a) (Å)</td>
<td>LDA</td>
<td>10.702</td>
</tr>
<tr>
<td></td>
<td>GGA-PBE</td>
<td>10.902</td>
</tr>
<tr>
<td></td>
<td>GGA-PW91</td>
<td>10.894</td>
</tr>
<tr>
<td>Oxygen positional parameter, (x)</td>
<td>LDA</td>
<td>0.334</td>
</tr>
<tr>
<td></td>
<td>GGA-PBE</td>
<td>0.333</td>
</tr>
<tr>
<td></td>
<td>GGA-PW91</td>
<td>0.333</td>
</tr>
<tr>
<td>Lattice parameter, (a) (Å)</td>
<td>LDA</td>
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</tr>
<tr>
<td></td>
<td>GGA-PBE</td>
<td>10.883</td>
</tr>
<tr>
<td></td>
<td>GGA-PW91</td>
<td>10.870</td>
</tr>
<tr>
<td>Oxygen positional parameter, (x)</td>
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</tr>
<tr>
<td></td>
<td>GGA-PBE</td>
<td>0.333</td>
</tr>
<tr>
<td></td>
<td>GGA-PW91</td>
<td>0.333</td>
</tr>
</tbody>
</table>
Optimization of slab dimensions (Section 2.2 of the paper)

Fig. A 4. Methane adsorption energy and dipole moment of the pyrochlore slab versus vacuum space between oxide slabs. For CH4 physisorption simulations on plane (111) lattice Rh, the two bottom layers of the pyrochlore slab were held fixed.
Species adsorption

**Table A 2.** Strongest adsorption sites and corresponding adsorption energies for all species considered in the reaction network for DRM on the (111) and (011) surfaces of the LRhZ pyrochlore.

<table>
<thead>
<tr>
<th>Species</th>
<th>Plane (111)</th>
<th>Plane (011)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>∆E_{ads} (eV)</td>
<td>Adsorbate structure</td>
</tr>
<tr>
<td>CH₄</td>
<td>-0.07</td>
<td>3-fold Rh-Zr-La</td>
</tr>
<tr>
<td></td>
<td>-0.05</td>
<td>atop Rh</td>
</tr>
<tr>
<td></td>
<td>-0.03</td>
<td>bridge Zr-La</td>
</tr>
<tr>
<td>CH₃</td>
<td>-2.38</td>
<td>bridge Zr-La</td>
</tr>
<tr>
<td>CH₂</td>
<td>-4.63</td>
<td>bridge Rh-Zr</td>
</tr>
<tr>
<td>CH</td>
<td>-7.22</td>
<td>3-fold Rh-Zr-Zr</td>
</tr>
<tr>
<td></td>
<td>-4.71</td>
<td>3-fold Zr-Zr-La</td>
</tr>
<tr>
<td></td>
<td>-3.22</td>
<td>atop La</td>
</tr>
<tr>
<td>C</td>
<td>-7.22</td>
<td>3-fold Rh-Zr-Zr</td>
</tr>
<tr>
<td></td>
<td>-5.00</td>
<td>3-fold Zr-Zr-La</td>
</tr>
<tr>
<td></td>
<td>-2.77</td>
<td>atop La</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>-3.02</td>
<td>bridge Rh-Zr</td>
</tr>
<tr>
<td>O</td>
<td>-7.36</td>
<td>3-fold Rh-Zr-Zr</td>
</tr>
<tr>
<td></td>
<td>-6.80</td>
<td>3-fold Rh-Zr-La</td>
</tr>
<tr>
<td></td>
<td>-6.46</td>
<td>bridge Zr-Zr</td>
</tr>
<tr>
<td>OH</td>
<td>-5.39</td>
<td>bridge Zr-La</td>
</tr>
<tr>
<td>H₂O</td>
<td>-0.79</td>
<td>atop Zr</td>
</tr>
<tr>
<td></td>
<td>-0.78</td>
<td>bridge Rh-La</td>
</tr>
<tr>
<td>H₂</td>
<td>-0.38</td>
<td>atop Rh (side)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For the highly unsaturated tightly bound species (CH, C, O) all found adsorption sites where included in this table; since at sites, where the adsorption strength is intermediate, these species might be more reactive.
Table A 3 cont. Strongest adsorption sites and corresponding adsorption energies for all species considered in the reaction network for DRM on the (111) and (011) surfaces of the LRhZ pyrochlore.

<table>
<thead>
<tr>
<th>Species</th>
<th>Plane (111)</th>
<th>Plane (011)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>∆E_{ads} (eV)</td>
<td>Adsorbate structure</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>-0.78</td>
<td>atop Zr (linear)</td>
</tr>
<tr>
<td>CH₂OH</td>
<td>-2.54</td>
<td>bridge Zr-La</td>
</tr>
<tr>
<td></td>
<td>-2.50</td>
<td>atop Zr (side)</td>
</tr>
<tr>
<td>CHOH</td>
<td>-2.18</td>
<td>atop Zr (linear)</td>
</tr>
<tr>
<td>COH</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH₃O</td>
<td>-3.87</td>
<td>atop La (linear)</td>
</tr>
<tr>
<td>CH₂O</td>
<td>-1.72</td>
<td>3-fold Rh-Zr-Zr</td>
</tr>
<tr>
<td>CHO</td>
<td>-3.61</td>
<td>3-fold Rh-Zr-Zr</td>
</tr>
<tr>
<td>CO</td>
<td>-1.63</td>
<td>atop Rh</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>-1.46</td>
<td>3-fold Zr-Zr-La</td>
</tr>
<tr>
<td>COOH</td>
<td>-3.38</td>
<td>bridge Rh-Zr</td>
</tr>
</tbody>
</table>

For the highly unsaturated tightly bound species (CH, C, O) all found adsorption sites where included in this table; since at sites, where the adsorption strength is intermediate, these species might be more reactive.
**Table A 4.** Adsorbate structures at the strongest adsorption sites for all species considered in the reaction network for DRM on the (111) and (011) surfaces of the LRhZ pyrochlore.

<table>
<thead>
<tr>
<th>Species</th>
<th>Plane (111)</th>
<th>Plane (011)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Adsorbed structure</td>
<td>Adsorbed structure</td>
</tr>
<tr>
<td>CH₄</td>
<td>3-fold Rh-Zr-La atop La</td>
<td>atop Rh 3-fold Zr-La-La</td>
</tr>
<tr>
<td></td>
<td>bridge Zr-La</td>
<td></td>
</tr>
<tr>
<td>CH₃</td>
<td>bridge Zr-La</td>
<td>3-fold Zr-La-La</td>
</tr>
<tr>
<td></td>
<td>atop Zr</td>
<td></td>
</tr>
</tbody>
</table>

*The atoms belonging to the adsorbate are labeled. The color code is as follows: La – green, Zr – light blue, Rh – dark blue, O – red, C – grey, H – white.*
Table A 3 cont. Adsorbate structures at the strongest adsorption sites for all species considered in the reaction network for DRM on the (111) and (011) surfaces of the LRhZ pyrochlore.

* The atoms belonging to the adsorbate are labeled. The color code is as follows: La – green, Zr – light blue, Rh – dark blue, O – red, C – grey, H – white.
Table A 3 cont. Adsorbate structures at the strongest adsorption sites for all species considered in the reaction network for DRM on the (111) and (011) surfaces of the LRhZ pyrochlore.

<table>
<thead>
<tr>
<th>Species</th>
<th>Plane (111)</th>
<th>Plane (011)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td><img src="image1" alt="3-fold Rh-Zr-Zr" /></td>
<td><img src="image2" alt="in bulk bridge Rh-La" /></td>
</tr>
<tr>
<td>H</td>
<td><img src="image3" alt="bridge Rh-Zr" /></td>
<td><img src="image4" alt="bridge Rh-La" /></td>
</tr>
</tbody>
</table>

* The atoms belonging to the adsorbate are labeled. The color code is as follows: La – green, Zr – light blue, Rh – dark blue, O – red, C – grey, H – white.
**Table A 3 cont.** Adsorbate structures at the strongest adsorption sites for all species considered in the reaction network for DRM on the (111) and (011) surfaces of the LRhZ pyrochlore.

<table>
<thead>
<tr>
<th>Species</th>
<th>Plane (111) Adsorbed structure</th>
<th>Plane (011) Adsorbed structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td><img src="image" alt="Image of O adsorption structure on (111) plane" /> 3-fold Rh-Zr-Zr</td>
<td><img src="image" alt="Image of O adsorption structure on (011) plane" /> 3-fold Zr-La-La</td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Image of O adsorption structure on (111) plane" /> 3-fold Rh-Zr-La bridge La-La</td>
<td><img src="image" alt="Image of O adsorption structure on (011) plane" /> bridge Zr-La-La</td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Image of O adsorption structure on (111) plane" /> bridge Zr-Zr</td>
<td><img src="image" alt="Image of O adsorption structure on (011) plane" /> bridge La-La</td>
</tr>
<tr>
<td>OH</td>
<td><img src="image" alt="Image of OH adsorption structure on (111) plane" /> bridge Zr-La</td>
<td><img src="image" alt="Image of OH adsorption structure on (011) plane" /> bridge La-La</td>
</tr>
</tbody>
</table>

*The atoms belonging to the adsorbate are labeled. The color code is as follows: La – green, Zr – light blue, Rh – dark blue, O – red, C – grey, H – white.*
**Table A 3 cont.** Adsorbate structures at the strongest adsorption sites for all species considered in the reaction network for DRM on the (111) and (011) surfaces of the LRhZ pyrochlore.

<table>
<thead>
<tr>
<th>Species</th>
<th>Plane (111) Adsorbed structure</th>
<th>Plane (011) Adsorbed structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>atop Zr</td>
<td>bridge La-La</td>
</tr>
<tr>
<td></td>
<td>bridge Rh-La</td>
<td>atop La</td>
</tr>
<tr>
<td>H₂</td>
<td>atop Rh (side)</td>
<td>3-fold Rh-La-La</td>
</tr>
<tr>
<td></td>
<td>3-fold Zr-La-La</td>
<td></td>
</tr>
</tbody>
</table>

*The atoms belonging to the adsorbate are labeled. The color code is as follows: La – green, Zr – light blue, Rh – dark blue, O – red, C – grey, H – white.*
Table A 3 cont. Adsorbate structures at the strongest adsorption sites for all species considered in the reaction network for DRM on the (111) and (011) surfaces of the LRhZ pyrochlore.

<table>
<thead>
<tr>
<th>Species</th>
<th>Plane (111) Adsorbed structure</th>
<th>Plane (011) Adsorbed structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃OH</td>
<td>atop Zr (linear)</td>
<td>atop La (linear)</td>
</tr>
<tr>
<td></td>
<td><img src="image_url" alt="Image" /></td>
<td><img src="image_url" alt="Image" /></td>
</tr>
<tr>
<td>CH₂OH</td>
<td>bridge Zr-La</td>
<td>bridge Zr-La</td>
</tr>
<tr>
<td></td>
<td><img src="image_url" alt="Image" /></td>
<td><img src="image_url" alt="Image" /></td>
</tr>
<tr>
<td>CHOH</td>
<td>atop Zr (linear)</td>
<td>atop Rh (linear)</td>
</tr>
<tr>
<td></td>
<td><img src="image_url" alt="Image" /></td>
<td><img src="image_url" alt="Image" /></td>
</tr>
<tr>
<td>COH</td>
<td>N/A</td>
<td>3-fold Zr-La-La</td>
</tr>
<tr>
<td></td>
<td><img src="image_url" alt="Image" /></td>
<td><img src="image_url" alt="Image" /></td>
</tr>
</tbody>
</table>

* The atoms belonging to the adsorbate are labeled. The color code is as follows: La – green, Zr – light blue, Rh – dark blue, O – red, C – grey, H – white.
**Table A 3 cont.** Adsorbate structures at the strongest adsorption sites for all species considered in the reaction network for DRM on the (111) and (011) surfaces of the LRhZ pyrochlore.

<table>
<thead>
<tr>
<th>Species</th>
<th>Plane (111)</th>
<th>Plane (011)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CH₃O</strong></td>
<td>atop La (linear)</td>
<td>3-fold Zr-La-La</td>
</tr>
<tr>
<td><strong>CH₂O</strong></td>
<td>3-fold Rh-Zr-Zr</td>
<td>3-fold Zr-La-La</td>
</tr>
<tr>
<td><strong>CHO</strong></td>
<td>3-fold Rh-Zr-Zr</td>
<td>3-fold Zr-La-La</td>
</tr>
<tr>
<td><strong>CO</strong></td>
<td>atop Rh</td>
<td>3-fold Zr-La-La</td>
</tr>
</tbody>
</table>

* The atoms belonging to the adsorbate are labeled. The color code is as follows: La – green, Zr – light blue, Rh – dark blue, O – red, C – grey, H – white.
**Table A 3 cont.** Adsorbate structures at the strongest adsorption sites for all species considered in the reaction network for DRM on the (111) and (011) surfaces of the LRhZ pyrochlore.

<table>
<thead>
<tr>
<th>Species</th>
<th>Plane (111) Adsorbed structure</th>
<th>Plane (011) Adsorbed structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>3-fold Zr-Zr-La</td>
<td>bridge Zr-La</td>
</tr>
<tr>
<td>COOH</td>
<td>bridge Rh-Zr</td>
<td>atop Zr</td>
</tr>
</tbody>
</table>

* The atoms belonging to the adsorbate are labeled. The color code is as follows: La – green, Zr – light blue, Rh – dark blue, O – red, C – grey, H – white.
Table A 5. Reaction enthalpies and activation energies (forward and reverse) for all elementary reaction steps considered in the reaction network for DRM on the (011) and (111) pyrochlore surfaces.

<table>
<thead>
<tr>
<th>Elementary Reaction</th>
<th>Plane (011)</th>
<th>Plane (111)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta H_{\text{rxn}}$ (eV)</td>
<td>$E_{\text{a,f}}$ (eV)</td>
</tr>
<tr>
<td>R1</td>
<td>-0.13</td>
<td>0.00</td>
</tr>
<tr>
<td>R2</td>
<td>-1.36</td>
<td>0.38</td>
</tr>
<tr>
<td>R3</td>
<td>-1.39</td>
<td>1.41</td>
</tr>
<tr>
<td>R4</td>
<td>-1.16</td>
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<tr>
<td>R5</td>
<td>0.56</td>
<td>3.74</td>
</tr>
<tr>
<td>R6</td>
<td>-2.93</td>
<td>0.00</td>
</tr>
<tr>
<td>R7</td>
<td>-2.32</td>
<td>1.31</td>
</tr>
<tr>
<td>R8</td>
<td>3.31</td>
<td>3.32</td>
</tr>
<tr>
<td>R9</td>
<td>-3.38</td>
<td>0.22</td>
</tr>
<tr>
<td>R10</td>
<td>3.14</td>
<td>3.15</td>
</tr>
<tr>
<td>R11</td>
<td>-1.13</td>
<td>0.66</td>
</tr>
<tr>
<td>R12</td>
<td>3.41</td>
<td>3.42</td>
</tr>
<tr>
<td>R13</td>
<td>0.16</td>
<td>1.83</td>
</tr>
<tr>
<td>R14</td>
<td>4.73</td>
<td>6.43</td>
</tr>
<tr>
<td>R15</td>
<td>-2.55</td>
<td>2.96</td>
</tr>
<tr>
<td>R16</td>
<td>1.61</td>
<td>3.34</td>
</tr>
<tr>
<td>R17</td>
<td>-1.91</td>
<td>1.66</td>
</tr>
<tr>
<td>R18</td>
<td>2.46</td>
<td>2.57</td>
</tr>
<tr>
<td>R19</td>
<td>-0.59</td>
<td>2.29</td>
</tr>
<tr>
<td>R20</td>
<td>3.26</td>
<td>3.49</td>
</tr>
<tr>
<td>R21</td>
<td>-1.83</td>
<td>1.74</td>
</tr>
<tr>
<td>R22</td>
<td>2.59</td>
<td>6.90</td>
</tr>
<tr>
<td>R23</td>
<td>-0.07</td>
<td>3.08</td>
</tr>
<tr>
<td>R24</td>
<td>1.96</td>
<td>5.49</td>
</tr>
</tbody>
</table>

$^\dagger$Adsorption processes were considered barrierless.

The values in bold were obtained by using rigorous DFT methods (CI-NEB), whereas the other values were estimated using the BEP relationship derived in the present work. In the cases the BEP relationship provided a negative activation energy, its value was replaced by 0.01 eV and the barrier in the opposite direction (forward/reverse) was adjusted based on the value for $\Delta H_{\text{rxn}}$. 

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**Table A 6 cont.** Reaction enthalpies and activation energies (forward and reverse) for all elementary reaction steps considered in the reaction network for DRM on the (011) and (111) pyrochlore surfaces.

<table>
<thead>
<tr>
<th>Elementary Reaction</th>
<th>Plane (011)</th>
<th>Plane (111)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta H_{\text{rxn}}$ (eV)</td>
<td>$E_{a,f}$ (eV)</td>
</tr>
<tr>
<td>R25 CH$_3$OH*+* ⇌ CH$_3$O*+H*</td>
<td>-2.94</td>
<td>1.44</td>
</tr>
<tr>
<td>R26 CH$_2$OH*+* ⇌ CH$_2$O*+H*</td>
<td>-2.41</td>
<td>0.12</td>
</tr>
<tr>
<td>R27 CHOH*+* ⇌ CHO*+H*</td>
<td>-4.40</td>
<td>1.30</td>
</tr>
<tr>
<td>R28 O*+H* ⇌ OH*+*</td>
<td>2.26</td>
<td>5.60</td>
</tr>
<tr>
<td>R29 OH*+H* ⇌ H$_2$O*+*</td>
<td>3.03</td>
<td>3.04</td>
</tr>
<tr>
<td>R30 H$_2$O* ⇌ H$_2$O(g)+*</td>
<td>0.93</td>
<td>0.93</td>
</tr>
<tr>
<td>R31 H*+H* ⇌ H$_2$+*</td>
<td>2.60</td>
<td>2.65</td>
</tr>
<tr>
<td>R32 H$_2$* ⇌ H$_2$(g)+*</td>
<td>0.19</td>
<td>0.19</td>
</tr>
<tr>
<td>R33 CO* ⇌ CO(g)+*</td>
<td>2.53</td>
<td>2.53</td>
</tr>
<tr>
<td>R34 CH$_3$OH* ⇌ CH$_3$OH(g)+*</td>
<td>0.78</td>
<td>0.78</td>
</tr>
</tbody>
</table>

$^+$ Adsorption processes were considered barrierless.

The values in **bold** were obtained by using rigorous DFT methods (CI-NEB), whereas the other values were estimated using the BEP relationship derived in the present work. In the cases the BEP relationship provided a negative activation energy, its value was replaced by 0.01 eV and the barrier in the opposite direction (forward/reverse) was adjusted based on the value for $\Delta H_{\text{rxn}}$. 
Fig. A 5 Main reaction pathway for DRM on the plane (111) of LRhZ. The black dashed lines in the pictures indicate bonds for which the length is provided (in Å). Keep in mind that the reactions presented are not balanced stoichiometrically. The atoms belonging to the adsorbate are labeled. The color code is as follows: La – green, Zr – light blue, Rh – dark blue, O – red, C – grey, H – white.
Fig. A 6 Reaction path for $\text{CH}_3^*+^* \rightleftharpoons \text{CH}_2^*+\text{H}^*$ on the plane (111) of LRhZ. Energetics and structures calculated using CI-NEB. The Rxn coordinate ‘0’ refers to $\text{CH}_3^*+^*$. The Rxn coordinate ‘4’ refers to $\text{CH}_2^*+\text{H}^*$. The Rxn coordinates ‘1’, ‘2’ and ‘3’ refer to the three intermediate images considered. The color code is as follows: La – green, Zr – light blue, Rh – dark blue, O – red, C – grey, H – white.
Fig. A 7 Reaction path for C*+O* ⇌ CO*++ on the plane (011) of LRhZ. Energetics and structures calculated using CI-NEB. The Rxn coordinate '0' refers to C*+O*. The Rxn coordinate '4' refers to CO*++*. The Rxn coordinates ‘1’, ‘2’ and ‘3’ refer to the three intermediate images considered. The color code is as follows: La – green, Zr – light blue, Rh – dark blue, O – red, C – grey, H – white.
Fig. A 8 Reaction path for \( \text{CHO}^{*+*} \rightleftharpoons \text{CO}^{*+H}^* \) on the plane (011) of LRhZ. Energetics and structures calculated using CI-NEB. The Rxn coordinate '0' refers to \( \text{CHO}^{*+*} \). The Rxn coordinate ‘4’ refers to \( \text{CO}^{*+H}^* \). The Rxn coordinates ‘1’, ‘2’ and ‘3’ refer to the three intermediate images considered. The color code is as follows: La – green, Zr – light blue, Rh – dark blue, O – red, C – grey, H – white.
Fig. A 9 Reaction path for $O^*+H^* \rightleftharpoons OH^{**}$ on the plane (011) of LRhZ. Energetics and structures calculated using CI-NEB. The Rxn coordinate '0' refers to $O^*+H^*$. The Rxn coordinate ‘4’ refers to $OH^{**}$. The Rxn coordinates ‘1’, ‘2’ and ‘3’ refer to the three intermediate images considered. The color code is as follows: La – green, Zr – light blue, Rh – dark blue, O – red, C – grey, H – white.
Fig. A 10 Reaction path for C*+OH* ⇌ COH*++* on the plane (011) of LRhZ. Energetics and structures calculated using CI-NEB. The Rxn coordinate '0' refers to C*+OH*. The Rxn coordinate ‘4’ refers to COH*++. The Rxn coordinates ‘1’, ‘2’ and ‘3’ refer to the three intermediate images considered. The color code is as follows: La – green, Zr – light blue, Rh – dark blue, O – red, C – grey, H – white.
Fig. A 11 Reaction path for $\text{COH}^{\ast\ast} \rightleftharpoons \text{CO}^{\ast} + \text{H}^{\ast}$ on the plane (011) of LRhZ. Energetics and structures calculated using CI-NEB. The Rxn coordinate '0' refers to COH$^{\ast\ast}$. The Rxn coordinate '4' refers to CO$^{\ast} + $H$^{\ast}$. The Rxn coordinates ‘1’, ‘2’ and ‘3’ refer to the three intermediate images considered. The color code is as follows: La – green, Zr – light blue, Rh – dark blue, O – red, C – grey, H – white.
Fig. A 12 Reaction path for COH*+* ⇌ CO*+H* on the plane (011) of LRhZ. Energetics and structures calculated using CI-NEB. The Rxn coordinate '0' refers to COH*+*. The Rxn coordinate '4' refers to CO*+H*. The Rxn coordinates ‘1’, ‘2’ and ‘3’ refer to the three intermediate images considered. The color code is as follows: La – green, Zr – light blue, Rh – dark blue, O – red, C – grey, H – white.
Fig. A 13 Reaction path for $\text{CH}^{*+*} \rightleftharpoons \text{C}^{*+}\text{H}^{*}$ on the plane (011) of LRhZ. Energetics and structures calculated using CI-NEB. The Rxn coordinate '0' refers to CH$^{*+*}$. The Rxn coordinate '4' refers to C$^{*+}\text{H}^{*}$. The Rxn coordinates '1', '2' and '3' refer to the three intermediate images considered. The color code is as follows: La – green, Zr – light blue, Rh – dark blue, O – red, C – grey, H – white.
Fig. A 14 Reaction path for $\text{H}^*+\text{H}^* \rightleftharpoons \text{H}_2^*+^*$ on the plane (011) of LRhZ. Energetics and structures calculated using CI-NEB. The Rxn coordinate '0' refers to $\text{H}^*+\text{H}^*$. The Rxn coordinate ‘4’ refers to $\text{H}_2^*+^*$. The Rxn coordinates ‘1’, ‘2’ and ‘3’ refer to the three intermediate images considered. The color code is as follows: La – green, Zr – light blue, Rh – dark blue, O – red, C – grey, H – white.
Table A 7. Detailed list of all tested adsorption sites, the converged structures and the corresponding adsorption energies on the (111) plane. If there is not a reported converged structure, it means the simulation did not converge under the stipulated tolerances.

<table>
<thead>
<tr>
<th>Starting structure</th>
<th>Converged structure</th>
<th>$\Delta E_{\text{ads}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$ atop on Zr</td>
<td>not adsorbed</td>
<td>0.46</td>
</tr>
<tr>
<td>CH$_4$ atop on La</td>
<td>not adsorbed</td>
<td>0.28</td>
</tr>
<tr>
<td>CH$_4$ atop on Rh</td>
<td>atop Rh</td>
<td>-0.05</td>
</tr>
<tr>
<td>CH$_4$ bridging Zr and La</td>
<td>bridge Zr-La</td>
<td>-0.03</td>
</tr>
<tr>
<td>CH$_4$ bridging Zr and Zr</td>
<td>not adsorbed</td>
<td>0.02</td>
</tr>
<tr>
<td>CH$_4$ bridging Rh and La</td>
<td>3-fold Rh-Zr-La</td>
<td>-0.07</td>
</tr>
<tr>
<td>CH$_4$ bridging Rh and Zr</td>
<td>3-fold Rh-Zr-La</td>
<td>-0.06</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Starting structure</th>
<th>Converged structure</th>
<th>$\Delta E_{\text{ads}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$ atop on Zr</td>
<td>atop Zr</td>
<td>-2.17</td>
</tr>
<tr>
<td>CH$_3$ atop on La</td>
<td>atop La</td>
<td>-1.72</td>
</tr>
<tr>
<td>CH$_3$ atop on Rh</td>
<td>atop Rh</td>
<td>-1.87</td>
</tr>
<tr>
<td>CH$_3$ bridging Zr and La</td>
<td>bridge Zr-La</td>
<td>-2.32</td>
</tr>
<tr>
<td>CH$_3$ bridging Zr and Zr</td>
<td>atop Zr</td>
<td>-2.17</td>
</tr>
<tr>
<td>CH$_3$ bridging Rh and La</td>
<td>bridge Zr-La</td>
<td>-2.38</td>
</tr>
<tr>
<td>CH$_4$ bridging Rh and Zr</td>
<td>atop Rh</td>
<td>-1.91</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Starting structure</th>
<th>Converged structure</th>
<th>$\Delta E_{\text{ads}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$ atop on Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_2$ atop on La</td>
<td>atop La</td>
<td>-2.39</td>
</tr>
<tr>
<td>CH$_2$ atop on Rh</td>
<td>bridge Rh-Zr</td>
<td>-4.63</td>
</tr>
<tr>
<td>CH$_2$ bridging Zr and La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_2$ bridging Zr and Zr</td>
<td>3-fold Zr-Zr-La</td>
<td>-2.24</td>
</tr>
<tr>
<td>CH$_2$ bridging Rh and La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_2$ bridging Rh and Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

* ‘linear’ and ‘orthogonal’ structures refer to the orientation of the adsorbate on atop binding. ‘broken (A+B)’ means that the species dissociatively adsorbed on the surface into species A and B.*
Table A 8 cont. Detailed list of all tested adsorption sites, the converged structures and the corresponding adsorption energies on the (111) plane. If there is not a reported converged structure, it means the simulation did not converge under the stipulated tolerances.

<table>
<thead>
<tr>
<th>Starting structure $^#$</th>
<th>Converged structure $^#$</th>
<th>$\Delta$E$_{ads}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH linear on Zr</td>
<td>3-fold Rh-Zr-Zr</td>
<td>-7.22</td>
</tr>
<tr>
<td>CH orthogonal on Zr</td>
<td>3-fold Rh-Zr-Zr</td>
<td>-7.22</td>
</tr>
<tr>
<td>CH linear on La</td>
<td>atop La (linear)</td>
<td>-3.20</td>
</tr>
<tr>
<td>CH orthogonal on La</td>
<td>atop La (linear)</td>
<td>-3.22</td>
</tr>
<tr>
<td>CH linear on Rh</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH orthogonal on Rh</td>
<td>3-fold Rh-Zr-Zr</td>
<td>-7.19</td>
</tr>
<tr>
<td>CH bridging Zr and La</td>
<td>3-fold Zr-Zr-La</td>
<td>-4.71</td>
</tr>
<tr>
<td>CH bridging Zr and Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH bridging Rh and La</td>
<td>3-fold Rh-Zr-Zr</td>
<td>-7.22</td>
</tr>
<tr>
<td>CH bridging Rh and Zr</td>
<td>3-fold Rh-Zr-Zr</td>
<td>-7.22</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Starting structure $^#$</th>
<th>Converged structure $^#$</th>
<th>$\Delta$E$_{ads}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C atop on Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>C atop on La</td>
<td>atop La</td>
<td>-2.77</td>
</tr>
<tr>
<td>C atop on Rh</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>C bridging Zr and La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>C bridging Zr and Zr</td>
<td>3-fold Zr-Zr-La</td>
<td>-5.00</td>
</tr>
<tr>
<td>C bridging Rh and La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>C bridging Rh and Zr</td>
<td>3-fold Rh-Zr-Zr</td>
<td>-7.22</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Starting structure $^#$</th>
<th>Converged structure $^#$</th>
<th>$\Delta$E$_{ads}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H atop on Zr</td>
<td>bridge Rh-Zr</td>
<td>-2.95</td>
</tr>
<tr>
<td>H atop on La</td>
<td>atop La</td>
<td>-1.76</td>
</tr>
<tr>
<td>H atop on Rh</td>
<td>atop Rh</td>
<td>-2.72</td>
</tr>
<tr>
<td>H bridging Zr and La</td>
<td>bridge Rh-Zr</td>
<td>-3.02</td>
</tr>
<tr>
<td>H bridging Zr and Zr</td>
<td>bridge Zr-Zr</td>
<td>-2.26</td>
</tr>
<tr>
<td>H bridging Rh and La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>H bridging Rh and Zr</td>
<td>atop Rh</td>
<td>-2.68</td>
</tr>
</tbody>
</table>

$^\#$ ‘linear’ and ‘orthogonal’ structures refer to the orientation of the adsorbate on atop binding. ‘broken (A+B)’ means that the species dissociatively adsorbed on the surface into species A and B.
Table A 9 cont. Detailed list of all tested adsorption sites, the converged structures and the corresponding adsorption energies on the (111) plane. If there is not a reported converged structure, it means the simulation did not converge under the stipulated tolerances.

<table>
<thead>
<tr>
<th>Starting structure #</th>
<th>Converged structure #</th>
<th>$\Delta E_{\text{ads}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O atop on Zr</td>
<td>3-fold Rh-Zr-La</td>
<td>-6.80</td>
</tr>
<tr>
<td>O atop on La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>O atop on Rh</td>
<td>3-fold Rh-Zr-Zr</td>
<td>-7.36</td>
</tr>
<tr>
<td>O bridging Zr and La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>O bridging Zr and Zr</td>
<td>bridge Zr-Zr</td>
<td>-6.46</td>
</tr>
<tr>
<td>O bridging Rh and La</td>
<td>3-fold Rh-Zr-La</td>
<td>-6.72</td>
</tr>
<tr>
<td>O bridging Rh and Zr</td>
<td>3-fold Rh-Zr-Zr</td>
<td>-7.35</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Starting structure #</th>
<th>Converged structure #</th>
<th>$\Delta E_{\text{ads}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH linear on Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>OH orthogonal on Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>OH linear on La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>OH orthogonal on La</td>
<td>atop La (linear)</td>
<td>-4.74</td>
</tr>
<tr>
<td>OH linear on Rh</td>
<td>bridge Zr-La</td>
<td>-5.37</td>
</tr>
<tr>
<td>OH orthogonal on Rh</td>
<td>bridge Zr-La</td>
<td>-5.33</td>
</tr>
<tr>
<td>OH bridging Zr and La</td>
<td>bridge Zr-La</td>
<td>-5.38</td>
</tr>
<tr>
<td>OH bridging Zr and Zr</td>
<td>bridge Zr-La</td>
<td>-5.38</td>
</tr>
<tr>
<td>OH bridging Rh and La</td>
<td>bridge Zr-La</td>
<td>-5.39</td>
</tr>
<tr>
<td>OH bridging Rh and Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

# ‘linear’ and ‘orthogonal’ structures refer to the orientation of the adsorbate on atop binding. ‘broken (A+B)’ means that the species dissociatively adsorbed on the surface into species A and B.
Table A 10 cont. Detailed list of all tested adsorption sites, the converged structures and the corresponding adsorption energies on the (111) plane. If there is not a reported converged structure, it means the simulation did not converge under the stipulated tolerances.

<table>
<thead>
<tr>
<th>Starting structure</th>
<th>Converged structure</th>
<th>$\Delta E_{ads}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2O$ atop on Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>$H_2O$ atop on La</td>
<td>atop La (O binds La and hydrogens point away from the surface)</td>
<td>-0.50</td>
</tr>
<tr>
<td>$H_2O$ atop on Rh</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>$H_2O$ bridging Zr and La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>$H_2O$ bridging Zr and Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>$H_2O$ bridging Rh and La</td>
<td>bridge Rh-La</td>
<td>-0.78</td>
</tr>
<tr>
<td>$H_2O$ bridging Rh and Zr</td>
<td>atop Zr (O binds Zr. One H points to the surface and the other points away from it)</td>
<td>-0.79</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Starting structure</th>
<th>Converged structure</th>
<th>$\Delta E_{ads}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2$ linear on Zr</td>
<td>atop Zr (orthogonal)</td>
<td>-0.05</td>
</tr>
<tr>
<td>$H_2$ orthogonal on Zr</td>
<td>atop Zr (orthogonal)</td>
<td>-0.07</td>
</tr>
<tr>
<td>$H_2$ linear on La</td>
<td>atop La (orthogonal)</td>
<td>-0.06</td>
</tr>
<tr>
<td>$H_2$ orthogonal on La</td>
<td>atop La (orthogonal)</td>
<td>-0.06</td>
</tr>
<tr>
<td>$H_2$ linear on Rh</td>
<td>atop Rh (linear)</td>
<td>-0.04</td>
</tr>
<tr>
<td>$H_2$ orthogonal on Rh</td>
<td>atop Rh (orthogonal)</td>
<td>-0.38</td>
</tr>
<tr>
<td>$H_2$ bridging Zr and La</td>
<td>bridge Zr-La</td>
<td>-0.06</td>
</tr>
<tr>
<td>$H_2$ bridging Zr and Zr</td>
<td>bridge Zr-Zr</td>
<td>-0.02</td>
</tr>
<tr>
<td>$H_2$ bridging Rh and La</td>
<td>broken (H + H)</td>
<td>-1.23</td>
</tr>
<tr>
<td>$H_2$ bridging Rh and Zr</td>
<td>broken (H + H)</td>
<td>-1.25</td>
</tr>
</tbody>
</table>

# ‘linear’ and ‘orthogonal’ structures refer to the orientation of the adsorbate on atop binding. ‘broken (A+B)’ means that the species dissociatively adsorbed on the surface into species A and B.
Table A 11 cont. Detailed list of all tested adsorption sites, the converged structures and the corresponding adsorption energies on the (111) plane. If there is not a reported converged structure, it means the simulation did not converge under the stipulated tolerances.

<table>
<thead>
<tr>
<th>Starting structure</th>
<th>Converged structure</th>
<th>$\Delta E_{\text{ads}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$OH (C-end binds linear on Zr)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_3$OH (O-end binds linear on Zr)</td>
<td>atop Zr (O-end binds linear)</td>
<td>-0.78</td>
</tr>
<tr>
<td>CH$_3$OH orthogonal on Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_3$OH (C-end binds linear on La)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_3$OH (O-end binds linear on La)</td>
<td>atop La (O-end binds linear)</td>
<td>-0.59</td>
</tr>
<tr>
<td>CH$_3$OH orthogonal on La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_3$OH (C-end binds linear on Rh)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_3$OH (O-end binds linear on Rh)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_3$OH orthogonal on Rh</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_3$OH bridging Zr and La</td>
<td>bridge Zr-La</td>
<td>-0.52</td>
</tr>
<tr>
<td>CH$_3$OH bridging Zr and Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_3$OH bridging Rh and La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_3$OH bridging Rh and Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Starting structure</th>
<th>Converged structure</th>
<th>$\Delta E_{\text{ads}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$OH (C-end binds linear on Zr)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_2$OH (O-end binds linear on Zr)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_2$OH orthogonal on Zr</td>
<td>atop Zr (orthogonal)</td>
<td>-2.50</td>
</tr>
<tr>
<td>CH$_2$OH (C-end binds linear on La)</td>
<td>atop La (linear)</td>
<td>-1.30</td>
</tr>
<tr>
<td>CH$_2$OH (O-end binds linear on La)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_2$OH orthogonal on La</td>
<td>not adsorbed</td>
<td>0.33</td>
</tr>
<tr>
<td>CH$_2$OH (C-end binds linear on Rh)</td>
<td>atop Rh (C-end binds Rh. Bent structure)</td>
<td>-1.86</td>
</tr>
<tr>
<td>CH$_2$OH (O-end binds linear on Rh)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_2$OH orthogonal on Rh</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_2$OH bridging Zr and La</td>
<td>bridge Zr-La</td>
<td>-2.54</td>
</tr>
<tr>
<td>CH$_2$OH bridging Zr and Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_2$OH bridging Rh and La</td>
<td>bridge Zr-La</td>
<td>-2.28</td>
</tr>
<tr>
<td>CH$_2$OH bridging Rh and Zr</td>
<td>bridge Zr-La</td>
<td>-1.88</td>
</tr>
</tbody>
</table>

* ‘linear’ and ‘orthogonal’ structures refer to the orientation of the adsorbate on atop binding. ‘broken (A+B)’ means that the species dissociatively adsorbed on the surface into species A and B.
Table A 12 cont. Detailed list of all tested adsorption sites, the converged structures and the corresponding adsorption energies on the (111) plane. If there is not a reported converged structure, it means the simulation did not converge under the stipulated tolerances.

<table>
<thead>
<tr>
<th>Starting structure#</th>
<th>Converged structure#</th>
<th>$\Delta E_{ads}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHO (C-end binds linear on Zr)</td>
<td>atop Zr (linear)</td>
<td>-2.18</td>
</tr>
<tr>
<td>CHO (O-end binds linear on Zr)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CHOH orthogonal on Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CHO (C-end binds linear on La)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CHO (O-end binds linear on La)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CHOH orthogonal on La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CHOH (C-end binds linear on Rh)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CHO (O-end binds linear on Rh)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CHOH orthogonal on Rh</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CHOH bridging Zr and La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CHOH bridging Zr and Zr</td>
<td>broken (H$_{isolated}$ + CHO)</td>
<td>-1.02</td>
</tr>
<tr>
<td>CHOH bridging Rh and La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CHOH bridging Rh and Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Starting structure#</th>
<th>Converged structure#</th>
<th>$\Delta E_{ads}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COH (C-end binds linear on Zr)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>COH (O-end binds linear on Zr)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>COH orthogonal on Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>COH (C-end binds linear on La)</td>
<td>transformed into CHO (atop La (orthogonal))</td>
<td>-3.71</td>
</tr>
<tr>
<td>COH (O-end binds linear on La)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>COH orthogonal on La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>COH (C-end binds linear on Rh)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>COH (O-end binds linear on Rh)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>COH orthogonal on Rh</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>COH bridging Zr and La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>COH bridging Zr and Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>COH bridging Rh and La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>COH bridging Rh and Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

# ‘linear’ and ‘orthogonal’ structures refer to the orientation of the adsorbate on atop binding. ‘broken (A+B)’ means that the species dissociatively adsorbed on the surface into species A and B.
Table A 13 cont. Detailed list of all tested adsorption sites, the converged structures and the corresponding adsorption energies on the (111) plane. If there is not a reported converged structure, it means the simulation did not converge under the stipulated tolerances.

<table>
<thead>
<tr>
<th>Starting structure#</th>
<th>Converged structure#</th>
<th>$\Delta E_{\text{ads}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$O (C-end binds linear on Zr)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_3$O (O-end binds linear on Zr)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_3$O orthogonal on Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_3$O (C-end binds linear on La)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_3$O (O-end binds linear on La)</td>
<td>atop La (linear)</td>
<td>-3.87</td>
</tr>
<tr>
<td>CH$_3$O orthogonal on La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_3$O (C-end binds linear on Rh)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_3$O (O-end binds linear on Rh)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_3$O orthogonal on Rh</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_3$O bridging Zr and La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_3$O bridging Zr and Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_3$O bridging Rh and La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_3$O bridging Rh and Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Starting structure#</th>
<th>Converged structure#</th>
<th>$\Delta E_{\text{ads}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$O (C-end binds linear on Zr)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_2$O (O-end binds linear on Zr)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_2$O orthogonal on Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_2$O (C-end binds linear on La)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_2$O (O-end binds linear on La)</td>
<td>atop La (O-end binds linear)</td>
<td>-1.10</td>
</tr>
<tr>
<td>CH$_2$O orthogonal on La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_2$O (C-end binds linear on Rh)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_2$O (O-end binds linear on Rh)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_2$O orthogonal on Rh</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_2$O bridging Zr and La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_2$O bridging Zr and Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_2$O bridging Rh and La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_2$O bridging Rh and Zr</td>
<td>3-fold Rh-Zr-Zr</td>
<td>-1.72</td>
</tr>
</tbody>
</table>

# ‘linear’ and ‘orthogonal’ structures refer to the orientation of the adsorbate on atop binding. ‘broken (A+B)’ means that the species dissociatively adsorbed on the surface into species A and B.
Table A 14 cont. Detailed list of all tested adsorption sites, the converged structures and the corresponding adsorption energies on the (111) plane. If there is not a reported converged structure, it means the simulation did not converge under the stipulated tolerances.

<table>
<thead>
<tr>
<th>Starting structure#</th>
<th>Converged structure#</th>
<th>$\Delta E_{ads}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHO (C-end binds linear on Zr)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CHO (O-end binds linear on Zr)</td>
<td>bridge Zr-La</td>
<td>-2.27</td>
</tr>
<tr>
<td>CHO orthogonal on Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CHO (C-end binds linear on La)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CHO (O-end binds linear on La)</td>
<td>atop La (orthogonal)</td>
<td>-1.90</td>
</tr>
<tr>
<td>CHO orthogonal on La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CHO (C-end binds linear on Rh)</td>
<td>3-fold Rh-Zr-Zr</td>
<td>-3.57</td>
</tr>
<tr>
<td>CHO (O-end binds linear on Rh)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CHO orthogonal on Rh</td>
<td>3-fold Rh-Zr-Zr</td>
<td>-3.61</td>
</tr>
<tr>
<td>CHO bridging Zr and La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CHO bridging Zr and Zr</td>
<td>bridge Zr-Zr</td>
<td>-2.48</td>
</tr>
<tr>
<td>CHO bridging Rh and La</td>
<td>bridge Zr-La</td>
<td>-1.55</td>
</tr>
<tr>
<td>CHO bridging Rh and Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Starting structure#</th>
<th>Converged structure#</th>
<th>$\Delta E_{ads}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO linear on Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CO orthogonal on Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CO linear on La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CO orthogonal on La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CO linear on Rh</td>
<td>atop Rh (C-end binds linear)</td>
<td>-1.63</td>
</tr>
<tr>
<td>CO orthogonal on Rh</td>
<td>atop Rh (C-end binds linear)</td>
<td>-1.62</td>
</tr>
<tr>
<td>CO bridging Zr and La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CO bridging Zr and Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CO bridging Rh and La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CO bridging Rh and Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

# ‘linear’ and ‘orthogonal’ structures refer to the orientation of the adsorbate on atop binding. ‘broken (A+B)’ means that the species dissociatively adsorbed on the surface into species A and B.
Table A 15 cont. Detailed list of all tested adsorption sites, the converged structures and the corresponding adsorption energies on the (111) plane. If there is not a reported converged structure, it means the simulation did not converge under the stipulated tolerances.

<table>
<thead>
<tr>
<th>Starting structure</th>
<th>Converged structure</th>
<th>$\Delta E_{\text{ads}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ orthogonal on Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CO$_2$ orthogonal on La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CO$_2$ orthogonal on Rh</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CO$_2$ bridging Zr and La</td>
<td>broken (CO + O)</td>
<td>-2.86</td>
</tr>
<tr>
<td>CO$_2$ bridging Zr and Zr</td>
<td>3-fold Zr-Zr-La</td>
<td>-1.46</td>
</tr>
<tr>
<td>CO$_2$ bridging Rh and La</td>
<td>3-fold Rh-Zr-La</td>
<td>-1.02</td>
</tr>
<tr>
<td>CO$_2$ bridging Rh and Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CO$_2$ linear on Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CO$_2$ linear on La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CO$_2$ linear on Rh</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Starting structure</th>
<th>Converged structure</th>
<th>$\Delta E_{\text{ads}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COOH (OH-end binds linear on Zr)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>COOH (O-end binds linear on Zr)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>COOH orthogonal on Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>COOH (OH-end binds linear on La)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>COOH (O-end binds linear on La)</td>
<td>atop La (orthogonal)</td>
<td>-2.43</td>
</tr>
<tr>
<td>COOH orthogonal on La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>COOH (OH-end binds linear on Rh)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>COOH (O-end binds linear on Rh)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>COOH orthogonal on Rh</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>COOH bridging Zr and La</td>
<td>not adsorbed</td>
<td>1.63</td>
</tr>
<tr>
<td>COOH bridging Zr and Zr</td>
<td>atop Zr (O-end binds Zr. Bent structure)</td>
<td>-3.04</td>
</tr>
<tr>
<td>COOH bridging Rh and La</td>
<td>3-fold Rh-Zr-La</td>
<td>-3.23</td>
</tr>
<tr>
<td>COOH bridging Rh and Zr</td>
<td>bridge Rh-Zr</td>
<td>-3.38</td>
</tr>
</tbody>
</table>

# ‘linear’ and ‘orthogonal’ structures refer to the orientation of the adsorbate on atop binding. ‘broken (A+B)’ means that the species dissociatively adsorbed on the surface into species A and B.

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Table A 16. Detailed list of all tested adsorption sites, the converged structures and the corresponding adsorption energies on the (011) plane. If there is not a reported converged structure, it means the simulation did not converge under the stipulated tolerances.

<table>
<thead>
<tr>
<th>Starting structure‡</th>
<th>Converged structure‡</th>
<th>∆E\textsubscript{ads} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH\textsubscript{4} atop on Zr</td>
<td>not adsorbed</td>
<td>0.05</td>
</tr>
<tr>
<td>CH\textsubscript{4} atop on La</td>
<td>atop La</td>
<td>-0.13</td>
</tr>
<tr>
<td>CH\textsubscript{4} atop on Rh</td>
<td>not adsorbed</td>
<td>0.02</td>
</tr>
<tr>
<td>CH\textsubscript{4} bridging Zr and La</td>
<td>3-fold Zr-La-La</td>
<td>-0.07</td>
</tr>
<tr>
<td>CH\textsubscript{4} bridging La and La = bridge Rh-Zr</td>
<td>not adsorbed</td>
<td>0.06</td>
</tr>
<tr>
<td>CH\textsubscript{4} bridging Rh and La</td>
<td>not adsorbed</td>
<td>0.80</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Starting structure‡</th>
<th>Converged structure‡</th>
<th>∆E\textsubscript{ads} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH\textsubscript{3} atop on Zr</td>
<td>atop Zr</td>
<td>-2.53</td>
</tr>
<tr>
<td>CH\textsubcript{3} atop on La</td>
<td>atop La</td>
<td>-2.04</td>
</tr>
<tr>
<td>CH\textsubscript{3} atop on Rh</td>
<td>atop Rh</td>
<td>-2.23</td>
</tr>
<tr>
<td>CH\textsubscript{3} bridging Zr and La</td>
<td>atop Zr</td>
<td>-2.57</td>
</tr>
<tr>
<td>CH\textsubscript{3} bridging La and La = bridge Rh-Zr</td>
<td>3-fold Zr-La-La</td>
<td>-2.58</td>
</tr>
<tr>
<td>CH\textsubscript{3} bridging Rh and La</td>
<td>bridge Rh-La</td>
<td>-1.78</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Starting structure‡</th>
<th>Converged structure‡</th>
<th>∆E\textsubscript{ads} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH\textsubscript{2} atop on Zr</td>
<td>3-fold Zr-La-La</td>
<td>-5.01</td>
</tr>
<tr>
<td>CH\textsubscript{2} atop on La</td>
<td>3-fold Zr-La-La</td>
<td>-4.77</td>
</tr>
<tr>
<td>CH\textsubscript{2} atop on Rh</td>
<td>atop Rh</td>
<td>-3.10</td>
</tr>
<tr>
<td>CH\textsubscript{2} bridging Zr and La</td>
<td>3-fold Zr-La-La</td>
<td>-5.03</td>
</tr>
<tr>
<td>CH\textsubscript{2} bridging La and La = bridge Rh-Zr</td>
<td>3-fold Zr-La-La</td>
<td>-5.30</td>
</tr>
<tr>
<td>CH\textsubscript{2} bridging Rh and La</td>
<td>atop Rh</td>
<td>-3.18</td>
</tr>
</tbody>
</table>

‘linear’ and ‘orthogonal’ structures refer to the orientation of the adsorbate on atop binding. ‘bridging La and La = bridge Rh-Zr’ means that the bridge La-La and bridge Rh-Zr site constitute the same position on the surface slab. ‘broken (A+B)’ means that the species dissociatively adsorbed on the surface into species A and B.
Table A 17 cont. Detailed list of all tested adsorption sites, the converged structures and the corresponding adsorption energies on the (011) plane. If there is not a reported converged structure, it means the simulation did not converge under the stipulated tolerances.

<table>
<thead>
<tr>
<th>Starting structure‡</th>
<th>Converged structure‡</th>
<th>$\Delta E_{ads}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH linear on Zr</td>
<td>3-fold Zr-La-La</td>
<td>-7.67</td>
</tr>
<tr>
<td>CH orthogonal on Zr</td>
<td>3-fold Zr-La-La</td>
<td>-7.67</td>
</tr>
<tr>
<td>CH linear on La</td>
<td>3-fold Zr-La-La</td>
<td>-6.29</td>
</tr>
<tr>
<td>CH orthogonal on La</td>
<td>3-fold Zr-La-La</td>
<td>-7.16</td>
</tr>
<tr>
<td>CH linear on Rh</td>
<td>atop Rh (bent structure)</td>
<td>-4.09</td>
</tr>
<tr>
<td>CH orthogonal on Rh</td>
<td>in bulk bridge Rh-La</td>
<td>-6.39</td>
</tr>
<tr>
<td>CH bridging Zr and La</td>
<td>3-fold Zr-La-La</td>
<td>-7.16</td>
</tr>
<tr>
<td>CH bridging La and La = bridge Rh-Zr</td>
<td>3-fold Zr-La-La</td>
<td>-7.67</td>
</tr>
<tr>
<td>CH bridging Rh and La</td>
<td>bridge Rh-La</td>
<td>-4.16</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Starting structure‡</th>
<th>Converged structure‡</th>
<th>$\Delta E_{ads}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C atop on Zr</td>
<td>3-fold Zr-La-La</td>
<td>-6.88</td>
</tr>
<tr>
<td>C atop on La</td>
<td>3-fold Zr-La-La</td>
<td>-6.69</td>
</tr>
<tr>
<td>C atop on Rh</td>
<td>in bulk bridge Rh-La</td>
<td>-7.11</td>
</tr>
<tr>
<td>C bridging Zr and La</td>
<td>bridge Zr-La</td>
<td>-4.52</td>
</tr>
<tr>
<td>C bridging La and La = bridge Rh-Zr</td>
<td>3-fold Zr-La-La</td>
<td>-6.51</td>
</tr>
<tr>
<td>C bridging Rh and La</td>
<td>bridge Rh-La</td>
<td>-4.82</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Starting structure‡</th>
<th>Converged structure‡</th>
<th>$\Delta E_{ads}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H atop on Zr</td>
<td>3-fold Zr-La-La</td>
<td>-3.13</td>
</tr>
<tr>
<td>H atop on La</td>
<td>3-fold Zr-La-La</td>
<td>-3.13</td>
</tr>
<tr>
<td>H atop on Rh</td>
<td>atop Rh</td>
<td>-1.97</td>
</tr>
<tr>
<td>H bridging Zr and La</td>
<td>3-fold Zr-La-La</td>
<td>-3.14</td>
</tr>
<tr>
<td>H bridging La and La = bridge Rh-Zr</td>
<td>3-fold Zr-La-La</td>
<td>-3.27</td>
</tr>
<tr>
<td>H bridging Rh and La</td>
<td>bridge Rh-La</td>
<td>-3.66</td>
</tr>
</tbody>
</table>

‡ ‘linear’ and ‘orthogonal’ structures refer to the orientation of the adsorbate on atop binding. ‘bridging La and La = bridge Rh-Zr’ means that the bridge La-La and bridge Rh-Zr site constitute the same position on the surface slab. ‘broken (A+B)’ means that the species dissociatively adsorbed on the surface into species A and B.
Table A 18 cont. Detailed list of all tested adsorption sites, the converged structures and the corresponding adsorption energies on the (011) plane. If there is not a reported converged structure, it means the simulation did not converge under the stipulated tolerances.

<table>
<thead>
<tr>
<th>Starting structure‡</th>
<th>Converged structure‡</th>
<th>(\Delta E_{\text{ads}}) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O atop on Zr</td>
<td>3-fold Zr-La-La</td>
<td>-8.99</td>
</tr>
<tr>
<td>O atop on La</td>
<td>3-fold Zr-La-La</td>
<td>-8.55</td>
</tr>
<tr>
<td>O atop on Rh</td>
<td>bridge La-La</td>
<td>-7.89</td>
</tr>
<tr>
<td>O bridging Zr and La</td>
<td>3-fold Zr-La-La</td>
<td>-8.55</td>
</tr>
<tr>
<td>O bridging La and La = bridge Rh-Zr</td>
<td>3-fold Zr-La-La</td>
<td>-8.07</td>
</tr>
<tr>
<td>O bridging Rh and La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Starting structure‡</th>
<th>Converged structure‡</th>
<th>(\Delta E_{\text{ads}}) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH linear on Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>OH orthogonal on Zr</td>
<td>bridge Zr-La</td>
<td>-5.49</td>
</tr>
<tr>
<td>OH linear on La</td>
<td>atop La (linear)</td>
<td>-5.01</td>
</tr>
<tr>
<td>OH orthogonal on La</td>
<td>atop La (linear)</td>
<td>-5.02</td>
</tr>
<tr>
<td>OH linear on Rh</td>
<td>bridge La-La</td>
<td>-4.90</td>
</tr>
<tr>
<td>OH orthogonal on Rh</td>
<td>bridge La-La</td>
<td>-5.84</td>
</tr>
<tr>
<td>OH bridging Zr and La</td>
<td>broken(O+H)</td>
<td>-7.31</td>
</tr>
<tr>
<td>OH bridging La and La = bridge Rh-Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>OH bridging Rh and La</td>
<td>bridge La-La</td>
<td>-5.19</td>
</tr>
</tbody>
</table>

‡ ‘linear’ and ‘orthogonal’ structures refer to the orientation of the adsorbate on atop binding. ‘bridging La and La = bridge Rh-Zr’ means that the bridge La-La and bridge Rh-Zr site constitute the same position on the surface slab. ‘broken (A+B)’ means that the species dissociatively adsorbed on the surface into species A and B.
Table A 19 cont. Detailed list of all tested adsorption sites, the converged structures and the corresponding adsorption energies on the (011) plane. If there is not a reported converged structure, it means the simulation did not converge under the stipulated tolerances.

<table>
<thead>
<tr>
<th>Starting structure‡</th>
<th>Converged structure‡</th>
<th>$\Delta E_{ads}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O atop on Zr</td>
<td>atop Zr (O binds Zr. One H orients parallel to the surface, and the other points away from the surface)</td>
<td>-0.55</td>
</tr>
<tr>
<td>H$_2$O atop on La</td>
<td>atop La (O binds La. One H points to the surface and the other points away from it)</td>
<td>-0.81</td>
</tr>
<tr>
<td>H$_2$O atop on Rh</td>
<td>broken (O+H+H)</td>
<td>-0.47</td>
</tr>
<tr>
<td>H$_2$O bridging Zr and La</td>
<td>atop La (O binds La. One H points to the surface and the other points away from it)</td>
<td>-0.81</td>
</tr>
<tr>
<td>H$_2$O bridging La and La = bridge Rh-Zr</td>
<td>bridge La-La</td>
<td>-0.93</td>
</tr>
<tr>
<td>H$_2$O bridging Rh and La</td>
<td>atop La (O binds La. One H points to the surface and the other points away from it. Bent structure)</td>
<td>-0.62</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Starting structure‡</th>
<th>Converged structure‡</th>
<th>$\Delta E_{ads}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$ linear on Zr</td>
<td>not adsorbed</td>
<td>0.00</td>
</tr>
<tr>
<td>H$_2$ orthogonal on Zr</td>
<td>atop Zr (linear)</td>
<td>-0.01</td>
</tr>
<tr>
<td>H$_2$ linear on La</td>
<td>atop La (orthogonal)</td>
<td>-0.05</td>
</tr>
<tr>
<td>H$_2$ orthogonal on La</td>
<td>atop La (orthogonal)</td>
<td>-0.06</td>
</tr>
<tr>
<td>H$_2$ linear on Rh</td>
<td>atop Rh (linear)</td>
<td>0.04</td>
</tr>
<tr>
<td>H$_2$ orthogonal on Rh</td>
<td>broken (H+H on Rh)</td>
<td>0.04</td>
</tr>
<tr>
<td>H$_2$ bridging Zr and La</td>
<td>3-fold Zr-La-La</td>
<td>-0.09</td>
</tr>
<tr>
<td>H$_2$ bridging La and La = bridge Rh-Zr</td>
<td>3-fold Rh-La-La</td>
<td>-0.19</td>
</tr>
<tr>
<td>H$_2$ bridging Rh and La</td>
<td>3-fold Rh-La-La</td>
<td>-0.08</td>
</tr>
</tbody>
</table>

‡ ‘linear’ and ‘orthogonal’ structures refer to the orientation of the adsorbate on atop binding. ‘bridging La and La = bridge Rh-Zr’ means that the bridge La-La and bridge Rh-Zr site constitute the same position on the surface slab. ‘broken (A+B)’ means that the species dissociatively adsorbed on the surface into species A and B.
Table A 20 cont. Detailed list of all tested adsorption sites, the converged structures and the corresponding adsorption energies on the (011) plane. If there is not a reported converged structure, it means the simulation did not converge under the stipulated tolerances.

<table>
<thead>
<tr>
<th>Starting structure ‡</th>
<th>Converged structure ‡</th>
<th>$\Delta E_{\text{ads}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$OH (C-end binds linear on Zr)</td>
<td>not adsorbed</td>
<td>0.04</td>
</tr>
<tr>
<td>CH$_3$OH (O-end binds linear on Zr)</td>
<td>atop Zr (O binds Zr. Bent structure)</td>
<td>-0.49</td>
</tr>
<tr>
<td>CH$_3$OH orthogonal on Zr</td>
<td>atop Zr (O binds Zr. Bent structure)</td>
<td>-0.45</td>
</tr>
<tr>
<td>CH$_3$OH (C-end binds linear on La)</td>
<td>atop La (C-end points toward surface)</td>
<td>-0.04</td>
</tr>
<tr>
<td>CH$_3$OH (O-end binds linear on La)</td>
<td>atop La (O-end binds linear on La)</td>
<td>-0.78</td>
</tr>
<tr>
<td>CH$_3$OH orthogonal on La</td>
<td>atop La (O-end binds to La. Bent structure)</td>
<td>-0.60</td>
</tr>
<tr>
<td>CH$_3$OH (C-end binds linear on Rh)</td>
<td>atop Rh (C-end points toward surface)</td>
<td>-0.01</td>
</tr>
<tr>
<td>CH$_3$OH (O-end binds linear on Rh)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_3$OH orthogonal on Rh</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_3$OH bridging Zr and La</td>
<td>atop Zr (O-end binds to Zr. Bent structure)</td>
<td>-0.52</td>
</tr>
<tr>
<td>CH$_3$OH bridging La and La = bridge Rh-Zr</td>
<td>broken (CH + H + H$_2$(g) + O)</td>
<td>-1.63</td>
</tr>
<tr>
<td>CH$_3$OH bridging Rh and La</td>
<td>bridge Rh-La</td>
<td>-0.38</td>
</tr>
</tbody>
</table>

‡ ‘linear’ and ‘orthogonal’ structures refer to the orientation of the adsorbate on atop binding. ‘bridging La and La = bridge Rh-Zr’ means that the bridge La-La and bridge Rh-Zr site constitute the same position on the surface slab. ‘broken (A+B)’ means that the species dissociatively adsorbed on the surface into species A and B.
Table A 21 cont. Detailed list of all tested adsorption sites, the converged structures and the corresponding adsorption energies on the (011) plane. If there is not a reported converged structure, it means the simulation did not converge under the stipulated tolerances.

<table>
<thead>
<tr>
<th>Starting structure‡</th>
<th>Converged structure‡</th>
<th>(\Delta E_{\text{ads}}) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_2)OH (C-end binds linear on Zr)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH(_2)OH (O-end binds linear on Zr)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH(_2)OH orthogonal on Zr</td>
<td>bridge Zr-La</td>
<td>-2.73</td>
</tr>
<tr>
<td>CH(_2)OH (C-end binds linear on La)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH(_2)OH (O-end binds linear on La)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH(_2)OH orthogonal on La</td>
<td>atop La (orthogonal)</td>
<td>-1.63</td>
</tr>
<tr>
<td>CH(_2)OH (C-end binds linear on Rh)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH(_2)OH (O-end binds linear on Rh)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH(_2)OH orthogonal on Rh</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH(_2)OH bridging Zr and La</td>
<td>bridge Zr-La</td>
<td>-2.17</td>
</tr>
<tr>
<td>CH(_2)OH bridging La and La = bridge Rh-Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH(_2)OH bridging Rh and La</td>
<td>bridge La-La</td>
<td>-2.29</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Starting structure‡</th>
<th>Converged structure‡</th>
<th>(\Delta E_{\text{ads}}) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHO(_2)H linear on Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CHO(_2)H orthogonal on Zr</td>
<td>broken (CH + OH)</td>
<td>-5.56</td>
</tr>
<tr>
<td>CHO(_2)H linear on La</td>
<td>atop La (C-end binds La. Bent structure)</td>
<td>-2.13</td>
</tr>
<tr>
<td>CHO(_2)H orthogonal on La</td>
<td>broken (CH + OH)</td>
<td>-3.30</td>
</tr>
<tr>
<td>CHO(_2)H linear on Rh</td>
<td>atop Rh (C-end binds Rh. Bent structure)</td>
<td>-2.75</td>
</tr>
<tr>
<td>CHO(_2)H orthogonal on Rh</td>
<td>broken (H + H + CO)</td>
<td>-3.88</td>
</tr>
<tr>
<td>CHO(_2)H bridging Zr and La</td>
<td>broken (CH + OH)</td>
<td>-6.38</td>
</tr>
<tr>
<td>CHO(_2)H bridging La and La = bridge Rh-Zr</td>
<td>broken (CH + OH)</td>
<td>-4.27</td>
</tr>
<tr>
<td>CHO(_2)H bridging Rh and La</td>
<td>broken (CH + OH)</td>
<td>-2.30</td>
</tr>
</tbody>
</table>

‡ ‘linear’ and ‘orthogonal’ structures refer to the orientation of the adsorbate on atop binding. ‘bridging La and La = bridge Rh-Zr’ means that the bridge La-La and bridge Rh-Zr site constitute the same position on the surface slab. ‘broken (A+B)’ means that the species dissociatively adsorbed on the surface into species A and B.
Table A 22 cont. Detailed list of all tested adsorption sites, the converged structures and the corresponding adsorption energies on the (011) plane. If there is not a reported converged structure, it means the simulation did not converge under the stipulated tolerances.

<table>
<thead>
<tr>
<th>Starting structure</th>
<th>Converged structure</th>
<th>$\Delta E_{\text{ads}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COH linear on Zr</td>
<td>broken (CO + H)</td>
<td>-4.60</td>
</tr>
<tr>
<td>COH orthogonal on Zr</td>
<td>broken (C + OH)</td>
<td>-5.65</td>
</tr>
<tr>
<td>COH linear on La</td>
<td>3-fold Zr-La-La</td>
<td>-4.95</td>
</tr>
<tr>
<td>COH orthogonal on La</td>
<td>3-fold Zr-La-La</td>
<td>-4.42</td>
</tr>
<tr>
<td>COH linear on Rh</td>
<td>broken (CO + H)</td>
<td>-5.33</td>
</tr>
<tr>
<td>COH orthogonal on Rh</td>
<td>broken (OH + C$_\text{in bulk}$)</td>
<td>-5.15</td>
</tr>
<tr>
<td>COH bridging Zr and La</td>
<td>broken (C + OH)</td>
<td>-4.42</td>
</tr>
<tr>
<td>COH bridging La and La = bridge Rh-Zr</td>
<td>broken (C + OH)</td>
<td>-4.09</td>
</tr>
<tr>
<td>COH bridging Rh and La</td>
<td>broken (C + OH)</td>
<td>-4.76</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Starting structure</th>
<th>Converged structure</th>
<th>$\Delta E_{\text{ads}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$O (C-end binds linear on Zr)</td>
<td>atop Zr (C-end binds linear on Zr)</td>
<td>-2.22</td>
</tr>
<tr>
<td>CH$_3$O (O-end binds linear on Zr)</td>
<td>atop Zr (O-end binds linear on Zr)</td>
<td>-4.14</td>
</tr>
<tr>
<td>CH$_3$O orthogonal on Zr</td>
<td>atop Zr (O-end binds Zr. Bent structure)</td>
<td>-4.05</td>
</tr>
<tr>
<td>CH$_3$O (C-end binds linear on La)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_3$O (O-end binds linear on La)</td>
<td>atop La (O-end binds linear on La)</td>
<td>-4.10</td>
</tr>
<tr>
<td>CH$_3$O orthogonal on La</td>
<td>atop La (O-end binds La. Bent structure)</td>
<td>-4.07</td>
</tr>
<tr>
<td>CH$_3$O (C-end binds linear on Rh)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_3$O (O-end binds linear on Rh)</td>
<td>atop La (O-end binds La. Bent structure)</td>
<td>-3.75</td>
</tr>
<tr>
<td>CH$_3$O orthogonal on Rh</td>
<td>bridge La-La</td>
<td>-3.89</td>
</tr>
<tr>
<td>CH$_3$O bridging Zr and La</td>
<td>atop Zr</td>
<td>-4.00</td>
</tr>
<tr>
<td>CH$_3$O bridging La and La = bridge Rh-Zr</td>
<td>3-fold Zr-La-La</td>
<td>-4.68</td>
</tr>
<tr>
<td>CH$_3$O bridging Rh and La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

‡ ‘linear’ and ‘orthogonal’ structures refer to the orientation of the adsorbate on atop binding. ‘bridging La and La = bridge Rh-Zr’ means that the bridge La-La and bridge Rh-Zr site constitute the same position on the surface slab. ‘broken (A+B)’ means that the species dissociatively adsorbed on the surface into species A and B.
**Table A 23 cont.** Detailed list of all tested adsorption sites, the converged structures and the corresponding adsorption energies on the (011) plane. If there is not a reported converged structure, it means the simulation did not converge under the stipulated tolerances.

<table>
<thead>
<tr>
<th>Starting structure‡</th>
<th>Converged structure‡</th>
<th>$\Delta E_{ads}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$O (C-end binds linear on Zr)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_2$O (O-end binds linear on Zr)</td>
<td>atop Zr (O-end binds linear on Zr)</td>
<td>-1.32</td>
</tr>
<tr>
<td>CH$_2$O orthogonal on Zr</td>
<td>bridge Zr-La</td>
<td>-1.54</td>
</tr>
<tr>
<td>CH$_2$O (C-end binds linear on La)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_2$O (O-end binds linear on La)</td>
<td>atop La (O-end binds linear on La)</td>
<td>-1.31</td>
</tr>
<tr>
<td>CH$_2$O orthogonal on La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_2$O (C-end binds linear on Rh)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_2$O (O-end binds linear on Rh)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_2$O orthogonal on Rh</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_2$O bridging Zr and La</td>
<td>3-fold Zr-La-La</td>
<td>-2.84</td>
</tr>
<tr>
<td>CH$_2$O bridging La and La = bridge Rh-Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CH$_2$O bridging Rh and La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Starting structure‡</th>
<th>Converged structure‡</th>
<th>$\Delta E_{ads}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHO (C-end binds linear on Zr)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CHO (O-end binds linear on Zr)</td>
<td>3-fold Zr-La-La</td>
<td>-4.95</td>
</tr>
<tr>
<td>CHO orthogonal on Zr</td>
<td>3-fold Zr-La-La</td>
<td>-4.36</td>
</tr>
<tr>
<td>CHO (C-end binds linear on La)</td>
<td>atop La (C and H bind La)</td>
<td>-1.96</td>
</tr>
<tr>
<td>CHO (O-end binds linear on La)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CHO orthogonal on La</td>
<td>atop La (orthogonal)</td>
<td>-2.29</td>
</tr>
<tr>
<td>CHO (C-end binds linear on Rh)</td>
<td>broken (CO + H)</td>
<td>-3.04</td>
</tr>
<tr>
<td>CHO (O-end binds linear on Rh)</td>
<td>3-fold Rh-La-La</td>
<td>-3.42</td>
</tr>
<tr>
<td>CHO orthogonal on Rh, alternative I</td>
<td>broken (CO + H)</td>
<td>-3.05</td>
</tr>
<tr>
<td>CHO orthogonal on Rh, alternative II</td>
<td>bridge Rh-La</td>
<td>-2.99</td>
</tr>
<tr>
<td>CHO bridging Zr and La</td>
<td>3-fold Zr-La-La</td>
<td>-4.47</td>
</tr>
<tr>
<td>CHO bridging La and La = bridge Rh-Zr</td>
<td>bridge La-La</td>
<td>-2.94</td>
</tr>
<tr>
<td>CHO bridging Rh and La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

‡ ‘linear’ and ‘orthogonal’ structures refer to the orientation of the adsorbate on atop binding. ‘bridging La and La = bridge Rh-Zr’ means that the bridge La-La and bridge Rh-Zr site constitute the same position on the surface slab. ‘broken (A+B)’ means that the species dissociatively adsorbed on the surface into species A and B.
Table A 24 cont. Detailed list of all tested adsorption sites, the converged structures and the corresponding adsorption energies on the (011) plane. If there is not a reported converged structure, it means the simulation did not converge under the stipulated tolerances.

<table>
<thead>
<tr>
<th>Starting structure‡</th>
<th>Converged structure‡</th>
<th>$\Delta E_{\text{ads}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO linear on Zr</td>
<td>atop La (orthogonal. C and O bind a deeper level La-atom)</td>
<td>-2.48</td>
</tr>
<tr>
<td>CO orthogonal on Zr</td>
<td>3-fold Zr-La-La</td>
<td>-2.14</td>
</tr>
<tr>
<td>CO linear on La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CO orthogonal on La</td>
<td>atop La (orthogonal)</td>
<td>-0.42</td>
</tr>
<tr>
<td>CO linear on Rh</td>
<td>atop Rh (linear)</td>
<td>-1.80</td>
</tr>
<tr>
<td>CO orthogonal on Rh</td>
<td>atop Rh (linear)</td>
<td>-1.78</td>
</tr>
<tr>
<td>CO bridging Zr and La</td>
<td>3-fold Zr-La-La</td>
<td>-2.17</td>
</tr>
<tr>
<td>CO bridging La and La = bridge Rh-Zr</td>
<td>3-fold Zr-La-La</td>
<td>-2.53</td>
</tr>
<tr>
<td>CO bridging Rh and La</td>
<td>atop La (orthogonal. C-end binds to La)</td>
<td>-0.16</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Starting structure‡</th>
<th>Converged structure‡</th>
<th>$\Delta E_{\text{ads}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ orthogonal on Zr</td>
<td>3-fold Zr-La-La</td>
<td>-2.62</td>
</tr>
<tr>
<td>CO$_2$ orthogonal on La</td>
<td>bridge La-La</td>
<td>-2.25</td>
</tr>
<tr>
<td>CO$_2$ orthogonal on Rh</td>
<td>bridge Rh-La</td>
<td>-1.43</td>
</tr>
<tr>
<td>CO$_2$ bridging Zr and La</td>
<td>3-fold Zr-La-La</td>
<td>-2.62</td>
</tr>
<tr>
<td>CO$_2$ bridging La and La</td>
<td>bridge Zr-La</td>
<td>-2.57</td>
</tr>
<tr>
<td>CO$_2$ bridging Rh and La</td>
<td>not adsorbed</td>
<td>0.20</td>
</tr>
<tr>
<td>CO$_2$ bridging Rh and Zr</td>
<td>bridge Zr-La</td>
<td>-2.93</td>
</tr>
<tr>
<td>CO$_2$ linear on Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CO$_2$ linear on La</td>
<td>atop La (orthogonal. One C-atom points away from the surface)</td>
<td>-0.59</td>
</tr>
<tr>
<td>CO$_2$ linear on Rh</td>
<td>3-fold Rh-La-La</td>
<td>-2.33</td>
</tr>
</tbody>
</table>

‡ ‘linear’ and ‘orthogonal’ structures refer to the orientation of the adsorbate on atop binding. ‘bridging La and La = bridge Rh-Zr’ means that the bridge La-La and bridge Rh-Zr site constitute the same position on the surface slab. ‘broken (A+B)’ means that the species dissociatively adsorbed on the surface into species A and B.
Table A 25 cont. Detailed list of all tested adsorption sites, the converged structures and the corresponding adsorption energies on the (011) plane. If there is not a reported converged structure, it means the simulation did not converge under the stipulated tolerances.

<table>
<thead>
<tr>
<th>Starting structure</th>
<th>Converged structure</th>
<th>( \Delta E_{ads} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COOH (OH-end binds linear on Zr)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>COOH (O-end binds linear on Zr)</td>
<td>atop Zr (orthogonal)</td>
<td>-2.90</td>
</tr>
<tr>
<td>COOH orthogonal on Zr</td>
<td>broken (CO + OH)</td>
<td>-4.41</td>
</tr>
<tr>
<td>COOH (OH-end binds linear on La)</td>
<td>broken ((CO_{2(g)} + H))</td>
<td>-2.96</td>
</tr>
<tr>
<td>COOH (O-end binds linear on La)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>COOH orthogonal on La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>COOH (OH-end binds linear on Rh)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>COOH (O-end binds linear on Rh)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>COOH orthogonal on Rh</td>
<td>broken (CO + OH)</td>
<td>-4.76</td>
</tr>
<tr>
<td>COOH bridging Zr and La</td>
<td>broken (CO + OH)</td>
<td>-3.81</td>
</tr>
<tr>
<td>COOH bridging La and La= bridge Rh-Zr</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>COOH bridging Rh and La</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

‡ ‘linear’ and ‘orthogonal’ structures refer to the orientation of the adsorbate on atop binding. ‘bridging La and La = bridge Rh-Zr’ means that the bridge La-La and bridge Rh-Zr site constitute the same position on the surface slab. ‘broken \((A+B)\)’ means that the species dissociatively adsorbed on the surface into species A and B.
References


Appendix B

Reactor System

**Fig. B 1** Reactor system assemble, side view (from left side).
Fig. B 2  a) Reactor system assemble, side view (from right side), b) Quartz wool isolation at the upper end of the furnace, c) Inside view of the furnace.
Fig. B 3 Control Panel, front view of the reactor system assemble.

Fig. B 4 Feeding manifold to the reactor. Labeled gases and Ar/He were used for Steady-State Isotopic Transient Kinetic Analysis (SSITKA).
**Fig. B 5** Quartz Reactor.

**Fig. B 6** Componentes of the Ultra-Torr Straight Union Tube Fitting.
Fig. B 7 2-position valve with an electric actuator.
Appendix C

Thermodynamic Considerations

The dependence of the change in standard Gibbs free energy (ΔG°_T) with temperature (T) can be calculated from the change in the standard enthalpy (ΔH°_T) using the Van’t Hoff equation:

\[
\frac{\partial (\Delta G^\circ_{T} / T)}{\partial T} = -\frac{\Delta H^\circ_{T}}{T^2}
\]  \(\text{(C.1)}\)

Or, in the integral form,

\[
\frac{\Delta G^\circ_{T}}{T} = -\int_{T_{r}}^{T} \frac{\Delta H^\circ_{T}}{T^2} dT + \frac{\Delta G^\circ_{R}}{T_{R}}
\]  \(\text{(C.2)}\)

With,

\[
\Delta H^\circ_{T} = \Delta H^\circ_{R} + \int_{T_{r}}^{T} C_p dT
\]  \(\text{(C.3)}\)

Where the subscript R refers to the reference temperature (normally 25 °C).

The heat capacity associated with the reactants and products (C_p) involved in the reaction can be expressed as,

\[
C_p = \sum_{\text{species}} v_i C_{p_i}
\]  \(\text{(C.4)}\)
Where \( \nu_i \) is the stoichiometric coefficient in the reaction and \( C_{pi} \) is the heat capacity of each individual species. \( C_{pi} \) is a function of temperature and can be expressed in the form of the Shomate Equation:

\[
C_{pi} = A_i + B_i(t) + C_i(t)^2 + D_i(t)^3 + E_i/(t)^2
\]

Where, \( t = \text{temperature (K)/1000} \) and \( A_i, B_i, C_i, D_i \) and \( E_i \) are coefficients specific to each molecule. Thus, eq. (C.4) transforms into

\[
C_p = \sum_{\text{species}} \nu_i C_{pi} = \sum_{\text{species}} \nu_i \left( A_i + B_i(T/1000) + C_i(T/1000)^2 + D_i(T/1000)^3 + E_i/(T/1000)^2 \right)
\]

\[
C_p = \sum_{\text{species}} \left( \nu_i A_i + \nu_i B_i(T/1000) + \nu_i C_i(T/1000)^2 + \nu_i D_i(T/1000)^3 + \nu_i E_i/(T/1000)^2 \right)
\]

\[
C_p = \sum_{\text{species}} \nu_i A_i + \sum_{\text{species}} \nu_i B_i(T/1000) + \sum_{\text{species}} \nu_i C_i(T/1000)^2 + \sum_{\text{species}} \nu_i D_i(T/1000)^3 + \sum_{\text{species}} \nu_i E_i/(T/1000)^2
\]

\[
C_p = \sum_{\text{species}} \nu_i A_i + (T/1000) \sum_{\text{species}} \nu_i B_i + (T/1000)^2 \sum_{\text{species}} \nu_i C_i + (T/1000)^3 \sum_{\text{species}} \nu_i D_i + \frac{1}{(T/1000)^2} \sum_{\text{species}} \nu_i E_i
\]

\[
C_p = A' + B' T + C' T^2 + D' T^3 + \frac{E'}{T^2} \quad \text{(C.5)}
\]

Where,
\begin{align*}
A' &= \sum_{\text{species}} v_i A_i \\
B' &= \frac{1}{10^{x}} \sum_{\text{species}} v_i B_i \\
C' &= \frac{1}{10^{x}} \sum_{\text{species}} v_i C_i \\
D' &= \frac{1}{10^{x}} \sum_{\text{species}} v_i D_i \\
E' &= 10^{x} \sum_{\text{species}} v_i E_i
\end{align*}

Hence,

\[
\int_{T_R}^{T} C_p dT = \int_{T_R}^{T} \left( A' + B' T + C' T^2 + D' T^3 + \frac{E'}{T^2} \right) dT
\]

\[
\int_{T_R}^{T} C_p dT = A'(T - T_R) + \frac{B'}{2}(T^2 - T_R^2) + \frac{C'}{3}(T^3 - T_R^3) + \frac{D'}{4}(T^4 - T_R^4) - E' \left( \frac{1}{T} - \frac{1}{T_R} \right) \quad \text{(C.6)}
\]

Therefore, plugging eq. (C.6) into eq. (C.3)

\[
\Delta H_T^o = \Delta H_R^o + A'(T - T_R) + \frac{B'}{2}(T^2 - T_R^2) + \frac{C'}{3}(T^3 - T_R^3) + \frac{D'}{4}(T^4 - T_R^4) - E' \left( \frac{1}{T} - \frac{1}{T_R} \right)
\]

And subsequently, recalling eq. (C.2)
\[
\frac{\Delta G^o_T}{RT} = \int_{T_R}^{T} \frac{1}{RT^2} \left( \Delta H^o_R + A'(T - T_R) + \frac{B'}{2}(T^2 - T_R^2) + \frac{C'}{3}(T^3 - T_R^3) \right) \left( T^4 - T_R^4 \right) + \frac{D'}{4} \left( T^4 - T_R^4 \right) - E' \left( \frac{1}{T} - \frac{1}{T_R} \right) \right) dT + \frac{\Delta G^o_R}{RT_R}
\]

\[
\frac{\Delta G^o_T}{RT} = \int_{T_R}^{T} \frac{1}{RT^2} \left( \Delta H^o_R + A'T + \frac{B'}{2}T^2 + \frac{C'}{3}T^3 + \frac{D'}{4}T^4 - \frac{E'}{T} \right) \left( A'T_R + \frac{B'}{2}T_R^2 + \frac{C'}{3}T_R^3 + \frac{D'}{4}T_R^4 - \frac{E'}{T_R} \right) dT + \frac{\Delta G^o_R}{RT_R}
\]

\[
\frac{\Delta G^o_T}{RT} = \int_{T_R}^{T} \frac{1}{RT^2} \left( \Delta H^o_R + A'T + \frac{B'}{2}T^2 + \frac{C'}{3}T^3 + \frac{D'}{4}T^4 - \frac{E'}{T} \right) \left( A'T_R + \frac{B'}{2}T_R^2 + \frac{C'}{3}T_R^3 + \frac{D'}{4}T_R^4 - \frac{E'}{T_R} \right) dT + \frac{\Delta G^o_R}{RT_R}
\]

\[
\frac{\Delta G^o_T}{RT} = \int_{T_R}^{T} \frac{1}{RT^2} \left( \Delta H^o_R + A'T + \frac{B'}{2}T^2 + \frac{C'}{3}T^3 + \frac{D'}{4}T^4 - \frac{E'}{T} \right) \left( A'T_R + \frac{B'}{2}T_R^2 + \frac{C'}{3}T_R^3 + \frac{D'}{4}T_R^4 - \frac{E'}{T_R} \right) dT + \frac{\Delta G^o_R}{RT_R}
\]

Where,

\[(C.7)\]
\[ A' = \sum_{\text{species}} \nu_i A_i \]
\[ B' = \frac{1}{10^3} \sum_{\text{species}} \nu_i B_i \]
\[ C' = \frac{1}{10^6} \sum_{\text{species}} \nu_i C_i \]
\[ D' = \frac{1}{10^6} \sum_{\text{species}} \nu_i D_i \]
\[ E' = 10^6 \sum_{\text{species}} \nu_i E_i \]

Eq. (C.7) allows calculating the change in the Gibbs free energy at different reaction temperatures.
Table C 1 Constants and thermodynamic values needed to calculate the standard Gibbs free energy at different temperatures for dry reforming of methane ($\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2$).†

\[ C_P = A + B(t) + C(t)^2 + D(t)^3 + E(t)^2, \text{ where } t = \text{temperature (K)/1000} \]

<table>
<thead>
<tr>
<th>Species</th>
<th>ν</th>
<th>T range (K)</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>-1</td>
<td>298-1200</td>
<td>24.99735</td>
<td>55.18696</td>
<td>-33.69137</td>
<td>7.948387</td>
<td>-0.13664</td>
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<tr>
<td>CH₄</td>
<td>-1</td>
<td>298-1300</td>
<td>-0.703029</td>
<td>108.4773</td>
<td>-42.52157</td>
<td>5.862788</td>
<td>0.678565</td>
</tr>
<tr>
<td>H₂</td>
<td>2</td>
<td>298-1000</td>
<td>33.066178</td>
<td>-11.363417</td>
<td>11.432816</td>
<td>-2.772874</td>
<td>-0.15856</td>
</tr>
<tr>
<td>CO</td>
<td>2</td>
<td>298-1300</td>
<td>25.56759</td>
<td>6.09613</td>
<td>4.054656</td>
<td>-2.671301</td>
<td>0.131021</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>A’</th>
<th>B’</th>
<th>C’</th>
<th>D’</th>
<th>E’</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.297E+01</td>
<td>-1.742E-01</td>
<td>1.072E-04</td>
<td>-2.470E-08</td>
<td>-</td>
</tr>
</tbody>
</table>

\[ \Delta H_R^\circ (\text{kJ/mol}) \quad 247.359 \]
\[ \Delta G_R^\circ (\text{kJ/mol}) \quad 170.840 \]
\[ \Delta S_R^\circ (\text{kJ/mol.K}) \quad 0.257 \]
\[ T_R (\text{K}) \quad 298 \]

Table C 2 Standard free energy of dry reforming of methane at different temperatures.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>T (K)</th>
<th>$\Delta G^\circ$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>298.15</td>
<td>170.84</td>
</tr>
<tr>
<td>100</td>
<td>373.15</td>
<td>151.23</td>
</tr>
<tr>
<td>200</td>
<td>473.15</td>
<td>124.23</td>
</tr>
<tr>
<td>300</td>
<td>573.15</td>
<td>96.60</td>
</tr>
<tr>
<td>400</td>
<td>673.15</td>
<td>68.58</td>
</tr>
<tr>
<td>500</td>
<td>773.15</td>
<td>40.33</td>
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<tr>
<td>600</td>
<td>873.15</td>
<td>11.94</td>
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<tr>
<td>650</td>
<td>923.15</td>
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</tr>
<tr>
<td>700</td>
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</tr>
<tr>
<td>800</td>
<td>1073.15</td>
<td>-44.97</td>
</tr>
<tr>
<td>900</td>
<td>1173.15</td>
<td>-73.42</td>
</tr>
<tr>
<td>1000</td>
<td>1273.15</td>
<td>-101.83</td>
</tr>
</tbody>
</table>
# Appendix D

Microkinetic Model: Rate Equations and Constants

## Table D 1. List of constants

<table>
<thead>
<tr>
<th>Constant</th>
<th>Definition</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega$</td>
<td>Surface area per active site</td>
<td>$1.28 \times 10^{-19}$</td>
<td>$m^2$/active site</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant</td>
<td>$1.3806488 \times 10^{-23}$</td>
<td>J/K</td>
</tr>
<tr>
<td>$R$</td>
<td>Gas constant</td>
<td>8.3144621</td>
<td>J/(K.mol)</td>
</tr>
<tr>
<td>$h$</td>
<td>Planck’s constant</td>
<td>$6.62606957 \times 10^{-34}$</td>
<td>J.s</td>
</tr>
<tr>
<td>$m_{CH_4}$</td>
<td>Molecular mass of CH$_4$</td>
<td>$2.6635 \times 10^{-26}$</td>
<td>kg</td>
</tr>
<tr>
<td>$m_{CO_2}$</td>
<td>Molecular mass of CO$_2$</td>
<td>$7.3080 \times 10^{-26}$</td>
<td>kg</td>
</tr>
<tr>
<td>$m_{H_2O}$</td>
<td>Molecular mass of H$_2$O</td>
<td>$2.9923 \times 10^{-26}$</td>
<td>kg</td>
</tr>
<tr>
<td>$m_{H_2}$</td>
<td>Molecular mass of H$_2$</td>
<td>$3.3542 \times 10^{-27}$</td>
<td>kg</td>
</tr>
<tr>
<td>$m_{CO}$</td>
<td>Molecular mass of CO</td>
<td>$4.6512 \times 10^{-26}$</td>
<td>kg</td>
</tr>
<tr>
<td>$m_{CH_3OH}$</td>
<td>Molecular mass of CH$_3$OH</td>
<td>$5.3204 \times 10^{-26}$</td>
<td>kg</td>
</tr>
<tr>
<td>$s$</td>
<td>BET surface area</td>
<td>8721.9</td>
<td>$m^2$/kg</td>
</tr>
</tbody>
</table>

$1 ev/molecule = 96153.8$ J/mol
Table D2. List of unknown variables and equations available to solve the time evolution of the system

<table>
<thead>
<tr>
<th>Type of equation system</th>
<th>Variable</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\theta_{\text{CH}_4}$</td>
<td>$\frac{d\theta_{\text{CH}<em>4}}{dt} = r</em>{\text{CH}_4}$</td>
</tr>
<tr>
<td>2</td>
<td>$\theta_{\text{CH}_3}$</td>
<td>$\frac{d\theta_{\text{CH}<em>3}}{dt} = r</em>{\text{CH}_3}$</td>
</tr>
<tr>
<td>3</td>
<td>$\theta_{\text{CH}_2}$</td>
<td>$\frac{d\theta_{\text{CH}<em>2}}{dt} = r</em>{\text{CH}_2}$</td>
</tr>
<tr>
<td>4</td>
<td>$\theta_{\text{CH}}$</td>
<td>$\frac{d\theta_{\text{CH}}}{dt} = r_{\text{CH}}$</td>
</tr>
<tr>
<td>5</td>
<td>$\theta_{\text{C}}$</td>
<td>$\frac{d\theta_{\text{C}}}{dt} = r_{\text{C}}$</td>
</tr>
<tr>
<td>6</td>
<td>$\theta_{\text{H}}$</td>
<td>$\frac{d\theta_{\text{H}}}{dt} = r_{\text{H}}$</td>
</tr>
<tr>
<td>7</td>
<td>$\theta_{\text{O}}$</td>
<td>$\frac{d\theta_{\text{O}}}{dt} = r_{\text{O}}$</td>
</tr>
<tr>
<td>8</td>
<td>$\theta_{\text{OH}}$</td>
<td>$\frac{d\theta_{\text{OH}}}{dt} = r_{\text{OH}}$</td>
</tr>
<tr>
<td>9</td>
<td>$\theta_{\text{H}_2\text{O}}$</td>
<td>$\frac{d\theta_{\text{H}<em>2\text{O}}}{dt} = r</em>{\text{H}_2\text{O}}$</td>
</tr>
<tr>
<td>10</td>
<td>$\theta_{\text{H}_2}$</td>
<td>$\frac{d\theta_{\text{H}<em>2}}{dt} = r</em>{\text{H}_2}$</td>
</tr>
<tr>
<td>11</td>
<td>$\theta_{\text{CH}_3\text{OH}}$</td>
<td>$\frac{d\theta_{\text{CH}<em>3\text{OH}}}{dt} = r</em>{\text{CH}_3\text{OH}}$</td>
</tr>
<tr>
<td>12</td>
<td>$\theta_{\text{CH}_2\text{OH}}$</td>
<td>$\frac{d\theta_{\text{CH}<em>2\text{OH}}}{dt} = r</em>{\text{CH}_2\text{OH}}$</td>
</tr>
<tr>
<td>13</td>
<td>$\theta_{\text{CHOH}}$</td>
<td>$\frac{d\theta_{\text{CHOH}}}{dt} = r_{\text{CHOH}}$</td>
</tr>
<tr>
<td>14</td>
<td>$\theta_{\text{COH}}$</td>
<td>$\frac{d\theta_{\text{COH}}}{dt} = r_{\text{COH}} = 0$, no stable configuration was found for COH, therefore, it is assumed as non-existent on the surface</td>
</tr>
</tbody>
</table>

This set of differential equations arises from the material balance for adsorbed species on the catalyst surface with the plane (111) being the one exposed. The selected system is a batch reactor.
Table D 3 cont. List of unknown variables and equations available to solve the time evolution of the system

<table>
<thead>
<tr>
<th>Type of equation system</th>
<th>Variable</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>This set of differential equations arises from the material balance for adsorbed species on the catalyst surface with the plane (111) being the one exposed. The selected system is a batch reactor. (continuation)</td>
<td>( \theta_{\text{CH}_3\text{O}} )</td>
<td>( \frac{d\theta_{\text{CH}<em>3\text{O}}}{dt} = r</em>{\text{CH}_3\text{O}} )</td>
</tr>
<tr>
<td></td>
<td>( \theta_{\text{CH}_2\text{O}} )</td>
<td>( \frac{d\theta_{\text{CH}<em>2\text{O}}}{dt} = r</em>{\text{CH}_2\text{O}} )</td>
</tr>
<tr>
<td></td>
<td>( \theta_{\text{CHO}} )</td>
<td>( \frac{d\theta_{\text{CHO}}}{dt} = r_{\text{CHO}} )</td>
</tr>
<tr>
<td></td>
<td>( \theta_{\text{CO}} )</td>
<td>( \frac{d\theta_{\text{CO}}}{dt} = r_{\text{CO}} )</td>
</tr>
<tr>
<td></td>
<td>( \theta_{\text{CO}_2} )</td>
<td>( \frac{d\theta_{\text{CO}<em>2}}{dt} = r</em>{\text{CO}_2} )</td>
</tr>
<tr>
<td></td>
<td>( \theta_{\text{COOH}} )</td>
<td>( \frac{d\theta_{\text{COOH}}}{dt} = r_{\text{COOH}} )</td>
</tr>
</tbody>
</table>

The empty Rh sites coverage (\( \theta^{*}\text{Rh} \)) and the empty non-Rh sites coverage (\( \theta^{*} \)) is determined from a total sites balance.

| | Variable | Equation |
| | \( \theta^{*}\text{Rh} \) | \( \theta_{\text{H}_2} + \theta_{\text{H}_2\text{O}} + \theta_{\text{CO}} + \theta_{\text{COOH}} + \theta_{\text{CHO}} + \theta_{\text{CH}_2} + \theta_{\text{CH}} + \theta_{\text{O}} + \theta^{*}\text{Rh} = 1 \) |
| | \( \theta^{*} \) | \( \theta_{\text{H}_2\text{O}} + \theta_{\text{CH}_2\text{OH}} + \theta_{\text{CO}_2} + \theta_{\text{CHOH}} + \theta_{\text{OH}} + \theta_{\text{COOH}} + \theta_{\text{CH}_2\text{O}} + \theta_{\text{C}} + \theta_{\text{OH}} + \theta^{*} = 1 \) |

This set of differential equations is based on the design equation for a batch reactor. These equations arise from the material balance for the gas phase species.

| | Variable | Equation |
| | \( n_{\text{CH}_{4}(g)} \) | \( \frac{dn_{\text{CH}_{4}(g)}}{dt}, n_{\text{CH}_{4}(g)}(t = 0) = n_{\text{CH}_{4},0} \) |
| | \( n_{\text{CO}_2(g)} \) | \( \frac{dn_{\text{CO}_2(g)}}{dt}, n_{\text{CO}_2(g)}(t = 0) = n_{\text{CO}_2,0} \) |
| | \( n_{\text{H}_2\text{O}(g)} \) | \( \frac{dn_{\text{H}_2\text{O}(g)}}{dt}, n_{\text{H}_2\text{O}(g)}(t = 0) = 0 \) |
| | \( n_{\text{H}_2(g)} \) | \( \frac{dn_{\text{H}_2(g)}}{dt}, n_{\text{H}_2(g)}(t = 0) = 0 \) |
| | \( n_{\text{CO}(g)} \) | \( \frac{dn_{\text{CO}(g)}}{dt}, n_{\text{CO}(g)}(t = 0) = 0 \) |
| | \( n_{\text{CH}_1\text{OH}(g)} \) | \( \frac{dn_{\text{CH}_1\text{OH}(g)}}{dt}, n_{\text{CH}_1\text{OH}(g)}(t = 0) = 0 \) |
Table D 4. Reaction enthalpies and activation energies (forward and reverse) for all reaction steps considered in the reaction network for DRM on the (111) plane of the LRhZ pyrochlore.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta H ) (eV)</th>
<th>( \Delta E_{\text{act,f}} ) (eV)</th>
<th>( \Delta E_{\text{act,r}} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1 ( \text{CH}_4(g)+* \rightleftharpoons \text{CH}_4* )</td>
<td>-0.07</td>
<td>0.00</td>
<td>0.07</td>
</tr>
<tr>
<td>R2 ( \text{CH}_4*+* \rightleftharpoons \text{CH}_3*+\text{H}* )</td>
<td>-0.57</td>
<td>0.89</td>
<td>1.46</td>
</tr>
<tr>
<td>R3 ( \text{CH}_3*+* \rightleftharpoons \text{CH}_2*+\text{H}* )</td>
<td>-0.26</td>
<td>0.81</td>
<td>1.07</td>
</tr>
<tr>
<td>R4 ( \text{CH}_2*+* \rightleftharpoons \text{CH}^<em>+\text{H}</em> )</td>
<td>-0.75</td>
<td>2.53</td>
<td>3.28</td>
</tr>
<tr>
<td>R5 ( \text{CH}^<em>+</em> \rightleftharpoons \text{C}^<em>+\text{H}</em> )</td>
<td>0.66</td>
<td>3.37</td>
<td>2.71</td>
</tr>
<tr>
<td>R6 ( \text{CO}_2(g)+* \rightleftharpoons \text{CO}_2* )</td>
<td>-1.46</td>
<td>0.00</td>
<td>1.46</td>
</tr>
<tr>
<td>R7 ( \text{CO}_2*+* \rightleftharpoons \text{CO}^<em>+\text{O}</em> )</td>
<td>-1.26</td>
<td>1.26</td>
<td>2.53</td>
</tr>
<tr>
<td>R8 ( \text{CO}_2*+\text{H}* \rightleftharpoons \text{COOH}^<em>+</em> )</td>
<td>0.72</td>
<td>1.47</td>
<td>0.74</td>
</tr>
<tr>
<td>R9 ( \text{COOH}^<em>+</em> \rightleftharpoons \text{CO}^<em>+\text{OH}</em> )</td>
<td>-1.55</td>
<td>0.10</td>
<td>1.65</td>
</tr>
<tr>
<td>R10 ( \text{CH}_3*+\text{OH}* \rightleftharpoons \text{CH}_3\text{OH}^<em>+</em> )</td>
<td>2.50</td>
<td>2.52</td>
<td>0.01</td>
</tr>
<tr>
<td>R11 ( \text{CH}_3\text{OH}^<em>+</em> \rightleftharpoons \text{CH}_2\text{OH}^<em>+\text{H}</em> )</td>
<td>-0.30</td>
<td>0.81</td>
<td>1.11</td>
</tr>
<tr>
<td>R12 ( \text{CH}_2*+\text{OH}* \rightleftharpoons \text{CH}_2\text{OH}^<em>+</em> )</td>
<td>2.46</td>
<td>2.47</td>
<td>0.01</td>
</tr>
<tr>
<td>R13 ( \text{CH}_2\text{OH}^<em>+</em> \rightleftharpoons \text{CHOH}^<em>+\text{H}</em> )</td>
<td>1.19</td>
<td>2.12</td>
<td>0.93</td>
</tr>
<tr>
<td>R14 ( \text{CH}^<em>+\text{OH}</em> \rightleftharpoons \text{CHOH}^<em>+</em> )</td>
<td>4.41</td>
<td>4.42</td>
<td>0.01</td>
</tr>
<tr>
<td>R15 ( \text{CHOH}^<em>+</em> \rightleftharpoons \text{COH}^<em>+\text{H}</em> )</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>R16 ( \text{C}^<em>+\text{OH}</em> \rightleftharpoons \text{COH}^<em>+</em> )</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>R17 ( \text{COH}^<em>+</em> \rightleftharpoons \text{CO}^<em>+\text{H}</em> )</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>R18 ( \text{CH}_3*+\text{O}^* \rightleftharpoons \text{CH}_3\text{O}^<em>+</em> )</td>
<td>1.45</td>
<td>2.50</td>
<td>1.05</td>
</tr>
<tr>
<td>R19 ( \text{CH}_3\text{O}^<em>+</em> \rightleftharpoons \text{CH}_2\text{O}^<em>+\text{H}</em> )</td>
<td>0.36</td>
<td>2.28</td>
<td>1.92</td>
</tr>
<tr>
<td>R20 ( \text{CH}_2*+\text{O}^* \rightleftharpoons \text{CH}_2\text{O}^<em>+</em> )</td>
<td>2.08</td>
<td>2.88</td>
<td>0.80</td>
</tr>
<tr>
<td>R21 ( \text{CH}_2\text{O}^<em>+</em> \rightleftharpoons \text{CHO}^<em>+\text{H}</em> )</td>
<td>-0.97</td>
<td>1.37</td>
<td>2.34</td>
</tr>
<tr>
<td>R22 ( \text{CH}^<em>+\text{O}^</em> \rightleftharpoons \text{CHO}^<em>+</em> )</td>
<td>1.86</td>
<td>4.01</td>
<td>2.16</td>
</tr>
<tr>
<td>R23 ( \text{CHO}^<em>+</em> \rightleftharpoons \text{CO}^<em>+\text{H}</em> )</td>
<td>0.14</td>
<td>2.40</td>
<td>2.26</td>
</tr>
<tr>
<td>R24 ( \text{C}^<em>+\text{O}^</em> \rightleftharpoons \text{CO}^<em>+</em> )</td>
<td>1.34</td>
<td>3.31</td>
<td>1.97</td>
</tr>
</tbody>
</table>

\( k_{15f} = k_{15r} = k_{16f} = k_{16r} = k_{17f} = k_{17r} = 0 \), \( \theta_{\text{COH}} = 0 \) since there was not found any stable structure for COH on the plane (111) when geometry optimization calculations were performed.
Table D 5 cont. Reaction enthalpies and activation energies (forward and reverse) for all reaction steps considered in the reaction network for DRM on the (111) plane of the LRhZ pyrochlore.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H$ (eV)</th>
<th>$\Delta E_{act,f}$ (eV)</th>
<th>$\Delta E_{act,r}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R25</td>
<td>-1.49</td>
<td>0.33</td>
<td>1.82</td>
</tr>
<tr>
<td>R26</td>
<td>-0.83</td>
<td>0.91</td>
<td>1.73</td>
</tr>
<tr>
<td>R27</td>
<td>-2.99</td>
<td>0.01</td>
<td>3.00</td>
</tr>
<tr>
<td>R28</td>
<td>0.44</td>
<td>1.74</td>
<td>1.30</td>
</tr>
<tr>
<td>R29</td>
<td>2.07</td>
<td>2.08</td>
<td>0.01</td>
</tr>
<tr>
<td>R30</td>
<td>0.79</td>
<td>0.79</td>
<td>0.00</td>
</tr>
<tr>
<td>R31</td>
<td>1.11</td>
<td>1.16</td>
<td>0.05</td>
</tr>
<tr>
<td>R32</td>
<td>0.38</td>
<td>0.38</td>
<td>0.00</td>
</tr>
<tr>
<td>R33</td>
<td>1.63</td>
<td>1.63</td>
<td>0.00</td>
</tr>
<tr>
<td>R34</td>
<td>0.78</td>
<td>0.78</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Rate equations considered in the micro-kinetic model

1) \( \text{CH}_4 \rightarrow \text{Rh} \)

\[
\frac{d\theta_{\text{CH}_4}}{dt} = k_{1f} \left( p_{\text{CH}_4(g)} \theta_{\text{Rh}}^{\text{eq}} - \theta_{\text{CH}_4} \right) + k_{2r} \theta_{\text{CH}_3} \theta_{\text{H}} - k_{2f} \theta_{\text{CH}_4} \theta^* 
\]

2) \( \text{CH}_3 \rightarrow \text{Rh} \)

\[
\frac{d\theta_{\text{CH}_3}}{dt} = k_{2f} \theta_{\text{CH}_4} \theta^* - k_{2r} \theta_{\text{CH}_3} \theta_{\text{H}} - k_{3f} \theta_{\text{CH}_3} \left( \theta_{\text{Rh}}^{\text{eq}} \right)^2 + k_{3r} \theta_{\text{CH}_2} \theta_{\text{H}} \theta^* - k_{10r} \theta_{\text{CH}_4} \theta_{\text{OH}} + k_{10f} \theta_{\text{CH}_2 \text{OH}} \theta^* - k_{18f} \theta_{\text{CH}_3} \theta_{\text{O}} + k_{18r} \theta_{\text{CH}_2 \text{O}} \theta_{\text{Rh}}^{\text{eq}} 
\]

or

\[
\frac{d\theta_{\text{CH}_3}}{dt} = k_{2f} \theta_{\text{CH}_4} \theta^* + k_{3r} \theta_{\text{CH}_2} \theta_{\text{H}} \theta^* + k_{10r} \theta_{\text{CH}_4} \theta_{\text{OH}} + k_{18r} \theta_{\text{CH}_2 \text{O}} \theta_{\text{Rh}}^{\text{eq}} - \left( k_{2r} \theta_{\text{H}} + k_{3f} \left( \theta_{\text{Rh}}^{\text{eq}} \right)^2 + k_{10f} \theta_{\text{OH}} + k_{18f} \theta_{\text{O}} \right) \theta_{\text{CH}_3} 
\]

3) \( \text{CH}_2 \rightarrow \text{Rh} \)

\[
\frac{d\theta_{\text{CH}_2}}{dt} = k_{3f} \theta_{\text{CH}_4} \left( \theta_{\text{Rh}}^{\text{eq}} \right)^2 - k_{3f} \theta_{\text{CH}_2} \theta_{\text{H}} - k_{4f} \theta_{\text{CH}_2} \theta_{\text{H}}^{\text{eq}} + k_{4f} \theta_{\text{CH}_2} \theta_{\text{H}} - k_{12f} \theta_{\text{CH}_2} \theta_{\text{OH}} + k_{12r} \theta_{\text{CH}_2 \text{OH}} \theta_{\text{Rh}}^{\text{eq}} - k_{20r} \theta_{\text{CH}_2} \theta_{\text{O}} + k_{20f} \theta_{\text{CH}_2 \text{O}} \theta_{\text{Rh}}^{\text{eq}} 
\]

or

\[
\frac{d\theta_{\text{CH}_2}}{dt} = k_{3f} \theta_{\text{CH}_4} \left( \theta_{\text{Rh}}^{\text{eq}} \right)^2 + k_{4f} \theta_{\text{CH}_2} \theta_{\text{H}} + k_{12r} \theta_{\text{CH}_2 \text{OH}} \theta_{\text{Rh}}^{\text{eq}} + k_{20r} \theta_{\text{CH}_2 \text{O}} \theta_{\text{Rh}}^{\text{eq}} - \left( k_{3r} \theta_{\text{H}} \theta^* + k_{4f} \theta_{\text{Rh}}^{\text{eq}} + k_{12f} \theta_{\text{OH}} + k_{20f} \theta_{\text{O}} \right) \theta_{\text{CH}_2} 
\]

4) \( \text{CH} \rightarrow \text{Rh} \)

\[
\frac{d\theta_{\text{CH}}}{dt} = k_{4f} \theta_{\text{CH}_2} \theta_{\text{H}}^{\text{eq}} - k_{4f} \theta_{\text{CH}} \theta_{\text{H}} - k_{5f} \theta_{\text{CH}} \theta_{\text{H}}^{\text{eq}} + k_{5r} \theta_{\text{CH}} \theta_{\text{H}} - k_{14f} \theta_{\text{CH}} \theta_{\text{OH}} + k_{14r} \theta_{\text{CH}_2 \text{OH}} \theta_{\text{Rh}}^{\text{eq}} - k_{22f} \theta_{\text{CH}} \theta_{\text{O}} + k_{22r} \theta_{\text{CH}_2 \text{O}} \theta_{\text{Rh}}^{\text{eq}} 
\]
or

\[ r_{\text{CH}^{*}} = \frac{d\theta_{\text{CH}}}{dt} = k_{4f} \theta_{\text{CH}_{2}} \theta^{*} + k_{5f} \theta_{\text{C}} \theta_{\text{H}} + k_{14f} \theta_{\text{COH}} \theta^{*} + k_{22f} \theta_{\text{CHO}} \theta^{*} - \]

\[ (k_{4f} \theta_{\text{H}} + k_{5f} \theta^{*} + k_{14f} \theta_{\text{OH}} + k_{22f} \theta_{\text{O}}) \theta_{\text{CH}} \]

5) \( \text{C}^{*}\text{Rh} \)

\[ r_{\text{C}^{*}} = \frac{d\theta_{\text{C}}}{dt} = k_{5f} \theta_{\text{CH}} \theta^{*} - k_{5f} \theta_{\text{C}} \theta_{\text{H}} - k_{16f} \theta_{\text{COH}} \theta^{*} - k_{24f} \theta_{\text{CO}} \theta^{*} + k_{24f} \theta_{\text{O}} \theta_{\text{CO}}^{*} \]

or

\[ r_{\text{C}^{*}} = \frac{d\theta_{\text{C}}}{dt} = k_{5f} \theta_{\text{CH}} \theta^{*} + k_{16f} \theta_{\text{COH}} \theta^{*} + k_{24f} \theta_{\text{CO}} \theta^{*} - \]

\[ (k_{5f} \theta_{\text{H}} + k_{16f} \theta_{\text{OH}} + k_{24f} \theta_{\text{O}}) \theta_{\text{C}} \]

6) \( \text{H}^{*}\text{Rh} \)

\[
\begin{align*}
\frac{d\theta_{\text{H}}}{dt} & = k_{2f} \theta_{\text{CH}_{2}} \theta^{*} - k_{3f} \theta_{\text{CH}} \theta_{\text{H}} + k_{31f} \theta_{\text{CH}_{3}} \left( \theta^{*} \right)^{2} - k_{3f} \theta_{\text{CH}_{2}} \theta^{*} + k_{4f} \theta_{\text{CH}_{2}} \theta^{*} + k_{5f} \theta_{\text{CH}} \theta^{*} + k_{8f} \theta_{\text{COH}} \theta^{*} + k_{15f} \theta_{\text{COH}} \theta^{*} - k_{11f} \theta_{\text{CH}_{2} \text{OH}} \theta_{\text{H}} + k_{3f} \theta_{\text{CH}_{2} \text{OH}} \theta^{*} - k_{6f} \theta_{\text{CO}} \theta_{\text{H}} +
\end{align*}
\]

or

\[
\begin{align*}
\frac{d\theta_{\text{H}}}{dt} & = k_{2f} \theta_{\text{CH}_{2}} \theta^{*} - k_{3f} \theta_{\text{CH}} \theta_{\text{H}} + k_{31f} \theta_{\text{CH}_{3}} \left( \theta^{*} \right)^{2} - k_{3f} \theta_{\text{CH}_{2}} \theta^{*} + k_{4f} \theta_{\text{CH}_{2}} \theta^{*} + k_{5f} \theta_{\text{CH}} \theta^{*} + k_{8f} \theta_{\text{COH}} \theta^{*} + k_{15f} \theta_{\text{COH}} \theta^{*} - k_{11f} \theta_{\text{CH}_{2} \text{OH}} \theta_{\text{H}} + k_{3f} \theta_{\text{CH}_{2} \text{OH}} \theta^{*} - k_{6f} \theta_{\text{CO}} \theta_{\text{H}} +
\end{align*}
\]

\[
\begin{align*}
& \text{or} \\
& \left( k_{5f} \theta_{\text{H}} + k_{16f} \theta_{\text{OH}} + k_{24f} \theta_{\text{O}} \right) \theta_{\text{C}}
\end{align*}
\]
7) \( O^{*}\text{Rh} \)

\[
r_{O^{*}} = \frac{d\theta_{O}}{dt} = k_7 \theta_{CO_2} \left( \theta^{*}\text{Rh} \right)^2 - k_7 \theta_{CO} \theta_{H} \theta^{*} - k_{18f} \theta_{CH_3} \theta_{O} + k_{18r} \theta_{CH_2O} \theta^{*}\text{Rh} - k_{20f} \theta_{CH_2 \theta_2} \theta_{O} + k_{20r} \theta_{CH_2O} \theta^{*}\text{Rh} - k_{22f} \theta_{CH} \theta_{O} + k_{22r} \theta_{CHO} \theta^{*}\text{Rh} - k_{24f} \theta_{C} \theta_{O} + k_{24r} \theta_{CO} \theta^{*}\text{Rh} - k_{28f} \theta_{O} \theta_{H} \theta^{*} + k_{28r} \theta_{OH} \left( \theta^{*}\text{Rh} \right)^2
\]

or

\[
r_{O^{*}} = \frac{d\theta_{O}}{dt} = k_7 \theta_{CO_2} \left( \theta^{*}\text{Rh} \right)^2 + k_{18r} \theta_{CH_2O} \theta^{*}\text{Rh} + k_{20r} \theta_{CH_2O} \theta^{*}\text{Rh} + k_{22r} \theta_{CHO} \theta^{*}\text{Rh} + k_{24r} \theta_{CO} \theta^{*}\text{Rh} + k_{28r} \theta_{OH} \left( \theta^{*}\text{Rh} \right)^2 - \left( k_7 \theta_{CO} \theta^{*} + k_{18f} \theta_{CH_3} + k_{20f} \theta_{CH_2} + k_{22f} \theta_{CH} + k_{24f} \theta_{C} + k_{28f} \theta_{OH} \right) \theta_{O}
\]

8) \( OH^{*} \)

\[
r_{OH^{*}} = \frac{d\theta_{OH}}{dt} = k_9 \theta_{COOH} \theta^* - k_9 \theta_{CO} \theta_{OH} - k_{10f} \theta_{CH_3} \theta_{OH} + k_{10r} \theta_{OH} \theta^* - k_{12f} \theta_{CH_2} \theta_{OH} + k_{12r} \theta_{CH_2OH} \theta^{*}\text{Rh} - k_{14f} \theta_{CH} \theta_{OH} + k_{14r} \theta_{CHOH} \theta^{*}\text{Rh} - k_{16f} \theta_{C} \theta_{OH} + k_{16r} \theta_{CHOH} \theta^{*}\text{Rh} + k_{28f} \theta_{O} \theta_{H} \theta^* - k_{28r} \theta_{OH} \left( \theta^{*}\text{Rh} \right)^2 - k_{29f} \theta_{OH} \theta_{H} + k_{29r} \theta_{H_2O} \theta^{*}\text{Rh}
\]

or

\[
r_{OH^{*}} = \frac{d\theta_{OH}}{dt} = k_9 \theta_{COOH} \theta^* + k_{10} \theta_{CH_2OH} \theta^* + k_{12} \theta_{CH_2OH} \theta^{*}\text{Rh} + k_{14} \theta_{CHOH} \theta^{*}\text{Rh} + k_{16r} \theta_{CHOH} \theta^{*}\text{Rh} + k_{28f} \theta_{O} \theta_{H} \theta^* + k_{29r} \theta_{H_2O} \theta^{*}\text{Rh} - \left( k_{9f} \theta_{CO} + k_{10f} \theta_{CH_3} + k_{12f} \theta_{CH_2} + k_{14r} \theta_{CH} \psi + k_{16f} \theta_{C} + k_{28r} \theta_{H_2O} \left( \theta^{*}\text{Rh} \right)^2 + k_{29r} \theta_{H} \right) \theta_{OH}
\]

9) \( H_2O^{*} \)

\[
r_{H_2O^{*}} = \frac{d\theta_{H_2O}}{dt} = k_{29f} \theta_{OH} \theta_{H} - k_{29r} \theta_{H_2O} \theta^{*}\text{Rh} + k_{30} \left( P_{H_2O(g)} \theta^* - K_{30, eq} \theta_{H_2O} \right)
\]

10) \( H_2^{*}\text{Rh} \)
\[ r_{H_2} = \frac{d\theta_{H_2}}{dt} = \frac{1}{2} k_{31f} \left( \theta_H \right)^2 - k_{31r} \theta_{H_2} \theta^{Rh} + k_{32r} \left( P_{H_2(g)} \theta^{eq} - K_{32,eq} \theta_{H_2} \right) \]

11) CH$_3$OH$^*$

\[ r_{CH_3OH^*} = \frac{d\theta_{CH_3OH}}{dt} = k_{10r} \theta_{CH_3OH} \theta^* - k_{10r} \theta_{CH_3OH} \theta^{Rh} + k_{11r} \theta_{CH_2OH} \theta^* - k_{11r} \theta_{CH_2OH} \theta^{Rh} + k_{25r} \theta_{CH_2OH} \theta^* + k_{25r} \theta_{CH_2OH} \theta^{Rh} + k_{34r} \left( P_{CH_3OH(g)} \theta^* - K_{34,eq} \theta_{CH_3OH} \right) \]

or

\[ r_{CH_3OH^*} = \frac{d\theta_{CH_3OH}}{dt} = k_{10r} \theta_{CH_3OH} \theta^* + k_{11r} \theta_{CH_2OH} \theta^* + k_{25r} \theta_{CH_2OH} \theta^* - k_{25r} \theta_{CH_2OH} \theta^{Rh} + k_{34r} \left( P_{CH_3OH(g)} \theta^* - K_{34,eq} \theta_{CH_3OH} \right) \]

12) CH$_2$OH$^*$

\[ r_{CH_2OH^*} = \frac{d\theta_{CH_2OH}}{dt} = k_{11r} \theta_{CH_2OH} \theta^{Rh} - k_{11r} \theta_{CH_2OH} \theta^* + k_{12r} \theta_{CH_2OH} \theta^* - k_{12r} \theta_{CH_2OH} \theta^{Rh} - k_{13r} \theta_{CH_2OH} \theta^{Rh} + k_{13r} \theta_{CHOH} \theta^* - k_{26r} \theta_{CHOH} \left( \theta^{Rh} \right)^2 + k_{26r} \theta_{CHOH} \theta^* \]

or

\[ r_{CH_2OH^*} = \frac{d\theta_{CH_2OH}}{dt} = k_{11r} \theta_{CH_2OH} \theta^{Rh} + k_{12r} \theta_{CH_2OH} \theta^* + k_{13r} \theta_{CHOH} \theta^* + k_{26r} \theta_{CHOH} \theta^* - k_{13r} \theta_{CHOH} \theta^* + k_{26r} \theta_{CHOH} \theta^* \]

or

\[ r_{CH_2OH^*} = \frac{d\theta_{CH_2OH}}{dt} = k_{11r} \theta_{CH_2OH} \theta^{Rh} + k_{12r} \theta_{CH_2OH} \theta^* + k_{13r} \theta_{CHOH} \theta^* + k_{26r} \theta_{CHOH} \theta^* \]

13) CHO$^*$

\[ r_{CHO} = \frac{d\theta_{CHO}}{dt} = k_{13r} \theta_{CHO} \theta^{Rh} - k_{13r} \theta_{CHO} \theta^* + k_{14r} \theta_{CHO} \theta^* - k_{14r} \theta_{CHO} \theta^{Rh} - k_{15r} \theta_{CHO} \theta^{Rh} + k_{15r} \theta_{COH} \theta^* - k_{27r} \theta_{COH} \theta^* - k_{27r} \theta_{COH} \theta^{Rh} \]

or

\[ r_{CHO} = \frac{d\theta_{CHO}}{dt} = k_{13r} \theta_{CHO} \theta^{Rh} + k_{15r} \theta_{CHO} \theta^{Rh} + k_{14r} \theta_{CHO} \theta^* + k_{27r} \theta_{CHO} \theta^* \]
\[
\begin{align*}
    r_{\mathrm{CHOH}} &= \frac{d\theta_{\mathrm{CHOH}}}{dt} = k_{13f} \theta_{\mathrm{CH}_2 \mathrm{OH}} \theta^*_{\mathrm{Rh}} + k_{14r} \theta_{\mathrm{CH}} \theta_{\mathrm{OH}} + k_{15r} \theta_{\mathrm{COH}} \theta_H + k_{27f} \theta_{\mathrm{CHO}} \theta_H \theta^* - \\
    &\left( k_{13r} \theta_H + k_{14r} \theta^*_{\mathrm{Rh}} + k_{15r} \theta^*_{\mathrm{Rh}} + k_{27f} \left( \theta^*_{\mathrm{Rh}} \right)^2 \right) \theta_{\mathrm{CHOH}} \\
\end{align*}
\]

14) COH*

\[
\begin{align*}
    r_{\mathrm{COH}} &= \frac{d\theta_{\mathrm{COH}}}{dt} = k_{15f} \theta_{\mathrm{CHOH}} \theta^*_{\mathrm{Rh}} - k_{15r} \theta_{\mathrm{COH}} \theta_H + k_{16r} \theta_{\mathrm{CO}} \theta_{\mathrm{OH}} - k_{16r} \theta_{\mathrm{COH}} \theta^*_{\mathrm{Rh}} - \\
    &k_{17r} \theta_{\mathrm{COH}} \left( \theta^*_{\mathrm{Rh}} \right)^2 + k_{17r} \theta_{\mathrm{CO}} \theta_H \theta^* = 0 \\
\end{align*}
\]

or

\[
\begin{align*}
    r_{\mathrm{COH}} &= \frac{d\theta_{\mathrm{COH}}}{dt} = k_{15f} \theta_{\mathrm{CHOH}} \theta^*_{\mathrm{Rh}} + k_{16r} \theta_{\mathrm{CO}} \theta_{\mathrm{OH}} + k_{17r} \theta_{\mathrm{CO}} \theta_H \theta^* - \\
    &\left( k_{15r} \theta_H + k_{16r} \theta^*_{\mathrm{Rh}} + k_{17f} \left( \theta^*_{\mathrm{Rh}} \right)^2 \right) \theta_{\mathrm{COH}} = 0 \\
\end{align*}
\]

15) CH₃O*

\[
\begin{align*}
    r_{\mathrm{CH}_3\mathrm{O}*} &= \frac{d\theta_{\mathrm{CH}_3\mathrm{O}}}{dt} = k_{18l} \theta_{\mathrm{CH}_3} \theta_O - k_{18r} \theta_{\mathrm{CH}_3\mathrm{O}} \theta^*_{\mathrm{Rh}} - k_{19f} \theta_{\mathrm{CH}_3\mathrm{O}} \left( \theta^*_{\mathrm{Rh}} \right)^2 + \\
    &k_{19l} \theta_{\mathrm{CH}_3\mathrm{O}} \theta_H \theta^* + k_{25l} \theta_{\mathrm{CH}_3\mathrm{OH}} \theta^*_{\mathrm{Rh}} - k_{25r} \theta_{\mathrm{CH}_3\mathrm{O}} \theta_H \\
\end{align*}
\]

or

\[
\begin{align*}
    r_{\mathrm{CH}_3\mathrm{O}*} &= \frac{d\theta_{\mathrm{CH}_3\mathrm{O}}}{dt} = k_{18f} \theta_{\mathrm{CH}_3} \theta_O + k_{19l} \theta_{\mathrm{CH}_3\mathrm{O}} \theta_H \theta^* + k_{25l} \theta_{\mathrm{CH}_3\mathrm{OH}} \theta^*_{\mathrm{Rh}} - \\
    &\left( k_{18r} \theta^*_{\mathrm{Rh}} + k_{19f} \left( \theta^*_{\mathrm{Rh}} \right)^2 + k_{25r} \theta_H \right) \theta_{\mathrm{CH}_3\mathrm{O}} \\
\end{align*}
\]

16) CH₂O*₆Rh

\[
\begin{align*}
    r_{\mathrm{CH}_2\mathrm{O}*_{\mathrm{Rh}}} &= \frac{d\theta_{\mathrm{CH}_2\mathrm{O}}}{dt} = k_{19l} \theta_{\mathrm{CH}_2\mathrm{O}} \left( \theta^*_{\mathrm{Rh}} \right)^2 - k_{19l} \theta_{\mathrm{CH}_2\mathrm{O}} \theta_H \theta^* + k_{20f} \theta_{\mathrm{CH}_2} \theta_O - k_{20r} \theta_{\mathrm{CH}_2\mathrm{O}} \theta^*_{\mathrm{Rh}} - \\
    &k_{21f} \theta_{\mathrm{CH}_2\mathrm{O}} \theta^*_{\mathrm{Rh}} + k_{21r} \theta_{\mathrm{CHO}} \theta_H + k_{26f} \theta_{\mathrm{CH}_2\mathrm{OH}} \left( \theta^*_{\mathrm{Rh}} \right)^2 - k_{26r} \theta_{\mathrm{CH}_2\mathrm{O}} \theta_H \theta^* \\
\end{align*}
\]

or

\[
\]
\[
\begin{align*}
\text{r}_{\text{CH}_3\text{O}^{*\text{Rh}}} &= \frac{d\theta_{\text{CH}_3\text{O}^{*\text{Rh}}}}{dt} = k_{19f} \theta_{\text{CH}_3\text{O}} (\theta_{\text{Rh}^{*\text{Rh}}})^2 + k_{20f} \theta_{\text{CH}_3\text{O}} \theta_{\text{O}} + k_{21r} \theta_{\text{CHO}} \theta_{\text{H}} + k_{26f} \theta_{\text{CH}_2\text{OH}} (\theta_{\text{Rh}^{*\text{Rh}}})^2 - \\
&\quad \left( k_{19r} \theta_{\text{H}} \theta^* + k_{20r} \theta_{\text{Rh}^{*\text{Rh}}} + k_{21r} \theta_{\text{Rh}^{*\text{Rh}}} + k_{26r} \theta_{\text{H}} \theta^* \right) \theta_{\text{CH}_3\text{O}}
\end{align*}
\]

17) CHO^{*\text{Rh}}

\[
\begin{align*}
\text{r}_{\text{CHO}^{*\text{Rh}}} &= \frac{d\theta_{\text{CHO}^{*\text{Rh}}}}{dt} = k_{21f} \theta_{\text{CH}_3\text{O}} (\theta_{\text{Rh}^{*\text{Rh}}})^2 - k_{21r} \theta_{\text{CHO}} \theta_{\text{H}} + k_{22f} \theta_{\text{CH}_3\text{O}} - k_{22r} \theta_{\text{CHO}} (\theta_{\text{Rh}^{*\text{Rh}}})^2 - \\
&\quad k_{23r} \theta_{\text{CHO}} \theta_{\text{H}} + k_{23f} \theta_{\text{CO}} \theta_{\text{H}} + k_{27f} \theta_{\text{CH}_2\text{OH}} (\theta_{\text{Rh}^{*\text{Rh}}})^2 - k_{27r} \theta_{\text{CHO}} \theta_{\text{H}} \theta^* \\
&\quad \text{or} \\
\text{r}_{\text{CHO}^{*\text{Rho}}} &= \frac{d\theta_{\text{CHO}^{*\text{Rho}}}}{dt} = k_{21f} \theta_{\text{CH}_3\text{O}} (\theta_{\text{Rh}^{*\text{Rh}}})^2 + k_{22f} \theta_{\text{CH}_3\text{O}} + k_{23r} \theta_{\text{CO}} \theta_{\text{H}} + k_{27f} \theta_{\text{CH}_2\text{OH}} (\theta_{\text{Rh}^{*\text{Rh}}})^2 - \\
&\quad \left( k_{21r} \theta_{\text{H}} + k_{22r} \theta_{\text{Rh}^{*\text{Rh}}} + k_{23r} \theta_{\text{Rh}^{*\text{Rh}}} + k_{27r} \theta_{\text{H}} \theta^* \right) \theta_{\text{CHO}}
\end{align*}
\]

18) CO^{*\text{Rh}}

\[
\begin{align*}
\text{r}_{\text{CO}^{*\text{Rh}}} &= \frac{d\theta_{\text{CO}^{*\text{Rh}}}}{dt} = k_{7r} \theta_{\text{CO}_2} (\theta_{\text{Rh}^{*\text{Rh}}})^2 - k_{7r} \theta_{\text{CO}} \theta_{\text{O}} \theta^* + k_{9r} \theta_{\text{COOH}} \theta^* - k_{9r} \theta_{\text{CO}} \theta_{\text{H}} + k_{17r} \theta_{\text{COH}} (\theta_{\text{Rh}^{*\text{Rh}}})^2 - \\
&\quad k_{17r} \theta_{\text{COOH}} \theta^* + k_{23r} \theta_{\text{CO}} \theta_{\text{H}} + k_{24r} \theta_{\text{CO}} \theta_{\text{O}} - k_{24r} \theta_{\text{Rh}^{*\text{Rh}}} + k_{33r} \left( P_{\text{CO}(g)} \theta_{\text{Rh}^{*\text{Rh}}} - K_{33,eq} \theta_{\text{CO}} \right) \\
&\quad \text{or} \\
\text{r}_{\text{CO}^{*\text{Rho}}} &= \frac{d\theta_{\text{CO}^{*\text{Rho}}}}{dt} = k_{7r} \theta_{\text{CO}_2} (\theta_{\text{Rh}^{*\text{Rh}}})^2 + k_{9r} \theta_{\text{COOH}} \theta^* + k_{17r} \theta_{\text{COH}} (\theta_{\text{Rh}^{*\text{Rh}}})^2 + k_{23r} \theta_{\text{CO}} \theta_{\text{H}} + k_{24r} \theta_{\text{CO}} \theta_{\text{O}} - \\
&\quad \left( k_{7r} \theta_{\text{O}} \theta^* + k_{9r} \theta_{\text{OH}} + k_{17r} \theta_{\text{H}} \theta^* + k_{23r} \theta_{\text{H}} + k_{24r} \theta_{\text{Rh}^{*\text{Rh}}} \right) \theta_{\text{CO}} + k_{33r} \left( P_{\text{CO}(g)} \theta_{\text{Rh}^{*\text{Rh}}} - K_{33,eq} \theta_{\text{CO}} \right)
\end{align*}
\]

19) CO_{2}^{*}

\[
\begin{align*}
\text{r}_{\text{CO}_2^{*}} &= \frac{d\theta_{\text{CO}_2^{*}}}{dt} = k_{6f} \left( P_{\text{CO}_2(g)} \theta_{\text{O}} \theta_{\text{CO}} \theta_{\text{H}} \theta_{\text{Rh}^{*\text{Rh}}} \theta_{\text{COOH}} \theta^* \right) - k_{7r} \theta_{\text{CO}_2} (\theta_{\text{Rh}^{*\text{Rh}}})^2 + k_{7r} \theta_{\text{CO}} \theta_{\text{O}} \theta^* - k_{6f} \theta_{\text{CO}_2 \theta_{\text{H}} + k_{9r} \theta_{\text{COOH}} \theta^*} \\
&\quad \text{or} \\
\text{r}_{\text{CO}_2^{*}} &= \frac{d\theta_{\text{CO}_2^{*}}}{dt} = k_{6f} \left( P_{\text{CO}_2(g)} \theta_{\text{O}} \theta_{\text{CO}} \theta_{\text{H}} \theta_{\text{Rh}^{*\text{Rh}}} \theta_{\text{COOH}} \theta^* \right) + k_{7r} \theta_{\text{CO}_2} \theta_{\text{O}} \theta^* + k_{5r} \theta_{\text{COOH}} \theta^* - \left( k_{7r} (\theta_{\text{Rh}^{*\text{Rh}}})^2 + k_{9r} \theta_{\text{H}} \right) \theta_{\text{CO}}
\end{align*}
\]

20) COOH^{*\text{Rh}}
\[ r_{\text{COOH}^{\text{abs}}} = \frac{d\theta_{\text{COOH}}}{dt} = k_{8f} \theta_\text{CO}_2 \theta_\text{H} - k_{8r} \theta_{\text{COOH}} \theta^* - k_{9f} \theta_{\text{COOH}} \theta^* + k_{9r} \theta_{\text{CO}} \theta_{\text{OH}} \]

or

\[ r_{\text{COOH}^{\text{abs}}} = \frac{d\theta_{\text{COOH}}}{dt} = k_{8f} \theta_\text{CO}_2 \theta_\text{H} + k_{9r} \theta_{\text{CO}} \theta_{\text{OH}} - \left( k_{9r} \theta^* + k_{9f} \theta^* \right) \theta_{\text{COOH}} \]

The previous set of equations, coupled with the design equation for the batch reactor (presented in the next section), provides the time evolution of the intermediates coverage.
Design equation for the batch reactor

Set of equations corresponding to the reactor design are:

\[
\frac{dn_{\text{CH}_4(g)}}{dt} = r_{\text{CH}_4(g)} \left( \frac{m_{\text{cat}} s}{N_a \omega} \right)
\]

\[
\frac{dn_{\text{CO}_2(g)}}{dt} = r_{\text{CO}_2(g)} \left( \frac{m_{\text{cat}} s}{N_a \omega} \right)
\]

\[
\frac{dn_{\text{H}_2\text{O}(g)}}{dt} = r_{\text{H}_2\text{O}(g)} \left( \frac{m_{\text{cat}} s}{N_a \omega} \right)
\]

\[
\frac{dn_{\text{CH}_2\text{OH}(g)}}{dt} = r_{\text{CH}_2\text{OH}(g)} \left( \frac{m_{\text{cat}} s}{N_a \omega} \right)
\]

\[
\frac{dn_{\text{CO}(g)}}{dt} = r_{\text{CO}(g)} \left( \frac{m_{\text{cat}} s}{N_a \omega} \right)
\]

\[
\frac{dn_{\text{H}_2(g)}}{dt} = r_{\text{H}_2(g)} \left( \frac{m_{\text{cat}} s}{N_a \omega} \right)
\]

Initial conditions:

\[n_{\text{CH}_4(g)}(t = 0) = n_{\text{CH}_4,0}\]

\[n_{\text{CO}_2(g)}(t = 0) = n_{\text{CO}_2,0}\]

\[n_{\text{H}_2\text{O}(g)}(t = 0) = 0\]

\[n_{\text{CH}_2\text{OH}(g)}(t = 0) = 0\]

\[n_{\text{CO}(g)}(t = 0) = 0\]

\[n_{\text{H}_2(g)}(t = 0) = 0\]
Model assumptions

The doping percentage (wt % Rh) of a Rh-substituted pyrochlore can be related to its molecular formula (La$_2$Zr$_{2-x}$Rh$_x$O$_7$) as follows:

\[
\text{wt\% \ Rh} = \frac{x \cdot M_{\text{Rh}}}{2M_{\text{La}} + (2-x) \cdot M_{\text{Zr}} + x \cdot M_{\text{Rh}} + 7M_{\text{O}}} \times 100
\]

\[
\left( \text{wt\% \ Rh} \right) \left( 2M_{\text{La}} + 2M_{\text{Zr}} + 7M_{\text{O}} \right) + \left( \text{wt\% \ Rh} \right) \left( x \cdot M_{\text{Rh}} - xM_{\text{Zr}} \right) = 100x \cdot M_{\text{Rh}}
\]

\[
\left( \text{wt\% \ Rh} \right) \left( 2M_{\text{La}} + 2M_{\text{Zr}} + 7M_{\text{O}} \right) = x \left( 100M_{\text{Rh}} - \left( \text{wt\% \ Rh} \right) \left( M_{\text{Rh}} - M_{\text{Zr}} \right) \right)
\]

\[
x = \frac{\left( \text{wt\% \ Rh} \right) \left( 2M_{\text{La}} + 2M_{\text{Zr}} + 7M_{\text{O}} \right)}{\left( 100M_{\text{Rh}} - \left( \text{wt\% \ Rh} \right) \left( M_{\text{Rh}} - M_{\text{Zr}} \right) \right)}
\]
Fig. D 1 Time evolution of gas phase species for DRM over 2 wt. % LRhZ pyrochlore catalysts at 800 °C and 1.1 atm.
Appendix E

Catalyst Synthesis

Reaction set-up

As described in the Chapter 3 of the present dissertation. The solution containing the metal precursors must be homogeneously heated up to around 130 °C and this temperature must be held until a viscous gel is formed. Fig. E. 1 shows the mantel (‘bucket-like mantel’) used to heat up the solution to this temperature. Since the inner diameter of the heating mantel was greater than the diameter of the glass container holding the solution, sand was used to conduct the heat from the internal wall of the mantel. The temperature was controlled using a thermocouple (not shown in Fig. E. 1), that goes into the sand pool, and a digital temperature controller. The top of the glass container holding the solution was covered with stainless steel mesh (SST 316, 250x250).

Fig. E 1 Heating mantel used to generate the viscous gel from the metal precursors.
Fig. E 2 Gel inside the glass container. The top of the container is covered with stainless steel mesh.

The rate of heat transfer through the sand media was low enough so that the gel migrated upwards in the glass container and did not reach the desired self-ignition temperature (around 270 °C); thus, a zipper-mantel (see Fig. E. 3) was used to bring the gel to ignition.
Alternative reaction set-up (not recommended)

To achieve homogeneous heating of the mixture with a fast heating rate, an oil-bath was used and a thermometer was place in the bath to control the temperature. This method is not recommendable to the high temperature the oil-bath has to be brought to,
and also, since the self-ignition reaction produces ashes, the contact of any ash with the oil bath may produce fire.

**Recommended reaction set-up**

Use the mantel of Fig. E. 1 but place metal beads instead of sand to improve the heating rate, so that the gel self-ignites inside the same mantel and therefore the zipper-mantel (Fig. E. 3) is not needed. Also, it is recommendable to use a taller container so that the ashes remain container inside it and a coarser stainless steel mesh, so that the pressure inside the glass container does not build up as much.

**Calcination**

![Fig. E 4 Furnace for calcination of the catalyst at 700 °C for 10 h.](image)
Heat treatment

Fig. E 5 Furnace for catalyst heat treatment under Argon at 1000 °C for 10 h.

Fig. E 6 Fresh catalysts synthesized (Rh-LZ, Rh-Pd-LZ) and provided by collaborators (LRhZ). Only the catalysts AFTER HEAT TREATMENT were tested for reaction.
Appendix F

Catalyst Characterization

Fig. F 1 PXD pattern for fresh catalysts Rh-LZ and Rh-Pd-LZ, before and after heat treatment under Argon at 1000°C for 10 h.
Scanning Electron Microscopy (SEM)

**Fig. F 2** SEM images of Rh-LZ (before heat treatment under Ar).
**Fig. F 3** SEM image of Rh-LZ (after heat treatment under Ar).

**Fig. F 4** SEM image of Rh-Pd-LZ (before heat treatment under Ar).
**Fig. F 5** SEM image of Rh-Pd-LZ (after heat treatment under Ar).

**Fig. F 6** SEM image of LRhZ (catalyst provided by collaborators at Louisiana State University: Dr. James Spivey and Dr. Devendra Pakhare -now at Pyrochem Catalyst Company-).
Energy-Dispersive X-ray spectroscopy (EDX)
Catalyst: Rh-LZ (before heat treatment under Ar)

Spectrum processing:
Peaks possibly omitted: 8.037, 8.901 keV
Quantitation method: Cliff Lorimer thin ratio section.
Processing option: All elements analyzed (Normalised)
Number of iterations = 1
Standardless

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<th>Atomic%</th>
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<tr>
<td>Zr K</td>
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<td>0.28</td>
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<tr>
<td>La L</td>
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<td>4.93</td>
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<tr>
<td>Totals</td>
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<td></td>
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</table>
Catalyst: Rh-LZ (before heat treatment under Ar)

Spectrum processing:
Peaks possibly omitted: 8.038, 8.904, 9.342 keV
Quantitation method: Cliff Lorimer thin ratio section.
Processing option: All elements analyzed (Normalised)
Number of iterations = 1
Standardless

<table>
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<th>Atomic%</th>
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<td>21.42</td>
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<td>Zr K</td>
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<td>6.01</td>
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<tr>
<td>Rh L</td>
<td>1.26</td>
<td>0.32</td>
</tr>
<tr>
<td>La L</td>
<td>35.71</td>
<td>6.84</td>
</tr>
<tr>
<td>Totals</td>
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</tbody>
</table>
Catalyst: LRhZ (2 wt. % La2Zr2-xRhxO7) provided by collaborators at Louisiana State University: Dr. James Spivey and Dr. Devendra Pakhare (now at Pyrochem Catalyst Company)

Spectrum processing:
Peaks possibly omitted: 8.040, 8.900 keV
Quantitation method: Cliff Lorimer thin ratio section.
Processing option: All elements analyzed (Normalised)
Number of iterations = 1
Standardless

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>42.07</td>
<td>76.67</td>
</tr>
<tr>
<td>O K</td>
<td>10.69</td>
<td>14.63</td>
</tr>
<tr>
<td>Zr K</td>
<td>13.85</td>
<td>3.32</td>
</tr>
<tr>
<td>Rh L</td>
<td>2.13</td>
<td>0.45</td>
</tr>
<tr>
<td>La L</td>
<td>31.26</td>
<td>4.93</td>
</tr>
</tbody>
</table>

Totals 100.00
**Catalyst: Rh-LZ (after heat treatment under Ar)**

Spectrum processing:
Peaks possibly omitted: 8.037, 8.893 keV
Quantitation method: Cliff Lorimer thin ratio section.
Processing option: All elements analyzed (Normalised)
Number of iterations = 1
Standardless

<table>
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<td>Zr K</td>
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<td>0.35</td>
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<tr>
<td>Rh L</td>
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<td>0.01</td>
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<tr>
<td>La L</td>
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<td>0.39</td>
</tr>
<tr>
<td><strong>Totals</strong></td>
<td><strong>100.00</strong></td>
<td><strong>100.00</strong></td>
</tr>
</tbody>
</table>
Catalyst: Rh-Pd-LZ (before heat treatment under Ar)

Spectrum processing:
Peaks possibly omitted: 8.039, 8.901, 18.870 keV
Quantitation method: Cliff Lorimer thin ratio section.
Processing option: All elements analyzed (Normalised)
Number of iterations = 1
Standardless

<table>
<thead>
<tr>
<th>Element</th>
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<th>Atomic%</th>
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<td>Zr K</td>
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<tr>
<td>Rh L</td>
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<td>0.14</td>
</tr>
<tr>
<td>Pd L</td>
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<td>0.00</td>
</tr>
<tr>
<td>La L</td>
<td>29.68</td>
<td>4.60</td>
</tr>
</tbody>
</table>

Totals 100.00
**Catalyst: Rh-Pd-LZ (after heat treatment under Ar)**

Spectrum processing:
Peaks possibly omitted: 8.040, 8.903 keV
Quantitation method: Cliff Lorimer thin ratio section.
Processing option: All elements analyzed (Normalised)
Number of iterations = 1

<table>
<thead>
<tr>
<th>Standardless</th>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
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<tbody>
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<td>79.82</td>
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<td></td>
<td>O K</td>
<td>11.07</td>
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<tr>
<td></td>
<td>Zr K</td>
<td>13.59</td>
<td>2.91</td>
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<tr>
<td></td>
<td>Rh L</td>
<td>0.97</td>
<td>0.18</td>
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<tr>
<td></td>
<td>Pd L</td>
<td>0.39</td>
<td>0.07</td>
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<tr>
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<td>La L</td>
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<tr>
<td><strong>Totals</strong></td>
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</table>
Thermogravimetric Analysis (TGA)

Carbon deposition for all catalysts was analyzed after 4 h time-on-stream at 800 °C, 1.1 atm and GHSV = 58800 cm³/gcat/h.

![TGA analysis for spent Rh-LZ at two heating rates: 2 and 10 °C/min.](image)

**Fig. F 7** TGA analysis for spent Rh-LZ at two heating rates: 2 and 10 °C/min.
Fig. F 8 TGA analysis for spent Rh-Pd-LZ at two heating rates: 2 and 10 °C/min.

Fig. F 9 TGA analysis for spent LRhZ at two heating rates: 2 and 10 °C/min (catalyst provided by collaborators at Louisiana State University: Dr. James Spivey and Dr. Devendra Pakhare -now at Pyrochem Catalyst Company-).
Appendix G

Safety Protocol for Handling Carbon Monoxide

There are two sources of carbon monoxide in the laboratory (room 202, Earle Hall): the CO cylinder and the CO produced in the reforming reaction. Follow this procedure before engaging in any activity that involves handling carbon monoxide (CO):

1. There are two CO detectors calibrated with two alarms each (low limit at 35 ppm and high limit at 200 ppm). Learn how to use the detectors by reading the manual. Remove the detectors from the laboratory to an area where there are not contaminant gases present. Test the detectors.

2. Place one detector at the pressure regulator of the CO cylinder.

3. Clip the other detector to your shirt (place it the closest you can to your nose/mouth).

4. Make sure all windows in the lab are open, and the door of the lab is closed.

5. On a regular basis, the CO cylinder is not in use since it serves calibration purposes only. However, before it is used, make sure to connect the line to the reactor system, snoop the just created connection and then open the valve. Hold your breath and look for leaks (at the same time it is advisable to remove the detector from your shirt and place it close to the connection - Remember to hold your breath and pull your head the furthest you can from the connection).

If a leak is detected, close the valve in the CO cylinder and leave the area. Come back after a few minutes and tighten up the connection. Then, repeat this step until there is not gas leaking.
6. Once the absence of leaks is confirmed you can clip the CO detector back to your shirt.

7. When the CO cylinder is not needed anymore, close the cylinder valve first and allow time for the CO in the line to be evacuated to the laboratory hood. Then, close the valve after the pressure regulator. When the CO is completely evacuated, snoop the connection between the CO line and the system (this is a way to increase safety and detect any CO that was not completely evacuated from the line yet), hold your breath and disconnect the CO line (if needed). If a CO leak is detected when disconnecting this line, keep holding your breath, further tighten the valve in the CO cylinder and leave the area. Wait a reasonable time and then (while holding your breath) check for CO presence by passing the CO detector around the disconnected line.

8. CO from the reaction is constantly produced. If the alarm sounds, hold your breath, shut down the furnace and close all valves that feed the reactants to the reactor (6 valves before the flowmeters of the reactor system and the valves placed on the wall). Leave the area and tell everybody in the building to evacuate. Call the Fire Department. **Important:** If you do not feel comfortable performing any procedure after the alarm sounds, leave the area, tell everybody to evacuate as soon as possible and call the Fire Department.
Appendix H

Microkinetic Model Code

The Micro-kinetic model presented in Chapter 4 was built using the open source software SUNDIALS (written in the programming language C). More specifically, the example ‘cvRoberts_dns’ was upgraded to the more complex system of equations treated (see Appendix D). ‘cvRoberts_dns’ is found in example files of the solver CVODE v2.7.0, which solves initial value problems for ordinary differential equation (ODE) systems.

/* Header files with a description of contents used */
#include <stdio.h>
#include <stdlib.h>
#include <math.h>

Ith(v,i) references the ith component of the vector v, where i is in the range [1..NEQ] and NEQ is defined below. The Ith macro is defined using the N_VIth macro in nvector.h. N_VIth numbers the components of a vector starting from 0.

Ith(A,i) references the (i,j)th element of the dense matrix A, where i and j are in the range [1..NEQ]. The IJth macro is defined using the DENSE_ELEM macro in dense.h. DENSE_ELEM numbers rows and columns of a dense matrix starting from 0.

#define Ith(v,i)       NV_Ith_S(v,i-1)     /* Ith numbers components 1..NEQ */
#define IJth(A,i,j)    DENSE_ELEM(A,i,j-1) /* IJth numbers rows,cols 1..NEQ */
/* Problem Constants */

#define NEQ 26 /* number of equations */
#define Y1 RCONST(0) // initial surface coverage
#define Y2 RCONST(0)
#define Y3 RCONST(0)
#define Y4 RCONST(0)
#define Y5 RCONST(0)
#define Y6 RCONST(0)
#define Y7 RCONST(0)
#define Y8 RCONST(0)
#define Y9 RCONST(0)
#define Y10 RCONST(0)
#define Y11 RCONST(0)
#define Y12 RCONST(0)
#define Y13 RCONST(0)
#define Y14 RCONST(0)
#define Y15 RCONST(0)
#define Y16 RCONST(0)
#define Y17 RCONST(0)
#define Y18 RCONST(0)
#define Y19 RCONST(0)
#define Y20 RCONST(0)

#define Y21 RCONST(2.174604E-06) // initial moles of CH4(g)
#define Y22 RCONST(2.174604E-06) // initial moles of CO2(g)
#define Y23 RCONST(0) // initial moles of H2O(g)
#define Y24 RCONST(0) // initial moles of CH3OH(g)
#define Y25 RCONST(0) // initial moles of CO(g)
#define Y26 RCONST(0) // initial moles of H2(g)

#define RTOL RCONST(1.0e-20) /* scalar relative tolerance */
#define SZERO RCONST(1.0e-8)
#define ATOL1 SZERO /* vector absolute tolerance components */
#define ATOL2 SZERO
#define ATOL3 SZERO
#define ATOL4 SZERO
#define ATOL5 SZERO
#define ATOL6 SZERO
#define ATOL7 SZERO
#define ATOL8 SZERO
#define ATOL9 SZERO
#define ATOL10 SZERO
#define ATOL11 SZERO
#define ATOL12 SZERO
#define ATOL13 SZERO
#define ATOL14 SZERO
#define ATOL15 SZERO
#define ATOL16 SZERO
#define ATOL17 SZERO
#define ATOL18 SZERO
#define ATOL19 SZERO
#define ATOL20 SZERO
#define ATOL21 SZERO
#define ATOL22 SZERO
#define ATOL23 SZERO
#define ATOL24 SZERO
#define ATOL25 SZERO
#define ATOL26 SZERO
#define T0 RCONST(0.0)      /* initial time */
#define TADD RCONST(30)
#define TMULT RCONST(10)     /* output time factor */
#define NOUT 52               /* number of output times */
#define T1 RCONST(1e-15)

/* Functions Called by the Solver */
static int f(realtype t, N_Vector y, N_Vector ydot, void *user_data);
static int g(realtype t, N_Vector y, realtype *gout, void *user_data);

/* Private functions to output results */
static void PrintOutput(realtype t, realtype y1, realtype y2, realtype y3, realtype y4, realtype y5, realtype y6, realtype y7, realtype y8, realtype y9, realtype y10, realtype y11, realtype y12, realtype y13, realtype y14, realtype y15, realtype y16, realtype y17, realtype y18, realtype y19, realtype y20, realtype y21, realtype y22, realtype y23, realtype y24, realtype y25, realtype y26);
static void PrintRootInfo(int root_f1, int root_f2);

/* Private function to print final statistics */
static void PrintFinalStats(void *cvode_mem);

/* Private function to check function return values */
static int check_flag(void *flagvalue, char *funcname, int opt);

int main()
{
    realtype reltol, t, tout;
    N_Vector y, abstol;
    void *cvode_mem;
    int flag, flagr, iout;
    int rootsfound[2];

    y = abstol = NULL;
    cvode_mem = NULL;
/* Create serial vector of length NEQ for I.C. and abstol */
y = N_VNew_Serial(NEQ);
if (check_flag((void *)y, "N_VNew_Serial", 0)) return(1);
abstol = N_VNew_Serial(NEQ);
if (check_flag((void *)&abstol, "N_VNew_Serial", 0)) return(1);

/* Initialize y */
ith(y,1) = Y1;
ith(y,2) = Y2;
ith(y,3) = Y3;
ith(y,4) = Y4;
ith(y,5) = Y5;
ith(y,6) = Y6;
ith(y,7) = Y7;
ith(y,8) = Y8;
ith(y,9) = Y9;
ith(y,10) = Y10;
ith(y,11) = Y11;
ith(y,12) = Y12;
ith(y,13) = Y13;
ith(y,14) = Y14;
ith(y,15) = Y15;
ith(y,16) = Y16;
ith(y,17) = Y17;
ith(y,18) = Y18;
ith(y,19) = Y19;
ith(y,20) = Y20;
ith(y,21) = Y21; /* last 6 variables correspond to moles in the gas phase */
ith(y,22) = Y22;
ith(y,23) = Y23;
ith(y,24) = Y24;
ith(y,25) = Y25;
ith(y,26) = Y26;

/* Set the scalar relative tolerance */
reltol = RTOL;
/* Set the vector absolute tolerance */
ith(abstol,1) = ATOL1;
ith(abstol,2) = ATOL2;
ith(abstol,3) = ATOL3;
ith(abstol,4) = ATOL4;
ith(abstol,5) = ATOL5;
ith(abstol,6) = ATOL6;
ith(abstol,7) = ATOL7;
ith(abstol,8) = ATOL8;
ith(abstol,9) = ATOL9;
ith(abstol,10) = ATOL10;
ith(abstol,11) = ATOL11;
ith(abstol,12) = ATOL12;
ith(abstol,13) = ATOL13;
ith(abstol,14) = ATOL14;
ith(abstol,15) = ATOL15;
Ith(abstol,16) = ATOL16;
Ith(abstol,17) = ATOL17;
Ith(abstol,18) = ATOL18;
Ith(abstol,19) = ATOL19;
Ith(abstol,20) = ATOL20;
Ith(abstol,21) = ATOL21;
Ith(abstol,22) = ATOL22;
Ith(abstol,23) = ATOL23;
Ith(abstol,24) = ATOL24;
Ith(abstol,25) = ATOL25;
Ith(abstol,26) = ATOL26;

/* Call CVodeCreate to create the solver memory and specify the */
/* Backward Differentiation Formula and the use of a Newton iteration */
cvode_mem = CVodeCreate(CV_BDF, CV_NEWTON);
if (check_flag((void *)cvode_mem, "CVodeCreate", 0)) return(1);

/* Call CVodeInit to initialize the integrator memory and specify the */
/* user's right hand side function in y'=f(t,y), the initial time T0, and */
/* the initial dependent variable vector y. */
flag = CVodeInit(cvode_mem, f, T0, y);
if (check_flag(&flag, "CVodeInit", 1)) return(1);

/* Call CVodeSVtolerances to specify the scalar relative tolerance */
/* and vector absolute tolerances */
flag = CVodeSVtolerances(cvode_mem, reltol, abstol);
if (check_flag(&flag, "CVodeSVtolerances", 1)) return(1);

/* Call CVDense to specify the CVDENSE dense linear solver */
flag = CVDense(cvode_mem, NEQ);
if (check_flag(&flag, "CVDense", 1)) return(1);

flag = CVodeSetMaxNumSteps(cvode_mem, 9000);

/* In loop, call CVode, print results, and test for error. */
/* Break out of loop when NOUT preset output times have been reached. */
printf("26-species kinetics problem


tout = RCONST(0.0);
iout = 0; tout = T1;
while(1) {
  flag = CVode(cvode_mem, tout, y, &t, CV_NORMAL);
  PrintOutput(t, Ith(y,1), Ith(y,2), Ith(y,3), Ith(y,4), Ith(y,5), Ith(y,6), Ith(y,7), Ith(y,8), Ith(y,9), Ith(y,10),
  Ith(y,11), Ith(y,12), Ith(y,13), Ith(y,14), Ith(y,15), Ith(y,16), Ith(y,17), Ith(y,18), Ith(y,19), Ith(y,20),
  Ith(y,21), Ith(y,22), Ith(y,23), Ith(y,24), Ith(y,25), Ith(y,26));

  if (check_flag(&flag, "CVode", 1)) break;
  if (flag == CV_SUCCESS) {
    iout++;
    tout *= TMULT;
  }
}
if (iout == NOUT) break;
}

/* Print some final statistics */
PrintFinalStats(cvode_mem);

/* Free y and abstol vectors */
N_VDestroy_Serial(y);
N_VDestroy_Serial(abstol);

/* Free integrator memory */
CVodeFree(&cvode_mem);

return(0);
}

/*
*-------------------------------
* Functions called by the solver
*-------------------------------
*/

/* f routine. Compute function f(t,y). */

static int f(realtype t, N_Vector y, N_Vector ydot, void *user_data)
{
    realtype y0, y1, y2, y3, y4, y5, y6, y7, y8, y9, y10, y11, y12, y13, y14, y15, y16, y17, y18, y19, y20, y21,
    y22, y23, y24, y25, y26, yd1, yd2, yd3, yd4, yd5, yd6, yd7, yd8, yd9, yd10, yd11, yd12, yd13, yd14, yd15,
    yd16, yd17, yd18, yd19, yd20, yd21, yd22, yd23, yd24, yd25, yd26;
    realtype w, kb, R, h, unit, T, AA, S, Sco2, Sch4, Sh2o, Sh2, Sco, s, rov;
    realtype mch4, mco2, mh2o, mh2, mco, mch3oh, mcat, Na, vol;
    realtype Pch4, Pco2, Ph2o, Pch3oh, Pco, Ph2;
    realtype HadsCO2, HadsCH4, HdesH2O, HdesH2, HdesCO, HdesCH3OH;
    realtype Kco2011, Kch4011, Kh2o011, Kh2011, Kco011, Kch3oh011;
    realtype deltaSch4, deltaSco2, deltaSh2o, deltaSh2, deltaSco, deltaSch3oh, Sh23D, Sh22D;
    realtype kf1, kf2, kf3, kf4, kf5, kf6, kf7, kf8, kf9, kf10, kf11, kf12, kf13, kf14, kf15, kf16, kf17, kf18,
    kf19, kf20, kf21, kf22, kf23, kf24, kf25, kf26, kf27, kf28, kf29, kf30, kf31, kf32, kf33, kf34;
    realtype kr1, kr2, kr3, kr4, kr5, kr6, kr7, kr8, kr9, kr10, kr11, kr12, kr13, kr14, kr15, kr16, kr17, kr18,
    kr19, kr20, kr21, kr22, kr23, kr24, kr25, kr26, kr27, kr28, kr29, kr30, kr31, kr32, kr33, kr34;
    realtype subscript, Rhpercentage, MLa, MZr, MO, MRh;
    realtype y0Rh, fracRh;
    realtype scaling, Tadj;

    kb=1.3806488e-23;    // J/K
    R=8.3144621;        // R=8.314 J/mol*K
    h=6.62606957e-34;   // J*s

    return(0);
}
mch4 = 2.6635e-26;  // kg
mco2 = 7.3080e-26;  // kg
mh2o = 2.9923e-26;  // kg
mh2 = 3.3542e-27;  // kg
mco = 4.6512e-26;  // kg
mch3oh = 5.3204e-26;  // kg
unit = 96153.8;  // 1 eV/molec equals 96153.8 J/mol
mcat = 0.008e-3;  // mass of catalyst, kg
Na = 6.02214129e23;  // Avogadro's number, molecules/mol
Tadj = 0;  // K
T = 650 + 273.15 + Tadj;  // Temperature, K
s = 8721.9;  // surface area of catalyst per mass of it, m2/kg
vol = 2.20749E-06;  // reactor volume, m3
MLa = 138.91;
MZr = 91.22;
MO = 16;
MRh = 102.91;
Rhpercentage = 0.32;
scaling = 0.66079;  // scaling factor for activation energies

double Eaf[35];
double Ear[35];
double kf[35];
double kr[35];

// Activation barriers for plane 111/*
// in the plane 111 there are 4 metal atoms in a surface of 5.126x10^-19 m2, therefore, ω=1.282x10^-19 m2
// per active site*/
w = 5.126e-19/4;  // m2 per active site
Eaf[1] = 0.00;  Ear[1] = 0.03;
Eaf[2] = 0.89;  Ear[2] = 1.46;
Eaf[3] = 0.81;  Ear[3] = 1.07;
Eaf[6] = 0.00;  Ear[6] = 1.02;
Eaf[8] = 1.47;  Ear[8] = 0.74;
Eaf[9] = 0.10;  Ear[9] = 1.65;
Eaf[10] = 2.52;  Ear[10] = 0.01;
Eaf[12] = 2.47;  Ear[12] = 0.01;
Eaf[13] = 2.12;  Ear[13] = 0.93;
Eaf[14] = 4.42;  Ear[14] = 0.01;
Eaf[16] = 20;  Ear[16] = 20;
Eaf[18] = 2.50;  Ear[18] = 1.05;
Eaf[19] = 2.28;  Ear[19] = 1.92;
Eaf[20] = 2.88;  Ear[20] = 0.80;
Eaf[21] = 1.37;  Ear[21] = 2.34;
Eaf[22] = 4.01;  Ear[22] = 2.16;
Eaf[23]= 2.40 ; Ear[23]= 2.26 ;
Eaf[25]= 0.33 ; Ear[25]= 1.82 ;
Eaf[26]= 0.91 ; Ear[26]= 1.73 ;
Eaf[27]= 0.01 ; Ear[27]= 3.00 ;
Eaf[28]= 1.74 ; Ear[28]= 1.30 ;
Eaf[29]= 2.08 ; Ear[29]= 0.01 ;
Eaf[30]= 0.50 ; Ear[30]= 0.00 ;
Eaf[31]= 1.16 ; Ear[31]= 0.05 ;
Eaf[32]= 0.02 ; Ear[32]= 0.00 ;
Eaf[33]= 1.62 ; Ear[33]= 0.00 ;
Eaf[34]= 0.52 ; Ear[34]= 0.00 ;

int i;
for (i = 0; i < 35; i++) {
    kf[i]=(kb*T/h)*exp(-(scaling*Eaf[i]*unit)/(R*T)); // reaction rate for the forward reaction
    kr[i]=(kb*T/h)*exp(-(scaling*Ear[i]*unit)/(R*T)); // reaction rate for the reverse reaction
}
i = 0;
for (i = 15; i < 18; i++) {
    kf[i]=0; // reactions ruled out, because no stable configuration for COH* was ever found
    kr[i]=0;
}

/*Desorption rate constants*/
kr[1]=(kb*T/h)*exp(-(scaling*Ear[1]*unit)/(R*T)); // 1/Pa.s, CH4
kr[6]=(kb*T/h)*exp(-(scaling*Eaf[6]*unit)/(R*T)); // 1/Pa.s, CO2
kf[30]=(kb*T/h)*exp(-(scaling*Eaf[30]*unit)/(R*T)); // 1/Pa.s, H2O
kf[32]=(kb*T/h)*exp(-(scaling*Eaf[32]*unit)/(R*T)); // 1/Pa.s, H2
kf[33]=(kb*T/h)*exp(-(scaling*Eaf[33]*unit)/(R*T)); // 1/Pa.s, CO
kf[34]=(kb*T/h)*exp(-(scaling*Eaf[34]*unit)/(R*T))); // 1/Pa.s, CH3OH

/*Adsorption rate constants*/
kf[1]=w/pow(2*3.14159*mch4*kb*T,0.5); // 1/Pa.s, CH4
kf[6]=w/pow(2*3.14159*mco2*kb*T,0.5); // 1/Pa.s, CO2
kr[30]=w/pow(2*3.14159*mh2o*kb*T,0.5); // 1/Pa.s, H2O
kr[32]=w/pow(2*3.14159*mh2*kb*T,0.5); // 1/Pa.s, H2
kr[33]=w/pow(2*3.14159*mco*kb*T,0.5); // 1/Pa.s, CO
kr[34]=w/pow(2*3.14159*mch3oh*kb*T,0.5); // 1/Pa.s, CH3OH

Kch4011=kf[1]/kr[1];  // equilibrium constant of CH4, 1/Pa
Kco2011=kf[6]/kr[6];  // equilibrium constant of CO2, 1/Pa
Kh2o011=kf[30]/kr[30]; // equilibrium constant of H2O, Pa
Kh2011=kf[32]/kr[32];  // equilibrium constant of H2, Pa
Kco011=kf[33]/kr[33];  // equilibrium constant of CO, Pa
Kch3oh011=kf[34]/kr[34]; //equilibrium constant of CH3OH, Pa*/

y1 = Ith(y,1); y2 = Ith(y,2); y3 = Ith(y,3);
y4 = Ith(y,4); y5 = Ith(y,5); y6 = Ith(y,6);
y7 = Ith(y,7); y8 = Ith(y,8); y9 = Ith(y,9);
y10 = Ith(y,10); y11 = Ith(y,11); y12 = Ith(y,12);
y13 = Ith(y,13); y14 = Ith(y,14); y15 = Ith(y,15);
y16 = Ith(y,16); y17 = Ith(y,17); y18 = Ith(y,18);
y19 = Ith(y,19); y20 = Ith(y,20);
y21 = Ith(y,21); y22 = Ith(y,22); y23 = Ith(y,23); y24 = Ith(y,24); y25 = Ith(y,25); y26 = Ith(y,26);
Pch4 = y21*(R)*T/vol;
Pco2 = y22*(R)*T/vol;
Ph2o = y23*(R)*T/vol;
Pch3oh = y24*(R)*T/vol;
Pco = y25*(R)*T/vol;
Ph2 = y26*(R)*T/vol;

kf1 = kf[1]; kf2 = kf[2]; kf3 = kf[3]; kf4 = kf[4]; kf5 = kf[5]; kf6 = kf[6]; kf7 = kf[7]; kf8 = kf[8];
kf9 = kf[9]; kf10 = kf[10];
kf11 = kf[11]; kf12 = kf[12]; kf13 = kf[13]; kf14 = kf[14]; kf15 = kf[15]; kf16 = kf[16]; kf17 = kf[17]; kf18 = kf[18]; kf19 = kf[19]; kf20 = kf[20];
kf21 = kf[21]; kf22 = kf[22]; kf23 = kf[23]; kf24 = kf[24]; kf25 = kf[25]; kf26 = kf[26]; kf27 = kf[27]; kf28 = kf[28]; kf29 = kf[29]; kf30 = kf[30];
kf31 = kf[31]; kf32 = kf[32]; kf33 = kf[33]; kf34 = kf[34];

kr1 = kr[1]; kr2 = kr[2]; kr3 = kr[3]; kr4 = kr[4]; kr5 = kr[5]; kr6 = kr[6]; kr7 = kr[7]; kr8 = kr[8];
kr9 = kr[9]; kr10 = kr[10];
kr11 = kr[11]; kr12 = kr[12]; kr13 = kr[13]; kr14 = kr[14]; kr15 = kr[15]; kr16 = kr[16]; kr17 = kr[17]; kr18 = kr[18]; kr19 = kr[19]; kr20 = kr[20];
kr21 = kr[21]; kr22 = kr[22]; kr23 = kr[23]; kr24 = kr[24]; kr25 = kr[25]; kr26 = kr[26]; kr27 = kr[27]; kr28 = kr[28]; kr29 = kr[29]; kr30 = kr[30];
kr31 = kr[31]; kr32 = kr[32]; kr33 = kr[33]; kr34 = kr[34];

subscript = Rhpercentage*(2*MLa+2*MZr+7*MO)/(100*MRh-Rhpercentage*(MRh-MZr));
fracRh = subscript/(4);
y0Rh = RCONST(fracRh)-(y1+y3+y4+y5+y6+y7+y10+y16+y17+y18+y20);
y0 = RCONST(1-fracRh)-(y2+y8+y9+y11+y12+y13+y14+y15+y19);

//y1 is CH4*Rh
yd1 = Ith(ydot,1) = RCONST(kf1)*(Pch4*y0Rh-y1/RCONST(Kch4011))+RCOSTR(kr2)*y2*y6-
RCOSTR(kf2)*y1*y0;

//y2 is CH3*
yd2 = Ith(ydot,2) =
(RCONST(kf2)*y1*y0+RCOSTR(kr3)*y3*y6+y0+RCOSTR(kr10)*y11*y0+RCOSTR(kr18)*y15+y0Rh)-
(RCONST(kr2)*y6+RCOSTR(kf3)*y0Rh+y0Rh+RCOSTR(kf10)*y8+RCOSTR(kf18)*y7)*y2;

//y3 is CH2*Rh
yd3 = Ith(ydot,3) =
(RCONST(kf3)*y2*y0Rh+y0Rh+RCOSTR(kr4)*y4*y6+RCOSTR(kr12)*y12*y0Rh+RCOSTR(kr20)*y16*y0Rh)-(RCOSTR(kr3)*y6*y0+RCOSTR(kf4)*y0Rh+RCOSTR(kf12)*y8+RCOSTR(kf20)*y7)*y3;

//y4 is CH*Rh
yd4 = Ith(ydot,4) =
(RCONST(kf4)*y3*y0Rh+RCOSTR(kr5)*y5*y6+RCOSTR(kr14)*y13*y0Rh+RCOSTR(kr22)*y17*y0Rh)-(RCOSTR(kr4)*y6+RCOSTR(kf5)*y0Rh+RCOSTR(kf14)*y8+RCOSTR(kf22)*y7)*y4;
//y5 is C*Rh
yd5 = 1th(ydot,5) = (RCONST(kf5)*y4*y0Rh+RCONST(kr16)*y14*y0Rh+RCONST(kr24)*y18*y0Rh) -
(RCONST(kf5)*y6+RCONST(kf16)*y8+RCONST(kf24)*y7)*y5;

//y6 is H*Rh
yd6 = 1th(ydot,6) =
(RCONST(kf2)*y1*y0+RCONST(kf3)*y2*y0Rh*y0Rh+RCONST(kf4)*y3*y0Rh+RCONST(kf5)*y4*y0Rh+
RCONST(kr8)*y20*y0+RCONST(kf11)*y11*y0Rh+
+RCONST(kf13)*y12*y0Rh+RCONST(kf15)*y13*y0Rh+RCONST(kf17)*y14*y0Rh*y0Rh+RCONST(kf19)*y15*y0Rh*y0Rh

+RCONST(kf21)*y16*y0Rh+RCONST(kf23)*y17*y0Rh+RCONST(kf25)*y11*y0Rh+RCONST(kf26)*y12*y0Rh*y0Rh

+RCONST(kf27)*y13*y0Rh*y0Rh+RCONST(kr28)*y8*y0Rh*y0Rh+RCONST(kr29)*y9*y0Rh+2*RCONST(kr31)*y20*
y0 Rh-(RCONST(kr2)*y2+RCONST(kr3)*y3*y0+RCONST(kr4)*y4+RCONST(kr5)*y5+
+RCONST(kr11)*y18+RCONST(kr19)*y14*y0+RCONST(kr15)*y18*y0+RCONST(kr17)*y18*y0+RCONST(kr19)*y16*y0

+RCONST(kr21)*y17+RCONST(kr23)*y18+RCONST(kr25)*y15+RCONST(kr26)*y16*y0

+RCONST(kf27)*y17*y0+RCONST(kf28)*y7*y0+RCONST(kf29)*y8+RCONST(kf31)*y6)*y6;

//y7 is O*Rh
yd7 = 1th(ydot,7) =
(RCONST(kf7)*y19*y0Rh*y0Rh+RCONST(kr18)*y15*y0Rh+RCONST(kr20)*y16*y0Rh+RCONST(kr22)*y17*
y0Rh+RCONST(kr28)*y8*y0Rh*y0Rh) -
(RCONST(kr7)*y18*y0+RCONST(kf18)*y2+RCONST(kf20)*y3+RCONST(kf22)*y4+RCONST(kf24)*y5+
+RCONST(kf28)*y6*y0)*y7;

//y8 is OH*
yd8 = 1th(ydot,8) =
(RCONST(kf9)*y20*y0+RCONST(kr10)*y11*y0+RCONST(kr12)*y12*y0+RCONST(kr14)*y13*y0R
h+RCONST(kr16)*y14*y0Rh+RCONST(kf28)*y7*y6*y0+
+RCONST(kr29)*y9*y0Rh-)
(RCONST(kr9)*y18+RCONST(kf10)*y2+RCONST(kf12)*y3+RCONST(kf14)*y4+RCONST(kf16)*y5+
+RCONST(kr28)*y0Rh*y0Rh+RCONST(kf29)*y6)*y8;

//y9 is H2O*
yd9 = 1th(ydot,9) = RCONST(kf29)*y8*y6+RCONST(kr29)*y9*y0Rh+RCONST(kr30)*(Ph2o*y0-
RCONST(Kh2o011))*y9;

//y10 is H2*Rh
yd10 = 1th(ydot,10) = 0.5*RCONST(kf31)*y6*y6-
RCONST(kr31)*y10*y0Rh+RCONST(kr32)*(Ph2*y0Rh-RCONST(Kh2011))*y10;

//y11 is CH3OH*
\[\text{yd11} = \text{Ith}(\text{ydot},11) = \text{RCONST}(kf10)\cdot y2\cdot y8 + \text{RCONST}(kr11)\cdot y12\cdot y6 + \text{RCONST}(kr25)\cdot y15\cdot y6 - (\text{RCONST}(kr10)\cdot y0 + \text{RCONST}(kf11)\cdot y0\text{Rh} + \text{RCONST}(kf25)\cdot y0\text{Rh})\cdot y11 + \text{RCONST}(kr34)\cdot (Pch3oh\cdot y0 - \text{RCONST}(Kch3oh011)\cdot y11);\]

//y12 is CH2OH*
\[\text{yd12} = \text{Ith}(\text{ydot},12) = (\text{RCONST}(kf11)\cdot y11\cdot y0\text{Rh} + \text{RCONST}(kf12)\cdot y3\cdot y8 + \text{RCONST}(kr13)\cdot y13\cdot y6 + \text{RCONST}(kr26)\cdot y16\cdot y6 \cdot y0) - (\text{RCONST}(kr11)\cdot y6 + \text{RCONST}(kr12)\cdot y0\text{Rh} + \text{RCONST}(kf13)\cdot y0\text{Rh})\cdot y12;\]

//y13 is CHOH*
\[\text{yd13} = \text{Ith}(\text{ydot},13) = (\text{RCONST}(kf13)\cdot y12\cdot y0\text{Rh} + \text{RCONST}(kf14)\cdot y4\cdot y8 + \text{RCONST}(kr15)\cdot y14\cdot y6 + \text{RCONST}(kr27)\cdot y17\cdot y6 \cdot y0) - (\text{RCONST}(kr13)\cdot y6 + \text{RCONST}(kr14)\cdot y0\text{Rh} + \text{RCONST}(kf15)\cdot y0\text{Rh})\cdot y13;\]

//y14 is COH*
\[\text{yd14} = \text{Ith}(\text{ydot},14) = (\text{RCONST}(kf15)\cdot y13\cdot y0\text{Rh} + \text{RCONST}(kf16)\cdot y5\cdot y8 + \text{RCONST}(kr17)\cdot y18\cdot y6 \cdot y0) - (\text{RCONST}(kr15)\cdot y6 + \text{RCONST}(kr16)\cdot y0\text{Rh} + \text{RCONST}(kf17)\cdot y0\text{Rh})\cdot y14;\]

//y15 is CH3O*
\[\text{yd15} = \text{Ith}(\text{ydot},15) = (\text{RCONST}(kf18)\cdot y2\cdot y7 + \text{RCONST}(kr19)\cdot y16\cdot y6 \cdot y0 + \text{RCONST}(kf25)\cdot y11\cdot y0\text{Rh}) - (\text{RCONST}(kr18)\cdot y0\text{Rh} + \text{RCONST}(kf19)\cdot y0\text{Rh} + \text{RCONST}(kr25)\cdot y6)\cdot y15;\]

//y16 is CH2O*Rh
\[\text{yd16} = \text{Ith}(\text{ydot},16) = (\text{RCONST}(kf19)\cdot y15\cdot y0\text{Rh} + \text{RCONST}(kf20)\cdot y3\cdot y7 + \text{RCONST}(kr21)\cdot y17\cdot y6 + \text{RCONST}(kf26)\cdot y12\cdot y0\text{Rh} - (\text{RCONST}(kr19)\cdot y6 + \text{RCONST}(kr20)\cdot y0\text{Rh} + \text{RCONST}(kf21)\cdot y0\text{Rh} + \text{RCONST}(kr26)\cdot y6 \cdot y0))\cdot y16;\]

//y17 is CHO*Rh
\[\text{yd17} = \text{Ith}(\text{ydot},17) = (\text{RCONST}(kf21)\cdot y16\cdot y0\text{Rh} + \text{RCONST}(kf22)\cdot y4\cdot y7 + \text{RCONST}(kr23)\cdot y18\cdot y6 + \text{RCONST}(kf27)\cdot y13\cdot y0\text{Rh} \cdot y0\text{Rh}) - (\text{RCONST}(kr21)\cdot y6 + \text{RCONST}(kr22)\cdot y0\text{Rh} + \text{RCONST}(kf23)\cdot y0\text{Rh} + \text{RCONST}(kr27)\cdot y6 \cdot y0)\cdot y17;\]

//y18 is CO*Rh
\[\text{yd18} = \text{Ith}(\text{ydot},18) = (\text{RCONST}(kf7)\cdot y19\cdot y0\text{Rh} + \text{RCONST}(kf9)\cdot y20\cdot y0 + \text{RCONST}(kf17)\cdot y14\cdot y0\text{Rh} + \text{RCONST}(kf23)\cdot y17\cdot y0\text{Rh} + \text{RCONST}(kf24)\cdot y5\cdot y7) - (\text{RCONST}(kr7)\cdot y7\cdot y0 + \text{RCONST}(kr9)\cdot y8 + \text{RCONST}(kr23)\cdot y6 \cdot y0 + \text{RCONST}(kr24) \cdot y0\text{Rh} \cdot y18 + \text{RCONST}(kr33)\cdot (Pco\cdot y0\text{Rh} - \text{RCONST}(Kco011))\cdot y18);\]

//y19 is CO2*
\[\text{yd19} = \text{Ith}(\text{ydot},19) = \text{RCONST}(kf6)\cdot (Pco2\cdot y0 - y19\cdot \text{RCONST}(Kco011)) + \text{RCONST}(kr7)\cdot y18\cdot y7\cdot y0 + \text{RCONST}(kr8)\cdot y20\cdot y0 - (\text{RCONST}(kf7)\cdot y0\text{Rh} \cdot y0\text{Rh} + \text{RCONST}(kf8)\cdot y6)\cdot y19;\]

//y20 is COOH*Rh
\[\text{yd20} = \text{Ith}(\text{ydot},20) = (\text{RCONST}(kf8)\cdot y19\cdot y6 + \text{RCONST}(kr9)\cdot y18\cdot y8) - (\text{RCONST}(kr8)\cdot y0 + \text{RCONST}(kf9)\cdot y0)\cdot y20;\]
//derivative of moles of CH4(g) with respect to time
yd21 = Ith(ydot,21) = RCONST(mcat*s/(Na*w))*RCONST(-kf1)*(Pch4*y0Rh-y1/RCONST(Kch4011));

//derivative of moles of CO2(g) with respect to time
yd22 = Ith(ydot,22) = RCONST(mcat*s/(Na*w))*RCONST(-kf6)*(Pco2*y0-y19/RCONST(Kco2011));

//derivative of moles of H2O(g) with respect to time
yd23 = Ith(ydot,23) = RCONST(mcat*s/(Na*w))*RCONST(-kr30)*(Ph2o*y0-RCONST(Kh2o011)*y9);

//derivative of moles of CH3OH(g) with respect to time
yd24 = Ith(ydot,24) = RCONST(mcat*s/(Na*w))*RCONST(-kr34)*(Pch3oh*y0-RCONST(Kch3oh011)*y11);

//derivative of moles of CO(g) with respect to time
yd25 = Ith(ydot,25) = RCONST(mcat*s/(Na*w))*RCONST(-kr33)*(Pco*y0Rh-RCONST(Kco011)*y18);

//derivative of moles of H2(g) with respect to time
yd26 = Ith(ydot,26) = RCONST(mcat*s/(Na*w))*RCONST(-kr32)*(Ph2*y0Rh-RCONST(Kh2011)*y10);

return(0);

/*
g routine. Compute functions g_i(t,y) for i = 0,1.
*/
static int g(realtype t, N_Vector y, realtype *gout, void *user_data)
{
    realtype y1, y3;

    y1 = Ith(y,1); y3 = Ith(y,3);
    gout[0] = y1 - RCONST(0.0001);
    gout[1] = y3 - RCONST(0.01);

    return(0);
}

/*/ 
* Private helper functions
*/
static void PrintOutput(realtype t, realtype y1, realtype y2, realtype y3, realtype y4, realtype y5, realtype
y6, realtype y7, realtype y8, realtype y9, realtype y10, realtype y11, realtype y12, realtype y13, realtype
y14, realtype y15, realtype y16, realtype y17, realtype y18, realtype y19, realtype y20, realtype y21,
realtype y22, realtype y23, realtype y24, realtype y25, realtype y26)
{
    #if defined(SUNDIALS_EXTENDED_PRECISION)
/*printf("At t = %0.4Le      y =%14.6Le  %14.6Le  %14.6Le  %14.6Le  %14.6Le  %14.6Le  %14.6Le 
"), t, y1, y2, y3, y4, y5, y6, y7, y8, y9, y10, y11, y12, y13, y14, y15, y16, y17, y18, y19, y20, y21, y22, y23, y24, y25, y26);*/
#elif defined(SUNDIALS_DOUBLE_PRECISION)
    printf("At t = %0.4le      y =%14.6le  %14.6le  %14.6le  %14.6le  %14.6le  %14.6le  %14.6le
"), t, y1, y2, y3, y4, y5, y6, y7, y8, y9, y10, y11, y12, y13, y14, y15, y16, y17, y18, y19, y20, y21, y22, y23, y24, y25, y26);
#else
    printf("At t = %0.4e      y =%14.6e  %14.6e  %14.6e  %14.6e  %14.6e  %14.6e  %14.6e
"), t, y1, y2, y3, y4, y5, y6, y7, y8, y9, y10, y11, y12, y13, y14, y15, y16, y17, y18, y19, y20, y21, y22, y23, y24, y25, y26);
#endif
return;
}

static void PrintRootInfo(int root_f1, int root_f2)
{
    printf("    rootsfound[] = %3d %3d
"), root_f1, root_f2);
    return;
}
/
* Get and print some final statistics 
*/

static void PrintFinalStats(void *cvode_mem)
{
    long int nst, nfe, nsetups, nje, nfeLS, nni, ncfn, netf, nge;
    int flag;

    flag = CVodeGetNumSteps(cvode_mem, &nst);
    check_flag(&flag, "CVodeGetNumSteps", 1);
    flag = CVodeGetNumRhsEvals(cvode_mem, &nfe);
    check_flag(&flag, "CVodeGetNumRhsEvals", 1);
    flag = CVodeGetNumLinSolvSetups(cvode_mem, &nsetups);
    check_flag(&flag, "CVodeGetNumLinSolvSetups", 1);
    flag = CVodeGetNumErrTestFails(cvode_mem, &netf);
    check_flag(&flag, "CVodeGetNumErrTestFails", 1);
    flag = CVodeGetNumNonlinSolvIters(cvode_mem, &nni);
    check_flag(&flag, "CVodeGetNumNonlinSolvIters", 1);
    flag = CVodeGetNumNonlinSolvConvFails(cvode_mem, &ncfn);
    check_flag(&flag, "CVodeGetNumNonlinSolvConvFails", 1);
    flag = CVDlsGetNumJacEvals(cvode_mem, &nje);
    check_flag(&flag, "CVDlsGetNumJacEvals", 1);
flag = CVDlsGetNumRhsEvals(cvode_mem, &nfeLS);
check_flag(&flag, "CVDlsGetNumRhsEvals", 1);

flag = CVodeGetNumGEvals(cvode_mem, &nge);
check_flag(&flag, "CVodeGetNumGEvals", 1);

printf("nFinal Statistics:n\n");
printf("nst = %-6ld nfe = %-6ld nsetups = %-6ld nfeLS = %-6ld nje = %ld\n",
nst, nfe, nsetups, nfeLS, nje);
printf("nni = %-6ld ncfn = %-6ld netf = %-6ld nge = %ld\n \n",
nii, ncfn, netf, nge);
}

/*
 * Check function return value...
 * opt == 0 means SUNDIALS function allocates memory so check if
 * returned NULL pointer
 * opt == 1 means SUNDIALS function returns a flag so check if
 * flag >= 0
 * opt == 2 means function allocates memory so check if returned
 * NULL pointer
 */

static int check_flag(void *flagvalue, char *funcname, int opt)
{
    int *errflag;

    /* Check if SUNDIALS function returned NULL pointer - no memory allocated */
    if (opt == 0 && flagvalue == NULL) {
        fprintf(stderr, "SUNDIALS_ERROR: %s() failed - returned NULL pointer\n", funcname);
        return(1);
    }

    /* Check if flag < 0 */
    else if (opt == 1) {
        errflag = (int *) flagvalue;
        if (*errflag < 0) {
            fprintf(stderr, "SUNDIALS_ERROR: \%s failed with flag = %d\n", funcname, *errflag);
            return(1);
        }
    }

    /* Check if function returned NULL pointer - no memory allocated */
    else if (opt == 2 && flagvalue == NULL) {
        fprintf(stderr, "MEMORY_ERROR: %s() failed - returned NULL pointer\n", funcname);
        return(1);
    }

    return(0);
}
Appendix I

Mass Spectrometer: Signal Processing

Correlation of MS signals to gas species concentration. Mathematical approach using material balances

\[
\frac{C_i}{C_{CO_2}} = \frac{C_{i - \text{calibration}}}{C_{CO_2 - \text{calibration}}} = \frac{C_{i - \text{calibration}}}{C_{CO_2 - \text{calibration}}}
\]

\[
\frac{I_i}{I_{CO_2}} = \frac{I_{i - \text{calibration}}}{I_{CO_2 - \text{calibration}}}
\]

\[
\frac{C_i}{I_{CO_2}} = \frac{C_{i - \text{calibration}}}{I_{CO_2 - \text{calibration}}}
\]

\[
C_i = a_i \frac{I_i}{I_{CO_2}}
\]

All concentrations can be obtained based upon the concentration of CO\(_2\) and the observed MS signals as follows.

\[
C_{CH_4\text{out}} = a_{CH_4} \frac{I_{CH_4\text{out}}}{I_{CO_2\text{out}}} C_{CO_2\text{out}} = X_{CH_4\text{out}} C_{CO_2\text{out}}
\]

\[
C_{H_2\text{out}} = a_{H_2} \frac{I_{H_2\text{out}}}{I_{CO_2\text{out}}} C_{CO_2\text{out}} = X_{H_2\text{out}} C_{CO_2\text{out}}
\]

\[
C_{CO\text{out}} = a_{CO} \frac{I_{CO\text{out}}}{I_{CO_2\text{out}}} C_{CO_2\text{out}} = X_{CO\text{out}} C_{CO_2\text{out}}
\]

The calibration information for CO is not needed in this approach. Neither is the calibration information for H\(_2\)O.

Carbon atoms balance

\[
F_{CH_4\text{in}} + F_{CO_2\text{in}} = F_{CO_2\text{out}} + F_{CH_4\text{out}} + F_{CO\text{out}}
\]
F_{\text{CH}_i} + F_{\text{CO}_2} = \left( F_{\text{CO}_2} + F_{\text{CH}_4} + F_{\text{CO}_2} \right) \frac{100F_{\text{Total}}}{100F_{\text{Total}}}

F_{\text{CH}_i} + F_{\text{CO}_2} = \left( C_{\text{CO}_2} + C_{\text{CH}_4} + C_{\text{CO}_2} \right) F_{\text{Total}} \frac{100}{100}

F_{\text{CH}_i} + F_{\text{CO}_2} = \left( C_{\text{CO}_2} + X_{\text{CH}_4} + C_{\text{CO}_2} + X_{\text{CO}_2} \right) F_{\text{Total}} \frac{100}{100}

100 \left( F_{\text{CH}_i} + F_{\text{CO}_2} \right) = \left( 1 + X_{\text{CH}_4} + X_{\text{CO}_2} \right) C_{\text{CO}_2} F_{\text{Total}}

\[ C_{\text{CO}_2} \frac{F_{\text{Total}}}{F_{\text{Total}}} \left( 1 + X_{\text{CH}_4} + X_{\text{CO}_2} \right) \] (I)

**Oxygen atoms balance**

\[ 2F_{\text{CO}_2} = 2F_{\text{CO}_2} + F_{\text{CO}_2} + F_{\text{H}_2}\text{O}_2 \]

\[ 2F_{\text{CO}_2} = \left( 2F_{\text{CO}_2} + F_{\text{CO}_2} + F_{\text{H}_2}\text{O}_2 \right) \frac{100F_{\text{Total}}}{100F_{\text{Total}}} \]

\[ 2F_{\text{CO}_2} = \left( 2C_{\text{CO}_2} + C_{\text{CO}_2} + C_{\text{H}_2}\text{O}_2 \right) F_{\text{Total}} \frac{100}{100} \]

\[ 2F_{\text{CO}_2} = \left( 2 + X_{\text{CO}_2} + X_{\text{H}_2}\text{O}_2 \right) C_{\text{CO}_2} F_{\text{Total}} \frac{100}{100} \] (II)

Plugging (I) into (II)

\[ 2F_{\text{CO}_2} = \left( 2 + X_{\text{CO}_2} + X_{\text{H}_2}\text{O}_2 \right) \left( F_{\text{CH}_i} + F_{\text{CO}_2} \right) \frac{100}{100} F_{\text{Total}} \]

\[ 2F_{\text{CO}_2} = \left( 2 + X_{\text{CO}_2} + X_{\text{H}_2}\text{O}_2 \right) \left( F_{\text{CH}_i} + F_{\text{CO}_2} \right) \frac{100}{100} F_{\text{Total}} \]

For an equimolar feed, \( F_{\text{CH}_i} = F_{\text{CO}_2} \)

\[ 1 = \frac{2 + X_{\text{CO}_2} + X_{\text{H}_2}\text{O}_2}{1 + X_{\text{CH}_4\text{out}} + X_{\text{CO}_2}} \]

\[ 1 + X_{\text{CH}_4\text{out}} + X_{\text{CO}_2} = 2 + X_{\text{CO}_2} + X_{\text{H}_2}\text{O}_2 \]

\[ 1 + X_{\text{CH}_4\text{out}} = 2 + X_{\text{H}_2}\text{O}_2 \]

\[ X_{\text{H}_2}\text{O}_2 = X_{\text{CH}_4\text{out}} - 1 \] (III)

**Hydrogen atoms balance**

\[ 4F_{\text{CH}_i} = 4F_{\text{CH}_4\text{out}} + 2F_{\text{H}_2}\text{O}_2 \]

\[ 2F_{\text{CH}_4\text{out}} = 2F_{\text{CH}_4\text{out}} + F_{\text{H}_2}\text{O}_2 \]

\[ 2F_{\text{CH}_4\text{out}} = 2F_{\text{CH}_4\text{out}} + F_{\text{H}_2}\text{O}_2 \]
\[
2F_{\text{CH}_4} = \left( 2F_{\text{CH}_4\text{out}} + F_{\text{H}_2\text{out}} + F_{\text{H}_2\text{O}_{\text{out}}} \right) \frac{100F_{\text{Total}}}{100F_{\text{Total}}} \\
2F_{\text{CH}_4} = \left( 2C_{\text{CH}_4\text{out}} + C_{\text{H}_2\text{out}} + C_{\text{H}_2\text{O}_{\text{out}}} \right) \frac{F_{\text{Total}}}{100} \\
2F_{\text{CH}_4} = \left( 2X_{\text{CH}_4\text{out}} C_{\text{CO}_{2\text{out}}} + X_{\text{H}_2\text{out}} C_{\text{CO}_{2\text{out}}} + X_{\text{H}_2\text{O}_{\text{out}}} C_{\text{CO}_{2\text{out}}} \right) \frac{F_{\text{Total}}}{100} \\
2F_{\text{CH}_4} = \left( 2X_{\text{CH}_4\text{out}} + X_{\text{H}_2\text{out}} + X_{\text{H}_2\text{O}_{\text{out}}} \right) C_{\text{CO}_{2\text{out}}} \frac{F_{\text{Total}}}{100} \tag{IV}
\]

Plugging (I) into (IV)

\[
2F_{\text{CH}_4} = \left( 2X_{\text{CH}_4\text{out}} + X_{\text{H}_2\text{out}} + X_{\text{H}_2\text{O}_{\text{out}}} \right) \left( \frac{F_{\text{CH}_4\text{in}} + F_{\text{CO}_{2\text{in}}}}{1 + X_{\text{CH}_4\text{out}} + X_{\text{CO}_{\text{out}}} \right)
\]

For equimolar feed, \( F_{\text{CH}_4\text{in}} = F_{\text{CO}_{2\text{in}}} \)

\[
1 = \frac{2X_{\text{CH}_4} + X_{\text{H}_2\text{out}} + X_{\text{H}_2\text{O}_{\text{out}}} \right)}{1 + X_{\text{CH}_4\text{out}} + X_{\text{CO}_{\text{out}}} \\
1 + X_{\text{CH}_4\text{out}} + X_{\text{CO}_{\text{out}}} = 2X_{\text{CH}_4\text{out}} + X_{\text{H}_2\text{out}} + X_{\text{H}_2\text{O}_{\text{out}}} \\
1 + X_{\text{CH}_4\text{out}} + X_{\text{CO}_{\text{out}}} = 2X_{\text{CH}_4\text{out}} + X_{\text{H}_2\text{out}} + X_{\text{H}_2\text{O}_{\text{out}}} \\
1 + X_{\text{CO}_{\text{out}}} = X_{\text{CH}_4\text{out}} + X_{\text{H}_2\text{out}} + X_{\text{H}_2\text{O}_{\text{out}}} \\
X_{\text{CO}_{\text{out}}} = X_{\text{CH}_4\text{out}} + X_{\text{H}_2\text{out}} + X_{\text{H}_2\text{O}_{\text{out}}} - 1 \tag{V}
\]

Plugging (III) into (V)

\[
X_{\text{CO}_{\text{out}}} = X_{\text{CH}_4\text{out}} + X_{\text{H}_2\text{out}} + X_{\text{CH}_4\text{out}} - 1 - 1 \\
X_{\text{CO}_{\text{out}}} = 2X_{\text{CH}_4\text{out}} + X_{\text{H}_2\text{out}} - 2 \tag{VI}
\]

The sum of all concentrations must be %100

\[
C_{\text{CH}_4\text{out}} + C_{\text{CO}_{2\text{out}}} + C_{\text{CO}_{\text{out}}} + C_{\text{H}_2\text{out}} + C_{\text{H}_2\text{O}_{\text{out}}} + C_{\text{He}} = 100 \\
\left( X_{\text{CH}_4\text{out}} + 1 + X_{\text{CO}_{\text{out}}} + X_{\text{H}_2\text{out}} + X_{\text{H}_2\text{O}_{\text{out}}} \right) C_{\text{CO}_{2\text{out}}} + C_{\text{He}} = 100
\]

Putting equations (III) and (VI) into the previous equation:

\[
\left( X_{\text{CH}_4\text{out}} + 1 + 2X_{\text{CH}_4\text{out}} + X_{\text{H}_2\text{out}} - 2 + X_{\text{H}_2\text{out}} + X_{\text{CH}_4\text{out}} - 1 \right) C_{\text{CO}_{2\text{out}}} + \frac{F_{\text{He}_{\text{in}}}}{F_{\text{Total}}} = 100 \\
\left( 4X_{\text{CH}_4\text{out}} + 2X_{\text{H}_2\text{out}} - 2 \right) C_{\text{CO}_{2\text{out}}} + \frac{F_{\text{He}_{\text{in}}}}{F_{\text{Total}}} = 100 \tag{VII}
\]

Recalling equation (I)

\[
C_{\text{CO}_{2\text{out}}} F_{\text{Total}} = \frac{100 \left( F_{\text{CH}_4\text{in}} + F_{\text{CO}_{2\text{in}}} \right)}{1 + X_{\text{CH}_4\text{out}} + X_{\text{CO}_{\text{out}}} \right) \tag{I}
\]

Rearranging (I)

\[
C_{\text{CO}_{2\text{out}}} F_{\text{Total}} = \frac{100 \left( F_{\text{CH}_4\text{in}} + F_{\text{CO}_{2\text{in}}} \right)}{1 + X_{\text{CH}_4\text{out}} + X_{\text{CO}_{\text{out}}} \right) \tag{I}
\]

Rearranging (I)
\[ \frac{C_{\text{CO}_2\text{out}} (1 + X_{\text{CH}_4\text{out}} + X_{\text{CO}_2\text{out}})}{\left( F_{\text{CH}_4\text{in}} + F_{\text{CO}_2\text{in}} \right)} = \frac{100}{F_{\text{Total}}} \]  

(VIII)

Plugging (VIII) into (VII)

\[ (4X_{\text{CH}_4\text{out}} + 2X_{\text{H}_2\text{out}} - 2)C_{\text{CO}_2\text{out}} + F_{\text{He}_{\text{in}}} \frac{C_{\text{CO}_2\text{out}} (1 + X_{\text{CH}_4\text{out}} + X_{\text{CO}_2\text{out}})}{\left( F_{\text{CH}_4\text{in}} + F_{\text{CO}_2\text{in}} \right)} = 100 \]

\[ C_{\text{CO}_2\text{out}} \left( (4X_{\text{CH}_4\text{out}} + 2X_{\text{H}_2\text{out}} - 2) + F_{\text{He}_{\text{in}}} \frac{(1 + X_{\text{CH}_4\text{out}} + X_{\text{CO}_2\text{out}})}{\left( F_{\text{CH}_4\text{in}} + F_{\text{CO}_2\text{in}} \right)} \right) = 100 \]

\[ C_{\text{CO}_2\text{out}} = \frac{100}{\left( (4X_{\text{CH}_4\text{out}} + 2X_{\text{H}_2\text{out}} - 2) + F_{\text{He}_{\text{in}}} \frac{(1 + X_{\text{CH}_4\text{out}} + X_{\text{CO}_2\text{out}})}{\left( F_{\text{CH}_4\text{in}} + F_{\text{CO}_2\text{in}} \right)} \right)} \]  

(IX)

Thus, recalling key equations:

\[ X_{\text{H}_2\text{O}_{\text{out}}} = X_{\text{CH}_4\text{out}} - 1 \]  

(III)

\[ X_{\text{CO}_2\text{out}} = 2X_{\text{CH}_4\text{out}} + X_{\text{H}_2\text{out}} - 2 \]  

(VI)

\[ C_{\text{CO}_2\text{out}} = \frac{100}{\left( (4X_{\text{CH}_4\text{out}} + 2X_{\text{H}_2\text{out}} - 2) + F_{\text{He}_{\text{in}}} \frac{(1 + X_{\text{CH}_4\text{out}} + X_{\text{CO}_2\text{out}})}{\left( F_{\text{CH}_4\text{in}} + F_{\text{CO}_2\text{in}} \right)} \right)} \]  

(IX)

\[ C_{\text{CH}_4\text{out}} = X_{\text{CH}_4\text{out}} C_{\text{CO}_2\text{out}} \]

\[ C_{\text{H}_2\text{out}} = X_{\text{H}_2\text{out}} C_{\text{CO}_2\text{out}} \]

\[ C_{\text{CO}_2\text{out}} = X_{\text{CO}_2\text{out}} C_{\text{CO}_2\text{out}} \]

\[ C_{\text{H}_2\text{O}_{\text{out}}} = X_{\text{H}_2\text{O}_{\text{out}}} C_{\text{CO}_2\text{out}} \]

\[ C_{\text{He}} = 100 - \left( C_{\text{CH}_4\text{out}} + C_{\text{CO}_2\text{out}} + C_{\text{CO}_2\text{out}} + C_{\text{H}_2\text{out}} + C_{\text{H}_2\text{O}_{\text{out}}} \right) \]

Given \( C_{\text{He}} = \frac{F_{\text{He}_{\text{in}}}}{F_{\text{Total}}} \cdot 100 \), then

\[ F_{\text{Total}} = \frac{F_{\text{He}_{\text{in}}}}{C_{\text{He}}} \cdot 100 \]
Appendix I

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Felipe was born in 1988 in Cali, Colombia. He is the oldest of three siblings and the only boy. He went to school (includes elementary-school, middle-school and high-school) to Colegio Lacordaire (graduated 2005); later on, he obtain his Bachelor’s degree in Chemical Engineering at Universidad del Valle (graduated 2011), and after that, he went to Clemson University to pursue his PhD in Chemical Engineering (graduated 2015). In Colombia, he had a wide variety of jobs; Tennis teacher, Math teacher, English teacher, German Teacher, Fairs Coordinator and Interpret.

During his undergraduate studies, Felipe went to Germany for a year as an academic exchange student (august 2009 – July 2010). There, he attended a German course in Mannheim (2 months); then, he moved to Erlangen to attend the Friedrich – Alexander Universitität (where he also worked as student assistant) for one semester and finally worked as an Intern.

At Clemson, Felipe’s soccer team made it to the second place twice in the World Soccer Fest of the Baptist Church. Felipe also played in two adult leagues in Greenville (South Carolina) and his team made one second place and one championship. He also played multiple intramural tournaments, but sadly, without reaching the finals. Felipe was also the recruiter of prospective graduate students from Colombia and the president of the Clemson chapter of SACNAS (Society for Advancement of Hispanics/Chicanos and Native Americans in Science). His combined computational and experimental research on Optimization of Pyrochlore Catalysts for the Dry Reforming of Methane was conducted under the guidance of Dr. David A. Bruce.