Optimization of Pyrochlore Catalysts for Dry Reforming of Methane

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1. Introduction
Dry Reforming of Methane (DRM)
The dry reforming of methane (DRM) using CO₂ has long been considered a viable method for converting methane from geologic or biological sources into syngas (a mixture of CO and H₂), which can then be readily converted into a variety of chemicals and particularly liquid fuels that are more easily shipped via pipeline.

Dry Reforming of Methane (DMR):

\[ \text{CH}_4 + \text{CO}_2 \rightarrow 2 \text{CO} + 2 \text{H}_2 \]

Unlike other methods to produce syngas, DRM involves the reaction of two greenhouse gases; there is no water supply dependence, and there is no oxygen consumption. Though dry reforming holds great promise, the high temperatures required for the reaction have made it very difficult to find catalysts that exhibit high activity for extended periods.

Pyrochlore Catalyst
Experimental efforts by others have shown that pyrochlores are active for DRM at high temperatures (~1000 K), obtaining high CO and CH₄ conversions. La₂Zr₂O₇ (LZ) is a highly stable oxide having a pyrochlore structure, which has shown good long term stability. [1]

Thus, efforts have been made to tailor its catalytic properties for DRM, showing Rh as a promising dopant to enhance the catalytic performance. In the present work, computational studies are being used to better understand the reaction mechanism and guide experimental efforts to optimize La₂Zr₂RhO₇ (LRZ) pyrochlores, so as to enhance catalyst activity for syngas production and lower rates of catalyst deactivation.

2. Objectives
- Perform quantum mechanics simulations to understand the reaction mechanism of DRM on 2% doped LRZ pyrochlore and develop a microscopic model of reactions.
- Validate the developed microscopic model with experimental reaction data.
- Propose variations in the Rh doping percentage and/or arrangement of the Rh atoms on the surface to reduce the highest activation barriers predicted by the simulations.

Pyrochlore Crystal Structure
- General Structure: A₂B₂O₇
  - A: rare-earth metal
  - B: transition metal
- In this work:
  - La₂Zr₂O₇ (LZ): rare-earth metal
  - La: rare-earth metal
  - Zr: transition metal

3. Computation Methods
- Density functional theory (DFT)
- Vienna Ab initio Simulation Package (VASP)
- Exchange-Correlation Functional: GGA-PBE
- Core electron states are described by the projector-augmented wave (PAW) method
- Climbing Image Nudge Elastic Band method
- 2X2X2 Monkhorst-Pack mesh
- Cut-off energy: 500 eV

4. Results and Discussion
4.1 Lattice Parameter Optimization
In order to identify the most adequate computational method, lattice parameter optimization was carried out for 2%LRZ using three different exchange-correlation functionals (LDA, GGA-PBE, GGA-PW91). All functionals gave results within an error of 5%. For this work, the GGA-PBE functional was employed, and a lattice parameter of 10.88 Å (0.2 % error compared to experiment[2]) was used for all further calculations.

4.2 Surface Energy Calculation
Surface energy for the planes (001), (011) and (111) were calculated to identify the thermodynamically most favorable surface.

For nonstoichiometric slabs:

\[ E_s = \frac{1}{2S} (\Delta H_{\text{react}} - \Delta H_{\text{products}} - nE_{\text{bulk}}) \]

\[ E_s \text{ is Surface energy} \]
\[ E_{\text{bulk}} \text{ is Free Energy of oxygen-terminated slab} \]
\[ E_{\text{metal-terminated slab}} \text{ is Free Energy of bulk} \]
\[ n \text{ is Stoichiometric factor} \]

Surface energies (eV/Å²) for different planes of 2%LRZ pyrochlore

- Plane (001) - partially reduced: 0.19 eV/Å²
- Plane (111) - partially reduced: 0.09 eV/Å²

The lower the surface energy, the more thermodynamically stable is the plane. Planes (111) and (001) are the most thermodynamically stable.

4.3 Adsorption energies
CO₂ and CO adsorption, comparison to experimental results
Adsorption energies of CO₂ and CO upon different adsorption sites were calculated for both the (111) and (011) planes. On some tested adsorption sites, no stable structure was found, suggesting that these sites were unfavorable adsorption sites.

CO₂ on (111), CO₂ on (011), CO on (111), CO on (011)

4.4 Reaction energies (∆Hrxn) and activation energies ∆Ea
Approximately 70 reactions are considered, and it is necessary to obtain ∆Ea for each reaction step before an accurate microkinetic model can be developed. Because transition state identification is a computationally expensive task, some of these activation energies were rigorously calculated using CI-NEB, while others were estimated using BEP correlations that relate the ∆Ea for a specific reaction to the more easily calculated heat of reaction. Brønsted-Evans-Polanyi (BEP) relationship:

\[ \Delta H_{\text{rxn}} = \alpha \Delta E_a \]

4.4 Conclusions
- Reaction potentially occurs on planes (011) and (111)
- Experimental results for CO₂ and CO adsorption match our computational results
- Adsorption strength on both planes is similar
- Diffusion between possible adsorption sites is limited
- BEP relationship for our system will reduce computational effort

4. On-going work
- Calculate activation barriers for additional elementary reaction steps using the CI-NEB method
- Find a more accurate BEP relationship for our system and find all activation barriers
- Develop a complete microkinetic model for the DRM reaction network

5. References
[4] Spivey, J., LSU, CALCD

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