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Effects on Hydrogen Adsorption and Activation on Platinum in a Fuel Cell Catalyst

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EFFECTS ON HYDROGEN ADSORPTION AND ACTIVATION ON PLATINUM IN A FUEL CELL CATALYST

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
Jack Z. Zhang
August 2011

Accepted by:
Dr. James G. Goodwin, Jr., Committee Chair
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Dr. Christopher L. Kitchens
ABSTRACT

Proton exchange membrane fuel cells are a highly efficient source of power generation that is needed to sustain the energy demands of today’s more environmentally conscience society. However, the presence of impurities in the hydrogen fuel stream, such as CO, H₂S, and NH₃ from the steam reforming/partial oxidation of hydrocarbons/methanol, can severely poison the Pt electrocatalyst present in the fuel cell electrode causing degradation in the fuel cell performance. To counter these poisoning effects, fuel cell manufacturers are forced to use higher Pt loadings, which dramatically increases material costs and prevents the successful commercialization of the technology. The focus of the present research is the investigation of the impurity effects on the activity of a Pt fuel cell catalyst for the adsorption and activation of hydrogen at typical fuel cell conditions. The degree of impact from each impurity is observed in terms of Pt surface atom availability, which is then related to fuel cell performance results.

The effect of CO on hydrogen activation on Pt fuel cell catalysts were found to be severe even at as low as 10 ppm. In the presence of water vapor, the maximum CO surface coverage found on the Pt/C catalyst was between 0.5-0.7 monolayer at typical fuel cell operating conditions. Reversibility of the poisoning showed only a partial recovery in available Pt surface sites, however, the amount of Pt surface sites recovered was enough to return the hydrogen activation reaction back to equilibrium, which is equivalent to a full recovery observed in fuel cell performance. The poisoning effect from tetrachloroethylene appears to be a combination of the processes occurring at the anode and cathode. The presence of the hydrogen is required to help decompose the
chlorocarbon at the low operating temperatures. Once decomposed, the oxygen enhances the poisoning by tetrachloroethylene or derivatives. Other impurities such as NH$_3$, paraffins (C$_3$-C$_7$), inert gases (He, N$_2$, Ar), and ethylene, were found to have little or no effect on the hydrogen activation on Pt fuel cell catalyst.
DEDICATION

I would like to dedicate this work to my beloved wife, family, and friends, whose support and guidance has been essential throughout my life and shaped me into the person I am today.
ACKNOWLEDGMENTS

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CHAPTER ONE
INTRODUCTION

In today’s society of ever growing energy demands and increasing concern over global pollution, the need for a more efficient and environmentally friendly source of power generation is becoming more and more apparent, especially for the automotive industry. While battery-powered vehicles have, at the moment, the largest share of the low-pollutant vehicle market, they alone are still not sufficient enough to sustain our energy consumption needs. Moreover, inherent problems such as requiring disposal treatment and large storage space plague the battery from being a more permanent solution. Proton exchange membrane fuel cells (PEMFCs), on the other hand, are one of the most promising technologies for achieving the desired result.

Originally developed by General Electric in the 1960s as an attractive means for generating power in the NASA Gemini spacecraft [1], PEMFCs are an electrochemical energy conversion device that converts hydrogen and oxygen into electricity, with heat and water as the only products. Because there is no combustion or moving parts, fuel is converted to electricity more efficiently than any other electrical generating technology available today. Furthermore, inherent properties such as low operating temperatures, rapid start-up, and high power density make PEMFCs even more attractive as an alternative source of power generation for transportation applications [2]. However, impurities present in the hydrogen fuel streams, such as CO, H$_2$S, and NH$_3$ from the steam reforming/partial oxidation of hydrocarbons/methanol, respectively, can poison the
Pt catalyst present in the fuel cell electrodes. This poisoning limits the activity of the Pt for adsorbing and activating hydrogen for the hydrogen oxidation reaction (HOR) leading to severe degradation in the fuel cell performance [3]. Moreover, in addition to the impurities directly present in the hydrogen fuel stream, other contaminants, such as chlorinated hydrocarbons, may be introduced into the fuel cell via outside sources. These impurities severely limit the amount of operational time required of PEMFCs and present a major barrier to the successful commercialization of the technology.

While research into fuel cell contamination has increased substantially in recent years, understanding of their potential impacts, poisoning mechanism, and viable mitigation strategies are still limited. For example, although it has been shown that the presence of even 10 ppm CO can have a significant effect on the electrical current output of a fuel cell, fundamental properties of the poisoning, such as the maximum surface coverage of CO on the Pt surface at typical fuel cell operating conditions, differs between the surface science and electrochemical communities. Hence, in order to improve our understanding of impurities and their effects on fuel cell performance, a more fundamental investigation into the effect of these impurities on the characteristics of the catalyst, such as the Pt surface atom availability, is required.

The main objective of this research was to study the effect of impurities and fuel cell components on the activity of Pt for adsorbing and dissociating hydrogen at typical fuel cell operating conditions. This work also presents a new non-destructive technique to quantitatively examine the impact of these impurities on the catalyst activity in relation to the amount of Pt surface atoms available.
1.1 Background

1.1.1 PEMFC Components

PEMFCs are highly efficient energy conversion systems that produce electricity via the electrochemical redox reaction between hydrogen and oxygen. As illustrated by Figure 1.1, the membrane electrode assembly (MEA) of a typical PEMFC generally consists of a gas diffusion layer on both sides, followed by the anode and cathode catalyst layers, and a perfluorosulfonic-acid membrane, such as Nafion®, in the middle.

Figure 1.1 General schematic of a PEMFC electrode assembly.
Contrary to the previous conventional method of catalyst layer preparation of simply hot-pressing the electrocatalysts to the membrane, current anode and cathode catalyst layers are obtained by directly impregnating the electrocatalysts with the perfluorinated ionomers in liquid form [1]. The resulting viscous ink is then applied to both sides of the membrane. This method of synthesis results in a much greater interfacial area of contact between the electrocatalysts and the ionomer, which greatly improves the proton transport process.

1.1.2 PEMFC Operation

In a PEMFC, hydrogen fuel enters at the anode, where the hydrogen oxidation reaction (HOR) occurs. The reaction, which is essentially the adsorption and dissociation of hydrogen gas by the Pt electrocatalyst, produces protons and electrons. The protons are then transported by the ionomer across the membrane usually via the Grötthuss or proton-hopping mechanism [4, 5]. The ionomer, being a non-electron conductive material, presents a barrier in the direct flow of electrons and forces them through an external circuit, where an electrical current is generated. At the same time, oxygen gas enters at the cathode and is adsorbed and dissociated on the Pt. The dissociated oxygen atoms will then undergo oxygen reduction reaction (ORR) with the electrons and hydrogen atoms from the anode to form H₂O and generate heat. A simplified overview of the electrochemical reactions that occur within a PEMFC is shown by the equations below:
Anode: \[ H_2 \leftrightarrow 2H^+ + 2e^- \]  \hspace{1cm} (1)

Cathode: \[ \frac{1}{2}O_2 + 2H^+ + 2e^- \leftrightarrow H_2O \]  \hspace{1cm} (2)

Overall: \[ H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O \]  \hspace{1cm} (3)

Due to the instability of the Nafion® ionomer at temperatures higher than 120°C and the importance of proper water management to fuel cell performance [6], PEMFCs are generally operated at temperatures between 70-110°C [7]. The open circuit voltage or the theoretical maximum voltage possible is 1.16 V [8]. When the electrical current is drawn from the unit, the system is shifted away from equilibrium, and an irreversible loss in electrical density occurs. This loss is usually referred to as polarization loss and can be summarized in three main categories: activation polarization, ohmic polarization, and concentration polarization. The activation polarization is influenced by the electrode kinetics, which in the absence of impurities, is most often due to the slower reaction kinetics of the ORR at the cathode [9, 10]. The ohmic polarization is due to ohmic losses caused most often by the resistance to the flow of protons across the membrane. Finally, the concentration polarization occurs at high current densities or when the fuel cell is starved of reactants.

1.1.3 Fuel Contaminants

Platinum has been widely used as the electrocatalyst for PEMFCs due to its excellent hydrogen oxidation and oxygen reduction catalytic activity. The Pt metal is usually supported on vulcanized carbon, in the form of Pt/C, because of the higher
surface area and electron conductive capabilities. More recently, investigations into the
use of carbon nanotubes as the support showed the material to allow for a better
dispersion of the Pt particles, compared to that of the vulcanized carbon at the same metal
loadings [11, 12], with similar catalytic activity in fuel cell performance.

In the absence of impurities, the amount of Pt needed to achieve the desired
current density is relatively low. For example, while conventional catalyst layers
generally contain a Pt loading of 4 mg cm\(^{-2}\) [13], ultra thin catalyst layers with Pt
loadings as low as 0.014 mg cm\(^{-2}\) using novel sputtering methods show no decrease in the
electrocatalytic activity and greatly enhances the utilization efficiency of the loaded Pt
[14]. In real life operation, however, the use of pure hydrogen and oxygen as fuel
becomes expensive and results in an impractical system, especially since the
concentration of impurities, such as CO for example, must be reduced to as low as 2-5
ppm in order for the loss in performance over the operational lifetime of a fuel cell to be
considered tolerable [15]. In addition, other impurities such as CO\(_2\), NH\(_3\), hydrocarbons,
sulfur, formaldehyde, formic acide, and halogenates can be present from different
hydrogen production processes or outside sources. Table 1.1 is the hydrogen fuel quality
standard set by the Society of Automotive Engineers (SAE) that prohibits the selling of
any hydrogen fuel containing impurities over the specified limit.
Table 1.1 Fuel quality standard for H\textsubscript{2} fuel used in fuel cells.

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</tr>
<tr>
<td>Total Hydrocarbons (maximum, ppm v/v)</td>
<td>2</td>
</tr>
<tr>
<td>Oxygen (maximum, ppm v/v)</td>
<td>5</td>
</tr>
<tr>
<td>Helium (maximum, ppm v/v)</td>
<td>100</td>
</tr>
<tr>
<td>Nitrogen and Argon (maximum, ppm v/v)</td>
<td>100</td>
</tr>
<tr>
<td>Carbon Dioxide (maximum, ppm v/v)</td>
<td>2</td>
</tr>
<tr>
<td>Carbon Monoxide (maximum, ppm v/v)</td>
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</tr>
<tr>
<td>Total Sulfur Compounds (maximum, ppm v/v)</td>
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</tr>
<tr>
<td>Formaldehyde (maximum, ppm v/v)</td>
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</tr>
<tr>
<td>Formic Acid (maximum, ppm v/v)</td>
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</tr>
<tr>
<td>Ammonia (maximum, ppm v/v)</td>
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</tr>
<tr>
<td>Total Halogenated Compounds (maximum, ppm v/v)</td>
<td>0.05</td>
</tr>
<tr>
<td>Particulates Size (maximum, µm)</td>
<td>10</td>
</tr>
<tr>
<td>Particulate Concentration (maximum, µg L\textsuperscript{-1} at NTP)</td>
<td>1</td>
</tr>
</tbody>
</table>

Fundamental understanding in the effects of these different impurities on fuel cell performance is still limited. Possible poisoning mechanisms from trace amounts of impurities can range from simple blocking of reaction sites for chemisorption to the more complicated scenario of impeding charge transfer and/or proton conduction. The
resulting effect is the loss in fuel cell performance where the poisoning can be either reversible or permanent, depending on the impurity.

### 1.2 Research Objectives

The primary research objective in the present study is to investigate in detail the effect of impurities on the activity of the hydrogen oxidation reaction with Pt as the electrocatalyst at typical fuel cell operating conditions. These impurities will include water, hydrocarbons, oxygen, inert gases (He, N\textsubscript{2}, Ar), CO, CO\textsubscript{2}, ammonia, and halogenated compounds. Specific objectives will be:

- Measurement of the effect of concentration (of the various impurities) on hydrogen chemisorption and activation on the Pt catalysts used as PEMFC electrodes.
- Proposal of a mechanism of action for each impurity.
- Development of strategies/means to reduce the impact of these impurities on fuel cell performance. Figure 1.2 illustrates a brief overview of the technical approach used in this study.
Figure 1.2 Overview of the technical approach for the study of impurity effect used in the present study.

1.3 References


CHAPTER TWO

THE EFFECT OF LOW CONCENTRATIONS OF CO ON H\textsubscript{2} ADSORPTION AND ACTIVATION ON Pt/C: PART 1 – IN THE ABSENCE OF HUMIDITY


The presence of CO in the H\textsubscript{2}-rich gas used as fuel for hydrogen fuel cells has a detrimental effect on PEMFC performance and durability at conventional operating conditions. This paper reports on an investigation of the effect of CO on H\textsubscript{2} activation on a fuel cell Pt/C catalyst close to typical PEMFC operating conditions using H\textsubscript{2}-D\textsubscript{2} exchange as a probe reaction and to measure hydrogen surface coverage. While normally limited by equilibrium in the absence of impurities on Pt at typical fuel cell operating temperatures, the presence of ppm concentrations of CO increased the apparent activation energy (E\textsubscript{a}) of H\textsubscript{2}-D\textsubscript{2} exchange reaction (representing H\textsubscript{2} activation) from approximately 4.5 – 5.3 kcal mole\textsuperscript{-1} [25,26] (in the absence of CO) to 19.3 – 19.7 kcal mole\textsuperscript{-1} (in the presence of 10 – 70 ppm CO), similar to those reported by Montano et al. [26]. Calculations based on measurements indicate a CO surface coverage of approximately 0.55 ML at 80\textdegree C in H\textsubscript{2} with 70 ppm CO, which coincide very well with surface science results reported by Longwitz et al. [5]. In addition, surface coverages of hydrogen in the presence of CO suggest a limiting effect on hydrogen spillover by CO. Regeneration of Pt/C at 80\textdegree C in H\textsubscript{2} after CO exposure showed only a partial recovery of Pt sites. However, enough CO-free Pt sites existed to easily achieve equilibrium conversion for
H$_2$-D$_2$ exchange. This paper establishes the baseline and methodology for a series of future studies where the additional effects of Nafion and humidity will be investigated.

2.1 Introduction

Today, with potential global warming and shrinking sources of liquid fossil fuels, applications for proton exchange membrane fuel cells (PEMFC) have broadened to the automotive industry due to their advantageous characteristics such as high current density, quick startup, and zero polluting emissions [1]. However, due to the typical low temperature of operation (ca. 80°C) and the choice of Pt as the electrocatalyst, the detrimental effects that impurities, especially CO from H$_2$ production via hydrocarbon reforming, have on the durability and performance of PEMFCs are some of the greatest impediments to their successful commercialization [2].

Depending on the Pt-loading in the electrode, studies show CO tolerances from 2-5 ppm for low Pt-loadings to as high as 20 ppm at higher Pt-loadings [3]. Modifications of the Pt electrode, such as alloying with Ru, have supposedly increased CO tolerances up to as much as 100 ppm [3]. In one report, continuous exposure to 50 ppm of CO for 6 h yielded less than a 3% voltage decrease in PEMFC performance while exposure to 70 ppm of CO for 6 h caused an 85% voltage drop [4].

While the poisoning effect that CO has on PEMFC performance is well documented, there exists differing opinions between the surface science and electrochemical communities regarding the extent and fundamental characteristics of this
poisoning. For example, results from high pressure scanning tunneling microscopy (HP STM) and density functional theory (DFT) calculations of adsorption of CO on Pt(111) over the pressure range \( P_{\text{CO}} = 10^{-6} \) to 760 Torr at room temperature show an increase in the ratio of amount of surface CO to Pt\(_S\) \((\text{CO/Pt}_S)\), where Pt\(_S\) indicates exposed surface atoms of Pt, from 0.5 to 0.7 [5-7]. While the authors related this ratio to the surface coverage of Pt\(_S\) by CO, the ambiguity in their definition of “surface coverage” and the lack of information accounting for bridge-bonded CO, where one molecule of CO occupies two Pt\(_S\) atoms, makes it uncertain whether the fraction of Pt\(_S\) surface covered by CO was 0.7 or 1.0. It is important to note that this CO/Pt\(_S\) ratio was also obtained in the absence of H\(_2\). In contrast, electrochemical results on Pt electrodes via cyclic voltammetry (CV) suggest a completely covered Pt surface \((\theta_{\text{CO/Pt}} = 1)\) at much lower CO concentrations of 100 ppm CO in the presence of H\(_2\) [8,9]. However, calculation of surface coverage based on CV measurement of peak currents is imprecise and is not an ideal quantitative technique [10]. While discrepancies between these results may be attributed to differences in experimental conditions and methods of measurement, Longwitz et al. [5] also pointed out that extreme care must be taken when relating UHV results to systems operating under realistic conditions, such as at atmospheric pressure.

Due to the number of ambiguities regarding CO poisoning on Pt, such as the ones outlined above, research was carried out to investigate the fundamental effect of CO on H\(_2\) activation on a commercial Pt/C catalyst used in fuel cells. This effect was studied utilizing H\(_2\)-D\(_2\) exchange (as a probe reaction related to hydrogen activation) and surface concentration measurements of hydrogen and CO at conventional PEMFC operating
conditions (80°C, 2 atm) and in the absence of humidity. While the presence of humidity would have a notable effect on the adsorption of CO on Pt, as shown qualitatively via ATR-IR and Raman spectroscopy by Ebbesen et al. [11] and Ren et al. [12], respectively, quantitative measurement of CO surface coverage on Pt using the new methodology involving H₂-D₂ must first be established in the absence of humidity before the additional effects of Nafion and water can be investigated. In addition, measurements in the absence of water vapor permit a more direct comparison to the results on this topic in the surface science literature. Comparison and verification of the exchange reaction as a valid test reaction for the electrocatalytic oxidation of H₂ on Pt can be found elsewhere [13].

2.2 Experimental

2.2.1 Catalyst Characterization

A commercial Pt fuel cell catalyst, 20 wt% Pt supported on carbon black (Vulcan XC-72, Cabot Co.) (Pt/C), was purchased from BASF. Nominal composition was confirmed via elemental analysis (performed by Galbraith Laboratories) and energy dispersive x-ray spectroscopy (EDX) (STEM-Hitachi HD2000 equipped with an Oxford INCA Energy 200 EDS).

BET surface area, pore size, and pore volume measurements were carried out with a Micromeritics ASAP 2020. Samples of Pt/C were degassed under vacuum (10⁻³ mm
Hg) at 100°C for 3 h prior to analysis. Results were obtained from N2 adsorption isotherms at -196°C.

H2 and CO chemisorption experiments were performed at various analysis temperatures (35°C and 80°C) in a Micromeritics ASAP 2010 equipped with a chemisorption controller station. Samples were pretreated in flowing H2 at 80°C for 3 h prior to analysis. Due to the presence of Nafion in the catalyst layer in a fuel cell, a low pretreatment temperature is necessary because of the thermal limitations of the Nafion. However, temperature programmed reduction (TPR) of Pt/C showed the catalyst to be fully reduced under the pretreatment conditions employed. After pretreatment, samples were evacuated (10^-5 mm Hg) at 80°C for 3 h prior to analysis. The temperature was then adjusted to the specified analysis temperature and the H2 or CO isotherms were obtained from 50 – 450 mm Hg at increments of 50 mm Hg. Volumetric uptakes of CO or H2 were used to determine total number of surface Pt atoms and metal dispersion by assuming stoichiometric ratios of 1:1 for CO:PtS and H:PtS. Average Pt particle size based on chemisorption results was calculated from Eq. (1) [14]:

$$\text{Average Pt Particle Size (nm)} = \frac{1.08}{\text{Metal Dispersion}}$$  \hspace{1cm} (1)

Transmission electron microscopy (TEM) images and EDX spectra were obtained using a STEM-Hitachi HD2000 analytical electron microscope. Samples for TEM imaging were prepared by suspending small amounts of the catalyst in isopropyl alcohol and agitating in a sonicator until an even dispersion of catalyst was observed. A small drop of the dispersed sample was then transferred onto a copper grid. Sample grids were
then allowed to dry at room temperature overnight prior to measurement. Approximate average Pt particle size of the catalyst was obtained by averaging diameters of 100+ particles from the TEM images. The result was further confirmed via X-ray Diffraction (XRD) (Scintag XDS 2000 powder diffractometer equipped with CuKα radiation) on as-received and reduced (80°C in H₂ for 3 h) then passivated Pt/C with a scanning range from 20° – 85° and a step-size of 0.02° min⁻¹.

Diffuse reflectance FT-IR measurements were carried out in a Nicolet 6700 FTIR spectrometer equipped with a Harrick diffuse reflectance infrared Fourier Transform (DRIFT) cell fitted with ZnSe windows. The DRIFTS study of Pt/C was complicated by the carbon support which is a strong absorber of the IR beam. In order to get a detectable signal, the Pt/C catalyst was mixed with KBr powder at a ratio of Pt/C:KBr = 1:100 by weight. The feed flow rate was fixed at 50 sccm. Prior to exposure to CO, the catalyst was pretreated in-situ at 350°C in a flow of H₂ for 1 h, followed by flushing with He for 30 min, and then cooled to the desired temperature for taking a reference spectrum. The higher pretreatment temperature of 350°C was used to ensure a clean Pt surface prior to the introduction of CO. As mentioned above, this high of a pretreatment temperature of Pt/C would not be possible for Nafion-Pt/C since degradation of Nafion occurs at temperatures higher than 120°C. However, for the purposes here, there is minimal difference in Pt/C reduced at 80°C or 350°C. FT-IR spectra of CO adsorption on Pt/Al₂O₃ [15,16] showed pretreatment temperature to have a negligible effect on band frequency.
After taking a reference spectrum, a gas mixture of 4% CO in H₂ (or pure CO) was fed to the reduced catalyst for 1 h, followed by flushing with He for 10 minutes prior to taking the spectra. All spectra reported here were taken at a resolution of 4 cm⁻¹. Interpretation of FT-IR results is limited qualitatively to the surface species present after the introduction of CO.

2.2.2 H₂-D₂ Exchange Reaction

Experiments were performed in a conventional plug flow, micro-reactor system pressurized at 2 atm (Figure 2.1). All gases were purchased from Scott Specialty Gases with Research grade purity. Similar to chemisorption, prior to reaction experiments, all catalyst samples were pretreated at 80°C in H₂ for 3 h. Measurements of the apparent activation energies (Eₐ) were obtained with catalyst samples of 10 mg of Pt/C mixed with 40 mg of XC-72 to achieve differential reaction conditions. Temperature for apparent Eₐ measurements was varied from 50°C – 90°C.

While the anodic feed stream for PEMFCs is primarily H₂, the use of Ar was required in this study, primarily for purging the system when measuring hydrogen surface concentration, see section 2.3. For calibration purposes, in order to maintain a relatively constant pressure inside the MS, the reactant mixture for the exchange reaction was also diluted with Ar. The effluent gas (comprised of H₂, D₂, Ar, and HD) was analyzed with a Pfeiffer Vacuum MS. Reactions in the absence of CO were performed by flowing 100 sccm of 20% H₂, 20% D₂, and 60% Ar through the catalyst bed. For experiments involving CO, the impurity concentration was varied by mixing flows of 500 ppm CO in
H₂ with pure H₂ and keeping the same overall reaction mixture as above. The exchange conversion was obtained via Eq. (2) using the H₂ (m/z = 2) and D₂ (m/z = 4) MS signals in the presence and absence of catalyst:

\[
\text{Conversion (\%) } = \frac{(\text{H}_2 \text{ or D}_2 \text{ Signal})_{\text{No Cat.}} - (\text{H}_2 \text{ or D}_2 \text{ Signal})_{\text{Cat.}}}{(\text{H}_2 \text{ or D}_2 \text{ Signal})_{\text{No Cat.}}} \quad (2)
\]

Except for time-on-stream (TOS) experiments, exchange results in the presence of CO were obtained at CO adsorption/desorption equilibrium such that no further change in HD signal was observed (steady-state).

2.2.3 H₂-D₂ Switch with Ar Purge (HDSAP)

Because the H₂-D₂ exchange reaction is always able to reach equilibrium in the absence of CO under the specified experimental conditions for even small amounts of catalyst (~1 mg), it cannot be used as a baseline in determining the degree of CO poisoning on the Pt/C catalyst. Instead, a better method of comparison had to be developed by measuring the surface concentration of hydrogen in the absence and presence of CO. Although temperature programmed desorption (TPD) can essentially provide a similar type of measurement, the high temperatures involved normally in TPD greatly alters the physical characteristics of the catalyst and could only be performed at the very end of an experiment. On the other hand, H₂-D₂ switch with an Ar purge (HDSAP) provided a non-destructive measurement that could be performed at any point during a particular experiment. Agreement of surface concentration of hydrogen
measurements obtained from HDSAP with those from static H\textsubscript{2} chemisorption was found for the Pt/C catalyst (as shown later).

Figure 2.1 Flow apparatus used for H\textsubscript{2}-D\textsubscript{2} exchange, HDSAP, and TPD measurements.
Due to the high porosity of XC-72 ($S_{\text{BET}} = 218 \text{ m}^2 \text{ g}^{-1}$), high concentration of Pt (20 wt% Pt/C), and the extremely fast rate of the exchange reaction, when a switch from H$_2$ is made directly to D$_2$ in the reactor, some of the gas-phase H$_2$ in the catalyst pores is still able to dissociate on the Pt particles and react with adsorbed deuterium atoms before it can diffuse out of the pores. The resulting estimation of hydrogen surface concentration from the amount of HD and H$_2$ formed would, thus, be a combination of both gas-phase H$_2$ inside the pores and surface hydrogen atoms at the time of the switch and, therefore, would be an over estimation of the desired quantity. A solution to this problem was arrived at by the addition of purging with an inert gas (Ar) between the switch from H$_2$ to D$_2$.

HDSAP measurements were initiated by flowing a gas mixture comprised of 20% H$_2$ and 80% Ar (total = 100 sccm) for 30 min. The H$_2$ was then turned off and 80 sccm of Ar was passed through the reactor for 30 min (purge period). This was done to purge as much of the gas-phase or weakly adsorbed H$_2$ from the catalyst as possible. Preliminary HDSAP experiments showed 30 min to be optimal for both exposure and purge times for our catalyst. Once the purge was complete, a flow of 20 sccm of D$_2$ (along with 80 sccm of Ar) was introduced to the catalyst. Two peaks for HD and H$_2$ were observed in the MS after the D$_2$ switch. The amount of HD and H$_2$ were calculated by integrating the area under these peaks and using the respective areas from the exchange reaction as calibration. Total surface concentration of hydrogen was calculated from the sum of the amounts of hydrogen (H) in HD and H$_2$, as given by Eq. (3):
Validation of this technique is given in the Results and Discussion section.

Due to the high detection limit of mass spectrometers (MS), measurements of hydrogen surface concentrations were performed on catalyst samples of 100 mg Pt/C. This did not present a problem since equilibrium surface concentration was being measured and not rates of adsorption/desorption.

2.2.4 TPD

For measurements of CO surface concentration at steady-state, TPD measurements were performed at the end of each experiment. After the last HDSAP measurement, flow was switched to 20 sccm Ar and allowed to stabilize for 10 min. Due to the possibility of some CO desorbing, the temperature was ramped directly from 80°C to 600°C, instead of cooling to 35°C, at a rate of 10°C min⁻¹ while following, via the MS, CO and other possible carbonaceous species (CH₄ and CO₂) desorbing. The latter two species were recorded in case that, at the higher temperatures during the ramp, CO reaction with surface H or O (from another CO) was able to occur. These signals were compared to TPD spectra of Pt/C not exposed to CO.
2.3 Results and Discussion

2.3.1 Catalyst Characterization

2.3.1.1 BET

BET surface area, pore size, and pore volume were 225 ± 12 m² g⁻¹, 16.4 ± 1.8 nm, and 0.63 ± 0.04 cm³ g⁻¹ for the carbon support (XC-72), respectively; and 186 ± 5.6 m² g⁻¹, 19.7 ± 4.2 nm, and 0.57 ± 0.01 cm³ g⁻¹ for Pt/C, respectively. Results for XC-72 correspond well to values in the literature [17,18]. While little change was observed for pore size and volume, the addition of Pt to the carbon support reduced the BET surface area by ca. 17%.

2.3.1.2 Average Particle Size (TEM and XRD)

Analysis of TEM images indicated a fairly even distribution of Pt particles on XC-72 in the Pt/C catalyst (Figure 2.2). Average Pt particle size for the as-received Pt/C was determined to be 4.0 ± 0.9 nm. Exposure of Pt/C to H₂ and H₂/Ar at 80°C for 24 h had no effect on its average particle size, suggesting that the sintering process is very slow at 80°C. Similar results were obtained via XRD using the Debye-Scherrer equation and the full width at half maximum (FWHM) of the Pt(111) diffraction peak for both the as-received and pretreated Pt/C (ca. 3 nm and 4 nm, respectively) (Figure 2.3). From left to right, 2θ values of 25°, 40°, 45°, 68°, and 81° in Figure 2.3 correspond to diffractions of graphite (002), Pt(111), Pt(200), Pt(220), and Pt(311), respectively [19,20]. The difference between the two values of the average Pt particle size determined by XRD
relates to the reduction of the oxide layer surrounding the metal particles during pretreatment. Thus, results from both TEM and XRD appear to suggest an average Pt particle size of approximately 4 nm for this catalyst when reduced.

**Figure 2.2** TEM image of as-received 20 wt% Pt/C.

2.3.1.3 Elemental Analysis

Elemental analysis results for Pt/C from Galbraith Laboratories and EDX showed a Pt loading of 19.2 wt% as well as a large amount of sulfur (~0.4 wt%). Similar amounts of sulfur were obtained from analysis results for the carbon support (XC-72) itself. Most likely, this sulfur was due to the vulcanization process used in producing the activated carbon support. It is important to note that, although sulfur helps in dispersing
Pt particles during impregnation, extended runs in PEMFCs showed faster degradation of fuel cell performance when sulfur-containing carbon supports were used [17,21,22]. However, due to the low temperature used in this investigation and the short experimental times, compared to the extended fuel cell runs, the sulfur present in the carbon support should have had a minimal effect.

Figure 2.3 XRD spectra of Pt/C (a) as-received and (b) pretreated in H₂ at 80°C.
2.3.1.4 Static H₂ and CO Chemisorption

Regardless of analysis temperature (35 – 80°C), the amount of CO uptake remained relatively constant (Table 2.1). This suggests that CO does not spill over onto the carbon support. Average Pt particle size calculated from CO chemisorption is higher than that from the TEM images; the difference in the results is due to the existence of linear and bridge-bonded CO on Pt, such that the overall stoichiometry CO:Pt₅ is actually < 1. Results from DRIFTS-FTIR experiments (Figure 2.4) exposing Pt/C at 80°C to 4% CO in H₂ and pure CO show the existence of linear-bonded and some bridge-bonded CO at 2059 cm⁻¹ and 1840 cm⁻¹ wavenumbers, respectively. Evidence of CHₓ species (wavenumber 1523 cm⁻¹) present on the Pt surface is also apparent. However, TPD results showed little or no desorption of CH₄ during the temperature ramp.

Table 2.1 Static H₂ and CO chemisorption results at 35 and 80°C for 20 wt% Pt/Cᵃ.

<table>
<thead>
<tr>
<th>Adsorption Gas</th>
<th>Analysis Temp. (°C)</th>
<th>Amount of CO/H Adsorbedb (µmol g.cat⁻¹)</th>
<th>Metal Dispersion (%)</th>
<th>Avg. Pt Particle Size (nm)c</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>35</td>
<td>190</td>
<td>19</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>200</td>
<td>20</td>
<td>5.4</td>
</tr>
<tr>
<td>H₂</td>
<td>35</td>
<td>215</td>
<td>22</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>255</td>
<td>26</td>
<td>4.2</td>
</tr>
</tbody>
</table>

ᵃPt/C was pretreated in H₂ at 80°C for 3 h.
ᵇExperimental error for all results was ca. ± 3%.
ᶜAvg. Pt particle size calculated from Eq. (1) assuming CO/Pt₅ = 1 and H/Pt₅ = 1.
Contrary to CO chemisorption results, depending on the analysis temperature (35°C vs. 80°C), the amount of H₂ uptake during H₂ chemisorption varied from 215 µmol H g.cat⁻¹ to 255 µmol H g.cat⁻¹, respectively. Although both concentrations yield average Pt particle sizes {4.2 – 4.9 nm, Eq. (1)} within the range observed by TEM, the former is closer to the estimated average size. Thus, due to the probability of H₂ spillover at higher temperatures, especially on a carbon support [23], and considering the CO chemisorption results, the actual concentration of surface Pt atoms on Pt/C is estimated to be approximately 215 µmol H g.cat⁻¹. The additional 40 µmol H g.cat⁻¹ uptake at 80°C is likely due to hydrogen spillover.

Figure 2.4 DRIFTS-FTIR spectra of 20 wt% Pt/C at 80°C after exposure to 4% CO+H₂ and 100% CO.
2.3.1.5 Validation of $H_2$ Surface Concentration Results from HDSAP

While Ar itself is inert, due to its employment as a diluent in HDSAP, its effect or lack thereof on hydrogen surface concentration should be established. In addition, any difference in hydrogen surface coverage with $H_2$ partial pressure between that of these studies (0.4 atm) and those of typical fuel cells (1 – 2 atm) must be addressed. This comparison was carried out by exposure of Pt/C to a gas mixture of (20/80) $H_2$/Ar (2 atm total pressure) for an extended period of time (24 h). The same procedure was performed for Pt/C exposed to pure $H_2$ (2 atm). The results (Table 2.2) suggest that the dilution of the feed stream by Ar and a variation in the partial pressure of $H_2$ (0.4 – 2 atm) has a minimal effect on the concentration of hydrogen on Pt/C.

**Table 2.2** Effect of Ar and time, in the absence of CO, on total surface concentration of hydrogen on Pt/C$^a$ from HDSAP.

<table>
<thead>
<tr>
<th>Exposure Gas$^b$</th>
<th>Surface H Concentration (µmol g.cat$^{-1}$)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>After Pretreatment</td>
</tr>
<tr>
<td>H$_2$ only</td>
<td>284</td>
</tr>
<tr>
<td>20 H$_2$/80 Ar mixture</td>
<td>291</td>
</tr>
</tbody>
</table>

$^a$Pt/C was pretreated at 80°C in H$_2$ for 3 h.
$^b$Total pressure = 2 atm.
$^c$Experimental error for all results was ca. ± 8%.

The hydrogen surface concentrations based on HDSAP, after both 12 and 24 h of exposure to either H$_2$ or H$_2$/Ar, in the absence of CO appear to be within experimental
error of that of static H₂ chemisorption at 80°C (Table 2.1). The slightly higher surface concentration of hydrogen from HDSAP, obtained immediately after pretreatment, may be due to surface functional groups on the carbon support, leftover from the impregnation process to achieve higher Pt dispersion [24]. Extended exposure to H₂ appeared to stabilize the concentration of hydrogen adsorbed on the catalyst. It is also important to note that, while the hydrogen surface concentration is able to be obtained by HDSAP immediately after pretreatment, the time required for complete chemisorption analysis is approximately 12 h under the conditions employed. Thus, accounting for these factors, the hydrogen surface concentrations obtained from HDSAP at 80°C in flow and from static chemisorption at 80°C appear to be the same. Therefore, HDSAP appears to be an excellent experimental method for the measurement of hydrogen surface concentration on Pt/C.

2.3.2 H₂-D₂ Exchange Reaction

In the absence of CO or other impurities, the exchange reaction is equilibrium-limited on even small quantities of Pt catalyst, even at 35°C. For this reason, in the absence of impurities, the hydrogen oxidation reaction (HOR, H₂ ↔ 2H⁺ + 2e⁻) is rarely the rate-limiting step in fuel cell operation, even at high current densities [3]. Such was the case here even using 0.5 mg of Pt/C for the conditions employed. For an equal molar flow of H₂ and D₂ at 80°C, equilibrium is approximately 45% conversion of H₂.

As will be shown later, the steady-state coverage of Pt₅ by CO is not 100%, even at as high as 200 ppm CO, under the experimental conditions employed. This partial
coverage allows H₂ activation (H₂-D₂ exchange) to occur on Pt₅ unoccupied by CO. Thus, the effect of CO poisoning is a function of both CO concentration and amount of Pt/C, such that, even at high CO concentrations, if sufficient unoccupied-Pt₅ sites are available, steady-state H₂-D₂ exchange conversion could be at equilibrium. Because of this and the differential conversion condition necessary to provide a good estimation of the apparent activation energy, Eₐ, small amounts of Pt/C (10 mg) was mixed with carbon support (XC-72) to obtain a catalytic bed length of ca. 1 cm and to allow an even dispersion of Pt/C. The carbon support did not appear to affect the reaction as preliminary experiments of Pt/C mixed with α-Al₂O₃ showed similar results. The steady-state H₂-D₂ exchange conversion and rate were obtained for 10 and 70 ppm CO. These data are tabulated in Table 2.3 and shown in an Arrhenius plot (Figure 2.5). It should be noted that, the steady-state H₂-D₂ exchange conversion for 10 ppm CO at 80–90°C was significantly greater than differential conditions (≤ 10%), and these points can be concluded to have deviated somewhat from the linear relationship with the data at lower temperatures.

The Eₐ in the absence of CO was not able to be obtained due to the reaction being limited by equilibrium at the experimental conditions used in this study, even for extremely small amounts of catalyst (ca. 0.5 mg). However, surface science studies of H₂-D₂ exchange on Pt(111) [25,26] have reported apparent Eₐ of 4.5 kcal mole⁻¹ and 5.3 kcal mole⁻¹ between a temperature range of 25°C and 300°C using molecular beam and low pressure experiments, respectively. However, it should be noted that these measurements may still be equilibrium affected, even at these conditions. Closer
inspection of the Arrhenius plot given in reference [26] reveals slight curvature in both the \( \text{H}_2\text{-D}_2 \) exchange data taken in the absence and in the presence of CO. Thus, because the exchange reaction is so fast, one has to be extra cautious when interpreting these results.

Table 2.3 Steady-state \( \text{H}_2\text{-D}_2 \) exchange conversion and rate on Pt/C in the presence of 10 and 70 ppm CO.\(^a\)

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>( \text{H}_2\text{-D}_2 ) Exchange Conversion (%)</th>
<th>Rate (( \text{mol g}^{-1} \text{ sec}^{-1} ))</th>
<th>( \text{H}_2\text{-D}_2 ) Exchange Conversion (%)</th>
<th>Rate (( \text{mol g}^{-1} \text{ sec}^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>35.6</td>
<td>486.5</td>
<td>17.2</td>
<td>234.9</td>
</tr>
<tr>
<td>80</td>
<td>23.4</td>
<td>320.4</td>
<td>8.4</td>
<td>115.0</td>
</tr>
<tr>
<td>70</td>
<td>11.7</td>
<td>160.3</td>
<td>3.6</td>
<td>49.6</td>
</tr>
<tr>
<td>60</td>
<td>5.1</td>
<td>69.4</td>
<td>1.4</td>
<td>19.4</td>
</tr>
<tr>
<td>50</td>
<td>2.0</td>
<td>27.8</td>
<td>0.6</td>
<td>8.3</td>
</tr>
</tbody>
</table>

\(^a\)10 mg Pt/C at 80°C in a \( \text{H}_2\text{-D}_2\text{-Ar} \) mixture at 2 atm with \( \text{H}_2\text{-D}_2 = 1 \), \( P_{\text{Ar}} = 1.6 \) atm.

Experimental error for all results was ca. ± 5%.

Introduction of even 10 ppm CO significantly increased the apparent activation energy of the exchange reaction in the surface science studies. In the present study, values for \( E_a \) of 19.3 kcal mol\(^{-1}\) and 19.7 kcal mol\(^{-1}\) were measured for Pt/C in the presence of 10 and 70 ppm CO (Figure 2.5), respectively. These results agree well with the value measured by Montano et al. [26] of 17.4 kcal mol\(^{-1}\) (200 mTorr \( \text{H}_2 \), 20 mTorr...)
D$_2$, 5 mTorr CO) on Pt(111), overlooking the slight potential curvature of their Arrhenius plot.

**Figure 2.5** Apparent activation energy of H$_2$-D$_2$ exchange on Pt/C in the presence of 10 and 70 ppm of CO. All reaction rates were obtained at steady-state for % H$_2$-D$_2$ conversion.

Comparison of activation energies obtained for the CO poisoning of ethylene hydrogenation on Pt(111) (9.6 kcal mole$^{-1}$ in the absence of CO and 20.2 kcal mol$^{-1}$ in the presence of CO), show a similar trend of increasing apparent activation energy upon CO
poisoning [26]. The increase in $E_a$ may be influenced by a restructuring of the Pt surfaces by CO [26-29], which can occur even at room temperature [27,30]. Restructuring of metal surfaces is common and occurs due to thermodynamic instabilities that arise most often when the adsorbate-substrate bonds are stronger than the bonds between the substrate atoms [31]. Scanning tunneling microscopy (STM) images of Pt(110) in the presence of CO at various temperatures indicate that the CO continuously “lifts” and roughens the Pt surface over time until the surface becomes thermodynamically stable [27]. This roughening of the Pt surface and decrease in the coordination numbers of metal atoms may perhaps inhibit formation of HD by limiting the rate of diffusion of H and D atoms on the Pt surface [26]. In addition, molecular beam studies show that the $\text{H}_2$-$\text{D}_2$ exchange reaction is structure sensitive at low pressures ($\sim 10^{-7}$ torr) of $\text{H}_2$ and $\text{D}_2$ [32]. However, the authors theorized that the exchange reaction is not structure sensitive at high pressures (1 atm) due to the reaction being so fast that equilibrium is usually achieved (in the absence of an impurity). The combination of (1) blocking of Pt sites, (2) surface restructuring, and (3) structure sensitivity of $\text{H}_2$-$\text{D}_2$ exchange reaction could explain why even a small amount of CO can have such a significant effect on the apparent activation energy for $\text{H}_2$ activation on Pt. As shown in Figure 2.5, an increase in CO concentration (70 ppm) did not seem to affect the apparent activation energy further. This suggests that an increase in CO concentration beyond 10 ppm does not affect the exchange mechanism significantly.
2.3.3 \( \text{H}_2 \) and \( \text{CO} \) Surface Concentration Measurements

2.3.3.1 Effect of CO on Hydrogen Surface Concentration

Figure 2.6 shows TOS measurements of hydrogen surface concentration on 100 mg of Pt/C in the presence of 10–200 ppm CO in 20% \( \text{H}_2 \) and 80% Ar. Table 2.4 gives the steady-state surface concentrations. As the CO concentration increased, the time required to reach steady-state coverage decreased. This is understandable as higher CO concentrations allowed for higher initial uptakes. However, what primarily dictated the rate of decline with TOS was that, for ppm concentrations of CO, it took a long time to populate the surface of 100 mg Pt/C to steady-state coverage, even if every molecule adsorbed.

Due to adsorption/desorption equilibrium of CO at 80\(^\circ\)C, the surface concentration of hydrogen never approached 0 at steady-state, even in as high a concentration as 200 ppm CO. Increasing CO concentration to 200 ppm, from 70 ppm, did not appear to significantly further decrease hydrogen surface concentration or exchange conversion. For example, at the calculated loading of Pt, it would have taken at least 8.8 h in the presence of 10 ppm CO for all of the available surface Pt atoms to have undergone full coverage with CO.

While steady-state hydrogen surface concentration is a function of CO concentration regardless of the amount of catalyst, \( \text{H}_2 \) activation or \( \text{H}_2\)-\( \text{D}_2 \) exchange conversion is not. Even though a large loss in hydrogen surface concentration was observed for 100 mg of Pt/C in the presence of 10 ppm CO, \( \text{H}_2\)-\( \text{D}_2 \) exchange at steady-state was still very close to equilibrium (ca. 42% vs 45% at equilibrium). Exposure of
100 mg of Pt/C to 200 ppm CO further decreased H$_2$-D$_2$ exchange conversion at steady-state to 22%. This result suggests that, although CO is blocking a large portion of the sites, there are still sufficient available Pt surface atoms remaining in the 100 mg of catalyst to cause the H$_2$-D$_2$ exchange reaction to achieve high conversions at steady-state.

**Figure 2.6** TOS measurement of hydrogen surface concentration as a function of CO concentration (10 – 200 ppm) on Pt/C at 80°C.

If, according to electrochemical results, the CO were completely covering the Pt ($\theta_{CO/Pt}=1$) in the presence of 100 ppm CO [8,9], the steady-state conversion of H$_2$-D$_2$ exchange at 200 ppm CO should be 0%. In addition, because steady-state CO coverage on Pt$_S$ is not 100%, even at relatively high concentrations (i.e., 200 ppm) of CO,
increasing the total amount of Pt/C also increases the total number of free Pt₈ sites unoccupied by CO, such that higher concentrations of CO are required before the poisoning effect can be observed. This is the reason why increasing the Pt loading in fuel cells has the false effect of increasing its CO tolerance [3]. This is important because, regardless of how much of the Pt surface is poisoned by CO, as long as there exists enough unpoisoned Pt surface atoms such that the HOR is not the rate-limiting step, no effect of CO poisoning is observed.

**Table 2.4** Steady-state H₂-D₂ exchange conversion and surface coverage of Pt/C by CO and hydrogen (from HDSAP and TPD).a

<table>
<thead>
<tr>
<th>CO Conc. (ppm)</th>
<th>Steady-State H₂-D₂ Exchange Conversionb</th>
<th>Surface H Concentration at Steady-State (μmol H g.cat⁻¹) [HDSAP]c</th>
<th>Surface CO Concentration (μmol CO g.cat⁻¹) [TPD]d</th>
<th>Surface Coverage of Pt by CO based on HDSAP (ML)ₑᶠ</th>
<th>Surface Coverage of Pt by CO based on TPD (ML)fg</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>45% Equil.</td>
<td>265</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>45% Equil.</td>
<td>121</td>
<td>51</td>
<td>0.44</td>
<td>0.24</td>
</tr>
<tr>
<td>10</td>
<td>42%</td>
<td>111</td>
<td>64</td>
<td>0.48</td>
<td>0.30</td>
</tr>
<tr>
<td>30</td>
<td>34%</td>
<td>99</td>
<td>70</td>
<td>0.54</td>
<td>0.33</td>
</tr>
<tr>
<td>70</td>
<td>26%</td>
<td>97</td>
<td>74</td>
<td>0.55</td>
<td>0.34</td>
</tr>
<tr>
<td>200</td>
<td>22%</td>
<td>95</td>
<td>72</td>
<td>0.56</td>
<td>0.33</td>
</tr>
</tbody>
</table>

a100 mg Pt/C.
bExperimental error for all results was ca. ± 3%.
cExperimental error for all results was ca. ± 8%.
dExperimental error for all results was ca. ± 5%.
eCalculated from Equation (4).
fCalculated from Equation (5).
gCalculations are based on a Pt surface concentration of 215 μmol Pt₈ g.cat⁻¹ obtained from static H₂ chemisorption at 35°C and assuming a stoichiometry of (1:1) for both H:Pt and CO:Pt.
Further TOS results with a lower concentration of CO (2 ppm) are shown in Figure 2.7. Even after 108 h of exposure to CO, equilibrium conversion was still observed for H₂-D₂ exchange. Surprisingly, a reduction of CO from 10 to 2 ppm, which should shift the adsorption/desorption equilibrium of CO, had only a small effect on the concentration of surface hydrogen at steady-state (Table 2.4). Analysis of CO coverage results on Pt(111) as a function of CO pressure also showed very little change between the equivalent 2 – 10 ppm partial pressure range (10⁻³ – 10⁻² Torr) [5].

![Graph showing surface concentration of hydrogen on Pt/C as a function of time in the presence of 2 ppm CO.](image)

**Figure 2.7** Surface concentration of hydrogen on Pt/C as a function of time in the presence of 2 ppm CO.
2.3.3.2 Surface Coverage of CO on Pt

Due to the ambiguity of surface coverage, the definition that will be employed in this section is based on the coverage of PtS by CO, such that if we have two nondissociated CO molecules bridge-bonded to four PtS atoms on the surface of a unit cell, we have a CO surface coverage of one monolayer \( \theta_{\text{CO/PtS}} = 1 \). In other words, we are focused on surface coverage by CO as blocked surface atoms of Pt (PtS).

Actual surface Pt concentration is speculated to be between 190 – 215 \( \mu \text{mol PtS g.cat}^{-1} \) from static CO and \( \text{H}_2 \) chemisorption results at 35°C, respectively. The reason for this difference can be attributed to the fact that a portion of the CO is bridge-bonded to two PtS atoms, which is evident from IR obtained at 80°C as well as literature [6]. Because the stoichiometric ratio of (1:1) for H:PtS is much more likely than that of CO:PtS, the PtS concentration of 215 \( \mu \text{mol PtS g.cat}^{-1} \) obtained from static \( \text{H}_2 \) chemisorption at 35°C was used as the basis for the surface coverage analysis. Eq. (4) was used for calculations involving hydrogen surface concentration obtained from HDSAP and Eq. (5) was used for calculations involving CO surface concentration obtained from TPD:

\[
\text{CO Surface Coverage (HDSAP)} = \frac{215 \ \mu\text{mol PtS g.cat}^{-1} - (\text{Surface H})_{x \text{ppm CO}}}{215 \ \mu\text{mol PtS g.cat}^{-1}} \tag{4}
\]

\[
\text{CO Surface Coverage (TPD)} = \frac{(\text{Surface CO})_{x \text{ppm CO}}}{215 \ \mu\text{mol PtS g.cat}^{-1}} \tag{5}
\]

These results are also tabulated in Table 2.4.
As expected, CO surface coverage calculated from HDSAP and TPD results both increase with CO concentration. The difference between these two results is due, in large part, to a portion of the CO being bridge-bonded such that the stoichiometric ratio of CO:Pt is less than 1. Thus, the true surface coverage of Pt by CO is most likely closer to the values calculated based on hydrogen surface concentration [HDSAP] than that of CO [TPD]. These results show a maximum coverage of Pt by CO to be approximately 0.44 ML (monolayer) and 0.56 ML for the CO concentrations of 2 and 200 ppm, respectively, at 80°C and 0.4 atm of H2. Further increases in CO concentration may alter CO coverage due to phenomena such as restructuring, formation of surface carbonyls, and other unforeseen variables. Furthermore, the presence of humidity may affect these results.

Considering the sum of hydrogen adsorbed (HDSAP) and the amount of CO able to be desorbed from the catalyst after exposure (TPD) and the fact that some of the CO molecules are bridge-bonded, the results from Table 2.4 appear to imply a limiting of hydrogen spillover by CO adsorption. In other words, the sum of 111 μmol H g.cat⁻¹ obtained at steady-state in 10 ppm CO (HDSAP) and the 64 μmol CO g.cat⁻¹ (TPD) appear to represent the surface concentration of unpoisoned and poisoned Pt, respectively, with the absence of hydrogen spillover. This can happen if CO is preferentially adsorbing at the outer-edges of Pt particles (i.e., Pt-C interface). Because spillover, either onto the carbon support or to the adjacent ionomer, plays an important role in proton transfer, interruption of this process can have a detrimental effect on fuel cell activity, regardless of how fast the HOR is occurring.
2.3.3.3 Reversibility of CO Poisoning

In contrast to NH$_3$ on Nafion, the adsorption of CO on Pt is not permanent but rather reversible at 80°C. This is illustrated very clearly from the adsorption/desorption equilibrium (< 1 ML) that is achieved even when Pt is exposed to relatively high concentrations of CO.

From electrochemical results obtained by Uribe et al. [33], it was found that the performance of a fuel cell, previously poisoned with CO, was able to be fully regenerated within a few minutes of purging the anode with pure H$_2$, which appears to suggest a complete removal of adsorbed CO. Jimenez et al. [4] utilized this apparent fast reversibility of CO in a fuel cell by continuously cycling between feed streams of pure H$_2$ and CO/H$_2$ mixture every couple of minutes to improve CO tolerance. Similar to the results obtained by Uribe et al. [33], the authors also concluded that the poisoning process is reversible with only the injection of pure H$_2$. However, due to the high Pt loadings (20 wt% Pt/C, 0.5 mg Pt cm$^{-2}$) employed and the short duration of their experiments (110 min), the system was most likely not at steady-state and would not have adsorbed enough CO to shift the HOR away from being equilibrium limited. In addition, it is again pertinent to point out that as long as there exists enough unpoisoned Pt surface atoms such that the HOR is not the rate-limiting step, no effect of CO poisoning should be observed.

Figure 2.8 shows the hydrogen surface concentrations of Pt/C sequentially exposed to 30 ppm CO followed by regeneration in H$_2$, both for 12 h. The process was repeated a second time on the same catalyst to see if poisoning of a previously poisoned
Pt surface would yield different results. After an initial 12 h exposure to 30 ppm CO, steady-state was reached (35% H₂-D₂ conversion). Regeneration of the catalyst in H₂ for 12 h allowed only a partial recovery of the Pt sites and hydrogen adsorption capacity (ca. 150 μmol H g.cat⁻¹). However, the amount of CO-free Pt surface atoms, even after 6 h of regeneration, was enough to allow the H₂-D₂ exchange reaction to achieve equilibrium conversion (~45%). Re-exposure of the regenerated catalyst to 30 ppm CO again resulted in a hydrogen surface concentration similar to that following the initial exposure to CO.

These results suggest that the adsorption/desorption equilibrium of CO on Pt is not affected by whether or not the surface is fresh or pre-poisoned and regenerated. However, while only a partial recovery was again achieved, H₂-D₂ exchange conversion after 6 h regeneration was at equilibrium under the conditions employed.

Therefore, purging with H₂ may appear to initially restore fuel cell performance, but this apparent recovery is not due to the complete removal of CO from the Pt sites. Rather, it appears that there is only a partial recovery of sites – but sufficient CO-free Pt sites are recovered to allow H₂ activation not to be the rate-limiting step any longer. Based on these results, the addition of a H₂ purge between CO exposures may help in slowing its poisoning effect, but it by no means totally reverses this poisoning, unless perhaps if extremely long purge times are used.
Figure 2.8 Reversibility of CO poisoning after exposure of Pt/C to 30 ppm CO for 12 h. Steady-state H$_2$-D$_2$ exchange conversion was at 35% in the presence of CO and at equilibrium (~45%) for all points following regeneration.
2.4 Conclusions

Comparison of HDSAP results to those of static H₂/CO chemisorption at 80°C and CO TPD show excellent agreement, thus validating HDSAP as an excellent technique for the measurement of hydrogen surface concentration on Pt in the absence and presence of CO at the experimental conditions employed. While the H₂-D₂ exchange reaction (a model for H₂ activation) is able to reach equilibrium very easily on Pt in the absence of CO, introduction of CO is able to shift the reaction away from equilibrium. This shift from reaction equilibrium is supported by the increase in apparent activation energy of H₂-D₂ exchange from 4.5 – 5.3 kcal mole⁻¹ [25,26] (in the absence of CO) to 19.3 – 19.7 kcal mole⁻¹ (in the presence of 10 – 70 ppm CO). Apparent activation energy results, in the presence of CO, agree well with those reported by Montano et al. [26] within experimental error.

Results from the H₂-D₂ exchange reaction, HDSAP, and TPD show that the catalyst surface is not fully saturated by CO in the presence of as high as 200 ppm CO in H₂ under the experimental conditions used (80°C and 0.4 atm H₂), which suggest that surface coverage estimations via cyclic voltammetry (CV) are inaccurate. Furthermore, comparisons of hydrogen surface concentration and CO measurements with that of static H₂ chemisorption at 35°C show a CO surface coverage of ca. 0.44–0.56 ML in 2–200 ppm of CO in H₂, respectively. Surface science results of CO surface coverage obtained via HP STM on Pt(111) for the range of CO studied were consistently ~0.1 ML higher than the values obtained in this study. However, considering the differences in
experimental conditions (i.e., room temperature, in the absence of hydrogen, and single crystal surface), CO surface coverage obtained from HDSAP show good agreement with those obtained from surface science.

Regeneration of Pt/C in H₂, at fuel cell conditions, after exposure to 30 ppm CO shows only a partial recovery of surface Pt sites. However, the amount of CO-free sites available from removal of CO in the gas stream can still be enough to achieve equilibrium conversion for H₂-D₂ exchange. This explains why a complete recovery of performance is observed in a fuel cell – not because all of the surface CO has been removed, but because enough has been removed to make H₂ activation not be the rate-limiting step. In addition, surface coverage of hydrogen and CO results at steady-state appear to imply a limiting effect on hydrogen spillover by CO, perhaps due to CO adsorption at Pt-C interface.

With the establishment of HDSAP as a valid technique for the measurement of hydrogen surface concentration on Pt, future research in this series will explore the effects of Nafion and humidity on H₂ activation and surface coverage on Pt in the presence and absence of CO and other impurities. The eventual goal of this work will be a better understanding of the effects of impurities on H₂ activation and hydrogen surface coverage of a Nafion-Pt/C catalyst at various levels of humidity, similar to those typical in a catalyst layer in a PEMFC.

2.5 References


CHAPTER THREE

THE EFFECT OF LOW CONCENTRATIONS OF CO ON H₂ ADSORPTION AND ACTIVATION ON Pt/C: PART 2 – IN THE PRESENCE OF H₂O VAPOR


CO affects H₂ activation on supported Pt in the catalyst layers of a PEMFC and significantly degrades overall fuel cell performance. This paper establishes a more fundamental understanding of the effect of humidity on CO poisoning of Pt/C at typical fuel cell conditions (80°C, 2 atm). In this work, direct measurements of hydrogen surface concentration on Pt/C were performed utilizing an H₂-D₂ switch with Ar purge (HDSAP). The presence of water vapor decreased the rate of CO adsorption on Pt, but had very little effect on the resulting CO surface coverage on Ptₜ (θₜ⁰) at steady-state. The steady-state θₜ⁰’s at 80°C for Pt exposed to H₂ (Pₜ₂ = 1 atm) and a mixture of H₂/H₂O (1 atm H₂, 10%RH) were 0.70 and 0.66 ML, respectively. Furthermore, total strongly-bound surface hydrogen measured after exposure to H₂/H₂O was, surprisingly, the sum of the exchangeable surface hydrogen contributed by each component, even in the presence of CO. In the absence of any evidence for strong chemisorption of H₂O on the carbon support with/without Pt, this additive nature and seemingly lack of interaction from the co-adsorption of H₂ and H₂O on Pt may be explained by the repulsion of strongly adsorbed H₂O to the stepped-terrace interface at high coverages of surface hydrogen.
3.1 Introduction

Recently, proton exchange membrane fuel cells (PEMFCs) have attracted a lot of attention because of their superior features compared to other energy conversion technologies, such as their high energy density, easy start-up, low operating temperature, transient ability, and zero pollution emissions [1-4]. It is believed that PEMFCs will be utilized in the future as a main source of power for portable, transportation, and stationary applications [5]. However, the cost of materials, loss of performance, and durability due to the presence of impurities in the fuel and oxygen streams are currently major barriers for the successful commercialization of PEMFCs.

Generally, a PEMFC utilizes a $\text{H}_2$ fuel stream produced by reforming of hydrocarbons [6] and purification by conventional methods (i.e., selective or preferential oxidation (PROX), membrane separation, pressure swing adsorption (PSA), etc.) [5, 7, 8] to obtain a high purity $\text{H}_2$ fuel containing only trace amounts of impurities (i.e., CO, CO$_2$, NH$_3$, SO$_2$, etc.). Of the impurities present, ppm levels of CO have been found to be one of the most detrimental impurities in degrading the electrochemical performance of the Pt catalyst in PEMFCs [9-11]. The impurity has been shown to severely affect the hydrogen oxidation reaction (HOR) at the anode via competitive adsorption with $\text{H}_2$ on Pt sites, thereby inhibiting the process of $\text{H}_2$ dissociation and limiting the electrode kinetics of the cell [6, 12-14]. It has been reported that operating fuel cells at high humidity, temperature, and anode potential [12, 14, 15] helps to increase CO tolerance due to higher oxidation rates of CO by $\text{OH}_{\text{ads}}$. 
During the past few decades, numerous experiments have been performed to determine and understand the effect of CO on overall fuel cell performance at various conditions \[6, 9, 14, 16\]. Many experiments (both in-situ and ex-situ) and mathematical simulations have been published. The methods have been helpful in isolating the effect of operating parameters on individual components of PEMFCs \[17, 18\]. However, all techniques have limitations and extraneous variables which may affect the interpretation of the results. For instance, electrochemical techniques (i.e., polarization curve, current interruption, electrochemical impedance spectroscopy, cyclic voltammetry, CO stripping voltammetry, etc.) typically are performed in an acidic solution \[15, 19, 20\], operate at much lower current density than operational fuel cells, and require very rapid acquisition of the transient data \[17, 21\]. Surface science techniques (e.g., X-ray photoelectron spectroscopy, scanning tunneling microscopy, low-energy ion scattering spectroscopy, etc.) require ex-situ investigations at non-ideal conditions (i.e., ultra high vacuum or relatively low pressures) \[22-25\]. These conditions are much too far removed from typical fuel cell environments and may cause complications in data interpretation by extrapolation. To date, limited studies have examined the effect of impurities on the activation of H\(_2\) on Pt-based catalysts at conditions related to actual fuel cell environments.

In this study, H\(_2\)-D\(_2\) exchange and a simple H\(_2\)-D\(_2\) switch with an Ar purge in between (HDSAP) technique was employed to quantitatively investigate the effect of CO on H\(_2\) dissociation and on the hydrogen surface concentration on Pt/C catalysts in the presence of water vapor. The HDSAP methodology, developed in our previous work
has proven to be a powerful approach for the time-on-stream (TOS) measurements of hydrogen surface concentrations on Pt in the absence of humidity. This convenient non-destructive approach has many benefits over other conventional performance tests, for example, simple material preparation, low cost, and time efficiency. It provides valuable information (hydrogen surface concentration on Pt catalysts) which could be reasonably used to predict performance of a partially poisoned-fuel cell. The knowledge of the effect of water vapor (humidity) and CO on the amount of hydrogen adsorbed on Pt/C obtained in this work provides fundamental insight for future investigations of the effect of humidity and CO on Nafion-Pt/C in the catalyst layer of the fuel cell.

3.2 Experimental

3.2.1 Materials

A commercial fuel cell catalyst from BASF (Pt supported on carbon (Vulcan XC-72, Cabot International)) with a nominal loading of ~20 wt% Pt was used as received. Research-grade gases were purchased from National Specialty Gases and Scott Specialty Gases. All characterizations and experiments were performed on the reduced catalyst.

3.2.2 Catalyst Characterization

Prior to the analysis of total BET surface area, pore volume, and pore size, catalyst samples were degassed in a vacuum at 5 x 10^{-3} \, \text{mmHg} and 110°C for 4 h. The
measurements of N₂ adsorption isotherms at -196°C were performed using a Micromeritics ASAP 2020 apparatus.

Static H₂ and CO chemisorption measurements were carried out at both 35°C and 80°C using a Micromeritics ASAP 2010 automated system. Catalyst samples were first reduced with H₂ at 80°C for 3 h and then evacuated at 10⁻⁵ mmHg and 80°C for another 3 h prior to the analysis. Preliminary temperature program reduction (TPR) results showed that Pt catalysts were completely reduced under these conditions and time periods [11]. Higher reduction temperatures were not used since the conditions used to pretreat fuel cell catalysts must stay <120°C because of the presence of Nafion on actual catalysts. After adjusting to the specified analysis temperature (35°C or 80°C), the H₂ and CO uptake isotherms were obtained by varying the partial pressure from 50 – 450 mmHg in increments of 50 mmHg. The metal dispersion of Pt/C was determined using the total chemisorption isotherms and assuming H:Ptₙ and CO:Ptₙ stoichiometries of 1:1.

Elemental analyses (Pt) of samples were performed by Galbraith Laboratory (Knoxville, Tennessee, USA).

Transmission electron microscopy (TEM) analysis was conducted using a STEM-Hitachi HD2000 to investigate the average Pt particle size. Samples were sonically dispersed in iso-propanol (Fisher Scientific), after which a small aliquot of the suspension was deposited on a standard copper grid (200 mesh copper Formvar/Carbon) and allowed to dry in air at ambient temperature overnight prior to the analysis.
3.2.3 Nomenclature

In order to provide a shorthand designation for the various treatment and adsorption conditions to which the catalyst was exposed, the following designations are used throughout this paper.

<table>
<thead>
<tr>
<th>Designation</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>/:</td>
<td>TOS = 0 h. The nomenclatures given before and after “/” were treatment or adsorption conditions prior to and after TOS = 0 h, respectively.</td>
</tr>
<tr>
<td>w:</td>
<td>in the presence of 10% RH; P_{H2O} = 0.023 atm</td>
</tr>
<tr>
<td>C:</td>
<td>30 ppm CO</td>
</tr>
<tr>
<td>H:</td>
<td>H_{2}; P_{H2} = 1 atm balanced with P_{Ar} = 1 atm</td>
</tr>
<tr>
<td>D:</td>
<td>D_{2}; P_{D2} = 1 atm balanced with P_{Ar} = 1 atm</td>
</tr>
<tr>
<td>hd:</td>
<td>H_{2} and D_{2}; P_{H2} = 0.5 atm and P_{D2} = 0.5 atm balanced with P_{Ar} = 1 atm</td>
</tr>
<tr>
<td>Hw:</td>
<td>H_{2} and H_{2}O; P_{H2} = 1 atm balanced with P_{Ar} = 0.977 atm and P_{H2O} = 0.023 atm</td>
</tr>
<tr>
<td>hdw:</td>
<td>H_{2}, D_{2}, and H_{2}O; P_{H2} = 0.5 atm and P_{D2} = 0.5 atm balanced with P_{Ar} = 0.977 atm and P_{H2O} = 0.023 atm</td>
</tr>
<tr>
<td>A:</td>
<td>Ar; P_{Ar} = 2 atm</td>
</tr>
<tr>
<td>ad:</td>
<td>Ar and D_{2}; P_{Ar} = 1.5 atm and P_{D2} = 0.5 atm</td>
</tr>
<tr>
<td>Aw:</td>
<td>Ar and H_{2}O; P_{Ar} = 1.977 atm balanced with P_{H2O} = 0.023 atm</td>
</tr>
<tr>
<td>adw:</td>
<td>Ar, D_{2}, and H_{2}O; P_{Ar} = 1.477 atm and P_{D2} = 0.5 atm balanced with P_{H2O} = 0.023 atm</td>
</tr>
</tbody>
</table>
The total pressure and temperature in the reactor were always kept at 2 atm and 80°C, respectively. Ar was used as an inert gas balance to maintain a total flow rate of 100 sccm and total pressure of 2 atm. The treatment and experimental conditions for each set of results are given in the legend of each figure. For clarification purposes, the nomenclature, for example, “Hw / HwC”, means that the Pt/C catalyst, after reduction, was equilibrated in a 100 sccm stream with $P_{H_2} = 1$ atm, $P_{Ar} = 0.977$ atm, and $P_{H_2O} = 0.023$ atm (equal to 10%RH) overnight at 80°C prior to the first (TOS = 0 h) hydrogen surface concentration measurement via HDSAP. The catalyst was then subsequently exposed to 30 ppm CO in the presence of 1 atm $P_{H_2}$ with 10%RH for further TOS measurements of hydrogen surface concentration. While most of the experiments involving water vapor were performed in the presence of both $H_2$ and water, in order to isolate the amount of surface hydrogen attributed to the water, a few of the experiments investigated the hydrogen surface concentration on Pt/C in the absence of $H_2$. The nomenclature, for example, “Aw / AwC”, means that the Pt/C catalyst, after reduction, was equilibrated in a 100 sccm gas stream with $P_{Ar} = 1.977$ atm and $P_{H2O} = 0.023$ atm (10%RH) overnight at 80°C before the first (TOS = 0 h) hydrogen surface concentration of Pt/C was measured with subsequent exposure to 30 ppm CO at 10%RH Ar (in the absence of $H_2$).

3.2.4 Measurements of hydrogen surface concentration from both $H_2$ and $H_2O$

Pt catalysts (~100 mg) were loaded between quartz wool (ChemGlass, Inc.) in a 10 mm quartz tubular reactor with a thermocouple close to the catalyst bed. Prior to the
experiments, the catalyst was reduced in a mixture of hydrogen [H] at 80°C and 2 atm for 3 h, known to be sufficient for total reduction of the Pt [11]. In this study, the hydrogen surface concentration on Pt/C was investigated by a H₂-D₂ switch with an Ar purge in between (HDSAP) technique and the gas composition of the effluent was monitored online via mass spectrometry (MS) (Pfeiffer Vacuum). The procedures and validation of this technique have been described in more detail elsewhere [11].

A well-mixed humidified stream was obtained in a heated flash chamber (maintained at 100°C) with an inner diameter of 3.75 cm, length of 10 cm, and filled with 10 mm glass beads (to decrease the dead space and to obtain better mixing and heat transfer). Pre-heated deionized liquid water, along with a dry gas mixture of H₂ and Ar, was injected into the flash chamber, in which the liquid water was quickly evaporated and the humidified stream was allowed to mix thoroughly via turbulence before entering the reactor. The relative humidity (RH) or partial pressure of water was controlled by the flow rate of deionized water into the flash chamber via a syringe pump (Genie pump, Kent Scientific Corporation). All experiments involving water vapor were performed at 10%RH, 2 atm, and 80°C; the water was fed at 1.45 μL (min)^{-1} for the gas flow rates used.

The TOS hydrogen surface concentration measurements were initiated by first exposing the catalyst to a humidified mixture of H₂, Ar, and CO (if a poisoning study) for 30 min. After the initial exposure phase, the catalyst was then purged with 50 sccm of Ar [A] at 80°C for 1 h to remove as much of the gas phase H₂ and weakly-adsorbed hydrogen on the Pt surface as possible. The time period for the Ar purge in this study
was fixed at 1 h due to evidence suggesting that, for these conditions and this system, the specified purge time yielded a nearly full coverage of hydrogen adsorption on surface Pt in the presence of H₂O (see section 3.3.2). If the Ar purge time was too short, the measured surface hydrogen would include weakly held and spillover hydrogen in addition to that adsorbed on the Pt surface, resulting in overestimation of hydrogen coverage. On the other hand, too long of an Ar purge time would result in an underestimation of surface hydrogen due to loss of some strongly-bound hydrogen from the Pt surface. During the Ar purge, the liquid DI water flow was also stopped to prevent any additional source of hydrogen other than that adsorbed on the surface. At the end of the purge phase, a 100 sccm mixture of D₂ [D] was introduced to the catalyst. Theoretically, the total hydrogen surface concentration on Pt/C should be obtained from all hydrogen species (H₂, HD, H₂O, and HDO) desorbed from the Pt surface. The hydrogen surface concentration on Pt/C obtained by the HDSAP technique represents the amount of adsorbed hydrogen that can be exchanged with (or displaced by) D₂. However, it was found that after the 1 h Ar purge, the MS signal intensities for the H₂O and HDO peaks were insignificant compared to those for H₂ and HD, as can be seen in Figure 3.1. Consequently, the very small amounts of H₂O and HDO desorbed from Pt/C catalysts were disregarded and the total amount of hydrogen adsorbed on Pt/C was calculated as follows:

\[
\text{Surface } H \left[ \frac{\mu \text{mol } H}{g} \right] = \frac{N_{\text{HD}} + 2N_{\text{H₂}}}{W_C} \quad (1)
\]
where $N_{HD}$ and $N_{H_2}$ are number of μmols of HD and H$_2$ desorbed from the surface of Pt/C, respectively, after the switch to D$_2$, and $W_C$ is the weight of the Pt/C catalyst.

![Graph showing MS signals during hydrogen sensing on Pt/C](image)

**Figure 3.1** Typical MS signals during the measurement of hydrogen surface concentrations on Pt/C [Hw / HwC] exposed to a mixture of H$_2$, water vapor, and CO.

### 3.2.5 Measurements of hydrogen surface concentration from only H$_2$O

In order to have an environment as similar as possible to normal PEMFC conditions, most experiments were conducted in the presence of both H$_2$ and H$_2$O, which made it unfeasible to distinguish directly the portion of the total hydrogen surface concentration measured by the HDSAP technique originating from either H$_2$ or H$_2$O. Thus, several experiments in the absence of H$_2$ were performed to specifically determine the amount of hydrogen surface concentration attributable to water. After the 3 h
reduction at 80°C in a mixture of H₂/Ar [H] and prior to the introduction of water vapor to the catalyst, the catalyst was exposed to a flow of 100 sccm of Ar [A] while the temperature was increased from 80°C to 250°C (10°C min⁻¹) and held at 250°C for 1.5 h. This was done to remove as much of the adsorbed hydrogen as possible from the Pt surface before the introduction of water so that any surface hydrogen measured from HDSAP would be primarily from the water and not the adsorbed hydrogen from the pretreatment process. After holding at 250°C for 1.5 h, the catalyst was cooled to 80°C at 8°C min⁻¹, and held at 80°C for 15 min before the introduction to gas mixtures without H₂ {[Aw] or [AwC]}. The catalyst was exposed to one of these specified gas mixtures for over 20 h with TOS HDSAP measurements at various intervals. The hydrogen surface concentration originating from dissociated water was determined from the amount of HD and H₂ that desorbed from Pt/C [Eq. (1)].

3.2.6 MS calibration for hydrogen surface concentration measurements

For calibration purposes of the MS, the isotopic exchange reactions H₂-D₂-H₂O and D₂-H₂O were carried out on Pt/C at 80°C and 2 atm with a total flow of 100 sccm during HDSAP measurements. All possible exchange reactions and their heats of reaction and equilibrium constants calculated based on the thermodynamic data given in ref. [26] are as follows:
The \( \text{H}_2\text{-D}_2\)-\( \text{H}_2\text{O}\) and \( \text{H}_2\text{O}\)-\( \text{D}_2\) exchange reactions were initiated by introducing 100 sccm mixtures of \([\text{hd}]\), \([\text{hdw}]\), \([\text{hdC}]\), or \([\text{hdwC}]\) and of \([\text{ad}]\), \([\text{adw}]\), \([\text{adC}]\), or \([\text{adwC}]\) to the catalyst, respectively. During the exchange reactions, the sum of the partial pressures of \( \text{H}_2\) and \( \text{D}_2\) was always kept at 1 atm to maintain a similar partial pressure of \( \text{H}_2\) as in the anode feed stream of a typical PEMFC. The real time MS signal was collected until steady. MS signals for the gas composition in the absence of the catalyst were obtained by switching the flow to bypass the catalyst bed. The conversions of \( \text{H}_2\) and \( \text{D}_2\) were calculated as follows:

\[
\text{H}_2 \text{ Conversion} = \frac{[\text{H}_2]_{\text{no cat.}} - [\text{H}_2]_{\text{cat.}}}{[\text{H}_2]_{\text{no cat.}}} \quad (8)
\]

\[
\text{D}_2 \text{ Conversion} = \frac{[\text{D}_2]_{\text{no cat.}} - [\text{D}_2]_{\text{cat.}}}{[\text{D}_2]_{\text{no cat.}}} \quad (9)
\]

where \([\text{H}_2]_{\text{cat.}}\) and \([\text{D}_2]_{\text{cat.}}\) vs. \([\text{H}_2]_{\text{no cat.}}\) and \([\text{D}_2]_{\text{no cat.}}\) were the MS signals of \( \text{H}_2\) and \( \text{D}_2\) when the gas mixture passed through and by-passed the catalyst bed, respectively.

After the conversions of the exchange reactions were obtained, a pulse calibration of \( \text{H}_2\) and HD was obtained by switching the reaction feed stream back to the catalyst where the flow of reaction effluent was directed through a 6-port valve equipped with a 2
mL sample loop and eventually to vent. A mixture of 100 sccm D₂ and Ar [D] acted as the carrier gas such that, upon switching the 6-port valve from “Load” to “Inject”, the reaction effluent in the sample loop was flushed to the MS, resulting in a pulse of H₂ and HD. Two peaks for H₂ and HD were observed and the calibrations of their areas were obtained based on the H₂ and D₂ conversions calculated previously [Eqs. (8, 9)]. The mixture of D₂ and Ar [D] was used as the carrier gas to mimic the conditions during the D₂ switch of HDSAP for the hydrogen surface concentration measurements (sections 3.2.4 – 3.2.5).

It was found that in the absence of water vapor, the H₂ and D₂ conversions of Eq. (2) were always at equilibrium and both equal to ca. 45% before and after exposure to 30 ppm CO at 80°C. In the presence of water vapor (P_H₂O = 0.023 atm, 10%RH), on the other hand, the conversions of H₂ and D₂ were ca. 40% and 50%, respectively, due to the contribution from H₂O for all CO exposure times, most likely still at equilibrium. This was expected due to the large amount of Pt/C catalyst used for HDSAP measurements (ca. 100 mg).

3.2.7 Measurements of the amount of water adsorbed on the Pt catalyst and carbon support at steady-state by temperature programmed desorption (TPD)

Samples (ca. 100 mg) were pretreated in a mixture of humidified H₂ and Ar [Hw] overnight. Prior to the start of TPD measurements, the flow of the pretreatment gas mixture was stopped and the reactor was purged with 30 sccm Ar at 80°C for 25 min. The temperature was then ramped at a rate of 10°C min⁻¹ from 80°C to 400°C while the composition of the gas effluent was analyzed online by MS.
3.3 Results

3.3.1 Characterization

Table 3.1 shows the physical properties of the Pt/C catalyst and the carbon support used in this study. The addition of Pt appeared to slightly decrease the BET surface area, pore volume, and pore size of the catalyst as would be expected due to the high loading of Pt. Table 3.2 summarizes the hydrogen and CO chemisorption results for the Pt/C catalyst. It can be observed that the amount of hydrogen adsorbed at 35°C was slightly less than that of 80°C due most likely to an increased amount of spillover of the chemisorbed hydrogen onto the carbon support at the higher temperature. However, the amounts of CO adsorbed on Pt/C at 35°C and 80°C were similar and equal within experimental error to the hydrogen uptake at 35°C. Images from TEM have shown that Pt was well-dispersed on the carbon support with an average Pt particle size of 2.6 ± 0.4 nm (see Appendix B), comparable to the average Pt particle size predicted by hydrogen or CO chemisorption (Table 3.2). It is important to note that the temperature ramp from 80°C to 250°C at 10°C min⁻¹ and held at 250°C for 1.5 h (used to measure hydrogen surface concentration from only H₂O) should have had a minor effect on the average Pt particle size as preliminary results exposing the Pt/C catalyst to 350°C for 2 h in H₂ gas increased the average particle size by only 0.9 nm, which is still similar to that predicted from static chemisorption results, within experimental error.
Table 3.1 BET characteristics of the Pt catalyst and carbon support.

<table>
<thead>
<tr>
<th>Material</th>
<th>BET surface area(^a) (m(^2) g(^{-1}))</th>
<th>Pore size diameter(^a) (nm)</th>
<th>Pore volume(^a) (cm(^3) g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon support (XC-72)</td>
<td>225</td>
<td>16.4</td>
<td>0.63</td>
</tr>
<tr>
<td>Pt/C (17.5 wt% Pt(^b))</td>
<td>170</td>
<td>15.9</td>
<td>0.44</td>
</tr>
</tbody>
</table>

\(^a\)Experimental error = ± 3%.
\(^b\)From Pt elemental analysis; experimental error = ± 5%.

Table 3.2 Static H\(_2\) and CO Chemisorption results at 35 and 80\(^o\)C for 20 wt% Pt/C.

<table>
<thead>
<tr>
<th>Chemisorption</th>
<th>Adsorption temperature ((^o)C)</th>
<th>Total H atoms or CO chemisorbed(^a) ((\mu)mol g(^{-1}))</th>
<th>(D_{Pt}) (%)(^b)</th>
<th>Avg. Pt particle size(^c) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H_2)</td>
<td>35</td>
<td>316</td>
<td>35</td>
<td>3.1</td>
</tr>
<tr>
<td>(H_2)</td>
<td>80</td>
<td>361</td>
<td>40</td>
<td>2.7</td>
</tr>
<tr>
<td>CO</td>
<td>35</td>
<td>292</td>
<td>33</td>
<td>3.3</td>
</tr>
<tr>
<td>CO</td>
<td>80</td>
<td>297</td>
<td>33</td>
<td>3.3</td>
</tr>
</tbody>
</table>

\(^a\)Determined by extrapolating the isotherm for total H/CO chemisorption in the linear region at high pressure to zero pressure; experimental error = ± 6%. Hydrogen chemisorbed is given as \(\mu\)mol of H atoms per g catalyst.

\(^b\)Pt %dispersion obtained by assuming H:Pt\(_s\) = 1 or CO/Pt\(_s\) = 1.

\(^c\)Average Pt particle sizes calculated from \((1.08 \times 100)/D_{Pt}\) [46].

3.3.2 Justification of using a 60 min Ar purge time for the HDSAP measurements

It is known that the kinetics of the H\(_2\)-D\(_2\) exchange reaction on Pt-based catalysts is very fast [27]. Because the aim of this study was to determine the amount of strongly-bound hydrogen associated with surface Pt, especially in the presence of CO, it was necessary to purge gas-phase H\(_2\) and weakly-adsorbed hydrogen to the degree possible to leave only the strongly-adsorbed hydrogen on Pt prior to the D\(_2\) switch (related to the
number of Pt surface atoms available for H\textsubscript{2} activation). A switch to a flow of gas-phase D\textsubscript{2} from a flow of gas-phase H\textsubscript{2} without or with too short of a purge time (with an inert gas such as Ar) would result in an overestimation of the amount of hydrogen chemisorbed on the Pt surface due to the inclusion of weakly held and spillover hydrogen [11], as mentioned in section 3.2.4. However, too long of a purge time would result in an underestimation due to the removal of strongly-bound hydrogen. An optimum purge time is hence necessary for accurate measurement of the hydrogen surface concentration on Pt/C. With this use of an Ar purge in between the H\textsubscript{2} and D\textsubscript{2} flows, the amount of strongly-adsorbed hydrogen can be determined from the amounts of both HD and H\textsubscript{2} formed after the switch to D\textsubscript{2} [Eq. (1)].

Figure 3.2 shows the hydrogen surface concentration on Pt/C measured by HDSAP for varying Ar purge times. Prior to these HDSAP measurements, Pt/C catalysts were treated at 80°C overnight (to ensure complete hydrogen coverage) with 100 sccm of gas mixtures containing H\textsubscript{2}, [H] and [H\textsubscript{w}], for experiments performed at 0%RH and 10%RH, respectively. Since HDSAP analysis is a non-destructive technique, all data points were consecutively collected using the same catalyst sample. After the measurement of a data point for a particular Ar purge time was completed, the catalyst was re-exposed again to the same original gas mixture at 80°C overnight before the next HDSAP measurement for a different Ar purge time was carried out. Results were identical regardless of whether a single or multiple measurements were done so long as the Ar purge time was the same.
Figure 3.2 Effect of an Ar purge time on strongly-bound hydrogen surface concentration on Pt/C measured by HDSAP after exposure to H₂ or H₂ with 10%RH at 80°C.

In Figure 3.2, the hydrogen surface concentrations on Pt/C equilibrated with a mixture of [H] and [Hw] decreased with an increase in Ar purge time and started to level off for purge times > 60 min. It can be seen that the difference in hydrogen surface concentrations on Pt/C at 0%RH and 10%RH appears to be constant after a 60 min Ar purge, suggesting that the addition of 10%RH caused an increase in the hydrogen surface concentration on Pt/C of ca. 211 μmol H g⁻¹. In addition, for the adsorption of only H₂ [H], the surface concentration of adsorbed hydrogen determined after the 60 min Ar
purge was ca. 321 µmol H g\(^{-1}\), approximately the amount of hydrogen determined by static H\(_2\) chemisorption. These results suggest that an Ar purge time of 1 h is just long enough to remove most of the weakly held and spillover hydrogen (preventing overestimation) but not too long such that much of the strongly-bound surface hydrogen is lost (preventing underestimation). Thus, all hydrogen surface concentration results presented in this study were obtained using an Ar purge time of 1 h.

3.3.3 Use of sequential HDSAP measurements

Although HDSAP is not a destructive technique, the interruption of an exposure to water vapor, hydrogen, and/or 30 ppm CO to Pt/C catalysts to make a HDSAP measurement could possibly influence the degree of CO poisoning and change the surface coverage of CO and adsorbed hydrogen species on the Pt surface for subsequent TOS HDSAP measurements. Therefore, for comparison purposes and to assess any such effect, two experiments for TOS hydrogen surface concentration measurements were carried out:

- **Sequential CO and humidity exposure study**: One Pt/C catalyst sample was used for multiple TOS HDSAP measurements where the flow of H\(_2\), H\(_2\)O, and/or CO was interrupted with an Ar purge [A] followed by the switch to D\(_2\) [D] for each measurement. For example, after the HDSAP measurement at TOS = 3 h, where the Pt/C catalyst was exposed to H\(_2\), H\(_2\)O, and/or CO for 3 h, the same catalyst sample was further exposed to another 3 h of the mixture for the HDSAP measurement at TOS = 6 h.
• **Non-sequential CO and humidity exposure study**: Different samples of Pt/C catalysts were used for each TOS measurement. For example, after the HDSAP measurement at TOS = 3 h, a new Pt/C sample is reduced and exposed to H₂, H₂O, and/or CO for 6 h for the HDSAP measurement at TOS = 6 h.

It was found that the hydrogen surface concentration for the first experiment (sequential) at TOS = 6 h \([329 \, (\mu\text{mol H}) \, (g)^{-1}]\) was equal within experimental error to that for the latter study (non-sequential) \([341 \, (\mu\text{mol H}) \, (g)^{-1}]\), both for a total TOS = 6 h. The results show that sequential HDSAP measurements with TOS did not significantly affect the concentration of hydrogen, water, or CO on the catalyst surface so long as the TOS exposure to a particular gas mixture was identical. Therefore, use of a single catalyst sample for complete TOS studies was valid.

**3.3.4 Effect of water vapor on the amount of hydrogen adsorbed on Pt/C in the absence of CO**

Figure 3.3 illustrates the hydrogen surface concentration on Pt/C at 80°C as a function of time-on-stream (TOS) exposure to H₂ and/or water vapor in the absence of CO. It shows that the steady-state, strongly-bound hydrogen surface concentration of the Pt/C catalyst treated with H₂ \([H / H]\) was ca. 321 \((\mu\text{mol H}) \, (g)^{-1}\), which is within the range of values obtained by static chemisorption (Table 3.2). Exposure of the catalyst to a mixture of both H₂ and water vapor \([H / H_w]\) (10%RH) resulted in an increase in the amount of exchangeable strongly-bound hydrogen by ca. 221 \((\mu\text{mol H}) \, (g)^{-1}\). Surprisingly, the amount of exchangeable hydrogen from water, in the absence of H₂, \([A / A_w]\) was the same, within experimental error, as the increase from the addition of water.
to H₂. [A / Aw] refers to the experiments where hydrogen surface concentration were measured after exposure only to water vapor (see Section 3.2.5).

**Figure 3.3** Variation of strongly-bound hydrogen surface concentration on Pt/C with TOS at various conditions and 80°C in the absence of CO.

### 3.3.5 Water uptake measurements for the carbon support and the Pt catalyst by TPD

The water uptakes of the carbon support and the Pt/C catalyst equilibrated at 80°C in a humidified mixture of H₂ [Hw] were also studied. It was found from TPD analysis that the total (strongly and weakly held) amounts of water adsorption on the carbon support and the Pt/C catalyst were 918 and 875 µmol H₂O g.carbon⁻¹, respectively. The
results imply that the addition of Pt does not cause an increase in water spillover to the support. The total amount of water sorption (weak and strong) on the Pt/C catalyst was equivalent to ca. 3% of the pore volume or ca. 0.15 ML surface coverage of the support, assuming the density of water is 1 g cm$^{-3}$ and the thickness of water monolayer on the catalyst is its critical diameter (0.5 nm), respectively.

3.3.6 Effect of pre-exposure to water vapor on the amount of hydrogen adsorbed in the presence of CO

Figure 3.4 shows the effect of water adsorption (at 10%RH) on the hydrogen surface concentration on Pt/C in the presence of 30 ppm CO. [H / HwC] refers to the co-fed experiments, where the Pt/C catalyst were pre-equilibrated with a mixture containing 1 atm P$_{H_2}$ in the absence of humidity at 80°C overnight before the catalyst was introduced to both water vapor and CO (30 ppm) in the presence of H$_2$ with the hydrogen surface concentration on Pt/C measured with TOS. [Hw / HwC] denotes the water-pre-exposure experiment, where the catalyst was pre-exposed to a 10%RH hydrogen mixture at 80°C overnight prior to the exposure to CO in H$_2$ with 10%RH. In Figure 3.4, a lower value of the initial hydrogen surface concentration is observed for the [H / HwC] experiment because the catalyst had not been exposed to water for TOS < 0 h. Thus, initially there was an increase in hydrogen surface concentration due to the presence of water vapor after TOS = 0. However, the profiles of hydrogen surface concentration after exposure to CO for these two experiments became identical after an introduction period of several hours, indicating that pre-exposure of Pt/C to water vapor does not appear to
have an effect on the resulting kinetics of CO adsorption (poisoning) in presence of water vapor.

![Graph showing the effect of water vapor on Pt/C poisoning by 30 ppm CO at 80°C.](image)

**Figure 3.4** Effect of water vapor (10%RH) on Pt/C poisoning by 30 ppm CO at 80°C.

3.3.7 *Effect of CO poisoning and its reversibility on hydrogen surface concentration in the presence/absence of H₂ and water vapor*

Figure 3.5 presents the effect of CO poisoning on the amount of hydrogen adsorbed on Pt/C at 0%RH or 10%RH and 80°C. It shows that the hydrogen surface concentrations of strongly-bound hydrogen on Pt/C catalysts not exposed to CO ([H / H], [Aw / Aw], and [Hw / Hw]) remained constant over 20 h but decreased with TOS exposure to 30 ppm of CO ([H / HC], [Aw / AwC], and [Hw / HwC]). This decrease in
the amount of hydrogen surface concentration measured due to H\(_2\) or H\(_2\)O adsorption, in the presence of CO, was almost certainly caused by the blocking of Pt surface sites by CO.

**Figure 3.5** Effect of CO exposure on the amount of strongly-bound hydrogen adsorbed on Pt/C at 80°C in the presence (10%RH) and absence of water vapor.

Figure 3.6 illustrates the hydrogen surface concentration on Pt during CO exposure and regeneration under various conditions at 80°C. The designation used in this section was slightly modified. The nomenclatures given before, between, and after “/” correspond to treatment conditions prior to TOS = 0 h, CO exposure conditions after TOS = 0 h, and regeneration conditions after TOS = 33 h, respectively. After the steady-state CO poisoning was obtained (TOS = 33 h), CO flow was stopped and regeneration was
initiated by flowing a gas mixture of H$_2$, water vapor, and/or Ar \{[H], [Hw], and [Aw]\} through the catalyst bed. In Figure 3.6, the filled and unfilled symbols illustrate the hydrogen surface concentration on Pt/C during 30 ppm CO exposure (TOS = 0-33 h) and regeneration phase (TOS = 33–97 h), respectively.

![Graph showing hydrogen surface concentration over time](image)

**Figure 3.6** CO poisoning and regeneration of Pt/C in the presence/absence of H$_2$ and water vapor (10%RH) at 80°C. (Filled symbols and unfilled symbols represent the hydrogen surface concentration on Pt/C exposed to 30 and 0 ppm CO, respectively.).

These results show that the presence of CO significantly affected the amount of exchangeable strongly-bound hydrogen on Pt/C regardless of whether the adsorbing gas consists of H$_2$ + H$_2$O, H$_2$, or just H$_2$O. The pseudo steady-state hydrogen surface
concentrations measured on Pt/C after CO exposure in the presence of only H\textsubscript{2} (no H\textsubscript{2}O, squares) and only H\textsubscript{2}O (no H\textsubscript{2}, stars) were ca. 96 µmol H g\textsuperscript{-1} and 131 µmol H g\textsuperscript{-1}, respectively. The pseudo steady-state hydrogen surface concentration measured on Pt/C after CO exposure in the presence of both H\textsubscript{2} and H\textsubscript{2}O (circles) was ca. 239 µmol H g\textsuperscript{-1}, which is the same, within experimental error, as the summation of the amount of exchangeable hydrogen contributed from H\textsubscript{2} and H\textsubscript{2}O adsorption individually and again exhibits the perfectly additive nature of the exchangeable hydrogen from the two species, even in the presence of CO. Also, it can be seen in Figure 3.6 that the kinetics of CO adsorption (reflected in the rate of decrease of the hydrogen surface concentration) at 10\%RH in the presence/absence of H\textsubscript{2} appeared to be slower than that at 0\%RH. Regeneration of the catalysts was initiated by stopping the flow of CO, which ultimately resulted in an increase in the amount of hydrogen surface concentration observed for all conditions. The steady-state hydrogen surface concentration of the catalyst regenerated in a flow of H\textsubscript{2} at 0\%RH [H / HC / H] was ca. 136 µmol H g\textsuperscript{-1}, which is in agreement with results obtained previously [11]. Regeneration of CO-poisoned Pt/C catalyst in a flow of H\textsubscript{2} at 10\%RH [Hw / HwC / Hw] resulted in a hydrogen surface concentration of ca. 345 µmol H g\textsuperscript{-1} at steady-state. It is clear that regeneration of the CO-poisoned catalysts in the presence of H\textsubscript{2} at 0\% or 10\%RH {[H / HC / H] and [Hw / HwC / Hw]} for long periods of time (64 h) yields incomplete recovery of the strongly-bound hydrogen uptake capacity and hydrogen surface concentration. In the absence of H\textsubscript{2}, [Aw / AwC / Aw] on the other hand, complete recovery in the strongly-bound hydrogen surface concentration (due to H\textsubscript{2}O) on Pt/C was observed after regeneration at 80\textdegree\textsuperscript{C} for
44 h. The combination of [H / HC / H] and [Aw / AwC / Aw] shown in Figure 3.6 (triangles) will be discussed in Section 3.4.2.

3.4 Discussion

3.4.1 The change in the total hydrogen surface concentration on Pt/C after exposure to water vapor (10%RH) in the absence of CO

It can be seen in Figure 3.3 that the total amount of strongly-bound hydrogen surface concentration on Pt/C exposed to [H / Hw] at steady-state was ca. 221 µmol H g⁻¹ higher than in the absence of any water vapor [H / H], which appeared to be essentially identical to the amount of strongly-bound hydrogen adsorbed on Pt/C (223 µmol H g⁻¹) after exposure to only water at 10%RH [A / Aw] in the absence of H₂. This direct increase in hydrogen surface concentration, attributed most likely to the (strong) adsorption of H₂O, appears to imply that, in the absence of any impurities, the adsorption of H₂ and H₂O on the Pt/C catalyst results in a total hydrogen surface concentration that is the summation of the amount of exchangeable strongly-bound hydrogen contributed by each species. In other words, the adsorption of H₂ and H₂O on the Pt/C catalyst would appear, at first glance, to take place on different sites such that the presence of H₂O does not have an effect on the chemisorption of H₂. While these results may seem surprising, the lack of effect from the adsorption of H₂O on H₂ chemisorption has been well documented in the literature [28-31]. Furthermore, the idea of heterogeneous sites on Pt surface for the adsorption of H₂ and H₂O has been proposed by Iida and Tamaru [30], who found that the activity of the exchange reaction between H₂O and D₂ on supported Pt
was similar regardless of whether the support is hydrophobic or hydrophilic. This suggests that the exchange reaction proceeds entirely on the Pt surface with the support having a negligible effect on the exchange activity.

The additional hydrogen surface concentration on Pt after exposure to [Hw] \{221 (\mu\text{mol H}) (g)^{-1}\}, observed in this study, was most likely due to the isotopic exchange of H$_2$O and D$_2$ on surface Pt during the switch to D$_2$ for HDSAP measurements. This is because it has been reported that the complete exchange reaction between H$_2$O and D$_2$ on surface Pt can take place rapidly even at 100 K [32], and water dissociation on a Pt surface is not thermodynamically favorable [14, 33] under the conditions of this study. Moreover, as mentioned previously, during the D$_2$ switch in HDSAP measurements, the MS signal intensities for the H$_2$O and HDO peaks were found to be minor compared to those for H$_2$ and HD. This observation implies that under these conditions (P$_{D_2}$ = 1 atm, P$_{Ar}$ = 1 atm, 80$^\circ$C), Pt-HDO and Pt-H$_2$O were still remaining on the catalyst surface after the isotopic exchange reaction. In order to prove this assumption, D$_2$ TPD measurement were performed after the switch to D$_2$. At the end of HDSAP measurements, flow was switched to 30 sccm 5% D$_2$ in Ar mixture and allowed to stabilize. Then, the temperature was ramped at rate of 10$^\circ$C min$^{-1}$ from 80$^\circ$C to 400$^\circ$C. It was found that the MS signal intensity for HDO started to increase at 90$^\circ$C, reaching a maximum at 200$^\circ$C, and the intensity for H$_2$O decreased corresponding to the increase in the intensity of HDO. The HDSAP and TPD results suggest that Pt-HDO and Pt-H$_2$O exist on the catalyst under the conditions studied (80$^\circ$C) and the measured hydrogen surface concentration is derived from hydrogen adsorbed on Pt and/or Pt-H$_2$O.
3.4.2 Hydrogen surface concentration on Pt/C after CO exposure and after regeneration

The CO surface coverage on Pt ($\theta_{CO}$) obtained from the hydrogen surface concentration was calculated by Eq. (10):

$$\theta_{CO} = \frac{(Surface\ H)_{0\%RH,\ No\ CO} - (Surface\ H)_{SS,\ 30\ ppm\ CO,\ Adj\ for\ %RH}}{(Surface\ H)_{0\%RH,\ No\ CO}}$$

(10)

Because it is more meaningful to calculate the coverage of CO on the Pt surface atoms, $(Surface\ H)_{0\%RH,\ No\ CO}$ denotes the hydrogen surface concentration measured on Pt/C in the absence of any H$_2$O or CO such that the amount of exchangeable hydrogen is equal to the amount of available surface Pt (assuming H:Pt is 1:1). Similarly, due to the overestimation in the amount of available Pt surface atoms (based on static H$_2$ chemisorption in the absence of H$_2$O and on TEM results) caused by the additional exchangeable hydrogen from H$_2$O, any meaningful calculation of CO surface coverage must adjust for that extra hydrogen surface concentration. Hence, due to the additive nature of hydrogen surface concentration from H$_2$ and H$_2$O, $(Surface\ H)_{SS,\ 30\ ppm\ CO,\ Adj\ for\ %RH}$ denotes the hydrogen surface concentration of Pt/C at steady-state in the presence of 30 ppm CO that has been adjusted (reduced) for the extra surface hydrogen contributed by the H$_2$O.

The steady-state CO surface coverage of Pt subjected to a dry hydrogen stream [H / HC] (see Figure 3.6) was calculated to be ca. 0.70 monolayer (ML), which is consistent with the maximum CO surface coverage of Pt in the presence of even low concentrations of H$_2$ (< 9.87 x 10$^{-6}$ atm) reported in surface science studies (0.5 – 0.79 ML) [22, 25, 34, 35]. The pseudo-equilibrium $\theta_{CO}$ on Pt/C exposed to a humidified hydrogen mixture [Hw
was calculated to be ca. 0.66 ML, after taking the additional amount of exchangeable hydrogen from H₂O into account. Considering the low activity of Pt for the dissociation of H₂O at the experimental conditions employed, this similarity in CO surface coverage on Pt surface in the absence and presence of water vapor suggests that the water has little or no effect on the poisoning behavior of CO on Pt, at least for Pt/C. However, if a secondary metal was added to the catalyst that could dissociatively adsorb H₂O and oxidize CO to CO₂, the presence of H₂O vapor would be beneficial in diminishing the poisoning effect of CO on Pt.

Based on the strongly-bound hydrogen surface concentrations determined for Pt/C individually exposed to a stream containing H₂ and H₂O with 30 ppm of CO, a comparison between the experimental and the estimated values of the amounts of strongly-bound hydrogen adsorbed on Pt/C during exposure to 30 ppm CO, H₂, and H₂O can be made. If we assume that the effects of CO and H₂O are additive, the estimated values {combination of [H / HC / H] and [Aw / AwC / Aw]} can be obtained by adding the amounts of hydrogen adsorbed on Pt/C exposed to a stream containing H₂ and CO [H / HC/ H] with those exposed to a stream containing H₂O and CO [Aw / AwC / Aw]. It can be observed in Figure 3.6 that these effects do seem to be additive in terms of steady-state amounts (compare circle data with triangle data). However, the profile for the actual experimental results [Hw / HwC / Hw] decreased with a slower rate during exposure to CO and increased with a faster rate during regeneration than the combined (i.e., summed) values during the CO-poisoning phase (TOS = 0-33 h) and the regeneration phase (TOS = 33-97 h), respectively. The steady-state surface coverages of
CO on Pt, after regeneration in a H$_2$ stream vs. a mixture of both H$_2$/H$_2$O, were found to be ca. 0.56 and 0.54 ML, respectively, after taking into account the extra hydrogen surface concentration due to adsorbed water. While the estimated total (weak and strong) coverage of water on the entire catalyst surface was relatively low (0.15 ML), the majority of the water was most likely in the pore structures of the carbon support due to pore condensation. Given this and the fact that most of the Pt particles were also in these pore structures, it can be speculated that the slower rate of CO poisoning in the presence of water may be attributed to the water acting as a barrier, through which the CO must diffuse in order to adsorb on the Pt surface sites. Although competitive adsorption of water with CO could also be argued as a cause for the slower rate of CO poisoning, the fact that the steady-state surface coverages of CO on Pt were the same in the presence and absence of water vapor suggests that the slower rate of diffusion of CO, through the water condensed in the pores of the carbon support, to be the more likely case. During regeneration, it is possible that the co-adsorption of water on Pt weakened the strength of Pt-CO bonding, resulting in a slightly faster CO desorption rate. These results also suggest that, even in the presence/absence of CO, the effects of H$_2$ and H$_2$O on the hydrogen uptake capacity of Pt/C at steady state are additive and the sites for H and H$_2$O adsorption could be somehow different. There are two possible explanations for this phenomenon: (1) H$_2$ adsorption on Pt sites and H$_2$O adsorption (strong and weak) on the carbon support, or (2) H$_2$ and H$_2$O adsorption (strong) on two different types of Pt sites and H$_2$O sorption (weak) on the carbon support.
The first hypothesis is not likely. In addition to what was found by Iida and Tamaru [30], results from static CO chemisorption show that the uptake of CO by the carbon support is negligible (∼0 µmol CO g⁻¹), suggesting that CO selectively adsorbed on/poisoned only Pt. Therefore, the decrease in the hydrogen (from H₂O) surface concentration on Pt after exposure to CO in a humidified stream in the absence of H₂ [Aw / AwC / Aw] (see Figure 3.5 and Figure 3.6) invalidates the first hypothesis.

While it is known that hydrogen can dissociatively adsorb on both flat and stepped Pt surfaces, a molecular beam study of the H₂-D₂ exchange reaction on Pt(111) and Pt(332) crystal surfaces [36] has found that, in the absence of water vapor and CO, the rate of H₂-D₂ exchange on the corner/edge terraces of the Pt surface is ca. 7 times higher than that on the planar surfaces. Given that the rate-limiting step of the H₂-D₂ exchange reaction is the dissociative adsorption of molecular hydrogen [37], the above results suggest the preferential adsorption of hydrogen on stepped Pt sites. Additionally, results from TPD experiments of hydrogen desorption from Pt(533) and calculation of the dissociative sticking probability for hydrogen on the (111) and (100) terraces of the Pt(533) crystal indicate that direct dissociation of molecular hydrogen takes place preferentially on step sites [38]. However, this does not mean that H₂ cannot adsorb on the planar surfaces of Pt, and, of course, rapid surface diffusion of H atoms would ensure that all Pt surface atoms would be rapidly covered, as evident from static chemisorption results. The adsorption of H₂O on Pt, on the other hand, has also been shown via scanning tunneling microscopy (STM) on an imperfect Pt(111) crystal surface [39] and TPD of adsorbed H₂O on a Pt(533) single crystal surface [40] to also preferentially
adsorb on stepped sites. In fact, the above TPD results suggest a stabilization of the water monolayer by the stepped sites [40]. This is important because if the above surface science and static hydrogen chemisorption results are true, then there exists no evidence suggesting that the strong adsorption of H₂ and H₂O occurs on different types of Pt sites, thus, invalidating the second hypothesis. The problem, however, is that, in addition to the additive nature observed from the hydrogen surface concentration measurements, results from DFT calculations by Olsen et al. [41] also suggest that the presence of H₂ does not appear to block adsorption sites for H₂O. So if the H₂ and H₂O can both adsorb on all available Pt surface sites, how does one explain the seemingly lack of interaction between the two species? A plausible solution to this question may lie not with the adsorption (strong) of the individual species, but with their interaction on the Pt surface.

TPD and reflective absorption infrared spectroscopy (RAIRS) results on the interaction of water and deuterium on this stepped Pt(533) crystal surface indicate that deuterium destabilizes adsorbed water via an electronic effect [42]. At high enough coverages of deuterium, this causes the surface to be hydrophobic. Prior to the adsorption of deuterium, adsorption of water was observed on both the (111) terraces and (100) steps of the Pt(533) surface. As deuterium was introduced, the adsorption of deuterium atoms at the step edges began to disrupt the stability of water on the steps. As the concentration of adsorbed deuterium increased, the stepped sites became saturated and deuterium started to adsorb on the terrace sites. Increasing deuterium surface concentration on the terraces appeared to induce hydrophobicity to the surface and, at low
coverages of water, the water molecules were repelled toward the steps to form so-called amorphous solid water (ASW) structures at the (100) step and (111) terrace interface on Pt(533) [42]. While exchange between adsorbed deuterium and H$_2$O could occur on both terraces and steps, this shift in concentration of water molecules to the step-terrace interfacial sites on the hydrophobic, deuterium-saturated Pt(533) crystal surface also appeared to shift the D$_2$-H$_2$O exchange process toward the stepped sites. This induction of a hydrophobic surface by the adsorbed deuterium may explain the additive nature observed in the present study for the strongly-bound hydrogen surface concentrations and the lack of interaction observed between the two species (H$_2$ and H$_2$O). Adsorption of CO on the stepped sites, on the other hand, has been shown to be able to sterically block water adsorption [40], thus decreasing the hydrogen surface concentration. However, while water does not appear to have much of an equilibrium effect on the adsorption/poisoning of Pt by CO, its presence apparently helps in the faster desorption of CO during regeneration of the poisoned Pt/C catalyst, probably due to electronic interactions between adsorbed (strong) H$_2$O and CO. The weakly-bound H$_2$O on the carbon support should not contribute in any way to the extra hydrogen surface concentration observed or its additive nature since it would be removed during the purge part of the HDSAP measurement.

It is important to note that this study used higher ppm levels of CO than expected in an operating fuel cell to create a greater effect of the impurity that would be more easily investigated. The degree of CO poisoning (e.g., kinetics, steady-state $\theta_{CO}$) observed in this study should be more severe than in a real fuel cell because of (a) the
high CO impurity level used (30 ppm) and (b) the fact that, during fuel cell operation, the anode potential enhances CO electro-oxidation and helps clean the Pt surface during fuel cell operation [14]. It is unlikely that oxidative removal of CO$_{ads}$ by OH$_{ads}$ occurs during HDSAP measurements because CO oxidation is not thermodynamically favorable [14, 43, 44] at the low potential (in the absence of an electric current) conditions extant in this study. The slower kinetics of CO poisoning and faster kinetics of CO desorption on the hydrogen uptake capacity in the presence of water vapor observed in this study suggest that higher CO tolerance would be expected for PEMFCs operating at higher relative humidity.

The disagreement between the results in the literature due to the limitation of electrochemical techniques has also been discussed. Although only partial recovery was found in this study (see Figure 3.6), under electrochemical conditions, complete recovery in performance of CO-poisoned PEMFCs has been reported after the fuel cell was operated in a neat H$_2$ for a short period of time (5-30 min) [9, 14, 21, 45]. The difference in the results can be attributed to two things: (1) electrochemical oxidation of some CO and (2) limitation of electrochemical techniques to identify a partially CO-poisoned Pt surface if sufficient Pt sites are regenerated to ensure that the hydrogen oxidation reaction (HOR) is equilibrium limited. It is likely that after regeneration in a neat H$_2$ stream for a certain period of time, there are enough unpoisoned Pt sites to obtain equilibrium H$_2$ dissociation due to the high Pt-loadings (20-40 wt% Pt) used in the conventional anode catalyst layer [11]. Therefore, the complete effect of CO poisoning on the catalyst cannot
be observed electrochemically. However, the hydrogen surface concentration measurement performed in this study does not have such a limitation.

3.5 Conclusions

It is known that CO is one of the most harmful impurities for PEMFC performance because of its effect on the hydrogen oxidation reaction (HOR) on the catalyst at the anode. In this study, direct measurements of the strongly-bound hydrogen surface concentration on Pt/C, used as a typical anode catalyst, exposed to CO and water vapor were performed via an H₂-D₂ switch with an Ar purge (HDSAP technique). Surprisingly, hydrogen surface concentration results from the co-adsorption of H₂ and H₂O on Pt/C showed that the total amount of strongly-adsorbed surface hydrogen to be the sum of the exchangeable amount of hydrogen attributed to each individual species. This additive nature observed for the strongly-bound hydrogen surface concentration associated with H₂ and H₂O on Pt/C was consistent regardless of whether in the presence/absence of CO, which suggests that the adsorption (strong) of H₂ and H₂O occurs entirely on the Pt and may be due to the induction of a hydrophobic Pt surface as suggested by surface science results.

It was found that the amount of strongly-bound hydrogen adsorbed on the Pt surface decreased with TOS CO exposure at both 0% and 10%RH. While the presence of water vapor helped to decrease the kinetics of CO adsorption during TOS, it only affected the steady-state CO surface coverage of Pt (θ_CO) at most slightly, as the steady-state θ_CO values were found to be 0.70 and 0.66 ML for Pt catalysts exposed to 30 ppm CO at 80°C.
in the presence of H\(_2\) (P\(_{H2}\) = 1 atm) and H\(_2\)/H\(_2\)O (P\(_{H2}\) = 1 atm and P\(_{H2O}\) = 0.023 atm), respectively. These experimental results suggest that the presence of H\(_2\)O has little effect on the adsorption on/poisoning of Pt/C by the CO at steady-state. However, the slower rate of poisoning of Pt/C by CO, observed in the presence of water, might indicate a decrease in the rate of diffusion of CO to the Pt surface, due to the condensation of water in the pores. On the other hand, the slower rate of diffusion of CO away from the Pt surface would not be observed by the hydrogen surface concentration measurement, as long as the CO does not re-adsorb on other Pt surfaces.

Reversibility of CO poisoning of the Pt catalyst during regeneration in gas containing H\(_2\), water, or a combination of H\(_2\)/H\(_2\)O was also investigated. It was found that the kinetics of CO poisoning reversibility were significantly faster when the catalyst was regenerated in a humidified H\(_2\) stream than in a dry H\(_2\) stream. This increase in the rate of CO desorption in the presence of water may be due to electronic interactions between CO and strongly-bound H\(_2\)O on the Pt surface. Accordingly, greater CO tolerance is expected for PEMFCs operating at high relative humidity due to a slower rate of CO poisoning and faster rate of CO desorption during regeneration (or after removal of CO from the gas stream). After regeneration, the remaining CO surface coverages on Pt treated in a H\(_2\) stream [H / HC / H] vs. a mixture of both H\(_2\)/H\(_2\)O [Hw / HwC / Hw], after accounting for the extra hydrogen surface concentration due to adsorbed water, were ca. 0.56 and 0.54 ML, respectively.

The quantitative results of hydrogen surface concentrations on Pt/C in the presence/absence of water vapor, reported for the first time in this work, provide an
enhanced fundamental understanding of the individual and combined effects of CO, water vapor, and H₂ on the amount of strongly-bound hydrogen on a Pt/C catalyst at typical fuel cell conditions.

3.6 References


CHAPTER FOUR

THE EFFECT AND SITING OF NAFLON® IN A Pt/C PEM FUEL CELL CATALYST

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This paper explores the effect and siting (location) of Nafion on Pt/C as exists in a PEM fuel cell catalyst layer. The addition of 30 wt% Nafion on Pt/C (Nfn-Pt/C) resulted in a severe loss of BET surface area by filling/blocking the smaller pore structures in the carbon support. Surprisingly, the presence of this much Nafion appeared to have only a minimal effect on the adsorption capability of either hydrogen or CO on Pt. Kinetic measurements of the H$_2$-D$_2$ exchange reaction (related to hydrogen activation) on Pt/C and Nfn-Pt/C in the presence of CO showed the $E_a$ for both catalysts to be the same. However, the presence of Nafion doubled the amount of time required to purge most of the gas-phase and weakly-adsorbed hydrogen molecules away from the catalyst during hydrogen surface concentration measurements. This strongly chemisorbed surface hydrogen was determined by a H$_2$/D$_2$ switch and exchange procedure. Nafion had an even more pronounced effect on the reaction of a larger molecule like cyclopropane. Results from the modeling of cyclopropane hydrogenolysis in an idealized pores suggest that partial blockage of only the pore openings by the Nafion for the meso-macropores is sufficient to induce diffusion limitations on the reaction. The facts suggest that most of the Pt particles are in the meso-macropores of the C support, whereas Nafion is present
primarily on the external surface of the C where it blocks significantly the micropores but only partially the meso-macropores.

4.1 Introduction

Proton exchange membrane fuel cells (PEMFCs) have been viewed by many as one of the most viable sources of clean energy available. Characteristics of PEMFCs, such as fast startup, high current density, and zero polluting emissions, render the technology ideal for automotive purposes [1].

Utilizing the redox reaction between hydrogen and oxygen to produce power, the general composition of a PEMFC consists of a proton transport membrane sandwiched in-between an anode and cathode catalyst layer. With the hydrogen oxidation reaction (HOR) occurring at the anode, oxygen reduction reaction (ORR) at the cathode, and the electrons produced conducted via an external circuit, fast transport of protons from the anode to the cathode depends almost entirely on the characteristics of the proton transport media utilized. For this purpose, most commercial PEMFCs favor a poly(perflourosulfonic acid) polymer, most commonly known as Nafion®, as the proton transport media due to their high proton conductivity, water uptake, and durability [2]. This Nafion constitutes the membrane as well as a part of the catalyst layers. In those layers it is present on the catalyst (typically Pt/C) in relatively large amounts (~30 wt%).

Before the protons produced from the HOR can reach the Nafion membrane, the activated hydrogen atoms must first be transported from the Pt site to a nearby Nafion
cluster. This first transport step can take place either directly, if the Nafion is in direct contact with the Pt particle, or by diffusion on the carbon support. For this purpose, it is very advantageous to have high loadings of Nafion in the catalyst layer of a PEMFC to ensure fast transport of activated hydrogen atoms from the Pt to local Nafion clusters and then to the Nafion membrane. While high loadings of Nafion in the catalyst are important for fast proton transfer, one would hypothesize a negative effect of Nafion content on the activity of Pt for the HOR, i.e., by blocking Pt surface atoms via physical and/or chemical interactions, thereby preventing them from adsorbing and activating hydrogen.

To date, possible negative impacts of high loadings of Nafion on Pt activity for hydrogen activation have been studied via electrochemical techniques, such as cyclic voltammetry (CV) and rotating disk electrodes (RDE), and have only identified the large amounts of Nafion present to be effectively impeding HOR by obstructing the flow of feed gas and shifting the reaction from being kinetically controlled to being controlled by the diffusion of reactant gases to the catalysts [3-5]. While rate measurements were presented in these studies, due to the large amounts of Pt employed and the extremely fast reaction rate of HOR on Pt in the absence of any impurities, it is unclear whether the results can really be interpreted kinetically and were not affected by the H₂ activation reaction being at equilibrium. Furthermore, the electrodes used for the rotating disk voltammetry studies were immersed in a H₂-saturated solution, generally H₂SO₄, with H₂-gas passing through the solution during the analysis. Such an environment may create adsorption/transport characteristics of the feed gas different than that in a fuel cell.
Finally, high rotation speeds in the RDE exceeding 10,000 rpm have been known to create turbulence in the solution and cause unknown contributions of migration and cavitation effects [6]. These sources of extraneous error combined with a lack of adequate kinetic data demand a further look at whether the impregnation of such high weight loadings of Nafion on the catalyst particles in the catalyst layer of a PEMFC has an effect on the properties of Pt/C and in particular on the hydrogen activation capability of Pt.

As a continuation of our previous work, where the fundamental effects of CO poisoning on hydrogen activation on Pt/C catalysts were investigated utilizing the H$_2$-D$_2$ exchange reaction [7], research was carried out to investigate the interaction of Nafion on the properties of Pt in a commercial Pt/C catalyst commonly used in fuel cells. In addition to general catalyst characterization by BET, TEM, and static H$_2$/CO chemisorption, experiments were performed utilizing the H$_2$-D$_2$ exchange reaction for kinetic measurements of hydrogen activation in the presence of CO (a catalyst poison). In the absence of CO, the exchange reaction was at equilibrium and kinetic measurements could not be made. A modified H$_2$ to D$_2$ switch procedure, H$_2$-D$_2$ switch with Ar purge (HDSAP), was also used to measure in-situ the surface concentrations of hydrogen and CO with time-on-stream (TOS). Furthermore, a structure sensitive reaction, cyclopropane hydrogenolysis, was employed as a characterization technique to magnify the obstructing effect, if any, of surface Pt sites by Nafion. All experimental results presented in this paper were obtained at conditions where reaction equilibrium was not a contributing factor. In addition, unlike the electrochemical studies, all reaction results
were obtained for the catalysts exposed only to the gas-phase, where solution effects can be ignored.

4.2 Experimental

4.2.1 Catalyst Preparation

A commercial Pt fuel cell catalyst, nominal 20 wt% Pt supported on carbon black (Pt/C), was purchased from BASF. It was confirmed by BASF that the carbon black support (Vulcan XC-72) was purchased in-bulk from Cabot Co. and used directly for the synthesis of the Pt/C catalyst.

Nafion supported on Pt/C (Nfn-Pt/C) catalysts were prepared via incipient wetness impregnation of the commercial 20 wt% Pt/C with a Nafion ionomer solution (LQ-1105, DuPont, 5 wt% Nafion) to give a target weight loading of 30 wt% for the Nafion. The 30 wt% loading of Nafion has been shown in the literature to be the optimum Nafion content in a PEMFC catalyst layer [8-11]. The impregnated material was dried at 90°C overnight in a static air oven, crushed, and sieved to obtain a particle size of 60 – 150 µm. The catalyst was then stored in the dark prior to use. Nominal Pt composition was confirmed via elemental analysis (performed by Galbraith Laboratories) for both Pt/C and Nfn-Pt/C.

In order to verify all the possible sources of surface hydrogen in Nfn-Pt/C, to be discussed later, separate samples of Nfn-Pt/C were exchanged with either NaCl to neutralize the protonated sulfonic sites (SO$_3^-$ - H$^+$) or exposed to 5000 ppm NH$_3$ gas to
form (SO$_3^-$ - NH$_4^+$). The Na$^+$-form of Nfn-Pt/C was prepared by ion-exchanging ca. 500 mg of Nfn-Pt/C with 30 mL of an aqueous solution of 0.1 M NaCl under constant agitation at room temperature for 2 days. The duration of the exchange process was adequate due to the solution containing only Na$^+$ ions. The exchanged sample was then filtered and rinsed 5 times with warm (70-80°C) deionized water to remove excess solution. The resulting sample was dried overnight, crushed, sieved (60 – 150 µm), and kept in the dark prior to use. The NH$_4^+$-form of Nfn-Pt/C was obtained by exposing the catalyst to 5000 ppm NH$_3$ for 2 h after reduction in H$_2$ at 80°C for 3 h. Due to the irreversible poisoning of Nafion by NH$_3$ [12], the high concentration of NH$_3$ was employed to ensure a fast and complete conversion of all available sulfonic sites to the ammonium form. As will be shown in section 4.3.3, no effect on the surface hydrogen was observed from the treatment of Pt/C catalyst to NaCl and/or NH$_3$ gas using the same methodologies described.

4.2.2 Characterization Methods

4.2.2.1 BET

BET surface area, pore size, and pore volume measurements were carried out with a Micromeritics ASAP 2020. Samples of Pt/C and Nfn-Pt/C were degassed under vacuum (10$^{-3}$ mm Hg) at 110°C for 4 h prior to analysis. Results were obtained from N$_2$ adsorption isotherms at -196°C.
4.2.2.2 Static H₂/CO Chemisorption

Chemisorption experiments using H₂ and CO were performed at 35°C and 80°C in a Micromeritics ASAP 2010 equipped with a chemisorption controller station. Due to the structural instability of Nafion at temperatures of 120°C and above, catalysts were first reduced in H₂ at 80°C for 3 h followed by an evacuation at 80°C (10⁻⁵ mm Hg) for another 3 h prior to the start of the analysis. Temperature programmed reduction (TPR) results had shown the Pt to be fully reduced at these conditions. After evacuation, the temperature was then adjusted to the specified chemisorption temperature and the H₂ or CO isotherms were obtained from 50–450 mm Hg at increments of 50 mm Hg. Volumetric uptakes of CO or H₂ on the catalysts were determined from the total adsorption isotherm of the specified gas by extrapolating the higher pressure region of the total isotherm, which was linear, to zero pressure. These values were then used in determining total Pt surface atom concentration (Pt₅) and metal dispersion by assuming stoichiometric ratios of 1:1 for CO:Pt₅ and H:Pt₅. Correlation with TEM has shown that this permits a reasonable estimation of metal particle size for Pt/C [7]. Calculation of average Pt particle size for Pt/C and Nfn-Pt/C were carried out using the metal dispersion calculated from the chemisorption results [7].

4.2.2.3 TEM and XRD

Transmission electron microscopy (TEM) images of Pt/C and Nfn-Pt/C were obtained using a TEM-Hitachi 9500, which offers 300kV high magnification TEM and is designed for atomic resolution. Preparation of copper sample grids is explained in detail
elsewhere [7]. Approximate Pt particle sizes of the catalysts were obtained by averaging diameters of 100+ particles from the TEM images. The results were further confirmed via X-ray Diffraction (XRD) (Scintag XDS 2000 powder diffractometer equipped with Cu Kα radiation) on as-received and reduced Pt/C and Nfn-Pt/C (80°C in H2 for 3 h) with a scanning range from 20°–85° and a step-size of 0.02°/min.

4.2.2.4 Surface Hydrogen Concentration Measurements

The method, H2-D2 switch with an Ar purge (HDSAP), was developed in our previous work [7] for determining in-situ hydrogen surface concentration on Pt. The use of HDSAP is preferred over other surface concentration measurements, such as TPD, due to the non-destructive nature of the methodology and its ability to obtain TOS measurements. This is especially important for Nfn-Pt/C due to the thermal instability of the polymer at temperatures higher than 120°C. Further explanation of the details and assumptions regarding HDSAP can be found elsewhere [7].

HDSAP measurements were initiated by flowing a gas mixture comprised of H2/Ar (50:50) at 100 cm³ min⁻¹ (sccm) for 30 min (exposure phase). The H2 was then turned off and 50 sccm of Ar was passed through the differential, plug flow reactor for 30 min or 50 min (purge phase) for Pt/C or Nfn-Pt/C, respectively. This was done to purge as much of the gas-phase or weakly adsorbed H2 from the catalyst as possible. In the case of Nfn-Pt/C, a longer purge time was required due to the addition of high weight loadings of Nafion (see Section 4.3.3). After the purge phase, a flow of 50 sccm of D2 (along with the 50 sccm of Ar) was introduced to the catalyst, resulting in two mass
spectrometer signals being observed for hydrogen-containing species (H₂ and HD). The amount of H₂ and HD were calculated by integrating the area under the peaks (signal vs. time) and using the area obtained from a pulse of known quantities of H₂ and HD via a 6-port valve equipped with a 2 mL sample loop as calibration. Total surface concentration of hydrogen was calculated by adding the amount of hydrogen (H) in H₂ and HD, as given by the equation below:

\[
\text{Surface H (μmol/g cat)} = \text{μmol HD/g cat} + 2 \times \text{μmol H₂/g cat}
\]

4.2.2.5 Cyclopropane Hydrogenolysis

In order to better determine whether or not the high weight loading of Nafion was blocking surface Pt atoms via either physical and/or chemical interactions, a surface sensitive reaction, cyclopropane hydrogenolysis, was performed on 1 mg and 2.5 mg of Pt/C and Nfn-Pt/C, respectively, at 30°C and 1 atm utilizing a conventional plug flow, micro-reactor system similar to the one described in reference [7]. The different amounts of Pt/C and Nfn-Pt/C used were based on the individual Pt loading such that the amount of Pt is kept the same. The catalyst was diluted uniformly with 39 mg and 37.5 mg of XC-72 for Pt/C and Nfn-Pt/C, respectively, to achieve a catalyst bed of ca. 1 cm in thickness. Prior to reaction, catalysts were first reduced in 100 sccm of H₂/Ar (50:50) for 3 h at 80°C and 1 atm, after which the temperature was decreased from 80°C to 30°C. Once the temperature was stable at 30°C, reaction was initiated by flowing a gas mixture of C₃H₆:H₂:Ar (1:49:150) (total flow = 200 sccm) through the catalyst bed and allowing
it to stabilize for 5 min before injecting the gas effluent into a Varian C gas chromatograph (GC) equipped with an FID detector for analysis. The FID was connected to a Restek RT-QPLOT column (30 m, 0.53 mm ID), capable of separating C₁–C₇ hydrocarbons. Due to the high activity of Pt for cyclopropane hydrogenolysis [13], low amounts of catalysts and a low partial pressure of C₃H₆ in the feed stream were required to achieve close to differential conditions for kinetic analysis. Variation of space velocities or particle sizes of the catalyst showed no change in reaction rate, indicating the lack of external and internal mass transfer effects, respectively. The apparent activation energy of cyclopropane hydrogenolysis on Pt/C from Arrhenius plots was found to be ca. 11.6 kcal mol⁻¹, which is well within the 8 – 12 kcal mol⁻¹ range reported by Kahn et al. [14], and confirms, along with the linearity of the Arrhenius plot, the absence of mass or heat transfer effects on the rate of reaction measurements for Pt/C, the reference catalyst.

4.2.3 H₂-D₂ Exchange Reaction

The H₂-D₂ exchange reaction was chosen as the model reaction for the HOR primarily because both reactions share the same rate-limiting step, the dissociative adsorption of hydrogen. Furthermore, as shown by Ross and Stonehart [15], for the temperature range of 30–80°C, the first-order rate constants for H₂-D₂ exchange on Pt and electrochemical hydrogen oxidation are in close agreement with each other. Thus, not only is the H₂-D₂ exchange reaction a good probe reaction for hydrogen activation, it is
also a very good model reaction for the electrocatalytic oxidation of hydrogen on Pt, within the temperature range specified.

Using a conventional plug flow, micro-reactor system pressurized at 2 atm, the catalyst samples were pretreated at 80°C in 100 sccm of H₂:Ar (50:50) gas mixture for 3 h. A detailed explanation and drawing of the experimental apparatus used for reactions involving H₂-D₂ exchange can be found elsewhere [7]. In order to keep the amount of Pt constant for comparison purposes, H₂-D₂ exchange rate measurements were obtained with catalyst samples of 5 mg Pt/C (having 17.5 wt% Pt) and 6.4 mg Nfn-Pt/C (having 13.7 wt% Pt) mixed with 35 mg and 33.6 mg of XC-72, respectively, to achieve a bed length of ca. 1 cm in thickness. Due to the high activity Pt exhibits for H₂-D₂ exchange, in addition to the low amounts of catalyst used, exposure of the catalysts to 30 ppm CO was done as a means to shift the exchange reaction away from equilibrium and into differential conversion as preferred for kinetic analysis.

After pretreatment, a gas mixture of H₂:Ar (50:50) containing 30 ppm CO was flowed over the catalyst at 80°C for 12 h to achieve CO adsorption/desorption equilibrium such that no further change in HD signal was observed (steady-state). After achieving steady-state, measurements of the apparent activation energies (Eₐ) were started by flowing a reactant gas mixture at 80°C and 2 atm comprised of H₂:D₂:Ar (25:25:50), still containing 30 ppm CO, over the catalyst for 15 min, with the effluent gas (comprised of the reactants H₂ and D₂, the product HD, and the inert Ar) being analyzed online with a Pfeiffer Vacuum mass spectrometer (MS). To obtain the MS signals of H₂ and D₂ in the absence of the catalyst for the purpose of calculating the exchange
conversion, the flow was switched to reactor bypass for 5 min. The exchange conversion for H$_2$ or D$_2$ was obtained via Eq. (2) using the H$_2$ (m/z = 2) and D$_2$ (m/z = 4) MS signals in the presence and absence of catalyst:

\[
\text{Conversion (\%)} = \frac{(H_2 \text{ or } D_2 \text{ Signal})_{N_0 \text{ Cat}} - (H_2 \text{ or } D_2 \text{ Signal})_{Cat}}{(H_2 \text{ or } D_2 \text{ Signal})_{N_0 \text{ Cat}}} \tag{5}
\]

Under differential conditions, reaction rates were calculated by multiplying the measured conversion with the initial molar flow rate of hydrogen and dividing by the weight of Pt in the catalyst bed.

In order to determine the apparent activation energy, $E_a$, the temperature was then decreased to 70°C, where the conversion was again obtained after reaching steady-state. This process was repeated for 60°C, 50°C, 90°C, and finally at 80°C again. The rate obtained at 80°C at the beginning of the experiment was the same as the rate measured at 80°C at the end of the experiment indicating that no deactivation occurred during the rate measurements. Similar to the cyclopropane hydrogenolysis experiments, variation of space velocities or particle size of catalyst showed no change in reaction rate, indicating the lack of external and internal mass transfer effects, respectively. The apparent activation energy of H$_2$-D$_2$ exchange on Pt/C, the reference catalyst, in the presence of CO from Arrhenius plots was found to be ca. 20 kcal mol$^{-1}$, the expected value [7], and confirms the absence of heat transfer effects on the rate of reaction measurements.
4.3 Results and Discussion

4.3.1 Catalyst Characterization

4.3.1.1 BET

BET surface area, pore size, and pore volume results for the carbon support (XC-72) were 225 m$^2$ g$^{-1}$, 16.4 nm, and 0.63 cm$^3$ g$^{-1}$, respectively, which correspond very well with literature values [16, 17]. While the addition of Pt to the carbon support (performed by BASF) did little to affect the average pore size (15.9 nm), reductions in the BET surface area (to 170 m$^2$ g$^{-1}$) and pore volume (to 0.44 cm$^3$ g$^{-1}$) were observed. This indicates that significant amounts of the Pt particles were likely situated in the pore structure rather than the surface of the carbon support.

Impregnation of Pt/C with Nafion resulted in a reduction of BET surface area and pore volume from 170 m$^2$ g$^{-1}$ and 0.44 cm$^3$ g$^{-1}$ to 38 m$^2$ g$^{-1}$ and 0.28 cm$^3$ g$^{-1}$, respectively, while increasing the average pore size to 32.7 nm. Due to the fact that the majority of a support’s surface area comes from its pore structure, this severe reduction in BET surface area suggests a filling/blocking of many of these pores by the Nafion, especially the smaller pores, while the slight reduction in pore volume suggests that the larger pores, which contribute most to pore volume were relatively open. Further analysis of pore size distribution for XC-72, Pt/C, and Nfn-Pt/C (Figure 4.1), based on the desorption differential distribution calculated by the Barrett-Joyner-Halenda (BJH) method [18, 19],
confirms, more or less, a substantial filling/blocking of the smaller pores by Nafion while the larger sized pores appears to be less significantly blocked.

![Figure 4.1 Pore size distributions for XC-72, Pt/C, and Nfn-Pt/C.](image)

4.3.1.2 Elemental Analysis

Elemental analysis results for Pt/C and Nfn-Pt/C from Galbraith Laboratories showed Pt loadings of 17.3 wt% and 13.7 wt%, respectively, and sulfur contents of 0.5 wt% and 1.2 wt%, respectively. The amount of sulfur obtained for Pt/C is similar to that
of the carbon support (XC-72). While the residual sulfur (ca. 0.5 wt%) in the Pt/C is most likely due to the vulcanization process used in producing the activated carbon support, the additional sulfur obtained for Nfn-Pt/C (ca. 0.7 wt%) can be directly attributed to the sulfonic sites present in the polymer. Calculation of Nafion-loading based on the sulfur content shows a Nafion content of ca. 22 wt% and a sulfonic site concentration of ca. 231 µmol H\(^+\)-SO\(_3\)\(^-\) per g of Nfn-Pt/C or 1688 µmol H\(^+\)-SO\(_3\)\(^-\) per g of Pt. Using 1.58 g cm\(^{-3}\) as the approximate density of Nafion [20] and the BET surface area obtained for Pt/C (170 m\(^2\) g\(^{-1}\)), rough calculations suggest that there is enough Nafion in Nfn-Pt/C to produce an equivalent monolayer coverage of the catalyst at least 1.5 nm in thickness. Analysis of EDX mapping for Nfn-Pt/C showed the sulfur and fluorine contents to be evenly distributed on the surface of the catalyst.

### 4.3.1.3 Average Particle Size (TEM and XRD)

Analysis of TEM images indicated an even distribution of Pt particles on the carbon support (XC-72) for both Pt/C (Figure 4.2a) and Nfn-Pt/C (Figure 4.2b) catalysts. Average Pt particle sizes for the as-received Pt/C and the as-prepared Nfn-Pt/C were determined to be 2.6 ± 0.4 nm and 2.8 ± 0.5 nm, respectively, indicating no apparent change in Pt particle size (within experimental error) during Nafion loading. Exposure of Pt/C to H\(_2\) and H\(_2\)/Ar at 80\(^\circ\)C for 24 hrs also had no effect on its average particle size (see Appendix B), suggesting that the sintering process is extremely slow at 80\(^\circ\)C. Similar results were obtained via XRD using the Debye-Scherrer equation and the full width at half maximum (FWHM) of the Pt(111) diffraction peak for both Pt/C and Nfn-Pt/C.
Due to the relatively small signal/noise ratio (S/N ~ 4), average Pt particle sizes from the XRD spectra were able to be determined to be ca. 3 nm for both catalysts, similar to the TEM results considering the difficulty of detecting Pt particles < 3 nm using Cu Kα radiation.

Figure 4.2 TEM images of (a) Pt/C and (b) Nfn-Pt/C.

Figure 4.3 XRD spectra of (a) Pt/C and (b) Nfn-Pt/C.
The XRD spectra also illustrate the lack of difference in the crystalline structure of Pt between Pt/C and Nfn-Pt/C. From left to right, 2θ values of 25°, 40°, 46°, 68°, and 81° in Figure 4.3 correspond to diffractions of graphite(002), Pt(111), Pt(200), Pt(220), and Pt(311), respectively [21, 22]. Thus, results from both TEM and XRD appear to suggest an average Pt particle size of approximately 2.6 – 2.8 nm for both catalysts.

4.3.1.4 Static H₂ and CO Chemisorption

Due to differing Pt loadings for Pt/C and Nfn-Pt/C, static chemisorption results were scaled to “per g of Pt” rather than “per g of catalyst” in order for a valid comparison. Similar to the static chemisorption results reported for Pt/C in our previous work [7], an increase in the amount of hydrogen uptake was observed for both Pt/C and Nfn-Pt/C when the analysis temperature was increased from 35°C to 80°C (Table 4.1), which can be directly attributed to hydrogen spillover onto the carbon support [22]. Surprisingly, the amounts of hydrogen uptake (on a Pt basis) for both Pt/C and Nfn-Pt/C were identical, within experimental error. Even the effect of analysis temperature on hydrogen spillover was roughly the same for both catalysts, suggesting that Nafion did not inhibit the hydrogen adsorption capability of Pt through either physical blocking or chemical interactions, even though such a large amount of Nafion was present. While some of the Pt may exist in the smaller sized pores of the carbon support, based on the severe loss of pores with pore sizes of 20 nm and below between Nfn-Pt/C and Pt/C (Figure 4.1) and the lack of an inhibition effect by the Nafion for the adsorption of H₂
mentioned above, it can be speculated that the majority of the Pt particles are most likely not in the smaller sized pores (≤ 20 nm).

**Table 4.1** Static H\textsubscript{2} and CO chemisorption results at 35\textdegree C and 80\textdegree C for Pt/C and Nfn-Pt/C.

<table>
<thead>
<tr>
<th>Catalyst\textsuperscript{a}</th>
<th>Adsorption Gas</th>
<th>Analysis Temp. (\textdegree C)</th>
<th>Amount of CO/H Adsorbed\textsuperscript{b} (\textmu mol (g Pt)\textsuperscript{-1})</th>
<th>Metal Dispersion (%)</th>
<th>Avg. Pt Particle Size (nm)\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C</td>
<td>H\textsubscript{2}</td>
<td>35</td>
<td>1806</td>
<td>35</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80</td>
<td>2063</td>
<td>40</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>35</td>
<td>1669</td>
<td>33</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80</td>
<td>1697</td>
<td>33</td>
<td>3.3</td>
</tr>
<tr>
<td>Nfn-Pt/C</td>
<td>H\textsubscript{2}</td>
<td>35</td>
<td>1861</td>
<td>36</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80</td>
<td>2160</td>
<td>42</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>35</td>
<td>1452</td>
<td>28</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80</td>
<td>1452</td>
<td>28</td>
<td>3.9</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Catalysts were pretreated in H\textsubscript{2} at 80\textdegree C for 3 h.  
\textsuperscript{b}Experimental error for all results was ca. ± 5%.  
\textsuperscript{c}Avg. Pt particle size calculated from:  
Avg. Pt Particle Size (nm) = \frac{1.08}{\text{Metal Dispersion}}\textsuperscript{1}, assuming CO/Pt\textsubscript{S} = 1 and H/Pt\textsubscript{S} = 1 [45].  

As expected, an increase in the analysis temperature had no effect on the amount of CO uptake because CO does not spill over onto the carbon support at these temperatures. However, lower amounts of CO uptake than hydrogen (in atoms) were observed for the same catalyst. For Pt/C, the difference between hydrogen and CO uptake can be explained by the existence of both linear and bridge-bonded CO on Pt, as
shown by DRIFTS results in our previous work [7], such that the overall stoichiometry of CO:Pt₅ is actually less than 1. The addition of Nafion to Pt/C resulted in a somewhat lower CO uptake than for Pt/C alone. While it may have been possible that the presence of Nafion has an effect on the interaction of CO with Pt such that the amount of linear and bridge-bonded CO on Pt for Nfn-Pt/C was different than that for Pt/C, due to the partial blocking of pores by the Nafion, evidenced by the pore size distribution (Figure 4.1), and the similarity between critical diameters of N₂ and CO (3.0 Å vs. 2.8 Å, respectively), the difference in CO uptake between Pt/C and Nfn-Pt/C may more likely to have been due to Nafion preventing CO from reaching some of the Pt surface. This blockage may not have been observed for hydrogen perhaps because the critical diameter, defined as the “diameter of a cylinder which can circumscribe the molecule in its most favorable equilibrium conformation” [23], for hydrogen is 2.4 Å whereas the critical diameter for CO is 2.8 Å. Thus, the larger sized CO molecule may have been obstructed by Nafion from reaching Pt particle surfaces in places where the smaller sized hydrogen molecule would have no problem. Based on the significant reduction in BET surface area from Pt/C to Nfn-Pt/C and the fact that N₂ molecules have a critical diameter of 3.0 Å, similar to that of CO, a comparable reduction in CO uptake should have occurred for Nfn-Pt/C if Pt particles were evenly distributed in the pore structure of the carbon support. However, the actual slight reduction in CO uptake for Nfn-Pt/C reaffirms the earlier hypothesis that the majority of the Pt particles are most likely not situated in the smaller pores (≤ 20 nm) of the carbon structure. In other words, the smaller Nafion-filledblocked pores that blocked N₂ molecules from getting through also blocked CO
molecules; however, because there were probably few or no Pt particles in those smaller pores, the amount of CO uptake measured by static chemisorption was not significantly reduced.

It should be noted that the physical characteristics of a catalyst can vary depending on the precursor used, method of preparation, treatment conditions, type of support, etc. For example, pore volume distributions of various carbon supports prepared via the oil-furnace or acetylene process [24] show that the majority of the pore diameters were less than 10 nm. The reason for such small pore diameters is most likely due to the fact that the carbon particles themselves ranged from 10-40 nm in diameter, whereas the size of carbon particles used in this study were ca. 60-150 µm in diameter. Thus, when comparing the physical characteristics between catalysts, all variables, such as the ones mentioned above, must be taken into consideration.

4.3.2 \( H_2-D_2 \) Exchange Reaction

Apparent activation energy \( (E_a) \) measurements for \( H_2-D_2 \) exchange reaction on Pt cannot be obtained in the absence of a catalyst poison due to the reaction being limited by equilibrium at the experimental conditions used in this study, even for very small quantities of catalysts. Therefore, prior to the gathering of kinetic data, catalysts were exposed to 30 ppm of CO to partially cover the Pt surface \( (\theta_{CO} \approx 0.71 \text{ monolayer}) \) and to shift the reaction away from equilibrium. All results reported in this section were obtained after the adsorption-desorption of CO had reached steady-state.
Similar to the results presented in our previous study [7], exposure of Pt/C to the CO resulted in an apparent $E_a$ of 20.3 ± 0.5 kcal mol$^{-1}$ for the poisoned Pt surface compared to an apparent $E_a$ of 4.5 – 5.4 kcal mol$^{-1}$ reported for an unpoisoned Pt surface [21, 25]. Similarly, exposure of Nfn-Pt/C to 30 ppm CO resulted in an apparent $E_a$ of ca. 21.5 ± 1.0 kcal mol$^{-1}$. No difference was observed in the rate of HD formation from H$_2$-D$_2$ exchange for Pt/C [1080 ± 50 µmol HD (g Pt)$^{-1}$ sec$^{-1}$] and Nfn-Pt/C [1065 ± 63 µmol HD (g Pt)$^{-1}$ sec$^{-1}$], both in the presence of 30 ppm CO. This similarity in both apparent activation energy and reaction rate between the two catalysts reaffirms that the Pt particles are most likely in the larger pore structures of the carbon support and that the Nafion does not appear to be inhibiting the adsorption of either hydrogen or CO on the Pt surface via any physical and/or chemical interactions.

4.3.3 In-situ TOS Surface Hydrogen Concentration via HDSAP

Due to the extremely fast reaction rate of H$_2$-D$_2$ exchange in the presence of Pt, any amount of hydrogen trapped either in the pores of the support or in the Nafion clusters at the onset of the D$_2$ switch during HDSAP would cause an overestimation in the hydrogen surface concentration measurement. Thus, while a purge time of 30 min was enough to remove most of the excess hydrogen trapped in the pores of Pt/C [7], the same amount of time might not be sufficient due to the presence of Nafion on the catalyst.

Figure 4.4 shows the amount of hydrogen surface concentration as a function of purge time used for HDSAP measurements. Total surface concentration of hydrogen was
calculated via Eq. 1 by measuring the amount of HD and H$_2$ formed at the onset of the D$_2$ switch. As can be observed from the figure, a 30 min purge time with Ar for Pt/C, prior to the introduction of D$_2$, yields a hydrogen surface concentration similar to that from static hydrogen chemisorption on Pt/C at 80°C.

![Graph showing effect of purge time on hydrogen surface concentration measurements on Pt/C, Nfn-Pt/C, and the NH$_4^+$ form of Nfn-Pt/C.]

**Figure 4.4** Effect of purge time on hydrogen surface concentration measurements on Pt/C, Nfn-Pt/C, and the NH$_4^+$ form of Nfn-Pt/C.

This result suggests that for Pt/C, a purge time of 30 min is sufficient to remove most of the excess hydrogen in the pores of Pt/C without affecting the strongly adsorbed hydrogen associated with Pt (H-Pt). However, in order for the hydrogen surface
concentration for Nfn-Pt/C to be similar to the theoretical total amount of exchangeable surface H, which is the sum of static hydrogen chemisorption at 80°C \[H-Pt \approx 2160 \ \mu\text{mol H (g Pt)}^{-1}\] and the concentration of sulfonic sites in the Nafion \[\text{SO}_3^- - \text{H}^+ \approx 1688 \ \mu\text{mol H (g Pt)}^{-1}\], a purge time of 50 min is required. This increase in purge time required was also observed for samples of Nfn-Pt/C exposed to NH₃ (gas), which increased the amount of exchangeable surface hydrogen from Nafion from 1 hydrogen atom per sulfonic site to 4 hydrogen atoms due to the formation of \text{SO}_3^- - \text{NH}_4^+. In contrast, exposure of Pt/C to NH₃ (gas) prior to HDSAP showed a negligible effect on the surface hydrogen concentration. A likely reason for the difference in HDSAP purge times required between Pt/C and Nfn-Pt/C may be due to the Nafion clusters acting as a barrier to the diffusion of gas-phase H₂ away from the catalyst, as suggested earlier. Thus, a purge time of 50 min was chosen for surface hydrogen measurements for Nfn-Pt/C. Increase in purge time appeared to have a negligible effect on the removal of H⁺ from the sulfonic sites during the Ar purge.

In order to verify whether the excess hydrogen is indeed from the sulfonic sites in the Nafion, separate samples of Nfn-Pt/C were poisoned by ion-exchanging the H⁺ cations with a non-proton containing cation, Na⁺. From these results, poisoning of sulfonic sites with Na⁺ cations (Figure 4.5) significantly decreased the hydrogen surface concentration from Na⁺-Nfn-Pt/C compared to Nfn-Pt/C, giving values close to those of Pt/C. The slightly higher surface hydrogen concentration found for Na⁺-Nfn-Pt/C than for Pt/C is due to a portion of the sulfonic sites being not fully exchanged with Na⁺ but still being in the protonated form (H⁺/Na⁺-Nfn-Pt/C). Exposure of H⁺/Na⁺-Nfn-Pt/C to
NH₃ (gas) resulted in the conversion of just the protonated sulfonic sites to the ammonium form (NH₄⁺/Na⁺-Nfn-Pt/C); calculations from the results suggest that ca. 4.5 out of 5.5 sulfonic sites had been poisoned with Na⁺. The Pt/C catalyst treated with NaCl in an identical fashion yielded surface hydrogen concentration results similar to those of untreated Pt/C, which confirmed that the Na⁺ was associated only with the Nafion. The poisoning results involving NH₃ and Na⁺ clearly show the excess surface hydrogen concentration measured for H⁺/Nfn-Pt/C to be from the protonated sulfonic sites in the Nafion.

Figure 4.5 Effect of sulfonic sites exchanged with Na⁺ ions on hydrogen surface concentration on Nfn-Pt/C.
In addition, these results also confirm the rapid transport of protons from the surface Pt atoms to nearby Nafion clusters and vice versa, which is the desired intent of having such a high weight loading of Nafion. Thus, contrary to the previous thought that contact must be maintained between the Pt particles and the polymer electrolyte in order for proton transport to take place [24, 26], surface diffusion of protons on the carbon support, while slower than on Pt [27], proves to be adequate for the reaction. The poisoning of the sulfonic sites by NH$_3$ did not appear to have an effect on this transport process (where D exchanges with NH$_4^+$).

4.3.4 Effect of Nafion on the Surface Coverage of ppm CO in H$_2$ on Pt

Possible effects of Nafion on the surface coverage of CO on Pt from ppm quantities of CO in H$_2$ were investigated indirectly via hydrogen surface concentration measurements. Similar to the CO surface coverage experiments performed on Pt/C in our previous work [7], TOS measurements of hydrogen surface concentration were measured for both Pt/C and Nfn-Pt/C over a 24 h period of exposure to 30 ppm CO in H$_2$.

The poisoning behavior of 30 ppm CO on Pt/C in terms of surface hydrogen concentration was analogous to the results presented in our previous study [7]. Surface coverage of Pt by CO for the Pt/C catalyst here was calculated to be ca. 0.71 monolayer (ML). The difference between the CO surface coverage of 0.71 ML measured for the current batch of Pt/C and the 0.54 ML for the batch used in our previous study under identical conditions were likely due to slight differences in the preparation method by BASF for the different batches of Pt/C, thus changing the innate properties of the catalyst
somewhat. Regardless, the measured CO surface coverage of 0.71 ML is similar to the 0.5 – 0.7 ML coverage range of CO observed on Pt(111) over the pressure range ($P_{CO}$) of $10^{-6}$ to 760 Torr at room temperature found via high pressure scanning tunneling microscopy (HP STM) and confirmed with calculations using density functional theory (DFT) [28-30].

From Figure 4.6, the poisoning behavior of 30 ppm CO on Nfn-Pt/C, after adjusting for the excess surface hydrogen from the sulfonic sites in Nafion, is similar to that for Pt/C. The hydrogen surface concentration for Nfn-Pt/C, after 24 h of exposure to 30 ppm of CO, was somewhat higher than that for Pt/C, 660 $\mu$mol H (g Pt)$^{-1}$ vs. 570 $\mu$mol H (g Pt)$^{-1}$, respectively. Upon closer inspection, it can be observed that the addition of Nafion resulted in an apparent slightly slower approach to steady-state than for Pt/C at the same concentration of CO, which may account for the difference in the surface hydrogen measured. While this may be argued to be related to the longer purge time required for HDSAP measurements for Nfn-Pt/C versus for Pt/C, the more likely possibility is that of the large Nafion clusters interfering with the rate at which CO reaches the surface Pt atoms as it was confirmed that the increase in required purge time between Pt/C and Nfn-Pt/C did not have an effect on the surface coverage of strongly-bound CO. Thus, the hydrogen surface concentration for Nfn-Pt/C was most likely not at steady-state at 24 h, and further exposure of Nfn-Pt/C to CO would have resulted in a hydrogen surface concentration even more similar to that of Pt/C. Regardless, the CO surface coverage for Nfn-Pt/C and for Pt/C after 24 h of exposure is the same (0.69 vs. 0.71, respectively), within experimental error. The CO surface coverage results show
that the Nafion does not, in general, appear to affect significantly the adsorption of CO on Pt at steady state. Similar to the effect Nafion has on the rate of diffusion of CO, the slightly lower CO uptake observed for Nfn-Pt/C, compared to Pt/C, from static chemisorption results is mostly likely due to the system not being perfectly at equilibrium (i.e., the equilibration interval was too low for Nfn-Pt/C).

Figure 4.6 Effect of Nafion on the surface coverage of CO on Pt/C and Nfn-Pt/C from 30 ppm of CO in H₂.
4.3.5 Effect of Nafion on the Activity of Pt/C for Cyclopropane Hydrogenolysis

Up until this point, the presence of such a high weight loading of Nafion has appeared to have a lack of effect on the activity of Pt for the adsorption of hydrogen and CO, which is extremely surprising considering the significant reduction in BET surface area from the impregnation of the Nafion and the large amount of Nafion present. Even if the majority of the surface Pt resided in the larger pore structures of the carbon support, one would think that the presence of such a large amount of Nafion would have at least some effect on the Pt via physical and/or chemical interactions. Because the results given so far have all involved the activation of hydrogen in one form or another, this apparent lack of effect from the Nafion may be due to the fast kinetics of hydrogen diffusion and activation and the structure insensitive characteristic of activation. To probe this issue further, a more structure sensitive reaction was employed to provide further insight. Use of a “demanding” or “structure sensitive” reaction is often very useful for investigating metal dispersion and metal decoration effects on specific activity in heterogeneous catalysts [31]. One should understand that the term “structure sensitivity” entails not just an effect of metal particle size on the observed rate or turn-over-frequency of the reaction; rather the reaction rate of a structure sensitive reaction depends on the coordination number of the active metal surface atoms and/or the number of contiguous metal surface atoms (site ensemble size) required for reaction to occur. Thus, as the name implies, these structure sensitive reactions are sensitive to changes in the surface structure of the catalyst and the availability of the surface atoms.
For this study, the hydrogenolysis of cyclopropane was chosen as a structure sensitive reaction mainly due to its lower reaction temperature requirement for Pt-based catalysts (0 – 80°C [32]). Other structure sensitive reactions, such as ethane hydrogenolysis, require operating temperatures in excess of 300°C and above [33, 34], which is problematic for the catalysts employed due to Nafion degradation at temperatures above 120°C. In addition, at temperatures below 150°C, only one product (propane) is formed from the reaction of cyclopropane with hydrogen over Pt catalysts, which greatly simplifies analysis [14, 35]. While there exists differing opinions as to whether hydrogenolysis of cyclopropane over Pt catalysts is structure sensitive [13, 36, 37] or structure insensitive [14, 35, 38, 39], results from a recent investigation [40] using K⁺-modified Pt/C catalysts confirm the reaction to be structure sensitive.

Reaction rate measurements were obtained using small amounts of catalyst (1.0–2.5 mg), low reaction temperature (30°C), and low concentration of reactants (0.05 atm C₃H₆ and 0.25 atm H₂), to ensure differential reaction conditions. In order to compare the rates, given the different wt% of Pt before and after loading Nafion, rates were calculated on a per weight Pt basis. Observed rates were calculated to be 557 µmol C₃H₈ (g Pt)⁻¹sec⁻¹ and 373 µmol C₃H₈ (g Pt)⁻¹sec⁻¹ for Pt/C and Nfn-Pt/C, respectively. Furthermore, determination of Eₐ from Arrhenius plots show the value for Nfn-Pt/C (5.4 kcal mol⁻¹) to be almost exactly half that of Pt/C (11.6 kcal mol⁻¹). This difference in Eₐ, where the measured (Nfn-Pt/C) is ca. half that of the intrinsic (Pt/C), is a very strong indication for the possibility of internal diffusion limitations, such that the reaction rate is shifted from being reaction-limited to diffusion-limited. Because Eₐ is an average value, interactions
between Nafion and Pt, such as preferential blocking of specific Pt surface atoms and/or electronic effects where the surface binding energies of species are different, may also have a similar effect in shifting the value of $E_a$ measured. However, since there exists no evidence thus far from all previous results suggesting that such an interaction exists, especially to the degree of reducing the values of $E_a$ (measured for Pt/C) by half, the possibility of internal diffusion limitations caused by the Nafion will be discussed.

In this case, because no signs of internal diffusion limitations are evident for Pt/C, it can only be concluded that the presence of internal diffusion limitations observed for Nfn-Pt/C is due to the Nafion. Based on previously mentioned evidence suggesting that the majority of the Pt appears to be in the larger pore structures ($> 30$ nm) of the carbon support and the lack of evidence suggesting the filling of these pores by the Nafion (i.e, only a subtle decrease in pore size distribution based on pore volume, Figure 4.1), it can be proposed that the main cause of internal diffusion limitations observed for Nfn-Pt/C is probably due to the partial blocking of pore openings by the polymer, such that the diameter of the entrance into a pore ($\delta$) is smaller than the diameter of the pore ($d$) itself (as illustrated by Figure 4.7).

Theoretical modeling of the effect of $\delta$ on the $E_a$ was performed using a single one-dimensional ideal cylindrical pore with a length of $L_l$ and a diameter of $d$; factors such as tortuosity, pore porosity, and constriction factor were all assumed to be unity. Using a similar scenario depicted by El-Kady and Mann [41] in their work regarding the deactivation of catalyst due to pore-mouth plugging from coke deposition, the Nafion
was assumed to form a membrane as an impenetrable barrier of thickness $L_2$ with an opening to the pore of diameter $\delta$.

Assuming a first-order irreversible reaction, which is a reasonable assumption for cyclopropane hydrogenolysis in the presence of a large excess of hydrogen [32], at steady-state, the mass-balance (in dimensionless form) for species A in the system is (Eqs. 3 and 4):

**Figure 4.7** Simplified scenario of blocking of pore opening by the Nafion in Nfn-Pt/C.
In membrane: \[ \frac{d^2 C_2}{d\eta^2} = 0 \] (6) 
In the pore: \[ \frac{d^2 C_1}{d\eta^2} - \left( \frac{4kL^2}{dD_{e,1}} \right) C_1 = 0 \] (7) 

with the following dimensionless variables:

\[ \eta = \frac{x}{L}, \quad C_1 = \frac{C_{A,1}}{C_{A,0}}, \quad C_2 = \frac{C_{A,2}}{C_{A,0}} \] (8)

These conservation of mass equations are derived based on Fick’s law for dilute solutions and can be found in any transport-related textbook [42]. The variable \( L \) is the total length of the system and is the sum of \( L_1 \) and \( L_2 \). \( C_{A,o} \) is the bulk concentration of species A outside of the pore, \( D_{e,1} \) is the effective diffusivity inside the pore, \( C_{A,1} \) and \( C_{A,2} \) are the concentration of species A in the pore and membrane, respectively. Boundary conditions used to solve the above differential equations are:

At \( \eta = 0 \) (end of the pore): \[ \frac{dC_1}{d\eta} = 0 \] (9) 
At \( \eta = 1 \): \[ C_2 = \Phi_2 \] (10) 
At \( \eta = L_1/L = \lambda_1 \): (interface between membrane and pore) \[ \Phi C_1 = C_2, \text{ where } \Phi = \frac{\Phi_2}{\Phi_1} \] (11) 
At \( \eta = L_1/L = \lambda_1 \): \[ D \frac{dC_1}{d\eta} = \frac{dC_2}{d\eta}, \text{ where } D = \frac{D_{e,1}}{D_{e,2}} \] (12)

where \( D_{e,2} \) is the effective diffusivity in the membrane, \( \Phi_1 \) and \( \Phi_2 \) are the partition coefficients for the pore and membrane respectively. The partition coefficient \( \Phi \) is the ratio of available volume to the void volume and is dependent on the molecular properties.
of the solute. So, for cyclopropane, which has a critical diameter of ca. 4.9 Å or 0.49 nm, the partition coefficients for the membrane and pore are calculated by:

\[
\begin{align*}
\text{Membrane:} & \quad \Phi_1 = \left(1 - \frac{0.49 \text{ nm}}{\delta}\right)^2 \\
\text{Pore:} & \quad \Phi_2 = \left(1 - \frac{0.49 \text{ nm}}{d}\right)^2
\end{align*}
\]

The effective diffusivities \(D_{e,1}\) and \(D_{e,2}\) are defined as:

\[
D_{e,1} = \frac{\varepsilon_1 \sigma_1 D_{K,1}}{\tau_1} \quad \text{and} \quad D_{e,2} = \frac{\varepsilon_2 \sigma_2 D_{K,2}}{\tau_2}
\]

For both pore and membrane, the parameters: constriction factor (\(\sigma\)) and tortuosity (\(\tau\)) are all assumed to be unity. The porosity for the ideal pore (\(\varepsilon_1\)) is also assumed to be unity while the porosity for the membrane (\(\varepsilon_2\)) is the ratio of the open area to the total area of the pore. The terms \(D_{K,1}\) and \(D_{K,2}\) are the Knudsen diffusion coefficients for the pore and membrane, respectively, and were calculated as follows:

\[
D_{K,1} = \frac{d}{3} \sqrt{\frac{8RT}{\pi M}} \quad \text{and} \quad D_{K,2} = \frac{\delta}{3} \sqrt{\frac{8RT}{\pi M}}
\]

where \(R\) is the gas constant, \(T\) is temperature, and \(M\) is the molecular weight of the solute. Solving for \(C_2\) and \(C_1\) from the differential equations (3) and (4) via the boundary conditions Eqs. (6–9) yields the following solutions:

\[
\begin{align*}
\text{In the membrane:} & \quad C_2 = \Phi_2 - \alpha_2 (1 - \eta) \\
\text{In the pore:} & \quad C_1 = \alpha_1 \cosh(\phi \eta)
\end{align*}
\]

where:
Approximation of average pore radius and pore length based on BET surface area, pore volume, gross volume of catalyst particle, and external surface area obtained for Pt/C show values of ca. 5 nm and 20 µm, respectively. The Arrhenius plot of the rate resulting from the concentration in the pore ($C_1$) is plotted in Figure 4.8 with varying values for the diameter of the opening in the membrane.

It can be observed from Figure 4.8 that in the case where opening in the membrane is equal to pore diameter (i.e., $\delta = d = 10$ nm), the theoretical $E_a$ is the intrinsic value and no evidence of internal diffusion limitations exists. As the value of $\delta$ decreases, the concentration in the pore ($C_1$) and the resulting $E_a$ does not start to be affected until $\delta$ is as low as 0.7 nm. Further decreases in $\delta$ beyond that point shifts the theoretical $E_a$ farther from its intrinsic value of 11.5 kcal mol$^{-1}$, until finally, at a value of 0.5 nm, the $\delta$ was so small that almost no solute, in this case cyclopropane with a critical diameter of ca. 0.49 nm, is able to diffuse into the pore, thus yielding an $E_a$ close to zero.

It should be noted that for all values of $\delta$, the concentration gradient, at steady-state, remained relatively constant throughout the pore. Even at a $\delta$ value of 0.55 nm, where the $E_a$ showed clear diffusion limitations, the steady-state concentration of cyclopropane in the pore was ca. a factor 0.6 that of the bulk and varied no more than 0.02% from one end of the pore to the other. This lack of a concentration gradient in the pore is
counterintuitive for a supposedly diffusion-influenced reaction. But this is just because most people are used to the effect of decreasing diameter of the pore. The real diffusion barrier is the membrane in the current case.

Figure 4.8 Effect of membrane opening on $E_a$ for cyclopropane hydrogenolysis on Pt/C using an idealized cylindrical pore model with the pore mouth partially covered by a (Nafion) membrane.
It is important to note that the model is based upon a simple mass-balance and does not take into account wall effects and other electronic interactions on diffusion. In the presence of these effects, the effect of membrane diameter may be even larger.

Increases in the number of openings in the membrane also increase the calculated \( E_a \) for the same opening diameter. For example, if there exists 5 openings in the membrane each with \( \delta = 0.55 \) nm, the calculated \( E_a \) would increase from 6.3 kcal mol\(^{-1}\) (only 1 opening) to 9.8 kcal mol\(^{-1}\) and the calculated \( E_a \) for \( \delta = 0.52 \) nm would increase from 2.8 kcal mol\(^{-1}\) to 6.8 kcal mol\(^{-1}\). However, because the model does not take into account wall effects and other electronic interactions, no definite conclusions can be made regarding this change.

Attempts were made to obtain actual cross-sectional spectra of a Nfn-Pt/C catalyst particle via both SEM/EDX and TEM/EDX by imbedding the catalyst particles in a resin. The dried resin was then either cut/polished for SEM/EDX analysis or sectioned via microtome for TEM/EDX analysis. Results from both methods proved to be inconclusive due mostly to the lack of penetration of the resin into the carbon support. The fragile nature of the carbon also proved to be troublesome.

Based on these and all previous results, it can be concluded that the effect of Nafion on Pt/C for cyclopropane hydrogenolysis appears to be limited to the induction of internal diffusion limitations by virtue of decreasing the effective diameter of the openings of the pores in the carbon support. The similar values of \( E_a \) observed for H\(_2\)-D\(_2\) exchange reaction on both catalysts, poisoned with ppm CO, suggests that either the openings of the pores or the openings in the Nafion structure itself overlaying the pores
were wide enough so that hydrogen diffusion was not affected. No blocking of Pt surface atoms by the Nafion via either physical and/or chemical interactions was observed. It is important to note that while the Nafion in this study was in the dry or unswelled state. Due to the apparent lack of interactions between the polymer and Pt surface and the minimal impact water vapor has for H\textsubscript{2} adsorption and activation on Pt/C [43], the effect that humidity would have on the this Nafion-Pt system of this study should also be minimal.

4.4 Conclusions

While the impregnation of 30 wt% Nafion on Pt/C had dramatic effects on the physical characteristics of Pt/C, such as the reduction of BET surface area from 170 m\textsuperscript{2} g.cat\textsuperscript{-1} to 37 m\textsuperscript{2} g.cat\textsuperscript{-1}, the overall effect of the Nafion on the adsorption capabilities of Pt for hydrogen and CO were minimal, based on both static chemisorption and in-situ surface hydrogen concentration results. Likewise, the similar rates of H\textsubscript{2}-D\textsubscript{2} exchange for Pt/C and Nfn-Pt/C poisoned with ppm CO suggests that the effect of Nafion on the poisoning behavior of CO on the reaction is also minimal. However, for cyclopropane, a molecule larger than CO, a clear decrease in the rate of hydrogenolysis was observed in going from Pt/C to Nfn-Pt/C. While this decrease might be thought to be attributable to the blocking of Pt surface atoms by Nafion, due to the lack of evidence suggesting such an interaction exists from static chemisorption, H\textsubscript{2}-D\textsubscript{2} exchange and hydrogen surface concentration results, the decrease in reaction rate is most likely due to internal diffusion.
limitations caused by the Nafion. Results from the modeling of a membrane (the Nafion in this case) over an idealized cylindrical pore show the effect of decreasing the size of the membrane opening, while keeping the pore diameter constant, to effectively decrease the value of $E_a$ as a result of diffusion limitations through the membrane but not in the pore. In contrast, the similar values of $E_a$ observed for H$_2$-D$_2$ exchange reaction on both Pt/C and Nfn-Pt/C suggests that the smaller effective pore openings in Nfn-Pt/C were not small enough to affect the smaller hydrogen molecules, as compared to cyclopropane. No blockage of Pt surface atoms by the Nafion via either physical and/or chemical interactions was observed. Based on all the measurements made, it appears that most of the Nafion is probably on the external surface of the carbon support, where it blocks micro pores significantly and partially blocks meso-macro pores. Most of the Pt particles appear to reside in the meso-macro pores.

Results from hydrogen surface concentration measurements on Pt/C and Nfn-Pt/C using H$_2$-D$_2$ exchange suggest a rapid diffusion of hydrogen and deuterium across the carbon surface at 80°C. The increase in the amount of total exchangeable hydrogen going from Pt/C to Nfn-Pt/C was confirmed to be from the protonated sulfonic sites in the Nafion. It should be noted that while contact between the polymer and Pt particles is not required for proton transport, recent results from a new evaluation method for the effectiveness of Pt/C electrocatalysts clearly show the benefits of ionic contact in improving the apparent utilization of Pt available [44].
4.5 References


CHAPTER FIVE

THE EFFECT OF LOW CONCENTRATIONS OF TETRACHLOROETHYLENE ON H$_2$ ADSORPTION AND ACTIVATION ON Pt IN A FUEL CELL CATALYST

The poisoning effect of tetrachloroethylene (TTCE) on the activity of a Pt fuel cell catalyst for the adsorption and activation of H$_2$ was investigated at 60°C and 2 atm using hydrogen surface concentration measurements. In the presence of only H$_2$, introduction of up to 540 ppm TTCE in H$_2$ to Pt/C at typical fuel cell conditions resulted in a reduction of available Pt surface atoms (measured by H$_2$ uptake) by ca. 30%, which was still not enough to shift the H$_2$-$\text{D}_2$ exchange reaction away from being equilibrium limited. Poisoning behavior of 30 ppm CO + 150 ppm TTCE on Pt/C in H$_2$ showed that poisoning effect from the CO to be dominant. Exposure of TTCE to Pt/C in a mixed redox environment (hydrogen+oxygen), similar to that at the cathode of a fuel cell, resulted in a much more significant loss of Pt surface atom availability, suggesting a role in TTCE decomposition and/or Cl poisoning. Regeneration of catalyst activity of poisoned Pt/C showed the highest level of recovery when regenerated in only H$_2$, with much less recovery in H$_2$+O$_2$ or O$_2$. The results from this study are in good agreement with those found in a fuel cell study by Martínez-Rodríguez et al. [2] and confirm that the majority of the poisoning from TTCE on fuel cell performance is most likely at the cathode, rather than the anode.
5.1 Introduction

With the ever decreasing supply of liquid fossil fuels and the fear of global warming looming on the horizon, the ongoing search for alternative energy, especially for the automotive industry, is of even greater importance. From the list of possible alternatives, including batteries, biofuels, and solar energy, proton exchange membrane fuel cells (PEMFC) have been shown to be the most promising due to their advantageous characteristics such as high current density, quick startup, and zero pollution emissions [1]. However, partly due to the detrimental effects impurities have on the durability and performance of PEMFCs, successful commercialization of this technology is still limited at best.

While the numbers of studies investigating the impurity effects on PEMFCs have been increasing rapidly in the past years, most of them have concentrated mainly on the impurities that are present in the hydrogen fuel stream as a result of hydrogen production from hydrocarbon reforming, namely CO, CO₂, and NH₃. There exists very limited information of other impurities, such as chlorinated hydrocarbons, that may be introduced into the fuel cell via other sources, such as the fueling station and/or during vehicle maintenance. Due to their non-polar nature, such compounds are used extensively in cleaning and degreasing applications as excellent solvents for organic materials. In fact, the International Organization for Standardization (ISO) and the Society of Automotive Engineers (SAE) have proposed the regulation of these chlorinated hydrocarbons as part
of the hydrogen fuel quality standards, setting the limit of total chlorinated species to be 0.05 ppm [2].

A recent study by Martínez-Rodríguez et al. [2] on the impact of one such chlorinated hydrocarbon, tetrachloroethylene (TTCE), also known as perchloroethylene (PCE), on the performance of a PEMFC showed a 98% degradation in current density in the span of 3 h when 30 ppm of TTCE was introduced into the hydrogen fuel stream. Furthermore, while a decrease in the concentration of TTCE did result in a slower rate of poisoning, the amount of current loss at steady-state after 200 h with 0.05 ppm TTCE was still 84% of its initial value. Compared to the cell polarization results in the presence of CO [3], it is clear that the impact of TTCE [2] on fuel cell performance is far greater, at similar concentration levels. Yet, results from the TTCE study [2] were inconclusive as to exactly how the impurity was causing such a detrimental effect on the fuel cell performance. For example, results from a hydrogen pump experiment \([\text{H}_2(\text{anode})/\text{N}_2(\text{cathode})]\), used to characterize changes in the anode and membrane during poisoning, and the electrochemical impedance spectroscopy (EIS) characterization of the membrane resistance before and after TTCE exposure showed that the poisoning effects of TTCE are neither related to the anode nor the membrane. On the other hand, analysis of both anode inlet and outlet showed a reduction in TTCE concentration from 164 ppm to 41 ppm, respectively, during open circuit, which was further reduced to 5.4 ppm upon application of a current. However, no TTCE was detected at the cathode outlet. Thus, while this fuel cell study was very informative in measuring and determining the effect of TTCE on overall fuel cell performance, more information is required in order to
understand the poisoning mechanism of the impurity, especially on the catalyst and associated reactions.

This study is a follow-up to the fuel cell work by Martínez-Rodríguez et al. [2] to further delineate the effect of TTCE on the H₂ activation and surface coverage of Pt in order to better understand the poisoning mechanism of the impurity. Due to the fast reaction rate of H₂ activation on Pt, kinetic measurements of the reaction could not be made at typical fuel cell operating conditions. Instead, a modified H₂-to-D₂ switch procedure, H₂-D₂ switch with Ar purge (HDSAP) [4, 5], was used to measure in-situ the surface concentrations of hydrogen on Pt/C and on Nafion-Pt/C with time-on-stream (TOS) in the presence of varying concentrations of TTCE (150-540 ppm). Chlorine elemental analyses were performed subsequently on the TTCE poisoned catalysts. Furthermore, in order to mimic conditions at the cathode, Pt/C was also exposed to 150 ppm TTCE under mixed redox conditions.

5.2 Experimental

5.2.1 Catalyst Preparation

A carbon supported Pt fuel cell catalyst (Pt/C), with a nominal Pt-loading of 20 wt\%, was purchased from BASF and used as-received. The carbon support used for the synthesis of the catalyst was Vulcan XC-72 (Cabot Co.).

The Nafion supported on Pt/C (Nfn-Pt/C) catalyst used in this study was the same as that prepared in our previous work [6]. Briefly, Nfn-Pt/C was prepared via incipient
wetness impregnation of the commercial 20 wt% Pt/C catalyst with a Nafion ionomer solution (LQ-1105, DuPont, 5 wt% Nafion) to give a target weight loading of 30 wt% for the Nafion. The high Nafion loading of 30 wt% has been shown in the literature to be the optimum Nafion content in a PEMFC catalyst layer [7-10]. The impregnated material was then dried at 90°C overnight in a static air oven, crushed and sieved to obtain a particle size distribution of 60 – 150 µm. The catalyst was then stored in the dark prior to use. Elemental analysis of Pt-content (performed by Galbraith Laboratories) showed a Pt-loading of ca. 17.5 wt% and 13.7 wt% for Pt/C and Nfn-Pt/C catalysts, respectively.

5.2.2 Characterization Methods

5.2.2.1 BET

The BET surface area, pore size, and pore volume measurements of Pt/C and Nfn-Pt/C were carried out using a Micromeritics ASAP 2020 unit. Samples of catalysts were degassed under vacuum (10⁻³ mm Hg) at 110°C for 4 h prior to analysis. Results were obtained from N₂ adsorption isotherms at -196°C.

5.2.2.2 TEM

Transmission electron microscopy (TEM) images of Pt/C and Nfn-Pt/C catalysts were obtained using a TEM-Hitachi 9500, which offers 300kV high magnification TEM and is designed for atomic resolution. The preparation method of copper sample grids was the same as that used in our previous work [5]. Briefly, catalyst samples were immersed in small aliquots of isopropyl alcohol and sonicated until an even dispersion of
the catalyst was observed. A small drop of the dispersed sample was then transferred onto a copper grid (200 mesh copper Formvar/carbon) and allowed to dry at room temperature overnight prior to measurement. Approximate Pt particle sizes of the catalysts were obtained by averaging diameters of 100+ particles from the TEM images.

5.2.2.3 Static H₂/CO Chemisorption

Static chemisorption experiments using H₂ and CO were performed at 35°C in a Micromeritics ASAP 2010 unit equipped with a chemisorption controller station. Prior to the start of the analysis, the catalysts were first reduced in flowing H₂ at 80°C for 3 h, followed by an evacuation at 80°C (10⁻⁵ mm Hg) for another 3 h. After evacuation, the temperature was then adjusted to 35°C and the H₂ or CO isotherms were obtained from 50–450 mm Hg pressure at increments of 50 mm Hg. Volumetric uptakes of H₂ or CO on the catalysts were determined from the total adsorption isotherms of the specified gas. These values were then used in the determination of total Pt surface atom concentration (Pt₅) and metal dispersion by assuming stoichiometric ratios of 1:1 for H:Pt₅ and CO:Pt₅. Calculation of average Pt particle size for Pt/C and Nfn-Pt/C were made using metal dispersion measured by chemisorption, which has been shown to correlate reasonably well with TEM results [5, 6].

5.2.2.4 Surface Hydrogen Concentration Measurements

The method, H₂-D₂ switch with an Ar purge (HDSAP), was developed and verified in our previous work [4-6] for determining in-situ the concentration of strongly
adsorbed surface hydrogen on Pt/C and Nfn-Pt/C. The use of HDSAP is preferred over other surface concentration measurements, such as TPD, due to the non-destructive nature of the methodology (Nafion is not stable above ca. 120°C) and its ability to obtain TOS measurements.

HDSAP measurements were initiated by first exposing the catalyst to a flowing gas mixture of H$_2$/Ar (1:1) at 100 cm$^3$ min$^{-1}$ (sccm) for 30 min. Afterwards, the H$_2$ was stopped and 50 sccm of Ar was passed through the plug flow reactor for 30 min [5] or 50 min [6] for Pt/C and Nfn-Pt/C, respectively. The purge with Ar was done to flush out as much of the gas-phase and/or weakly adsorbed H$_2$ from the catalyst as possible. After the Ar purge, a flow of 50 sccm of D$_2$ (along with the 50 sccm of Ar) was introduced to the catalyst, resulting in two transient signals being observed for hydrogen-containing species (H$_2$ and HD) in the Pfeiffer Vacuum mass spectrometer (MS). The amount of H$_2$ and HD were calculated by integrating the area under the peaks (signal vs. time) and using the area obtained from a pulse of known quantities of H$_2$ and HD via a 6-port valve equipped with a 2 mL sample loop as calibration. Total surface concentration of hydrogen was calculated by adding the amount of hydrogen (H) in H$_2$ and HD, as given by the equation below:

$$\text{Surface H (µmol/g, cat)} = \mu\text{mol HD/g, cat} + 2 \times \mu\text{mol H}_2/g, \text{cat}$$

(1)

After the initial measurement of hydrogen surface concentration on the freshly reduced catalyst, specified concentrations of TTCE were exposed to the catalyst by flowing 10 sccm of either H$_2$ or Ar through a KIN-TEK Trace Source$^\text{TM}$ permeation tube type LFH filled with approximately 30 mL of the liquid component. Based on the
emission rate of the membrane inside the tube, control of the TTCE concentration at the outlet was maintained by placing the permeation tube in an insulated oven and adjusting its temperature accordingly. The calibrated effluent of the permeation tube was diluted further with a mixture of \( \text{H}_2/\text{Ar} \) or \( \text{H}_2/\text{O}_2/\text{Ar} \), depending on the experiment, to achieve a total flow rate of 100 sccm and the desired concentration of TTCE. Time-on-stream (TOS) measurements of the effect of TTCE exposure of Pt/C and Nfn-Pt/C on hydrogen surface concentration were taken sequentially such that one sample could be used for the entire experiment. Preliminary results showed that the Ar purge periodically did not have any effect on the poisoning behavior of TTCE compared to an uninterrupted exposure of Pt/C to either 150 or 540 ppm TTCE for 12 h (non-sequential), resulting in the same 12 h hydrogen surface concentration being measured as one with HDSAP measurements periodically during a 12 h run (sequential).

**5.2.3 \( \text{H}_2\)-\( \text{D}_2 \) Exchange Reaction**

The \( \text{H}_2\)-\( \text{D}_2 \) exchange reaction was chosen as the model reaction for the hydrogen oxidation reaction (HOR) primarily because both reactions share the same rate-limiting step, which is the dissociative adsorption of hydrogen. Furthermore, as shown by Ross and Stonehart [11], for the temperature range of 30–80\(^\circ\)C, the first-order rate constants for \( \text{H}_2\)-\( \text{D}_2 \) exchange on Pt and electrochemical hydrogen oxidation are in close agreement with each other. Thus, not only is the \( \text{H}_2\)-\( \text{D}_2 \) exchange reaction a good probe reaction for hydrogen activation, it is also a very good model reaction for the electrocatalytic oxidation of hydrogen on Pt, within the temperature range specified.
Using a conventional plug flow, micro-reactor system maintained at 60°C and 2 atm, the H₂-D₂ exchange reaction was started by flowing a reactant gas mixture comprised of (25:25:50) H₂:D₂:Ar, with the specified concentration of impurity, over the catalyst for 15 min. The reactor effluent gas (comprised of the reactants H₂ and D₂, the product HD, and the inert Ar) was analyzed online with a MS. To obtain the MS signals of H₂ and D₂ in the absence of the catalyst for the purpose of calculating the exchange conversion, the flow was switched to reactor bypass for 5 min. The exchange conversion for H₂ or D₂ was obtained via Eq. (2) using the H₂ (m/z = 2) and D₂ (m/z = 4) MS signals in the presence and absence of catalyst:

\[
\text{Conversion (\%)} = \frac{(H₂ \text{ or } D₂ \text{ Signal})_{\text{No Cat.}} - (H₂ \text{ or } D₂ \text{ Signal})_{\text{Cat.}}}{(H₂ \text{ or } D₂ \text{ Signal})_{\text{No Cat.}}} \times 100\%
\]  

\[2\]

5.3 Results and Discussion

5.3.1 Catalyst Characterization

5.3.1.1 BET

The BET surface area, pore size, and pore volume results for the carbon support (XC-72) were 225 m² g⁻¹, 16.4 nm, and 0.63 cm³ g⁻¹, respectively, which correspond very well with literature values [12, 13]. Similar results were observed for the carbon-supported Pt catalyst where the BET surface area, pore size, and pore volume were found to be 170 m² g⁻¹, 15.9 nm, and 0.44 cm³ g⁻¹, respectively. Due to the fact that the bulk of the surface area of a support comes from its pores, reductions in the BET surface area and pore volume suggests that significant amounts of the Pt particles were most likely
situated in the pore structure rather than just on the external surface of the carbon support granules.

Addition of Nafion to Pt/C resulted in a further reduction of BET surface area and pore volume to 38 m$^2$ g$^{-1}$ and 0.28 cm$^3$ g$^{-1}$, respectively, while increasing the average pore size to 32.7 nm. As was shown in our previous work [6], the severe reduction in BET surface area was due to a substantial filling/blocking of the smaller pores by the Nafion, while the larger sized pores appear to have been much less affected.

5.3.1.2 Average Particle Size

Measurements of average Pt particle sizes for the Pt/C and Nfn-Pt/C catalysts were obtained from TEM images and were determined to be 2.6 ± 0.4 nm and 2.8 ± 0.5 nm, respectively, indicating no apparent change in Pt particle size (within experimental error) from the addition of Nafion [6]. Furthermore, analysis of TEM results indicated a relatively even distribution of Pt particles on the carbon support for both catalysts.

5.3.1.3 Static H$_2$ and CO Chemisorption

Due to differing Pt loadings for Pt/C and Nfn-Pt/C, static chemisorption results were scaled to a “per g of Pt” basis rather than “per g of catalyst” in order for a more valid comparison (Table 5.1). The results can easily be converted back to “per g of catalyst” basis by dividing by the appropriate Pt weight fraction for the associated catalyst (i.e., 17.5 wt% and 13.7 wt% for Pt/C and Nfn-Pt/C, respectively). Surprisingly, the addition of such large amounts of Nafion did not appear to affect the ability of the Pt
to adsorb either hydrogen or CO since the amounts of hydrogen and CO uptake were relatively similar for both catalysts, within experimental error. Furthermore, based on the severe loss of pores with pore sizes of 20 nm and below due to being filled/blocking by the Nafion [6] and the fact that N₂ molecules have a critical diameter similar to that of CO (3.0 Å vs. 2.8 Å, respectively), the minimal effect Nafion had on the amount of CO uptake also suggests that the majority of the Pt particles were most likely not situated in the smaller pores of the carbon support. A more in-depth analysis of these results and the reasoning behind our conclusions can be found elsewhere [6], as the point of this work is not on the effect of Nafion.

Table 5.1 Static H₂ and CO chemisorption results at 35°C for Pt/C and Nfn-Pt/C.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Adsorption Gas</th>
<th>Analysis Temp. (°C)</th>
<th>Amount of CO/H Adsorbed [µmol (g Pt)^{-1}]</th>
<th>Metal Dispersion (%)</th>
<th>Avg. Pt Particle Size (nm)^c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C</td>
<td>H₂</td>
<td>35</td>
<td>1806</td>
<td>35</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>35</td>
<td>1669</td>
<td>33</td>
<td>3.3</td>
</tr>
<tr>
<td>Nfn-Pt/C</td>
<td>H₂</td>
<td>35</td>
<td>1861</td>
<td>36</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>35</td>
<td>1452</td>
<td>28</td>
<td>3.9</td>
</tr>
</tbody>
</table>

^aCatalysts were pretreated in H₂ at 80°C for 3 h.
^bExperimental error for all results was ca. ± 5%.
^cAvg. Pt particle size calculated from:
Avg. Pt Particle Size (nm) = \(\frac{1.08}{\text{Metal Dispersion}}\), assuming CO/Ptₜ = 1 and H/Ptₜ = 1 [29].

Comparison of the average Pt particle sizes from chemisorption results, calculated based on the metal dispersion, with those obtained from TEM shows good
agreement, within experimental error. This suggests that the amount of PtS measured from hydrogen chemisorption, based on the assumed stoichiometric ratio of 1:1 for H:PtS, is reasonably accurate and that the Pt surface is essentially not blocked by Nafion [6].

5.3.2 Hydrogen Surface Concentration Measurements

5.3.2.1 Effect of TTCE Poisoning on Pt in H₂ for Pt/C

Figure 5.1 shows the TOS measurements of hydrogen surface concentration on 100 mg of Pt/C in the presence of 150–540 ppm TTCE in a (50/50) H₂/Ar mixture at 60°C and 2 atm. Even in the presence of such high concentrations of TTCE, the hydrogen surface concentration, at steady-state, showed a loss of only 18% when exposed to 150 ppm TTCE over a 12 h period. Increase in the TTCE concentration resulted in a further decrease in hydrogen surface concentration such that at 290, 400, and 540 ppm TTCE, the reductions in hydrogen surface concentration were ca. 24%, 29%, and 35%, respectively. While the loss in hydrogen surface concentration is not minor, it should be noted that, due to the extremely high activity Pt has for adsorbing and activating hydrogen, a much more substantial loss in Pt surface atoms (ca. 66%) is required to shift the reaction away from equilibrium for the conditions used and to start inhibiting the performance of a PEMFC [5]. Because of this, the conversion of H₂-D₂ exchange on Pt, even in the presence of 540 ppm TTCE, remained at equilibrium at steady-state. This result can also be observed from fuel cell hydrogen pump experiments, where polarization scans using a H₂(anode)/N₂(cathode) setup, with 30 ppm TTCE in the anode feed, showed that the impurity had no effect on the overpotential of the hydrogen
oxidation reaction (HOR) over a 4 h period [2]. However, introduction of the same TTCE concentration to a H₂(anode)/O₂(cathode) fuel cell for 3 h showed almost a complete degradation in fuel cell performance.

![Graph](image)

**Figure 5.1** Effect of TTCE exposure on the hydrogen surface concentration on Pt/C in the presence of only H₂.

Even though the exposure of Pt/C to TTCE was not able to shift the H₂-D₂ exchange reaction away from equilibrium, the loss of up to 35% of available Pt surface
atoms was determined and was a cause of concern. According to hydrodechlorination studies (dechlorination in the presence of hydrogen) of chlorinated hydrocarbons, coke, chlorine deposition, and possibly HCl are attributed to be the main possible reasons for catalyst deactivation [14-18]. However, the majority of these deactivation effects were observed more for the hydrodechlorination of chloroalkanes instead of the chloroalkenes. For example, hydrodechlorination of trichloroethane (TCA) and dichloroethane (DCA) on 3 wt% Pt/η-alumina at 250°C in 10% H₂ started to deactivate as early as 8 h TOS. However, no signs of deactivation were evident for dichloroethylene (DCE) at the same conditions for up to 24 h TOS, with the conversion of DCE at 100% for the entire duration and the product distribution being primarily ethane and HCl [19]. Further addition of an equimolar amount of HCl to a feed stream with 1 mol% DCE had essentially no effect on the initial activity or stability of a Pt/η-alumina catalyst at 250°C, proving that the presence of HCl does not contribute to the deactivation of the catalyst.

While no deactivation was observed above for the hydrodechlorination of DCE on Pt/η-alumina at higher reaction temperatures, at lower temperatures such as 60°C, the hydrogenation of Cl-species on the Pt surface may not be as fast, resulting in a reduction of hydrogen surface concentration or Pt surface atoms available for adsorbing hydrogen on the Pt/C catalyst. However, elemental analysis of Cl concentration (performed by Galbraith Laboratories) using ion chromatography for Pt/C samples exposed to 150, 290, 400, or 540 ppm TTCE for 12 h resulted in a retention of only ca. 13, 20, 23, and 26 μmol Cl g.cat⁻¹, respectively. While this low concentration of Cl would not account for the reduction in hydrogen surface concentration on a 1:1 Cl:Pt₅ basis, surface science
results for Cl adsorption on Pt(100) single crystals suggest that the stoichiometric ratio of Cl to Pt₅ is actually closer to 1:2 [20]. Furthermore, results from low-energy electron diffraction (LEED) for the adsorption of Cl on Pt(110) and Pt(111) single crystals show clear evidence of surface reconstruction [21]. Thus, based on this and the steady-state behavior of TTCE poisoning on the hydrogen surface concentration of Pt in the presence of excess H₂, it can be concluded that the poisoning effect of the impurity, at the lower reaction temperatures, is mainly due to the deposition of Cl-species on the Pt surface, resulting in Pt₅ blockage, effects on the chemisorption of hydrogen on neighboring Pt surface atoms, and/or Pt surface reconstruction. It should also be noted that, similar to how electropositive alkali metal atoms can affect not only the site they are adsorbed on but also four neighboring sites through electrostatic interactions [22], the presence of electronegative Cl atoms on a Pt surface can potentially poison multiple active Pt sites for adsorbing and dissociating H₂ [23, 24].

5.3.2.2 Reversibility of TTCE Poisoning on Pt in H₂ for Pt/C

Figure 5.2 shows the regeneration of Pt/C after exposure to 150 ppm TTCE in H₂ for 12 h. The regeneration was performed by flowing a mixture of (50/50) H₂/Ar over the poisoned catalyst at 60°C and 2 atm for a period of 22 h with hydrogen surface concentration measurements at 1.5, 3, 6, and 22 h of regeneration. As can be observed from the figure, some partial recovery of the Pt surface is evident after only 1.5 h of regeneration. However, similar to the results observed for the regeneration of CO poisoning on Pt/C [5], complete recovery of hydrogen surface concentration could not be
achieved, even after 22 h of exposure to H$_2$. Elemental analysis of Cl on the poisoned Pt/C, after 22 h of regeneration, shows a concentration of ca. 7 µmol Cl g.cat$^{-1}$ remaining of the original 13 µmol Cl g.cat$^{-1}$. This lack of a complete recovery may be due to the difficulty in removing adsorbed Cl and/or in reconstructing at 60°C the surface modified by the adsorption of Cl-species.

Figure 5.2 Regeneration in H$_2$ after TTCE poisoning for Pt/C.
5.3.2.3 Effect of Nafion on TTCE Poisoning on Pt in H\textsubscript{2} for Nfn-Pt/C

The effect of Nafion on the poisoning behavior of TTCE on Pt is shown in Figure 5.3. It should be noted that, based on the effect Nafion has for obstructing the diffusion of gas-phase H\textsubscript{2} away from the catalyst, the purge time used for the hydrogen surface concentration measurements for Nfn-Pt/C was increased to 50 min [6].

**Figure 5.3** Effect of Nafion on the poisoning behavior of TTCE in H\textsubscript{2} on Pt.
Similar to the effect Nafion has in obstructing the rate of diffusion of CO to the Pt surface [6], the presence of the polymer apparently also decreased the diffusion of TTCE to the Pt surface. After taking into account the excess protons available from the sulfonic sites in the Nafion, the effect of Cl on the strongly adsorbed hydrogen surface concentration on the Pt surface for Nfn-Pt/C was the same as for Pt/C, within experimental error. No evidence of physical and/or chemical interaction between the Nafion and the Pt surface atoms exists based on these results, as also previously found [6].

5.3.2.4 Co-adsorption of TTCE and CO on Pt in H₂ for Pt/C

The poisoning effect of 150 ppm TTCE + 30 ppm CO on Pt/C was investigated via hydrogen surface concentration measurements, with the results plotted in Figure 5.4. While the poisoning effect of two impurities is always interesting due to possible synergistic effects, the co-poisoning experiment was further motivated by FT-IR results suggesting that the presence of Cl on the Pt surface may block similar sites for CO adsorption. In a study by Gracia et al. [25], two batches of Pt/SiO₂ catalysts were prepared with one using a Pt-precursor containing Cl (H₂PtCl₆) and the other using a Pt-precursor without Cl [Pt(NH₃)₄(NO₃)₂]. Results from FT-IR obtained by exposing each catalyst to 0.3% CO in He at varying temperatures (45-200°C) show a significant reduction in the absorbance for the IR band corresponding to the linear-bonded CO, especially at the lower temperatures.
Based on Figure 5.4, the poisoning behavior of 150 ppm TTCE + 30 ppm CO on the hydrogen surface concentration of Pt/C appears to have been relatively similar to that of 30 ppm CO by itself, suggesting that the poisoning effect of CO is more dominant over that of Cl. This result is somewhat surprising, especially considering the highly electronegative nature of Cl. Furthermore, theoretical surface science studies of electrostatic adsorbate-adsorbate interactions show that an adsorbing molecule like CO,
which extracts electrons from the surface, will be destabilized by nearby electronegative atoms like Cl [22, 26]. This result suggests that the presence of Cl should decrease the adsorption behavior of CO and is in agreement with what was observed from the FT-IR results mentioned above. So why then is CO the dominant poison in our CO + TTCE study? While the presence of such large amounts of H₂ may have some effect on the adsorption of the two impurities, the reason is more likely due to the method of Cl deposition or, more specifically, the hydrodechlorination of TTCE. In other words, unlike the Pt/SiO₂ study [25], where Cl was directly deposited on the catalyst using a Pt-precursor containing Cl, the surface Cl in our study is from the decomposition reaction of TTCE.

Whenever a reaction involves the breaking of chemical bonds, in this case four C-Cl bonds to form ethane and HCl, that reaction is often structure sensitive, requiring site containing up to 12 contiguous surface metal atoms in order to carry out the reaction. Even the H₂-D₂ exchange reaction, which is essentially hydrogen activation, exhibits evidence of structure sensitivity at specific reaction conditions [27]. Furthermore, the extent to which the reaction is structure sensitive does not need to be extreme for the presence of a small amount of impurity to completely poison the reaction. For example, for a moderately structure sensitive reaction such as cyclopropane hydrogenolysis, a K⁺-coverage on the Pt surface of ca. 0.4 resulted in a 90% reduction in the rate of propane formation (i.e., from 96 to 10 µmol g.cat⁻¹ s⁻¹) [28]. Thus, if the hydrodechlorination of TTCE is structure sensitive, as the surface coverage of CO increases, the rate of TTCE decomposition would decrease, resulting in a much slower deposition of Cl on the Pt
surface. It should be emphasized that this is just a hypothesis as data regarding the structure sensitivity of the hydrodechlorination of TTCE is extremely limited. However, with such a hypothesis, all the results can be explained. One can also hypothesize that if Cl$_2$ gas was used instead of TTCE, at the same Cl concentrations, the poisoning effect of Cl would most likely be more severe. However, this is outside the scope of this paper.

5.3.2.5 Effect of TTCE Poisoning on Pt in O$_2$ and H$_2$+O$_2$

While the exposure of Pt/C to TTCE in a reducing environment (H$_2$) has been shown to have a negligible effect on the activity of Pt for adsorbing and activating H$_2$ and only a small effect on hydrogen surface coverage, the detrimental effect the impurity has on the performance of a fuel cell still remains to be answered. While no TTCE was detected at the cathode outlet during any of the fuel cell tests, this does not eliminate the possibility of chlorinated species being present at the cathode. In fact, it was hypothesized by Martínez-Rodríguez et al. [2] based on their results that the poisoning effect observed in their fuel cell was most likely due to the migration of a chlorinated compound, resulting from the decomposition of TTCE, across the membrane to the cathode where the oxygen reduction reaction (ORR) was poisoned.

The effect of TTCE in O$_2$ alone was first investigated. Exposure of the Pt/C to 1.8% O$_2$ for 1 h at 60°C and 2 atm, followed by a H$_2$ exposure time of 30 min, was shown to be adequate to saturate the Pt surface with hydrogen [5], i.e., the amount of surface hydrogen obtained after the O$_2$ exposure was the same as before O$_2$ exposure, suggesting that the amount of available Pt surface atoms remained the same. Increase in the duration
of exposure to 1.8% O₂ to 3 h resulted in a minor loss of available Pt surface atoms based on the measured hydrogen surface concentration (from 322 to 288 µmol H g.cat⁻¹). This slight reduction in the Pt surface atom availability was most likely due to the H₂ exposure time of 30 min being too short to completely re-reduce all of the oxidized Pt surface atoms. However, in order to allow for a valid comparison and based on the relatively minor loss in hydrogen concentration, the H₂ exposure time of 30 min was used for all subsequent experiments involving O₂.

Exposure of Pt/C to 150 ppm TTCE in 1.8% O₂ in Ar (no H₂) for 3 h showed no further decrease in Pt surface atom availability (as measured by hydrogen uptake), suggesting that the O₂ in conjunction with TTCE was not the cause for the severe deactivation observed in the fuel cell. This is most likely because, at low temperatures (<100°C) and in the absence of H₂, the decomposition of TTCE on Pt in O₂ is nearly 0% [18], resulting in almost no deposition of Cl on the Pt surface.

In order to fully investigate the effect chlorinated compounds might have on the ORR, it is important to duplicate the mixed redox conditions present (hydrogen + O₂) at the cathode of a fuel cell, where water vapor is also produced. To this end, the poisoning effect of 150 ppm TTCE on Pt/C was investigated in a mixture of 4% H₂ and 1.8% O₂ in Ar. Besides being below the flammability range of a H₂ + O₂ mixture, the 2:1 ratio of H₂:O₂ was chosen due to evidence suggesting a reasonably high conversion of TTCE in this stoichiometric mixture at low temperatures (ca. 20% at 75°C) [18]. In addition, the combination of both H₂ and O₂ on Pt also allows for the investigation of the effect that
water vapor might have on the TTCE poisoning, which, at the partial pressures of H₂ and O₂ used would be equivalent to ca. 30 %RH, assuming 100% conversion.

Figure 5.5 Comparison of exposure and 150 ppm TTCE poisoning of Pt/C in different gases (H₂, O₂, and H₂ + O₂). Effect of different regeneration gases. The data point for exposure to O₂ for 3 h has been moved slightly to the right due to overlapping with the data point for exposure to O₂+TTCE.

From Figure 5.5, it can be observed that the exposure of Pt/C to the mixture of 4% H₂/1.8% O₂ in Ar for 3 h resulted in a slight increase in the hydrogen surface concentration measured. This excess surface hydrogen was most likely contributed by the formation and retention of some H₂O on the catalyst surface, and should not be
confused with an increase in Pt surface atom availability [4]. In contrast to the lack of effect observed in the presence of H2, exposure of Pt/C to 150 ppm TTCE in the H2-O2 mixture for 3 h resulted in a substantial decrease in Pt surface atom availability. The effect of this poisoning was repeated 5 times at the same conditions on fresh samples of Pt/C, with reproducibility being < ±5%. Furthermore, based on the fuel cell hydrogen pump results [H2(anode)/N2(cathode)] of Martínez-Rodríguez et al. [2], with 30 ppm TTCE in the humidified anode feed, no decrease in the overpotential of the HOR was observed over a 4 h period in the presence of H2 + H2O. This suggests that the significant loss in the hydrogen surface concentration on Pt/C, from the exposure of TTCE in the H2-O2 mixture, was not due to either H2 or H2O, but clearly shows the role O2 plays in enhancing the deactivation process of the catalyst. It should be re-emphasized that, in the absence of H2, no effect from Cl poisoning was observed due to the TTCE being unable to decompose in O2 at the lower reaction temperatures, resulting in little or no deposition of Cl on the Pt surface.

Thus, the poisoning effect of TTCE on the performance of a fuel cell is really the combination of processes that are occurring at both the anode and the cathode. In other words, while the addition of TTCE to the anode has a minor effect on the Pt surface atom availability, the presence of the H2 plays a crucial role in initiating the poisoning process by facilitating the decomposition of TTCE to ethane and HCl. Once formed, the HCl then migrates from the anode to the cathode, where the presence of O2 enhances the poisoning effect from the halogen. Without the H2 being present to first decompose the TTCE via hydrodechlorination, the poisoning effect from the TTCE would most likely
not be as severe, as $O_2 +$ TTCE had no further effect on the Pt surface atom availability compared to $O_2$ by itself. This is again due to the fact that the decomposition of TTCE on Pt in $O_2$ is nearly 0% at the lower temperatures ($< 100^\circ C$) [18].

Similar to the results observed in the performance recovery studies of a fuel cell poisoned with TTCE [2] and what was shown in Figure 5.2, regeneration of the poisoned Pt/C in 4% $H_2$ showed an almost complete recovery of Pt surface atom availability (based on hydrogen uptake) in 1.5 h. In contrast, regeneration of the poisoned Pt/C in 1.8% $O_2$ or 4% $H_2 + 1.8% O_2$ resulted in little recovery in the same period of time. Interestingly, subsequent exposure to 1.8% $O_2$, with no TTCE, following regeneration in 4% $H_2$ showed a re-poisoning (i.e., loss of Pt surface atom availability) of the catalyst. This re-poisoning effect from subsequent exposure to $O_2$, after regenerating in $H_2$, was also observed by Martínez-Rodríguez et al. [2] and was suggested to be from residual TTCE desorbing from the gas lines. However, due to the fact that all gas lines were heated to 100$^\circ C$ with heating tape in our experimental system and the long time since TTCE was removed from the feed stream, a more likely reason may be associated with a study by Garcia et al. [25], where it was suggested that $O_2$ facilitates the migration of adsorbed Cl from the support to the metal surface, a process which $H_2$ helps reverse. However, more work is needed to validate this hypothesis.
5.4 Conclusions

The poisoning effect of TTCE on the ability of Pt to activate and adsorb $\text{H}_2$ was investigated at $60^\circ\text{C}$ and 2 atm using hydrogen surface concentration measurements on both Pt/C and Nfn-Pt/C catalysts exposed to varying concentrations of the impurity (150-540 ppm). Even at as high as 540 ppm TTCE, the reduction in hydrogen surface concentration was observed to be only ca. 33%, which was not enough to shift the $\text{H}_2$-$\text{D}_2$ exchange reaction away from being equilibrium limited. Decrease in the concentration of TTCE resulted in a decrease in the amount of surface hydrogen lost. As expected, the addition of Nafion to Pt/C decreased the rate of TTCE poisoning, due to the polymer inhibiting the rate of diffusion [6], but had very little/no effect on the poisoning behavior of TTCE at steady-state. Considering the high activity Pt has for the adsorption and activation of $\text{H}_2$, these results suggest that the presence of TTCE should have no observable effects on the HOR, due to not being able to shift the reaction away from equilibrium. These results also suggest that the detrimental loss in fuel cell performance in the presence of TTCE is not from the anode but most likely from the cathode.

Co-adsorption of CO and TTCE (30 ppm CO + 150 ppm TTCE) on Pt/C in $\text{H}_2$ showed that the poisoning effect from the mixture to be primarily dominated by the CO. This result is surprising considering overwhelming evidence from FT-IR [25] and surface science studies [22-24, 26] suggesting that the presence of Cl should actually destabilize the adsorption of CO due to electrostatic adsorbate-adsorbate interactions. However, because the deposition of Cl on the Pt surface is from the hydrodechlorination of TTCE,
it can be speculated that the structure sensitivity of the reaction plays a role. The presence of CO, which has a much more direct method of adsorption, would then severely poison the reaction and limit the deposition of Cl. It should be emphasized that this is only speculation at this point as data regarding the structure sensitivity of the hydrodechlorination of TTCE is extremely limited.

While only a slight reduction in amount of available Pt surface atoms (measured based on H$_2$ uptake from HDSAP) was observed from the exposure of TTCE to Pt/C in a H$_2$-only environment, a much more significant loss of available Pt surface atoms was observed when the catalyst was exposed to TTCE in the presence of both H$_2$ and O$_2$. This increase in the poisoning effect of TTCE was found to be contributed by the combination of H$_2$ and O$_2$, as the absence of either one resulted in little/no poisoning at the experimental conditions studied (60°C and 2 atm). This enhancement in the poisoning effect of TTCE in the presence of O$_2$ clearly shows the role O$_2$ plays in enhancing the deactivation process of the catalyst and further confirms that the actual poisoning of fuel cell performance by TTCE is at the cathode, rather than the anode. Similar to the recovery results obtain in a fuel cell [2], regeneration of Pt surface atoms (based on hydrogen surface concentration measured) of a poisoned Pt/C showed the highest level of recovery when regenerated in only H$_2$, followed distantly by H$_2$+O$_2$ and O$_2$.

5.5 References


There has been debate in the past as to whether or not cyclopropane hydrogenolysis is a structure sensitive reaction. This paper addresses the structure sensitivity of cyclopropane hydrogenolysis on Pt using K\textsuperscript{+} addition to Pt/C and compares the results to those for CO hydrogenation, a classic structure insensitive reaction. Kinetic parameters determined for both reactions show the effect of K\textsuperscript{+} on Pt to be limited to simple site blockage at the reaction conditions used. Determination of the site ensemble size (number of contiguous surface metal atoms) required for reaction using Martin’s model suggests that cyclopropane hydrogenolysis requires a site ensemble size of ca. 7, whereas the structure insensitive CO hydrogenation reaction requires only an ensemble size of ca. 1. In addition, evidence suggests that K\textsuperscript{+} decorates Pt non-uniformly.

6.1 Introduction

The reaction of cyclopropane with hydrogen has been studied extensively on a wide variety of metal catalysts [1-8], and in particularly Pt [1, 3, 9-13]. This hydrogenolysis reaction, termed so due to the characteristic ring opening of
cyclopropane, has been observed to yield three different sets of products depending on the metal and conditions used:

\[ cC_3H_6 + H_2 \rightarrow C_3H_8 \] (1)

\[ cC_3H_6 + 2H_2 \rightarrow CH_4 + C_2H_6 \] (2)

\[ cC_3H_6 + 3H_2 \rightarrow 3CH_4 \] (3)

Reactions (2) and (3), termed “selective” and “non-selective hydrocracking”, respectively, have been observed to occur on metals such as Fe, Os, and Ru with a shift toward the latter reaction as temperature increases [3, 5, 7, 8]. However, on metals such as Pt, Pd, Ir, and Rh, only reaction (1) has been observed [3, 4, 11, 13].

The structure sensitivity of the three cyclopropane reactions has been widely debated in the literature; and within this debate, the structure sensitivity of reaction (1) on Pt has particularly been discussed. Early works by Boudart et al. [9] and Kahn et al. [12] comparing the specific activity of the hydrogenolysis reaction as a function of metal surface area and dispersion showed the turnover frequency (TOF) to vary by a factor of only 2 for various loadings of Pt on alumina/silica and for certain Pt single crystal planes investigated. Based on the hypothetical vast differences in surface structural characteristics of the metal between supported and single crystals of Pt, the authors concluded that the reaction was structure insensitive to particle size, nature of support, or method of preparation. Later, work by Gallaher et al. [4] on La$_2$O$_3$-supported Rh, which, like Pt, is only active for reaction (1), showed the reaction rate to increase linearly with an increase in Rh dispersion, and suggested that the activity vs. dispersion on a TOF basis is constant and similar in behavior to that of other structure insensitive reactions.
On the other hand, Otero-Schipper et al. [13] confirmed the factor of 2 difference in TOF observed by Boudart et al. [9] but found it to be beyond experimental uncertainty for a wide range of dispersed Pt/SiO₂ catalysts. They concluded that, for this difference to be real, the reaction must be at least moderately structure sensitive. Similar conclusions have been suggested in more recent works by Jackson et al. [11] and Sajkowski et al. [6], in which the activity of cyclopropane hydrogenolysis appeared to depend on the particle size of the various supported Pt and Ru catalysts investigated. It should be noted that, while Ru is active for reactions (1) and (2), both reactions appear to have the same rate determining step, which is the ring opening of cyclopropane and formation of a common intermediate [6].

It should be pointed out that the “structure sensitivity” of a particular reaction entails not just (a) an effect of particle size related to crystal planes exposed on the observed rate or TOF of the reaction. Parameters that can also affect the rate of a structure sensitive reaction are: (b) coordination numbers of the active metal surface atoms in the active sites and (c) the number of contiguous metal surface atoms or ensemble size required for reaction. A general change in particle size and/or dispersion can potentially change the characteristics of all three parameters above, and, depending on how “structure sensitive” the specific reaction is, the effect on the resulting reaction kinetics can be moderate to significant. In addition to particle size, the shape of a metal particle may also be an issue. However, a more specific investigation of structure sensitivity of a reaction on a metal catalyst can be made without varying metal particle
size but by decoration of the metal surfaces using an additive or poison that effectively blocks surface metal atoms.

This paper reports, for the first time, the results of an investigation into the structure sensitivity of cyclopropane hydrogenolysis on Pt using a series of K\textsuperscript{+}-doped Pt/C catalysts prepared via sequential impregnation of the pre-reduced supported metal catalyst to prevent modification of the particle size distribution. Potassium was chosen due to evidence suggesting the promoter-metal interactions to be limited to simple site blocking on Pt and other noble metals if impregnated sequentially [14, 15]. The methodology of this investigation is similar to that of Hoost and Goodwin [15] and utilizes the statistical dependence of the rate of structure-sensitive reactions on simple site blockage originally established and reviewed in detail by Martin [16] in determining the approximate ensemble size required for reaction. In addition, results for the hydrogenation of CO, a classic structure-insensitive reaction, on the K\textsuperscript{+}-modified Pt/C catalysts are also presented to contrast to those for cyclopropane hydrogenolysis. Due to the low temperature required for cyclopropane hydrogenolysis, if this reaction were shown to be structure sensitive, it could be used to characterize Pt catalyst surfaces in catalysts not stable at higher temperatures, such as Nafion-Pt/C, which is used as the anode catalyst in proton exchange membrane fuel cells (PEMFCs).
6.2 Experimental

6.2.1 Catalyst Preparation

A commercial carbon supported Pt (Pt/C) with a nominal Pt loading of 20 wt%, was purchased from BASF and used as received. It was confirmed by BASF that the carbon black support (Vulcan XC-72) was purchased in-bulk from Cabot Co. and used directly for the synthesis of the Pt/C catalyst.

A portion of the purchased Pt/C catalyst were impregnated sequentially via incipient wetness with aqueous KNO₃ solutions of varying concentrations to prepare a series of K⁺-doped catalysts with theoretical \((\text{K/Pt}_T)_{\text{atom}}\) ratios of 0, 0.1, 0.2, 0.4, and 0.8, where \(\text{Pt}_T\) stands for the total amount of Pt available. In order to obtain a more uniform distribution of the potassium for each batch, the KNO₃ (Sigma Aldrich, 99.999% purity) was dissolved in 30 mL of distilled water and added drop-wise to the catalyst until incipient wetness was achieved. The wet catalyst was then placed in a static oven at 90°C for ca. 20 min to dry and the process was repeated until the entire solution has been used. The K⁺-free Pt/C catalyst was treated with only distilled water to check for possible effects from the impregnation process. After impregnation, the material was dried at 90°C overnight in a static air oven, then crushed, and sieved to obtain a catalyst particle size distribution of 60 – 180 µm. Nominal Pt and K compositions were confirmed via elemental analysis (performed by Galbraith Laboratories) for all catalysts. The K⁺-modified Pt/C catalysts are designated as \(xx\text{K/Pt}\) to indicate \((\text{K/Pt}_T)_{\text{atom}} = xx/100\). It should be noted that the \((\text{K/Pt}_T)_{\text{atom}}\) ratio is based on the total amount of Pt in the catalyst.
6.2.2 Characterization Methods

6.2.2.1 BET

Physical characteristics of the catalysts such as BET surface area, pore size, and pore volume measurements were performed in a Micromeritics ASAP 2020 unit. Samples of as-received Pt/C and K⁺-promoted Pt/C catalysts were degassed under vacuum (10⁻³ mm Hg) at 110°C for 4 h prior to analysis. Results were obtained from N₂ adsorption isotherms at -196°C.

6.2.2.2 Static H₂ Chemisorption

Static chemisorption experiments using H₂ were performed at 35°C in a Micromeritics ASAP 2010 equipped with a chemisorption controller station. Catalysts were first reduced in H₂ at 80°C for 3 h followed by an evacuation at 80°C (10⁻⁵ mm Hg) for another 3 h prior to the start of the analysis. A low reduction temperature of 80°C was chosen in order to be able to apply the results of this study to an investigation of temperature sensitive catalysts such as Nafion® supported on Pt/C. Nafion® polymer is an integral part of PEMFC Pt/C catalysts but is structurally unstable at higher temperatures. While no Nafion® was present on the Pt/C catalyst investigated here, the low reduction temperature was used to adhere to conditions employed for fuel cell catalysts. Temperature programmed reduction (TPR) results has shown Pt/C catalysts to be fully reduced at these conditions [17]. After evacuation, the temperature was adjusted to 35°C and the H₂ isotherms were obtained from 50–450 mmHg at increments of 50 mmHg. Volumetric uptakes of CO or H₂ on the catalysts were determined from the total
adsorption isotherm of the specified gas by extrapolating the linear portion of the isotherm in the higher pressure region to zero pressure. These values were then used in determining total available Pt surface atom concentration (Pt$_S$) and metal dispersion by assuming stoichiometric ratios of 1:1 for H:Pt$_S$. Calculation of average Pt particle size was carried out using the metal dispersion approximated from the chemisorption results and has been shown to correlate very well with the average Pt particle size results obtained from TEM images [17].

6.2.2.3 TEM and XRD

Transmission electron microscopy (TEM) images of Pt/C and K$^+$-promoted catalysts were obtained using a TEM-Hitachi 9500, which offers 300kV high magnification TEM and is designed for atomic resolution. Preparation of copper sample grids is explained in detail elsewhere [17]. Approximate Pt particle sizes of the catalysts were obtained by averaging diameters of 100+ particles from the TEM images. The results were further confirmed via X-ray Diffraction (XRD) (Scintag XDS 2000 powder diffractometer equipped with Cu Kα radiation) with a scanning range from 20°–85° and a step-size of 0.02°/min.

6.2.3 Cyclopropane Hydrogenolysis

Cyclopropane hydrogenolysis reaction rate results were obtained at 30°C and 1 atm utilizing a conventional plug flow, micro-reactor system similar to the one described in reference [17] with a tubular quartz reactor with an internal diameter of ca. 5 mm. Due
to the high activity of Pt for this reaction \cite{3}, low amounts of catalysts and a low partial pressure of \( \text{C}_3\text{H}_6 \) (American Gas Group, UHP) in the feed stream were required in order to achieve differential conditions for adequate kinetic analysis. To this end, 1.5–5 mg of the xxK/Pt catalysts (depending on activity) were diluted uniformly with 38.5–35 mg of XC-72, respectively, to achieve a catalyst bed of ca. 1 cm in thickness. Prior to reaction, the catalysts were reduced in 100 sccm of \( \text{H}_2:\text{Ar} \) (50:50) (National Specialty Gases, UHP) for 3 h at 80°C and 1 atm. After reduction, the temperature was decreased from 80°C to 30°C and stabilized. Reaction was initiated by flowing a gas mixture of \( \text{C}_3\text{H}_6:\text{H}_2:\text{Ar} \) (1:50:149) (total flow = 200 sccm) through the catalyst bed and allowing the reaction to stabilize for 5 min before sampling the gas effluent with a Varian 3800 GC equipped with FID and a Restek RT-QPLOT column (30 m, 0.53 mm ID). It is meaningful to note again that high space velocity and low partial pressure of \( \text{C}_3\text{H}_6 \) were required to achieve differential conditions due to the high activity Pt has for this reaction. All reaction rates reported were those for initial reaction (TOS = 5 min) to avoid possible complications from catalyst deactivation due to carbon deposition \cite{18}. The measured apparent activation energy of 12 kcal mol\(^{-1}\) for Pt/C, obtained by variation of reaction temperature from 30–50°C in increments of 5°C and from an Arrhenius plot of the data, is within the 8–12 kcal mol\(^{-1}\) range observed for this reaction on Pt-based catalysts in the literature \cite{12}. This agreement in the value of \( E_{\text{app}} \) and the linearity of the Arrhenius plot confirm the absence of mass and heat transfer effects.
6.2.4 CO Hydrogenation

The hydrogenation of CO on Pt was done to contrast to cyclopropane hydrogenolysis. Rate measurements of methanation on the Pt/C catalysts were taken at 392°C due to evidence indicating the dominant role of K⁺ on Pt for this reaction to be simple site-blockage in this higher temperature range [14]. The reaction temperature of 392°C was also required due to the low activity of Pt for this reaction. The reaction rate measurements were made using 100 mg of catalyst loaded in a fixed-bed differential reactor (316 stainless steel) with a length of ca. 300 mm and an internal diameter of ca. 5 mm.

The catalyst, placed in between quartz wool plugs, was positioned in the middle of the reactor with a thermocouple close by to allow accurate temperature control. Prior to reaction, the catalyst was first reduced in 22 sccm H₂ for 3 h at 80°C and 1.8 atm. After reduction, the temperature was ramped at 5°C/min from 80°C to 392°C, still in the flow of H₂. Once the temperature was stabilized, reaction was initiated by flowing a H₂:CO (12:1) mixture with a total flow rate of 22 sccm through the catalyst bed to achieve the same partial pressures of H₂ and CO used by Bajusz et al. [14]. The high relative partial pressure of H₂ to CO was employed to produce primarily methane as the product to simplify analysis.

Initial reaction data were collected after 5 min of reaction using a Varian 3800 GC equipped with both a flame ionization detector (FID) and thermal conductivity detector (TCD). The FID was connected to a Restek RT-QPLOT column (30 m, 0.53 mm ID), capable of separating C₁–C₇ hydrocarbons, while the TCD was connected to a Restek
Hayesep® Q column (1.83 m, 3.18 mm ID) used to separate CO and other inorganic gases. At these conditions, the reaction conversion was kept low (less than 0.5% in all cases) and differential behavior could be assumed. Specific activities were determined and are reported in terms of the rate of CH₄ formation per gram of catalyst. The formation of higher hydrocarbons was minimal and was excluded from our analysis.

Apparent activation energy ($E_{\text{app}}$) of CO hydrogenation on Pt/C was obtained by varying the reaction temperature from 380–410°C at increments of 10°C and determined to be 26 kcal mol⁻¹. Based on the linearity of the Arrhenius plot, the agreement of $E_{\text{app}}$ with literature values [14], and the lack of an effect of space velocity in this range on rate, it could be concluded that there were no mass or heat transfer effects on the rate of reaction.

In addition to the measurement of reaction rate data, steady-state isotopic transient kinetic analysis (SSITKA) was employed to understand the effect of K⁺-loading on surface kinetic parameters such as average surface residence times and surface concentrations of intermediates for the formation of CH₄. The reaction conditions utilized for these measurements were the same as above. These parameters were determined from isotopic transient curves, obtained by switching between (95% $^{12}$CO + 5% Ar) and ($^{13}$CO), using SSITKA data analysis [19]. The switch was made with a Valco four-port valve with an electric actuator to minimize turbulence effects and variation of flow rates, while two back-pressure regulators were also employed to minimize pressure disturbance effects. The 5% Ar present in $^{12}$CO was used as an inert tracer to determine the gas hold-up time of the entire reaction system. The
isotopic concentrations were followed by an online mass spectrometer (MS, Pfeiffer Vacuum) capable of high-speed data acquisition. An example of the normalized transients for CO and CH₄ obtained by switching from $^{12}$CO to $^{13}$CO during the reaction can be observed in Figure 6.1.

![Normalized transient curves for $^{12}$CO, $^{12}$CH₄, and Ar resulting from an isotopic switch, during CO hydrogenation at 392°C on 40K/Pt.](image)

**Figure 6.1** Typical normalized transients for $^{12}$CO, $^{12}$CH₄, and Ar resulting from an isotopic switch, during CO hydrogenation at 392°C on 40K/Pt.

The average residence time of CH₄ ($\tau_{\text{CH}_4}$) was obtained from the area between the normalized transient curves for CH₄ and the inert tracer (Ar). The concentrations of reversibly adsorbed CO (N$_{\text{CO}}$) and of the active surface intermediates leading to the formation of CH₄ (N$_{\text{CH}_4}$) were calculated by equations (2) and (3) below, respectively:
$N_{CO} = \text{Rate}_{CO} \times \tau_{CO} = F_{0,CO}(1 - x)\tau_{CO}$

$N_{CH_4} = \text{Rate}_{CH_4} \times \tau_{CH_4} = F_{0,CO}(x)\tau_{CH_4}$

where $x$ is the reaction conversion and $F_{0,CO}$ is the initial flow rate of CO.

**6.3 Results and Discussion**

**6.3.1 Catalyst Characterization**

The effects of the impregnation process on the physical characteristics of the catalyst were minimal as the BET surface area, average pore size, and pore volume measured for 00K/Pt were the same as those for the as-received Pt/C (Table 6.1). However, with the addition of K\(^+\), a noticeable decrease in BET surface area with increasing K\(^+\) concentration was evident. The loss of such a large amount of surface area (up to ca. 37%) is most likely due to blockage of some of the smaller pore structures in the support by K\(^+\) species. This is substantiated by the increase in the average pore size from ca. 16 to 19 nm. The effect of K\(^+\)-loading on the total pore volume of the catalysts appears to have been minimal, but this parameter is mainly a function of the larger pores.

Results from TEM and XRD spectra of the as-received Pt/C, 00K/Pt, 40K/Pt, and 80K/Pt catalysts showed no differences in the average Pt particle size ($2.6 \pm 0.4$ nm, $2.6 \pm 0.4$ nm, $2.7 \pm 0.3$ nm, and $2.7 \pm 0.4$ nm, respectively) determined for these catalysts. This was expected as the mild conditions used during the sequential impregnation process should not alter the metal particle size or dispersion of the Pt.
Table 6.1 BET surface area, average pore size, and pore volume of K+-doped Pt/C.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET SA* (m²/g.cat)</th>
<th>Pore Size* (nm)</th>
<th>Pore Volume* (cm³/g.cat)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C</td>
<td>170</td>
<td>15.9</td>
<td>0.44</td>
</tr>
<tr>
<td>00K/Pt</td>
<td>171</td>
<td>16.4</td>
<td>0.45</td>
</tr>
<tr>
<td>10K/Pt</td>
<td>159</td>
<td>16.2</td>
<td>0.44</td>
</tr>
<tr>
<td>20K/Pt</td>
<td>151</td>
<td>17.2</td>
<td>0.43</td>
</tr>
<tr>
<td>80K/Pt</td>
<td>107</td>
<td>19.1</td>
<td>0.48</td>
</tr>
</tbody>
</table>

*Experimental error was less than ±6%.

Table 6.2 Surface coverage of Pt by K⁺.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>K/Ptₜᵃ (atomic)</th>
<th>K⁺ impreg.ᵃ (µmol/g.cat)</th>
<th>Ptₛᵇ,c (µmol/g.cat)</th>
<th>θₚᵗᵈ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C</td>
<td>0.00</td>
<td>0</td>
<td>286</td>
<td>-</td>
</tr>
<tr>
<td>00K/Pt</td>
<td>0.00</td>
<td>0</td>
<td>278</td>
<td>1.0</td>
</tr>
<tr>
<td>10K/Pt</td>
<td>0.07</td>
<td>63</td>
<td>270</td>
<td>0.97</td>
</tr>
<tr>
<td>20K/Pt</td>
<td>0.15</td>
<td>135</td>
<td>264</td>
<td>0.95</td>
</tr>
<tr>
<td>40K/Pt</td>
<td>0.29</td>
<td>260</td>
<td>252</td>
<td>0.90</td>
</tr>
<tr>
<td>80K/Pt</td>
<td>0.53</td>
<td>475</td>
<td>177</td>
<td>0.64</td>
</tr>
</tbody>
</table>

ᵃBased on elemental analysis results from Galbraith Laboratories.
ᵇFrom static H₂ chemisorption at 35°C using the total adsorption isotherm and assuming (1:1) H:Ptₛ.
ᶜExperimental error was less than ±5%.
ᵈBased on Ptₛ of the 00K/Pt catalyst determined from static H₂ chemisorption at 35°C.

Elemental analysis results from Galbraith Laboratories showed an actual Pt loading of ca. 18 wt% for all catalysts, compared to the nominal loading of 20 wt%. The amount of K measured was 0.0, 0.24, 0.54, 1.02, and 1.82 wt% for the 00–80K/Pt catalysts, respectively. Based on these Pt and K loadings, consequent calculation of the actual (K/Ptₜ)ₐtom ratios for the K⁺-doped catalysts resulted in ratios of 0.07, 0.15, 0.29, and 0.53 for the 10–80K/Pt catalysts, respectively (Table 6.2). Even though subsequent
rinsing with distilled water of the KNO₃ solution containers were done to impregnate as much of the K⁺ as possible, it appears that a portion of the K⁺ was inevitably lost during the impregnation process.

In addition to Pt and K, elemental analysis (performed by Galbraith) and EDX confirmed the existence of large amounts of sulfur present in the bulk (ca. 0.5 wt% or 5000 ppm) and on the surface (ca. 0.2 wt% or 2000 ppm) of the Pt/C catalyst, respectively. Similar concentrations of sulfur were detected for the carbon support itself and is due to the vulcanization process (treatment with sulfur) used to produce a better dispersion of the Pt particles [20], especially at such high metal loadings. While most of the sulfur appears to be in the interior rather than on the surface of the carbon support (total S concentration = 0.5 wt% with ca. 0.2 wt% being the equivalent relative concentration on the surface), exposure of the catalyst to high temperatures could potentially cause the sulfur in the interior to migrate to the surface of the support and onto the Pt surface, thereby poisoning the reaction. In fact, results from EDX analysis of a similar but different batch of Pt/C catalysts after 48 h at 450°C in the presence of H₂ showed relative surface concentration of sulfur to double from ca. 0.1 to 0.24 wt%.

However, based on the relatively minor loss of hydrogen uptake capability of the catalyst (static chemisorption) from the prolonged thermal treatments (no treatment: 288 µmol/g.cat, compared to 252 µmol/g.cat after heating at 450°C for 50 h in H₂) and taking into account sintering effects, the presence and increase in surface sulfur did not appear to affect significantly or poison many Pt surface sites. Thus, because of the low reduction temperature used (80°C), the low reaction temperature used for cyclopropane
hydrogenolysis, and fast ramp rate (5°C/min) to 392°C from 80°C used in our study of CO hydrogenation, the migration/poisoning effect of the sulfur on the initial reaction rates should be minimal. Even so, only initial rate data, collected after 5 min of reaction, will be used in the discussion of structure sensitivity for both CO hydrogenation and cyclopropane hydrogenolysis on the Pt/C catalysts.

![Graph](image)

**Figure 6.2** Relationship of amount of K⁺ impregnated to the amount of surface Pt (based on static H₂ chemisorption, 35°C).

While more than enough K⁺ was added to completely block all Pt surface atoms available, results from static hydrogen chemisorption (Table 6.2) and a plot of available surface Pt vs. the amount of K⁺ added (Figure 6.2) clearly show that only a small portion
(ca. 12%) of the K\textsuperscript{+} impregnated on the Pt/C to be associated with surface Pt (i.e., blocking it) for the 10–40K/Pt catalysts. This increased to ca. 21% for 80K/Pt. Repeat analyses of specific samples show the experimental error to be well below ±5%, suggesting the K\textsuperscript{+} to be more or less well distributed throughout each sample of catalyst.

6.3.2 Cyclopropane Hydrogenolysis

Due to the high activity of Pt for cyclopropane hydrogenolysis and the high weight loading of Pt in the catalysts, low amounts of catalyst and a low partial pressure of cyclopropane were required to keep the conversion below 15%. While this conversion is a little high for perfect differential reactor behavior, it has been found that the rate of this reaction on Pt increased linearly up to 50% conversion [9]. As expected, propane was the only product observed from this reaction on Pt. Table 6.3 shows the initial (5 min) reaction rate data obtained for cyclopropane hydrogenolysis on the various K\textsuperscript{+}-doped Pt/C catalysts and Figure 6.3 shows a plot of initial rate of this reaction as a function of K\textsuperscript{+}-coverage on Pt (1 – \( \theta_{\text{Pt}} \)).

Initial reaction rate results for cyclopropane hydrogenolysis on the as-received Pt/C and 00K/Pt catalysts were the same, within experimental error. For the xxK/Pt catalysts, rate decreased with increasing K\textsuperscript{+}-loading. As can be seen from Figure 6.3, most of the significant reduction in initial reaction rate data was before a K\textsuperscript{+}-coverage of 0.15, with rate leveling off as K\textsuperscript{+}-coverage increased further. Calculation of the TOF for cyclopropane hydrogenolysis based on the amount of exposed Pt surface atoms (Pt\textsubscript{S}) obtained from static H\textsubscript{2} chemisorption showed an overall decrease of ca. a factor of 6
(0.34 s\(^{-1}\)–0.06 s\(^{-1}\)) for the range of K\(^+\)-coverage investigated. Comparison of TOF of Pt/C with those of other supported Pt catalysts reported in literature (Pt/Al\(_2\)O\(_3\) [9] and Pt/SiO\(_2\) [9, 13]) show the values to be in agreement within the same order of magnitude, which is very good considering differences in catalyst preparation, composition, and reaction conditions.

Table 6.3 Initial reaction results\(^a\) of cyclopropane hydrogenolysis on K\(^+\)-modified Pt/C catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Initial (R_p)(^b) ((\mu)mol/g.cat-s)</th>
<th>TOF(^c) (s(^{-1}))</th>
<th>(E_{\text{app}})(^d) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>00K/Pt</td>
<td>96</td>
<td>0.34</td>
<td>11.9</td>
</tr>
<tr>
<td>10K/Pt</td>
<td>81</td>
<td>0.30</td>
<td>11.7</td>
</tr>
<tr>
<td>20K/Pt</td>
<td>69</td>
<td>0.26</td>
<td>10.9</td>
</tr>
<tr>
<td>40K/Pt</td>
<td>41</td>
<td>0.16</td>
<td>10.1</td>
</tr>
<tr>
<td>80K/Pt</td>
<td>10</td>
<td>0.06</td>
<td>10.4</td>
</tr>
</tbody>
</table>

\(^a\)30°C, 1 atm, H\(_2\)/C\(_3\)H\(_5\)/Ar = 50/1/149 sccm.
\(^b\)Initial reaction rate for the formation of propane: Error < ±7%.
\(^c\)Based on Pt\(_S\) from static H\(_2\) chemisorption.
\(^d\)Apparent activation energy: Error < ±10%.

The apparent activation energy (\(E_{\text{app}}\)) of 11.9 kcal/mol measured for the non-modified Pt/C catalyst is in agreement with what has been reported in the literature [12] for Pt catalysts. The relatively constant \(E_{\text{app}}\), within experimental error, with the addition of K\(^+\) suggests the lack of electronic and/or promotion effects between the Pt and K\(^+\)-species for cyclopropane hydrogenolysis, such that the reaction mechanism and heats of adsorption remain relatively essentially the same. Thus, K\(^+\) appears to act only as a blocking agent for this reaction.
Figure 6.3 Initial rates of cyclopropane hydrogenolysis and CO hydrogenation as a function of $K^+$-coverage on Pt surface.

### 6.3.3 CO Hydrogenation

The reaction of CO and hydrogen on Pt was performed to provide a comparison to the rate data for cyclopropane hydrogenolysis. Even at the high reaction temperature of 392°C utilized, required due to the low intrinsic activity of Pt for this reaction, the reaction conversion on the 18 wt% Pt/C (100 mg) was less than 0.5%, compared to 1.5% reaction conversion for 4.5 wt% Pt/SiO$_2$ (25–35 mg) at the same reaction temperature [14]. This difference in catalytic activity between the two catalysts may be due to differences in metal-support interactions and the fact that the carbon support used had
been vulcanized. As mentioned previously, the main reason for choosing 392°C was due to evidence for K⁺-modified Pt/SiO₂ indicating that, at this high temperature range, the dominant role of K⁺ on Pt for methanation was simple site blockage [14]. Table 6.4 lists the initial reaction rate data and surface kinetic parameters, as determined by SSITKA, for CO hydrogenation on the various K⁺-doped Pt/C catalysts. Figure 6.3 gives a plot of the initial rate of CO hydrogenation as a function of K⁺-coverage on Pt (1 – θ₉).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>R_M a (10⁻³ μmol/g.cat-s)</th>
<th>τ_CO b (s)</th>
<th>N_CO c (μmol/g.cat)</th>
<th>τ_M b (s)</th>
<th>N_M d (μmol/g.cat)</th>
<th>1/τ_M (s⁻¹)</th>
<th>E_app (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>00K/Pt</td>
<td>74</td>
<td>2.4</td>
<td>30</td>
<td>5.0</td>
<td>0.37</td>
<td>0.20</td>
<td>26.3</td>
</tr>
<tr>
<td>20K/Pt</td>
<td>64</td>
<td>2.3</td>
<td>29</td>
<td>4.8</td>
<td>0.31</td>
<td>0.21</td>
<td>28.5</td>
</tr>
<tr>
<td>40K/Pt</td>
<td>55</td>
<td>2.4</td>
<td>30</td>
<td>4.8</td>
<td>0.25</td>
<td>0.20</td>
<td>27.9</td>
</tr>
<tr>
<td>80K/Pt</td>
<td>47</td>
<td>2.5</td>
<td>32</td>
<td>4.8</td>
<td>0.20</td>
<td>0.21</td>
<td>28.2</td>
</tr>
</tbody>
</table>

aRate of CH₄ formation: Error = ± 2 × 10⁻³ μmol/g.cat s.
bAverage surface residence time of rev. ads. CO: Error = ± 0.2 s.
cSurface concentration of rev. ads. CO: Error = ± 5%.
dSurface concentration of carbon-containing intermediates leading to CH₄: Error = ± 4%.

As seen in Figure 6.3, decrease in the initial reaction rate was relatively proportional to the increase in K⁺-coverage from 0–0.1 and began to level off as K⁺-coverage increases to 0.36. Thus, the overall subtle decrease in rate with increasing fraction of Pt surface covered by K⁺ suggests that this reaction is less sensitive to surface structure than cyclopropane hydrogenolysis. Surface parameters measured by SSITKA for CO hydrogenation show that, considering the large amount of surface Pt atoms available based on static H₂ chemisorption, only a small portion (ca. 10%) appeared to be
occupied by reversibly adsorbed CO ($N_{CO}$) at 392°C and even less (ca. 1%) for the formation of active intermediates (in terms of carbon atoms) that led to the production of CH$_4$ ($N_M$). The fact that the average residence time of the carbon-based intermediates leading to the formation of CH$_4$ ($\tau_M$) remained constant with $K^+$-coverage suggests that the decrease in the activity of the catalyst was solely attributable to the blockage of the sites that were active for the formation of CH$_4$. The quantity, $1/\tau_M$, is a measure of the TOF of reaction based on the sites active for the formation of methane. The relatively constant value of $1/\tau_M$ for the various $K^+$-doped catalysts suggests either uniform poisoning or, more likely, the lack of variation in activity among the different sites available, which is what would be expected for a structure insensitive reaction. The reason for the decrease in rate is clearly due to a loss in surface intermediates (sites), $N_M$, with increasing amounts of $K^+$, since Rate = $(1/\tau_M)N_M$. Similar to what was observed for cyclopropane hydrogenolysis, comparison of TOF ($1/\tau_M$) obtained for CO hydrogenation on Pt/C to that for Pt/SiO$_2$ [14] shows the values to be similar with an order of magnitude.

The $E_{app}$ of 26.3 kcal/mol measured for CO hydrogenation on the non-doped (bare) Pt/C is similar to the literature value of 27 kcal mol$^{-1}$ [14]. Similar to cyclopropane hydrogenolysis results, the lack of variation (within experimental error) in $E_{app}$ between the bare and $K^+$-doped Pt/C catalysts observed for this reaction also indicates the absence of any electronic or promotion effects caused by $K^+$. All results suggest that the effect of $K^+$ as a Pt modifier for both reactions appears to have been limited to simply blocking active sites.
6.3.4 Structure Sensitivity Analysis

While the variation in the TOF for cyclopropane hydrogenolysis is an indication of structure sensitivity, that evidence alone is not enough as confirmation. Utilizing the simplified exponential expression relating the statistical dependence of rate on site blockage by a blocking agent presented by Hoost and Goodwin [15] and originally proposed by Martin [16], the ensemble size required for a specific reaction can be approximated by the following equation:

\[
\frac{R}{R_{P=0}} = (1 - \theta_p)^{N_E}
\]

where \( R \) is the reaction rate of the doped catalyst (K\(^+\)-doped Pt/C), \( R_{P=0} \) is the rate of the non-doped (non-blocked) catalyst (Pt/C), \( N_E \) is the ensemble size required for the reaction, and \( \theta_p \) is the fraction of the surface metal blocked by the blocking agent or poison P. This simplified expression is only valid when the number of available surface atoms on a particle is greater than the site ensemble size, which is usually the case for supported catalysts.

Figure 6.4 shows the semi-logarithmic plot of the normalized initial rates of reaction \((R/R_{P=0})\) as a function of fraction of Pt surface exposed \((\theta_p)\) for both cyclopropane hydrogenolysis and CO hydrogenation. The slopes of the individual curves should yield the value for \( N_E \) or ensemble size required for reaction. As one would expect for a structure insensitive reaction, data points for CO hydrogenation on the semi-log plot follow the same trend as that of a uniformly poisoned reaction with an ensemble size requirement of ca. 1 (single-atom ensemble model). While there is some slight deviation from the theoretical line, the difference is minimal. Similarly, interpretation of
the decrease in initial rate with $K^+$-coverage for $\theta_{Pt} = 1–0.8$ suggests the ensemble size required for cyclopropane hydrogenolysis to be ca. 7 (7-atom ensemble model). As the $K^+$-coverage increased to give $\theta_{Pt} < 0.8$, a deviation from the 7-atom ensemble theoretical line predicted by Martin’s model can be observed. This variation, as clearly shown by the modeling results of Hoost and Goodwin [15], is indicative of preferential blockage of certain surface planes of the metal by the blocking agent (in this case $K^+$).

**Figure 6.4** Fraction of Pt surface exposed vs. normalized initial reaction rates for cyclopropane hydrogenolysis and CO hydrogenation.
Although a key assumption in Martin’s ensemble model is uniform poisoning of the metal surfaces, the reality, however, is that this is rarely the case. Monte Carlo simulations performed by Strohl and King [21] on various supported bimetallic (but non-alloying) systems (Cu-Pt, Ag-Pt, and Au-Pt) showed non-uniform decoration of the Pt surface by the other metal. All three metals (Cu, Ag, and Au), based on the simulation, preferentially adsorb on surface sites of low coordination with varying degrees of filling. For example, Au completely filled lower coordinated Pt surfaces at lower fractions of the metal adsorbed than Ag, followed by Cu. Furthermore, the simulation also showed that, depending on the “bonding nature” of the species, the blocking behavior of the Cu atoms differed from that of Au and Ag. Such non-uniform decoration by K⁺ of a metal surface has been shown for K⁺/Ru/SiO₂ [15].

Thus, it would appear that K⁺ preferentially blocks certain Pt planes on Pt particles such that the distribution of the alkali species is non-uniform. As a result, this non-uniform blocking behavior would, of course, have dramatic effects on the activities observed for structure-sensitive reactions. In other words, if the K⁺ were to preferentially adsorb on surface Pt sites with the lowest activity for the reaction, the resulting minor loss in overall activity with increasing coverage could result in the misinterpretation of the reaction as being structure insensitive. Conversely, if the opposite were true, then the complete loss in activity with only a fraction of the surface Pt covered would lead to the misinterpretation of the reaction to being extremely structure sensitive. Given the large decrease in rate with K⁺-coverage and the existence of probable preferentially blockage of certain Pt surface structures with higher activities, it can be concluded that
cyclopropane hydrogenolysis on Pt is definitely structure sensitive. The ensemble size required for cyclopropane hydrogenolysis of Pt is possibly less than 7, however, but likely greater than 2, the value found for cyclopropane hydrogenolysis on Ni-Cu/SiO$_2$ by Cale and Richardson [2]. Specific possibilities for the required ensemble size will not be discussed here as more data is needed.

6.4 Conclusions

The structure sensitivity of cyclopropane hydrogenolysis on Pt was investigated via a series of K$^+$-doped Pt/C catalysts. While the BET surface area and average pore diameter decreased with K$^+$-loading, sequential impregnation of the alkali species had no effect on the average Pt particle size as determined from TEM and XRD. Static H$_2$ chemisorption results confirm that, of the large amount of K$^+$ added, only a small portion (ca. 10–20%) was associated with surface Pt atoms. Sulfur poisoning of Pt due to sulfur contained in the carbon support from vulcanization was not evident.

Based on the surface parameters, as determined from SSITKA, and apparent activation energies, the effect of K$^+$ on the Pt for both reactions appear to be limited to simple site blockage. No evidence indicating promotion or true poisoning effects were observed at the reaction conditions employed. Initial reaction rate results for cyclopropane hydrogenolysis on the as-received Pt/C and 00K/Pt catalysts were the same, within experimental error, indicating also no effect due to aqueous impregnation.
The value for the site ensemble size required for cyclopropane hydrogenolysis on Pt, based on Martin’s model [16], was estimated to be ca. 7, whereas, CO hydrogenation, a classic structure insensitive reaction, appears to require a site ensemble size of ca. 1, as might be expected. In addition, calculation of TOF (based on H$_2$ chemisorption) for cyclopropane hydrogenolysis show a decrease with increasing K$^+$-loading, while the TOF (based on 1/$\tau_M$ from SSITKA) for CO hydrogenation remained essentially constant. Based on these results and the extremely high probability of non-uniform distribution of K$^+$ on specific Pt surfaces, as suggested by Monte Carlo simulations for bimetallic systems [21], reaction results for K$^+$-modified Ru/SiO$_2$ [15], and the deviation observed from the ensemble model at the higher K$^+$ coverages, it can be concluded that the significant loss of rate with increasing K$^+$-coverage for cyclopropane hydrogenolysis is dependent not only on the number of Pt surface atoms exposed, but also on the Pt surface planes exposed and the availability of sites with higher numbers of contiguous atoms for reaction. The evidence clearly shows that cyclopropane hydrogenolysis on Pt is structure sensitive.

6.5 References


CHAPTER SEVEN
SUMMARY AND RECOMMENDATIONS

7.1 Summary

In the present research, the effects of CO, water, Nafion®, and tetrachloroethylene on the activity of Pt for the adsorption and activation of hydrogen were investigated at typical PEMFC operating conditions. The degrees of impact from the impurities were characterized in terms of both H₂-D₂ exchange reaction and Pt surface atom availability. The H₂-D₂ exchange reaction was shown to be similar in both the elementary surface reaction and rate constant to the electrocatalytic oxidation of H₂ on Pt at temperatures close to ca. 50°C. Other impurities investigated but were not discussed due to having little or no effect on the H₂ activation and Pt surface atom availability were inert gases (He, N₂, Ar), paraffins (C₃-C₇), ethylene, and NH₃ (see Appendix C).

The reaction rate of hydrogen activation on Pt is extremely fast in the absence of any CO. Measurement of the apparent activation energy for the reaction on Pt, in the absence of CO, was estimated to be ca. 4.5-5.3 kcal mole⁻¹ from surface science studies. Exposure of the catalyst to 10 ppm CO increased the apparent activation energy to 19.3 kcal mole⁻¹. Increasing the CO concentration to 70 ppm resulted in no further increase in apparent activation energy, within experimental error. While reaction rate measurements of H₂-D₂ exchange on the Pt/C were possible in the presence of CO, the reaction is limited by equilibrium on as little as 1 mg of the 20 wt% Pt/C catalyst in the absence of
CO, even at room temperature. Because of this, no reaction rate measurements were possible on the unpoisoned catalyst at the experimental conditions employed. Results involving Pt surface atom availability using hydrogen surface concentration measurements show a steady-state CO surface coverage of approximately 0.55 ML at 80°C in H₂ with 70 ppm CO. The CO surface coverage did not appear to increase when the CO concentration was increased to 200 ppm, suggesting that the CO surface coverage of ca. 0.55 ML to be close to maximum for the Pt/C catalyst investigated. Regeneration of Pt/C at 80°C in H₂ after CO exposure showed only a partial recovery of Pt surface sites. However, enough CO-free Pt sites existed to easily achieve equilibrium conversion for H₂-D₂ exchange reaction.

In the presence of water vapor, a reduction in the rate of CO adsorption was observed from time-on-stream (TOS) results. However, the water vapor had very little effect on the steady-state CO surface coverage on Pt surface sites (Ptₛ). For example, the steady-state surface coverage of Ptₛ by CO at 80°C for Pt exposed to H₂ (PᵢH₂ = 1 atm) and a mixture of H₂/H₂O (1 atm H₂, 10%RH) were 0.70 and 0.66 ML, respectively. Interestingly, the amount of strongly-bound surface hydrogen measured after exposure to a mixture of H₂/H₂O was the sum of the exchangeable surface hydrogen contributed by each component, even in the presence of CO. Since TPD results show no evidence for the strong adsorption of H₂O on the carbon support, with/without Pt, this additive nature in the strong-bound surface hydrogen and seemingly lack of interaction from the co-adsorption of H₂ and H₂O on Pt may be attributed to the repulsion of strongly adsorbed H₂O to the stepped-terrace interface at high coverages of surface hydrogen. Regardless,
no effect from the presence of water vapor was observed on the activity of Pt for the adsorption and activation of hydrogen. It should be emphasized that the increase in surface hydrogen present on the Pt/C catalyst in the presence of water vapor does not indicate an increase in catalytic activity. The activity of the catalyst is obtained from the amount of Pt surface atoms available, which does not increase when exposed to water vapor.

An investigation into the effect and siting of the Nafion® was necessary due to the high loading (ca. 30 wt%) used in conventional PEMFC catalyst layers. While high loadings of the ionomer in the catalyst layer is favorable to ensure fast proton transport, one can imagine that the addition of such large amounts of the Nafion® can potentially block Pt surface atoms via physical and/or chemical interactions. In fact, physisorption results showed a severe loss in BET surface area from the addition of Nafion® due most likely to the filling/blocking of the smaller pore structures in the carbon support. However, static H₂ and CO chemisorption results indicated only a minimal effect from the Nafion® on the adsorption capability of either hydrogen or CO on Pt, which is extremely surprising. Even measurements of apparent activation energy of H₂-D₂ exchange reaction in the presence of CO on Pt/C and Nfn-Pt/C resulted in similar values for both catalysts. This lack of effect from the Nafion® on the Pt was found, from cyclopropane hydrogenolysis modeling results, to be due to the partial blockage of only the pore openings. The experimental results suggest that most of the Pt particles are in the meso-macropores of the carbon support, whereas Nafion is present primarily on the external surface of the carbon, where it blocks significantly the micropores but only
partially the meso-macropores. Since no evidence suggesting physical and/or chemical interactions between the Nafion® and Pt surface atoms, this study also suggests that transport of protons can take place without direct contact between the ionomer and metal surface, unlike previously thought.

Finally, the poisoning effect of a relatively unknown impurity, tetrachloroethylene (TTCE), was investigated due to a recent fuel cell study showing a much more severe degradation in fuel cell performance from TTCE than from similar concentrations of CO, when present in the hydrogen fuel stream. Interestingly, while the poisoning effect from the CO can be attributed to the blocking of Pt surface sites at the anode of the fuel cell, results from both the fuel cell study and Pt surface atom availability measurements indicate no observable effects from the TTCE on the HOR. The real poisoning effect, however, was observed when the Pt/C catalyst was exposed to the TTCE in a mixed redox environment (H₂ + O₂), similar to that at the cathode of a fuel cell. It was found that the poisoning effect of TTCE on the performance of a fuel cell is really the combination of two processes: hydrodechlorination of TTCE and the enhanced poisoning effect of Cl-species in the presence of O₂. Regeneration of the poisoned catalyst in H₂ showed the highest level of recovery. The results from this study confirm that the majority of the poisoning from TTCE on fuel cell performance takes place most likely at the cathode, rather than the anode.

The structure sensitivity of cyclopropane hydrogenolysis was investigated due to the need of a structure sensitive reaction in the study involving Nafion®. A debate also existed among the scientific community in regards as to whether or not the reaction is
really structure sensitive. Traditional structure sensitive reactions, such as ethane hydrogenolysis, could not be employed due to the requiring of reaction temperatures well in excess of 120°C, which can cause structure instability leading to the degradation of the ionomer. The structure sensitivity study was performed using K⁺ addition to Pt/C and comparing the reaction results to those for CO hydrogenation, a classic structure insensitive reaction. Kinetic parameters determined for both reactions show the effect of K⁺ on Pt to be limited to simple site blockage at the reaction conditions used. Determination of the site ensemble size (number of contiguous surface metal atoms) required for reaction using Martin’s model suggests that cyclopropane hydrogenolysis requires a site ensemble size of ca. 7, whereas the structure insensitive CO hydrogenation reaction requires only an ensemble size of ca. 1. This confirms that the hydrogenolysis of cyclopropane on Pt is indeed structure sensitive.

The results from this study provided a critical insight into the effects CO, water, Nafion®, and TTCE have on the activation of H₂ on a Pt fuel cell catalyst through Pt surface atom availability based on hydrogen uptake. In addition, due to the fast rate of proton transport observed between the ionomer and the Pt surface, this new method of measurement may also be helpful in investigating the possible effects some impurities may have on the process of proton conduction.
7.2 Recommendations

The following are a few suggested mitigation strategies based on the results observed in this study:

- While the presence of water vapor did not have an observable effect on the CO surface coverage on Pt at steady-state, it did decrease the rate of CO adsorption or poisoning. Thus, in order to prolong the operational lifetime of a fuel cell in the presence of CO, it would appear that higher levels of relative humidity would be favorable. A possible drawback from this suggestion may be an increase in water management issues.

- Even though the presence of Nafion® did not have an effect on the catalytic activity of Pt/C, it did show, based on the cyclopropane hydrogenolysis results, that the ionomer can prevent molecules of larger critical diameters from having easy access to the Pt particles situated in the pores of the carbon support. Thus, for larger-sized molecules, such as tetrachloroethylene, the use of a molecular sieve in the gas diffusion layer (GDL) of a PEMFC may help in reducing their impact. A possible drawback from this suggestion may be increased diffusion-related issues in the GDL.

- Finally, for impurities like CO, whose poisoning effect is somewhat reversible, an increase in the operating temperature of a fuel cell would
help decrease the poisoning effect observed and/or increase the concentration of the impurity tolerable.

Obviously, more work is still needed in studying the poisoning effects of the many other impurities that can be introduced into the hydrogen feed stream. Furthermore, while limitations exist for the new method of measuring the in-situ Pt surface atom availability using hydrogen uptake, it shows promise and should definitely be further investigated.
APPENDICES
APPENDIX A

HYDROGEN SURFACE CONCENTRATION MEASUREMENTS FROM HDSAP

The calibration peak (Figure A.1) is obtained by flowing known partial pressures of H₂ and D₂ over the catalyst and directing the effluent into a 6-port valve with a 2 mL sample loop. Once the flow is stabilized, the content within the sample loop is injected into the mass spectrometer.

![Figure A.1 Example of a calibration peak used to calculate, from the HDSAP profile, the concentration of surface hydrogen at time-on-stream.](image)

After the calibration peak, HDSAP (Figure A.2) is started by exposing the catalyst to 30 min of H₂ (P_H₂ = 1 atm), purging with Ar for x min (x = 30 min for Pt/C and 50 min for Nfn-Pt/C), followed by D₂ (P_D₂ = 1 atm) switch via 4-port valve. The amount of
surface hydrogen is calculated by taking the area under both the H\textsubscript{2} and HD peaks (with the final leveled off value as background) (Figure A.3) and comparing them to the area under the calibration peak. The final surface hydrogen concentration is obtained by \((C_{\text{H}_2} \times 2) + C_{\text{HD}}\).

\textbf{Figure A.2} Typical HDSAP measurement.
Figure A.3 Example of a H$_2$ and HD peak resulting from the D$_2$ switch during HDSAP.
APPENDIX B

TEM IMAGES OF Pt/C WITH VARIOUS PRETREATMENT CONDITIONS

Figure B.1 TEM image of fresh, untreated 20 wt% Pt/C.

Figure B.2 TEM image of 20 wt% Pt/C exposed to 50/50 H₂/Ar for 3 h at 80°C and 2 atm.
Figure B.3 TEM image of 20 wt% Pt/C exposed to H₂ for 24 h at 80°C and 2 atm.

Figure B.4 TEM image of 20 wt% Pt/C exposed to 50/50 H₂/Ar for 24 h at 80°C and 2 atm.
## APPENDIX C

### OVERVIEW OF IMPURITY EFFECTS

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Effect on FC Performance</th>
<th>Max. Conc. Tested</th>
<th>Max. $P_i$ (atm)</th>
<th>Effect on Pt/C&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Effect on Nafion&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inerts (N&lt;sub&gt;2&lt;/sub&gt;, Ar, He)</td>
<td>No</td>
<td>50 – 80%</td>
<td>1.0 – 1.6</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>TBD</td>
<td>500 ppm</td>
<td>0.0005</td>
<td>TBD</td>
<td>No</td>
</tr>
<tr>
<td>CO</td>
<td>Major</td>
<td>2-50 ppm</td>
<td>to 0.00005</td>
<td>Major</td>
<td>No</td>
</tr>
<tr>
<td>NH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Major</td>
<td>10-5000 ppm</td>
<td>to 0.005</td>
<td>Minimal</td>
<td>Major</td>
</tr>
<tr>
<td>Formic acid</td>
<td>TBD</td>
<td>400 ppm</td>
<td>0.0004</td>
<td>TBD</td>
<td>No</td>
</tr>
<tr>
<td>Ethylene</td>
<td>TBD</td>
<td>400 ppm</td>
<td>0.0004</td>
<td>Minimal</td>
<td>No</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>TBD</td>
<td>250 ppm</td>
<td>0.00025</td>
<td>TBD</td>
<td>No</td>
</tr>
<tr>
<td>Perchloroethylene</td>
<td>Major</td>
<td>30-400 ppm</td>
<td>0.0004</td>
<td>Major</td>
<td>No</td>
</tr>
<tr>
<td>Tetrahydrofuran (THF)</td>
<td>Yes – but reversible</td>
<td>400 ppm</td>
<td>0.0004</td>
<td>TBD</td>
<td>No</td>
</tr>
<tr>
<td>Propane (C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;)</td>
<td>No</td>
<td>100 ppm</td>
<td>0.0001</td>
<td>Minimal</td>
<td>No</td>
</tr>
<tr>
<td>Butane (C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;)</td>
<td>No</td>
<td>100 ppm</td>
<td>0.0001</td>
<td>Minimal</td>
<td>No</td>
</tr>
<tr>
<td>Pentane (C&lt;sub&gt;5&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;)</td>
<td>No</td>
<td>100 ppm</td>
<td>0.0001</td>
<td>Minimal</td>
<td>No</td>
</tr>
<tr>
<td>Hexane (C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;14&lt;/sub&gt;)</td>
<td>No</td>
<td>100 ppm</td>
<td>0.0001</td>
<td>Minimal</td>
<td>No</td>
</tr>
<tr>
<td>Heptane (C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;16&lt;/sub&gt;)</td>
<td>No</td>
<td>100 ppm</td>
<td>0.0001</td>
<td>Minimal</td>
<td>No</td>
</tr>
<tr>
<td>Cations (Na&lt;sup&gt;+&lt;/sup&gt;, Ca&lt;sup&gt;2+&lt;/sup&gt;, Fe&lt;sup&gt;3+&lt;/sup&gt;)</td>
<td>Major</td>
<td>NA</td>
<td>NA</td>
<td>Minimal</td>
<td>Major</td>
</tr>
</tbody>
</table>

<sup>a</sup>Impurities were exposed to Pt/C catalyst at 80oC over a 24 h period.

<sup>b</sup>Impurities were exposed to a Nafion membrane at 80oC over a 24 h period.

**Figure C.1** Overview of impurity effects on overall fuel cell performance, Pt/C catalyst, and Nafion membrane.