



The effect of low concentrations of CO on H₂ adsorption and activation on Pt/C: Part 2—In the presence of H₂O vapor

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ABSTRACT

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 Pt₅ (θ_{CO}) at steady-state. The steady-state θ_{CO} s at 80 °C for Pt exposed to H₂ ($P_{H_2} = 1$ 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.

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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 H₂ 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 H₂ fuel containing only trace amounts of impurities (i.e., CO, CO₂, NH₃, SO₂, 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 H₂ on Pt sites, thereby inhibiting the process of H₂ 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] help to increase CO tolerance due to higher oxidation rates of CO by OH_{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

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the activation of H₂ on Pt-based catalysts at conditions related to actual fuel cell environments.

In this study, H₂–D₂ exchange and a simple H₂–D₂ switch with an Ar purge in between (HDSAP) technique was employed to quantitatively investigate the effect of CO on H₂ 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 [11], 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.

2. Experimental

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.

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 5×10^{-3} mmHg and 110 °C for 4 h. The measurements of N₂ adsorption isotherms at –196 °C were performed using a Micromeritics ASAP 2020 apparatus. BET surface area is that for the whole catalyst including the Pt and the C support.

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 to 450 mmHg in increments of 50 mmHg. The metal dispersion of Pt/C was determined using the total chemisorption isotherms and assuming H:Pt₅ and CO:Pt₅ stoichiometries of 1:1.

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

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.

Designation	Treatment
/	TOS = 0 h. The nomenclatures given before and after “/” were treatment or adsorption conditions prior to and after TOS = 0 h, respectively
w	in the presence of 10%RH; $P_{\text{H}_2\text{O}} = 0.023$ atm
C	30 ppm CO
H	H ₂ ; $P_{\text{H}_2} = 1$ atm balanced with $P_{\text{Ar}} = 1$ atm
D	D ₂ ; $P_{\text{D}_2} = 1$ atm balanced with $P_{\text{Ar}} = 1$ atm
hd	H ₂ and D ₂ ; $P_{\text{H}_2} = 0.5$ atm and $P_{\text{D}_2} = 0.5$ atm balanced with $P_{\text{Ar}} = 1$ atm
Hw	H ₂ and H ₂ O; $P_{\text{H}_2} = 1$ atm balanced with $P_{\text{Ar}} = 0.977$ atm and $P_{\text{H}_2\text{O}} = 0.023$ atm
hdw	H ₂ , D ₂ , and H ₂ O; $P_{\text{H}_2} = 0.5$ atm and $P_{\text{D}_2} = 0.5$ atm balanced with $P_{\text{Ar}} = 0.977$ atm and $P_{\text{H}_2\text{O}} = 0.023$ atm
A	Ar; $P_{\text{Ar}} = 2$ atm
ad	Ar and D ₂ ; $P_{\text{Ar}} = 1.5$ atm and $P_{\text{D}_2} = 0.5$ atm
Aw	Ar and H ₂ O; $P_{\text{Ar}} = 1.977$ atm balanced with $P_{\text{H}_2\text{O}} = 0.023$ atm
adw	Ar, D ₂ , and H ₂ O; $P_{\text{Ar}} = 1.477$ atm and $P_{\text{D}_2} = 0.5$ atm balanced with $P_{\text{H}_2\text{O}} = 0.023$ atm

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 $P_{\text{H}_2} = 1$ atm, $P_{\text{Ar}} = 0.977$ atm, and $P_{\text{H}_2\text{O}} = 0.023$ 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 H₂ 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 H₂. The nomenclature, for example, “Aw/AwC”, means that the Pt/C catalyst, after reduction, was equilibrated in a 100 sccm gas stream with $P_{\text{Ar}} = 1.977$ atm and $P_{\text{H}_2\text{O}} = 0.023$ 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 H₂).

2.4. Measurements of hydrogen surface concentration from both H₂ and H₂O

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 on-line 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

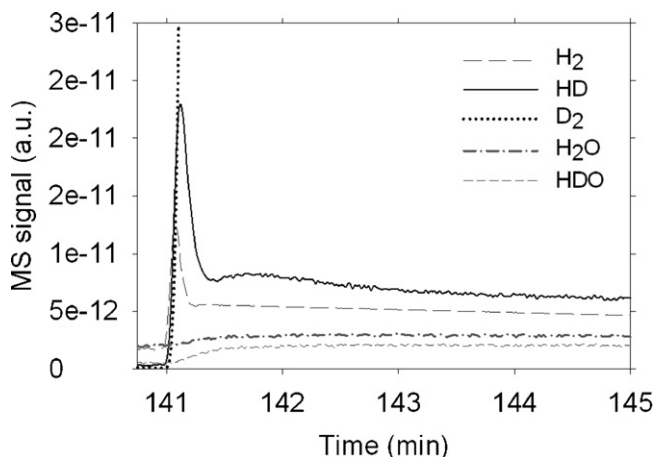


Fig. 1. Typical MS signals during the measurement of hydrogen surface concentrations on Pt/C [Hw/HwC] exposed to a mixture of H₂, water vapor, and CO.

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 3.2). 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 Fig. 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:

$$\text{surface H}[(\mu\text{mol H})\text{g}^{-1}] = \frac{N_{\text{HD}} + 2N_{\text{H}_2}}{W_{\text{C}}} \quad (1)$$

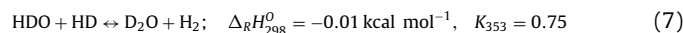
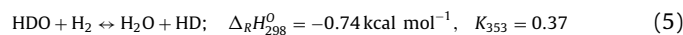
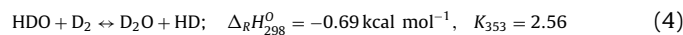
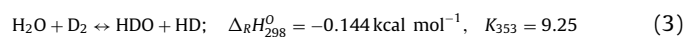
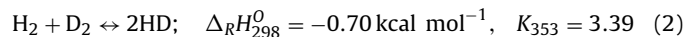
where N_{HD} and N_{H_2} are number of μmol of HD and H₂ desorbed from the surface of Pt/C, respectively, after the switch to D₂, and W_{C} is the weight of the Pt/C catalyst.

2.5. Measurements of hydrogen surface concentration from only H₂O

In order to have an environment as similar as possible to normal PEMFC conditions, most experiments were conducted in the presence of both H₂ and H₂O, which made it unfeasible to distinguish directly the portion of the total hydrogen surface concentration measured by the HDSAP technique originating from either H₂ or H₂O. Thus, several experiments in the absence of H₂ 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)].

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 H₂-D₂-H₂O and H₂O-D₂ exchange reactions were initiated by introducing 100 sccm mixtures of [hd], [hdw], [hdC], or [hdwC] and of [ad], [adw], [adC], or [adwC] to the catalyst, respectively. During the exchange reactions, the sum of the partial pressures of H₂ and D₂ was always kept at 1 atm to maintain a similar partial pressure of H₂ 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 H₂ and D₂ 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 H₂ and D₂ 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 H₂ and HD was obtained by switching the

Table 1
BET characteristics of the Pt catalyst and carbon support.

Material	BET surface area ^a (m ² g ⁻¹)	Pore size diameter ^a (nm)	Pore volume ^a (cm ³ g ⁻¹)
Carbon support (XC-72)	225	16.4	0.63
Pt/C (17.5 wt% Pt ^b)	170	15.9	0.44

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

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) and (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 2.4 and 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 ($P_{\text{H}_2\text{O}} = 0.023$ 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).

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. Results

3.1. Characterization

Table 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 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 (data not shown here), comparable to the average Pt particle size predicted by hydrogen or CO chemisorption (see Table 2). It is important to note that the procedure used to measure hydrogen surface concentration from only H₂O (temperature ramp from 80 °C to 250 °C at 10 °C min⁻¹ and holding at 250 °C for 1.5 h) should have had a only a minor effect on the average Pt particle size. This is because an experiment exposing the Pt/C catalyst to 350 °C for 2 h in H₂ resulted in an average particle size ca. 0.9 nm larger, but that was still within experimental error and similar to that predicted from static chemisorption results.

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

It is known that the kinetics of the H₂–D₂ 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 H₂ and weakly adsorbed hydrogen to the degree possible to leave only the strongly adsorbed hydrogen on Pt prior to the D₂ switch (related to the number of Pt surface atoms available for H₂ activation). A switch to a flow of gas-phase D₂ from a flow of gas-phase H₂ 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 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 H₂ and D₂ flows, the amount of strongly adsorbed hydrogen can be determined from the amounts of both HD and H₂ formed after the switch to D₂ [Eq. (1)].

Fig. 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 mix-

Table 2
Chemisorption results.

Chemisorption	Adsorption temperature (°C)	Total H atoms or CO chemisorbed ^a (μmol g ⁻¹)	D_{Pt} (%) ^b	Avg. Pt particle size ^c (nm)
H ₂	35	316	35	3.1
H ₂	80	361	40	2.7
CO	35	292	33	3.3
CO	80	297	33	3.3

^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 μmol 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 $(1.08 \times 100)/D_{\text{Pt}}$ [46].

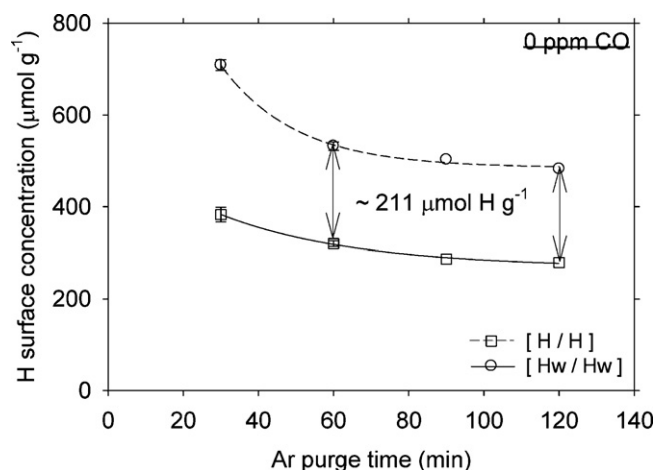


Fig. 2. Effect of an Ar purge time on strongly bound hydrogen surface concentration on Pt/C measured by HDSAP after exposure to H₂ or H₂ with 10%RH at 80 °C.

tures containing H₂ [H] and [Hw], 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.

In Fig. 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 H₂ 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. 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 H₂, H₂O, and/or CO was interrupted with an Ar purge [A] followed by the switch to D₂ [D] for each measurement. For example, after the HDSAP measurement at TOS = 3 h, where the Pt/C catalyst was exposed to H₂, H₂O, and/or CO for 3 h, the same

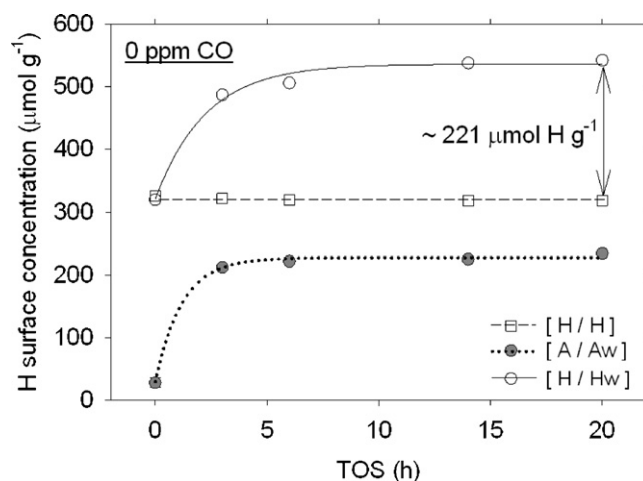


Fig. 3. Variation of strongly bound hydrogen surface concentration on Pt/C with TOS at various conditions and 80 °C in the absence of CO.

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 μmol H g⁻¹] was equal within experimental error to that for the latter study (non-sequential) [341 μmol 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.

3.4. Effect of water vapor on the amount of hydrogen adsorbed on Pt/C in the absence of CO

Fig. 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 μmol H g⁻¹, which is within the range of values obtained by static chemisorption (Table 2). Exposure of the catalyst to a mixture of both H₂ and water vapor [H/Hw] (10%RH) resulted in an increase in the amount of exchangeable strongly bound hydrogen by ca. 221 μmol H g⁻¹. Surprisingly, the amount of exchangeable hydrogen from water, in the absence of H₂ [A/Aw] 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 2.5).

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

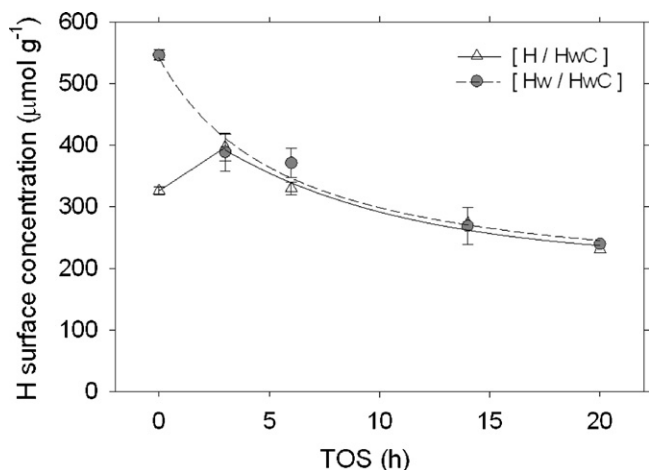


Fig. 4. Effect of water vapor (10%RH) on Pt/C poisoning by 30 ppm CO at 80 °C.

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.

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

Fig. 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 Fig. 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

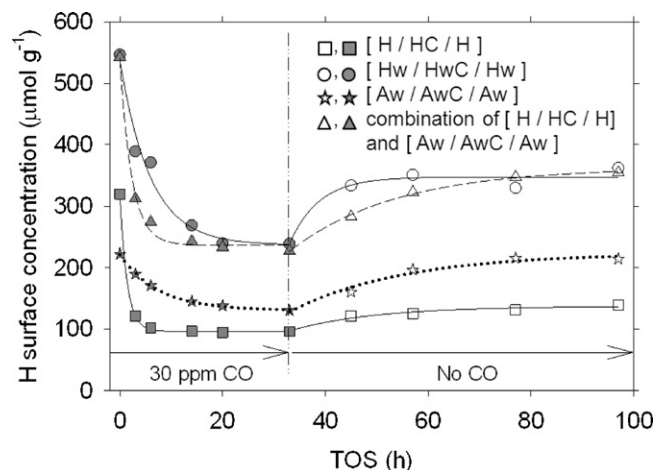


Fig. 6. CO poisoning and regeneration of Pt/C in the presence/absence of H_2 and water vapor (10%RH) at 80 °C. (Filled symbols and unfilled symbols represent the hydrogen surface concentration on Pt/C exposed to 30 and 0 ppm CO, respectively.)

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.

3.7. Effect of CO poisoning and its reversibility on hydrogen surface concentration in the presence/absence of H_2 and water vapor

Fig. 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_2O adsorption, in the presence of CO, was almost certainly caused by the blocking of Pt surface sites by CO.

Fig. 6 illustrates the hydrogen surface concentration on Pt during CO exposure and regeneration under various conditions at 80 °C. The designations 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,

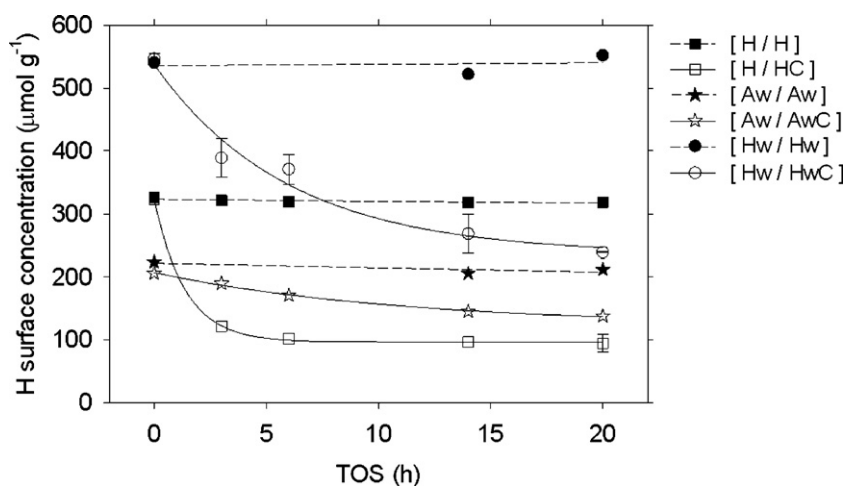


Fig. 5. Effect of CO exposure on the amount of strongly bound hydrogen adsorbed on Pt/C at 80 °C in the presence (10%RH) and absence of water vapor.

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 H₂, water vapor, and/or Ar {[H], [Hw], and [Aw]} through the catalyst bed. In Fig. 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. 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 H₂+H₂O, H₂, or just H₂O. The pseudo steady-state hydrogen surface concentrations measured on Pt/C after CO exposure in the presence of only H₂ (no H₂O, squares) and only H₂O (no H₂, stars) were ca. 96 μmol H g⁻¹ and 131 μmol H g⁻¹, respectively. The pseudo steady-state hydrogen surface concentration measured on Pt/C after CO exposure in the presence of both H₂ and H₂O (circles) was ca. 239 μmol H g⁻¹, which is the same, within experimental error, as the summation of the amount of exchangeable hydrogen contributed from H₂ and H₂O 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 Fig. 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 H₂ 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 H₂ at 0%RH [H/HC/H] was ca. 136 μmol H g⁻¹, which is in agreement with results obtained previously [11]. Regeneration of CO-poisoned Pt/C catalyst in a flow of H₂ at 10%RH [Hw/HwC/Hw] resulted in a hydrogen surface concentration of ca. 345 μmol H g⁻¹ at steady-state. It is clear that regeneration of the CO-poisoned catalysts in the presence of H₂ 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 H₂ [Aw/AwC/Aw] on the other hand, complete recovery in the strongly bound hydrogen surface concentration (due to H₂O) on Pt/C was observed after regeneration at 80 °C for 44 h. The combination of [H/HC/H] and [Aw/AwC/Aw] shown in Fig. 6 (triangles) will be discussed in Section 4.2.

4. Discussion

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 Fig. 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 μmol H g⁻¹}, observed in this study, was most likely due to the isotopic exchange of H₂O and D₂ on surface Pt during the switch to D₂ for HDSAP measurements. This is because it has been reported that the complete exchange reaction between H₂O and D₂ 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 D₂ switch in HDSAP measurements, the MS signal intensities for the H₂O and HDO peaks were found to be minor compared to those for H₂ and HD. This observation implies that under these conditions ($P_{D_2} = 1$ atm, $P_{Ar} = 1$ atm, 80 °C), Pt–HDO and Pt–H₂O were still remaining on the catalyst surface after the isotopic exchange reaction. In order to prove this assumption, D₂ TPD measurements were performed after the switch to D₂. At the end of HDSAP measurements, flow was switched to 30 sccm 5% D₂ in Ar mixture and allowed to stabilize. Then, the temperature was ramped at rate of 10 °C min⁻¹ from 80 °C to 400 °C. It was found that the MS signal intensity for HDO started to increase at 90 °C, reaching a maximum at 200 °C, and the intensity for H₂O decreased corresponding to the increase in the intensity of HDO (data not shown here). The HDSAP and TPD results suggest that Pt–HDO and Pt–H₂O exist on the catalyst under the conditions studied (80 °C) and the measured hydrogen surface concentration is derived from hydrogen adsorbed on Pt and/or Pt–H₂O.

4.2. Hydrogen surface concentration on Pt/C after CO exposure and after regeneration

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

$$\theta_{CO} = \frac{(\text{surface H})_{0\%RH, No CO} - (\text{surface H})_{SS, 30 ppm CO, Adj. for \%RH}}{(\text{surface H})_{0\%RH, No CO}} \quad (10)$$

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 H₂O or CO such that the amount of exchangeable hydrogen is equal to the amount of available surface Pt (assuming H:Pt_S is 1:1). Similarly, due to the overestimation in the amount of available Pt surface atoms (based on static H₂ chemisorption in the absence of H₂O and on TEM results) caused by the additional exchangeable hydrogen from H₂O, 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 H₂ and H₂O (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 H₂O.

The steady-state CO surface coverage of Pt subjected to a dry hydrogen stream [H/HC] (see Fig. 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 H₂ (<9.87 × 10⁻⁶ atm) reported in surface science studies (0.5–0.79 ML) [22,25,34,35]. The pseudo-equilibrium θ_{CO} on Pt/C exposed to a humidified hydrogen mixture [Hw/HwC] 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 Fig. 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 H₂ stream vs. a mixture of both H₂/H₂O, 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 H₂ and H₂O on the hydrogen uptake capacity of Pt/C at steady state are additive and the sites for H and H₂O adsorption could be somehow different. There are two possible explanations for this phenomenon: (1) H₂ adsorption on Pt sites and H₂O adsorption (strong and weak) on the carbon support, or (2) H₂ and H₂O adsorption (strong) on two different types of Pt sites and H₂O 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 ($\sim 0 \mu\text{mol CO g}^{-1}$), 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 Figs. 5 and 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(1 1 1) and Pt(3 3 2) 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(5 3 3) and calculation of the dissociative sticking probability for hydrogen on the (1 1 1) and (1 0 0) terraces of the Pt(5 3 3) 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(1 1 1) crystal surface [39] and TPD of adsorbed H₂O on a Pt(5 3 3) 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(5 3 3) 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 (1 1 1) terraces and (1 0 0) steps of the Pt(5 3 3) 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 (1 0 0) step and (1 1 1) terrace interface on Pt(5 3 3) [42]. While exchange between adsorbed deuterium and H₂O 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(5 3 3) crystal surface also appeared to shift the D₂–H₂O 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 (H₂ and H₂O). 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) H₂O and CO. The weakly bound H₂O 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 θ_{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 Fig. 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.

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 H_2 – D_2 switch with an Ar purge (HDSAP technique). Surprisingly, hydrogen surface concentration results from the co-adsorption of H_2 and H_2O 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 H_2 and H_2O on Pt/C was consistent regardless of whether in the presence/absence of CO, which suggests that the adsorption (strong) of H_2 and H_2O 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 ($P_{\text{H}_2} = 1$ atm) and $\text{H}_2/\text{H}_2\text{O}$ ($P_{\text{H}_2} = 1$ atm and $P_{\text{H}_2\text{O}} = 0.023$ atm),

respectively. These experimental results suggest that the presence of H_2O 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 $\text{H}_2/\text{H}_2\text{O}$ 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_2O 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 $\text{H}_2/\text{H}_2\text{O}$ [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 H_2 on the amount of strongly bound hydrogen on a Pt/C catalyst at typical fuel cell conditions.

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