

# Selective CO oxidation over Pt/alumina catalysts for fuel cell applications

Akkarat Manasilp, Erdogan Gulari\*

Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2136, USA

Received 16 August 2001; received in revised form 15 October 2001; accepted 30 October 2001

## Abstract

It has been demonstrated that even traces of CO present in the hydrogen rich feed gas to proton exchange membrane (PEM) fuel cells can poison the platinum anode electrode and dramatically reduce the power output. The tolerable level of CO is around 10 ppm. In this paper, we present the results of selective CO oxidation in simulated reformat gas over single-step sol–gel prepared Pt/alumina catalysts. The effect of water vapor, carbon dioxide, CO and oxygen concentrations, temperature, and Pt loading on the activity and selectivity are presented. Our results show that a 2% Pt/alumina sol–gel catalyst can selectively oxidize CO down to a few ppm with constant selectivity and high space velocity. Water vapor in the feed increases the activity of the catalysts dramatically and in the absence of water vapor, CO<sub>2</sub> in the feed stream decreases the activity of the catalysts significantly. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Selective oxidation of CO; Pt/alumina catalyst; Sol–gel synthesis; Fuel processing; Fuel cell

## 1. Introduction

Spurred on by the promise of significantly higher efficiency and almost no emission of pollutants, proton exchange membrane (PEM) fuel cells have been extensively studied in the last two decades for many applications especially for low emission vehicles [1–4]. Pure hydrogen is the ideal fuel for the PEM fuel cell. Currently, there is no available technology for safely storing enough hydrogen to give a PEM fuel cell powered vehicle acceptable range. On demand generation of hydrogen by reforming methanol or other liquid hydrocarbon fuels in a fuel processor is the only means of providing the needed hydrogen and the driving range. Catalytic steam reforming of

methanol or partial oxidation of gasoline followed by water gas shift reaction will produce a gas stream with 40–75% H<sub>2</sub>, 15–20% CO<sub>2</sub>, ~10% H<sub>2</sub>O, 0–25% N<sub>2</sub> and 0.5–1% CO. Many studies have shown the negative effect of CO on the performance of PEM fuel cell [5,6]. Palladium-based membrane purification, catalytic methanation, and selective catalytic CO oxidation are the methods of reducing the CO in the feed to 10 ppm or less, necessary for operation of the fuel cell, with minimal loss of hydrogen. Of these three methods selective CO oxidation is the most promising and lowest cost approach. However, hydrogen oxidation competes with CO oxidation leading to the loss of fuel efficiency. In order to reduce CO to the desired level and to minimize H<sub>2</sub> consumption, selective and active catalysts are needed.

Purifying H<sub>2</sub> by selectively oxidizing trace amounts of CO by catalytic oxidation over a Pt-based catalyst

\* Corresponding author. Tel.: 1+734-763-5941;  
fax: 1+734-763-0459.  
E-mail address: gulari@umich.edu (E. Gulari).

is not new. The first patent for selectively oxidizing CO in hydrogen by a Pt/alumina catalyst was awarded to Engelhard in 1963 [7]. Platinum catalysts supported on alumina (Pt/Al<sub>2</sub>O<sub>3</sub>) have been used to oxidize CO [8,9]. Oh and Sinkevitch studied selectivity and activity of alumina supported Pt, Ru and Rh with a gas stream containing 900 ppm CO, 800 ppm O<sub>2</sub> and 0.85% H<sub>2</sub> and found Ru and Rh to be very selective compared to Pt/alumina [10]. Kahlich et al. [11] studied the kinetics of the selective CO oxidation in H<sub>2</sub>-rich gas on Pt/Al<sub>2</sub>O<sub>3</sub> in detail and observed that over 0.5% Pt/alumina it is not possible to have more than 80% conversion of 1% CO with 1% O<sub>2</sub> in the presence of hydrogen even at temperatures as high as 250 °C. They also observed that the presence of hydrogen increases the rate of CO oxidation by as much as a factor of five. Based on their model they estimated that the best temperature for preferential oxidation of CO over a Pt/alumina catalyst is ~200 °C and that 2.5 times the stoichiometric amount of oxygen would be needed to completely oxidize 1% CO. Their integral and differential measurements of selectivity of CO oxidation were roughly equal at 40%. Igarashi et al. [12] investigated the selectivity and activity of Pt supported on zeolites (A-type, mordenite and x-type) and on Al<sub>2</sub>O<sub>3</sub>. Their results show that Pt/alumina had the highest activity but the selectivities of Pt/A and Pt/mordenite catalysts were somewhat better. In a feed stream of 1% CO and 1% O<sub>2</sub> in hydrogen, their catalysts showed maximum conversions of 60–80% above 200 °C and maximum selectivities of 30–60% with a catalyst weight to flow rate of 0.06 g/(s cm<sup>3</sup>). Their results also show that the selectivity on CO approaches 100% as the oxygen to CO ratio approaches zero. Igarashi et al. [12] also found that 1% CO in the gas feed was never completely oxidized on a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst even though the O<sub>2</sub> amount added into the inlet gas was high (~3% O<sub>2</sub>). They obtained 100% conversion of 1% CO at 200 °C with a two-stage catalytic reactor with a Pt/mordenite catalyst. The overall gas composition was 1% CO, 0.7% O<sub>2</sub> and H<sub>2</sub> as balance. Korotkikh and Farrauto [13] investigated selective oxidation of 1% CO by a proprietary Pt/alumina catalyst promoted by a base metal oxide in a stream of mostly hydrogen with oxygen. They were able to observe high selectivity and activity at low temperatures.

While CO oxidation is a well-studied reaction, selective oxidation of CO in hydrogen, CO<sub>2</sub>, H<sub>2</sub>O rich stream is not nearly as well studied. Indeed most of the previous studies referenced above were with dry streams with no CO<sub>2</sub> in the feed. Because CO<sub>2</sub>, CO, H<sub>2</sub> and H<sub>2</sub>O are all tied together by the water gas shift reaction it is important to study selective CO oxidation with a realistic gas mixture. In this manuscript, we report the results of our investigation of selective oxidation of CO with sol–gel prepared Pt/alumina catalysts and the effect of reaction gases including CO<sub>2</sub> and H<sub>2</sub>O. We chose the single-step sol–gel method for several reasons: (1) it gives a high surface area support with a narrow distribution of pores; (2) based on our previous experience the crystallite size of the platinum in the final product is largely independent of the metal loading; (3) there appears to be more interactions between the support and the metal crystallite (some of which are actually buried in alumina) based on the observed resistance to sintering.

## 2. Experimental

### 2.1. Catalyst preparation

Aluminum oxide supported platinum (Pt) catalysts with 1, and 2 wt.% Pt loading were prepared by the single-step sol–gel technique [14]. The desired amount of aluminum isopropoxide was weighted, and then added into a beaker of hot deionized water at 80 °C. After 30 min of aging with continuous stirring, nitric acid (HNO<sub>3</sub>) was added to start the hydrolysis reaction resulting in a fibrillar sol. Pt was incorporated by adding a desired amount of solution of hydrogen hexachloroplatinate(IV) hydrate in 1,3-butanediol to the aluminum hydroxide sol at the room temperature followed by mixing and aging until gelation occurred. The gel was dried in air at 110 °C overnight, then calcined at 500 °C for 13 h. After calcination, the catalyst was ground and sieved to obtain a 100–140 mesh powder.

X-ray diffraction (XRD) was used to identify the phases present in our samples. A Rigaku rotating anode XRD system generating Cu K $\alpha$  radiation was used to obtain XRD patterns. The BET surface area and average pore radius of catalysts were measured

by an Autosorb-1 gas sorption system (Quantachrome Corporation).

## 2.2. Reactor system

Selective carbon monoxide oxidation was performed in an integral reactor. The amount of the catalyst used was 70 mg. Catalyst powder was packed in to the glass tube reactor between two quartz wool plugs. The size of the catalyst bed was approximately 3 mm in diameter and 4 mm in height. The reaction temperature was measured with a K-type thermocouple in contact with the top of the catalyst bed. Because of the small size of the catalyst bed and the use of He as balance in the gas stream, it was assumed that there was no significant temperature profile in the catalyst bed. The activity tests for the selective to CO oxidation were conducted with a mixture of 1% CO, 0–25% CO<sub>2</sub>, 0.5–1.35% O<sub>2</sub>, 60% H<sub>2</sub>, 0 and 10% H<sub>2</sub>O and He as balance. The total gas flow rate was 40 ml/min. Prior to activity tests, we purged catalysts under hydrogen flow at 450 °C for 5 h.

Outlet gas compositions from the reactor were analyzed by using a HP 5890 gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). A 80/100 mesh carbosphere (Altech) column was used to detect H<sub>2</sub>, CO, O<sub>2</sub>, and CO<sub>2</sub>. To quantitatively analyze for carbon dioxide the oven temperature was ramped from room temperature to 80 °C. In addition, FTIR was used to detect CO at low concentrations (ppm level). An ice cooled water condenser was used to trap excess water downstream of the reactor, before the outlet gas entered the GC and FTIR.

The CO conversion was obtained by comparing the concentration of CO in the feed and in the reactor outlet. Selectivity was defined as the ratio of oxygen used to oxidize CO to CO<sub>2</sub> to the total amount of oxygen used in the reactor (obtained by subtracting the outlet concentration from the feed concentration). Because of the large amounts of water vapor and CO<sub>2</sub> in the reactant stream the CO and O<sub>2</sub> concentrations were measured directly. The amount of oxygen not used in oxidizing CO to CO<sub>2</sub> was assumed to be used in oxidizing hydrogen. Note that there was no methane formation in any of our experimental runs.

## 3. Results and discussion

### 3.1. Catalyst characterization

The sol–gel process used to produce the Pt/alumina catalysts yielded a BET surface area of ~325 m<sup>2</sup>/g alumina with a narrow pore size distribution centered at  $D \sim 6$  nm. For this process we prepared two catalysts: 1% Pt and 2% Pt. Pt crystallite sizes were estimated from the line broadening of the Pt(1 1 1) peak to be ~22 nm for both catalysts. The dispersions measured by CO chemisorption were 8.9% for the 1% Pt and 5.7% for the 2% Pt catalysts. The discrepancy between the two results is simply due to the fact that X-rays are more sensitive to the larger crystallites. Based on past experiences with single-step Pt/alumina sol–gel catalysts we estimate that as much as half to the Pt is buried in alumina and is not accessible.

### 3.2. Activity tests

Fig. 1a shows the activities of the two catalysts as a function of temperature for a dry gas composition of 1% CO, 1% O<sub>2</sub>, 65% H<sub>2</sub> and He as balance. At 110 °C the integral conversions are 15 and 20% over the 1 and 2% Pt catalysts. Increasing the temperature to 170 °C increased the CO conversion from 20 to 80% for a 2% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst and from 15 to 55% for a 1% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. Increasing the temperature further to 210 °C resulted in dramatic decreases in the CO conversion to 12 and 10%, respectively for both catalysts. Fig. 1b shows that the selectivities of the two catalysts are comparable and essentially stay constant (~45–50% all the way up to 170 °C, the peak conversion temperature. Above 170 °C the CO selectivity rapidly drops to ~10% at 210 °C. This drop can be explained by the oxygen conversion shown in Fig. 1c. We see that the difference in oxygen conversion parallels the difference in CO conversion for the two catalysts resulting in a constant selectivity. However, at the peak conversion temperature of 170 °C there is very little oxygen left in the reactor and all of the oxygen is consumed at 190 °C. This results in a rapid drop in CO conversion as well as selectivity. These observations are in qualitative agreement with those of Kahlich et al. [11]. They observed a maximum conversion temperature of ~200–250 °C and a selectivity of ~25–40% all the way to 250 °C. The difference in

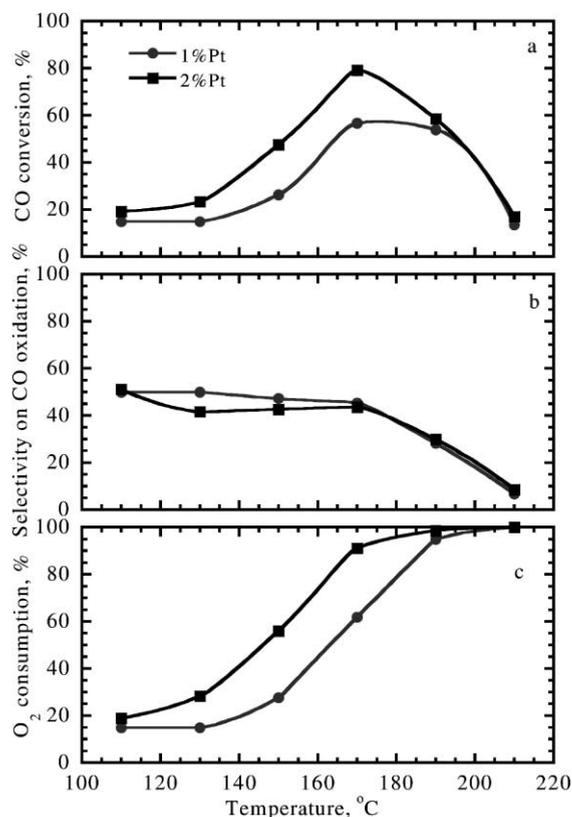


Fig. 1. Activity and selectivity as a function of temperature for 1 and 2% Pt supported on  $\text{Al}_2\text{O}_3$  (single-step sol-gel). Gas composition: 1% CO, 1%  $\text{O}_2$ , 60%  $\text{H}_2$  and He as balance.

the peak conversion temperature is most likely due to our higher metal loading. Almost perfect constancy of our selectivity can be explained if one assumes that below 170 °C the surface of the catalyst has a constant ratio of adsorbed CO to adsorbed  $\text{H}_2$  [11]. Since CO adsorbs very strongly on platinum, the surface must be CO covered until the desorption temperature of CO is reached ( $\sim 160$  °C) or the gas phase CO concentration becomes essentially zero. Korotkikh and Farrauto [13] also observed a similar behavior.

### 3.3. $\text{O}_2$ effect on activity and selectivity

The dependence of CO conversion and selectivity on CO oxidation on  $\text{O}_2$  concentration in the gas feed is shown in Fig. 2. Fig. 2a shows that the conversion increases dramatically with increasing oxygen

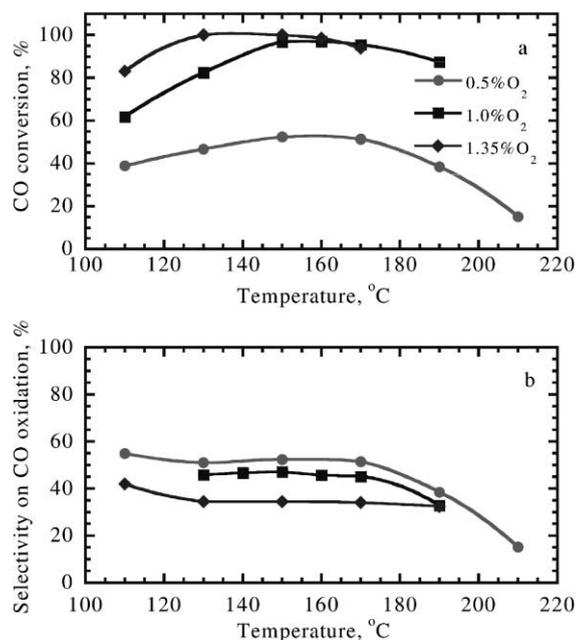


Fig. 2. The effect of  $\text{O}_2$  in the gas feed on CO conversion and selectivity as a function of temperature for a 2%  $\text{Pt}/\text{Al}_2\text{O}_3$  catalyst. Gas composition: 1% CO, vary  $\text{O}_2$ , 25%  $\text{CO}_2$ , 60%  $\text{H}_2$ , 10%  $\text{H}_2\text{O}$  and He as balance.

concentration (note that the feed also has 10%  $\text{H}_2\text{O}$ ). At stoichiometric  $\text{O}_2$  concentration, 0.5%  $\text{O}_2$  the maximum conversion attainable is  $\sim 51\%$  at 151 °C, identical to what was observed with a dry gas mixture (Fig. 1a). However, the peak is much shallower and broader in temperature. Increasing the  $\text{O}_2$  concentration to twice the stoichiometric ratio (1%  $\text{O}_2$ ) increases the peak conversion to  $\sim 98\%$  at 150 °C (compared to  $\sim 80\%$  with the dry gas mixture). Further increasing the oxygen concentration to 1.35% results in 100% conversion of 1% CO between 130 and 150 °C. Fig. 2b shows that the selectivities are in inverse order,  $\sim 35$ , 50 and 55% for 1.35, 1 and 0.5%  $\text{O}_2$  feeds, respectively.

### 3.4. $\text{H}_2\text{O}$ effect

Fig. 3 shows the dramatic effect of water on the activity of the catalyst (2%  $\text{Pt}/\text{Al}_2\text{O}_3$ ) more clearly. Including 10% water in the feed has dramatically enhanced the CO oxidation reaction especially at low temperatures as shown in Fig. 3a. At 130 °C the

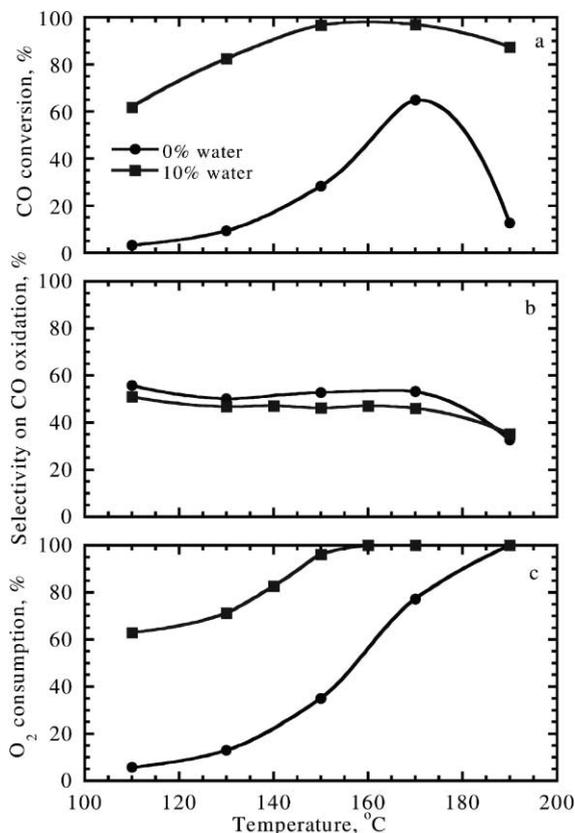


Fig. 3. The effect of water in the gas feed on CO conversion and selectivity as a function of temperature for a 2% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. Gas composition: 1% CO, 1% O<sub>2</sub>, 25% CO<sub>2</sub>, 60% H<sub>2</sub>, 0 and 10% H<sub>2</sub>O and He as balance.

conversion is 10% when there is no water vapor in the feed adding 10% water increases the conversion to 80%. The activity is increased over the whole temperature range we investigated (110–190 °C). For the low conversion temperatures (110 and 190 °C) the conversion has increased by approximately 10-fold. A smaller but similar enhancement by of water was observed by Kahlich et al. [11] and Muraki et al. [15]. From the data it is clear that the addition of the water vapor reduces the activation energy for CO oxidation drastically. Because most of our data is in the integral reactor region, calculation of an accurate activation energy is problematic. However, using the lowest conversion temperatures a very rough estimate of the CO oxidation activity in the presence of water was made to obtain ~37 kJ

compared to ~74 kJ observed in the absence of water vapor.

Compared to the dramatic increase in activity the changes observed in selectivity are very small but consistent. The presence of water has decreased the selectivity by ~3–5% over the temperature range of 110–170 °C. This small change in selectivity indicates that the presence of water increases the rate of both CO and hydrogen oxidation. This is borne out by the oxygen conversion data shown in Fig. 3c. In the presence of water in the feed all of the oxygen is consumed at 160 °C. There can be several reasons for the enhancing effect of water. One is that water enhances the water gas shift reaction and as a result more CO is converted into CO<sub>2</sub>, the second possibility is that the hydroxyl group formed on the catalyst upon adsorption of water is a better oxidant than oxygen and increases the oxidation rate of CO and hydrogen. A third possibility is the modification of the ratio of the Pt<sup>0</sup> to Pt(O)<sub>x</sub> sites in the presence of water vapor. The reduced metal could exist only when there is no oxygen in the gas stream. The changes in the ratio of these two types of Pt sites can change the activity and the selectivity of the catalyst directly. Kahlich et al. [11] proposed that perhaps the formate groups formed on alumina in the presence of water participate in the reaction and increase the rate of CO oxidation. We could not measure the hydrogen concentration accurately enough to be able to determine whether the amount of hydrogen increased due to water gas shift reaction or not. However, one indirect piece of evidence against the water gas shift mechanism contributing to CO oxidation is the complete oxidation of CO. If indeed the Pt/alumina was a reasonably good water gas shift catalyst we should have several 100 ppm of CO left in the outlet of the reactor which we did not see for the case of 1.35% O<sub>2</sub> feed and as discussed later for the case of 0.5% CO and O<sub>2</sub>. We tested the contribution of forward water gas shift reaction to CO oxidation over this catalyst with a 1% CO, 10% H<sub>2</sub>O + He to find CO conversions of 2, 11 and 14% at 170, 190 and 210 °C, respectively. In comparison, a 2% impregnation Pt/sol-gel alumina catalyst gave conversions of 7, 20 and 52%. Clearly, the conversion rates seen for the single-step sol-gel catalyst are not enough to account for the significant increases seen due to addition of water to the simulated reformer gas. Based on past work carried in our

laboratory for methanol synthesis, we believe the rate of formate formation and decomposition on alumina is too slow to account for the significant increases we see in CO and hydrogen oxidation in the presence of water vapor.

### 3.5. CO<sub>2</sub> effect

In reality, the gas streams that are produced from reformers and water gas shift reactors contain about 20–25% CO<sub>2</sub>. Therefore, it is crucial to know how this catalyst performs with this much CO<sub>2</sub> in the feed. Fig. 4 shows the effect of 25% CO<sub>2</sub> on CO conversion in a dry feed gas. CO conversion at 110 °C was 20, and 5% for the run without CO<sub>2</sub> and the run with 25% CO<sub>2</sub>, respectively. The peak conversion also drops from 80

to 65%. On the high temperature side of the peak in conversion, the decrease in CO conversion is more dramatic but reaches an almost constant level of 10% at 180 °C.

The CO oxidation selectivity given in Fig. 4b shows an unusual behavior. Until the peak conversion temperature of 170 °C the selectivity is higher for the CO oxidation reaction in the presence of 25% CO<sub>2</sub>. This observation is in agreement with the other findings discussed above, i.e. the lower the conversion the higher the selectivity. However, above the peak conversion temperature, CO oxidation selectivity drops sharply and is lower than the run without CO<sub>2</sub>, again there is a constant limiting selectivity of ~8% at high temperatures. This observation too is consistent with the assumption that there may be reverse water gas shift reaction limiting the CO oxidation at high temperatures. To determine the extent of reverse water gas shift reaction, we used a feed composition of 25% CO<sub>2</sub> and 70% H<sub>2</sub> in the feed with no CO and H<sub>2</sub>O. In agreement with the known thermodynamics of the water gas shift reaction, we found that an increase in reaction temperatures increases CO formation. At 170 °C, CO formed was 1200 ppm and at 210 °C, CO formed was 2400 ppm. Again these conversions can be compared to 870, 2000 and 3930 ppm we observed with the same feed and reaction temperatures with a 0.5% impregnation Pt/sol-gel alumina catalyst (we do not have data for a 2% impregnation catalyst but suspect that the conversions over it would have been at a factor of two higher).

The oxygen conversion data shown in Fig. 4c shows that in the presence of CO<sub>2</sub> the conversion of oxygen is lower over the complete range of temperatures studied. Thus, CO<sub>2</sub> slows the oxidation of both CO and H<sub>2</sub>. It is well known that over reducible metal oxide supports carbonates are formed which prevent the participation of support oxygen in CO oxidation reaction [16]. It is a small possibility that in the single-step sol-gel catalysts the interface between alumina and platinum crystallites contain mobile oxygen which is blocked by CO<sub>2</sub> adsorbing on the same sites [17]. The other likely explanation is that at low temperatures dissociation of CO<sub>2</sub> on Pt yields a higher effective CO concentration on the catalyst surface and, thus, reduces the rate of oxidation. However, as the reverse water gas shift reaction data given above shows the

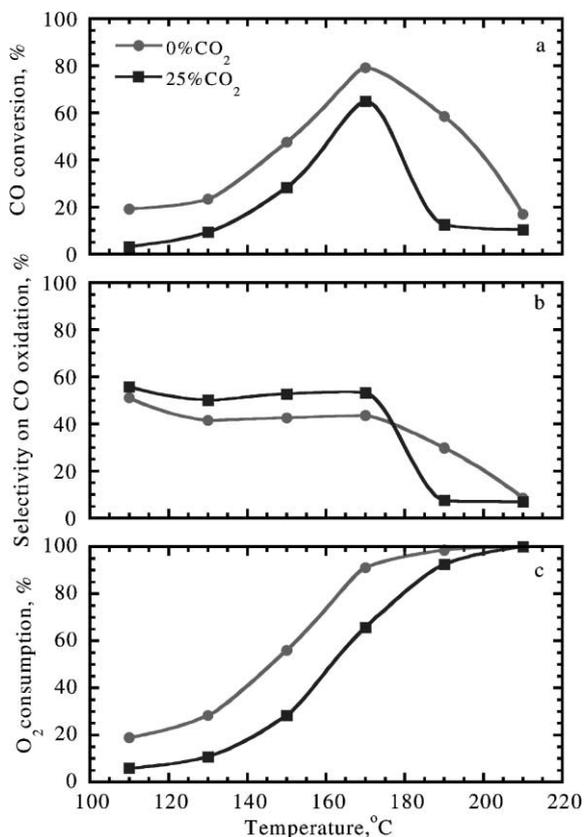


Fig. 4. The effect of CO<sub>2</sub> in the gas feed on CO conversion and selectivity as a function of temperature for a 2% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. Gas composition: 1% CO, 1% O<sub>2</sub>, 0 and 25% CO<sub>2</sub>, 60% H<sub>2</sub> and He as balance.

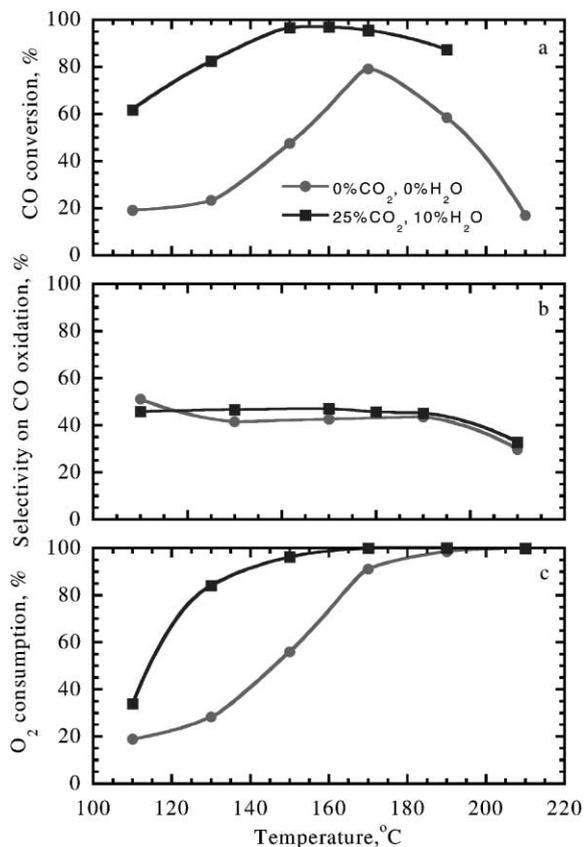


Fig. 5. The combination of CO<sub>2</sub> and water effect on CO oxidation reaction and selectivity on CO oxidation as a function of temperature for a 2% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. Gas composition: 1% CO, 1% O<sub>2</sub>, 0 and 25% CO<sub>2</sub>, 0 and 10% H<sub>2</sub>O, 60% H<sub>2</sub> and He as balance.

increase in the CO concentration is at most on the order of 10–20%, not enough to cause the dramatic decrease observed.

### 3.6. Combined H<sub>2</sub>O and CO<sub>2</sub>

We also fed water and CO<sub>2</sub> together into the reactor and observed the overall performance of this catalyst as shown in Fig. 5a–c. Interestingly, although CO<sub>2</sub> in the feed retarded the CO oxidation reaction and water promoted the CO oxidation reaction, the combination of CO<sub>2</sub> and water together increased the CO conversion from 80 to 97%. Also, the maximum CO conversion temperature shifted down from 170 °C for the run without CO<sub>2</sub> and water to 150 °C

for the run with 25% CO<sub>2</sub> and 10% water. Overall the conversion versus temperature and selectivity curves shown in Fig. 5a and b are almost identical with the data shown in Fig. 2a and b for the case of 10% water but no CO<sub>2</sub> in the feed. Thus, the positive effect of water is more dominant than the negative effect of CO<sub>2</sub> in the feed. Oxygen conversion was also higher for the feed that contained water and CO<sub>2</sub> when compared to the feed without water and CO<sub>2</sub>. When only H<sub>2</sub>O is added without CO<sub>2</sub> the activity is higher by a few percent and the decrease in activity on the high temperature side of the peak conversion is somewhat less.

Comparing CO oxidation activities and selectivities between a 2% Pt/Al<sub>2</sub>O<sub>3</sub> single-step sol-gel made catalyst and a 2% Pt/commercial alumina impregnation catalyst, we found that the first catalyst gave higher CO conversion and higher selectivity at the same temperatures than the second catalyst did. At 150 °C, maximum CO conversion for the 2% Pt/commercial alumina was 80% and its selectivity was 42% while maximum CO conversion for the 2% Pt/alumina single-step sol-gel catalyst was 97% and its selectivity was 48%. This could be because of the differences in Pt crystalline size, surface area of catalyst and the support effect. Total surface area of the 2% Pt/commercial alumina is 150 m<sup>2</sup>/g while that of the 2% single-step sol-gel Pt/alumina is 320 m<sup>2</sup>/g. Pt crystalline size for the impregnation catalyst made with the commercial alumina is less than 3 nm compared to ~20 nm for the single-step sol-gel Pt/alumina catalyst. Unfortunately, due to the overlap of the alumina peaks with those of Pt peaks we could not determine if there were significant differences in the oxidation states of Pt prepared by the different methods.

### 3.7. Space velocity effect

The dependence of CO conversion and selectivity on flow rate was studied in two experiments and the results are shown in Fig. 6. We increased the space velocity from 34,000 to 60,000 cm<sup>3</sup>/(h g). Increasing the space velocity decreased the CO conversion at the same temperature. With 1% CO, 1% O<sub>2</sub>, 20% CO<sub>2</sub>, 10% H<sub>2</sub>O, 60% H<sub>2</sub>, and He as balance, maximum CO conversion for the low space velocity run was 99% at 160 °C and for the high space velocity run was 91%

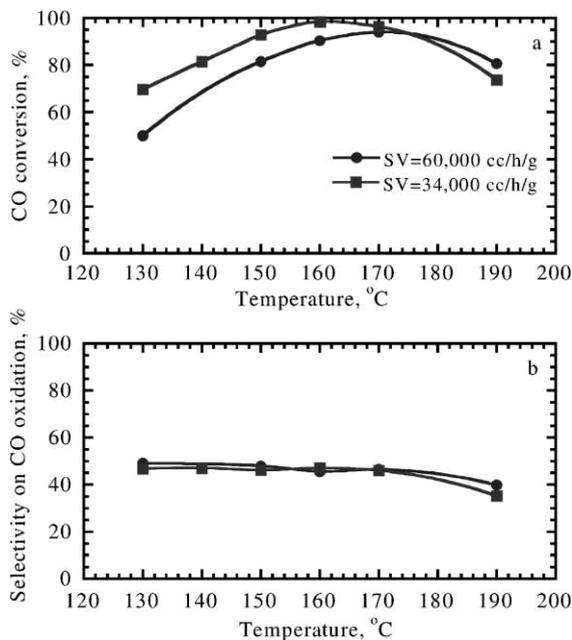


Fig. 6. Dependence of CO oxidation and selectivity on CO oxidation on space velocity and temperature for a 2% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. Gas composition: 1% CO, 1% O<sub>2</sub>, 20% CO<sub>2</sub>, 60% H<sub>2</sub>, 10% H<sub>2</sub>O and He as balance.

at 170 °C. As expected the selectivity did not change with space velocity.

### 3.8. CO concentration effect

It is well known that over platinum there is an inverse relationship between the reaction rate and CO partial pressure. To verify that this is also the case, when there is hydrogen, water and CO<sub>2</sub> in the feed, we reduced the CO concentration and O<sub>2</sub> concentration to 0.5%. Using the 2% Pt catalyst and a feed gas composition of 0.5% CO, 0.5% O<sub>2</sub>, 20% CO<sub>2</sub>, 10% H<sub>2</sub>O, 65% H<sub>2</sub> and He as balance, we obtained the results shown in Fig. 7. Under these conditions we were able to reach 100% CO conversion in the temperature range of 140–155 °C. We did not detect any CO in the reactor outlet with a sensitivity of 5 ppm. The selectivity was constant at 50% from 110 to 170 °C. Since the selectivity of this case is somewhat (50% versus 48%) higher than the case of 1% CO and 1% O<sub>2</sub> feed, an optimal design for fuel processor gas that contains more than 0.5% CO would be to have several stages

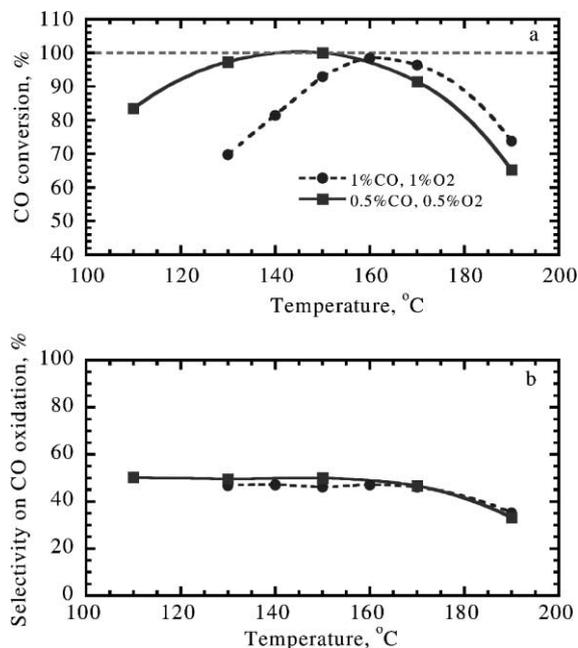


Fig. 7. Variation of maximum conversion with CO and O<sub>2</sub> concentration and temperature. Gas composition: 0.5% and 1% CO, 0.5 and 1% O<sub>2</sub>, 20% CO<sub>2</sub>, 60% H<sub>2</sub>, 10% H<sub>2</sub>O and He as balance.

and inject part of the air/oxygen at each stage so that the highest CO selectivity and complete CO conversion is guaranteed.

## 4. Conclusions

Our results show that the single-step sol–gel made Pt/alumina catalysts have the high levels of activity and selectivity necessary for catalyzing preferential oxidation of 1% or less CO in the hydrogen rich fuel processor gas all the way down to a few ppm of CO. Addition of water vapor to the feed has a significant positive effect. It reduces the activation energy for both CO oxidation and hydrogen oxidation, thus, the conversion is increased significantly without changing the selectivity. We speculate that this is because of participation of the hydroxyl groups, formed by the dissociative adsorption of H<sub>2</sub>O on Pt. The sol–gel technique provides a high surface area stable catalyst and despite the fact that some of the Pt is not accessible to gas phase species, results in high activity catalysts.

In comparison to the strongly positive effect of water vapor presence of realistic amounts of CO<sub>2</sub> in the feed has a detrimental effect on the activity of the catalysts. This can be either due to the reverse water gas shift reaction, formation of carbonates on the support or an increase in the effective surface concentration of CO by dissociative adsorption of CO<sub>2</sub>. The fact that we were able to reach final CO concentrations in the single digit ppm range indicates that water gas shift reaction is far away from equilibrium on this catalyst when there is water vapor and oxygen in the feed. Indeed if we compare the performance of the single-step sol–gel catalyst to impregnation catalysts (with sol–gel alumina support) we observe that the single-step catalyst is much less active both for the forward and reverse water gas shift reactions.

### Acknowledgements

Ms. A. Manasilp would like to thank The Thai Government for a Ph.D. fellowship. Partial financial support of this project by the NSF CTS Grant #9985449 is gratefully acknowledged.

### References

- [1] S. Gottesfeld, US Patent 4,910,099 (20 March 1990).
- [2] H.F. Oetjen, V.M. Schmidt, U. Stimming, F. Trila, J. Electrochem. Soc. 143 (1996) 3838.
- [3] C.D. Dudfield, R. Chen, P.L. Adcock, J. Power Sources 86 (2000) 214.
- [4] C. Sishtlla, G. Koncar, S. Gamburzev, A.J. Appleby, J. Power Sources 71 (1998) 249.
- [5] B. Rohland, V. Plzak, J. Power Sources 84 (1999) 183.
- [6] M. Gotz, H. Wendt, Electrochim. Acta 43 (1998) 3847.
- [7] M. Brown, A. Green, US Patent 3,088,919.
- [8] A. Cohn, US Patent 3,216,783 (9 November 1965).
- [9] V.J. Vlastnik, F.J. Armellini, F.A. Jordano, Los Alamos National Laboratory, August 1987.
- [10] S.H. Oh, R.M. Sinkevitch, J. Catal. 142 (1993) 254.
- [11] M.J. Kahlich, H.A. Gasteiger, R.J. Behm, J. Catal. 171 (1997) 93.
- [12] H. Igarashi, H. Uchida, M. Suzuki, Y. Sasaki, M. Watanabe, Appl. Catal. A: Gen. 159 (1997) 159.
- [13] O. Korotkikh, R. Farrauto, Catal. Today 62 (2000) 249.
- [14] G.E. Yoldas, Ceram. Bull. 54 (1975) 298.
- [15] H. Muraki, S.-I. Matunaga, H. Shinjoh, M.S. Wainwright, D.L. Trimm, J. Chem. Tech. Biotechnol. 52 (1991) 415.
- [16] E. Gulari, C. Guldur, S. Srivannavit, S. Osuwan, Appl. Catal. A: Gen. 182 (1999) 147.
- [17] T. Inui, K. Fujimoto, T. Uchijima, M. Masai (Eds.), *New Aspects of Spillover Effect in Catalysis*, Elsevier, Amsterdam, 1993, p. 27.