

Removal of Carbon Monoxide from Hydrogen-rich Fuels over CeO₂-promoted Pt/Al₂O₃

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ABSTRACT

A comparative study of catalytic CO oxidation and selective CO oxidation over Pt/Al₂O₃ and CeO₂-promoted Pt/Al₂O₃ catalysts has been investigated for the removal of a trace amount of CO from the reformed gas. The catalysts were prepared by sol gel and incipient wetness impregnation. CO oxidation and selective CO oxidation were carried out with a 5%Pt/Al₂O₃ and a 5%Pt/15%CeO₂/Al₂O₃. The presence of 15%CeO₂ in the 5%Pt/Al₂O₃ dramatically improves the activities to CO oxidation and selective CO oxidation at low temperature (<180°C). FTIR results indicate that CO could react with lattice oxygen from ceria and release CO₂ as a product. Low space velocity would obtain high CO conversion at low temperatures while high space velocity would obtain high CO conversion at high temperatures. The results also show that a 5%Pt/15%CeO₂/Al₂O₃ can completely oxidize 1% CO at 180°C with selectivity of 52% and space velocity of 70,000 cm³·g⁻¹·h⁻¹. Under the realistic gas feed with 1%O₂, this catalyst is very stable and retains its activity and selectivity at 180°C during 72 h.

Keywords: CO Oxidation; CeO₂-Pt/alumina; CO Adsorption; Selective CO Oxidation; Fuel Processing

1. Introduction

The polymer-electrolyte-membrane fuel cell (PEMFC) has been attracting significant attention in several applications including electric vehicles and residential power-generations. This is because of its many attractive features such as high power density, rapid start-up, and high efficiency [1, 2]. As the PEMFCs utilize hydrogen gas as a fuel and since hydrogen can be produced by means of a fuel reformer followed by water gas shift reaction for further conversion of CO to H₂, carbon monoxide is always present in the hydrogen stream. Generally, catalytic steam reforming of methanol or partial oxidation of gasoline followed by water gas shift reaction will produce a gas stream with 40%-75% H₂, 15%-20% CO₂, ~10% H₂O, 0-25% N₂ and 0.5%-1.0% CO. This amount of CO contained in the reformed gas is high enough to poison the Pt anode of PEM fuel cells and in turn dramatically degrades the fuel cell potential and energy conversion efficiency [3, 4]. Experimentally, it has been found that the tolerable level of CO without harmful effects is about 10 ppm [5]. This means the 0.5%-1.0% CO needs to be reduced to 10 ppm or less in order to increase the use of proton exchange membrane (PEM) fuel cells running with on-board generated hydrogen. The most economical and straightforward technique for this pur-

pose is selective catalytic oxidation of CO in the H₂-rich reformed gas using O₂ or preferential oxidation (PROX). This method needs a suitable catalyst to enhance the CO oxidation reaction with minimal oxidation of hydrogen which is the desired fuel. The crucial requirement for the PROX reactor is a high CO conversion with high selectivity. A number of catalysts have been investigated for the PROX reaction [6-10]. Noble metals supported on alumina such as Pt, Au, Ru and Pd, have been proposed as ideal catalysts for PROX reaction, especially Pt/Al₂O₃, Pt/Fe₂O₃/Al₂O₃, Pt/CeO₂, Pt/CeO₂-ZrO₂, Pt/zeolite [11-13]. An improvement in the selectivity at low temperatures is needed. Oxidation of CO on alumina-supported Pt catalysts is known to take place via the Langmuir-Hinshelwood mechanism. Kahlich et al. [14] studied the kinetics of selective CO oxidation in H₂-rich gas on Pt/Al₂O₃ and observed that CO conversion never reached 100% for a 0.5%Pt/Al₂O₃. The maximum CO conversion was ~80% at temperatures as high as 250 °C. Other studies reported that CO conversion occurred in the reaction temperature range of 200°C-250°C [15] or else needed high oxygen concentration for complete elimination of CO, corresponding to lower selectivity. We have previously [16] investigated the catalytic activity of 2%Pt/Al₂O₃, which was prepared by the sol-gel method, in selective CO oxidation reaction under the

excess H₂ gas stream. We found that 2% Pt was well dispersed in alumina supports. Therefore, it can selectively oxidize CO down to ppm level with constant selectivity and high space velocity. The performance of Pt catalysts can be improved by modifying supports such as adding alkali metals into supports [17] or by promoting with other metal oxides such as Fe₂O₃ or CeO₂ [18]. Serre, et al. [19] found that the presence of CeO₂ in a 2%Pt/Al₂O₃ after a reductive pretreatment drastically enhanced the activity of the catalyst to CO oxidation. The promoting effect of ceria was attributed to the enhancement of the metal dispersion and the stabilization of Al₂O₃ support toward thermal sintering. Moreover, ceria can be a chemically active component, working as an oxygen store that releases lattice oxygen in the presence of reductive gases and re- placement of the lattice oxygen with oxygen gas when oxygen gas is present in excess [20]. Parinyaswan et al. [21] investigated the performance of Pt-Pd/CeO₂ catalysts for selective CO oxidation. This catalyst could maximally convert 83% CO to CO₂ with selectivity of 60% at 90°C with a gas feed containing 1% CO, 1% O₂, 25% CO₂ and 10% H₂O. This means there would still be 1,700 ppm of CO left in the gas feed and this gas could dramatically deplete the efficiency of a PEM fuel cell in a very short time. The authors suggest a multi-stage reactor to reduce CO to below 10 - 100 ppm for the use of this catalyst with PEM fuel cells. Silva et al. [22] studied the effect of the presence of ceria with Pt over alumina catalysts for the partial oxidation of methane reaction. They reported that the addition of ceria in alumina led to the formation of a homogenous solid solution, which exhibited a high-oxygen storage capacity. Brown et al. [23] compared the activities of Pt over alumina with ceria-promoted Pt over alumina in the production of hydrogen from methanol decomposition. They reported that promoting with ceria had a positive effect on activity and selectivity. Indeed, the use of ceria coupled with alumina as a support for Pt might enhance the catalytic selective CO oxidation of platinum over alumina catalysts. Son et al. [24,25] investigated the performance of Ce-Pt/ γ -Al₂O₃ for selective oxidation of CO in H₂ for PEFCs. They found that the addition of 5% Ce in the Pt over alumina dramatically enhanced CO conversion and selectivity at low temperatures. The catalyst completely converted 1%CO to CO₂ at 200°C with 50% selectivity. Although the effect of other gases such as CO₂ and H₂O was studied, their gas compositions containing 1% CO, 2.3% H₂O, 10.09% CO₂ and H₂ as balance were far from a realistic gas composition containing 40%-75% H₂, 0.5%-2.0% CO, 15%-20% CO₂, 10% H₂O and 0-25% N₂ by volume. Therefore, the activity of promoted platinum over alumina with ceria for preferential CO oxidation still needs to be investigated.

In order to obtain a better understanding of the activity of the ceria promoted platinum alumina catalyst to the

selective CO oxidation, 5%Pt/15%CeO₂/Al₂O₃ and 5% Pt/Al₂O₃ catalysts were tested for their activities to both CO oxidation in H₂ free-stream and CO oxidation in the presence of excess H₂-containing feed stream and the obtained results were compared with others reported in literatures. All supports in this work were prepared by sol gel method. The CO coverage of the catalysts was also studied using FTIR. The FTIR results were used to explain the enhancement of catalyst activity in the presence of ceria. It should be pointed out that all gases containing in reformed gas affect to the selectivity to CO oxidation of the catalysts as reported in literatures. Therefore, the effect of space velocity on the activity of the catalyst was investigated. These results will lead us to the proper operating conditions in order to obtain high selectivity and high CO conversion of ceria promoted Pt alumina catalyst.

2. Experimental

2.1. Catalyst Preparation

A cerium aluminum oxide supported platinum (Pt) catalyst with 5.0 wt% Pt loading was prepared by sol gel technique [26] and incipient wetness impregnation. Aluminum is protoxide; cerium (III) acetate and hydrogen hex anchor oplatinate (IV) hydrate were obtained from Aldrich. Preparation of supports containing cerium aluminum oxide began with dissolving the desired amount of aluminum is protoxide in hot demonized water at 80°C. After 30 min of aging with continuous stirring, nitric acid (HNO₃) was added to start the hydrolysis reaction resulting in a fibrillar sol. Then, the known amount of cerium (III) acetate was incorporated into the solution at room temperature. The solution was stirred overnight to obtain uniformity. The obtained solution was heated to 60°C and kept at this temperature until gelation occurred. The gel was dried in air at 110°C overnight, and then calcined at 500°C for 13 hours. After calcination, the resulting powder was ground and sieved to obtain a 100-140 mesh powder. Incipient wetness impregnation was used to deposit platinum into the support. With this method, a desired amount of solution of hydrogen hexachloroplatinate (IV) hydrate was added into a cerium alumina support and then mixed together until the mixture uniformly. The obtained solid was dried in air at 110°C overnight, and then calcined at 500°C for 13 hours. The final powder was 5% Pt/15% CeO₂/Al₂O₃. In this work, the activity of this catalyst was compared with activity of a 5% Pt/ Al₂O₃. For a 5% Pt/Al₂O₃ analogous preparation techniques were used such that the Al₂O₃ support was prepared by sol gel and Pt was impregnated in the support by incipient wetness impregnation. Before testing the activities of these catalysts, the catalysts were purged with H₂ at 400°C for 5 hrs.

2.2. Characterization

The BET surface area and average pore radius of catalysts were determined with adsorption-desorption isotherms of N_2 at 77 K using a MicroMeritics ASAP 2010 instrument. Average crystalline sizes of oxides were determined by Scherrer's equation using the X-ray line broadening from X-ray diffraction, Bruker AXS model D 8 Discover equipped with a $CuK\alpha$ radiation with a nickel filter. Diffraction intensity was measured in the 2 theta ranges between 20° and 85° , with a step of 0.02° for 8 s per point.

2.3. Catalytic Activity

CO oxidation and CO oxidation in the H_2 -rich stream was performed in a fixed-bed reactor. The reaction temperatures inside the reactor were measured with a K-type thermocouple placed on the top of the catalyst bed and were controlled by a temperature controller (OMEGA: CN3251). The amount of catalyst used in each run was 68 mg. The total gas flow rates of the reaction mixture were $40\text{ cm}^3\cdot\text{min}^{-1}$ and $80\text{ cm}^3\cdot\text{min}^{-1}$, corresponding to the space velocity of $70,000\text{ cm}^3\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ and of $35,000\text{ cm}^3\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, respectively. For CO oxidation, the activity tests were conducted with a feed mixture of 1% CO, 1% O_2 and He as balance. For selective CO oxidation, a feed mixture contained 1% CO, 0.5%-1% O_2 , 0-10% H_2O , 0-20% CO_2 , 55% H_2 and He as balance. A volumetric flow controller with an accuracy of $0.5\text{ cm}^3\cdot\text{min}^{-1}$ was used for measuring the total gas flow rate at the bypass (for calibration purposes) and at the outlet of the reactor.

A Varian CP-4900 micro gas chromatograph (micro GC) equipped with 2 channels (A and B) was used for analysis of the outlet gas compositions from the reactor. Channel A was used to detect H_2 , O_2 , CO and CH_4 by a Molsieve 5A PLOT column. Channel B was used to detect CO_2 by a PoraPLOT Q column. Along with GC, FTIR was used to detect CO at low concentrations (ppm level) in the outlet gas from the reactor. Because water deteriorates the performance of these columns, an ice cooled water condenser was used to remove water from the gas streams before entering the GC and FTIR.

The CO conversion was obtained by comparing the CO concentration in the feed measured at the bypass line and the CO concentration in the outlet stream from the reactor. Selectivity was defined as the ratio of oxygen consumed by CO oxidation to the total oxygen consumption (obtained by subtracting the O_2 concentration at the reactor outlet from the O_2 concentration in the feed). The amount of O_2 not used in the CO oxidation reaction was assumed to oxidize H_2 in the H_2 oxidation reaction. Importantly, there was no methane formation observed under reaction conditions performed in this study.

3. Results and Discussion

3.1. Characterization of the Catalysts

The alumina support prepared via the sol gel method yielded a BET area of $227.8\text{ m}^2/\text{g}$ with an average pore size of 5.3 nm while the sol gel made 15% CeO_2/Al_2O_3 had a BET area of $230.0\text{ m}^2/\text{g}$ with an average pore size of 5.2 nm. Pt crystalline sizes were estimated from the line broadening of Pt (111) peaks. For both a 5%Pt/ Al_2O_3 catalyst and a 5%Pt/15% CeO_2/Al_2O_3 catalyst, no Pt (111) peaks were observed indicating that Pt metal was well impregnated and dispersed on the supports for both catalysts. For ceria structure in a 5%Pt/15% CeO_2/Al_2O_3 fresh catalyst reduced under hydrogen, XRD results matched with those for CeO_2 with average CeO_2 crystallite sizes of ~ 6.8 nm. Dispersions measured by CO chemisorption were 48% for the 5%Pt/ Al_2O_3 and 54% for the 5%Pt/15% CeO_2/Al_2O_3 .

3.2. Activity Tests for CO Oxidation with Free- H_2 Gas Stream

The two catalysts were tested for their activities in CO oxidation as a function of temperature under gas feed containing 1%CO, 1% O_2 and He as balance as seen in **Figure 1**.

At 100°C the integral conversions were 2% and 10% over the 5%Pt/ Al_2O_3 and the 5%Pt/15% CeO_2/Al_2O_3 catalysts. Increasing the temperature to 150°C increased the CO conversion from 2% to 27% for the 5%Pt/ Al_2O_3 and from 10% to 60% for the 5%Pt/15% CeO_2/Al_2O_3 . Further increasing reaction temperature to 170°C increased the CO conversion to 70% for the 5%Pt/ Al_2O_3 and to 98.9% for the 5%Pt/15% CeO_2/Al_2O_3 . Finally, CO completely converted to CO_2 at 180°C for both catalysts. Clearly, the catalyst containing ceria showed better activity in CO oxidation, especially at low temperatures. For the 5%Pt/ Al_2O_3 , it has been known that CO strongly chemisorbs over Pt sites from room temperatures to 150°C

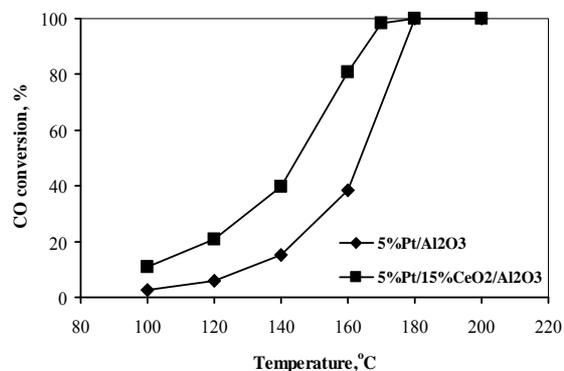
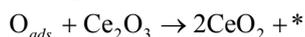
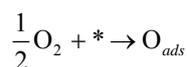
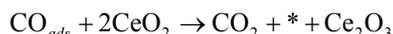


Figure 1. Activities of platinum over alumina and promoted platinum over alumina catalysts to CO oxidation. Gas composition: 1%CO, 1% O_2 and He as balance.

[14,27]. At these temperatures, the competition between CO molecules and O₂ molecules over the active sites is crucial. The reaction occurs when O₂ molecules adsorb and dissociate next to CO molecules. At temperatures less than 150°C, Pt sites are occupied by CO molecules. This leads to low activity of platinum over alumina catalysts in the CO oxidation reaction. Increasing reaction temperature above 150°C dramatically increases the rate of reaction due to desorption of CO molecules from the active sites and leaving available sites for O₂ molecules to be adsorbed. The addition of ceria enhances the rate of reaction of the catalyst. This is due to the oxygen storage property proposed as following [28]:



where “*” stands for an adsorption site on platinum and “ads” for an adsorbed species. From this model, the key point of high activity of the 5%Pt/15%CeO₂/Al₂O₃ catalyst at low reaction temperatures (<150°C) results from a capacity of ceria to switch between the two-oxidation states Ce⁴⁺ and Ce³⁺. Ce³⁺ returns back to Ce⁴⁺ by gaseous oxygen molecules. This phenomenon occurs even at room temperature. However, 170°C is high enough for CO molecules to desorb from active sites and leave the active sites available for other reactant molecules to be adsorbed and reacted [29]. Therefore, both catalysts performed comparably above 170°C. FTIR was used to check the chemisorbed CO species. The results are shown in **Figure 2**. Before the test, the catalyst pellet diluted with KBr was purged with helium at 200°C until catalyst surface was clean. Then, the sample was cooled to 100°C under a helium purge. After the temperature of the sample reached 100°C, the sample was purged with gas stream containing 1% CO balance with helium. The adsorption of CO over the catalyst sample was recorded.

Figure 2(a) shows the CO adsorption over the 5%Pt/15%CeO₂/Al₂O₃ pellet. A strong peak at 2062 cm⁻¹ was observed. This peak corresponds to CO adsorbed over Pt/CeO₂/Al₂O₃ [30]. Other peaks at 2395-2312 cm⁻¹ were also observed and these peaks indicate the presence of gas phase CO₂. The intensity of the CO₂ band slowly decreased with time and finally disappeared. The formation of CO₂ was due to CO oxidation reaction and the O₂ reactant must have come from lattice of CeO₂. This result was in agreement with a model of oxygen transport in Pt/ceria catalyst [31]. Next, the same experiment was carried out with the 5%Pt/Al₂O₃. The results are shown in **Figure 2(b)**. A strong peak at 2085 cm⁻¹ was observed. This peak corresponds to CO adsorbed on Pt with neighboring oxidized Pt [32]. Unlike platinum over ceria-promoted alumina catalyst, no peak of CO₂ gas phase

was observed. This means that in the absence of gas phase O₂ no CO oxidation reaction occurs with this catalyst. The CO adsorbed on Pt peak for promoted Pt catalyst appeared at 2062 cm⁻¹ while that of Pt/Al₂O₃ appeared at 2085 cm⁻¹ [29,32]. The downward shift of CO adsorbed wave number may be due to inducing of C-O bond weakening for CO adsorbed on Pt by Ce [19]. The reduction of the bond strength of adsorbed CO makes it more reactive with an oxygen atom from ceria lattice into CO adsorbed near Pt-CeO₂ interface followed by desorption of CO₂ leaving Pt site available for other gas molecules. Therefore, the presence of a small amount of ceria could enhance the activity of platinum over alumina due to its oxygen storage property.

3.3. Effect of Ceria on the Activity of Catalysts

The effect of ceria on the activity of catalysts was shown in **Figure 3**.

Figure 3(a) shows the activities of the two catalysts as function of reaction temperature for a dry gas composition of 1%CO, 1%O₂, 55%H₂ and He as balance. At 110°C, CO conversions were 46% and 60% over the 5%Pt/Al₂O₃ and the 5%Pt/15%CeO₂/Al₂O₃ catalysts. Increasing reaction temperatures further to 180°C led to dramatic increases in CO conversion from 46% to 90% for the 5%Pt/Al₂O₃ and from 60% to 99.3% for the 5%Pt/15%CeO₂/Al₂O₃. At 190°C, CO conversion reached a maximum of approximately 99.97% for the 5%Pt/15%CeO₂/Al₂O₃ while CO conversion reached a maximum of approximately 93.70% for the 5%Pt/Al₂O₃. Further increasing reaction temperature to 230°C resulted in decreases in CO conversion to 57% for the 5%Pt/Al₂O₃ and 89% for the 5%Pt/15%CeO₂/Al₂O₃. **Figure 3(b)** shows oxygen consumption as a function of reaction temperature. For the 5%Pt/Al₂O₃, O₂ was quickly consumed by the reactions. O₂ conversion increased from 79% to 100% when reaction temperature increased from 110°C

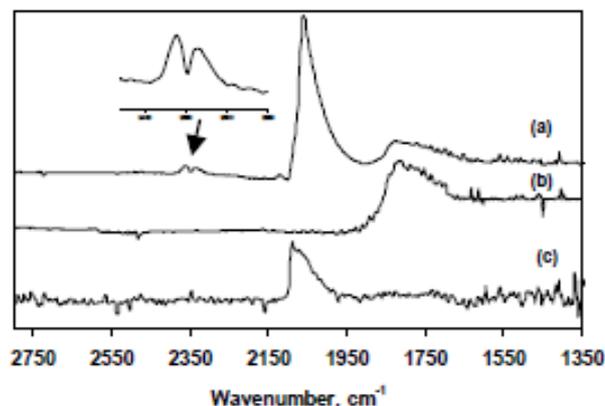


Figure 2. FTIR study for CO adsorbed over catalysts under 1%CO in He at 100°C: (a) 5%Pt/15%CeO₂/Al₂O₃, (b) 15%CeO₂/Al₂O₃ and (c) 5%Pt/Al₂O₃.

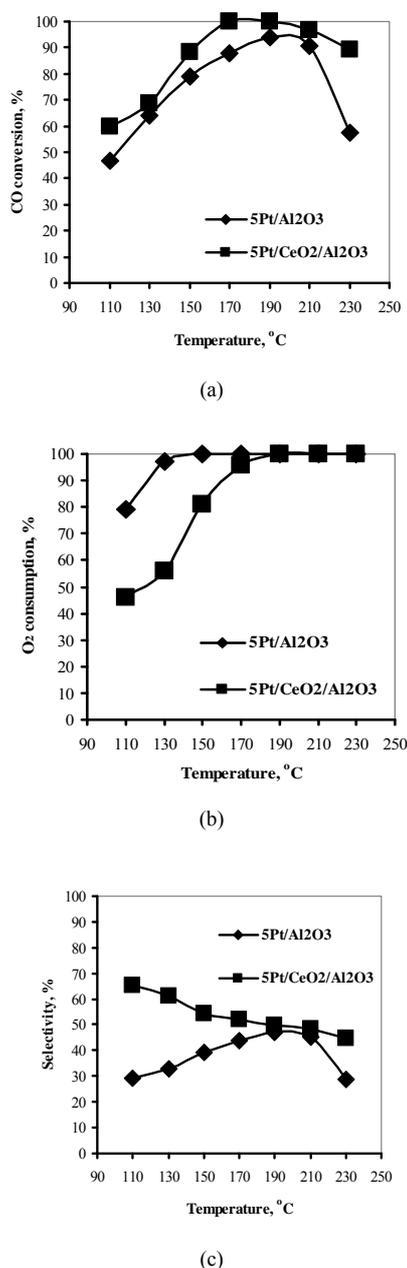


Figure 3. Comparison of activities to selective CO oxidation of the 5%Pt/Al₂O₃ and the 5%Pt/15%CeO₂/Al₂O₃ catalysts as a function of temperature. Gas composition: 1%CO, 1%O₂, 55%H₂ and He as balance.

to 150°C. Unlike the 5%Pt/Al₂O₃, O₂ conversion for the 5%Pt/15%CeO₂/Al₂O₃ slowly increased from 46% to 56%, 81%, 86% and 100% when reaction temperature increased from 110°C to 130°C, 150°C, 170°C, and 190°C, respectively. These results led to differences in selectivity for CO oxidation as shown in **Figure 3(c)**. As mentioned previously, no methane formation was observed under these operating conditions. Consequently, selectivity was defined as the ratio of oxygen used for

CO oxidation to total oxygen consumed by the reactions. As shown in **Figure 3(c)**, the selectivity's of the two catalysts are different. At 110°C, selectivity was 29% for the 5%Pt/Al₂O₃. This means that oxygen consumed by the reactions mostly goes to H₂ oxidation. At the same temperature, selectivity was 65% for the 5%Pt/15%CeO₂/Al₂O₃. This means that the presence of ceria in the catalyst enhanced the rate of CO oxidation. Further increases reaction temperature to 180°C increased selectivity to 44% for the 5%Pt/Al₂O₃ but decreased selectivity to 50% for the 5%Pt/15%CeO₂/Al₂O₃. At 230°C, selectivity of both catalysts dropped to 28% for the 5%Pt/Al₂O₃ and 45% for the 5%Pt/15%CeO₂/Al₂O₃. The decrease of selectivity for both catalysts at high temperatures is due to the competition between CO oxidation and H₂ oxidation reactions. At high temperatures, the H₂ oxidation reaction occurs faster than the CO oxidation reaction [32]. Further investigation of the 5%Pt/15%CeO₂/Al₂O₃ catalyst was conducted to understand its behavior under different reaction conditions.

3.4. Space Velocity Effect

The dependence of CO conversion and selectivity on flow rate is shown in **Figures 4(a)-(c)**.

Space velocity was increased from 35,000 to 70,000 cm³·g⁻¹·h⁻¹. Considering at the same temperatures, increasing the space velocity decreased the CO conversion and decreased the O₂ consumption. With 1% CO, 1% O₂, 20% CO₂, 10% H₂O, 55% H₂ and He as balance, maximum CO conversion for the low space velocity run was 100% at 150°C while maximum CO conversion for the high space velocity run was 100% at 180-190°C. Selectivity did not change with space velocity at temperatures less than 150°C. At higher temperatures, selectivity for the low space velocity run was lower than that for the high space velocity run. This result indicates that the use of this catalyst depends on the reaction condition. Low space velocity would obtain high CO conversion at low temperatures while high space velocity would obtain high CO conversion at high temperatures.

Activities of 1%Pt-1%CeO₂ over activated carbon [33] were compared with those of 5%Pt/15%CeO₂/Al₂O₃ in selective CO oxidation under realistic gas compositions. Although the authors reported that their catalyst is very active to CO oxidation in H₂-excess stream and CO conversion drastically increased with the presence of CO₂, combining both CO₂ and H₂O in the gas feed stream resulted in CO conversion of 100% and selectivity to CO oxidation of 50% at 150°C with space velocity of 24,000 cm³·g⁻¹·h⁻¹. Unlike this catalyst, CO conversion of the 5%Pt/15%CeO₂/Al₂O₃ decreased with the presence of CO₂ in the gas stream. This is due to the carbonate formation blocking the available active sites. However, combining both CO₂ and H₂O in the gas feed enhanced

the activity of the catalyst especially at low temperatures (<160°C). Under the realistic gas composition, our catalyst obtained 100% CO conversion at 140-150°C with selectivity in CO oxidation of 50%-52% and space velocity of 35,000 cm³·g⁻¹·h⁻¹.

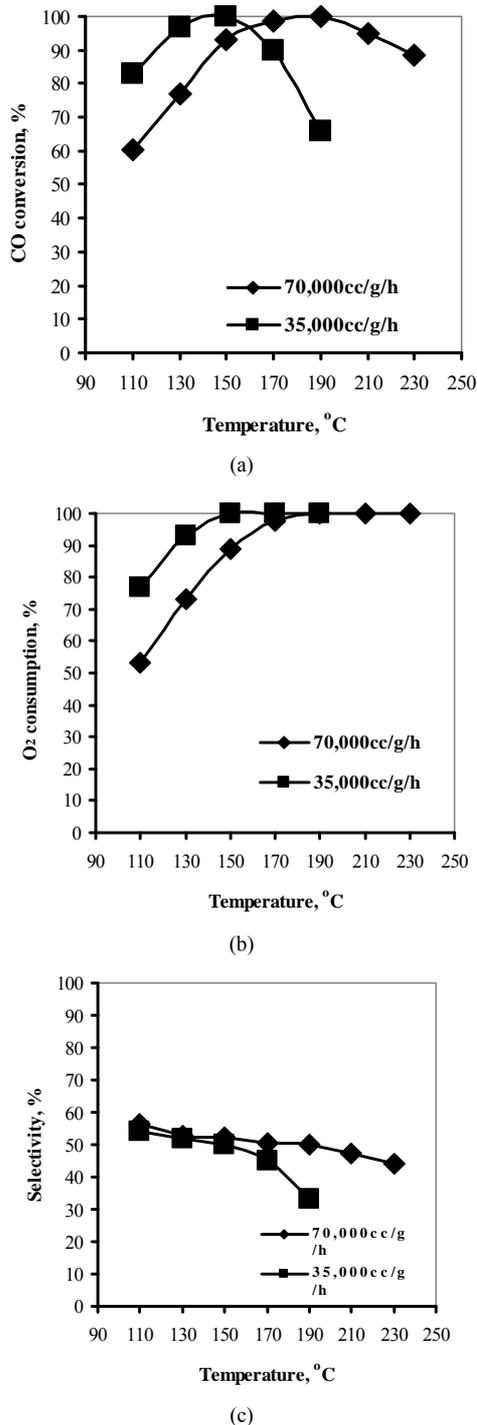


Figure 4. Dependence of CO conversion and selectivity of CO oxidation on space velocity and temperature for a 5%Pt/15%CeO₂/Al₂O₃. Gas composition: 1%CO, 1%O₂, 10%H₂O, 20%CO₂, 55%H₂ and He as balance.

In our work, 5%Pt/15%CeO₂/Al₂O₃ demonstrated excellent performance in preferential CO oxidation. This catalyst is very stable under the realistic gas conditions during 72 hr of use. The higher selectivity in CO oxidation could obtain under the low O₂ concentration.

4. Conclusions

The CO poisoning of PEMFCs is a major problem to deplete the efficiency and energy conversion of PEMFCs. To remove a trace amount of CO in the reformed gas is essential. In this work, the catalytic performance of promoted platinum over alumina with ceria in selective CO oxidation in the presence of excess hydrogen has been studied. The addition of ceria improved the catalytic activity in oxidation reactions. It resulted from the oxygen storage property of ceria. Space velocity also affected the CO conversion. High CO conversion at low temperature was obtained when low space velocity was chosen. Finally, the 5%Pt/15%CeO₂/Al₂O₃ is an excellent catalyst for removal of trace CO in reformed gas. It reduces 1% CO in the realistic reformed gas to less than 10 ppm with selectivity of 52% at 180°C with space velocity of 70,000 cm³·g⁻¹·h⁻¹.

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