Effect of platinum on ceria supported copper catalysts for PrOx process in fuel processors

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Abstract

The CO preferential oxidation (PrOx) is one of the critical steps in hydrogen production and purification for Polymer Electrolyte Membrane Fuel Cell (PEMFC). This reaction was investigated in the presence of excess hydrogen over Cu/CeO₂, Pt/CeO₂ and Cu-Pt/CeO₂ catalysts. The ceria supports were prepared via precipitation method and Cu-Pt/CeO₂ catalyst was synthesized by sequential impregnation on ceria. The catalysts were characterized by XRD. Comparison of ceria supported copper and platinum showed that the activity of copper catalysts are higher than platinum in PrOx process. Effect of platinum addition on ceria supported copper was investigated, and the results showed that Pt promoter have positive effect on CO conversion in low temperature (<110°C). Promotion of Cu with Pt increases the CO conversion by 30% in comparison with un-promoted Cu catalyst. It is mentioned that the platinum addition to copper only promotes the Cu catalyst at low temperature. At higher temperatures, reverse WGS reaction occurs and decreases the CO conversion.

1. Introduction

The preferential oxidation of CO (PrOx) is one of the critical steps in hydrogen production and purification for PEMFC, since the anode catalyst in PEM is strongly poisoned even by ppm level of CO in the H₂ rich gas [1-3]. The CO-PrOx process used after steam reforming and WGS for removal of trace contaminant CO in the H₂ rich gas. Among the current available methods, CO-PrOx is most economical and efficient approach to reduce CO to the desired level without excessive hydrogen consumption [4]. The main reactions in CO-PrOx involved are:

CO Oxidation: \( CO + \frac{1}{2} O₂ \rightarrow CO₂ \)  \hspace{1cm} (1)

H₂ Consumption: \( H₂ + \frac{1}{2} O₂ \rightarrow H₂O \)  \hspace{1cm} (2)

The CO conversions were calculated based on the carbon monoxide consumption in the reaction as follows:
X_{CO}(\%) = \frac{[CO_{in}] - [CO_{out}]}{[CO_{in}]} \times 100 \quad (3)

The selectivity of the CO oxidation in the presence of excess hydrogen was calculated from the oxygen mass balance as follows:

\[ \text{Se}_{CO} = 0.5 \times \frac{[CO_{in}] - [CO_{out}]}{[O_{in}] - [O_{out}]} \times 100 \quad (4) \]

And, the excess of oxygen factor (\lambda) is defined as:

\[ \lambda = 2 \times \frac{F_{CO}^{in}}{F_{CO}^{out}} \quad (5) \]

where \( F \) is the molar flow of the specie. Among the different catalysts, CuO/CeO\(_2\) catalysts have been recently proposed as a promising candidate for the selective removal of CO from reformates streams due to their high activity and remarkable selectivity [5]. The well-known enhancement of oxidation activity of copper, when supported on reducible oxides like CeO\(_2\), was attributed to a synergistic effect [6]. It is proposed that well-dispersed CuO on CeO\(_2\), which is reducible at a lower temperature with respect to bulk CuO, could adsorb CO better. As a result, this catalyst exhibited higher activity/selectivity for low-temperature CO oxidation and CO-PrOx [7]. To increase the catalytic activity of the catalysts, many metals have been used as promoter, such as Pt, Au, Zn, Ni, Co … [8-13]. Nowadays, platinum catalysts are not used alone for CO-PrOx process. Several researchers have made use of Pt as catalyst promoter in this process. Junichiro Kugai et al. synthesized Pt-Cu/γ-Fe\(_2\)O\(_3\) by a unique radiolytic process and their physical properties and catalytic activity for CO preferential oxidation were investigated for various Pt/Cu atomic ratios. Regardless of the low Pt loading, the sample with 10% Pt and 90% Cu (percents is in atomic) exhibited the highest activity at 100°C, near the 70% CO conversion [14]. Pt-Ni/γ-Al\(_2\)O\(_3\) catalysts were prepared by Eun-Yong Ko et al. with co-impregnation and sequential impregnation method. Comparison between test results of this catalysts showed that the 1%Pt-1.5%Ni/γ-Al\(_2\)O\(_3\) prepared by co-impregnation has high activity, about 90%, which is the highest CO conversion with 43% CO\(_2\) selectivity at 100°C [15]. J L Ayastuy et al. synthesized Pt-Sn/γ-Al\(_2\)O\(_3\) by sequential impregnation with Pt/Sn atomic ratios of 1.92, 0.53, 0.28, and then studied catalytic performance in PrOx process. The optimum Pt/Sn atomic ratio was found to be 0.53. In a wide range of performance with respect to temperature, the catalyst with optimum Pt to Sn ratio showed a maximum CO conversion of 78% for \( \lambda = 2 \) with constant selectivity (about 40%) and with 31% CO yield [16]. Hernan P. Bideberripe et al. studied a bimetallic Pt-Ge catalyst prepared by a controlled surface reaction (ion exchange) and studied the PrOx performance of this catalyst. The good activity of the bimetallic catalyst can be assigned to the presence of a “noble metal-oxidized metal promoter” ensemble site in close contact, the noble metal (Pt) being the CO adsorption site and the oxidized metal promoter (Ge) the O\(_2\) adsorption site. CO conversions of these catalysts were about 55% at 230°C with 50% CO\(_2\) selectivity [17]. CeO\(_2\)-supported Pt-Cu bimetallic catalysts were synthesized by J. Kugai et al. with radiolytic process and their PrOx activities were evaluated in relation to structural properties of the catalysts. These Pt-Cu bimetallic catalysts showed much lower light-off temperature than monometallic Cu. The best CO-PrOx performance related to Pt\(_{10}\)Cu\(_{90}\) catalyst [18].

Due to good activity of copper catalysts and positive effect of platinum, in this study the effect of Pt addition to performance of ceria supported Cu catalysts in CO-PrOx process was investigated. Cu-Pt/CeO\(_2\) catalyst was synthesized by sequential impregnation method in order to study the CO preferential oxidation performance and compare it with copper catalyst. In addition, the effect of catalyst synthesis Cu-Pt/CeO\(_2\) bimetallic was evaluated in comparison with the physical mixture of Cu and Pt catalysts. Sequential impregnated method has not been used for Cu-Pt/CeO\(_2\) catalyst in previous studies. The purpose of this work is enhanced catalytic activity of copper catalysts.

2. Experimental

2.1. Materials

In this work, copper nitrate [Cu(NO\(_3\))\(_2\)·3H\(_2\)O, Merck, 99.5%], hexa-chloro-platinic acid [H\(_2\)PtCl\(_6\)·6H\(_2\)O, Merck, 40%], cerium nitrate [Ce(NO\(_3\))\(_3\)·6H\(_2\)O, Fluka, 99.5%] and commercial ceria [CeO\(_2\), Loba chemie, 99.95%] as the precursors and ammonia [NH\(_3\), Merck, 25%] as the precipitate agent have been used. All these substances were pure and required no further purification.
2.2. Catalysts Preparation

Monometallic catalysts 7%Cu/CeO$_2$ and 0.5%Pt/CeO$_2$ were prepared by impregnation from aqueous solution of copper nitrate, hexa-chloro-platinic acid and commercial ceria to compare the activities in CO-PrOx process. These catalysts were dried for 12h at 120°C and then calcined in air at 500°C for 4h.

Ceria support was prepared by precipitation method, cerium nitrate as precursor and ammonia as precipitate agent and the resulting suspension was left to settle for 6h. The precipitate was filtered and washed with deionized water, and then the ceria cake dried overnight at 120°C. The dried precipitate was calcined at 600°C for 6h. Cu-Pt/CeO$_2$ catalyst with 7 wt.% Cu and 0.5 wt.% Pt were synthesized by sequential impregnation method on ceria prepared by precipitation method; the precursor was dried for 12h at 120°C and later calcined in air at 500°C for 4h between the two impregnation steps.

2.3. Catalysts Analysis

The XRD patterns were recorded on an X-ray diffractometer (PANalytical X’Pert-Pro) using a Cu K$_\alpha$ monochromatized radiation source and a Ni filter in the range 2θ=20-80°.

The surface areas (BET), mean pore diameter and total pore volume were determined by nitrogen adsorption at -196.15°C using an automated gas adsorption analyzer (Gimini, Micromeritics). Inlet and outlet gases were analyzed by a Shimadzu-8A chromatograph equipped with a TCD, Carbosieve column, and GC data’s analyzed by Chromanit software.

2.4. Catatest

Activity test were carried out at 60-200°C temperature range and atmospheric pressure in a fixed bed quartz reactor (8 mm inner diameter). Also, 120 mg catalyst with 40-60 mesh was charged in the reactor for each test. The feed composition was selected based on reformate composition after WGS process and contains large amount of H$_2$, small amount of CO (1-2%) and suitable amount of O$_2$ according to stoichiometric ratio. In this work, feed gas composition was 2% CO, 2% O$_2$ and 96% H$_2$ (vol.%, dry basis). The total flow rate was 40 ml/min corresponding to a space velocity of 20000 h$^{-1}$. The catalysts pretreated at 400°C for 1 h in O$_2$ stream with a flow rate of 20 ml/min before the tests. An scheme of setup (catatest) system is shown in Figure 1.

3. Results and Discussion

3.1. Catalyst Characterization

The XRD patterns of CeO$_2$ and Cu-Pt/CeO$_2$ catalysts are presented in Figure 2. The crystalline mean particle sizes of catalyst have been determined by the X-ray broadening technique employing the Scherrer formula as:

$$d_{XRD} = \frac{0.9 \, \lambda}{FWHM \, \cos \theta}$$

Where $\lambda$ is the X-ray wavelength (1.5406 Å), $FWHM$ (in Rad) is the full width at half maximum of the characteristic peak (111) of sample and $\theta$ is the diffraction angle for the (111) plane. For Cu-Pt/CeO$_2$ sample, the peak of Pt not specified because Pt loading is less than 1.0 wt.%, it means Pt loading onto Cu catalyst does not affect the crystal phase of catalyst. For ceria, the main characteristic peaks are associated with the Face-Centered Cubic (FCC) fluorite structure. The main peak (2θ = 28.8°) corresponds to the (111) reflection of ceria and average calculated crystal size of ceria was 17 nm. The main peak (2θ = 35 and 38°) corresponds to the CuO and average calculated crystal size was 19 nm for 7%CuO/CeO$_2$, and 7%Cu-0.5%Pt/CeO$_2$. The surface area of synthesized CeO$_2$ by precipitation method was 74.5 m$^2$/g, total pore volume 0.18 m$^3$/g and average pore diameter about 9.6 nm. As can be seen in Figure 3(a), adsorption/desorption isotherm of ceria is relatively narrow, this proves that the fine particles are obtained.
that makes the large surface area and resulting in high catalytic activity of catalyst containing this support. Figure 3(b) shows the pore size distribution of the CeO$_2$, which is less than 10 nm and about 5 nm.

3.2. Catalyst Activity

3.2.1. Comparison of Cu and Pt

For comparison of Cu and Pt catalyst activity in the CO-PrOx process, two samples with 7% Cu and 0.5% Pt on commercial ceria were synthesized by impregnation method at similar conditions. CO conversion and CO$_2$ selectivity of these catalysts shows in Figure 4. As shown in Figure 4, CO conversion of Pt catalyst was very lower than Cu catalyst, but CO$_2$ selectivity of this sample was more than Cu catalyst. Therefore, selection of Cu as main active site in catalyst is correct. It is noteworthy that Pt catalysts performance strongly dependent on the support and with specification changes of support changed.

Figure 4: CO conversion and CO$_2$ selectivity of Cu and Pt catalysts. Operating conditions: 96% H$_2$, 2% CO, 2% O$_2$, $\lambda = 2$ & GHSV = 20000 h$^{-1}$.

3.2.2. Effect of Pt on Cu Catalyst Performance

Based on the our results and studies, Pt catalysts singly not suitable in CO-PrOx process operation
because of lower CO conversion toward some catalysts such as Cu catalysts, moreover, the cost of platinum catalysts are very more than Cu catalysts and use of Pt as main active site isn’t affordable. So, in this study, the CuO/\(\text{CeO}_2\) was selected as primary catalyst and the effect of Pt as promoter of Cu catalyst investigated. Therefore, 7%Cu-0.5%Pt/\(\text{CeO}_2\) catalyst synthesized by sequential impregnation method and was tested in operation conditions explained. Catalytic activity of this catalyst in comparison with 7%Cu/\(\text{CeO}_2\) shows in Figure 5. CO conversion of Cu-Pt catalyst in low temperature (<110°C) was much more than Cu catalyst and this increase due to the positive effect of adding Pt. For example, CO conversion of 7%Cu/\(\text{CeO}_2\) at 80°C was 50%, while in 7%Cu-0.5%Pt/\(\text{CeO}_2\) was more than 90%, that due to synergistic effect of Pt and Cu in low temperatures. In 100°C, CO conversion of 7%Cu-0.5%Pt/\(\text{CeO}_2\) reached to 96% with 48% CO\(_2\) selectivity. The use of platinum as a Cu catalysts promoter at high temperature is not recommended, because of reverse WGS reaction, carbon monoxide and water produced and finally CO conversion and CO\(_2\) selectivity decreased.

3.2.3. Physical Mixing of Cu and Pt Catalyst

To evaluate the effectiveness of synthesis catalyst in comparison with physical mixing of Cu and Pt catalysts, the catalytic test carried out with 10 wt.% of 0.5%Pt/\(\text{CeO}_2\) and 90 wt.% of 7%Cu/\(\text{CeO}_2\) catalyst, these catalysts were in 40-60 mesh and mixed physically. Figure 6 shows that even the physical addition of a platinum catalyst at low temperatures has increased the CO conversion of Cu catalysts. However, by synthesize of Cu-Pt/\(\text{CeO}_2\) catalyst with sequential impregnation method, the better results achieved due to proper distribution of active sites and better contact between metals.

Figure 5: Activity of Cu and Cu-Pt catalysts. Operating conditions: 96% \(\text{H}_2\), 2% CO, 2% \(\text{O}_2\), \(\lambda = 2\), and GHSV = 20000 h\(^{-1}\).

Figure 6: Performance of mixed and synthesized catalysts. Operating conditions: 96% \(\text{H}_2\), 2% CO, 2% \(\text{O}_2\), \(\lambda = 2\), and GHSV = 20000 h\(^{-1}\).

Figure 7 shows the CO conversion and CO\(_2\) selectivity of 7%Cu-0.5%Pt/\(\text{CeO}_2\) catalyst synthesized by sequential impregnation method in this work and that of Pt\(_{10}\)/Cu\(_{90}\)/\(\text{CeO}_2\) by J. Kugay et al. through radiolytic process [18]. As shown in Figure 7, the rate of CO conversion of impregnated catalyst is more than Pt\(_{10}\)/Cu\(_{90}\)/\(\text{CeO}_2\) catalyst. For example, CO conversion of our catalyst is 96%, 36% higher than Pt\(_{10}\)/Cu\(_{90}\)/\(\text{CeO}_2\) catalyst at 100°C, CO\(_2\) selectivity of 7%Cu-0.5%Pt/\(\text{CeO}_2\) catalyst
less than $\text{Pt}_{20}\text{Cu}_{80}/\text{CeO}_2$ catalyst, however, the catalytic activity in CO-PrOx process is more important to remove trace amount of CO from produced hydrogen.

Figure 7: CO-PrOx performance for 7%Cu-0.5%Pt/\text{CeO}_2 $\alpha \neq 2$ and $\text{Pt}_{20}\text{Cu}_{80}$ catalyst $\alpha \neq 1$ [18].

4. Conclusion

The preferential oxidation (PrOx) process is one of the most effective methods for the removal of CO trace from the reformate stream. CO-PrOx is a process to convert CO in a H$_2$ rich gas mixture to CO$_2$ with minimum H$_2$ consumption. Ceria supported Cu catalysts are of the best catalysts for this process. In this study, 7%Cu/\text{CeO}_2 catalyst was prepared by impregnation method and 7%Cu-0.5%Pt/\text{CeO}_2 catalyst was synthesized by sequential impregnation to investigate the effect of Pt as promoter. Results indicated that the addition of Pt increased the CO conversion at low temperatures (<110°C), but CO$_2$ selectivity decreased. Therefore, platinum is useful when CO-PrOx process is necessarily carried out at low temperatures, which with the addition of only 0.5% Pt, CO conversion increases nearly 40% due to synergistic effect of Cu and Pt. At 100°C, CO conversion of 7%Cu-0.5%Pt/\text{CeO}_2 reached 96% with 48% CO$_2$ selectivity, a significant progress in the results in comparison with that of other researchers. At higher temperatures (>110°C), due to reverse WGS reaction, carbon monoxide and water are produced, and finally, CO conversion and CO$_2$ selectivity decreased.

5. References


[18] J. Kugai, T. Moriya, S. Seino, “CeO\textsubscript{2}-sup-