Selective catalytic oxidation of CO in the presence of H₂ over gold catalyst

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Abstract

The proton exchange membrane fuel cells with potentially much higher efficiencies and almost zero emissions offer an attractive alternative to the internal combustion engines for automotive applications. A critical issue in fuel cell system is the small (∼ 0.5%) amount of CO present from output of fuel reformer. This amount of CO can deteriorate the performance of fuel cells. Consequently, an additional gas conditioning process is required to minimize CO content in reformed gas. The proposed research study focuses on preferential oxidation of CO in a simulated reformed gas to CO₂ by using selective CO oxidation catalysts. In this work, the effects of preparation method, O₂, water vapor, and CO₂ concentration in feed stream on the selective CO oxidation over Au/CeO₂ catalysts were investigated in the temperature range of 323–463 K. Catalytic stability test was also performed.

We find that the activity of Au catalyst depends very strongly upon the preparation method, with co-precipitation prepared Au/CeO₂ catalyst exhibiting the highest activities.
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Keywords: CO oxidation; Gold catalyst; Ceria; Co-precipitation; Fuel cell

1. Introduction

In the past, the world has widely relied on the energy from burning fossil fuels, which are expected to be depleted in the near future. Extensive uses of fossil fuels have created air pollution, acid rain, and the greenhouse effect. Scientists have been searching for alternative means of powering vehicles more efficiently without creating any pollution. The proton exchange membrane (PEM) fuel cell has been attracting much attention in improving fuel efficiency and cleanliness of automobiles [1]. This is due to low temperature of operation, fast cold start, perfect CO₂ tolerance by the electrolyte and a combination of high power density and high energy conversion efficiency. Normally, pure hydrogen is the ideal fuel for the fuel cell system since it simplifies system integration, maximizes system efficiency, and provides zero emission. However, since no effective and potentially safe means of storing adequate amount of hydrogen in a vehicle exists, on-board hydrogen generation by steam reforming of methanol or partial oxidation of liquid hydrocarbons followed by water gas shift reaction are alternative ways of giving a fuel cell powered vehicle adequate range. These technologies not only produce hydrogen as a main product but also has side products with a small amount of 1% CO. Many studies have shown the negative effect of CO on the performance of PEM fuel cell since the electrodes of the fuel cell are typically made of platinum which is very sensitive to CO poisoning [2,3]. Selective catalytic CO oxidation is perhaps the most promising method of reducing CO in the feed to a 10 ppm or lower range with a minimal loss of hydrogen.

The preferential catalytic oxidation of CO was first studied by Oh and Sinkevitch [4] with alumina
supported ruthenium (Ru), rhodium (Rh) and platinum (Pt). Ru and Rh were very selective compared to Pt for oxidizing CO in the presence of H₂ diluted with N₂ at 403 K. However, a gas composition of 900 ppm CO, 800 ppm O₂ and 0.85% H₂ in N₂ background was very different from the reformed gas that is generated by reforming a liquid hydrocarbon or methanol. The concept of using a zeolite support on Pt catalysts was applied for this reaction by Watanabe et al. [5] and Igarashi et al. [6].

Kinetic studies of selective CO oxidation on Pt/Al₂O₃ and Au/Fe₂O₃ catalysts in a simulated reformed gas (75% H₂, the rest is N₂) over a wide range of CO concentrations (0.02–1.5%) were reported by Kahlich et al. [7,8]. In addition to the noble metal catalysts other catalysts have also been investigated such as CoO catalyst [9], and Pt promoted deposited on a monolith catalyst [10]. The supported Au catalysts have been found to be very active for CO oxidation reaction [11–13]. Recently, the metal oxide supports such as Al₂O₃ [14], MnO [15], Fe₂O₃ [16], MgO–Al₂O₃ [17] were found to promote the activity of Au on selective CO oxidation and the catalytic combustion of volatile organic compounds [18].

Among the different metal oxides used as the support of Au for CO oxidation, cerium oxide or ceria (CeO₂) is one of the interesting metal oxides. CeO₂ is the oxide of the rare-earth metal cerium, which may exist in several compositions, due to the capacity of Ce to switch between the two oxidation states of Ce³⁺ and Ce⁴⁺. A number of functions have been ascribed to ceria, including promoting water gas shift activity [19–21], maintaining the dispersion of the catalytic metals [2,22] and stabilizing the surface area of the support [23]. Extensive research, in particular during the past decade, has shown that ceria has beneficial effects on a number of catalytic reactions.

Due to a facile redox reaction cycle, ceria exhibits oxygen storage capacity and improves the CO and hydrocarbon oxidation. Summers and Ausen [24] claimed that ceria donated oxygen to Pt in their study of the oxidation of CO on Pt/CeO₂ catalyst. For CO oxidation, ceria has been found to lower the activation energy, increase the reaction rate and suppress the usual CO inhibition effect [25]. The percentage loading of Ce has been shown to affect CO oxidation on Pt [26]. Ceria promotes the activity of Pt in both lean and rich reactant gases for CO oxidation [27]. Consequently, we chose CeO₂ as the support for studying selective catalytic oxidation of CO in the presence of H₂ based on the aforementioned properties of ceria.

From preliminary results, we found that Au/CeO₂ catalysts also work very well for the selective CO oxidation. Therefore, the objectives of this work are to optimize the operating conditions for preferential oxidation of CO by O₂ in the presence of H₂ over the temperature range of 323–463 K, which are suitable for fuel cell applications, and to study the effect of preparation method on the catalytic activity of Au/CeO₂ catalysts.

2. Experimental

2.1. Catalyst preparation

Three methods of the catalyst preparation; impregnation, co-precipitation and sol–gel were used in this work.

Impregnation method: The Au catalysts were obtained by impregnation of the commercial ceria support with an aqueous solution of HAuCl₄·xH₂O (Alfa Aesar) containing the appropriate amount of Au. The catalysts were dried overnight at 383 K and calcined at 773 K for 5 h.

Co-precipitation method: An aqueous solution of Na₂CO₃ (1 M) was added into an aqueous mixture of HAuCl₄·xH₂O and Ce(NO₃)₃·6H₂O (Fluka) and was kept at room temperature and constant pH of 8.0. The precipitate was aged for an hour and then was washed several times with distilled water until there was no excess anions. After washing with deionized water, the catalysts were dried overnight at 383 K and calcined at 773 K for 5 h.

Sol–gel method: The single step sol–gel catalysts were prepared by hydrolyzing a solution of Ce acetate (Alfa Aesar) and HAuCl₄·xH₂O with NH₄OH. The reaction mixture was kept at 353 K while the pH was maintained between 9.0 and 9.5. Then, HNO₃ was added until gelation, the catalysts were dried overnight at 383 K and calcined at 773 K for 5 h.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were used to obtain information about the structure and composition of crystalline materials. A Rigaku X-ray diffraction system equipped with a graphite monochromator and a Cu tube for generating a CuKα radiation was used to obtain the XRD patterns.

The Brunauer–Emmett–Teller (BET) method was used to determine the surface area and pore size of the catalysts by N₂ adsorption/desorption at 77 K. Specific surface area was determined using an Autosorb-1 surface area analyzer.

The particle morphology of the catalysts was observed by a Scanning Electron Microscope (SEM) using JEOL JSM-5410 LV scanning microscope operated at 15 kV. The Transmission Electron Microscopy (TEM) images were attained using a JEM 2010 operating at 200 kV in bright and dark field modes. Crystallinity and crystal structure of the samples were evaluated from the selected area of electron diffraction patterns.

2.3. Activity measurement

Catalytic activity studies were conducted in a pyrex glass U-tube reactor having an internal diameter of 6 mm
at atmospheric pressure. One hundred mg of catalyst was packed between glass wool plugs in the middle of the reactor. The reactant gas typically consisted of 1% CO, 0.5–2% O₂, 2% CO₂, 2.6% H₂ O, 40% H₂ and helium. The space velocity was 30,000 ml g⁻¹ h⁻¹. The reactant gas was passed through filters to remove particles and a check valve to prevent a reverse flow. The individual stream flow rate was controlled by mass flow controllers to achieve the desired composition.

The reactant and product were analyzed by an on-line gas chromatograph, (Hewlett Packard 5890 Series II equipped with a thermal conductivity detector). The column utilized in the chromatograph was a Carbosphere, 80/100 mesh, 10 ft × 1/8 in stainless-steel packed column.

The CO conversion was calculated based on the carbon dioxide formation. The selectivity of CO oxidation was defined as the oxygen consumption for CO oxidation divided by the total oxygen consumption. There was no methane formation observed under reaction conditions performed in this study.

3. Results and discussion

3.1. Catalyst characterization

Table 1 lists the BET surface areas, ceria crystallite sizes and Au particle sizes of the Au/CeO₂ catalysts studied. The surface area varies significantly with the catalyst preparation method. The CeO₂ crystallites sizes of the catalysts were determined from X-ray line-broadening using the Debye Scherrer equation and the results are also shown in Table 1. The sol–gel method gave the largest CeO₂ crystallite size while the co-precipitation method gave the smallest CeO₂ crystallite size on Au catalysts. The sizes of CeO₂ crystallites are inversely correlated with the surface areas of the catalysts. The SEM pictures of Au/CeO₂ catalysts for impregnation, co-precipitation and sol–gel are given in Fig. 1. The typical XRD patterns of the CeO₂ in the Au/CeO₂ samples prepared by three different methods are shown in Fig. 2. It is apparent that the patterns consist of eight main reflections, typical of a cubic, fluorite structure of CeO₂ corresponding to (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), and (4 0 0) planes. XRD patterns of Au/CeO₂ co-precipitation catalyst showed no metal peaks indicating that the metallic particle size of the catalyst might be smaller than 5 nm. This observation was also confirmed by TEM investigations. The evidence of Au in metallic form on impregnation and sol–gel catalysts was observed at 2θ = 38.2° and the average Au crystallite sizes were 29 and 30 nm, respectively.

The TEM picture of 1% Au/CeO₂ co-precipitation catalyst shown in the Fig. 3(a) reveals the presence of the gold particles as dark spots in the catalyst. The existence of Au particles on CeO₂ support was verified by using EDS focusing on the regions containing highly contrast spots under TEM. For 1% Au/CeO₂ co-precipitation catalyst, the Au particles were seen as highly contrast spots both on and inside the support and the average particle size of Au is about 4.5 nm. Fig. 3(b) shows the Au particle size distribution of co-precipitation catalyst.

3.2. Catalytic activity

3.2.1. Temperature dependence

Fig. 4 illustrates the effect of catalyst preparation method on the catalytic activity of 1% Au/CeO₂. The Au/CeO₂ co-precipitation catalyst has the best performance among the three methods of catalyst preparation. The CO conversion showed a peak on all of the catalysts. The temperature at which the activity of the Au/CeO₂ co-precipitation catalyst was maximum was 383 K. The reaction at 383 K is the most suitable temperature for the fuel cell operating temperature level (353–393 K). At higher temperature, there is a continuous decrease in selectivity, indicating higher activation energy for the H₂ oxidation than for the CO oxidation. The low temperature behavior of the selectivity is in agreement with the studies of Igarashi et al. [6] and Kahlisch et al. [7].

The morphologies of Au/CeO₂ co-precipitation catalyst by SEM and XRD are very different from those of impregnation and sol–gel catalysts. It was found that the co-precipitation catalyst has a crystallite size of about 4.5 nm which is much smaller than those prepared by impregnation and sol–gel methods which have Au crystallite sizes of 29 and 30 nm, respectively. The results obtained with the Au/CeO₂ catalyst prepared by co-precipitation method were similar to those observed with the co-precipitation catalyst reported by Haruta et al. [12].

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Table 1
Catalyst surface area, ceria crystallite size and Au particle size

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Preparation method</th>
<th>BET surface area (m²/g)</th>
<th>Ceria crystallite size (nm)</th>
<th>Au particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% Au/CeO₂</td>
<td>Impregnation</td>
<td>104.2</td>
<td>17.4</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>Co-precipitation</td>
<td>124.1</td>
<td>14.5</td>
<td>&lt; 5</td>
</tr>
<tr>
<td></td>
<td>Sol–gel</td>
<td>66.7</td>
<td>38.6</td>
<td>2–8</td>
</tr>
</tbody>
</table>

*Ta *Not measured.
and Scirè et al. [18]. Besides, from SEM pictures, we observed only crystalline ceria on Au/CeO$_2$ co-precipitation catalyst which is also confirmed by the XRD results. It is then concluded that the Au/CeO$_2$ co-precipitation catalyst exhibits much higher activity than other two catalysts due to the aforementioned characteristics. It has been reported that the high activity of Au/CeO$_2$ catalyst might be related to the capacity of Au nanoparticles to weaken the Ce–O bond. Thus, the mobility/reactivity of the surface lattice oxygen is increased [18].

The performance of Au catalysts in this work can be compared with Au/MnO$_x$ and Au/Fe$_2$O$_3$ catalysts available in the literature. Kahlich et al. [8] and Torres Sanchez et al. [15] reported that the high activity and selectivity at the considerably lower temperature of 393 and 353 K were observed over Au/MnO$_x$ and Au/Fe$_2$O$_3$ catalysts, respectively. However, their reactant gas mixture used containing CO, O$_2$ and H$_2$ was not a typical simulated reformed gas. In addition, Au/CeO$_2$ co-precipitation catalyst is most active at 383 K which is suitable for the system connected directly to PEM fuel cells. This catalyst shows much higher activity and selectivity when compared to the Ag-based composite oxide catalysts reported by Gülür and Balıkçı [28]. However, recent work by Avgouropoulos et al. [29] at similar reaction conditions shows that CuO–CeO$_2$ sol–gel catalyst exhibited very high activity with selectivity close to 90%.

3.2.2. Effects of O$_2$ and water vapor concentration

The CO conversion and selectivity as a function of O$_2$ concentration in the feed, for the Au/CeO$_2$ co-precipitation catalyst is shown in Fig. 5. As expected, the CO conversion increases with increasing O$_2$ concentration while the CO selectivity decreases with increasing O$_2$ concentration. With 0.5%, 1% and 2% O$_2$ concentration the maxima in
CO conversion are \( \sim 70\% \), 92% and 98% at 383 K, respectively. The selectivities at the point of maximum conversion for 0.5%, 1%, and 2% \( \text{O}_2 \) concentration are 64%, 62% and 48%, respectively. The optimal \( \text{O}_2 \) concentration needed for oxidizing 1% \( \text{CO} \) in the feed is 1% with high selectivity and minimal loss of hydrogen.

In general, it is believed that the catalytic activity of the catalyst is liable to be suppressed in the presence of water vapor. The effect of water vapor in the feed stream on the \( \text{CO} \) oxidation activity and selectivity of \( \text{Au/\text{CeO}_2} \) co-precipitation catalyst is shown in Fig. 6. The feed gas mixture was humidified by bubbling through a container of temperature controlled water, yielding 10% water vapor in the reactant gas. Under the humidified condition, water lowered CO conversion in the region of temperature lower than 373 K compared to the unhumidified condition.

This is due to the strong adsorption of water on the active site [30]. However, at high temperatures water seemed to be slightly favorable to the catalyst activity since it provides...
a hydroxyl group which is necessary for reaction to take place [12,31,32]. The selectivity of the catalyst was slightly affected by the presence of water vapor which is similar to CuO–CeO₂ catalyst [29].

3.2.3. Effect of CO₂ concentration

Fig. 7 shows the effect of CO₂ addition to the feed stream on the activity of the Au/CeO₂ co-precipitation catalyst. Increasing CO₂ concentration from 2% to 20% reduced the activity of the Au/CeO₂ catalyst. The maximum in conversion dropped from ~ 92% to ~ 85% with a shift of 30 K to higher temperatures. The selectivity of the catalyst was not significantly impacted by the presence of CO₂ in the feed.

3.2.4. Deactivation test

Catalytic stability of Au/CeO₂ co-precipitation catalyst was tested at the temperature of 383 K. As can be seen from Fig. 8, the CO conversion and selectivity were maintained for 2 days with very slight loss of activity. The result shows good stability of the Au/CeO₂ co-precipitation catalyst as compared with Au/Fe₂O₃, CuO–CeO₂ and Au/TiO₂ catalysts reported by Kahlich et al. [8], Avgouropoulos et al. [29] and Lin et al. [13], respectively.

4. Conclusions

In this study, the catalytic activity of 1% Au/CeO₂ catalysts prepared by three different methods was investigated for the selective CO oxidation over the temperature range of 323–463 K. We found that 1% Au/CeO₂ co-precipitation catalyst is the most active, exhibiting high activity and good selectivity at 383 K. The presence of water vapor in the feed stream lowered the CO conversion only in the lower temperature region. Increasing CO₂ concentration in the feed
stream significantly reduced the CO conversion. However, both water vapor and CO2 showed no significant effect on the CO selectivity. The optimal amount of O2 required for oxidizing 1% CO in the feed is 1%. The catalyst was found to be quite stable in the deactivation test.

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References


