

MnO_x modified Co₃O₄-CeO₂ catalysts for the preferential oxidation of CO in H₂-rich gases

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Received 16 October 2007; received in revised form 13 December 2007; accepted 8 January 2008

Available online 18 January 2008

Abstract

In this work, MnO_x modified Co₃O₄-CeO₂ catalysts were prepared and used for preferential oxidation of CO in hydrogen-rich gases. The catalytic performance tests results showed that the catalyst with Co:Ce:Mn molar ratio of 8:1:1 exhibited the best low-temperature CO oxidation activity and higher selectivity for CO-PROX reaction among tested catalysts. 100% CO conversion could be obtained over this catalyst at 80–180 °C with the feeding gas of 1 vol.% CO, 1 vol.% O₂, 50 vol.% H₂ and N₂ balance under the space velocity of 40,000 ml h⁻¹ g_{cat}⁻¹. Adding CO₂ and/or water was unfavorable for CO removal, even so complete oxidation of CO was still achieved over this catalyst with the reaction stream of 20 vol.% CO₂, 10 vol.% H₂O, 1 vol.% CO, 1 vol.% O₂, 50 vol.% H₂ and N₂ balance under high space velocity of 80,000 ml h⁻¹ g_{cat}⁻¹ at reaction temperature range of 160–180 °C. The catalysts were characterized by XRD, TEM, EDX, TPR and XPS techniques and the results showed that adding MnO_x into Co₃O₄-CeO₂ led to more uniform mixing of Co₃O₄ and CeO₂ particles and led to finely dispersed and high valence state cobalt oxides species, which contributed to high catalytic activity of Co-Ce-Mn mixed oxides catalysts.

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Keywords: MnO_x; Co₃O₄; CeO₂; Preferential oxidation; CO; Hydrogen

1. Introduction

Proton exchange membrane fuel cell (PEMFC) is an attractive technology for power generation mainly due to its high efficiency and environmental friendship [1]. Hydrogen as fuel for PEMFC can be produced by steam reforming or autothermal reforming of hydrocarbons in combination with water gas shift (WGS) reaction. The effluent gases from the WGS reaction process typically contain about 40–75 vol.% H₂, 20–25 vol.% CO₂, 10 vol.% H₂O, N₂ (if air is an oxidant), and 0.5–2 vol.% CO [2]. The anodes of fuel cells, however, can easily be poisoned by CO. The content of CO in the streams, as a result, must be reduced to below 10 ppm for Pt anode and below 100 ppm for CO-tolerant alloy anodes before feeding [3]. Several different methods for CO removal have been studied including purification with metal membrane, preferential oxidation (PROX) of CO, and CO methanation. Among

all of them, preferential oxidation of CO with oxygen or air is now considered as the simplest and most effective method for removing CO from hydrogen-rich streams [4].

The reported promising catalysts for CO-PROX can be grouped into three types: (1) supported noble metal catalysts, such as Pt, Pd or Rh [5–11], (2) nano-gold catalysts [12–17] and (3) base metal oxides catalysts which mainly concentrate on CuO-CeO₂ [18–22]. Noble metal catalysts and CuO-CeO₂ catalyst are active for CO-PROX in higher reaction temperature range of 150–300 °C. Gold catalysts exhibit high activity for CO oxidation at lower temperature, ca. <100 °C. High activity at low reaction temperature is favorable for improving the cold-start properties in fuel cell system and for compacting the PROX unit and the PEM fuel cell stacks [23]. However, CO removal to below 10 ppm is hard to be achieved over gold catalysts due to their high activities for hydrogen oxidation, although Au catalysts are reported to be very active for CO oxidation at low temperature. Therefore, developing catalysts for CO-PROX with high selectivity as well as good low-temperature activity is of great significance.

CoO_x/CeO₂ catalysts are very active for CO oxidation and their high activities are ascribed to finely dispersed and high

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valence state CoO_x which results from the synergistic interaction between cobalt oxides and ceria [24,25]. At present, little information on $\text{CoO}_x/\text{CeO}_2$ for CO-PROX reaction has been published, although a few catalysts containing cobalt, such as CoFe_2O_4 , Co-Pt/TiO_2 , Co/SrCO_3 , were reported for CO-PROX [26–28].

In our previous work, the catalytic performance of $\text{Co}_3\text{O}_4\text{-CeO}_2$ catalysts for preferential oxidation of CO in hydrogen-rich gases was examined and it was found that adding a small amount of ceria into Co_3O_4 led to obvious improvement of the catalytic activity for CO-PROX [29].

In this work, it was found that MnO_x modified $\text{Co}_3\text{O}_4\text{-CeO}_2$ exhibited much better catalytic performance for CO preferential oxidation at low temperature ($<80^\circ\text{C}$) and exhibited a broad temperature window for complete CO removal.

2. Experimental

2.1. Catalyst preparation

MnO_x modified $\text{Co}_3\text{O}_4\text{-CeO}_2$ catalysts were prepared by coprecipitation method as described in the previous work [29]. The aqueous solutions of $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ were mixed at desired ratios. Then the mixed solutions and a sodium carbonate solution were gradually and simultaneously dropped into a continuously stirred flask at a pH value of 8.5–9.5. After an aging period of 4 h, the resulting precipitates were filtered and washed with hot water until no pH change, and then they were dried under static air at 80°C for 24 h and calcined at 350°C for 5 h. The so prepared catalysts were denoted as $a\text{Co-}b\text{Ce-}c\text{Mn}$, in which a , b and c represented the molar ratio of Co, Ce and Mn.

2.2. Catalytic performance tests

The catalytic performance tests were carried out with a fixed bed flow reactor system under atmospheric pressure. Catalysts were preoxidized with gas mixture of 5 vol.% O_2/N_2 at 300°C for 40 min on-line. Then the reactor was cooled to reaction temperature. The reaction gas mixture consisted of 1 vol.% CO, 1 vol.% O_2 , 50 vol.% H_2 and N_2 balance. The influence of CO_2 and/or H_2O on the preferential oxidation of CO was examined by adding 20 vol.% CO_2 and/or 10 vol.% H_2O into the feeding gases. The outlet gas mixtures from the reactor were analyzed with a gas chromatograph system equipped with TCD and FID detectors. A nickel catalytic converter was used for detecting trace amount of CO. Thus, CO content below 10 ppm could be detected.

2.3. Catalyst characterization

X-ray diffraction (XRD) measurements were performed by using X'pert Pro diffractometer equipped with a $\text{Co K}\alpha$ X-ray tube operating at 40 kV and 40 mA. The particle size of the samples was calculated by the Sherrer formula.

Transmission electron microscopy (TEM) analysis of catalysts was performed using a Philips G2 F-20 Microscope equipped with energy-dispersive X-ray (EDX) instrument.

Temperature-programmed reduction (TPR) experiments were performed in a micro-flow reactor fed with 5.0% H_2/Ar mixture flowing at a rate of 30 ml/min. The weight of tested samples was 50 mg. Prior to each tests, the samples were treated with N_2 gas at 40°C for 30 min. Then the temperature was raised from 40 to 930°C at a heating rate of $10^\circ\text{C}/\text{min}$. The hydrogen consumption was measured by TCD detector, calibrated by the peak area of known amounts of CuO .

X-ray photoemission spectroscopy (XPS) analysis of catalysts was performed using PERKIN ELMER PHI 1600 spectrometer equipped with a $\text{Mg K}\alpha$ source at a beam power of 250 W. Extended spectra (survey) were collected in the range of 0–1350 eV (187.85 eV pass energy). The binding energy (BE) was calibrated with a reference of taking the C 1s photoelectron peak located at 284.6 eV of “adventitious” carbon.

3. Results and discussion

3.1. Catalytic performance

Fig. 1 shows CO conversion and selectivity to CO oxidation for PROX reaction over 8Co-1Ce and Co-Ce-Mn catalysts with different molar ratios. As could be seen from Fig. 1, catalytic activity was improved markedly by adding a small amount of MnO_x to Co-Ce mixed oxides. CO could be completely oxidized to CO_2 over 8Co-1Ce-1Mn catalyst at a low temperature of 80°C , which was rarely observed over base metal oxides catalysts [18–22,24,25] and was even comparable to noble metal catalysts [6–11].

Besides, 8Co-1Ce-1Mn catalyst exhibited high selectivity for CO oxidation, which was higher than gold catalysts. At the reaction temperature of 80°C , CO conversion and corresponding selectivity were 100% and 98.2%, respectively, over 8Co-1Ce-1Mn catalyst. Gold-based catalysts were characterized with high low-temperature activity for CO oxidation, while their selectivities for CO-PROX were relatively poor. Chang et al. [13] found 1% $\text{Au/Mn}_{0.5}\text{-Ce}_{0.5}\text{O}_2$ exhibited very good catalytic performance for CO-PROX and Grisel et al. [17] also gave an excellent work on $\text{Au/MnO}_x/\text{MgO}/\text{Al}_2\text{O}_3$ for CO-PROX. However, due to poor selectivity caused by H_2 oxidation in CO-PROX process, CO was hard to be removed to below 10 ppm over both of these Au catalysts.

8Co-1Ce-1Mn catalyst exhibited an interesting and attractive character, that is, complete oxidation of CO could be obtained in a broad reaction temperature range from 80 to 180°C , as presented in Fig. 1a.

The activity of Co-Ce-Mn catalysts for CO oxidation decreased sharply with increasing the molar ratio of MnO_x . Complete CO removal could hardly be obtained over 4Co-1Ce-4Mn. This indicated that MnO_x was not the key active component for CO oxidation.

Fig. 2 presents the influence of space velocity on CO conversion over 8Co-1Ce-1Mn catalyst. As space velocity was doubled, the curve of CO conversion changed a little; as it was trebled, 100% CO conversion could still be achieved between 120 and 180°C , indicating that this catalyst was very active.

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