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Enhanced catalytic performance of Au/CuO–ZnO catalysts containing low CuO content for preferential oxidation of carbon monoxide in hydrogen-rich streams for PEMFC

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ABSTRACT

In this study, effects of Au and CuO loadings in Au/CuO–ZnO nanocatalysts for preferential oxidation of carbon monoxide in H_2-rich streams (PROX) are investigated. CuO–ZnO supports were synthesized by a co-precipitation method. Au was also incorporated into the catalysts by a deposition-precipitation procedure. The catalysts were characterized by XRD, BET surface area, FESEM, HRTEM, H_2-TPR, FTIR, and CO-TPD. 2–10 nm Au nanoparticles are dispersed on CuO–ZnO support and significantly enhance the reducibility of CuO. The Au/CuO–ZnO catalysts containing low amount of CuO were found to be more active for PROX compared to the Au/ZnO catalyst. Moreover, as more CuO is added to Au/ZnO, the CO_2 selectivity increases in the whole PROX temperature range. The catalyst containing 2 wt% Au and 1 wt% CuO on ZnO exhibited the highest activity and selectivity in the operating temperature range of PEM fuel cells. The activity of this catalyst also remained almost intact during 900 min of PROX time on stream at 80 °C.

1. Introduction

Nowadays, increasing demands for clean fuel have attracted much attention to fuel cell systems based on hydrogen fuel with high efficiency and the least air pollutants. Among different types of fuel cells, polymer electrolyte membrane fuel cells (PEMFC) have obtained much more interest due to the moderate operating temperature range of 80–120 °C and convenient application for electric vehicles as well as residential power generations [1,2]. The hydrogen-rich stream is supplied by processing of natural gas or methanol in partial oxidation and/or steam reforming, along with water gas shift reactions [1–3]. The produced gas typically contains 45.0–75.0 vol% H_2, 0.5–2.0 vol% CO, 10.0–30.0 vol% CO_2 and 5.0–10.0 vol% H_2O [4,5].

Carbon monoxide has a poisoning effect on the Pt and/or Pt–Ru anode of PEMFC and even small amounts of CO in the hydrogen stream can significantly deteriorate its performance. Therefore, lowering the CO content of PEMFC feed to a trace-level (below 10 ppm), has great importance for increasing the anode efficiency [5,6]. Various methods have been proposed for the CO removal comprising selective

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diffusion, pressure swing adsorption, selective CO oxidation, and CO methanation. However, the catalytic preferential oxidation (PROX) of CO in H_2-rich gas is considered as a promising method and the most cost-effective way to eliminate CO from the reformed fuels [1,6].

An efficient PROX catalyst must meet certain requirements: (i) high CO conversion and oxidation rate at a wide operating temperature range of 80–120 °C, (ii) high selectivity for CO oxidation reaction with respect to undesired H_2 oxidation, and (iii) stability within time on stream.

Compared to the conventional Pt-based catalysts [6,7] and metal oxides such as CuO/CeO_2 [6,8], highly dispersed Au nanoparticles have shown superior activity with higher selectivity at lower temperatures [1,4–6]. In general, three factors can influence the performance of Au supported catalysts: (a) size of Au nanoparticles, (b) oxidation state of the active sites, and (c) interaction between Au species and the support [9,10].

The preparation method of Au catalyst affects Au particle size and its interaction with the support. The deposition-precipitation method is the most recommended method for preparing an Au catalyst. This method results in deposition of Au nanoparticles with high dispersion.

Due to superior activity of Au catalysts in PROX, its performance has been studied on various supports [11–16]. Furthermore, mixture of active metals such as Au–Cu [17–19], Au–Pt [20,21] and Au–Ag [22,23] supported catalysts have been investigated in CO oxidation and PROX reactions, in which bimetallic Au–Cu catalysts have exhibited high activity and selectivity compared to the monometallic Au supported one. The promoting effect of Cu on the supported Au catalysts can be ascribed to the effect of Cu on the size of Au particles and proper interaction of Au clusters with the support. Also a low amount of CuO on supports such as Al_2O_3 and SiO_2 can facilitate the CO oxidation reaction in the presence of H_2 by increasing the ability of the support to supply oxygen and/or providing additional active sites for adsorption of the reactants [17–19].

In this investigation, Au is dispersed by deposition-precipitation on CuO–ZnO prepared by a co-precipitation method, and the thus obtained Au/CuO–ZnO catalysts containing various amounts of Au and CuO were applied for the preferential oxidation of CO in H_2-rich streams.

2. Experimental method

2.1. Catalyst preparation

The 0.5, 1.0, 2.0 and 5.0 wt% CuO–ZnO supports, were synthesized via a co-precipitation method. An aqueous solution of 0.50 M $Na_2CO_3{\cdot}1H_2O$ was added drop-wise into a mixture of 0.03 M $Zn(NO_3)_3{\cdot}6H_2O$ and $Cu(NO_3)_2{\cdot}3H_2O$ solutions under vigorous stirring at 65 °C. The resulted solution was aged at pH of 8.5 for 15 min at the same temperature, then filtered and washed with plenty of warm deionized water to remove the interfering ions. The precipitates were dried overnight at 100 °C and calcined in air at 300 °C for 3 h. Also a batch of ZnO without CuO was prepared by the same method.

Various amount of Au (1.0, 2.0 and 5.0 wt%) was loaded on to the CuO–ZnO supports by deposition-precipitation (DP) method. Simultaneously, an aqueous solution of $HAuCl_4$ and proper amount of 0.10 M $Na_2CO_3{\cdot}1H_2O$ were added drop-wise into the slurry of CuO–ZnO at 50 °C and constant pH of 8 under vigorous mixing. The resulted slurry was aged for 30 min and then filtered, washed, and dried at 100 °C under air atmosphere followed by crushing and sieving to a mesh size of 50–120. The final catalysts is denoted as xAu/yCuO-ZnO, where x and y vary from 1.0 to 5.0 wt% and 0 to 5.0 wt%, respectively.

2.2. Catalyst characterization

The structure of the catalysts was determined by X-ray powder diffraction (XRD),with a Bruker AXS D8 advanced diffractometer using Cu Kα radiation (λ = 1.5406Å). The samples were scanned over the range of 2θ = 20–80° at a rate of 0.05°/s and the average crystallite size of the catalysts was determined based on Scherrer's equation. Field emission scanning electron microscopy (FESEM) was performed using a HITACHI S-4160 instrument in order to study the morphology of the catalysts. High resolution transmission electron microscopy (HRTEM) analysis was performed using a JEOL JEM-2100 (200 kV) microscope equipped with an EDS analytical system. The powdered samples were ultrasonically dispersed in ethanol and the obtained suspensions were deposited on to a thin carbon film supported on a copper micro-grid.

For each catalyst, about 70 Au particles were measured in order to determine the average particle size and size distribution of Au particles. BET tests were carried out using an automated gas adsorption analyzer (Tristar 3020, Micromeritics), and H_2-temperature programmed reduction (TPR) tests were performed by a Quantachrome CHEMBET-3000 apparatus. The specific surface areas of the samples were determined by nitrogen adsorption-desorption using BET method. The H_2-TPR experiments were performed on 100 mg of each catalyst with a

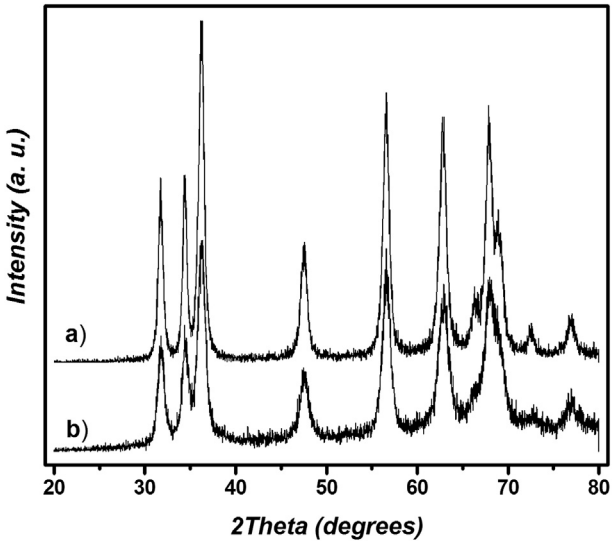

Fig. 1 – XRD patterns of ZnO (a), and 2Au/5CuO–ZnO (b) catalysts.