Copper-cerium oxides supported on carbon nanomaterial for preferential oxidation of carbon monoxide

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Abstract: The Cu_xO-CeO_2/Fe@CNSs, Cu_xO-CeO_2/MWCNTs-Co and Cu_xO-CeO_2/MWCNTs-Ni catalysts were prepared by the impregnation method and characterized by transmission electron microscopy, scanning electron microscopy, X-ray powder diffraction, H_2-temperature programmed reduction and N_2 adsorption-desorption techniques. It was found that the Fe nanoparticles were encapsulated into the multi-layered carbon nanospheres (CNSs). However, the multi-wall carbon nanotubes (MWCNTS) were generated on the Co/Al_2O_3 and Ni/Al_2O_3 precursor. The addition of carbon nanomaterial as supports could improve structural properties and low-temperature activity of the CuO-CeO_2 catalyst, and save the used amount of metal catalysts in the temperature range with high selectivity for CO oxidation. The copper-cerium oxides supported on carbon nanomaterial had good resistence to H_2O and CO_2.

Keywords: carbon nanomaterial; copper-cerium oxides; hydrogen; CO oxidation; rare earths

Proton-exchange membrane fuel cells are the most suitable and commercially viable hydrogen-based cells for power generation[1]. Preferential oxidation of CO (CO-PROX) is regarded as the simplest and most effective method for the removal of CO in the hydrogen-rich streams[2]. A proper catalyst for CO-PROX should have high activity, selectivity and stability from 80 to 200 ºC[3,4].

CuO-CeO_2 catalysts are widely investigated as alternative to noble metals for CO-PROX due to good catalytic performance[5]. The current problem is that it is difficult for CuO-CeO_2 catalysts to possess high surface area by common preparation methods. In contrast to the wide investigation on CuO-CeO_2 catalysts[4,6,7], little attention has been paid to the application of the supported CuO-CeO_2 catalysts. Carbon nanomaterial is a promising support for improving activity and selectivity of the catalysts because of their favorable structure and unique properties[8,9]. In 2010, Zhang et al.[10] found that the CeO_2/CuO/CNT nanocomposites have an excellent catalytic performance for CO oxidation with the lowest T_{50} at 113.5 ºC.

In this work, copper-cerium oxides were loaded on the Fe@CNSs, MWCNTs-Co, and MWCNTs-Ni supports in order to improve the structural properties and activity of CuO-CeO_2 catalysts for preferential oxidation of carbon monoxide.

1 Experimental

1.1 Catalyst preparation

1.1.1 Preparation of supports

The $Fe(NO_3)_3 \cdot 9H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were dissolved in 50 mL distilled water in an ultrasonic bath. The above solution was added dropwise to aqueous solution of urea and aged for 24 h. The sample was dried at 80 ºC for 12 h and calcined in a muffle furnace at 500 ºC for 5 h to obtain the Fe/Al_2O_3 precursor. Subsequently, the Co/Al_2O_3 and Ni/Al_2O_3 precursor were prepared by the similar method.

The Fe/Al_2O_3, Co/Al_2O_3 and Ni/Al_2O_3 precursor were transferred into the porcelain boats in a tube furnace, respectively. First, the samples were purged for 10 h in an Ar stream in order to remove the air. After heating to 650 ºC at a heating rate of 2 ºC/min, the H_2/Ar mixture (V_{H_2}=10%) was switched on and the samples were reduced for 2 h. Then the samples were heated to 800 ºC in an Ar stream. The CH_4/H_2 (V_{CH_4}=20%) mixture was passed into the tube furnace as a carbon source for 160 min. Finally, the samples were naturally cooled to ambient temperature in an Ar stream. The black powders obtained are denoted as Fe@CNSs, MWCNTs-Co, and MWCNTs-Ni, respectively.

1.1.2 Preparation of catalysts

The Fe@CNSs, MWCNTs-Co, and MWCNTs-Ni were suspended in the concentrated HNO$_3$ (68 wt.%) and treated under ultrasonic condition for 3 h, respectively. After filtration, the supports were washed thoroughly with deionized water until the PH value was adjusted to approximately 7.0, and then dried at 80 ºC for 12 h.

The treated Fe@CNSs, MWCNTs-Co, and MWCNTs-Ni supports were added into an aqueous solution including Cu(NO$_3$)$_2$·3H$_2$O and Ce(NO$_3$)$_3$·6H$_2$O and impregnated for 24 h, respectively. Then the solvent was evaporated slowly at 80 ºC for 12 h in a vacuum oven. Further, the temperature was increased to 350 ºC at a rate of 2 ºC/min and the solid mixture was calcined at 350 ºC for 3 h in N$_2$ atmosphere. The obtained catalysts were labeled as Cu$_x$O-CeO$_2$/Fe@CNSs, Cu$_x$O-CeO$_2$/MWCNTs-Co and Cu$_x$O-CeO$_2$/MWCNTs-Ni (20 wt.% CuO, Cu/Ce molar ratio=1:1). The CuO-CeO$_2$ catalyst prepared by the surfactant-templated method[7] was used as the reference sample (Cu/Ce molar ratio=1:1).

1.2 Catalyst characterization

Transmission electron microscopy images were taken on an FEI JEM-2010 transmission electron microscope. The sample was dispersed into ethanol with the ultrasonic treatment, and a drop of the suspension was placed on a copper grid for TEM observation. Scanning electron microscopy images were obtained on an FEI SIRION200 scanning electron microscope. The samples were coated with a thin layer of Au before scanning. Powder X-ray diffraction patterns were recorded on a PANalytical X'pert PRO diffractometer with Cu Kα source (λ= 0.15406 nm). N$_2$ adsorption-desorption isotherms were obtained at liquid nitrogen temperature (–196 ºC) using a Micrometrics ASAP2020 adsorption apparatus. The surface area and pore size distribution were determined by the Brunauer-Emmett-Teller (BET) and the Barrette-Joynere-Halenda (BJH) methods, respectively. H$_2$ temperature-programmed reduction was conducted on a Micromeritics Apparatus (AutoChem II 2920). The reduction gas was 10% H$_2$/Ar gas mixture and the flow rate of gas was 50 mL/min. Before reduction, the sample was pretreated at 200 ºC for 1 h in a N$_2$ stream, and then cooled to room temperature. The H$_2$/Ar mixture was switched on and the sample was heated with a heating rate of 10 ºC/min. The reaction was performed from room temperature to 900 ºC.

1.3 Catalytic performance tests

The catalytic performance for PROX was carried out in a quartz reactor. The reaction mixture consisted of 1% CO, 1% O$_2$ and 50% H$_2$ (volume fraction) with N$_2$ as balance gas. The space velocity was 40000 mL/g$_{cat}$/h. The reaction was operated between 35 and 215 ºC. Product and reactant analyses were conducted by a

GC-2014C gas chromatograph. A 5A molecular sieve column was used to separate CO, O$_2$ and N$_2$. CO$_2$ was separated by a TDX column. Water was trapped before the gasses entered the GC and CO$_2$ was absorbed before entering the 5A molecular sieve. The water vapor (10 vol.%) and CO$_2$ (15 vol.%) was introduced into the reaction mixture when studying the effect of H$_2$O and CO$_2$ on the catalytic performance. The conversion of CO (C_{CO}) and the selectivity for CO oxidation (S_{CO_2}) were calculated according to the following Eqs. (1) and (2), respectively[11].

$$C_{CO}=([CO]_{in}-[CO]_{out}/[CO]_{in}\times100\% \tag{1}$$

$$S_{CO_2}=0.5([CO]_{in}-[CO]_{out}/([O_2]_{in}-[O_2]_{out})\times100\% \tag{2}$$

2 Results and discussion

2.1 Transmission electron microscopy

Fig. 1 shows transmission electron microscopy images of the supports. It can be observed from Fig. 1(a) that the Fe nanoparticles are encapsulated into the multi-layered
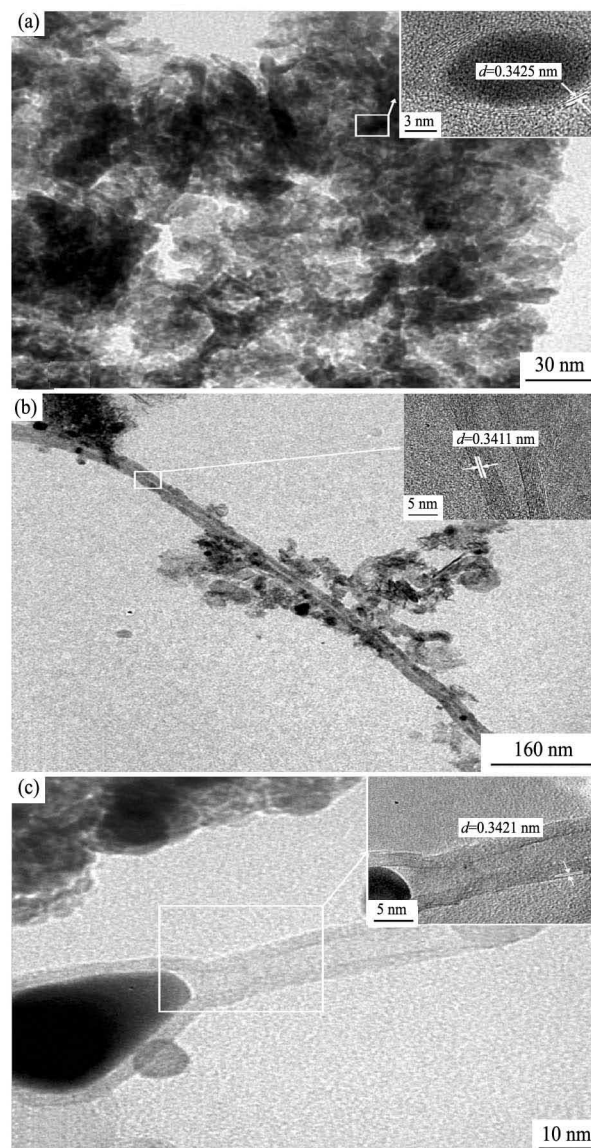

Fig. 1 TEM images and HRTEM images (insets) of the supports
(a) Fe@CNSs; (b) MWCNTs-Co; (c) MWCNTs-Ni