Preferential oxidation of CO in excess hydrogen over a nanostructured CuO–CeO$_2$ catalyst with high surface areas

Zhigang Liu [a,b], Renxian Zhou [a,*], Xiaoming Zheng [a,*]

[a] Institute of Catalysis, Zhejiang University, Hangzhou 310028, PR China
[b] School of Chemistry and Chemical Engineering, Hunan University, Changsha, Hunan 410082, PR China

ARTICLE INFO

ABSTRACT

CuO–CeO$_2$ is prepared by coprecipitation and ethanol washing and characterized using BET, HR-TEM, XRD and TPR techniques. The results show that CuO–CeO$_2$ is nanosized (r_{TEM} = 6.5 nm) and possesses high surface area (S_{BET} = 138 m^2 g^{-1}). Furthermore, some lattice defects in the surface of CuO–CeO$_2$ are found, which are beneficial to enhance catalytic performance of CuO–CeO$_2$ in preferential oxidation of CO in excess hydrogen (PROX). Consequently, the nanostructured CuO–CeO$_2$ exhibits perfect catalytic performance in PROX. Namely, CO content can be lowered to less than 100 ppm at 150 °C with 100% selectivity of O$_2$ in the presence of 8% CO$_2$ and 20% H$_2$O at 120,000 ml g$_{cat}^{-1}$ h^{-1}.

1. Introduction

PROX has been attaining an increasing interest in the past years because of the potential application of polymer electrolyte membrane (PEM) fuel cells in the future [1–3]. Catalysts for this reaction request having a compromise between catalytic performance and cost of catalysts. Novel metal or rare metal catalysts such as Au, Pt, Rh, Ru often possess a very excellent catalytic performance in PROX [4–9]. However, they have an unavoidable problem, i.e., they are expensive. Activity of CuO–CeO$_2$ catalysts in PROX exhibits several orders of magnitude higher than that of conventional copper-based catalysts and comparable or superior to platinum catalysts [10–12]. Liu and Flytzani-Stepphanopoulos [13] reported that formation of copper clusters and strong interaction of copper with cerium oxide were desirable to achieve a high activity for CO oxidation. Therefore, CuO–CeO$_2$ catalyst can obtain easily, due to its low cost, a very good compromise between catalytic performance and cost, and is a promising catalyst in PROX. However, CuO–CeO$_2$ catalysts reported in literatures [14] often possess surface areas lower than 100 m^2 g^{-1}, which generally cause to the depression of catalytic performance of CuO–CeO$_2$ catalyst in PROX. Therefore, preparation of nanostructured CuO–CeO$_2$ catalyst with higher surface area is attracting more attentions [15–17]. Ethanol is used to dehydration in coprecipitation process to achieve higher surface area and smaller particle size. For example, Xu et al. [18] reported that ethanol was used in ZrO$_2$ preparation by coprecipitation and found that ZrO$_2$ with ethanol washing (S = 53 m^2 g^{-1}, d = 15–20 nm) had a higher surface area and smaller particle size in comparison with ZrO$_2$ without ethanol washing (S = 27 m^2 g^{-1}, d = 40–200 nm).

In this study, we prepared a nanostructured CuO–CeO$_2$ catalyst with high surface area by coprecipitation and ethanol washing. The CuO–CeO$_2$ catalyst exhibits an excellent catalytic performance in PROX and can reduce CO content to less than 100 ppm with 100% selectivity at 150 °C in a feed of 1% CO, 1% O$_2$, 50% H$_2$, 8% CO$_2$, 20% H$_2$O and Ar in balance.

2. Experimental

Sample one (expressed as 5CuC-ET) is synthesized by coprecipitation. The aqueous solution of 0.362 mol L^{-1} KOH is added dropwise within 30 min to the mixture of 0.055 mol L^{-1} Ce(NO$_3$)$_2$ and 0.008 mol L^{-1} Cu(NO$_3$)$_2$ solutions with vigorous stirring, and then aged for about 20 min. The pH value of supernate is 12.5 and the pH value of precipitate should be washed to 7.0 with deionized water, following to be washed with 200 ml ethanol before dried at 105 °C for 1 h. The dried sample is heated for about 2 h at 500 °C. Obtained product is crushed and sieved to 60–80 meshes. The loading of Cu in CuO–CeO$_2$ catalyst is 5.0 wt%. BET surface area of CuO–CeO$_2$ catalyst is 138 m^2 g^{-1}.

Sample two (expressed as 5CuC-WA) is synthesized following the above process except the ethanol washing. BET surface area of CuO–CeO$_2$ catalyst is 117 m^2 g^{-1}.

* Corresponding authors. Tel.: +86 571 88273272; fax: +86 571 88273283.
E-mail address: liuzhigang@hnu.cn (R. Zhou).

The activity measurement is carried out in a fixed micro-reactor (quartz glass, 4 mm i.d., 6 mm o.d., length 250 mm) at atmospheric pressure. Reactor temperature is measured by K-type thermocouple located at the top of packed catalyst bed and controlled by a temperature controller. The mass of catalyst used in experiments ranges from 50 mg to 200 mg, and $CuO–CeO_2$ catalyst is diluted with inert alumina particles (60–80 meshes) with a dilution ratio of 1:1 by mass. A desired mixture of gases (i.e. 50% H_2, 1.0% O_2, 1.0% CO, 0–8% CO_2 and Ar in balance) is achieved by adjusting the ratio of flows with mass flow controllers (Scientific Alicat Int., USA). Water vapor is introduced into reacting gases bubbling through a heated water bath.

Reactor inlet and outlet streams are measured using an on-line gas chromatograph equipped with a thermal conductivity detector (TCD) and a flame ionized detector (FID). H_2 and O_2 are separated by a carbon molecular sieve (TDX-01) column and detected using TCD. CO and CO_2 are separated by a carbon molecular sieve (TDX-01) column, then converted to methane by a methanation reactor and analyzed by FID.

Taking into consideration of the existence of CO_2 in feedstock, CO conversion is calculated based on the CO decrease as follows:

$$\% \text{ of conversion of co} = \frac{[co]_{in} - [co]_{out}}{[co]_{in}} \times 100$$

And the selectivity is defined as the oxygen consumed by CO oxidation, namely:

$$\% \text{ of selectivity} = \frac{0.5([CO]_{in} - [CO]_{out})}{[O_2]_{in} - [O_2]_{out}} \times 100$$

Specific area of samples is obtained at $-196\,°C$ using a Coulter Omnisorp 100CX. Prior to the measurement, samples are pretreated at 250 °C for 2 h. TEM profiles are conducted using a JEOL JEM-2010 (HR) microscope operating at 100 kV. X-ray powder diffraction (XRD) patterns are recorded on a Rigaku D/Max 2550PC powder diffractometer using nickel-filtered Cu Kα radiation. H_2 temperature-programmed reduction (TPR) is carried out using a conventional reactor equipped with TCD. 50 mg catalyst and 5% H_2/95% Ar (40 ml/min flowing velocity) are applied in this study. The heating rate is 10 °C/min from 30 to 350 °C.

3. Results and discussion

3.1. TEM and XRD

TEM images of 5CuC-ET are given in Fig. 1. The average particle size of 5CuC-ET, seen from Fig. 1a, is about 6.5 nm. Generally speaking, CuO exists in the $CuO–CeO_2$ catalyst by several possible forms, that is, CuO clusters, bulk CuO and solid solution of CuO and CeO_2 [18,19]. Due to low copper atomic weight and poor contrast, CuO particles can not be distinguished from cerium even in the high resolution electron microscopy image (shown in Fig. 1b). However, CeO_2 crystal lattice can be clearly distinguished (seen f area in Fig. 1b). Especially, some lattice defects are found (seen e area in Fig. 1b), which are beneficial to form reactive centers or yield active oxygen species [20].

According to the literature [21], possible oxygen species are showed in following:

$$O_2 = O_2^- = O_2^{2-} = O^- = O_{lat}^{2-}$$
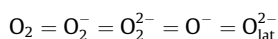
When increasing catalyst treatment temperature, the equilibrium shifts to the right. Therefore, superoxide species and peroxide species are supposed as the reactive oxygen species at low temperature ranges (e.g. from 100 °C to 170 °C) in PROX [21]. A superoxide species forms from the adsorption of an oxygen molecule on a single unsaturated surface cerium ion. Formation of peroxide species
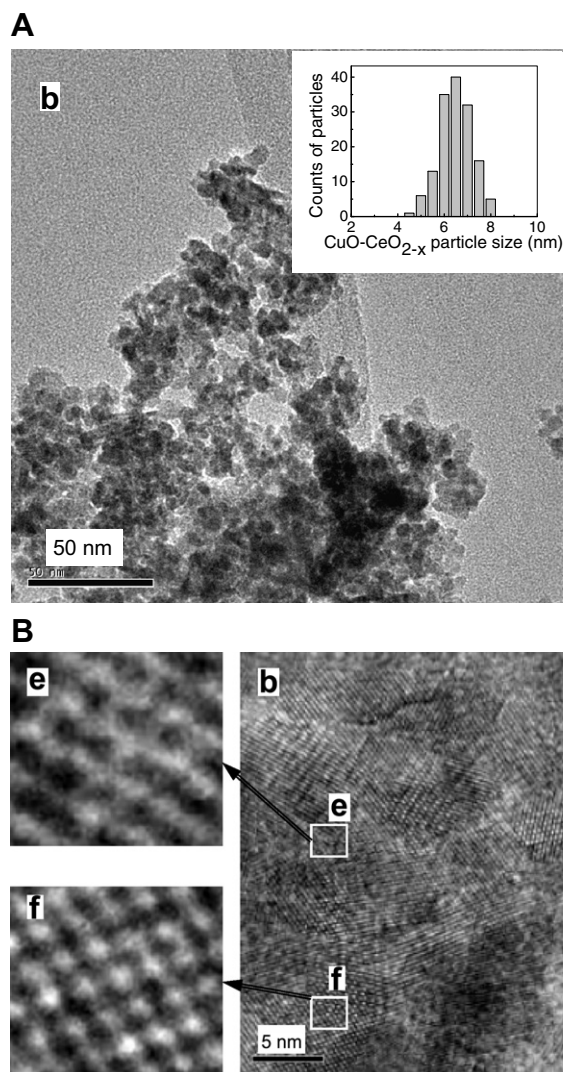

Fig. 1. (a) TEM image of 5CuC-ET (b) HR-TEM image of 5CuC-ET.

increases with the extent of reduction of cerium oxide surface. However, reactive oxygen species is not formed on conventionally prepared CeO_2, and their formation on nano-structured CeO_2 ($S_{BET} = 180\ m^2\,g^{-1}$; $R = 5$ nm) is enhanced by the presence of gold [22]. Evidently, high surface area and nano-sized $CuO–CeO_2$ is beneficial to yield active oxygen species and enhance catalytic performance of $CuO–CeO_2$ catalyst in PROX.

Fig. 2 illustrates XRD patterns of $CuO–CeO_2$ catalysts and pure CeO_2. The major peaks are due to CeO_2 crystal phases and no CuO phases are found by XRD within its detection limit. The absence of CuO peaks may be attributed to fine dispersion of CuO or amorphous phase on the surface of ceria [23], which gives a weak response and can't be detected. From Fig. 2, it also can be found that the peaks of 5CuC-ET are broader than those of the other catalysts, which indicate that 5CuC-ET has a smallest particle size and ethanol washing is beneficial to yield nanostructured $CuO–CeO_2$ catalysts.

3.2. H_2-TPR

H_2-TPR profiles of $CuO–CeO_2$ catalysts are revealed in Fig. 3. The over lapping reduction peaks are present: a low-intensity, low-temperature peak at 176 °C (α peak) and a higher-intensity peak