Preferential oxidation of CO in excess H_2 over CeO_2/CuO catalyst: Effect of calcination temperature

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Abstract

Different from the classical configuration CuO/CeO_2 catalyst, the inverse configuration CeO_2/CuO catalyst (atomic ratio of Ce/Cu = 10/100) was prepared by impregnation method. Five calcination temperatures were selected to investigate the interaction between CeO_2 and CuO support. It is found that as calcination temperature increased from 500 to 900 °C, sintering of CeO_2 particles on the support occurred together with the diffusion of a portion of Ce^{4+} ions into CuO crystals, forming solid solution. Formation of interface complex Ce–O–Cu was suggested by TPR measurements. The catalyst calcined at 700 °C gives the highest activity for preferential oxidation of CO in excess H_2 stream.

Key words

preferential oxidation; carbon monoxide; cerium oxide; cupric oxide; TPR

1. Introduction

Proton exchange membrane fuel cell (PEMFC) generally requires a H_2-rich stream with CO content less than 10 ppm. The gas mixture obtained by steam reforming of natural gas (mainly methane) and the following water-gas shift reaction (WGS) still contains ca. 0.5%–2% CO besides ca. 18% CO_2. For small scale PEMFC stacks, e.g., the one in house use, the unit to remove CO from the reforming-WGS gas mixture should be small as possible as can in volume. Selective methanation of CO is a way to remove CO from the gas mixture, while methanation of a part of CO_2 is also accompanied. Thus a relatively large amount of hydrogen is consumed, which decreases electric power output of PEMFC. In contrast, preferential oxidation of CO in excess H_2 (CO-PROX) is a more suitable way to remove CO from the gas mixture. CuO/CeO_2 composite has been proved to be a promising catalyst for CO-PROX due to its good activity and low cost relative to noble metal supported catalysts [1]. Several methods such as co-precipitation, citrate, urea-nitrate combustion and impregnation methods were reported to prepare CuO/CeO_2 catalyst in literatures [2−6]. It seems that the urea-nitrate combustion method is better than the citrate method [2,4]. In comparison of co-precipitation method with impregnation method, Gamarra et al. [3] reported that the one prepared by impreg-

nation method with atomic ratio of Cu/Ce = 0.022 is better. On the other hand, calcination temperature of the catalyst has a great influence on the catalytic activity for CO oxidation [7−9]. Jung et al. [7] reported that the calcination at 700 °C is optimal for CuO/CeO_2 catalyst prepared by co-precipitation method at Cu content of 5.1 wt%. On the mechanism of CO-PROX, it is proposed that the catalytically active center for CO oxidation is Cu–O–Ce structure on the interface of CuO and CeO_2 phases as shown in Equation (1) [10−12]. The symbol "□" represents oxygen vacancy.

$$Cu^{2+} - O^{2-} - Ce^{4+} + CO = Cu^{+} - \square - Ce^{3+} + CO_2 \quad (1)$$
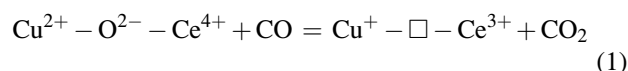
Martínez-Arias et al. [13] detected superoxide ion O_2^- by EPR technique on the partially reduced CuO/CeO_2 sample prepared by the method of incipient wetness impregnation of CeO_2 support using an aqueous solution of $Cu(NO_3)_2$. Temperature-programmed reduction (TPR) in H_2-N_2 mixture gas suggests several different states of CuO_x dispersed on CeO_2 support, i.e., highly dispersed CuO_x with strong interacting with the support, well dispersed CuO_x clusters, and CuO crystallites [8,9,14,15]. Formation of solid solution Cu–Ce–O is also confirmed [3,7,16]. Shan et al. [16] reported a solid solution $Cu_xCe_{1-x}O_y$ ($x \leq 0.1$) formed after calcination at 650 °C. And they found at a larger x value, the segregated

CuO phase became present [16]. CuO crystallites on CeO_2 support can be recognized by XRD. Moreover, due to the interaction between CuO_x and CeO_2, an extent of reduction of CeO_2 in CuO/CeO_2 catalyst would occur concurrently with CuO_x species at the reduction temperature of CuO_x, even though pure CeO_2 itself began to be reduced only at a much higher temperature [14,15].

The inverse configuration CeO_2/CuO catalyst was firstly designed by Hornes et al. as an alternative to the classical configuration CuO/CeO_2 for preferential oxidation of CO in excess H_2 stream [17]. The inverse system, synthesized by microemulsion method, showed a better activity for CO-PROX than $Cu_{0.2}Ce_{0.8}O_2$ reference catalyst [17]. The idea of the authors was that, using large size of CuO particles as support to decease the reducibility of the catalytically active centers, and therefore to obtain a wider temperature window with high CO conversion and high selectivity to CO_2 of O_2 for CO-PROX. Another merit of the inverse system is the decreased usage of rare earth metal oxide CeO_2.

We followed the inverse design of the work [17], and prepared CeO_2/CuO catalyst (atomic ratio of Ce/Cu = 10/100) by impregnating a commercial CuO powder with $Ce(NO_3)_3$ solution. Five calcination temperatures, i.e., 500, 600, 700, 800 and 900 °C, were selected to investigate the interaction between cerium oxide component and CuO support.

2. Experimental

2.1. Catalyst preparation

5 g commercial CuO powder (Beijing Chemicals, China) was used as support. 5 mL water-ethanol mixture (2 mL distilled water plus 3 mL ethanol (95%)) was taken to dissolve an appropriate amount of cerium nitrate (Tianjin Fuchen Chemicals, China). After CuO powder was added into the cerium nitrate solution, the solid-liquid mixture was stirred into slurry with glass rod and agitated supersonically at 60 °C for 15 min with continuous stirring by hand, in order to evaporate the excess liquid. Then, the resulting solid was dried in oven at 120 °C for 4 h. At last the solid was calcined in a muffle furnace at a given temperature for 2 h. Five calcination temperatures, i.e., 500, 600, 700, 800 and 900 °C, were selected to investigate the effect of calcination temperature. CeO_2/CuO catalysts obtained at the five calcination temperatures all had the same atomic ratio of Ce/Cu equal to 10/100, so they were denoted as 10 at.% CeO_2/CuO in the text of this paper.

2.2. Catalyst characterization

Phase identification of the five CeO_2/CuO catalysts was carried out on an X-ray diffractometer (Shimadzu XRD-6000, Japan) with Cu K_α radiation at the fixed measurement parameters. Temperature-programmed reduction (TPR) experiments were performed on the apparatus (PX2000, Pengxiang Co., Tianjin, China), where a $20\%H_2$-N_2 mixture gas was flowing at 20 mL/min over the sample (20 mg) during the heating process at 10 °C/min from room temperature to 900 °C. Specific surface area (SSA) and pore volume were measured by BET method at liquid nitrogen temperature (Belsorp-Max, Japan).

Catalytic activity of CeO_2/CuO catalysts for CO-PROX was tested in a fixed-bed flow reactor under atmospheric pressure. 200 mg catalyst (60−80 mesh) was loaded into a U-type quartz tube reactor (6 mm i.d.). The CO-containing gas was composed of 2 vol% CO, 75 vol% H_2 and 23 vol% N_2, flowing at 100 mL/min controlled by a mass flow controller (MFC). Air was co-fed by another MFC, set at 15 mL/min. Reaction products' analyses were performed on a gas chromatograph with a thermal conductivity detector (TCD). In the oven of the gas chromatograph, a packed column (Shincarbon ST 50/80, Shimadzu Column Packing, Japan) was connected to separate H_2, O_2, N_2, CO and CO_2 in the reaction products.

3. Results and discussion

3.1. XRD phase identification

XRD patterns of the five CeO_2/CuO catalysts obtained at different calcination temperatures are shown in Figure 1. It is seen that the diffraction of CeO_2 phase has a growing intensity with calcination temperature increasing. This can be ascribed to a continuous sintering of CeO_2 phase dispersed on CuO support. Besides, it can also be envisaged that a portion of Ce^{4+} ions were capable of diffusing into CuO crystals forming solid solution at high calcination temperatures. The intensities of the two most intense XRD peaks (plane (−111) at 2θ = ca. 35.56°, plane (111) at 2θ = ca. 38.72°) of CuO phase in CeO_2/CuO catalysts are shown in Figure 2. It is clear that the peak intensity increased at first and then decreased on plane (111) as the calcination temperature rose from 500 to 900 °C. Whereas, the pure CuO samples had an increasing trend in intensity with calcination temperature rising, if considering the baseline count fluctuation of XRD equipment, for the same XRD peak as shown in Figure 3.
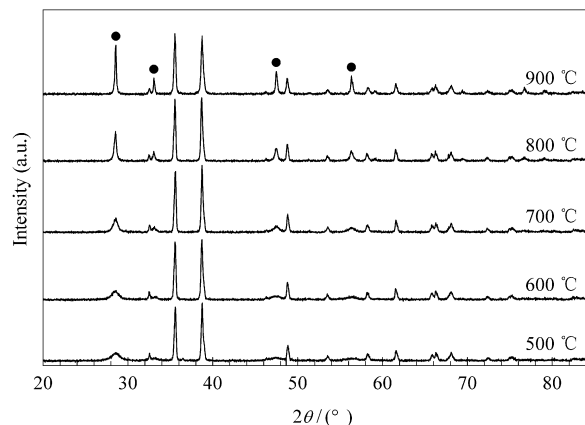

Figure 1. XRD patterns of CeO_2/CuO catalysts calcined at different temperatures. The black full circles denote CeO_2 phase. Other peaks belong to CuO phase