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Influence of Ethanol Washing in Precursor on CuO–CeO_2 Catalysts in Preferential Oxidation of CO in Excess Hydrogen

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Abstract In this study, influence of ethanol washing in precursor on CuO–CeO_2 catalysts in preferential oxidation of CO in excess hydrogen (PROX) was investigated. BET, FTIR and TPR techniques were used. The results showed that ethanol washing was beneficial to improve the catalytic performance of CuO–CeO_2 catalysts in the PROX. The CO conversion over CuO–CeO_2 catalysts without ethanol washing was only 85% at 190 °C, while the highest CO conversion over CuO–CeO_2 catalysts with 200 mL ethanol washing was beyond 99% at 120 °C. XRD and TPR results showed that ethanol washing depressed the growth of CuO–CeO_2 catalysts and improved the reducibility of CuO–CeO_2 catalysts. The FTIR measurement proved that the absorption water was decreased by the way of ethanol washing, indicating that the amount of the H–O–H bridge between adsorption water and precursor of CuO–CeO_2 catalysts was decreased and depressed the growth of CuO–CeO_2 catalysts.

Keywords CuO–CeO_2 · Preferential oxidation · CO · Fuel cell · Ethanol washing

1 Introduction

The PROX is the most effective method used to eliminate CO in the application of polymer electrolyte membrane (PEM) fuel cells [1–4]. 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 [5–7]. Therefore, CuO–CeO_2 catalysts can be considered to be a promising catalyst in PROX, due to a good compromise between catalytic performance and cost of catalysts.

For CuO–CeO_2 catalysts, preparation methods have a critical influence. Preparation methods reported include co-precipitation [8–10], urea-nitrate combustion method [11, 12], sol-gel peroxo route [13, 14], etc. Avgouropoulos et al. [6] investigated the difference among four CuO–CeO_2 catalysts prepared using co-precipitation, citrate-hydrothermal, urea-nitrates combustion, and impregnation methods. They found that the combustion-prepared sample exhibited the best catalytic performance, followed by the citrate-hydrothermal-prepared sample. And the impregnated was least active. However, CuO–CeO_2 catalysts synthesized by Kim et al. [15] using co-precipitation methods, with BET specific surfaces of 91 m^2/g, showed superior performance in PROX, namely, these catalysts reduced CO content to less than 100 ppm below 170 °C in a feed of 1% CO, 1% or 1.25% O_2, 50% H_2 in the presence of H_2O and CO_2.

Guzman et al. [16] had found that the reactive oxygen species were not formed on conventionally prepared CeO_2, and their formation on nano-structured CeO_2 was enhanced by the presence of gold. Therefore, preparation of nano-structured CuO–CeO_2 catalysts with higher surface areas had been attracting more attentions. Ethanol was used to dehydration in coprecipitation process to achieve higher surface areas and smaller particle sizes. For example, Xu et al. [17] reported that ethanol was used in ZrO_2 preparation by coprecipitation and found that ZrO_2 with ethanol dehydration (S = 53 m^2 g^{-1}, d = 15–20 nm) had a higher surface area and a smaller particle size in comparison with ZrO_2 without ethanol dehydration (S = 27 m^2/g, d = 40–200 nm).

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In this study, the influence of ethanol washing on catalytic performance of CuO–CeO_2 catalysts in PROX had been investigated. And BET, XRD, FTIR and TPR were used to characterize CuO–CeO_2 catalysts.

2 Experimental

2.1 Catalyst Preparation

CuO–CeO_2 catalyst was prepared by coprecipitation according to literature [18]. The obtained precipitate was washed with water to 7.0 of pH value and then washed with different amount of ethanol before dried at 105 °C for about 3 h. The dried sample was thermally heated at 500 °C for about 2 h. And the samples which were washed with 0, 20, 40, 60 and 200 mL ethanol were designated as 5CuC-0, 5CuC-20, 5CuC-40, 5CuC-60 and 5CuC-200, respectively. All treated catalysts were crushed and sieved to 60–80 meshes. The loading of Cu in all catalysts was 5% in weight.

2.2 Evaluation of Catalytic Performance

Activity measurement was carried out in a fixed-bed microreactor (quartz glass, 4 mm i.d., 6 mm o.d., length 250 mm) at atmospheric pressure. The reactor temperature was measured by a K-type thermocouple located at the top of the packed catalyst bed and controlled by a temperature controller. The mass of catalyst used in the experiments was 50 mg, and the catalyst was diluted with inert alumina particles (60–80 meshes) with a dilution ratio of 1:1 of mass. A desired mixture of gases (i.e. 50% H_2, 1.0% O_2, 1.0% CO, 10.0% CO_2, 20.0% H_2O and Ar in balance) was controlled by the mass flow controllers (Alicat Scientific Inc., USA). The water vapor was introduced by allowing reaction gases to bubble through a heated water bath.

The reactor inlet and outlet streams were measured using an on-line gas chromatograph equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). H_2 and O_2 were separated by a carbon molecular sieve (TDX-01) column and detected using TCD. CO and CO_2 were separated by a carbon molecular sieve (TDX-01) column, then converted to methane by a methanation reactor and analyzed by FID. The FID detection limit for CO is less than 3 ppm.

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

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

The O_2 selectivity is defined as the oxygen consumed by CO oxidation, namely:

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

2.3 Characterization of Catalysts

The specific surface areas of samples were obtained at −196 °C using a Coulter Omnisorp 100 CX. Prior to the measurement, samples were pretreated at 250 °C for 2 h. X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/Max 2550PC powder diffractometer using nickel-filtered Cu$K\alpha$ radiation. FT-IR measurement was carried out on a Nicolet Magna-IR 560 spectrophotometer. H_2 temperature-programmed reduction (TPR) was carried out using a conventional reactor equipped with TCD. About 50 mg catalyst and 40 mL/min flow rate of 5% H_2/Ar were applied in this study. The heating rate was 10 °C/min from 30 to 350 °C.

3 Results and Discussion

3.1 Catalytic Performance of CuO–CeO_2 Catalysts

Figure 1 revealed the difference of catalytic performance among 5CuC-0CP, 5CuC-20CP, 5CuC-40CP, 5CuC-60CP and 5CuC-200CP in PROX. From Fig. 1, it could be seen that addition of ethanol had a beneficial effect on the catalytic performance of CuO–CeO_2 catalysts. In the case of 5CuC-0CP, the peak conversion of CO was 85.2% at 190 °C. In contrast, the peak conversion of CO over 5CuC-20CP was 97.9% at 190 °C. When increasing the amount of ethanol, the peak conversions of CO over 5CuC-40CP, 5CuC-60CP and 5CuC-200CP were 99.3% at 175 °C, 99.4% at 160 °C and 99.5% at 120 °C, respectively. It was evident that enough amount of ethanol used to replace water in hydroxide precursors of CuO–CeO_2 catalysts could be beneficial to enhance catalytic activity of CuO–CeO_2 catalysts in PROX.

Selectivity of O_2 declined in the turn of 5CuC-0CP, 5CuC-20CP, 5CuC-40CP, 5CuC-60CP and 5CuC-200CP. The selectivity of O_2 had a converse trend in comparison with the conversion of CO, indicating that the oxidation of CO and H_2 was sensitive to the properties of the catalysts and had a similar reaction pathway, namely, CO and H_2 competed for the adsorption centers, the reaction centers and oxygen etc [9]. Secondly, the selectivity of O_2 had a converse trend with the temperatures, indicating that higher reaction temperatures were favorable for the oxidation of H_2. Competing for the similar activation centers was the key for the selective oxidation of CO and H_2. Generally, lower reaction temperatures were beneficial to absorb and activate CO and higher reaction temperatures were

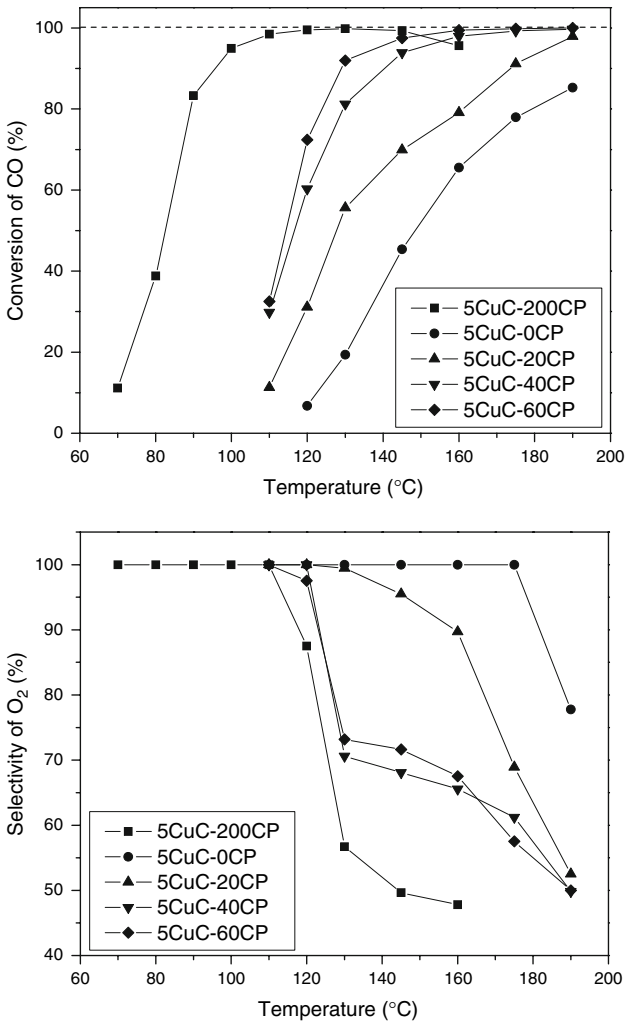

Fig. 1 The activity and selectivity of CuO–CeO_2 catalysts washed with different amount of ethanol, at a space velocity of 120,000 mL g^{-1} h^{-1}, in a feed of 1.0% CO, 1.0% O_2, 50% H_2, balance Ar

beneficial to absorb and activate H_2 in the surface of CuO–CeO_2 catalysts [19]. Therefore, with the increase of reaction temperatures, more and more oxygen were consumed by the reaction with hydrogen (i.e. $2H_2 + O_2 = 2H_2O$) and caused the decrease of selectivity of O_2.

3.2 Structure of CuO–CeO_2 Catalysts

Table 1 listed the washing amount of ethanol, particle sizes, surface areas and catalytic activity of CuO–CeO_2 catalysts. From Table 1, it could be seen that with the increase of washing amount of ethanol, the particle sizes and surface areas of CuO–CeO_2 catalysts decreased from 13.1 to 5.4 nm and increased from 117 to 138 m^2 g^{-1}, respectively. Especially, when the amount of ethanol was equal to or larger than 40 mL, the surface areas of CuO–CeO_2 catalysts had little change.

Table 1 Characteristics of CuO–CeO2 catalysts and comparison of their activity in CO oxidation

Catalysts	Washing amount (mL)	$D_{(111)}$[a] (nm)	S_{BET} (m^2 g^{-1})	T_{50}[b] (°C)
5CuC-0	0	13.1	117	148
5CuC-20	20	10.2	122	128
5CuC-40	40	9.4	139	117
5CuC-60	60	6.1	139	114
5CuC-200	200	5.4	138	82

[a] From line broadening of CeO_2 (111) peak

[b] W/F = 0.03 g s cm^{-3}

Figure 2 showed the XRD patterns of CuO–CeO_2 catalysts washed with different amount of ethanol. The distinct fluorite-type oxide structure of CeO_2 was observed in all samples [20]. In addition, no observed shift in the diffraction lines of CeO_2 could be found in these catalysts, indicating that no solid solutions appeared in the CuO–CeO_2 catalysts. However, it should also be noted that the XRD peaks of CeO_2 were rather broad and shifts of small magnitude could be undetectable [21]. From Fig. 2, it could be seen that with the increase of ethanol amount, the peaks were broader and weaker, which indicated that the particle sizes of CuO–CeO_2 catalysts became smaller with the increase of ethanol amount.

Figure 3 showed the FTIR spectra in the region 400–4,000 cm^{-1} of the precursor of CuO–CeO_2 catalysts. Residual water and hydroxyl group were detected with a large band at around 3,430 cm^{-1} and a band at around 1,530 cm^{-1}, due to the bending vibrations of associated

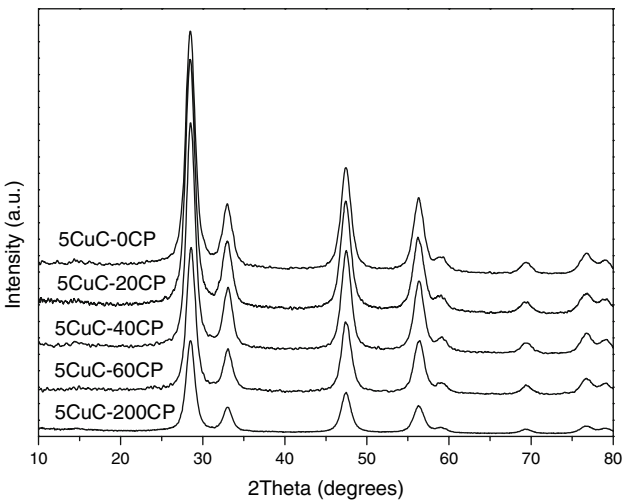

Fig. 2 XRD patterns of CuO–CeO_2 catalysts washed with different amount of ethanol

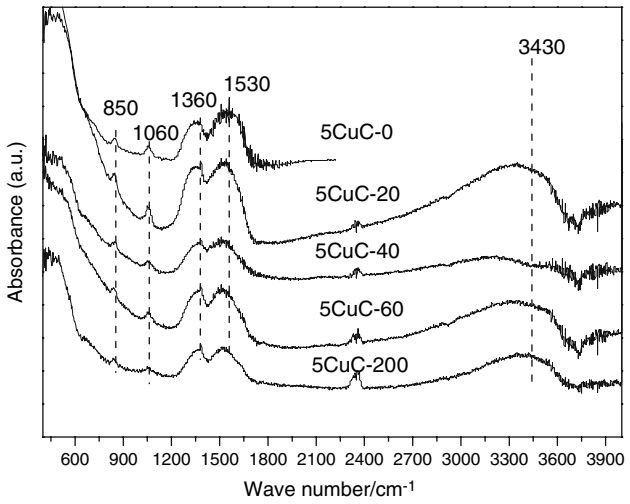

Fig. 3 Infrared spectra of CuO–CeO_2 catalysts washed with different amount of ethanol

water. Another species of strong bands was located at around 1,360 cm^{-1}, which maybe associated with the formation of nitrate like species. The IR absorption bands at about 1,060 cm^{-1} and 850 cm^{-1} were typical of carbonate like species. Obviously, there existed small amount of nitrate and carbonate like species in the precursor of CuO–CeO_2 catalysts. It also could be seen that the signal of the adsorption water decreased with the ethanol amount increased, indicating that the adsorption water also decreased with the ethanol amount increased. The influence of adsorption water on the preparation of CuO–CeO_2 catalysts could be explained according to Fig. 4. The H–O–H bridge was formed because of the hydrogen bonding between adsorption water and precursor of CuO–CeO_2 catalysts. When heating the precursors of CuO–CeO_2 catalysts, the H–O–H bridge enhanced the dehydration reaction between near particles of the precursors of CuO–CeO_2 catalysts and caused the growth of CuO–CeO_2 catalysts. Therefore, when adsorption water was decreased by the way of ethanol washing, the amount of the H–O–H bridge between adsorption water and precursor of CuO–CeO_2 catalysts was also decreased, which depressed the dehydration reaction between near particles of the precursors of CuO–CeO_2 catalysts and improved the dispersion of nano-structured CuO–CeO_2 catalysts.

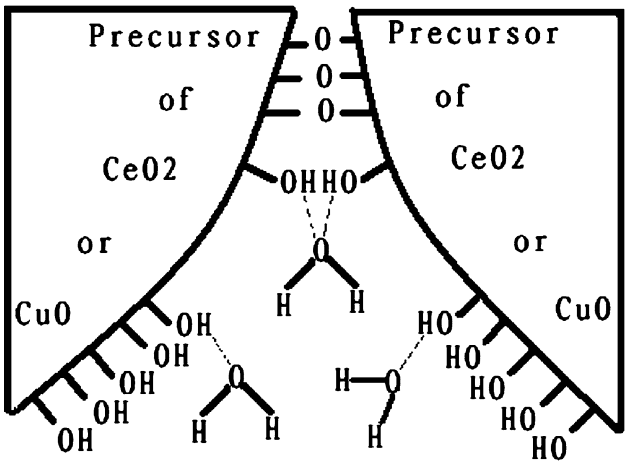

Fig. 4 Influence of water on the growth of CuO–CeO_2 catalysts

3.3 The Redox Properties of CuO–CeO_2 Catalysts

The H_2-TPR profiles of CuO–CeO_2 catalysts washed with different amount of ethanol were illustrated in Fig. 5. The over lapping reduction peaks consisted of a low-intensity, low-temperature peak at 164 °C (α peak) and a high-intensity peak at 180 °C (β peak). According to literature [11, 21, 22], α peak was attributed to reduction of copper ions strongly interacting with CeO_2 and β peak was assigned to the reduction of larger CuO particles less associated with ceria. It should be noted that, compared with the reduction profile of pure CuO characterized by a single peak at 293 °C [22], the reduction temperature of CuO was lowered. In case of 5CuC-0CP, α peak and β peak had a slight shift to lower temperature and H_2-consumption amount was lower than that of CuO–CeO_2 catalysts washed with ethanol. In addition, with increasing in the amount of ethanol, the areas of α peak were increased. However, there was no evident shift among peaks of CuO–CeO_2 catalysts washed with ethanol (Table 2).

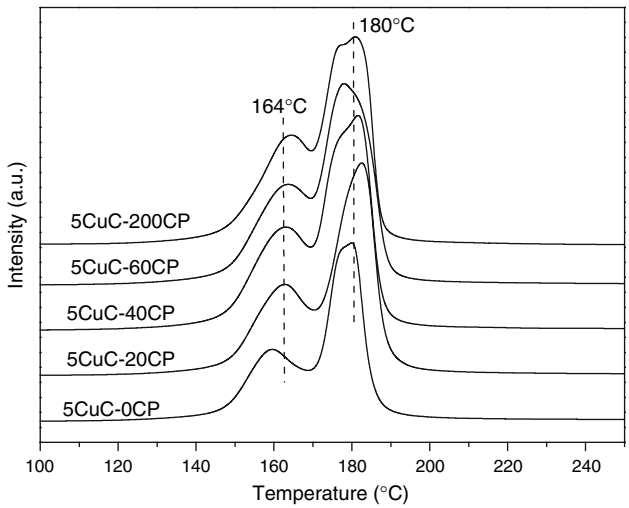

Fig. 5 TPR profiles of CuO–CeO_2 catalysts washed with different amount of ethanol

Table 2 H_2-consumption amount of $CuO–CeO_2$ catalysts washed with different amount of ethanol

Catalysts	α Peak (mmol g_{cat}^{-1})	β Peak (mmol g_{cat}^{-1})
5CuC-0CP	182	258
5CuC-20CP	258	319
5CuC-40CP	259	364
5CuC-60CP	288	379
5CuC-200CP	325	479

[a] $W/F = 0.03$ g s cm^{-3}

4 Conclusions

Different amount of ethanol washing (i.e. 0, 20, 40, 60, and 200 mL) had a strong influence on catalytic performance of $CuO–CeO_2$ catalysts in preferential oxidation of CO in excess hydrogen, namely, the catalytic performance of $CuO–CeO_2$ catalysts in preferential oxidation of CO in excess hydrogen had been strongly improved. The CO conversion of 5CuC-0CP was only 85.2% at 190 °C, while the highest CO conversion of 5CuC-200CP is beyond 99% at 120 °C. XRD and TPR results showed that ethanol washing depressed the growth of $CuO–CeO_2$ catalysts and improved the dispersion of $CuO–CeO_2$ catalysts. The FTIR measurement proved that the absorption water was decreased by the way of ethanol washing, indicating that the amount of the H–O–H bridge between adsorption water and precursor of $CuO–CeO_2$ catalysts was decreased and depressed the growth of $CuO–CeO_2$ catalysts.

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