Methanol synthesis from carbon monoxide and hydrogen over ceria-supported copper catalyst prepared by a coprecipitation method

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High catalytic activity in the synthesis of methanol from carbon monoxide and hydrogen can be produced with ceria-supported copper catalysts prepared by a coprecipitation method. The activity at 468 K is comparable with that produced with commercial copper–zinc catalysts at 503–523 K, while it is still unstable. Although the reaction atmosphere is reductive, metallic copper particles on cerium oxide are oxidized during the reaction and the catalyst is activated. Hence, formation of the copper oxide species is indispensable for the appearance of the high catalytic activity.

KEY WORDS: methanol synthesis; copper; cerium oxide; EXAFS; formation of copper oxides.

1. Introduction

In the commercial process for methanol production, copper–zinc catalysts are usually employed in the synthesis of methanol from carbon oxides and hydrogen above 520 K [1]. Although the process suffers a large recycling cost of unreacted gas, the exothermic reaction does not operate at lower temperatures, which promises higher equilibrium conversion, because of insufficient catalytic activity. About two decades ago an intermetallic compound of copper–cerium was found to be active in methanol synthesis above 580 K [2]. Nix *et al.* [3] reported the structural change of $CeCu_2$ alloy to $CeO_{2-x} + CeH_{2+x} + Cu$ phases during the activation process and its catalytic activity at 398 K, but activity such as space–time yield was not reported. We also found that the activity of copper interacting with cerium oxide is as high as that of palladium in weight of metal basis [4]. Here, we will report that a high activity for methanol synthesis can be produced with ceria-supported copper catalysts prepared by a coprecipitation method.

2. Experimental

Ceria-supported copper catalysts (n wt% Cu/CeO_2, where n represents the content of copper) were prepared by coprecipitation from an aqueous mixture of $Cu(CH_3COO)_2$ and $Ce(NO_3)_3{\cdot}6H_2O$ with addition of an aqueous solution of Na_2CO_3 with vigorous stirring at 343 K. After being washed with distilled water, the precipitate was dried at 393 K for 12 h and finally calcined in air at 623 K for 12 h. The densities of the catalysts were 3.2 kg dm^{-3} regardless of the samples.

Catalytic tests were performed in a fixed-bed continuous flow reactor. The powdered catalyst (0.5 g) was placed in a stainless steel tubular reactor of 9 mm i.d. and reduced in a stream of 10 vol% of hydrogen diluted with nitrogen (3.6 dm^3 h^{-1}, 0.1 MPa) at 573 K for 6 h. A mixture of carbon monoxide (33 vol%) and hydrogen (67 vol%) was fed with a flow rate of 3.6 dm^3 h^{-1} in STP at 468 K and at 2.0 MPa. The outlet gas was analyzed with two on-line gas chromatographs (Ohkura Riken type 802 with TCD and type 103 with FID).

The BET surface areas of the samples were determined from the isotherms of nitrogen physisorption at 77 K. The XRD patterns of the samples were recorded with a MAC Science MO3X diffractometer using nickel-filtered Cu K_α radiation in air. Profiles of EXAFS for the samples were taken at room temperature in fluorescence mode for *K*-edges of Cu at beam-line BL01B1 of SPring-8. The Fourier transformation was performed on k^3-weighted EXAFS oscillations in the range 30–145 nm^{-1}. Normalization of the EXAFS was done by dividing the absorption intensity by the height of the absorption edge. A cubic spline background subtraction was carried out. The samples were sealed with polyethylene films under a nitrogen atmosphere.

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3. Results and discussion

Methanol was selectively synthesized from carbon monoxide and hydrogen over Cu/CeO_2 catalysts at 468 K, while a trace amount of methane was sometimes detected. At the initial stage of the reaction the activity increased steeply and reached maxima at about 6 h on-stream, then gradually decreased (table 1). The activity of 25 wt% Cu/CeO_2 was highest at 0.5 h on-stream (35.0 mol dm^{-3} h^{-1}), but the activities of 5 wt% and 10 wt% Cu/CeO_2 became higher at 6.5 h on-stream (39.3 and 40.9 mol dm^{-3} h^{-1}, respectively) than that of 25 wt% Cu/CeO_2 (26.9 mol dm^{-3} h^{-1}). The activities of the catalysts are comparable with that produced with 15 wt% Pd/CeO_2 prepared by a coprecipitation method [5]. The activity of commercial copper–zinc catalysts at 2 MPa was 14–27 mol dm^{-3} h^{-1} at 503–523 K calculated from the data in table 7 of ref. [2] assuming that the activity relates to the reaction pressure. Thus, Cu/CeO_2 can produce similar activity to that of a commercial copper catalyst at a lower reaction temperature by *ca.* 30–50 K while the activity is still unstable.

The BET surface area of the Cu/CeO_2 samples decreased with an increase in the copper content, but even the surface area of 40 wt% Cu/CeO_2 was as high as 97 m^2 g^{-1} (see table 1).

After reduction of 10–40 wt% Cu/CeO_2 in a hydrogen stream at 573 K for 6 h, XRD peaks were recorded at 43.3° and 50.4° in 2θ attributed to metallic copper (figure 1), while no peaks except for those attributed to CeO_2 were observed with 5 wt% Cu/CeO_2 [6]. Interestingly the mean crystallite sizes of Cu determined from the peak broadening using Sherrer's equation were 33–34 nm regardless of the copper content except for 5 wt% Cu/CeO_2 [7]. After the reaction for 25 h intensities of the peaks attributed to metallic copper decreased, and XRD peaks at 36.5° attributed to Cu_2O and at 35.6 and 38.8° to CuO appeared with 25 and 40 wt% Cu/CeO_2 [6]. Formation of Cu–O bonding after the reaction was also confirmed with the Fourier transform of the extended X-ray absorption fine structure (FT-EXAFS) spectra of the catalysts after the reaction (figure 2). This shows that copper particles were oxidized during the reaction although the reaction gas is reductive. Hence,

Table 1
Catalytic activity of copper supported on cerium oxide for methanol synthesis at 468 K.

Catalyst	Space–time yield of methanol (mol dm^{-3} h^{-1}) (time on-stream)			BET surface area (m^2 g^{-1})
	0.5 h	6.5 h	24.5 h	
5 wt% Cu/CeO_2	5.1	39.3	28.3	191
10 wt% Cu/CeO_2	19.2	40.9	29.4	166
25 wt% Cu/CeO_2	35.0	43.9	26.9	157
40 wt% Cu/CeO_2	12.1	29.9	18.9	97

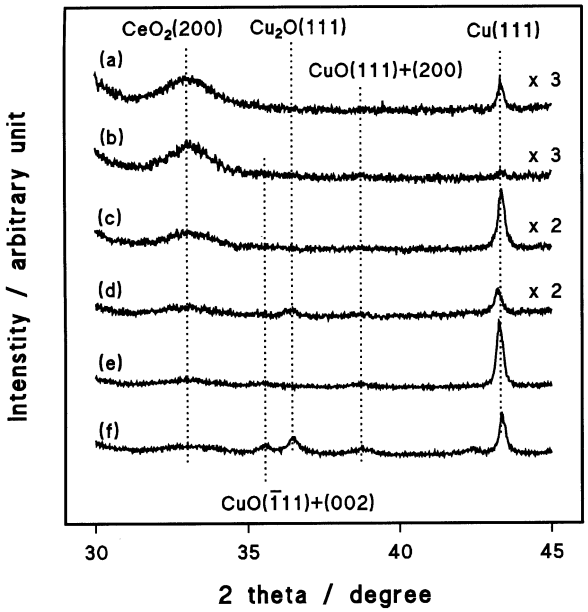

Figure 1. Powder XRD patterns of copper supported on cerium oxide. (a) 10 wt% Cu/CeO_2 after reduction with hydrogen at 573 K for 6 h, (b) after reaction at 468 K for 25 h, (c) 25 wt% Cu/CeO_2 after reduction, (d) after reaction for 25 h, (e) 40 wt% Cu/CeO_2 after reduction, (f) after reaction for 25 h.

the formation of the copper oxide species is probably due to the interaction with cerium oxide, and such a phenomenon was observed with palladium supported on cerium oxide [8]. The mean crystallite sizes of Cu_2O determined from the XRD peaks at 36.5° were 14 and 17 nm for 25 and 40 wt% Cu/CeO_2 after the reaction, respectively, while the sizes of metallic copper were 32 and 33 nm, respectively. Since the mean crystallite size of Cu metal was not significantly changed after the

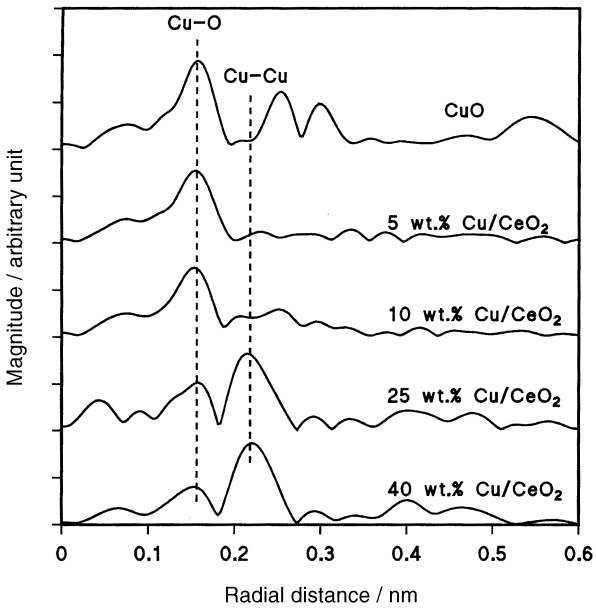

Figure 2. Fourier-filtered Cu *K*-edge pseudoradial distribution functions of copper supported on cerium oxide after reaction at 468 K for 25 h.

reaction, the formation of small Cu_2O particles was not simply due to oxidation of the metallic copper particles during the reaction, but rather due to partial dispersion of copper from the large copper particles to the surface of cerium oxide during the reaction. Thus, the copper oxide species formed should interact strongly with cerium oxide. The activity of Cu/CeO_2 is generally low at the initial stage of the reaction; it seems that metallic copper particles produced by the pretreatment with hydrogen are less active and new active species are formed during the reaction process. Hence, the high catalytic activity should be caused by the strong interaction between copper and cerium oxide. However, copper cannot be directly oxidized with cerium oxide because the oxidation takes place in the presence of carbon monoxide during the reaction, suggesting that oxygen in carbon monoxide plays an important role in the oxidation. The mechanism is not clear at this point, but a small quantity of carbon dioxide and/or water, which can oxidize copper, must be formed during the reaction because slight formation of methane was detected. Rabo *et al.* [9] pointed out the possibility of disproportionation of carbon monoxide to carbon dioxide and carbon which will be converted to methane in presence of hydrogen on the surface of metal. The redox property of cerium oxide may enhance oxidation of copper with carbon dioxide and/or water.

Fakley *et al.* [10] proposed carboxyl species such as Cu–O–CH–O–Ce formed on the periphery between a copper cluster and cerium oxide as an intermediate of the methanol synthesis from carbon monoxide and hydrogen over a Ce–Cu alloy catalyst. Further oxidation of copper may cause the deactivation of Cu/CeO_2. However, the catalyst is under the reductive reaction condition, and the oxidation state of copper should be controlled by the interaction between the metal and the support. Since the redox property of cerium oxide changes with the addition of other oxides such as zirconium oxide [11], the catalytic activity may be stabilized by the addition of the third component.

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