Catalysis Letters Vol. 79, Nos. 1–4, April 2002 (© 2002)

A comparative study of palladium and copper catalysts in methanol synthesis

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Received 20 August 2001; accepted 14 December 2001

Catalytic activity of copper supported on cerium oxide (Cu/CeO_2) in methanol synthesis from carbon monoxide and hydrogen at 473 K is similar to that of ceria-supported palladium (Pd/CeO_2) Both catalysts contain 0.3 mmol g^{-1} of the active metals and the activities on a mole basis of the active metals are significantly higher than that of a commercial copper catalyst. Analyses by EXAFS suggest that the particle size of copper in Cu/CeO_2 is similar to that of palladium in Pd/CeO_2. The activity of copper supported on silica is very low even at 523 K although the particle size of copper is close to that in Cu/CeO_2. Hence, cerium oxide promotes the activity of copper as can be seen in Pd/CeO_2.

KEY WORDS: methanol synthesis; copper; palladium; cerium oxide; silica; EXAFS.

1. Introduction

Two major catalytic systems, supported copper and palladium catalysts, exhibit high activity and selectivity for the methanol synthesis from carbon oxides and hydrogen [1–4]. Palladium was said to be more active than copper in methanol synthesis on a mole basis of active metal, especially from carbon monoxide and hydrogen [1,2], and actually some palladium catalysts are comparable with or more active than copper–zinc catalysts [5–7]. Hence, as a catalyst metal for methanol synthesis palladium seems to be more active than copper. However, Nix *et al.* [8] reported that a catalyst, of which the precursor is $CeCu_2$ alloy, is active even at 398 K, but they did not make a comparison with conventional catalysts. In the present report, we will show that the activity of copper supported on cerium oxide is similar to that of the ceria-supported palladium even on a mole basis of the active metal and cerium oxide is an effective promoter of copper.

2. Experimental

Ceria-supported palladium and copper catalysts with a metal loading of 0.3 mmol g^{-1} (Pd/CeO_2 and Cu/CeO_2, respectively) were prepared by the deposition–precipitation method from an aqueous solution of palladium acetate (Kanto Chemical, GR grade) or copper acetate (Ishizu Pharmaceutical Co., GR) in which cerium oxide (Daiichi Kigenso Kagaku Kogyo, 98 m^2 g^{-1}) was dispersed. The metal hydroxide was exclusively precipitated on the surface of cerium oxide by gradual addition of a sodium carbonate solution and the pH value of the mixture was maintained at 10 for 1 h. The resulting solids, washed with distilled water, were dried at 393 K for 12 h, then calcined at 723 K for 1 h (Pd catalyst) or 623 K for 12 h (Cu catalyst) in air. Silica-supported palladium and copper catalysts containing 0.3 mmol g^{-1} of the metal (Pd/SiO_2 and Cu/SiO_2, respectively) were prepared by the conventional impregnation technique. After silica (Fuji-Silicia G-10, 272 m^2 g^{-1}) was impregnated with palladium acetate or copper acetate by evaporation of the mixture at 353 K, the resulting wet solid was heated with the same procedure as described above.

Profiles of the extended X-ray absorption fine structure (EXAFS) for the reduced catalysts were recorded at room temperature in transmission mode for *K*-edges of Pd and in fluorescence mode for *K*-edges of Cu at beam-line BL01B1 of SPring-8, Japan. The samples were reduced with hydrogen (0.02 MPa) at 573 K for 1 h (Pd samples) or for 6 h (Cu samples) in a vacuum line and sealed with polyethylene films in nitrogen atmosphere. The Fourier transform was performed on k^3-weighted EXAFS oscillations in the range 30–150 nm^{-1}. Inverse Fourier transforms were obtained within the windows of 0.18–0.53 nm for Pd *K*-edges and 0.18–0.51 nm for Cu *K*-edges in *r* space. The Pd–Pd and Cu–Cu references were derived from the EXAFS of Pd and Cu foils, respectively. The analysis was performed with a program of "REX" supplied by Rigaku.

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Methanol synthesis from carbon monoxide and hydrogen (molar ratio of CO/H_2, 1:2) was performed with a fixed-bed continuous flow reactor operated at 2.0 MPa and at 473 K (flow rate, $7.2\,dm^3\,h^{-1}\,g^{-1}$). Prior to the reaction, the catalysts were reduced in a stream of 10 vol% hydrogen diluted in nitrogen at 573 K for 1 h (Pd catalysts) or for 6 h (Cu catalysts).

3. Results and discussion

3.1. Structural analysis

The Fourier transform of the Pd *K*-edge EXAFS for Pd/SiO_2 was a typical pattern of metallic palladium, but the magnitude of the peaks for Pd/CeO_2 was significantly smaller (figure 1). The coordination numbers of the first Pd–Pd shell determined by curve-fitting were 10.6 and 7.4 for Pd/SiO_2 and Pd/CeO_2, respectively (table 1). The parameters for the higher shells obtained were not exact because of the noise signal, but the multi-shell fitting can increase the accuracy of the first-shell parameters (figure 2). Since the coordination number relates generally to the particle size of the metal, the mean particle size on Pd/SiO_2 is probably larger than on Pd/CeO_2 [9]. The sizes can be estimated as 3 and 1 nm, respectively, from the coordination number by the standard method proposed by Greegor and Lytle [9] assuming spherical particles, while Clausen *et al.* [10] criticized the procedure on the basis of molecular dynamics simulations and they showed that the size determined by the standard method is underestimated. The Fourier transform of the Cu K-edge EXAFS for Cu/SiO_2 was similar to that of Cu/CeO_2, and the profiles evidence that the copper particles are metallic. The coordination numbers of the first Cu–Cu shell were 6.7 and 7.1, respectively, showing that the dispersions of the metal on the copper catalysts are similar to that for Pd/CeO_2.

Table 1
EXAFS parameters of the palladium and copper catalysts reduced with hydrogen

Sample	Interaction	Interatomic distance, *R* (nm)	Coordination number, *N*	Debye–Waller factor, σ (nm)
Pd foil	Pd–Pd	0.275	12.0	0.0061
	Pd–Pd	0.48	24	0.006
	Pd–Pd	0.55	12	0.007
Pd/CeO_2	Pd–Pd	0.275	7.4	0.0083
	Pd–Pd	0.48	6	0.008
	Pd–Pd	0.55	3	0.008
Pd/SiO_2	Pd–Pd	0.275	10.6	0.0074
	Pd–Pd	0.48	18	0.006
	Pd–Pd	0.54	7	0.006
Cu foil	Cu–Cu	0.256	12.0	0.0060
	Cu–Cu	0.44	24	0.006
	Cu–Cu	0.51	12	0.007
Cu/CeO_2	Cu–Cu	0.255	7.1	0.0059
	Cu–Cu	0.44	12	0.006
	Cu–Cu	0.51	3	0.006
Cu/SiO_2	Cu–Cu	0.258	6.7	0.0055
	Cu–Cu	0.44	16	0.006
	Cu–Cu	0.51	8	0.006

3.2. Methanol synthesis

Hydrogenation of carbon monoxide to methanol was selectively catalyzed over Pd/CeO_2 at 473 K. The activity increased at the initial stage of the reaction and the space–time yield (STY) of methanol reached

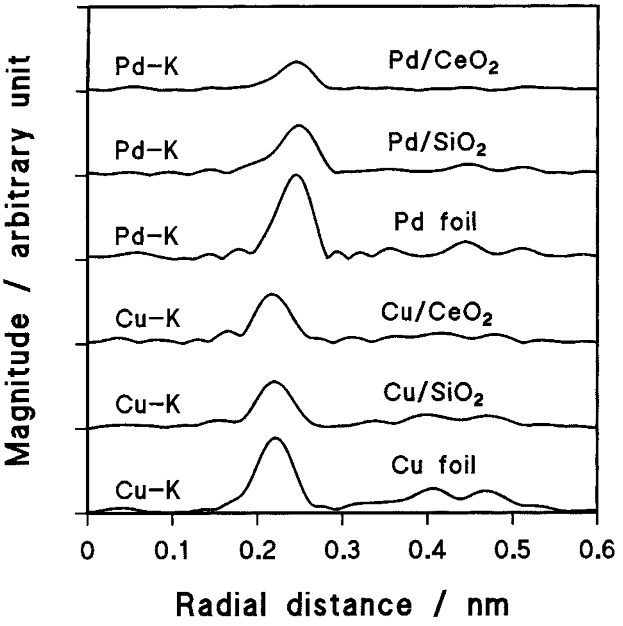

Figure 1. Fourier-filtered pseudoradial distribution functions of palladium and copper catalysts reduced with hydrogen.

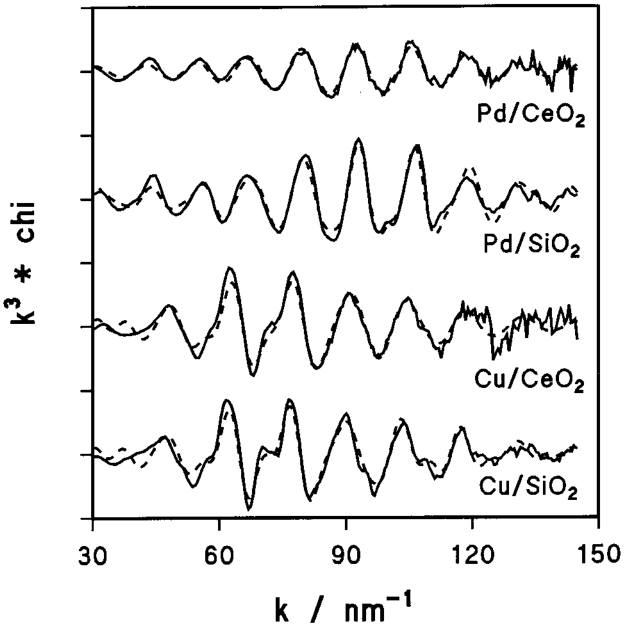

Figure 2. k^3-Weighted Pd and Cu *K*-edge EXAFS oscillations of palladium and copper catalysts reduced with hydrogen.

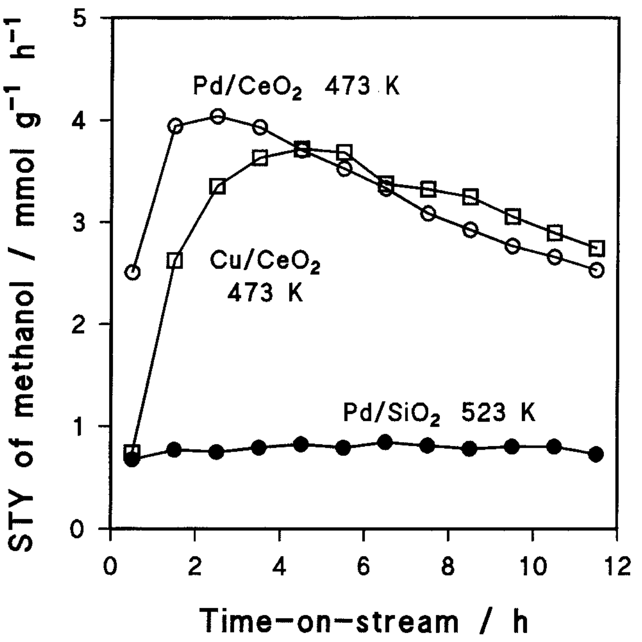

Figure 3. Methanol synthesis from carbon monoxide and hydrogen over palladium and copper catalysts at 0.20 MPa.

4.0 mmol g^{-1} h^{-1} which was 3.7% in the conversion (figure 3). The activity of Pd/CeO$_2$ gradually decreased after the activation. A commercial copper–zinc catalyst containing 2.1 mmol g^{-1} of Cu produced a STY around 3 mmol g^{-1} h^{-1} under the same conditions while the catalyst was pretreated with hydrogen at 523 K for 6 h. The activity is inconsistent with the reaction data of commercial catalysts in ref. [2] assuming that the STY relates to the reaction pressure. On a mole basis of copper the yield is calculated to be 1.4 h^{-1}. Since the mole basis yield of palladium in Pd/CeO$_2$ is 13 h^{-1}, palladium seems to be a very efficient metal in comparison with copper. When silica was the support of palladium, the activity was very low at 473 K while methanol was selectively produced with a STY of 0.8 mmol g^{-1} h^{-1} at 523 K (see figure 3), showing that interaction between palladium and the support is important as well as the dispersion of the active metal [11].

On the other hand, no activity was found with Cu/SiO$_2$ even at 523 K, as reported by Bartley and Burch [12]. However, the activity of Cu/CeO$_2$ containing 2 wt% of copper increased gradually in the initial stage of the reaction and reached 3.7 mmol g^{-1} h^{-1} of STY of methanol at 4.5 h-on-stream while it decreased gradually after that (see figure 3). The activity is very close to that of Pd/CeO$_2$, which contains 3 wt% of palladium. The initial increase in the activity suggests formation of active species during the reaction. Since no activity was found with Cu/SiO$_2$ in which copper is dispersed as well as in Cu/CeO$_2$, cerium oxide should contribute to the catalytic activity. Fakley *et al.* [13] discussed formation of a formate intermediate at the periphery between copper and cerium oxide in alloy-based catalysts. In the case of palladium supported on ceria, the presence of cationic palladium species and formation of Pd–O–Ce during the methanol synthesis were confirmed, showing that palladium particles are strongly in contact with ceria under the reaction conditions [6,14]. Since the major product is carbon monoxide in hydrogenation of carbon dioxide over Pd/CeO$_2$ [15], the methanol synthesis cannot proceed *via* formation of carbon dioxide and this supports formation of the formate species at the periphery of palladium and cerium oxide. Such interaction between copper and cerium oxide may occur during the reaction, and it can account for formation of the formate intermediate at the periphery.

In conclusion, the activity of copper for methanol synthesis is comparable with palladium when copper is activated on cerium oxide, which is a promising support of copper and palladium.

Acknowledgments

The synchrotron radiation experiment was performed with the approval of the Japan Synchrotron Radiation Research Institute (Proposal No. 2000B0137-NX-np). W.S. acknowledges the fellowship of the New Energy and Industrial Technology Development Organization of Japan.

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