Low-temperature Methanol Synthesis Catalyzed over Pd/CeO$_2$

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Methanol is effectively synthesized from carbon monoxide and hydrogen at a reaction temperature as low as 170 °C over Pd/CeO$_2$ in which the palladium species are cationic after reduction with hydrogen at 300 °C.

The methanol synthesis from carbon oxides and hydrogen over copper-zinc catalysts is usually operated above 250 °C and at a reaction pressure of more than 5 MPa. Because of the thermodynamic limitation, the yield of methanol is not high enough for the one-pass operation, which is a break-through of the methanol production system. In order to realize it, the reaction must be carried out at 170 °C or less, however, the catalytic activity of copper-zinc catalysts is insufficient at the low temperatures.[1]

Although high potential of palladium as a catalyst for the methanol synthesis has been claimed, the actual activity on a weight of catalyst basis has been disappointing.[1-3] Ponec pointed out that Pd$^+$ species on the surface are active in the methanol synthesis, but stabilization of the species by promoters was not successful.[3,4] In the present paper we will show that the cationic palladium species are mainly present in Pd/CeO$_2$ prepared by the coprecipitation method and the catalyst is practically active for the methanol synthesis even at 170 °C.

Palladium supported on cerium oxide (Pd/CeO$_2$) was prepared by coprecipitation from an aqueous mixture of PdCl$_2$ (Kishida Chemical, GR grade) and Ce(NO$_3$)$_3$ · 6H$_2$O (Kishida, 98%) by addition of an aqueous solution of 0.15 M Na$_2$CO$_3$ with vigorous stirring. The coprecipitate was filtered, dried in vacuum for 20 h, and finally calcined in air at 500 °C. The palladium content was 15 wt%.

The X-ray photoelectron spectrum (XPS) of Pd/CeO$_2$ was recorded at room temperature with a Shimadzu ESCA-KM. The sample were reduced with hydrogen (0.02 MPa) at 300 °C for 1 h in the spectrometer. Binding energies were determined by reference to the C 1s binding energy of 284.6 eV.

The powder X-ray diffraction (XRD) pattern of the sample reduced at 300 °C was recorded with a Rigaku Rotaflex 20 diffractometer using nickel-filtered CuKα radiation.

Catalytic tests were performed in a fixed bed continuous flow reactor. A catalyst (0.5 g, 50-75 mesh), diluted with 2.0 g of quartz sand, was placed in a stainless steel tubular reactor of 9 mm-i.d. After the pre-reduction in a stream of 10 vol% hydrogen diluted with nitrogen (3.6 dm^3 h^{-1}) at 0.1 MPa, a mixture of carbon monoxide (33 vol%) and hydrogen (67 vol%) was introduced at a reaction temperature, then, pressure was raised (total flow rate, 1.8 dm^3 h^{-1} in STP). The effluent gas was analyzed with two on-line gas chromatographs (Okura Riken Co. Ltd., type 802 with TCD and type 103 with FID). Yields and selectivities were calculated on the basis of carbon numbers.

The BET surface area of the sample after reduction with hydrogen at 300 °C for 1 h was determined from the isotherm of nitrogen physisorption.

In the Pd 3d$_{5/2}$ region, there were peaks at 335.9 and 338.2 eV in the XPS of Pd/CeO$_2$ reduced at 300 °C (Figure 1). The major binding energy of 335.9 eV is significantly higher than that of palladium metal at 335.0 eV and lower than that of PdO at 336.3 eV.[5] In the case of 5 wt% PdO/MgO, the energy is 336.5 eV.[6] Thus, palladium in the sample is probably cationic despite the reduction at 300 °C, suggesting strong interaction between palladium particles and cerium oxide. The valence of the palladium species can be estimated to be close to +1 on the basis of the binding energy. The binding energy of 338.2 eV for the minor peak is significantly higher than that of PdO, implying that a part of palladium interacts directly with cerium oxide.

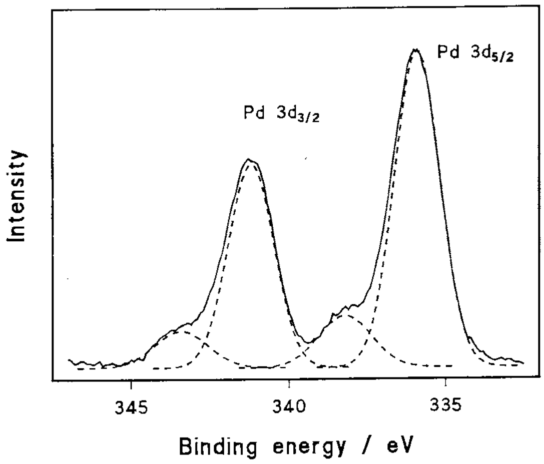

Figure 1. XPS of Pd 3d region for 15 wt% Pd/CeO$_2$ reduced with hydrogen at 300 °C.

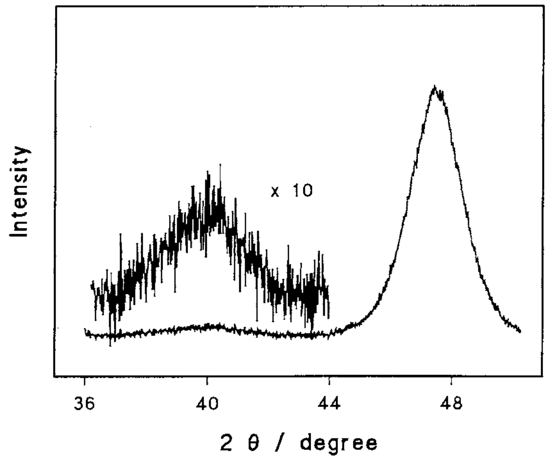

Figure 2. XRD pattern of 15 wt% Pd/CeO$_2$ reduced with hydrogen at 300 °C.

The major peaks of Ce 3d$_{5/2}$ and O 1s were at 882.6 eV and 529.8 eV, respectively. The surface molar ratio of Pd/Ce/O for the sample reduced at 300 °C was estimated as 4/32/64 from the XPS peak areas using the atomic sensitivity factors of Pd 3d (4.6), Ce 3d

(10), and O 1s (0.66).

Although the sample contained 15 wt% of palladium, the major XRD peak for metallic palladium at 39.9° in 2θ was very weak and broad in the pattern for the sample reduced at 300 °C (Figure 2).[8] The approximate mean crystallite size of palladium can be calculated as 3 nm from the line broadening of the peak using the equation of Sherrer.[9] However, there may be a substantial number of palladium particles smaller than 3 nm, which are invisible to X-rays. The small particles can result in formation of cationic palladium species because a binding energy of 336.1 eV for Pd $3d_{5/2}$ was reported for 0.09 wt% Pd/Al_2O_3 reduced at 400 °C while the sample contained 2-3 nm palladium metal particles.[10] The XRD peaks attributable to cerium oxide were recorded at $2\theta = 28.6°$, 33.1°, and 47.5°, and the crystallite size of cerium oxide is estimated as 4 nm from the width of the peak at 47.5°.[8]

Methanol was synthesized at 170 °C from flowing carbon monoxide and hydrogen at 3.0 MPa over Pd/CeO_2 (Figure 3). The activity was low at the initial stage, but increased significantly up to 15 h-on-stream at 3.0 MPa. The catalyst yielded 16.3% of methanol and 1.4% of ethanol after 24 h-on-stream. The by-product was methane of which selectivity was always less than 0.5%. At 200 °C the catalyst yielded 18.3% of methanol even under a lower reaction pressure of 2.0 MPa. The space time yield (STY) of methanol is generally employed for comparison of methanol synthesis catalysts, and that produced with Pd/CeO_2 at 170 °C was 8.7 mmol h^{-1} g^{-1} at 24 h-on-stream and it is comparable with those of copper catalysts for methanol synthesis at reaction temperatures above 200 °C.[1,11] The STY with impregnated 4 wt% Pd/CeO_2 was reported to be only 0.7 mmol h^{-1} g^{-1} at 230 °C and at 3 MPa,[2] while the binding energy of Pd $3d_{5/2}$ was 334.8 eV.[7]

The BET surface area of the sample reduced at 300 °C was 120 m^2 g^{-1}. The surface area of palladium is roughly estimated as 7 m^2 g^{-1} from the BET surface area and the surface molar ratio using the atomic cross sections of Pd (0.060 nm^2), Ce^{4+} (0.022 nm^2), and O^{2-} (0.023 nm^2).[12] Determination of the palladium surface area by adsorption of hydrogen or carbon monoxide was unsuccessful because cerium oxide also adsorbed or consumed the adsorbates. A tentative turn-over frequency (TOF) for Pd was calculated as 45 h^{-1} from the methanol yield at 170 °C and at 3 MPa. Since the TOF for Cu in Cu/ZnO catalysts at 250 °C and at 5 MPa calculated from the data in Ref. 13 is 39 h^{-1}, palladium may produce the activity similar to that of copper at a significantly lower temperature by 80 °C. It was reported that high temperature reduction of palladium supported on cerium causes strong metal-support interaction (SMSI) which may improve the activity of palladium in the methanol synthesis.[2,7] However, in this study the catalyst was only reduced at 300 °C for 1 h, suggesting that the high activity is not due to migration of cerium on the surface of palladium.[14,15]

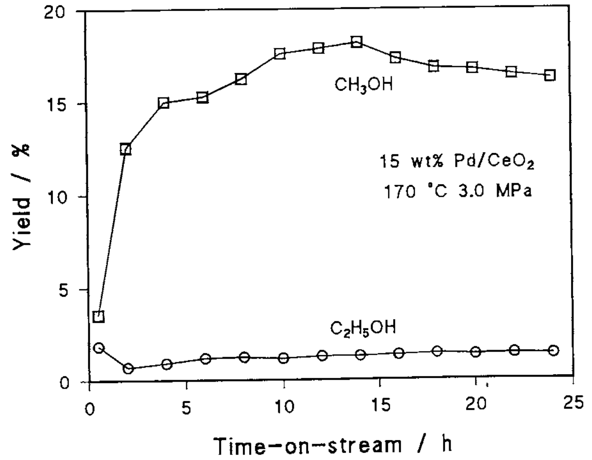

Figure 3. Catalytic activity of 15 wt% Pd/CeO_2 for methanol synthesis at 170 °C. F/W, 3.6 dm^3 g^{-1} h^{-1}.

Assuming that the palladium particles are spherical with 3 nm in diameter, the surface area of 15 wt% of palladium should be 25 m^2 g^{-1}, instead of 7 m^2 g^{-1}. This simple calculation shows that palladium in the coprecipitated catalyst is not effectively exposed on the surface and the higher catalytic activity will be produced with a less quantity of palladium by improvement in the preparation technique.

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