Catalysis Letters 64 (2000) 23–25

Methanol synthesis from carbon monoxide and hydrogen catalyzed over Pd/CeO_2 prepared by the deposition–precipitation method

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Ceria-supported palladium catalysts prepared by the deposition–precipitation method are highly active for the methanol synthesis from carbon monoxide and hydrogen in comparison with the catalyst prepared by the conventional impregnation method. Analyses by EXAFS show that palladium particles can be dispersed very well on the surface of ceria by both the methods, implying that the higher activity of the catalysts prepared by deposition–precipitation is not simply due to the particle size of palladium. Cationic palladium species are present in the samples prepared by deposition–precipitation after reduction with hydrogen at 300 °C, suggesting that the active species are produced by strong contact between palladium particles and the support.

Keywords: methanol synthesis, palladium supported on ceria, cationic palladium, ultrafine Pd particle, EXAFS of Pd, XPS of Pd 3d

1. Introduction

Although a high potential of palladium as a catalyst for the methanol synthesis from carbon oxides and hydrogen has been claimed, the actual activity on a weight of catalyst basis is disappointing compared with conventional copper catalysts [1–6]. Ponec pointed out that Pd^+ species on the surface are active in the methanol synthesis, however, stabilization of the species by promoters was not successful [7–9]. In the case of the methanol decomposition to carbon monoxide and hydrogen (the reverse reaction of the synthesis), the cationic palladium species is considered to be also highly active and the species can be produced by interaction between nanometer-size palladium particles and the support such as ceria [10]. Matsumura et al. reported the formation of cationic palladium species in Pd/ZrO_2 prepared by the deposition–precipitation method while no such species can be observed in the sample prepared by the conventional impregnation technique [11]. In this paper we will show a high performance of Pd/CeO_2 prepared by deposition–precipitation for the methanol synthesis.

2. Experimental

Two ceria-supported palladium catalysts were prepared from different palladium precursors by the deposition–precipitation method. Powder of CeO_2 (Daiichi Kigenso Kagaku Kogyo, Grade A), whose surface area was 98 $m^2\,g^{-1}$, was dispersed in an aqueous solution of $PdCl_2$ (Kishida Kagaku, GR grade) or $Pd(NO_3)_2$ (Kishida, GR). Palladium hydroxide was exclusively precipitated on the surface of CeO_2 by addition of 1 M Na_2CO_3 solution to the palladium solution and the pH value of the solution was maintained at 10 for 1 h. The resulting solid was washed with distilled water, then vacuum-dried for 1 day and calcined at 500 °C for 5 h in air. The BET surface areas were 107 $m^2\,g^{-1}$ for the sample prepared from $PdCl_2$ (DP-$PdCl_2$) and 105 $m^2\,g^{-1}$ for that from $Pd(NO_3)_2$ (DP-$Pd(NO_3)_2$). The palladium contents of both the samples were 3 wt%. The other sample, IMP-$Pd(NO_3)_2$, was prepared by the conventional impregnation technique from an aqueous solution of $Pd(NO_3)_2$ using the same CeO_2 powder (Pd content 3 wt%). It was also vacuum-dried for 1 day, then calcined at 500 °C for 5 h in air. The surface area was 93 $m^2\,g^{-1}$.

Catalytic tests were performed with a fixed-bed continuous-flow reactor. A catalyst (0.5 g, 50–75 mesh) diluted with 2 g of quartz sand was placed in a stainless tube reactor of which i.d. was 9 mm. After the catalyst was reduced in a stream of 10 vol% hydrogen diluted with nitrogen (3.6 $dm^3\,h^{-1}$) at 300 °C for 1 h under atmospheric pressure, a mixture of carbon monoxide (33 vol%) and hydrogen (67%) was fed at 250 °C (flow rate, 1.8 $dm^3\,h^{-1}$ in STP). The reaction pressure was kept at 2.0 MPa using a back-pressure valve placed on the exit of the reactor. The outlet gas was analyzed with two on-line gas chromatographs (Okura Riken type 802 with TCD for hydrogen, carbon oxides, and methane, and type 103 with FID for hydrocarbons, methanol, and dimethyl ether). Yields were calculated on the basis of the quantity of carbon monoxide converted to products.

Profiles of EXAFS for the samples were taken at room temperature in transmission mode for K-edges of Pd at beam-line BL01B1 of SPring-8. The samples were reduced with hydrogen (0.02 MPa) at 300 °C for 1 h in a vacuum line and sealed with polyethylene films in nitrogen

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atmosphere. The Fourier transformation was performed on k^3-weighted EXAFS oscillations in the range of 3–15 Å^{-1}. Normalization of the EXAFS function was done by dividing the absorption intensity by the height of the absorption edge. A cubic spline background subtraction was carried out. Inverse Fourier transform was obtained within the windows 1.8–2.8 Å in r space. The Pd–Pd reference was derived from the EXAFS of Pd foil. The analysis was performed with a program of "REX" supplied by Rigaku.

X-ray photoelectron spectra were recorded at room temperature with a Shimadzu ESCA-KM. The samples 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.

3. Results and discussion

Methanol was effectively synthesized from carbon monoxide and hydrogen at 250 °C over the palladium catalyst prepared by deposition–precipitation (figure 1). The catalytic activity of DP-PdCl$_2$ gradually increased for the first 4 h, and then decreased while the selectivity was always more than 95%. The major by-product was methane and a slight amount of dimethyl ether was also detected. The maximum yield was 12.6% with the selectivity of 96.6%. The activity of DP-Pd(NO$_3$)$_2$ was lower than that of DP-PdCl$_2$, however, it was significantly higher than that of IMP-Pd which produced the maximum yield of 1.2% with the selectivity of 94.8%. The maximum methanol yield produced with DP-Pd(NO$_3$)$_2$ was 7.8% with the selectivity of 95.9%. The space time yield (STY) of methanol is generally employed for comparison of methanol synthesis catalysts, and that produced with DP-PdCl$_2$ was 6.7 mmol h^{-1} g^{-1} at the maximum and it was comparable with those of copper catalysts for methanol synthesis [3,12]. The STY with IMP-Pd(NO$_3$)$_2$ was only 0.6 mmol h^{-1} g^{-1} at the maximum while that with impregnated 1.6% Pd/CeO$_2$ was reported to be 0.07 mmol h^{-1} g^{-1} at 250 °C and at 1.5 MPa by Sudhakar and Vannice [5].

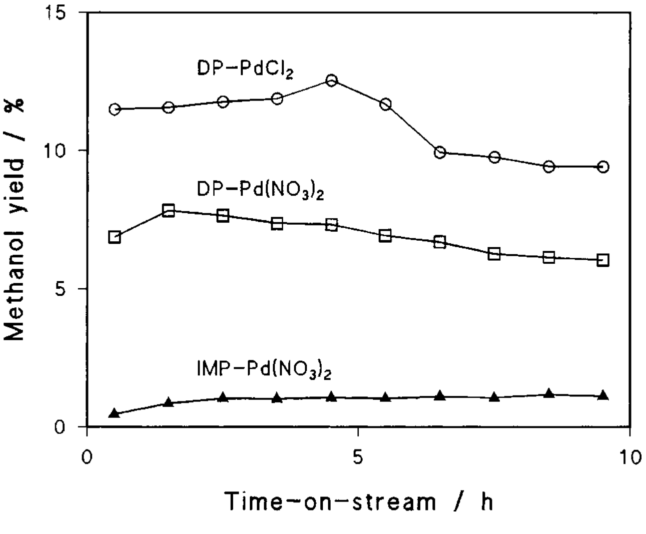

Figure 1. Methanol synthesis from carbon monoxide and hydrogen over 3 wt% Pd/CeO$_2$ at 250 °C. Reaction conditions: pressure 2.0 MPa, $F/W = 3.6$ dm^3 h^{-1} g^{-1}.

The Pd K-edge EXAFS (extended X-ray absorption fine structure) spectra of the palladium catalysts reduced at 300 °C were recorded. The XANES (X-ray absorption near-edge structure) spectra for the three samples were similar to that of palladium foil (figure 2). The Fourier transformation of the spectra show the presence of metallic Pd–Pd bonding at 2.4 Å in all the samples (figure 3) [13]. The coordination numbers and distances of Pd–Pd determined by curve-fitting are described in table 1. Prediction of particle size for metallic species from the EXAFS data has gained widespread use. The standard procedure was proposed by Greegor and Lytle [14,15] and the particle sizes of palladium in DP-PdCl$_2$, DP-Pd(NO$_3$)$_2$, and IMP-Pd(NO$_3$)$_2$ can be estimated as 0.5, 1.2, and 0.6 nm, respectively. Clausen et al. criticized the procedure on the

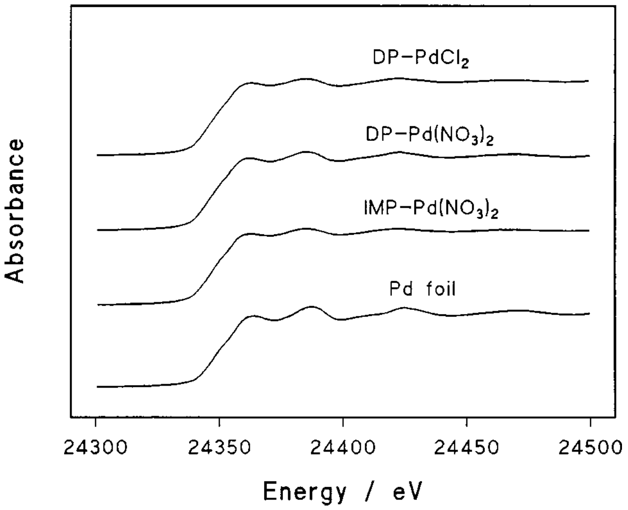

Figure 2. Pd K-edge XANES spectra of 3 wt% Pd/CeO$_2$ reduced at 300 °C.

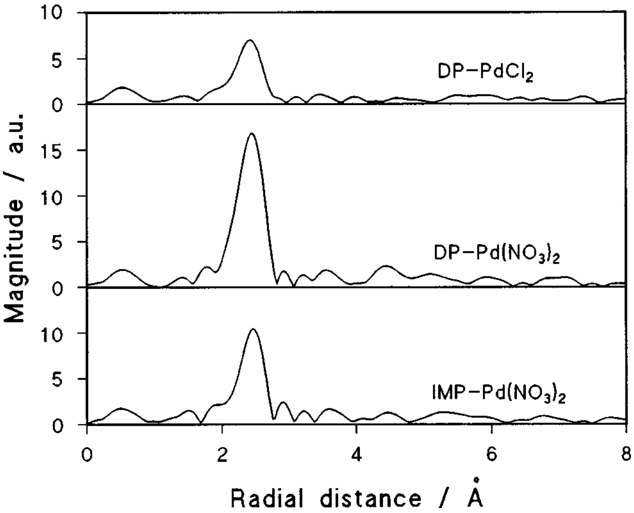

Figure 3. Fourier-filtered Pd K-edge pseudoradial distribution functions of 3 wt% Pd/CeO$_2$ reduced at 300 °C.

Table 1
EXAFS parameters of 3 wt% Pd/CeO_2 reduced at 573 K.

Sample	Interatomic distance, $R_{\mathrm{Pd-Pd}}$ (Å)	Coordination number, N	Debye–Waller factor, σ (Å)
Pd foil	2.74	12.0	0.070
DP-$PdCl_2$	2.71	4.1	0.082
DP-$Pd(NO_3)_2$	2.73	7.3	0.071
IMP-$Pd(NO_3)_2$	2.72	4.6	0.074

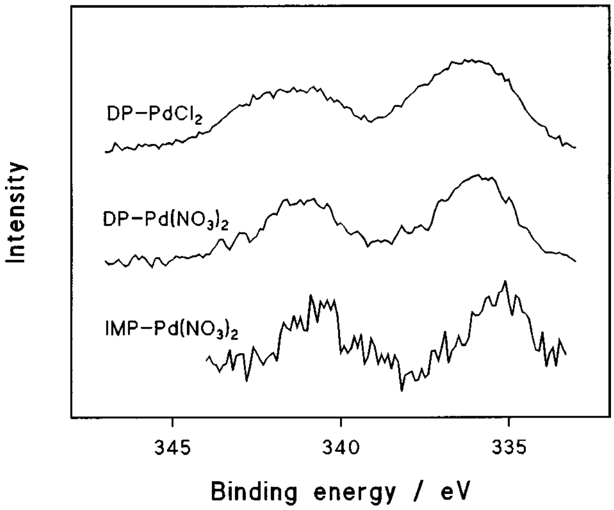

Figure 4. XPS of Pd 3d region for 3 wt% Pd/CeO_2 reduced at 300 °C.

basis of molecular dynamics simulations and they showed that the particle size determined by the standard method is underestimated [16]. However, it is strongly suggested that palladium particles in the impregnated sample are dispersed as well as in DP-$PdCl_2$ and the particle size for DP-$Pd(NO_3)_2$ is considerably larger. Hence, the difference in the activity between the catalysts prepared by impregnation and deposition–precipitation is not simply due to the dispersion of palladium particles. The Debye–Waller disorder factor decreased with an increase in the particle size estimated, but the decrease was small, suggesting that the palladium particles on the samples are fairly well crystallized.

Surface analyses of the palladium samples reduced at 573 K *in situ* were performed by X-ray photoelectron spectroscopy (figure 4). The binding energies of Pd $3d_{5/2}$ for DP-$Pd(NO_3)_2$ and DP-$PdCl_2$ were 335.9 and 336.2 eV, respectively, and considerably higher than that for IMP-$Pd(NO_3)_2$ (335.1 eV). The binding energies of O 1s were 529.6–529.8 eV, regardless of the samples. The binding energy for palladium metal is 335.0 eV [17]. The higher binding energies for the samples prepared by deposition–precipitation show that the surface palladium species are cationic although the EXAFS data evidence that the palladium particles take metallic structure. Kili et al. reported that Pd $3d_{5/2}$ at 336.8 ± 1 eV is attributed to PdO in Pd/γ-Al_2O_3 modified with cerium or lanthanum oxide [18]. Hence, the valence of the palladium species on DP-$Pd(NO_3)_2$ and DP-$PdCl_2$ can be estimated to be close to $1+$, and the cationic species may be the active sites of methanol synthesis, as proposed by Ponec [7–9]. The higher activity of the latter catalyst is probably caused by the higher dispersion of palladium particles. The cationic species will be produced by electron transfer from palladium to ceria, showing the strong interaction between palladium particles and the support. It is supposed that formation of palladium hydroxide takes place mainly on basic sites on cerium oxide in the process of deposition–precipitation and chemical bonding such as Pd–O–Ce can be formed in the interface of palladium particles and the support during the calcination process. Consequently, the high activity of the catalyst prepared by deposition–precipitation may be due to the strong contact which produces cationic palladium species being active in the methanol synthesis.

Acknowledgement

The synchrotron radiation experiment was performed with the approval of the Japan Synchrotron Radiation Research Institute (Proposal No. 1999A0032-NX-np). WS acknowledges the fellowship of the New Energy and Industrial Technology Development Organization of Japan.

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