Catalytic activity of palladium supported on mesoporous zirconium oxide in low-temperature methanol decomposition

Mahendra P. Kapoor, Yuichi Ichihashi, Wen-Jie Shen and Yasuyuki Matsumura *

National Institute of Advanced Industrial Science and Technology, Ikeda, Osaka 563-8577, Japan
E-mail: yasuyuki@rite.or.jp

Received 9 February 2001; accepted 10 July 2001

Methanol decomposition to hydrogen and carbon monoxide can be effectively catalyzed at 160–220 °C over palladium supported on mesoporous zirconium oxide by the deposition–precipitation method. The electronic state and the particle size of palladium in the catalyst are very similar to those of palladium supported on non-porous zirconium oxide, but the palladium surface area of the former sample is smaller than that of the latter. However, the activity of the mesoporous catalyst is significantly higher than that of the non-porous catalyst, implying a promotional effect of the mesoporous structure.

KEY WORDS: palladium; mesoporous zirconium oxide; methanol decomposition; EXAFS; XPS

1. Introduction

Palladium is active for the catalytic methanol decomposition to carbon monoxide and hydrogen while this endothermic reaction is applicable to the energy recovery of the waste heat from methanol-fueled automobiles and from industries [1–6]. The activity is enhanced by the strong interaction between palladium and the support which produces active palladium species [1–3]. Zirconium oxide is one of the effective supports of palladium, especially when the catalyst is prepared by the deposition–precipitation method [1]. As a support material mesoporous compounds such as MCM-41 are often advantageous because of their porous structure with large surface area which may give high dispersion of the catalytic metals [7]. Hence, it can be expected that zirconium oxide with mesoporous structure will be an effective support of palladium. In the present paper, we will show that the activity of palladium supported on mesoporous zirconium oxide is significantly high in comparison with non-porous zirconia support.

2. Experimental

Mesoporous zirconium oxide with a high surface area was synthesized according to the method reported by Ciesla *et al*. [8] except that ammonium carbonate was used instead of ammonium sulfate. The synthesized material was dried at 90 °C overnight and calcined in air at 400 °C for 4 h. Formation of the mesoporous structure was confirmed with the X-ray diffraction pattern in which peaks at 2.7°, 5.4°, and 7.9° in 2θ (Cu Kα) were present. The BET surface area determined from the physisorption isotherm of nitrogen was 365 $m^2\ g^{-1}$.

Palladium was supported on the mesoporous zirconium oxide by the deposition–precipitation method described elsewhere [3]. Palladium hydroxide was exclusively precipitated on the oxide in a $PdCl_2$ (Kanto Kagaku, GR grade) aqueous solution by gradual addition of 1 M Na_2CO_3 solution. After it had been washed with distilled water several times, the solid was dried at 120 °C overnight and calcined in air at 300 °C for 3 h. The sample (Pd/ZrO_2-MS) contained 3 wt% of palladium. After the loading of palladium the XRD peak originally present at 2.7° (d-spacing, 3.3 nm) shifted to 2.2° (4.0 nm), but the peak intensities were similar. The BET surface area decreased to 254 $m^2\ g^{-1}$. For a comparison purpose palladium supported on a commercial zirconium oxide powder (Daiichi Kigenso Kagaku Kogyo, RC-100) was also prepared by the same procedure as described above. The sample (Pd/ZrO_2) also contained 3 wt% of palladium and the BET surface area was 91 $m^2\ g^{-1}$.

Catalytic reaction was performed in a fixed-bed continuous-flow reactor under atmospheric pressure. A catalyst (0.20 g) diluted with 1.0 g of quartz sand being inert under the reaction conditions was sandwiched with quartz wool plugs in a quartz tube reactor of 6 mm i.d. The samples were reduced in a flow of 20 vol% hydrogen diluted with argon (flow rate, 9.6 $dm^3\ h^{-1}$) for 1 h at 300 °C, then 20 vol% of methanol was fed with an argon carrier (total flow rate 4.8 $dm^3\ h^{-1}$) at a desired temperature. The outlet gas was analyzed with an on-stream gas chromatograph (Yanagimoto G2800) equipped with a Porapak-T column (4 m) and a thermal conductivity detector.

X-ray photoelectron spectra (XPS) were recorded at room temperature with a Shimadzu ESCA 750. After reduction with hydrogen (0.02 MPa) at 300 °C for 1 h in a vacuum line, the sample was mounted in air to a sample holder. In order

---

[*] To whom correspondence should be addressed. Present address: Research Institute of Innovative Technology for the Earth, Kizu-cho, Soraku-gun, Kyoto 619-0292, Japan.

1011-372X/01/1000-0139$19.50/0

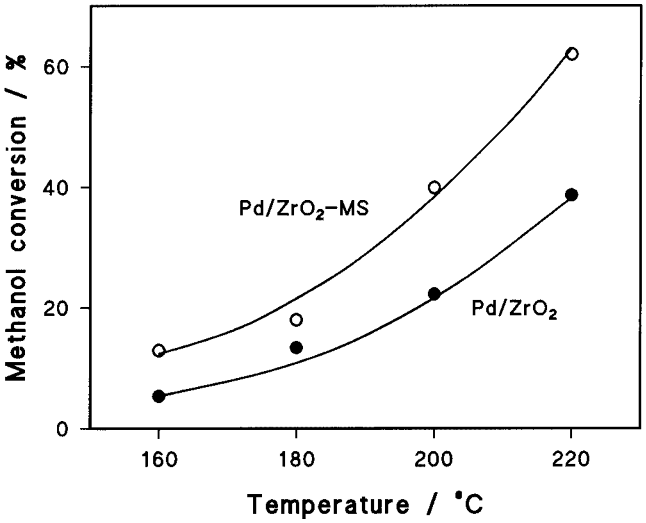

Figure 1. Catalytic activity of palladium supported on mesoporous and non-porous zirconium oxide to methanol decomposition.

to remove surface adsorbates, Ar ion sputtering for 0.5 min at 2 kV and 20 mA was carried out just before the measurement. Binding energies were corrected by the reference of the C 1s line at 284.6 eV.

EXAFS profiles for the samples were taken at room temperature in transmission mode for K-edges of Pd at beamline 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 atmosphere. The Fourier transformation was performed on k^3-weighted EXAFS oscillations in the range of 30–150 nm^{-1}. Inverse Fourier transform was obtained within the windows 0.19–0.53 nm in r space. The Pd–Pd reference was derived from the EXAFS of Pd foil.

Adsorption experiments were performed with a vacuum system equipped with Baratron vacuum gauges after the samples were reduced with hydrogen at 300 °C for 1 h.

3. Results and discussion

Palladium supported on mesoporous zirconium oxide (Pd/ZrO_2-MS) effectively catalyzed the selective methanol decomposition to carbon monoxide and hydrogen at 160–220 °C. The activity was significantly higher than that for Pd/ZrO_2 whose support was non-porous zirconium oxide (figure 1). This finding shows that the mesoporous compound is an effective support of the palladium catalyst for the methanol decomposition.

X-ray photoelectron spectroscopy was employed for analysis of the electronic state of palladium in the samples because the valence of palladium is believed to relate to the catalytic activity in the methanol decomposition [1–3]. In order to observe the palladium particles inside the pores, reduced Pd/ZrO_2-MS was ground to fine powder in air at room temperature. It was confirmed that the handling in air does not seriously affect the XPS spectra of palladium by the reference of the XPS of a sample reduced *in situ*. As shown in figure 2, the XPS peaks of Pd 3d and Zr 3p overlapped in the spectrum; however, the peaks of Pd 3d can be separated using Gaussian functions with the separation of 5.3 eV between the Pd $3d_{5/2}$ and Pd $3d_{3/2}$ peaks [9]. The spectrum was similar to that of the sample prepared without grinding. The binding energy of Pd $3d_{3/2}$ for Pd/ZrO_2-MS was 340.8 eV and this is almost the same as that for Pd/ZrO_2 (340.7 eV); the peaks of Zr $3p_{3/2}$ were at 332.7 and 332.8 eV, respectively. Since the energy of Pd $3d_{3/2}$ for metallic palladium is 340.2 eV and that for PdO will be 341.4 eV assuming the separation of 5.3 eV from the energy of Pd $3d_{5/2}$ [9], the binding energy for the palladium samples strongly suggests the presence of cationic palladium species whose valence is close to $1+$ in the catalysts after the reduction; whereas the species are considered to be active in the methanol decomposition [1–3]. Hence, both the samples contain the active palladium species, but it does not account for the difference in activity.

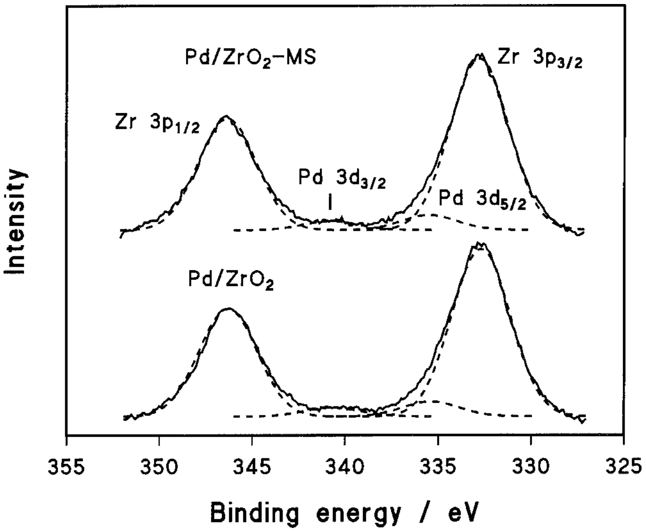

Figure 2. X-ray photoelectron spectra of Pd 3d and Zr 3p for palladium supported on mesoporous and non-porous zirconium oxide.

In order to analyze the physical state of palladium, the Pd K-edge EXAFS (extended X-ray absorption fine structure) spectra of the palladium catalysts reduced at 300 °C were recorded. The X-ray absorption near-edge structure (XANES) of Pd/ZrO_2-MS was very similar to that of Pd/ZrO_2 (not shown). The Fourier transforms of the Pd K-edge EXAFS show the presence of metallic Pd–Pd bonding at 0.24 nm (figure 3). The coordination number of the first Pd–Pd shell for Pd/ZrO_2-MS determined by curve-fitting was 9.9 (Pd–Pd distance, 0.275 nm) which is very close to 9.4 (0.275 nm) for Pd/ZrO_2. The EXAFS parameters for the higher shells were not exact, but they were included in the calculation to increase the accuracy of the first-shell fitting (table 1). The calculated curve of k^3-weighted Pd K-edge EXAFS oscillations well fit the experimental data (figure 4). Since the coordination number relates basically to the number of atoms in a particle, the mean size of palladium particles in Pd/ZrO_2-MS is similar to that for Pd/ZrO_2. Predic-

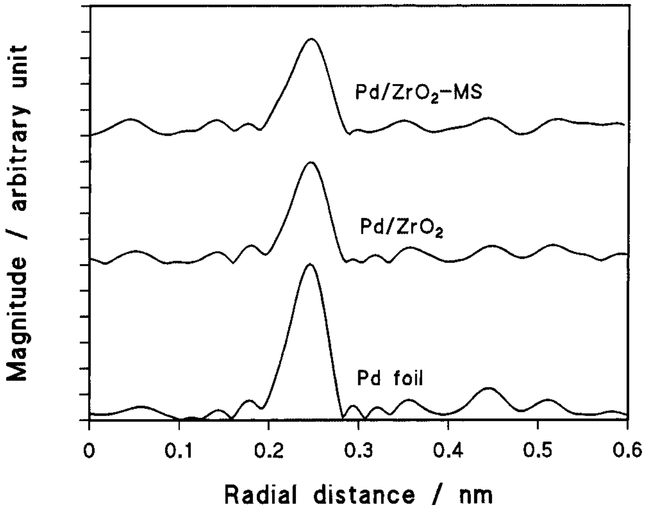

Figure 3. Fourier-filtered Pd K-edge pseudoradial distribution functions of palladium supported on mesoporous and non-porous zirconium oxide.

Table 1
EXAFS parameters of Pd–Pd interaction for palladium catalysts reduced at 300 °C.

Sample	Interatomic distance, R (nm)	Coordination number, N	Debye–Waller factor, σ (nm)
Pd foil	0.275	12.0	0.0060
	0.389	6.0	0.0061
	0.476	24.0	0.0060
	0.550	12.0	0.0062
Pd/ZrO_2-MS	0.275	9.9	0.0070
	0.38	8	0.008
	0.48	13	0.006
	0.55	5	0.006
Pd/ZrO_2	0.275	9.4	0.0068
	0.39	5	0.005
	0.48	16	0.006
	0.55	11	0.006

tion of particle size for metallic species from the coordination number has gained widespread use. The mean particle sizes of palladium in both the samples can be estimated as *ca.* 2 nm on the basis of the standard procedure proposed by Greegor and Lytle assuming spherical particles, while the size is appreciably larger when the shape of the particle is flat [10]. In case of the samples prepared by the deposition–precipitation technique, metals often contact strongly with the surface of the support and the shape of the metal particle is rather flat and close to a hemisphere [11]. No XRD peak of Pd(111) at around 40° in 2θ was recorded with both samples reduced at 300 °C, suggesting that the crystallite size is smaller than 4 nm.

In order to determine the surface area of palladium, adsorption of hydrogen was carried out at room temperature with the samples reduced at 300 °C (figure 5). The metallic surface area of palladium can be calculated from the quantity of hydrogen chemisorbed on the surface assuming that hydrogen atoms are stoichiometrically adsorbed on palladium atoms whose site density is 1.3×10^{19} m^{-2} [12].

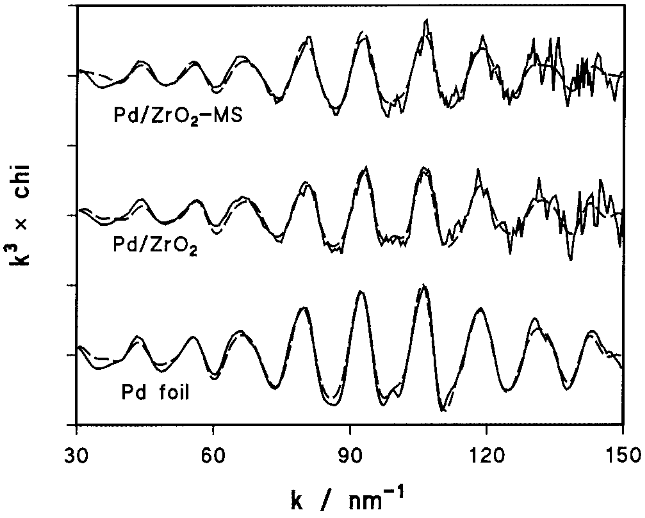

Figure 4. k^3-weighted Pd K-edge EXAFS oscillations of palladium supported on mesoporous and non-porous zirconium oxide. Solid line, experimental data; broken line, calculated fit.

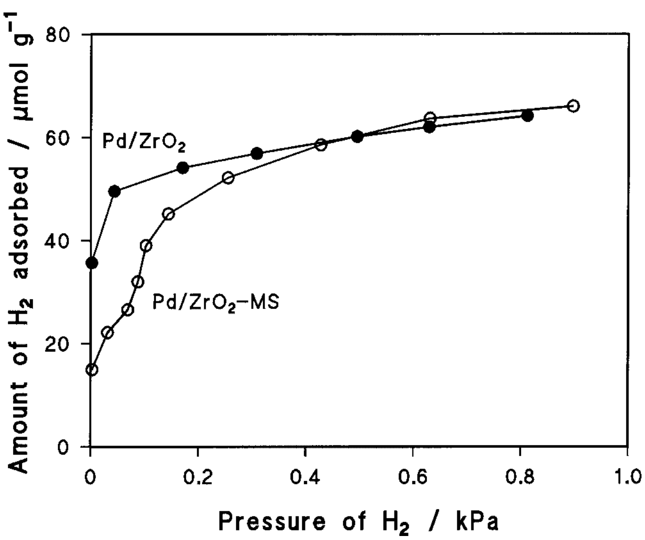

Figure 5. Hydrogen adsorption at room temperature on palladium supported on mesoporous and non-porous zirconium oxide.

The area for Pd/ZrO_2 was 3.2 m^2 g-cat^{-1} on the basis of the amount of hydrogen irreversibly adsorbed (35 μmol g^{-1}). Although the result of EXAFS indicates that the particle size of palladium in Pd/ZrO_2-MS is close to that for Pd/ZrO_2, the palladium area for Pd/ZrO_2-MS was only 1.4 m^2 g-cat^{-1} (the amount of hydrogen irreversibly adsorbed, 15 μmol g^{-1}). The drastic decrease in the BET surface area from 365 to 254 m^2 g^{-1} in the process of palladium modification on the mesoporous compound shows the possibility that a considerable part of palladium particles are confined in blind pores while the particle size is probably close to the pore size. The increase in the *d*-spacing of the mesoporous compound from 3.3 to 4.0 nm by the loading of palladium may suggest that the presence of palladium particles expand the pore structure. However, the amount of hydrogen reversibly adsorbed on Pd/ZrO_2-

MS was similar to that for Pd/ZrO_2 (see figure 5), indicating that a major part of palladium in the mesopores can contact with hydrogen which mainly absorbed in the bulk phase. Thus, it can be supposed that palladium particles are three dimensionally in contact with the wall of the mesopore which results in the smaller area of the palladium surface.

Although the catalytic activity should relate to the surface area of palladium and the lower area is a disadvantage of Pd/ZrO_2-MS, the activity is higher than that of Pd/ZrO_2. Interaction between palladium and zirconium oxide is an important factor of the catalytic activity, especially in the case of the catalyst prepared by deposition–precipitation [1]. Since no catalytic activity was found with zirconium oxide, the perimeter of palladium and the support should be highly active. In the case of Pd/ZrO_2-MS, the palladium particles are considered to be surrounded by the wall of zirconium oxide; hence, the proportion of the perimeter to a whole palladium surface will be larger than in Pd/ZrO_2 and it may cause the higher activity. On the perimeter, concentration of methanol is supposed to be higher because zirconium oxide can adsorb methanol [13], and this may be another advantage of the three dimensional structure to the methanol decomposition. The similar effect was observed with nickel supported on a porous glass of which the pore diameter is close to the nickel particles in the catalyst [14].

Acknowledgement

The synchrotron radiation experiment was performed with the approval of the Japan Synchrotron Radiation Research Institute (Proposal No. 2000A0410-NX-np).

References

[1] Y. Matsumura, M. Okumura, Y. Usami, K. Kagawa, H. Yamashita, M. Anpo and M. Haruta, Catal. Lett. 44 (1997) 189.
[2] Y. Usami, K. Kagawa, M. Kawazoe, Y. Matsumura, H. Sakurai and M. Haruta, Appl. Catal. A 171 (1998) 123.
[3] W.-J. Shen and Y. Matsumura, Phys. Chem. Chem. Phys. 2 (2000) 1519.
[4] National Research Council, *Catalysis Looks to the Future* (National Academy Press, Washington, DC, 1992).
[5] W.H. Cheng, Appl. Catal. A 130 (1995) 13.
[6] W.H. Cheng, C.Y. Shiau, T.H. Liu, H.L. Tung, J.F. Lu and C.C. Hsu, Appl. Catal. A 170 (1998) 215.
[7] C.A. Koh, R. Nooney and S. Tahir, Catal. Lett. 47 (1997) 199.
[8] U. Ciesla, S. Schacht, G.D. Stucky, K.K. Unger and F. Schuth, Angew. Chem. Int. Ed. Eng. 35 (1996) 541.
[9] C.D. Wagner, W.N. Riggs, L.E. Davis and J.F. Joulder, *Handbook of X-ray Photoelectron Spectroscopy*, ed. G.E. Muileuberg (Perkin–Elmer, MN, 1978).
[10] R.B. Greeegor and F.W. Lytle, J. Catal. 63 (1980) 476.
[11] T. Akita, K. Tanaka, S. Tsubota and M. Haruta, J. Electron Microsc. 49 (2000) 657.
[12] S.-Y. Wang, S.H. Moon and M.A. Vannice, J. Catal. 71 (1981) 167.
[13] M.-Y. He, J.M. White and J.G. Ekerdt, J. Mol. Catal. 30 (1985) 415.
[14] Y. Matsumura, K. Kuraoka, T. Yazawa and M. Haruta, Catal. Today 45 (1998) 191.