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Low-temperature decomposition of methanol to carbon monoxide and hydrogen with low activation energy over Pd/ZrO_2 catalyst

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Palladium nano-particles in 2 wt% Pd/ZrO_2 prepared by the deposition–precipitation method interact strongly with zirconium oxide. The catalyst is significantly active to the methanol decomposition to carbon monoxide and hydrogen at less than 500 K with the apparent activation energy of ca. 80 kJ mol^{-1} compared with 2 wt% Pd/ZrO_2 prepared by the impregnation technique which produces the activation energy of ca. 100 kJ mol^{-1}.

Keywords: palladium supported on zirconium oxide, dehydrogenation of methanol, deposition–precipitation method, XAFS, XPS

1. Introduction

The decomposition of methanol to carbon monoxide and hydrogen at low temperature is attracting growing interest for use of methanol-fueled vehicles and for other heat-recovery systems [1]. Copper, nickel, and palladium are known to be active for the methanol decomposition to carbon monoxide and hydrogen; however, the activity at low temperatures below 500 K is not sufficiently high [1–4]. Zirconium oxide has been reported as an effective support for palladium [3,4], and, interestingly, a rough calculation for 1 wt% Pd/ZrO_2 prepared by the impregnation method at 543–583 K gives an apparent activation energy of ca. 90 kJ mol^{-1} on the basis of the kinetic data reported by Fukuhara et al. [4] while the enthalpy change of the reaction is 98.0 kJ mol^{-1} at 500 K. In the present paper we show that the catalytic activity of Pd/ZrO_2 at low temperatures around 500 K can be further improved by the catalyst preparation using the deposition–precipitation method. Over the catalyst the apparent activation energy can be reduced to 80 kJ mol^{-1} while the dehydrogenation takes place through several elementary steps on the catalyst surface.

2. Experimental

A palladium catalyst was prepared from 0.01 M HCl aqueous solution of $PdCl_2$ (Kishida Chemicals Co. Ltd.) in which ZrO_2 powder (Daiichi Kigenso Kagaku Kogyo Co. Ltd., RC-100, specific surface area 83.8 $m^2\ g^{-1}$) was dispersed. Palladium hydroxide was exclusively precipitated on the surface of ZrO_2 by addition of 1 M NaOH solution to the $PdCl_2$ 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 773 K for 5 h in air. The content of palladium metal in the sample (denoted as Pd-dep) was determined as 2.0 wt% by emission spectral analysis and the sodium content was less than 0.01 wt%. The other sample was prepared by the conventional impregnation technique from an aqueous solution of $PdCl_2$ using the same ZrO_2 powder. The sample (Pd-imp) containing 2 wt% of palladium was also vacuum-dried for 1 day, then calcined at 773 K for 5 h in air.

Adsorption experiments were performed with a vacuum system equipped with Baratron vacuum gauges after the samples were reduced with hydrogen (20 kPa) at 673 K for 1 h. X-ray absorption near edge structures (XANES) of the samples reduced with hydrogen were taken in transmission mode for K-edges of Pd at beamline 10B of the Photon Factory in Tsukuba, Japan. X-ray photoelectron spectra (XPS) were recorded with the samples reduced with hydrogen in a Shimadzu ESCA-KM.

Catalytic reaction was performed with a conventional fixed-bed flow reactor under atmospheric pressure. A catalyst (0.05–0.20 g; when the quantity is less than 0.20 g, ZrO_2 was used as a filler and the total mass was kept at 0.20 g) was sandwiched with quartz wool plugs in a quartz tube reactor (i.d. 6 mm). The materials other than the catalysts were confirmed to be inert in the reaction. The catalyst was reduced in a flow of 20 vol% hydrogen in argon at 673 K for 1 h, then 25% of methanol was fed with an argon carrier at 453–513 K.

3. Results and discussion

The adsorption isotherms of hydrogen at room temperature for Pd-dep and Pd-imp reduced with hydrogen at 673 K were similar, and the quantities of hydrogen irreversibly adsorbed were 34 μmol g^{-1} for the former and 30 μmol g^{-1} for the latter. On the basis of these values, mean particle diameters of palladium are tentatively calculated as 3.1 nm for Pd-dep and 3.5 nm for Pd-imp assuming that the particles are spherical and the site density of a palladium atom is 1.3×10^{19} m^{-2} [5]. It is consistent with the result that no peaks attributed to palladium were recorded in the XRD patterns of these samples after the reduction. The BET surface areas for the samples were 92.5 m^2 g^{-1} for Pd-dep and 81.1 m^2 g^{-1} for Pd-imp.

Despite the poor S/N ratio caused by the interference of zirconium, significantly different XANES were recorded for both the two samples reduced at 673 K. The XANES for Pd-imp was similar to that for palladium black (metallic palladium); however, in the spectrum of Pd-dep the absorption peak at ca. 24380 eV was small (figure 1). The shape of the latter is rather close to that for oxidized palladium particles [6], suggesting that palladium particles of Pd-dep are not fully metallic but oxidized, at least in part.

The oxidized state of Pd in Pd-dep is also supported by the XPS of the samples reduced in situ. Although the peaks for Pd 3d were observable for Pd-imp at 334.6 and 340.5 eV which are close to the binding energies for palladium metal [7], the peaks for Pd-dep were not obvious by overlap with the peaks for Zr 3p at 332.8 and 346.4 eV and the binding energy of Pd 3d$_{3/2}$ can be read at 341.4 eV (figure 2). The mixed peak of Pd 3p$_{3/2}$ and O 1s for Pd-imp was deconvoluted into Pd 3p$_{3/2}$ at 532.2 eV and O 1s at 530.1 eV, but the peak for Pd-dep was resolved into three peaks at 532.6 eV for Pd 3p$_{3/2}$, at 530.0 eV for O 1s, and at 531.8 eV. The higher binding energies of Pd 3d$_{3/2}$ and Pd 3p$_{3/2}$ for Pd-dep evidence that palladium in Pd-dep is cationic. The peak of O 2s for Pd-dep was also deconvoluted into two peaks at 21.5 and 22.7 eV, but that for Pd-imp was single at 21.6 eV (not shown). Thus, the peak at 531.8 eV can be assigned to O 1s, suggesting presence of oxygen strongly interacting with palladium. The hydroxyl groups on the surface of the support would be responsible for the peak because Pd-dep was prepared in an alkaline solution. However, no such peaks at 531.8 or 22.7 eV were recorded with a different aliquot of zirconium oxide pretreated with 1 M NaOH solution for 1 h and washed with distilled water, then heated at 773 K for 5 h. Although the binding energies of the Zr 3d$_{5/2}$ peak for both the samples were the same, 182.2 eV, the shape of the Zr 3d peaks for Pd-dep was different from that for Pd-imp. That is, the splitting between Zr 3d$_{5/2}$ and 3d$_{3/2}$ was 2.1 eV for Pd-dep, discernibly smaller than 2.3 eV observed for Pd-imp, which is usual for Zr 3d peaks [7]. This difference is probably a reflection of the strong interaction between palladium particles and the surface of zirconium oxide via oxygen in Pd-dep. The bonding of Pd–O–Zr in Pd-dep may be formed in the process of the catalyst preparation.

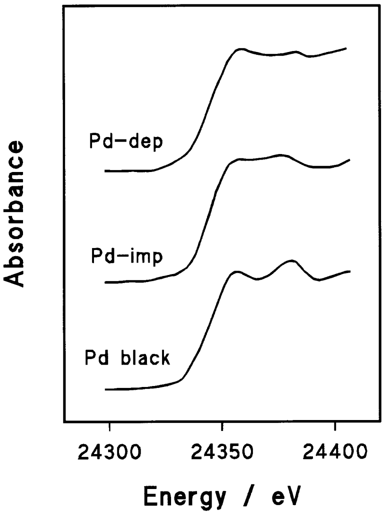

Figure 1. XANES of Pd K-edge for palladium supported on zirconium oxide reduced with hydrogen at 673 K for 1 h.

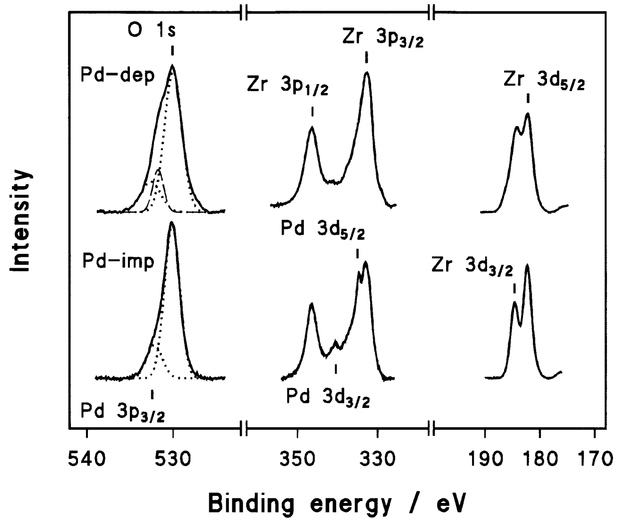

Figure 2. X-ray photoelectron spectra for palladium supported on zirconium oxide reduced with hydrogen at 673 K for 1 h. The peak intensities are normalized using atomic sensitivity factors for O 1s (0.66), Zr 3p$_{3/2}$ (0.72), and Zr 3d$_{5/2}$ (1.5) [8].

The selective decomposition of methanol to carbon monoxide and hydrogen was catalyzed over both samples at reaction temperatures around 500 K; however, Pd-dep was significantly more active than Pd-imp (figure 3). The conversion of methanol was not proportional with the contact time (W/F) even at low conversions less than 10%. The curves can be fitted with the equation $X = a(W/F)^b$, where X is the conversion and b is in the range from 0.55 to 0.72. The value of ΔG at 453 K is -10.9 kJ mol^{-1}, and the equilibrium conversion

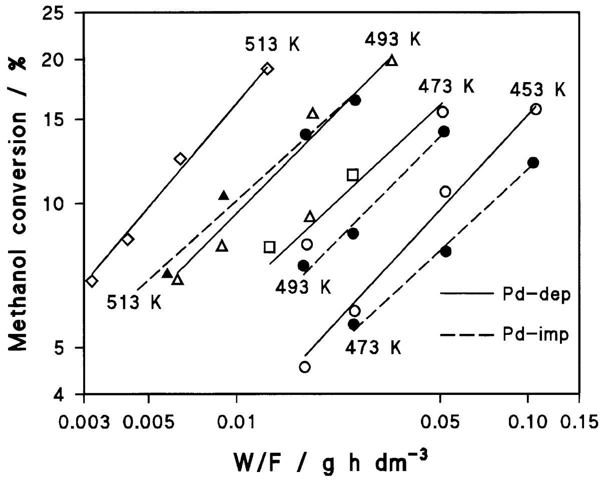

Figure 3. The catalytic activity of palladium supported on zirconium oxide to methanol decomposition. The data are plotted with logarithmic scales. Amount of catalyst: (○, ●) 0.20 g; (□) 0.10 g; (△, ▲) 0.07 g; (◇) 0.05 g.

is nearly 100% under the reaction conditions. Hence, the relation between conversion and contact time is not caused by the reverse reaction, but rather due to poisoning of the active sites with carbon monoxide produced. The rates of the reaction were determined from the tangents of the curves at $X = 7.0$, 10.0, and 13.0%. Apparent activation energies obtained from the Arrhenius plots were 75.1, 76.9, and 78.3 kJ mol^{-1} for Pd-dep at $X = 7.0$, 10.0, and 13.0%, respectively. On the other hand the activation energies for Pd-imp are 102.5, 99.6, and 97.5 kJ mol^{-1}, respectively. The values are higher than that calculated from the data reported by Fukuhara et al. for 1 wt% Pd/ZrO$_2$ at 543–583 K by ca. 10 kJ mol^{-1} [4].

These experimental results show that the palladium particles strongly interacting with zirconium oxide is advantageous in the methanol decomposition. The decomposition of methanol over palladium is roughly comprised of three steps: (1) dissociative adsorption of methanol to form surface methoxyl groups, (2) decomposition of the surface methoxyl groups to surface carbon monoxide and hydrogen, and (3) desorption of surface carbon monoxide and hydrogen [9–13]. Fukuhara et al. discussed that step (2) is a rate-determining step [4] and the strong interaction between palladium nano-particles and zirconium oxide may reduce the activation energy of this process while further investigation is necessary for the clarification of the mechanism.

Acknowledgement

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