

Interaction between palladium and the support in Pd/CeO₂ prepared by deposition–precipitation method and the catalytic activity for methanol decomposition

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Abstract

Adsorption of carbon monoxide on cerium oxide at room temperature can proceed over 3 wt.% Pd/CeO₂ prepared by a deposition–precipitation method. The quantity of carbon monoxide adsorbed is largely excessive to the content of palladium in the sample while the amount of carbon monoxide adsorbed on 3 wt.% Pd/CeO₂ prepared by the conventional impregnation technique is small. The catalyst prepared by deposition–precipitation is highly active for the methanol decomposition to carbon monoxide and hydrogen at 160°C–220°C compared with the impregnated sample. Analyses by XPS show presence of cationic palladium species in the former catalyst after the reaction while only metallic species can be found in the latter, appearing that there is strong interaction between the palladium species and the support in the catalyst prepared by deposition–precipitation. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Metal–support interaction is often observed on palladium supported on cerium oxide [1–6]. Suppression of carbon monoxide adsorption on ceria-supported palladium occurs after reduction with hydrogen at 500°C while recovery of the adsorption after reoxidation was reported [3]. The phenomenon is generally understood as strong metal–support interaction (SMSI), that is, migration of cerium on the surface of palla-

dium and/or metal encapsulation [1,2]. The reduction temperature affects the catalytic properties to reactions such as hydrogenation of carbon monoxide [4], hydrogenation of benzene [5], and oxygen exchanging of carbon monoxide [6].

Shim et al. [7] reported that Pd–CeO₂ formed from CePd₃ intermetallic compound enhances hydrogenation of butene, butadiene, and butyne, and the behavior is interpreted by spillover of hydrogen and electron transfer from palladium to cerium. When the support of palladium is zirconium oxide, electron transfer from palladium to the support can be observed and it results in promotion of the catalytic activity to methanol decomposition [8]. However, no such

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electron transfer was reported with Pd/CeO₂ prepared by the conventional impregnation method [9]. In the present work, we will show that palladium particles interact with the support strongly and enhance adsorption of carbon monoxide on the support of Pd/CeO₂ prepared by a deposition–precipitation technique. The catalyst is active for the methanol decomposition to carbon monoxide and hydrogen while the endothermic reaction is applicable to energy-recovery system for waste heat [10].

2. Experimental

Palladium supported on cerium oxide (Pd–DP) was prepared from 0.01 M HCl aqueous solution of PdCl₂ (Kishida Chemicals) in which CeO₂ powder (Daiichi Kigenso Kagaku Kogyo) was dispersed. Palladium hydroxide was exclusively precipitated on the surface of CeO₂ by addition of 1 M Na₂CO₃ solution to the PdCl₂ solution and the pH value of the mixture was maintained at 10 for 1 h. The resulting solid was washed with distilled water until no chlorine anion was detected in the rinse water with an AgNO₃ reagent; then it was vacuum-dried for 1 day and calcined at 500°C for 5 h in air. The content of palladium was 3 wt.% and the BET surface area of the sample as prepared was 107 m² g⁻¹. The other sample (Pd–IMP) was prepared by the conventional impregnation technique from an aqueous solution of Pd(NO₃)₂ using the same CeO₂ 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 m² g⁻¹.

Temperature-programmed desorption (TPD) of carbon monoxide from the palladium samples was carried out using a system equipped with a thermal conductivity detector (TCD). A sample (0.20 g) was reduced with 5 vol% of hydrogen diluted with argon (1.8 dm³ h⁻¹) at 300°C for 1 h, then, it was kept under a stream of argon at 300°C for 0.5 h. After cooling the sample to room temperature, carbon monoxide was sup-

plied for 1 h and excessive carbon monoxide on the sample was removed with a flow of argon for 0.5 h. In the measurement, the sample was heated with a rate of 300°C h⁻¹ under an argon flow (1.8 dm³ h⁻¹).

The catalytic tests were performed with a fixed-bed flow reactor under atmospheric pressure. A catalyst (0.20 g, 50–75 mesh) 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. After the catalyst was first reduced with 20 vol% hydrogen in argon (flow rate, 9.6 dm³ h⁻¹) at 300°C for 1 h, 20 vol% of methanol diluted with argon (total flow rate, 4.8 dm³ h⁻¹) was fed at a desired reaction temperature. The effluent gas was analyzed with an on-line gas chromatograph (Yanagimoto G2800) equipped with TCD and a column of Porapak T (4 m).

X-ray photoelectron spectra (XPS) were recorded at room temperature with a Shimadzu ESCA 750. The samples were Ar ion-sputtered for 0.5 min at 2 kV and 20 mA just before the measurement. Binding energies were corrected by the reference of the C 1s binding energy at 284.6 eV.

Powder XRD patterns of the catalysts were recorded with a Rigaku Rotaflex 20 diffractometer using nickel-filtered CuK α radiation (40 kV, 150 mA).

3. Results and discussions

TPD of carbon monoxide was carried out after reduction of the sample with hydrogen at 300°C followed by adsorption of carbon monoxide at room temperature. There was a small desorption peak around 80°C and a major peak around 200°C in the profile of Pd–DP (Fig. 1). Cordatos and Gorte [11] suggested formation of carbon dioxide by reduction of cerium oxide during the TPD of carbon monoxide from Pd/CeO₂ above 200°C. However, according to the literature, the peak of carbon dioxide was

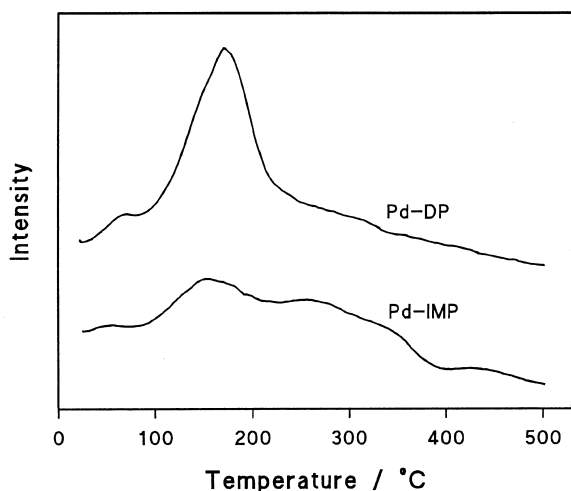


Fig. 1. TPD of carbon monoxide for 3 wt.% Pd/CeO₂.

almost diminished after reduction of the sample. Thus, formation of carbon dioxide is probably negligible in our samples because they were reduced with hydrogen at 300°C for 1 h. The quantity of carbon monoxide desorbed from Pd-DP was estimated as 1.2 mmol g⁻¹ from the peak area. On the other hand, the desorption peak was small in the case of Pd-IMP (see Fig. 1). The amount of carbon monoxide desorbed was estimated to be 0.3 mmol g⁻¹. Since the quantity for Pd-DP is extremely larger than the content of palladium (0.3 mmol g⁻¹), carbon monoxide is mainly adsorbed on the surface of the ceria support in the case of Pd-DP. It is known that irreversible adsorption of carbon monoxide takes place on unmodified ceria reduced at 400°C or above [12,13], but no significant adsorption occurs on ceria reduced at 300°C. Bensalem et al. [14] observed that carbon monoxide is irreversibly adsorbed mainly on palladium sites in impregnated Pd/CeO₂ reduced at 300°C while the surface of ceria support is significantly reduced. It is known that adsorption of carbon monoxide on the surface of ceria without reduction is enhanced by elevation of adsorption temperature [15], suggesting that adsorption of carbon monoxide on ceria is activated at room temperature on Pd-DP in which strong interaction between palladium par-

ticles and the support may take place. The enhancement of the adsorption is not due to presence of residual chlorine on the sample because the use of chlorine-containing metal precursors usually disturbs the adsorption of carbon monoxide on cerium oxide [2].

The catalytic activity of Pd-DP for the methanol decomposition was significantly higher than that of Pd-IMP at 160°C–220°C (Fig. 2). Methanol was selectively decomposed to carbon monoxide and hydrogen. It is noteworthy that the conversion produced by the former catalyst at 160°C was seven times larger than that of the latter. The formation rate of carbon monoxide for Pd-DP at 200°C was 59 mmol g⁻¹ h⁻¹ and the rate produced with 10 wt.% Ni/SiO₂, which is a typical catalyst of methanol decomposition, at 250°C was 41 mmol g⁻¹ h⁻¹ [16], appearing that the palladium catalyst is highly active.

Surface analyses of the palladium samples were performed by X-ray photoelectron spectroscopy. The binding energy of Pd 3d_{5/2} for Pd-DP taken out from the reactor after the reaction at 180°C was 336.1 eV (Fig. 3). The value was considerably higher than that for Pd-IMP (335.1 eV). The binding energy for palladium metal is 335.0 eV and that for palladium oxide is 336.3 eV [17]; in the case of 5

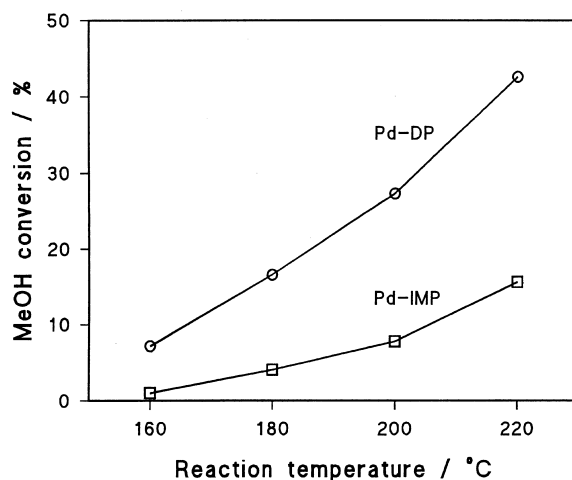


Fig. 2. Catalytic activity of 3 wt.% Pd/CeO₂ for methanol decomposition to carbon monoxide and hydrogen.

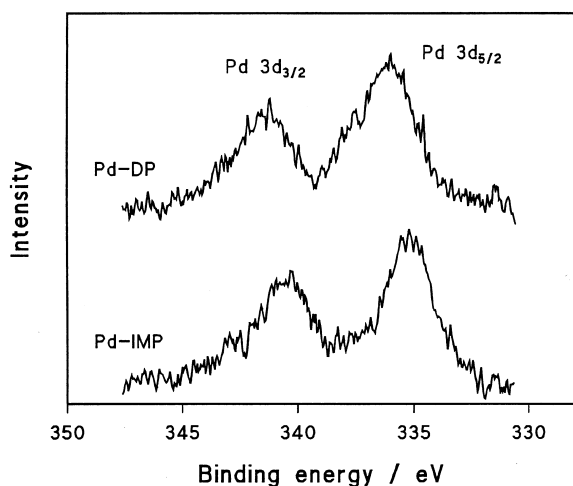


Fig. 3. XPS of 3 wt.% Pd/CeO₂ after reaction at 180°C.

wt.% PdO/MgO, the energy was 336.5 eV [18]. The high binding energy for Pd–DP shows that palladium in Pd–DP is cationic although it was reduced at 300°C, while the cationic species is considered to be highly active in the methanol decomposition [9,19]. This species can be produced by electron transfer from palladium to ceria, showing the strong interaction between palladium particles and the support as mentioned above. The surface atomic ratios of Pd/Ce were determined as 0.044 for Pd–DP and 0.047 for Pd–IMP from the peak areas of Pd 3d and Ce 3d using the atomic sensitivity factors of 4.6 and 10, respectively [20]. Since XPS reflects the condition of few surface atomic layers, dispersion of palladium on the surface depends roughly on the ratio of Pd/Ce and the dispersion for Pd–IMP may be similar to that for Pd–DP. With palladium particles whose crystallite size is 3 nm or above, an XRD peak at ca. 40° in 2θ is detectable under the experimental conditions empirically. However, no such peak was detected in the XRD patterns for either of the samples after reaction, suggesting palladium particles are highly dispersed. 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 process of dehydration. We may infer that the high activity of the palladium catalyst prepared by deposition–precipitation is caused by the strong interaction between palladium particles and the support.

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