Effects of Pd Dispersion on the Catalytic Activity of Pd/SiO₂ for Ethylene Hydroformylation

Nobuo Takahashi,* Tatsushi Tobise, Isao Mogi, Makoto Sasaki,
Akihiko Mijin, Toshiyuki Fujimoto,[†] and Masaru Ichikawa[†]
Kitami Institute of Technology, 165 Koencho, Kitami, Hokkaido 090
[†] Catalysis Research Center, Hokkaido University, Sapporo 060

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Synopsis. In ethylene hydroformylation over Pd/SiO_2 catalysts with 17—85% Pd-dispersion, the turnover frequency for propionaldehyde formation increased with the Pd dispersion, particularly in the region of higher dispersion, suggesting the responsibility of atoms at the corners and at edges on the surface of Pd metal particles for this reaction.

Much attention has been focused on the preparation of heterogeneous rhodium catalysts for olefin hydroformylation by several groups.[1-5] Few studies concerning the preparation of solid catalysts containing transition metals other than Rh, however, have been reported. Kobayashi has reported that Pd/SiO_2 was active for ethylene hydroformylation, where its catalytic acitivity was found to be comparable to that on Rh/SiO_2.[6] Details concerning the catalytic behavior of Pd/SiO_2, however, have not been clarified. In the present work, we have studied the effects of Pd dispersion on the activity and selectivity of Pd/SiO_2 catalysts for gas-phase ethylene hydroformylation.

Experimental

Catalysts were prepared by a conventional impregnation method from palladium chloride (dissolved in HCl), palladium nitrate (dissolved in H_2O), or dinitrodiamminepalladium (dissolved in aqueous ammonia). The specific surface area of silica gel used was 420 m^2 g^{-1} (obtained from Nishio Ind. Ltd.). The amounts of Pd loaded were determined by atomic absorption spectrophotometry.

The apparatus used was a fixed-bed type reactor with a continuous flow at atmospheric pressure. The pretreatment of the catalyst with oxygen-flow (50 cm^3(STP) min^{-1}) at 573 K for 3 h was followed by reduction with hydrogen (50 cm^3(STP) min^{-1} at 673 K for 3 h). After the sample was cooled below 323 K in a hydrogen flow, a mixture of He–C_2H_4(20%)–CO(20%)–H_2(20%) (total flow rate=100 cm^3(STP) min^{-1}) was fed to start the reaction. The catalyst bed was then heated to 373 K, at which temperature the reaction was performed. The time at which the temperature reached 373 K was noted as the time on stream of zero. The conversion of ethylene was kept below 20% in all catalytic runs by controlling the amount of catalyst used. The concentrations of products in the effluent gas stream were determined by gas chromatography.

Measurements of carbon monoxide chemisorption were carried out at room temperature by using a conventional glass-made static system. The amount of CO required for a monolayer coverage of a Pd metal surface (q_m) was estimated by extrapolating the flat part of an adsorption isotherm to the zero of the equilibrium pressure for adsorption. Assuming that each surface palladium atom can adsorb one CO molecule, the dispersion of Pd (%-exposed) was evaluated from the value of q_m.

EXAFS measurements of the Pd K-edge of the sample were carried out at Beam Line 10-B in the Photon Factory of the National Laboratory for High Energy Physics (KEK-PF) with a Si(311) channel-cut monochrometer. An EXAFS analysis was performed with the EXAFS1 and EXAFS2 programs.[7]

Results and Discussion

Pd/SiO_2 catalysts with a wide range of Pd-dispersions (from 17 to 85%) were prepared as shown in Table 1. The reaction products during ethylene hydroformylation over Pd/SiO_2 were found to be propionaldehyde and ethane. As shown in Fig. 1, the rates for the formation of both products decreased with the time on stream to reach the stationary-state reaction. In the present work, the catalytic acitivity was evaluated in terms of the turnover frequency for time on stream of 10 h (denoted by TOF(PA) and TOF(E) for propionaldehyde and ethane formation, respectively). The values for TOF(PA) were estimated to be 2.2×10^{-2} and 30.6×10^{-2} min^{-1} on catalysts I and III, respectively. The value on Rh/SiO_2 (1.0 wt%Rh) with 40% dispersion was found to be 0.5×10^{-2} min^{-1}. Thus, Pd/SiO_2 with a high dispersion of Pd was found to be very effective for ethylene hydroformylation, compared with Rh/SiO_2. However, the values for TOF(E) (1.5 and 7.1 min^{-1} on I and III, respectively) were much higher than that on Rh/SiO_2 (0.5×10^{-2} min^{-1}).

The effects of the dispersion of palladium on the turnover frequencies are shown in Fig. 2. The value for TOF(PA) gradually increased with an increase in the dispersion of Pd up to ca. 70%, and then sharply in the

Table 1. %-Exposed of Pd on Pd/SiO_2 Prepared

Catalyst	Pd compound	Pd loaded 10^{-6} mol g^{-1}	CO adsorbed 10^{-6} mol g^{-1}	%-Exposed
I	$Pd(NO_3)_2$	118	20	17
II	$Pd(NO_2)_2(NH_3)_2$	47	40	85
III	$Pd(NO_2)_2(NH_3)_2$	94	78	83
IV	$Pd(NO_2)_2(NH_3)_2$	188	145	77
V	$PdCl_2$	47	34	72
VI	$PdCl_2$	94	61	65
VII	$PdCl_2$	188	99	53

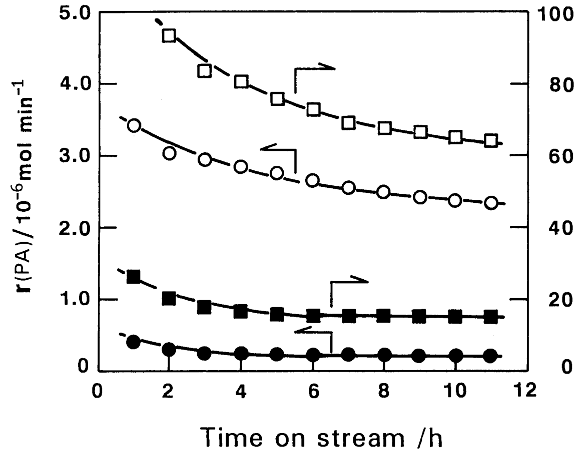

Fig. 1. Changes in the formation of propionaldehyde (●,○) and ethane (■,□) during ethylene hydroformylation at 373 K. ●,■: on catalyst-I (0.500 g); ○,□: on catalyst-III (0.100 g).

region >70%. While the effect of Pd-dispersion on TOF(E) was found to be similar to that on TOF(PA), the TOF(PA)/TOF(E) ratio increased with an increase in the dispersion of Pd (Fig. 2). Highly dispersed Pd/SiO_2 was thus found to be much more effective for ethylene hydroformylation than a catalyst with low Pd-dispersion, not only regarding activity but also regarding selectivity.

The increase in the dispersion results in an increase in number of protruding atoms, such as those at corners and at edges on the surface of metal particles.[8,9] In the case of Pd/SiO_2, the IR-bands attributed to CO adsorbed on Pd were observed at 2088 and 1950 cm^{-1} for a linear-type CO and a bridged-type CO, respectively. The (linear-CO)/(bridged-CO) ratio increased with an increase in the Pd-dispersion, indicating an increase in the ratio of the protruding atoms against the total number of Pd atoms. This result agrees with that already reported by Sheu et al.[9] Furthermore, we conducted an EXAFS evaluation for samples I (17% Pd dispersion) and III (83% dispersion) of Pd/SiO_2 catalysts. Fourier transforms of $k^3\chi(k)$ of Pd K-edge EXAFS spectra on both samples, which were stored under an air atmosphere, are shown in Figs. 3-(A) and 3-(B), respectively. The EXAFS spectrum 3-(A) for I showed an appreciable contribution of Pd backscatter at 0.26 nm before the phase-shift correction. A curve-fitting analysis provided the distance between Pd–Pd as 0.272 nm with a coordination number (CN) of 7.6. These values resemble those on a Pd foil (Pd–Pd: 0.272 nm and CN: 12), suggesting that the predominant Pd species on I is relatively large Pd metal particles. On the other hand, the EXAFS spectrum 3-(B) for III showed the contribution of O(oxygen) backscatter (Pd–O: 0.199 nm, CN: 2.0), indicative of PdO-like species as the predominant Pd species on this sample. Under the exposure of samples I and III to air, it was found that Pd particles on III are much more easily oxidized than those on I due to the higher exposure of Pd atoms. The absence of PdO-like species on I under an air atmosphere is based on a lower metal dispersion, where only the surface layer of Pd particles is oxidized.

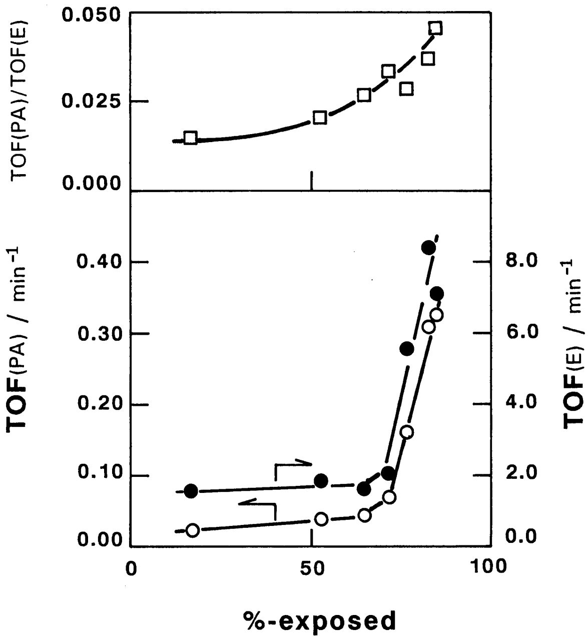

Fig. 2. Effects of Pd dispersion on the catalytic behavior of Pd/SiO_2 for ethylene hydroformylation (at 373 K). ○, TOF(PA); ●, TOF(E); □, TOF(PA)/TOF(E).

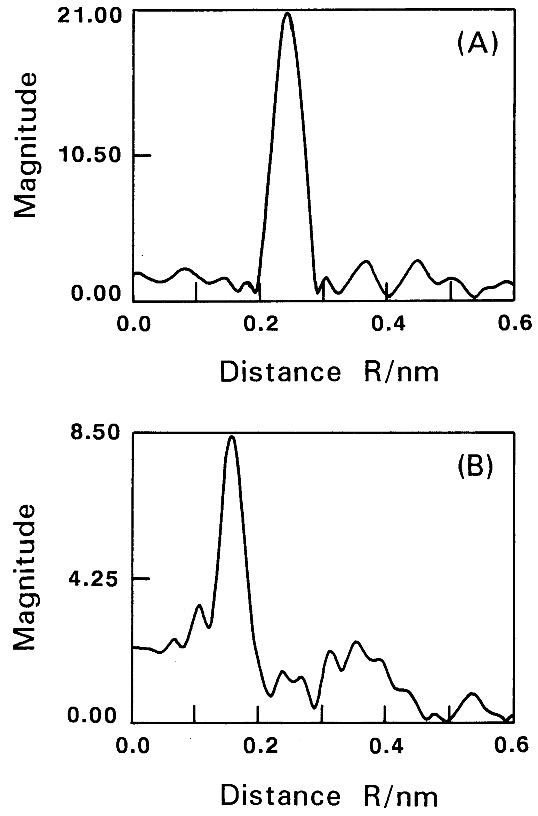

Fig. 3. Fourier transforms of $k^3\chi(k)$ for Pd K-edge EXAFS of Pd/SiO_2. (A) Pd/SiO_2-I (17%-exposed), (B) Pd/SiO_2-III (83%-exposed).

The changes in the particle size may also induce changes in the electronic state of metal atoms at the surface. In case of Rh/SiO_2, which showed a similar effect of Rh-dispersion on TOF(PA), the infrared wavenumbers for CO adsorbed on the highly dispersed Rh/SiO_2 were found to be lower than those on a catalyst with low Rh-dispersion.[8) This suggests that the Rh-dispersion affected the electronic state of surface Rh atoms. However, almost no appreciable changes in the stretching frequency of both CO bands were observed in the case of Pd/SiO_2, suggesting that the effects of Pd-dispersion on the electronic state of surface Pd atoms were not important.

Consequently, the enhancement in TOF(PA) on highly dispersed Pd/SiO_2 should be attributed to an increase in the number of protruding corner and edge-site Pd atoms located on the metal particles.

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