Effect of Support Texture on Enantioselective Hydrogenation of (*E*)-α-Phenylcinnamic Acid with Cinchonidine-Modified Palladium Catalysts

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The texture of support materials has decisive influence on the behavior of cinchonidine-modified palladium catalysts in the enantioselective hydrogenation of (*E*)-α-phenylcinnamic acid, which suggests an important role of pore diffusion in the determination of the selectivity. Palladium metal particles located in micropores of the support have detrimental effect; nonporous ultra fine materials are preferable.

Palladium catalysts modified by cinchona alkaloids catalyze the enantioselective hydrogenation of C=C double bonds in α,β-unsaturated acids.[1,2] The enantiomeric excesses (e.e.) of up to 72%, 52%, and 22% have been reported for the hydrogenations of (*E*)-α-phenylcinnamic acid (**1**) with a $\mathrm{Pd/TiO_2}$ catalyst,[3] (*E*)-2-methyl-2-pentenoic acid with a $\mathrm{Pd/Al_2O_3}$ catalyst,[4] and tiglic acid with a $\mathrm{Pd/SiO_2}$ catalyst,[5] respectively, all modified with cinchonidine. We have shown that the preparation variables of the palladium catalysts, as well as the reaction conditions, influence the catalytic performance in the hydrogenation of **1**.[6,7] The highest e.e. of 2,3-diphenylpropionic acid (**2**) was obtained with a 5wt%$\mathrm{Pd/TiO_2}$ catalyst prepared by a precipitation method and reduced at 473K in a hydrogen flow before use.[3] On the contrary, the pretreatment of a $\mathrm{Pd/SiO_2}$ catalyst at elevated temperatures resulted in drastic decreases both in the activity and in the enantioselectivity. It was suggested that the Pd particles, located in the micropores of a support with a high surface area, become inaccessible to the bulky substrate and the modifier after the heat treatment. This means that both the pore size distribution and the location of Pd metal particles within the pore structure of the support may strongly affect the catalytic performance. In order to confirm this idea, we have examined $\mathrm{Pd/SiO_2}$ catalysts prepared with various silica supports having different textures, and also some commercial Pd/C catalysts designed with different Pd locations within the pore structure.

A series of 5wt%$\mathrm{Pd/SiO_2}$ catalysts were prepared by an impregnation method with $\mathrm{Pd(NH_3)_4Cl_2}$ and calcined at 673 K for 5 h. The silicious mesoporous materials with uniform pore diameters, MCM-41 (2.2 nm) and KIT-1 (2.8 nm), were synthesized according to the literatures.[8,9] A macroporous $\mathrm{SiO_2}$ (JRC-SIO-7) was obtained from Catalysis Society of Japan. Another series of 5wt%$\mathrm{Pd/SiO_2}$ catalysts were prepared by a precipitation-deposition method with $\mathrm{PdCl_2}$ and $\mathrm{Na_2CO_3}$ according to the procedures described previously.[3,7] Three kinds of $\mathrm{SiO_2}$ were employed: silica-**1** (Fluka Cab-osil M-5, 197 m^2/g, nonporous), silica-**2** (Fuji Silysia Chemical FL60D, 300 m^2/g, average pore diameter:10nm), and silica-**3** (Wakogel C-200, 370 m^2/g, broad pore-size distribution[10] from 2 to 20 nm). The Pd/C catalysts were obtained from Johnson Matthey. The hydrogenation reactions were carried out at 298 K in 1,4-dioxane containing 2.5vol% of water under an atmospheric pressure of hydrogen. Procedures of modification and product analyses are the same as described in our previous papers.[7,11]

Table 1. Effect of support structure on catalytic properties of impregnated 5wt%$\mathrm{Pd/SiO_2}$ catalysts in the enantioselective hydrogenation of (*E*)-α-phenylcinnamic acid[a]

Support	Surface area m^2g^{-1}	Average pore diameter/nm	r_0[b] mmol $h^{-1}g^{-1}$	e.e.[c] %
MCM-41	1162	2.2	0.4	27
KIT-1	790	2.8	0.8	32
JRC-SIO-7	82	46.2	2.3	38

[a] Reaction conditions; catalyst: 100 mg, solvent: 1,4-dioxane (containing 2.5vol% water) 10 cm^3, substrate: 1 mmol, modifier: cinchonidine 0.02 mmol, H_2: 0.1 MPa, reaction temperature: 298 K. [b] Initial reaction rate. [c] Enantiomeric excess of **2** at full conversion.

Table 1 compares the catalytic performance of three $\mathrm{Pd/SiO_2}$ catalysts, prepared by an impregnation method with mesoporous or macroporous supports having uniform pore sizes, and reduced *in situ* by stirring in the solvent at 298 K for 1 h under an atmospheric pressure of hydrogen. Both the activity and the enantioselectivity increased with increasing pore diameter of the support materials, suggesting the important effect of pore diameter on this reaction. This observation seems reasonable because Pd metal particles located in the pores will behave as selective sites only when the bulky molecules of both the modifier and the substrate (each size *ca.* 1 nm) effectively diffuse to them and form intermediate complexes (*ca.* 1.7 nm) on the surface.[11] Palladium metal particles in smaller pores will be more difficult to be modified during the modification procedure, and the unmodified Pd will behave as nonselective sites as far as the substrate molecules can reach them. Those in much smaller pores will be inaccessible even for the substrate molecules and lead to a lower activity of the catalyst.

Three kinds of 5wt%$\mathrm{Pd/SiO_2}$ catalysts, prepared by a precipitation-deposition method with different silica gels having different pore structures, were used to examine the effect of reduction temperatures. The results are shown in Figure 1. The catalyst, reduced at 298 K as described above, showed a similar enantioselectivity to each other irrespective of the difference in the support texture, while the activity varied significantly. Similar tendency has been reported for Pd catalysts prepared by the precipitation method with various support materials.[7] This is probably because Pd species, precipitated only on the exterior surface of the support, become active sites after the low-temperature reduction. A striking difference was observed in their selectivities when these catalysts were reduced in a hydrogen flow at elevated temperatures, although the activity of all these catalysts decreased with increasing reduction temperature as expected from the sintering. The enantioselectivity of the catalyst supported on nonporous silica gel (Pd/silica-**1**) was increased by this pretreatment,

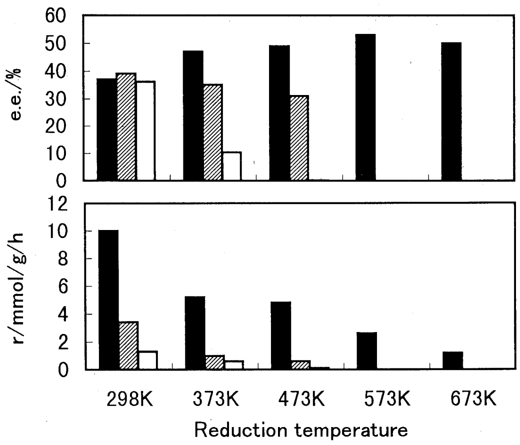

Figure 1. Effect of reduction temperature on enantioselectivity of precipitated 5wt%Pd/SiO_2 catalysts with different support texture. Reaction conditions except catalyst amount (20 mg) as for Table 1. ■: Pd/silica-**1**, ▨: Pd/silica-**2**, □: Pd/silica-**3**.

similarly to the behavior of the Pd/TiO_2 catalyst reported previously.[7] The increase in the selectivity as a result of the heat treatment has been explained by a decrease in Pd dispersion and by the removal of surface contaminations. The heat treatment of the other two catalysts diminished their selectivities to a small extent for the catalyst supported on a wide-pore silica (Pd/silica-**2**) and to a large extent for that supported on a silica with micropores (Pd/silica-**3**). These results can be explained similarly to the impregnated catalysts mentioned above. Palladium metal particles sintered by the heat treatment will narrow the pores and hinder the diffusion of large molecules, thereby lowering the selectivity as well as the activity. Therefore, nonporous and ultra fine particles seem to be suitable as the support materials. This may be one reason for the highest e.e. obtained with a Pd/TiO_2 catalyst[3]; the TiO_2 employed (JRC-TIO-3, Catalysis Society of Japan) was practically nonporous (30-40 nm particles, 40 m^2/g).

Blaser et al. have reported similar influence of support texture on the enantioselective hydrogenation of α-ketoesters with cinchonidine-modified 5%Pt/Al_2O_3 catalysts; best results were observed using aluminas with relatively small surface area, high pore volume and rather large pores.[12] They concluded, however, that the texture of support is less important for the selectivity of Pt/Al_2O_3 catalysts. In contrast to the reaction of α-ketoesters on Pt catalysts, the hydrogenation of α,β-unsaturated acids on Pd catalysts is markedly suppressed in the presence of the modifier. Therefore, the contribution of nonselective Pd sites, such as located in micropores of the support, to overall hydrogenation will be much larger for the Pd catalyst system than for the Pt system.

Table 2 shows the catalytic properties of some commercial Pd/C catalysts with different location of Pd metal within the pore structure of charcoal.[13] The catalysts were reduced *in situ* at 298 K before use. The type-A catalyst with Pd metal located on the exterior surface of the support (so-called eggshell type) was found to be preferable. The type-B catalyst with Pd located deeper within the pore structure showed a lower selectivity, and the type-C catalyst with Pd evenly dispersed throughout the support structure had a much lower selectivity and also a much lower activity in spite of the high dispersion of Pd metal. These behaviors of Pd/C catalysts also support the idea mentioned above. The enantioselective hydrogenation of the bulky intermediate complex of the substrate and the modifier can take place only on Pd metal particles located on or near to the exterior surface, or in relatively wide pores of the charcoal.

Table 2. Textural and catalytic properties of commercial 5wt%Pd/C catalysts in the enantioselective hydrogenation of (*E*)-α-phenylcinnamic acid[a]

Catalyst	Pd distribution[b]	S_M[c] m^2g^{-1}	r_0[d] mmol $h^{-1}g^{-1}$	e.e.[e] %
5R38H[f]	Type-A	13.4	5.0	49
5R90[f]	Type-B	12.4	7.2	32
LR385	Type-C	39.9	2.3	22

[a] Reaction conditions; catalyst: 20 mg, others as for Table 1. [b] Type-A: Pd located on the exterior surface of the charcoal, type-B: Pd located deeper within the pore structure, type-C: Pd evenly dispersed throughout the support structure. [c] Pd metal surface area. [d] Initial reaction rate. [e] Enantiomeric excess of **2** at full conversion. [f] Prereduced by the supplier.

These results strongly suggest that Pd metal particles located in micropores has detrimental effect on this reaction. Therefore, the relatively poor selectivities, reported with the smaller substrates,[4,5] could be attributed to the easier diffusion of the substrate molecules within the micropores, *i.e.*, the larger contribution of the nonselective Pd sites in micropores to the overall hydrogenations. The pore diffusion should be taken into account for further studies of this catalytic system.

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