Communications

Mesoporous Silica-Supported Pd Nanoparticles; Highly Selective Catalyst for Hydrogenation of Olefins in Supercritical Carbon Dioxide

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The selective hydrogenation of olefins has been considered to be a key synthetic method for research and industrial processes. In particular, because a low solubility of gaseous hydrogen in conventional organic solvents results in a slow reaction rate in a gas−liquid system, supercritical carbon dioxide (scCO$_2$) completely miscible with hydrogen has been investigated as one of alternative media for both homogeneous and heterogeneous catalytic hydrogenations.[1−4] Carbon dioxide is also important in chemical technology, particularly as an environmentally friendly reaction medium. In contrast to the homogeneous catalysts showing a difficulty in removal from the reaction mixtures, the combination of scCO$_2$ and solid supported catalysts provides several advantages for a green chemistry reaction system; no organic solvent is included, the CO$_2$ solvent and supported catalysts are easily separated from the reactants and products, and the catalysts can be recycled.

Palladium metal (Pd) has been used in a variety of technologically important applications including catalysts and gas sensors.[5,6] Typically, commercially available supported catalysts such as Pd/C and Pd/Al$_2$O$_3$ are used in many hydrogenation reactions in both liquid solvents and scCO$_2$.[7,8] Although their catalytic performances are enhanced in scCO$_2$ rather than in conventional organic solvents, the broad size distribution and poor dispersion of Pd particles deposited on open surface of supports should be improved for a high selectivity and a low structure sensitivity of catalytic reactions.[9] When these supported catalysts are used for the hydrogenation of olefins including a benzyl group, hydrogenolysis generally accompanies the hydrogenation. Some additives are used as catalyst poison to avoid such a deprotection of the benzyl group.[10,11] One approach to designing the catalysts available for the selective hydrogenation without additives is to use supports with confined spaces for Pd metal particles. Obviously, the porous materials with a well-defined pore geometry are attractive as supports and adsorbents for highly selective catalytic reactions by Pd.[12] It was reported that the enantioselectivity of the asymmetric Pd(II) organometallic catalysts can be improved when

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Scheme 1. Hydrogenation of 4-Methoxycinnamic Acid Benzyl Ester in the Supercritical CO$_2$
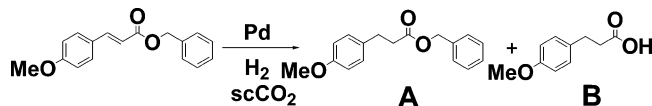
constrained inside the mesoporous silica.[13−15] The Pd(0) nanoparticles immobilized on SBA-15 and PAMAM−SBA-15 composites showed high catalytic selectivity for the hydrogenation and cross-coupling reactions, respectively.[16,17] In the present work, we explored the catalytic performance of SBA-15-supported Pd nanoparticles for the selective hydrogenation of olefins in scCO$_2$. 4-Methoxycinnamic acid benzyl ester was selected to compare the selectivity for the hydrogenation of the C=C bond and benzyl ester moiety. In the metal-catalyzed hydrogenation reactions, the benzyl group has been widely used as an excellent protecting group for the hydroxy group and carboxylic acid group. However, an improvement of chemoselectivity between benzyl groups and other sensitive groups such as C=C, C≡C, and C≡N is still a challenge for the effective hydrogenation reactions.[18,19] In a conventional reduction environment with hydrogen, the metal-catalyzed hydrogenation of the C=C bond and benzyl ester moiety in 4-methoxycinnamic acid benzyl ester could result in two different products, as represented in Scheme 1. Interestingly, Pd nanoparticles highly dispersed in the mesopores of SBA-15, coupled with favorable mass transport of reactants in the supercritical fluid medium, induced a remarkable enhancement of catalytic selectivity for the hydrogenation of this olefin in scCO$_2$.

Mesoporous SBA-15 was prepared according to the literature procedure.[20] Palladium(II) hexafluoroacetylacetonate (Pd(hfac)$_2$) was selected as a Pd precursor because of its high solubility in scCO$_2$.[21] Pd(hfac)$_2$ (Pd, 10.0 wt %) was dissolved in THF (10 mL) containing SBA-15, and this mixture was stirred for 24 h, evaporated, and dried under a vacuum for 4 h. Pd(hfac)$_2$/SBA-15 was loaded into the stainless holder at ambient condition, placed in a 200 mL high-pressure stainless steel reactor sealed with a high-pressure needle valve at both ends and equipped with a pressure gauge, and then allowed to equilibrate to 60 °C. Carbon dioxide was then added to 100 bar using a high-pressure syringe pump (Isco Inc. Model 260D) that was maintained at the desired temperature using a water jacket. The reaction was allowed to stand for a period of 5 h. The recovered powder was rapidly washed with THF to eliminate Pd(hfac)$_2$ adsorbed on the external surface of SBA-15,

calcined in air at 400 °C for 3 h, and then reduced for 1 h in a H$_2$(4%) + Ar(96%) mixed-gas atmosphere at 300 °C to form Pd/SBA-15. The formation of Pd metal was confirmed by X-ray powder diffraction patterns showing characteristic reflections from the (111) and (200) Pd crystal planes (see the Supporting Information, Figure S1). The final quantity of loaded Pd was determined to be 1.61 wt % by ICP measurement. It is noted that the amount of Pd is dependent on both the initial concentration of Pd(hfac)$_2$ solution and the CO$_2$ pressure. Transmission electron microscopy (TEM) observations of Pd/SBA-15 were made with a Philips CM200 operating at 200 kV.

TEM images of Pd/SBA-15 are shown in Figure 1, where the location and size of Pd particles are revealed. A well-ordered 2D hexagonal array of channel-like mesopores is retained after scCO$_2$ treatment. Pd nanoparticles are mainly dispersed inside the mesoporous channels of SBA-15 where the size (∼ 6 nm) is limited by the mesopore diameter. The synthesis and deposition of nanoparticles inside the pores of mesoporous materials have become rather commonplace.[22] The incorporation of Pd into the pores of several mesoporous materials such as FSM-16 and HMM-1 has been carried out in the solid−liquid system[23,24] as well as the chemical vapor transport system.[25] The loading processes of metal precursors in conventional liquid deposition techniques usually suffer from a mass transfer limitations, and this may give rise to difficulties associated with high dispersion in the narrow channels of supports. In contrast, the lack of surface tension between interfaces of supports and scCO$_2$ minimizes the mass-transport resistance through the mesopores and results in highly improved dispersion of Pd nanoparticles.

The hydrogenation of 4-methoxycinnamic acid benzyl ester synthesized according to the literature[26] was performed in a stainless steel batch reactor (10 mL). Substrate (0.05 g, 1.86×10^{-4} mol) and Pd/SBA-15 catalyst (50:1 substrate: catalyst molar ratio) were loaded into the CO$_2$ cell, and the reactor was then sealed and flushed two times with CO$_2$. After the cell was heated to 45 °C, hydrogen gas (H$_2$, 12 bar) was introduced into the cell and CO$_2$ was subsequently charged by utilizing a syringe pump. The mixture was continuously stirred by a magnetic stirrer in the reaction. The same procedure was carried out using commercial Pd/C (5 wt % Pd) and Pd/Al$_2$O$_3$ (5 wt % Pd) catalysts for comparison. The amount of catalysts was chosen to achieve approximately the same quantity of Pd loading as in Pd/SBA-15. After the reaction was completed, the cell was cooled to room temperature and then depressurized carefully. The residue in the reactor was collected with acetone and dissolved into CDCl$_3$ after removing the acetone. Hydrogenation conversion and product distribution from 4- methoxycinnamic acid benzyl ester catalyzed by Pd metal were determined by ^{1}H NMR (JEOL AL-300) (see the Supporting

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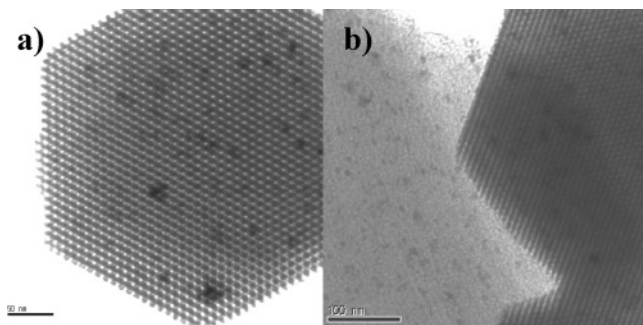
Figure 1. TEM images (a) parallel (bar = 50 nm) and (b) perpendicular (bar = 100 nm) to the channel direction of Pd/SBA-15.

Table 1. Conversion and Product Distribution for Pd-Catalyzed Selective Hydrogenation of 4-Methoxycinnamic Acid Benzyl Ester in scCO₂
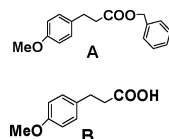
catalyst	CO_2^{*a} (bar)	time (min)	temp (°C)	total	A	B
Pd/SBA-15	80	60	45	33.1	92	8
Pd/SBA-15	120	60	45	66.7	97	3
Pd/SBA-15	150	60	45	100	93	7
Pd/SBA-15	200	60	45	54.9	92	8
Pd/SBA-15	150	30	45	100	97	3
Pd/SBA-	150	10	45	100	95	5
Pd/SBA-15	120	60	25	100	88	12
Pd/C	150	10	45	100	38	62
Pd/Al₂O₃	150	10	45	92	64	36

conversion (%) spans total, A, B columns

^{a} CO₂* = pressure of carbon dioxide. In a general experiment, 0.05 g (1.86 × 10⁻⁴ mmol) of ester and corresponding catalysts (50:1 substrate:catalyst mole ratio) were put into a CO₂ cell. Pressure of H₂ = 12 bar.

Information, Figure S2). A TEM image of the used catalyst shows that the mesoporous structure of silica is retained and no agglomeration of Pd particles is induced during the reaction (see the Supporting Information, Figure S3). The Pd content in the catalyst was reduced by ~0.2 wt % after the hydrogenation reaction, indicating that the Pd nanoparticles could be leached from the silica support in our experimental conditions.

Table 1 summarizes the catalytic results for the Pd/SBA-15, Pd/Al₂O₃, and Pd/C catalysts tested for the hydrogenation of 4-methoxycinnamic acid benzyl ester in scCO₂. Under the conditions used, two products were observed: one of them is the reduced form only in the C=C moiety (A in Scheme 1), whereas the other is fully reduced one (B in Scheme 1) through an additional hydrogenolysis. The total

conversion is enhanced with increasing CO₂ pressure, and a maximum conversion is obtained at 150 bar without changing other conditions. When the pressure is further increased to 200 bar, the conversion is significantly lowered to 54.9%. Such a decrease in conversion is not attributed to the CO₂ solubility of the reactants because they are completely dissolved above 80 bar. Rather, the dilution effect would be responsible for the low reaction rate at higher CO₂ pressure (200 bar).[27] The reaction for only 10 min is sufficient for the complete conversion (100%) when the hydrogenation is carried out at 150 bar, 45 °C. Compared with commercially available Pd catalysts deposited on an open surface of Al₂O₃ or carbon (C) supports, Pd/SBA-15 shows similar catalytic activity but significantly higher selectivity for the hydrogenation reactions in scCO₂. Thus, wel-dispersed Pd nanoparticles with a narrow size distribution in the channel of mesoporous support would be efficient in catalytic selectivity when the reaction is carried out in supercritical fluid media possessing favorable transport property.

In conclusion, we propose the potential of Pd/SBA-15, in which the dispersion of Pd nanoparticles is highly improved by using scCO₂, as an effective catalyst for versatile hydrogenation reactions performed particularly in scCO₂ solvent. The development of similarly supported catalysts would be an attractive prospect with potential for both economic and environmental advantages. For this purpose, present preliminary examination could be extended to encompass other heterogeneous catalysts and mesoporous supports of different pore sizes and other widely applicable transformations in scCO₂. To illuminate the origin of highly enhanced catalytic selectivity, we have similar investigations in progress with several mesoporous supports of different pore sizes and various olefinic substrates.

Supporting Information Available: Wide-angle XRD pattern of Pd/SBA-15, TEM image of Pd/SBA-15 after the reaction, NMR spectra of hydrogenation products, and yield percent calculation method (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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