

Selective catalytic activity of ball-shaped Pd@MCM-48 nanocatalysts

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Remarkable selectivity is achieved in the cleavage of benzyl ethers using ball-shaped palladium nanocatalysts, Pd@MCM-48, in an MCM-48 matrix. The unique nanocatalysts not only feature unprecedented complete hydrogenolysis selectivity of a benzyl ether over hydrogenation of a double bond, but also demonstrate selective cleavage of unsubstituted benzyl ether over substituted benzyl ethers.

Nano-structured catalytic materials have drawn attention for their potential durability, reactivity and selectivity in chemical processes due to their unique structural properties.¹ One interesting method to prepare nano-structured catalysts is templated synthesis in which active catalysts are encapsulated inside channels and pores of a host. With the development of practical synthetic routes for mesoporous silicate materials, extensive research effort has been focused on their applications to catalytic reactions.^{2,3} Although there have been several recent reports on the template-assisted metallic nanocatalysts demonstrating increased reactivity,⁴ the improvement of selectivity is very challenging in organic reactions.⁵

Recently, we described the preparation of well-defined ball-shaped Pd nanomaterials inside a cubic phase MCM-48 matrix.⁶ Nanostructuring was accomplished by chemical vapor infiltration of Pd(hfac)₂ (hfac = 1,1,1,5,5,5-hexafluoro-acetylacetonate) into the template matrix MCM-48, followed by mild thermal decomposition under H₂ gas to generate pure Pd metal inside the template. The MCM-48 matrix has pore size of ~3 nm and Pd@MCM-48 is composed of ball shaped isolated Pd domains of ~38 nm in diameter (Fig. 1). The Pd metal surface area measured by CO chemisorption is 12 m² g⁻¹ Pd with a metal dispersion of 3.3%. The observed Pd surface area of our sample is about 3–10 times lower than those obtained from one dimensional matrix systems such as MCM-41,⁷ which is not surprising since those Pd are well dispersed inside linear pore channels while ours are highly localized ball types with Pd surface accessibility only at the end of pore channels. Since the Pd domains of ~38 nm are arranged with an ordered array of nanoscale exposed-surface inside pore channels, nanostructured Pd@MCM-48 may offer unexpected catalytic activities for organic reactions.

First, the hydrogenation activity was compared with those of Pd/SiO₂ and Pd/C on various olefins ranging from a terminal olefin to a trisubstituted olefin to observe for a possible discrimination of substitution patterns of olefins by the catalyst.^{5d,8} The reduction rate with Pd@MCM-48 was about 1.5 to 5 times slower than those with Pd/SiO₂ or Pd/C and did not show

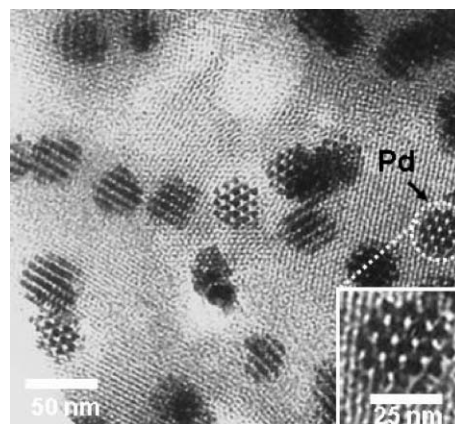


Fig. 1 Transmission electron micrograph of Pd@MCM-48 nanocatalyst.

significant discrimination among olefins relative to Pd/SiO₂ or Pd/C (Table 1). The slower reduction rate with Pd@MCM-48 was presumed to be due to the difference in exposed surface area of Pd since the hydrogenation reaction rate was reported to be independent of pore diffusion.⁹ However, when considering the accessible Pd surface area of Pd/SiO₂ and Pd/C (~243 m² g⁻¹ Pd) obtained by CO chemisorption is about 20 times higher than that (~12 m² g⁻¹ Pd) of Pd@MCM-48, the hydrogenation reactivity of Pd@MCM-48 per accessible Pd surface area can be considered far higher than that of Pd/C. Similar catalytic activity has been observed previously in other supported Pd catalysts.⁷

When Pd@MCM-48 was tested as the catalyst for hydrogenolysis of benzyl ether **1**, contrary to the anticipation that the silica support would provide an acidic environment to facilitate the

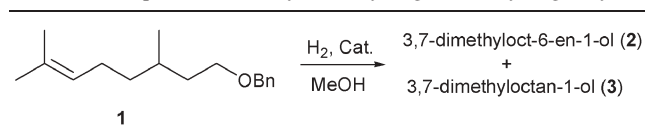
Table 1 Comparison of hydrogenation rate^a

Substrate	Relative rate		
	5% Pd/C	3% Pd/SiO ₂ ^b	Pd@MCM-48
Methyl-3-butenolate	2.9	2.5	1
<i>trans</i> -2-Pentenyl benzoate	1.1	0.89	0.23
4-Methyl-4-pentenyl pivaloate	0.4	0.3	0.27
Cyclohex-3-enylmethyl benzoate	0.7	0.7	0.26
3,7-Dimethyloct-6-enyl benzoate	0.08	0.05	0.03

^a The hydrogenation reaction of a mixture of equimolar amount of olefins and dodecanol as the standard with 10% catalyst (w/w to the total amount of mixture of olefins) under hydrogen atmosphere (1 atm) was monitored by gas chromatography (Column : NB-54, 30 m capillary column, conditions; temp.: gradient from 80 °C to 210 °C (10 °C min⁻¹), flow rate : 30 ml min⁻¹). ^b The catalyst was prepared by conventional wet infiltration & reduction method using MCM-48 as the support.

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Table 2 Comparison of catalysts on hydrogenation/hydrogenolysis^a


Catalyst	Product ratio (2 : 3)
Pd@MCM-48 (5 wt%)	100 : 0
Pd/SiO ₂ (3 wt%) ^b	70 : 30
Pd/C (5 wt%)	45 : 55
Pd(OH) ₂ /C (10 wt%)	80 : 20

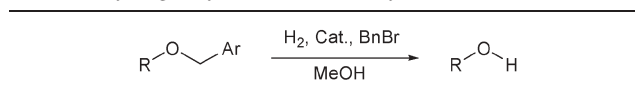
^a The hydrogenation/hydrogenolysis reaction with 10% catalyst under hydrogen atmosphere (1 atm) was monitored by gas chromatography until all the starting material was consumed. ^b The catalyst was prepared by conventional wet infiltration & reduction method using MCM-48 as the support.

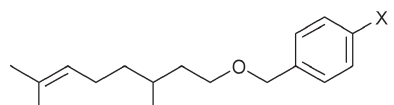
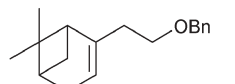
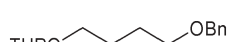
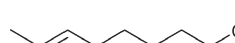



hydrogenolysis reaction,¹⁰ the initial hydrogenolysis rate was found to be two times slower than that of Pd/C as similarly observed in the hydrogenation experiments. Interestingly, however, the hydrogenolysis reaction with Pd@MCM-48 appeared to proceed much faster than the olefin hydrogenation, as a quantitative yield of selective hydrogenolysis product **2** was obtained without the formation of the hydrogenation product **3** when compound **1**, which contained both an olefin and a benzyl ether, was subjected to Pd@MCM-48 catalyzed reaction conditions (Table 2).

This extraordinary selectivity has not been observed with conventional Pd catalysts. When Pd/C catalyst was used for the same reaction, equal amounts of **2** and **3** were observed. Even Pd(OH)₂ on carbon, known to be the most reactive and selective catalyst for the hydrogenolysis reaction, showed increased but far from complete selectivity in our comparison experiment. The reduction using Pd/SiO₂ as the catalyst indicated that Pd/SiO₂ did not discriminate two functional groups well. The low selectivity obtained from the reaction with Pd/SiO₂ prepared in the conventional way as the catalyst, indicated that the silica support itself did not contribute to the selectivity.

We also found that the hydrogenolysis reaction was facilitated by the addition of benzyl bromide (15 mol%): the reaction completed in 30 minutes with benzyl bromide compared with 4 hours without benzyl bromide. When benzyl bromide was added to the reaction, the reaction mixture became quite acidic after the reaction (pH = 2) while the pH of the reaction mixture at the beginning of the reaction was neutral. The effect of benzyl bromide can be explained by the increased reaction rate due to the increased concentration of protons generated from the hydrogenolysis reaction of benzyl bromide.¹⁰ We then investigated the generality and selectivity of the hydrogenolysis of various alcohols using both benzyl ethers and substituted benzyl ethers (Table 3).

When the hydrogenolysis reaction was tested using various substituted benzyl ethers, to our surprise, only the unsubstituted benzyl ether was cleaved. This result was quite different from the reported reactivity of substituted benzyl ethers toward Pd catalyzed hydrogenolysis reactions as electron donating groups facilitated the hydrogenolysis reaction and electron withdrawing groups retarded the reaction.¹¹ Moreover, only the unsubstituted benzyl ethers of primary alcohols reacted with our new catalyst while the benzyl ethers of the secondary and tertiary alcohols were not reactive. On the other hand, hydrogenolysis reaction of the

Table 3 Hydrogenolysis of various benzyl ethers^a


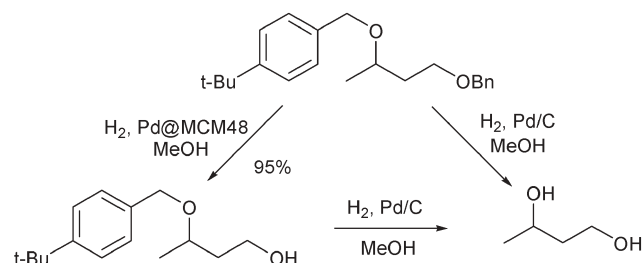
Substrate	Yield ^b
	X = H >99% X = Me N.R. ^c X = OMe N.R. X = Ph N.R. X = <i>t</i> -Bu N.R. X = CN N.R.
	95%
	76%
	N.R.
	N.R.
	N.R.
	N.R.

^a The hydrogenolysis reaction was carried out with 10% catalyst and benzyl bromide (15 mol%) under hydrogen atmosphere (1 atm) until all the starting material was consumed. ^b Isolated yield. ^c No reaction after 24 hours.

substrates (Table 3) using Pd/SiO₂ as the catalyst not only cleaved all the substituted benzyl ethers but also reduced the double bonds completely. The unusual nano-structural feature of Pd@MCM-48 was presumed to be responsible for this extraordinary selectivity toward the unsubstituted benzyl ethers of primary alcohols.

This remarkable selectivity toward the unsubstituted benzyl ethers of primary alcohols could be applied to organic synthesis since the catalyst would allow differential deprotection of alcohols in the same molecule, as shown in Scheme 1. If two alcohol functional groups in the molecule were protected with differently substituted benzyl ethers, those protecting groups could be deprotected selectively in sequence.

Here, we have demonstrated that ball-shaped Pd nanocatalysts show a unique catalytic activity with exceptional selectivity for benzyl ether hydrogenolysis to produce primary alcohols. Although the exact catalytic mechanism needs to be further

**Scheme 1** Selective deprotection of benzyl alcohols.

studied, this report demonstrates that nano-structured mesoporous materials exhibit interesting catalytic activity through cooperative properties such as nanoscale domained Pd catalytic centers within confined reaction geometry.

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