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In situ synthesized Pd nanoparticles supported on B-MCM-41: an efficient catalyst for hydrogenation of nitroaromatics in supercritical carbon dioxide[†]

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In situ synthesis of Pd nanoparticles supported on boron (B)-substituted MCM-41 (B-MCM-41) with Si/B ratio varying from 100 to 5 was carried out by hydrothermal method using H₃BO₃ as B source. The textural properties as well as thermal stability of the resultant material were investigated by XRD, TEM, FTIR and TG-DTA. Highly ordered materials were obtained depending on the Si/B ratio, which also influenced the particle size of Pd as well as dispersion. Pd/B-MCM-41 was a promising catalyst for the hydrogenation of nitrobenzene in supercritical carbon dioxide with exceptionally faster reaction rate [turnover frequency (TOF) = 5.2×10^5 h⁻¹ (144 s⁻¹)] and high yield of aniline (100%). The observed reaction rate was strongly influenced by the Pd particle size related to Si/B ratio and physical properties of CO₂ such as pressure- and temperature-dependent solvent power. A comparison of catalytic activity with the Pd supported only on silica material of similar particle size inferred that the presence of even a small amount of B significantly changes the reaction rate from 70 (only Si) to 105 s^{-1} (Si/B = 100). In addition, TOF of Pd/B-MCM-41 was high when compared with other Pd catalysts supported on Al-MCM-41 and Ga-MCM-41 obtained by a similar method, and follows the order: B (144 s⁻¹) > Ga (31.2 s⁻¹) > Al (10.2 s^{-1}) . The remarkable advantage of the present catalytic system involves low metal content (~1%), easy separation and it is successfully employed for the hydrogenation of substituted nitroaromatics, nitrile and phenol under mild reaction conditions. Furthermore, the catalyst was recyclable up to the 7th recycle without any loss of catalytic activity.

Introduction

A selective catalyst is a highly desirable candidate for the greenness of chemical transformation, because it improves the efficiency of the reaction by lowering the energy input and by avoiding the use of stoichiometric reagents.¹ Thus, development of an efficient catalyst for a heterogeneous system is one of the challenging areas in catalysis.

Supported metal nanoparticles are potential heterogeneous catalysts used for various types of reaction. Mesoporous materials, which was discovered by Beck *et al.* in 1992,² seem to be ideal hosts for metal nanoparticles because of very high surface areas to immobilize catalytically active species on, or the ability to provide nano-size confinement inside the pore system.³ The mesoporous molecular sieve MCM-41 (a member of the M41S family) possesses a hexagonally arranged uniform pore structure. The important characteristics of this novel material are large BET surface area, high porosity, and controllable narrow pore size distribution. Those characteristics manifest themselves

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as a very promising candidate as catalyst support. Generally, the synthesis procedure of MCM-41 involves multidentate binding of the silicate oligomers to the cationic surfactant, preferential silicate polymerization in the interface region, and charge density matching between the surfactant and the silicate.^{4–7}

Beginning with a relatively inert all-silica MCM-41, great chemical and catalytic diversity may be generated by isomorphous substitution with trivalent cations in Si framework. The substitution of Si by B is expected to modify structural properties of MCM-41 and was first described by Oberhagemann et al. using quaternary ammonium salts of different chain length as the template.⁸ After that several authors described the synthesis and characterization depending on B precursor (Na₂B₄O₇ or H₃BO₃) or using alkylamine as surfactant to obtain highly ordered uniform hexagonal mesopores in the resultant material and stability of B in the framework.^{9–12} It was observed that, like Al, B has been confirmed to occupy tetrahedral framework sites. However, in comparison with Al-substituted MCM-41, less literature is available on the catalytic activity of B-containing materials because of its small size and propensity for trigonal coordination. Borosilicate molecular sieves are only mildly acidic, which particularly make them more suitable for catalysts demanding low acidity.13-17

Supported Pd catalysts are widely used in a number of hydrogenation reactions and in various organic syntheses due to their unique properties of absorbing large quantities of hydrogen.¹⁸

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Several methods have been described in the literature for the synthesis of noble metal nanoparticles supported on mesoporous materials, such as direct incorporation,¹⁹ incipient wetness impregnation^{20–22} and ion exchange.²³ In addition to those, photocatalytic reduction and gamma irradiation were also used to prepare metal nanoparticles on MCM-41 support.²⁴

The present study describes the hydrothermal method of *in situ* synthesis of Pd nanoparticles on B-MCM-41 using H_3BO_3 as B source. The catalytic performance was investigated for the hydrogenation of nitrobenzene in supercritical carbon dioxide (scCO₂) under mild conditions and the results are compared with Al- and Ga-supported Pd catalyst obtained by similar methods.

Results and discussion

Physicochemical characterization of the catalysts

Elemental analysis of the calcined product confirmed the Pd loading of all the samples including Al and Ga-MCM-41 were ~1%. The colour of the as-synthesized B-MCM-41 was white and changed to grey after incorporation of Pd (Pd/B-MCM-41), which is taken as an initial indication of the presence of Pd in the material. After calcination, the parent material (B-MCM-41) remains white, while Pd/B-MCM-41 turns orange and suggesting the migration of Pd²⁺ to the surface, by reaction with SiOH groups of defect sites. A similar result was reported by Kawabata *et al.*²⁵ on the synthesis of Pd-containing Al-MCM-41 and attributed to the migration of Pd²⁺ ions from inside the framework to the surface due to the insufficient substitution of Pd²⁺ ions for both Si⁴⁺ and Al³⁺ sites in the lattice. It has to be mentioned that for Si/B ratio, the gel ratio has been considered throughout the manuscript.

X-ray diffraction pattern of Pd/B-MCM-41

Fig. 1a exhibits the XRD pattern of Pd/B-MCM-41 with different Si/B ratios. All materials show typical low angle (1 0 0) reflections characteristic of MCM-41 along with the smaller Bragg peaks. Beck et al.² indexed those peaks for the hexagonal unit cell and the cell parameter (a_0) was calculated using the formula $a_0 = 2d_{100}/\sqrt{3}$. It has to be mentioned that the quality of the main peak varied significantly depending on the Si/B ratio. For high Si/B ratios, the major peak was more sharp and appears at $2\theta = 2.120^{\circ}$ along with three well-resolved peaks. However, the scattering pattern of materials with low Si/B ratio exhibits a major peak of decreased intensity with the absence of smaller peaks originated from the ordered two-dimensional structures. It was observed that the unit cell parameter a_0 slightly decreased with increasing B content and corresponds well with the literature^{9–12,26,27} (Table 1). Furthermore, decrease in a_0 of B-MCM-41 compared to the pure Si analogue is evidence for B in the silicate framework.9,10,28

To detect the Pd nanoparticles, XRD measurement was also performed at higher angle regions ($2\theta = 30^{\circ}$ to 90°), and are displayed in Fig. 1b. Independent of the Si/B ratio of calcined sample, five distinctive peaks at $2\theta = 33.8$, 42.0, 54.8, 60.7 and 71.4, corresponding to the diffraction lines of PdO (1 0 1), (1 1 0), (1 1 2), (1 0 3) and (2 1 1), respectively, appeared after the incorporation of Pd in B-MCM-41. Particle sizes were



Fig. 1 (a) Low-angle XRD pattern of Pd/B-MCM-41 with different Si/ B ratio. (b) Higher-angle XRD pattern of Pd/B-MCM-41 with different Si/B ratio.

Table 1 Physical properties of Pd/B-MCM-41

Si/B ratio	<i>d</i> ₁₀₀ (nm)	A_0 (nm)	Average Pd particle size ^a (nm)	Weight loss of template at 120–320 °C
Only Si	4.6	5.31		38.6
100	4.2	4.85	10.9	35.1
25	4.1	4.73	19.5	33.4
10	4.0	4.62	21.5	30.2
5	3.8	4.38	22.6	28.5

^a From XRD using Scherer's equation.



Fig. 2 TEM images along with particle size distribution of (a) Si/B = 100 and (b) Si/B = 5.

calculated from the XRD line broadening of the peak at $2\theta = 33.8$ using Scherer's equation,²⁹ which shows that there is a change in the average particle size from 10.9 to 22.6 nm with the change in Si/B ratio from 100 to 5 (Table 1). Moreover, after hydrogenation the diffraction lines of PdO disappeared and a new peak corresponding to Pd⁰ appeared at $2\theta = 40.1$.

TEM of Pd/B-MCM-41

The pore structure of MCM-41 and the presence of Pd nanoparticles were directly visible through TEM observation. Fig. 2a and b shows TEM images of Pd/B-MCM-41 with Si/B = 100 and Si/B = 5, respectively, through the pore axis and their corresponding particle size distributions. The image corresponding to Si/B = 100 exhibits the regular ordered hexagonal channel, characteristics of MCM-41. However, increasing B content damaged regular order. In addition, TEM also focused on Pd particles supported on B-MCM-41. In each case, Pd particles were almost spherical in shape and distributed throughout the support matrix. Calculation of particle size distribution (Fig. 2) confirmed average particle size of 12.1 nm for low B-containing material (Si/B = 100), whereas larger particles of average size = 23.1 nm found in the high B-containing material (Si/B = 5). These observations correspond well with the results of XRD measurement.

FTIR spectra of Pd/B-MCM-41

Fig. 3 represents FTIR spectra of Pd/B-MCM-41 of different Si/B ratios along with the Si-only material. FTIR spectra of calcined Pd/B-MCM-41 show a series of bands in the region of $500-1400 \text{ cm}^{-1}$ characteristic of SiO₄ tetrahedra and their modification after B substitution. The presence of an IR band at 1380 and 940 cm⁻¹ confirmed B substitution in the silicate framework and representing the tri- and tetra-coordinated B, respectively.³⁰ All B-containing samples developed a band at



Fig. 3 FTIR spectra of (a) only Si, (b) Si/B = 100, (c) Si/B = 25, (d) Si/B = 10 and Si/B = 5.

1380 cm⁻¹ and the increased intensity of the band might be correlated with the increased B content of the materials. Generally, the tetrahedral form of B is stable only with Na counterbalancing, but is unstable in the H form (when H_3BO_3 was used as B precursor).²⁷ However, the spectra of Si/B = 5 developed a small shoulder (Fig. 3e) at 940 cm⁻¹ representative of tetrahedral B, which was absent in the other B-containing materials. In the pure Si material, instead of the band at 1380 cm⁻¹, a 960 cm⁻¹ band due to silanol group typical of calcined MCM-41 material was observed.

Thermogravimetric analysis

The thermal analysis pattern of Pd/B-MCM-41 was very similar to that of Pd-containing Si material (ESI; Fig. 1s[†]). Total weight loss occurred in three distinctive steps. The first step was associated with the loss of physically adsorbed water in the temperature range of room temperature to 120 °C along with a weight loss of $\sim 2-3\%$, and related to the hydrophobicity of the material. The second stage of weight loss corresponding to desorption and decomposition of the template from the pores occurred at 120–320 °C. There was a distinctive difference depending on the Si/B ratio. For example, weight loss in the described region is 35.1 and 28.5% for Si/B = 100 and Si/B = 5, respectively, indicating that with increasing B content a larger part of the template is removed at high temperature as template cation bonded to the siloxy group decomposes at low temperature,² which is confirmed from the analysis of Si-only material (Table 1).





Scheme 1 Possible reaction pathway of nitrobenzene hydrogenation.

However, it is equally likely that less template was incorporated into the composite of high B-containing material. If there was more B, less electrostatic attraction between the metal precursor and surfactant results in less incorporation of CTAB in the resultant material. Finally, the weight loss of 7–8% from 320 to 455 °C can be assigned to coke calcination, and the weight loss of 3–4% above 455 °C should be the loss of silanol groups present in the framework (dehydroxylation). These results correspond well with those reported previously.³¹ For all the materials, a sharp DTA peak was observed and attributed to the strong endothermic process due to the combustion and removal of the surfactant from pores of MCM-41 matrix.

Catalytic activity

Scheme 1 depicts one of the possible reaction paths of hydrogenation of nitrobenzene in $scCO_2$ as described in the literature.³² Selective hydrogenation of nitrobenzene in $scCO_2$ was conducted in a batch reactor using Pd/B-MCM-41 catalyst.

For optimization of the reaction conditions, maximum conversion and highest selectivity of aniline were set as targeted parameters. Despite of the low structural order, Pd/B-MCM-41 (Si/B = 5) was chosen as the catalyst because of high B content. The CO₂ and H₂ pressure, temperature, and the reaction time were considered as parameters for optimization.

Variation of CO₂ pressure

Fig. 4 exhibits variation of reaction rate (TOF) with CO₂ pressure under the studied reaction condition ($P_{\rm H_2} = 2$ MPa, temperature = 50 °C and reaction time = 5 min). Notably, \sim 7 times increase in TOF was observed with the change in CO₂ pressure from 6 to 14 MPa. The highest TOF (144 s^{-1}) was obtained at 12 MPa of CO₂ pressure. Visual inspection of the phase behaviour (ESI; Fig. 2s[†]) conducted in a view-cell under similar conditions revealed that the mixture of nitrobenzene, H₂, and CO₂ transforms from a two-phase system (nitrobenzene and CO₂-H₂) to a single homogeneous phase (nitrobenzene-CO₂-H₂) with the change in the CO_2 pressure. In the lower pressure region of 6-10 MPa, a biphasic system prevailed, and a single homogeneous phase was obtained at or above 12 MPa. As the pressure changed from 6 to 12 MPa, the reaction rate (TOF) increased from 23.3 to 144 s^{-1} . This is attributed to the transition from bi-phase to single phase of substrate-CO2-H2 system. Thus, elimination of the gas-liquid interface was crucial to achieve highest performance of Pd/B-MCM-41 as hydrogenation catalyst. Independent to CO₂ pressures, aniline was the only product detected.



Fig. 4 Variation of CO₂ pressure; reaction conditions: catalyst = 0.1 g, substrate = 2.0 g, $P_{\rm H_2} = 2$ MPa, temperature = 50 °C, time = 5 min.



Fig. 5 Variation of H₂ pressure; reaction conditions: catalyst = 0.1 g, substrate = 2.0 g, $P_{CO_2} = 12$ MPa, temperature = 50 °C, time = 5 min.

Effect of H₂ pressure

 H_2 pressure is one of the important parameters to optimize the reaction condition in scCO₂.^{18d,e} The dependence of TOF on H_2 pressure was studied at the fixed CO₂ pressure (12 MPa), reaction time (5 min) and temperature of 50 °C (Fig. 5). The TOF of nitrobenzene hydrogenation was found to be very sensitive to the H_2 pressure. When the pressure was changed from 0.5 to 2.0 MPa, the TOF increased from 46.3 to 144 s⁻¹ without affecting the product selectivity, probably due to the enhanced concentration of H_2 in the system. Further increase of pressure to 4 MPa did not change the conversion, however, the selectivity of aniline decreased. Thus, an optimum pressure of 2 MPa was chosen to achieve the targeted conversion, which is lower than the pressure required for Si-only material indicating a possible effect of the presence of B in MCM-41.

Effect of reaction temperature

Generally, solvent properties of CO_2 are strongly influenced by the pressure and temperature. Thus, fine tuning of temperature can also change the density of CO_2 and consequently the solvent strength. To explore the effect of temperature, the reaction was conducted at 35 to 70 °C using Pd/B-MCM-41 of Si/B ratio 5



Fig. 6 Temperature *vs.* TOF over Pd/B-MCM-41; reaction conditions: catalyst = 0.1 g, substrate = 2.0 g, $P_{CO_2} = 12$ MPa, $P_{H_2} = 2$ MPa, time = 5 min.

and 100 with the reaction time fixed at 5 min. In each case, the conversion of nitrobenzene increased with temperature. For example Si/B = 5 shows a conversion of 62% at 35 °C, which increased to 100% when the temperature rose to 50 °C at a fixed pressure of CO₂ (12 MPa). Taking into the account of low conversion data at 35 °C, it might be concluded that although a single phase was formed between nitrobenzene, CO₂ and H₂, the kinetic effect was in action to enhance the reaction rate rather than phase behaviour. Furthermore, Fig. 6 shows changes in reaction rate along with temperature, depending on Si/B ratio. As the temperature changes from 35 to 50 °C, the rate of the reaction (TOF) also increased. In addition, with the decrease in Si/B ratio from 100 to 5, TOF changes from 43 (35 °C) to 105 s^{-1} (50 °C) and 89 (35 °C) to 144 s⁻¹ (50 °C), respectively. Hence, it might be concluded that (i) independent of the B content and other related parameters like particle size, structural order, etc., increase in temperature increased the reaction rate and (ii) low B-containing material exhibited lower TOF even at higher temperature of 70 °C. Thus, an optimum temperature of 50 °C was chosen for all experiments as the highest conversion was achieved at that temperature within the reaction time of 5 min using Si/B = 5 catalyst.

Effect of reaction time

The effect of reaction time on the conversion of nitrobenzene was evaluated on two Pd/B-MCM-41 catalysts with Si/B ratios of 100 and 5 (Fig. 7a). In each case, the reaction was comparatively fast, but complete conversion can be achieved within the shortest reaction time of 5 min only when Si/B = 5 was used. For these two catalysts, Pd particle sizes are different (Table 1). Thus, to explain these observations there are two primary factors to be considered: (i) effect of Pd particle size and (ii) B content, which controlled the structural order. It has to be mentioned that only support material was inactive and, hence, catalytic activity of the metal-containing catalysts arises unambiguously due to the presence of active metal species present on the support. Generally, the variation in catalytic activity depends on the dispersion of metal. This factor is further influenced by B content of the support material. (i) Effect of Pd particle size: the



Fig. 7 (a) Time dependence of nitrobenzene conversion using Pd/ B-MCM-41; reaction conditions: catalyst = 0.1 g, substrate = 2.0 g, $P_{\rm CO_2} = 12$ MPa, $P_{\rm H_2} = 2$ MPa, temperature = 50 °C. (b) Effect of particle size on reaction rate.

dependence of nitrobenzene hydrogenation rate on particle size is shown in Fig. 7b, which indicates that the initial TOF calculated per surface Pd atom increases with the particle size. The changes in particle size from ~10 to 20 nm increased the TOF from 59 to 144 s⁻¹. Hence, larger Pd particles were considered to be more active than smaller ones, assuming that all the particles took part in the reaction. Although there was a sharp change of TOF with particle size, it is difficult to comment on the structure sensitivity because the studied range of particle size was limited. A similar phenomenon was also reported previously in the liquid-phase hydrogenation of nitrobenzene in methanol over Pd/C at 50 °C.³³ (ii) B content: presence of B incorporates weak acidity on the support surface, as described by many researchers, and it might change catalyst morphologies such as metal dispersion, etc. We had compared the results between low B content (Si/B = 100) and Si-only material. The rate was comparatively higher for Si/B = 100 (TOF = 105 s^{-1}) rather than Sionly catalysts (TOF = 70 s⁻¹) although both of them contain Pd particles of similar size (~10 nm) and highly ordered structures. On the basis of these results it might be concluded that even in the presence of a small amount of B the reaction rate increased, which implies that weak acid sites or hydrophobicity (related to the B species) participate in the reaction process under the studied reaction conditions. To check the role of support containing acid sites, the hydrogenation of nitrobenzene was conducted on ~1% Pd-containing Al and Ga-MCM-41 under similar reaction conditions as described for Pd/B-MCM-41. Generally, Al-MCM-41 possesses stronger surface acidity than its B counterpart^{34,35} and the order of acid strength is $Al > Ga \gg B$.³⁶ Following the comparison of reaction rate (TOF) between Pd supported on B-MCM-41 (Si/B = 10; particle size = 21.5 nm), Al-MCM-41 (Si/Al = 10; particle size = 18.9 nm) and Ga-MCM-41 (Si/Ga = 10; particle size 21.2 nm), the order is B $(140 \text{ s}^{-1}) > \text{Ga} (31.2 \text{ s}^{-1}) > \text{Al} (10.2 \text{ s}^{-1})$. In each case, Pd particle size was chosen as ~20 nm (ESI Fig. 3s:† low angle and higher angle XRD pattern of Pd-containing Al and Ga-MCM-41). Thus, acidity of support could not be the responsible factor for high activity of the catalyst. Substitution of a trivalent cation like B, Al and Ga modified the hydrophobic properties of Si-MCM-41 and the hydrophobicity order for substituted Si surfaces is $B > Ga > Al.^{37,38}$ Primarily, the order of hydrophobicity (prevents limited access of the substrate due to the stronger water adsorption) seems to be a possible deciding factor for higher reaction rate of Pd/B-MCM-41. However, information gathered from the TG analysis of Si-only and B-MCM-41 (Si/B = 100) reveals a different scenario as similar hydrophobicity (almost the same amount of water loss) was detected for both of the materials. As mentioned before, only Si and B-MCM-41 (Si/B = 100) possess significant differences in the reaction rate. Therefore, higher reaction rate of Pd/B-MCM-41 cannot be directly related to the hydrophobic nature of the support. It might be speculated that the presence of B in the support material causes an electronic interaction with Pd.^{39a} This brings about an increase in the metal's electron density, causing it to interact more strongly with H_2 adsorbed on the metal surface⁴⁰ and remarkably increases the reaction rate. A similar result was also observed during the liquid-phase hydrogenation of nitrobenzene over Pt supported on borate.39b

Hydrogenation of other substrates

The optimized reaction conditions (50 °C, 5 min, $P_{\rm CO_2} = 12$ MPa and $P_{\rm H_2} = 2$ MPa) of nitrobenzene have been applied for the hydrogenation of different nitroaromatics with electron-withdrawing group (-Cl) and electron-donating group (-OMe) and the results are shown in Table 2. The hydrogenation of o, m and *p*-chloronitrobenzene results in the corresponding amine with a very high selectivity of >99% and conversion follows the order of p > m > o (entries 1–3). A similar reaction over 5% Pd/C catalyst was also described by Ichikawa et al. in scCO₂ and obtained 100% conversion with 82.1% selectivity of chloroaniline at 40 °C, reaction time = 150 min, $P_{\rm H_2}$ = 1.1 MPa and $P_{\rm CO_2}$ = 10 MPa.⁴¹ Other compounds such as nitroanisoles also behaved in a similar manner (entries 4-6) though conversion was lower than halonitroaromatics. In each case, only the nitro group was hydrogenated, which might be attributed to the capability of the nitro group attached to the ring to pull electrons more strongly compared to other functional groups. As a result it could be easily attracted to the catalyst surface and be hydrogenated instead of the other groups.⁴² The potential of the catalyst is once again described by the hydrogenation of nitrile (-CN; electron-withdrawing group) and phenol (-OH; electron-donating group) (Table 2; entries 6 and 7). It has to be mentioned that, similar to nitro compounds, only -CN was hydrogenated to

Table 2Hydrogenation of different substrates on Pd/B-MCM-41 in $scCO_2^a$

Entry	Substrate	Conversion (%)	Product (selectivity %)
1		68.2	NH ₂ (100) CI
2		82.2	NH ₂
3		100	CI
4	Me NO2	53.5	(100) OMe
5	MeO	66.9	MeO (100)
6	MeO-NO2	89.2	MeONH ₂
7 ^b	✓N	60.2	(99.0)
8	он	98.5	(100) (100)

^{*a*} Reaction conditions: entries 1–6: catalyst = 0.1 g, substrate = 2.0 g, $P_{CO_2} = 12$ MPa, $P_{H_2} = 2$ MPa, temperature = 50 °C; time = 10 min. Entry 7 catalyst = 0.1 g, substrate = 1.0 g, $P_{CO_2} = 10$ MPa, $P_{H_2} = 2$ MPa, temperature = 50 °C; time = 2 h. Entry 8: catalyst = 0.1 g, substrate = 1.0 g, $P_{CO_2} = 12$ MPa, $P_{H_2} = 4$ MPa, temperature = 50 °C; time = 4 h. ^{*b*} Dibenzylamine = 1%.

primary amine with a selectivity of 99%. The hydrogenation of phenol (Table 2; entry 8), where ring hydrogenation is more preferable because of presence of the –OH group (electron-donating group), results in cyclohexanone as the only product. The ring hydrogenation was activated by acidity of the support⁴³ due to the presence of B in the support material, as confirmed by comparison with Pd/MCM-41 (only Si) catalyst under similar reaction conditions (temperature = 50 °C, time = 4 h, $P_{CO_2} = 10$ MPa, $P_{H_2} = 4$ MPa) as described previously.⁴⁴

Comparison with organic solvents

For comparison, hydrogenation of nitrobenzene was conducted in neat organic solvents like hexane and ethanol, and the results are shown in Table 3. In each case the amount of catalyst, substrate, H₂ pressure, temperature and reaction time were similar to those in scCO₂. In ethanol the reaction was also fast (Table 3: entry 2) and comparable with scCO₂ (Table 3; entry 1). However, the selectivity of aniline dropped (73.2%) due to the

 Table 3
 Nitrobenzene hydrogenation in different solvent and catalyst recycling

Entry	Solvent		Selectivity (%)	
		Conversion (%)	Aniline	Others
1	scCO ₂	100	100	0.0
2^a	Ethanol	100	73.2	26.8^{b}
3 ^{<i>a</i>}	Hexane	33.6	100	0.0
4^c	1st recycle	84.0	100	0.0
5	4th recycle	84.1	100	0.0
6	8th recycle	80.2	100	0.0

^{*a*} Solvent = 5 ml, only H₂ of 2 MPa. ^{*b*} Nitrosobenzene (3.8%), azoxybenzene (12.7%) and azobenzene (10.3%); reaction conditions: catalyst = 0.1 g, substrate = 2.0 g, P_{CO_2} = 12 MPa, P_{H_2} = 2 MPa, temperature = 50 °C; time = 5 min. ^{*c*} Recycling after shorter reaction time of 2 min (entries 4–6).

formation of by-products such as nitrosobenzene (3.8%), azoxybenzene (12.7%) and azobenzene (10.3%). It is well-known that scCO₂ has a low dielectric constant ($\varepsilon = 1.2-1.6$) under all conditions and it is believed that there are some similarity between the behaviour of CO₂ and hexane. Hydrogenation of nitrobenzene in hexane under the studied reaction conditions exhibited very low conversion (33.1%) (Table 3; entry 3), but aniline was the only product detected. This is excellent support to suggest that scCO₂ is a unique medium to achieve high activity and selectivity due to better solubility of H₂.

Again, a comparison with our previous work (catalyst = 5% Pd/C, conversion = 52%, selectivity = 100% reaction time = 10 min, $P_{\rm H_2}$ = 4 MPa and $P_{\rm CO_2}$ = 14 MPa; temperature = 35 °C) related to the hydrogenation of nitrobenzene using Pd catalyst in scCO₂ revealed that the reaction was exceptionally faster over Pd/B-MCM-41 catalyst.^{32a}

Catalyst recycling

Recycling of catalyst is one of the most important criteria for B-containing catalyst. Potential recyclability of the catalyst was conducted with a reaction time of 2 min under the similar reaction conditions as described before. After the designated reaction time, the catalyst was filtered and then transferred to another reactor containing fresh nitrobenzene. The process was repeated for eight successive runs. The conversion was consistent until the 7th run and then dropped to 80.2% without any change in the selectivity (Table 3; entries 4–6). TEM observations of the catalyst after the 4th recycle confirmed its stability, whereas some changes of particle size in comparison to the parent material (Fig. 2) were observed after the 8th recycle (see ESI, Fig. 4s \dagger).

Conclusions

In conclusion, Pd nanoparticles supported on B-MCM-41 were synthesized successfully by a hydrothermal method. Different characterization techniques revealed that, depending on Si/B ratio, structural order as well as Pd particle size varied. Investigation of the catalytic activity of Pd/B-MCM-41 suggested that

Experimental

processes.

Synthesis, characterization techniques and catalytic activity measurements

didate for further development of other clean chemical

it is an excellent catalyst for the hydrogenation reaction of nitro-

benzene under very mild conditions. The reaction was extremely fast due to the presence of B in the support and aniline was the only product formed. Furthermore, the effect of B can then be understood from the comparison with silica-only material. When the hydrogenation of nitrobenzene was conducted over Pd/ Al-MCM-41 and Pd/Ga-MCM-41, the reaction rate followed the order of B > Ga > Al. The described reaction system is free from any by-product formation and long-term catalytic activity can be achieved, as observed from recycling of the catalyst. This simple low metal-containing catalyst was also adaptable for successful chemo-selective hydrogenation of substituted nitroaromatics as

Materials. Tetraethyl orthosilicate (TEOS) as silica source, boric acid (H₃BO₃), sodium aluminate and gallium nitrate were taken as B, Al and Ga sources, respectively. All of the abovementioned chemicals, sodium hydroxide and nitrobenzene were purchased from Wako Pure Chemicals. Cetyltrimethylammonium bromide (CTAB) and PdCl₂ were from Aldrich Chemical Co. and used as received. CO₂ (>99.99%) has been provided by the Nippon Sanso Co. Ltd.

Synthesis. Hydrothermal synthesis of Pd/B-MCM-41 has been carried out as follows: Typically, sodium hydroxide and CTAB were added to de-ionized water and stirred until dissolved. After that, the required amount of H₃BO₃ was introduced slowly under stirring and stirring was continued for another 1 h, followed by the addition of 1 wt% solution of Pd salt and again stirred for another 1 h. Finally, TEOS was added to the solution with stirring for another 1 h and the gel mixture was autoclaved at 140 °C for 48 h. Final gel composition was: 1 TEOS, x B, 0.45 Na₂O, 0.12 CTAB, 118 H₂O, where x = 0.01-0.2. The solid product was then filtered, washed thoroughly with de-ionized water followed by oven drying at 60 °C. The synthesized material was calcined at 550 °C for 8 h in air to remove the template. For comparison, Pd supported on Al and Ga-MCM-41 materials were also synthesized in a similar manner. The resultant product was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR) and thermogravimetric-differential thermal analysis (TG-DTA).

Catalytic activity. All the reactions were conducted in a 50 ml stainless steel batch reactor and the details are given elsewhere.⁴⁴ Briefly, 0.1 g of catalyst and 2 g of the reactant were introduced into the reactor and placed in an oven with fan heater to maintain the desired temperature. At first H₂ of required pressure is introduced into the reactor. After that liquid CO₂ was charged using a high-pressure liquid pump (JASCO) and then compressed to the desired pressure. The reaction mixture was stirred during the reaction. The liquid product was separated from the catalyst and identified by GC-MS (Varian Saturn 2200), followed by

quantitative analysis using a GC (HP 6890) equipped with capillary column and flame ionization detector. For all results reported, the selectivity is defined as follows:

% selectivity = conc. of the product/total conc. of products $$\times\,100$$

For organic solvent in place of CO_2 , 5 ml of organic solvent has been used.

Catalyst characterization techniques

In order to have an approximation of the elemental composition and metal loading in Pd/B-MCM-41 samples, energy dispersive spectroscopy (EDS) was carried out with XL 30 s Philips Co. equipment coupled Scanning Electron Microscope. The analyses were randomly taken in several sample zones to have a representative value of the elemental composition.

Powder X-ray diffraction pattern was recorded on a Rigaku-RAD-X system using monochromatized Cu K α radiation (λ = 1.542 Å). In general, the diffraction data were collected using continuous scan mode with a scan speed of 2° min⁻¹ over the scan range $2\theta = 1.5-15^{\circ}$ and for wide-angle ($2\theta = 30-70^{\circ}$) measurements.

Transmission electron microscopy (TEM) of the material was recorded on a Philips Technai operating at 200 kV. The powder was suspended in ethanol by ultrasonic method. A drop of this solution was placed on a grid with a holey carbon copper film and then allowed to dry, covered by a watch glass.

Fourier-transform infrared spectra (FT-IR) were taken at room temperature on a Horiba spectrometer FT-720. Before measurement, samples were ground with KBr and pressed into thin wafers.

Thermogravimetric analysis was carried out by using a Rigaku Thermoflex TAS200 unit. About 10 mg of the sample was placed in a platinum pan and was heated at a heating rate of 10 $^{\circ}$ C min⁻¹.

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