

Hydrogenation of Phenol in Supercritical Carbon Dioxide Catalyzed by Palladium Supported on Al-MCM-41: A Facile Route for One-Pot Cyclohexanone Formation

M. Chatterjee,^{a,*} H. Kawanami,^{a,*} M. Sato,^a A. Chatterjee,^b T. Yokoyama,^a and T. Suzuki^a

^a Research Center for Compact Chemical Process, AIST, 4-2-1 Nigatake, Miyagino-ku, Sendai 983-8551, Japan
Fax: (+81)-22-237-5215; phone: (+81)-22-237-5211; e-mail: c-maya@aist.go.jp or h-kawanami@aist.go.jp

^b Accelrys KK, Nishishinbashi TS Bldg. 11F, 3-3-1 Nishishinbashi, Minato-Ku, Tokyo 105-0003, Japan
Fax: (+81)-03-3578-3873; phone: (+81)-3-3578-3860

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Abstract: The hydrogenation of phenol has been carried out in supercritical carbon dioxide (scCO₂) under very mild reaction conditions at the temperature of 50°C over palladium supported Al-MCM-41 (metal loading ~1%). This palladium catalyst is shown to be highly active and promotes the selective formation of cyclohexanone (~98%), an industrially important compound, in a “one-pot” way. The effects of different variables like carbon dioxide and hydrogen pressure, reaction time and also silica/alumina ratio of the MCM-41 support along with palladium dispersion are presented and discussed. The pressure effect of carbon dioxide is significantly prominent in terms of conversion and cyclohexanone selectivity. Moreover, the silica/alumina ratio was also found to be an important parameter to enhance the effectiveness of the catalyst as it exhibits a remarkable increase in phenol conversion from 20.6% to 98.4% as the support changes from only silica MCM-41 to Al-MCM-41. A plausible mechanism for the hydrogenation of phenol to cyclohexanone over the palladium catalyst has been proposed. The proposition is vali-

dated by transition state calculations using density functional theory (DFT), which reveal that cyclohexanone is a favorable product and stabilized by <19 kcal mol⁻¹ over cyclohexanol in scCO₂ medium. Under similar reaction conditions, phenol hydrogenation was also carried out with rhodium, supported on Al-MCM-41. In contrast to the palladium catalyst, a mixture of cyclohexanone (57.8%) and cyclohexanol (42.2%) was formed. Detailed characterization by X-ray diffraction and transmission electron microscopy confirmed the presence of metal nanoparticles (palladium and rhodium) between 10–20 nm. Both the catalysts exhibit strikingly different product distributions in solventless conditions compared to scCO₂. This method can also be successfully applied to the other hydroxylated aromatic compounds.

Keywords: density functional theory (DFT); one-pot process; Pd/Al-MCM-41; phenol hydrogenation; Rh/Al-MCM-41; supercritical carbon dioxide

Introduction

Cyclohexanone is known as one of the key intermediates in the synthesis of caprolactam and adipic acid, which are the main ingredients for the preparation of Nylon 6, Nylon 66 and polyamide resin.^[1] Industrially, cyclohexanone is obtained by a two-step process involving the hydrogenation of phenol to cyclohexanol followed by the dehydrogenation to cyclohexanone.^[2] However, there are many deficiencies existing mainly in the dehydrogenation of cyclohexanol such as the reaction temperature, the fact that the conversion is constrained due to the thermodynamic equilibrium and the poor hydrogen utilization. Thus, a one-step

process for the synthesis of cyclohexanone is preferred over the two-step process to avoid energy consumption and also in terms of the capital cost. Generally, the hydrogenation of phenol to cyclohexanone is carried out mainly in the gas phase with Pd^[3] or Pt catalysts.^[4] It has also been studied extensively in the liquid phase to obtain cyclohexanone^[5] and also in an aqueous system,^[6] which results in cyclohexanol or a mixture of cyclohexanol and cyclohexanone instead of only cyclohexanone.

Despite the fact that the reaction has been studied over several catalysts and different reaction environments, the nature of the catalyst support is an important issue, which has a strong impact on the product

selectivity. It is generally accepted that phenol adsorbs on the support while Pd adsorbs H_2 and consequently supplies it to the aromatic ring by a spill-over mechanism.^[7] Depending on the acid-base properties of the support, the adsorption geometry of phenol varies and changes the product selectivity from cyclohexanone to cyclohexanol or *vice versa*. So far, Pd supported on MgO ,^[8] mesoporous CeO_2 and ZrO_2 ^[9] have been considered as the most potent catalysts to obtain cyclohexanone with high selectivity in gas phase conditions. However, gas phase hydrogenation suffers from disadvantages like harsh reaction conditions, generation of by-products, which lowers the yield of desired product and the deactivation of the catalyst due to the coke deposition which is unavoidable.

Supercritical carbon dioxide ($scCO_2$) is a well-known environmentally benign “green” reaction medium for rapid and selective organic synthesis and various other industrial processes. Over the past few years, several heterogeneously catalyzed reactions have been successfully carried out in $scCO_2$, often with higher reaction rates and different product distributions, as well as high selectivity, in comparison with those obtained in conventional organic solvents.^[10] Recently, the hydrogenation of phenol has also been reported in $scCO_2$ using Rh/C ^[11a] and Rh/CNF .^[11b] The maximum selectivity for cyclohexanone was 17% (10 MPa of H_2 , 12 MPa of CO_2) and 43.3% (4 MPa of H_2 , 12–14 MPa of CO_2), over Rh/C and Rh/CNF , respectively.

Here, we demonstrate the one-step formation of cyclohexanone by phenol hydrogenation under very mild conditions using the Pd/Al-MCM-41 catalyst in $scCO_2$ as it has already been proved a promising medium to improve the efficiency of the catalyst. The result has also been compared with that of $Rh/Al-MCM-41$ to check the effect of the nature of metal on the product distributions.

Mesoporous material seems to be an ideal host for metal nanoparticles due to its very high surface area to immobilize catalytically active species on it or for providing a nanosize confinement inside the pore system.^[12] To provide additional functions to siliceous mesoporous material, Si can be easily substituted by Al, which in turn improves the catalytic activity because of the generation of acid sites, hydrothermal stability and the dispersion of nanoparticles on the material. Compared to other conventional supports, mesoporous material is exhibiting superior catalytic activity and significant enhancement of selectivity in $scCO_2$ during the selective hydrogenation of different organic compounds.^[13]

Results and Discussion

Characterization of Catalysts

Pd/Al-MCM-41

Analysis of the calcined product confirmed that the Pd loadings of all the samples are ~1%. The change of color from white (parent Al-MCM-41) to grey is taken as an initial indication of the presence of Pd^{2+} into the structure. After calcination, the material turns orange and this suggests the migration of Pd^{2+} to the surface of Al-MCM-41, by reaction with Si-OH groups of defect sites due to insufficient substitution of Pd^{2+} ions for both Si^{4+} sites and Al^{3+} sites in the lattice of Al-MCM-41.^[14]

Figure 1a exhibits the XRD pattern of Pd/Al-MCM-41 with different Si/Al ratios. All materials show typical low angle (100) reflections along with the smaller Bragg's peaks limited only to the higher Si/Al ratio. For low Al containing material, the most intense (100) XRD line appeared at $2\theta = 2.180^\circ$, whereas after increasing the Al content with the change of the Si/Al ratio to 8.5, the main peak is shifted to the lower value of $2\theta = 1.660^\circ$ with a decrease in the intensity as well; a likely explanation is that the reduced scattering intensities of the Bragg reflections might be caused by the introduction of scattering materials into the pores.^[15] However, the scattering pattern of higher Al containing Pd-Al MCM-41 (Si/Al = 16 and 8.5) does not show a series of Bragg's peak originating from the ordered two-dimensional hexagonal structure of MCM-41. Therefore, the reduced peak intensity of the material could be due to the disordered mesoporous structure. As the Si/Al ratio changes from 100 to 8.5, the main XRD peak was shifted towards the lower angle and the corresponding d spacing of Pd/AlMCM-41 increases from 4.05 nm to 5.32 nm. The unit cell parameters ($a_0 = 2d_{100}/\sqrt{3}$) for different Si/Al ratios are 4.6 nm (Si/Al = 100), 4.9 nm (Si/Al = 50), 5.7 nm (Si/Al = 16) and 6.1 nm (Si/Al = 8.5). The increase in basal (100) spacing indicates that the incorporation of Al generally results in an enhancement of the d_{100} spacing. This is consistent with the presence of tetrahedral Al in the framework and is attributed to the longer Al-O bond length compared to the Si-O bond.^[16]

To detect the Pd nanoparticles, XRD measurements are performed at the higher angle region ($2\theta = 30^\circ$ to 70°), and are displayed in Figure 1a as inset. In the calcined sample, five distinctive peaks at $2\theta = 33.8$, 42.0 , 54.8 , 60.7 and 71.4 corresponding to PdO are observed. Particle sizes are calculated from the XRD line broadening of the peak at $2\theta = 33.8$ using Scherrer's equation.^[17] There is a change of the particle size from 12 to 28 nm with the change in Si/Al ratio from 100 to 8.5. After reaction, the diffraction

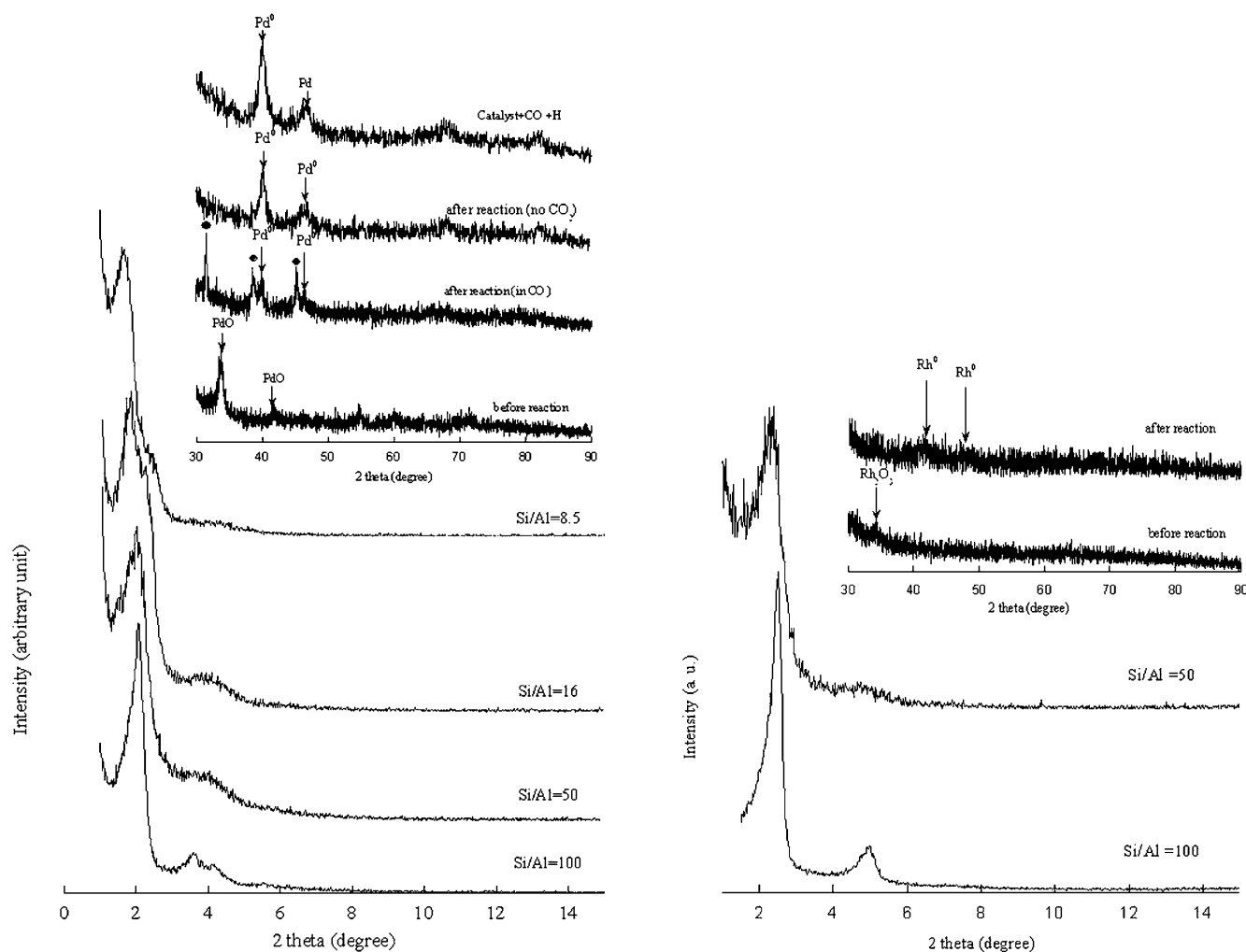


Figure 1. X-ray diffraction pattern of (a, left) Pd/Al-MCM-41; inset shows higher angle diffraction for Pd and (b, right) Rh/Al-MCM-41; inset shows higher angle diffraction for Rh.

lines of PdO disappear and a peak corresponding to Pd(0) appears at $2\theta = 40.1$ along with some unidentified peaks marked with circles (Figure 1a; inset). No such peaks are observed after the reaction in solventless conditions. However, it is unreasonable to predict the possibility of interaction between CO₂ and metal as no such peaks are found in the absence of phenol (catalyst-CO₂-H₂). Hence, it can be speculated that the interaction of the catalyst with CO₂ and H₂ is different when phenol is present in the system.

Rh/Al-MCM-41

The XRD pattern of calcined Rh/Al-MCM-41 of Si/Al=100, 50 exhibits a single peak in the low angle region (100) along with the other Bragg peaks thus confirming the hexagonal structure (Figure 1b). Compared to the Si/Al=100 material, the peak position

has been shifted to the lower value for Si/Al=50 and consequently a_0 has increased from 3.9 nm to 4.5 nm. Moreover, for higher Al containing materials (Si/Al=16 and Si/Al=8.5) the structures are collapsed after calcination, probably due to the incorporation of the much larger Rh (ionic radii of Rh³⁺=0.8 Å). XRD patterns of the higher angle region of the calcined Rh/Al-MCM-41 sample exhibit a peak at $2\theta = 34.3^\circ$ indicating the presence of Rh₂O₃ particles with orthorhombic symmetry^[18] and the particle sizes (10 nm–20 nm) are calculated from the XRD pattern in a similar manner as described for Pd/Al-MCM-41.

TEM of Pd/Al-MCM-41

Figure 2a shows a TEM image of Pd/Al-MCM-41 (Si/Al=100) through the pore axis. The image exhibits the regular ordered hexagonal channel, characteristic

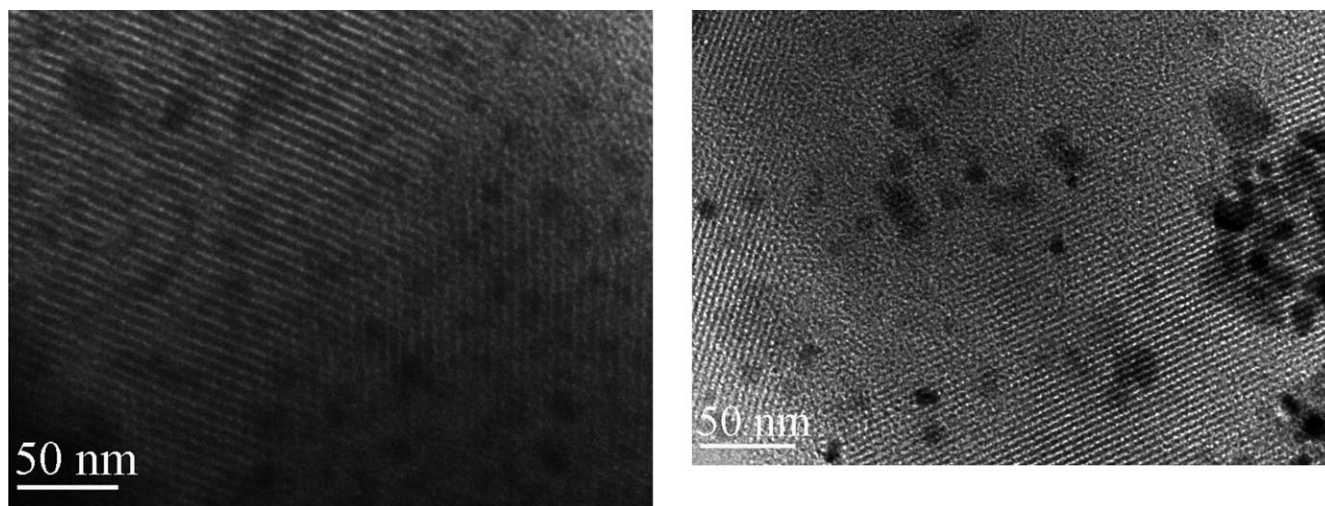


Figure 2. TEM image of (a, *left*) Pd/AlMCM-41 (Si/Al=100) and (b, *right*) Rh/AlMCM-41 (Si/Al=100).

of MCM-41. The Pd particles are spherical and distributed throughout the MCM-41 matrix. Calculation of the particle size distribution confirms the presence of mainly 10–12 nm particles, which corresponds well with the XRD measurements of wide angle line broadening. However, the higher Al content (Si/Al=8.5) material reveals a disordered structure with larger PdO particles as observed by TEM (not shown).

TEM of Rh/Al-MCM-41

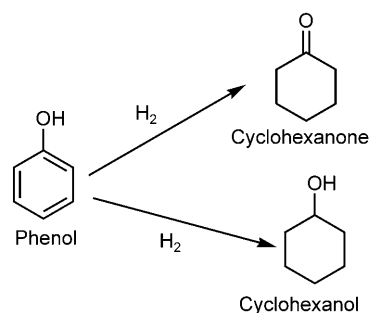
The structure of Rh/Al-MCM-41 is evident from the TEM image of the material (Figure 2b; Si/Al=100). An ordered array of channels has been observed. The regular array was totally disrupted when the Al content increased. It is evident from the image that Rh particles are spherical and randomly distributed. An average particle size of ~10 nm is revealed from the calculation of the particle size distribution.

Hydrogenation of Phenol

Scheme 1 exhibits the probable reaction pathway of the hydrogenation of phenol to cyclohexanone and cyclohexanol under the studied reaction conditions (P_{CO_2} = 12 MPa, P_{H_2} = 4 MPa, T = 50 °C) in scCO_2 medium.

Effect of Different Catalysts

It is well-known that noble metals possess the ability to generate atomic hydrogen,^[19] so Pd-, Pt- and Rh-



Scheme 1. Reaction path for the hydrogenation of phenol in scCO_2 over Pd/Al-MCM-41 and Rh/Al-MCM-41.

containing catalysts were chosen for the hydrogenation of phenol and the results are shown in Table 1. It is evident that the Rh catalyst generally produces a mixture of cyclohexanone and cyclohexanol independent of the support and the highest conversion of phenol (100%) is observed when the Rh/Al-MCM-41 or Rh/MCM-41 catalyst was used (Table 1; entries 3 and 4). On the other hand, Pt and Pd catalysts show cyclohexanone as the major product with very high selectivity (Table 1 entries 6–10). However, the phenol conversion is very low over the Pt catalyst (>10%) whereas Pd/Al-MCM-41 exhibits excellent conversion and selectivity to cyclohexanone (Table 1; entry 10). As the aim of this study is to optimize the reaction conditions to obtain high selectivity for cyclohexanone, the hydrogenation of phenol has been carried out over Pd and the results are compared with those from Rh/Al-MCM-41.

Table 1. Hydrogenation of phenol over various noble metal catalyst in supercritical carbon dioxide.^[a]

Entry	Catalyst	Conversion [%]	Selectivity	
			Cyclohexanone	Cyclohexanol
1	Rh/Al ₂ O ₃	35.1	32.1	67.9
2	Rh/C	62.1	21.1	78.9
3	Rh/MCM-41	100.0	46.5	53.5
4	Rh/Al-MCM-41	100.0	52.8	47.2
5	Pt/C	2.5	100.0	0.0
6	Pt/Al ₂ O ₃	8.4	91.0	9.0
7	Pd/C	12.0	60.2	39.8
8	Pd/Al ₂ O ₃	46.0	70.1	29.9
9	Pd/MCM-41	20.0	86.4	13.6
10	Pd/Al-MCM-41	98.4	97.8	2.2
11	Pd/Al-MCM-41	98.6	97.8	2.2
12	Pd/Al-MCM-41	98.2	97.9	2.1
13	Pd/Al-MCM-41	96.4	97.7	2.3
14	Pd/Al-MCM-41	90.2	97.8	2.2

^[a] Reaction conditions: catalyst = 0.1 g, phenol = 1.0 g; temperature = 50 °C; P_{CO₂} = 12 MPa, P_{H₂} = 4 MPa, time = 4 h; entries 11–14 recycling data.

Effect of CO₂ Pressure

Pd/Al-MCM-41

Figure 3a shows the effect of CO₂ pressure from 7 MPa to 14 MPa and compared with the solventless conditions on the hydrogenation of phenol over Pd/Al-MCM-41 at the fixed temperature of 50 °C and hydrogen pressure of 4 MPa. A strong influence of the CO₂ pressure has been observed on the conversion and the selectivity. At 7 MPa, the conversion is as low as 46% and the selectivity of cyclohexanone is 57.4%. The conversion and selectivity of cyclohexanone are enhanced from 46.4% to 98.4% and 57.4% to 97.8%, respectively, as the CO₂ pressure changes from 7 MPa to 14 MPa and above 14 MPa the selectivity remains constant. In comparison with the higher pressure region, a noticeable difference in the product distribution has been found at the lower pressure of 7 MPa, where CO₂ mainly exists in the gas phase. At the lower pressure of CO₂ (< 8 MPa), the product is

composed of 1:1 mixtures of cyclohexanone and cyclohexanol, whereas cyclohexanone is the sole product at higher pressure (> 10 MPa). Again, under the solventless conditions, a mixture of cyclohexanone and cyclohexanol was formed and the conversion decreased to 28.9% due to the mass transfer limitation.

Rh/Al-MCM-41

The scenario of the CO₂ pressure effect has been changed completely when Rh/Al-MCM-41 is used (Figure 3b). Under the similar reaction conditions of Pd, apparently no significant influence of CO₂ pressure is observed on the conversion of the phenol hydrogenation; in each case, the conversion of phenol is 100% within the reaction time of 4 h. However, a trivial effect of CO₂ pressure was observed when the reaction time changed to 0.5 h; the phenol conversion changes from 68.2% to 52.1% with the increase in pressure from 7–12 MPa. Again, at the lower pressure

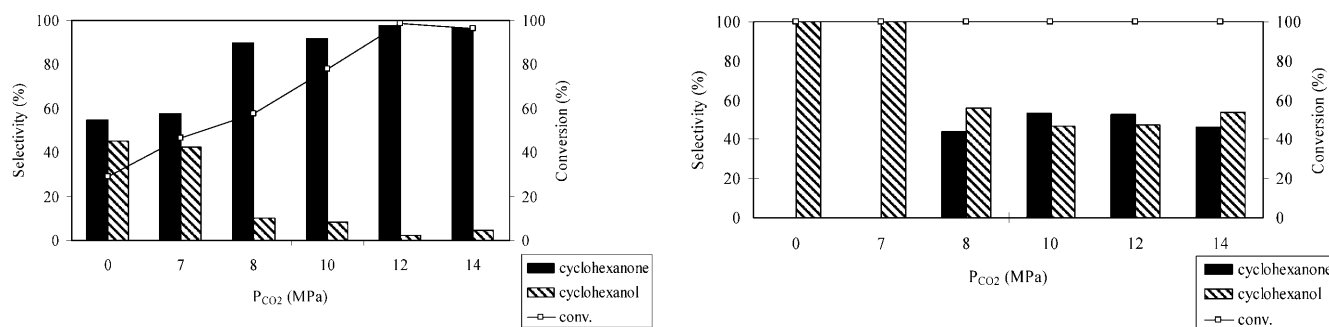


Figure 3. Effect of CO₂ pressure on the conversion and selectivity of (a, left) Pd/Al-MCM-41 and (b, right) Rh/Al-MCM-41. Reaction conditions: catalyst = 0.1 g, phenol = 1.0 g; temperature = 50 °C; P_{H₂} = 4 MPa, time = 4 h.

of CO₂, cyclohexanol is the main product with 100% selectivity, while on increasing the pressure from 8–14 MPa, a mixture of cyclohexanone and cyclohexanol is formed. The ratio of the product changes from 1:1.3 to 1:0.9 (cyclohexanone:cyclohexanol) as the pressure is enhanced from 8 MPa to 14 MPa. Surprisingly, complete conversion and highest selectivity (100%) of cyclohexanol is achieved when the hydrogenation of phenol is carried out in the solventless conditions (Figure 3b).

It is observed that, for both catalysts, the product distribution at lower pressure follows different trends to that of the liquid CO₂ phase condition. Hence, it is expected that the reaction mechanism of phenol hydrogenation in gas phase conditions of CO₂ is similar to that of the solventless conditions but differs from that in the liquid phase conditions. Visual observation of the phase behavior, under similar conditions revealed that in the higher CO₂ pressure (>10 MPa) region, the mixture of substrate, CO₂ and H₂ transforms from a binary (liquid-gas) phase to a homogeneous phase. This transition is accompanied by the intrinsic change in product selectivity and also the conversion. Thus, elimination of the gas-liquid interface is crucial to achieve highest performance of Pd/Al-MCM-41 but it is not necessary for the Rh/Al-MCM-41 catalyst.

Effect of Hydrogen Pressure

Pd/Al-MCM-41

Figure 4a shows the dependence of hydrogen pressure on the conversion and selectivity over Pd/Al-MCM-41 at fixed temperature (50 °C) and CO₂ pressure (12 MPa). The degree of phenol conversion is very sensitive to the hydrogen pressure. When the pressure changes from 1 to 4 MPa, the conversion increases from 50.2% to 98.4% as the concentration of hydrogen is enhanced in the system. Nevertheless, there is a

slight change in the selectivity of cyclohexanone from 86.5% to 97.8% along with the hydrogen pressure.

Rh/Al-MCM-41

Variation of conversion and selectivity as a function of hydrogen pressure over Rh/Al-MCM-41 under the similar reaction conditions as for Pd/Al-MCM-41 is shown in Figure 4b. At 1 MPa, the conversion of phenol is low (46.1%). Increasing the pressure to 4 MPa the conversion is enhanced to 100% and it also affects the product distribution over Rh/Al-MCM-41. When conversion is low (46.1%), then selectivity of cyclohexanone is comparatively high at 71.2%, but increasing conversion of phenol is accompanied by a complete hydrogenation to cyclohexanol. The enhancement of the activity and selectivity of cyclohexanol attributes to the increased concentration of hydrogen in the reaction mixture.

Therefore, hydrogen pressure is an important parameter to influence the conversion and selectivity for both Pd- and Rh/Al-MCM-41.

Effect of Reaction Time

The effect of reaction time on the hydrogenation of phenol over Rh- and Pd/Al-MCM-41, suggests that the rate of the reaction does not differ considerably under the studied reaction conditions (Figure 5a and Figure 5b). For instance, 65.6% and 52.1% conversion are achieved within 0.5 h over the Pd and Rh catalyst, respectively. The conversion of phenol on Pd/Al-MCM-41 remains unchanged after the extension of reaction time from 3 to 5 h and the deactivation of the catalyst could be suspected. However, the recycling of the catalyst was straightforward (Table 1 entries 11–14). Only after the 3rd recycle did the activity of the catalyst start to decrease. Moreover, the selectivity of cyclohexanone for the Pd catalyst re-

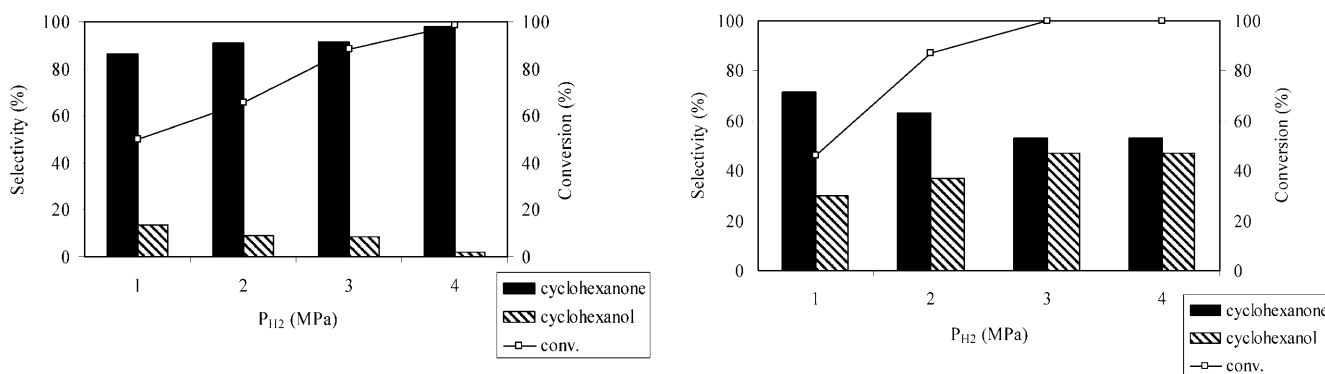


Figure 4. Variation of H₂ pressure on the conversion and selectivity of (a, left) Pd/Al-MCM-41 and (b, right) Rh/Al-MCM-41. Reaction conditions: catalyst = 0.1 g, phenol = 1.0 g; temperature = 50 °C; P_{CO₂} = 12 MPa, time = 4 h.

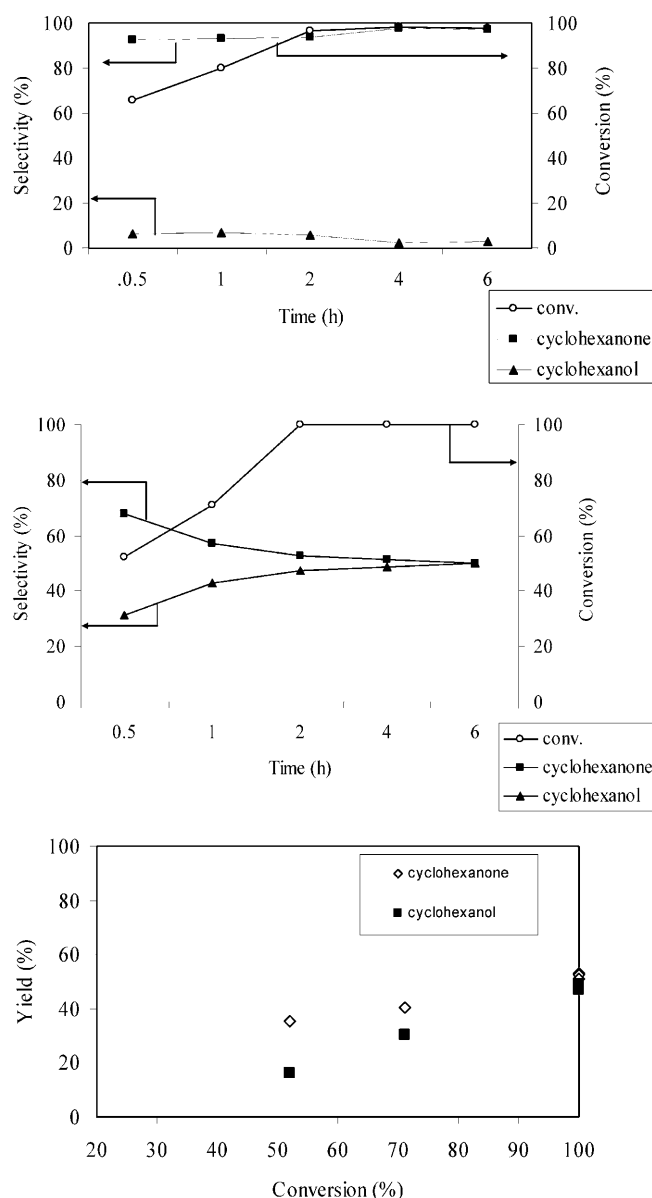


Figure 5. Variation of reaction time on the conversion and selectivity of (a, top) Pd/Al-MCM-41 and (b, middle) Rh/Al-MCM-41. Reaction conditions: catalyst = 0.1 g, phenol = 1.0 g; temperature = 50 °C; P_{CO_2} = 12 MPa, P_{H_2} = 4 MPa. (c, bottom) Variation of the yield of cyclohexanone and cyclohexanol with conversion over Rh/Al-MCM-41.

mained unaffected by the reaction time. No leaching of Pd has been detected in the supernatant after the reaction.

The product distribution of phenol hydrogenation over Rh/Al-MCM-41 differs as the time changes from 0.5 h to 2 h, but remains constant as soon as the conversion reaches its maximum of 100%. The decreasing selectivity of cyclohexanone and simultaneous increasing selectivity of cyclohexanol takes place within 2 h of reaction time and then remains constant. This

result leads us to believe that initially cyclohexanol is formed at the expense of cyclohexanone. To verify this result, the yield of each product versus conversion using Rh/Al-MCM-41 was plotted and is shown in Figure 5c. Interestingly, the yields of both cyclohexanol and cyclohexanone increase with increasing phenol conversion, attributing the independent formation of cyclohexanone and cyclohexanol. Chary et al.^[20] observed a similar pattern during the vapor phase hydrogenation of phenol over Pd/C catalyst. Again, to confirm the independent formation of cyclohexanol, the hydrogenation of cyclohexanone was carried out under similar reaction conditions as for phenol, but no cyclohexanol was observed. Hence, it can be inferred that the cyclohexanone and cyclohexanol are two independent products and not obtained with the expense of others in scCO_2 over Rh/Al-MCM-41.

Therefore, depending on the nature of the catalyst's active site, phenol can interact with the surface through the aromatic ring, or the hydroxy group, where the former ended up with the complete hydrogenation.^[21] Furthermore, Pd- and Rh/Al-MCM-41 catalysts both maintained their catalytic activity for at least 20 h of reaction time. This indicates that the catalysts are free from deactivation under the studied reaction conditions.

As we have mentioned before (Figure 3a and Figure 3b), there is a considerable difference in the conversion and selectivity as the reaction was carried out in solventless conditions using Pd- and Rh/Al-MCM-41. The importance of scCO_2 medium is evident from the difference in the rate of phenol hydrogenation on Pd/Al-MCM-41 catalyst. In solventless conditions, the conversion is poor (14.3%) whereas a radical change in the conversion (65.6%) is achieved in scCO_2 within the reaction time of 0.5 h. It seems to be reasonable to explain the enhanced activity in scCO_2 medium because of increased solubility of hydrogen in the medium, which decreases the mass transfer limitations. In addition, a drastic change in the product distribution is also evident from the Figure 3a. A mixture of cyclohexanone and cyclohexanol is formed under the solventless conditions whereas cyclohexanone has been obtained in scCO_2 medium. The difference in product distribution depending on the presence and absence of scCO_2 , is suggesting a change in the adsorption geometry of phenol influenced by the electronic structure of the metal active site. Namely, the solvent influences the polarity of the catalyst surface^[22] and a modification in electronic structure has also been predicted in scCO_2 , which strongly affects the catalytic activity and the selectivity of the reaction.^[23]

In contrast to Pd/Al-MCM-41, the rate of the reaction decreased in scCO_2 (52.1% conversion in 0.5 h) compared to the solventless conditions (98.0% con-

version in 0.5 h) over Rh/Al-MCM-41 catalyst. Thus, initial conversion in CO₂ and solventless condition shows marked difference and at present it is not possible to predict the exact cause behind the decrease in conversion because of the complicated nature of kinetics of this solid (catalyst)-liquid (solvent+substrate)-gas (H₂) system. The yields of cyclohexanone and cyclohexanol, change from 30.1% and 21.4 to 4.7% and 93.1%, respectively, as the reaction was performed in the absence of solvent. This result can be explained by considering the fact that when the substrate molecule interacts with the catalyst the process of adsorption of substrate to the catalyst surface proceeds through the interaction between the substrate and the catalyst and consequently a surface complex can be formed (reactant-metal). The magnitude of the reaction rate of the heterogeneously catalyzed reaction depends on the stability of the surface complex, which varies implicitly with the molecular structure of the substrate.^[24] Thus, one could expect a probable change in the reaction rate between only phenol in solventless conditions and phenol solvated in CO₂ which interacts with the catalyst. However, it is too early to comment on the reduction of the reaction rate as it needs a detailed study of the molecular structural changes of phenol in scCO₂ over Rh/Al-MCM-41.

From the above results, it can be concluded that the hydrogenation of phenol exhibits different types of product distribution even under the same reaction conditions due to the difference in the nature of the active metal ion. Furthermore, the reaction paths for the hydrogenation of phenol considerably differ between scCO₂ and solventless conditions independent of the nature of the metal. As our main concern is cyclohexanone, which is formed over Pd catalyst, the following part will continue with a more detailed study on combining the nature of the catalyst and its active site.

From Table 1, it is evident that, depending on the support, the catalytic activity changes. Indeed, according to the literature,^[25] the hydrogenation of phenol over Pd catalyst occurs when hydrogen is activated on Pd and phenol is adsorbed as a phenolate species over the support close to the metal particles. A significant alteration in conversion is also found when Pd is supported on the Al-MCM-41 instead of only silica MCM-41 (entry 9; Table 1).

Effect of Si/Al Ratio

The effect of the Si/Al ratio on the activity and selectivity over Pd/Al-MCM-41 catalyst is shown in Figure 6. The Pd catalyst supported on Al-MCM-41 exhibits much higher activity than Pd-MCM-41 (only silica support). The introduction of Al leads to a dra-

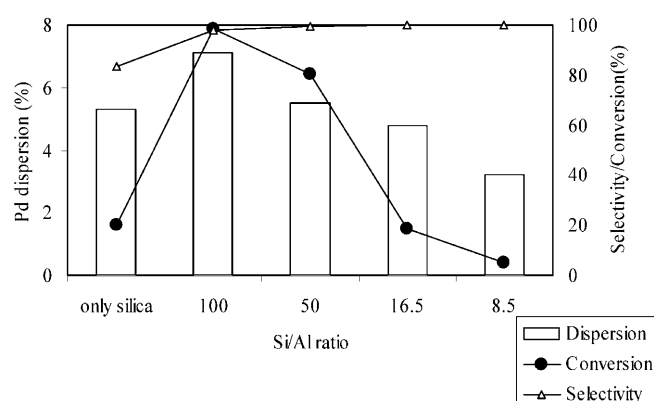


Figure 6. Effect of Pd dispersion and Si/Al ratio on phenol conversion and cyclohexanone selectivity over Pd catalyst.

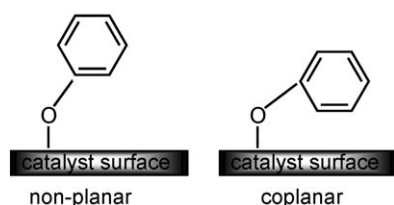
matic change in the phenol conversion from 20% (only silica) to 98.4% (Si/Al=100) and also the selectivity of cyclohexanone changes from 78.4% to 97.8%. The promoting effect of Al could be attributed to the increase of surface acidity. It is well known that incorporation of Al to MCM-41 might serve as acid sites and thus enhance the activity. The phenol molecule can adsorb on the acidic site either by the donation of π -electrons of the benzene ring or through the OH group and the later is more favorable under the present reaction conditions. The best result is obtained over Pd/Al-MCM-41 when Si/Al=100, among the catalysts of varying Si/Al ratios. This expression of conversion and selectivity might be related to the acidity of the mesoporous support. It is commonly assumed that the acid sites within the molecular sieve structure are essential for enhancement of the catalytic activity.^[26] However, when the Al content increases with the change in the Si/Al ratio from 50 to 8.5, the acidity changes from 161 to 381 $\mu\text{moles/g}$ and the conversion of phenol was decreased from 80.3% to 18.5%. Thus, the higher acidity of the support lowers the conversion of phenol. This result can be explained by the fact that in the MCM-41 structure, the incorporation of Al leads to the formation of tetrahedral Al³⁺ in the framework. For high Al contents, most Al atoms are anchored on the outer surface rather than incorporated into the framework of MCM-41^[27] and the growing part of the acid sites (tetrahedral Al³⁺) might be neutralized by non-framework cationic Al species which blocks the strong acid sites.^[28] In addition, increasing the Al content could cause some deterioration in the pore structure as well as in the texture of the mesoporous material,^[29] which is clearly observed from the Figure 1a and harmful for the activity of the catalyst. A similar result has been obtained by Li et al. during the Ullmann reaction over a Pd-containing Al-MCM-41 catalyst.^[30] This observation is in contrast to the results of Neri et al.^[9] who observed a significant decrease in the se-

lectivity of cyclohexanone during the vapor phase hydrogenation of phenol, with increasing acidity of the support and a preference of Pd/MgO over Pd/Al₂O₃, which could be due to the difference in reaction conditions.

To gain an insight into the relation between the nature of the catalyst and its activity, the effect of particle size distribution, which is related to the product selectivity, has also been studied. Figure 6 exhibits the dispersion of Pd depending on the Si/Al ratio and also the sole silica material. The Pd metal dispersion varies from 7.1% to 3.2% as the Si/Al ratio changes from 100 to 8.5 and indicated that, with increasing Al content, the Pd particle size increases. Although a slight change in the selectivity from 97.8% to 100% is evident, this is within the experimental error range. Hence, the selectivity to cyclohexanone seems to be structure insensitive.

Possible Mechanistic Considerations of the “One-Pot” Formation of Cyclohexanone

Regarding the mechanism of the hydrogenation of phenol and the formation of cyclohexanone in the vapor phase over Pd/Al-MCM-41, it is reported that the adsorption orientation of the phenol molecule changes from co-planar to non-planar depending on the acidity and basicity of the medium and results in the formation of cyclohexanol and cyclohexanone, respectively (Scheme 2).^[9] However, it is interesting to observe that, in scCO₂, cyclohexanone is formed ex-



Scheme 2. Orientation of phenol adsorption on the catalyst surface.

clusively when an optimum amount of Al is present in the support, which is in contrast to the described mechanism for the vapor and liquid phase hydrogenation of phenol. There are two possible interactions: (i) catalyst-substrate and (ii) catalyst-substrate-solvent. To understand the plausible reaction routes, a comparison is made between the phenol hydrogenation in scCO₂ and in conventional organic solvents like ethanol and hexane under the same reaction conditions. Unfortunately, the phenol conversions in ethanol (24.7%) and hexane (9.1%) are extremely poor. The selectivity of cyclohexanone in ethanol (42.1%) is strikingly low compared to those in the scCO₂ medium and hexane (65.1%). Hence, it is confirmed that the mechanism of the phenol hydrogenation reaction must be different depending on the nature of the solvent. In scCO₂, the solubility of H₂ is higher and the increasing phenol conversion in scCO₂ correlates well with the presence of a high concentration of H₂ because of the larger solubility and absence of mass transfer limitations. According to the product distribution, it is evident that phenol prefers a non-planar orientation for adsorption on Pd/Al-MCM-41 rather than a co-planar one as cyclohexanone is the main product. One probable explanation could be that phenol is a polar compound and its attraction towards ethanol would be stronger as the polarity of the solvent is higher. From the DFT calculations (details are given in the Experimental Section) on the optimized geometry of phenol in CO₂ and in ethanol, it is proved that phenol is less stable in CO₂ by *ca.* 8 kcal mol⁻¹ (Table 2). Thus, it can be suggested that, for ethanol as medium, less phenol is available to the catalyst active site, as it will prefer to stay solvated. So, more space will be accessible for the phenol molecule to adsorb co-planar on the surface. On the contrary, as scCO₂ is a quadrupolar solvent and the interaction between solvent and substrate will be less than for substrate-catalyst, more phenol will be attracted to the catalyst active site. As a result, the concentration of phenol over the catalyst surface will be increased and less space is available to adsorb on the catalyst surface and that might be reasonable for phenol to

Table 2. Total energy, stabilization energy of reactant and products in ethanol and CO₂ medium and transition state calculation to identify the reaction energy of cyclohexanone and cyclohexanol.

Molecule	Solvent	Total energy (Hartree)		Stabilization energy (kcal mol ⁻¹)	
reactant + Pd	CO ₂	-474.6736518		8.0965040747	
reactant + Pd	Ethanol	-474.6865544			
Energy of reactant (Hartree)	Energy of product cyclohexanol (Hartree)	Energy of cyclohexanone (Hartree)	Energy for transition state (Hartree)	Energy of reaction (kcal mol ⁻¹)	Feasibility of reaction (kcal mol ⁻¹)
-474.5717	-474.7984		-474.7630	-142.274	
-474.5717		-474.8128	-474.3430	-161.301	-19.027

adsorb preferably in a non-planar way. Depending on the mode of adsorption, either co-planar or non-planar geometry results in a shifting of the selectivity. To confirm this proposition, transition state calculations have been performed and the results are shown in Table 2. This shows that the barrier height of cyclohexanone formation is *ca.* 19 kcal mol⁻¹ less than that of cyclohexanol, which makes it a stable product in CO₂ and hence confirms the highest selectivity of cyclohexanone.

However, it is difficult to predict the exact reaction route of phenol hydrogenation because heterogeneous catalysis in scCO₂ is very complicated system and the interaction of organic molecules in the channel system of molecular sieves are far from being understood completely.

Hydrogenation of Other Hydroxy Aromatic Compounds

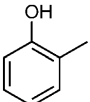
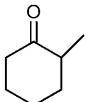
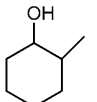
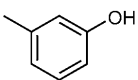
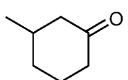
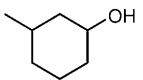
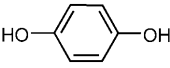
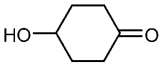
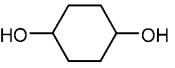
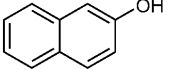
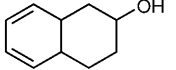
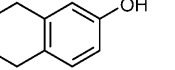
To explore the scope of the application of Pd/Al-MCM-41, this method has been extended to the other hydroxy aromatic compounds under the similar reaction conditions and the results are shown in Table 3. Interestingly, the ring hydrogenation is observed in every case and the partial hydrogenation products are formed with reasonable selectivity. Indeed, the hydrogenation of *o*-cresol produces methyl cyclohexanone with *ca.* 78% selectivity and interestingly the dihydroxybenzene derivative produces hydroxycyclohexanone with 80% selectivity (entries 1–3; Table 3). Generally, the presence of electron-releasing substituents on the aromatic ring influences the acidity due to the resonance/or inductive effect and activates the ring. From these results (Table 3) it is obvious that the selectivity of the ketone product is higher. For explaining the much higher selectivity of the ketone intermediate over a Pd catalyst, it requires the regioselective

addition of hydrogen to phenols, which maintains the resonance energy as much as possible and produces a series of hydrogenation intermediates. Differences in the resonance stabilization energy between the transition states may play a significant role to determining the product selectivity. On the other hand, the formation of the fully hydrogenated product may be accounted for by the decrease in the contribution of the phenoxide ion or an increase in the strength of the adsorption to suppress the contribution of the resonance energy.^[31] The hydrogenation of naphthol reflects a relatively good selectivity to the tetrahydronaphthol compound (*ca.* 85%) (entry 4; Table 3), possibly due to the generation of a cationic intermediate through the kinetically favored C-1 (naphthalene is also stabilized by resonance structures) that maintains one benzene ring intact.

Conclusions

In conclusion, we have demonstrated the hydrogenation of phenol over Pd/Al-MCM-41, which effectively promotes the formation of cyclohexanone; an industrially important compound, in scCO₂. From the results it is confirmed that for this reaction scCO₂ is an essential medium because it enhances the catalytic activity substantially by lowering the mass transfer limitation between solid and gas phases. Furthermore, as the reaction has occurred at a mild temperature of 50 °C it reduces the energy consumption and is also cost effective. The reaction is free from any by-product formation and long-term catalytic activity can be achieved. A detailed study on Pd/Al-MCM-41 has revealed a significant increase in phenol conversion with the incorporation of Al on the mesoporous support due to the acidity of the support material. The reaction is classified as a structure insensitive reaction as the particle size translates no impact on selectivity.

Table 3. Hydrogenation of hydroxy aromatic derivatives with Pd/AlMCM-41.^[a]

Entry	Substrate	Conversion [%]	Selectivity [%]	
1		79.1	 	77.3:22.7
2		65.6	 	89.1:10.1
3		30.0	 	79.9:20.1
4		83.0	 	84.8:5.2

^[a] Reaction conditions: catalyst = 0.1 g; phenol = 1.0 g; temperature = 50 °C; P_{CO₂} = 12 MPa; P_{H₂} = 4 MPa; time = 4 h.

A plausible mechanism of phenol hydrogenation has been predicted over Pd/Al-MCM-41, which exhibits a strong effect of the nature of the reaction medium. The transition state calculations of the reaction using DFT confirmed the stability of cyclohexanone in CO₂ and thus its high selectivity. Alterations of the process variables like CO₂ and H₂ pressure served to increase the conversion of phenol but the selectivity to cyclohexanone remain unaltered. An appreciable catalytic performance in terms of conversion and selectivity is also observed for the Rh/Al-MCM-41 catalyst. However, the product distribution differs considerably in comparison with that of the Pd/Al-MCM-41 and the mixture of cyclohexanone and cyclohexanol is formed. In summary, this study provides a greener and simpler way for the formation of cyclohexanone from an environmental hazardous material like phenol. The nature of the solvent medium and the metal active site are the most important factors to determine the product distribution. Successful application of this method is also possible to the other hydroxy aromatic compounds.

Experimental Section

Catalyst Synthesis

Materials: Tetraethyl orthosilicate (TEOS) as silica source, sodium aluminate as aluminium source and sodium hydroxide were purchased from Wako Pure Chemicals. Cetyltrimethylammonium bromide (CTAB), PdCl₂ and RhCl₃ were from Aldrich Chemical Co. All materials were used as received. CO₂ (>99.99%) has been provided by the Nippon Sanso Co. Ltd.

Hydrothermal Synthesis of Pd/Al-MCM-41: Typically, sodium hydroxide and CTAB were added to de-ionized water and stirred until dissolved. After that, TEOS along with the required amount of sodium aluminate are introduced slowly under the stirring condition and with continued stirring for another 1 h. A 1 wt% solution of Pd salt was introduced in to the gel and again stirred for 2 h. The final gel composition is : 1 TEOS: x Al: 0.45 Na₂O: 0.12 CTAB: 118 H₂O, where x=0.01–0.11. The gel was then autoclaved at 140 °C for 48 h. The solid product was filtered, washed thoroughly with de-ionized water followed by oven drying at 60 °C. To remove the template, the material was calcined at 550 °C for 8 h in air.

For the sake of comparison, Rh/Al-MCM-41 has also been synthesized in the similar manner. Finally, the product was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). These two catalysts have been termed as Pd/Al-MCM-41 and Rh/Al-MCM-41, respectively.

Catalytic Activity

All the reactions were carried out in a 50-mL stainless steel batch reactor and the details are given elsewhere.^[13] Briefly, 0.1 g of catalyst and 1 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 at the required pressure was 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 simply by filtration and identified by GC-MS, 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:

$$\% \text{ selectivity} = \frac{\text{concentration of the product}}{\text{total concentration of the products}} \times 100.$$

For organic solvent in place of CO₂, 5 mL of organic solvent were used.

Catalyst Characterization

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

Transmission electron microscopy (TEM) of the material was recorded on Philips Technai operating at 200 kV. The powder was suspended in ethanol by an 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.

Phase Behavior Studies

Visual observation of phase behavior of phenol under the studied reaction condition was studied with a 10-mL high pressure view cell fitted with a sapphire window. The cell is placed over a magnetic stirrer for stirring the content and connected to a pressure controller, to regulate the pressure inside the view cell. In addition to that a temperature controller was also used to maintain the desired temperature of 50 °C. Phenol was introduced into the view at a constant hydrogen pressure of 4 MPa while the CO₂ pressure was varied in the range of 7–14 MPa and the phase behavior of phenol-H₂-CO₂ system was monitored.

Computational Methodology

All the calculations related to the transition state were performed with density functional theory (DFT)^[32] using the DMol³ code^[33] of Accelrys Inc. BLYP exchange correlation functional^[34a] and DNP basis set.^[34b] In order to consider the effect of solvent, we employed the conductor-like screening model (COSMO) solvation method within the DFT formalism as in the program DMol³ of Accelrys Inc.^[35] In this method, the solute molecules form a cavity within the dielectric continuum of permittivity ϵ that represents the solvent. The charge distribution of the solute polarizes the dielectric medium. The response of the dielectric medium is described by the generation of screening (or polarization) charges on the cavity surface. The cavity surface is obtained as a superimposition of spheres centered at the atoms, discarding all parts lying on the interior part of the surface.

The spheres are represented by a discrete set of points, the so-called basic points; eliminating the parts of the spheres that lie within the interior part of the molecule thus amounts to elimination of the basic grid points that lie in the interior of the molecule. The radii of the spheres are determined as the sum of the van der Waals radii of the atoms of the molecule and of the probe radius. The surviving basic grid points are then scaled to lie on the surface generated by the spheres of van der Waals radii alone. The basic points are then collected into segments, which are also represented as discrete points on the surface. The screening charges are located at the segment points. The transition state calculations were performed using the synchronous transit methods as included in the DMol³ module of Accelrys Inc.

Complete linear synchronous transit (LST)/quadratic synchronous transit (QST) begins by performing an LST/optimization calculation. The TS approximation obtained in that way is used to perform QST maximization. From that point, another conjugate gradient minimization is performed. The cycle is repeated until a stationary point is located or the number of allowed QST steps is exhausted. DMol³ uses the *nudged elastic band (NEB)* method for minimum energy path calculations. The NEB method introduces a fictitious spring force that connects neighboring points on the path to ensure continuity of the path and projection of the force so that the system converges to the *minimum energy path (MEP)*, which is as well called intrinsic reaction co-ordinate if the co-ordinate system is mass weighted. We also calculated the vibration mode to identify the negative frequency to confirm the transition state.

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