PAPER

Selective reduction of phenol derivatives to cyclohexanones in water under microwave irradiation

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Selective reduction of phenol to cyclohexanone over the Pd/C catalyst in the presence of a hydrogen source of $HCOONa/H_2O$ has been studied. Surprisingly, phenol was transformed efficiently to cyclohexanone in an excellent yield of above 98% under microwave irradiation. The influence of some parameters like reaction temperature, time and amount of hydrogen donor, as well as the reaction pathway has been discussed. The combination of microwave irradiation and $HCOONa/H_2O$ was certified to be effective for the reduction of phenol as well as its derivatives to their corresponding cyclohexanones.

Introduction

Water is the most abundant, cheap, safe, and environmentally benign solvent in nature and the study of organic reaction in/ on water is an important theme of current research from the point of green chemistry.[1] Ordinarily, the solubility of organic substrates is the key factor for the performance of chemical transformations in water. For example, the hydrogenation of phenol could be carried out in the aqueous phase successfully at a moderate temperature for that phenol is completely water soluble at temperatures higher than 66 °C. But, the products of cyclohexanone and cyclohexanol are only slightly soluble in water under the reaction conditions, which may facilitate the product separation from the aqueous phase.[2] Cyclohexanone is widely utilized in industrial production of caprolactam and adipic acid, which are the monomers for manufacturing nylon-6, nylon-6,6 and polyamide resins.[3] Traditionally, cyclohexanone is produced *via* the oxidation of cyclohexane and the hydrogenation of phenol. The oxidation of cyclohexane requires high temperature, and the yield of cyclohexanone is quite low (<10%) due to the low conversion and the formation of some byproducts like cyclohexanol and cyclohexyl hydroperoxide.[4] The hydrogenation of phenol is usually going through two different processes: (1) phenol is hydrogenated to cyclohexanol and then the produced cyclohexanol dehydrogenates to cyclohexanone at high temperatures;[5,6] (2) phenol is selectively hydrogenated to cyclohexanone directly over the suitable catalysts under the optimized conditions.[7–11] The gas phase phenol hydrogenation is usually performed at high temperature over supported Pd[7–10] or Pt[11] catalysts, it was reported that the selectivity of cyclohexanone could be reached up to 95% over 5% Pt–0.4–4% Cr/C[11] and nanotubular titanate supported Pd catalysts[9] at 200 °C. However, gas phase hydrogenation suffers from some disadvantages like harsh reaction conditions and the catalyst deactivation induced by the unavoidable coke deposition.[12] Much interest has been focused on the liquid phase phenol hydrogenation because of the relatively mild conditions and the cost and energy savings.[2,13,14] However, the selectivity of cyclohexanone often decreases with phenol conversion, because cyclohexanone can be further hydrogenated to cyclohexanol in the consecutive reaction. Thus, it is a great challenge to obtain a high selectivity (>95%) at an elevated phenol conversion (>80%).[13,15] Recently, some effort has been made to improve the yield of cyclohexanone. For example, Titirici *et al.* investigated the phenol hydrogenation using a hydrophilic carbon support palladium catalyst in the aqueous phase, and a 95% selectivity of cyclohexanone was obtained at 99% conversion of phenol, which was attributed to the hydrophilic carbon support, it pushes the hydrophobic cyclohexanone away from the surface of Pd nanoparticles, inhibiting its further hydrogenation.[16] Moreover, Han *et al.* reported that the combination of Pd catalysts and solid Lewis acids was an efficient catalytic system for the hydrogenation of phenol to cyclohexanone in CH_2Cl_2 and compressed CO_2, a selectivity of cyclohexanone above 99.9% was obtained at the complete conversion of phenol.[17] Most recently, Wang *et al.* researched the phenol hydrogenation using mesoporous carbon nitrides supported palladium nanoparticles ($Pd@mpg-C_3N_4$) in the aqueous phase, and >99% selectivity of cyclohexanone was obtained at >99% conversion of the phenol under the mild conditions.[18] Corma *et al.* reported that Pd supported on hydroxyapatite, carbon and

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alumina are chemoselective catalysts for the hydrogenation of phenol to cyclohexanone.[19] Furthermore, it was reported that the selectivity to cyclohexanone could be improved in the presence of dense phase carbon dioxide,[12,17,20–22] because the presence of CO_2 could prohibit the further hydrogenation of cyclohexanone to cyclohexanol.[21]

In this work, a new method was developed for the selective reduction of phenol and its derivatives with an alternative hydrogen source of $HCOONa/H_2O$ under microwave irradiation. That the microwave irradiation could promote some organic reactions has been reported and well reviewed in the literature.[1] Under microwave irradiation, α,β-unsaturated carbonyl compounds could be transformed to saturated carbonyl compounds over the supported palladium catalyst, and 100% chemoselectivity was achieved in the presence of hydrogen source of $MeOH/HCOOH/H_2O$ (1 : 2 : 3),[23] and ketones could be transformed to alcohols with a yield of 98% in the presence of catalytic amounts of lithium isopropoxide and 2-propanol.[24] Herein, phenol and its derivatives were reduced efficiently and selectively to their corresponding cyclohexanones, and above 98% yield to cyclohexanone was achieved at the complete conversion of phenol in the presence of HCOONa and H_2O under microwave irradiation. We offer a safe, facile, and environmentally benign process for the production of cyclohexanones.

Experimental

Materials

$HCOONa·2H_2O$, diethyl ether, toluene and all the substrates are of analytical grade and used without further purification. 5% Pd/C, 5% Pd/Al_2O_3, 10% Pd/C, 5% Pt/C, 5% Ru/C, and 5% Rh/C were purchased from WAKO. Gases of H_2 (99.999%), O_2 (99.9%), CO (99.999%) and CO_2 (99.999%) were used as delivered.

Reduction of phenol in the presence of $HCOONa/H_2O$

The microwave-assisted reactions were performed in a 10 ml quartz tube under microwave irradiation (Initiator, Biotage, Sweden). In a typical reaction, phenol (0.625 mmol), $HCOONa·2H_2O$ (1.875 mmol, 3 eq.), 10% Pd/C (5.3 mg), and deionized water (2 ml) were added to the quartz tube. Then, the reaction vessel was sealed and the reaction was carried out under microwave irradiation at 80 °C with a stirring speed of 900 rpm. After the reaction, the mixture was cooled and extracted with diethyl ether and the resulted organic solution was analyzed by a gas chromatograph (GC-shimadzu-2010, FID, capillary column, Rtx-50 30 m × 0.25 mm × 0.25 μm) and identified by gas chromatograph/mass spectrometry (GC/MS, Agilent 5890). Toluene as the internal standard substance was mixed to the sample in order to determine the conversion level and selectivity. The conversion was calculated by moles of phenol consumed divided by initial moles of phenol used, and the selectivity was determined by moles of product i divided by total moles of product obtained. Cyclohexanone and cyclohexanol are the only reaction products observed under the experimental conditions used, and the carbon balance values calculated from phenol, cyclohexanone and cyclohexanol are around 100%. The gas phase sample was collected and analyzed by a TCD detector

(TDX-01, 2 m) and identified with pure H_2, O_2, CO and CO_2 to confirm the production of hydrogen and CO during the reaction.

Hydrogenation of phenol with molecular hydrogen

The hydrogenation reaction with molecular hydrogen was performed in a 50 ml Teflon-lined high-pressure stainless steel batch reactor with oil heating. Phenol (0.625 mmol), 10% Pd/C (5.3 mg), deionized water (2 ml) and H_2 (2 MPa) were introduced into the reactor. The reaction was performed at 80 °C with a stirring speed of 900 rpm, and the following procedures are the same as described above.

Results and discussion

$HCOOH–NEt_3$ azeotropic mixture and HCOONa as alternatives to molecular hydrogen have attracted more attention in the catalytic transfer hydrogenations.[25,26] Herein, the reduction of phenol in aqueous solution was studied under the different conditions, and the results are shown in Table 1. When the reaction was carried out in an autoclave with oil heating and molecular hydrogen as the reducing reagent, the selectivity to cyclohexanone was lower than 80% and it decreased with hydrogen pressure (entries 1 and 3), as well as it decreased with conversion irrespective of the hydrogen pressure (entries 1–4). By comparison, when HCOONa was used as the reducing reagent, the selectivity to cyclohexanone reached about 98% at a similar conversion (entries 3 and 6), however, the turnover frequency (TOF) was much lower than that obtained using molecular hydrogen (entries 1–6). It was assumed that the hydrogen was produced from the formate and proton supplied by water as described in the literature (eqn (1)),[27,28] and then the hydrogenation occurred through the produced hydrogen molecules (eqn (2)). To confirm this, the reduction of phenol with $HCOONa/H_2O$ as the hydrogen source was performed in an open flask and refluxed with N_2 flow, the result showed a much low conversion ($<1.0%$, entry 7), it directly confirmed that the transfer hydrogenation was insignificant, but the hydrogenation should be more remarkable under the reaction conditions. Moreover, hydrogen was detected in the reaction product (gas phase) by TCD analysis. The above results demonstrated that the reduction of phenol catalyzed with the Pd/C catalyst in the presence of HCOONa in water was going through hydrogen production (eqn (1)) and conventional hydrogenation reaction (eqn (2)), rather than a hydrogen transfer reaction. The concentration of hydrogen produced from organic hydrogen donor HCOONa and water was lower compared to the case of using hydrogen gas. Lower hydrogen concentration may disfavor the step of hydrogenation of 1-hydroxycyclohexene to cyclohexanol. Thus the relatively lower TOF and higher selectivity to cyclohexanone were obtained (entries 1–6). In addition, the effect of the microwave irradiation was checked for the present reaction, as seen the reaction rate under microwave irradiation was about 30 times higher than those under conventional heating conditions (entries 5, 6, 8), furthermore, a 98% selectivity to cyclohexanone at the complete conversion of phenol was achieved in the presence of HCOONa (entry 8). Under microwave irradiation, the production of hydrogen *via* a decomposition process (eq. (1)) could be improved remarkably,[29] as well as the hydrogenation of phenol (eqn (2)) was accelerated

**Table 1** Results for the reduction of phenol under different conditions with 10% Pd/C[a]

Entry	Hydrogen source	Heating method	Time/min	Conv. (%)	TOF[b]/min^{-1}	Selectivity (%)	
						Cyclohexanone	Cyclohexanol
1	0.2 MPa H$_2$	CH	60	58.1	11.4	79.4	20.6
2	0.2 MPa H$_2$	CH	90	84.3	11.1	69.8	30.2
3	2 MPa H$_2$	CH	45	66.0	17.3	65.1	34.9
4	2 MPa H$_2$	CH	90	100	—	14.7	85.3
5[c]	HCOONa	CH	120	32.2	3.2	99.8	0.2
6[c]	HCOONa	CH	300	63.6	2.5	98.1	1.9
7[c,d]	HCOONa	CH	300	1.0	0.04	100	—
8[c,e]	HCOONa	MW	15	100	—	98.0	2.0

[a] Reaction conditions: phenol 0.625 mmol, 10% Pd/C 5.3 mg, substrate/catalyst = 125/1, H$_2$O 2 ml, 80 °C. The reactions were performed in a sealed Teflon-lined high-pressure stainless steel batch reactor (50 ml). CH: conventional heating method, MW: microwave irradiation. [b] Turnover frequency; which was given as the overall rate of phenol conversion normalized by the number of active sites over the specified time. The number of active sites was calculated by (the metal dispersion) × (the total number of supported metal atoms). The Pd dispersion (D) was calculated from the following equation: dispersion = $6(v_m/a_m)/d$, where v_m and a_m are equal to 14.70 Å^3 and 7.93 Å^2, respectively, and the average diameter (d) of Pd particles was determined to be 10.5 nm through the measurement from the TEM images. [c] HCOONa·2H$_2$O 1.875 mmol. [d] The reaction was performed in an open flask and refluxed under N$_2$ flow under the similar conditions. [e] The reaction was performed in a sealed quartz tube (10 ml) under microwave irradiation.

significantly. So the hydrogenation of phenol was performed very fast and the high selectivity to cyclohexanone could be obtained under microwave irradiation in the presence of HCOONa and water. Herein, HCOONa was selected as the hydrogen donor, and several parameters were discussed for the reduction of phenol under the microwave irradiation.

$$HCOONa + H_2O \xrightarrow{\text{Pd/C}} H_2 + NaHCO_3 \quad (1)$$

$$\text{C}_6\text{H}_5\text{-OH} + 2H_2 \xrightarrow{\text{Pd/C}} \text{cyclohexanone} \quad (2)$$

The reaction temperature exhibited a large effect on the reaction rate, with increasing temperature from 60 to 90 °C, the conversion increased from 13.3 to 96.0% as shown in Fig. 1. When the temperature was further enhanced up to 110 °C, the conversion decreased, which may be attributed to the thermodynamic limitations[30] and/or to desorption of phenol and catalytically active hydrogen from the catalyst surface at high temperature.[31,32] The selectivity to cyclohexanone changed slightly with the increase in temperature under conditions used.
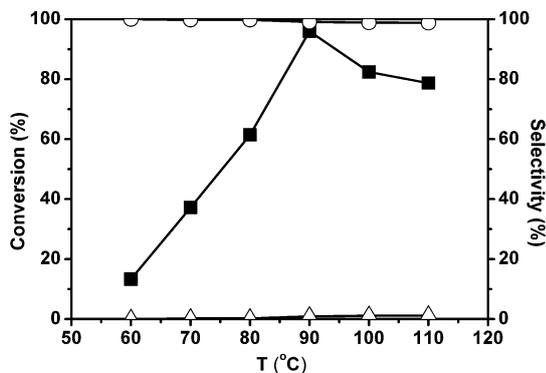

Fig. 1 Influence of temperature on the reduction of phenol under microwave irradiation. Reaction conditions: phenol 0.625 mmol, 10% Pd/C 5.3 mg, substrate/catalyst = 125/1, HCOONa·2H$_2$O 1.875 mmol, H$_2$O 2 ml, 5 min. (■) Conversion of phenol and selectivity to (○) cyclohexanone; (△) cyclohexanol.
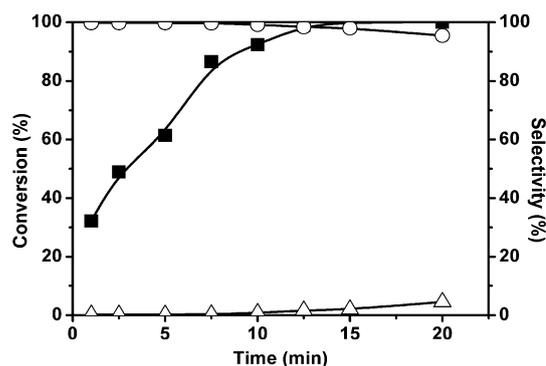
Fig. 2 Variation of conversion and selectivity with reaction time on the reduction of phenol under microwave irradiation. Reaction conditions: phenol 0.625 mmol, 10% Pd/C 5.3 mg, substrate/catalyst = 125/1, HCOONa·2H$_2$O 1.875 mmol, H$_2$O 2 ml, 80 °C. (■) Conversion of phenol and selectivity to (○) cyclohexanone; (△) cyclohexanol.

The plot of phenol conversion and product selectivity *versus* reaction time was shown in Fig. 2. The reaction was very fast and cyclohexanone was produced as the predominant product (99.8% in selectivity) until the conversion reached 86%, and then cyclohexanone slowly transferred to cyclohexanol but the selectivity was still above 98% at the complete conversion of phenol after reaction for 15 min. Cyclohexanone and cyclohexanol were produced throughout the reaction progress, but 1-hydroxycyclohexene was not detected. Based on the above results and literature,[13,33] a possible reaction pathway for phenol reduction in the present system was discussed. According to Scheme 1, 1-hydroxycyclohexene was formed as an intermediate which might be easily converted into either the cyclohexanone *via* isomerization (step II) or the cyclohexanol *via* further hydrogenation (step III). The cyclohexanol should not form from 1-hydroxycyclohexene (step III) for that the selectivity to cyclohexanol was lower than 0.2% at the first 7.5 min, but produced from the subsequent hydrogenation of cyclohexanone (step IV) as its selectivity increased with a consumption of cyclohexanone after the conversion of phenol reached 86%. Step II that is isomerization of 1-hydroxycyclohexene
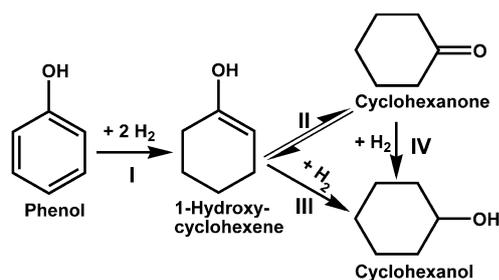
Scheme 1 Proposed route for hydrogenation of phenol.

to cyclohexanone should be much faster than step I that is hydrogenation of phenol to 1-hydroxycyclohexene. However, it should be noted that, when molecular hydrogen was used, cyclohexanol was formed with a selectivity above 20% even at conversion lower than 70% (entries 1 and 3 in Table 1), suggesting that step III may happen, but step IV should be much faster compared with the cases of HCOONa.

The effect of the amount of HCOONa was checked and the results are illustrated in Table 2. The selectivity to cyclohexanone was independent of the amount of HCOONa, and the values were above 98% at any alternative condition. But, the activity increased with HCOONa amount (entries 1 and 5, 4 and 7, 6 and 8). The conversion of phenol was about 50% after reaction for 60 min and it did not change with extending reaction time when 1 eq. HCOONa was used (entries 2 and 3), because the hydrogen donor was not enough to supply sufficient hydrogen for the reaction. When the amount of HCOONa was increased to 2 and 3 eq., the conversion reached 100% after reaction proceeded for 30 and 15 min, respectively (entries 5 and 7). It suggests that 2 eq. of HCOONa were required for supplying enough hydrogen to reduce phenol to cyclohexanone from the stoichiometry of the reaction.

Under the microwave irradiation, the activities of several noble metal catalysts were checked and compared. As per the results listed in Table 3, the conversion was 8.9% and the selectivity to cyclohexanone was 99.8% over 5% Pd/C, while the conversion increased to 18.3% with a similar selectivity of cyclohexanone over 5% Pd/Al$_2$O$_3$, but the conversion reached up to 61.4% with a similar cyclohexanone selectivity over the 10% Pd/C catalyst, indicating that the support and Pd loading had a large influence on the reaction rate. As shown in Fig. 3, the average Pd particle size was about 17.7 nm for 5% Pd/C and 10.5 nm for 10% Pd/C from the TEM images, suggesting that the particle size affected the catalytic activity. The similar

Table 3 Results of reduction of phenol with different catalysts under microwave irradiation[a]

Entry	Catalyst	Conversion (%)	TOF/min^{-1}	Selectivity (%)	
				Cyclohexanone	Cyclohexanol
1	5% Pd/C	8.9	35.4	99.8	0.2
2	5% Pd/Al$_2$O$_3$	18.3	—	99.9	0.1
3	10% Pd/C	61.4	144.9	99.8	0.2
4[b]	5% Pt/C	−(84.1)	—	−(38.1)	−(61.9)
5[b]	5% Ru/C	−(39.8)	—	−(1.5)	−(98.5)
6[b]	5% Rh/C	0.1 (76.9)	—	100 (65.8)	−(34.2)

[a] Reaction conditions: phenol 0.625 mmol, substrate/catalyst = 125/1, HCOONa·2H$_2$O 1.875 mmol, H$_2$O 2 ml, 5 min, 80 °C. [b] The data in parentheses are the results of reduction of phenol with 0.2 MPa H$_2$ in 15 min.
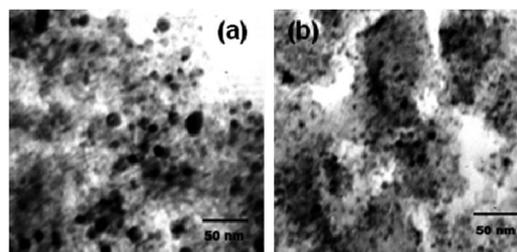
Fig. 3 TEM images of (a) 5% Pd/C and (b) 10% Pd/C catalysts.

results were also reported that the TOF increased with decreasing Pd crystallite size for the phenol hydrogenation in vapor phase over the Pd/CeO$_2$ catalyst.[7] Moreover, Pd presented much higher activity than those of Pt, Ru, Rh catalysts, as for 5% Ru/C, Pt/C and Rh/C, they did not show any activity in the present catalytic system with HCOONa (entries 4–6), even though Ru/C, Pt/C and Rh/C were effective catalysts for the hydrogenation of phenol with molecular hydrogen as shown in Table 3. It was reported that the formate could decompose to produce hydrogen over the Pd/C catalyst in water at reaction temperatures from 70 to 140 °C.[27,28] However, such a catalytic activity may not occur over the supported Pt, Ru and Rh catalysts under present reaction conditions.
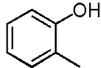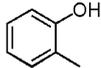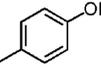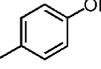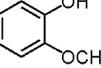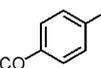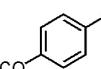
The efficiency of the present catalytic system was examined for several phenol derivatives under the similar reaction conditions, and the results are shown in Table 4. As can be seen, the ring hydrogenation of these substrates could be performed to a certain extent within 40 min, and the corresponding

Table 2 Effect of the amount of HCOONa for reduction of phenol under microwave irradiation[a]

Entry	Mole ratio of HCOONa/phenol	Time/min	Conversion (%)	Selectivity (%)	
				Cyclohexanone	Cyclohexanol
1	1	30	35.9	99.9	0.1
2	1	60	49.3	99.8	0.2
3	1	90	49.3	99.5	0.5
4	2	15	75.7	99.8	0.2
5	2	30	99.3	99.2	0.8
6	3	5	61.4	99.8	0.2
7	3	15	100	98.0	2.0
8	4	5	68.8	99.4	0.6

[a] Reaction conditions: phenol 0.625 mmol, 10% Pd/C 5.3 mg, substrate/catalyst = 125/1, H$_2$O 2 ml, 80 °C.

Table 4 Results of reduction of phenol derivatives under microwave irradiation[a]

Entry	Substrate	Time/min	Conversion (%)	Selectivity (%)	
1	o-methylphenol	10	30.1	2-methylcyclohexanone 100	2-methylcyclohexanol 0
2	o-methylphenol	30	59.4	2-methylcyclohexanone 100	2-methylcyclohexanol 0
3	p-methylphenol	10	76.9	4-methylcyclohexanone 92.9	4-methylcyclohexanol 7.1
4	p-methylphenol	15	95.4	4-methylcyclohexanone 92.8	4-methylcyclohexanol 7.2
5	o-methoxyphenol	40	12.4	2-methoxycyclohexanone 86.3	2-methoxycyclohexanol 13.7
6	p-methoxyphenol	20	20.3	4-methoxycyclohexanone 97.6	4-methoxycyclohexanol 2.4
7	p-methoxyphenol	40	33.2	4-methoxycyclohexanone 97.3	4-methoxycyclohexanol 2.7

[a] Reaction conditions: substrate 0.625 mmol, 10% Pd/C 5.3 mg, substrate/catalyst = 125/1, HCOONa·$2H_2O$ 1.875 mmol, H_2O 2 ml, 80 °C.

cyclohexanones were produced as the main product with the selectivity above 92% except for o-methoxyphenol (86.3%). o-Methyl cyclohexanone was produced as the sole product with 100% selectivity (entries 1 and 2), and p-methyl cyclohexanone was produced with a selectivity of about 93% (entries 3 and 4), and o- and p-methoxycyclohexanone were produced with selectivity of about 86% and 97% from the hydrogenation of o- and p-methoxyphenol, respectively (entries 5–7). It was clear that the selectivity to cyclohexanones was independent of the reaction conversion, but depended on the molecular structure largely. The reaction rate and product selectivity depended significantly on the chemical nature of the substituent and its position relative to the −OH group. Steric effects resulted in a lower conversion for the substitution at the *ortho*-position compared with the *para*-position (entries 1 and 3; 5 and 7). The effect of the substituent is consistent with the Hammett parameters (σ). The electron-releasing substituents lowered the reactivity of phenol ring, and the conversion of phenol with the MeO group (σ: −0.27) was much lower than that with the methyl group (σ: −0.17) (entries 4 and 7). Moreover, the phenolic substrates with electron-withdrawing group like o-chlorophenol and p-nitrophenol have also been examined. But for o-chlorophenol, the hydro-dechlorination of o-chlorophenol to phenol occurred firstly; while for p-nitrophenol, p-aminophenol was mainly produced under the reaction conditions.

The recycling of catalyst has been investigated and the results are shown in Table 5. After the first run, the reaction mixture was centrifuged, and then the catalyst was separated from the liquid mixture by decantation. The catalyst was

Table 5 Recycling of 10% Pd/C catalyst[a]

Run	Conversion (%)	Selectivity (%)	
		Cyclohexanone	Cyclohexanol
1	76.3	99.2	0.8
2	37.7	99.4	0.6
3	32.9	99.5	0.5

[a] Reaction conditions: phenol 0.625 mmol, 10% Pd/C 5.3 mg, substrate/catalyst = 125/1, HCOONa·$2H_2O$ 1.875 mmol, H_2O 2 ml, 80 °C, 6 min.

washed three times and then introduced into the reactor with H_2O, and fresh phenol and HCOONa·$2H_2O$ were charged into the reactor again for the recycling runs. The activity decreased obviously at the second run but decreased slightly at the third run, the selectivity to cyclohexanone did not change and it was higher than 99%. For the heterogeneous catalysis, metal species leaching during the reaction is one problem for recycling. In this work, Pd leaching was not detected in the filtrate by ICP analysis (iCAP6300, Thermo USA, the detection limit was 0.1 ppm), but CO was detected in the gas phase of the reaction product by TCD analysis and which might be responsible for the deactivation. Baiker and co-workers reported that the hydrogenation of carbonyl compounds over the Pt/C catalyst in scCO$_2$ provided CO as a side product, which might strongly bind to the Pt metal on the catalyst surface, resulting in serious catalyst deactivation.[34,35] Bianchi and co-workers reported that the FTIR spectra of the adsorbed CO species (linear and bridged species) were formed on Pd/Al$_2$O$_3$, Pd/CeO$_2$/Al$_2$O$_3$, and Pd/La$_2$O$_3$/CeO$_2$/Al$_2$O$_3$ at adsorption temperatures

from 300 to 800 K.[36] In this work, CO may be formed by the thermal decomposition of HCOONa[37] or the reduction of CO_2 produced from $NaHCO_3$ and/or HCOONa.[34,35]

Conclusions

In conclusion, a new environmentally benign and effective process was developed for the reduction of phenol derivatives to cyclohexanones. Under the assistance of microwave, the hydrogenation of phenol was performed very fast and cyclohexanone was produced with a yield of >98% in the presence of a hydrogen source of HCOONa and water under the mild conditions. The reduction of phenol with HCOONa in water was not going through the hydrogen transfer reaction pathway, but the hydrogen production and hydrogenation pathway. It is worth expecting a practical utilization of the present process for phenol and its derivatives transfer to their corresponding cyclohexanones in near future.

Acknowledgements

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