Hydrogenation of Phenol to Cyclohexanone over Bifunctional Pd/C-Heteropoly Acid Catalyst in the Liquid Phase
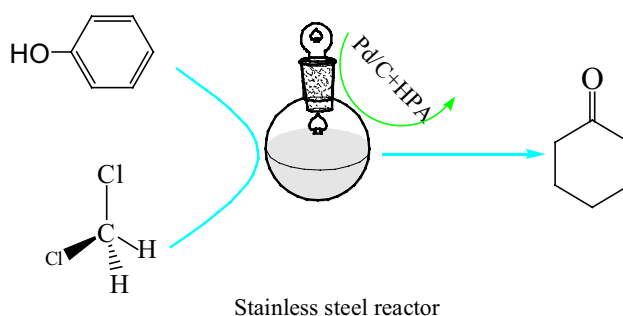
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Abstract

Cyclohexanone is an important intermediate in the manufacture of polyamides in chemical industry, but direct selective hydrogenation of phenol to cyclohexanone under mild conditions is a challenge. Hydrogenation of phenol to cyclohexanone has been investigated in the presence of the composite catalytic system of Pd/C-heteropoly acid. 100% conversion of phenol and 93.6% selectivity of cyclohexanone were achieved within 3 h under 80 °C and 1.0 MPa hydrogen pressure. It has been found that a synergetic effect of Pd/C and heteropoly acid enhanced the catalytic performance of the composite catalytic system which suppressed the hydrogenation of cyclohexanone to cyclohexanol.

Graphic Abstract

Stainless steel reactor

Keywords Cyclohexanone · Catalysis · Hydrogenation · Pd/C-heteropoly acid · Phenol

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1 Introduction

Cyclohexanone is well 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 [1–3]. The process for the production of cyclohexanone in industry contains the oxidation of cyclohexane [4] and the hydrogenation of phenol [5]. Compared with the hydrogenation of phenol, the oxidation of cyclohexane has almost disadvantage because it requires high temperature and high pressure, and generates a large number of undesirable byproducts. In the route of the hydrogenation of phenol, cyclohexanone is generally produced through one-step or two-step process [6]. The two-step process involves hydrogenation of phenol to cyclohexanol

followed by dehydrogenation to cyclohexanone [7]. In contrast, the one-step selective hydrogenation of phenol to cyclohexanone is more advantageous. For instance, it avoids the endothermic dehydrogenation step. The one-step hydrogenation of phenol can be conducted in either the gas phase or liquid phase, and the selectivity of cyclohexanone is largely dependent on the catalyst properties. Currently, the supported Pd catalysts is frequently used in the hydrogenation of phenol [8, 9]. Pd/Al_2O_3 catalysts obtained approximately 50~60% selectivity of cyclohexanone with 20% conversion of phenol in the gas-phase hydrogenation (160 °C) at 0.2 MPa hydrogen pressure [10]. At 160 °C and 0.45 MPa hydrogen pressure, 95% selectivity with 40% conversion was obtained when Pd supported on calcined Mg/Al hydrotalcite was used [11]. When Ba-modified Pd/Al_2O_3 was used, the conversion of phenol reached 100% and the selectivity of cyclohexanone was up to 80% in situ hydrogenation (220 °C) at 3.5 MPa hydrogen pressure [9]. Palladium nanoparticles supported on polyaniline-functionalized carbon nanotubes (Pd-PANI/CNT) has a high activity towards the direct hydrogenation of phenol to cyclohexanone, and the phenol conversion and the cyclohexanone selectivity were more than 99% under atmospheric pressure of hydrogen in aqueous media at 80 °C for 9 h [12]. Zhong and coworkers reported that Pd nanoparticle supported on a mesoporous-graphitic carbon nitride (Pd@mpg-C_3N_4) showed high activity and promoted the formation of cyclohexanone under atmospheric pressure of hydrogen in aqueous media without additives. Phenol conversion reaching 99% and cyclohexanone selectivity was more than 99% at 65 °C. Even at room temperature, 99% conversion and 96% selectivity could still be obtained [13, 14]. Gas phase phenol hydrogenation requires normally high temperature (150–300 °C), and generates carbonaceous deposits (coking) in the course of the reaction leads to deactivation of the supported catalyst. In contrast, liquid-phase process reduces cost and energy savings, because hydrogenation reaction is performed at relatively low temperature. However, another important and inherent drawback of current liquid-phase hydrogenation relates to the high cost and the complex preparation process of the catalyst. In this regard, a highly selective catalyst for the liquid-phase hydrogenation is still desirable.

Catalysis by heteropoly acids (HPAs) and related polyoxometalate compounds is a field of increasing importance. HPAs have several advantages as catalysts, such as a very strong Brønsted acidity, and fast reversible multi electron redox transformations, which makes it become a new multifunctional catalytic material [15] and uses on the hydration [16], esterification [17], condensation [18], polymerization [19], alkylation [20], and oxidation reactions [21] with good catalytic performance. HPAs have been reported in the hydrogenation reaction. Joshi et al. reported that 12-molybdophosphoric acid-catalyzed transfer hydrogenation of nitroaromatics with excellent catalytic performance in homogeneous phase [22]. Co-based catalysts modified with Keggin type HPA salts showed the improving of selectivity on hydrogenation of crotonaldehyde [23]. The one-pot transformation of (+)-citronellal to menthol over Pd-$H_3PW_{12}O_{40}$/SiO_2 catalyst obtained 92% yield of menthol with 100% citronellal conversion and 85% stereo selectivity of the desired (-)-menthol [24]. The results indicated that the catalyst modified with HPAs had better catalytic performance for the hydrogenation than traditional catalysts. Therefore, the hydrogenation of phenol using the bifunctional Pd/C-HPA catalyst in the liquid phase was studied in this paper.

2 Experimental Section

2.1 Materials

Pd/C (10 wt%) was purchased from Sigma Aldrich. Phosphotungstic acid (PTA, $H_3O_{40}PW_{12}\cdot xH_2O$, Mw = 2880) and tungstosilicic acid (TTA, $H_8Si(W_2O_7)_6\cdot xH_2O$, Mw = 2915) were purchased from Sinopharm Chemical Reagent. H_2 (99.99 wt%) was produced by Qingdao Analytical Instrument Company. Other chemicals (analytic purity) were commercially available and used without further purification.

2.2 Hydrogenation Reaction

The hydrogenation reaction was carried out in the stainless steel reactor equipped with a magnetic stirrer. Amounts of phenol, Pd/C-HPA and solvent were added into the reactor. The reactor was flushed with 0.2 MPa H_2 for five times to remove air and 1.0 MPa H_2 was introduced. Then the mixture was heated to a desired temperature and reacted for a certain time. After the reaction was finished, the reactor was cooled to room temperature and depressurized. The reaction mixture was centrifuged to separate the catalysts and got the product mixture. The separated catalysts were directly used in the recycle experiments. The sample of the upper layer were characterized qualitatively with HP6890/5973 GC/MS equipped with an HP-5MS column, 30 m × 0.25 mm × 0.25 μm, and its quantitative analysis were determined by GC using HP6890 GC equipped with an HP-5 column, 30 m × 0.32 mm × 0.25 μm. The contents of the reactants and products were directly showed by the system of GC chemstation according to the area of each chromatograph peak. The conversion of phenol was defined as Conv. %, which was the wt% of phenol consumed in the reaction. The selectivity of one product was calculated by Sel. % = Wp/W$_{all}$ × 100, where Wp was the mass of one product, and W$_{all}$ was the total mass of all products, including cyclohexanone and cyclohexanol. All the experiments were repeated for five times to confirm the results effectiveness.

3 Results and Discussion

Liquid-phase phenol hydrogenation reduces cost and energy savings, because the reaction can be performed at relatively low temperature. Many researchers have contributed to this area, and multiple catalysts had been screened, such as Rh/C [25], Pd/hydrophilic C [13], Pd/Mg and Pd/Fe [26], and Pd/C [26]. Han and co-workers achieved both excellent conversion and selectivity in the hydrogenation of phenol by using Pd/C, Pd/Al$_2$O$_3$ or Pd/NaY assisted by the Lewis acid AlCl$_3$ [27]. However, the fact that these hosts contain Lewis acids such as AlCl$_3$ imposes severe limitations on their used in hydrogenation reactions in general and adds another chemical sensitivity restricting substrates purities and reaction conditions. HPA is a new multifunctional and organic catalysts. It shows higher catalytic activity and selectivity when HPA catalyzes organic reactions [17], and it can be used in multiphase reactants as phase transference catalysts. Liu and co-workers achieved both excellent conversion and selectivity in the hydrogenation of furfural and cinnamic aldehyde by using modified heteropoly acid salt catalyst [28]. On this basis, we have investigated the hydrogenation of phenol to cyclohexanone in the presence of the composite catalytic system of Pd/C-Heteropoly acid.

3.1 The Effects of the Different Catalysts on the Reaction Results

The activities of different catalysts for the hydrogenation of phenol were investigated and the results were showed in Table 1. It was seen that cyclohexanone and cyclohexanol were the only reaction products observed over the entire range of conditions studied, and the catalysts had a remarkable influence on the selective hydrogenation of phenol to cyclohexanone. Pd/C was used as the standard catalyst to compare with other catalysts as it showed good catalytic performances in many hydrogenations [29]. However, Pd/C catalyst presented low catalytic activity for the hydrogenation of phenol. The conversion of phenol and the selectivity to cyclohexanone were only 61.2% and 89.4%, respectively. And even the too much cyclohexanone was hydrogenated to perform cyclohexanol (Entry 2). The HPAs catalysts, such as phosphotungstic acid (PTA), phosphomolybdic acid (PMA) and tungstosilicic acid (TSA) showed no catalytic activity for the hydrogenation (Entries 3–5). In contrast, the composite catalytic systems consisting of Pd/C and HPA showed an excellent catalytic activity for the hydrogenation (Entries 6–8). Especially, the composite catalytic system Pd/C-PTA had 100% conversion of phenol and 93.6% selectivity to cyclohexanone

Table 1 Effects of different catalysts on the results of the hydrogenation

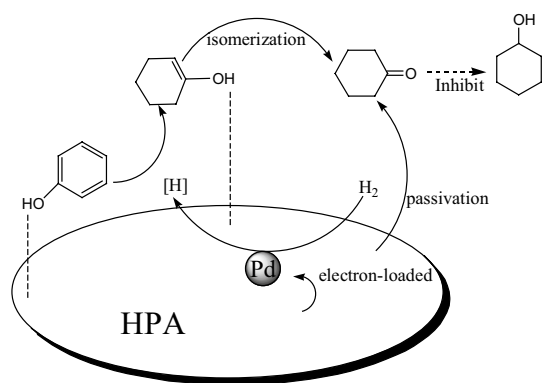| Entry	Reagent	Catalyst	Conv. (%)	Sel. (%)[b]	
				C=O	C–OH
1	Phenol	Blank	0	/	/
2	Phenol	Pd/C	61.2	89.4	10.6
3	Phenol	PTA	0	/	/
4	Phenol	PMA	0	/	/
5	Phenol	TSA	0	/	/
6	Phenol	Pd/C-PTA	100	93.6	6.4
7	Phenol	Pd/C-PMA	100	66.3	33.7
8	Phenol	Pd/C-TSA	100	90.5	9.5
9	Phenol	Pd/C-PTA-Na	100	89.5	10.5
10	Phenol	Pd/C-AcNa	67.6	90.9	9.1
11	Phenol	Pd/C-H$_3$PO$_4$	100	83.5	16.5
12	Phenol	Pd/C-ZnCl$_2$	1.6	88.0	12.0
13[a]	Phenol	Pd/C-ZnCl$_2$	100	91.8	8.2
14	Cyclohexanone	Pd/C-PTA	61.8	/	100
15	Cyclohexanone	Pd/C	2.8	/	100
16[b]	Phenol	Pd/C-PTA	100	80.0	20.0
17	Phenol	Pd/C-AlCl$_3$	81.39	93.78	6.22

Phenol 0.1 g, Pd/C 0.005 g, HPA 0.05 g, $T=80$ °C, $t=3$ h, $P(H_2)=1.0$ MPa, dichloromethane 10 ml

PTA Phosphotungstic acid, *PMA* Phosphomolybdic acid, *TSA* Tungstosilicic acid, *C=O* Cyclohexanone, *C–OH* Cyclohexanol

[a]Phenol 0.1 g, Pd/C 0.05 g, ZnCl$_2$ 0.03 g, $T=100$ °C, $t=6$ h

[b]Phenol 10.0 g, Pd/C 0.5 g, HPA 5.0 g

were achieved (Entry 6). The good catalytic performance may be attributed to the synergistic effect originating from the Pd/C and PTA, as well the unique acid property and the exhibiting fast reversible multi electron redox transformations of PTA. In order to determine the effects of the acidic properties on the hydrogenation, sodium phosphotungstate(PTA-Na), HCOONa and H$_3$PO$_4$ were selected and used as the co-catalysts (Table 1, Entries 9–11). The results showed that the catalytic performance of the catalytic system Pd/C-PTA-Na was similar with that the catalytic system Pd/C-PTA, but it's catalytic performance worse than Pd/C-PTA. These results demonstrated that HPA and Pd/C have good synergistic effect on the hydrogenation of phenol to cyclohexanone. And Pd/C-AlCl$_3$ was used as catalyst to catalyze the hydrogenation of phenol, under the same reaction conditions, the conversion of phenol was significantly lower than that of Pd/C-HPA (Table 1, Entries 6 and 17). Otherwise, although Pd/C-ZnCl$_2$ could reach high conversion and good selectivity, its catalyst dosage is much more than the Pd/C-HPA (Table 1, Entries 6 and 13[b]). This may be due to the larger volume of HPA's anion, regular tetrahedron and eight surface body structure that has a good symmetry, which can promote

Scheme 1 Reaction mechanism of phenol over Pd/C-Heteropoly acid

Table 2 Effects of solvents on the hydrogenation of phenol catalyzed by Pd/C-PTA

Entry	Solvent	Conv. (%)	Sel. (%)	
			C=O	C–OH
1	Dichloromethane	100	93.6	6.4
2	Cyclohexane	99.4	34.0	66.0
3	Tetrahydrofuran	98.3	76.2	23.8
4	1-Chlorobutane	97.3	78.9	21.1
5	Trichloromethane	8.6	92.4	7.6
6	H$_2$O	99.91	15.91	84.09

Solvent 10 mL, others the same as Table 1

the catalytic reaction. The results can be explained by the reaction mechanism showed in Scheme 1. One of the carbons in benzene ring tends to become highly nucleophilic, thereby facilitating attack of the benzene ring by an incipient electrophile. Compared with the palladium adsorption on phenol, heteropoly acid had stronger adsorption performance for phenol through the formation of hydrogen bonding. Therefore, phenol can easily interact with heteropoly acid through the hydroxyl group to form the strong O–H–O interactions, and H$_2$ that adsorbed and activated by Pd formed the active hydrogen. Then when the O–H–O interactions meets with the active hydrogen, benzene ring of phenol is partially hydrogenated to the enol intermediate, which is unstable and isomerize rapidly to form cyclohexanone. Due to the charge density of heteropoly acid is low and the transition metal element in the heteropoly acid anions is easy to transfer electrons, thereby accept the lone pair of electrons from the cyclohexanone carbonyl oxygen atom to form a common election pair, and to achieve passivation of the hydrogenation activity of cyclohexanone carbonyl. It's inhibits the reaction further hydrogenation. What's more, there only a weaker H-bridge donor, so the cyclohexanone leaves the surface of the catalyst quickly, and being replaced by a more strongly binding from new phenol molecule. Based on the experimental data presented here and the literature results, it was concluded that in the hydrogenation of phenol, these two types of activation worked cooperatively, resulting in high activity and selectivity for producing cyclohexanone.

3.2 The Effects of the Reaction Conditions on the Reaction Results

The effect of solvents on the hydrogenation of phenol to cyclohexanone were showed in Table 2. Among the investigated solvents, when dichloromethane was used as solvent, the hydrogenation exhibited the best conversion of phenol (nearly 100%) and selectivity of cyclohexanone (93.6%).

When the other solvents investigated were used, the results of the hydrogenation were not satisfied. This may be due to that the solvents had different effects on the solubility of organics or hydrogen, the absorption and desorption of the catalyst surface, which effects on the reaction rate. The phenol and the polar solvent have a greater force, so in the polar solvents, the adsorption of phenol on the surface of the catalyst is relatively less, which is not conducive to the hydrogenation of phenol. Therefore, the influence of other factors on the reaction was discussed by using dichloromethane as solvent in the following experiments.

Table 3 showed the effects of catalyst amounts and some reaction conditions on the hydrogenation of phenol. With increasing of the amount of Pd/C, the conversion of phenol increased gradually (Table 3, Entries 1–3). When the dosage of Pd/C was 0.005 g, the conversion of phenol reached 100%, and the selectivity of cyclohexanone was 93.6%. After that, when more catalyst Pd/C was used, the selectivity of cyclohexanone decreased gradually. This may be because that the excessive amount of catalyst provides the hydrogenation activity center too much, and the cyclohexanone is easily hydrogenated to cyclohexanol. Therefore, the amount of Pd/C as raw material 5 wt% was appropriate. The effect of the amount of PTA on the hydrogenation was similar with that amount of Pd/C (Table 3, Entries 2, 4, 5). This may be because that the active centers of the catalysts increased with increasing of amount of PTA, so as to improve the catalytic performance. But when PTA was excessive, the PTA maybe covers the surface of the hydrogenation centers, resulting in decrease of the activity of the catalyst. To a certain extent, the amount of Pd/C and PTA own the synergistic catalytic effect. Therefore, the nice conversion of phenol and selectivity of cyclohexanone could be obtained at an appropriate mass ratio of Pd/C and PTA (1:10). The reaction temperature had a considerable effect on the hydrogenation (Table 3, Entries 2, 6, 7). 100% conversion of phenol and 93.6% selectivity of cyclohexanone were obtained within 3 h under the mild conditions of 80 °C and 1.0 MPa hydrogen pressure. With the temperature continues rise, little effect on

Table 3 Hydrogenation of phenol with Pd/C-PTA catalyst using dichloromethane as solvent

Entry	Pd/C(g)	PTA(g)	T(°C)	H_2 (MPa)	Time(h)	Conv. (%)	Sel. (%)	
							C=O	C–OH
1	0.004	0.05	80	1.0	3	90.4	93.9	6.1
2	0.005	0.05	80	1.0	3	100	93.6	6.4
3	0.006	0.05	80	1.0	3	100	89.5	10.5
4	0.005	0.03	80	1.0	3	96.2	94.0	6.0
5	0.005	0.07	80	1.0	3	100	82.0	18.0
6	0.005	0.05	60	1.0	3	75.1	94.4	5.6
7	0.005	0.05	100	1.0	3	100	60.7	39.3
8	0.005	0.05	80	1.5	3	100	80.7	19.3
9	0.005	0.05	80	2.5	3	100	55.1	44.9
10	0.005	0.05	80	1.0	2	100	83.6	16.4
11	0.005	0.05	80	1.0	4	100	89.0	11.0

Conditions: phenol 0.1 g, dichloromethane solvent 10 mL, unless otherwise noted

the reaction conversion rate, but the selectivity of cyclohexanone decreased significantly (Table 3, Entries 2, 7). This is probably because that, when the temperature rises, not only conducive to Pd/C hydrogenation activity generated more centers to facilitate the hydrogenation reaction of phenol; and also promote phosphotungstic acid generated more activity center, improve the catalyst the dispersion of the active ingredient to improve the selectivity of cyclohexanone [30]. But when the temperature is too high, the heteropoly acid active branch decomposition and dispersion caused by uneven reunion, affecting the activity of the catalyst. Thus, the optimum reaction temperature is 80 °C. Within 3 h of reaction at 80 °C and 1.0 MPa H_2, at an appropriate mass ratio of Pd/C and PTA (1:10), the conversion of phenol attained 100% and the selectivity for cyclohexanone was 93.6%.

3.3 Reusability of Catalyst

Reaction conditions: 0.055 g Pd/C-Heteropoly acid in the first run (no further addition), 0.1 g Phenol in each run, $T = 80$ °C, $t = 3$ h, $P(H_2) = 1.0$ MPa dichloromethane solvent 10 mL.

Figure 1 showed the result of reusability of the composite catalytic system of Pd/C-Heteropoly acid in the hydrogenation of phenol. It was found that the catalyst still exhibited high selectivity after using 5 times, but the conversion of phenol decreased slightly. This stem from the generation of carbonaceous deposits (coking) in the course of the reaction leads to deactivation of the catalyst. However, the Lewis acidity still in heteropoly acid cation which can inhibits the cyclohexanone further hydrogenate to cyclohexanol. The results indicated that the structure of the heteropoly acid was unchanged even after being reused for five cycles, supporting its good reusability. To further clarified, the coking problem of the solid catalyst is also appearance in this
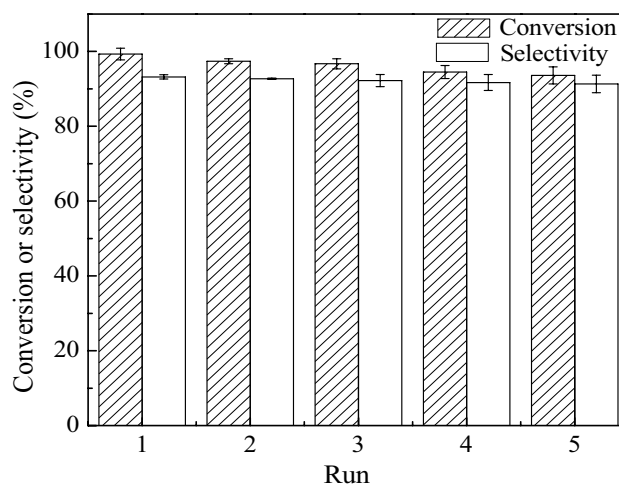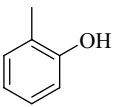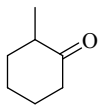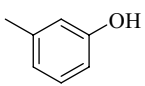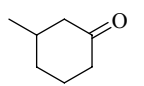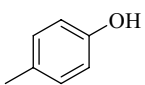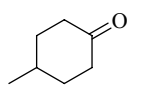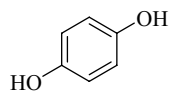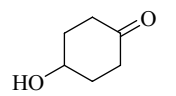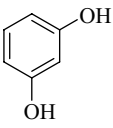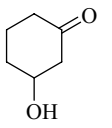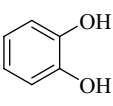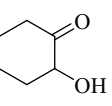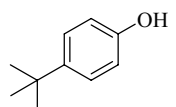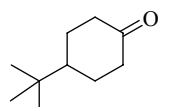

Fig. 1 Recycling of catalyst in the hydrogenation of phenol

reaction. Therefore, a lot of research work still needs to be done that about how to avoid catalyst coking which leads to reduced catalytic activity.

3.4 Generality of Pd/C-Heteropoly Acid Performance for the Other Hydrogenations

To illustrate the general applicability of Pd/C-Heteropoly acid, the method was extended to ring hydrogenation of other hydroxylated aromatic compounds. Table 4 showed the results of these hydrogenations. As can be seen, 100% conversion of phenol was achieved in all cases, and the selectivity toward substituted cyclohexanones were excellent (>96%). As expected, methyl phenol derivatives gave methyl cyclohexanones with both excellent conversions and selectivity (Table 4, Entries 1–3). However, it takes 12 h for o-cresol to reach the same conversion rate as other derivatives. Hydrogenation of hydroquinone, resorcinol and

Table 4 Results of reduction of phenol derivatives over the Pd/C-Heteropoly acid

Entry	derivative	$T(^oC)$	Time(h)	Conv.(%)	product	Sel.(%)
1		80	12	99		90.6
2		80	3	99		92.4
3		80	3	99		91.5
4		80	3	99		94.3
5		80	3	99		91.7
6		80	3	99		90.1
7		100	3	99		92.3

Conditions: Pd/C-Heteropoly acid 0.055 g, substrate 0.5 mmol, $P(H_2) = 1.0$ MPa

pyrocatechol (Table 4, Entries 4–6) were produce very valuable hydroxyl cyclohexanones, again with high conversion and selectivity. Furthermore, this Pd/C-Heteropoly acid catalyst is predicted to be active in the hydrogenation of other phenol derivatives, such as naphthalene, methoxyphenol, aminophenols, etc. Work focused on more detailed hydrogenation studies of Pd/C-Heteropoly acid material is going on.

4 Conclusions

Within the present study, a new and more sustainable method for the hydrogenation of phenol to cyclohexanone was developed by employing the composite catalytic system of Pd/C-Heteropoly acid. By varying the reaction conditions (e.g. the temperature and the amount of Pd/C-Heteropoly acid), the composite catalytic system of Pd/C-Heteropoly acid showed 100% conversion and high selectivity for the hydrogenation of phenol to cyclohexanone under the preferred reaction conditions, such as the amount of the catalyst 5% of the starting material, the catalyst system is a heteropoly acid and Pd/C that mass ratio of 10, the reaction temperature is 80 °C, hydrogen pressure is 1.0 MPa, the reaction time is 3 h. The composite catalyst system was stable and could be reused five times, the catalytic activity without obvious decrease.

Compliance with Ethical Standards

Conflict of interest There are no conflicts to declare.

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