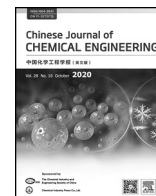




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Article

Phenol hydrogenation to cyclohexanone over palladium nanoparticles loaded on charming activated carbon adjusted by facile heat treatment

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ABSTRACT

Selective phenol hydrogenation is a green approach to produce cyclohexanone. It still remains a big challenge to prepare efficient supports of the catalysts for the phenol hydrogenation via a simple and cost-effective approach. Herein, a facile approach was developed, i.e., direct calcination of activated carbon (AC) under argon at high temperature, to improve its structure and surface properties. The modified AC materials were supported with Pd nanoparticles (NPs) to fabricate the Pd/C catalysts. The as-prepared Pd/C600 catalyst exhibits superior catalytic performance in the phenol hydrogenation, and its turnover frequency (TOF) value is 199.2 h^{-1} , 1.31 times to that of Pd/C-raw. The Pd/C600 catalyst presents both better hydrophobicity and more structural defects, contributing to the improved dispersibility in the reaction solution (phenol-cyclohexane), the better Pd dispersion and the smaller Pd size, which result in the enhancement of the catalytic performance. Furthermore, the as-prepared Pd/C600 catalyst shows a good recyclability.

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1. Introduction

Cyclohexanone (as an important fine chemical) is widely used as a feedstock for synthesizing adipic acid and caprolactame [1]. The industrial production of cyclohexanone includes cyclohexane oxidation and phenol hydrogenation [2–5]. Compared with cyclohexane oxidation, the selective phenol hydrogenation avoids harsh reaction conditions (higher temperature and pressure) and difficult separation, and has been regarded as a green and sustainable technology in the manufacture of cyclohexanone [6]. For phenol hydrogenation, hydrogen is first activated by active components like Pd, and phenol is adsorbed on the catalyst surface. Then, the benzene ring of phenol partially hydrogenates to form the enol. Finally, the enol isomerizes easily to generate cyclohexanone [3]. However, many researchers have found that cyclohexanone is easily further hydrogenated to produce the byproduct cyclohexanol [1]. Therefore, it is urgently needed to design and prepare a catalyst with excellent activity and outstanding cyclohexanone selectivity for the hydrogenation of phenol.

A series of supported noble metal catalysts like Pd-based catalysts have been used for the phenol hydrogenation [7,8]. It is generally known that the catalytic activity of a supported catalyst can be greatly enhanced by suitably selecting and controlling its support. Due to low cost, easy processability, excellent physicochemical stability and wide

availability, activated carbon (AC) has been widely adopted as supports of supported catalysts [9,10]. However, according to the previous literature, the AC was restricted due to its inferior to firmly anchor the noble metal active sites, resulting in the aggregation of these metal nanoparticles (MNPs) [11]. Hence, the design and preparation of functional AC are vital. To date, a number of approaches are devolving to adjust the surface properties of AC. One approach is to develop carbon materials with hierarchical porous nanostructure, which can not only facilitate the mass transfer, but can also be favorable for the dispersion of MNPs by enlarging the specific surface area [12]. Yang *et al.* prepared hierarchically porous carbon through an ammonium oxalate activation route by using cellulose as the carbon precursor, which had an amazing ability in stabilizing and dispersing Ru NPs [13]. Another effective approach is to dope the carbon with heteroatom metal-free (N, O, P, etc.), which can promote great varieties of intrinsic properties: increasing the hydrophilicity, generating more defects, promoting higher MNP dispersion by reinforcing interactions between the MNPs and the support, thereby making the modified carbon materials as charming supports for heterogeneous catalysts [14–17]. Doping the carbon with O can increase its oxygen-containing groups, which can stabilize the MNPs on the carbon surface. Li *et al.* synthesized an O-doping carbon by pretreating with different concentrations of HNO_3 , resulting in superior catalytic performance by increasing the Pd dispersion [18]. Nevertheless, most of these reported approaches suffer from various degrees of weakness such as expensive raw materials, tedious and harsh preparation processes, and requirement of environmentally unfriendly reagents. Therefore, it is still a significant challenge to develop

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a low-cost and simple way to fabricate fascinating AC supports for loading MNPs.

Herein, we developed a facile approach for preparing excellent-performance AC supports by direct calcination under argon at high temperature. Then, the Pd NPs were loaded on the modified AC materials to fabricate the Pd/C catalysts with enhanced catalytic performance in the hydrogenation of phenol. The factors which affected the catalytic properties of the Pd/C catalysts were discussed in detail.

2. Experimental

All the chemicals used in the preparation of the Pd@C catalysts and the phenol hydrogenation to cyclohexanone were obtained commercially [19].

2.1. Catalyst preparation

2.1.1. High temperature modification of AC

2 g of AC was calcined in a tube furnace under argon atmosphere at a certain temperature for 3 h with a heating rate of $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. The as-modified carbon is named as CT, where T represents the calcination temperature. The AC without high temperature treatment is marked as C-raw.

2.1.2. Synthesis of supported Pd catalysts

The Pd/C catalyst was synthesized by a wet impregnation method with $\text{Pd}(\text{OAc})_2$ as the precursor. Typically, 0.043 g of $\text{Pd}(\text{OAc})_2$ and 1 g of AC materials were added into 25 ml of acetone and stirred at $30\text{ }^{\circ}\text{C}$ for 12 h. Rotary evaporation was performed to remove the acetone. The black solid obtained after drying in an oven at $60\text{ }^{\circ}\text{C}$ overnight is marked as Pd/CT or Pd/C-raw.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) was conducted on a Rigaku Miniflex 600 diffractometer in the 2θ of 10° – 80° with a scanning rate of $20\text{ }(^{\circ})\cdot\text{min}^{-1}$. The defect degree of various catalysts was characterized by Raman measurements (Horiba LabRam HR800). N_2 adsorption/desorption was measured to evaluate structural parameters of various catalysts on a Micromeritics ASAP 2010 apparatus. Inductively coupled plasma emission spectroscopy (ICP, Optima 2000DV) was performed to measure the Pd content of each catalyst. CO chemisorption was determined to measure the dispersion of Pd NPs using a Micromeritics ASAP 2010 apparatus. Transmission electron microscopy (TEM) was performed to observe the morphologies of the Pd NPs on a JEOL JEM 2100 microscope. The samples for the TEM characterization were the recovered catalysts after the hydrogenation reaction [3]. X-ray photoelectron spectrometry (XPS) was used for analyzing the electron valence state and surface elemental composition of the catalysts on an ESCALAB 250Xi apparatus. A DropMeterA-100P apparatus was used to measure the water contact angles (WCAs) of various catalysts.

2.3. Catalytic tests

A 50 ml micro autoclave was used to conduct phenol hydrogenation to cyclohexanone (Fig. 1). In a typical experimental procedure, 5 ml of reaction solution (1 wt% of phenol-cyclohexane) was placed in the autoclave and then 0.1 g of the Pd/C catalyst was added. The air in the autoclave was purged out by hydrogen (0.1 MPa H_2 , 5 times). After that, the reaction was performed at $80\text{ }^{\circ}\text{C}$ with a stirring rate of $100\text{ r}\cdot\text{min}^{-1}$. The mass transfer resistance could be eliminated at the stirring rate of $100\text{ r}\cdot\text{min}^{-1}$ (data not shown here). After 30 min of reaction, the catalyst was separated from the mixture by filtration. The filtrate was analyzed by a Shimadzu GC-2014 gas chromatograph with a hydrogen flame ion detector and a PE-20 M capillary column (30 m in length, 0.25 mm in diameter).

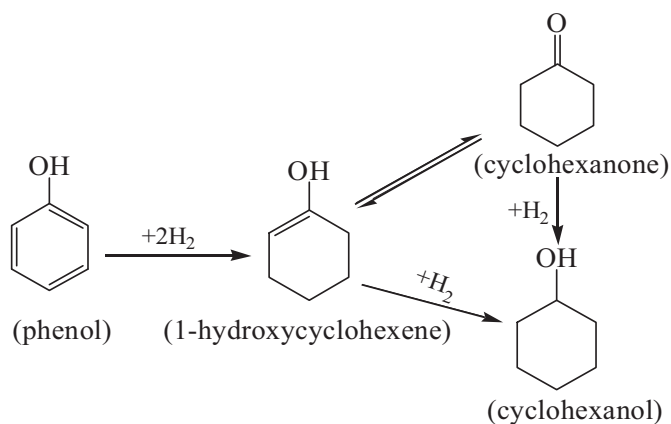


Fig. 1. Illustration of phenol hydrogenation reaction mechanism.

3. Results and Discussion

3.1. Microstructure of the Pd/C catalysts

Three typical catalysts (Pd/C-raw, Pd/C600 and Pd/C800) were characterized in detail to study the influence of high temperature calcination on the microstructure of the Pd/C catalysts.

The XRD patterns of three catalysts with different calcination conditions are similar (Fig. 2). Two distinct broad diffraction peaks of all Pd/C catalysts at 2θ of 23° and 43° are related to the (002) and (100) crystal planes of amorphous carbon, respectively. These results indicate that all Pd/C catalysts possess relatively low graphitization degree [19]. A distinct characteristic peak at about 26° is detected in all Pd/C catalysts, which can be attributed to stereotypes of carbon [19]. Furthermore, no Pd NPs diffraction peaks are detected in three catalysts, mainly due to the good dispersion of Pd on the AC carriers [20]. Raman spectra of three catalysts (Fig. 3) show two obvious peaks at about 1583 (G-band) and 1335 (D-band) cm^{-1} corresponding to graphite and disordered carbon, respectively [21]. In general, the intensity ratio of the $I_{\text{D}}/I_{\text{G}}$ is used to assess the defect degrees of samples [22]. The larger $I_{\text{D}}/I_{\text{G}}$ ratios acquired from the Pd/CT catalysts indicate that more defects are generated during direct calcination at high temperature. When the calcination temperature increases from 0 to $600\text{ }^{\circ}\text{C}$, the ratio of $I_{\text{D}}/I_{\text{G}}$ increases from 0.92 to 1.04, indicating that proper temperature can increase structural defects, ascribing to the removal of impurities on the surface of AC [23]. The value of $I_{\text{D}}/I_{\text{G}}$ further increases to 1.13 at $800\text{ }^{\circ}\text{C}$, indicating that excessively high temperature can lead to the collapse of the framework, resulting in more defects in the structure [24].

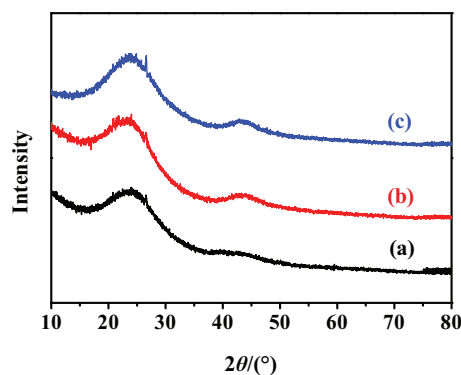


Fig. 2. XRD patterns of various catalysts: (a) Pd/C-raw, (b) Pd/C600, (c) Pd/C800.

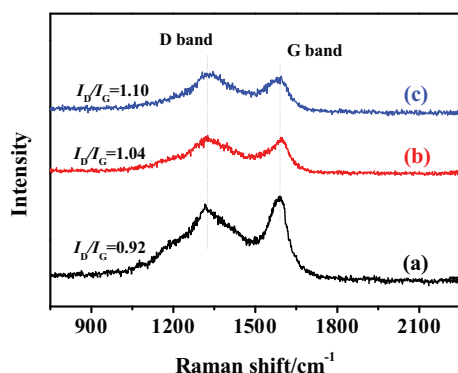


Fig. 3. Raman spectra of various catalysts: (a) Pd/C-raw, (b) Pd/C600, (c) Pd/C800.

The effects of calcination temperature on the textural properties of the Pd/C catalysts were investigated by nitrogen adsorption–desorption measurements. As depicted in Fig. 4, the Pd/C-raw and Pd/CT catalysts exhibit type I/IV isotherms. The typical hysteresis loop at relative high pressure ($0.41 < P/P_0 < 1.0$) and the steep increase at $P/P_0 < 0.02$ suggest the presence of mesopores and the rich microporous nature in the Pd/C catalysts, respectively [25]. With increasing the calcination temperature, the nitrogen adsorption amount decreases significantly, thereby reduced surface area and pore volume (Table 1). As compared to the Pd/C-raw catalyst, the S_{BET} of the Pd/C800 catalyst decreases from 1327 to 659 $\text{m}^2 \cdot \text{g}^{-1}$ and the pore volume also decreases from 0.64 to 0.36 $\text{cm}^3 \cdot \text{g}^{-1}$. The reason for the reduced S_{BET} and pore volume is probably due to the structure collapse induced by high temperature calcination.

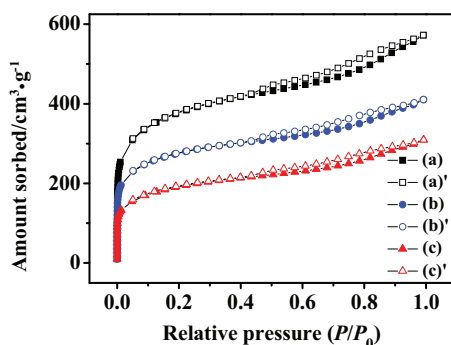


Fig. 4. N_2 adsorption-desorption isotherms of various catalysts: (a) Pd/C-raw, (b) Pd/C600, (c) Pd/C800.

Table 1
Textural properties of various catalysts

Catalysts	$S_{\text{BET}}/\text{m}^2 \cdot \text{g}^{-1}$		Pore volume/ $\text{cm}^3 \cdot \text{g}^{-1}$	
	Total	Meso	Total	Meso
Pd/C-raw	1327	492	0.64	0.50
Pd/C600	980	329	0.43	0.34
Pd/C800	659	276	0.36	0.28
Recovered Pd/C600	837	324	0.40	0.39

XPS was employed to confirm the electron valence state and surface elemental composition of each catalyst. As illustrated in Fig. 5, the wide XPS spectra provide a clear view that the N, O, C, and Pd elements exist in the framework of the Pd/C catalysts. The O content significantly

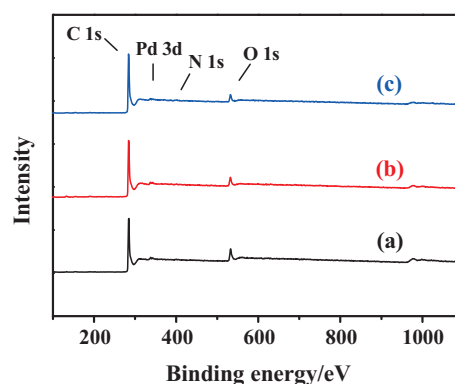


Fig. 5. XPS spectra of various catalysts: (a) Pd/C-raw, (b) Pd/C600, (c) Pd/C800.

decreases from 10.31% to 6.92% with increasing the calcination temperature from 0 to 800 $^{\circ}\text{C}$ (Table 2), revealing that the oxygen species on the surface of the Pd/C catalysts are decomposed at high calcination temperature. The O 1s spectrum can be assigned to four different peaks in each Pd/C catalyst (Fig. 6), namely, C=O (531.8 eV), C—O (533.3 eV), COOH (534.5 eV) and H_2O (536.5 eV) [26,27]. Notably, the H_2O adsorbed on the surface of the Pd/C catalysts is obviously decreased with the increase of calcination temperature (Table 3), indicating that the hydrophobicity of the Pd/C catalysts is increased during calcination at high temperature, which is conducive to disperse uniformly in the reaction solution (phenol-cyclohexane). To detect the difference of the hydrophilicity of the Pd/C catalysts, the WCAs were examined, and the results are illustrated in Fig. 7. The WCA of the Pd/C-raw catalyst is 24.5° , while those of Pd/C600 and Pd/C800 are 58.9° and 81.1° . The results indicate that the higher calcination temperature of AC makes the hydrophobicity of the Pd/C catalysts gradually increase, which can be ascribed to the removal of H_2O adsorbed on the surface of AC.

Table 2
Atomic proportion of diverse elements on various catalysts surface

Catalysts	Atomic proportion/%			
	C1s	Pd3d	N1s	O1s
Pd/C-raw	88.79	0.22	0.68	10.31
Pd/C600	91.47	0.21	0.89	7.43
Pd/C800	91.98	0.19	0.92	6.92

TEM was performed to investigate the distribution and morphology of the supported Pd NPs on AC. It is seen from Fig. 8 that the Pd NP sizes for three samples are in the nanometer range, but the Pd particle sizes are quite different. The average Pd sizes in Pd/C600 (4.3 nm) and Pd/C800 (5.0 nm) are significantly smaller than those in Pd/C-raw (8.0 nm) (Table 4), which may be due to the presence of more structure defects generated by calcination at high temperature (Fig. 3) and the structure defects can anchor Pd NPs from aggregating [18,28]. When the calcination temperature rises from 600 to 800 $^{\circ}\text{C}$, the Pd average size increases from 4.3 to 5.0 nm, attributing to the reduced surface area and pore volume with excessively high temperature (Fig. 4, Table 1). Further, the Pd/C catalysts were subjected to CO chemisorption measurements and the results are shown in Table 4. The Pd dispersion of Pd/C-raw, Pd/C600 and Pd/C800 is 19.1%, 35.6% and 29.0%, respectively. Apparently, the calcination temperature dramatically influences the dispersion of the Pd NPs. The higher Pd dispersion of the Pd/CT catalysts might be due to the generated structure defects (Fig. 3) [18,28]. However, it is found that the order of Pd dispersion (Pd/C600 > Pd/C800 > Pd/C-raw) is inconsistent with the order of structure defects

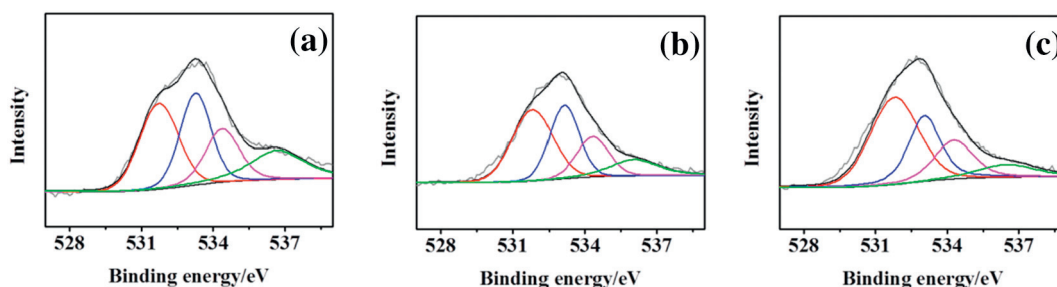


Fig. 6. O1s spectra of various catalysts: (a) Pd/C-raw, (b) Pd/C600, (c) Pd/C800.

Table 3

Oxygen species proportion from XPS O1s on various catalysts surface

Functional groups	XPS binding energy/eV			
	531.8 C=O	533.3 C–O	534.5 COOH	536.5 H ₂ O
Pd/C-raw	32.1	28.7	19.5	19.7
Pd/C600	39.3	29.5	18.3	12.9
Pd/C800	45.9	26.3	18.5	9.3

(Pd/C800 > Pd/C600 > Pd/C-raw), which might be ascribed to the obvious decrease in the surface area of the Pd/C800 catalyst (Fig. 4, Table 1).

ICP was performed to measure the Pd content of three catalysts. As seen from Table 4, the Pd content is decreased with increasing calcination temperature. The results indicate that the AC modified with high temperature is not conducive for the Pd loading, which is related to its decreased surface area (Fig. 4 and Table 1) and O content (Fig. 5 and Table 2) [18].

3.2. Catalytic performance of the Pd/C catalysts

The results of the hydrogenation of phenol over different Pd/C catalysts at 80 °C are depicted in Fig. 9. Interestingly, the cyclohexanone selectivity of all samples is above 96.0%, which is ascribed to the presence of nitrogen of AC itself (Fig. 5 and Table 2). Nitrogen can increase the basicity of the catalysts, which is beneficial to form cyclohexanone by making the phenol adsorb on the catalysts in a non-planar mode [8]. The major byproduct is cyclohexanol, and no obvious other derivatives are produced [19]. Meanwhile, the catalytic activity of the Pd/C catalysts significantly varies with different calcination temperatures. When increasing the calcination temperature from 0 to 600 °C, the catalytic activity of the Pd/C catalysts obviously increases from 47.2% to 88.3%, but then decreases to 46.9% while further increasing the calcination temperature to 800 °C, and the Pd/C600 catalyst exhibits the most outstanding catalytic activity. The TOF values of the as-prepared Pd/C-raw, Pd/C600 and Pd/C800 were calculated based on the Pd atoms on the catalyst surface [29]. The TOF value of Pd/C600 is 199.2 h⁻¹, 1.31 times

higher than that of Pd/C-raw (151.8 h⁻¹), and 1.36 times higher than that of Pd/C800 (146.5 h⁻¹).

For heterogeneous catalytic reactions, the catalytic stability is another important nature besides the activity and selectivity. The Pd/C600 catalyst was selected as the representative for investigating the stability of the as-prepared Pd/CT catalysts in the phenol hydrogenation. In order to better study the catalytic stability, the catalytic activity of Pd/C600 is increased to 96% by prolonging the reaction time to 40 min. As shown in Fig. 10, the phenol conversion of the Pd/C600 catalyst only decreases slightly from 96% to 93% and the cyclohexanone selectivity maintains at 95% after five cycles. The XRD patterns of the fresh and the recovered Pd/C600 catalysts are similar (Figs. 2 and 11(a)), demonstrating the maintained crystal structure of Pd/C600. The results of ICP analysis show that the Pd content of the recovered Pd/C600 catalyst after five cycles is similar with the fresh Pd/C600 (about 1.0 wt%, Table 4), suggesting that the leaching of Pd during the catalytic cycles can be negligible. N₂ sorption isotherms of the fresh and the recovered Pd/C600 catalysts are almost the same (Figs. 4 and 11b), and the slight reduction in the surface area owing to the adsorption of reaction products is responsible for the slight decrease of phenol conversion after five reaction cycles. These results indicate that the as-prepared Pd/C600 catalyst exhibits a good catalytic stability in the hydrogenation of phenol.

3.3. Influence mechanism of high temperature modification

The above results imply that the increased catalytic performance of the Pd/C catalysts (Fig. 9) is ascribed to the modified AC with superior microstructure and surface properties (Fig. 12). Hydrophobicity affects the catalytic performance of the Pd/C catalysts by affecting the dispersibility of the catalysts in the reaction solution (phenol-cyclohexanone). The Pd/C catalyst with better dispersibility is more convenient for the reactants to contact, thereby higher catalytic activity by improving the mass transfer. From the results of WCAs (Fig. 7), the order of the hydrophobicity of various Pd/C catalysts is Pd/C800 > Pd/C600 > Pd/C-raw. However, the catalytic activity of the as-prepared Pd/C catalysts shows a different order of Pd/C600 > Pd/C800 > Pd/C-raw (Fig. 9), indicating that the hydrophobicity is not the only factor in determining the catalytic activity of the Pd/C catalysts. According to the TEM and CO

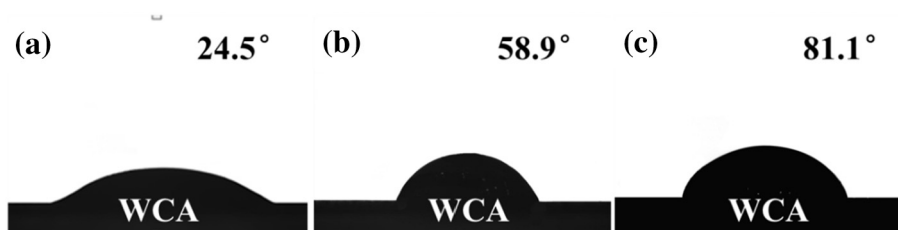


Fig. 7. Water contact angles of various catalysts: (a) Pd/C-raw, (b) Pd/C600, (c) Pd/C800.

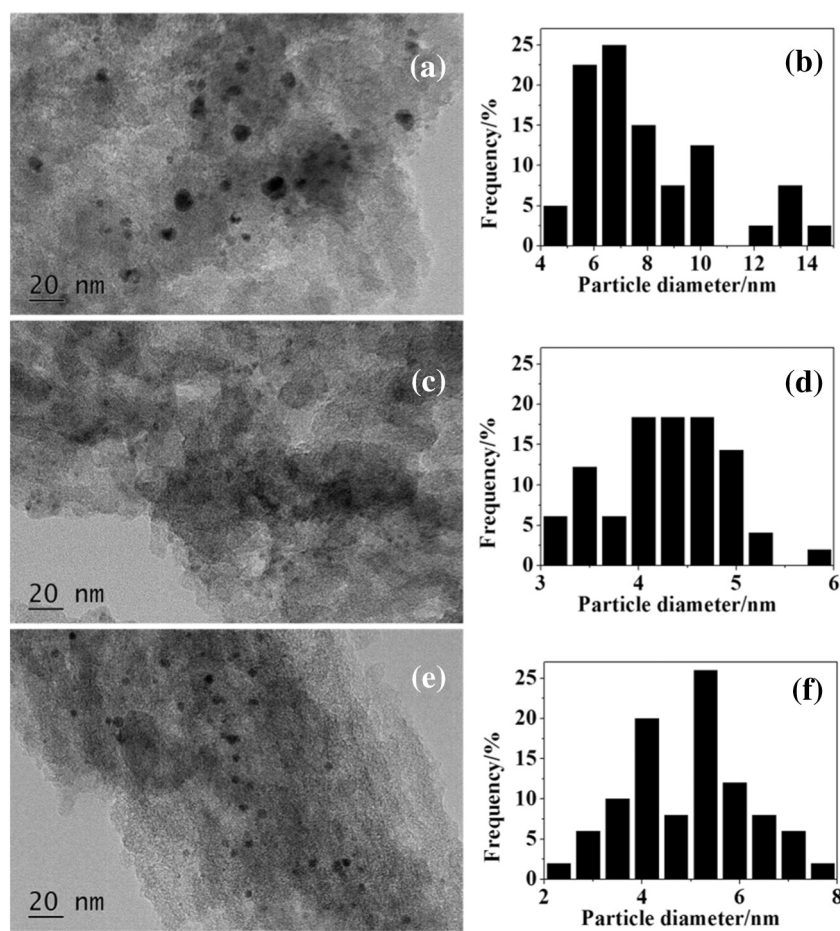


Fig. 8. TEM images and Pd particle sizes of various catalysts: (a, b) Pd/C-raw, (c, d) Pd/C600, (e, f) Pd/C800.

chemisorption results (Fig. 8 and Table 4), the Pd/C600 catalyst which has higher Pd dispersion and smaller Pd size exhibits higher catalytic activity, which is in accordance with the results reported in the literature [3]. It's not difficult for us to understand that the higher Pd dispersion and the smaller Pd size imply more efficient Pd atoms for hydrogen activation, thereby higher catalytic activity. According to the above analyses, it could be concluded that the AC modification with high temperature can obviously increase the hydrophobicity, decrease the Pd size and improve the Pd dispersion of the Pd/C catalyst, which in turn significantly enhances the catalytic activity of the Pd/C catalyst in the phenol hydrogenation. And the Pd dispersion and Pd size are the dominant factors.

4. Conclusions

In summary, AC was modified via high temperature calcination and loaded with Pd NPs to prepare the Pd/C catalysts for the phenol

hydrogenation to produce cyclohexanone, and the related influence mechanism was researched. The modification by high temperature calcination significantly affects the activity of the Pd/C catalysts, owing to its great tremendous impact on the hydrophilicity/hydrophobicity, Pd dispersion and Pd size of the Pd/C catalysts. Among them, the Pd dispersion and Pd size are the dominant factors. Better hydrophobicity, better

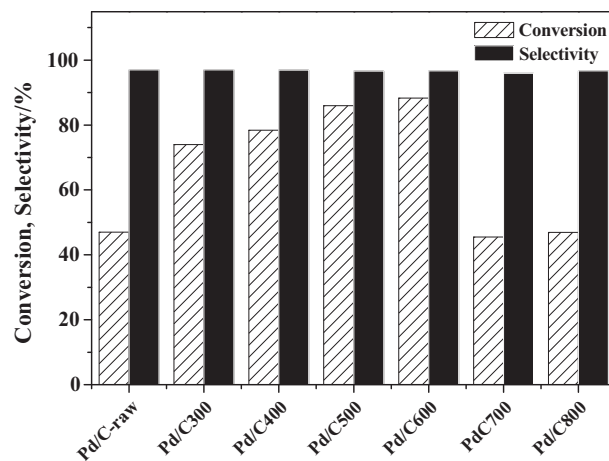


Fig. 9. Hydrogenation of phenol over various catalysts (catalyst 0.1 g, 1 wt% of phenol-cyclohexane solution 5 ml, 80 °C, 0.1 MPa H₂, 30 min).

Table 4

Pd content, dispersion and size of various catalysts

Catalysts	Pd/C-raw	Pd/C600	Pd/C800	Recovered Pd/C600
Pd content ^① /wt%	1.38	1.06	0.94	1.01
Pd dispersion ^② /%	19.1	35.6	29.0	–
Pd size ^③ /nm	8.0	4.3	5.0	–

^① Analyzed by ICP.

^② Calculated from CO chemisorption.

^③ Average size as conducted by TEM.

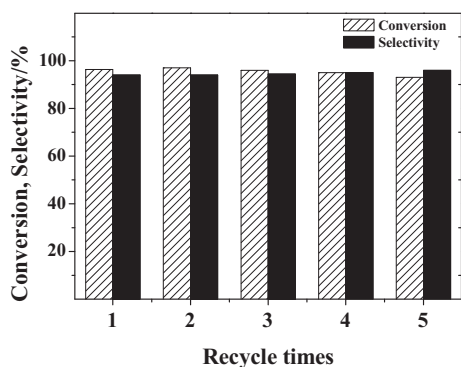


Fig. 10. Stability tests of Pd/C600 (catalyst 0.1 g, 1 wt% of phenol-cyclohexane solution 5 mL, 80 °C, 0.1 MPa H₂, 40 min).

Pd dispersion and smaller Pd size are beneficial for the improvement of the catalytic performance of Pd/C in the phenol hydrogenation to produce cyclohexanone in cyclohexane.

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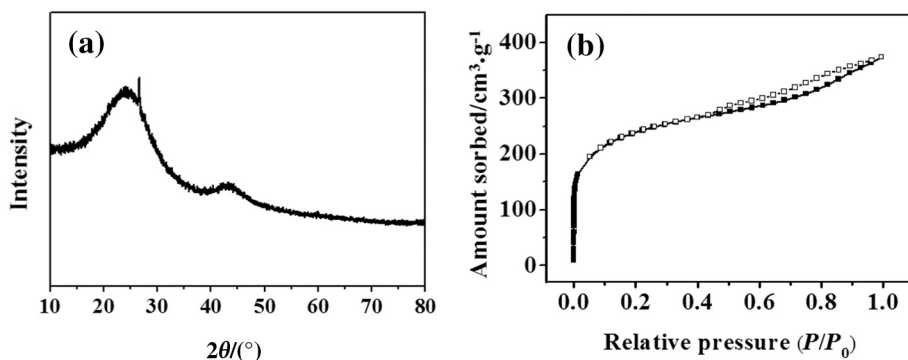


Fig. 11. (a) XRD pattern, (b) N₂ sorption isotherms of Pd/C600 after 5 cycles.

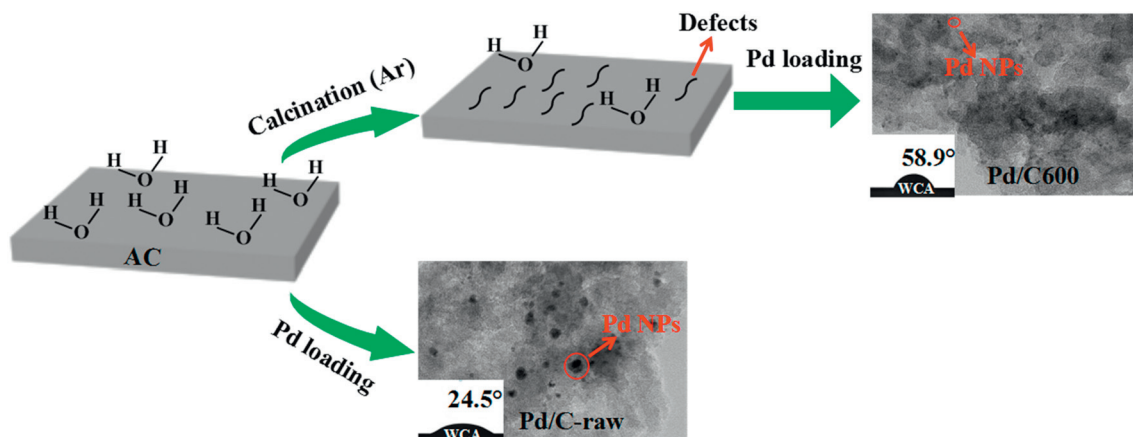


Fig. 12. Influence mechanism of AC modification with high temperature.

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