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Highly selective hydrogenation of 3,4-dichloronitrobenzene over Pd/C catalysts without inhibitors

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A series of Pd-only catalysts supported on activated carbon pretreated with HNO_3 or EDTA-2Na for liquid phase selective hydrogenation 3,4-dichloronitrobenzene (DCNB) to corresponding 3,4-dichloroaniline (DCAN) are investigated. Characterization of the catalysts is performed by N_2 adsorption/desorption, TPD, XRD and TPD techniques. The selectivity to DCAN is not only correlate with the Pd particle average size, but also correlate with distribution of Pd particles sizes. The surface groups of activated carbon can influence the average size and distribution of Pd particles. Pretreated activated carbon with HNO_3, forms various oxygen-containing groups on the surface, results in large average size but wide-distributed Pd particles. On the contrast, pretreated activated carbon with EDTA-2Na results in large average size and narrow-distributed of Pd particles simultaneously. More than 60% Pd particles sizes are distributed in the 20–30 nm range of the 2% Pd loading catalyst pretreated with 1 M EDTA-2Na, of which the selectivity to DCAN is up to 99.61%.

1. Introduction

Halogenated anilines are important intermediates for synthesis of organic fine chemicals, such as dyes, drugs, herbicides, and pesticides. The main routes to their production involve the Bechamp reaction [1] in a metal–acid system or selective hydrogenation over heterogeneous catalysts. The hydrogenation is now preferred, owing to its lower impact on the environment since no acid effluents are produced. The catalysts for the hydrogenation have been well-studied, such as platinum [2,3], palladium [4], rhodium [5], nickel [6], and copper chromite [7] catalysts. Depending on the halogen and its position relative to the nitro group in the halogenated nitrobenzene, dehalogenation can vary from negligible to near 100% [8,9]. To improve the hydrogenation selectivity, the catalyst preparations are modified (alloying [10], metal/support interaction [11–13], etc.) or specific additives (promoters or inhibitors) [14,15] are used in the reaction system.

Coq et al. [16–18] reported the hydrogenation of *p*-chloronitrobenzene over platinum catalysts. They find that the hydrogenation of *p*-chloronitrobenzene is a structure sensitivity reaction; the selectivity to *p*-chloroaniline is affected by changing the size of Pt particles. The highest yields in haloamines are obtained on large Pt particles [16]. In the preparation of the supported metal catalyst, the great concern has been to produce metal particles that are well dispersed with sizes as small as possible in order to maximize the surface-to-volume ratio [19–23]. Now the narrow particle size distribution should become an important concern as well for the selectivity purpose [24]. Various techniques to prepare nanosized materials have been investigated. Whereas these techniques hardly concern how to produce catalysts have large metal particles with narrow particle size distribution apply to some special reactions, such as hydrogenation of halogenated nitrobenzenes.

Activated carbon has some advantages as catalyst support [25]. However, the chemical inertness of carbon might result in a low reactivity, thus creating an interaction between the activated carbon and supported metal precursors, which sometimes impacts the deposition of the metals significantly. The activation pretreatment in an oxidation environment is generally believed to be an available way for the introduction of oxygen-containing groups onto the activated carbon [26–28].

3,4-Dichloronitrobenzene (DCNB) as the reactant is representative and special, because of dehalogenation can occur to generate chloroaniline (3-chloroaniline or 4-chloroaniline), can also further occur to generate aniline. In this study, a series of Pd-only catalysts supported on activated carbon pretreated with HNO_3 or EDTA-2Na have been prepared and characterized from a structural and textural point of view. In particular, we investigated the effects of introducing different surface group on the activated carbon using a combination of BET, temperature programmed desorption (TPD), X-ray diffraction (XRD) and transmission electron microscopy (TEM) and liquid phase selective hydrogenation of 3,4-dichloronitrobenzene (DCNB) to corresponding 3,4-dichloroaniline (DCAN) catalytic tests, focusing on the surface group of activated

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carbon, the average size and distribution of Pd particles. Based on various characterizations, the promoting effect of pretreatment of activated carbon on the catalytic selectivity is discussed briefly.

2. Experimental

2.1. Catalyst preparation

A commercially starting activated carbon with particle size less than 61 μm (250 mesh), BET surface area of 1703 m^2/g and 0.48 wt% ash was made from coconut shells (Fujian Xinsen Carbon Co., Ltd.). The activated carbon was pretreated with different concentrations of HNO_3 (from 0.8 M to 14.9 M) at 366 K for 4 h. The pretreated activated carbon was then filtered, rinsed in deionized water until pH = 7 and eventually dried at 383 K for 10 h.

The activated carbon was also pretreated with different concentrations of EDTA-2Na (from 0.4 M to 1.2 M) at 323 K for 4 h. The pretreated activated carbon was then filtered, rinsed in deionized water until pH = 7 and eventually dried at 383 K for 10 h.

A desired volume of H_2PdCl_4 aqueous solution was added into an aqueous suspension of the pretreated activated carbon at 80 °C. After stirred 6 h, the solution pH of 10–11 was reached by addition of NaOH solution; then the precipitated $Pd(OH)_2$ was reduced by hydrazine hydrate. The Pd/C catalyst was filtered, rinsed in deionized water until pH = 7 and eventually outgassed in a vacuum at 383 K for 10 h. The actual Pd loading was determined by ICP (inductively coupled plasma atomic emission spectrometer). Residual Cl was not found on the catalyst surface by EDS detection.

2.2. Catalytic testing

Liquid phase hydrogenation of 3,4-dichloronitrobenzene was conducted as follows: 100 ml methanol, 10.0 g 3,4-dichloronitrobenzene, 0.1 g catalyst were mixed in a 1000 ml steel autoclave equipped with a magnetic stirrer and an electric heating system. The reactor was first filled with N_2 three times in succession to exclude the inside air. Then it was filled with H_2 to replace N_2 three times, followed by heating slowly till 353 K. When the hydrogen pressure reached 1.0 MPa, the hydrogenation was started immediately by stirring the reaction mixture vigorously. The stirring rate was kept at 600 rpm to eliminate the external diffusion effects. Less than 61 μm particle size of activated carbon can eliminate internal diffusion on the reaction. The reaction products were analyzed by gas chromatography (SHIMADZU GC14B) from which the DCNB conversion and the yield of DCAN were obtained. The capillary column DB-225 with an i.d. of 0.32 mm and a length of 30 m equipped with an FID detector was used.

2.3. Characterization techniques

The textural properties of the activated carbons were analyzed by low temperature N_2 adsorption/desorption using a Quantachrome NOVA-1000e gas absorption analyzer. A 50 mg sample was heated to 523 K and held at that temperature for 12 h to remove the adsorbed species. The specific surface areas were calculated using the BET equation.

The amount of oxygen-containing groups (carboxyl, lactonic, and phenol) on the activated carbon pretreated with HNO_3 was determined by adsorption neutralization with $NaHCO_3$, Na_2CO_3, and NaOH solutions, respectively. A 500 mg sample was equilibrated with 25 ml of 0.1 M $NaHCO_3$, $NaCO_3$, or NaOH for 24 h, respectively, and then 25 ml of 0.1 M HCl was added to aliquots and back-titrated with 0.1 M NaOH after boiling off the CO_2 [29,30].

The amount of surface groups on the activated carbon were determined by temperature-programmed desorption (TPD) of CO_2 under helium stream. 100 mg sample was loaded in a quartz cell and treated at room temperature for 1 h in a He stream at 50 ml/min. Then the sample was heated at 5 K/min up to 1173 K. The decomposition products (CO_2) of surface groups were measured by on-line mass spectrometry.

X-ray diffraction patterns (XRD) of Pd/C catalysts were collected in the 2θ angle between 15° and 75°, at a step width of 0.04° and by a counting 1 s at each step with a SCINTAG X'TRA X-ray diffractometer (ARL) with Cu Ka radiation. The Pd particle size was calculated by the Schrrer formula.

TEM analysis was performed with a JEOL JEM-200CX instrument operating at 160 kV. The total Pd particle count was used to derive Pd sizes from TEM analysis. The Pd particle size of Pd/C catalysts, ds, was calculated by the following equation: $ds = \Sigma n_i d_i^3 / \Sigma n_i d_i^2$, where visible particle size d_i on the micrographs was measured by a computerized system. The standard deviation is 4.87.

3. Results and discussion

3.1. Textural and surface group characterization of activated carbon

The structure parameters of the activated carbons pretreated with different concentration HNO_3 are listed in Table 1. The pretreatment with low concentrations (0.8 M) HNO_3 can appreciably increase the structure parameters of the activated carbon. Some impurities blocking pore canals of activated carbon can be removed by the low concentration HNO_3 for the improvement of structure properties of activated carbons [29]. However, an opposite effect of pretreatment with high concentrations (from 1.7 M to 14.9 M) HNO_3 on the structure parameters has been observed. In particular, the structure parameters will be decreased significantly when the pretreatment is carried out with undiluted (14.9 M) HNO_3. Tamon et al. [30] also found that the BET surface area and pore volume of activated carbon had been decreased greatly by the strong oxidation of 13.2 M HNO_3. At the same time, various oxygen containing groups (carboxyl, lactone, phenol, etc.) form on the surface of activated carbons during the pretreatment with HNO_3. The amount of oxygen-containing groups on the activated carbon pretreated with different concentrations of HNO_3 measured by Boehm's method [31] is presented in Table 2. The experimental results indicate that the amount of oxygen-containing groups and the total groups on the activated carbons are highly dependent upon the HNO_3 concentration used. This influence will be increased with the increase of HNO_3 concentration.

The structure parameters of the activated carbons pretreated with different concentration EDTA-2Na are listed in Table 3. Con-

Table 1
Structure parameters of the AC pretreated with different concentrations of HNO_3.

HNO_3 concentration (mol/l)	S_{BET} (m^2/g)	V_{micro} (cm^3/g)	V_{total} (cm^3/g)	D (nm)
Untreated	1703	0.662	1.065	1.28
0.8	1787	0.692	1.098	1.27
1.7	1655	0.648	1.049	1.30
3.5	1548	0.633	1.020	1.28
7.7	1252	0.540	0.851	1.24
14.9	664	0.288	0.417	1.17

Table 2
Oxygen-containing groups of the AC pretreated with different concentrations of HNO_3.

HNO_3 concentration (mol/l)	Carboxyl group (mmol/g)	Lactonic group (mmol/g)	Phenol group (mmol/g)	Total groups (mmol/g)
Untreated	0.121	0.005	0.079	0.205
0.8	0.484	0.127	0.212	0.823
1.7	0.519	0.152	0.349	1.020
3.5	0.751	0.274	0.366	1.391
7.7	1.278	0.322	0.464	2.084
14.9	1.422	0.650	0.655	2.727

Table 3
Structure parameters of the AC pretreated with different concentrations of EDTA-2Na.

EDTA-2Na concentration (mol/l)	S_{BET} (m^2/g)	V_{micro} (cm^3/g)	V_{total} (cm^3/g)	D (nm)
Untreated	1703	0.662	1.062	1.29
0.4	1787	0.710	1.167	1.30
0.8	1812	0.728	1.185	1.30
1.0	1846	0.738	1.210	1.31
1.2	1839	0.742	1.213	1.31

trast pretreatment with HNO_3, pretreatment with EDTA-2Na does not destroy the structure of activated carbons. Moreover, pretreatment with different concentrations EDTA-2Na can increase the structure parameters of the activated carbon. Some impurities blocking pore canals of activated carbon can be removed by EDTA-2Na for the improvement of structure properties of activated carbons.

Fig. 1 shows the CO_2 TPD profiles of pretreated activated carbon, in which there are three CO_2 desorption peaks at ~500, ~600, and ~873 K, respectively. The CO_2 desorption peaks of activated carbon pretreated with 14.9 M HNO_3 are attributed to carboxylic acids, lactones, and carboxylic anhydrides [32–34]. Furthermore, the CO_2 desorption peaks of activated carbon pretreated with 1 M EDTA-2Na are obviously attributed to the carboxyl of EDTA. According to the height of CO_2 desorption peaks, the amount of surface groups on the activated carbon pretreated with 14.9 M HNO_3 are much more than the activated carbon pretreated with 1 M EDTA-2Na.

3.2. Catalytic properties of the Pd/C catalysts

The liquid phase hydrogenation of DCNB is a complicated process, and many by-products are involved. It followed the reaction pathways described in the literature [35]. The liquid phase hydrogenation process goes through nitroso and hydroxylamine intermediate stages, different side reactions occur in different reaction conditions. However, the dechlorination reaction is the main side reaction. We investigated the effect of activated carbons pretreated with different concentration of HNO_3 on the hydrogenation of DCNB over Pd(5%)/C catalysts. The result is listed in Table 4. It could be seen clearly that the catalytic properties of Pd/C catalysts correlate with HNO_3 concentration closely. With the increase HNO_3 concentration, the catalytic activity (reaction time) decreased but selectivity to DCAN increased remarkably. The selectivity of DCAN on Pd/C catalyst pretreated with undiluted (14.9 M) HNO_3 achieved 97.15%. Since the activated carbon pretreated by nitric acid change the number of oxygen-containing groups. This means that the number of oxygen-containing groups can affect the number of palladium active sites of Pd/C catalyst, which get reflected in the catalytic activity.

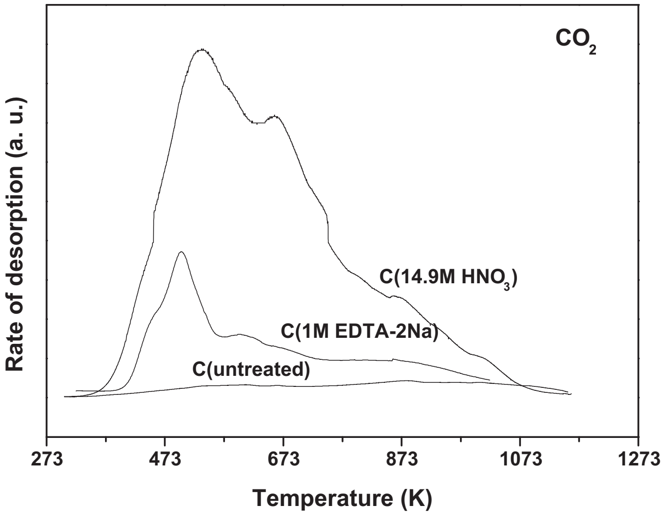

Fig. 1. CO_2 gas evolution profiles of the pretreated activated carbon in TPD.

Table 5 lists the catalytic properties for hydrogenation of DCNB over Pd(5%)/C catalysts pretreated with different concentrations of EDTA-2Na. It can be seen that the catalytic activity decreased but selectivity to DCAN increased equally, and the selectivity to DCAN increased gradually with the concentration of EDTA increasing. EDTA pretreatment concentrations 1.0 and 1.2 mol/l, respectively, the reaction results are very close. This may be due to the concentration of more than 1.0 mol/l EDTA after its adsorption on the catalyst surface becomes saturated. However, there is a great probability of dehalogenation side reactions taking place. As activity and selectivity of the high correlation, this means that just by changing the concentration of EDTA to change the number of Pd active sites is not enough, also need to adjust the amount of Pd loading.

Furthermore, we investigated the effect of Pd loading on the hydrogenation of DCNB over Pd/C catalysts pretreated with 1 M concentration of EDTA-2Na. The results are listed in Table 6. It can be seen that the effect of Pd loading on the catalytic properties of Pd/C catalyst is remarkable. When the Pd loading decreased (from 5% to 2%), the time of complete reaction prolonged gradually, it implied that the activity of Pd/C catalyst reduced, whereas, the selectivity to DCAN improved observably. As the Pd loading decreased more to 1%, the activity and selectivity of Pd/C dropped simultaneously. The selectivity to DCAN of the Pd/C catalyst with 2% Pd loading was the highest, 99.61%. Comparing with the Pd/C catalyst pretreated with undiluted (14.9 M) HNO_3, the catalytic property of Pd/C catalyst pretreated with 1 M concentration of EDTA-2Na had surpassed. At the same time, the value of Pd loading can be reduced (from 5% to 2%) to save the noble metal. Furthermore, Nitric acid in the treatment process will be activated decomposition of NOx, but the EDTA solution was added later can be recycled.

Table 4
Catalytic properties for hydrogenation of 3,4-dichloronitrobenzene over Pd(5%)/C catalysts pretreated with different concentrations of HNO_3.[a]

HNO_3 concentration (mol/l)	Reaction time (min)	Conversion (%)	Selectivity of productions		
			3,4-Dichloroaniline (%)	Chloroaniline (%)	Aniline (%)
0.8	21	100	64.71	5.92	29.37
1.7	25	100	75.69	3.46	20.85
3.5	32	100	87.36	2.73	9.91
7.7	39	100	94.10	1.33	4.57
14.9	53	100	97.15	0.52	2.33

[a] Reaction conditions: 0.1 g catalyst; 10.0 g 3,4-dichloronitrobenzene; 100 ml methanol; $PH_2 = 1.0$ MPa; $T = 353$ K; stirring rate = 600 rpm.

Table 5
Catalytic properties for hydrogenation of 3,4-dichloronitrobenzene over Pd(5%)/C catalysts pretreated with different concentrations of EDTA-2Na.[a]

EDTA-2Na concentration (mol/l)	Reaction time (min)	Conversion (%)	Selectivity of productions		
			3,4-Dichloroaniline (%)	Chloroaniline (%)	Aniline (%)
0.4	18	100	79.23	13.73	7.04
0.8	23	100	88.09	8.14	3.77
1.0	25	100	91.37	6.05	2.58
1.2	27	100	91.81	5.80	2.39

[a] Reaction conditions: 0.1 g catalyst; 10.0 g 3,4-dichloronitrobenzene; 100 ml methanol; $PH_2 = 1.0$ MPa; $T = 353$ K; stirring rate = 600 rpm.

3.3. Characterization of the Pd/C catalysts

Table 7 presents the Pd particle size of Pd/C catalysts, which is determined by XRD and TEM, respectively. This experimental result indicates that Pd particle size of Pd/C catalysts is highly dependent upon the HNO_3 concentration. Pretreatment of activated carbon with HNO_3 might significantly affect the physicochemical properties of activated carbon and further influence the Pd dispersion [28]. The pretreatment of activated carbon with a high concentration of HNO_3 will result in oxygen-containing groups assembling densely on the activated carbon [28,32,33,36]. The presence of a large number of oxygen-containing groups on the dispersion of palladium is detrimental.

Fig. 2 shows the relation between the selectivity to DCAN and the average size of Pd particles. It could be seen clearly that the variety trends of the average sizes of Pd particles and the selectivity to DCAN accompanied with the concentration of HNO_3 increasing are especially coincident. It means that the selectivity to DCAN correlates with the average sizes of Pd particles of Pd/C catalysts closely. Increasing the average sizes of Pd particles of Pd/C catalysts can improve the selectivity to DCAN of products. The highest yields of DCAN are obtained on the largest Pd particles on the activated carbon pretreated with the highest (undiluted) concentration of HNO_3. Coq et al. [16–18] had studied the behavior of some Pt catalysts in relation to the size of the platinum particles for monometallic Pt/Al_2O_3 catalysts for the hydrogenation of *p*-chloronitrobenzene. It was also found that the selectivity to *p*-chloroaniline is affected by changing the size of Pt particles. They had obtained the same results that the highest yields of *p*-chloroaniline achieved on large Pt particles. We speculate that absorption capacity of chloroaniline products on the large Pd or Pt particles is weak. Easy desorption of chloroaniline products helps to reduce the dehalogenation side reactions.

Fig. 3 illustrates the TEM micrograph and Pd particles sizes distribution of Pd(5%)/C catalyst pretreated with 14.9 M concentration of HNO_3. It can be seen that the palladium particles are broad dispersed. After pretreated with HNO_3, various oxygen-containing groups, such as carboxylic acids, lactones, carboxylic anhydrides,

Table 6
Catalytic properties for hydrogenation of 3,4-dichloronitrobenzene over Pd/C catalysts with different loadings of Pd.[a]

Loading of Pd (wt%)	Reaction time (min)	Conversion (wt%)	Selectivity of productions		
			3,4-Dichloroaniline (%)	Chloroaniline (%)	Aniline (%)
5	25	100	91.37	6.05	2.58
3	37	100	97.85	2.04	0
2	46	100	99.61	0.39	0
1	59	100	99.17	0.83	0

[a] Reaction conditions: 0.1 g catalyst (pretreated with 1.0 M concentration of EDTA-2Na); 10.0 g 3,4-dichloronitrobenzene; 100 ml methanol; $PH_2 = 1.0$ MPa; $T = 353$ K; stirring rate = 600 rpm.

Table 7
Average sizes of Pd particles on the AC pretreated with different concentrations of HNO_3.

Characterization methods	Average sizes of Pd particles (nm) Concentration of HNO_3 (mol/l)				
	0.8	1.7	3.5	7.7	14.9
XRD[a]	–[b]	7.4	9.8	13.5	22.0
TEM	2.7	6.8	9.1	13.6	20.0

[a] The average size of Pd crystal particles on Pd/C catalysts were calculated by Schrrer formula.

[b] The diffraction peaks of Pd crystal are too dispersion to calculate the average size of Pd crystal particles on Pd/C catalysts.

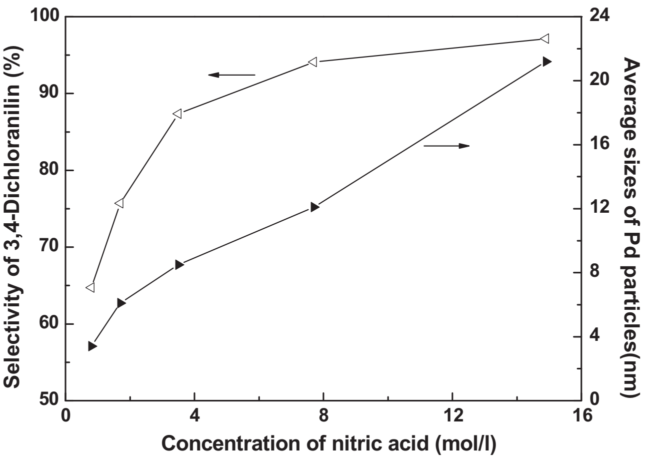

Fig. 2. Effects of HNO_3 concentration used in the pretreatment of AC on the selectivity of 3,4-dichloroaniline and average sizes of Pd particles of Pd/C catalysts.

phenols, ethers, and carbonyls (and quinones) distribute on the surface of the activated carbon [32–34]. The interaction between each the oxygen-containing group and Pd precursor is different, which was considered to be due to the no uniform distribution of the Pd particle size.

Table 8
Average sizes of Pd particles of Pd(2%)/C catalyst pretreated with 1 M EDTA-2Na.

Characterization methods	Average sizes of Pd particles (nm)
XRD[a]	23.4
TEM	21.8

[a] The average size of Pd crystal particles on Pd/C catalysts were calculated by Schrrer formula.

Table 8 presents the average size of Pd particles of Pd(2%)/C catalyst pretreated with 1.0 M EDTA-2Na. The surface area of activated carbon pretreated with EDTA-2Na are much higher than that of activated carbon pretreated with undiluted (14.9 M) HNO_3, and the Pd loading on activated carbon pretreated with 1.0 M concentration of EDTA-2Na does not achieve half of Pd loading on activated carbon pretreated with undiluted (14.9 M) HNO_3. Whereas, the average size of Pd particles of Pd(2%)/C catalyst pretreated with 1.0 M concentration of EDTA-2Na is similar to that of Pd(5%)/C catalyst pretreated with undiluted (14.9 M) HNO_3. We presume that there are strong chelation between the Pd and EDTA, which adsorbed on activated carbon support. EDTA is a multi-tooth ligand, can form a chelate with a number of palladium cations. This chelation results in the Pd particles stacking on the activated carbon on the conditions of big surface area of support and low loading of metal.

Fig. 4 shows the TEM micrograph and the Pd particles sizes distribution of Pd(2%)/C catalyst pretreated with 1 M concentration of EDTA-2Na. It can be seen that the distribution of sizes of Pd particles was much narrower than that of the Pd(5%)/C catalyst pretreated with undiluted (14.9 M) HNO_3. The sizes of a majority of Pd particles were in range of from 20 nm to 30 nm. We consider that excellent catalytic property of Pd(2%)/C catalyst pretreated with 1 M concentration of EDTA-2Na can be attributed to the large Pd particles and narrow distribution of Pd particles sizes.

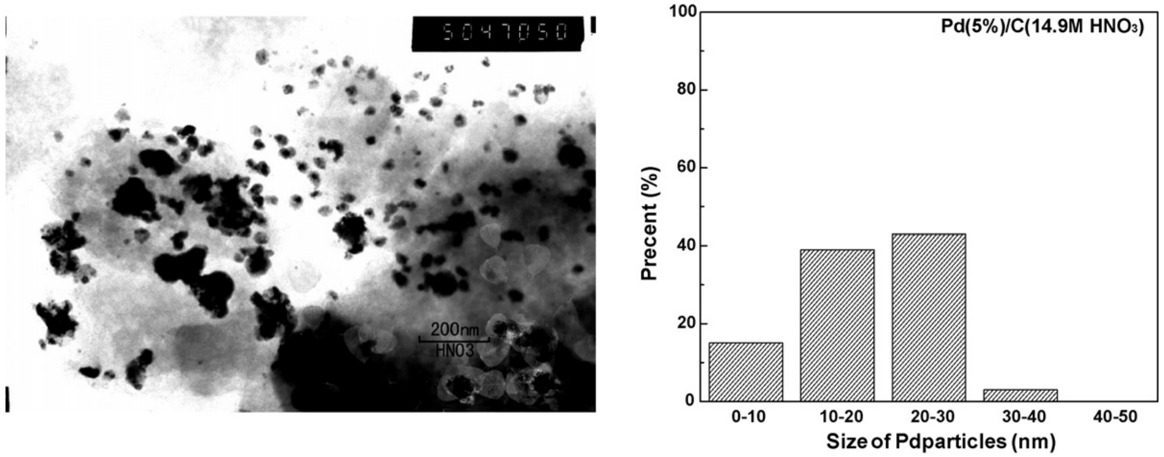

Fig. 3. TEM micrograph and Pd particles sizes distribution of Pd(5%)/C catalysts pretreated with 14.9 M HNO_3.

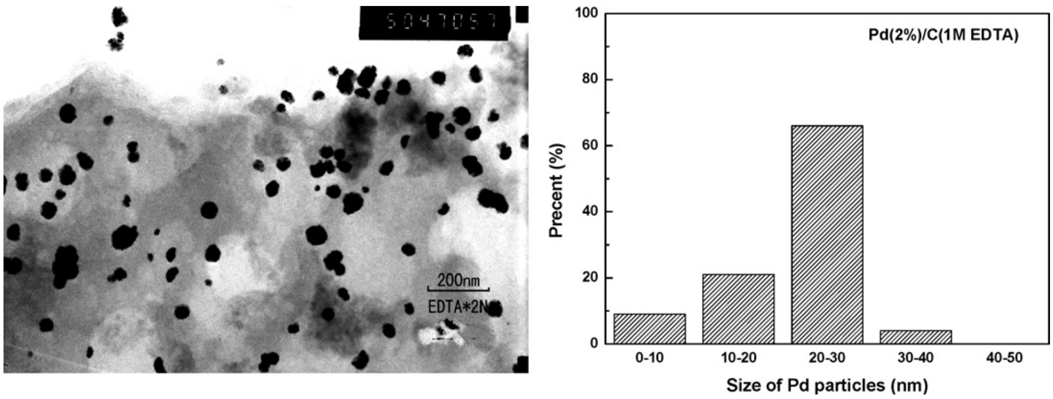

Fig. 4. TEM micrograph and Pd particles sizes distribution of Pd(2%)/C catalysts pretreated with 1.0 M EDTA-2Na.

4. Conclusion

In the liquid phase hydrogenation of DCNB, the selectivity to DCAN correlates not only with the Pd particle average size of Pd/C catalyst, but also with distribution of Pd particles sizes. Through the above discussions, we have concluded that well-distributed large Pd particles can effectively restrain the dehalogenation side reactions. It is confirmed that the surface groups of activated carbon can influence the average size and distribution of Pd particles. Pretreatment of activated carbon with special chemical solution is a useful method to adjust the surface groups of activated carbon. Common pretreated with HNO_3, on the condition of high concentration, form various oxygen-containing groups on the surface of the activated carbon. And it results in large average size but bad-distributed Pd particles on activated carbon support. On the contrast, pretreated with EDTA-2Na results in large average size and well-distributed of Pd particles on activated carbon support simultaneously. The strong chelation between the Pd and the single surface group of activated carbon support, EDTA, is the major reason. It is worthwhile to note that the pretreated activated carbon with EDTA-2Na has some definite advantages: (i) the reaction process need no more inhibitors to reduce hydrogenolysis by-products; (ii) high (99.61%) selectivity to DCNB; and (iii) low (2%) loading of Pd.

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