

## 酸处理活性炭催化水合肼还原硝基苯

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**摘要:** 以水合肼为还原剂, 采用硝酸、盐酸、硫酸及氮气或氢气气氛处理的活性炭为催化剂, 考察了其催化硝基苯还原反应性能。结果表明, 经化学处理后, 活性炭表面形成了各种含氧官能团, 它们可引发水合肼分解, 并影响硝基苯的吸附。活性炭表面形成的含氧官能团越多, 其催化硝基苯还原速率越快。其中经盐酸处理的活性炭表面形成的含氧官能团最多, 因而表现出最高的硝基苯还原活性。

**关键词:** 活性炭; 水合肼; 硝基苯; 加氢; 红外光谱

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## Reduction of Nitrobenzene with Hydrazine Hydrate Catalyzed by Acid-Treated Activated Carbon

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**Abstract:** Activated carbons, which were modified by chemical treatment in aqueous solutions of HNO<sub>3</sub>, HCl, and H<sub>2</sub>SO<sub>4</sub> or in gaseous N<sub>2</sub> and H<sub>2</sub>, have been tested as catalysts in the reduction of nitrobenzene using hydrazine hydrate as hydrogen donor. Fourier transform infrared spectroscopy analysis and Boehm titration reveal that the chemical treatment leads to the formation of various oxygen functional groups on the surface of the activated carbon. These oxygen functional groups can induce the decomposition of hydrazine hydrate and influence the adsorption of nitrobenzene on the surface of the activated carbon. The catalytic activity is correlated to that of the oxygen functional groups, which suggests that an abundance of surface oxygen functional groups is favourable for this reaction. The activated carbon treated by hydrochloric acid had the largest amount of oxygen functional groups and exhibited the highest activity for nitrobenzene reduction to aniline.

**Key words:** activated carbon; hydrazine hydrate; nitrobenzene; hydrogenation

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Activated carbon (AC) is usually used as a substrate for loading active catalytic centers due to its high surface area, tunable porosity, and high stability in caustic and acidic conditions [1–3]. Both the texture and surface chemistry of AC support have a distinct effect on the catalytic performance of AC supported catalysts [4,5]. However, there are examples of the application of AC itself as catalyst for

chemical reactions [6–12]. For example, Díaz Velásquez et al. [11] reported that surface modified activated carbons catalyzed the oxidative dehydrogenation of isobutane. Sun et al. [12] investigated selective hydrogen transfer to anthracene and its derivatives over an AC, and found that the AC can split gaseous hydrogen into atoms and catalyze the monatomic hydrogen transfer to aromatic rings.

Generally, the catalytic properties of AC itself can be modified to develop desirable physicochemical properties by adequate choice of activation procedures. For example, AC can be modified via physical approaches to change of their properties for different applications. It was reported that heat treatment in an inert atmosphere can selectively remove some of the oxygen functional groups [13]. Surface carboxylic acid groups of carbons disappear after treatment in H<sub>2</sub> at 723 K [14]. In addition, surface properties of activated carbons can be also modified by adding inorganic acids. The modification of AC mainly changes the surface chemistry of the carbons and sometimes alters their specific surface area and porosity [15,16]. Moreover, both strongly and weakly polar oxygen functional groups can be introduced by acid modification. These polar surface oxygen groups remarkably influence the catalytic activity and selectivity by tuning the preferential reactant adsorption and product desorption [17].

Here, we employed an AC as a metal-free catalyst for the reduction of nitrobenzene. The product, aniline, is an important intermediate in the fine chemicals industry. It is mainly produced by the selective hydrogenation of nitrobenzene over metals, especially noble metal catalysts such as Ni, Pt, Ru, and Pd [18] under hydrogen at a relatively high temperature. In addition, there exists little literature on the application of AC in the reduction of nitro compounds [19,20]. The present study investigates the characterization and application of modified activated carbons as catalysts in the hydrogenation of nitrobenzene using hydrazine hydrate as hydrogen donor. The relationship between the catalytic performance and the oxygen functional groups on activated carbon surfaces is discussed in detail.

## 1 Experimental

### 1.1 Chemicals

All chemicals used for the experiments were of AR grade, including activated carbon, nitric acid (HNO<sub>3</sub>, 65%), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 98%), hydrochloric acid (HCl, 37%), hydrazine hydrate (N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, 80%), and ethanol. These reagents were purchased from Tianjin Kermel Chemical Reagents Company. Nitrobenzene (AR grade) was supplied by China Medicine Group Shanghai Chemical Reagent Company.

### 1.2 Catalyst preparation

Activated carbon was firstly boiled in deionized water for 2 h and then washed by deionized water, and labeled D-AC. The D-AC was separately modified by three different acids, hydrochloric acid, sulfuric acid, and nitric acid, and denoted

as H-AC, S-AC, and N-AC. This modification was carried out by stirring 50 g D-AC in different acid solutions at 50 °C for 24 h. After filtration, the modified ACs were carefully washed by deionized water and then dried at 105 °C overnight.

In addition, the H-AC was treated in nitrogen atmosphere heating at a rate of 10 °C/min to 400, 600, and 800 °C, respectively, then keeping at those temperatures for 10 h and denoted as H-AC-400N<sub>2</sub>, H-AC-600N<sub>2</sub>, H-AC-800N<sub>2</sub>. The H-AC was also treated in hydrogen atmosphere heating at a rate of 10 °C/min to 600 °C and keeping for 4 h, and denoted as H-AC-600H<sub>2</sub>.

### 1.3 Catalyst characterization

XRD patterns were obtained on an X-ray diffraction instrument (D8 Advance, Bruker) equipped with a graphite monochromator and with a Cu K<sub>α</sub> radiation source. It was operated under the following conditions: tube voltage 40 kV, current 40 mA, and scanning range  $2\theta = 10^\circ - 70^\circ$ . The specific surface area was measured by the nitrogen adsorption-desorption method at liquid nitrogen temperature. The measurements were carried out using a Micromeritics instrument (ATUOSORB-JMP, Quantachrome) apparatus after sample degassing at 200 °C for 12 h. The specific surface area was calculated using the BET model. Fourier transform infrared spectra (FT-IR) were recorded between 400 and 4000 cm<sup>-1</sup> with a Bruker AXS TENSOR 27 spectrometer. The samples were diluted in KBr to a 0.1% [carbon + KBr] content. Corrections were made with respect to the mass of carbonaceous material in the pellets. The spectrum of the diluent itself was obtained and subtracted from those of the mixture. Boehm titration was used for quantifying various surface functional groups on AC. This method depends on the reaction of basic solutions having different pK<sub>b</sub> values with functional groups having different pK<sub>a</sub> values [15]. General Boehm titration procedure: an AC sample mass of 0.5 g was suspended in 25 ml 0.1 mol/L standard basic solution and shaken in a closed container for 24 h. The slurry was filtered to remove AC. An aliquot of 10 ml was back-titrated with 0.1 mol/L HCl. The amounts of various oxygen functional groups were determined according to the Boehm method [21].

### 1.4 Catalytic testing

Catalytic tests were carried out in a 50 ml glass reactor with a condenser. The reactor was heated by a water recirculating bath. A standard run is described as follows: catalyst (0.3 g) was dissolved in ethanol (5 ml), then, nitrobenzene (0.5 ml, 4.89 mmol) and hydrazine hydrate (0.75 ml, hydrazine hydrate:nitrobenzene molar ratio = 2.5:1) was

added. The mixture solution was stirred at 80 °C. At the end of the reaction, the catalyst was removed and the reaction products were analyzed using a gas chromatograph (Agilent-6890N) equipped with a capillary column (HP-5; 0.25  $\mu\text{m} \times 0.32 \text{ mm} \times 30 \text{ m}$ ) and a flame ionization detector.

## 2 Results and discussion

### 2.1 Catalyst characterization

The XRD patterns of the D-AC, H-AC, S-AC, and N-AC samples are shown in Fig. 1. The sharp, narrow peak at 26.1° in the patterns of all the samples indicates the presence of a highly graphitized fraction in the AC samples [14]. The broader peak at  $2\theta$  values from 20° to 30° of all the samples denotes strong small angle scattering and is indicative of an amorphous material with high porosity. Furthermore, the weaker broad peak at 43.3° indicates that the (100) and (101) peaks have merged to yield a single (10) reflection which demonstrates a relatively high degree of randomness in these samples. Our data suggest that the samples treated by different acids show the same XRD structure and are completely consistent with AC.

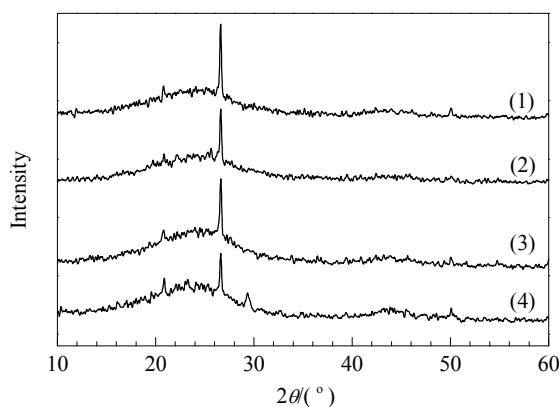


Fig. 1. XRD patterns of ACs. (1) H-AC; (2) S-AC; (3) N-AC; (4) D-AC.

Table 1 gives the specific surface area and the results of Boehm titration. The different acid treatment of ACs led to a slight decrease in specific surface area, and this decrease in the BET surface area may be due to blocking of the narrow pores by the surface complexes introduced by the acid treatment [22]. Therefore, acid treatment influences the chemical structure of the AC surface as further discussed (introduction of oxygen functional groups). The Boehm method uses bases of different strengths to differentiate surface functionalities of various acidic strengths. It is assumed that a base of certain strength is able to neutralize those functional surface groups which are more acidic (i.e. less basic). It is generally accepted that  $\text{NaHCO}_3$  ( $\text{p}K_{\text{NaHCO}_3}$

Table 1 Surface properties of various activated carbons

Sample	BET surface area ( $\text{m}^2/\text{g}$ )	Carboxyl (mmol/g)	Lactone (mmol/g)	Phenol (mmol/g)	Total acidity (mmol/g)
D-AC	433.9	0.018	0.018	0.018	0.054
H-AC	386.7	0.207	0.027	0.180	0.414
N-AC	405.2	0.126	0.090	0.063	0.279
S-AC	370.8	0.163	0.061	0.102	0.326

= 6.37) neutralizes only carboxyl groups on the carbon surface,  $\text{Na}_2\text{CO}_3$  ( $\text{p}K_{\text{Na}_2\text{CO}_3} = 10.25$ ) titrates carboxyls and lactones,  $\text{NaOH}$  ( $\text{p}K_{\text{NaOH}} = 15.74$ ) neutralizes carboxyl, lactone, and phenolic groups [23]. As expected, treating by acids results in a significant increase of AC acidity, which is demonstrated by a fivefold to eightfold increase of the amount of acidic groups (Table 1). The amounts of acidic functional groups on AC increase in the order of D-AC < N-AC < S-AC < H-AC. Furthermore, the amount of carboxylic groups increased to a greater extent than phenolic groups on the activated carbon. Likewise, the increase of the amounts of carboxylic groups, phenolic and lactone groups of ACs is consistent with the amount of total acidity.

FT-IR analysis can be used to determine the presence of surface functional groups on AC. The effects of  $\text{HCl}$ ,  $\text{HNO}_3$ , and  $\text{H}_2\text{SO}_4$  treatment on the surface functional groups on AC were examined, and representative FT-IR bands are shown in Fig. 2. For the D-AC sample the bands of stretching O–H vibrations are revealed in the range of 3150–3650  $\text{cm}^{-1}$  [14]. These may be attributed to surface hydroxyl groups and chemisorbed water [15]. The weak peaks at 2922 and 2854  $\text{cm}^{-1}$  can be assigned to various C–H stretching vibrations [14]. The strong adsorption bands at 1630 and 1387  $\text{cm}^{-1}$  are assigned to carboxylic groups [14,24,25]. The broad peak between 1000 and 1200  $\text{cm}^{-1}$  can be attributed to the phenolic groups [24]. The increase of the relative intensity of the bands in the range of 3150–3650  $\text{cm}^{-1}$  indicates an increased content of hydroxyl

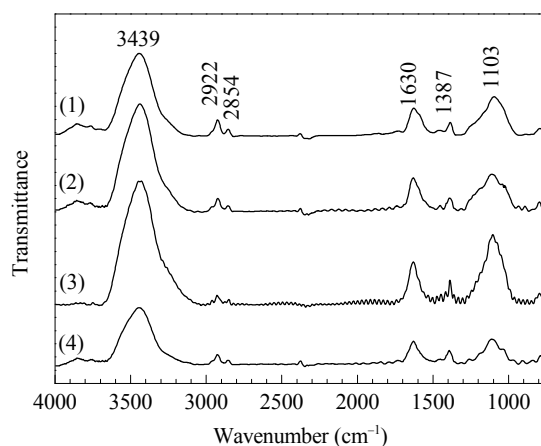


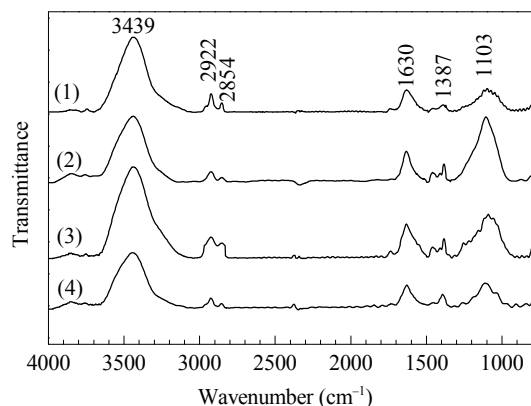
Fig. 2. FT-IR spectra of ACs. (1) S-AC; (2) N-AC; (3) H-AC; (4) D-AC.

groups in N-AC, H-AC, and S-AC, also suggesting that the AC treated by acids generates a large number of carboxylic groups. In addition, a slight increase in the intensity of the band at  $1387\text{ cm}^{-1}$  was observed, which can be assigned to carboxylic O–H stretching vibration. However, the peaks at  $1630$  and  $1103\text{ cm}^{-1}$  in the three spectra were different.

The bands at  $1630$  and  $1103\text{ cm}^{-1}$  corresponding to carboxylic C=O stretching and phenolic C–O and O–H stretching modes increased slightly in the N-AC and S-AC samples and significantly in the H-AC sample, implying that HCl treatment increased the amount of the oxygen functional groups most. It is worth emphasizing that the H-AC sample treated by HCl (an acid without oxidation ability) increased the relative intensity of the band at  $1000\text{--}1200\text{ cm}^{-1}$ . This corresponds to a relative increase of single-bonded oxygen functional groups such as phenols, ethers, and lactones [15,26]. Leony Leon et al. [26] suggested that two types of interaction may occur when  $\text{H}^+$  and  $\text{Cl}^-$  adsorb on carbon, i.e. one process is described in terms of pyrone-type structures and the other one is of the electron donor-acceptor interaction type.

These results implied that treatment by acid increased the concentration of oxygen functional groups such as carboxylic and phenol groups on the activated carbon surface. Moreover, the HCl treatment increased the amount of the oxygen functional groups most. This is consistent with the results of Boehm titration. However, this information alone is not sufficient to investigate the change of functional groups on the surface of ACs. Because of this, two additional tests for the change of surface functionalities were carried out.

The H-AC sample was thermally treated at  $400$ ,  $600$ , and  $800\text{ }^\circ\text{C}$  in nitrogen respectively, to investigate the change of its surface functionalities. The FT-IR spectra of the H-AC samples treated at different temperatures are given in Fig. 3. When the H-AC was treated in  $\text{N}_2$  at  $600\text{ }^\circ\text{C}$ , the peaks at  $1630$  and  $1387\text{ cm}^{-1}$  corresponding to carboxylic C=O and O–H stretching, respectively [14,24,25], increased significantly, they whereas decreased greatly at  $800\text{ }^\circ\text{C}$ . In addition, the broad band between  $1000$  and  $1200\text{ cm}^{-1}$  corresponding to phenolic C=O and O–H stretching vibrations [24] showed the same trend. From these results, it can be suggested that the increase of these functional groups results from the conversion of functional groups in a low oxidation state to such in a high oxidation state by means of  $\text{N}_2$  treatment [24]. Meanwhile, the great decrease of these functional groups at  $800\text{ }^\circ\text{C}$  is attributed to the partial release of these groups or conversion into other functionalities [24]. In contrast the bands at  $2922$  and  $2854\text{ cm}^{-1}$  corresponding to C–H stretching vibrations [14] showed an opposite trend. This may be due to conversion to other oxygen functional groups. In addition, a slight decrease of the bands in the



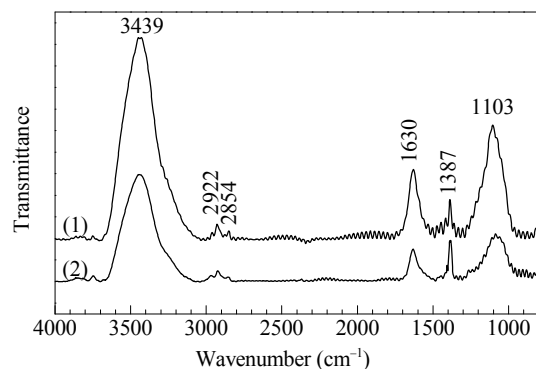
**Fig. 3.** FT-IR spectra of ACs. (1) H-AC-800N<sub>2</sub>; (2) H-AC-600N<sub>2</sub>; (3) H-AC-400N<sub>2</sub>; (4) D-AC.

range of  $3150\text{--}3650\text{ cm}^{-1}$  may be due to release of chemisorbed water. These results indicate that oxygen functional groups such as carboxylic and phenolic groups increased when the sample was treated at  $600\text{ }^\circ\text{C}$  in nitrogen.

FT-IR spectra of the H-AC before and after treating in  $\text{H}_2$  at  $600\text{ }^\circ\text{C}$  are compared in Fig. 4. A remarkable decrease of the band at  $1630\text{ cm}^{-1}$  and a slight decrease of the band at  $1387\text{ cm}^{-1}$  corresponding to carboxylic C=O and O–H stretching vibrations, respectively, implied that the carboxylic groups significantly decreased after treating in  $\text{H}_2$ . Similarly, a significant decrease of the broad band between  $1000$  and  $1200\text{ cm}^{-1}$  indicates that the phenolic groups decreased greatly after treating in  $\text{H}_2$ . In addition, a decrease of the relative intensity of the band in the range of  $3150\text{--}3650\text{ cm}^{-1}$  indicated a decreased content of hydroxyl groups, which may be due to the decrease of carboxylic groups or release of chemisorbed water. These results imply that the oxygen functional groups such as carboxylic and phenol groups decreased significantly after  $\text{H}_2$  treatment at  $600\text{ }^\circ\text{C}$ .

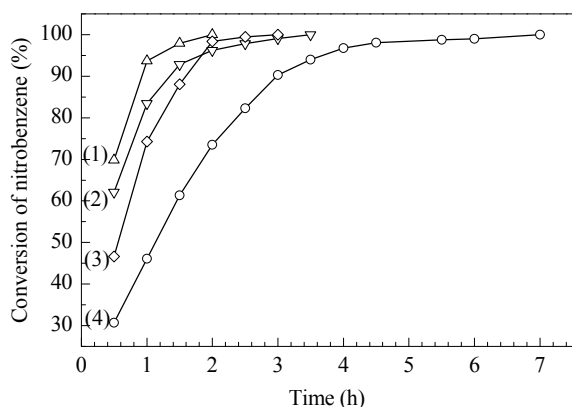
## 2.2 Catalytic activity

We study the catalysis of nitrobenzene hydrogenation by



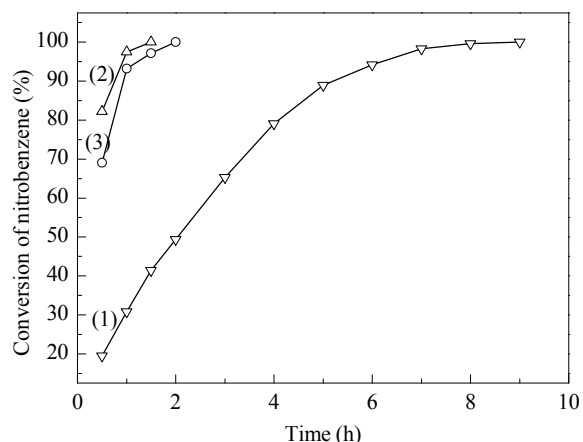
**Fig. 4.** FT-IR spectra of ACs. (1) H-AC; (2) H-AC-600H<sub>2</sub>.

modified ACs using hydrazine hydrate as reductant. The time to reach 100% nitrobenzene conversion is considered to be the best measure of the catalytic activity for this reaction [27]. The effect of acid treatment on nitrobenzene hydrogenation is shown in Fig. 5. A blank test without catalyst is first performed. In the absence of AC, nitrobenzene is not reduced by hydrazine hydrate, indicating that the catalyst is essential for this reaction. As shown in Fig. 5, all ACs under investigation showed similar behavior for nitrobenzene hydrogenation. After 1 h of reaction the nitrobenzene conversions over the D-AC, H-AC, S-AC, and N-AC were 46.09%, 93.67%, 83.47%, and 74.26%, respectively. The time to reach 100% nitrobenzene conversion is 2 h for the H-AC, 3 h for the N-AC, 3.5 h for S-AC, and 7 h for the D-AC, respectively. The H-AC, N-AC, and S-AC samples showed higher activity than the D-AC, and the H-AC shows the highest activity among these samples. From Fig. 2 the amount of oxygen functional groups on the surface of the ACs had increased after acid treatment implying the amount of the oxygen functional groups on the surface of AC may be conducive to the catalytic activity.



**Fig. 5.** Effect of different acids treatment on catalytic activity. (1) H-AC; (2) S-AC; (3) N-AC; (4) D-AC. Reaction conditions: nitrobenzene 4.89 mmol, ethanol 5 ml, 0.3 g catalyst,  $n(\text{hydrazine hydrate}):n(\text{nitrobenzene}) = 2.5$ , 80 °C.

Because the H-AC showed the highest activity among all the catalysts, the H-AC was thermally treated in nitrogen at 400, 600, and 800 °C, respectively, to investigate the effect of the oxygen functional groups on catalytic activity. The results are indicated in Fig. 6. After 1.5 h of reaction, the conversion of nitrobenzene reached 100% for the H-AC-600N<sub>2</sub>, 97.12% for the H-AC-400N<sub>2</sub>, and 41.44% for the H-AC-800N<sub>2</sub>, respectively. The H-AC-600N<sub>2</sub> showed the best catalytic activity expressed as a decrease in the time to reach 100%. From the FT-IR results shown in Fig. 3, the amount of oxygen functional groups on the surface of the H-AC increased slightly as the treatment temperature increased from 400 to 600 °C in N<sub>2</sub> atmosphere, but greatly decreased with further increase of the treatment temperature

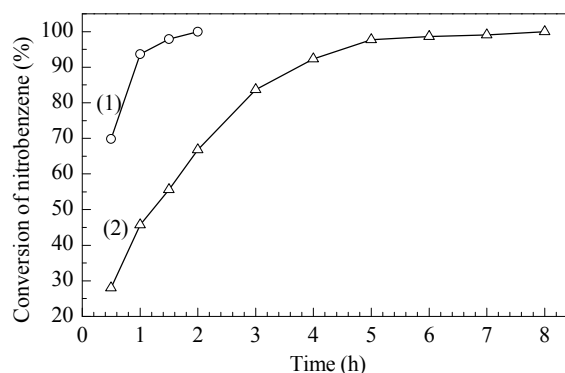


**Fig. 6.** Effect of nitrogen treatment on the catalytic activity. (1) H-AC-800N<sub>2</sub>; (2) H-AC-600N<sub>2</sub>; (3) H-AC-400N<sub>2</sub>. Reaction conditions are the same as in Fig. 5.

up to 800 °C. The AC treated at excessively higher temperatures (800 °C) result in relatively low catalytic activities, and it is likely to be due to the decrease in the amount of the oxygen functional groups on the H-AC surface.

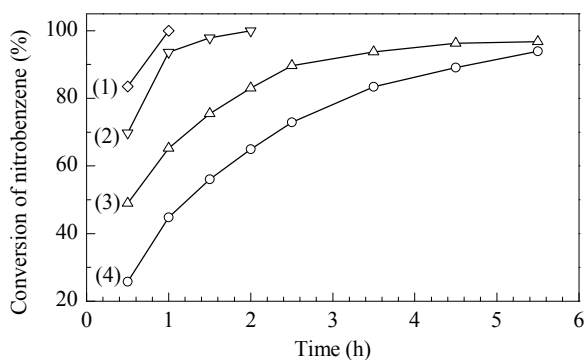
The H-AC sample was also thermally treated in H<sub>2</sub> at 600 °C to further investigate the effect of the oxygen functional groups on catalytic activity. The result is shown in Fig. 7. Over the H-AC sample the reaction completed within only 2 h. However, the conversion of nitrobenzene reached 100% in 8 h over the H-AC-600H<sub>2</sub> sample. This result indicates that the reaction rate decelerated significantly after hydrogen treatment at 600 °C. As it is shown in Fig. 4, the bands at 1630, 1387, and 1103 cm<sup>-1</sup> corresponding to carboxylic C=O and O-H and phenolic C-O and O-H stretching vibrations also decreased after hydrogen treatment. This result indicates that the decrease of the amount of oxygen functional groups is unfavourable to the hydrogenation of nitrobenzene. Therefore, the amount of oxygen functional groups on the surface of activated carbon is a key factor for this reduction.

The performance dependence of the H-AC sample on re-



**Fig. 7.** Effect of hydrogen treatment on the catalytic activity. (1) H-AC; (2) H-AC-600H<sub>2</sub>. Reaction conditions are the same as in Fig. 5.

action temperature has been studied over the range between 60 and 90 °C. The influence of the reaction temperature on the conversion of nitrobenzene is shown in Fig. 8. At 60 °C, the conversion of nitrobenzene was 56.05% after 2 h of reaction. With increasing the temperature to 70 °C, nitrobenzene conversion increased to 75.48% at 2 h. When the temperature reached to 80 °C, the reaction completed within 2 h. The results show that the reaction rate was accelerated with increasing temperature. In addition, the reaction completed within an hour at 90 °C, and the reaction rate was too fast to study the reaction mechanism. Therefore, the reaction temperature of 80 °C is more appropriate.

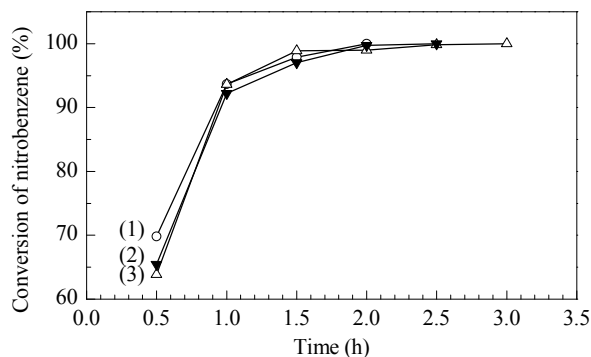


**Fig. 8.** Effect of different reaction temperature on catalytic activity. (1) 90 °C; (2) 80 °C; (3) 70 °C; (4) 60 °C. Reaction conditions are the same as in Fig. 5 except reaction temperature.

The reuse of the H-AC was investigated to determine if the relatively simple catalysts can be reused. The result is shown in Fig. 9. With the H-AC as catalyst, the reaction completed within 2 h in the first experiment. After the reaction had completed, two methods of recycling the H-AC were applied. First, the H-AC was separated from the products, washed by ethanol several times, dried under air at 105 °C for 12 h. Then the H-AC was used for next reaction. The reaction completed within 3 h, implying the reaction rate decreased in the second experiment. Second, for the external regeneration after the use in the batch reactor, the H-AC was separated from the products, washed by ethanol several times, dried under air at 105 °C for 12 h, and treated in N<sub>2</sub> at 600 °C for 4 h. After the re-treatment the reaction completed within 2.5 h. This indicates that the catalytic activity of the H-AC can be improved if it is subjected to a thermal reactivation.

### 2.3 Adsorption of nitrobenzene by activated carbons

To find out how the adsorption of nitrobenzene was affected on the AC samples, the isothermal adsorption of nitrobenzene was carried out by suspending with 0.3 g of the AC samples in a mixture of 0.5 ml nitrobenzene and 5 ml ethanol (solvent) in a closed vessel at 80 °C for 4 h (without



**Fig. 9.** Reuse of the catalyst. (1) Fresh H-AC; (2) Recycled H-AC; (3) Re-treated H-AC. Reaction conditions are the same as in Fig. 5.

hydrazine hydrate). The final bulk liquid phase was analyzed and its composition was compared with that of the starting mixture. Table 2 shows the relative variation in the bulk liquid phase after equilibration. Acid-treated activated carbons showed greater capacity for nitrobenzene adsorption. The amount of nitrobenzene adsorbed on AC samples descends in the orders of H-AC > S-AC > N-AC > D-AC. According to the results from Fig. 2 the H-AC sample had more surface oxygen functional groups than any other sample, indicating that the surface oxygen functional groups were the important factor in the increase of nitrobenzene adsorption, which can accelerate the reaction rate. Therefore, the increase in the amount of the surface oxygen functional groups is consistent with the increase of the reaction rate.

### 2.4 Decomposition of hydrazine hydrate

When equilibrating the mixture of hydrazine hydrate and ethanol (solvent) in the presence of the modified ACs, the decomposition of hydrazine hydrate was observed. Therefore, the decomposition of hydrazine hydrate was investigated by a solution of hydrazine hydrate in ethanol in the presence of H-AC, S-AC, N-AC, D-AC samples, respectively (without nitrobenzene). The experiments were carried out at 80 °C for several hours and hydrazine decomposition gives NH<sub>3</sub> and N<sub>2</sub>. The gases released during the reaction was measured with a gas burette, and then passed through a trap containing 1.0 mol/L hydrochloric acid to ensure the absorption of ammonia. It can be seen that the N-AC sample showed the highest decomposition rate of hydrazine hydrate

**Table 2** Adsorption of nitrobenzene on catalysts

Sample	Change of nitrobenzene concentration in the bulk liquid phase after equilibration
H-AC	1.176%
N-AC	0.192%
S-AC	1.050%
D-AC	0.065%

and the decomposition was completed within 2 h (Fig. 10). The decomposition rates of hydrazine hydrate were in following orders of N-AC > S-AC > H-AC  $\approx$  D-AC. A high decomposition rate of hydrazine hydrate resulted in the greater decrease of the hydrazine hydrate concentration, which decreased the reaction rate of the reduction of nitrobenzene. Hence, the rate of the reduction of nitrobenzene over modified ACs is in contrast with the decomposition rate of hydrazine hydrate.

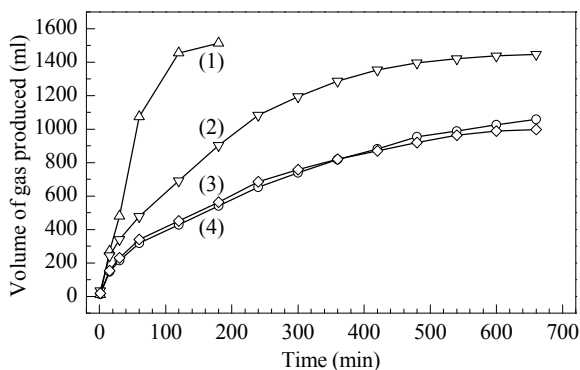


Fig. 10. Effect of different acids treatment on decomposition of hydrazine hydrate. (1) N-AC; (2) S-AC; (3) H-AC; (4) D-AC.

### 3 Conclusions

Activated carbons treated by simple inorganic acids were directly used as catalysts in the reduction of nitrobenzene in the presence of hydrazine hydrate. Our experiment results show that catalytic activities can be attributed to the oxygen functional groups on activated carbon. The activated carbons treated by different acids have different amounts of oxygen functional groups which influence adsorption of reactants and decomposition of hydrazine. Activated carbon treated by hydrochloric acid, which has the most oxygen functional groups, has shown to be the most active catalyst in this reaction. Therefore, the amount of oxygen functional groups on activated carbon plays an important role in this reaction. These oxygen functional groups of activated carbon mainly include carboxylic groups, phenolic and lactone groups. We will investigate which kind of oxygen functional group is more effective for this reaction in the future.

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