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ARTICLE

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_3, HCl, and H_2SO_4 or in gaseous N_2 and H_2, 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

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_2 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

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detail.

1 Experimental

1.1 Chemicals

All chemicals used for the experiments were of AR grade, including activated carbon, nitric acid (HNO_3, 65%), sulfuric acid (H_2SO_4, 98%), hydrochloric acid (HCl, 37%), hydrazine hydrate ($N_2H_4 \cdot H_2O$, 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 ºC for 24 h. After filtration, the modified ACs were carefully washed by deionized water and then dried at 105 ºC overnight.

In addition, the H-AC was treated in nitrogen atmosphere heating at a rate of 10 ºC/min to 400, 600, and 800 ºC, respectively, then keeping at those temperatures for 10 h and denoted as H-AC-400N_2, H-AC-600N_2, H-AC-800N_2. The H-AC was also treated in hydrogen atmosphere heating at a rate of 10 ºC/min to 600 ºC and keeping for 4 h, and denoted as H-AC-600H_2.

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_α radiation source. It was operated under the following conditions: tube voltage 40 kV, current 40 mA, and scanning range $2\theta = 10^\circ$–70°. 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 ºC 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^{-1} 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_b values with functional groups having different pK_a 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 ºC. 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 μm × 0.32 mm × 30 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 2θ 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

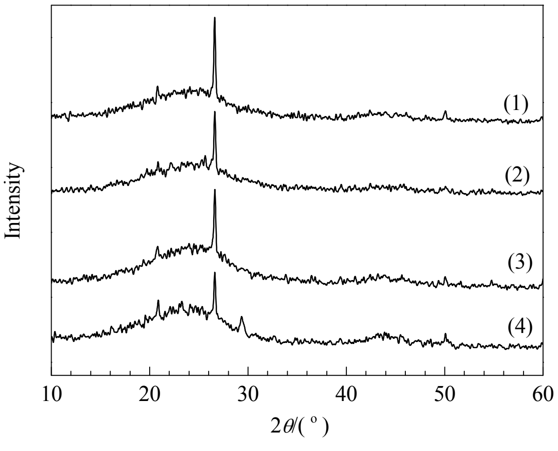

Fig. 1. XRD patterns of ACs. (1) H-AC; (2) S-AC; (3) N-AC; (4)