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Editor's Choice paper

Nitrogen and oxygen-doped metal-free carbon catalysts for chemoselective transfer hydrogenation of nitrobenzene, styrene, and 3-nitrostyrene with hydrazine

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ABSTRACT

An activated carbon (AC) was treated by hydrogen peroxide and ammonia to dope oxygen and nitrogen on its surface. The surface-functionalized AC catalysts were used for the transfer reduction of nitrobenzene, styrene, and 3-nitrostyrene by hydrazine hydrate. The reduction of nitrobenzene and 3-nitrostyrene was promoted over the oxygen- and nitrogen-doped catalysts compared to the parent AC catalyst. Those were less active for the reduction of styrene but active for the reduction of vinyl group of 3-nitrostyrene. However, the nitrogen dopant suppressed the reduction of vinyl group of 3-vinylaniline. The functionalized AC catalysts are likely to facilitate the adsorption and activation of nitro group of the nitro substrates through interactions with polarized surface induced by the oxygen and nitrogen hetero dopants. This should make it possible to reduce the vinyl group of 3-nitrostyrene on the surface. The nitrogen dopant hindered the reduction of the vinyl group of 3-vinylaniline because the adsorption through its amino group should become difficult on the surface of basic nature induced by the nitrogen doping. The AC serves as an electrical conductor and its performance should be enhanced by the surface functionalization and this would contribute to the formation of reducing species such as diimide and proton from hydrazine on the surface. The present results show that oxygen- and/or nitrogen-doped, functionalized carbon materials could be promising as metal-free multi-task catalysts.

1. Introduction

Carbon materials are known to act as an effective catalyst in several organic reactions [1]. Nitrogen-doped carbon and carbon nitride materials may act as interesting and promising metal-free catalysts in chemical and electrochemical reactions. Several review articles demonstrate the development of the catalysis of those carbon materials including nitrogen species [2–4]. For example, Bitter et al. prepared nitrogen-doped carbon materials in the form of nanotube by chemical vapor deposition of acetonitrile and pyridine on supported metal particles [5]. They showed that these nitrogen-doped carbon materials were active for Knoevenagel reactions. The present authors doped nitrogen to an activated carbon (AC) and a carbon black by treating in a stream of pure ammonia and a mixture of ammonia and air at temperatures of 400–800 °C and indicated that these catalyzed Knoevenagel condensation and transesterification reactions [6]. It is known that the former two reactions can be catalyzed by base catalysts and the latter by metal or metal oxide catalysts. Those bulk carbon materials are useful for practical preparation and application. Thomas et al. prepared well-designed carbon nitride materials and showed their catalytic actions in Friedel-Craft reactions and cyclization of functional nitrile and alkynes [3]. Their work is important for discussing the structure of active sites working on the surface of nitrogen-doped carbon materials, which may be different depending on the nature of chemical reactions of interest. Recently, Chizari et al. reported that nitrogen-doped carbon nanotubes served as metal-free catalysts for the selective transformation of harmful hydrogen sulfide into solid sulfur [7].

For considering and judging the potential of nitrogen-doped carbon materials as metal-free catalysts, it is desirable and interesting to further examine their catalytic actions in other reactions. In the present work, the surface of a parent AC material was modified by nitrogen doping and wet treatments with hydrogen peroxide and hydrazine and the catalytic performance of these carbon materials prepared was tested in liquid-phase reduction with hydrazine for monofunctional aromatic substrates of nitrobenzene and styrene and a bifunctional substrate of 3-nitrostyrene. The influence of the

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surface modifications on the reaction rate and the product selectivity was examined. The surface properties of the carbon materials prepared were examined by nitrogen adsorption and X-ray photoelectron spectroscopy, and the quantity of basic sites on their surfaces was also measured. The reaction results were discussed by considering possible interactions of nitro, vinyl, and amino groups with the surface modified with nitrogen and oxygen species and possible impact of the surface treatments on the electrical properties of the AC derived materials.

It is well-known that hydrazine can serve as an effective reducing agent for various organic synthetic reactions [8]. A few workers examined the reduction of aromatic nitro compounds to corresponding aniline over activated carbon or graphite in the presence of iron chloride [9,10]. Good yields of aniline products (>90%) were obtained for several nitro substrates. Larsen et al. discussed the reaction mechanisms of carbon-catalyzed transfer hydrogenation of nitrobenzene by hydrazine [11]. In the literature, we could find only a few works that consider the use of metal-free carbon materials for the reduction of aromatic mononitro- and dinitro-compounds by hydrazine. The reduction of aliphatic and aromatic nitro compounds by hydrazine was studied by Gowda et al. [12,13] using zinc and magnesium catalysts and by Kappe et al. [14] using iron oxide nanocrystals.

2. Experimental

2.1. Sample preparation

A commercially available AC (GL Science) was used as a parent carbon material and it was modified in different manners to change its surface properties. A weighted AC sample (500 mg) was placed in a quartz reactor and a stream of either pure NH_3 or NH_3 90% + air (10%) was passed at a rate of 100 cm^3 min^{-1} at room temperature for 30 min [6]. Then, the sample was heated at 10 K min^{-1} up to a temperature lower by 100 K than the desired value and then at 5 K min^{-1} to the desired temperature. The sample was treated at this temperature for 1 h and then cooled to 300 °C, at which the gas stream was changed to pure N_2 and the sample was further cooled to room temperature. The parent AC was also subjected to a wet treatment with either hydrazine or hydrogen peroxide. The AC sample (2.0 g) was placed in a Teflon-coated autoclave (100 cm^3) followed by introduction of hydrazine hydrate (2.0 cm^3, Wako) and distilled water (20 cm^3). The mixture was treated at 100 °C and at a stirring speed of 400 rpm for 5 h. The solid sample so treated was washed with water and ethanol (Wako) and dried under ambient conditions for 1 day. The hydrogen peroxide treatment was made by using 0.3 g of the same AC and 15 cm^3 of 30% hydrogen peroxide (Wako) in the same procedures as used in the hydrazine treatment.

2.2. Surface area and XPS measurement

The textural properties of those carbon samples so prepared were measured by nitrogen adsorption/desorption (Quantachrome NOVA 1000). Total surface area was determined by the Brunauer, Emmet and Teller's (BET) equation. Chemical nature of their surfaces was examined by X-ray photoelectron spectroscopy (XPS) on JEOL JPS-9200 with monochromatic Al-Kα radiation [6]. The charge-up shift correction of the binding energy was made by using C1s binding energy at 284.5 eV.

2.3. Measurement of basic sites

The amount of basic sites was determined by back titration at room temperature. An AC sample (100 mg) was added to 0.01 M hydrochloric acid solution (15 cm^3) (Wako) in a glass bottle with a cap and the mixture was stirred by a magnetic stirrer overnight. After separation of the solid AC sample by filtration, a certain volume of solution (10 cm^3) was sampled and titrated by 0.01 M sodium hydroxide solution (Wako). The amount of basic sites was calculated from the initial amount of hydrochloric acid used and the amount of sodium hydroxide added to reach the point of neutralization, which was determined by titration curve measured (pH value of solution vs. amount of sodium hydroxide added).

2.4. Activity measurement

The catalytic performance of several carbon materials prepared was tested in liquid-phase reduction of nitrobenzene, styrene, and 3-nitrostyrene by hydrazine. The Teflon-coated reactor was loaded with carbon catalyst, substrate, and hydrazine hydrate, purged by 0.2 MPa N_2, and heated to a reaction temperature of 100 °C on a heating place. The reaction mixture was stirred by a magnetic stirrer at 100 °C for a certain period of time. The multiphase reaction mixture was so mixed at a stirring rate of >400 rpm that the influence of agitation was negligible. Then, the reactor was cooled by ice water and the liquid phase was separated by filtration. The liquid mixture was analyzed by gas chromatography (GL Science 390B) using decane as an internal standard. The conversion was determined from the amounts of substrate before and after reaction and the selectivity from the amount of a product divided by the total amount of all products detected.

3. Results and discussion

3.1. Textural and chemical properties of modified carbon materials

The parent AC was treated with hydrogen peroxide, ammonia, and hydrazine hydrate. Table 1 shows the textural properties of several carbon materials prepared. The parent AC has a surface area of 1047 m^2 g^{-1} and its surface contains oxygen in 10% (entry 1). The content of oxygen was found to decrease to 6% by treatment with hydrazine (entry 2) while it increased to 15% by treatment with hydrogen peroxide (entry 3). The treatments of ammonia (90% in air) at 400 °C, 600 °C, and 800 °C supplied nitrogen in 3–4% to the surface of AC (entries 4–6). The content of oxygen was slightly decreased by the treatments at 400, 600, and 800 °C. The material treated with hydrogen peroxide and then ammonia had an oxygen content of 6.1% and a nitrogen content of 5.3% (entry 7). Compared to these changes in the chemical nature, the surface area did not change so much by those surface treatments. The treatments by hydrogen peroxide and/or ammonia caused the weight of AC to decrease by 10–40% (entries 3–7).

The basic character of AC catalysts may be important for the adsorption of reacting species on their surface, as will be discussed later. The amounts of basic sites were determined by back titration for a few selected samples at room temperature, in which a strong acid of hydrochloric acid ($pK_a = -7.0$) [15] was used. The results obtained are also given in Table 1, indicating that the amount of basic sites of the parent AC is 0.426 mmol g^{-1} (entry 1) and it decreases to 0.163 mmol g^{-1} on the treatment with hydrogen peroxide (entry 3). The treatment with ammonia was observed to produce larger amounts of basic sites (entries 4, 6 and 7). The amount of basic sites was 0.615 mmol g^{-1} for the sample treated at 400 °C and 0.758 mmol g^{-1} for the one treated at a higher temperature of 800 °C. The sample treated by hydrogen peroxide and ammonia also had a large amount of basic sites of 0.710 mmol g^{-1}.

3.2. Reduction of nitrobenzene and styrene

Those surface-modified carbon materials were applied for the liquid-phase reduction of either nitrobenzene or styrene by