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Regular Article

N-doped nanoporous carbon as efficient catalyst for nitrobenzene reduction in sulfide-containing aqueous solutions

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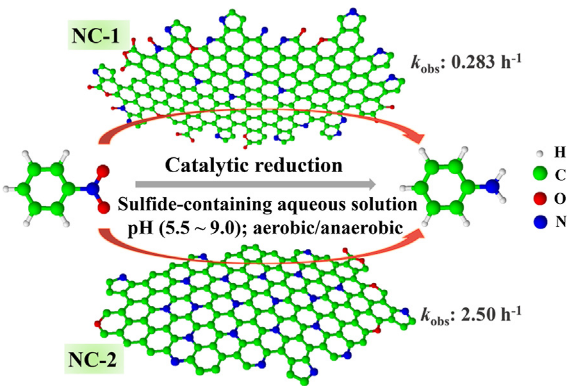
GRAPHICAL ABSTRACT



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ABSTRACT

Metal-free N-doped porous carbon (NC) materials have been demonstrated to be promising catalysts in contaminated environment remediation. Two NC materials (NC-1 and NC-2) were prepared by sol-gel routes. Their catalytic properties were investigated for the reduction of nitrobenzene (NB) in sulfide-containing aqueous solution. Both NC-1 and NC-2 can efficiently catalyze the reduction of NB to aniline (AN) under ambient conditions, but also can be reused for more than 5 times. The reaction fits excellently to the pseudo-first-order kinetic. Compared with NC-1 material, NC-2 shows much higher removal efficiency (rate constant k_{obs}: 0.283 h^{-1} vs. 2.50 h^{-1}). The important features of NC material, including high specific surface area, suitable surface functional groups (especially nitrogen-containing groups), and enhanced electron transfer ability, should be mainly factors for its excellent catalytic activity. This work demonstrates that N-doped carbon materials have great potential for degradation of NB to AN in the natural aquatic environment.

1. Introduction

The extended usage of nitroaromatic compounds like nitrobenzene (NB) in synthesis of medicine, dyes and agrochemicals has led to the continued release of such toxic organic compound into

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environment [1]. As a persistent pollutant, NB is quite stable under nature conditions, and easily accumulated in aquatic environment for years, thus bringing incredible effects on human beings and the aquatic ecological environment. Up to now, different methods have been developed for degrading NB in aquatic system, such as photodegradation [2–4], ultrasound degradation [5], biodegradation [6,7] and chemical reduction methods [8,9]. Among them, chemical reduction method is more efficient for converting NB, but need consume more energy or require great quantities of chemicals (as reducing agents), which may cause secondary pollution. Currently, it is still very significant to develop more economical and effective method to solve the pollution problems caused by the discharge of NB into aquatic environment.

Recently, catalytic reduction method has drawn more attention for it can effectively transform NB at very mild conditions to aniline (AN), a much less toxic compound, which is considerably easier degraded or mineralized [10,11]. So far, a number of supported noble metal catalysts have been reported to be efficient for the reduction of NB by selecting suitable reducing agents [12–15]. However, the high cost of noble metal limit it large-scale application. Alternatively, some cost-effective metal catalysts (Cu and Fe_3O_4) are also active for the reduction of NB [16,17]. However, these catalysts are not very stable due to the leaching of metal ingredient into the water body. Interestingly, a few recent literatures suggested that some carbon materials, including black carbon and graphic oxides, could be directly used as metal-free catalysts for the reduction of nitro aromatic compounds by sulfide in water [18,19]. The main reason for choosing sulfide as reductant is due to the fact that sulfur compounds are abundant in anaerobic aquatic environments [20]. These progresses are very significant since it reveals that carbon materials can function as active catalysts to reduce NB to AN.

As an important member of carbon materials, N-doped carbon materials have shown great advantages for some important catalytic reactions [21–24]. Particularly, it was reported that N-doped carbon materials could act as active catalysts for the reduction of nitro aromatic components with hydrogen, hydrazine, or $NaBH_4$ [25–29]. For example, N- and O-doped carbon showed good catalytic activity for the hydrogenation of nitrobenzene, styrene, and 3-nitrostyrene with hydrazine [25]. The N-doped graphitic mesoporous carbon exhibited excellent catalytic activity for the reduction of nitrobenzene with hydrazine hydrate in a sealed pressure tube [26]. N-doped graphene, N-doped nanotubes and mesoporous N-doped carbon exhibited catalytic activity in the reduction of 4-nitrophenol to 4-aminophenol with $NaBH_4$ [27–29]. Besides, N-doped diamond and porous carbon materials also showed outstanding electro-catalytic activities for the reduction of nitrobenzene [30,31].

Previously, our co-authors reported that a series of NC materials can be used as efficient catalysts or catalyst supports for some catalytic oxidation and transesterification reactions [32,33]. In this work, we tried to study the catalytic performance of NC materials for the reduction of NB by sodium sulfide in water. The NC-catalyzed reaction kinetics were investigated in detail, and the effects of a variety of parameters, such as thermal treat temperature of NC catalysts, the dosage of catalysts, and the pH values of reaction system on the catalytic performance were also studied. It was found that the thermally treated NC material shows excellent catalytic activity and recyclability for the reduction of NB with sodium sulfide under very mild conditions.

2. Materials and methods

2.1. Preparation of NC materials

The preparation method of NC materials was described in previous literatures [32]. First, citric acid, sucrose, $Al(NO_3)_3{\cdot}9H_2O$ and H_3PO_4 with mole ratio of 0.5/1.0/1.0/1.0 were mixed at room temperature in 500 mL three-necked bottle containing 200 mL redistilled water. Ammonia solution was dropped to adjust the pH value of the mixture to 5.0. After removing water by heating the system at 80 °C, the resultant solid composite was pretreated at 300 °C in muffle furnace and carbonized at 800 °C in tube furnace with argon flow. The carbonized sample of NC-1 was recovered after treating with 4 M HNO_3 solution, washed with deionized water, and dried at 110 °C. In addition, a part of NC-1 sample was treated at 800 °C in argon atmosphere to obtain a thermally treated sample, denoted as NC-2.

2.2. Characterization of NC materials

N_2 adsorption/desorption isotherms were measured by Micromeritics ASAP 2010 analyzer (Micromeritics Instrument Co., U.S.). Raman spectra were recorded with a LabRAM HR Evolution (Horiba). The X-ray diffraction (XRD) patterns were recorded on a Shimadzu XRD-6000 diffractometer (40 kV, 30 mA) using Ni-filtered Cu Ka radiation (Shimazu, Japan). The Fourier transformation infrared spectroscopy (FT-IR) spectra were recorded on a Thermo Nicolet 6700 spectrometer. The chemical state and composition of NC materials were studied by X-ray photoelectron spectroscopy (XPS) (Thermo, ESCA LAB250, U.S.).

Boehm titration method was used to determine the surface acidic/basic properties of NC materials present in aqueous solution. Typically, 0.1 g of NC sample was placed respectively in the following 0.05 mol/L solution (10 mL): sodium hydroxide, sodium carbonate, sodium bicarbonate, or hydrochloric acid. The vials were sealed and shaken for 24 h at 30 °C and filtrated, then known quantity of hydrochloric acid was added to each filtrate. The amounts of acidic/basic sites of various types (phenolic, lactonic and carboxylic groups, etc.) were calculated according to the method reported in literature [34].

2.3. Experimental setup

The batch experiments for anaerobic conditions were conducted in an anaerobic chamber under a 2% H_2 balance N_2 gas, while the experiments for aerobic conditions were exposed to the air. For the anaerobic batch experiments, an aqueous solution with 0.05 M Tris-HCl was pre-purged with nitrogen gas at least 30 min. Typically, a fresh solution of Na_2S (800 mM) and NB (8 mM) were pre-purged with nitrogen gas to remove the dissolved oxygen. NC materials were weighed and put into a 40 mL glass vial to make the concentration ranging from 0 to 500 mg/L (0, 30, 60, 125, 250, 500). The 0.05 M Tris-HCl solution was fixed the pH to 7.0 and then sub-packed into 40 mL glass vial together with the solutions of NB and Na_2S at a desired proportion to set the initial concentrations of NB (80 μM) and Na_2S (8 mM). The solution-filled vials were sealed with polytetrafluoroethylene (PTFE)-lined screw cap immediately and taken out the anaerobic chamber to a shaking table (HZQ-F160, HDL Apparatus, China)at 30 ± 1 °C to allow the NC materials well disperse. During the reaction, a subset of vials were taken out and sampled at appointed time. The volume of the sample should be no less than 0.5 mL. The obtained samples were filtered through 0.22 μm membrane (Analytical Instrument, China) before analysis.

All reaction data were collected in duplicate or in triplicate. The change in pH values was found to be less than 0.2 pH unit during the reaction process for all experiments. All kinetic experiments were carried out over a time period of at least one half-life of NB reduction. All samples were stored in small agilent bottle (1.5 mL) in a freezer at 4 °C.