



Nitrobenzene-assisted reduction of phenylacetylene with hydrazine over nitrogen-doped metal-free activated carbon catalyst: Significance of interactions among substrates and catalyst



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ABSTRACT

A nitrogen-doped activated carbon (AC) can catalyze the reduction of nitrobenzene with hydrazine but not phenylacetylene. When nitrobenzene coexists in the reaction mixture, however, phenylacetylene can also be reduced. Nitrobenzene is likely to assist the adsorption of phenylacetylene on the surface of AC catalyst through molecular interactions between the two substrates, allowing their simultaneous reduction to aniline and styrene. For these interactions to occur, nitrogen and/or oxygen species doped on the surface of AC are involved. The results demonstrate a new interesting catalytic function of nitrogen- and oxygen-doped metal-free carbon materials.

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1. Introduction

The doping of nitrogen to carbon materials attracts increasing attention as an interesting and effective method for modifying, improving, and creating their chemical functions. Different methods of nitrogen doping have been reported, as demonstrated in recent review articles [1–6], including chemical vapor deposition, polymerization using nitrogen-containing compounds such as acetonitrile, pyridine, cyanide, and melamine, and others. Those nitrogen-doped metal-free carbon materials (carbon nitride in some cases) are active catalysts for various reactions such as Knoevenagel condensation, transesterification, Friedel-Crafts reaction, cyclization, coupling of carbon dioxide and epoxide, and oxidation. In addition, theoretical consideration suggests that the doping of nitrogen species modify the electronic structure of neighboring carbon atoms and deliver new catalytic functions on the surface of carbon materials [7]. Thus, the nitrogen-doped carbon materials are expected to act as *metal-free* multi-functional catalysts useable for various chemical transformations that are usually catalyzed by various metal and metal oxide catalysts.

The present authors prepared nitrogen-doped carbon materials by a simple method in which an activated carbon (AC) was treated

by a mixture of ammonia and air at temperatures of 400–800 °C. Those nitrogen-doped AC materials were shown to catalyze different types of organic reactions including Knoevenagel condensation [8,9], transesterification [8], reduction [10], and oxidation [11,12]. One of interesting results obtained is chemoselectivity in the reduction of aromatic substrates by hydrazine [10]. It was indicated that nitrogen and oxygen species existing on the surface of AC did serve as active sites for this reduction. Nitrobenzene was reduced to aniline but not styrene; however, vinyl group, as well as nitro group, of 3-nitrostyrene was reduced. It is assumed that the adsorption of nitrobenzene and 3-nitrostyrene occurs on the surface of nitrogen-doped AC through interactions of their nitro group with the catalyst. In the following course of study on the catalysis of nitrogen-doped AC materials, other interesting features have been obtained in the reduction of phenylacetylene and other organic substrates by hydrazine. Phenylacetylene cannot be reduced, similar to styrene, but its reduction can occur by the coexistence of reducible nitrobenzene. These results will be reported in the present work.

2. Experimental

A selected nitrogen-doped AC sample was used as a catalyst, which was prepared by treating a commercial AC (from GL Science, having a BET surface area of 1047 m² g⁻¹ and an O content of 10%) with hydrogen peroxide at 130 °C and then with ammonia at 800 °C [10,12]. The AC sample so prepared was found to have a

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Table 1
Reduction of phenylacetylene (PA) to styrene (ST) by hydrazine over nitrogen-doped AC catalyst in the presence of organic additives.

Entry	Additive	Conversion of additive (%)	Conversion of PA (%)	Selectivity to ST (%)
1	–	–	6	91
2	Benzyl cyanide	0	4	88
3	Benzaldehyde	100	7	85
4	Nitrobenzene	89	28	64
5	Aniline	0	8	76

Reaction conditions: catalyst 10 mg, phenylacetylene 0.5 cm³, additive 0.5 cm³, hydrazine 4.0 cm³, N₂ 0.2 MPa, 100 °C, 2 h.

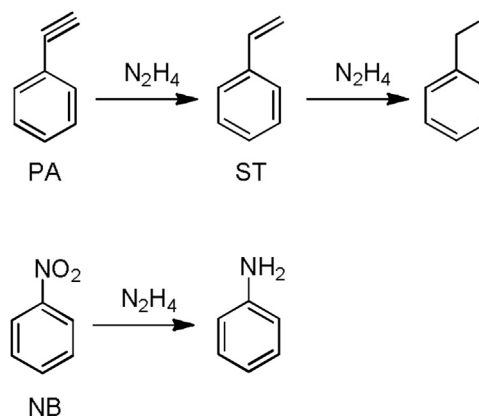
BET surface area of 1198 m² g⁻¹ and contain N and O species in 3.1% and 5.3%, respectively, from XPS measurements. The reduction of phenylacetylene was conducted with this catalyst in an autoclave at 100 °C in the same procedures as described elsewhere [10] and styrene and ethylbenzene were observed to form as products under the conditions used.

The possibility of molecular interactions between phenylacetylene and nitrobenzene was examined by FTIR spectroscopy in attenuated total reflection (ATR) mode [13]. The measurements were made for phenylacetylene, nitrobenzene, and their mixture in 1:1 in volume at room temperature. The FTIR–ATR spectra were also collected at a reaction temperature of 100 °C and the spectra obtained were the same as obtained at room temperature.

3. Results and discussion

Table 1 shows the influence of different organic additives on the reduction of phenylacetylene. Under the conditions used, nitrobenzene was observed to transform to aniline exclusively. The conversion obtained in the absence of any additive was 6% (entry 1) and comparable small conversion values were also obtained with benzyl cyanide, benzaldehyde, and aniline (entries 2, 3, 5). It is interesting, in contrast, that an enhanced conversion of 28% was achieved in the presence of nitrobenzene (entry 4). Although reducible nitrobenzene and benzaldehyde gave similar conversion values of 89% and 100%, respectively, the former promoted the reduction of phenylacetylene but not the latter. In addition, further reduction of the first-step product of styrene to ethylbenzene was promoted by nitrobenzene compared to benzaldehyde (entries 3, 4). For comparison, the parent unmodified AC sample was used instead of the nitrogen-doped one. When nitrobenzene and phenylacetylene were reacted alone, the conversion was observed to be 27% and 6%, respectively, under the same conditions as used for Table 1. Even when nitrobenzene was also present in the reaction mixture, the conversion of phenylacetylene was not enhanced. It is important to note that the promotional effect of coexisting nitrobenzene on the reduction of phenylacetylene appears in the presence of the nitrogen-doped AC sample.

Next, the reduction of phenylacetylene was conducted in the presence of different amounts of nitrobenzene. The total volume of reaction mixture and the concentration of phenylacetylene were fixed by using ethylene glycol as a diluent. The conversion of nitrobenzene was controlled to be <25% by using a short reaction time of 20 min in order to avoid the influence of a significant change in the nitrobenzene concentration in the liquid phase. Under the conditions used, styrene, ethylbenzene, and aniline were observed to form as products (Scheme 1). Nitrobenzene was hydrogenated to aniline in 100% selectivity. The results obtained are shown in Table 2 and Fig. 1. The non-catalytic reduction of phenylacetylene alone occurred to a small extent and the nitrogen-doped AC catalyst was inactive (entries 1, 6). When nitrobenzene was added, the conversion of phenylacetylene was enhanced and the enhancement was even more significant in the presence of catalyst than in



Scheme 1. Reduction of phenylacetylene (PA) and nitrobenzene (NB) by hydrazine. ST: styrene.

Table 2
Reduction of phenylacetylene (PA) by hydrazine over nitrogen-doped AC in the presence of different amounts of nitrobenzene (NB).

Entry	Amount of NB (cm ³)	Conversion of NB (%)	Conversion of PA (%)	Selectivity to ST (%)
(a) In the absence of catalyst				
1	0	–	4.2	84
2	0.5	3.5	8.1	83
3	1.0	2.1	7.6	80
4	1.5	1.3	7.0	82
5	2.0	1.4	7.1	80
(b) In the presence of catalyst				
6	0	–	4.5	87
7	0.5	22	15	73
8	1.0	14	15	75
9	1.5	12	13	78
10	2.0	11	14	76

Reaction conditions: catalyst 10 mg, phenylacetylene 0.25 cm³, additive + ethylene glycol 2.0 cm³, hydrazine 6.0 cm³, N₂ 0.2 MPa, 100 °C, 20 min.

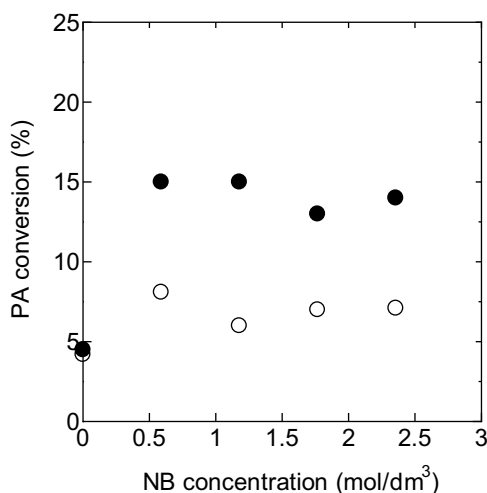


Fig. 1. Influence of nitrobenzene (NB) concentration on phenylacetylene (PA) conversion in PA reduction by hydrazine in the presence (●) and absence (○) of nitrogen-doped carbon catalyst. Reaction conditions: catalyst 10 mg, phenylacetylene 0.25 cm³, additive + ethylene glycol 2.0 cm³, hydrazine 6.0 cm³, N₂ 0.2 MPa, 100 °C, 20 min.

the absence of catalyst. That is, the nitrogen-doped AC catalyst is involved in the reduction of phenylacetylene assisted by nitrobenzene. The results show that the reduction of phenylacetylene is not further promoted by increasing the amount of nitrobenzene from 0.5 cm³, at which molar ratio of nitrobenzene against phenyl-

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