Journal of Molecular Catalysis A: Chemical 393 (2014) 257–262

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Editor's Choice paper

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

Shin-ichiro Fujita, Hiroyuki Watanabe, Ayaka Katagiri, Hiroshi Yoshida, Masahiko Arai*

Division of Chemical Process Engineering, Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan

ARTICLE INFO

Article history:
Received 27 March 2014
Received in revised form 16 June 2014
Accepted 17 June 2014
Available online 26 June 2014

Keywords:
Chemoselective hydrogenation
Hydrazine
Carbon catalyst
Nitrogen doping
Oxygen doping

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

---

* Corresponding author. Fax: +81 11 706 6594.
E-mail address: marai@eng.hokudai.ac.jp (M. Arai).

http://dx.doi.org/10.1016/j.molcata.2014.06.021
1381-1169/

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

Table 1
Textural properties of different carbon catalysts prepared.

Entry	Surface treatment	Surface area[a] ($m^2 g^{-1}$)	Burn-off (%)	Surface composition[b] O (%)	Surface composition[b] N (%)	Amount of basic sites[c] ($mmol\,g^{-1}$)
1	No treatment	1047		10	0	0.426
2	N_2H_4	–[d]		6.1	0	–[d]
3	H_2O_2	1188	37	15	0	0.163
4	NH_3 90%, 400 °C	1180	10	8.1	1.7	0.615
5	NH_3 90%, 600 °C	1116	17	7.4	2.6	–[d]
6	NH_3 90%, 800 °C	1260	27	8.2	4.1	0.758
7	$H_2O_2 \rightarrow NH_3$ 90%, 600 °C	–[d]	55	6.1	5.3	0.710

[a] Determined by nitrogen adsorption (BET surface area).
[b] Determined by XPS.
[c] Determined by back titration using hydrochloric acid and sodium hydroxide.
[d] Not measured.

Table 2
Results of reduction of nitrobenzene, styrene, and 3-nitrostyrene by hydrazine using different carbon catalysts.

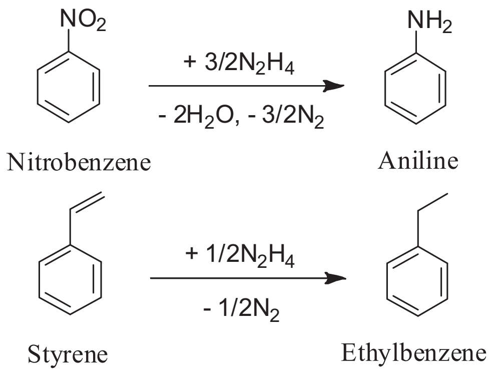
Entry	Surface treatment	Conversion (%) Nitrobenzene	Conversion (%) Styrene	Conversion (%) 3-Nitrostyrene	Selectivity in 3-nitrostyrene reduction[a] (%) **1**	**2**	**3**
1	No catalyst	26	11	55	58	16	26
2	No treatment	40	14	62	46	20	34
3	N_2H_4	36	–[b]	–[b]			
4	H_2O_2	80	13	97	13	29	58
5	NH_3 90%, 600 °C	42	–[b]	56	45	21	34
6	NH_3 90%, 800 °C	47	13	–[b]			
7	$H_2O_2 \rightarrow NH_3$ 90%, 600 °C	67	18	93	10	54	36

Reaction conditions: catalyst 10 mg, nitrobenzene 8.5 mmol (styrene 8.0 mmol, 3-nitrostyrene 3.8 mmol), hydrazine 4 cm^3, temperature 100 °C, and time 2 h.
[a] **1**: 3-ethylnitrobenzene; **2**: 3-vinylaniline; **3**: 3-ethylaniline.
[b] Not measured.

hydrazine (Scheme 1), in which aniline and ethylbenzene were respectively detected to form as products under the conditions used. Table 2 shows that the reduction of nitrobenzene occurred in the absence of catalysts and gave a conversion of 26% (entry 1). The parent AC was inherently active with a conversion of 40% (entry 2). The treatment with hydrazine indicated no activity improvement (entry 3) and that with ammonia increased the conversion slightly (entries 5 and 6). The conversion was significantly enhanced to 80% on the treatment with hydrogen peroxide (entry 4). This improvement was somewhat canceled by additional treatment with ammonia at 600 °C, the conversion being 67% (entry 7). In contrast, the reduction of styrene was only a little improved by the presence of catalysts and the surface treatments had hardly positive impact on the performance of AC (entries 2, 4 and 6). But a marginal activity improvement was observed with the treatment with hydrogen peroxide and ammonia, the conversion being increased to 18% (entry 7).

The results of Tables 1 and 2 imply that the reduction of nitrobenzene may be improved by the presence of surface oxygen and/or nitrogen. Fig. 1 gives a plot of nitrobenzene conversion (aniline yield) against the total amount of surface oxygen and nitrogen, which includes the reaction results over the AC-based materials shown in Table 2 and a few other samples surface-treated under different conditions. Fig. 1 suggests that both surface oxygen and nitrogen species contribute to the formation of working active sites. These active sites should adsorb and activate a polar nitro group of nitrobenzene but not a less polar vinyl group of styrene, which will be discussed later. As reported previously [6], there are a few different types of either nitrogen or oxygen on the surface-modified AC samples. However, these surface nitrogen and oxygen dopants should almost equally contribute to the production of active sites for the reduction of nitro compounds by hydrazine under the conditions used.

For comparison, the reduction of nitrobenzene was also examined by gaseous hydrogen (2 MPa) using an AC catalyst modified by



Scheme 1. Reduction of nitrobenzene and styrene by hydrazine.

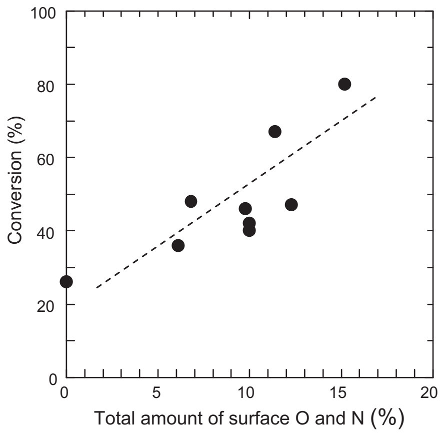
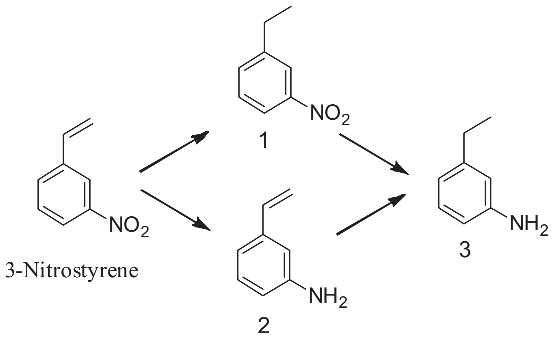


Fig. 1. Plot of the conversion of nitrobenzene reduction against the total amount of surface oxygen and nitrogen for several treated and untreated AC catalysts.



Scheme 2. Reduction of 3-nitrostyrene to 3-ethylnitrobenzene (**1**), 3-vinylaniline (**2**), and 3-ethylaniline (**3**).

ammonia at 800 °C while keeping the other conditions unchanged (Table 2). No reaction was found to occur, indicating that nitrobenzene was not reduced by gaseous hydrogen under the conditions used.

3.3. *Reduction of 3-nitrostyrene*

The results of the reduction of a bifunctional substrate of 3-nitrostyrene (Scheme 2) are also presented in Table 2. The parent AC catalyst gave a conversion of 62% (entry 2), slightly larger than a conversion of 55% in the absence of catalyst (entry 1). The treatment with hydrogen peroxide was effective to enhance its activity, increasing the conversion to 97% (entry 4). In addition, the treatment caused a significant change in the product selectivity (entries 1, 2 and 4). The untreated AC gave 3-ethylnitrobenzene **1** in the largest selectivity of 46% (entry 2) while the hydrogen peroxide-treated AC produced **1** in a selectivity 13% but 3-ethylaniline **3** in 58% (entry 4). These results imply that nitro group of 3-nitrostyrene becomes more reactive on the surface of AC modified by hydrogen peroxide, which has a larger content of oxygen (Table 1). The treatment with ammonia gave a catalyst that had a similar catalytic activity as observed with the parent AC (entries 2 and 5). A larger conversion of 93% was also obtained with the catalyst treated by hydrogen peroxide and then ammonia (entry 7). This catalyst gave a similar smaller selectivity to **1** (10%) but a larger selectivity to **2** (54%) as compared to the catalyst treated with hydrogen peroxide alone. Similar to nitrobenzene (Fig. 1), the total conversion tends to increase with the total amount of surface oxygen and nitrogen species (Fig. 2).

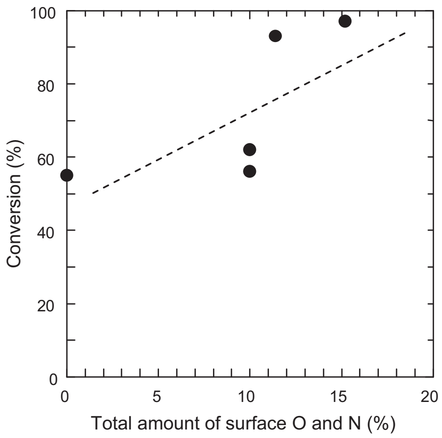


Fig. 2. Plot of the conversion of 3-nitrostyrene reduction against the total amount of surface oxygen and nitrogen for several treated and untreated AC catalysts.

Table 3
Influence of a small quantity of water on the results of 3-nitrostyrene reduction by hydrazine over two selected catalysts.

Entry	Surface treatment	Water[a]	Conversion (%)	Selectivity (%)[b]		
				1	**2**	**3**
1	H_2O_2	–	14	53	36	11
2	H_2O_2	○	19	41	48	11
3	$H_2O_2 \rightarrow NH_3$ 90%, 600 °C	–	14	69	24	7
4	$H_2O_2 \rightarrow NH_3$ 90%, 600 °C	○	18	46	45	9

Reaction conditions: catalyst 10 mg, 3-nitrostyrene 3.8 mmol, hydrazine 4 cm^3, water 0.02 cm^3, temperature 100 °C, and time 10 min.

[a] Water added (○); not added (–).

[b] **1**: 3-ethylnitrobenzene; **2**: 3-vinylaniline; **3**: 3-ethylaniline.

Fig. 3 shows the plot of product selectivity against 3-nitrostyrene conversion for the two selected catalysts of entries 4 and 7 of Table 2. For the AC catalyst modified by hydrogen peroxide, the selectivity to **1** decreased with conversion, that to **2** also decreased but more slightly, and that to the final product of **3** increased; **3** was formed more dominantly through the reduction of **1** rather than **2**. The selectivity at a conversion close to 100% was **3** > **2** > **1**. In contrast, for the catalyst treated by hydrogen peroxide and ammonia, the selectivity to **1** decreased more markedly with conversion while that to either **2** or **3** increased. At a high conversion of about 90%, the selectivity to **2** was larger than that to **3** and the selectivity to **1** was the smallest. These results indicate an interesting fact that the presence of surface nitrogen suppresses the reduction of **2** to **3**; namely, the reduction of the vinyl group of **2** becomes more difficult. At an early stage of reaction, **1** is formed in a large quantity and so the reduction of its vinyl group cannot be inhibited.

The reduction of a nitro group by hydrazine yields two water molecules. The influence of water on the conversion and selectivity was examined by making reaction runs in the presence of a small quantity of water at the start of reaction. The results obtained are given in Table 3, indicating that the presence of water did not affect the total conversion so much for the two AC catalysts (used in the runs of Fig. 3) but changed the product selectivity. The selectivity to **2** was increased by water while that to **1** was decreased; the selectivity to **3** was similar at similar conversion levels (entries 1 and 2, entries 3 and 4). The effects of water were not different between the two catalysts. These results suggest that the difference in the selectivity pattern observed with the two catalysts is caused by that in the contents of surface oxygen and nitrogen species (Table 1). The presence of water does not induce such a negative effect as catalyst deactivation. The effects of water observed are difficult to explain at present and further work is needed. We should consider the interactions of water molecules with the surface of catalyst and the reacting species of substrate and/or intermediate. It is known that water will act as a reaction promoter in organic synthetic reactions with homogeneous catalysts in which water could change the reactivity of reactive functional groups at the aqueous–organic interface [16]. For those using heterogeneous catalysts, water will also serve as a promoter in different manners [17]. Infrared spectroscopy may be useful to examine the interactions of water with organic substrates and intermediates [18,19].

Furthermore, the influence of reaction temperature was examined using a selected catalyst. Table 4 shows the results of reaction runs at 60, 80, and 100 °C, in which the reaction time was varied to compare the product selectivity at similar conversion levels. When the temperature was raised, the selectivity to **1** tended to increase while that to **2** decrease but not so markedly. Then, one may say that the reduction temperature does not affect the product selectivity so much under the conditions used. Table 4 shows again that the catalyst is selective for the production of **2** through the reduction of the nitro group in the reduction of 3-nitrostyrene after considering

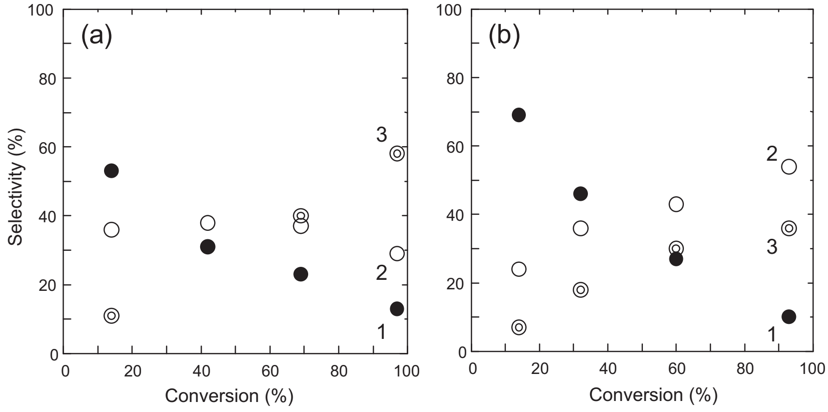


Fig. 3. Plot of the product selectivity against the total conversion of 3-nitrostyrene reduction by hydrazine over two selected AC catalysts treated by hydrogen peroxide and by hydrogen peroxide and ammonia. (a) Entry 4 and (b) Entry 7 of Table 2. **1**: 3-ethylnitrobenzene; **2**: 3-vinylaniline; **3**: 3-ethylaniline.

the contribution of non-catalytic reduction in which the product **1** is produced through the reduction of the vinyl group in a larger selectivity.

3.4. Implication of surface hetero dopants in the reduction

Carbon can serve as an adsorbent and an electrical conductor [8,11] and these functions should be taken into account to discuss the above-mentioned impact of the surface modifications of AC on its catalytic performance. The present AC-derived materials can be a catalyst for the reduction of nitrobenzene and 3-nitrostyrene by hydrazine but not for styrene; the doping of oxygen and nitrogen species promotes the reduction of nitro groups but the reduction of vinyl group of vinylaniline is suppressed by the presence of surface nitrogen species, resulting in an increase in its selectivity. It is difficult at present to discuss the structural features of the surface modified AC materials in detail. However, the authors consider a possibility that the doping of either a 5B element of nitrogen or a 6B element of oxygen to produces some polar sites on the surface of AC composed of a 4B element of carbon. These polar sites are likely to adsorb polar nitro group of nitrobenzene and 3-nitrostyrene and, hence, the surface-treated AC materials may act as a catalyst for the reduction of their nitro group. Less polar vinyl group is difficult to be adsorbed on those polar sites and so styrene cannot be reduced; for 3-nitrostyrene, however, it can be adsorbed on the AC catalysts through its nitro group and there is a chance for its vinyl group to be reduced to some extent. For vinylaniline, in contrast, the reduction of its vinyl group is not possible because the adsorption of the vinylaniline is difficult to occur due to repulsive interactions of its amino group with basic sites formed on the surface of AC by the doping of nitrogen. Beier et al. used supported platinum particles for reduction of 3-nitrostyrene by hydrogen and showed that the selectivity to vinylaniline was enhanced in the presence of basic ionic liquid, which suppressed its further hydrogenation to ethylaniline [20], similar to the present treated AC surface of basic nature.

A few previous works assume possible reaction pathways for the transfer hydrogenation with hydrazine as shown in Scheme 3 [8,12,14]. Ozaki et al. showed the effectiveness of nitrogen- and/or boron-doped carbon materials as a Pt-free electrode in proton exchange membrane fuel cells [21–25]. Namely, those surface-modified carbon materials may act as high-performance electrical conductors. A similar change in the electrical properties is assumed to occur for the present AC materials through the surface treatments. This may contribute to facilitate the formation of diimide N_2H_2, along with two electrons and two protons H^+, from hydrazine N_2H_4 on the carbon surface. The diimide and/or proton would then attack the nitro group of nitrobenzene and 3-nitrostyrene adsorbed on the surface and the vinyl group of the latter substrate, as discussed above. Ikeda et al. discussed possible structures of active sites for oxygen reduction reaction on the surface-modified carbon electrode via first-principles molecular dynamics simulation [25]. Such a model calculation will give an insight into the working active sites for the present transfer hydrogenation of organic substrates with hydrazine over the nitrogen- and oxygen-doped AC catalysts, for which detailed surface characterization is not easy.

Probably, those effects on the adsorption of the substrates and the reactivity of the reducing agent would be responsible for the catalytic performance of nitrogen- and oxygen-doped AC materials in the chemoselective hydrogenation of nitrobenzene, styrene, and 3-nitrostyrene. It is interesting that the doping of hetero atoms to the surface of carbon-based catalysts, which produces polar sites (C—N, C—O) on their surface, is an effective way in promoting

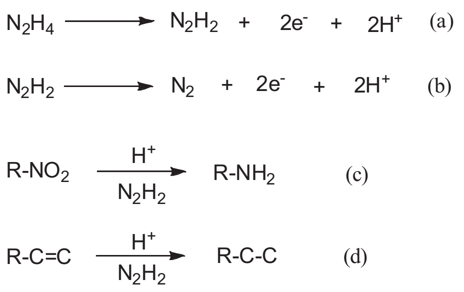
Table 4
Influence of reaction temperature on the reduction of 3-nitrostyrene by hydrazine over a selected catalyst (entry 4 of Table 2).

Entry	Temperature (°C)	Time (min)	Conversion (%)	Selectivity[a] (%)		
				1	2	3
1	60	225	63 (22)[b]	18 (69)[b]	45 (21)[b]	37 (10)[b]
2	80	90	67 (24)[b]	16 (72)[b]	43 (17)[b]	41 (11)[b]
3	100	60	69 (35)[b]	23 (50)[b]	37 (25)[b]	40 (25)[b]

Reaction conditions: catalyst 10 mg, 3-nitrostyrene 3.8 mmol.

[a] **1**: 3-ethylnitrobenzene; **2**: 3-vinylaniline; **3**: 3-ethylaniline.

[b] Figures in parentheses are conversion and selectivity values obtained in the absence of catalyst.



Scheme 3. Possible pathways for the reduction of nitro and vinyl groups by hydrazine [8,12,14].

organic synthetic reactions and controlling their product distribution patterns. A similar phenomenon appears with a quadrupole molecule of CO_2, which interacts with nitro and other functional groups of organic substrates, promoting the rate of liquid-phase reaction and the product selectivity in selective hydrogenation and other reactions [26–29].

4. Conclusions

The catalytic performance of AC was enhanced by the surface treatments with hydrogen peroxide and/or ammonia for the reduction of nitrobenzene and 3-nitrostyrene by hydrazine but not for styrene. The total amount of surface oxygen and nitrogen dopants is responsible for the enhancement of the reduction; namely, both dopants are involved in the catalysis. In addition, the nitrogen dopant can suppress the reduction of vinylaniline to the final product of ethylaniline, increasing the selectivity to vinylaniline. The oxygen and nitrogen dopants should change the surface properties of AC, which can serve as an adsorbent and an electrical conductor. These dopants are likely to contribute to the adsorption and activation of the nitro group. For 3-nitrostyrene, this may also facilitate the reduction of its vinyl group, in contrast to styrene that has no other functional group. The nitrogen dopant would form basic sites on which the vinylaniline is difficult to be adsorbed through its amino group; as a result, its further reduction should be suppressed. The doping of oxygen and nitrogen species would further influence the formation of reducing species such as diimide N_2H_2 and proton H^+ from hydrazine on the surface of AC. The present results demonstrate that the doping of surface oxygen and/or nitrogen is promising for the preparation of metal-free multi-task carbon catalysts, which can enhance the reaction rate and tune the product selectivity in organic synthetic reactions.

Acknowledgement

This work was supported by Japan Society for the Promotion of Science Grant-in-Aid for Challenging Exploratory Research 23656499.

References

[1] J.L. Figueiredo, M.F.R. Pereira, in: P. Serp, J.L. Figueiredo (Eds.), Carbon Materials for Catalysis, Wiley, NJ, USA, 2009, pp. 131–155.
[2] D. Yu, E. Nagelli, F. Du, L. Dai, J. Phys. Chem. Lett. 1 (2010) 2165–2173.
[3] A. Thomas, A. Fischer, F. Goettmann, M. Antonietti, J.-O. Müller, R. Schlögl, J.M. Carlsson, J. Mater. Chem. 18 (2008) 4893–4908.
[4] L.S. Panchakarla, A. Govindaraj, C.N.R. Rao, Inorg. Chim. Acta 363 (2010) 4163–4174.
[5] S. van Dommele, K.P. de Jong, J.H. Bitter, Chem. Commun. (2006) 4859–4861.
[6] N. Kannari, S. Okamura, S. Fujita, J. Ozaki, M. Arai, Adv. Synth. Catal. 352 (2010) 1476–1484.
[7] K. Chizari, A. Deneuve, O. Ersen, I. Florea, Y. Liu, D. Edouard, I. Janowska, D. Begin, C. Pham-Huu, ChemSusChem 5 (2012) 102–108.
[8] A. Furst, R.C. Berlo, S. Hooton, Chem. Rev. 65 (1965) 51–68.
[9] T. Hirashima, O. Manabe, Chem. Lett. 4 (1975) 259–260.
[10] B.H. Han, D.H. Shin, S.Y. Cho, Tetrahedron Lett. 26 (1985) 6233–6234.
[11] J.W. Larsen, M. Freund, K.Y. Kim, M. Sidovar, J.L. Stuart, Carbon 38 (2000) 655–661.
[12] S. Gowda, D.C. Gowda, Ind. J. Chem. B 42 (2003) 180–183.
[13] G.R. Srinivasa, K. Abiraj, D.C. Gowda, Ind. J. Chem. B 42 (2003) 2885–2887.
[14] D. Cantillo, M.M. Moghaddam, C.O. Kappe, J. Org. Chem. 78 (2013) 4530–4542.
[15] J. McMurry, Organic Chemistry, 5th ed., Brooks/Cole, London, 2000, pp. 53.
[16] R.N. Butler, A.G. Coyne, Chem. Rev. 110 (2010) 6302–6337.
[17] H. Yoshida, S. Fujita, M. Arai, Catal. Today (2014), http://dx.doi.org/10.1016/j.cattod.2014.03.078.
[18] X. Meng, H. Cheng, S. Fujita, Y. Yu, F. Zhao, M. Arai, Green Chem. 13 (2011) 570–752.
[19] H. Wan, A. Vitter, R.V. Chaudhari, B. Subramaniam, J. Catal. 309 (2014) 174–184.
[20] M.J. Beier, J.-M. Andanson, A. Baiker, ACS Catal. 2 (2012) 2587–2595.
[21] J. Ozaki, T. Anahara, N. Kimura, A. Oya, Carbon 44 (2006) 3358–3361.
[22] J. Ozaki, N. Kimura, T. Anahara, A. Oya, Carbon 45 (2007) 1847–1853.
[23] T. Ikeda, M. Boero, S. Huang, K. Terakura, M. Oshima, J. Ozaki, J. Phys. Chem. C 112 (2008) 14706–14709.
[24] S.M. Lyth, Y. Nabae, S. Moriya, S. Kuroki, M. Kakimoto, J. Ozaki, S. Miyata, J. Phys. Chem. C 113 (2009) 20148–20151.
[25] T. Ikeda, M. Boero, S. Huang, K. Terakura, M. Oshima, J. Ozaki, S. Miyata, J. Phys. Chem. C 114 (2010) 8933–8937.
[26] X. Meng, H. Cheng, S. Fujita, Y. Hao, Y. Shang, Y. Yu, S. Cai, F. Zhao, M. Arai, J. Catal. 269 (2010) 131–139.
[27] H. Yoshida, K. Kato, X. Meng, S. Narisawa, S. Fujita, J. Wang, Z. Wu, F. Zhao, M. Arai, J. Phys. Chem. C 115 (2011) 2257–2267.
[28] S. Fujita, T. Tanaka, Y. Akiyama, K. Asai, J. Hao, F. Zhao, M. Arai, Adv. Synth. Catal. 350 (2008) 1615–1625.
[29] H. Yoshida, S. Fujita, M. Arai, B.M. Bhanage, in: B.M. Bhanage, M. Arai (Eds.), Transformation and Utilization of Carbon Dioxide, Springer, New York, 2014, pp. 369–388.