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Nitrogen-Doped Carbon Materials Prepared by Ammoxidation as Solid Base Catalysts for Knoevenagel Condensation and Transesterification Reactions

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Abstract: Nitrogen-doped carbon materials were prepared by ammoxidation of commercial carbon sources (carbon black and activated carbon) and applied as base catalysts for Knoevenagel and transesterification reactions. It was shown that these carbon materials were active and the activities were different depending on the ammoxidation conditions (temperature and ammonia concentration in air) and carbon sources used. The bulk, textural, and surface properties of the nitrogen-doped carbon materials were examined by several methods to clarify possible factors determining their final catalytic activities. The activated carbon-derived catalysts were more active than the carbon black-derived ones. The surface area and porosity were not responsible for this difference between the two carbon sources but the difference in the reactivity with oxygen was important. The reactivity of carbon sources with oxygen should influence the doping of nitrogen onto their surfaces by ammoxidation with ammonia and air and the resulting activities as base catalysts. The catalytic activity increases with the amount of nitrogen doped and, therefore, the nitrogen doped should be responsible for the catalytic activities. In addition, the activities are maximal at a ratio of nitrogen to oxygen of around 1, suggesting the importance of cooperative functions of nitrogen and oxygen on the surface of carbons.

Keywords: ammoxidation; base catalysts; carbon; Knoevenagel condensation; nitrogen doping; transesterification

Introduction

Recently several authors have reported the preparation and design of interesting functional carbon-based materials. Toda et al. successfully made a solid acid catalyst of amorphous carbon materials in which a sulfonite group was introduced.[1] Ozaki et al. tailored nitrogen- and/or boron-doped carbon materials *via* controlled carbonization of polymers, which were effective as the electrode in proton exchange membrane fuel cells.[2] Nitrogen-doped carbon materials were also prepared by Favia et al.[3] using cold plasma treatment with ammonia and oxygen and by Bitter et al.[4] using chemical vapor deposition of compounds such as acetonitrile and pyridine containing both carbon and nitrogen on supported metal particles. The latter authors used their nitrogen-doped carbon nanotube materials so prepared for Knoevenagel reactions. Those results indicate the attractive potential of the preparation of carbon materials having various chemical and electrochemical functions. A recent communication has discussed possible functions of nitrogen-containing carbon alloys,[5] in which different modes of carbon bonding coexist in the absence and presence of other foreign atoms like nitrogen. In addition, previous XPS studies showed the presence of various types of nitrogen species in nitrogen-doped carbon materials, which could have different chemical functions.[6] Thomas et al. prepared graphitic carbon nitride materials using a well-designed synthetic chemistry, in which the materials were made by polymerization of cyanamide, dicyanamide, or melamine.[7] Various materials with different structures and properties can be obtained depending on reaction conditions. These carbon nitride materials are active catalysts for Friedel–Crafts and cyclization reactions. Very recently, Jin et al. have prepared carbon nitride nanoparticles using mesoporous silica nanoparticles as a template and indicated that these are active catalysts for transesterification reactions.[8]

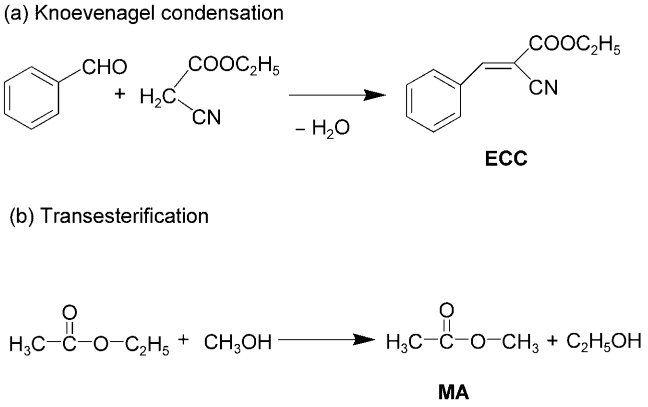
Those previous results demonstrate that nitrogen-containing carbon materials can be *metal-free* active catalysts for electrochemical and organic synthetic reactions. The synthesis and catalytic application of nitrogen-modified carbon materials is a challenging task with scientific and industrial significance. As known from the above-mentioned works, there are three approaches to the preparation of nitrogen-containing carbon materials, which are (i) synthetic chemistry using small building-unit molecules, (ii) carbonization of nitrogen-containing macromolecules, and (iii) doping of nitrogen to bulk carbon materials. In the present work, our attention is paid to the last method in which the doping procedures are easy. A useful method of nitrogen doping is amination or ammoxidation, in which a carbon sample is thermally treated with ammonia or a mixture of ammonia and air.[9] It was reported quite early by Rideal and Wright that nitrogen-containing carbon materials so prepared were active for the oxidation of aqueous oxalic acid.[9a] Stöhr et al. reported that the formation of H_2O from H_2 and O_2 was catalyzed by carbon materials activated by thermal treatment with ammonia.[9b] Other authors also indicated previously the catalytic potentials of nitrogen-doped carbon materials treated with ammonia as fuel cell cathodes and catalysts for the oxidation of oxalic acid and others.[9c–e] To the best of our knowledge, however, only a few works[4,7,8] have been reported so far to apply such nitrogen-doped carbon materials prepared *via* ammoxidation and other methods for organic synthetic reactions.

Considering the previous results and the theoretical expectation of interesting chemical functions of nitrogen-doped carbon materials, the present authors have prepared nitrogen-doped carbon materials *via* ammoxidation of active carbon and carbon black under different conditions and examined their potential as solid base catalysts, as a part of a study on the preparation of new solid base catalysts.[10] Base-catalyzed chemical reactions are of practical importance to the production of drugs, fragrances, and chemical intermediates.[11] The use of solid base catalysts is currently recommended, as compared with homogeneous ones, because of their easy separation and recycling procedures. The safe nature and low cost of carbon materials are also practically important. The ammoxidized carbon materials have been shown to be active for such reactions as Knoevenagel condensation and transesterification reactions.[12] The structural features of the nitrogen-doped carbon catalysts prepared have been examined by different methods including nitrogen adsorption/desorption, XPS, XRD, and so on, from which the quantity and chemical state of the nitrogen doped and the catalytically active working sites have been discussed.

Results and Discussion

Catalytic Activities

The nitrogen-doped carbon materials prepared were applied for base-catalyzed Knoevenagel and transesterification reactions (Scheme 1). The influence of ammoxidation conditions such as treatment gas and heating schedule was first examined using CB as a carbon source and Knoevenagel condensation as a test reaction. Table 1 presents the catalytic activities of CB-based materials prepared under different conditions. The raw CB material was heat-treated with gas (1) (NH_3 + air, NH_3, or N_2) at increasing temperatures up to 600 °C, kept at this temperature for 1 h, cooled to a certain switching temperature at which the gas was changed from gas (1) to gas (2) (N_2 or air), and further cooled down to room temperature. When the whole treatment was made with pure N_2 alone, a low ethyl cyanocinnamate (ECC) yield of 8% was obtained (entry 1). The reaction was found to proceed in the absence of catalyst, giving a very small ECC yield of 5%. So, the raw CB was less active for the present Knoevenagel reaction. When pure NH_3 was used for gas (1), the catalytic activity was enhanced and the ECC yield was larger for a lower switching temperature (entries 2–5). The lowest temperature of 25 °C gave the largest yield of 50%, which, however, should be ascribable to the presence of NH_3 itself physisorbed on the carbon. When air was used during the cooling from 600 °C to room temperature, an ECC yield of 14% was obtained



Scheme 1. Base-catalyzed reactions studied. ECC = ethyl cyanocinnamate, MA = methyl acetate.

Table 1. Influence of ammoxidation conditions on the activity of CB-based catalysts for Knoevenagel condensation.[a]

Entry	Ammoxidation conditions[b]			ECC
	Gas (1)	Temp. [°C]	Gas (2)	yield [%]
1	N_2	600	N_2	8
2	NH_3	600	N_2	12
3	NH_3	300	N_2	13
4	NH_3	100	N_2	19
5	NH_3	25	N_2	50
6	NH_3	600	air	14
7[c]	NH_3	600	air	21
8	NH_3 (90%)+air	600	air	24
9	NH_3 (90%)+air	300	air	27
10	NH_3 (90%)+air	100	air	46

[a] For reaction conditions, see the text.

[b] A carbon sample was heat-treated with a stream of gas (1) at 100 $cm^3 min^{-1}$ and at increasing temperatures up to 600 °C, kept at 600 °C for 1 h, and cooled to the temperature given. Then, the treatment gas was switched with a stream of gas (2) and cooled down to room temperature.

[c] A carbon sample was heat-treated in air at increasing temperatures up to 600 °C, with NH_3 at this temperature for 1 h, and then cooled in air to room temperature.

(entry 6), which was comparable to that obtained with N_2 for gas (2) (entry 2). When the CB was treated with air instead of NH_3 at increasing temperatures up to 600 °C, the ECC yield increased from 12% to 21% (entries 2, 7). When NH_3 (90%)+air was used for gas (1) and air for gas (2), the ECC yield was significantly enhanced (entries 2/8, 3/9, 4/10). These results indicate an important fact that the coexistence of O_2 (in air) with NH_3 is required to prepare more active carbon-based catalysts. The authors speculate that the O_2 molecules break chemical bonds such as C–C, C–O, and/or C–H at the surface of carbon and assist the doping of nitrogen from NH_3.

The influence of ammoxidation conditions was further examined with the two carbon sources CB and AC, which were treated with NH_3 and/or air at different temperatures. The treatment gas mixture was changed to air at a switching temperature of 300 °C. This switching temperature was selected to avoid the influence of physisorbed NH_3 residues on the carbon materials. When the samples prepared with switching temperatures of 100 °C and 300 °C were heat-treated at a rate of 15 °C min^{-1} in an argon stream, the desorption of NH_3 was measured by a mass spectrometer and observed to occur at temperatures of 100–400 °C for the former sample but not for the latter. Figure 1 gives the results of Knoevenagel and transesterification reactions with the carbon materials ammoxidized at different temperatures. For the former reaction for which a 5% ECC yield was obtained in the absence of catalyst, the AC-derived samples were more active than the CB-derived ones. A maximum yield appeared at 700 °C for the former samples but at a lower temperature of 600 °C for the latter ones. The maximum yield was two-fold larger than that with the sample prepared at 400 °C for either the AC or the CB carbon source. For the transesterification reaction giving a methyl acetate (MA) yield of 10% without catalyst, the product yield simply increased with temperature less significantly for the AC-derived samples compared with the results of Knoevenagel condensation. The CB-derived sample prepared at 400 °C was inactive for transesterification but those prepared at higher temperatures had similar catalytic activities. The CB and AC carbon materials took catalytic activities for the base-catalyzed reactions by ammoxidation and the effects of ammoxidation temperature were different depending on the starting carbon sources and the chemical reactions. The difference in the reactivity to O_2 between the two raw carbon materials, which will be described later, may be responsible; this difference should be crucial for the doping of nitrogen and the generation of catalytically active sites. In addition, the difference in the temperature effects between Knoevenagel and transesterification reactions suggests that the structural features of working active sites are different between the two reactions.

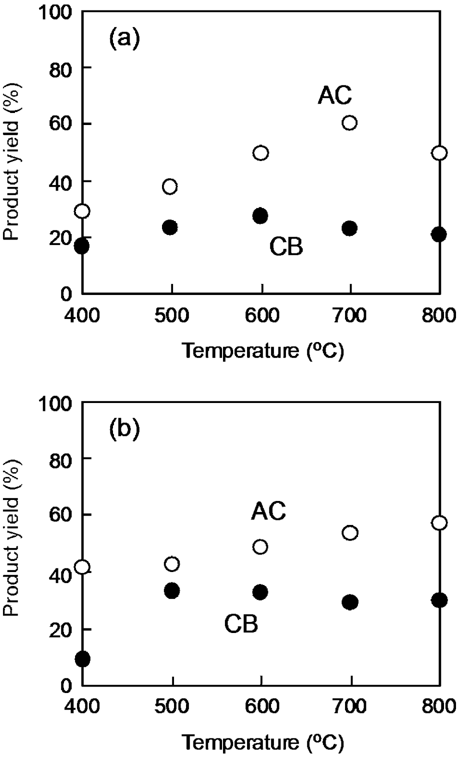


Figure 1. Results of (**a**) Knoevenagel condensation and (**b**) transesterification reaction using nitrogen-doped AC- and CB-derived carbon catalysts prepared *via* ammoxidation at different temperatures (NH_3 concentration 90%, ammoxidation time 1 h).

Figure 2 shows the influence of NH_3 concentration at a treatment temperature of 600 °C. When the NH_3 concentration was 90% or lower, the product yield did not change with the concentration so much for the two reactions. Namely, the ammoxidized carbon materials had similar catalytic activities irrespective of the NH_3 concentration used. For Knoevenagel condensation with the catalyst samples prepared with 60% and 70% NH_3, a small amount of benzoic acid (<2.5%) was detected to form along with a trace amount of benzaldehyde dibutyl acetal. It was likely that the presence of 40–30% O_2 caused the production of O-containing surface functional groups on the carbon materials facilitating the oxidation of benzaldehyde to benzoic acid and this acid catalyzed the formation of acetal from benzaldehyde and 1-butanol (solvent). At a 100% of NH_3, however, the product yields were decreased, indicating again the importance of the coexistence of O_2. An interesting exception was the AC-based sample treated with 100% NH_3 for the transesterification, which indicated the highest activity. These results also suggest that Knoevenagel and transesterification reactions are catalyzed by different active sites.

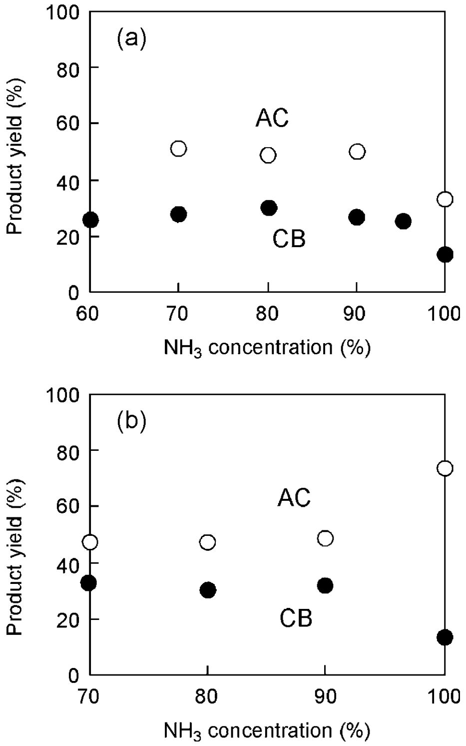


Figure 2. Results of (**a**) Knoevenagel condensation and (**b**) transesterification reaction using nitrogen-doped AC- and CB-derived carbon catalysts prepared *via* ammoxidation with different NH_3 concentrations (ammoxidation temperature 600 °C, time 1 h).

The CB and AC carbon materials were ammoxidized with 90% NH_3 at 600 °C for different periods of time and longer treatments were observed to be less effective (see Supporting Information, Figure S1). The amoxidation treatments for 2 h and 1 h were sufficient to activate the CB and AC samples, respectively. This difference would be explained by a difference in the reactivity with O_2 between the two carbon sources, as will be discussed later with thermogravimetric results.

One of merits of using heterogeneous catalysts is their possibility of easy separation and recycling. So, the recycling test was conducted with a CB-derived carbon sample prepared by ammoxidation at 600 °C. After the first reaction run, the catalyst was separated by suction filtration, dried in air at 120 °C overnight, and used for the next run. For transesterification reaction, the CB-based carbon catalyst was able to be recycled without significant loss of activity for three repeated runs (see Supporting Information, Figure S2). For Knoevenagel condensations, unfortunately, the catalyst was observed to lose its activity for the second run. When the catalyst was further treated in an N_2 stream at 300 °C for 1 h after the drying at 120 °C, its initial activity was recovered by 50% but not completely. The change of product yield with reaction time indicated the loss of activity (see Supporting Information, Figure S3). A possible factor for this catalyst deactivation was water formed during the reaction (Scheme 1). However, this was unlikely because the activity was not completely recovered by heat treatment at a high temperature of 300 °C as mentioned above and the activity was not found to be influenced by addition of a porous material like zeolite as a water catcher in the reaction mixture. Another possible factor was benzoic acid, which would form by oxidation of benzaldehyde and poison the active base sites. This was also unlikely because no positive effects appeared even when the liquid reaction mixture was pretreated by bubbling with an argon stream to remove the dissolved O_2 and the reaction was run in an argon atmosphere using a glove-box. At present, the catalyst deactivation during the Knoevenagel reaction cannot be explained satisfactorily. It is speculated that a small quantity of the product ECC is adsorbed on and poisons the active sites of the nitrogen-doped carbon catalysts. Another possibility is the base-catalyzed hydrolysis of the ester yielding an acid, which could then deactivate the active basic sites.

Bulk and Textural Properties

The changes of bulk and textural properties of CB and AC carbon materials with the ammoxidation were examined. The weight loss and the surface area of the carbon samples were measured after the ammoxidation with 90% NH_3 at different temperatures for 1 h (see Supporting Information, Figure S4). The ammoxidation caused the weight loss of the CB- and AC-derived samples, which were about 5% and 15%, at 600 °C. The weight loss was larger for the latter than the former. The weight decreased by more than 20% on the ammoxidation at 800 °C. The surface areas of the raw CB and AC samples were 1400 $m^2 g^{-1}$ and 1200 $m^2 g^{-1}$, respectively, and did not change so much on ammoxidation at 600 °C and 800 °C. The surface areas of the AC-derived samples were smaller than those of the CB-derived ones although the former were more active than the latter for Knoevenagel and transesterification reactions. The total pore volume of the raw AC material was 0.58 $cm^3 g^{-1}$, which was found to increase to 0.62 and 0.70 $cm^3 g^{-1}$ on the ammoxidation at 600 °C and 800 °C, respectively. The raw CB material had a larger pore volume of 3.26 $cm^3 g^{-1}$, changing to 3.28 and 3.57 $cm^3 g^{-1}$ for the samples prepared at 600 °C and 800 °C, respectively. Furthermore, it was found that the pore size distribution did not change so much with the ammoxidation for either CB or AC carbon material. Similar results were reported by Jansen and van Bekkum[9g]; these authors modified carbon materials by amination and ammoxidation at temperatures between 200 °C and 420 °C and observed that their pore structures were virtually unchanged by these treatments. Those textural features are unable to explain the significant differences in the catalytic activity among the various nitrogen-doped carbon catalysts prepared, which depend on the ammoxidation conditions and carbon sources used (Figure 1 and Figure 2). The chemical properties of their surfaces should be responsible for their base catalysis, as will be discussed later.

The reactivity of the two CB and AC carbon sources with O_2 was examined by thermogravimetric analysis in which the sample was heated in air at a rate of 10 °C min^{-1} up to 800 °C. The weight loss was observed to start at 550 °C for the former sample but at a lower temperature of 450 °C for the latter (not shown). That is, the AC was more reactive with O_2 than the CB, which should be crucial for determining the easiness of nitrogen doping on ammoxidation, the structure of nitrogen-containing active sites formed, and thus the final catalytic activities. The amount of nitrogen doped was observed to be larger for the AC compared to the CB, as described later (see Figure 4).

Surface Chemical Properties

The ammoxidized carbon samples were examined by XPS and it was confirmed that nitrogen was doped onto the CB and AC materials and the extent of nitrogen doping depended on ammoxidation conditions and carbon sources used. Figure 3 gives XPS traces for the carbon materials ammoxidized with 90% NH_3 at different temperatures. The amount of nitrogen doped was estimated by measuring the total area of the N 1*s* spectrum obtained. In Figure 4 the product yield of either Knoevenagel or transesterification reactions is plotted against the amount of N relative to C. It is clear that a positive correlation exists between the N/C ratio and the product yield, that is, the catalytic activity for either reaction. The doping of nitrogen is responsible for the catalytic activity of ammoxidized CB and AC materials. A wide range XPS analysis was also made for the CB and AC carbon samples but we did not detect the presence of metal species such as Fe, which had a possibility of playing some role in the nitrogen doping through oxidation of carbon.

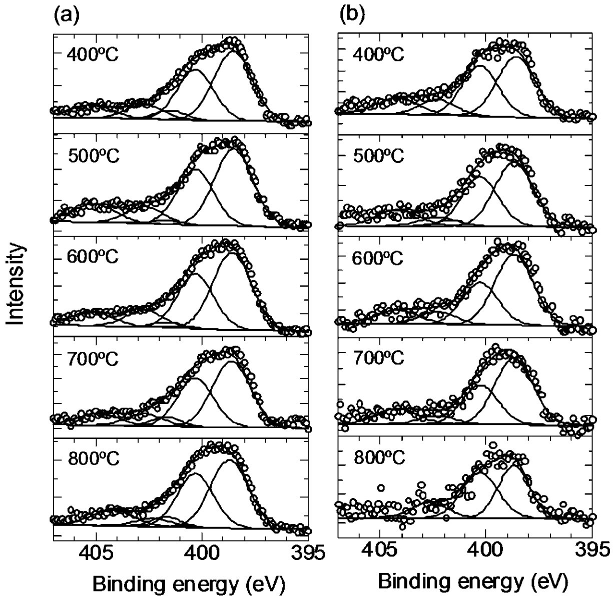


Figure 3. XPS spectra of AC- (**a**) and CB (**b**)-based catalysts prepared by ammoxidation with 90% NH_3 for 1 h at the different temperatures given.

The XPS data (Figure 3) indicated the presence of several nitrogen species of different electronic states (Scheme 2). The relative amounts of these different nitrogen species were estimated by deconvolution of the spectra. Figure 5 shows the results for the AC- and CB-derived samples ammoxidized with 90% NH_3 at different temperatures. The assignment of the binding energies to the corresponding chemical states of nitrogen was made according to previous work.[6a,13] Although the activities of those nitrogen-doped carbon catalysts were different as mentioned above, they were very similar in the distribution of the different nitrogen species. The fraction of pyridine-type nitrogen (398.5 eV) was comparable to that of pyrrole-/pyridone-type nitrogen (400.5 eV) each in about 40% with small amounts of quaternary (401.5 eV) and oxidized (402.5 eV) N species and adsorbed NO_x

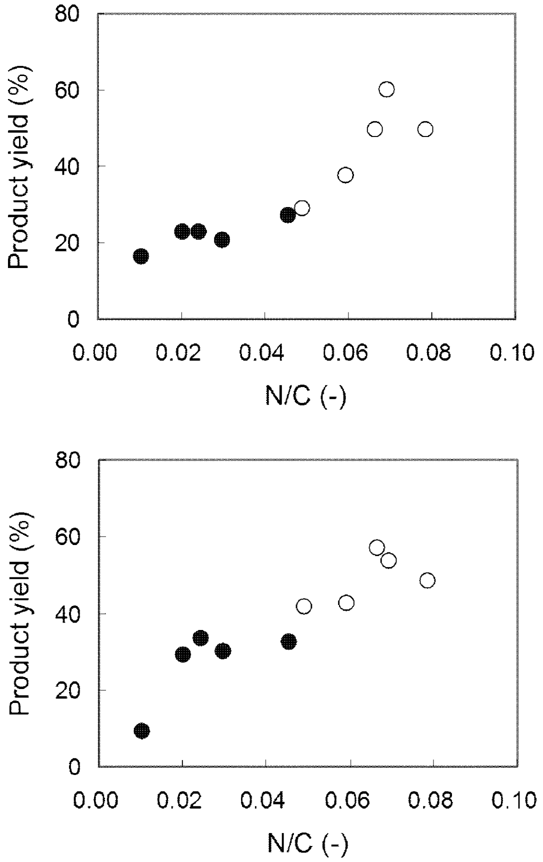


Figure 4. Plot of the product yield in (*top*) Knoevenagel condensation and (*bottom*) transesterification reaction against the N content for nitrogen-doped AC- (open circle) and CB-derived (closed circle) carbon catalysts.

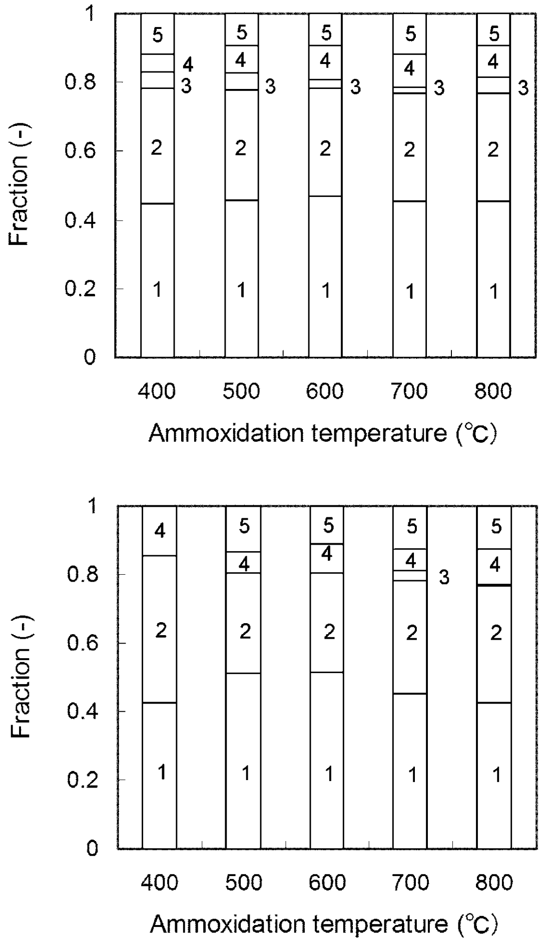
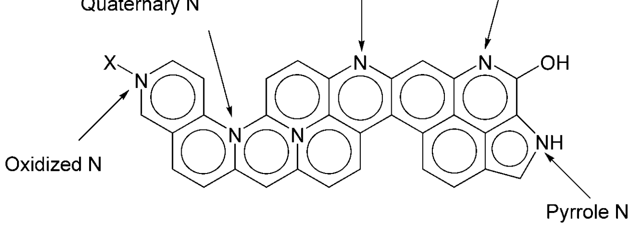


Figure 5. Distributions of N species of (*top*) AC- and (*bottom*) CB-derived carbon catalysts prepared by ammoxidation with 90% NH_3 at the different temperatures given. 1 = pyridine-type; 2 = pyrrole/pyridone-type; 3 = quaternary-type, 4 = oxidized-type; 5 = adsorbed NO_x.

(405.0 eV). The different states of nitrogen doped should be unlikely to indicate the same catalytic activity.[4,5,14] At present, unfortunately, it was impossible to specify the type of nitrogen doped that is involved in the catalytically active sites. Previously Bitter et al. reported, for nitrogen-containing carbon nanotubes prepared by chemical vapor deposition of C- and N-containing precursors (acetonitrile, pyridine), that the initial activity in Knoevenagel condensations increased with the amount of pyridine-type nitrogen included.[4] The binding energy of pyridine-type nitrogen is lower than those of the other types of nitrogen, implying that the density of electrons is smaller and the Lewis basicity would be weaker. We cannot deny a possibility that the other types of nitrogen than the pyridine-type one may also contribute to the basic active sites for Knoevenagel and transesterification reactions. Previously the present authors studied the same transesterification reaction with mesoporous smectite-like catalysts and reported that the reaction was catalyzed by basic sites of medium strength, which was examined by temperature programmed desorption of CO_2.[10] It was further found that the nitrogen-doped carbon materials were inactive for Knoevenagel condensation between benzaldehyde and diethyl malonate $CH_2(CO_2C_2H_5)_2$ instead of ethyl cyanoacetate $CH_2(CN)CO_2C_2H_5$ under the present reaction conditions. The abstraction of a proton from the methylenic group is the first and rate-determining step[12a] and it may be more difficult for diethyl malonate than for ethyl cyanoacetate. This indicates that



Scheme 2. Possible structures of nitrogen doped to carbon.

such strong basic sites are absent in the nitrogen-doped carbon catalysts prepared.

An interesting relationship was found when the activity for either Knoevenagel condensation or transesterification reaction was plotted against the N/O atomic ratio of the nitrogen-doped carbon catalysts (Figure 6). For both reactions, the maximum activities appeared at an N/O ratio of 0.8–1.0, indicating the importance of the presence of the same amounts of surface N and O species. The authors believe that there operates some cooperation of N- and O-containing sites, which promotes these two reactions. A possible model for such cooperation is the pyridone-type of nitrogen depicted in Scheme 2, in which OH group is attached to the C atom next to the N atom of the pyridone ring. The H of the OH group may form hydrogen bonding with the negatively polarized O atom of the carbonyl group of one substrate (benzaldehyde, ethyl acetate) and the hydrogen bonding is likely to increase the positive nature of the C atom. A carbanion would be produced from the counterpart substrate (ethyl cyanoacetate, methanol) by the catalytic action of basic N sites. The cooperation of the hydrogen bonding and the basic N site would promote the nucleophilic attack of the carbanion to the carbonyl substrate. This could explain the maximum activity of the nitrogen-doped catalyst at an N/O ratio of around 1 (Figure 6).

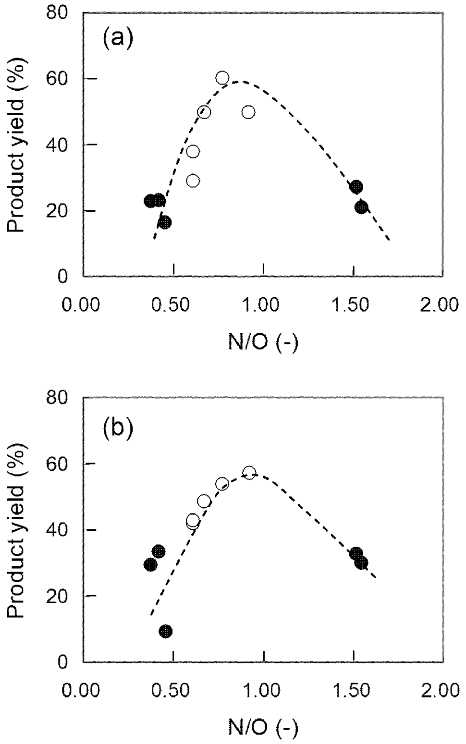


Figure 6. Plots of the product yield in Knoevenagel condensation (**a**) and transesterfication reaction (**b**) against the N/O ratio for the AC- (open circles) and CB- (closed circles) derived nitrogen-doped carbon catalysts

The above discussion is based on a possible structure of carbon surfaces as depicted in Scheme 2, in which different states of doped nitrogen species are distinguished by XPS. It was previously reported that there existed various functional groups on the surface of carbon materials such as carbonyl, carboxylic anhydride, lactonic, quinoline-like, xanthene, and ether groups.[15] These functional groups would exist on the present starting carbon materials and be formed and changed by the ammoxidation. These oxygen-containing groups should be considered for more a detailed discussion on the mechanisms of nitrogen doping and the catalytic actions of doped nitrogen species and neighbor functional groups in organic synthetic reactions.

To further give light on the features of our nitrogen-doped carbon catalysts, the same reactions were conducted with pyrrole, pyridine and piperidine similar to their structural moieties (Scheme 2). The active AC-derived sample ammoxidized with 90% NH_3 at 600°C for 1 h was selected, which was doped with a larger amount of nitrogen. This carbon sample contained nitrogen in 6.6 mol% as estimated from XPS and so 0.55 mmol nitrogen was included in a 0.1 g of the sample. Similar molar amounts of pyrrole, pyridine and piperidine were used for the reaction runs under the identical conditions. Table 2 shows that pyrrole and pyridine were almost inactive for the Knoevenagel condensation and transesterification while piperidine was active for both reactions. The activity of the nitrogen-doped carbon catalyst was comparable to

Table 2. Comparison of a nitrogen-doped carbon catalyst with homogeneous catalysts of pyridine and piperidine.

Entry	Catalyst	ECC yield [%][a]	MA yield [%][b]
1	N-doped carbon[c]	50	49
2	pyrrole[d] (pK_a 0.4)[e]	9	–[i]
3	pyridine[f] (pK_a 5.25-5.5)[e]	15	8
4	piperidine[g] (pK_a 11)[e]	89[h]	50

[a] Yield of ethyl cyanocinnamate in Knoevenagel condensation at 80°C for 1 h.

[b] Yield of methyl acetate in transesterification at 140°C for 4 h.

[c] AC-derived material ammoxidized with 90% NH_3 at 600°C. 0.1 g.

[d] 0.038 cm^3.

[e] Refs.[12b,16]

[f] 0.044 cm^3.

[g] 0.054 cm^3.

[h] The substrate ethyl cyanoacetate was completely consumed but a by-product of butyl cyanocinnamate was also formed.

[i] Not measured.

Table 3. Results of Knoevenagel condensation reactions of ethyl cyanoacetate with different carbonyl substrates.[a]

Substrate	Benzaldehyde	Butyraldehyde	Acetophenone	Benzophenone
Yield[b] [%]	60	55	–[c]	–[c]

[a] AC derived catalyst prepared *via* ammoxidation with 90% NH_3 at 700 °C for 1 h was used. *Reaction conditions:* catalyst 100 mg; ethyl cyanoacetate 9.4 mmol; carbonyl substrate 9.9 mmol; solvent 1-butanol 4 cm^3; temperature 80 °C; time 1 h.

[b] Knoevenagel coupling products.

[c] No reaction occurred.

that of the piperidine for transesterification. It was also active for Knoevenagel condensation but less active than the piperidine. It is important, however, that such an undesired by-product as butyl cyanocinnamate was not formed with the nitrogen-doped carbon catalyst. Thus, one can say that the nitrogen-doped carbon materials will function as effective basic catalysts comparable or similar to the molecular basic catalyst of piperidine.

Finally, the performance of nitrogen-doped carbon catalyst was further tested for Knoevenagel condensation reactions of ethyl cyanoacetate with different aldehydes and ketones under the same conditions. Table 3 presents the results with benzaldehyde, butyraldehyde, acetophenone, and benzophenone using an AC-derived catalyst prepared through ammoxidation with NH_3 90% at 700 °C for 1 h. The nitrogen-doped catalyst was also active for butyraldehyde, similar to benzaldehyde, in which no by-product was observed. However, it was inactive for acetophenone and benzophenone. It is known that ketones are generally less reactive than aldehydes.[12a]

The present results demonstrate that the ammoxidation of carbon materials is an attractive method for the production of *metal-free* carbon-based catalysts for organic synthetic reactions. The use of carbon materials has several merits for green chemistry due to their chemical/physical natures. Further studies are in progress in our laboratories to apply the ammoxidized carbon catalysts for other reactions (oxidation, for example) and to examine nitrogen-doped catalysts prepared from other carbon sources different in the structure compared to AC and CB used in the present work.

Conclusions

The following conclusions are drawn from the present work on the carbon materials that were chemically modified by ammoxidation with NH_3 and air.

The ammoxidized carbon materials are active catalysts for base-catalyzed Knoevenagel condensation and transesterification reaction.

The doping of nitrogen onto the carbon surfaces is responsible for the catalytic activities for these reactions. The amount of nitrogen doped depends on ammoxidation conditions (temperature and NH_3 concentration) and carbon sources used. The doping of nitrogen is promoted by the coexistence of oxygen with NH_3 and the higher reactivity of parent carbon materials to oxygen.

The textural properties (surface area and porosity) are unimportant for determining the activities of the ammoxidized carbon catalysts. The ratio of surface N/O species is important and the maximum activities appear at the ratio of 0.8–1.0, suggesting cooperation of N- and O-containing sites for the two reactions.

The ammoxidation of carbon materials is an interesting route for the production of *metal-free* carbon-based catalysts for organic synthetic reactions.

Experimental Section

Nitrogen Doping to Carbon Materials

Two different raw carbon materials, carbon black (CB, Ketjen Black EC600 JD) and activated carbon (AC, GL Science 60/80 mesh), were used. A weighed (about 150 mg) carbon sample was placed in a quartz reactor and heated to 400–800 °C (mainly 600 °C) in a stream of gas (1) (NH_3 + air, NH_3, or N_2) at a flow rate of 100 $cm^3 min^{-1}$. The sample was treated at this temperature for 1 h and cooled to a certain temperature, at which the treatment gas was changed to gas (2) (N_2 or air), and further cooled down to room temperature. The doping of nitrogen to the carbon materials was confirmed by X-ray photoelectron spectroscopy.

Catalytic Activity Measurements

The catalytic activity of those nitrogen-doped carbon samples prepared was tested for Knoevenagel condensation and transesterification reactions using a Teflon-lined autoclave (50 cm^3) under conditions: for the former, benzaldehyde 9.9 mmol, ethyl cyanoacetate 9.4 mmol, solvent 1-butanol 4 cm^3, catalyst 100 mg, temperature 80 °C, time 1 h; for the latter, ethyl acetate 10 mmol, ethanol 200 mmol, catalyst 100 mg, temperature 140 °C, time 4 h. After the reaction run, the reaction mixture was suction filtered, toluene was added to the separated liquid mixture as an internal standard, and the liquid mixture was analyzed by gas chromatography (Shimadzu GC14-B with Zebron ZB-50 column) and mass spectrometry (Shimadzu QP5050 A with GL Science TC-17 column). To examine the catalyst recycling, the separated solid carbon catalyst was dried in air at 120 °C overnight and then used for the next reaction run.

Characterization of Carbon-Based Catalysts

The textural properties of the carbon samples so prepared were measured by nitrogen adsorption/desorption (Quantachrome NOVA 1000). X-ray photoelectron spectroscopy (XPS) (Perkin–Elmer EACA-5600) was used to examine C1*s*, N1*s*, and O1*s* core levels for the nitrogen-doped carbon samples. The charge-up shift correction of binding energy was made by setting the C1*s* binding energy of the carbonized sample at 284.5 eV. No sample pretreatment was made before the XPS measurements.

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