Preparation of Nitrogen-Doped Carbon from Polyacrylonitrile and its Application as a Solid-Base Catalyst

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N-doped carbon (N carbon) materials were prepared from a commercial polyacrylonitrile (PAN) by calcination and subsequent ammoxidation and these were used for a model reaction of Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate. The catalytic activity of the calcined PAN for the reaction was very low, but it was greatly enhanced by the ammoxidation and the enhancement depended on both the calcination and ammoxidation temperatures. X-ray photoelectron spectra indicated the presence of pyridine-type and

pyrrole-/pyridone-type N species and the amount of the former N species was well correlated with the catalytic activity. It was suggested that the presence of pyridine-type N in the graphene structure is significant for the emergence of the catalytic activity. The most active N-carbon catalyst prepared in the present study was much more active than solid-based catalysts reported so far including N carbon derived from activated carbon, N-doped carbon nanotubes, and a few metal oxide based catalysts.

Introduction

Base-catalyzed chemical reactions are important for the production of drugs, fragrances, and chemical intermediates.^[1] From the viewpoints of economy and green chemistry, the use of solid-base catalysts for those reactions is desirable, because they are more easily separable and recyclable than homogeneous catalysts such as alkali alkoxides and organic amines. However, fewer efforts have been made for solid base catalysis than for solid acid catalysis.^[1] So, the development of effective solid-based catalysts is still an important issue.

Recently, the use of N-doped carbon (N-carbon) materials as solid-based catalysts has been reported. Von Dommele et al. and Wang et al. reported the preparation of N-doped carbon nanotubes by chemical vapor deposition using N-containing compounds of nitriles, pyridine, or amines and showed that the obtained carbon nanotubes are effective as solid-base catalysts for Knoevenagel condensation reactions.^[2,3] Several groups reported the preparation of mesoporous graphitic carbon nitride materials by polymerization of cyanamide, di-cyanamide, or melamine.^[4] These carbon nitride materials were shown to be active catalysts for various reactions including Friedel–Crafts reaction, cyclization, coupling of CO₂ and epox-

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Among the methods to prepare N-carbon materials described above, the ammoxidation is the easiest and applicable to preparation of large quantities of N-carbon materials from commercially available carbon sources. According to our previous work, however, the amount of N species doped by the ammoxidation was limited, which is a disadvantage to get more active N-carbon catalysts. Polyacrylonitrile (PAN) that contains N atoms in its structure is frequently used as a precursor for the manufacture of carbon fiber because of its superior chemical and physical properties.^[7] The processes of the carbon fiber production from PAN involves three steps of oxidative stabilization, carbonization, and graphitization.^[7] In Scheme 1 the

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Scheme 1. Possible structure changes of PAN in the course of oxidative stabilization and carbonization steps for the production of carbon fiber.

possible chemical reactions in the course of the oxidative stabilization and carbonization steps is presented.^[7,8] In the first step, PAN is calcined in air at a few hundred °C. This changes PAN to carbon in the ladder structure through oxidation, dehydrogenation, and cyclization. In the second step, the cyclized ladder structure grows in lateral direction by polycondensation, which is accompanied with the elimination of N atoms. Although PAN itself contains a large fraction of N atoms, most of them were unfortunately removed during the second step. Thus, if the ladder-structure carbon is ammoxidized, N-carbon material containing a large amount of N species may be obtained. Considering this possibility, we have prepared N-doped carbon materials via ammoxidation of the calcined PAN and used for Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate to ethyl cyanocinnamate (ECC, Scheme 2). The



Scheme 2. Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate to ethyl cyanocinnamate (ECC).

ammoxidation of the calcined PAN significantly enhanced its catalytic activity depending on both the calcination and ammoxidation temperatures. The structural and chemical features of the N-carbon catalysts were examined by acid–base titration, XPS, and XRD, from which the catalytically active working sites were deduced. It was suggested that not only the kind and quantity of doped N species but also the structure of carbon atoms around the doped N atoms is an important factor determining the catalytic activity of N carbon. The N-

carbon catalysts prepared from PAN were shown to be much more active than a few types of solid-based catalysts reported so far.

Results and Discussion

In Table 1, the reaction results obtained with the carbon catalysts prepared and the quantities of basic sites on them are

Table 1. Catalytic activities of carbon catalysts prepared from PAN for Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate ^[a] and the amount of basic sites on them.							
Entry	Catalyst	ECC yield [%]	ECC formation rate $[mmol g^{-1} h^{-1}]$	N _{base} [mmol g ⁻¹]			
1	PAN-C200	10	10	0.342			
2	PAN-C200-AO400	76	75	0.592			
3	PAN-C200-AO600	98	153 ^(b)	0.964			
4	PAN-C400	8	8	0.321			
5	PAN-C400-AO400	99	129 ^[b]	0.811			
6	PAN-C500	7	7	0.249			
7	PAN-C500-AO400	94	199 ^[b]	1.122			
[a] Reaction conditions: catalyst 100 mg, benzaldehyde 9.9 mmol, ethyl cyanoacetate 9.4 mmol, 1-butanol 4 cm ³ , temperature 80 °C, reaction time 1 h. [b] Determined from reaction results using 30 mg of catalyst.							

listed. The calcined PAN samples gave low ECC yields (Table 1, entries 1, 4, and 6), which were almost the same with the one obtained without any catalyst (\approx 6%). Therefore, the catalytic activity of the calcined PAN is practically negligible. If PAN calcinated at 200 °C (PAN-C200) was N doped by ammoxidation at 400 °C, its catalytic activity was significantly enhanced and the enhancement was larger by the N doping at a higher temperature of 600 °C (entries 1-3). The temperature for the calcination of PAN also affected the catalytic activity of N carbon derived from the resulting carbon samples. If the ammoxidation was performed at 400 °C for PAN-C500, PAN-C400, and PAN-C200, the activity was in the order PAN-C500-AO400> PAN-C400-AO400 > PAN-C200-AO400 (entries 2, 5, and 7). Thus, N doping on the calcined PAN can give active catalysts for the Knoevenagel condensation reaction and the activity of N carbon depends on its preparation conditions.

The numbers of basic sites (N_{base}) on the carbon catalysts were determined by acid-base titration (Table 1). The calcined PAN possessed some amounts of basic sites and the ammoxidation treatment increased the number of basic sites on them. In Figure 1 the catalytic activity of N carbon is plotted against N_{base} . The activity almost linearly increased as N_{base} increased, but the plot intersected with *x*-axis at the position near which the data of the calcined PAN gathered. These suggest that the basic sites produced by the ammoxidation are responsible for the enhanced catalytic activity and the nature of basic sites existing over the calcined PAN (before the ammoxidation) is different from that of those produced by the ammoxidation.

The surfaces of the carbon samples were analyzed by XPS. XPS spectra in the N1s region are depicted in Figure 2. The N1s spectrum revealed the presence of pyridine-type N





Figure 1. Relationship between the ECC formation rate and N_{base} . (•) Calcined and subsequently ammoxidized PAN and (\odot) calcined PAN. Numbers correspond to the entry numbers in Table 1.



Figure 2. N1s XPS spectra of carbon samples prepared from PAN. Numbers correspond to entry numbers in Table 1.



Scheme 3. Possible structures of N species doped on carbon.

(398.5 eV), N(1), and pyrrole-/pyridone-type N (400 eV), N(2) (Scheme 3).^[9] Their surface concentrations were determined from the deconvoluted spectra (Table 2). After calcination, some amounts of N species originating in PAN could remain (Table 2, entries 1,4,6). Those amounts were not changed much by the ammoxidation (entries 1–5). However, among the calcined PANs, PAN-C500 could give the N-carbon catalyst con-

Table 2. Surface concentrations of N species over various carbon samples.							
Entry	Sample	N(1) [%]	N(2) [%]				
1	PAN-C200	12.7	3.3				
2	PAN-C200-AO400	9.8	8.1				
3	PAN-C200-AO600	15.3	6.3				
4	PAN-C400	9.6	6.4				
5	PAN-C400-AO400	8.5	6.2				
6	PAN-C500	7.9	8.6				
7	PAN-C500-AO400	17.3	8.9				

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taining the largest amount of N species after the ammoxidation.

The relationship between the concentration of N species and the catalytic activity was examined. In Figure 3, the activity



Figure 3. Relationship between the catalytic activity and the surface concentration of N(1) species. (\bullet) Calcined and ammoxidized PAN and ($_{\odot}$) calcined PAN. Numbers correspond to those in Table 1.

is plotted against the concentration of N(1) species. For Ncarbon catalysts, the activity was found to increase with the concentration of N(1) species, although some scatter was observed in the plot. Such trend could not be seen in the correlation between the activity and the concentration of N(2) species (Figure S1). It is strongly suggested that N(1) species is involved in the active sites for the reaction. A similar conclusion was made by van Dommele et al. for N-doped carbon nanotube catalysts.^[2] However, this is not the case for PAN-C200 and PAN-C400. Their activities were very low, although N(1) species existed over them and those amounts were similar to the ones over the active catalysts of the ammoxidized N-carbons. (Table 2). This issue will be discussed later.

To investigate structural changes in the course of the calcination, diffuse reflectance FTIR spectra of PAN and PAN-C200 were measured (Figure 4). The spectrum of PAN displayed the absorption bands of CH_2 (2940 and 1456 cm⁻¹), C=N (2242 cm⁻¹), C=O (1740 cm⁻¹), CH (1373 cm⁻¹), and C-C (1237 cm⁻¹) groups.^[8] After the calcination (Figure 4b), the intensities of these bands were largely decreased and new absorption bands appeared at 1674, 1632, and 810 cm⁻¹. Those new bands were ascribable to C=C stretching, C=N stretching, and C=C-H bending vibrations, respectively.^[8] These observations strongly suggest that dehydrogenation and cyclization



Figure 4. Diffuse reflectance FTIR spectra of a) PAN and b) PAN-C200.

occur in the course of the calcination, resulting in the ladder structure as illustrated in Scheme 1.

In Figure 5, XRD patterns of PAN, PAN-C200, PAN-C200-AO400, and PAN-C200-AO600 are illustrated. PAN showed a strong peak at approximately 17°. This peak disappeared after the calcination (PAN-C200). The disappearance would be ascribed to the formation of carbon in the ladder structure from the PAN polymer chain as suggested by FTIR measurements described above. When PAN-C200 was ammoxidized at 400 °C, the peak at approximately 25° ascribed to the (002) reflection peak of graphite^[10] became stronger and sharper. Such effects on the (002) peak were more significant for the ammoxidation at 600 °C. Similar results were also obtained with PAN-C400 and PAN-C500 (Figure S2). Taking account of the above-mentioned carbonization processes in the carbon fiber



Figure 5. XRD patterns of a) PAN, b) PAN-C200, c) PAN-C200-AO400, and d) PAN-C200-AO600.

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production from PAN (Scheme 1), the present results obtained with XRD suggest that, during the ammoxidation of the calcined PAN, the ladder structure would link up in lateral direction, producing a graphene-like layer, and the resulting layers would be stacked, forming graphite structures.

On the basis of the results described above, the structure of active sites for the Knoevenagel condensation reaction over N carbon was considered. As shown in Figure 3, the activity of N carbon increased with the amount of N(1) (pyridine-type) species; however, our previous work has already shown that the pyridine molecule has a weaker basicity than N carbon prepared from AC and, hence, the catalytic activity of the former for the Knoevenagel condensation reaction is much lower than that of the latter.^[6] It was also found that the ammoxidation of PAN-C200 and PAN-C400 significantly enhanced their catalytic activities without large changes in the amounts of N(1) species over them (Tables 1 and 2), but it caused some change in their structures as suggested by XRD results (Figure 5). Thus, the N atoms existing on the surface of the calcined PAN are unlikely to be active sites by themselves and the presence of N atoms in a large conjugated graphene-like structure would probably be requisite. Kondo et al. showed that N atoms doped on graphite could modify the electronic conjugated system of the graphite surface and N(1) species would give Lewis basic nature to neighboring C atoms the number of which could be more than 10.^[9d] Lewis basic sites including both doped N and neighboring C atoms would activate methylene group of ethyl cyanoacetate. The significance of the size of the graphene-like structure can explain the low activities of PAN-C200 and PAN-C400 the structures of which are supposed to be the ladder structure. In addition, the difference in the size of the graphene-like structure might be the reason for the slight scatter observed in the plot of Figure 3.

In Table 3, the Knoevenagel condensation reaction rate of the most active PAN-C500-AO400 is compared with those of several solid-base catalysts reported so far. In our previous study, N-carbon catalysts were prepared from a commercial AC by ammoxidation.^[6] Among them, the most active N carbon (AC-AO700) exhibited an ECC reaction rate of 60 mmol $g^{-1}h^{-1}$ under the same reaction conditions as used here. Thus, PAN

Table 3. Comparison of catalytic activities of various solid-base catalysts for Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate to ECC.							
Entry	Catalyst	7 ^[a] [°C]	ECC formation rate $[mmol g^{-1} h^{-1}]$	e Reference			
1	PAN-C500-AO400	80	199	Present study			
2	AC-AO700 ^[b]	80	50	[6]			
3	N-CNT ^[c]	78	17	[2]			
4	N-CNT ^[c]	80	45	[3]			
5	Na–SM ^[d]	60	8	[11]			
6	MgO	60	29	[12]			
7	HT ^[e]	60	3	[12]			
[a] Reaction temperature. [b] Prepared from a commercial activated carbon by the ammoxidation at 700 °C. [c] N-doped carbon nanotube. [d] Na containing smectite. [e] Mg–AI mixed oxide prepared from Mg–AI hydrotalcite (Mg/AI=3).							



can give more active catalysts than AC. Our previous study also showed that the same N species were formed on AC by the ammoxidation, but their amounts were smaller than those of the present N-carbon catalysts prepared from PAN.^[6] This might be the reason for the lower catalytic activity of N-carbon prepared from AC compared to that of the N-carbons prepared from PAN. The catalytic activity of N-doped carbon nanotube^[2,3] was also lower than that of PAN-C500-AO400 (Table 3, entries 3, 4). Other types of solid-base catalysts such as smectite, MgO, and a Mg–AI mixed oxide were also used for the same reaction.^[11,12] They had lower activity than PAN-C500-AO400, even if the difference of the reaction temperature was taken into account (entries 1, 5–7). Thus, PAN-C500-AO400 is the most active among the solid-based catalysts listed in Table 3.

As listed in Table 2, the surface concentration of N(1) over PAN-C200-AO600 was higher than that over PAN-C200-C400. This would be a possible reason for the higher activity of the former N-carbon catalyst. For N doping on carbon materials, the dissociation of C-C bond is considered to be required.^[13] The rate of the dissociation would be faster at higher temperatures, which would promote the N doping. Table 2 also shows that the amount of N(1) species tended to decrease with increasing calcination temperature and no N species was detected by XPS over PAN-C500. The calcination at high temperatures would cause the evolution of N atoms, probably as HCN.^[7] Therefore, N atoms originating from the source PAN polymer would disappear by the calcination at 500 °C (PAN-C500). Despite of this, PAN-C500-AO400 contained the largest amount of N(1) species and, hence, it was the most active (Tables 1 and 2). When PAN was calcined at 500 °C, approximately 90% of the PAN sample was burned off. Such a significant burn-off did not occur for the calcination of PAN at 200 and at 400 °C. Hence, PAN-C500 would contain a larger amount of deficient sites than PAN-C200 and PAN-C400. Jansen and Bekkum propose N-doping mechanisms in which carboxylic groups contribute to the doping^[13] and our previous work showed that O₂ molecules promote N-doping of AC using NH₃.^[6] Probably, the deficient sites over the calcined PAN involve O species and some kind of those O species that can promote N-doping. It is highly probable that the larger amount of those deficient sites over PAN-C500 resulted in the larger amount of doped N species. It is difficult, at present, to precisely depict what reactions occur in the course of the ammoxidation of the calcined PAN. The ladder structure of the calcined PAN and the amount and nature of N and O atoms in it may depend on the calcination conditions. Detailed study on this issue may give more effective N-carbon catalysts.

Conclusions

N-carbon catalysts were prepared from polyacrylonitrile (PAN) by calcination and subsequent ammoxidation. The catalytic activity of the calcined PAN for the Knoevenagel condensation reaction was greatly enhanced by the ammoxidation depending on both the calcination and ammoxidation temperatures. XRD measurements suggested the occurrence of the growth in the graphite structure. X-ray photoelectron spectra indicated the presence of pyridine-type and pyrrole-/pyridone-type N species. The catalytic activity of the ammoxidized N-carbon was correlated with the amount of pyridine type N species, suggesting that they are involved in the catalytically active sites; however, such N species on the calcined PAN samples were practically inactive. On the basis of these observations, it has been suggested that the presence of pyridine-type N atoms in the large graphene structure is significant for the emergence of the catalytic activity. The most active N carbon prepared from PAN was much more active than other solidbase catalysts reported so far including N carbon derived from activated carbon, N-doped carbon nanotubes, and a few inorganic solid-base catalysts.

Experimental Section

Raw starting carbon materials were prepared from PAN powder (copolymer containing 3 mol% ethyl vinylacetate) supplied by Mitsubishi Rayon by the calcination in air at 200, 400, or 500 °C for 3 h. Those carbon materials were named as PAN-C200, PAN-C400, and PAN-C500, respectively. Nitrogen doping on these samples was performed by ammoxidation. A weighed carbon sample (\approx 150 mg) was placed in a quartz reactor and heated to 400 or 600 °C in a stream of 90 vol.% NH₃-air at 100 cm³min⁻¹. The carbon sample was treated at this temperature for 1 h, cooled to 300 °C, at which the treatment gas was then changed to air, and further cooled to room temperature. N-carbon samples thus prepared were designated as PAN-C200-AO600, PAN-C500-AO400 etc., for which the first and the second numbers represent the temperatures for the calcination and for the ammoxidation, respectively.

The catalytic activity of those N-carbon materials prepared was tested for Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate. The reaction was performed in a Teflon-lined autoclave (100 cm³) at 80 °C for 1 h using the catalyst (100 mg), benzaldehyde (9.9 mmol), ethyl cyanoacetate (9.4 mmol), and 1-butanol solvent (4 cm³). After the reaction run, the reaction mixture was suction-filtered, ethyl benzene was added to the separated liquid mixture as an internal standard, and the liquid mixture was diluted with 1-butanol to 25 cm³ and analyzed by gas chromatography (Shimadzu GC14-B with Zebron ZB-50 column) and mass spectrometry (Shimadzu QP5050A with GL Science TC-17 column). A few reaction runs were also performed with 30 mg of the catalyst.

The textural properties of the carbon samples prepared were measured by nitrogen adsorption/desorption (Quantachrome NOVA 1000). The surface area was determined by the BET equation. XPS measurements of the samples were conducted on JEOL JPS-9200 using monochromatic AIK_{α} radiation. The charge-up shift correction of the binding energy was done by using C_{1s} binding energy at 284.5 eV. Diffuse-reflectance FTIR spectra of PAN and PAN-C200 were measured on a JASCO FTIR-620. A spectrum of KBr was used as the background. The numbers of basic sites on the carbon samples were determined by acid-base titration. An amount of approximately 0.1 g of the carbon sample was dispersed in $0.01\,\ensuremath{\text{m}}$ HCl solution (15 cm³) under stirring overnight. Then, the sample was separated by filtration and the concentration of HCl in the filtrate was determined by titration with 0.01 M NaOH solution. The amount of basic sites was determined from the decrease of the HCl concentration.



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