



Title	Preparation of Nitrogen-Doped Carbon from Polyacrylonitrile and its Application as a Solid-Base Catalyst
Author(s)	Fujita, Shin-ichiro; Katagiri, Ayaka; Watanabe, Hiroyuki; Asano, Sayaka; Yoshida, Hiroshi; Arai, Masahiko
Citation	Chemcatchem, 7(18), 2965-2970 <a href="https://doi.org/10.1002/cctc.201500337">https://doi.org/10.1002/cctc.201500337</a>
Issue Date	2015-09-15
Doc URL	<a href="http://hdl.handle.net/2115/62798">http://hdl.handle.net/2115/62798</a>
Rights	This is the accepted version of the following article: ChemCatChem, September 14 2015, 7(18), pp.2965-2970, which has been published in final form at <a href="http://onlinelibrary.wiley.com/doi/10.1002/cctc.201500337/abstract">http://onlinelibrary.wiley.com/doi/10.1002/cctc.201500337/abstract</a> .
Type	article (author version)
File Information	Fujita-CCC7(18).pdf



[Instructions for use](#)

# **Preparation of nitrogen-doped carbon from polyacrylonitrile and its use as a solid base catalyst**

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

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

## **Abstract**

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 base catalysts reported so far including N-carbon derived from activated carbon, N-doped carbon nanotubes, and a few metal oxide based catalysts.

## **1. Introduction**

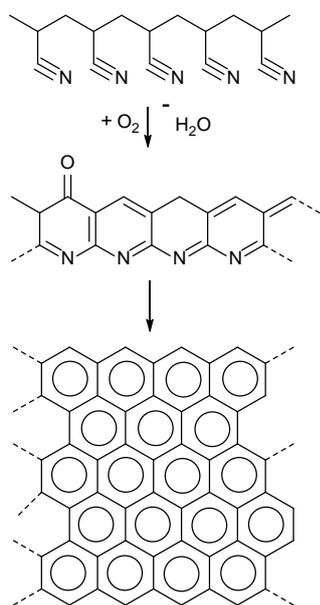
Base-catalyzed chemical reactions are important for the production of drugs, fragrances, and chemical intermediates.<sup>[1]</sup> From the viewpoints of economy and green

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 compared to solid acid catalysis.<sup>[1]</sup> So, the development of effective solid base catalysts is still an important issue.

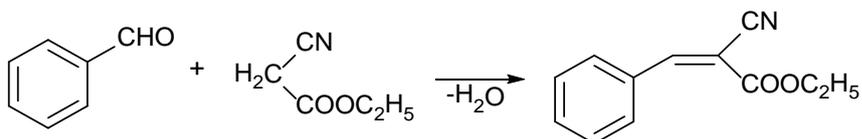
Recently, the use of N-doped carbon (N-carbon) materials as solid base catalysts has been reported. Von Dommele et al. and Wang et al. reported the preparation of N-doped carbon nanotubes by chemical vapor deposition using N containing compounds of nitriles, pyridine, or amines and showed that the obtained carbon nanotubes are effective as solid base catalysts for Knoevenagel condensation reactions.<sup>[2,3]</sup> Several groups reported the preparation of mesoporous graphitic carbon nitride materials by polymerization of cyanamide, dicyanamide, or melamine.<sup>[4]</sup> These carbon nitride materials were shown to be active catalysts for various reactions including Friedel-Crafts reaction, cyclization, coupling of CO<sub>2</sub> and epoxide, transesterification, and Knoevenagel condensation. Ma and co-workers prepared N-doped graphenes by a high temperature treatment of graphene with ammonia or acetonitrile and showed that those N-doped graphenes are active for a few oxidation reactions using an organic peroxide compound;<sup>[5]</sup> however, they did not examine the applicability of the N-doped graphenes for base-catalyzed reactions. Another method to prepare N-carbon materials is the ammoxidation of bulk carbon materials in which source carbon materials are treated at elevated temperatures in a mixture of NH<sub>3</sub> and air. Our group has also reported that N-carbons prepared by ammoxidation of commercial carbon black and activated carbon (AC) can act as solid base catalysts for Knoevenagel condensation and transesterification reactions.<sup>[6]</sup> X-ray photoelectron spectroscopy (XPS) measurements of N-carbons prepared showed the presence of a few different types of N species. The activity of N-carbon materials tended to increase with the amount of N doped and so the presence of N on their surface is significant for the genesis of the activity for the reactions.

Among the methods to prepare N-carbon materials described above, the ammoxidation is the easiest and applicable to prepare large quantities of N-carbon materials from commercially available carbons. 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.<sup>[7]</sup> The processes of the carbon fiber production from PAN involve three steps of oxidative stabilization, carbonization, and graphitization.<sup>[7]</sup> Scheme 1 represents the possible chemical reactions in the course of the oxidative stabilization and carbonization steps.<sup>[7,8]</sup> In the first step, PAN is calcined in air at few hundreds °C. This changes PAN to carbon in the ladder structure via oxidation, dehydrogenation, and cyclization. In the second step, the cyclized ladder structure grows in lateral direction via polycondensation, which is accompanied by the elimination of N atoms. Although PAN itself contains a large fraction of N atoms, most of them was unfortunately removed during the second step. So, if the ladder-structure carbon is ammoxidized, N-carbon containing a large amount of N species may be obtained. Considering this possibility, the present authors 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 (Scheme 2). The 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 have been examined by acid-base titration, XPS, and X-ray diffraction (XRD), from which the catalytically active working sites have been discussed. It has been 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 also an important factor determining the catalytic activity of N-carbon. The N-carbon catalysts prepared from PAN have been shown to be much more active than a few types of solid base catalysts reported so far.



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



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

## Results and Discussion

Table 1 lists the reaction results obtained with the carbon catalysts prepared and the quantities of basic sites on them. The calcined PAN samples gave low ECC yields (entries 1, 4, and 6), which were almost the same with the one obtained without any catalyst (c.a. 6%). So, the catalytic activity of the calcined PAN is practically negligible. When 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. When the ammoxidation was carried out at 400 °C for PAN-C500, PAN-C400, and PAN-C200, the activity was in an order of 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.

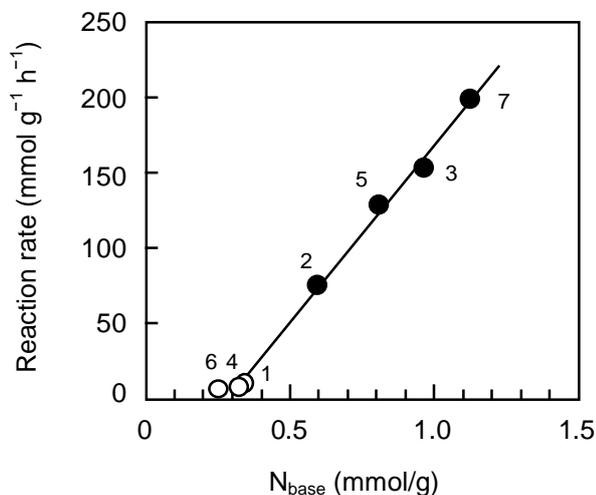
**Table 1.** Catalytic activities of carbon catalysts prepared from PAN for Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate<sup>[a]</sup> and the amount of basic sites on them.

Entry	Catalyst	ECC yield (%)	ECC formation rate (mmol g <sup>-1</sup> h <sup>-1</sup> )	N <sub>base</sub> (mmol/g)
1	PAN-C200	10	10	0.342
2	PAN-C200-AO400	76	75	0.592
3	PAN-C200-AO600	98	153 <sup>[b]</sup>	0.964
4	PAN-C400	8	8	0.321
5	PAN-C400-AO400	99	129 <sup>[b]</sup>	0.811
6	PAN-C500	7	7	0.249
7	PAN-C500-AO400	94	199 <sup>[b]</sup>	1.122

<sup>[a]</sup> Reaction conditions: catalyst 100 mg, benzaldehyde 9.9 mmol, ethyl cyanoacetate 9.4 mmol, 1-butanol 4 cm<sup>3</sup>, temperature 80°C, reaction time 1 h.

<sup>[b]</sup> Determined from reaction results using 30 mg of catalyst.

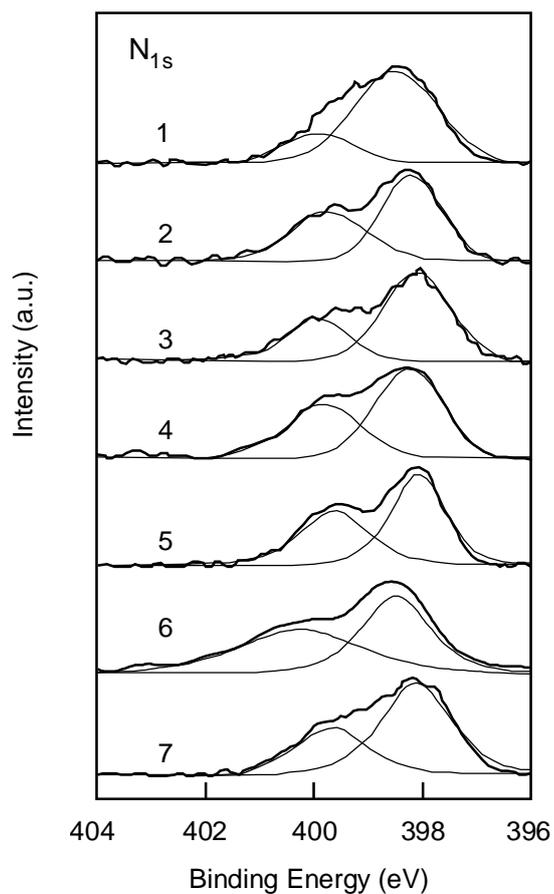
The numbers of basic sites (N<sub>base</sub>) on the carbon catalysts were determined by acid–base titration (Table 1). The calcined PAN possessed some amounts of basic sites and the ammoxidation treatment increased the number of basic sites on them. Figure 1 plots the catalytic activity of N-carbon against N<sub>base</sub>. The activity almost linearly increased as N<sub>base</sub> 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.



**Figure 1.** Relationship between the ECC formation rate and  $N_{\text{base}}$ . (●) Calcined and subsequently ammoxidized PAN and (○) calcined PAN. Numbers correspond to those in Table 1.

Surface of the carbon samples were analyzed by XPS. XPS spectra in the  $N_{1s}$  region are depicted in Fig. 2. The  $N_{1s}$  spectrum revealed the presence of pyridine-type N (398.5 eV), N(1), and pyrrole-/pyridone-type N (400 eV), N(2) (Scheme 3).<sup>[9]</sup> Their surface concentrations were determined from the deconvoluted spectra (Table 3). After the calcination at 200 and 400 °C, some amounts of N species originating in PAN could remain (entries 1, 4). Those amounts were not changed so much by the ammoxidation (entries 1-5). However, among the calcined PANs, PAN-C500 could give the N-carbon catalyst containing the largest amount of N species after the ammoxidation.

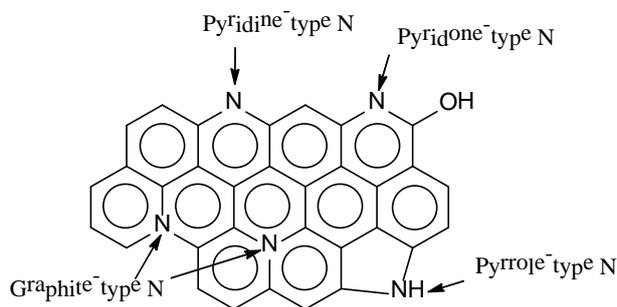
The relationship between the concentration of N species and the catalytic activity was examined. In Figure 3, the activity is plotted against the concentration of N(1) species. For N-carbon catalysts (black circles), the activity was found to increase with the concentration of N(1) species, although 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 (Fig. 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.<sup>[2]</sup> 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.



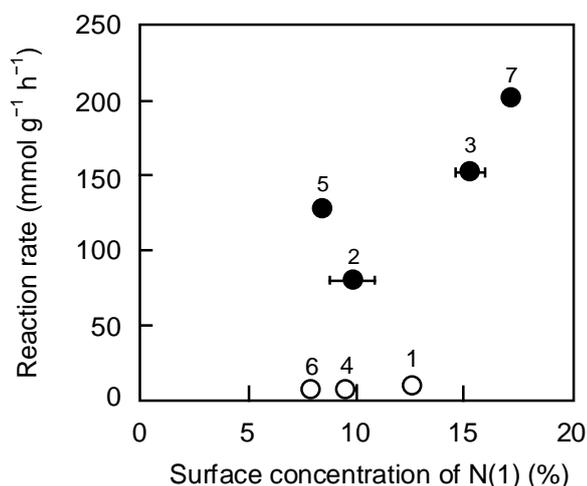
**Figure 2.**  $N_{1s}$  XPS spectra of carbon samples prepared from PAN. Numbers correspond to those in Table 1.

**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	7.9
3	PAN-C200-AO600	15.3	7.0
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

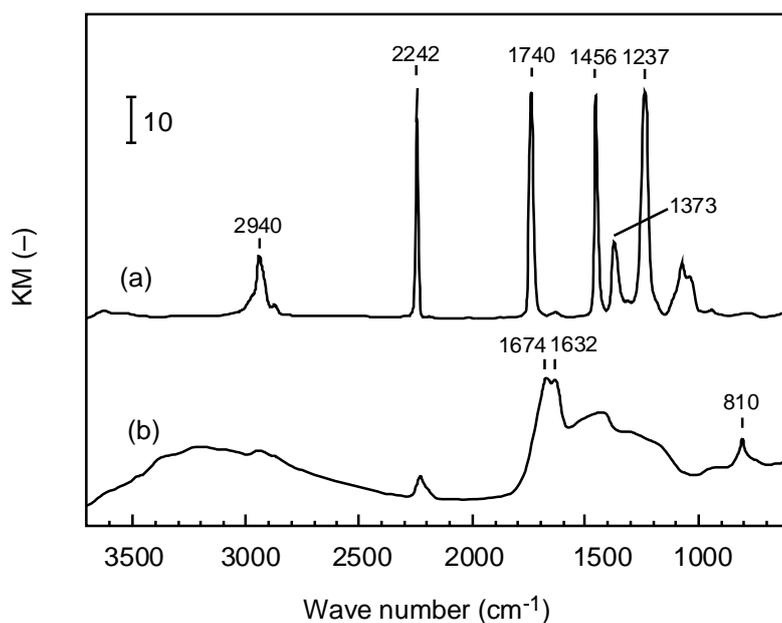


**Scheme 3.** Possible structures of N species doped on carbon.



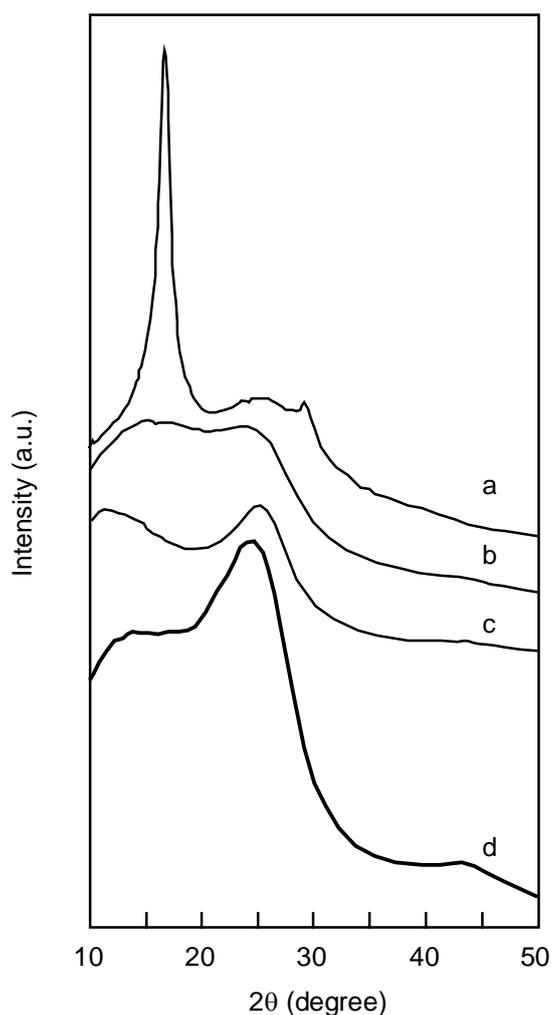
**Figure 3.** Relationship between the catalytic activity and the surface concentration of N(1) species. (●) Calcined and ammoxidized PAN and (○) calcined PAN. Numbers correspond to those in Table 1.

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 showed the absorption bands of CH<sub>2</sub> (2940 and 1456 cm<sup>-1</sup>), C≡N (2242 cm<sup>-1</sup>), C=O (1740 cm<sup>-1</sup>), CH (1373 cm<sup>-1</sup>), and C–C (1237 cm<sup>-1</sup>) groups.<sup>[8]</sup> After the calcination (Fig. 4b), the intensities of these bands were largely decreased and new absorption bands appeared at 1674, 1632, and 809 cm<sup>-1</sup>. Those new bands were ascribable to C=C stretching, C=N stretching, and C=C–H bending.<sup>[8]</sup> These observations strongly suggest that dehydrogenation and cyclization occur in the course of the calcination, resulting in the ladder structure as illustrated in Scheme 1.



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

Figure 5 illustrates XRD patterns of PAN, PAN-C200, PAN-C-200-AO400, and PAN-C200-AO600. PAN showed a strong peak at around  $17^\circ$ . 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  $400^\circ\text{C}$ , the peak around  $25^\circ$  ascribed to the (002) reflection peak of graphite<sup>[10]</sup> became stronger and sharper. Such effects on the (002) peak were more significant with the ammoxidation at  $600^\circ\text{C}$ . Similar results were also obtained with PAN-C400 and PAN-C500 (Fig. S2). Taking account of the above-mentioned carbonization processes in the carbon fiber 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.



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

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 already showed that pyridine molecule has 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 the latter.<sup>[6]</sup> 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 (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 electronic conjugated system of the graphite surface and N(1) species would give Lewis basic nature to neighboring C atoms whose number could be more than 10.<sup>[9d]</sup> 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 whose structures 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.

Table 3 compares the Knoevenagel condensation reaction rate of the most active PAN-C500-AO400 with those of several solid base catalysts reported so far. In our previous study, N-carbon catalysts were prepared from a commercial AC by the ammoxidation.<sup>[6]</sup> Among them, the most active N-carbon (AC-AO700) showed an ECC reaction rate of 60 mmol g<sup>-1</sup> h<sup>-1</sup> under the same reaction conditions as used in the present ones. Thus, PAN can give more active catalysts compared to 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.<sup>[6]</sup> This might be the reason for the lower catalytic activity of N-carbon prepared from AC compared to the N-carbons prepared from PAN. The catalytic activity of N-doped carbon nanotube<sup>[2,3]</sup> was also lower than PAN-C500-AO400 (entries 3, 4). Other types of solid base catalysts such as smectite, MgO, and a Mg-Al mixed oxide were also used for the same reaction.<sup>[11,12]</sup> 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 base 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. For N-doping on carbon materials, the dissociation of C-C bond is considered to be required.<sup>[13]</sup> The rate of the dissociation would be faster at higher temperatures for the N-doping. Table 2 also shows that the amount of N(1) species tended to decrease with increasing calcination temperature (entries 1, 4, and 6). The calcination at high temperatures would cause the evolution of N atoms, probably as HCN.<sup>[7]</sup> Despite of the smallest amount of N(1) species over PAN-C500, 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, about 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 defect sites than PAN-C200 and PAN-C400. Jansen and Bekkum propose N-doping mechanisms in which carboxylic groups contribute to the doping <sup>[13]</sup> and our previous work shows that O<sub>2</sub> molecules promote N-doping of AC using NH<sub>3</sub>.<sup>[6]</sup> Probably, the defect sites over the calcined PAN involve O species and some kind of those O species can promote N-doping. It is highly probable that the larger amount of those defect sites over PAN-C500 resulted in the larger amount of doped N species. At present, it is difficult 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.

**Table 3.** Comparison of catalytic activities of various solid base catalysts for Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate to ethyl cyanocinnamate (ECC).

Entry	Catalyst	Temperature <sup>[a]</sup> (°C)	ECC formation rate (mmol g <sup>-1</sup> h <sup>-1</sup> )	Reference
1	PAN-C500-AO400	80	199	Present study
2	AC-AO700 <sup>[b]</sup>	80	50	[6]
3	N-CNT <sup>[c]</sup>	78	17	[2]
4	N-CNT <sup>[c]</sup>	80	45	[3]
5	Na-SM <sup>[d]</sup>	60	8	[11]
6	MgO	60	29	[12]
7	HT <sup>[e]</sup>	60	3	[12]

<sup>[a]</sup> Reaction temperature

<sup>[b]</sup> Prepared from a commercial activated carbon by the ammoxidation at 700 °C.

<sup>[c]</sup> N-doped carbon nanotube.

<sup>[d]</sup> Na containing smectite.

<sup>[e]</sup> Mg-Al mixed oxide prepared from Mg-Al hydrotalcite (Mg/Al = 3).

## Conclusions

In the present study, N-carbon catalysts were prepared from PAN by the 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. XPS 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 solid base 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 (co-polymer 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 carried out by the ammoxidation. A weighed carbon sample (c.a. 150 mg) was placed in a quartz reactor and heated to 400 or 600°C in a stream of 90 vol.% NH<sub>3</sub>-air at 100 cm<sup>3</sup>/min. 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. where the first and the second numbers represent the temperatures for the calcination and for the ammoxidation, respectively.

The catalytic activity of those N-carbons prepared was tested for Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate. The reaction was carried out in a Teflon-lined autoclave (100 cm<sup>3</sup>) at 80°C for 1 h using 100 mg of the catalyst, 9.9 mmol of benzaldehyde, 9.4 mmol of ethyl cyanoacetate, and 4 cm<sup>3</sup> of 1-butanol solvent. 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 cm<sup>3</sup> 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 carried out with 30 mg of the catalyst.

The textural properties of the carbon samples prepared were measured by nitrogen adsorption/desorption (Quantachrome NOVA 1000). Surface area was determined by the Brunauer, Emmet and Teller's (BET) equation. X-ray photoelectron spectroscopy (XPS) measurements of the samples were made on JEOL JPS-9200 using monochromatic Al-K $\alpha$  radiation. The charge-up shift correction of the binding energy was made by using C<sub>1s</sub> 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 back ground. The numbers of basic sites on the carbon samples were determined by acid–base titration. About 0.1 g of the carbon sample was dispersed in 15 cm<sup>3</sup> 0.01 M HCL solution 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.

**Keywords:** carbon • nitrogen doping • solid base catalyst • ammoxidation • Knoevenagel condensation

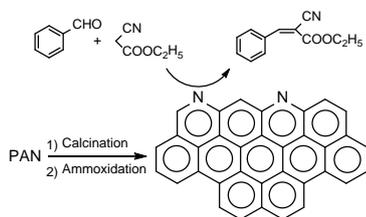
## References

- [1] H. Hattori, *Chem. Rev.* **1995**, 95, 537-558; K. Tanabe, W. Hölderich, *Appl. Catal. A: Gen.* 181 (1999) 399-434; H. Hattori, *Appl. Catal. A: Gen.* **2001**, 22, 247-259; R. J. Davis, *J. Catal.* **2003**, 216, 396-405; Y. Ono, *J. Catal.* **2003**, 216, 406–415.
- [2] S. van Dommele, K.P. de Jong, J.H. Bitter, *Chem. Commun.* **2006**, 46, 4859-4861.
- [3] L. Wang, L. Wang, H. Jing, N. Bing, *Catal. Commun.* **2001**, 15, 78-81.
- [4] F. Goettmann, A. Fischer, M. Antonietti, A. Thomas, *Angew. Chem. Int. Ed.* **2006**, 45, 4467-4471; F. Goettmann, A. Thomas, M. Antonietti, *Angew. Chem. Int. Ed.* **2007**, 46, 2717-2720; A. Thomas, A. Fischer, F. Goettmann, M. Antonietti, J.-O. Müller, R. Schlögl, J.M. Carlsson, *J. Mater. Chem.* **2008**, 18, 4893-4908; X. Jin, V.V. Balasubramanian, S.T. Selvan, D.P. Sawant, M.A. Chari, G.Q. Lu, A. Vinu, *Angew. Chem. Int. Ed.* **2009**, 48, 7884-7887; M. Bismillah, B.H. Min, Y.H. Mo, S.E. Park, *Green Chem.* **2011**, 13, 1416-1421; J. Xu, K. Shen, B. Xue, Y.X. Li, Y.

- Cao, *Catal. Lett.* **2013**, *143*, 600-609. J. Xu, K.Z. Long, T. Chen, B. Xue, Y.X. Li, Y. Cao, *Catal. Sci. Technol.* **2013**, *3*, 3192-3199.
- [5] W, Li, Y. Gao, W. Chen, P. Tang, W. Li, Z. Shi, D.S. Su, J. Wang, D. Ma, *ACS Catal.* **2014**, *4*, 1261-1266; Y. Gao, G. Hu, J. Zhong, Z. Shi, Y. Zhu, D.S. Su, J. Wang, X. Bao, D. Ma, *Angew. Chem. Int. Ed.* **2013**, *52*, 2109-2113.
- [6] N. Kan-nari, S. Okamura, S. Fujita S, J. Ozaki, M. Arai, *Adv. Synth. Catal.* **2010**, *352*, 1476-1484.
- [7] E. Fitzer, W. Frohs, M. Heine, *Carbon* **1986** *24*, 387-395; M.S.A. Rahaman, A.F. Ismail, A. Mustafa, *Carbon* **2007**, *92*, 1421-1232.
- [8] M.M. Coleman, G.T. Sivy, *Carbon* **1981**, *19*, 123-126; G.T. Sivy, B. Gordon, M.M. Coleman, *Carbon* **1983**, *21*, 573-578; H. Kakida, K. Tashiro, M. Kobayashi, *Polym. J.* **1996**, *28*, 30-34.
- [9] a) M.P. Woods, E.J. Biddinger, P.H. Matter, B. Mirkelamoglu, U.S. Ozkan, *Catal. Lett.* **2010**, *136*, 1-8; b) E. Raymundo-Piñero, D. Cazorla-Amorós, A. Linares-Solano, J. Find, U. Wild, R. Schlögl, *Carbon* **2002**, *40*, 597-608; c) S. Maldonals, S. Morin, K.J. Stevenson, *Carbon* **2006**, *44*, 1429-1437; d) T. Kondo, S. Casolo, T. Suzuki, T. Shikano, M. Sakurai, Y. Harada, M. Saito, M. Oshima, M.I. Trioni, G.F. Tantardini, J. Nakamura, *Phys. Rev. B* **2012**, *86*, 35436.
- [10] J.B. Aladekomo, R.H. Bragg, *Carbon* **1990**, *28*, 897-906; T.D. Shen, W.Q. Ge, K.Y. Wang, M.X. Quan, J.T. Wang, W.D. Wei, C.C. Koch, *Nanostruct. Mater.* **1996**, *7*, 393-399; Z.Q. Li, C.J. Lu, Z.P. Xia, Y. Zhou, Z. Luo, *Carbon* **2007**, *45*, 1686-1695.
- [11] S. Fujita, B.M. Bhanage, D. Aoki, Y. Ochiai, N. Iwasa, M. Arai, *Appl. Catal. A: Gen.* **2006**, *313*, 151-159.
- [12] M.J. Climent, A. Corma, S. Iborra, A. Velty, *J. Mol. Catal. A: Chem.* **2002**, *182-183*, 327-342.
- [13] R.J.J. Jansen, H. van Bekkum, *Carbon* **1994**, *32*, 1507-1516.

## Graphical abstract

### Layout 1

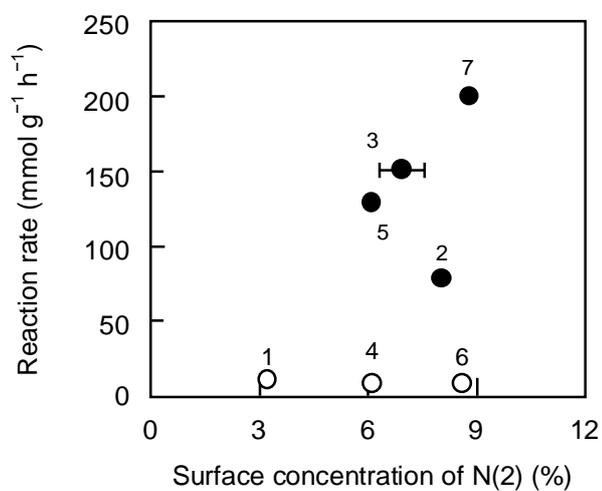


N-carbon catalysts highly active for Knoevenagel condensation have been prepared by the calcination and subsequent ammoxidation of polyacrylonitrile. The catalytic activity depended on both the calcination and ammoxidation temperatures. The significance of pyridine-type N atoms in large graphene structure for the catalytic activity has been suggested.

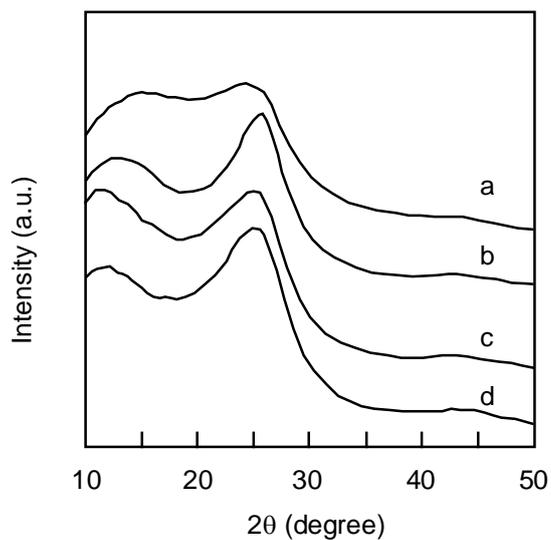
After the calcination, some amounts of N species originating in PAN could remain (entries 1, 4, 6). Those amounts were not changed so much by the ammoxidation. However, among the calcined PAN, PAN-C500 could give the N-carbon catalyst containing the largest amount of N species after the ammoxidation.

Left column

## Supporting Information



**Figure S1.** Relationship between the catalytic activity and the surface concentration of  $\text{N}(2)$  species. Numbers correspond to those in Table 1.



**Figure S2.** XRD patterns of (a) PAN-C400, (b) PAN-C400-AO400, (c) PAN-C500, and (d) PAN-C500-AO400.