[Regular Paper]

Activated Carbon Fibers Prepared from Quinoline and Isoquinoline Pitches

Isao MOCHIDA^{†1)*}, Kay Hyeok AN^{†1)}, Yozo KORAI^{†1)}, Takashi KOJIMA^{†2)},
Makoto KOMATSU^{†2)}, and Masaaki YOSHIKAWA^{†3)}^{†1)} Institute of Advanced Material Study, Kyushu University, Kasuga, Fukuoka 816-8580^{†2)} Corporate Research Laboratory, Mitsubishi Gas Chemical Co., Inc., Tsukuba, Ibaraki 300-4247^{†3)} Research & Development Center, Osaka Gas Co., Ltd., Torishima, Konohana-ku, Osaka 554-0051

(Received May 14, 1998)

Nitrogen enriched activated carbon fibers (ACFs) were prepared from isotropic quinoline and isoquinoline pitches produced by the catalytic action of HF/BF₃ through spinning, stabilization, carbonization, and oxidative activation. The pitches exhibited excellent spinnability, and the resultant fibers had mechanical properties comparable to those of commercial fibers. The surface areas and nitrogen contents of the ACFs, obtained hereby were 740–860 m²/g and 4–5.6%, respectively, at around 50 wt% of burn-off. FT-IR and XPS analyses identified the surface oxygen and nitrogen functional groups on the stabilized and activated fibers. The ACFs from isoquinoline pitch (IQP-ACF) exhibited higher basicity (1.3 meq/g) than commercial ACFs of similar surface areas (0.68 and 0.25 meq/g for PAN (FE-300) and coal tar pitch (OG-8A) based ACFs, respectively) due to a higher basic nitrogen content on the surface. The activation appears to expose basic nitrogen atoms, which were located under the surface. The basicity of ACF from quinoline pitch (QP-ACF) was much lower than that of IQP-ACF, however, QP-ACF adsorbed 74 mg/g of SO₂, which was 1.4 and 2.3 times higher than that over FE-300 and OG-8A. In contrast, IQP-ACFs showed less adsorption of SO₂ than that of QP-ACF and FE-300, but more than that of OG-8A. Oxidation activity of ACF surface may participate in the adsorption of SO₂ in the form of SO₃ or H₂SO₄. The oxygen functional groups under the influence of neighboring nitrogen atoms may be the active sites for the oxidative adsorption.

1. Introduction

The surface functional groups and compositions of activated carbon fibers (ACF) are key properties that control the fibers' practical performance. There are several reports and approaches that describe the modification of carbon fiber surfaces by oxidation, sulfonation, and nitrogenation^{1)–3)}. One approach is to include the designed functionality as a building block in the synthesis of the fiber. For example, the oxidative stabilization of polyacrylonitrile has been proved to induce the pyridine ladder in the stabilized fiber^{4),5)}.

The authors have reported the acidic oligomerization of quinoline and isoquinoline into pitches, which can be used to produce a coke of high nitrogen content^{6),7)}. Hence, the spinning, stabilization, carbonization, and activation of such pitches are also expected to provide active carbon fibers with high nitrogen contents. However, when AlCl₃ is used as the condensation catalyst, it is hard to remove it from the pitch, disturbing the effective preparation of the fibers⁸⁾. In comparison, Fei *et al.* have produced nitrogen-rich ACF from a shale oil residue without using a catalyst⁹⁾. As it is a

derivative of natural product, its nitrogen species are difficult to control.

In the present study, the preparation of carbon fibers (CF) and that of activated carbon fibers (ACF) were examined using isotropic pitches produced from quinoline and isoquinoline by HF/BF₃, which is recovered and regenerated completely^{10)–12)}. Such ACFs inherit nitrogen functionality as carried by the starting substrates. Increase in the surface area by activation can increase its basicity by exposing the nitrogen atoms, which are located under the surface of the fiber. A previous report has described that the coke from isoquinoline showed much higher basicity than that from quinoline⁶⁾. Hence, the production of CF and ACF with high basicity can be expected from an isoquinoline pitch precursor. The adsorption of SO₂ on these ACFs was also examined.

2. Experimental

2.1. Preparation of Nitrogen-containing Pitches by HF/BF₃ Catalyst

Nitrogen containing-pitches were prepared from commercially available quinoline and isoquinoline by the condensation reaction in the presence of HF/BF₃ at

* To whom correspondence should be addressed.

Table 1 Some Properties of QP and IQP

Pitch	S.P. [°C]	Yield [wt%]	C.Y. [wt%]	Elemental analysis [wt%]					Solubility [wt%]			O.T.
				C	H	N	H/C	N/C	BS	BI-PS	PI	
QP	216	44	82	83.84	4.32	10.35	0.618	1.106	20.0	50.0	30.0	Isotropic
IQP	230	45	76	84.22	4.02	6.76	0.573	0.069	28.8	68.4	2.8	Isotropic

S.P.: softening point, C.Y.: carbon value at 600°C, O.T.: optical texture.

230°C and 340°C under 2-3 kg/cm² and 7-10 kg/cm² of autogenous pressure, respectively, in an autoclave for 4 h. After the reaction, HF/BF₃ and unreacted quinoline or isoquinoline were removed by distillation. Some properties of the resultant pitches are summarized in Table 1.

2.2. Spinning, Stabilization and Activation

The nitrogen-containing pitches were spun into fibers of *ca.* 12-14 μ m in diameter with a steel spinneret under nitrogen pressure of 2.0-6.0 kg/cm². The diameter and length of the nozzle were both 0.25 mm ($L/D = 1$) for quinoline pitch (QP), and both 0.5 mm ($L/D = 1$) for isoquinoline pitch (IQP). The pitch fiber derived from QP (QP-PF) was oxidatively stabilized at 300°C in air containing 2 vol% of NO₂ to accelerate the stabilization at lower temperatures. The IQP-PF was stabilized at two different temperatures, 280°C and 300°C, in air containing 2 vol% of NO₂. The stabilized fibers were carbonized at 600, 900, and 1200°C for 1 h in an argon flow. The heating rate was 10°C/min. The stabilized fibers were activated with steam at 850°C for 7-15 min. Surface areas were measured by the BET method using N₂ adsorption isotherms at 77 K.

2.3. Characterizations of the Precursor Pitches and Fibers

FT-IR (JEOL, JIR-100) spectra of the stabilized and activated carbon fibers were observed using the KBr disc procedure.

Tensile strength, Young's modulus, and strain to break were measured at room temperature using monofilaments according to the procedure defined in Japanese Industrial Standard (JIS R-7601) using an Instron type tensile testing machine (Instron 4200 series) with a head speed of 0.5 mm/min.

XPS spectra were obtained by an ESCA 100 (Shimadzu Co.) spectrometer using non-monochromatic Mg K α radiation (1253.6 eV) at 10 kV and 30 mA.

2.4. Titration and SO₂ Adsorption

Back titration experiments were carried out using a pH meter (HI 9025C) to measure the basicity of nitrogen-containing ACFs. About 0.1 g of ACF was immersed in aq. 0.1 N HCl. The mixture was titrated with aq. 0.1 mol/l NaOH after mechanical stirring for 24 h. A blank experiment was carried out by titrating aq. 0.1 mol/l HCl without immersing the ACF.

The SO₂ adsorption capacity of ACFs was measured by gravimetric analysis at 30°C using a flow of dry He

containing 2000 ppm of SO₂. In these experiments, the ACF samples were first pretreated by heating at 150°C for 1 h to remove any water that might be present on the samples.

3. Results

3.1. Properties of High Nitrogen Content Pitches

The yield, softening point, solubility, elemental analyses and optical texture of the pitches are summarized in Table 1. The pitches were derived from quinoline and isoquinoline by catalytic action of HF/BF₃ and both exhibited perfect isotropy on the optical microscope. The N/C atomic ratio of the quinoline pitch (QP) was similar to that of quinoline, indicating that there had been no denitrogenation from the heterocyclic ring during the condensation. For QP showed higher H/C ratio and lower solubility in benzene and pyridine were shown than those for isoquinoline pitch (IQP).

Isoquinoline was found to lose nitrogen during condensation, reducing the N/C ratio from 0.11 to 0.07. The main fraction of the IQP was benzene insoluble

(a) and (b) QP-SF, (c) and (d) IQP-SF-280, (e) and (f) IQP-SF-300.

Fig. 1 Scanning Electron Micrographs of Stabilized Fibers Derived from QP and IQP

Table 2 Some Properties of Stabilized Fibers and Activated Carbon Fibers Derived from QP and IQP

Run No.	Elemental analysis [wt%]							B-off [wt%]	S.A. [m ² /g]	N.P [ml/g]	Basicity [meq/g]	SO ₂ [mg/g]
	C	H	N	O(dif.)	H/C	N/C	O/C					
QP-ACF ^{a)}	80.8	1.7	5.6	12.0	0.25	0.06	0.11	46.6	738	43.2	0.70	74
(QP-SF) ^{b)}	71.8	3.0	11.5	13.4	0.51	0.14	0.14					
IQP-ACF-280 ^{a)}	79.0	1.8	3.9	15.3	0.28	0.04	0.15	49.6	862	42.5	0.75	43
(IQP-SF-280) ^{b)}	72.9	2.9	7.6	15.3	0.48	0.09	0.16					
IQP-ACF-300 ^{a)}	76.3	2.0	4.5	17.3	0.31	0.05	0.17	52.1	750	38.7	1.13	38
(IQP-SF-300) ^{b)}	70.2	2.6	8.5	17.3	0.45	0.10	0.18					
FE-300	78.1	1.4	4.5	16.0	0.22	0.05	0.15	—	850	43.0	0.68	53
OG-8A	91.2	0.9	0.6	7.0	0.12	0.01	0.06	—	840	47.5	0.25	32

a) Activated fibers: activated with steam at 850°C for 15 min(QP-CF, IQP-CF-280) or 7 min(IQP-CF-300). b) Stabilized fibers. FE-300: polyacrylonitrile based ACF(Toho Rayon Co.). OG-8A: Coal tar pitch based ACF(Osaka Gas Co.). B-off.; Burn-off, S.A.; surface area, N.P; amount of 0.1 N NaOH necessary for adjusting the neutralizing point, SO₂; amount of SO₂ absorbed on ACF at 30°C in He containing 2000 ppm of SO₂.

(BI) but pyridine soluble(PS). The pyridine insoluble(PI) fraction, however, was very small.

3. 2. Carbon Fibers from High Nitrogen-content Pitches

The shapes and surfaces of the stabilized fibers derived from QP and IQP after stabilization (QP-SF and IQP-SF, (a), (b), respectively) under SEM are shown in **Fig. 1**. IQP-SF-280 and -300, (c), (d) possessed a smooth surface, while that of QP-SF was slightly rough, indicating a more facile spinnability of IQP.

Elemental analyses of the stabilized fibers are summarized in **Table 2**. QP-SF contained 11.5%, and IQP-SF-280 and IQP-SF-300 contained 7.6-8.5% nitrogen, respectively. QP-SFs had a higher content of nitrogen than IQP-SFs, which, however, contained more oxygen. It is to be noted that IQP-SF-300 contained slightly more nitrogen than IQP-SF-280. It is pointed out that a less extent of condensation with IQP requires stabilization with more reactive NO₂.

Weight losses of QP-SF and IQP-SFs during carbonization were 18-39 wt% and 24-47 wt% in the temperature range from 600 to 1200°C, respectively. QP-SF gave higher carbonization yield than IQP-SFs, indicating that a higher content of insoluble fraction of larger molecular weight in QP may be responsible for the higher carbonization yield of the resultant fiber.

The behavior of nitrogen during carbonization is illustrated in **Fig. 2**. The nitrogen in QP-SF decreased much more rapidly over the range from 600 to 900°C than that both in IQP-SF-280 and -300. As a result, QP-carbon fiber(QP-CF) and IQP-carbon fiber(IQP-CF-280) had the same N/C ratio after carbonization at 900°C. The IQP-CF-300 maintained a higher N/C ratio than IQP-CF-280 during carbonization, although denitrogenation of the former fiber was greater in the range of from 900 to 1200°C.

Table 3 summarizes some mechanical properties of the carbon fibers carbonized at 950°C. Since com-

Fig. 2 Variation of N/C in CF Derived from QP and IQP as Function of Carbonization Temperature

Table 3 Some Mechanical Properties of Nitrogen Containing Carbon Fibers Carbonized at 950°C for 1 h

CF	Average diameter [μm]	Tensile strength [MPa]	Young's modulus [GPa]	Elongation [%]
QP-CF	13.8	106	7	1.5
IQP-CF-280	13.6	78	4	1.8
IQP-CF-300	11.9	92	4	2.2

mercially available isotropic pitch based carbon fibers are reported to have 70-100 MPa for tensile strength and 4-10 GPa for modulus, the mechanical properties of QP and IQP based carbon fibers and commercial fibers are competitive. The fiber derived from QP showed higher tensile strength and modulus than those of the fiber from IQP.

3. 3. Activation

Figure 3 illustrates the extent of burn-off as a function of activation time at 850°C. Both burn-offs of QP-ACF and IQP-ACF-280 increased linearly with

Fig. 3 Weight Loss of QP-SF and IQP-SF as Function of Activation Time at 850°C

Fig. 4 Surface Area of QP-SF and IQP-SF as Function of Burn-off at 850°C

activation time, although the extent of burn-off was slightly higher for the latter. The IQP-SF-300 (IQP-ACF-300) showed the largest burn-off among the three fibers. After only 7 min of activation, the burn-off increased to 52 wt% and it reached 62 wt% by 10 min and then became much less.

Figure 4 illustrates the changes in the surface area as a function of burn-off. The surface area of QP-ACF increased more rapidly at low burn-offs than that of IQP-ACF-280, whose surface area increased with burn-off, and the surface area of IQP-ACF-300 increased very rapidly at high burn-offs. Shapes and surfaces ACFs under SEM are shown in **Fig. 5**. These ACFs showed smooth surface and diameters almost the same as those of the respective stabilized fibers even after burn-off, indicating that very small pores were introduced on the ACF surfaces. **Table 2** summarizes some properties of the activated carbon fibers at a similar degree of burn-off around 50 wt%. The surface areas of the activated carbon fibers here

(a) and (b) QP-ACF, (c) and (d) IQP-ACF-280, (e) and (f) IQP-ACF-300.

Fig. 5 Scanning Electron Micrographs of the ACFs Derived from QP and IQP

observed in the range from 740 to 860 m²/g, IQP-ACF-280 were the highest. The nitrogen content of IQP-ACF-300 was higher than that of IQP-ACF-280, but lower than that of QP-ACF by 1%. **Table 2** also includes the properties of two commercial ACFs namely, polyacrylonitrile based (FE-300, Toho Rayon Co.) and coal tar pitch based (OG-8A, Osaka Gas Co.). The surface areas of the ACFs here observed were much the same as those of commercial ones at almost same burn-off level of 50%.

3.4. Structural Characteristics of Stabilized Fibers and ACFs

Figure 6 illustrates the FT-IR spectra of stabilized (**Fig. 6 (A)**) and activated carbon fibers (**Fig. 6 (B)**). The QP-SF showed intense peaks at 1253, 1176, and 1120 cm⁻¹ due to the presence of phenoxyl (Ar-O), etheric (C-O-C), and hydroxyl groups (C-OH), respectively, and a shoulder at 1710 cm⁻¹ (carbonyl), indicating oxygenation during stabilization.

The bands at 1710 cm⁻¹ for IQP-SF-280 and -300 were more intense, indicating a higher content of carbonyl groups, although the bands in the range 1253 to 1120 cm⁻¹ were much smaller than those of QP-SF.

Upon carbonization and activation, the band at 1710 cm⁻¹ decreased, and broad intense bands appeared in the range 1300-1100 cm⁻¹ on IQP-ACFs, indicating that carbonyl groups (1710 cm⁻¹) were degraded by activation while phenoxyl and C-O-C groups were introduced on the IQP-ACFs. The major oxygen functional groups of QP-ACF were not changed by

activation. However, the total amount of oxygen functional groups decreased.

The C_{1s} spectra of stabilized and activated carbon fibers obtained by XPS analyses are shown in **Figs. 7 (A)** and **7 (B)**. The C_{1s} spectra of the stabilized fibers

Fig. 6 The FT-IR Spectra of Stabilized Fibers(A) and Their ACFs(B)

clearly indicate that the main oxygen functional groups are carbonyl groups the IQP-SFs and ether groups(C-O-C) for QP-SF. The carboxyl groups, which could not be detected by FT-IR on QP-SF, were found in the XPS spectra of QP-SF as well as of IQP-SF. The oxygen functional groups after activation are shown in **Fig. 7 (B)**. The overall oxygen functional groups on the surface were lower in concentration than those of the stabilized fibers. The width at a half maximum(FWHM) of the main C_{1s} peak of ACFs was smaller than that for the stabilized fibers. The relative intensities of O_{1s} and N_{1s} against C_{1s} calculated from the XPS spectra are summarized in **Table 4**. The nitrogen content of the ACF surface increased compared with while the oxygen content decreased, comparing to the corresponding stabilized fibers. The activation may eliminate some oxygen functional groups introduced during stabilization, and expose the nitrogen atoms located under the surface of the stabilized fiber.

3. 5. Basicity of Nitrogen Rich ACFs

Figure 8 illustrates the back titration curves of ACFs with NaOH. The blank curve was obtained by titration of aq. HCl(0.1 N) in the absence of ACF. The basicities of commercial ACFs, FE-300 and

Table 4 Composition of Stabilized Fibers and Their Activated Fibers from XPS Spectra

Run No.	C_{1s}	N_{1s}	O_{1s}	N_{1s}/C_{1s}	O_{1s}/C_{1s}
QP-CF	74.15	10.27	15.58	0.119	0.158
IQP-CF-280	75.85	5.39	18.76	0.061	0.185
IQP-CF-300	74.75	5.84	19.41	0.067	0.194
QP-ACF	74.89	14.08	11.03	0.161	0.110
IQP-ACF-280	78.24	12.31	9.45	0.135	0.091
IQP-ACF-300	73.29	14.05	12.66	0.164	0.129

Fig. 7 XPS C_{1s} Spectra of Stabilized Fibers(A) and Their ACFs(B)

(A) QP-ACF, IQP-ACF-280, and IQP-ACF-300, (B) FE-300 and OG-8A.

Fig. 8 Titration Curves of Various ACFs after 0.1 g of ACF Was Immersed for 24 h in 5 ml of aq. HCl(0.1 N)

OG-8A were also included to compare with those of QP-ACF and IQP-ACFs.

The amount of NaOH(0.1 N) necessary for neutralization increased in the following order; IQP-ACF-300 > IQP-ACF-280 $\approx$ QP-ACF $\approx$ FE-300 > OG-8A. The basicities calculated from the amount of NaOH are summarized in Table 2. The basicity of IQP-ACF-300(1.13 meq/g) was the highest among the ACFs, while OG-8A was lowest (0.25 meq/g). The IQP-ACF-280(0.75 meq/g) and QP-ACF (0.70 meq/g) both possessed basicity similar to that of FE-300(0.68 meq/g). The basicities of QP-ACF and IQP-ACFs were larger by about four times than those of their coke produced at 600°C, which had basicities of 0.19 meq/g for QP-coke and 0.28 meq/g for IQP-coke, respectively, as described previously in paper⁶⁾.

3. 6. Adsorption of SO₂

The amounts of SO₂ adsorbed on the ACFs at 30°C from 2000 ppm of SO₂ in helium are summarized in Table 2. The QP-ACF adsorbed 74 mg/g of SO₂, which was larger than that on FE-300 and that on OG-8A by 1.4 and 2.3 times, respectively, although its

surface area was smaller.

The IQP-ACF-280 and -300 adsorbed 43 and 38 mg/g of SO₂, respectively, however both amounts were certainly less than those adsorbed on QP-ACF and FE-300 in spite of their greater basicity. Other than acid-base interaction is suggested.

4. Discussion

Nitrogen-containing pitches with excellent spinnability properties were successfully prepared from quinoline and isoquinoline by the condensation reaction in the presence of HF/BF₃ that suggested future commercialization of such pitches.

The present study has revealed that nitrogen-rich ACFs derived from QP and IQP possess very high basicity. The nitrogen contents in the ACFs decreased by 47-60% of those in their stabilized fibers upon activation. However, the ACFs showed much higher basicity than the corresponding coke of higher nitrogen content produced from the same pitch. It is evident that the activation uncovered the basic nitrogen atoms, which were otherwise hidden under the surface. The XPS data proved that nitrogen atoms were concentrated on the surface of the fibers during activation, although the total nitrogen contented, observed by elemental analysis decreased. The surface-bond nitrogen atoms, which displayed high basicity might be useful as adsorption and activation sites in base-catalyzed reactions.

The concentration of surface-bond nitrogen atoms on the three ACFs analyzed by XPS were similar(Table 4). However, IQP-ACFs exhibited much higher basicity than QP-ACF. Different locations of the nitrogen in quinoline and isoquinoline rings appeared responsible. The nitrogen in quinoline could be captured in the condensed ring because of its alpha position, while that in isoquinoline can be basic because of its beta-position in spite of the ring condensation as was reported in papers^{6),7)}. The nitrogen atoms captured in the condensed ring will not show basicity unless their lone pair electrons are liberated.

SO₂ adsorption may reflect the ability of the ACFs to promote oxidation as well as their basicity because SO₂ can be adsorbed in the form of SO₃ or H₂SO₄^{13),14)}. The greater adsorption capacities of QP-ACF and FE-300 than those of IQP-ACFs and OG-8A may indicate that the nitrogen atom according to its location¹⁵⁾ in the ring influences the oxidation activity of the oxygen functional groups because the elemental composition of ACF surface is much the same.

The stabilization temperature of IQP-SFs influenced the composition and properties of IQP-CFs and IQP-ACFs; moreover, however temperatures allowed 2% more oxygen up-take upon stabilization, improved the tensile strength of the resultant carbon fiber, and left

more oxygen and nitrogen on the resultant ACF, which led to greater basicity. Higher temperatures may promote the oxidative condensation at stabilization to maintain a better alignment of carbon planes and to stabilize the nitrogen containing-rings by dehydrogenation and coupling of hexagonal planes. Such structure of the stabilized fiber may be inherited in the carbonized fiber of better tensile strength and of more nitrogen content.

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要 旨

キノリンおよびイソキノリンピッチから調製した活性炭素繊維

持田 勲^{†1)}, 安 啓熾^{†1)}, 光来要三^{†1)}, 小島 孝^{†2)}, 小松 眞^{†2)}, 吉川正晃^{†3)}

^{†1)} 九州大学機能物質科学研究所, 816-8580 福岡県春日市春日公園 6-1

^{†2)} 三菱ガス化学(株)総合研究所, 300-4247 茨城県つくば市和台 22

^{†3)} 大阪ガス(株)開発研究所, 554-0051 大阪市此花区西島 6-19-9

キノリンおよびイソキノリンを HF/BF₃ で重合した等方性のピッチを紡糸, 不融化, 炭化, 賦活して窒素濃度の高い活性炭素繊維を調製した。ピッチの紡糸性は極めて良く, また生成した活性炭素繊維の機械的性質は上市されているものに匹敵する性能を示した。本実験で製造した炭素繊維の表面積, 窒素含有率は, 50 wt% 程度のバーンオフでそれぞれ 740 ~ 860 m²/g および 4 ~ 5.6% であった。不融化および賦活した繊維の表面には酸素および窒素官能基が存在することが FT-IR と XPS で確かめられた。イソキノリンピッチから製造した活性炭素繊維 (IQP-ACF) は表面に塩基性の窒素が多く, 既に上市されているほぼ同程度の表面積のポリアクリロニトリル系の FE-300 や

ピッチ系の OG-8A の塩基性 (それぞれ 0.68 および 0.25 meq/g) より強い塩基性 (1.3 meq/g) を示した。賦活により内部の窒素が表面に露出されたものと思われる。キノリンピッチから製造した活性炭素繊維 (QP-ACF) は IQP-ACF より塩基性はかなり弱い, 74 mg/g の SO₂ を吸収し, これは FE-300 や OG-8A のそれぞれ 1.4 および 2.3 倍に達した。これに対し, IQP-ACF の SO₂ 吸着量は FE-300 より少なかったが, OG-8A より大きかった。これは吸着 SO₂ を SO₃ や H₂SO₄ に転換する酸化活性に違いがあるため, 窒素官能基の近傍にありその影響を受ける酸素官能基が酸化的吸着の活性点であろう。

Keywords

Nitrogen compound, Polynuclear aromatics, Quinoline, Isoquinoline, Activated carbon fiber