Pitch Based Activated Carbon Fibers from Quinoline and Isoquinoline

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1. INTRODUCTION

Active carbons, which carrying its large amount of micropore and high surface area, are widely used for gas purification and separation, de-odorization, and water purification as the adsorbents and catalyst supports. They are usually in pelletized, granular, powdered, or molded form.

Resent development of active carbons in fiber form(activated carbon fiber, ACF) is broadening applications of active carbons due to its unique characteristics. Thin-fiber shape assures fast adsorption and desorption kinetics compared with pelletized or granular active carbons, reducing the volume of adsorption vessel. Unique pore structure of ACF is the origin of this characteristic.

Recently, the outstanding properties of ACF justify its high price in wide areas. For example, purification of atmosphere and water, capture and recovery of solvent[1,2], de-ordering[3], methane storage[4], electrodes for Li-battery[5], double layer capacitor[6] and fuel cell[7], CO2 capture[8], and gas separation[9].

Pollution of atmosphere and water is still a major environmental problems in the developed as well as developing countries. Active carbons have already applied for removal of SOx and NOx. Recently, ACF has received much attention in the application for the environmental protection.

The surface nitrogen functional groups of ACFs play important roles in controlling the properties and performances. Even very small content of nitrogen atoms on ACF surface can influence significantly the surface chemical and electrochemical properties, which are directly related with their performances.

The effects of nitrogen functional groups on adsorption properties and catalytic activity of active carbon and ACF have been studied extensively by many authors. Mochida et al. have reported remarkable catalytic performances of PAN based ACFs, which carry 3-10 wt% of nitrogen atoms, for the adsorption of SO_2, removal of SOx, and the reduction of NO with NH_3, although the performances depended on the kind of PAN-ACF and post-treatment[10].

Juntgen et al.[11] reported that relationship between NO reduction activity and the nitrogen content of the active carbon. Treatment of the carbon at elevated temperatures by NH_3 has resulted in improved SCR(selective catalytic reduction) activity, which increase linearly with nitrogen content of treated carbon between 1 and 3 wt%. Above at this level the enhancement was saturated.

Mochida[12] found that PAN based ACF had most excellent catalytic activity among ACFs for the dehydrochlorination of 1,2-dichloroethane into vinyl chloride. The conversion and selectivity over PAN based ACF at 633K after two hours were 50% and 99.9%, respectively. In this reaction, the initial catalytic activity of PAN based ACFs correlated with their nitrogen content.

In the present study, the preparation of activated carbon fibers was examined, using isotropic pitches produced from quinoline and isoquinoline by the aid of HF/BF_3 which is recovered and regenerated completely[13]. Such ACFs inherit the nitrogen functionality as carried by the starting substrates. Increasing the surface area by activation can increase its basicity, by exposing nitrogen atoms which are located under the surface of the fiber.

Hence the production of ACF with high basicity can be expected from quinoline and isoquinoline pitch precursor. The adsorption of SO_2 was also examined on these ACFs.

2 EXPERIMENTAL

2.1 Preparation of nitrogen-containing pitches by HF/BF_3 catalyst

Nitrogen containing-pitches were prepared from commercially available quinoline and isoquinoline by the condensation reaction in the presence of HF/BF_3 at 503 and 613K for 4hr under 2 - 3 and 7 - 10 kg/cm² of autogenous pressure, respectively, in an autoclave. After the reaction, HF/BF_3 and unreacted quinoline or isoquinoline were removed by distillation.

2.2 Spinning, stabilization, and activation

The nitrogen-containing pitches were spun into fibers of ca. 12 ~ 14μm in diameter under nitrogen pressure of 2.0 - 6.0 kg/cm² from a steel spinneret. The pitch fiber derived from QP(QP-PF) was oxidatively stabilized at 573K in air containing 2 vol.% of NO_2. The IQP-PF was stabilized at two different temperatures of 553 and 573K in air containing 2 vol.% of NO^2. The stabilized fibers were activated with steam at 1123K for 7 - 15 min. Surface areas were measured according to the BET method using N_2 adsorption isotherms at 77K.

2.3 Titration and SO_2 adsorption

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

The SO_2 adsorption capacity of the ACFs was measured by gravimetric analysis at 303K using a flow of dry He containing 2000 ppm of SO_2. In these experiments, the ACF samples were first pretreated by heating to 150Åé for 1hr to remove any water that might be present on the ACF.

3 RESULTS AND DISCUSSION

3.1 General properties of nitrogen containing-pitches

The yield, softening point, solubility, elemental analyses and optical texture of the pitches are summarized in Table 1. Both pitches were derived from quinoline and isoquinoline by the catalytic action of HF/BF_3 and both exhibited perfect isotropy under the optical microscope. The N/C of the quinoline pitch(QP) was similar to that of quinoline, indicating that there had been no denitrogenation of the heterocyclic ring during condensation. The QP showed a higher H/C ratio and lower solubility in benzene and pyridine than the 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 BI-PS, while the PI fraction was very small.

3.2 Activation

The stabilized fibers were activated with steam at 1123K for 7 - 15 min.

Figure 1 illustrates the extent of burn-off as a function of activation time. The burn-off of QP-ACF(from QP-SF) and IQP-ACF-280(from IQP-SF-280) both increased linearly with activation time, although the extent of burn-off was slightly higher for the latter than the former. The IQP-ACF-300(from IQP-SF- 300) showed the largest burn-off among

the three fibers; after only 7 min of activation increased, the burn-off to 52 wt%; the burn-off reached 62% after 10 min and then became much slower.

Figure 2 illustrates the changes of surface area as a function of burn-off. The surface area of QP-ACF increased more rapidly at low burn-offs than those of IQP-ACF-280 and 300. The surface area of IQP-ACF-300 increased very rapidly at high burn-offs. The surface area of IQP-ACF-280 increased monotonously with burn-off.

Table 2 summaries some properties of the activated carbon fibers at a similar degree of burn-off around 50 wt%. The surface areas of the present activated carbon fibers were between 740 to 860 m2/g, IQP-ACF-280 showing the highest surface area. 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 properties of two commercial ACFs, polyacrylonitrile based(FE-300, Toho Rayon) and pitch based(OG-8A, Osaka Gas) ones. The surface areas obtained with the present ACFs were much the same to those of commercial ones.

No significant changes in the shape and surface of the fibers were observed after the activation

3.2 Basicity of nitrogen rich ACFs

Figure 3 illustrates the back titration curves of the ACFs with NaOH. The blank curve was obtained by the titration of aq. HCl(0.1N) in the absence of ACF. The basicities of commercial ACFs, FE-300 and OG-8A, were also included to compare those of QP-ACF and IQP-ACFs. The amount of NaOH(0.1N) necessary for neutralization increased in the following order; IQP-ACF-300, IQP-ACF-280, QP-ACF ,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 largest among the ACFs, while OG-8A was least basic(0.25meq/g). The QP-ACF-280(0.75 meq/g) and QP-ACF (0.70 meq/g) possessed similar basicity 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 873K which had basicities of 0.19 meq/g for QP-coke and 0.28 meq/g for IQP-coke, respectively.

3.3 Adsorption of SO_2

The amounts of SO_2 adsorbed on the ACFs at 303K from 2000 ppm of SO_2 in helium are summarized in Table 2. The QP-ACF adsorbed 74 mg/g of SO_2 which was larger than those on FE-300 and OG-8A by 1.4 and 2.3 times, respectively, in spite of the fact that its surface area was smaller.

The IQP-ACF-280 and 300 adsorbed 43 and 38 mg/g of SO_2, respectively, both of which were certainly less than those on QP-ACF and FE-300 in spite of larger basicity. Other than acid-base interaction is suggested.

4. CONCLUSION

Nitrogen enriched ACFs were succesfully prepared from isotropic quinoline and isoquinoline pitches. The ACFs exhibted higher basicity and adsorption amount of SO_2 than commercial ACFs which have similar surface areas.

5. REFERENCES

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Table 1. Some properties of QP and IQP.

Pitch	S.P. (°C)	Yield (wt%)	C.Y. (wt%)	Elemental Analyses(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	0.106	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, Yield : wt% of pitch product, C.Y. : carbon value at 600°C, O.T. : optical texture, BS : benzene soluble, BI-PS : benzene insoluble-pyridine soluble, PI : pyridine insoluble.

Table 2. Some properties of stabilized fibers and activated carbon fibers derived from QP and IQP.

Run No.	Elemental analysis(wt%)							W.L	S.A.	N.P	basicity	SO_2
	C	H	N	O(dif.)	H/C	N/C	O/C	(wt%)	(m^2/g)	(ml/g)	(meq/g)	(mg/g)
QP-ACF *	80.8	1.7	5.6	12.0	0.25	0.06	0.11	46.6	738	43.2	0.70	74
(QP-SF) #	71.8	3.0	11.5	13.4	0.51	0.14	0.14					
IQP-ACF-280 *	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) #	72.9	2.9	7.6	15.3	0.48	0.09	0.16					
IQP-ACF-300 *	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) #	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

*: Stabilized fibers, #: Activated fibers
FE-300 : polyacrylonitrile based ACF(Toho Rayon)
OG-8A : pitch based ACF(Osaka Gas)
W.L. : weight loss at activation, S.A. : surface area
N.P : Amount of 0.1N NaOH necessary for adjusting for neutrializing point
SO_2 : Amount of SO_2 absorbed on ACF at 30°C in He containing 2000ppm of SO_2.

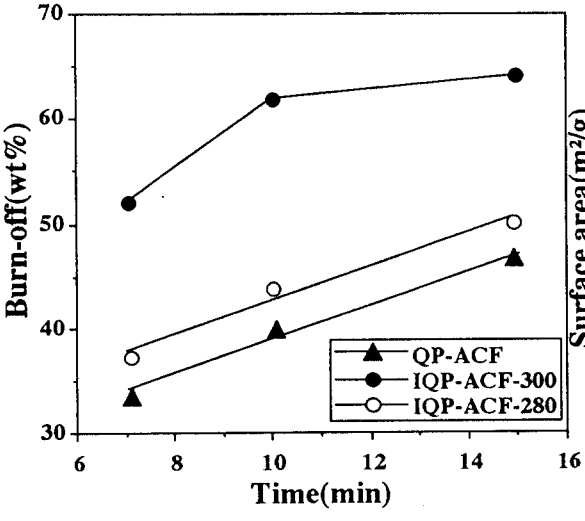

Fig. 1. Weight loss of ACF derived from QP and IQP as funtion of activation time at 850°C.

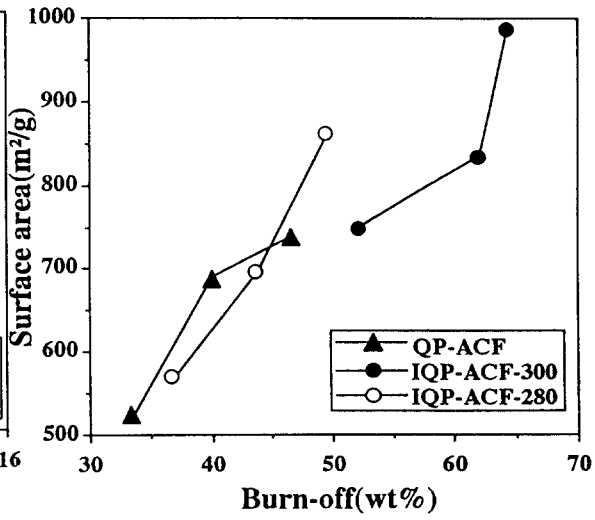

Fig. 2. Surface area of ACF derived from QP and IQP as funtion of burn-off at 850°C.

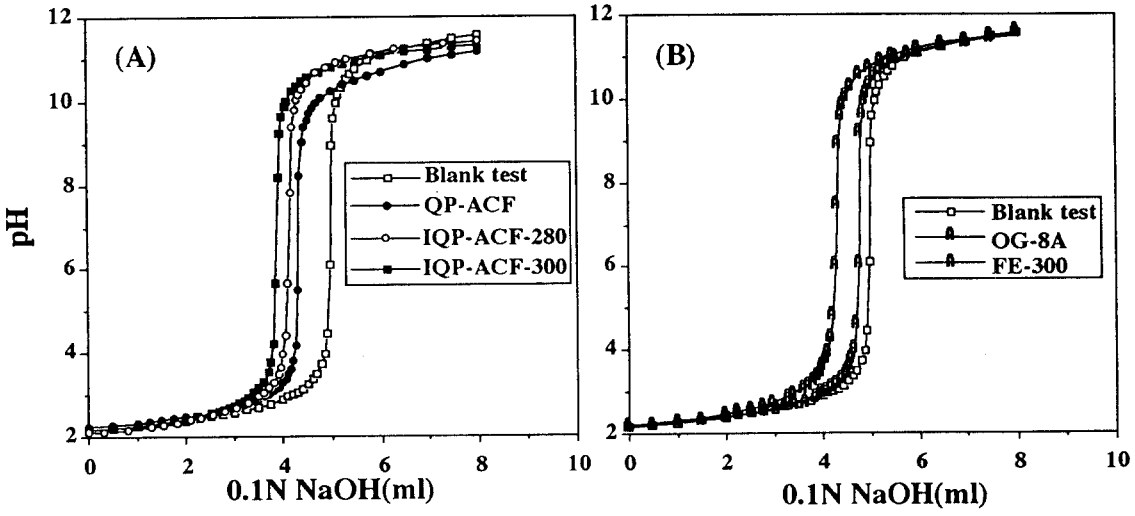

Fig. 3. Titration curves of various ACFs after 0.1 g of ACF was immersed for 24hr in 5ml of aq. HCl(0.1N). (A) QP-ACF andIQP-ACFs, (B) FE-300 and OG-8A.