



Catalytic removal of SO₂ over ammonia-activated carbon fibers

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Abstract

Nitrogen-containing functional groups were introduced onto the surface of activated carbon fibers (ACF) by activating an ethylene tar pitch-based carbon fiber with ammonia water. The activity of the ACF for the conversion of SO₂ to aq. H₂SO₄ in the presence of H₂O and O₂ is significantly higher than that of other commercial ACF studied before. Both the SO₂ adsorption capacity and oxidation activity of ACF are enhanced very much by the nitrogen-containing functional groups. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

SO₂ is one of the major pollutants in the atmosphere. Several methods have been established for the removal of SO₂ from flue gas, e.g., wet desulfurization (with CaO, H₂O) and dry desulfurization (with active coke) etc. However, much effort is still needed to improve the cost/performance ratio for the SO₂ removal.

Recently, a series of papers have reported that activated carbon fibers may be a good candidate to remove SO₂ into aq. H₂SO₄ in the presence of H₂O and O₂ without any carbon loss [1–10]. Much better efficiency can be obtained after heat treatment of ACF at optimum temperatures [1–14].

In a previous paper, we found that cellulose-based activated carbon fiber had the highest activity among the ACFs so far examined, although the ACFs had similar surface areas [1]. This was attributed to its largest amount of oxygen-containing functional groups. Thus, this should indicate that the surface chemistry does play an important role in the catalytic removal of SO₂. Activated carbon with nitrogen-containing functional groups was reported also to benefit the oxidation of SO₂. However, the role of such groups was not very clear [11,15–17].

The introduction of nitrogen-containing functional groups could be implemented in many ways [16–20], such as by carbonizing and activating the mixtures of the carbon precursor and ammonia or its derivatives [16,17], by heat-treating the carbonaceous materials with NH₃ or HCN [18,19], or by depositing the nitrogen-containing agent into the activated carbon [20]. In the present paper, nitrogen-containing functional groups were directly introduced onto the surface of ACF by using NH₃·H₂O as the activation agent. Based on the present results, the types and role of nitrogen-containing functional groups can be discussed, and optimum modification of the ACF surface to obtain even higher activity for SO₂ removal can be expected.

2. Experimental

2.1. Preparation of ACFs

A pitch-based carbon fiber which was derived from ethylene tar was activated by steam (H-series) and ammonia water (N-series) at 800–915°C. The designed concentration of ammonia water (NH₃·H₂O) was introduced into the snake-like stainless steel tube furnace. The temperature of the furnace was above 200°C, thus the vaporization of ammonia water was achieved. The prepara-

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Table 1
Conditions of preparation and properties of samples

Sample	Conditions of preparation				Properties							
	Activation Temp. (°C)	Activation time (h)	Activating agent	Activation yield (%)	Elemental analysis (wt%)					S_{BET} m ² /g	V ml/g	D Å
					C	H	S	O*	N			
H-1	800	5	steam	70	92.13	1.03	0.32	6.51	0.01	717	0.34	5.4
H-2	890	1.5	steam	31	95.79	0.77	0.45	2.99	0.00	1748	0.83	6.1
H-3	890	1	steam	39	95.82	0.73	0.43	3.01	0.01	1469	0.59	5.8
N-1	915	1	NH ₃ (g)	95	–	–	–	–	–	–	–	–
N-2	915	1	10.5 M ammonia water	73	96.26	0.70	0.35	2.24	0.45	671	0.30	5.1
N-3	915	1	7 M ammonia water	63	94.24	0.71	0.35	3.73	0.97	918	0.37	5.4
N-4	915	1	3.5 M ammonia water	41	94.62	0.70	0.31	3.25	1.12	1480	0.61	5.9
N-5	915	1	2.3 M ammonia water	39	94.72	0.63	0.44	3.83	0.38	1592	–	–
N-4 (HT1000)	N-4 was heat-treated in N ₂ at 1000°C for 1 h				97.71	0.69	0.17	1.16	0.27	1470	0.59	5.8

* By difference; S_{BET} , specific surface area; V, total pore volume; D, average pore width; –, not measured.

tion conditions and some properties of resultant ACFs are summarized in Table 1.

Heat treatment of N-4 was carried out at 1000°C for 1 h in N₂ to obtain N-4 (HT1000)

2.2. SO₂ removal

SO₂ removal was carried out in a fixed bed flow reactor as described elsewhere [21–23]. ACF was packed in a tubular glass reactor of 8 mm diameter and the packing height was about 0.1 g/10 mm. The concentrations of SO₂, O₂ and H₂O in model flue gas were 1000 ppm, 5vol% and 10vol%, respectively, under the balance of N₂. The weight of ACF, the total flow rate and reaction temperature were 0.05–0.25 g, 100 ml/min and 30°C, respectively. The SO₂ concentration was detected with a flame photometric detector.

2.3. Adsorption of SO₂

The adsorption capacity of ACF for SO₂ of 2000 ppm with or without 5vol% O₂ was calculated separately by the difference of weight of ACF before and after adsorption. The adsorption temperature, adsorption time, and gas flow rate were 30°C, 1 h, and 100 ml/min, respectively. The adsorption capacity of ACFs for H₂O of 4vol% in N₂ flow was measured at 30°C by weighing the sample after 4 h adsorption.

2.4. Analysis of SO₂ and SO₃ on the surface of ACF after SO₂+O₂ adsorption

The ACF after SO₂+O₂ adsorption was heated from room temperature to 450°C by temperature-programmed desorption, the evolved gas bubbled through a solution of H₂O₂ (5vol%), and formed H₂SO₄ was determined by

titrating with NaOH solution. The amount of H₂SO₄ was used to calculate the total sulfur amount on ACF after SO₂+O₂ adsorption.

The ACF after SO₂+O₂ adsorption was extracted twice with 10 ml H₂O. The sulfur in the form of SO₂, and thus transformed into H₂SO₃ by extraction, was detected by titration with solution of iodine. With the same portion of solution, the dissolved SO₃ (in the form of H₂SO₄) was determined by titration with NaOH solution.

2.5. Characterization of ACF

XPS was performed using a VG Scientific ZSCALAB-220I-XL apparatus. The C1s and N1s spectra were obtained using MgK_α X-ray at 15 kV and 15 mA. The pressure inside the vacuum system was maintained at 1.25×10⁻⁸ Torr. The carbon C1s line (284.6 eV) was used as calibration. A software package, Eclipse V2.1, was used for peak fitting and quantification.

The specific surface area and pore structure of ACFs were determined by using an ASAP-2000 instrument. The former was measured by the isotherm of N₂ (77 K), and the latter was calculated by the H–K method.

3. Results

3.1. Introduction of N-containing functional groups

Table 1 summarizes the properties of ACFs activated with steam and ammonia water. The reaction between carbon fiber and NH₃ does takes place (Sample N-1), although the gasification rate is rather low even at 915°C. The N-containing groups appear on the surface probably due to the reaction of carbon with NH₂· or NH· radicals [18], which are formed by NH₃ decomposition at high

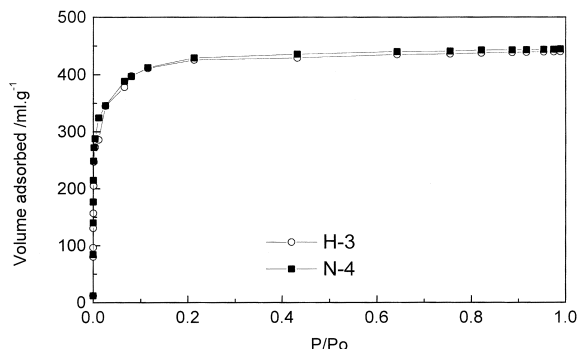
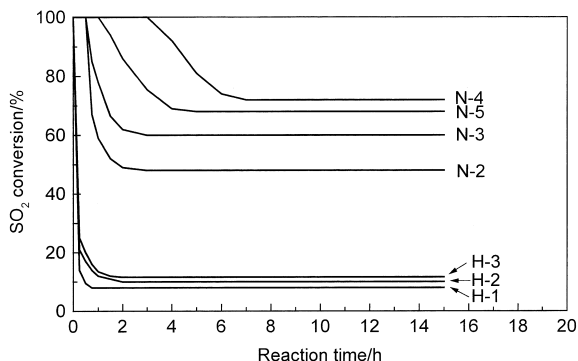


Fig. 1. Nitrogen adsorption isotherms for ACFs.

Fig. 2. Activity of ACFs for SO₂ removal at 30°C.

temperature. The specific surface area and burn-off of resultant ACFs increase with lower NH₃ concentration (Samples N-2–N-5). In other words, the gasification appears to be inhibited to some extent when ammonia is added to the water vapor. A possible explanation for this phenomenon may be as follows [18]: the reaction of H₂O and carbon matrix creates active sites, the latter react with NH₂· and NH· radicals to form more stable nitrogen groups, thus the active sites become ‘deactivated’. So the higher the concentration of NH₃ in the activating agent, the more serious is the ‘deactivation’ of active sites.

The elemental analysis indicated that nitrogen is successfully introduced onto the N-series ACF. While almost no nitrogen is detected in the H-series ACF (H-1–H-3). A higher oxygen content in ACF of lower surface area activated by steam is observed (H-1). Both H-series and N-series ACF of higher surface areas show similar oxygen contents.

The nitrogen adsorption isotherms of ACFs activated with steam and the solution of ammonia is shown in Fig. 1. Both ACFs contain mainly micropores. The average pore diameters of ACFs are also similar when they have similar surface area, as shown in Table 1 (H-3 and N-4).

Some data derived from the N1s spectrum of N-4 are given in Table 2. When compared with elemental analysis (1.18%) and surface N/C atomic ratio (1.09%), it can be concluded that most of the nitrogen exists on the surface of ACF.

3.2. Activities of ACFs for SO₂ removal

The activities of ACFs for SO₂ removal in the presence of O₂ and H₂O are shown in Fig. 2. The N-series ACFs show higher activity than the H-series, even though the N-series ACFs have lower surface areas. The N-series ACFs has even higher activity than the PAN-based ACFs reported before [2], although the latter also has a high nitrogen content (4.5% and 5.8%).

Fig. 3 shows the activity of heat-treated N-4 and H-3 samples at their optimum heat treatment temperature for SO₂ removal. Although they have similar surfaces, the activity of N-4 ACF is still higher than that of H-3.

3.3. Adsorption of SO₂ and H₂O

From Table 3 it can be seen that the SO₂ adsorption

Table 2
XPS curve-fit data for C1s peaks of N-4 and H-3 and for N1s peaks of N-4

Groups	N-4		H-3	
	Binding energy (eV)	Relative intensity (%)	binding energy (eV)	relative intensity (%)
C–C	284.5	69	284.7	66
C–O	286.2	10	286.4	13
C=O	287.7	7	287.4	8
COOH	289.1	5	289.1	7
$\pi \rightarrow \pi^*$	291.2	9	291.2	6
	N-4 before desulfurization		N-4 after desulfurization	
Nitrogen-containing functional groups	401.7	10	401.6	26
	400.1	58	400.1	64
	398.6	32	398.3	10

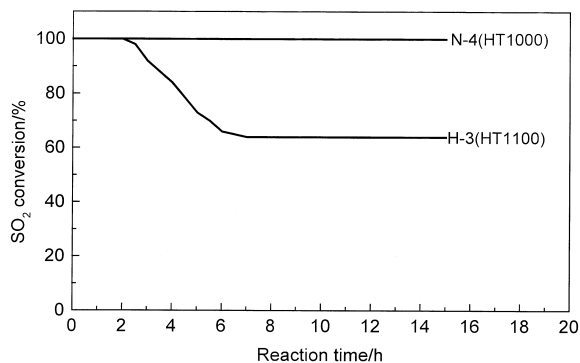


Fig. 3. The desulfurization activity of H-3 and N-4 at optimum heat treatment temperature.

Table 3

The adsorption capacities of ACFs for SO_2 , $\text{SO}_2 + \text{O}_2$ and H_2O at $30^\circ\text{C}/\text{mg}\cdot\text{g}^{-1}$

	N-4	H-3
SO_2	36	18
$\text{SO}_2 + \text{O}_2$	60	25
H_2O	398	332

capacity of N-4 is larger than that of H-3, regardless of the presence of O_2 . In addition, a higher adsorption capacity of H_2O is also observed for sample N-4.

Table 4 summarizes the total sulfur uptakes ($\text{SO}_2 + \text{SO}_3$) and the relative contents of SO_2 and SO_3 which are washed out by water. The remaining sulfur is considered to be in the form of SO_3 since it has a strong affinity for the ACF surface [15–24]. The amount of sulfur present in the form of SO_3 in N-4 is larger than in H-3, while the amount of sulfur present in the form of SO_2 in N-4 is less than in H-3. This is evidence for the higher catalytic oxidation activity of N-4.

4. Discussion

Ammonia-activated ACFs show a higher activity than steam-activated ACFs, regardless of their surface area. Sample N-4 also has higher activity than H-3, with similar

Table 4

The total amount of sulfur after adsorption of $\text{SO}_2 + \text{O}_2$ and the amounts of sulfur (SO_2 and SO_3) in washing solution

Sample	(mg/g) ^a	(%) ^b	(%) ^c	(%) ^d
H-3	11.2	24.4	35.7	39.9
N-4	28.3	15.1	49.8	35.1

^a The total sulfur content of ACF after $\text{SO}_2 + \text{O}_2$ adsorption.

^b Sulfur present in the form of SO_2 in washing solution.

^c Sulfur present in the form of SO_3 in washing solution.

^d Sulfur not washed out.

specific area, after heat treatment in N_2 at their respective optimum temperature. These results suggest the important role of surface functional groups in the ACFs.

Table 2 presents C1s XPS deconvolution results of samples N-4 and H-3. They both have the same types and similar amounts of oxygen-containing groups. Thus, the remarkably high activity of N-4 for SO_2 removal can be attributed to the nitrogen-containing functional groups.

It is necessary to know the types of nitrogen-containing groups in ACFs before the study of the influence of nitrogen-containing groups on the activities of ACFs for SO_2 removal is performed. The N1s spectra and deconvolution results for sample N-4 before and after desulfurization are shown in Fig. 4 and Table 2. Both N1s regions indicate the presence of three different species. The peak with binding energy at 398.5 eV can be ascribed to pyridine-like structures [25–29], the other two peaks at 400.1 eV and 401.6 eV correspond to pyrrolic-like nitrogen or pyridone [25,27–33] and quaternary nitrogen which includes protonated pyridinic nitrogen [25,28,36,37], respectively. The changes of the relative intensity of these nitrogen-containing species before and after desulfurization are observed, especially the peaks at 398.5 eV and 401.6 eV, where the relative intensity of the peak at 398.5 eV evidently decreases after desulfurization, whereas the intensity of the peak at 401.6 eV increases after desulfurization. This may be due to the following reasons: (a) a lone electron pair in the plane of pyridine-like ring may easily

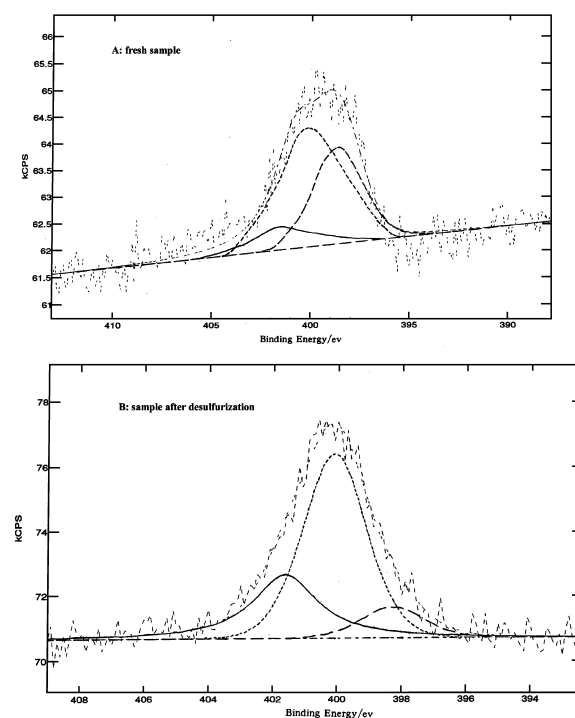


Fig. 4. N1s spectra of N-4 ACF.

react H_2SO_4 to form the protonated pyridinic nitrogen (H_2SO_4 is produced by the oxidation and hydration of SO_2 over ACF in the presence of O_2 and H_2O); (b) pyrrole-like nitrogen is difficult to react with the protons due to the fact that there are no unpaired electrons on the nitrogen atom of pyrrole, so it contributes little to the 401.6 eV peak. Therefore, it can be suggested that a part of quaternary nitrogen after desulfurization results from the conversion of pyridine-like nitrogen for sample N-4 before desulfurization. Other nitrogen groups, such as amides, lactams and imides, will react with H_2SO_4 to be decomposed upon desulfurization. Thus, we conclude that the nitrogen-containing groups on the surface of ACFs during the desulfurization are pyridone-, pyrrole-, pyridine-like, and quaternary nitrogen.

Continuous SO_2 removal over ACFs is carried out by the following processes [1–9]: SO_2 adsorbed on the ACF is oxidized into SO_3 by O_2 from the gas phase. The reaction of SO_3 and H_2O which condensed in ACF pores produces H_2SO_4 , which is washed by excess amount of condensed H_2O to recover the SO_2 adsorption sites. Thus, a new cycle of adsorption and oxidation of SO_2 and production and elution of H_2SO_4 starts again. This continuous operation makes SO_2 removal possible. Hence, ACFs which have higher adsorption capacity for SO_2 and H_2O , higher catalytic activity for oxidation of SO_2 to SO_3 and easier elution of H_2SO_4 from the surface of ACFs have higher desulfurization activities. Pyridine groups show relatively strong basicity, and they have strong affinity for acidic molecules such as SO_2 to enhance ACF's adsorption capacity. This is confirmed in Table 3. The adsorption capacities of N-4 for SO_2 and $\text{SO}_2 + \text{O}_2$ are higher than those of H-3. In addition, the more pyridine-like nitrogen species, the higher is the catalytic activity for the oxidation reaction [33]. Pyrrole-like species are believed to be the active part of nitrogen-containing functional groups [38]; Stohr et al. [19] found that ammonia-treated activated carbons show a higher catalytic activity than HCN-treated carbons for the oxidation reaction which involve O_2 . Strelko et al. [34] suggest that the treatment with ammonia results in the formation of pyrrole nitrogen. The latter has the highest charge mobility in a carbon matrix and the best donor–acceptor properties. This is because the insertion of nitrogen atoms into the graphite lattice can lower the band gap, thus producing higher electron mobility and lower electron work function at the carbon/gas interface compared with pure carbons. Therefore, pyrrole nitrogens improve the catalytic activity of carbon. They can increase the electroreductive ability of ACF for the adsorption of molecular oxygen [38], resulting in O_2^- having a higher oxidation ability than molecular oxygen. The higher oxidation ability of O_2^- was also reported by others [19,35,36]; for example, Stohr et al. [19] suggest that O_2^- is likely to control the catalytic properties of carbons in oxidation reactions. Matzner and Boehm [37] also postulated that this activity is due to

formation of O_2^- from adsorbed O_2 . As for quaternary nitrogen, which corresponds to nitrogen atoms incorporated in the graphite layers, its function is not clear, but it is estimated that the effective charge on the nitrogen atom increases when going from top to center and 'valley' positions [32], so quaternary nitrogen of center and 'valley' positions may show a positive influence on catalytic activity [34]. With respect to the pyridone, its role is not understood.

The presence of H_2O also has considerable influence on desulfurization activity, because on the one hand it reacts with SO_3 to form H_2SO_4 , and on the other hand and also more importantly, it behaves as a regeneration medium to wash H_2SO_4 from the SO_2 adsorption sites [1,2,4,6,13]. It is suggested [18,32] that nitrogen-containing groups may offer polar sites for H_2O adsorption due to their stronger polarity, thus ACFs with nitrogen-containing groups show higher adsorption affinity for H_2O than pure carbons.

Based on the analysis above, nitrogen-containing groups favour adsorption of SO_2 and H_2O and oxidation of SO_2 . However, which types of nitrogen-containing groups play the most important role still needs to be studied.

5. Conclusion

Using the solution of ammonia and water as an activation agent has proved to be an efficient way to directly introduce nitrogen-containing functional groups onto the surface of ACFs. The resultant ACFs show much higher activity for SO_2 removal in the presence of O_2 and H_2O than other commercial ACFs of similar surface areas. This effect can be attributed to the presence of nitrogen-containing functional groups since they are able to enhance the adsorption capacity of SO_2 and H_2O and the catalytic activity for oxidation of SO_2 to SO_3 .

Acknowledgements

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