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Adsorption of Ammonia on the Sulfuric Acid Treated ACF

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Abstract

For the adsorption of ammonia, activated carbon fibers (ACFs) were subjected to sulfuric acid treatment in order to modify the surface functional groups. The surface acid and base value of ACFs were measured using titration and FT-IR spectrometry. SEM was used to investigate the surface morphology. Acid treatments by H_3PO_4, H_2SO_4, and HNO_3 were performed to increase the adsorption capacity of NH_3. As a result, Cellulose-based ACF has high adsorption capacity for ammonia. The ammonia removal efficiency of ACF was the maximum which was treated by 15 wt% sulfuric acid at 100°C for 60 min. The average pore diameter little increased from 19 Å to 20.8 Å and the specific surface area of ACF considerably decreased and acid values increased by 15 wt% sulfuric acid treatment. Ammonia reacted with sulfonyl radicals. After adsorption of ammonia, white material was grown on the surface of ACF through the adsorption of ammonia and it was determined to ammonium sulfate.

Keywords : *Functional Groups, Chemical Treatment, Microporosity*

1. Introduction

Although activated carbon fibers (ACFs) have excellent adsorption properties due to their large surface area and pore volume, they didn't possess sufficient adsorption capacity for polar gases with low molecular weight such as ammonia. The lack of adsorption capacity for polar gases has been complemented by impregnating some additives into the micropores or by developing functional groups on carbon surface. The chemical treatment of ACFs by acids changes the surface area, pore volume and the amount of functional groups. Fu *et al*. [1] reported the chemical activation of ACF by phosphoric acid prepared a large surface area as well as good adsorption properties for organic vapors and small molecular weight chemicals in water. Kutics [2] reported the surface area decreased from 1496 to 1010 m^2/g and the amount of strong carboxyl radicals increased from 0.064 to 2.34 meq/g by nitric/sulfuric acid treatment of phenol resin based ACF at 90°C, 0.1h. Mochida [3] reported the adsorption behaviors of ammonia on ACFs acidified with sulfuric acid. Oya [4] has reported that phosphorous-supported ACF that was prepared by impregnation of phosphoric acid exhibits its high adsorption performances against alkaline gases including ammonia.

In this study, ACFs were subjected to sulfuric acid treatment in order to modify the surface functional groups and the adsorption performances of ammonia were described.

2. Experimental

Various ACFs (cellulose based, KF-1500, Toyobo Co., PAN based, FX-200, Toho Rayon Co., phenol resin based, Kuractive 15, Kuraray Chemical Co., pitch based, A-15, Osaka Gas Co.) were used as base materials. The specific surface area of all ACFs was about 1500 m^2/g except PAN based ACF (700 m^2/g, nitrogen content 6-8%). ACFs were dried at 105°C for one night and immersed in hot aqueous solution of sulfuric, nitric and phosphoric acid at the same concentrations. The ACFs were taken out and dried at 105°C. Nitrogen adsorption isotherms of acid treated ACFs for BET surface areas were obtained at 77 K by volumetric method [5]. The microporous volume was determined from the isotherms using *t*-method [6]. The pH of ACFs was measured with ASTM D 3838. About 1.0 g of each sample was added to 20 ml distilled water and shaken over 12 h, and the pH was measured after filtration. The acid and base values on the carbon surface were determined by Boehm's method [7]. In case of acid value, about 1.0 g of the sample was added to 100 ml of 0.1 N NaOH solution and shaking it for 24 h, then the solution was filtered through membrane paper and titrated with 0.1 N HCl solution. Likewise, the base value was determined by converse titration.

Ammonia adsorption was performed in ACF packed glass column (I.D = 0.6 cm, L = 36 cm, packed density 0.18 g/cm^3) at room temperature. The concentration of ammonia in inlet air was controlled to 100 ppm by flow controller. The

concentration of ammonia in outlet air was analyzed by gas chromatography (HP 5890 II : TCD).

The surface functional groups of activated carbon fibers were analyzed by FT-IR spectrophotometry using a Bomem MB-100 series equipped with a DTGS (deuterated triglycine sulfate) detector. The sample chamber was continuously purged with dry nitrogen at the rate 15 L/min to prevent interference of carbon dioxide and water vapor.

3. Results and Discussion

3.1. Ammonia removal efficiency of various ACFs

Fig. 1 shows the ammonia removal efficiency of various ACFs. The total adsorbed amount of ammonia was 5.45 mg/g for cellulose-based, 2.8 mg/g for PAN-based, 2.0 mg/g for phenolic resin-based, and 2.25 mg/g for pitch-based ACF, respectively. The cellulose based ACF shows larger adsorption capacity than others for ammonia.

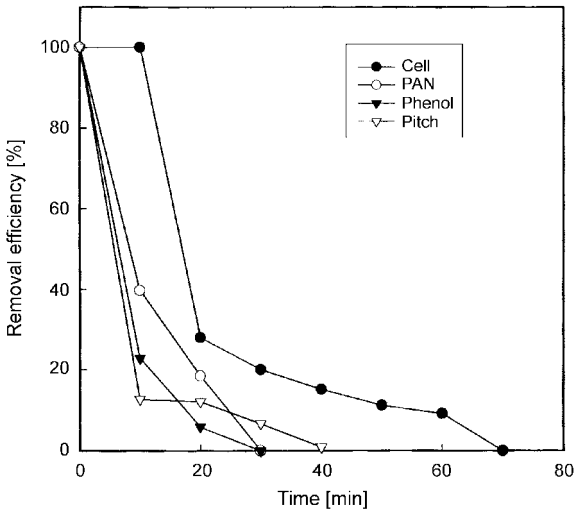

Fig. 1. Adsorption characteristics of ammonia on ACFs.

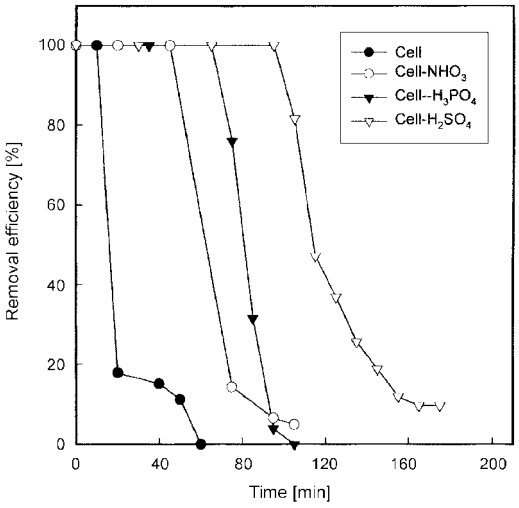

Fig. 2. Effect of surface treatment of ACFs on the ammonia removal efficiency.

Fig. 2 shows the effect of various acids (4.5 wt%) treatment of cellulose based ACF on the removal efficiency of ammonia at room temperature. The adsorption capacity increased remarkably by the acid surface treatment, especially by the sulfuric acid treatment. The total adsorbed amount of ammonia was 92 mg/g for sulfuric acid treatment, 21 mg/g for phosphoric acid treatment, and 15.5 mg/g for nitric acid treatment. The removal efficiency of cellulose-based ACF increased about 17 times for ammonia by the sulfuric acid treatment. This is because of the reaction of ammonia with sulfonyl group to produce ammonium sulfate. Mochida [3] reported that the adsorption capacities of ACFs were remarkably increased about 50-70 times by acidification with sulfuric acid. He have shown that the amount of adsorbed ammonia was 43 mg/g for PAN-based FE-200, 66 mg/g for phenol resin-based 210-20, 52 mg/g for pitch-based A-5, respectively. However, these data couldn't be directly compared to ours because of different level of specific surface area and treatment conditions. And unfortunately there is no data for cellulose-based ACF in Mochida's result.

Fig. 3 shows the ammonia removal efficiency of surface treated ACFs at different sulfuric acid concentrations (100°C). From the figures, the total adsorbed ammonia was 72.8 mg/g for 10 wt%, 89.9 mg/g for 15 wt%, 82.7 mg/g for 18 wt%, and 90.3 mg/g for 20 wt%. The 15 wt% was recommended as the proper sulfuric acid concentration for surface treatment of ACF.

3.2. Characterization of ACFs before and after acid treatments

Fig. 4 shows the pore size distribution of cellulose-based

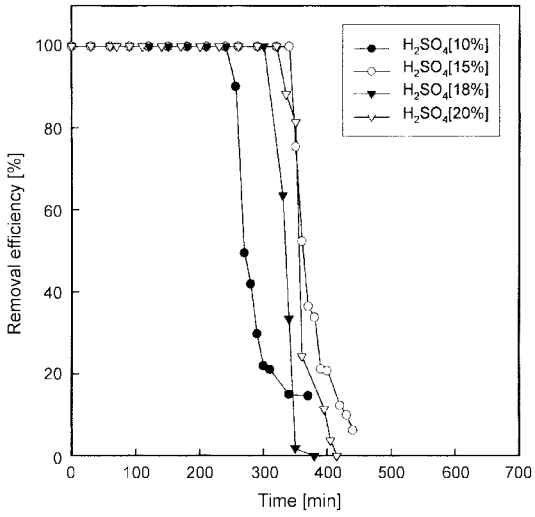

Fig. 3. Effect of H_2SO_4 treatment concentration on the ammonia removal efficiency.

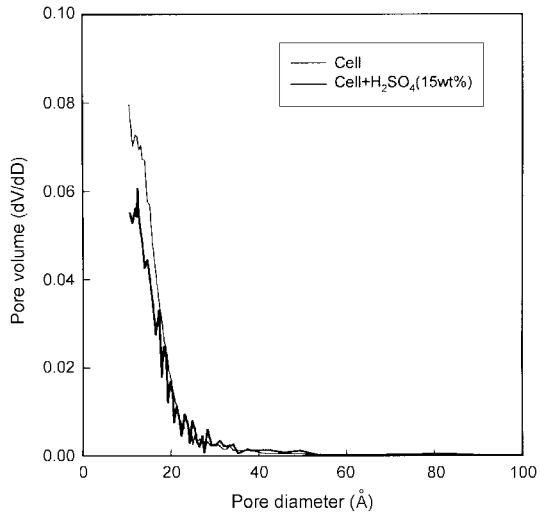

Fig. 4. Pore diameter distribution of ACF (Cell) treated with H_2SO_4.

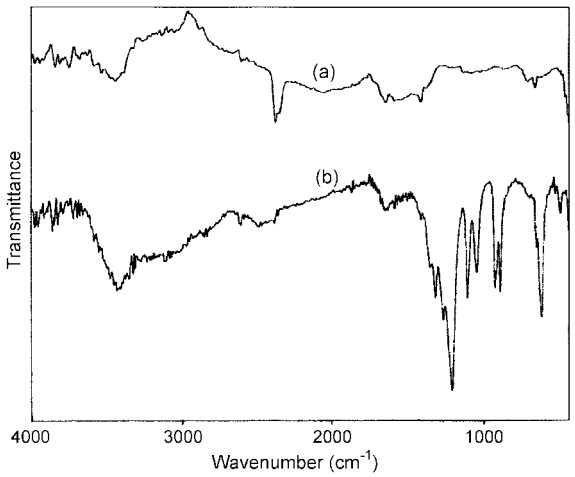

Fig. 5. FT-IR of cellulous-based ACFs.
(a) before treatment
(b) after treatment with H_2SO_4

Table 1. Pore characteristics of sulfuric acid treated cellulose-based ACF

	Specific surface area (m^2/g)	Total pore volume (cc/g)	Micropore volume (cc/g)	Average pore diameter (Å)
Before	1015	0.487	0.453	19.2
After	861	0.449	0.399	20.8

ACFs before and after sulfuric acid treatment (15 wt%). There are some fluctuations for acid treated ACF in the range of 20-40 Å. These results suggested that sulfuric acid treatment of ACF in liquid phase caused the blocking of the some narrow pores by the surface complexes introduced. Kutics [2] reported very similar result of the decrease of specific surface area by nitric/sulfuric acid treatment.

Table 1 shows that pore characteristics of cellulose-based ACFs before and after sulfuric acid treatments (15 wt%). The average pore diameter increased from 19.2 to 20.8 Å and the specific surface area was considerably decreased from 1015 to 861 m^2/g by the sulfuric acid treatment. The decrease of total pore volume was mainly due to the decreased of micropore volume. The average pore diameter was slightly increased by the sulfuric acid treatment. Turk [8] reported that the chemical treatment occupies some of the pore volume and surface area.

Table 2 shows the surface properties of the ACF in this work. The results of the Boehm's titration show that natures of pure cellulose-based ACF was amphoteric with slight basic properties, whereas sulfuric acid treated ACF being acidic-rich properties. That is probably due to the existence of surface functional groups by sulfuric acid treatment. Also acid and base values largely depend on the pH of the activated carbon fiber surfaces measured.

Table 2. Surface characteristics of sulfuric acid treated cellulose-based ACF

Samples	PH	Acid values [meq · g^{-1}]	Base values [meq · g^{-1}]
Cellulose ACF	7.05	270	330
ACF treated with sulfuric acid	2.63	1058	15

3.3. FT-IR spectra of ACF

Fig. 5 shows the FT-IR spectra of cellulose-based ACFs before (a) and after (b) sulfuric acid treatment. From the figure (a), the adsorption band peak located around 3440 cm^{-1} is the stretching vibration of phenolic radicals (-OH), the band around 1628 cm^{-1} shows the peak of carboxyl radicals (-COOH), and the complex band around 1400-1600 cm^{-1} shows the aromatic band (-C=C) and various substitution modes of the aromatic ring [9]. These functional groups were the characteristics of ACF surface. Some of these functional groups were changed to sulfonyl groups by the sulfuric acid treatment. From the figure (b), new strong adsorption band peaks were developed around the 1176 cm^{-1} (-SO) by the introduction of sulfonyl radicals, which were not shown in the untreated ACF surface.

The stretching vibration peaks of phenolic radicals are still around 3430 cm^{-1} and carboxyl radicals around 1628 cm^{-1}. This means the adsorption characteristics of acid treated ACFs on organic or inorganic materials might be different

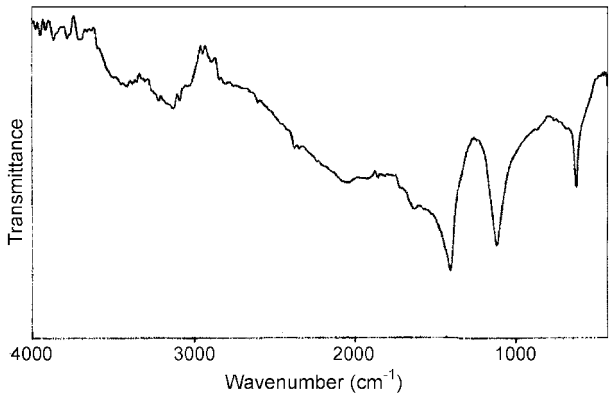

Fig. 6. FT-IR spectrum of sulfuric acid treated ACF after adsorption of ammonia.

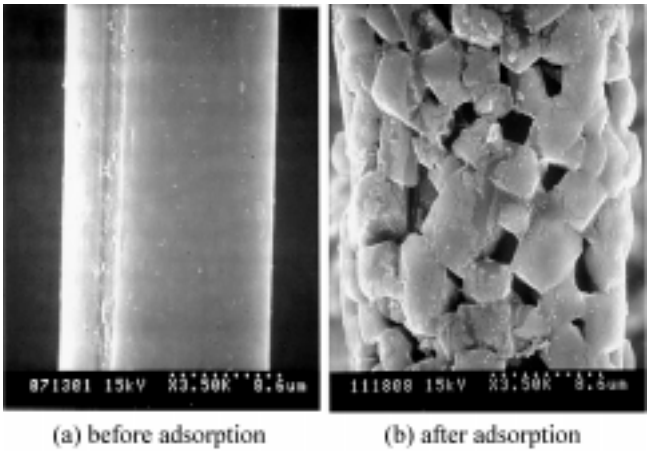

Fig. 7. SEM photos of ACF treated with H_2SO_4
(a) before adsorption and (b) after ammonia adsorption.

from that of untreated ACFs. The high removal efficiency of ammonia by sulfuric acid treated ACF suggested that the ammonia has reacted with sulfonyl radicals and produced ammonium sulfate. Mochida [3] also reported the formation of ammonium sulfate on the surface of sulfuric acid treated ACF with ammonia.

Fig. 6 shows the FT-IR spectrum of sulfuric acid treated ACF after ammonia adsorption. There were stretching vibration peaks of amine radicals (-NH_2) around 1402 cm^{-1} and peaks of phenolic radicals (-OH) around 3450 cm^{-1}. There were also -NH peak around 3125 cm^{-1} and carboxyl radicals around 1626 cm^{-1}. This means ammonia reacted with sulfonyl radicals. However, ammonia didn't react with carboxyl radicals. Some of these results were different from Mochidas result. He reported that sulfuric acid provided two kinds of adsorption sites on the surface of ACF. One is that sulfuric acid adsorbed on ACF induces organic acids. Such an organic acid adsorbed ammonia at room temperature. The amount of adsorption is correlated to the amount of carboxylic groups on ACFs [10]. The other is that sulfuric acid staying on ACF reacts with ammonia to form ammonia sulfate.

3.4. Identification of ACF adsorbed materials

Fig. 7 shows the SEM photos of ACF after ammonia adsorption. There are much white cristal type materials grown on the surface of sulfuric acid treated ACF. This is believed ammonium sulfate produced by the reaction of sulfonyl radicals with ammonia.

The TGA analysis of the white material that was grown on the surface of ACF was performed. The ammonium sulfate was also TGA analized to compare the curve with that of the white material. From the coincide of two curves, the white material was confirmed to ammonium sulfate.

4. Conclusion

Acid treated cellulose-based ACF shows good efficiency for the removal of ammonia. The adsorption efficiency of 15 wt% sulfuric acid treated ACF for ammonia was about 17 times higher than non-treated ACF. The decrease of total pore volume by acid treatment was mainly due to the blocking of some narrow micropores. The average pore diameter was slightly increased by the sulfuric acid treatment. Boehm's titration shows that sulfuric acid treated ACF was being acidic-rich properties. That is due to the development of surface functional groups by sulfuric acid treatment. By the result of FT-IR, ammonia reacted not only sulfonyl radicals but also phenolic radicals and didn't react with carboxyl radicals. After adsorption process of ammonia, white materials were found at the surface of ACF for the removal of ammonia and it was confirmed to ammonium sulfate.

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