ADSORPTION OF AMMONIA ON SURFACE MODIFIED ACF

C.S.Shin, K.H.Kim, B.K.Choi, †J.W.Shim, †S.K.Ryu
Dept. of Safety Eng., Chungbuk Nat'l Univ., Cheongju 301-763, Korea
†Dept. of Chemical Eng., Chungnam Nat'l Univ., Taejon 305-764, Korea

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. Fu[1] reported the chemical activation of ACF by phosphoric acid prepared a large surface area as well as good adsorption properties for organic vapors. Oya[2] has reported that phosphorous-supported ACF which was prepared by impregnation of phosphoric acid exhibits high adsorption performance against alkaline gases including ammonia. In this study, the adsorption performances of ammonia by surface modified ACFs with acids was described.

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 ACFs were subjected to different acid treatments in order to modified the surface functional groups and microporosity. Ammonia adsorption was performed in ACF packed glass column(I.D 0.6cm, L 36cm, packed density 0.18g/cm³) at room temperature. The concentration of ammonia in inlet air was controlled 100ppm by flow controller. The concentration of ammonia in outlet air was analyzed by GC(FPD : CP-9001, FID, TCD : 5890 II).

Results and Discussion

Fig.1 shows the ammonia removal efficiency of various ACFs. Cellulose based ACF shows prominent efficiency than others. The total adsorbed amount of ammonia were 5.40mg/g for cellulose-based, 2.75mg/g for PAN-based, 2.02mg/g for phenolic resin-based, and 2.25mg/g for pitch-based ACF, respectively. Fig.2 shows the effect of various acid treatment of cellulose based ACF on the removal efficiency of ammonia. The adsorption capacity increased remarkably by the acid surface treatment, especially by the sulfuric acid treatment. The total adsorbed amount of ammonia were 31.6mg/g for sulfuric acid(4.5%) treatment, 20.7mg/g for phosphoric acid(4.5%) treatment, and 15.2mg/g for nitric acid(4.5%) treatment. The removal efficiency of cellulose-based ACF increased about 5.9 times for ammonia by the sulfuric acid treatment. The adsorbed amount of ammonia was 92mg/g for sulfuric acid treatment at 100℃, 15wt%. Fig.3 shows the SEM photos of ACF after ammonia adsorption. There are much white crystal type materials grown on the surface of sulfuric acid treated ACF. This is believed that ammonium sulfate was produced by the reaction of sulfonyl radicals with ammonia. The FT-IR spectra of cellulose based ACFs after sulfuric acid treatment shows that new strong adsorption band peaks were developed around the 1176cm (-SO) and around 580, 750-1000cm (-SO) by the introduction of sulfonyl radicals, which were not shown on the untreated ACF surface. The FT-IR spectrum of sulfuric acid treated ACF after ammonia adsorption also shows that there are stretching vibration peaks of amine radicals ($-NH_2$) around 1402cm, week peaks of N-H around 3450cm, aromatic C-H ring peaks around 3125cm, and carboxyl radicals around 1626cm. The white materials which was grown on the surface of sulfuric acid treated ACF through the adsorption of ammonia was determined to ammonium sulfate by TGA analysis. Table 1 shows that the specific surface area of cellulose-based ACF was considerably decreased by the sulfuric acid treatment. However, the total pore volume and the micropore volume were not so much changed and the average pore diameter was slightly increased by treatment. These results suggested that sulfuric acid treatment of ACF in liquid phase caused the blocking of the narrow pores by the surface complexes introduced. Kutics[3] reported very similar result of the decrease of specific surface area by nitric/sulfuric acid treatment.

References

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[3] Kutics, K. and Suzuki, M. : extended abstracts, 2nd Korea-Japan Symposium on Separation Technology, June 1-2, Seoul, Korea, 1990; 395-398.

Acknowledgments

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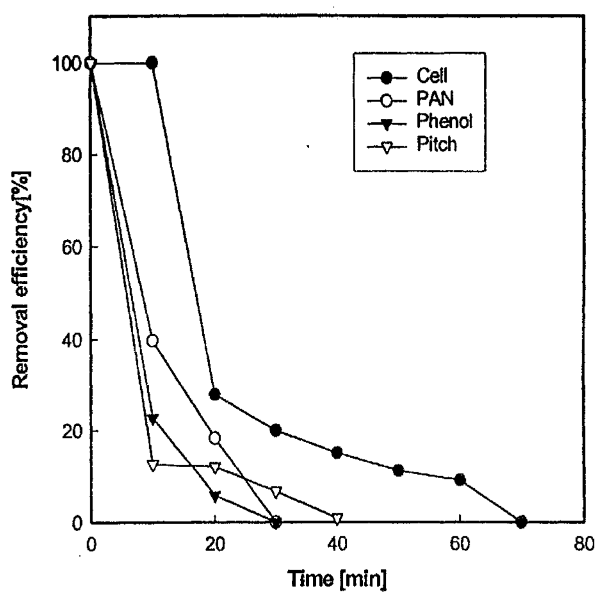


Fig 1. Ammonia removal efficiency of various ACFs.

Table 1. Pore characteristics of sulfuric acid (15%) treated cellulose-based ACF.

	Before	After
Specific surface area (㎡/g)	1015	862
Total pore volume (cc/g)	0.487	0.449
Micropore volume (cc/g)	0.453	0.399
Average pore diameter (Å)	19.2	20.8

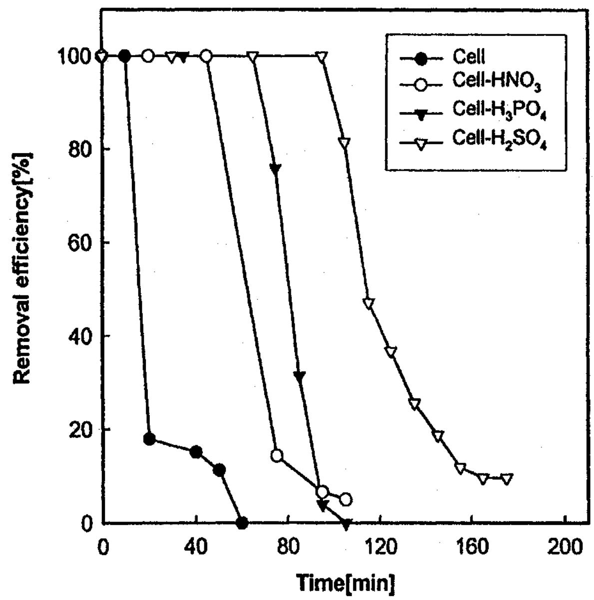
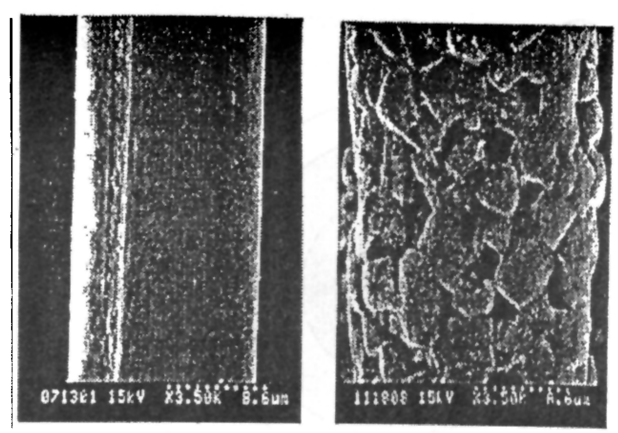


Fig 2. Ammonia removal efficiency of surface modified cellulose-based ACFs with various acids at 25℃, 4.5wt%.



(a) (b)

Fig 3. SEM photos of ACF surface before(a) and after(b) NH_3 adsorption.