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# Regenerative Removal of Ammonia in the Atmosphere with Active Carbon Fibers

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Active carbon fibers (ACF) further activated with sulfuric acid adsorbed ammonia at room temperature up to 2 - 3% by weight before its break-through in repeated runs after the regeneration at 185 °C. The adsorption capacity of ACF was correlated to the amount of carbon dioxide evolved at a temperature range of 200 - 400 °C.

Because ammonia is an origin of unpleasant smell,[1] its handy removal is most wanted to be developed. Active carbon has been widely applied for the adsorption of various substances, however its acidity is too weak to adsorb ammonia irreversibly and effectively at room temperature.[2] Although impregnation of sulfuric acid on active carbon allows adsorption of ammonia,[3] elution of sulfuric acid and difficulty of its regeneration limit its broad application.

In the present letter, active carbon fiber is reported to adsorb a large quantity of ammonia after further activation with sulfuric acid where sulfuric acid was impregnated and heated to introduce acidic oxygen functionalities on the surface of active carbon fiber.[4]

Commercial active carbon fibers (ACF) prepared from PAN (PAN-FE-200), pitch (OG-5A), and phenol-resin (ACN-210-20) were used in the present study. An active carbon impregnated with sulfuric acid (TURUMI-AX) was also studied for comparison.

The active carbon fibers were immersed and stirred in sulfuric acid. The mixture was dried in a rotary evaporator and heated at 250 °C under nitrogen flow for 4 - 6 h. The amounts of remaining sulfuric acid was

determined by titration of the extract from the ACF with boiling water.

Adsorption of ammonia (100 ppm in helium) was carried out at room temperature in a fixed bed flow reactor ($W/F=5\times10^{-3}$g ml$^{-1}$). ACF was heated at 185 °C for 1 h under He flow before the adsorption. Ammonia flowing out from the bed was oxidized into nitrogen oxide, and quantified continuously with a NOx meter (ECL-77A, YANAGIMOTO Co., Ltd.). The regeneration was carried out at 185 °C for 3 - 5 h under He flow (100 ml min$^{-1}$).

The TPD analyses of ACFs were performed in a temperature range of room temperature to 1000 °C at the heating rate of 10 °C min$^{-1}$.[5] The evolved gases were analyzed by Quadrapole Mass Spectrometer (TE-600, ANELVA).

Figure 1 illustrates the break-through profiles of ammonia removal by

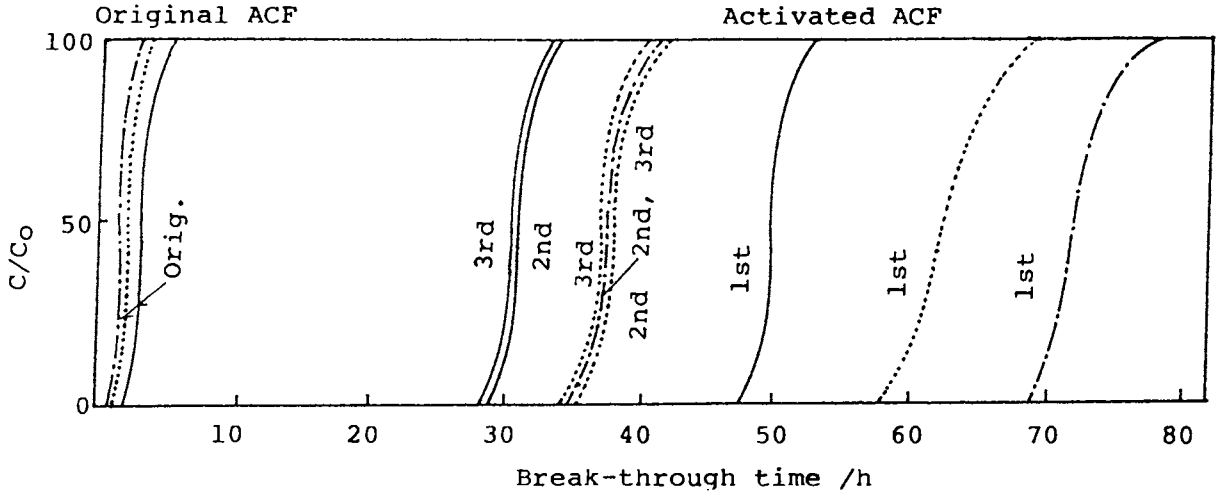


Fig.1. Break-through profiles of ammonia on ACFs and activated ones.

Adsorption; at room temperature

$NH_3$=100ppm, $W/F=5\times10^{-3}$g min ml$^{-1}$

Regeneration; 185 °C, carrier gas : He=100 ml min$^{-1}$

——— PAN-FE-200, ····· OG-5A, —·—·— ACN-210-20

as-received ACFs and their activated ones with sulfuric acid. PAN-FE-200, ACN-210-20 and OG-5A could continue the complete capture of ammonia for only 50-70 min in the 1st run. Impregnation of sulfuric acid and successive heat treatment at 250 °C prolonged the time of complete capture to as long as 48, 57, and 68 h with activated PAN-FE-200, OG-5A, and ACN-210-20, respectively. The regeneration at 185 °C restored the adsorption abilities in the second run, allowing the complete capture of ammonia for 28, 36, and 34 h,

respectively. The third and thereafter runs after the regeneration maintained essentially the same periods of complete capture.

Table 1 summarizes the adsorption capacities of ACFs activated with sulfuric acid until their respective break-through. PAN-FE-200 adsorbed 4.3 wt% of dry ammonia in the first run. The amount decreased to 2.6 wt% in the second run and stayed around the value in the successive runs. Such amounts of adsorbed ammonia were much larger than that on a commercial active carbon impregnated with sulfuric acid. The amount of the latter material decreased markedly in the successive runs to be essentially null by 5th run. Moisture (20% relative humidity at 20 °C) usually increased the amount of ammonia adsorption.

Table 1. Amount of adsorbed ammonia in the regenerative test[a)]

| Sample | Adsorption amount(wt%) | | |
|---|---|---|---|
| | 1st | 2nd | 3rd |
| PAN-FE-200 | 4.3 | 2.6 | 2.7 |
| ACN-210-20 | 6.6 | 3.1 | 3.1 |
| OG-5A | 5.2 | 3.3 | 3.0 |
| TURUMI-AX | 1.2 | 0.7 | 0.3 |

a) Adsorption; at room temperature, $NH_3$:100 ppm, W/F=5x10$^{-3}$g·min·ml$^{-1}$ Regeneration; 180 °C, carrier gas: He= 100 ml min$^{-1}$

ACF and their activated ones evolved carbon dioxide in a temperature range of 250 - 400 °C in the TPD analysis. The activation with sulfuric acid increased its amount. The amounts from ACFs in the temperature range of 250 - 400 °C are well correlated with the averaged amount of adsorbed ammonia until the break-through in the second and thereafter runs as shown in Fig. 2.

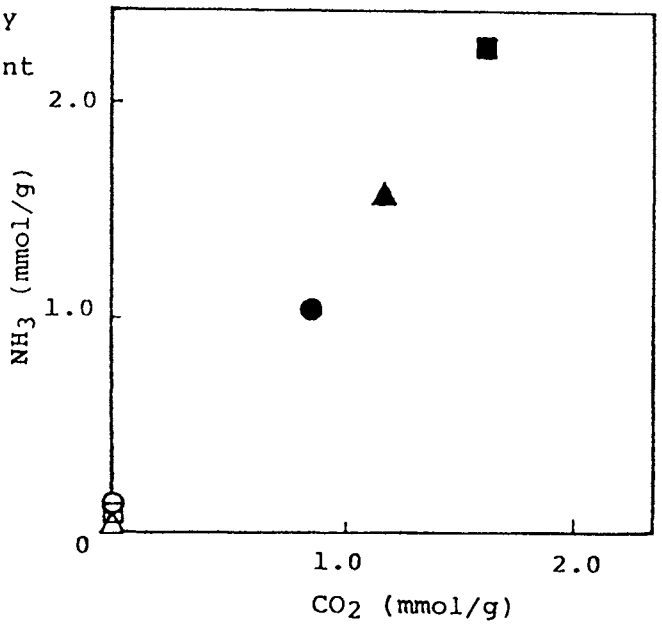


Fig.2. Correlation between amount of ammonia adsorption until break-through and evolved $CO_2$ from ACFs and then activated ones
○:PAN-FE-200, □:OG-5A, △:ACN-210-10
(Original:open, Activated:closed)

The present study revealed that some ACFs further activated with sulfuric acid exhibited a fairly large amount of ammonia adsorption

at its low concentration. The adsorption appears irreversible at room temperature but its major portion desorbs at 185 °C to restore adsorption ability in the repeated cycles of adsorption and desorption.

Sulfuric acid provided two kinds of adsorption sites on the surface of ACF. Sulfuric acid adsorbed on ACF induces organic acids when it is reduced above 250 °C. Such an organic acid may adsorb ammonia at room temperature and release it at elelvated temperatures. The amount of such adsorption is correlated to the amount of evolved $CO_2$ in TPD which comes from carboxylic groups on ACF.[5] Sulfuric acid staying on ACF reacts with ammonia to form ammonia sulfate, which will decompose above 450 °C, accompanying the reduction of $SO_3$.

The activation as well as regeneration temperatures are very influential on the amount of reversible adsorption of ammonia. The former temperature governs the oxidation of ACF-surface by impregnated $H_2SO_4$ to produce the carboxylic group and thermal decomposition of the group. The optimum temperature is experimentally defined 250 °C. Lower temperature leaves sulfuric acid unreacted on the ACF surface to provide large amount of irreversible adsorption and chance of their elution under wet conditions. On the contrary, higher temperature allows the complete reaction of sulfuric acid and decomposition of the carboxylic group. The second temperature should be selected to evolve ammonia completely without any decomposition of the carboxylic group.

References

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