

STATE OF NO_x OVER PITCH BASED ACTIVE CARBON FIBER AT THE INITIAL STAGE OF NO-NH₃ REACTION

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INTRODUCTION

Removal of NO in the atmosphere as well as the flue gas is still an objective to increase the efficiency. The present authors have reported a significant catalytic activity of pitch based active carbon fiber for the reductive[1,2] and oxidative[3] removal of NO at room temperature, especially after the ACF was heat-treated at a proper temperature [4,5]. The problem to be solved is the inhibition of humidity above 70% relative humidity (rh). [6,7]. Hence the enhancement of the activity in the humid area is the major target to be explored.

In the present study, adsorption and reduction of NO over pitch based active carbon fiber (ACF) was analyzed especially at the initial stage of NO-NH₃ reaction where the high rate of NO removal was observed over the ACF in the humid air, although the activity decreased gradually to the stationary level. The analyses of NO adsorption and reduction over the ACF may suggest plausible ways how to maintain or regenerate such an activity for more efficient process of NO removal.

EXPERIMENTAL

The ACF examined in the present study was a pitch based active carbon fiber supplied by Osaka Gas Co. (OG-8A, surface area 800m²/g). The ACF was heat-treated at 850°C to develop the highest activity for NO reduction with NH₃ (OG-8A-H850).

The reactivity and adsorption of NO-NH₃ (200 and 300ppm respectively in air) was studied by a conventional flow reactor at 25 to 70°C. The ACF of 0.5g (8cm length) was packed in the reactor. The flow rate of the total gas was fixed at 100 ml/min. Humidity of air was controlled by feeding H₂O in the reactor.

By analyzing the outlet NO and NH₃ concentrations by NO_x meters (NH₃ was oxidized before the analysis), the removal and desorption of NO were quantified to calculate the adsorption and the reduction of NO.

The desorption of NO and NH₃ adsorbed on the ACF during the NO-NH₃ reaction and their single flow was performed by program heating up to 300°C the ACF bed in the flowing He of 100ml. The heating rate was 3.3°C/min.

RESULTS

Removal of NO in the reactor with NH₃ over OG-8A-H850

Figure 1 illustrates the removal of NO in the presence of NH₃ in dry and humid (80%rh) air over OG-8A-H850 at 25 to 70°C by W/F : 5x10⁻³g·min/ml. NO was completely removed for initial 20min at 25°C in dry air and then its removal decreased gradually for 120min to give a stationary removal of 98%. The higher temperature shortened the periods of complete removal and gradual reduction, reducing the stationary removal. Thus the stationary removal obtained at 40, 55 and 70 was 85, 75 and 50%, respectively.

Relative humidity of 80% eliminated the period of complete removal under the present conditions and reduced the stationary removal to 20, 60, 50 and 40%, respectively, at 25, 40, 55 and 70°C. It should be noted that an intermediate temperature of 40°C allowed the largest removal of NO in humid air of 80%rh, being very contrast to the reaction in dry air.

Adsorption of NO and NH₃ at the early stage of the reaction

Figure 2 illustrates the temperature programmed desorption of adsorbed NO and NH₃ over OG-8A-H850 after for the NO-NH₃ reaction at 25°C for 3h.

NO started to desorb at 30°C, slowly up to 60°C, after which the desorption became may rapid to reach a maximum at 80°C. Further heating provide another maximum at 180°C. The total amount of desorbed NO was 7x10⁻²mmol/g ACF.

Ammonium started to desorb immediately after the switch of carrier gas and increased rapidly its concentration to the maximum at 40°C. The second maximum of small concentration was found at 230°C.

Figure 3 summarizes the amounts of adsorbed NO after 3h reaction at several reaction temperatures, as measured by the procedure described in Figure 2. The amount under dry conditions decreased monotonously at higher temperatures. In contrast, the amount at 80%rh showed the maximum at 40°C where the inhibition of H₂O may be reduced.

The conversion of NO by 3h shown in Figure 1 includes the amounts of reduced as well as adsorbed NO. The amounts of reduced NO thus calculated are plotted also in Figure 3. The amount of NO by 3h under dry conditions was much the same up to 55°C, then decreased sharply. Hence the conversion decreasing at the higher reaction temperature shown Figure 1 decreases reduction of NO reduction as well as adsorption.

In contrast, the amount of NO reduction was much higher at 40 - 70°C than at 25°C in humid air. Inhibition by H₂O on reduction and adsorption of NO is reduced at higher temperature where the adsorption of H₂O is minimized.

Figure 4 shows the adsorption amount of NO alone over OG-8A-H850 for 3h where adsorption appeared saturated. The amount of NO adsorption were very similar to those during NO-NH₃ in the same temperature range, indicating that the adsorption of NO is saturated regardless of NH₃ presence.

Reactivity of NO adsorbed during the NO-NH₃ reaction

Figure 5 illustrates the desorption profiles of NO during the NO-NH₃ reaction over OG-8A-H850 after the reaction with 300ppm NH₃ alone for 3h at 25 - 55°C. Desorption amount of NO was markedly reduced by the reaction with NH₃. NO desorbing at the lower temperature was reduced more readily by the reaction. The higher temperature reduced more NO of desorption.

DISCUSSION

The present study focussed the early stage of NO-NH₃ reaction over a pitch based active carbon fiber of fairly large surface heat-treated at 850°C. At the initial stage, NO was completely removed by adsorption and reduction over the ACF. The adsorption took place rapidly to contribute principally to the removal at the very initial stage, however its contribution decreases as the progress of run because the adsorption approaches the saturation. After the saturation of the adsorption, the NO removal becomes stationary. Although humidity reduces both adsorption and reduction, the situation of the NO removal over the ACF was basically common.

The higher reaction temperature reduces the adsorption of NO to decrease its reduction in dry air as previously reported and hence NO removal decreases. In contrast, the higher reaction temperature up to 40°C increased both adsorption and reduction in humid air because the inhibition of H₂O due to its adsorption decreases markedly up to 40°C. A particular temperature of 40°C allows the highest removal by compromising adsorptions of NO and H₂O.

The adsorbed NO at the early stage stayed unreduced while NO and NH₃ are fed. However NH₃ alone can reduce NO, the higher temperature up to 45°C accelerating the reduction. It should be noted that two adsorbed species of NO are present on the ACF, of which desorption temperatures are very different and that the NO species desorbing at the lower temperature is more reactive with NH₃. It is also worthwhile to note that the stationary reduction of NO does not appear to reflect such adsorbed species. More details of NO adsorbed species are of value to be analyzed. The lower stationary removal of NO in humid air is a task to be overcome for the practical application. The removal of NO at early stage which includes both adsorption and reduction can be applied for the complete removal where the regeneration of adsorption ability by reducing adsorbed NO and NO removal can be practically cycled. The optimization is the next target of the study.

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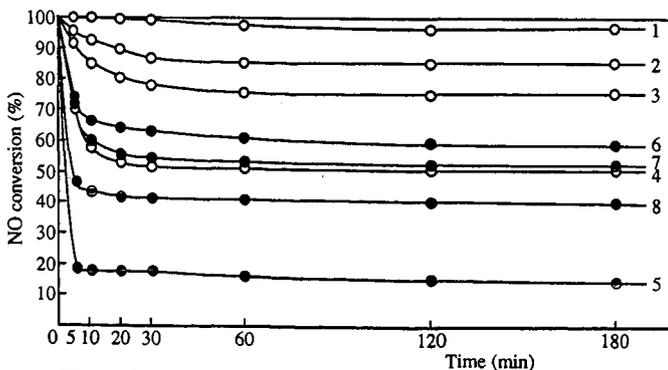


Fig.1 NO-NH₃ reaction profile over ACF OG-8A-H850 in dry and wet air
 NO : NH₃ = 1:1.5 (NO = 200ppm), O₂ = 10%, N₂ balance
 W/F = 5 × 10⁻³ g · min · ml⁻¹, W = 0.5g, Time : 180min
 Dry (r.h. = 0%) : ○ 1. 25°C, 2. 40°C, 3. 55°C, 4. 70°C
 Wet (r.h. = 80%) : ● 5. 25°C, 6. 40°C, 7. 55°C, 8. 70°C

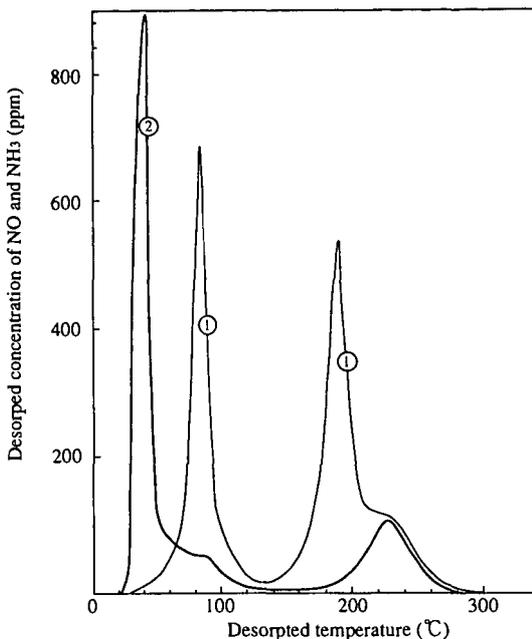


Fig. 2 Desorption profile of NO and NH₃ after NO-NH₃ reaction over OG-8A-H850

Reaction : NO : NH₃ = 1 : 1.5 (NO = 200 ppm), O₂ = 10%, N₂ balance
 W = 0.5g, W/F = 5 × 10⁻³ g · min · ml⁻¹, Temp. = 25°C
 r.h = 0%, Time = 180 min
 Desorption : Flow gas (He) = 100 ml/min, Temp. : 25 - 300°C
 H.R. = 3.3°C/min
 ○ 1 NO, ○ 2 NH₃

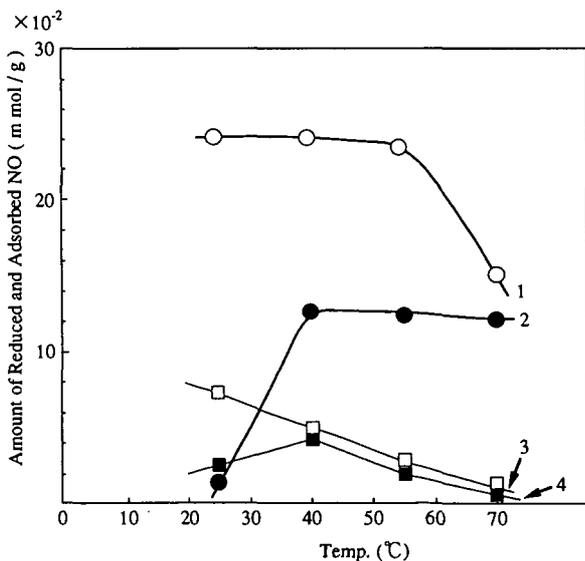


Fig. 3 NO reduction and adsorption over OG-8A-H850

NO : NH₃ = 1 : 1.5 (NO = 200 ppm), N₂ balance, O₂ = 10%
 W/F = 5 × 10⁻³ g · min · ml⁻¹, W = 0.5, F = 100 ml/min, Time : 180min
 ○ : 1. Reduction (Dry, rh = 0%) □ : 3. Adsorption (Dry, rh = 0%)
 ● : 2. (Wet, rh = 80%) ■ : 4. (Wet, rh = 80%)

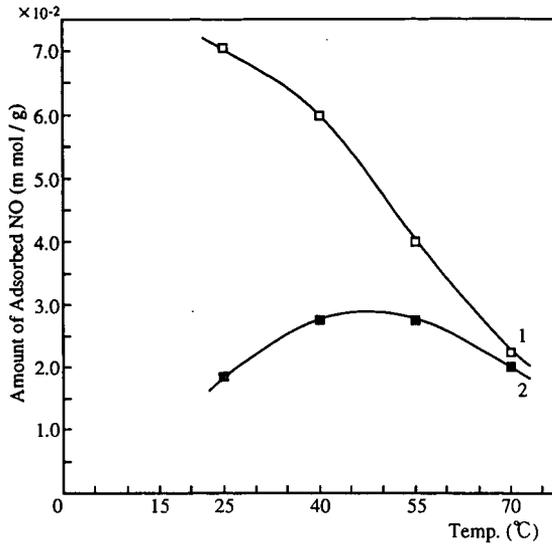


Fig. 4 Adsorption amount of NO alone over OG-8A-H850

NO : 300ppm, W/F = $5 \times 10^{-3} \text{ g} \cdot \text{min} \cdot \text{ml}^{-1}$, W = 0.5g, Time : 180min
 1 : Dry (r.h. = 0%), 2 : Wet (r.h. = 80%)

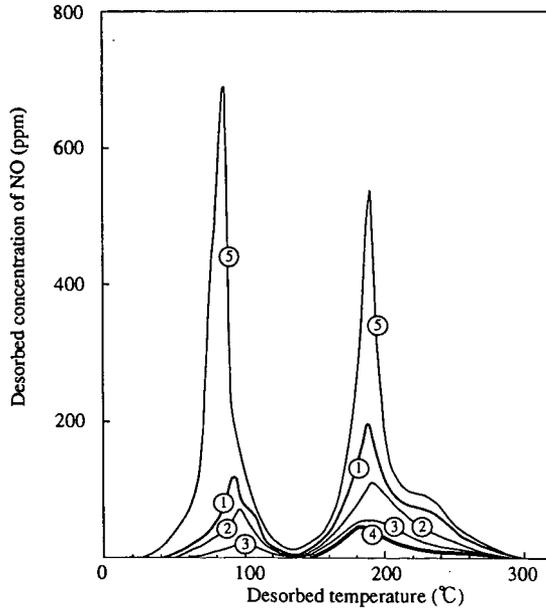


Fig.5 Desorption after regeneration with NH_3 of adsorbed NO during NO- NH_3 reaction

ACF : OG-8A-H850 (Pitch based)
 Reaction : NO : NH_3 = 1 : 1.5 (NO = 200ppm), O_2 = 10%, N_2 balance,
 W / F = $5 \times 10^{-3} \text{ g} \cdot \text{min} \cdot \text{ml}^{-1}$, r.h. = 0%, Time : 180min
 Regeneration : NH_3 = 300 ppm, O_2 = 10%, N_2 balance
 W/F = $5 \times 10^{-3} \text{ g} \cdot \text{min} \cdot \text{ml}^{-1}$, W = 0.5g
 r.h = 0%, Temp. : 25 - 55°C, Time : 180min
 Desorption : Flow gas (He) = 100 ml/min, Temp. : 25 - 300°C, H.R. = 3.3°C/min
 ① Regen. Temp. = 25°C ④ Regen. Temp. = 55°C
 ② " " = 35°C ⑤ Non-Regen.
 ③ " " = 45°C