

NITRIC OXIDE(NO) REMOVAL ON COPPER IMPREGNATED ACTIVATED CARBON FIBERS

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Introduction

Nitric oxide(NO) is an important atmospheric pollutant[1]. It is necessary to investigate effective methods for removing NO from the atmospheric environment. There are many studies on the removal of NO through unarmful species such as N₂ and O₂. The selective catalytic reduction (SCR) of NO in flow gases has been investigated, as proven and applicable technology, by using reducing agents such as CO, H₂, NH₃, and aliphatic carboxylic acid [3,7]. But the disadvantage of the process is that it requires a complex and expensive setup for safely handling NH₃, which is a hazardous chemical, results in catalyst plugging, fouling, in the processing of it [4]. Activated carbon has attracted much attention for the reduction of NO [2,4,7]. Sometimes, NO should be decomposed in the high temperature adsorbent packing tower. In recent years, theoretical and applied aspects of the catalytic decomposition of NO by the metal (Ni, Fe, Cu, K, and Na) on carbon prepared by impregnation with an aqueous solution of nitrate or acetate of metal have been elucidated in research. Especially, copper metal shows the most efficient catalytic activity toward the reduction of NO onto N₂ and O₂ [1,5]. ACF is a newly developed carbon adsorbent and not so much reports as well as activated carbons in using catalyst supports for the removal of atmospheric pollutants. In this paper, copper was impregnated on ACF to decompose NO gas by catalytic decomposition at 300-400 °C, and the decomposition mechanism was investigated.

Experimental

2.1 Cu-impregnated ACF

ACF (KF-1500, Toyobo Co.) was wet-chopped to 3-4mm length, added to Cu(NO₃)₂ · 3H₂O solution. The Cu(NO₃)₂ impregnated ACF was heated up to 500 °C to obtain Cu-particles on ACF[8]. The adsorption characteristics of Cu-impregnated ACFs were measured by N₂ adsorption at 77 K. The samples denoted in Cu-3, Cu-5, Cu-10, and Cu-20 were 3, 5, 10, and 20wt% Cu-impregnated ACFs, respectively. SEM and XRD analysis were carried out to investigate the scattering of Cu particles on ACF surface.

2.2 NO decomposition

Figure 1 shows the schematic view of experimental apparatus. In order to investigate the NO decomposition, Cu-impregnated ACFs were placed in a conventional adsorption-bed quartz column and heated up to reaction temperature under N₂ flow. Then, NO/He gas was flowed into the column in the absence of O₂. The effluent gas was monitored with a stack gas analyzer. The decomposition of NO was determined from the concentration of NO in the effluent stream. XRD analysis was performed to investigate the change of copper particles during the catalytic reaction with NO gas.

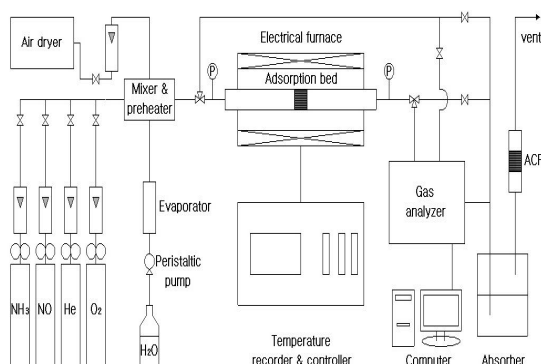


Figure 1. Schematic view of the experimental apparatus

Results and Discussion

3.1 Characteristics of Cu-impregnated ACF

Table 1 shows the characteristics of Cu-impregnated ACFs. The BET specific surface area and the micropore volume decreased as the amount of Cu-impregnation increased, resulting in the increase of average pore diameter. It is known that Cu particles blocked the entrance of narrow micropores. Nevertheless, the ACFs have great potential as adsorption materials being the type I, within the range of well-developed micropores according to the BET classification.

Table 1. Characteristics of Cu-impregnated ACFs

ACF (wt%)	BET surface area (m ² /g)	Total pore volume (cc/g)	Micropore volume (cc/g)	Average pore dia. (Å)
Cu-0	1497	0.83	0.79	14.9
Cu-3	1270	0.51	0.50	16.1
Cu-5	1146	0.46	0.45	16.1
Cu-10	1005	0.42	0.40	16.5
Cu-15	797	0.34	0.32	16.8
Cu-20	659	0.31	0.28	18.5

Figure 2 shows the TGA curves of 10wt% Cu-impregnated ACFs in air and N₂ surrounding. The Cu(NO₃)₂ was decomposed to form CuO and Cu₂O between 225 °C and 255 °C. These copper oxides decomposed again remaining Cu particles as a form of ACF-C_(s)(Cu) through heat treatment up to 500 °C. The Cu particles were confirmed by the XRD analysis, the result was well agreed with those of Marquez-Alvarez [2]. Figure 3 shows the SEM photos of Cu-impregnated ACF surface. The amounts of surface-adsorbed Cu particles increased as the increase of copper oxide compound concentration. Some Cu particles have a tendency to aggregate through the heat treatment.

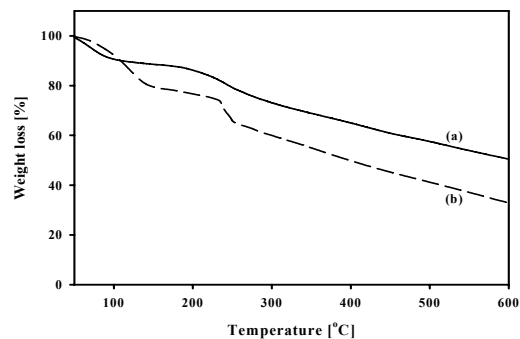


Figure 2. TGA curves of Cu-impregnated ACFs in (a) N₂ and (b) air.

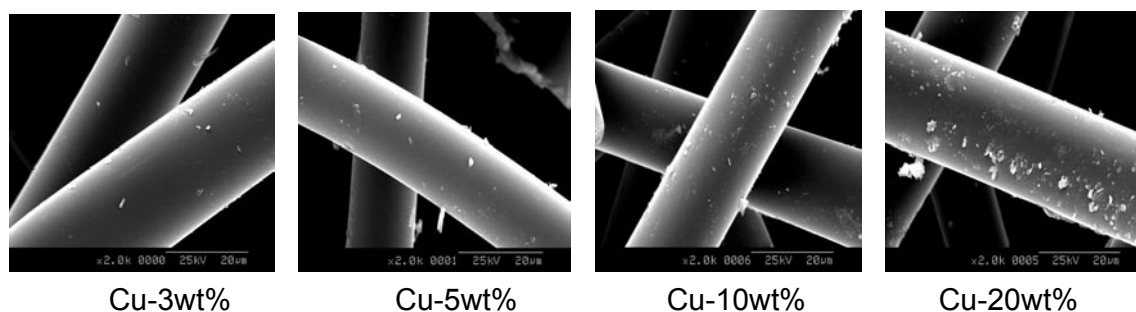


Figure 3. SEM photos of Cu-impregnated ACFs.

3.2 Removal of NO through Cu-impregnated ACF packing column

Figure 4 shows the breakthrough curves of NO on as received ACFs at 20°C and 300°C. The breakthrough times were very short and both curves were steep just after the breakpoints, which means that the adsorption capacity of NO on ACF was very poor in spite of large specific surface area. Figure 5 shows the breakthrough curves of NO on Cu-impregnated ACFs at 400°C. NO gas was effectively decomposed for a very long time. Also, the 10wt% Cu-impregnated ACF shows the lowest NO concentration in the outlet stream, however the 5wt% Cu-impregnated ACF decomposed NO gas very well too, even though the impregnated amounts was far smaller than 20wt% ACF. Park [5] reported that 5wt% Cu-plating on activated carbon was the optimum amounts for the removal of NO gas. Yoshikawa [7] reported that NO conversion by catalytic reaction with transition metal-oxides was directly proportional to the amount of impregnated catalysts and the reaction temperature. Figure 6 shows the XRD profiles of the 10wt% Cu-impregnated ACFs (A) before catalytic reaction, (B) after reaction with NO for 325min., and (C) after reaction with NO for 900min. at 400°C.

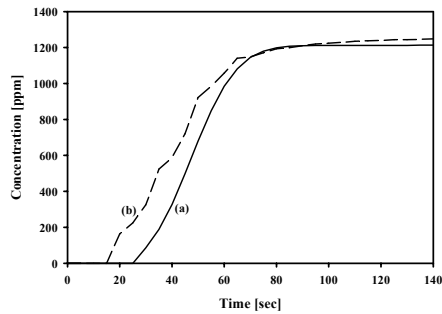


Figure 4. Breakthrough curves of NO on ACFs at 20°C(a) and 300°C(b).

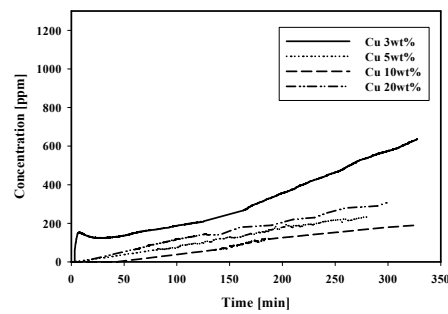


Figure 5. Breakthrough curves of NO on Cu impregnated ACF at 400°C.

The profile (A) shows only the Cu peaks at $2\theta = 43.3$ and 50.5 . The profile (B) shows Cu_2O peaks at $2\theta = 36.4$, 42.3 , and 61.3 besides Cu peaks, which means some of Cu particles converted into Cu_2O during the first catalytic reaction stage with NO gas at 400°C . The profile (C) shows that Cu_2O converted into CuO during the second catalytic reaction stage with NO gas. Regeneration of ACF-C(Cu) from ACF-C(CuO) was carried out by simply heating it in N_2 surrounding. Park and Jang [6] reported that there was no CuO peaks during the NO gas decomposition by ACF/Cu catalyst at 400°C . However, Marquez-Alvarez et al.[2] have reported the existence of Cu_2O by the carbon-supported copper catalytic removal of NO gas. There was little consumption of ACF in mass during the catalytic decomposition of NO gas to N_2 by copper. Therefore, following NO gas decomposition mechanism can be suggested by Cu-impregnated ACF at 400°C .

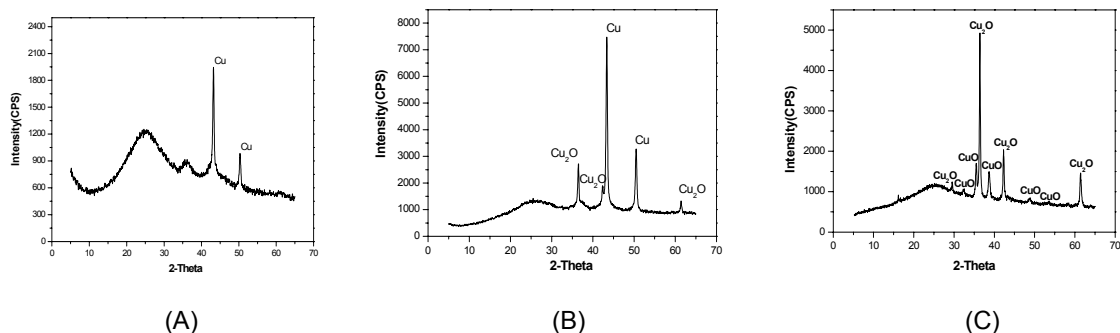
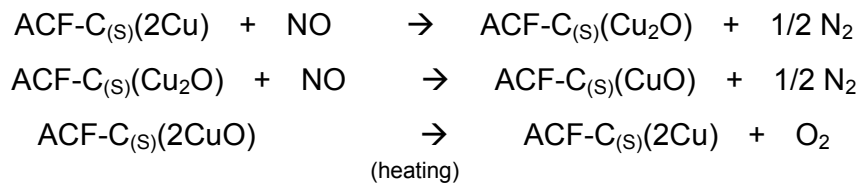


Figure 6. XRD profiles of the Cu-impregnated ACFs at 400°C , (A) before reaction, (B) after reaction with NO for 325min., and (C) after reaction with NO for 900min.

Conclusions

The catalytic decomposition of NO gas has been performed by Cu-impregnated activated carbon fibers at 300-400 °C in helium surrounding. Initial NO concentration was 1300ppm. The as-received ACF adsorbed NO very little, even though it has a high specific surface area. However, NO was effectively decomposed by 5-10wt% Cu-impregnated ACF at 400 °C. The concentration of NO was maintained less than 200ppm for 6 hours in this system. The Cu-impregnated ACF-C(Cu) deoxidized NO to N₂ and was reduced to ACF-C(Cu₂O) in the initial stage. The ACF-C(Cu₂O) also deoxidized NO to N₂ and was reduced to ACF-C(CuO). This ACF-C(CuO) was converted into ACF-C(Cu) by heating it in N₂ surrounding, which can be used again. There was little consumption of ACF in mass during the catalytic decomposition of NO to N₂ by copper. The catalytic decomposition was accelerated by increasing the reaction temperature.

Acknowledgements

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