Remarkable Activity Enhancement of Pitch Based Active Carbon Fibers by Heat-treatment for Oxidative SO_2 Removal

Isao Mochida, Keiichi Kuroda, Yuji Kawabuchi, Shizuo Kawano, Yuji Matsumura,† and Masaaki Yoshikawa†
Institute of Advanced Material Study, Kyushu University, 6-1 Kasuga-koen, Kasuga, Fukuoka 816
†Research and Development Center, Osaka Gas Co., Ltd., 6-19-9 Torishima, Konohana-ku, Osaka 554

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Oxidative capture and recovery of SO_2 in form of H_2SO_4 was examined over pitch based active carbon fibers (P-ACF-OG-15A and -20-A). The fiber calcined at 1100 °C was found to exhibit a remarkable activity to remove completely 1000 ppm SO_2 at a contact time of $1x10^{-3}$ g·min ·ml^{-1} with 10% H_2O at 30 °C. Hydrophobicity appears important to show such a high activity.

The present authors have proposed a novel system for the removal of SO_2 in the flue gas where SO_2 is adsorbed, oxidized and hydrated over polyacrylonitrile based active carbon fibers (PAN-ACF) to be continuously recovered in the form of aq. H_2SO_4.[1-3] Higher activity of ACF and less amount of humidity are requisite for smaller volume of the reactor, recovery of more concentrated H_2SO_4 and less consumption of water to reduce the cost of flue gas cleaning. The present authors have found significant enhancement of the catalytic activity of PAN-ACF by the heat treatment at 800 °C.[4,5] Such enhancement was found with pitch based ACF for the oxidation and reduction of NO in humid air.[6,7] There a some reports that the pitch based ACF showed specific adsorption ability to SO_2.[8,9] Although we aim the oxidation and hydration of SO_2 on the ACF, the pitch based ACF can be expected to show high activity. In the present study, catalytic activities of pitch based ACFs of high surface area were examined for the oxidative removal of SO_2. Pitch based ACF of as-received form has been reported to be inferior to PAN-ACF in the oxidative adsorption of SO_2.[5] However, the heat-treatment is expected to enhance its catalytic activity as observed in NO reactions.[6,7] Hence the heat-treatment at rather high temperatures above 1000 °C was examined to find higher activity. The hydrophobic surface of pitch based ACF can be expected to require smaller amount of H_2O for the complete removal of SO_2. OG series of pitch based ACF OG-15A and OG-20A were supplied by Osaka gas Co.. They were heat-treated in nitrogen gas at varying temperatures. Some of their properties are summarized in Table 1. SO_2 removal was carried out at 30 °C, using a fixed bed flow reactor. Weights of ACF were 0.1 and 0.25 g. The total flow rate was 100 ml·min^{-1}. The model flue gas contained SO_2 of 1000 ppm, O_2 of 5 vol% and H_2O of 5, 7.5 and 10 vol% in nitrogen. Aq.H_2SO_4 was recovered at the outlet of the reactor. SO_2 concentrations in the inlet and the outlet gases were observed continuously by a flame photometric detector (FPD).

Table 1. Some properties of pitch based active carbon fibers

ACFs	Ultimate analysis (wt%)					Surface area (m²/g)
	C	H	N	O	Ash	
OG-20A	93.9	0.9	0.3	4.6	0.5	2149
OG-20A-H1000[a]	95.8	0.6	0.3	2.8	0.5	1721
OG-20A-H1100[a]	97.5	0.1	0.2	1.6	0.6	1720
OG-20A-H1200[a]	98.0	0	0.2	1.2	0.6	1683
OG-15A	93.9	0.9	0.7	4.1	0.4	1927
OG-15A-H1000[a]	95.8	0.6	0.6	2.5	0.5	1547
OG-15A-H1100[a]	96.6	0.2	0.5	2.2	0.5	1485
OG-15A-H1200[a]	97.6	0.1	0.4	1.4	0.5	1307

[a] Calcination temperature (℃).

Figure 1 illustrates the desulfurization profiles of 1000 ppm SO_2 by as-received and heat-treated, OG-20A at W/F (Weight/Flow) = $1x10^{-3}$ g·min ·ml^{-1}, 10% humidity and 30 °C. The favorable influences of the heat-treatment at higher temperature up to 1100 °C were definite. Thee heat-treatment at 1000 °C increased the stationary removal up to 80 from 5% over the as-received OG-20A. A further higher temperature of 1100 °C removed completely SO_2 of 1000 ppm for at least 15 h. High temperature of 1200 °C decreased the activity to 40% removal.

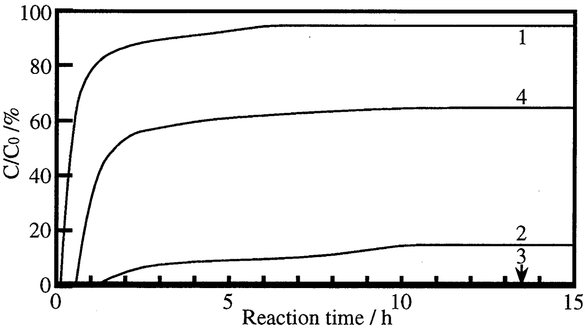

Figure 1. Breakthrough profiles of SO_2 over pitch-ACFs of OG-20A
SO_2 1000 ppm, O_2 5 vol%, H_2O 10 vol%
W/F : 1.0×10^{-3}g min mL^{-1} , Reaction Temp 30 ℃
1: OG-20A
2: OG-20A-H1000
3: OG-20A-H1100
4: OG-20A-H1200

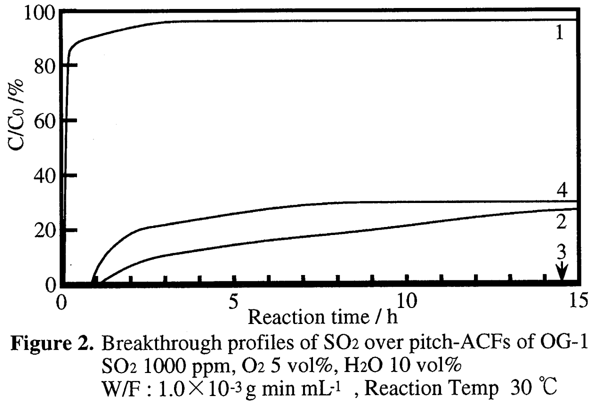

Figure 2. Breakthrough profiles of SO_2 over pitch-ACFs of OG-15A
SO_2 1000 ppm, O_2 5 vol%, H_2O 10 vol%
W/F : 1.0×10^{-3}g min mL^{-1} , Reaction Temp 30 ℃
1: OG-15A
2: OG-15A-H1000
3: OG-15A-H1100
4: OG-15A-H1200

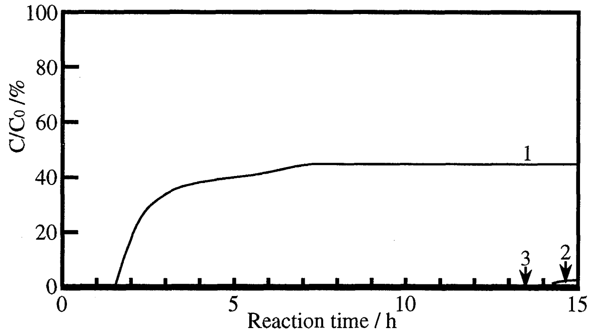

Figure 3. Breakthrough profiles of SO_2 over heat-treated pitch-ACF at several humidity
SO_2 1000 ppm, O_2 5 vol%
W/F : 1.0×10^{-3}g min mL^{-1} , Reaction Temp 30 ℃
ACF : OG-20A-H1100
H_2O 1 : 5vol%, 2 : 7.5vol%, 3 : 10vol%

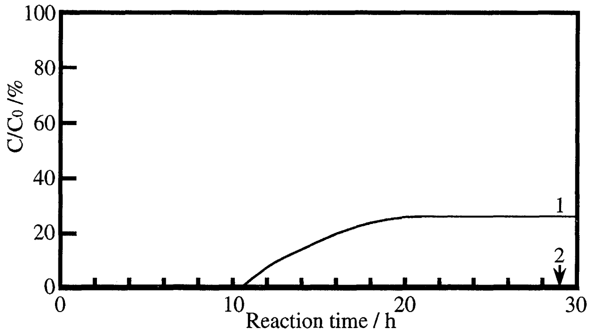

Figure 4. Breakthrough profiles of SO_2 over OG-20A-H1100 by larger W/F under lower humidity
SO_2 : 1000 ppm, O_2 : 5 vol%, H_2O : 5 vol%
Reaction Temp 30 ℃
W/F 1: 2.5×10^{-3}g min mL^{-1}
2: 5.0×10^{-3}g min mL^{-1}

There is certainly an optimum temperature of the heat-treatment with this particular OG-20A of very large surface area. Longer contact time of W/F = $2.5x10^{-3}$ g·m in/ml allowed a complete removal of SO_2 over OG-20A-H900.

Figure 2 illustrates the catalytic activity of as-reseived OG-15A of slightly smaller surface area, and its heat-treated forms at 1000, 1100, and 1200 (H1000, H1100, and H1200) at W/F $1x10^{-3}$ g ·min/ml and 10% H_2O. The heat treatment above 1000°C was also very effective in enhancing the activity of this fiber, allowing complete removal of SO_2 by the heat treatment at 1100 °C. The activities of their as-reseived ACFs were much the same regardless of their surface area. However, heat-treatment at 1100 °C provided OG-20A of larger surface area with higher activity.

Figure 3 illustrates the effects of humidity on the SO_2 removal over OG-20A-H1100 at 30°C. Lower concentration of H_2O decreased the extent of SO_2 removal, providing 100% removal at 10% H_2O, 96% at 7.5% H_2O, and 55% at 5% H_2O.

Figure 4 illustrates the conversion of SO_2 over OG-20A-H1100 when W/F was varied at a fixed humidity. Complete removal of SO_2 at 5% H_2O required W/F of $5x10^{-3}$ g ·min/ml. It should be noted that larger W/F allowed the complete removal of SO_2 by the saturated humidity at the reaction temperature.

The present letter reported a remarkably high activity of a pitch based active carbon fiber of very large surface area after the heat-treatment at unusually high temperature of 1100 °C. The activity observed in the present study allowed the complete removal of 1000 ppm SO_2 at room temperature by the space velocity of ca.8000 h^{-1} over OG-20A-H1100. Such a activity was ca.3 times higher than that observed with the best heat-treatment PAN-ACF in previous papers.[4] A very small volume of reactor is designed by such a high activity.

The heat-treatment at 1100 °C eliminated almost completely the surface oxygen functional groups. The site produced through such elimination may be active for the SO_2 oxidation, although no structural evidence for such sites is obtained. Enhanced hydrophobicity is another advantage of the ACF heat treated at 1100 °C. Further higher temperature of the heat-treatment reduced significantly the surface area through the graphitization probably removing the active sites.

ACF of larger surface area is prepared by the larger burn off which increases the cost of ACF. In this case, OG-15A is much more reasonable than OG-20A. although the activity of the former fiber was slightly inferior. Although Pitch ACF of moderate activation and high activity is a practical target in the successive study, the present letter clarifies definitely the possibility that the very high activity acceptable for the practically desulfurization of atmosphere as well as the flue gas is obtainable with pitch based ACF of reasonable price after the adequate heat-treatment. The second point of interest is the lowest humidity for the complete SO_2 removal. OG-20A-H1100 of the highest activity in this letter achieved complete removal of SO_2 at 5% H_2O when W/F was as large as $5x10^{-3}$ g·m in/ml. Although it is not clear yet whether higher humidity or larger W/F is feasible in practice, their compensating roles are proved in this study.

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