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Continuous Removal of SO_2 in the Model Flue Gas over PAN-ACF with Recovering Aqueous H_2SO_4

Seiki KISAMORI, Shizuo KAWANO, and Isao MOCHIDA
Institute of Advanced Material Study, Kyushu University, 6-1 Kasuga-koen, Kasuga, Fukuoka 816

SO_2 was adsorbed, oxidized, hydrated, and recovered continuously as aq. H_2SO_4 at 30-100 ℃ on a polyacrylonitrile based active carbon fiber (PAN-ACF-FE-300). SO_2 of 1000 ppm in a model flue gas was removed completely for longer than 60 h at 30 and 50 ℃ by $W/F=5.0x10^{-3}$ g min ml^{-1} by supplying sufficient humidity of 10 and 20 vol%, respectively. The heat-treatment of the ACF at 800 ℃ was found very effective to enhance the catalytic activity.

More energy-saving, deeper removal of SO_2 in the flue gas has been expected to be developed for the better environment with smaller increase of the cost. Although the wet desulfurization of flue gas using calcium hydroxide in water has been widely commercialized,1) desulfurization of higher efficiency is expected. The desulfurization consumes calcium hydride, to produce gypsum of low value as by-product, requiring a large amount of water and leaking ca. 50 ppm of SO_2. Oxidative adsorption of SO_2 in the form of H_2SO_4 on active carbon or coke around 130 ℃ is a basis for a dry process.2-4) The present authors have reported a remarkably large capacity of PAN-ACF among various ACFs for such an oxidative adsorption.5,6) Such a dry process using carbon adsorbents should heat up the adsorbents after the SO_2 adsorption to recover SO_2 adsorbed in the form of H_2SO_4 on the carbon surface and to regenerate the adsorption ability. At the same time, oxygen functional groups which are introduced by adsorption and desorption of SO_2 should be removed because such oxygen functional groups reduce SO_2 adsorption ability of ACF.7,8) The reduction of SO_3 into SO_2 at the recovery consumes the carbon as carbon dioxide or monoxide. The carbon adsorbent loses its weight and adsorption ability very rapidly, when flue gas of large SO_2 concentration is charged. Such energy and carbon consumption is one of the critical disadvantages.2,7) Hitachi has proposed extraction of adsorbed SO_2 on active carbon with water, however, it took so much water to obtain a diluted H_2SO_4.9)

The present paper proposes a solution of the problem, by recovering aq. H_2SO_4 continuously from the surface of PAN-ACF at the SO_2 removal temperature without any carbon loss. PAN-ACF is certainly active to oxidize catalytically SO_2 into SO_3 even at room temperature. Hence continuous hydration of SO_3 may allow the flow of aq. H_2SO_4 from the ACF surface to the reservoir, liberating the active sites for the oxidation and hydration of the successive SO_2 molecule. The present process can be applicable to remove SO_2 in the atmosphere as well as flue gas without any difficulty.

FE-300 was supplied by Toho Rayon Co. and was heat-treated in nitrogen at 800 ℃ for 1 h. It is abbreviated as FE-300-800.

SO_2 removal was carried out at 30-100 ℃ using a fixed bed flow reactor which is illustrated in Fig.1. A model flue gas containing SO_2 of 1000 ppm, O_2 of 5 vol% and H_2O of 10-30 vol% in nitrogen was used. H_2SO_4 was trapped at the outlet of the reactor as illustrated in Fig.1. A part of H_2O was condenced to dew drops in the reactor when water vaper of 10 and 20 vol% was introduced at 30 and 50 ℃, respectively. Therefore, concentrations of SO_2 and H_2O in the model gas were increased slightly and the total flow rate was decreaced slightly in those cases compared with other cases. SO_2 concentrations in inlet and outlet gases were observed continuously by frame photometric detector (FPD). Weights of ACF examined and the total flow rate were 0.25, 0.5, and 1.0 g, and 100 ml min^{-1}, respectively.

Figure 2 illustrates the break-through profiles of SO_2 at several temperatures through the bed of FE-300-800. The gas carried 10 vol% water in all cases. SO_2 was adsorbed completely at 100 ℃ until 5.1 h (the break-through time, T_0), no SO_2 being detected at all at the outlet of the reactor, and then SO_2 started to leak, its concentration increasing rather rapidly to 100% of the inlet SO_2 after 10.5 h. SO_2 of 4.0 mmol g^{-1} was captured on the ACF at 100 ℃. Lower temperature of 80 ℃ extended the break-through time to 8.5 h until SO_2 was detected at the outlet of the reactor. After the break-through, SO_2 concentration at the outlet increased rather gradually by 24 h until it reached to 65% of the inlet concentration, and that of the outlet stayed at the same level later on until at least 45 h. Further lower temperature of 50 ℃ extended the break-through time to 10.5 h. At this temperature, the outlet concentration increased very slowly to 25% after 25 h. While the removal of SO_2 continued, some elusion of aq. H_2SO_4 was observed at outlet of the reactor. At room temperature of 30 ℃, SO_2 was completely removed at least 60 h while no SO_2 was observed at the outlet. Elusion of aq. H_2SO_4 was clearly observed at the outlet.

Activity of as-received FE-300 at 30 ℃ is also illustrated in Fig.2. Although the ACF also removed SO_2 continuously as aq. H_2SO_4 at 30 ℃, the activity was certainly inferior to that of the heat-treated one.

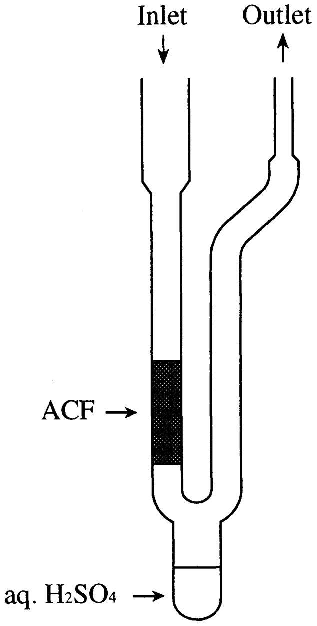

Fig.1. Reactor for desulfurization.

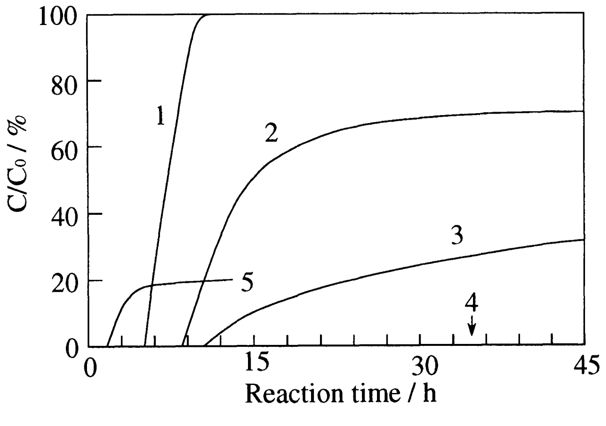

Fig.2. Breakthrough Profiles of SO_2 through FE-300 (as-received PAN-ACF) and FE-300-800 (heat-treated FE-300) at Several Temperatures; SO_2 1000 ppm, O_2 5 vol%, H_2O 10 vol%; W/F=5.0×10^{-3}g min ml^{-1}
1:FE-300-800 at 100 ℃, 2:FE-300-800 at 80 ℃, 3:FE-300-800 at 50 ℃, 4:FE-300-800 at 30 ℃, 5:FE-300 at 30 ℃;
No.4 adsorbed SO_2 completely until 60 h.

Figure 3 summarizes the influences of H_2O concentration on the break-through profiles of SO_2 through FE-300-800 at 80 and 50 ℃. Higher concentration of H_2O (20 and 30 vol%) extended slightly the break-through time at 80 ℃ and reduced markedly the stationary concentration of SO_2 at the outlet after the concentration became steady. The stationary concentration under 10, 20, and 30 vol% H_2O were 60, 55 and 10%, respectively. The influence of H_2O concentration was more drastic at 50 ℃. H_2O concentration of 20 vol% allowed a steady SO_2 removal of 100%, no SO_2 being detected for 60 h, whereas 10 vol% H_2O provided 30% steady concentration at the outlet. When the steady removal of SO_2 was achieved, elusion of aq. H_2SO_4 was observed. Hence, SO_2 is adsorbed, oxidized, and hydrated into aq. H_2SO_4 on the ACF surface which flows out from the bed to be stored in the reservoir at the reactor outlet (Fig.1). Thus, the removal of SO_2 is expected to continue. Enough water is necessary to hydrate SO_3 and to dilute H_2SO_4 to flow smoothly through the ACF bed.

Figure 4 summarized the influences of W/F (Flow rate was fixed at 100 ml min^{-1}) on the break-through profiles of SO_2 through FE-300-800 at 100 and 30 ℃ when humidity was fixed at 10 vol%. In the case of 100 ℃, break-through time (T_0) was extended drastically with increasing of W/F. When the weight of the ACF increased from 0.25 g to 1.0 g, T_0 was extended markedly from 1.8 h to 18 h. The concentration of SO_2 at the outlet was saturated to be 100% by 10-15 h when ACF of 0.25 and 0.5 g was used, respectively. When the ACF was increased to 1.0 g, SO_2 concentration at the outlet increased very slowly but continuously even 45 h after SO_2 adsorption started. Larger amount of ACF may allow the better contact of the gas with the fiber and some storage of adsorbed H_2SO_4 to fill the void in its bed.

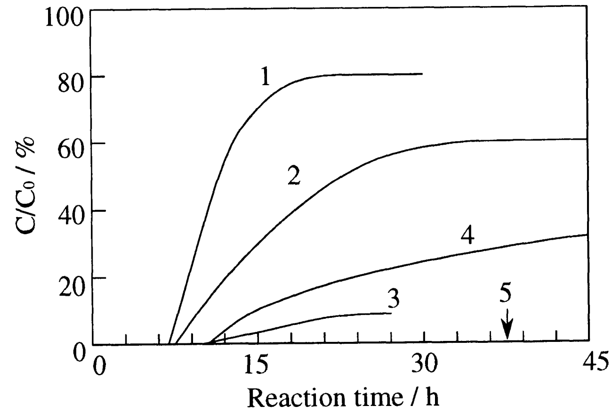

Fig.3. Effect of H_2O Concentration for SO_2 Removal; SO_2 1000 ppm, O_2 5 vol%, W/F=5.0×10^{-3} g min ml^{-1} ; ACF:FE-300-800
1:H_2O 10 vol%, 80 ℃; 2:H_2O 20 vol%, 80 ℃;
3:H_2O 30 vol%, 80 ℃; 4:H_2O 10 vol%, 50 ℃;
5:H_2O 20 vol%, 50 ℃;
No.5 adsorbed SO_2 completely until 60 h.

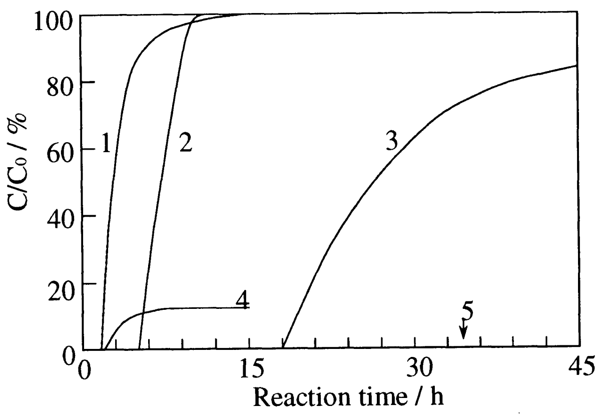

Fig.4. Influence of W/F for SO_2 removal; SO_2 1000 ppm, O_2 5 vol%, H_2O 10 vol%; ACF : FE-300-800
1:100 ℃, W/F=2.5×10^{-3}g min ml^{-1}
2:100 ℃, W/F=5.0×10^{-3}g min ml^{-1}
3:100 ℃, W/F=1.0×10^{-2}g min ml^{-1}
4: 30 ℃, W/F=2.5×10^{-3}g min ml^{-1}
5: 30 ℃, W/F=5.0×10^{-3}g min ml^{-1}
No.5 adsorbed SO_2 completely until 60 h.

The ACF removed SO_2 completely for 60 h at least by W/F = 5.0x10^{-3} g min ml^{-1} at 30 ℃. However, 0.25 g of ACF removed SO_2 completely for 2.0 h, and then SO_2 started to leak. SO_2 concentration in the outlet increased continuously to 10% by 7.5 h, and stayed at the level until 15 h at least, leaving aq. H_2SO_4 in the reservoir.

The oxidation and hydration of adsorbed SO_2 were found to proceed on the PAN-ACF surface at a temperature range of 30-100 ℃. The surface of the activated carbon was found to oxidize SO_2 efficiently and rapidly. The key point of the present study is to achieve the continuous recovery of aq. H_2SO_4 by supplying H_2O vapor onto ACF. The results indicate that the necessary concentration of water vapor is very much dependent on the reaction temperature, being 20 vol% at 50 ℃ and 10 vol% at 30 ℃ when the W/F was large enough. Higher reaction temperature requires more supply of water. A H_2SO_4 can flow only when it is diluted to a certain concentration by the sufficient water on the ACF surface. Water is condensed on the ACF from the gas phase basically according to the relative humidity, although H_2SO_4 itself may adsorb water.

Fiber form of ACF may be favorable for smooth flow of aq. H_2SO_4 through the adsorbent bed. Flue gas sometimes requires further reduction of NOx after the desulfurization. Hence the temperature of desulfurization should be balanced since higher temperature is favorable for the reduction while lower desulfurization temperature requires less water. The flow of aq. H_2SO_4 may depend also on the surface structure of ACF. It is worthwhile to note that the heat-treatment at 800 ℃ increased significantly the ability of SO_2 recovery. The oxidation appears to be enhanced. Such treatment may introduce the active site for adsorption[6,7] and oxidation of SO_2 through the evolution of CO and CO_2 by decomposition of surface oxygen functional groups on ACF. Kinetic study and search for better ACF are now in progress to perform the compete removal of SO_2 with less amount of water supply.

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