Kinetic Study on the H_2SO_4 Recovery Desulfurization over PAN-ACF and its Analysis

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Introduction

Removal of SO_2 and NOx from flue gas is important because they cause acid rain. Current SO_2 removal from flue gas has been carried out by wet desulfurization using a calcium hydroxide slurry. Significant leakage of SO_2, consumption of lime stone, energy and water, and the production of $CaSO_4$ are the problems of the method. SO_2 adsorption on active carbon is one of the expected dry methods. SO_2 is oxidized and hydrated to sulfuric acid on active carbon. Problems of this method are limited capacity, difficulty of regeneration and oxidative loss of active carbon as CO and CO_2 by the regeneration. Regeneration by washing to recover aq. H_2SO_4 requires a large amount of water.

The present authors have reported that PAN-ACF can completely capture SO_2 in form of aq. H_2SO_4 which can be recovered continuously with an addition amount of water. The objective of the present report is to study the reaction kinetics in terms of SO_2, O_2 and H_2O concentrations over variable amount of the ACF.

Experimental section

FE series of PAN-ACFs were supplied by Toho Rayon Co.. They were heat-treated in nitrogen gas at 800°C. SO_2 removal was carried out at 30°C using a fixed bed flow reactor. Weights of ACF were 0.25, 0.5, 0.75 and 1.0g. The total flow rate was 100ml min^{-1}. The model flue gas containing 10-1000ppm of SO_2, 0-500ppm of NO, 0-15vol% of O_2 and 0-20vol% of H_2O in nitrogen was used. 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) and NOx gases were analyzed by NOx meter (ECL-88US, Yanagimoto Co.,Ltd.).

Result

Figure 1 illustrates the influence of O_2 concentrations over PAN-ACF-FE-300-800 at 30°C. Without oxygen, SO_2 concentration in the outlet gas increased very sharply to be 100% of the inlet gas within 1h. More than 3% of oxygen allowed 62% SO_2 removal regardless of oxygen concentration by W/F (weight/flow rate) of 2.5×10^{-3} g min ml^{-1} in 10vol% of H_2O.

Figure 2 illustrates the break-through profiles of SO_2 at H_2O of 5-10% at 30°C. SO_2 was removed completely for longer than 20h when the concentration of H_2O was 10%. While SO_2 leaked out when the concentration of H_2O decreased to 7.5% or less.

Figure 3 illustrates the break-through profiles of SO_2 at several concentrations of SO_2 by the same H_2O concentration at 30°C. The rate of stationary removal increased with decreasing SO_2 concentration. The stationary conversion were 70% at 1000ppm SO_2, 90% at 750ppm and 100% below 500ppm. SO_2 was removed completely for at least 20h when the concentration of SO_2 was below 500ppm. 5% of H_2O was enough to remove of 20ppm completely for longer than 200h by W/F of 2.5×10^{-3} g min ml^{-1}. W/F compensates to some extent the concentrations of H_2O and SO_2.

Figure 4 illustrates the influence of NO of 500ppm at SO_2 of 500ppm removal over PAN-ACF-FE-300-800 by W/F of 2.5×10^{-3} g min ml^{-1} at 30°C. Without NO, SO_2 was removed completely for longer than 20h. while a concentration of NO of 500ppm reduced the stationary removal of SO_2 to 60%. More H_2O and a larger W/F increased SO_2 removal in the presence of NO. NO started to leak after 3h, no stationary NOx removal being observed under the present conditions.

References
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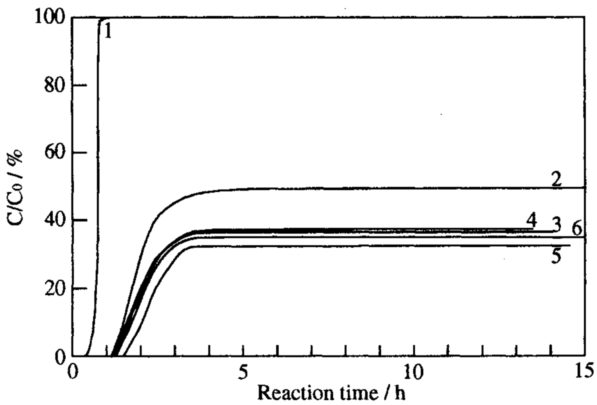

Fig. 1 Breakthrough profiles of SO_2 at several concentrations of O_2 over FE-300-800
SO_2 : 1000ppm, H_2O : 10 vol%
$W/F = 2.5\times10^{-3}$ g · min · ml^{-1}
Reaction Temp. 30℃
O_2 1 : 0%, 2 : 2%, 3 : 3%, 4 : 4%, 5 : 5%, 6 : 10%

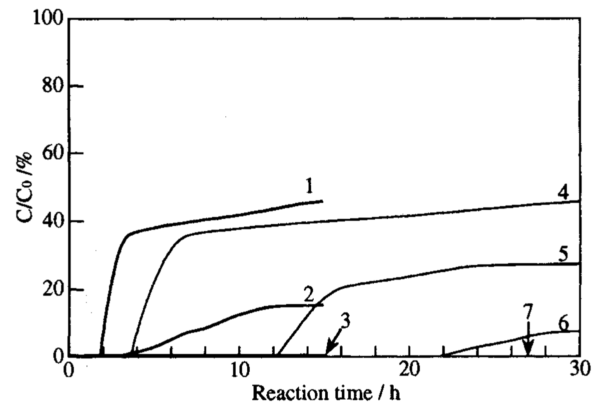

Fig. 2 Breakthrough profiles of SO_2 over FE-300-800 at several concentrations of H_2O and at several weights of ACFs
SO_2 : 500ppm, O_2 : 5 vol%, Reaction Temp. 30℃
H_2O 1 : 5%, $W/F = 2.5\times10^{-3}$ g · min · ml^{-1}
2 : 7.5%, $W/F = 2.5\times10^{-3}$ g · min · ml^{-1}
3 : 10%, $W/F = 2.5\times10^{-3}$ g · min · ml^{-1}
W/F 4 : 2.5×10^{-3} g · min · ml^{-1}, H_2O : 5 vol%
5 : 5.0×10^{-3} g · min · ml^{-1}, H_2O : 5 vol%
6 : 7.5×10^{-3} g · min · ml^{-1}, H_2O : 5 vol%
7 : 1.0×10^{-2} g · min · ml^{-1}, H_2O : 5 vol%

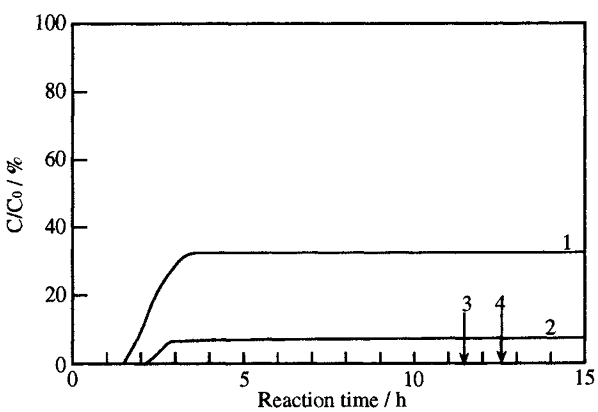

Fig. 3 Breakthrough profiles of SO_2 at several concentrations of SO_2 over FE-300-800
O_2 : 5 vol%, H_2O : 10 vol%
$W/F = 2.5\times10^{-3}$ g · min · ml^{-1}
SO_2 1 : 1000ppm, 2 : 750ppm, 3 : 500ppm, 4 : 250ppm
No.3 and No.4 adsorbed SO_2 completely for least 20hours

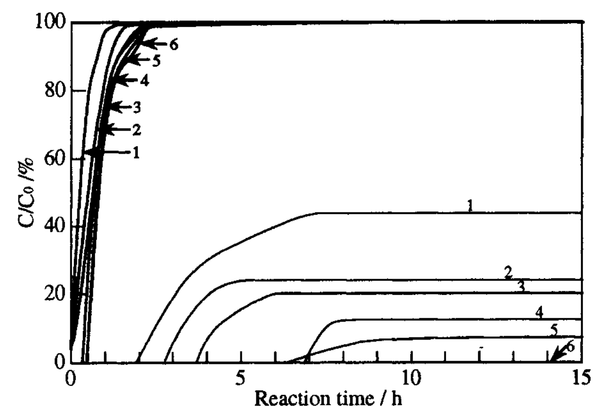

Fig. 4 Breakthrough profiles of SO_2 and NO over FE-300-800 at 30℃
SO_2 : 500 ppm, NO : 500 ppm, O_2 : 5 vol%,
$W/F = 2.5\times10^{-3}$ g · min · ml^{-1} (1, 2, 3)
$W/F = 5.0\times10^{-3}$ g · min · ml^{-1} (4, 5, 6)
H_2O 1, 4 : 10 vol%, 2, 5 : 15 vol%, 3, 6 : 20 vol%
SO_2 : 1, 2, 3, 4, 5, 6 ——
NO : 1, 2, 3, 4, 5, 6 ——