Influences of Oxygen Concentration on the Removal of SO_2 over Pitch Based Activated Carbon Fibers

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Introduction

The present authors reported that the pitch based activated carbon fiber (ACF) was very effective to remove SO_2 at 30°C in the model flue gas(1000ppm SO_2,5vol% O_2,10vol% H_2O). However, the real flue gas of low oxgen concentration >3.8% reduced the efficiency very markedly for the complete removal of SO_2 at 50 °C, requiring larger W/F and/or higher H_2O concentration to reduce the advantage of the present scheme of desulfurization over ACF. In the present study, the effects of oxygen concentration was investigated on the removal efficiency of ACF by changing the flow rate.

Experimental

OG series pitch based ACF of large surface area, OG-20A was supplied by Osaka Gas Co. ACF was heat-treated in argon gas at 1100 °C (OG-20A-H1100). SO_2 removal was carried out at 50-70°C using a fixed bed flow reactor of U type glass. ACF was packed densely in the reactor tube (8 mm in diameter). The length of ACF bed was ca. 30mm when 0.10 ~ 0.75g of ACF was loaded. The flow rate was usually 100ml/min. A model flue gas containing SO_2 1000ppm, O_2 3,4,5vol%, and H_2O 10vol% in nitrogen was used. Aq. H_2SO_4 was trapped at the bottom of the reactor. The concentrations of SO_2 in the inlet and outlet gases were observed continuously by a flame photometric detector (R268Y; Hamamatsu Photonics). SO_2 adsorption was measured under flowing helium containing SO_2(1000ppm) and O_2(0 ~10%) at a flow rate of 150ml/min at 30°C over the ACF (200mg) suspended in quartz basket in a micro balance (CAHN 1000).

Results

Figure 1 illustrates the breakthrough and stationary SO_2 concentration over OG-20A-H1100 in up flow and down flow reactors at 50°C, where the oxygen concentration was varied at the constant H_2O concentration of 10vol%. In the down flow reactor, oxygen concentration of 3 and 5vol% provided the breakthrough times and stationay concentration of 19.5h, 30% and 22h, 24% respectively. Higher oxygen content slightly improved the SO_2 removal. In a marked contrast, up flow reactor emphasized very much the favorable effect of higher oxygen concentration. 5vol% O_2 allowed complete removal while 3vol% provided much the same results as observed in the down flow reactor.

Figure 2 illustrate the SO_2 removal profiles at 70°C. Up flow reactor gave better removal, but the difference was very small. Higher oxygen content allowed the longer breakthrough and lower stationary SO_2 concentartion than those by 3vol% O_2, although improvement was very limited.

Figure 3 illustrates adsorption up-takes of SO_2 over OG-20A-H1100 at 30°C when oxygen concentration was varied from zero to 10vol%. Significant increase of SO_2 adsorption was definite when 1vol% O_2 was introduced. Steady increase of SO_2 adsorption was observed up to 10h. 5vol% increased the amount significantly whereas 10vol% increased very slightly in comparision with that by 5vol% O_2.

Discussion

The present study revealed that the oxygen concentration about 5vol% influences a little in the oxidative removal of 1000ppm SO_2 over Pitch Based ACF. However less than 5vol% may influence the paformance. The oxidative removal of SO_2 over the ACF proceeds through adsorption, oxidation, hydration of SO_2, and elution of H_2SO_4. When sufficient O_2 is supplied, the rate determining step is the elution of H_2SO_4 while low oxygen concentration blow 5vol%, the oxidation step may involved in the rate determining steps even if much excess of O_2 5vol% compared to 0.1% SO_2 is supplied. Poor activation of O_2 on the ACF is suggested. Another interesting observation is that up flow reactor provides higher SO_2 removal under the conditions of 5vol% O_2, 10vol% H_2O and 5X10-3 g min ml-1. If the eluting H_2SO_4 occupies the active site to some extent both oxygen and SO2 adsorptions are hindered by H_2SO_4. In the down flow reactor, H_2SO_4 flows from the top to the bottom of the ACF bed while the up flow H_2SO_4 occupies only the lower part where the last SO_2 was oxidized into H_2SO_4. Hence the up flow can give high concentration while the apper part of the bed is not occupied with H_2SO_4. In other words, elution of H_2SO_4 always passes through the site occupied by H_2SO_4, increasing the free sites opened by H_2SO_4 elution.

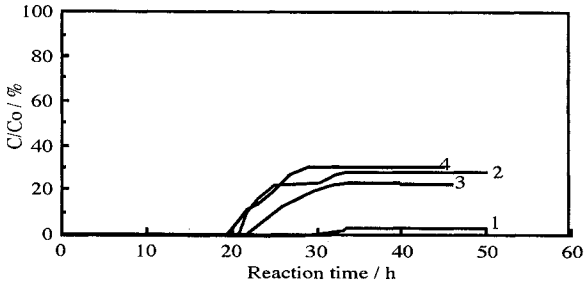

Fig. 1 Breakthrough profiles of SO_2 at some concentration of oxygen over OG-20A-H1100

SO2 1000ppm , H2O 10vol%
W/F=5.0X10-3 g min ml-1
Sample OG-20A-H1100
Reaction Temperature 50°C
Up flow type:1,2 Down flow type:3,4

1.O2 : 5vol%, 2.O2 : 3vol%
3.O2 : 5vol%, 4.O2 : 3vol%

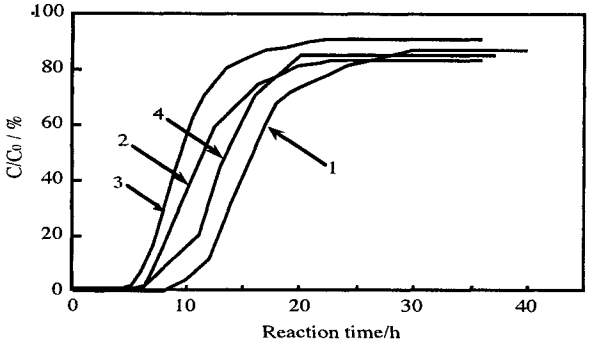

Fig. 2 Breakthrough profiles of SO_2 at some concentration of oxygen over OG-20A-H1100

SO_2 1000ppm, H_2O 10vol%
W/F=5.0X10-3 g min ml-1
Sample OG-20A-H1100
Reaction temperature 70°C
Up flow type:1,2,3
Down flow type:4

1. O2 : 5vol%
2. O2 : 4vol%
3. O2 : 3vol%
4. O2 : 5vol%

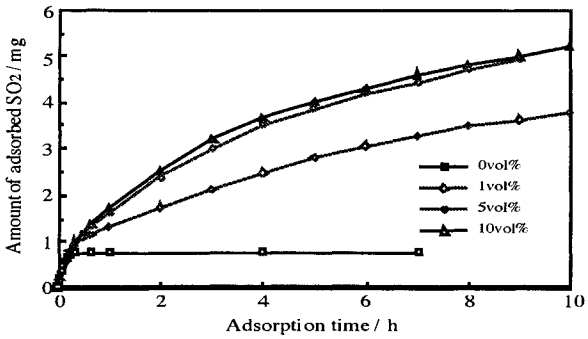

Fig.3 Adsorption profiles of SO_2 over OG20A-H1100 in a micro balance

Flow rate 150ml/min (He balance)
Sample OG-20A-H1100 (200mg)
Adsorption temperature 30°C
SO_2 1000ppm, O_2 0, 1, 5, 10vol%