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Simultaneous removal of H_2S and COS using activated carbons and their supported catalysts

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Abstract

Adsorption and catalytic decomposition of H_2S and COS were investigated over active carbons using a flow reactor with fixed bed in the temperature range from 300 to 450 °C. Active carbons removed very effectively COS at a relatively high temperature of 400 °C, some portion being decomposed to CO over active carbons. Although H_2S was also removed by active carbons at 400 °C, the removal capacity of H_2S was much smaller than that of COS and H_2S was hardly decomposed over active carbons. The impregnation of Fe on the active carbon enhanced very much the removal of both COS and H_2S; however, their decomposition behaviors were much different. It is found that the decomposition of H_2S was enhanced by Fe-supported activated carbon derived from a brown coal, while no decomposition of COS took place over the same Fe-supported active carbon. These results indicate that H_2S may be dominantly removed through the reaction with metal to produce metal sulfide, while COS may be preferably adsorbed as COS itself in the pore of active carbon and then may react with carbon surface to be decomposed to CO. Such contrast adsorption and decomposition behaviors of COS and H_2S are discussed based on their chemical reactivity over active carbon-supported catalyst.

Keywords: Hydrogen sulfide; COS; Active carbon; Metallic catalyst; Supported catalyst

1. Introduction

Removal of sulfur-containing compounds is one of the most important technologies for the utilization of gasified products derived from various feedstocks such as biomass, waste and solid fossil fuels. Especially, gaseous sulfur compounds of H_2S and COS are severe catalyst poisons against the following processes of steam reforming for hydrogen production or Fischer–Tropsch (F–T) synthesis [1,2].

Various researches for H_2S removal have been already reported in details for the purification of gasified products derived from various feedstocks [3–5]; however, removal of COS is not concerned yet as much as H_2S, because COS are not the major sulfur compounds produced from the gasification of biomass and other wastes feedstocks [6,7]. In addition, the removal of COS have been reported to be more difficult at low temperatures in the range from room temperature to around 200 °C than H_2S, since COS is rather inactive compared to H_2S probably due to its neutrality and similarity to CO_2. COS is sometimes produced through the reaction of H_2S with CO_2, although this reaction can be reversible to produce again H_2S and CO_2 from the reaction of COS with H_2O depending upon the adsorption conditions.

Carbon-based adsorbents such as active carbons and activated carbon fibers have been widely applied for the purification procedures of gas and water, and the selective adsorption of a specific compound from various gaseous mixtures produced from gasification and other conversion processes [8–10]. Although gaseous sulfur compounds such as H_2S and COS contaminated in the synthetic gas products

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have been conventionally removed by cold and wet procedures; recently, hot gas cleaning procedures are required to be developed for the utilization of highly purified synthetic gas for F–T synthesis and hydrogen of high purity for fuel cell application. For the complete removal of H_2S, higher temperatures around 500 °C are preferred because H_2S is captured completely by the reaction with catalytic materials such as ZnO and Fe_2O_3 in a absorption manner [3–5].

In the present study, the adsorption behaviors of H_2S and COS are investigated using active carbon adsorbents in the middle temperature range of 300–450 °C, because tarry compounds produced from biomass gasification have been reported to be effectively removed in this temperature range [11,12]. Sulfur-containing and other contaminants such as vaporized alkali metals are expected to be captured with the tarry byproducts at the same time. Another advantage is that the following catalytic processes of F–T synthesis are operated around 300 °C, hence a directly coupled gasification process of biomass can be designed by the combination of such hot gas cleaning with catalytic F–T synthesis.

2. Experimental

One hundred parts per million of H_2S and COS mixed standard gas in N_2 balance was used for the adsorption treatments.

Three types of activated carbons: a commercial active carbon (abbreviated as AC), a wood-derived activated carbon (red pine derived abbreviated as RP) and brown coal-derived activated carbons (abbreviated as Yallourn (YL) and Loy Young (LY)) were used in the present study. Two forms of them were prepared; one is particle form (abbreviated as PA; particle size: ca. 3 mm) and the other form is powder form (abbreviated as PO; particle size <100 mesh), respectively. RP powder was prepared in water at 200 °C for 10 h using autoclave before the activation reaction.

The activation reactions of heat-treated biomass and brown coals were performed at 800 °C for 30 min under CO_2 flow of 100 cm^3/min. Their surface areas, total pore volumes and average pore diameters are summarized in Table 1.

The demineralization of coal was performed with 18% HCl aqueous solution at 50 °C for 10 h, followed by filtration, washing with water and drying at 80 °C under nitrogen flow.

The impregnation was performed by mixing of $FeCl_3$ and $Ca(OH)_2$ with YL coal, precipitating Fe onto the brown coal, followed by filtration, washing and drying at 50 °C [13]. The impregnated amount of Fe was approximately 5 wt% before the activation treatment.

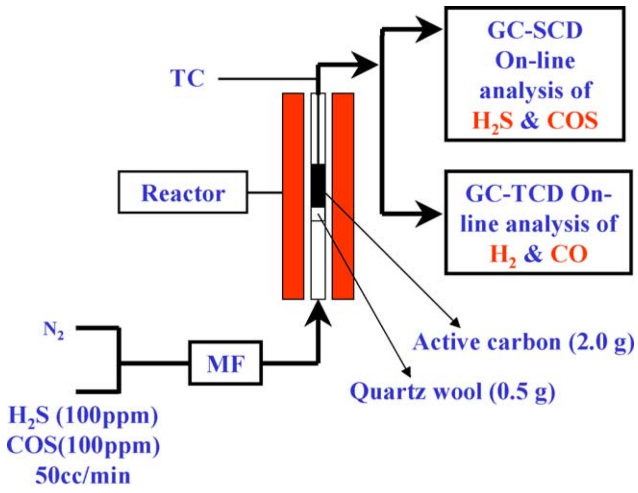

Fig. 1. Fixed bed flow-reactor with continuous online GC analyses. TC, thermocouple; MF, mass flow controller.

Fig. 1 shows a simplified illustration of flow-type adsorption reactor with fixed bed of active carbon and online measurements of GC-sulfur chemiluminescence detector (SCD) for the quantitative analysis of sulfur compounds and micro-GC-thermal conductivity detector (TCD) system for the detection of CO and H_2 as decomposed products.

3. Results and discussion

3.1. Non-catalytic adsorption of H_2S and COS over activated carbons

Fig. 2 illustrates the adsorption results of 100 ppm H_2S and COS in N_2 over a commercial activated carbon (AC–PA: particle) at room temperature. The reference data for the adsorption of H_2S and COS over quartz–wool were also plotted in Fig. 2, showing essentially no adsorption of H_2S and COS over the quartz–wool at room temperature. In comparison of the breakthrough curves of H_2S and COS over AC–PA, both of them were completely adsorbed in the initial 30 min, and then gradually started to breakthrough at 50 min, their concentrations being saturated to around 55 and 95 ppm for H_2S and COS, respectively. So, their saturated adsorption amounts were approximately estimated

Table 1
Pore distribution of different active carbons

Sample	AC–PA	AC–PO	RP–PO	YLFe–PO	YL–PO
BET surface area (cm/g)	990.74	1059.77	473.61	562.48	555.12
Total pore volume (cm^3/g)	0.53	0.55	0.22	0.27	0.29
Average pore diameter (A)	21.24	20.60	18.93	19.18	20.18

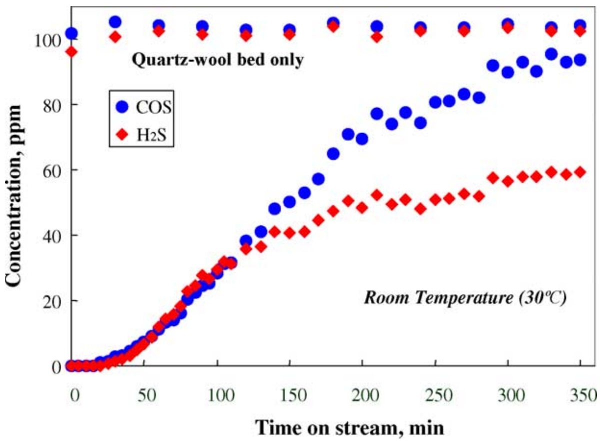

Fig. 2. COS and H_2S adsorption over AC–PA at room temperature.

to ca. 45 and 5 ppm, respectively. It is noted that a certain amount of H_2S be adsorbed on the active carbon particles (AC–PA) even at room temperature.

Fig. 3 describes the breakthrough profiles of H_2S and COS over AC–PA at variable temperatures in the temperature range from 300 to 450 °C. In the case of COS, the adsorption amount increased with adsorption temperatures, the outlet concentrations being saturated at around 10, 30 and 100 ppm at 450, 400 and 300 °C, respectively. It is found that COS was decomposed above 400 °C over the active carbon, while no decomposition of COS took place at 300 °C. In contrast, the adsorption profiles of H_2S did not change so much regardless of the adsorption temperatures, three breakthrough curves being similar in the temperature range from 300 to 450 °C; H_2S started to breakthrough at the initial 50 min, and then the concentration was gradually saturated to about 90 ppm at 350 min. It is also pointed out that no formation of H_2 was observed, showing the thermal stability of H_2S on the active carbon even at 450 °C. Based on these results, it is suggested that about a half portion of COS may be adsorbed into the pores of the active carbon without its decomposition even at relatively high temperature around 400 °C, although the reactions with H_2S and/or a very small amount of water in the pore of active carbon may contribute to the disappearance of COS to some extent.

Fig. 4 compares the effects of particle sizes of active carbon (AC) on the adsorption behaviors of H_2S and COS at

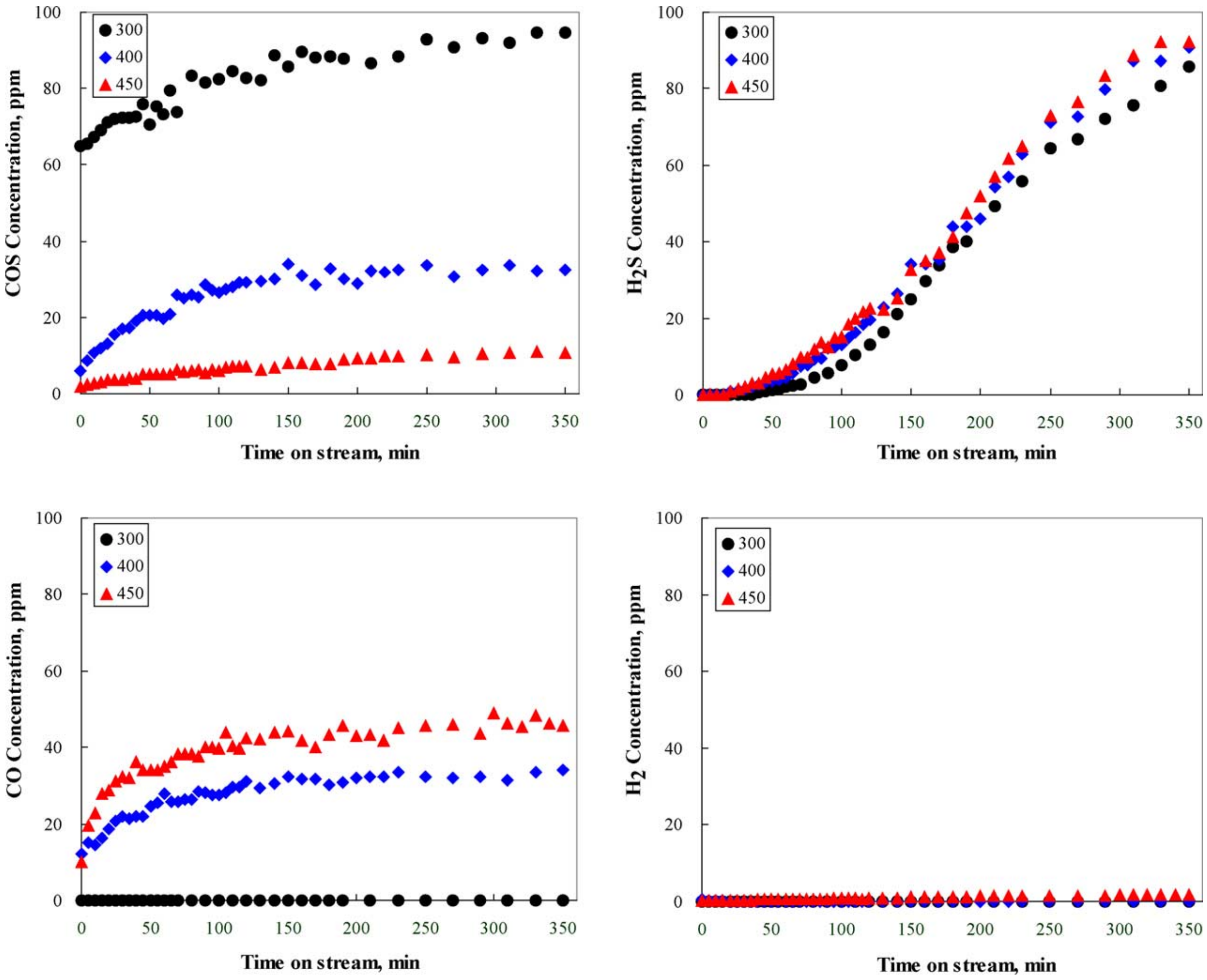

Fig. 3. Adsorption and decomposition of COS and H_2S at different temperatures (AC–PA).

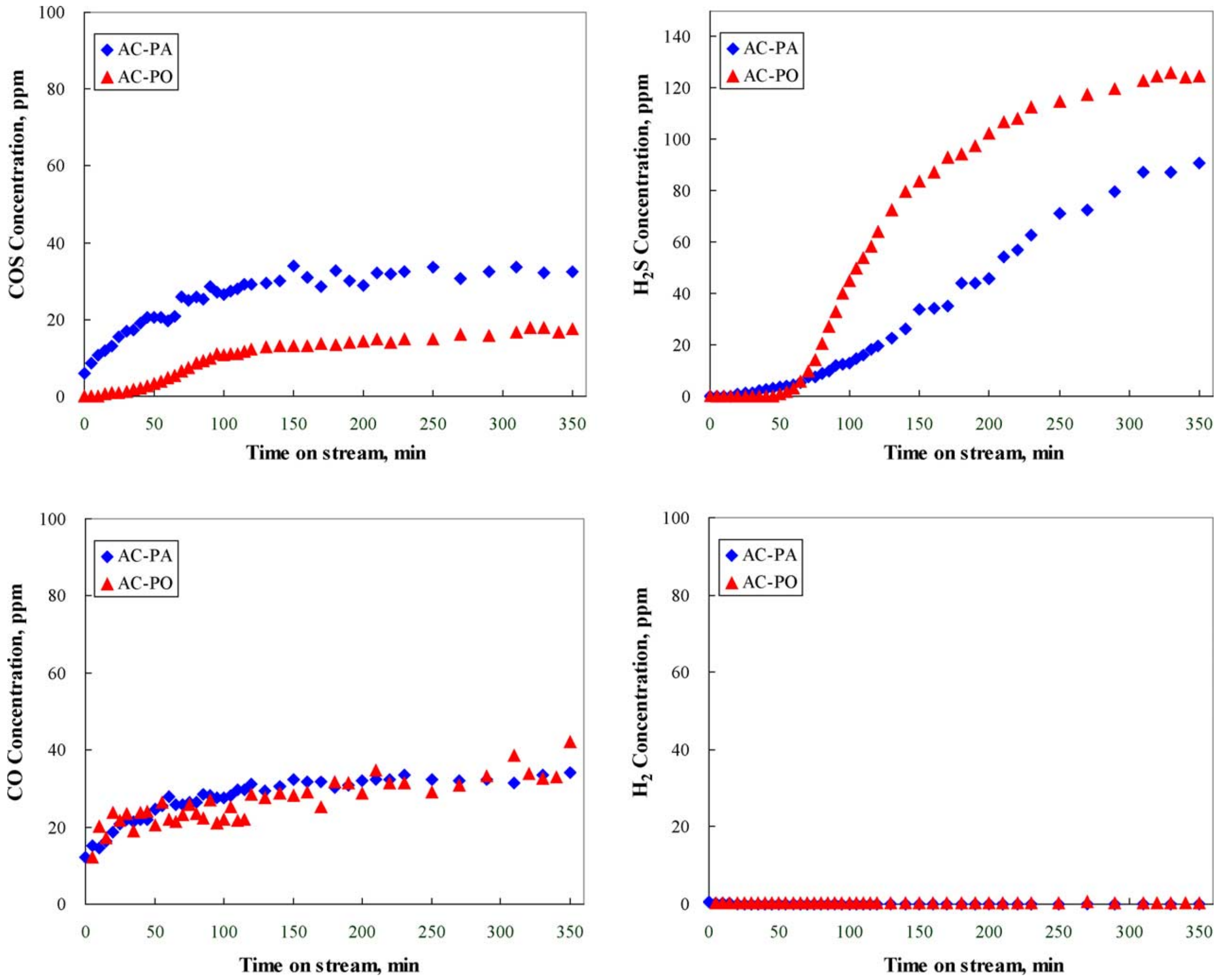

Fig. 4. Influence of particle size of active carbon on adsorption and decomposition of COS and H_2S at 400 °C.

400 °C. The finer particles of the active carbon adsorbed more amount of COS, the outlet concentrations being 10 ppm over AC–PO (powder) and 30 ppm over AC–PA (particle), respectively. The decomposed amount of COS was much the same regardless of the forms of active carbon. On the other hand, in the case of H_2S, AC–PA showed the larger adsorption capacity than AC–PO and no decomposition of H_2S was observed over the two activated carbons with different particle sizes. These results suggest that a considerable portion of COS may adsorb into the pores of active carbon; however, H_2S may mainly adsorb in a chemical manner by the interaction with metal components in the active carbon.

3.2. *Effects of metal supporting to activated carbon on the adsorption of H_2S and COS*

Fig. 5 illustrates the influence of different active carbons on the adsorption and decomposition of H_2S and COS at 400 °C. Compared to a commercial active carbon of AC–PO, a biomass derived (RP–PO) and a coal derived (YL–PO) gave the better adsorption capacity for COS, while the decomposition ratio of COS was lower than that of AC–PO. In the case of H_2S, YL–PO exhibited the highest adsorption capacity among the three adsorbents, H_2S being never desorbed until 350 min. Based on the analysis of metal contents in YL coal as shown in Table 2, it is suggested that higher concentrations of Fe may contribute to the much higher adsorption capacity compared to the other adsorbents.

Fig. 6 illustrates the influence of Fe impregnation and demineralization of YL coal on the adsorption behaviors of COS and H_2S. In the case of COS, the impregnation of Fe on the active carbon (YLFe–PO) and the demineralization of YL coal (YLD–PO) were not influential so much on the adsorption capacity, indicating that the adsorption of COS may not be enhanced by the catalytic effects of metals in the adsorbent.

On the other hand, the supporting of Fe to YL–PO significantly enhanced the adsorption of H_2S, showing complete removal of H_2S in the longer adsorption time of 1000 min, although YL–PO without Fe supporting gave the slightly lower adsorption capacity than YLFe–PO, probably because Fe metals in the original YL coal may be highly

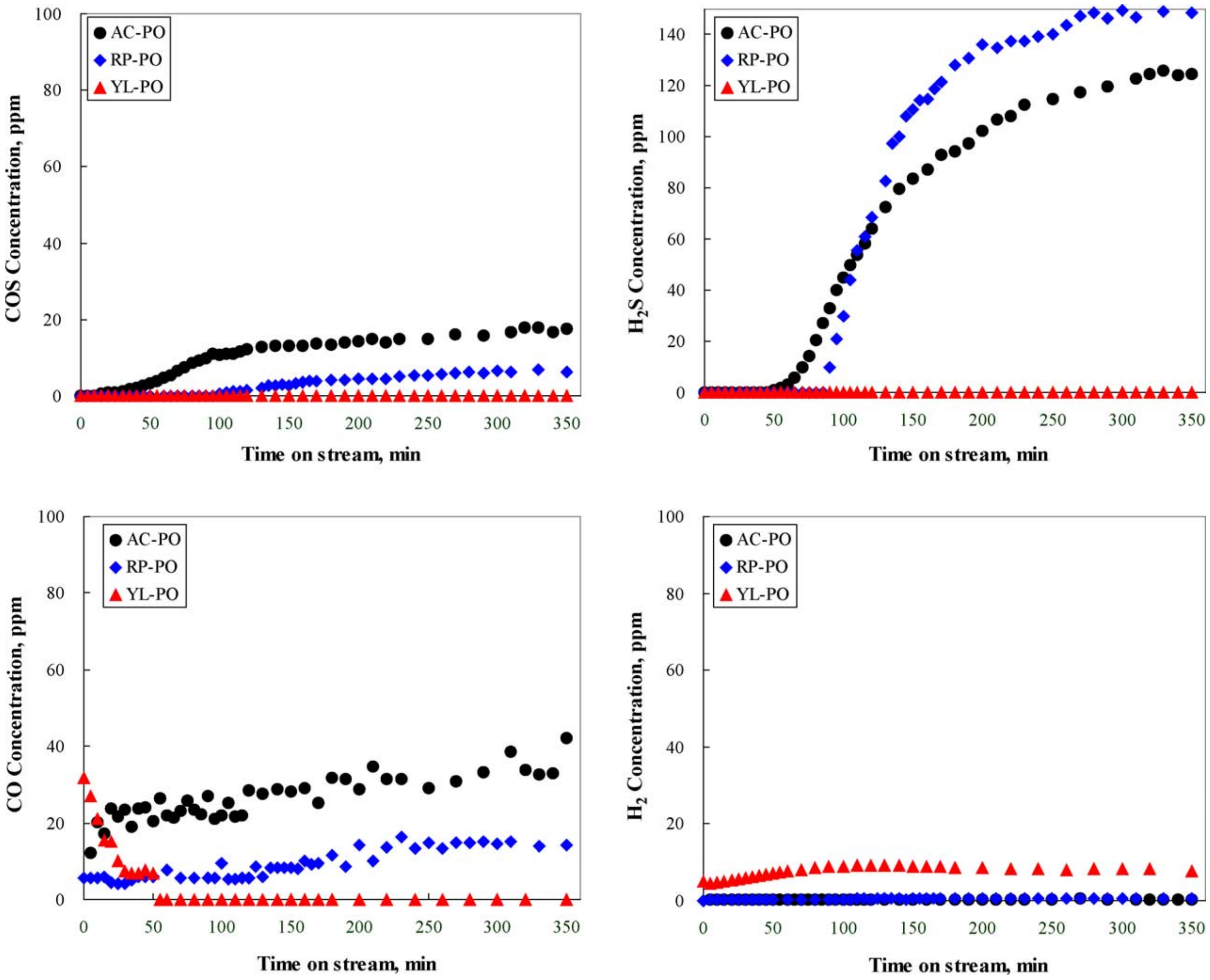

Fig. 5. Influence of different active carbons on adsorption and decomposition of COS and H_2S at 400 °C.

dispersed in YL–PO even after the activation procedure. The demineralization of YL coal significantly decreased the adsorption capacity of H_2S, showing a breakthrough profile before 200 min. Therefore, the Fe metal content in the adsorbent is very important for the removal of H_2S. The decomposition of H_2S was not enhanced so much by Fe supporting on the active carbon derived from brown coal.

Fig. 7 shows the influence of coal type on the removal of COS and H_2S at 400 °C. The active carbon derived from Loy Young coal was named LY. In the case of COS, the breakthrough curves were not influenced by the coal type, although the YL–PO gave the higher adsorption capacity. The same tendency was obtained for the removal of H_2S; however, the difference in the adsorption capacity was much larger than that of COS. It is suggested that the contents of metals such as Fe and/or Ca in the original coals may be most influential on the removal of H_2S.

Table 3 summarizes the breakthrough (BT) times and adsorption capacities of COS and H_2S obtained by various active carbons. Fe-supported YL–PO (shortly YLFe–PO) exhibited the longest BT times and the largest adsorption capacity for both of COS and H_2S, reflecting from the catalytic desulfurizaton effect by Fe supporting. It is also pointed out that the higher surface area of the commercial active carbon of AC may not directly contribute to the effective removal of gaseous sulfur compounds compared to the active carbons derived from wood biomass (RP) and brown coals of which surface area are about half of the commercial one. These results indicate that the remaining metals in the active carbons derived from biomass and brown coals, especially Fe content in brown coals, should be one of the most influential factors for the removal of COS and H_2S. And in comparison of the adsorption and decomposition behaviors of COS with H_2S, such catalytic desulfurization by Fe is more effective for H_2S; however, in

Table 2
Metal contents of YL coal before and after the demineralization treatment with 18% HCl aqueous solution

Sample	Ash (wt%, d)	Metal content (wt%, d)						
		Fe	Ca	Na	Mg	Al	Si	K
YL	1.57	0.38	0.17	0.07	0.19	0.02	0.10	0.01
YLD	0.15	0.05	0.02	0.02	0.03	0.01	0.10	0.00

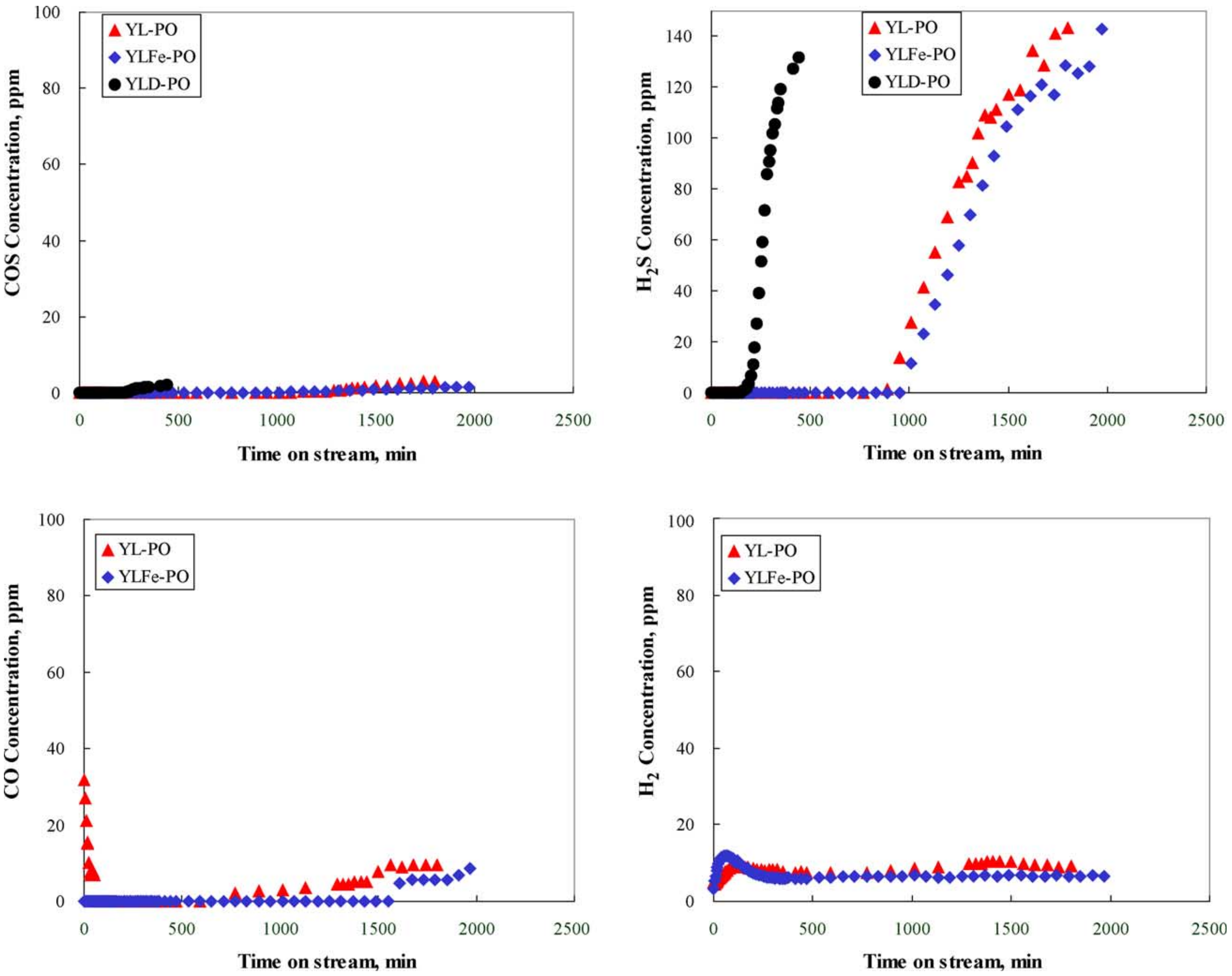

Fig. 6. Influence of Fe impregnation and demineralization on the adsorption behaviors of COS and H_2S over the active carbon (YL–PO) at 400 °C.

other words, COS seems to be removed by the interactions with the pore surface of active carbons.

Based on the results, it is revealed that COS may be more effectively removed by active carbons regardless of its neutrality compared to H_2S. It is also suggested that the outlet concentration of H_2S above 100 ppm in the adsorption reaction may be due to exchange reactions of COS with a small amount of H_2O in the pore of active carbon (that is;

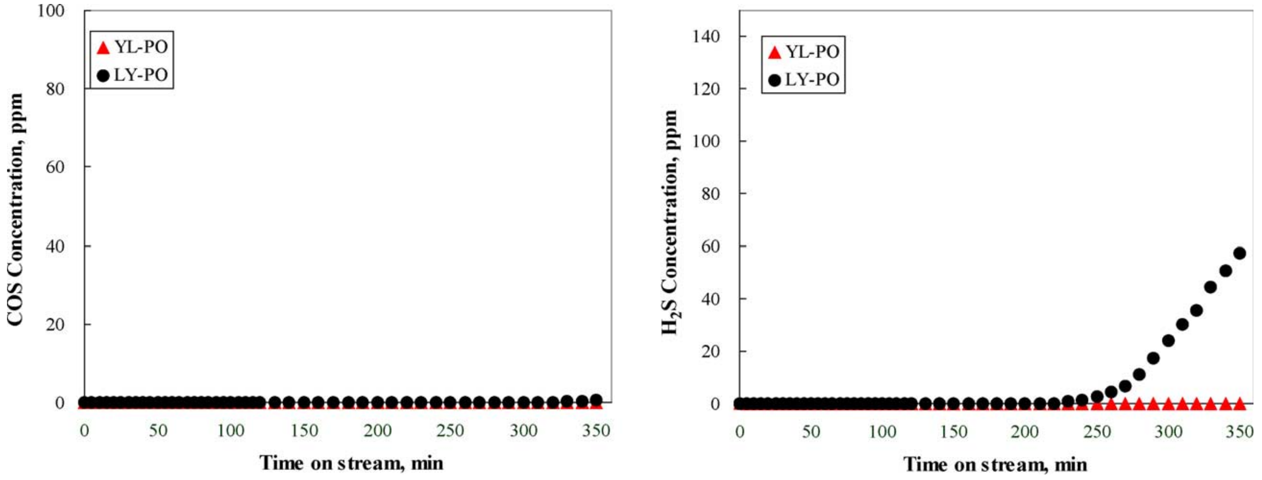

Fig. 7. Influence of coal type on the removal of COS and H_2S at 400 °C.

Table 3
Breakthrough (BT) time and adsorption capacity of COS and H_2S over various active carbons at 400 °C

Sample	AC–PA	AC–PO	RP–PO	YLFe–PO	YL–PO
COS BT time (min)	0	15	90	1100	1000
COS capacity (cm^3/g)	0.000	0.039	0.234	2.860	2.600
H_2S BT time (min)	20	50	100	1000	900
H_2S capacity (cm^3/g)	0.051	0.128	0.255	2.550	2.230

$COS + H_2O \rightarrow CO_2 + H_2S$), which may contribute to a relatively larger adsorption capacity of COS.

4. Conclusion

The present study revealed that active carbons removed very effectively COS at a relatively high temperature of 400 °C, some portion being decomposed to CO over active carbons. While H_2S was also removed by active carbons at 400 °C, the removal capacity of H_2S was much smaller than that of COS and H_2S was hardly decomposed over active carbons. Although the impregnation of Fe on the active carbon enhanced very much the removal of both COS and H_2S, their decomposition behaviors were much different, suggesting that the decomposition of H_2S may be enhanced by Fe-supported active carbon, while COS may not decompose over the same Fe-supported active carbon. These results indicate that H_2S may be dominantly removed through the reaction with metal to produce metal sulfide, while COS may be preferably adsorbed as COS itself in the pore of active carbon and then may react with carbon surface to be decomposed to CO. Remaining metals such as Fe in the active carbons derived from brown coals also exhibited the catalytic effect on the removal of COS and H_2S, especially enhancing the desulfurization of H_2S to form metal sulfide.

It is indicated that active carbons with a suitable surface area around 500 m^2/g and a highly dispersed Fe species should be designed for simultaneous removal of COS and H_2S, and such active carbons can be prepared from brown coal and biomass resources at a relatively lower cost.

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