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A study on the characteristics of the SO_2 reduction using coal gas over SnO_2-ZrO_2 catalysts

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Abstract

SO_2, which is an air pollutant causing acid rain and smog, can be converted into elemental sulfur in direct sulfur recovery process (DSRP). SO_2 reduction was performed over catalyst in DSRP. In this study, SnO_2-ZrO_2 catalysts were prepared by a co-precipitation method, and CO and coal gas, which contains H_2, CO, CO_2 and H_2O, were used as reductants. The reactivity profile of the SO_2 reduction over the catalysts was investigated at the various reaction conditions as follows: reaction temperature of 300–550 °C, space velocity of 5000–30,000 $cm^3/g_{\text{-cat.}}$ h, [reductant]/[SO_2] molar ratio of 1.0–4.0 and Sn/Zr molar ratio of SnO_2-ZrO_2 catalysts 0/1, 2/8, 3/5, 5/5, 2/1, 3/1, 4/1 and 1/0. SnO_2-ZrO_2 (Sn/Zr = 2/1) catalyst showed the best performance for the SO_2 reduction in DSRP on the basis of our experimental results. The optimized reaction temperature and space velocity were 325 °C and 10,000 $cm^3/g_{\text{-cat.}}$ h, respectively. The optimal molar ratio of [reductant]/[SO_2] varied with the reductants, that is, 2.0 for CO and 2.5 for coal gas. SO_2 conversion of 98% and sulfur yield of 78% were achieved with the coal gas.

Keywords: SO_2 reduction; Coal gas; SnO_2-ZrO_2 catalysts; Sulfur recovery process

1. Introduction

SO_2 is mainly generated by the oxidation of the S-component in the combustion process. Harmful SO_2 causes many problems such as the plant corrosion, the respiratory disease, and the acid rain. Therefore, it is necessary to remove SO_2 from exhaust gas. Various regenerable and alternative energy technologies were developed in recent years due to the limitation of fossil fuel resources. The integrated gasification combined cycle (IGCC) system is considered as one of the most thermally efficient, economically attractive, and environmentally acceptable technologies for power generation from coal. The main components in an IGCC power plant are coal gasification unit, gas cleanup system and power generation facilities. Hot gas desulfurization (HGD) is a very important process in the gas cleanup system, and its main role is to remove harmful sulfur compounds, which exists in the form of hydrogen sulfide (H_2S) under the highly reducing conditions of the gasifier, from the coal-derived fuel gas. HGD process consists of a sulfidation process and a regeneration process in which the sulfidated sorbents can be regenerated using O_2.

$$MO + H_2S \rightarrow MS + H_2O \quad \text{(Sulfidation process)}$$

$$MS + \tfrac{3}{2}O_2 \rightarrow SO_2 + MO \quad \text{(Regeneration process)}$$

SO_2 generated during the regeneration of sorbents can be reduced by using the reductants, such as CO, H_2, CH_4 and C (carbon), over the catalyst in direct sulfur recovery process (DSRP).

$$SO_2 + C \rightarrow CO_2 + S \tag{1}$$

$$SO_2 + 2H_2 \rightarrow S + 2H_2O \tag{2}$$

$$SO_2 + 2CO \rightarrow 2CO_2 + S \tag{3}$$

$$2SO_2 + CH_4 \rightarrow 2S + CO_2 + 2H_2O \tag{4}$$

Transition metal oxides and solid acid catalysts mainly have been utilized as the suitable catalysts in DSRP. Recent

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Table 1
Optimal reaction conditions and results reported in other studies

Reaction condition		Result		Reference
Catalyst	Temperature (°C)	SO_2 conversion (%)	Sulfur yield (%)	
CoS_2–TiO_2	400	98.6	95	[1]
Co_3O_4–TiO_2	400	100	97	[2]
Ti–Co oxides	350	90	85.5	[3]
$Ce_{1-x}Zr_xO_2$	425	92.6	91.4	[4]
Ce–(La, Gd)O_2	500	98	95	[5]

researches for the SO_2 reduction over these catalysts are listed in Table 1. It is recently reported that elements in group IV including transition elements, such as La, Ti, Ce and Zr, are used for SO_2 reduction [1–5]. In this study, SnO_2-ZrO_2 catalysts were prepared by co-precipitation method and used in DSRP. The reaction characteristics in terms of the reaction conditions were investigated and the reaction conditions, such as temperature, space velocity, molar ratio of [reductant]/[SO_2] and H_2O content, were optimized.

2. Experimental

2.1. Preparation of the catalysts

2.1.1. SnO_2 and ZrO_2 catalysts

SnO_2 and ZrO_2 catalysts were prepared by the precipitation method. Tin chloride pentahydrate ($SnCl_4{\cdot}5H_2O$), the precursor for SnO_2, and zirconyl nitrate hydrate ($ZrO(NO_3)_2{\cdot}6H_2O$), the precursor for ZrO_2 were dissolved in the distillated water, respectively. Ammonium hydroxide was added to each solution of the precursor up to pH 9–10, and the white precipitate was formed. This precipitated slurry was warmed in the water bath, dried at 110 °C overnight and then calcined at 600 °C for 4 h in air in an electric furnace. And finally, the product was ground and sieved to 80–100 mesh size.

2.1.2. Physical mixture catalysts of SnO_2 and ZrO_2

Physical mixture catalysts with different Sn/Zr molar ratios were prepared by physically mixing SnO_2 and ZrO_2 which were prepared by the precipitation method.

2.1.3. Co-precipitated SnO_2-ZrO_2 catalysts

SnO_2-ZrO_2 catalysts with Sn/Zr molar ratios corresponding to 1/4, 3/5, 5/5, 2/1, 3/1 and 4/1 were prepared by co-preparation method. The same precursor materials with the specified ratios and procedure as described in Section 2.1.1 were employed. Symbols of the prepared SnO_2-ZrO_2 catalysts are shown in Table 2.

2.2. Analysis of the catalysts

Characterization of the catalysts was performed by X-ray diffractometer (XRD; Rigaku, D/MAX-2500) with Ni-filtered Cu Kα to analyze the catalysts.

Table 2
Symbols of the prepared catalysts

Sn/Zr molar ratio	SnO_2-ZrO_2 catalysts prepared by physical mixing	SnO_2-ZrO_2 catalysts prepared by co-precipitation method
	Type	
	SZ-PM series	SZ-CP series
2/8	SZ-PM28	SZ-CP28
3/5	SZ-PM35	SZ-CP35
5/5	SZ-PM55	SZ-CP55
2/1	SZ-PM21	SZ-CP21
3/1	SZ-PM31	SZ-CP31
4/1	SZ-PM41	SZ-CP41

2.3. Characteristics of the reaction under the various conditions

A vertical fixed-bed quartz tube reactor with 1/2 in. diameter was used for the reaction test. The reactant gas at the various [reductant]/[SO_2] molar ratios, space velocity and H_2O content with N_2 diluent was fed into the reactor. SO_2 of 2 vol.% was used as a main reactant and the catalyst of 0.5 g was packed in a fixed bed reactor. The gaseous products were analyzed by a gas chromatogragh (Shimazu 8A) equipped with thermal conductivity detector. H_2 was used as the carrier gas. Porapak T and Hayesep Q were used as the column materials to separate SO_2, COS, CS_2, H_2S and CO_2. SO_2 conversion, sulfur selectivity and sulfur yield were defined by the following equations:

$$SO_2\,\text{conversion}\,(\%) = \frac{[SO_2]_{in} - [SO_2]_{out}}{[SO_2]_{in}} \times 100$$

$$\text{Sulfur selectivity}\,(\%) = \frac{[SO_2]_{in} - [SO_2]_{out} - [COS]_{out} - [H_2S]_{out}}{[SO_2]_{in}} \times 100$$

$$\text{Sulfur yield}\,(\%) = SO_2\,\text{conversion} \times \text{sulfur selectivity}$$

3. Results and discussion

3.1. XRD analysis of catalysts

XRD patterns of SnO_2 and ZrO_2 were compared with the patterns of SZ-PM catalysts at six different Sn/Zr mole ratios as shown in Fig. 1. XRD patterns corresponding to SnO_2 and ZrO_2 were confirmed in the database of JCPDS card. When comparing SnO_2, ZrO_2 and SZ-PM catalysts, the peaks corresponding to SnO_2 and ZrO_2 were observed in the XRD patterns of SZ-PM catalysts. The peak intensities of SnO_2 and ZrO_2 in SZ-PM catalysts varied in accordance with the molar ratio of Sn to Zr. So, it could be confirmed that crystallization condition of SnO_2 and ZrO_2 were observed in SZ-PM catalysts. Fig. 2 shows XRD patterns of the fresh, and the used SZ-CP catalysts. Reaction was performed at 325 °C for 4 h. The mole ratio of [CO]/[SO_2] was fixed to 2.0. Unlike the SZ-PM catalysts, for the catalysts with low content of ZrO_2, the peaks

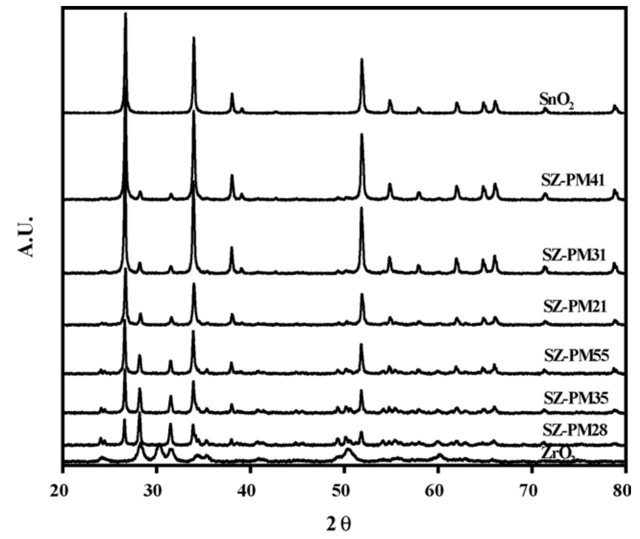

Fig. 1. XRD patterns of SZ-PM catalysts calcined at 600 °C.

for crystalline ZrO_2 were not clearly observed. This indicates that the ZrO_2 could not be well crystallized due to the presence of SnO_2 or may exist in very fine particles. For the catalysts with high content of ZrO_2, such as SZ-CP35 and SZ-CP28, the peaks for crystalline ZrO_2 were observed. Unlike the ZrO_2-only catalyst, the ZrO_2 appeared to be mostly the tetragonal phase, and the monoclinic phase was hardly seen. This may be due to the presence of SnO_2, which inhibits the transformation of the tetragonal phase to the monoclinic phase. Since the peaks were broad, ZrO_2 seemed to be present as small crystallities. In addition, it was observed that the used SZ-CP catalysts had similar crystallites and the used SZ-CP catalysts had similar XRD patterns to the fresh SZ-CP catalysts. This shows that the transformation, which may cause the deactivation, did not occur in SZ-CP catalysts.

3.2. SO_2 reduction by CO

The performance of the prepared catalysts for the SO_2 reduction by CO was evaluated in this section.

3.2.1. SO_2 reduction by CO over SnO_2

The SO_2 reduction by CO over SnO_2 was conducted to evaluate the performance of SnO_2. Fig. 3 shows the effect of the reaction temperature on the SO_2 conversion and sulfur yield. Space velocity was maintained at 10,000 $cm^3/g_{\text{-cat.}}$ h and the molar ratio of $[CO]/[SO_2]$ was fixed at 2.0. The temperature was varied in the range of 350–550 °C. In this case, the light-off temperature was 350 °C. The higher reaction temperature, the higher SO_2 conversion and yield were obtained. At 550 °C, 45% of SO_2 conversion and 32% of sulfur yield were achieved. It was reported that the SO_2 reduction by CO was difficult to occur below 400 °C over the other catalyst systems [1–5]. Consequently, although the efficiency of SO_2 reduction was low, the SO_2 reduction was able to be achieved at low temperature below 400 °C in this study.

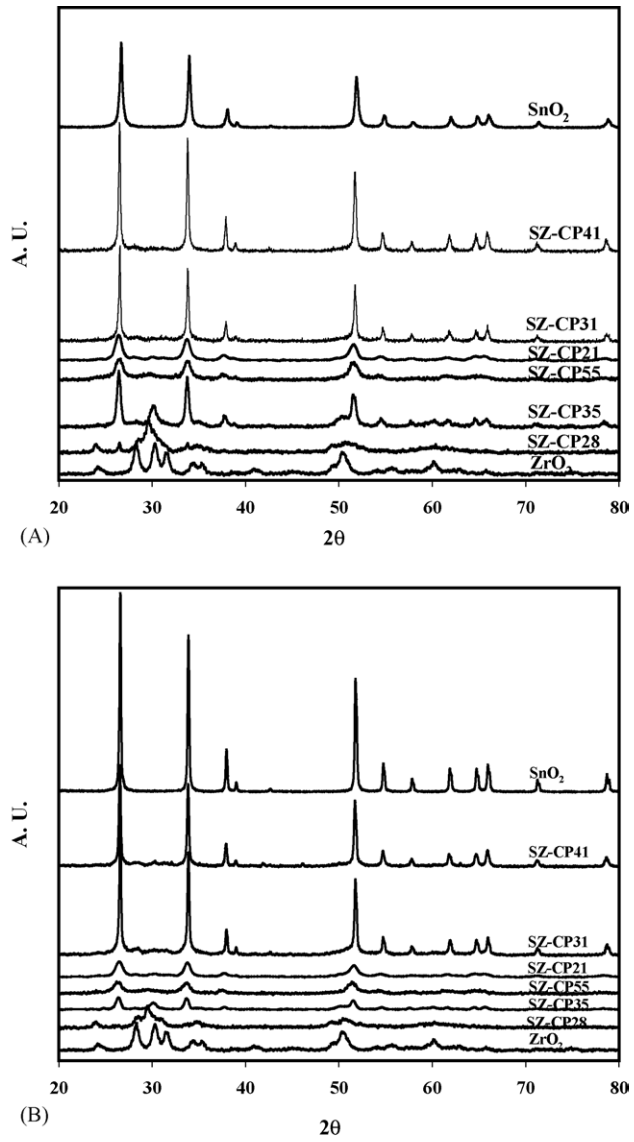

Fig. 2. XRD patterns of SZ-CP catalyts calcined at 600 °C: (A) Fresh catalysts and (B) used catalysts at the reaction temperature of 325 °C for 4 h and $[CO]/[SO_2]$ of 2.0.

3.2.2. SO_2 reduction by CO over ZrO_2

The performance of ZrO_2 for the SO_2 reduction by CO was also evaluated in this study. The experiment was carried out by varying temperature from 450 °C to 800 °C at space velocity of 10,000 $cm^3/g_{\text{-cat.}}$ h with $[CO]/[SO_2]$ molar ratio of 2.0. Fig. 4 shows the effect of the reaction temperature on the SO_2 conversion and the sulfur yield. The light-off temperature was 490 °C, while the optimal reaction temperature was in the range of 550–650 °C. SO_2 conversion of near 100% and sulfur yield of 92% were achieved in the temperature range of 550–650 °C. Our experimental results showed that ZrO_2 catalyst achieved higher SO_2 removal efficiency than that of SnO_2, but ZrO_2 required much higher temperature than SnO_2.

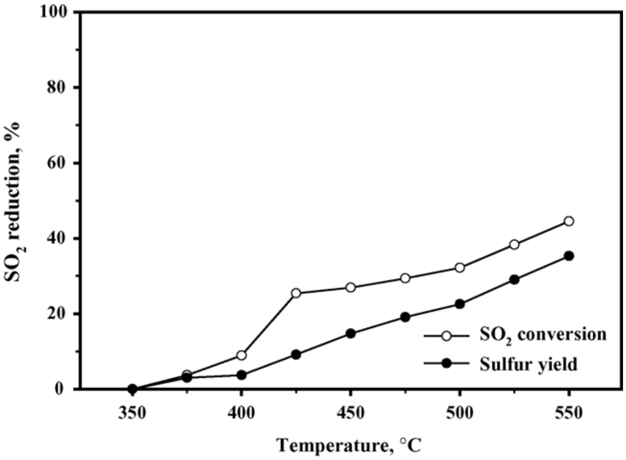

Fig. 3. The effect of the reaction temperature on the SO_2 reduction by CO over SnO_2 (Space velocity of 10,000 $cm^3/g_{-cat.}$ h, [CO]/[SO_2] molar ratio of 2.0).

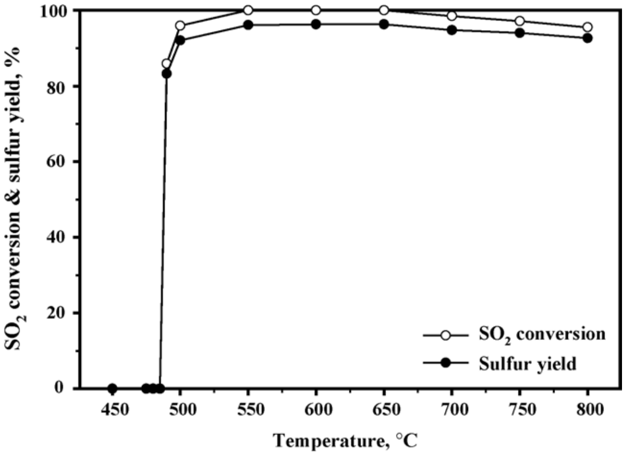

Fig. 4. The effect of the reaction temperature on the SO_2 reduction by CO over ZrO_2 catalyst (Space velocity of 10,000 $cm^3/g_{-cat.}$ h, [CO]/[SO_2] molar ratio of 2.0).

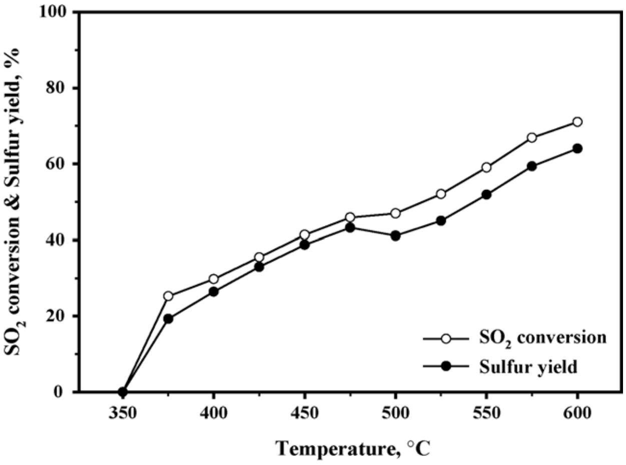

Fig. 5. The effect of the reaction temperature on the SO_2 reduction by CO over SZ-PM21 catalyst (Space velocity of 10,000 $cm^3/g_{-cat.}$ h, [CO]/[SO_2] molar ratio of 2.0).

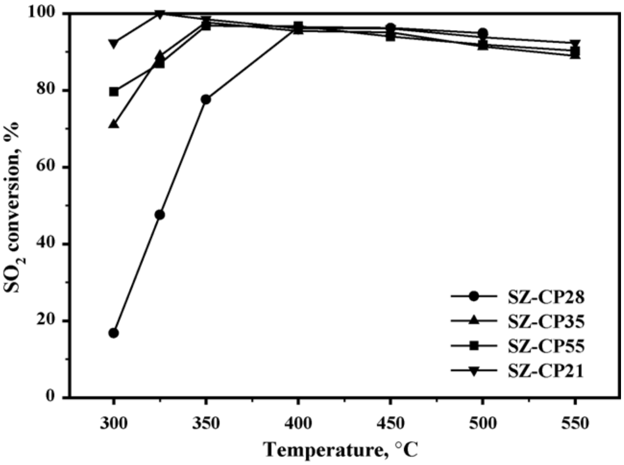

Fig. 6. The effect of the reaction temperature on the SO_2 reduction by CO over SZ-CP catalysts (Space velocity of 10,000 $cm^3/g_{-cat.}$ h, [CO]/[SO_2] molar ratio of 2.0).

3.2.3. SO_2 reduction by CO over SZ-PM21 catalyst

SZ-PM21 catalyst was prepared by mixing SnO_2 and ZrO_2 with Sn/Zr molar ratio of 2/1. Fig. 5 shows the effect of temperature on the SO_2 conversion and the sulfur yield with SZ-PM21 catalyst. The light-off temperature was 350 °C, the same as for SnO_2. However, SO_2 conversion and sulfur yield over SZ-PM21 were higher than those over SnO_2. The reactivity of SO_2 reduction by CO over SZ-PM21 catalyst was higher than that of SnO_2 catalyst and, however, it was lower than that of ZrO_2 especially at high temperatures.

3.2.4. SO_2 reduction by CO over SZ-CP catalysts

The effects of the Sn/Zr molar ratio and reaction temperature on the SO_2 conversion and sulfur yield for the SZ-CP catalysts are shown in Figs. 6 and 7, respectively. The temperature was varied over the range of 300–550 °C at space velocity of 10,000 $cm^3/g_{-cat.}$ h with [CO]/[SO_2] molar ratio of 2.0. The light-off temperature over SZ-CP catalysts appeared as low as below 300 °C, and SO_2 conversion and sulfur yield were very

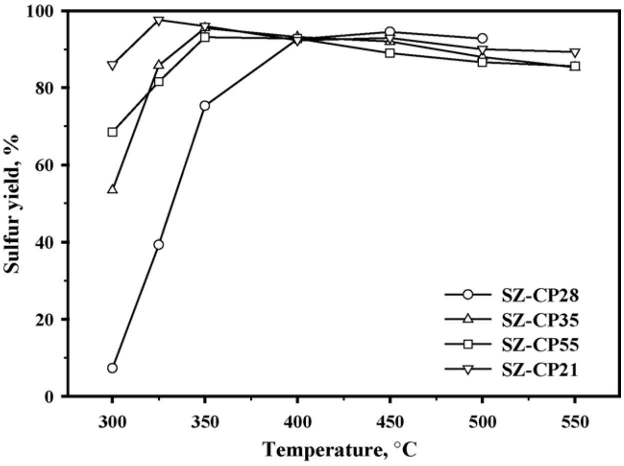

Fig. 7. The effect of the reaction temperature on the SO_2 reduction by CO over SZ-CP catalyst (Space velocity of 10,000 $cm^3/g_{-cat.}$ h, [CO]/[SO_2] molar ratio of 2.0).

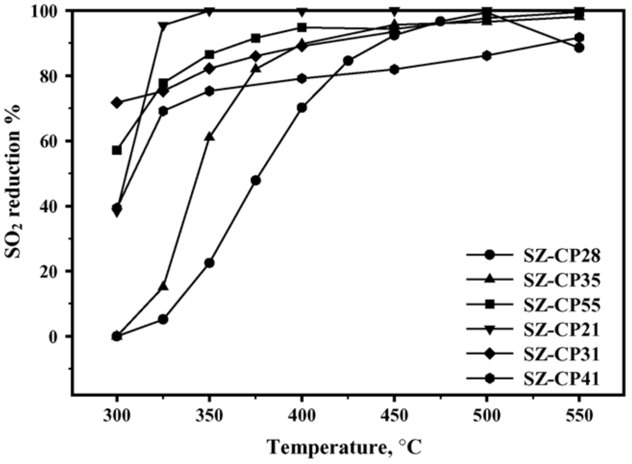

Fig. 8. The effect of the reaction temperature on SO_2 reduction by coal gas over SZ-CP catalysts (Space velocity of 10,000 cm^3/g$_{\text{-cat.}}$ h, $[H_2 + CO]/[SO_2]$ molar ratio of 2.5 and H_2O content of 2.0 vol.%).

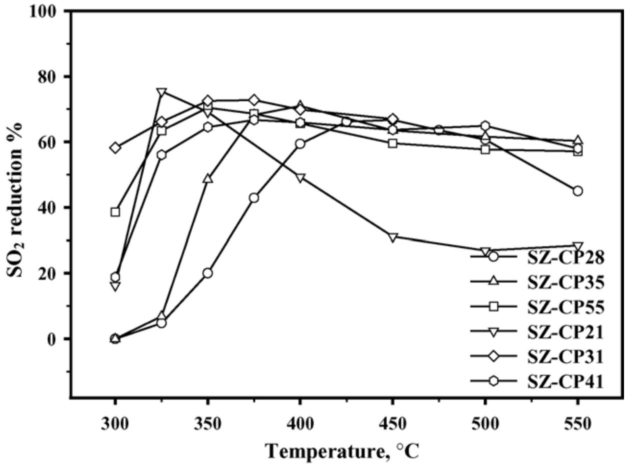

Fig. 9. The effect of the reaction temperature on SO_2 reduction by coal gas over SZ-CP catalysts (Space velocity of 10,000 cm^3/g$_{\text{-cat.}}$ h, $[H_2 + CO]/[SO_2]$ molar ratio of 2.5 and H_2O content of 2.0 vol.%).

high. SZ-CP21 catalyst among SZ-CP catalysts showed the best performance, and its optimal reaction temperature was 325 °C. At 325 °C SO_2 conversion of near 100%, and sulfur yield of 97% were achieved with SZ-CP21. At higher Sn content and temperature, SO_2 conversion and sulfur yield decreased gradually.

Performance of each SnO_2 and ZrO_2 catalyst was evaluated in DSRP. In case of SnO_2 catalyst, light-off temperature was 350 °C, and its SO_2 conversion and sulfur yield were 45% and 35%, respectively, at 550 °C. In case of ZrO_2 catalyst, light-off temperature was 490 °C, and SO_2 conversion and sulfur yield were 100% and 92%, respectively, over the temperature range of 550–650 °C. For the physical mixture of SnO_2 and ZrO_2, the light-off temperature was the same as that of the SnO_2-only catalyst, but the reactivity was higher, especially in the temperature range from 350 °C to 500 °C. This indicates that there is a synergy effect occurring, although it is not so great. For the SZ-CP catalysts, in contrast, the light-off temperature became considerably lower and the reactivity increased tremendously. This clearly shows that there is a noticeable synergy effect in this case. A reason for this may be due to intimate contact between SnO_2 and ZrO_2, probably due to fine particle of ZrO_2. SnO_2 may initiate the reduction, leading to formation of a more reactive intermediate, and then this intermediate may be quickly converted to sulfur probably by fine ZrO_2 particles. A more detailed study is further needed to better understand this.

3.3. SO_2 reduction by coal gas over SZ-CP catalysts

On the basis of the experimental results for performance evaluation of catalysts, the SO_2 reduction by coal gas containing H_2, CO, CO_2 and H_2O was conducted over all SZ-CP catalysts with various molar ratios of Sn to Zr. Figs. 8 and 9 show the effect of the reaction temperature and Sn/Zr molar ratio of SZ-CP catalysts on the SO_2 conversion and sulfur yield. The reaction temperature was varied in the range of 300–550 °C and space velocity was maintained to 10,000 cm^3/g$_{\text{-cat.}}$ h. $[H_2 + CO]/[SO_2]$ molar ratio and H_2O content were 2.5 and 2.0 vol.%, respectively. SZ-CP21 catalyst again showed the best performance and its optimal reaction temperature was 325 °C. Under these operating conditions, SO_2 conversion was about 98% and sulfur yield was about 78%. The reactivity with coal gas as the reductant was lower than the one with CO only.

3.4. Optimization of the reaction conditions

Among SZ-CP catalysts, SZ-CP21 catalyst was selected as the best catalyst for the SO_2 reduction by coal gas. A series of experiments were performed by varying space velocity, $[H_2 + CO]/[SO_2]$ molar ratio and H_2O content in order to find out an optimum operating condition for SZ-CP21 catalyst.

3.4.1. Optimization of the space velocity

Optimization of the space velocity was conducted in the range of 5000–30,000 cm^3/g$_{\text{-cat.}}$ h with 2.0 $[H_2 + CO]/[SO_2]$ molar ratio and 2.0 vol.% H_2O at 325 °C. Fig. 10 shows the

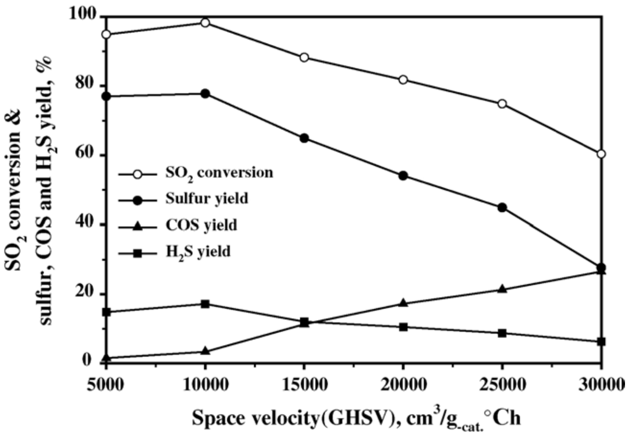

Fig. 10. The effect of the space velocity on the SO_2 reduction by coal gas over SZ-CP21 catalyst (Temperature of 325 °C, $[H_2 + CO]/[SO_2]$ molar ratio of 2.5 and H_2O content of 2 vol.%).

effect of the SO_2 conversion and sulfur, COS and H_2S yield in terms of the space velocity. It was observed that the optimal space velocity was 10,000 $cm^3/g_{\text{-cat.}}$ h in this study. In Fig. 10, the SO_2 conversion and sulfur yield started to decrease from the space velocity of 10,000 $cm^3/g_{\text{-cat.}}$ h due to the decrease of the contact time between the catalyst and reactants as the space velocity increased. Fig. 10 shows the yield of sulfur, H_2S and COS as a function of the space velocity. The COS yield increased with increasing the space velocity because COS was produced by the reaction between CO and SO_2, and enough time was not given to be converted to elemental sulfur. H_2S was produced by reaction between H_2 and SO_2, and its selectivity decreased with the space velocity.

3.4.2. *Optimization of the [H_2 + CO]/[SO_2] molar ratio*

In order to investigate the effect of [H_2 + CO]/[SO_2] molar ratio on the SO_2 reduction and to optimize the space velocity, a series of experiments were carried out by varying [H_2 + CO]/[SO_2] molar ratio as shown in Fig. 11. Fig. 11 shows the effect of the [H_2 + CO]/[SO_2] molar ratio on the SO_2 conversion and sulfur, COS and H_2S yield over SZ-CP21 catalyst. The variation of the [H_2 + CO]/[SO_2] molar ratio was conducted at 325 °C with space velocity of 10,000 $cm^3/g_{\text{-cat.}}$ h and H_2O content of 2.0 vol.%. When [H_2 + CO]/[SO_2] molar ratio is 1.0, the SO_2 conversion and sulfur yield were 43% and 38%, respectively. The higher [H_2 + CO]/[SO_2] molar ratio, the higher SO_2 conversion and sulfur yield upto 2.5 due to excessive SO_2. On the other hand, the higher [H_2 + CO]/[SO_2] molar ratio, the lower SO_2 conversion and sulfur yield from 2.5, and higher values due to the excessive H_2 and CO. From our experimental results, the optimal [H_2 + CO]/[SO_2] molar ratio was 2.5 and the SO_2 conversion and sulfur yield were about 98% and 78%. This result was not consistent with the stoichiometric [H_2 + CO]/[SO_2] molar ratio of 2.0 as seen in Eqs. (2) and (3). It was indicated that an excessive amount of reductants was required to achieve higher SO_2 conversion and sulfur yield since the oxidative atmosphere was promoted by CO_2 and H_2O contained in coal gas.

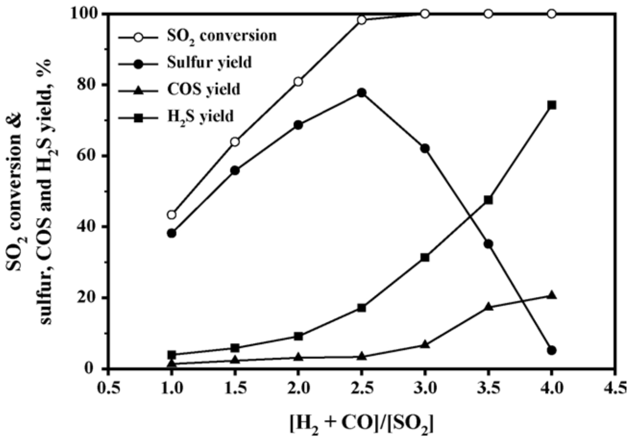

Fig. 11. The effect of the [H_2 + CO]/[SO_2] molar ratio on the SO_2 reduction by coal gas over SZ-CP21 catalyst (Temperature of 325 °C, space velocity of 10,000 $cm^3/g_{\text{-cat.}}$ h and H_2O content of 2.0 vol.%).

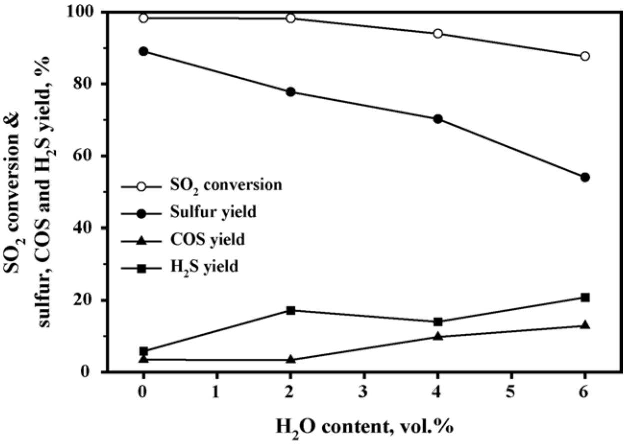

Fig. 12. The effect of the H_2O content on the SO_2 reduction by coal gas over SZ-CP21 catalyst (Temperature of 325 °C, space velocity of 10,000 $cm^3/g_{\text{-cat.}}$ h and [H_2 + CO]/[SO_2] molar ratio of 2.5).

3.4.3. *The effects of H_2O content on the SO_2 reduction by coal gas*

A small amount of H_2O was contained in coal gas from IGCC power plant system. Thus, the effect of H_2O content on the SO_2 reduction by coal gas over SZ-CP21 catalyst was investigated with the H_2O content up to 6 vol.% and the results are presented in Fig. 12. With no H_2O, SO_2 conversion and sulfur yield were about 98% and 89%, respectively. The higher was H_2O content, the lower SO_2 conversion and sulfur yield were obtained. It was believed that SO_2 conversion was decreased due to the decrease of the reactivity over the catalyst by H_2O, and that sulfur selectivity was decreased because of the increase of the selectivity of COS and H_2S as shown in Fig. 12. When 2 vol.% H_2O was contained in coal gas, SO_2 conversion and sulfur yield were about 98% and 78%, respectively.

4. Conclusion

The effect of the various reaction conditions, such as the reaction temperature, space velocity [reductant]/[SO_2] and H_2O content on the SO_2 reduction was investigated by the SO_2 reduction, by CO and coal gas over SnO_2, ZrO_2, physical mixture of SnO_2 and ZrO_2, and co-precipitated SnO_2-ZrO_2 catalysts in this study. The conclusions are as following:

(1) For the SO_2 reduction by CO over SnO_2 catalyst, light-off temperature was 350 °C, and SO_2 conversion and sulfur yield was about 45% and 32%, respectively, at 550 °C.
(2) In case of the SO_2 reduction by CO over ZrO_2 catalyst, light-off temperature was 490 °C and SO_2 conversion and sulfur yield was about 100% and 92%, respectively, at 550–650 °C.
(3) In case of the SO_2 reduction by CO over SZ-PM21 catalyst, light-off temperature was 350 °C and SO_2 conversion and sulfur yield was about 100% and 92%, respectively, at 550–650 °C. In this study, light-off temperature was same as that of SnO_2 but SO_2 removal efficiency was higher than that of SnO_2.

(4) In case of the SO_2 reduction by CO over SZ-CP catalysts, the best catalyst was SZ-CP21 catalyst. In addition, light-off was started below 300 °C, and SO_2 conversion and sulfur yield was about 100% and 97%, respectively, at 325 °C over SZ-CP21 catalyst. In our result, light-off temperature was lower than that of pure SnO_2 and pure ZrO_2, while, SO_2 removal efficiency was higher than those of SnO_2 and ZrO_2.

From our experimental results, it was concluded that the synergy effect between the reactivity of SnO_2 at low temperature and the high SO_2 reduction efficiency of ZrO_2 results in the high SO_2 reduction efficiency over SZ-CP catalysts at low temperature. The optimized reaction conditions of the SO_2 reduction by coal gas containing H_2, CO, CO_2 and H_2O over SZ-CP21 catalyst were obtained as follows: the optimal reaction temperature, space velocity and molar ratio of $[H_2 + CO]/[SO_2]$ were 325 °C, 10,000 $cm^3/g_{\text{-cat.}}$ h and 2.5, respectively. Also, it was confirmed that the SO_2 reduction by coal gas over SZ-CP catalysts was applicable to DSRP in IGCC power plant system.

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