



Catalytic reduction of sulfur dioxide with carbon monoxide over tin dioxide for direct sulfur recovery process

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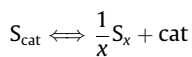
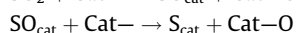
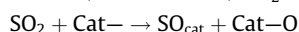
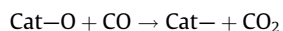
ABSTRACT

SO₂ reduction by CO over SnO₂ catalyst was studied in this work. The parameters were the reaction temperature, space velocity (GHSV) and [CO]/[SO₂] molar ratio. The optimal temperature, GHSV and [CO]/[SO₂] molar ratio were 550 °C, 8000 h⁻¹ and 2.0, respectively. Under these conditions, the SO₂ conversion and sulfur selectivity were about 78% and 68%, respectively. The following reaction pathway involving two mechanisms was proposed in SO₂ reduction by CO over SnO₂ catalyst: in the first step involving Redox mechanism, the elemental sulfur was produced by the mobility of the lattice oxygen between SO₂ and SnO₂ surface. In the second step, COS was formed by the side reaction between elemental sulfur and CO or metal sulfide and CO. In the third step involving COS intermediate mechanism, the abundant elemental sulfur was produced by the SO₂ reduction by COS which was produced in the second step and was more effective reducing agent than CO.

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1. Introduction

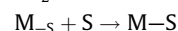
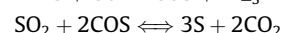
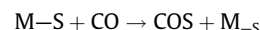
SO₂ is a toxic and corrosive sulfur compound which corrodes equipment, generates acid rain and pollutes and acidifies the soil. To treat SO₂, throwaway processes such as the lime or limestone scrubbing process are the prevailing methods of flue gas desulfurization. Furthermore, SO₂ treatment can be performed by the direct sulfur recovery process (DSRP), in which SO₂ is converted into elemental sulfur with a reducing agent over a catalyst (Happel et al., 1977; Liu et al., 1994, 1996). The carbonaceous materials, carbon monoxide, natural gas and hydrogen have been used as the various reducing agents in the reduction process of SO₂ (Haas and Khalafalla, 1973; Gangwal et al., 1991; Liu et al., 1996). The various catalysts such as Ce–Zr, Sn–Zr, Co–Mo, transition metals and Al₂O₃ have been used in DSRP (Ma et al., 1996, 1997; Han et al., 2006). In DSRP, the mechanism of SO₂ reduction is thought to depend on the types of catalyst and reducing agent. Redox mechanism and COS intermediate mechanism have been generally suggested for the SO₂ reduction by CO. The reaction pathway for the Redox mechanism involves the lattice oxygen mobility of the metal oxide, as below:



(Cat–: oxygen vacancy and SO_{cat}: SO₂ species reduced after the adsorption).

The Redox mechanism has the following reaction and catalytic characteristics: relatively high reaction temperature, near zero COS formation, high storage capacity and mobility of lattice oxygen of an applicable oxide catalyst, involves active sites consisting of lattice oxygen vacancies and sulfate group formation after the reaction (Haas and Khalafalla, 1973; Happel et al., 1975; Gangwal et al., 1991; Horváth, 2003).

It is known that the COS intermediate mechanism involves the surface reaction between SO₂ and COS on the Lewis and Brønsted acid sites after COS is formed elsewhere by the reaction between CO and sulfur or metal sulfides, as below (Lee and Han, 2002; Ma et al., 1996, 1997):



The COS intermediate mechanism has the following reaction and catalytic characteristics: a relatively low reaction temperature, high COS formation, involves the active Lewis and Brønsted acidic sites, the partial transformation of metal oxide into metal sulfide and high activity of an applicable catalyst in the reaction between SO₂ and COS.

In this work, the SO₂ reduction by CO over SnO₂ catalyst was conducted under various conditions such as the temperature, space velocity (GHSV) and [CO]/[SO₂] molar ratio. The reaction characteristics were compared with two conventional mechanisms, which have been proposed for the reduction of SO₂ by CO.

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At same time, the possible reaction pathway will be suggested as the applicable mechanism for the SO₂ reduction by CO over SnO₂ catalyst.

2. Experimental

2.1. Preparation and activity test of the catalyst

The precipitation method was employed to prepare the SnO₂ catalyst. Tin chloride pentahydrate (SnCl₄ · 5H₂O, Aldrich), as the precursor was dissolved in the distilled water with stirring. Ammonium hydroxide was added to the solution of the precursor to bring the pH up to 9–10, whereupon a white precipitate was formed. This precipitated slurry was warmed in a water bath at 80 °C for 3 h. After drying the viscous liquid at 110 °C for 24 h, the solid was calcined at 600 °C for 4 h in an electric furnace.

After crushing the solid product, selected particles with a size of 0.075–0.15 mm were used as the catalyst in the reactivity test of SO₂ reduction by CO. The reduction of SO₂ was performed as follows: a gas mixture with the [CO]/[SO₂] molar ratio (20000 ppmv SO₂ in N₂ balance) of 1.0–4.0 and GHSV of 5000–30000 h⁻¹ was fed into the reactor. When a steady state was attained, the outlet concentration of SO₂, COS and the other by-products were determined by a gas chromatograph (Shimadzu-8A) equipped with a thermal conductivity detector. In the SO₂ reduction by CO, the SO₂ conversion, sulfur yield and the selectivity of SO₂ and COS were calculated by following equations:

$$\text{SO}_2 \text{ conversion (\%)} = \frac{[\text{SO}_2]_{\text{in}} - [\text{SO}_2]_{\text{out}}}{[\text{SO}_2]_{\text{in}}} \times 100$$

$$\text{Sulfur selectivity (\%)} = \frac{[\text{SO}_2]_{\text{in}} - [\text{SO}_2]_{\text{out}} - [\text{COS}]_{\text{out}}}{[\text{SO}_2]_{\text{in}}} \times 100$$

$$\text{COS selectivity (\%)} = \frac{[\text{COS}]_{\text{out}}}{[\text{SO}_2]_{\text{in}}} \times 100$$

$$\text{Sulfur yield (\%)} = \text{SO}_2 \text{ conversion} \times \text{Sulfur selectivity}$$

In the SO₂ reduction by COS, the sulfur yield was calculated by following equation:

$$\text{Sulfur yield (\%)} = \frac{[\text{SO}_2]_{\text{in}} + [\text{COS}]_{\text{in}} - [\text{SO}_2]_{\text{out}} - [\text{COS}]_{\text{out}}}{[\text{SO}_2]_{\text{in}} + [\text{COS}]_{\text{in}}} \times 100$$

2.2. Characterization of the fresh and used SnO₂ catalysts

The phase composition of the catalysts was analyzed by X-ray diffractometer (XRD; Rigaku, D/MAX-2500, Ni-filtered Cu K α radiation) and elemental composition of the fresh and used SnO₂ catalysts were analyzed using an energy dispersive X-ray spectrometer (EDX, KEVEX SIGMA, FISONs Co.).

X-ray photoelectron spectroscopy (XPS) was conducted using an ESCALAB 250 XPS spectrometer fabricated by VG Scientifics and equipped with a focused (spot size 100 Å) and monochromatized Al K α anode ($h\nu = 1486.6$ eV). The binding energies corresponding to the C1s peak at 284.6 eV are given with an accuracy of ± 0.2 eV. The samples were obtained and delivered to a XPS instrument after the used SnO₂ catalyst was pretreated in N₂ atmosphere and the temperature was gradually dropped to room temperature.

CO-TPR (temperature-programmed reduction) of SnO₂ catalyst was conducted by a thermal conductivity detector (TCD, AUTOSORB-1, Quantachrome Co.) for measuring the degree of the reduction. After the SnO₂ catalyst of 0.5 g was pretreated in N₂ atmosphere for 2 h at 250 °C to remove the impurities like H₂O. Then, the temperature was adjusted to room temperature. CO-TPR analysis was performed by injecting 5 vol% CO and then the temperature was raised from room temperature up to 575 °C at a

rate of 5 °C min⁻¹. The TCD-signal corresponds to the reduction degree of the SnO₂ catalyst.

3. Results and discussion

3.1. Effect of the reaction temperature

Fig. 1 shows the results of activity test as a function of time in the SO₂ reduction by CO over SnO₂ catalyst. The fixed reaction conditions were GHSV of 10000 h⁻¹ and the [CO]/[SO₂] molar ratio of 2.0. The reaction temperature was varied from 350 to 550 °C. The light-off temperature for the conversion of SO₂ was 375 °C and then the SO₂ conversion was more than 4%. During the reaction time of 4 h, the activity was stable after approximately 30 min and remained constant without any variation such as a catalyst deactivation. SO₂ conversion increased as the reaction temperature increased. The dependence of the selectivities of sulfur and COS on temperature was different from the SO₂ conversion. The COS selectivity was increased and the sulfur selectivity was decreased with increasing the reaction temperature in the range below 425 °C. It was inferred that the COS formation was promoted, while the formation of elemental sulfur was not, depending on the reaction temperature. Above 425 °C, the selectivity of sulfur was increased and the selectivity of COS was decreased as the reaction temperature increased. The highest COS selectivity was obtained at 425 °C. However, the most desirable catalytic activity was a high sulfur yield, which was obtained simultaneously with a high SO₂ conversion and sulfur selectivity. Consequently, the sulfur yield was increased as the reaction temperature increased. The highest sulfur yield was obtained at 550 °C, at which the SO₂ conversion was about 45% and the sulfur selectivity was about 80%.

3.2. Effect of GHSV

Fig. 2 shows the SO₂ conversion and the selectivities of COS and sulfur with the GHSV in the SO₂ reduction by CO over SnO₂ catalyst. The temperature and [CO]/[SO₂] molar ratio were fixed at 600 °C and 2.0, respectively, and GHSV was varied from 5000 to 30000 h⁻¹. The SO₂ conversion decreased from 83% to 37% as GHSV increased from 5000 to 30000 h⁻¹. This result might be associated with the decrease of the contact time between the reactant and the catalyst surface. The variation of the selectivities of sulfur and COS with GHSV was different from the SO₂ conversion. Below 8000 h⁻¹, the COS selectivity decreased from 37% to 32% and the sulfur selectivity was increased from 63% to 68% as GHSV was increased from 5000 to 8000 h⁻¹. Above 8000 h⁻¹, as GHSV increased, the sulfur selectivity was decreased simultaneously with the decrease of the SO₂ conversion from 68% to 52% and the COS selectivity was increased from 32% to 49%. The sulfur yield also was decreased due to the decrease of the SO₂ conversion and sulfur selectivity. As a result, the optimal GHSV was 8000 h⁻¹ and then the SO₂ conversion of 78% and sulfur selectivity of 68% were obtained at 8000 h⁻¹.

3.3. Effect of the [CO]/[SO₂] molar ratio

Fig. 3 shows the effect of the [CO]/[SO₂] molar ratio on the SO₂ reduction by CO over SnO₂ catalyst. The [CO]/[SO₂] molar ratio was varied from 1.0 to 4.0 with the fixed reaction temperature of 600 °C and GHSV of 8000 h⁻¹. As the [CO]/[SO₂] molar ratio was increased from 1.0 to 4.0, the SO₂ conversion was increased from 47% to about 100%. It was concluded that the SO₂ conversion was increased by increasing the [CO]/[SO₂] molar ratio because the SO₂ concentration became critical and decreased as the CO concentration was further increased. The COS selectivity was increased, but the sulfur selectivity was simultaneously de-

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