

# Synergistic catalysis effect in SO<sub>2</sub> reduction by CO over Sn–Zr-based catalysts

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## Abstract

In this study, the synergistic effect observed in the SO<sub>2</sub> reduction by CO over SnO<sub>2</sub>–ZrO<sub>2</sub> catalysts was investigated in detail. From the reactivity tests of the various catalysts, it was established that the applicable mechanism of this study was different from the conventional mechanisms such as the redox and COS intermediate mechanisms. It could be explained by postulating that the synergistic effect of the Sn–Zr-based catalyst was obtained in the SO<sub>2</sub> reduction by CO as the following mechanistic pathway: In the first step involving the redox mechanism, SO<sub>2</sub> was converted into elemental sulfur and other by-products such as COS because of the lattice oxygen mobility afforded by the redox properties of the SnO<sub>2</sub> catalyst. In the second step involving the COS intermediate mechanism, COS produced in the first step was the more effective reducing agent than CO and reacted with SO<sub>2</sub> over the ZrO<sub>2</sub> catalyst, and then the productivity of elemental sulfur was improved. At that time, the reaction rate of SO<sub>2</sub> + 2COS → 3S + 2CO<sub>2</sub> must have been faster than that of CO + S → COS. The high reactivity of the SnO<sub>2</sub>–ZrO<sub>2</sub> (Sn/Zr = 2/1) catalyst at low temperature was thus caused by a synergistic effect resulting of the simultaneous interaction between the redox mechanism and COS intermediate mechanism.

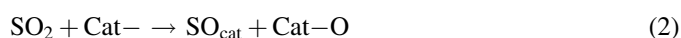
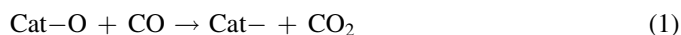
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**Keywords:** SO<sub>2</sub> reduction by CO; Sn–Zr-based catalyst; Redox mechanism; COS intermediate mechanism; Synergistic effect

## 1. Introduction

The Direct Sulfur Recovery Process (DSRP), in which SO<sub>2</sub> can be converted into elemental sulfur over a catalyst, is a dry SO<sub>2</sub> reduction process using a reducing agent. The reducing agents used for the reduction of SO<sub>2</sub> are CO, H<sub>2</sub>, C (carbon) and CH<sub>4</sub>. The various mechanisms for the SO<sub>2</sub> reduction by CO over the various catalysts have previously been proposed. Among the various proposed mechanisms, the redox mechanism involves the catalytic properties to move and store the lattice oxygen to simultaneously reduce SO<sub>2</sub> and oxidize the catalyst through its mobility. Consequently, the SO<sub>2</sub> reduction to convert SO<sub>2</sub> into elemental sulfur can proceed due to the lattice oxygen mobility between the lattice oxygen vacancy of the catalyst and SO<sub>2</sub>. The abundant storage capacity and the easy mobility of the lattice oxygen are necessary for the redox

mechanism. The pathway could be explained as follows [1,2]: In the first step, the surface of the catalyst is reduced by a reducing agent, and then the lattice oxygen vacancies, which play an active role in the oxidation and reduction process using the catalyst, are formed. In the second step, after the adsorption of SO<sub>2</sub>, the re-oxidation of the catalyst proceeds through the lattice oxygen mobility into the lattice oxygen vacancies from SO<sub>2</sub>, and then the elemental sulfur might be separated from SO<sub>2</sub>. The redox mechanism can be expressed as follows (Eqs. (1)–(4)):



In accordance with the redox mechanism, the elemental sulfur is preferentially produced by the direct SO<sub>2</sub> reduction by

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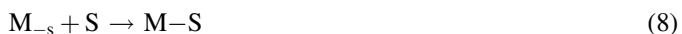
E-mail address: [tjlee@ynu.ac.kr](mailto:tjlee@ynu.ac.kr) (T.J. Lee).

CO, whereas COS is a secondary by-product from the reaction between elemental sulfur and CO (Eq. (5)):



The pathway of the reduction and re-oxidation can be explained by the redox mechanism involving the catalytic properties of the high lattice oxygen mobility. The majority of fluorite type metal oxides such as Ce-based oxides having the mobility of lattice oxygen are known as the applicable catalysts for the  $\text{SO}_2$  reduction [3–9].

The COS intermediate mechanism has been suggested as the other mechanism for the  $\text{SO}_2$  reduction by CO. In this mechanism, it has been known that COS is a by-product produced in the reaction between elemental sulfur and CO and plays an important role as an essential intermediate. Moreover, COS is known to be a more effective reducing agent than CO for the conversion of  $\text{SO}_2$  into elemental sulfur. In the 1970s, the COS intermediate mechanism was suggested for the  $\text{SO}_2$  reduction by CO over Fe/alumina catalyst [10,11]. A two-stage reactor for the  $\text{SO}_2$  reduction by CO was designed based on the COS intermediate mechanism [12–14]. Recently, the COS intermediate mechanism model was used for explaining the  $\text{SO}_2$  reduction of by CO over  $\text{La}_2\text{O}_3$  catalyst or transition metal-based catalysts [15–17]. In the COS intermediate mechanism, it was known that the transition metal-based catalyst is transformed into the metal sulfide. Consequently, COS is produced by the side reaction between CO and the metal sulfide after the adsorption of CO on the surface of the metal sulfide, and then the elemental sulfur vacancies are formed on the surface of the metal sulfide and are filled by the produced elemental sulfur. The COS intermediate mechanism can be represented as follows (Eqs. (6)–(8)):



The high COS selectivity with having the low  $\text{SO}_2$  conversion can be shown in the  $\text{SO}_2$  reduction by CO over transition metal supported alumina catalysts along COS intermediate mechanism [18]. The COS production and the  $\text{SO}_2$  reduction by the produced COS must be accompanied in the COS intermediate mechanism. In the  $\text{SO}_2$  reduction by COS over Fe/alumina catalyst, the Lewis and Brönsted acidic sites of Fe/alumina catalyst were suggested as the active sites [19].

In the previous study, it was reported that the high reactivity was obtained at low temperature in the  $\text{SO}_2$  reduction by CO over  $\text{SnO}_2$ - $\text{ZrO}_2$  catalyst. It might be due to the synergistic effect obtained by the coexistence of  $\text{SnO}_2$  and  $\text{ZrO}_2$ . In this study, the reaction characteristics of the  $\text{SO}_2$  reduction by CO over the Sn-Zr-based catalysts were systematically investigated in order to explain the synergistic effect in detail. These results of this study suggested that the reaction pathway of the  $\text{SO}_2$  reduction by CO over Sn-Zr-based catalyst proceeds by different mechanisms from the redox and COS intermediate mechanisms.

## 2. Experimental

### 2.1. Preparation of the catalysts and the reactivity test

The  $\text{SnO}_2$  and  $\text{ZrO}_2$  catalysts were respectively prepared by a precipitation method and the  $\text{SnO}_2$ - $\text{ZrO}_2$  (Sn/Zr = 2/1) catalyst was prepared by a co-precipitation method as follows: Tin chloride pentahydrate ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ , Aldrich) and zirconyl nitrate hydrate ( $\text{ZrO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Aldrich) were used the precursors corresponding to each catalyst. After the proper amounts of the precursors corresponding to the desired Sn/Zr molar ratio were dissolved in distilled water with stirring vigorously, the co-precipitate was produced by adding  $\text{NH}_4\text{OH}$  solution up to the pH range of 9–10. The solution containing the co-precipitate was dehydrated in a water bath at  $80^\circ\text{C}$ . The viscous liquefied slurry was dried at  $110^\circ\text{C}$  overnight in a drying oven and the resulting solid product was calcined at  $600^\circ\text{C}$  for 4 h in an electric furnace. After the catalyst was sieved, the selected particles with diameters of 0.075–0.150 mm were employed in the reactivity test. The schematic symbols of the various catalysts prepared by their different chemical and physical mixing methods are listed in Table 1.

The reactivity test of the  $\text{SO}_2$  reduction by CO was conducted using a quartz-based tubular reactor with a diameter of 1/2 in. The gas mixture with the desired  $[\text{CO}]/[\text{SO}_2]$  molar ratio was fed into the reactor after its temperature was raised to the desired reaction temperature. The basic concentration of  $\text{SO}_2$  and the  $[\text{CO}]/[\text{SO}_2]$  molar ratio were 2 vol% (diluted by  $\text{N}_2$ ) and 2.0, respectively, and the space velocity (GHSV) was 8000 ml/g<sub>cat</sub> h or 10,000 ml/g<sub>cat</sub> h. During a steady state of reactivity, the concentrations of  $\text{SO}_2$ , COS,  $\text{H}_2\text{S}$  and other by-products were determined by a gas chromatograph (Shimadzu-8A) equipped with a thermal conductivity detector and a packed column of 1/8 in. with Hayesep Q (8 ft) and Porapak T (2 ft).

### 2.2. Characterization of the Sn-Zr-based catalysts

The prepared catalysts were characterized by  $\text{H}_2$ -TPR (temperature-programmed reduction) analysis (Quantachrome Co., Autosorb-1 model) using the following procedure. After the pretreatment of 0.5 g of the Sn-Zr-based catalyst in flowing  $\text{N}_2$  for 2 h at  $250^\circ\text{C}$  and subsequent cooling down, the  $\text{H}_2$ -TPR was initiated by the injection of 5 vol%  $\text{H}_2$ . At the same time, the temperature of the catalyst sample was raised from room temperature up to  $600^\circ\text{C}$  at a heating rate of  $5^\circ\text{C}/\text{min}$ .

The crystalline forms of the fresh and used catalysts were analyzed by X-ray diffractometer (XRD; Rigaku, D/MAX-2500) with Ni-filtered Cu  $\text{K}\alpha$  radiation.

The redox property of the SZ-CP21 catalyst was investigated by reducing and re-oxidizing the SZ-CP21 catalyst. The reducing agent and oxidizing agent were 4 vol% CO and 2 vol%  $\text{SO}_2$ , respectively. Under the space velocity of 10,000 ml/g<sub>cat</sub> h, the reduction and re-oxidation of the SZ-CP21 catalyst were performed at  $325^\circ\text{C}$  sequentially.

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