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The catalytic reduction of SO_2 to elemental sulfur with H_2 or CO

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Abstract

In the catalytic reduction of SO_2 to elemental sulfur using a stoichiometric amount of H_2 or CO, sulfided Co/Al_2O_3 or Co/TiO_2 catalysts had bifunctional properties; cobalt sulfide generates H_2S (with H_2 as reductant) or COS (with CO as reductant) as reaction intermediate and then production of sulfur can be achieved by the reaction between the reaction intermediate (H_2S or COS) and SO_2 over Al_2O_3 or TiO_2.

Keywords: Bifunctional role; Catalytic reduction; Elemental sulfur; SO_2; H_2S; COS

1. Introduction

As recent regulation for the environmental problem becomes more strict in the near future, developing of control technologies for the SO_x emission in either flue gas or in oxygen-free tail gas has been paid a significant attention. Commercial technologies for the removal of SO_x from flue gas (flue gas desulfurization, FGD) are based on a throwaway process such as lime or limestone scrubbing [1]. Other recovery technologies such as adsorption and absorption are under development [2–4]. In conjunction with this development and for the recovery of SO_x in oxygen-free gas, the best choice would be the selective reduction of SO_2 to elemental sulfur which is easy to treat, handle, and transport.

The reduction of sulfur oxide to sulfur has been studied in early 1930s using reducing agents such as carbonaceous material [5], carbon monoxide [6–10], natural gas [11–13], and hydrogen [14–16]. In spite of many efforts to find efficient catalysts and reductants, there is no commercialized process due to high reaction temperature and low sulfur yield for practical application. Recently, we have reported that sulfided $Co–Mo/Al_2O_3$ (or sulfided Co/Al_2O_3) can convert SO_2 selectively to sulfur with hydrogen at lower temperature than have ever reported [17,18]. Also, Liu et al. [19] and Ma et al. [20] reported that composite oxides (or mixed oxysulfide) showed good sulfur yield using carbon monoxide as reductant even though reaction temperature is still somewhat high.

Here, we report that cobalt supported on (or mixed with) Al_2O_3 or TiO_2 shows high catalytic activity for the reduction of SO_2 with H_2 or CO. Bifunctional roles of proposed catalysts were investigated in relation to their high catalytic activity at low reaction temperature.

2. Experimental

2.1. Preparation of catalysts

Al_2O_3-supported cobalt (Co/Al_2O_3) was prepared by pore-filling impregnation of γ-Al_2O_3 (Aldrich, sur-

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face area is 250 m^2/g, and pore volume is 0.65 cm^3/g) with cobalt nitrate ($Co(NO_3)2{\cdot}6H_2O$) solution. The cobalt loading was fixed at 10 wt% on the metal basis. After drying over night at 110°C, it was calcined at 450°C for 2 h in a flow of air. Before the reaction, Co/Al_2O_3 catalyst was pre-sulfided in a flow of H_2S containing gas (10 vol% H_2S in H_2 balance) at 400°C for 2 h. In order to investigate the reaction mechanism, CoS_2 (Alfa, 60/80 mesh, 99.9% purity), γ-Al_2O_3 (Aldrich, 60/80 mesh), and a physical mixture of the two were also employed. Co_9S_8 was made by sulfiding of CoS_2 in a flow of 10 vol% H_2S/H_2 gas at 400°C. TiO_2 was purchased from JRC (Japan). Its form was rutile and surface area was 45 m^2/g.

2.2. *Reaction tests*

A vertical, fixed-bed flow reactor made of 1 in. pyrex tube was used for the reaction test at atmosphere. Sulfur dioxide (Solkatronic) and hydrogen (or carbon monoxide) (Union Carbide) were mixed and diluted in helium using mass flow controllers. A sulfur condenser was attached at the effluent side of the reactor, and its temperature was maintained constant at 110°C to condense sulfur vapor without condensing water vapor. From the condenser up to the gas chromatograph, all the lines and fittings were heated above 120°C. A line filter was installed after the condenser to trap any sulfur mist that was not collected by the condenser. The gaseous products were analyzed by a gas chromatograph and a thermal conductivity detector. The conversion of SO_2, the selectivity of sulfur are defined as follows:

$$\text{Conversion of } SO_2(\%) = \frac{(SO_2)_{\text{inlet}} - (SO_2)_{\text{outlet}}}{(SO_2)_{\text{inlet}}} \times 100,$$

$$\text{Selectivity of sulfur}(\%) = \frac{(SO_2)_{\text{inlet}} - (SO_2)_{\text{outlet}} - (H_2S \text{ or } COS)_{\text{outlet}}}{(SO_2)_{\text{inlet}} - (SO_2)_{\text{outlet}}} \times 100,$$

where each term represents concentration of sulfur dioxide and hydrogen sulfide (or carbonyl sulfide).

3. Results and discussion

3.1. *Catalytic reduction of SO_2 with H_2*

The reaction was carried out at a constant feed ratio of H_2/SO_2=2.0, the stoichiometric ratio to reduce SO_2 selectively to elemental sulfur, not to H_2S. Gas hourly space velocity was fixed at 3600 h^{-1}. Fig. 1 shows the conversion of SO_2 and the selectivity of sulfur for sulfided Co/Al_2O_3 catalyst with time on stream. The selectivity of sulfur shows high values above 90% at all reaction temperatures. The conversion decreases at the initial stage of the reaction. After showing a minimum point, it increases again and reaches a steady state. This implies that there might be some changes in catalyst structure during the reaction.

In order to investigate catalyst phases during the reaction, the catalyst was analyzed by XRD. During the reaction, cobalt phases of Co_9S_8, Co_3S_4, and CoS_2 were found depending on the reaction time. Fig. 2 shows the relative portion of cobalt phases at corresponding conversion and time on stream. The cobalt phase before the reaction was Co_9S_8 that is thermodynamically stable at pre-sulfiding condition (10 vol% H_2S/H_2 at 400°C) [21]. As reaction time goes on, the Co_9S_8 phase was slowly transformed to Co_3S_4 and CoS_2, and only the CoS_2 phase remained after 180 min of the reaction. It is clear that the cobalt

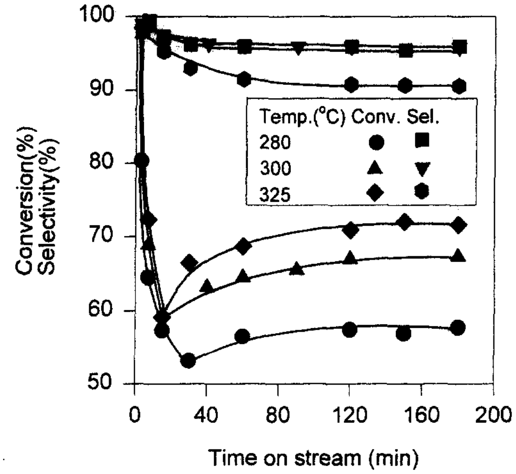

Fig. 1. The conversion of SO_2 and selectivity of sulfur with time on stream at various reaction temperatures on sulfided Co/Al_2O_3 catalysts (H_2/SO_2=2.0, 5% SO_2, GHSV=3600 h^{-1}).

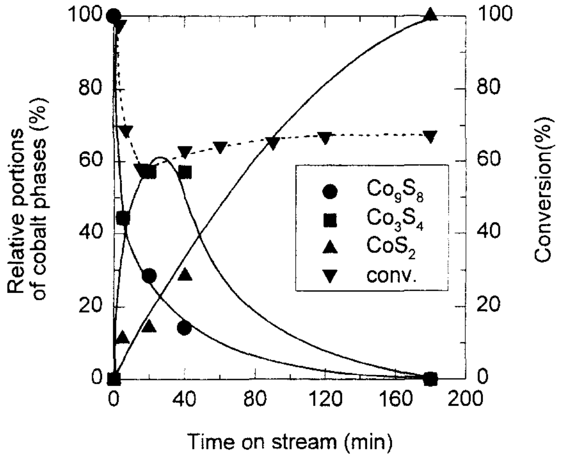

Fig. 2. Relative portions of cobalt phases and conversion of SO_2 with time on stream (H_2/SO_2=2.0, 5% SO_2, temperature=300°C).

phase in Co/Al_2O_3 catalyst experiences a phase transformation from sulfur deficient form (Co_9S_8) to sulfur-rich form (CoS_2) through the incorporation of produced sulfur during the reaction. Owing to this phase transformation, the conversion of SO_2 with time on stream has the transient period at the initial reaction stage.

For the transformation of Co_9S_8 to sulfur-rich CoS_2 during the reaction, the reactant SO_2 in the feed must be consumed. As shown in Table 1, Co_9S_8 has nearly zero activity compared with CoS_2. Therefore, the initial high conversion of SO_2 over Co_9S_8 phase in Fig. 1 must result from the consumption of SO_2 for the phase transformation of Co_9S_8. As the sulfur consumption for the structural transformation decreases exponentially, the conversion of SO_2 at initial stage is also decreased coinciding with phase transformation of Co_9S_8. As the new cobalt phases such as, Co_3S_4 and CoS_2, are generated, the conversion of SO_2 increases again as shown in Fig. 2. The conversion keeps increasing while the Co_3S_4 phase begins to decrease, indicating that the Co_3S_4 is probably less active than the CoS_2. Therefore, it is concluded that the active phase in the reaction is CoS_2, which is generated by incorporation of sulfur into Co_9S_8 during the reaction.

Table 1 shows the conversion of SO_2 and selectivity of sulfur over various kinds of catalysts. CoS_2 catalyst shows a high conversion of SO_2, but the selectivity of sulfur is zero, indicating that the reactant SO_2 is converted to H_2S. Over a physical mixture of CoS_2 and Al_2O_3, both the conversion and selectivity of sulfur is very high. In order to confirm the role of cobalt and alumina, the following experiment was carried out as shown in Table 1 (from third row to sixth row). When only alumina was used (third row), there was zero conversion of SO_2. It establishes that alumina is inert in this reaction. The case of fifth row in Table 1, where CoS_2 was packed on the top of Al_2O_3 bed showed high values of conversion of SO_2 and selectivity of sulfur. Since the CoS_2 produced only H_2S (second row in Table 1), the generation of sulfur must result from a reaction that is catalyzed by the bottom alumina. When the packing order was reversed, placing the alumina on the top of CoS_2 bed, as in the case of sixth row in Table 1, the production of sulfur was negligible. In other words, when alumina is located on the top in the reactor bed, it has no catalytic function and only the bottom layer of CoS_2 produces H_2S as in the case of single CoS_2 bed used (second row in Table 1). These results clearly show that Co/Al_2O_3 catalyst has bifunctional role in the reaction. The metal sulfide in Co/Al_2O_3 catalyst fully hydrogenates SO_2 to H_2S, and then alumina catalyzes the reaction of SO_2 and H_2S (Claus reaction)

Table 1
The conversion of SO_2 and selectivity of sulfur over a separate bed of Co_9S_8, CoS_2, and Al_2O_3, and a combination or a physical mixture of CoS_2 and Al_2O_3 (H_2/SO_2=2.0, 5% SO_2, temperature=300°C, GHSV=3600 h^{-1})

Catalyst	Conversion (%)	Selectivity (%)
Co_9S_8	1.5	75.0
CoS_2	17.5	0.0
Al_2O_3	0.0	0.0
Physical mixture of CoS_2 (1 g) and Al_2O_3 (1 g)	12.3	96.5
CoS_2 (1 g, top)/Al_2O_3 (1 g, bottom)	12.8	98.3
Al_2O_3 (1 g, top)/CoS_2 (1 g, bottom)	7.9	0.0

to produce elemental sulfur.

Metal sulfide site : $SO_2 + 3H_2 \rightarrow H_2S + 2H_2O$ (1)

Al_2O_3 site : $SO_2 + 2H_2S \leftrightarrow 3S + 2H_2O$ (2)

Overall reaction : $SO_2 + 2H_2 \rightarrow S + 2H_2O$ (3)

According to the above reaction scheme, the role of metal sulfide is generation of reaction intermediate (H_2S) and only the alumina has a role of producing sulfur.

3.2. *Catalytic reduction of* SO_2 *with* CO

The reduction of SO_2 with CO on a physical mixture of TiO_2 (1 g) and CoS_2 (1 g) was carried out at various reaction temperatures from 300°C to 500°C using a stoichiometric feed ratio of $CO/SO_2=2.0$.

$$2CO + SO_2 \rightarrow 2CO_2 + S \quad (4)$$

The conversion of SO_2 and selectivity of elemental sulfur is shown in Fig. 3. The light-off temperature was about 300°C and the conversion reached equilibrium after 400°C. The selectivity of elemental sulfur had a maximum value at 400°C. These results show that the mixture catalyst has better activity and lower light-off temperature compared to other mixed oxides [19].

The comparison of conversion and selectivity between the physical mixture of CoS_2–TiO_2 and titania is shown in Table 2. TiO_2 had a good activity at 400°C, but the conversion dropped below 10% at 350°C. However, the physical mixture catalyst showed about 80% conversion of SO_2 at 350°C. The addition of CoS_2 to TiO_2 improves the activity of SO_2 reduction by CO showing a synergy effect. To investigate the role of CoS_2 in the mixture catalyst, the reaction was carried out on a single bed of CoS_2. The conversion of SO_2 was very low, while COS was continuously produced. Therefore, it is assumed that the COS is not generated by the reaction of SO_2 with CO, but by the reaction with CoS_2. This was confirmed by observing continuous generation of COS after passing CO through a bed of CoS_2 at 350°C. When CoS_2 was contacted with CO for a long time, there was slow decrease of COS formation and this was followed by a sudden drop of COS.

Table 2
Comparison of conversion of SO_2 and selectivity of sulfur between mixture of CoS_2–TiO_2 and TiO_2 ($CO/SO_2=2.0$, 2% SO_2, temperature=400°C, GHSV=3000 h^{-1})

Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)
CoS_2–TiO_2	350	84.5	98.8
TiO_2	350	7.6	99.3
CoS_2–TiO_2	400	98.6	97.6
TiO_2	400	97.9	97.1

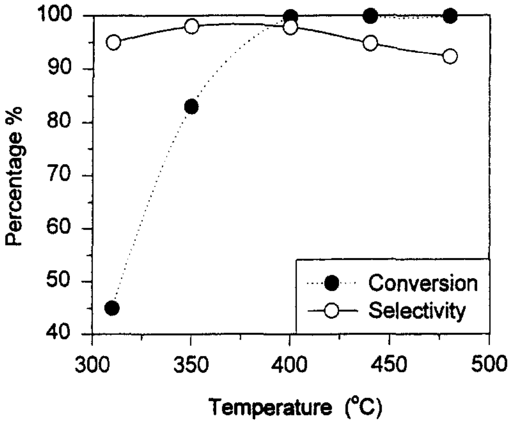

Fig. 3. The conversion of SO_2 and selectivity of sulfur on the mixture of CoS_2–TiO_2 ($CO/SO_2=2.0$, 2% SO_2, GHSV=3000 h^{-1}).

The integration of the amount of sulfur for COS generation was equal to the amount of sulfur that can be removed by transformation of CoS_2 to CoS. The phase transformation was also confirmed by XRD. These results suggest that CO reacts with sulfur in CoS_2 to produce COS:

$$CoS_2 + CO \rightarrow CoS + COS \quad (5)$$

In the case of TiO_2, it is suggested that the reduction of SO_2 by CO follows a redox mechanism [8,19,22].

$$\text{Cat-O} + CO \rightarrow \text{Cat-[ ]} + CO_2 \quad (6)$$

$$\text{Cat-[ ]} + SO_2 \rightarrow \text{Cat-O} + SO \quad (7)$$

$$\text{Cat-[ ]} + SO \rightarrow \text{Cat-O} + S \quad (8)$$

The reaction is started by the reduction of TiO_2 by CO. When the reduced Cat-[ ]s are formed, SO_2 gives one oxygen to reduced Cat-[ ] and turns into SO. The mobile SO gives remaining one oxygen to other Cat-[ ] and elementary sulfur is generated. To confirm

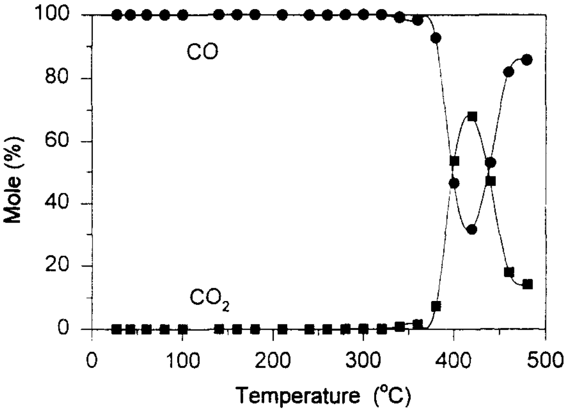

Fig. 4. CO reaction over TiO_2 (4% CO/He, 2 g TiO_2, flow rate: 50 cm^3/min).

elementary steps of the redox mechanism on TiO_2, CO reaction on TiO_2 was carried out as shown in Fig. 4. The result shows that TiO_2 has an oxygen source for the oxidation of CO. Production of CO_2 had light-off temperature of 380°C.

The proposed redox mechanism of TiO_2 cannot explain the synergy effect of mixture catalyst at 350°C because of low activity of TiO_2 with CO at 350°C.

It has been reported that COS can react with SO_2 to generate elemental sulfur [20].

$$2COS + SO_2 \rightarrow 3S + 2CO_2 \qquad (9)$$

The high activity on the physically mixed catalyst at 350°C probably indicates that TiO_2 has a good activity for the reaction (9). Hence, at the low temperature region below 350°C, the modified redox mechanism is proposed.

$$CoS_2 + CO \rightarrow CoS + COS \qquad (10)$$

$$TiO_2 + COS \rightarrow TiO[\,] + CO_2 + S \qquad (11)$$

$$2TiO[\,] + SO_2 \rightarrow 2TiO_2 + S \qquad (12)$$

First, CoS_2 reacts with CO to produce COS intermediate. Similar to CO, COS is able to reduce TiO_2 to create an oxygen vacancy, and the oxygen vacancy is used for generation of elemental sulfur. According to the literature [23,24], it was reported that COS can be decomposed on metal oxide. Indeed we observed the production of CO_2 and elemental sulfur during the reaction of COS with TiO_2 as shown in Eq. (11). The result indicates that COS can be easily activated on TiO_2 at lower temperature than CO. Therefore, the synergy effect on the mixtures of CoS_2 and TiO_2 at low temperatures can be explained by formation of the COS intermediate from CoS_2, the good ability of COS to create oxygen vacancy on TiO_2, and subsequent reaction of SO_2 on TiO_2 vacancy to produce elemental sulfur. Thus, there are bifunctional roles of cobalt sulfide and titania in the reduction of SO_2 with CO, which is similar to the case of the reduction of SO_2 with H_2 on sulfided Co/Al_2O_3 catalyst.

4. Conclusion

The catalytic system composed of mixtures of sulfided $Co–Al_2O_3$ or $CoS_2–TiO_2$ (mixed catalyst) had unique reaction properties of bifunctionality for the reduction of SO_2 with H_2 or CO to elemental sulfur. In the case of H_2 as reductant, the reaction occurred via two individual steps on two different sites; first, SO_2 was fully hydrogenated to H_2S on CoS_2 site and then it was followed by the Claus reaction between SO_2 and H_2S to produce elemental sulfur on Al_2O_3 site. When CO was used for the reduction of SO_2, COS was generated by the reaction between CO and CoS_2. This was followed by the reaction of COS and SO_2 on TiO_2 to produce elemental sulfur through the redox mechanism. Therefore, the reduction of SO_2 always occurs via two individual reaction steps and the component of catalyst has its own roles for each individual step. Cobalt sulfide generates the reaction intermediate (H_2S or COS) and then the intermediate and SO_2 reacts on Al_2O_3 or TiO_2 to produce elemental sulfur.

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