JOURNAL OF CATALYSIS **158,** 251–259 (1996)
ARTICLE NO. 0024

On the Synergism between La_2O_2S and CoS_2 in the Reduction of SO_2 to Elemental Sulfur by CO

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Received April 5, 1995; revised September 5, 1995; accepted September 6, 1995

In our study of the catalytic reduction of SO_2 to elemental sulfur by CO in the presence of La_2O_2S and CoS_2, a synergistic effect between the two sulfides was observed which not only increased the catalytic activity but also suppressed the formation of the side-product COS. It was also found that the crystal phase of CoS_2, which can be easily reduced by CO, could be retained when La_2O_2S coexisted even in small quantities. A mechanism was proposed based on the COS intermediate mechanism and the remote control concept. © 1996 Academic Press, Inc.

INTRODUCTION

The catalytic reduction of SO_2 in a combustion product gas stream by CO has received much attention because this dry desulfurization method conveniently uses one of the exhaust constituents as the reducing agent, yields a product of commercial value in the form of almost pure elemental sulfur, and generates no secondary pollution. Furthermore, the process is single-stage and is easier to design and operate. Several types of catalysts have been investigated for this reaction including iron-alumina (1), copper-alumina (2, 3), mixed oxides of cerium and transition metals (4–6), copper cobaltate (4), cerium oxide (5), and perovskite oxides (4, 7–12).

It is interesting to note that an apparent synergistic effect between the active components of the catalysts used for the SO_2–CO reaction often exists. Kahlafalla *et al.* (1) observed a synergism for the iron–alumina catalyst system and found no measurable reaction rates in the 400–600°C range with alumina or iron alone; but when a mixture of the two was used, a substantial amount of the sulfur dioxide was removed and mixtures containing 43% freshly reduced iron exhibited a sharp increase in the catalytic activity. Happel *et al.* (13) found lanthanum and titanium oxides to be inactive, however, the lanthanum oxide catalytic activity increased drastically when a small amount of titanium (3%) was added, and they identified the two active phases in this mixture after reaction to be La_2O_3 and $La_2O_3 \cdot TiO_2$. Baglio (14) reported that the reduction of SO_2 to elemental sulfur was minimal when either CoS_2 or La_2O_2S was used alone; however, a conversion of over 77% was obtained when a mixture of CoS_2 and La_2O_2S with a 2 : 1 molar ratio was used.

In a previous work (12), we studied the change in structure of the perovskite oxide $LaCoO_3$ and its derivatives formed by the partial substitution of the *A* and/or *B* ions. We found that the perovskite structure was no longer retained when used as catalyst in the reaction of SO_2 with CO and that a complicated mixture of sulfides was formed. We also found that La_2O_2S and CoS_2 always existed in catalysts with high activity and we proposed a mechanism based on the cooperative actions between the two active phases. Carbon monoxide first reacts with CoS_2 to form the intermediate COS, to be followed by the reduction reaction between COS and SO_2 to form elemental sulfur catalyzed by La_2O_2S. Some of the sulfur formed migrates from the surface of the oxysulfide to the CO-reduced CoS_2, thus maintaining the activity of the CoS_2 (also known as remote control (15)).

In this paper, experimental results will be presented to substantiate the existence of synergism between La_2O_2S and CoS_2 in the reduction of SO_2 by CO. The consequences of the synergism are increased activity, suppression of the formation of COS, and stabilization of the CoS_2 phase. These effects are very pronounced when only a small amount of La_2O_2S is added to CoS_2 and the results are consistent with the proposed mechanism.

EXPERIMENTAL

Lanthanum oxysulfide, La_2O_2S, with a specific surface area of 3.37 $m^2\ g^{-1}$ was prepared from lanthanum oxide according to the method of Fang *et al.* (16). Cobalt sulfide, CoS_2, was prepared using the method of Kuznetsov *et al.* (17): a stoichiometric mixture of metallic cobalt and sulfur powder was placed in a quartz ampoule and sealed under vacuum. The quartz ampoule was placed in a protective

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0021-9517/96 $12.00

metallic bomb and was slowly heated at less than 100°C h^{-1} to 650°C. After holding at this temperature for 2 h, the sample was cooled down to room temperature very slowly (less than 10°C h^{-1}). The sample had a specific surface area of 0.72 m^2 g^{-1}.

The oxysulfide and the sulfide were individually ground to pass through a 200-mesh sieve, and 0.5-g catalyst samples of different mole fractions $\{Fm = CoS_2/(La_2O_2S + CoS_2)\}$ were prepared. Thorough mixing was achieved by shaking and rotating the sample in a small glass vessel for 10 min by hand. The samples were resulfidized *in situ* in the reaction gas mixture at 600°C for 2 h before catalytic activity measurements. A summary of some of the properties of the catalysts is listed in Table 1.

The structure of the catalysts before and after the reaction was characterized using X-ray diffraction (Philips MPD-1880 I X-ray diffractometer, Cu$K\alpha$ radiation, $\lambda = 1.542$ Å). The surface area of La_2O_2S and CoS_2 was measured using BET method, and the surface area of the mixtures was calculated based on the weight ratio of the constituents; see Table 1.

The catalytic reaction was carried out in a fixed-bed flow reactor made from a 2-cm-diameter, 50-cm-long quartz tube heated externally using an electric furnace. The temperature of the catalyst bed was controlled to within 1°C. The feed gas, containing 0.5 mol% SO_2 and 1.0 mol% CO in UHP nitrogen, was fed into the reactor from the top at a constant flow rate of 180 ml/min measured at atmospheric pressure. The effluent of the reactor was split and sent to an on-line nondispersive infrared SO_2 analyzer (CFA-321A, Horiba) and a HP 5980 Series II gas chromatograph. The GC had two columns: molecular sieve and Porapak Q, and two TCD detectors, one for measuring CO and one for measuring the sulfur-containing compounds: SO_2, COS, H_2S, CO_2, and CS_2. Elemental sulfur was condensed from the product gas stream by an ice-bath trap and a filter with a pore size of 2 μm. Steady-state activity measurements were made using 0.5 g of catalyst with a space velocity of 21,600 ml g^{-1} h^{-1} except for the first experiment where 1 g of catalyst was used (SV = 10,800 ml g^{-1} h^{-1}).

TABLE 1

Some Physical Characteristics of Catalysts Used

Molar fraction (Fm)	Weight fraction (Fw)	Weight of CoS_2 (g)	Weight of La_2O_2S (g)	Specific surface area (m^2/g)
0.0	0.0000	0.0000	0.5000	3.37
0.1	0.0384	0.0192	0.4808	3.27
0.3	0.1336	0.0668	0.4332	3.02
0.5	0.2645	0.1323	0.3597	2.67
0.7	0.4563	0.2281	0.2719	2.16
0.9	0.7640	0.3820	0.1180	1.35
1.0	1.0000	0.5000	0.0000	0.72

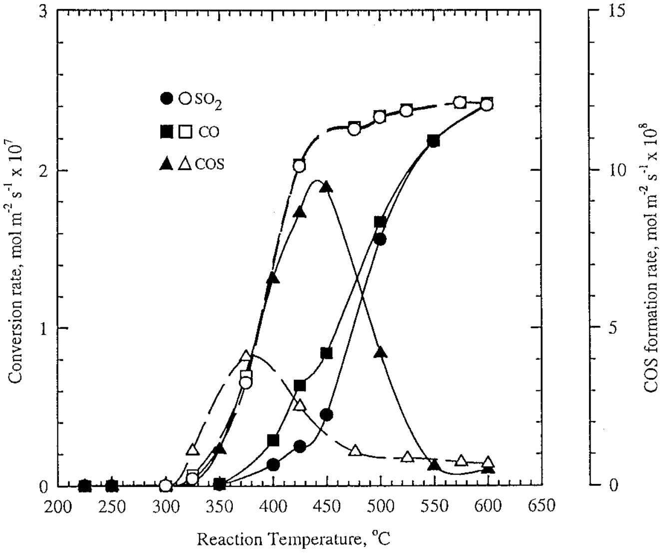

FIG. 1. SO_2 and CO conversion and COS formation rate over resulfidized La_2O_2S/CoS_2 (1:1 rolar ratio).

RESULTS AND DISCUSSION

The two compounds used in this study were La_2O_2S and CoS_2. For the sake of definition, we will use the term *catalyst* when these compounds were used as individual catalyst and *active component* when they were synergistic partners in a catalyst system. We also define the *catalytic activity* to be the SO_2 conversion rate at a given reaction temperature, and the *selectivity* to be the inverse proportion of the formation rate of the side-product COS at a given SO_2 conversion rate.

The Cooperative Working State of the Catalyst

In our first experiment, 1 g of a mechanical mixture of La_2O_2S and CoS_2, Fm = 0.5, was used to catalyze the reduction reaction. The experiment was carried out by first heating the catalyst in 50°C steps from room temperature to 600°C, then cooling in the same manner to a temperature when the reaction was cut off. In each step of the heating and the cooling process, the temperature was held constant until the SO_2 concentration in the effluent no longer changed for a period of at least 30 min. COS was the only by-product with a ratable concentration level. The results are presented in Fig. 1. The CO consumption rates as shown were divided by 2 according to the stoichiometry of the CO and SO_2 reaction.

From Fig. 1, it can be seen that the reaction system in the cooling path represented by the broken-line curves exhibits a higher catalytic activity and selectivity than that in the heating path represented by the solid-line curves; the difference between the two is due to the fact that the La_2O_2S and CoS_2 mixture in the cooling stage has already experienced a heating or resulfidization process, while in the heating path it started out as a fresh mechanical mixture. It is apparent that the mechanical mixture experienced changes in the heating stage; in other words, a synergistic state of the catalysts was established after the heating stage or resulfidization of the mechanical mixture at high temperature, and the active components began to work cooperatively as a catalyst system.

Our earlier work (12) on perovskite oxides showed that the COS intermediate mechanism could be used to describe this type of reaction system. The COS formed reacted with SO_2 to form elemental sulfur, thus playing a role in the rate of SO_2 conversion. The mechanism can be presented in equation form as

$$MS_x + CO = MS_{x-1} + COS \qquad [1]$$

$$2COS + SO_2 = 3/2\, S_2 + 2CO_2 \qquad [2]$$

$$MS_{x-1} + S = MS_x, \qquad [3]$$

where MS_x is a metal sulfide. These equations are useful in explaining some of the results obtained in this study.

The results presented in Fig. 1 indicate that in the heating stage:

(i) Below 450°C, the rate of COS formation increased with the reaction temperature before decreasing to a very low level. COS is produced in the reaction of CO with CoS_2 (Reaction [1]).

(ii) The consumption rate of CO was always higher than the conversion rate of SO_2 and the difference between the two rates increased at first and then decreased after reaching a maximum. The maximum COS formation rate occurred at about 450°C directly above the hump in the CO curve. The start in the decrease of the rate difference was due to the increase in the SO_2 conversion rate (signified by steeper slopes) thus indicating an acceleration in the reaction between COS and SO_2 (Reaction [2]). The hump in the CO consumption curve suggested that COS formation was promoted by the temperature increase at the beginning thus using up more CO, however, the COS formed could also be decomposed according to COS = CO + S, and this rate increased with temperature rapidly at temperatures higher than 450°C (14). The eventual resumption of the CO consumption rate at higher temperature was due to Reaction [2] which shifted Reaction [1] to the right.

In the cooling stage:

(i) There was no significant difference between the CO and SO_2 conversion rates, indicating that the sulfide was no longer reduced by CO.

(ii) The formation rate of the side-product COS was lower, and the maximum shifted towards the lower temperature side indicating an increase in the catalytic activity of Reaction [2].

In our earlier study on perovskite oxides for the reduction of SO_2 to elemental sulfur we found the active catalysts always contained a small amount of CoS_{2-x} (x = 0.903–1.25, e.g., $CoS_{1.097}$) in addition to the major phases La_2O_2S and CoS_2. The CoS_{2-x} phase is the product of the reduction of CoS_2 by CO and is able to accept the sulfur formed by the sequential reaction between the intermediate COS and SO_2 (Reaction [2]) catalyzed by La_2O_2S, so that the CoS_2 in the working catalyst was always maintained at an appropriate concentration thus completing the reaction cycle. Therefore, the CoS_{2-x} phase played the role of the sulfur carrier and was a vital component in the reduction of SO_2 by CO. Since the mechanical mixture of La_2O_2S and CoS_2 in its initial state did not contain any CoS_{2-x}, it could be deduced that there was no link between the La_2O_2S and the CoS_2 phases; however, as the reaction temperature increased, the reaction of CO with CoS_2 intensified as indicated by a higher CO consumption rate and a higher COS formation rate, inducing the formation of the CO-reduced cobalt sulfides CoS_{2-x}, and the mechanical mixture as a whole was resulfidized.

At temperatures above 450°C, the existence of the CoS_{2-x} phase and the increase in reaction temperature promoted the reaction between COS and SO_2, thus increasing the SO_2 conversion rate and reducing the formation rate of COS as shown in Fig. 1. Since the reaction between COS and SO_2 produced elemental sulfur, an equilibrium between CoS_{2-x} and CoS_2 was established. The resulfidization process apparently cooperatively linked the separate phases of the catalyst system and as a result there was an increase in catalytic activity and selectivity in the cooling phase of the experiment. Indeed, XRD analysis of the catalyst after reaction revealed the existence of the CoS_{2-x} phase, and the diffraction pattern of the resulfidized mechanical mixture was very similar to that of the sulfidized $LaCoO_3$ (see Fig. 2); the latter has been shown to be an active catalyst for the reduction of SO_2 by CO.

It is recognized, therefore, that a mechanical mixture of La_2O_2S and CoS_2 must be resulfidized before a synergistic effect can take place; this suggests that the coexistence of the three phases is a necessary condition for the reduction reaction to be effective, and from the discussion given above, there is evidence that the reduction of SO_2 by CO follows the COS intermediate mechanism.

Influence of Synergistic Effect on SO_2 Conversion

The samples listed in Table 1, representing a full range of catalyst compositions, were resulfidized at 600°C for 2 h before catalytic activities were measured at different

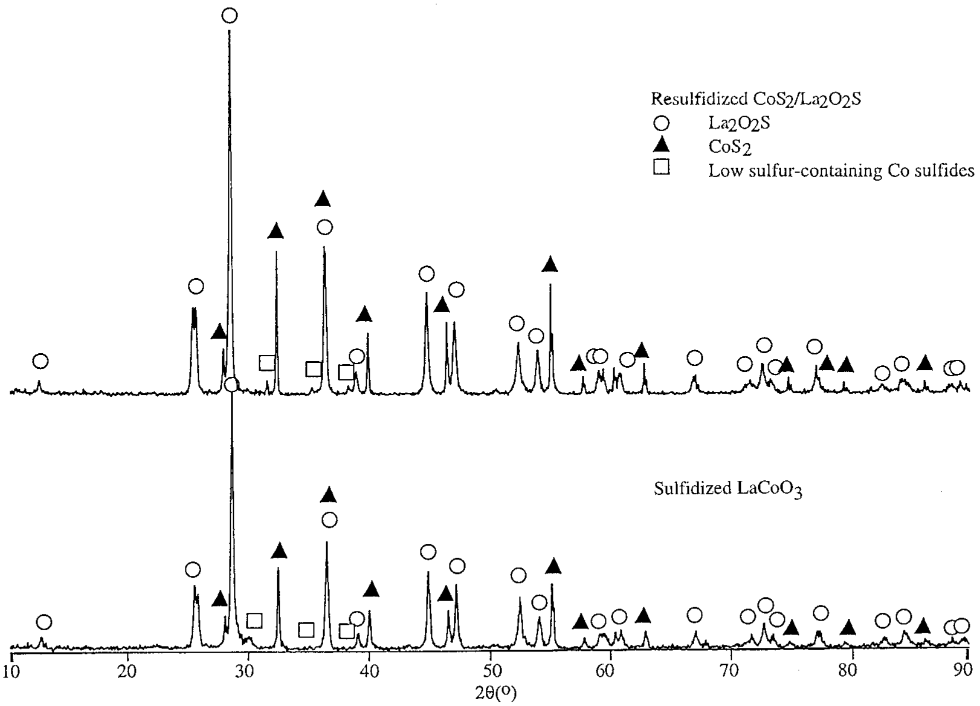

FIG. 2. Powder diffraction patterns of resulfidized La_2O_2S/CoS_2 (Fm = 0.5) and sulfidized $LaCoO_3$.

temperatures for the determination of the synergistic effect. The results are plotted in Figs. 3a and 3b. The solid lines are the activities of catalysts containing both active components. The broken lines, called the base-line activities, are the activities calculated by taking the arithmetic sums of the experimentally determined activities when either one of the two active components is substituted with quartz powder of the same sieve size. The quartz powder has been previously proven to be catalytically inactive for this system. For example, for a Fm = 0.5 catalyst (con-

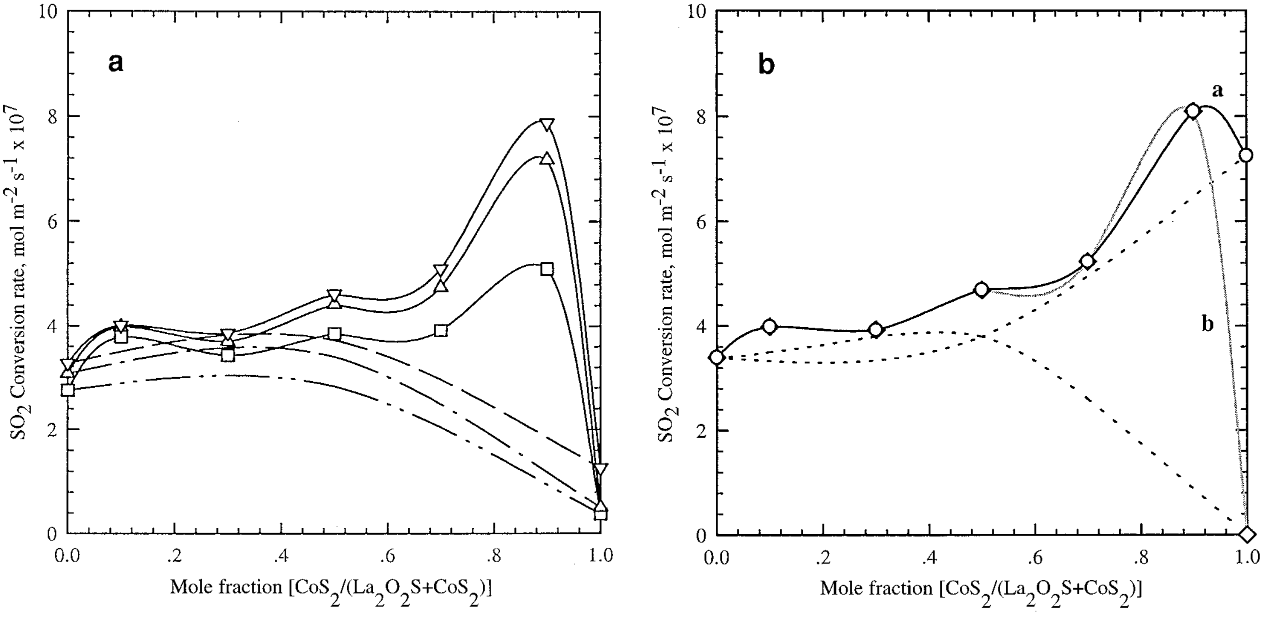

FIG. 3. Effect of catalyst composition on SO_2 conversion rate. (a) 450°C: (□) phase cooperation, (–··–) without phase cooperation; 500°C: (△) phase cooperation, (–·–) without phase cooperation; 550°C: (▽) phase cooperation, (——) without phase cooperation; (b) 600°C: (○, ◇) phase cooperation, (----) without phase cooperation.

taining 0.1323 g of CoS_2 and 0.3597 g of La_2O_2S) the baseline activity was obtained by summing the individual activities measured from samples containing 0.1323 g CoS_2 and 0.3597 g quartz powder, and 0.3597 g La_2O_2S and 0.1323 g quartz powder. The existence of synergistic effects is signified when the solid lines are higher than the broken lines.

It is evident from Fig. 3a that the solid-line curves are always above the broken-line curves for a given temperature; i.e., there is an increase in the SO_2 conversion rate due to the cooperation of the two distinct active phases which in turn suggests the existence of synergism. Figure 3a also shows that the activity of catalysts consisting of the two active components is always higher than the single component catalysts. This is particularly pronounced for the almost inactive CoS_2. However, adding a small amount of CoS_2 to La_2O_2S (Fm = 0.1, i.e., 4 wt% of CoS_2) increased the SO_2 conversion rate while adding a small amount of La_2O_2S (Fm = 0.9, i.e., 23.6 wt% of La_2O_2S) to the otherwise inactive CoS_2 improved the catalytic activity even more significantly. This strong cooperative effect is due to the fact that even though CoS_2 readily reacts with CO to form COS it is inactive in the further reaction of COS with SO_2, whereas La_2O_2S fills this void because it is active, thus completing the overall desulfurization reaction. This phenomenon also provides evidence of the existence of the COS intermediate mechanism in the present system.

At 600°C, CoS_2 exhibited a marked increase in SO_2 conversion rate, even higher than that of La_2O_2S. Moreover, the synergistic effect was apparently weaker. This can be seen from curve (a) in Fig. 3b.

The increase in reaction temperature from 550 to 600°C caused a 32% increase in SO_2 conversion (from 6 to 38%) for CoS_2, while for La_2O_2S it was only 4% (from 82 to 86%). This is because the surface area of CoS_2 is only one-fifth of that of La_2O_2S thus the specific activity of CoS_2 is proportionally higher. However, this specific activity cannot be maintained and the SO_2 conversion gradually decreased to zero after 10 h of reaction. The deactivation of the pure CoS_2 phase is due to the depletion of the active lattice sulfur and more discussion will follow. The same was not observed for the La_2O_2S-containing catalysts. Despite the deactivation of the pure CoS_2 phase the synergistic effect at 600°C was still prominent (see curve (b) in Fig. 3b).

In our study, we found that La_2O_2S by itself was catalytically active in the reduction of SO_2 by CO which contradicted the work by Bagilio (14) where they found that La_2O_2S was active only for the reaction between COS and SO_2. We shall report these findings elsewhere in a different paper.

Influence of Synergistic Effect on COS Formation

When an intermediate of a sequential reaction exists as a stable product, the overall reaction rate and the selectivity are strongly dependent on the ratio of the formation and consumption rates of the intermediate. To obtain high conversion of SO_2 and low production of COS, a proper ratio of the extent of the CO–CoS_2 and the COS–SO_2 reactions must exist. If the reduction of SO_2 by CO follows an intermediate mechanism, represented by Reactions [1] to [3], then a synergistic effect on the COS formation rate is expected. The results shown in Fig. 4 demonstrate this point.

The solid-line curves are the COS formation rate of the two-component systems while the broken lines are for single catalysts. The following observations can be made by examining the results shown in Fig. 4:

(i) The formation of the intermediate COS was very much dependent on temperature, and the formation curves could be distinctly divided into two groups: one made of La_2O_2S containing catalysts, be it one- or two-component, the other was CoS_2. There was also a pronounced temperature gap, almost 150°C, where the maximum COS formation rate occurred for the two groups: 550°C for CoS_2, and around 400°C for the La_2O_2S containing group. This means that the maximum COS formation temperature can be decreased drastically when La_2O_2S is added to CoS_2 even in small quantities.

The existence of the temperature gap can be explained by studying the following reaction system:

$$\mathrm{CO} + \mathrm{CoS_2} \xrightarrow{[4]} \mathrm{CoS_{2-x}} + \mathrm{COS} \begin{array}{l} \xrightarrow{[5a]} \mathrm{CO} + \mathrm{S} \\ \xrightarrow[\mathrm{La_2O_2S}]{+\mathrm{SO_2}\ [5b]} \mathrm{CO_2} + \mathrm{S_2}. \end{array}$$

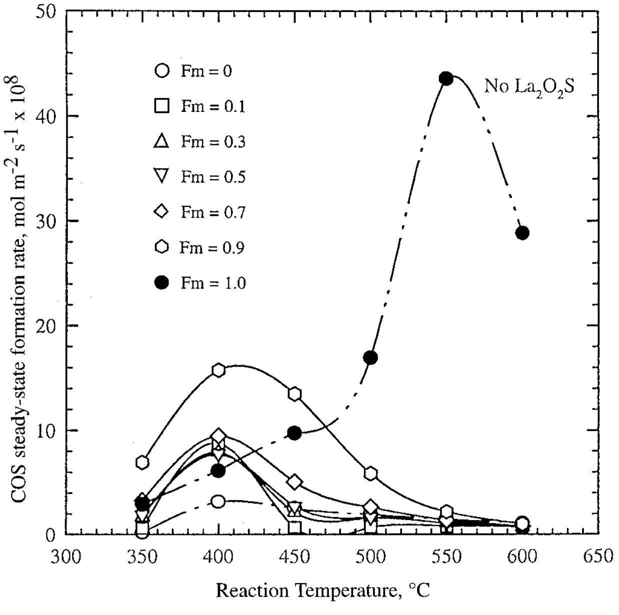

FIG. 4. Temperature dependence of COS formation rate.

When CoS_2 is used as a single catalyst, Reaction [5b] will not take place. The net formation of COS is thus determined by Reactions [4] and [5a] and the maximum COS formation is at 550°C.

For the La_2O_2S containing catalysts, Reaction [5b] is catalyzed by La_2O_2S. All three reactions affect the net COS formation. Actually, Reaction [5a] can be ignored because it is not catalytic. Thus the rate is slow when compared to Reaction [5b], and furthermore, it is inhibited by the formation of elemental sulfur via Reaction [5b]. On the other hand, it has been proven that Reaction [5b] can be initiated at a temperature ranging from 350 to 450°C at a gas space velocity of 6,000 to 90,000 h^{-1} (14), and our experiments were conducted in this range of gas space velocities. In the presence of La_2O_2S and when the temperature is right, the COS can react with SO_2 as soon as it is formed by Reaction [4]. Consequently, the maximum formation of COS shifts to the low temperature side.

(ii) Below 420°C, more COS was formed by catalysts containing both La_2O_2S and CoS_2 than the one-component catalyst and the reasons are as follows:

- La_2O_2S is more stable than CoS_2 in the interaction with CO implying that less COS will be formed on La_2O_2S than on CoS_2.
- the CoS_2 as shown in Fig. 4 was a stand-alone catalyst and it was reduced by CO in a high temperature resulfidization step, therefore further interaction between CO and the low-sulfur-containing sulfide became poor. Evidence shall be provided in the following discussion.
- In the two-component catalysts, an equilibrium was established between CoS_2 and $CoS_{1.097}$ as discussed previously, and labile sulfur from CoS_2 was made available for reaction with CO.

(iii) The COS formation rate decreased rapidly around 450°C for the two-component catalysts showing signs of the oxidation of COS by SO_2 and the corresponding change in SO_2 conversion rate substantiated this. The peak widths narrowed gradually when the Fm value decreased and the catalyst at Fm = 0.1 showed the most pronounced change. It is apparent that with a smaller Fm value there is more La_2O_2S in the catalyst system and more active sites are available on the catalyst surface for Reaction [5b]. However, this is not evident when the two catalysts are used as individual catalysts thus providing another proof of the synergistic effect.

The synergistic effect can also be observed by studying the formation of COS using a similar treatment as presented in the section concerning the SO_2 conversion and the results are shown in Fig. 5. The solid lines represent the COS formation rates catalyzed by catalysts containing both active components, while the broken lines (base-lines) represent the formation rates without phase cooperation.

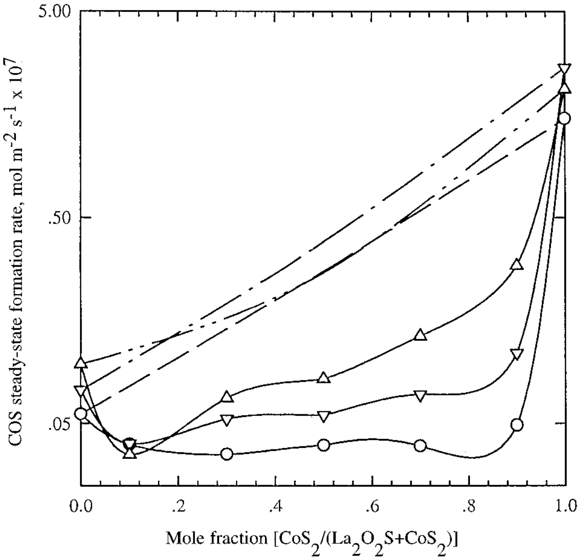

FIG. 5. Influence of the cooperation between La_2O_2S and CoS_2 on COS formation. 600°C: (○) phase cooperation, (——) without phase cooperation; 550°C: (▽) phase cooperation, (–·–) without phase cooperation; 500°C: (△) phase cooperation, (–··–) without phase cooperation.

As before, the difference between a corresponding set of base and solid lines for a given temperature at a given Fm value can be considered as an indicator of the existence of synergistic effects. It can be seen that by adding either one of the two active components to the other significantly suppresses the formation of COS and the effect is most drastic when a small amount of La_2O_2S is added to CoS_2.

The fact that the synergistic effect is always stronger on the right side of the *x*-axis in the figures (adding small amounts of La_2O_2S to CoS_2) than the left side (adding small amounts of CoS_2 to La_2O_2S), may be due to the following reasons: (1) CoS_2 is only active for the formation of COS and a second active phase is needed to complete the reaction cycle; (2) La_2O_2S by itself is an active catalyst for the overall reaction; and (3) the existence of small amounts of either of the two compounds in another may result in a large difference in the surface area contribution. For example, in a Fm = 0.1 sample about 15% of the total surface area is due to the CoS_2 phase while the contribution of La_2O_2S phase in a Fm = 0.9 sample is about 30%.

Structure Characterization

All catalyst samples after reaction were characterized using XRD; the diffractograms are shown in Fig. 6. For reference, X-ray diffractograms of fresh La_2O_2S and CoS_2 prepared according to the methods described previously are also presented. Based on this information it is possible in principle to compose X-ray diffractograms for any fresh catalyst containing these two components.

Figure 6 shows that the Fm = 1.0 catalyst (containing

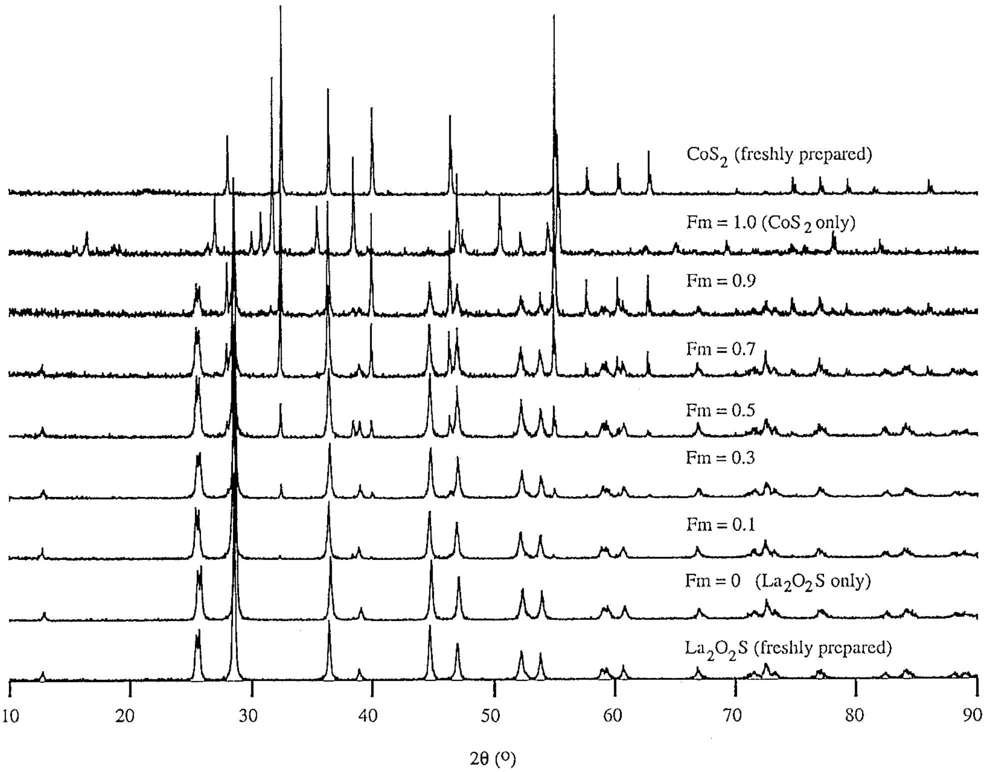

FIG. 6. X-ray diffractograms of the catalysts before and after reaction.

no La_2O_2S) was completely reduced and formed a mixture of low-sulfur-containing sulfides such as $CoS_{1.097}$, $CoS_{1.035}$, Co_3S_4, and Co_4S_3 after reaction. For Fm = 0.9, 0.7 and 0.5, containing 23.6, 54.4, and 73.6 wt% of La_2O_2S, respectively, only a small portion of the CoS_2 was changed to the low-sulfur-containing sulfides. Catalysts with Fm = 0.3 and 0.1, containing 86.6 and 96.2 wt% of La_2O_2S, respectively, showed patterns which could be composed from the individual fresh components, because the concentration of the low-sulfur-containing sulfides was too low to be detected by XRD analysis. These results provide evidence of the existence of low-sulfur-containing sulfides in the two-component catalysts. Moreover, the existence of the La_2O_2S phase apparently inhibited the complete reduction of CoS_2 to low-sulfur-containing sulfides.

Reaction Mechanism

There are two mechanisms suggested in the literature for the catalytic reduction of SO_2 to elemental sulfur by CO. The first one is the redox mechanism (5, 10, 13)

$$\text{Cat-O} + \text{CO} = \text{Cat-}\square + \text{CO}_2 \qquad [6]$$

$$\text{Cat-}\square + \text{SO}_2 = \text{Cat-O} + \text{SO} \qquad [7]$$

$$\text{Cat-}\square + \text{SO} = \text{Cat-O} + \text{S}, \qquad [8]$$

where Cat-□ presents a reduced catalyst surface. It seems that only a single catalyst phase is involved in the redox mechanism and that oxygen vacancies are the active sites; furthermore, the mechanism does not involve the formation of COS.

The second mechanism is the COS intermediate mechanism (14, 18) represented by Reactions [1] to [3] in an earlier section. In the COS intermediate mechanism the reducing agent CO reacts first with the sulfur in the sulfides, preferably the unstable sulfides (19), to form the intermediate COS, which is then oxidized by SO_2 on the other active phase. A part of the sulfur formed reacts with the CO-reduced low-sulfur-containing sulfides and the high-sulfur-containing sulfide is recovered; the rest of the sulfur leaves with the exhaust as a product.

Reaction [1] has been demonstrated using iron (18) and cobalt disulfide (14). These are relatively unstable sulfides and therefore can be more easily reduced by CO.

It has also been shown that the Reaction [2] can be catalyzed by alumina (18) or La_2O_2S (14). It was suggested (20) that in the case of alumina the carbonyl sulfide will chemisorb cationically on the alumina Lewis acid sites and the sulfur dioxide will chemisorb anionically on the Brønsted sites, allowing the adsorbed species to react according to a Langmuir–Hinshelwood mechanism.

In our experiment, high COS formation and low SO_2

conversion rates were observed when the catalyst contained only CoS_2, this is because CoS_2 is active in Reaction [1] but inactive in Reaction [2]. However, as expected, SO_2 conversion rate increased drastically when a small portion of La_2O_2S was added to CoS_2. Our results provide evidence of the existence of Reactions [1] and [2].

Furthermore, the following observations may provide the evidence needed for the existence of Reaction [3]:

(i) The activity of CoS_2 decreased to zero after about 10 h of reaction, and the CoS_2 phase was found to be completely reduced to a mixture of $CoS_{1.097}$, $CoS_{1.035}$, Co_3S_4, and Co_4S_3.

(ii) The CoS_2 phase was maintained when La_2O_2S was added because Reaction [2] took place to provide the sulfur needed for Reaction [3].

(iii) A small amount of the CoS_{2-x} phase, the intermediate of Reactions [2] and [3], was always found in catalysts containing La_2O_2S and CoS_2 after reaction.

Thus, the apparent role of Reaction [3] in the overall reaction is to keep an equilibrium of the CoS_2 phase with the rest of the system, so that the activity of the catalyst system can be maintained. In order to explain the strong cooperative effects between the distinct phases in this system, a remote control mechanism proposed by Delmon and Matralis (21) is used. The theory says that "a donor phase *D* emits a surface mobile (spillover) species. This spillover species reacts with the surface of the acceptor phase *A*, distinct from *D*, and creates active and selective catalytic sites on *A*." Our experimental findings prompted us to think that it is reasonable to apply this concept to the COS intermediate mechanism. Although the spillover of sulfur has not been studied to the extent of hydrogen and oxygen, the possibility of sulfur spillover in HDS catalysis has been suggested (22). The reaction mechanism presented in Fig. 7 is proposed based on our earlier results using perovskite oxides as catalysts, and is substantiated by the present work on the individual active components.

Our expeirmental results indicate that not only CoS_2 but also La_2O_2S can react with CO to form COS; the difference is that the formation rate for La_2O_2S is lower. It is now apparent that a synergistic effect is present in both systems, FeS_2–Al_2O_3 and CoS_2–La_2O_2S; there are, however, differences.

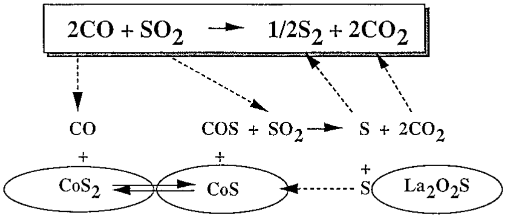

FIG. 7. Remote control mechanism [12].

Haas and Khalafalla (18) concluded that Al_2O_3 does not sulfidize readily except when a metal is present to form the metal sulfide needed for the reaction with CO to form COS. In contrast, our work indicates that La_2O_2S by itself possesses the dual functions of forming COS and of catalyzing the oxidation of the COS formed with SO_2, so that we were able to significantly promote the reduction of SO_2 to elemental sulfur using La_2O_2S alone. Nevertheless, when CoS_2 was added to La_2O_2S, the overall reaction rate was accelerated because of the higher rate of COS formation on CoS_2.

CONCLUSIONS

There exists a synergism between La_2O_2S and CoS_2 for the reduction of SO_2 by CO to elemental sulfur. Since the synergism is the consequence of the cooperation between the individual active components based on the COS intermediate mechanism, it follows that not only the SO_2 conversion but also the amount of COS formed (i.e., the selectivity) will be influenced. Our experimental results show that the activity as well as the selectivity can be increased when the catalyst is a mixture of La_2O_2S and CoS_2.

The activity of a mixture of La_2O_2S and CoS_2 can be increased when a small portion of the CoS_2 is reduced to a low-sulfur containing sulfide, e.g., $CoS_{1.097}$. The low-sulfur-containing sulfide plays the role of a sulfur acceptor to control the amount of active sulfur sites in the CoS_2 phase and thus keeps the formation of the intermediate COS going.

The addition of La_2O_2S, even in small amounts, can inhibit a complete reduction of CoS_2 to low-level sulfides.

The formation rate of the side-product COS for a two-component system is lower than the stand-alone catalysts at temperatures higher than 500°C.

Based on the results obtained from an earlier investigation on perovskite oxide catalysts, we proposed a COS intermediate mechanism modified using the remote control concept. The present work on composite sulfide catalysts and the study of the intermediate product COS provides further evidence that this mechanism is valid.

Contrary to the work by others, the La_2O_2S samples prepared in this work are active in the reduction of SO_2 by CO.

ACKNOWLEDGMENTS

The authors appreciate the invaluable technical support provided by K. L. To and H. S. Tsui of the Research Centre, HKUST. The Materials Preparation and Characterisation Centre has been more than generous in performing XRD and surface analysis on our behalf, and we are indebted to its staff. This project was financially supported in part by HKUST Grant Phase0.RC02.

REFERENCES

1. Khalafalla, S. E., Foester, E. F., and Haas, L. A., *Ind. Eng. Chem. Prod. Res. Dev.* **10,** 133 (1971).
2. Querido, R., and Short, W. L., *Ind. Eng. Chem. Prod. Res. Dev.* **12,** 10 (1973).
3. Hibbert, D. B., and Tseung, A. C. C., *J. Chem. Soc. Faraday Trans. 1* **74,** 1981 (1978).
4. Bazes, J. G. I., Caretto, L. S., and Nobe, K., *Ind. Eng. Chem. Prod. Res. Dev.* **14,** 264 (1975).
5. Liu, W., and Flytzani-Stephanopoulos, M., *in* "Environmental Catalysis" (J. N. Armor, Ed.), Am. Chem. Soc., Symp. Ser., Vol. 552, p. 375. Am. Chem. Soc., Washington, DC, 1994.
6. Liu, W., Sarofim, A. F., and Flytzani-Stephanopoulos, M., *Appl. Catal. B* **4,** 167 (1994).
7. Happel, J., Hnatow, M. A., Bajars, L., and Kundrath, M., *Ind. Eng. Chem. Prod. Res. Dev.* **14,** 154 (1975).
8. Hibbert, D. B., and Tseung, A. C. C., *J. Chem. Tech. Biotech.* **29,** 713 (1979).
9. Hibbert, D. B., and Champbell, R. H., *Appl. Catal.* **41,** 273 (1988).
10. Hibbert, D. B., and Champbell, R. H., *Appl. Catal.* **41,** 289 (1988).
11. Palilla, F. C., U.S. Patent 3 931 393, 1976.
12. Ma, J., Fang, M., and Lau, N. T., *in* "First World Conference—Environmental Catalysis, Pisa, Italy, May 1–5, 1995."
13. Happel, J., Leon, A. L., Hnatow, M. A., and Bajars, L., *Ind. Eng. Chem. Prod. Res. Dev.* **16,** 150 (1977).
14. Baglio, J. A., *Ind. Eng. Chem. Prod. Res. Dev.* **21,** 38 (1982).
15. Karroua, M., Matralis, H., Grange, P., and Delmon, B., *J. Catal.* **139,** 371 (1993).
16. Fang, M., Ma, J., and Lau, N. T., U.S. patent pending.
17. Kuznetsov, V. G., Sokolova, M. A., Palkina, K. K., and Popova, Z. V., *Inorg. Mater.* (*USSR*) **1,** 617 (1965).
18. Haas, L. A., and Khalafalla, S. E., *J. Catal.* **29,** 264 (1973).
19. Haas, L. A., and Khalafalla, S. E., *J. Catal.* **30,** 451 (1973).
20. Khalafalla, S. E., and Haas, L. A., *J. Catal.* **24,** 121 (1972).
21. Delmon, B., and Matralis, H., *in* "New Aspects of Spillover Effect in Catalysis" (T. Inui *et al.,* Eds.), p. 25. Elsevier, Amsterdam, 1993.
22. Kabe, T., Ishihara, A., Qian, W., Ogawa, S., and Sakuno, H., *in* "New Aspects of Spillover Effect in Catalysis" (T. Inui *et al.,* Eds.), p. 341. Elsevier, Amsterdam, 1993.