Activation of La_2O_3 for the Catalytic Reduction of SO_2 by CO

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Lanthanum oxide by itself has been reported to be inactive for the reduction of SO_2 by CO; however, we discovered that La_2O_3 can be activated in a reaction gas atmosphere if previously hydrated. The active phase of the activated lanthanum oxide was identified to be lanthanum oxysulfide by using X-ray diffraction. This showed that the activation was in essence a sulfidization of the oxide. An activation mechanism is proposed based on the surface acidic and basic properties resulting from the dehydroxylation of the lanthanum hydroxide. © 1996 Academic Press, Inc.

INTRODUCTION

Sulfur dioxide discharged into the atmosphere as a product of combustion processes, such as coal-fired power plants, is one of the major components of acid rain and other forms of atmospheric pollution. Numerous flue gas desulfurization (FGD) processes have been commercialized (1), and most of them are wet scrubbing processes. Dry flue gas SO_2 reduction methods are highly desirable, especially if the sulfur can be recovered in a salable form. The catalytic reduction of SO_2 by CO has received much attention because it offers a dry desulfurization method using a flue gas constituent as the reducing agent, while producing elemental sulfur.

Among many of the catalysts investigated for the reaction between SO_2 and CO, lanthanum oxide has been considered to be inactive by researchers. Palilla (2) observed that the activity of La_2O_3 was much lower than that of the $LaCoO_3$ perovskite oxide; Happel *et al.* (3) reported that pure lanthanum oxide is inactive; and Bajars (4) used a La_2O_3 catalyst pretreated in a mixture of 75 vol% CO and 25 vol% N_2 at 600°C and obtained not only a low conversion of SO_2 but also a substantial formation of COS. Despite these reports, it is not difficult to notice that in many of these studies lanthanum is a vital component of some of the active catalysts developed (2–10). On the other hand,

summarizing what has been learned from the work on the catalytic oxidative coupling of methane using lanthanum catalysts (11), it becomes apparent that the difference in the catalytic performance reported by the various research groups may be due to the extreme sensitivity of lanthanum oxide to water vapor and CO_2. Indeed, the freshly high-temperature-calcined hexagonal *A*-form La_2O_3 can suffer bulk hydration and carbonation in less than 24 h of exposure to the atmosphere (12). Furthermore, it has been found that the lanthanum in the perovskite-type oxides is sulfidized into sulfides, oxysulfide, and/or oxysulfate after reaction (8, 9, 13); thus, it is the general belief that lanthanum in the oxide form cannot be responsible for the catalytic activity. In the literature, there is little detailed description on the preparation of the La_2O_3, and even more scarce is the discussion on whether lanthanum oxide and/or its sulfidized derivatives are good catalysts for the SO_2 reduction reaction. Therefore, we decided to evaluate the performance of lanthanum oxide in the catalytic reduction of SO_2 by CO.

In the present paper, the findings of our study of the activation of hydrated La_2O_3, prepared from different starting materials and/or pretreatment conditions, for the reduction of SO_2 by CO are reported. Catalyst samples before and after the reaction were characterized by X-ray powder diffraction (XRD) to relate the phase composition to the activation behavior and catalytic performance, and a mechanism is proposed to describe the role of hydration in the activation process.

EXPERIMENTAL

In our earlier investigation of the catalytic reduction of SO_2 by CO using perovskite type oxides as catalyst, we found that the oxides can be activated in the reaction gas stream due to a sulfidization process (9). We also learned that the lanthanum, coordinated by 12 oxygen ions in a perovskite oxide, can be sulfidized into sulfide, oxysulfide, and/or oxysulfate, depending on the particular chemical environment. The same activation method was used in this work.

A fixed-bed flow reactor (a 2-cm diameter by 50-cm-long quartz tube) was used in this study. The reactor was heated

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Sample no.	Supplier	Assay (%)	Surface area ($m^2\,g^{-1}$)	Particle size (mesh)
1	Yiaolong Non-Ferrous Metals Co. Ltd.	99.99	5.4	120–400
2	Fluka Chemika	97.0	6.1	120–200
3	BDH Lab. Supplies	99.5	5.2	120–200
4	Merck	99.995	4.7	120–200
5	Sigma Chemical Co.	99.5	5.6	120–200

externally in an electrical furnace and the temperature of the catalyst bed was controlled to within $1°C$. The feed gas entered from the top of the reactor at a constant flow rate and passed through the catalyst bed into a section where the reaction products were treated and measured. The reactor was operated at atmospheric pressure.

Sulfur dioxide concentration in the feed and effluent was measured using an on-line nondispersive infrared analyzer (CFA-321A, Horiba). A second on-line infrared gas analyzer (VIA-510, Horiba) was used to determine the carbon dioxide concentration in effluent. A HP 5980 Series II Gas Chromatograph with two columns (one molecular sieve and one Porapak Q) and two TCD detectors was used to analyze CO, CO_2, and the sulfur-containing compounds such as SO_2, COS, H_2S, and CS_2. The effluent stream composition was measured after the elemental sulfur has been condensed by passing the effluent through an ice-bath trap and a filter with a pore size of $2\ \mu m$.

For safety reasons and better control, the feed gas consisting of 0.5 vol% SO_2, 1.0 vol% CO, and balanced with UHP nitrogen was prepared in a gas blender. The feed flow rate was held at $180\ ml\ min^{-1}$ measured at atmospheric pressure for all activation experiments performed.

Five lanthanum oxide samples purchased from different sources were used in the activation study. The specific surface area and the particle size of the samples are summarized in Table 1. All experiments were conducted using 0.5 g of the lanthanum oxides without any pretreatment.

In addition to the above as-received samples, catalyst precursors prepared by different pretreatment methods were also investigated. The preparation of the precursors are described in the following paragraphs.

The phase pure La_2O_3 was prepared by first calcining the oxide powder purchased from Yiaolong at $900°C$ for 12 h. It was then quickly transferred to the reactor and calcined *in situ* at $600°C$ under a dry air stream for half an hour before performing the activation experiments.

The hydration and carbonation of lanthanum oxide were carried out by exposing the calcined La_2O_3, as described above, in a sealed vessel containing water vapor or with CO_2 produced from dry ice for 1 week. Alternatively, sim-

ilar results can be obtained by simply exposing the La_2O_3 powder to ambient air for one week.

LaOOH was prepared by the *in situ* decomposing of the hydrated product $La(OH)_3$ at $400°C$ under vacuum for 4 h.

The BET surface area of the lanthanum compounds before and after activation was determined using Micromeritics ASAP2010, and the bulk structure was characterized using X-ray powder diffraction (Philips MPD-1880 I X-ray diffractometer, Cu$K\alpha$ radiation, $\lambda = 1.542$ Å).

RESULTS

Activation of Pure and Pretreated La_2O_3

La_2O_3. A freshly prepared La_2O_3 sample was heated in the reactor to $600°C$ in air purified by activated carbon and molecular sieve 5A for 30 min before the reaction gas mixture was introduced. In our reaction system, SO_2 is a reactant, while CO_2 is a product; therefore, by following the concentration change of these two compounds in the reactor, we can interpret what is happening inside the reactor. Curve a in Figs. 1a and 1b shows the concentration changes of SO_2 and CO_2 in the reactor. The SO_2 concentration decreased at the beginning of the reaction and returned almost to the feed concentration after about 5 min, while the CO_2 curve showed a small peak before decreasing to zero. If the CO_2 formed was due to the reaction of SO_2 and CO, then the molar ratio between the consumption and formation rates would be 1 : 2. By integrating the peak areas under the corresponding curves, the amount of SO_2 consumed and CO_2 formed were estimated to be 0.049 and 0.019 mmol, respectively, indicating there must exist another pathway for the disappearance of SO_2, or the formation of CO_2 was not due to the above mentioned reaction alone. Furthermore, the small CO_2 peak and the deep SO_2 valley have also been observed when the feed contained no SO_2 or CO, thus the CO_2 could be formed by the reaction of CO with the active oxygen species adsorbed on the surface. We can in turn say that the consumption of SO_2 was due to the adsorption on La_2O_3.

After 6 h of treatment, only a minimal change in the SO_2 and CO_2 concentrations was observed showing that the A-La_2O_3 could not be easily activated. This result is consistent with the reports in the literature.

$La(OH)_3$. A calcined La_2O_3 powder sample was exposed to an atmosphere saturated with water vapor for 1 week. XRD analysis revealed that the La_2O_3 was transformed to $La(OH)_3$. The hydrated lanthanum oxide was activated in the same manner described earlier, and the results are shown as curve b in Figs. 1a and 1b.

It is very interesting to see that there was a second sharp decrease in the SO_2 concentration after about 6 min, while the CO_2 concentration increased synchronously; after 1 h we observed the deposition of elemental sulfur in the cold
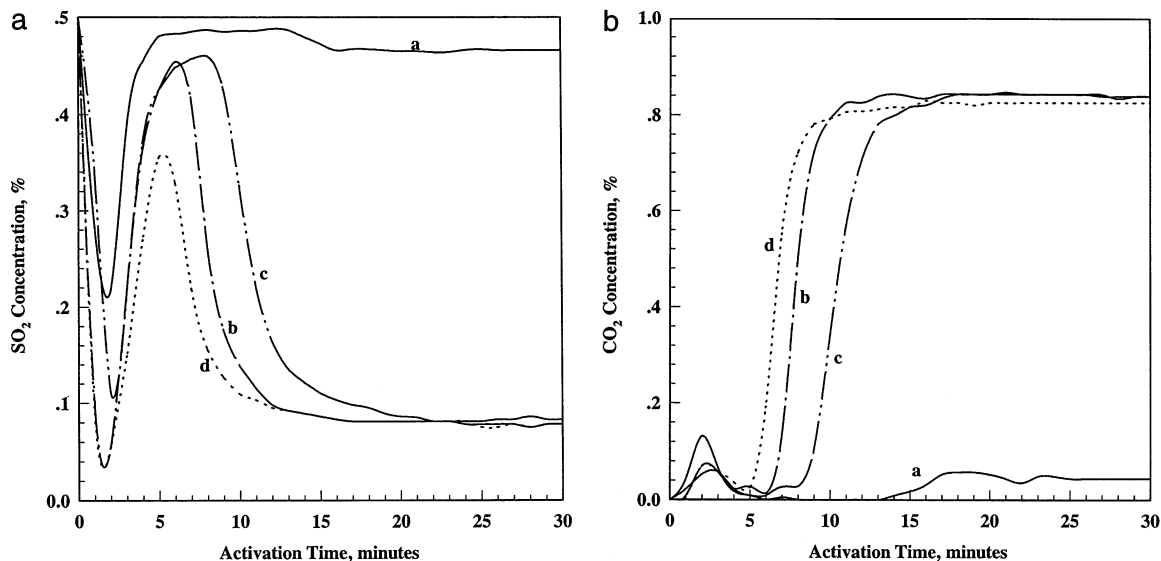
FIG. 1. Change in (a) SO_2 and (b) CO_2 concentration during activation. Curve a: A-La_2O_3; Curve b: $La(OH)_3$; Curve c: La_2O_3 exposed to dry ice vapor; Curve d: La_2O_3 exposed to air.

trap. This clearly shows that sulfur dioxide was catalytically reduced to sulfur and the water-vapor-pretreated lanthanum oxide could be and was activated. Furthermore, the decrease in the SO_2 concentration at the beginning was much greater than that for the unexposed A-La_2O_3, indicating that the adsorption of SO_2 on the oxide was significantly promoted by the hydration process.

La_2O_3 exposed to dry ice vapor.   A calcined La_2O_3 powder sample was exposed to CO_2 produced from dry ice in a closed vessel for one week and it was found that this sample could also be easily activated. See curve c in Figs. 1a and 1b. This sample behaved virtually the same as $La(OH)_3$, differing only in that the second sharp decrease in SO_2 occurred some 5 min later and the adsorption of SO_2 was weaker (0.073 mmol).

Indeed, XRD analysis revealed that after such a treatment, the sample was almost all $La(OH)_3$ with only a small quantity of La_2OCO_3. The formation of $La(OH)_3$ was probably due to the moisture in the atmosphere condensed by the dry ice. This implies that the hydration of lanthanum oxide is much easier than carbonation and is consistent with the observation made by Bernal *et al.* (12). They observed the lanthanum hydroxide in three different air-stabilized lanthanum samples was only partially transformed to the hydroxycarbonate phase, and there was no further progress of the carbonation reaction after exposing the samples to atmospheric CO_2 for more than 3 years.

La_2O_3 exposed to air.   A sample of the calcined La_2O_3 powder was exposed to air at room conditions (relative humidity, 85–95%) for one week and the activation curve of the air-exposed sample is presented in Figs. 1a and 1b

(curve d) for comparison to the other samples. As can be seen, the pretreatment of lanthanum oxide in air is also very effective in achieving activation. The adsorption of SO_2 of this catalyst was the same as the sample treated with water vapor. It was found that the major phase after the exposure was also $La(OH)_3$.

Comparison of untreated La_2O_3 samples purchased from different sources.   The activities of six as-received lanthanum oxide samples from different sources after activation are summarized in Table 2. The activity is defined as the average specific SO_2 conversion rate at 600°C at the termination of activation; i.e., the SO_2 concentration in the effluent does not change any more. The samples from Yiaolong and Fluka were found to be more active than the other three, while the sample from Merck was almost inactive. It should be mentioned that the containers of the Yiaolong and Fluka samples were opened a year ago, while the activation experiments using samples from

TABLE 2

Activities of Untreated Lanthanum Oxide Samples after Activation

		SO₂	
Sample	Surface area ($m^2\ g^{-1}$)	Conversion (%)	Ave. specific conv. ($mol\ m^{-2}\ s^{-1}$) $\times 10^7$
Yiaolong	4.0	94.6	3.1
Fluka	6.0	86.5	1.9
BDH	4.9	61.2	1.7
Merck	3.1	6.1	0.3
Sigma	4.9	77.1	2.1

Sigma, BDH, and Merck were conducted immediately after opening the storage bottles. XRD analysis revealed that the Yiaolong sample was completely changed to the hydroxide, the Merck sample maintained the pure La_2O_3 phase, and the other samples were found to be partially hydrated to different extent.

Influence of the dehydroxylation of La(OH)₃ on activation.   According to Bernal *et al.* (12, 14), LaOOH is formed in the decomposition of lanthanum hydroxide at 377°C before forming the oxide at a higher temperature:

$$La(OH)_3 \underset{\leftarrow 377°C \, (-2H_2O)}{\rightarrow} 2\,LaOOH \underset{\leftarrow 527°C \, (-H_2O)}{\rightarrow} La_2O_3 \qquad [1]$$
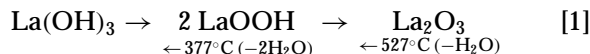
In this work we prepared the lanthanum oxyhydroxide *in situ* in the reactor in an inert atmosphere at a decomposition temperature of 400°C. The activation course of the decomposed product is shown in Fig. 2, and it can be seen that the SO_2 concentration, after an initial decrease, did not return to as high a level as that shown in Fig. 1a, indicating that the reactivity of the dehydrated product LaOOH increased significantly.

Effect of water during the activation of La₂O₃.   So far we have demonstrated that the prehydrated lanthanum oxide can be easily activated to catalyze the reduction of SO_2 by CO; there is, however, still another way to hydrate the oxide: by injecting water into the reaction gas stream during activation. This method has practical significance because flue gas usually contains water vapor in addition to sulfur dioxide.

In this experiment, an *in situ* calcined La_2O_3 was used as the starting material. Figure 3 shows the lanthanum oxide could not be activated after about 90 min of exposure
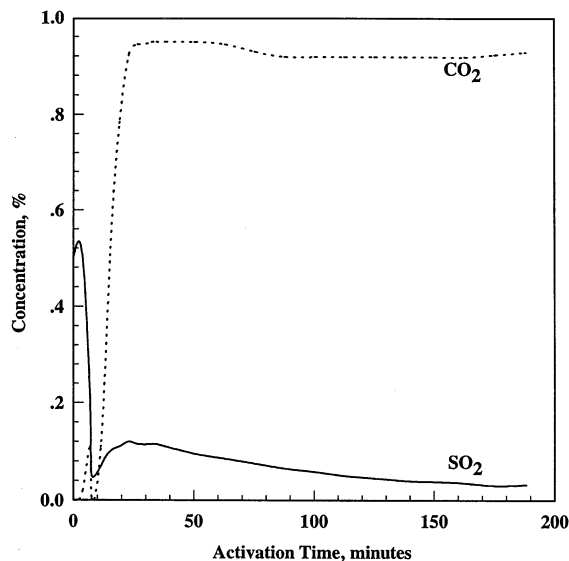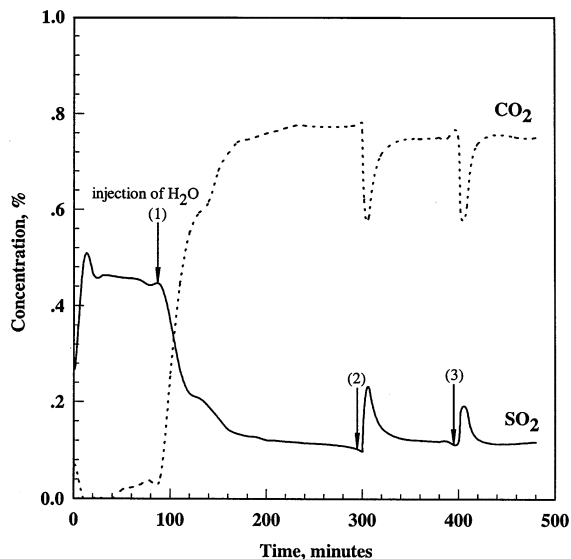

FIG. 3.   Activation of La_2O_3 by means of water injection.

in the bone-dry reactive gas mixture, however, activation was initiated as soon as 0.05 ml of water was injected into the gas stream. Furthermore, it can be seen that the further injection of water had no influence on the steady-state concentrations of SO_2 and CO_2.

Phase composition.   All of the samples before and after activation were characterized using XRD. The phase composition identified are summarized in Table 3. Some of the diffractograms are presented in Figs. 4a and 4b. The results show that La_2O_2S was always formed after activation, and if the major phase in the starting material was $La(OH)_3$, then La_2O_2S existed as the major phase. In the case of the Yiaolong sample, the only identifiable phase was La_2O_2S after activation.

DISCUSSION

Active Phase

From the results shown in Table 2, lanthanum oxysulfide was found to exist in all catalysts after activation, strongly suggesting that La_2O_2S was the active phase for the reduction reaction. Indeed, there is a relationship between the catalytic activity and the La_2O_2S content in the catalyst. The relationship is shown in Fig. 5, where the relative La_2O_2S content was calculated from diffractograms of some of the samples after activation according to the following equation:

$$P_i = I_i \bigg/ \sum I_i \times 100. \qquad [2]$$

Here P_i is the content of a species in phase i in % and I_i is the first intensive diffraction peak of the ith phase. This is also consistent with the observations made in our

FIG. 2.   Activation of decomposed $La(OH)_3$ sample.

TABLE 3

Phase Composition of Catalysts Used[a]

Description of sample	Before activation	After activation
As received, Yiaolong	La(OH)$_3$	La$_2$O$_2$S
As received from Fluka Chemika	La$_2$O$_3$, La(OH)$_3$	La$_2$O$_3$, La(OH)$_3$, La$_2$O$_2$S, (La$_2$O$_2$S$_2$)
As received from BDH Lab. Supplies	La$_2$O$_3$, La(OH)$_3$	La$_2$O$_3$, La$_2$O$_2$S
As received from Merck	La$_2$O$_3$	La$_2$O$_3$, (La$_2$O$_2$S)
As received from Sigma	La$_2$O$_3$, La(OH)$_3$	La$_2$O$_3$, La$_2$O$_2$S
Dissolved, precipitated, and calcined at 900°C for 12 h	La$_2$O$_3$	La$_2$O$_3$, (La$_2$O$_2$S), (La(OH)$_3$)
Exposure to saturated water vapor for 1 week	La(OH)$_3$	La$_2$O$_2$S, (La$_2$O$_3$)
Exposure to CO$_2$ (dry ice) for 1 week	La(OH)$_3$, (La$_2$O$_2$CO$_3$)	La$_2$O$_2$S, (La$_2$O$_3$), (La$_2$O$_2$CO$_3$)
Exposure to atmospheric air for 1 week	La(OH)$_3$, (La$_2$O$_2$CO$_3$, La$_2$O(CO$_3$)$_2$)	La$_2$O$_2$S, (La$_2$O(CO$_3$)$_2$)
Decomposed *in situ* for 4 h	LaOOH, La$_2$O$_3$, La(OH)$_3$	La$_2$O$_2$S$_2$, La$_2$O$_2$S, La$_2$O$_3$, (La$_2$S$_3$)

[a] Minor phases are in parentheses.

previous investigation using perovskite oxides as catalyst, where La$_2$O$_2$S was always found to exist as the major phase in the active catalysts (9).

Effect of Hydration

The activation results and XRD analysis showed that the hydration of lanthanum oxide, regardless of the method used, promotes the sulfidization of the oxide to oxysulfide. Using Eq. [2], the content of La(OH)$_3$ in the sample before activation and the La$_2$O$_2$S concentration after activation can be correlated and a linear relationship is obtained, as shown in Fig. 6. This shows the effect of hydration on the activation of the catalyst.

It is customary to characterize an oxide by its acid and base properties which in turn are dependent on the degree of dehydroxylation. In addition, surface OH groups themselves can play the role of acidic or basic sites. The influence of surface hydroxyl groups on the adsorption properties and catalytic activity of rare-earth oxides has been reported for several systems in literature and was reviewed by Netzer and Bertel (15). Tsyganenko *et al.* (16) investigated the acid and base properties of lanthanum oxide by

means of CO adsorption and found that both acidic and basic sites existed on the surface of hydroxylated samples after evacuation at various temperatures. The removal of certain OH groups after outgassing treatment led to the formation of coordinatively unsaturated La ions which are strong Lewis acid sites. It was found that after outgassing at 573°K, the La(OH)$_3$ phase decomposed and the bounding of the OH groups to one lanthanum atom was formed, providing strong Lewis base (or Brønsted acid) sites. It was further found that the pretreatment of the catalyst at temperatures ≥773°K resulted in the formation of basic O^{2-} sites because of the dehydroxylation. Li *et al.* (17) reported that surface unsaturated sites on CeO$_2$ can be generated by dehydroxylation at high temperatures, and these sites are vital to the activation of CO to form carbonate and inorganic carboxylate species. A severe change in the surface properties would be experienced when a lanthanum oxide was rehydrated and dehydroxylated, and it would have the capability in promoting the interaction of SO$_2$ and/or CO with the surface and thus achieving activation. This phenomenon will be discussed in the following section.
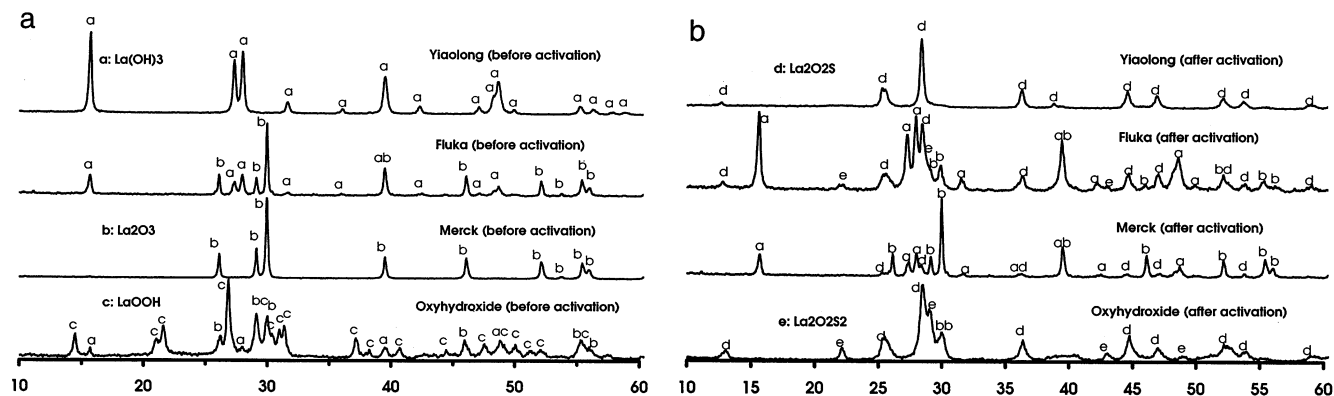

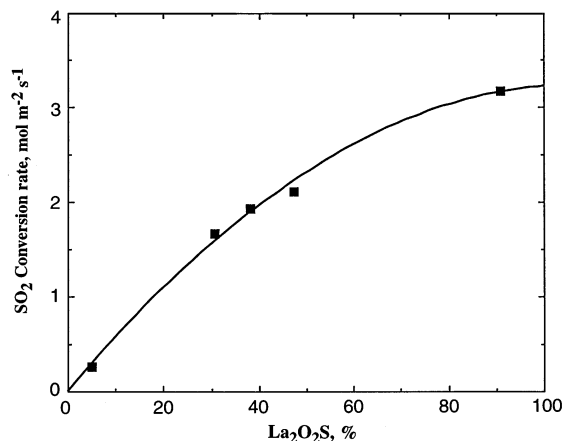FIG. 4. X-ray diffractograms of some samples (a) before and (b) after activation.

FIG. 5. Relationship between La_2O_2S content and specific activity.

FIG. 7. Chemisorption of CO and SO_2 on dehydrated La_2O_3 surface.

sorption of CO on Lewis acid sites is cationic and the adsorption of SO_2 on the basic part of a Brønsted sites is anionic; thus, the interaction between the two adsorbates on two neighboring sites could be the transfer of one oxygen atom from SO_2 to CO, resulting in the formation of a more reactive intermediate, sulfur monoxide, which then reacts with the carbon monoxide and the solid to form lanthanum oxysulfide. If there were no such Lewis–Brønsted pairs present on the solid, such as the case with lanthanum oxide, the formation of SO and the conversion of lanthanum oxide to oxysulfide would be difficult, because the SO formation step is endoenergic and the chance of interaction between SO_2 and CO is low. This is why lanthanum oxide calcined at high temperature cannot be activated, but can be after rehydration. Based on the results and discussion above, the following activation mechanism can be proposed:

$$2La(OH)_3 \rightarrow 2LaOOH + 2H_2O \qquad [3]$$

$$CO + SO_2 \rightarrow CO_2 + SO \qquad [4]$$

$$CO + SO \rightarrow CO_2 + S \qquad [5]$$

$$2LaOOH + CO \rightarrow La_2O_2\square + CO_2 + H_2O \qquad [6]$$

$$La_2O_2\square + S \rightarrow La_2O_2S \qquad [7]$$

Here $\square$ represents lattice oxygen vacancy. Reaction [6] suggests that it may be easier for the adsorbed CO to obtain an oxygen atom during the decomposition of LaOOH to La_2O_3, because of the formation of structural defects and the existence of edges or steps where oxygen has a lower coordination number. The overall gas-solid reaction is shown as follows:

$$2La(OH)_3 + 3CO + SO_2 \rightarrow La_2O_2S + 3CO_2 + 3H_2O. \quad [8]$$

It was observed that COS was formed during activation, and Fig. 8 is the time-dependent COS concentrations measured for the lanthanum oxide exposed to air. It can be seen that the formation of COS increased gradually and reached a constant level of about 90 ppmv after about 300 min. Carbonyl sulfide can be formed by the reaction of carbon monoxide with elemental sulfur:

$$CO + S \rightarrow COS. \qquad [9]$$

Activation Mechanism

The foregoing discussion points out that (1) the rehydration of the lanthanum oxide increases its adsorption of SO_2 and greatly promotes activation; (2) it is easier to activate the LaOOH formed by the decomposition of $La(OH)_3$ (the first step in Reaction [1]); (3) the dehydration may lead to the formation of a surface with both acidic and basic sites; and (4) the activated catalyst is lanthanum oxysulfide. It is known that CO can adsorb on coordinatively unsaturated metal cations (Lewis acid sites) formed by the removal of certain OH groups (16), while SO_2 is a strong Lewis acid and therefore will preferably attach to the basic part of a Brønsted site (18). Thus we can pictorially represent the chemisorption of CO and SO_2 as shown in Fig. 7 in a way analogous to the surface model for alumina (19). The ad-
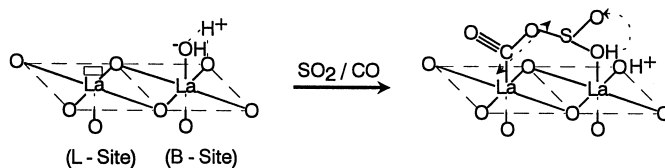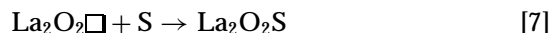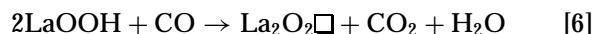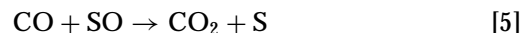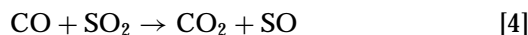

FIG. 6. The effect of $La(OH)_3$ content in the starting material on the formation of La_2O_2S in the catalyst.

Thus the formation of COS is dependent on the amount of

sulfur in the reaction system. Elemental sulfur can be produced by Reaction [5] as well as by the following reactions catalyzed by lanthanum oxysulfide:

$$SO_2 + 2CO \rightarrow 2CO_2 + S \qquad [10]$$

$$SO_2 + 2COS \rightarrow 2CO_2 + 3S. \qquad [11]$$
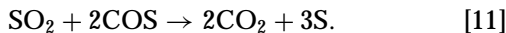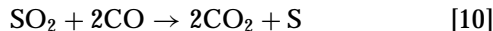
Intuitively, sulfur plays a balancing act in Reactions [7] and [9]–[11] during the activation and reduction reactions. As activation progresses, less sulfur is consumed by Reaction [7] while at the same time more La$_2$O$_2$S is produced, which in turn catalyzes Reactions [10] and [11] to produce more sulfur leading to the formation of COS by Reaction [9]. However, upon the completion of the activation process, Reaction [7] is no longer involved and the formation of COS is now determined by the competition between Reactions [9], [10], and [11].

The role of these reactions can be unraveled by examining the stoichiometry: Reaction [8] shows that the stoichiometry of CO and SO$_2$ during activation is 3 : 1 and is 2 : 1 for the reduction reaction (Reaction [10]).

In this experiment, a feed stoichiometric ratio of 2 : 1 was used. If Reaction [8] were the dominant reaction, the conversion of CO would be 50% higher than that of SO$_2$; on the other hand, if Reaction [10] dominated, there would be no difference between the two conversions.

It can be seen in Fig. 9 that the difference between the CO and SO$_2$ conversions was very large and negative at the beginning of the reaction because of the strong adsorption of SO$_2$. In this stage no or only little sulfur was available to form COS; see Fig. 8. Thereafter, the conversion of CO became higher than SO$_2$, but by no more than 20%, indicating that in addition to sulfidization desulfur-
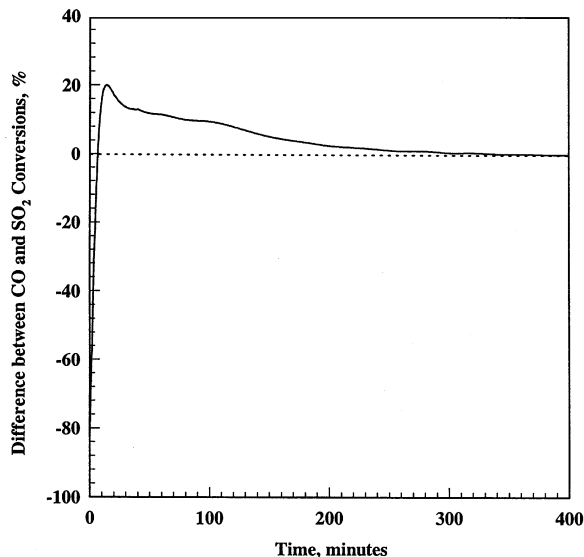

FIG. 9. Difference in SO$_2$ and CO$_2$ conversion during activation.

ization also took place. As time progressed, the difference decreased gradually because of the increasing contribution of desulfurization. As a result more and more sulfur became available for the formation of COS, as reflected in Fig. 8. After about 300 minutes, the difference decreased to zero upon the completion of sulfidization. This is also consistent with the constant formation of COS shown in Fig. 8. It is estimated that complete sulfidization requires only about 50 min for 0.5 g of La(OH)$_3$ using a reactive gas containing 0.5 mol% SO$_2$ and 1.0 mol% CO when no desulfurization reaction occurred. Therefore we believe Reaction [10] is a part of the activation process and longer activation time is needed.

CONCLUSION

Lanthanum oxide can be activated to catalyze the reduction of SO$_2$ by CO to elemental sulfur. The activation is achieved by the rehydration of lanthanum oxide to the hydroxide prompting the creation of Lewis and Brønsted sites in the subsequent dehydroxylation of the hydroxide. These sites are able to chemisorb SO$_2$ and CO simultaneously, promoting the formation of reactive SO species and lattice oxygen vacancies which readily accept sulfur. The activation is a gas/solid sulfidization reaction between the reaction gas mixture and the pretreated oxide. The active phase formed after the sulfudization is found to be lanthanum oxysulfide, La$_2$O$_2$S. The catalytic performance of this material has been investigated and will be reported elsewhere.
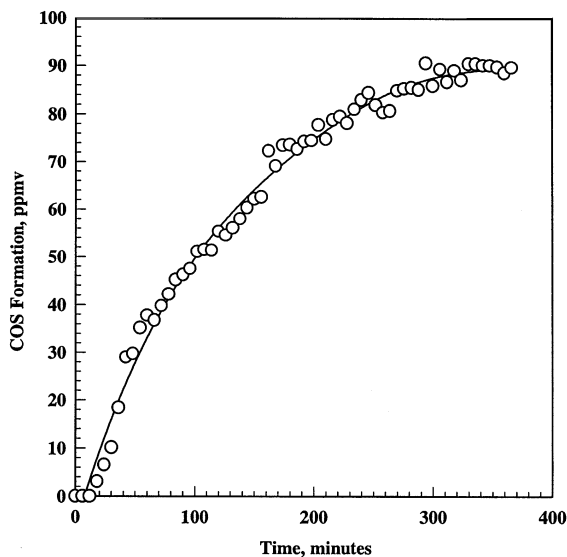
FIG. 8. Time-dependent COS concentration during activation.

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