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On the Formation of Carbonyl Sulfide in the Reduction of Sulfur Dioxide by Carbon Monoxide on Lanthanum Oxysulfide Catalyst; A study by XPS and TPR/MS

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Both the X-ray photoelectron spectroscopy (XPS) and temperature-programmed reaction, coupled with mass spectrometry (TPR/MS), are used to study the formation of carbonyl sulfide in the reduction of sulfur dioxide on lanthanum oxysulfide catalyst. It was found that the lattice sulfur of the oxysulfide is released and reacts with carbon monoxide to form carbonyl sulfide when the oxysulfide is heated. The oxysulfide is postulated to form sulfur vacancies at a temperature lower than that for the formation of carbonyl sulfide and atomic sulfur is released in the process. The atomic sulfur can either enter the gas phase and leave the oxysulfide catalyst or react with carbon monoxide to form carbonyl sulfide.

Key Words: **lanthanum hydroxide; lanthanum oxysulfide; catalytic reduction of sulfur dioxide; carbonyl sulfide; XPS; TPR/MS.**

INTRODUCTION

Ma *et al.* (1,2) demonstrated that properly sulfidized lanthanum oxide could effectively catalyze the reduction of sulfur dioxide by carbon monoxide to elemental sulfur. The active material was found to be lanthanum oxysulfide. Based on the results of kinetic measurements and powder X-ray diffraction (XRD) study, they postulated that lanthanum oxysulfide was bifunctional for the reduction of sulfur dioxide (2). Carbon monoxide reacts with lanthanum oxysulfide to form carbonyl sulfide, which then reacts with sulfur dioxide on the lanthanum oxysulfide to produce sulfur and carbon dioxide. A portion of the product sulfur then goes back into the lanthanum oxysulfide phase to replenish the sulfur lost in the formation of carbonyl sulfide,

$$\mathrm{CO} + \mathrm{La_2O_2S} = \mathrm{COS} + \mathrm{La_2O_2}\,\square, \qquad [1]$$

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

$$\mathrm{La_2O_2}\,\square + 1/2\,\mathrm{S_2} = \mathrm{La_2O_2S}, \qquad [3]$$

where $\square$ is a sulfur vacancy. On the other hand, Baglio (3) showed that lanthanum oxysulfide had only minimal catalytic activity for the reduction of sulfur dioxide by carbon monoxide and no carbonyl sulfide was found, but it was active for the reaction of sulfur dioxide with carbonyl sulfide. This suggests that the formation of carbonyl sulfide is a critical step in the catalytic reduction of sulfur dioxide on lanthanum oxysulfide. Despite the importance of this step in the catalytic desulfuriztion reaction, no detailed mechanistic study of the step has ever been reported and previous kinetic studies were not precise enough to reveal the mechanism. This study was initiated to study the formation of carbonyl sulfide on lanthanum oxysulfide using X-ray photoelectron spectroscopy (XPS) and temperature-programmed reaction coupled with mass spectrometry (TPR/MS) techniques. These methods are surface sensitive and can measure the changes in the surface of lanthanum oxysulfide during the formation of carbonyl sulfide.

METHODS

Catalyst Preparation

Two batches of catalyst samples each starting with 1 g of lanthanum hydroxide powder (Yiaolong Chemicals, PRC) were prepared using the sulfidization procedure reported by Ma *et al.* (1,2). The particle size and BET surface area of the powder were reported elsewhere (1). Batch H was sulfidized with 1.0% carbon monoxide and 0.5% sulfur dioxide (both 99.9% pure) in 99.99% pure nitrogen at a space velocity of about 22,000 ml $(\text{g-h})^{-1}$ at 600°C, while Batch O was calcined in air at 900°C to oxide prior to sulfidization. All samples were cooled to room temperature in the sulfidization reactor (a 2-cm diameter by 50-cm length quartz tube, heated externally by an electric furnace) in nitrogen flush. The samples were ground and thoroughly homogenized in a corundum mortar before any further processing and analyses were performed.

One half of each batch was retained for characterization studies and they were designated as Samples H1 and O1. The remaining halves of each batch, designated as Samples H2 and O2, were resulfidized and then subjected to carbon

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TABLE 1

Sample Treatment

Sample	Starting material	Sulfidization	Reduction
H1	Lanthanum hydroxide	$SO_2:CO = 1:2$ at 873 K	None
H2	Sample H1	$SO_2:CO = 1:2$ at 873 K	CO at 873 K
O1	Lanthanum hydroxide calcined at 1173 K	$SO_2:CO = 1:2$ at 873 K	None
O2	Sample O1	$SO_2:CO = 1:2$ at 873 K	CO at 873 K

monoxide reduction twice. The carbon monoxide reduction stream contained 1.0% carbon monoxide in nitrogen at the same space velocity as the sulfidization stream. Table 1 shows the conditions for the preparation of these samples.

All samples were characterized using powder X-ray diffraction (XRD) using Philips Powder X-ray System, Model MPD-1880I, with copper anode before subjected to XPS analysis. The X-ray power was 50 mA at 40 kV. The diffraction scanning was from 10° to 90° at a rate of 0.02° per second. The powder samples were pressed into aluminum sample holders without any pretreatment.

XPS

All XPS analyses were performed in a Perkin-Elmer Surface Science Analysis System, Model PHI 5600, equipped with a monochromatic aluminum Kα X-ray source (1486.6 eV). The powder samples were pressed into cup-shaped sample mounts for direct insertion into the instrument. Low energy flooding electrons were used to neutralize the charges built up on the samples and the binding energy scale was adjusted to make the adventitious carbon peak at 284.5 eV. Multiplex scans of carbon C 1s, oxygen O 1s, sulfur S 2p, and lanthanum La 3d were acquired at a constant pass energy of 23.5 eV. The atomic concentrations of the carbon, oxygen, sulfur, and lanthanum in the surface was calculated as follows: (1) baseline corrections were made based on the integral method, (2) peak areas were counted and scaled with the atomic sensitivity factors of the elements for the specific configurations of the XPS system, and (3) the scaled areas were normalized to yield atomic concentrations in percentage.

In order to validate the XPS results, lanthanum oxysulfide powder (Johnson Matthey) packed under argon was acquired and used as the comparison standard. The powder was transferred to the instrument in nitrogen atmosphere. Multiplex scans of C 1s, O 1s, S 2p, and La 3d was acquired at the same pass energy and its atomic concentrations were calculated with the same methodology as the sulfidized samples. A portion of the Johnson Matthey lanthanum oxysulfide powder was exposed to the atmosphere for a few days and examined with XPS to study the effects of atmospheric moisture on the samples.

TPR/MS

Lanthanum hydroxide powder (0.1 g) was sulfidized and activated in an electrically heated quartz TPD/TPR cell of 1 cm in diameter, purged by a stream made up of 8 ml min^{-1} 5% sulfur dioxide (purity 99.9%) and 10% carbon monoxide (purity 99.9%) in helium (purity 99.999%) and 90 ml min^{-1} helium. The sample was heated from 20 to 600°C at 10°C min^{-1} and kept at 600°C for 2 h. The elemental sulfur produced by the catalytic reaction deposited at the exit due to cooling. The sulfidized sample was cooled to room temperature by a stream of 90 ml min^{-1} helium with the reactor taken outside of the furnace and before transferred to a sulfur-free quartz cell. The transferred sample was heated from 20 to 600°C at 10°C min^{-1} in a stream composed of 8 ml min^{-1} 10% carbon monoxide in helium and 90 ml min^{-1} helium. Since the carbonyl sulfide measured in TPR can be attributed to the carbon monoxide reduction reaction, and the desorption of the residual carbonyl sulfide adspecies left behind from the prior sulfidization reaction, the relative contributions of these two sources were quantified by activating another 0.1 g lanthanum hydroxide using the same sulfidization procedure and then heated from 20 to 600°C at 10°C min^{-1} in 90 ml min^{-1} helium in a sulfur-free quartz cell prior to TPR. The carbonyl sulfide (mass number 60) in the effluent was monitored with a process quadrupole mass spectrometer (MS-250, Extrel Corporation).

RESULTS AND DISCUSSIONS

Sulfidization and Reduction

Powder XRD (see Table 2) showed that both Samples H1 and H2 were completely transformed to lanthanum oxysulfide, while Samples O1 and O2 were only partially transformed and had some lanthanum oxide and hydroxide left in the samples. This is consistent with what was reported by Ma *et al.* (1) in that lanthanum hydroxide is more readily sulfidized than lanthanum oxide. On the other hand, Sample O2 has more lanthanum oxysulfide than Sample O1 showing that the subsequent sulfidization promotes the transformation.

TABLE 2

Phase Compositions of Sulfidized and Reduced Samples

Sample	Phases identified
Lanthanum oxysulfide[a]	La_2O_2S
Lanthanum hydroxide[b]	$La(OH)_3$
H1	La_2O_2S
H2	La_2O_2S
O1	La_2O_2S, La_2O_3, $La(OH)_3$
O2	La_2O_2S, La_2O_3, $La(OH)_3$

Note. Phases are listed from left to right in the order of abundance.

[a] Purchased from Johnson Matthey.

[b] Purchased from Yiaolong Chemicals.

TABLE 3

Comparison of the La $3d_{5/2}$ and O 1s of Lanthanum Oxide and Hydroxide Obtained in the Current Work and Those in Literature

Peak	B.E. (eV)	Delta (eV)	Remark	Source
La $3d_{5/2}$	835.5	4.3	Lanthanum metal exposed to water	(7)
		4.5	Lanthanum metal exposed to oxygen	(7)
		3.7	Lanthanum hydroxide	(8)
		4.5	Lanthanum oxide	(8)
	834.4	3.8	Lanthanum hydroxide	This work
O 1s	530.5		Oxide	(7)
	532.8		Hydroxide	(7)
	528.6		Oxide	(5)
	between 530.5 and 531.5		Carbonates	(5)
	530.9			This work

Upon carbon monoxide reduction, a minute amount of carbonyl sulfide was detected in addition to the carbon dioxide in the effluent using a gas chromatograph (Hewlett Packard 5890 Series II with a thermal conductivity detector and a 6 ft long 1/8 inch diameter Teflon column packed with Porapak Q). The concentration was estimated in the order of 10 ppmv. Both the completely and partially sulfidized lanthanum oxide catalysts produced carbonyl sulfide in the reduction.

XPS Analyses

The XPS spectra of lanthanum hydroxide are shown in Fig. 1 and the positions of the O 1s and La 3d peaks are comparable to the published data (Table 3). For C 1s, the most intense peak is attributed to the adventitious carbon and its binding energy is assigned to 284.5 eV. The less intense peak at 5 eV higher arises from surface carbon-oxygen species (C-O) such as carbonate, since lanthanum oxide readily adsorbs the carbon dioxide in the air (4).

The XPS spectra of lanthanum oxysulfide are shown in Fig. 2. Exposing to the atmosphere does not produce significantly different spectra, except that the exposed oxysulfide has a relatively more intense oxygen peak at 528.6 eV. This more intense peak is attributed to the atmospheric oxygen species adsorbed on the lanthanum oxysulfide. The most intense S 2p peak is attributed to the oxysulfide and the less intense one at higher binding energy is associated to the surface sulfur-oxygen species (S-O).

Reduction with carbon monoxide does not yield significantly different XPS spectra, except that the small hump at 163 eV is removed and the sulfur-oxygen peak becomes smaller. The small hump is attributed to elemental sulfur (5), probably the surface sulfur produced in the catalytic reduction between carbon monoxide and sulfur dioxide, retained in the sample. Reducing the sample with carbon monoxide removes the retained sulfur.

Semiquantitative Analysis of XPS Results

In the analysis to follow, the catalyst is assumed to be a collection of solid crystal cores composed of lanthanum, oxygen, and sulfur covered with carbon-oxygen (C-O) and sulfur-oxygen (S-O) adspecies. The solid cores are made up of lanthanum oxysulfide, lanthanum oxide, and lanthanum hydroxide as indicated by XRD. The adventitious carbon is ignored in the analysis because it is inherent to the XPS technique and it is unlikely to participate in the catalytic reduction and the transformation of the catalyst. The surface sulfur associated with the small hump at 163 eV is treated as a part of the solid core in the quantitative calculation and is accounted for in the atomic concentration of the sulfur in the solid core, S_{core}. The atomic concentration of oxygen in the solid core, O_{core}, is given by the difference between the overall concentration of oxygen, $O_{overall}$, and the oxygen concentration of the adspecies C-O, $O_{C\text{-}O}$, and S-O, $O_{S\text{-}O}$.

$$O_{core} = O_{overall} - O_{C\text{-}O} - O_{S\text{-}O}. \qquad [4]$$

The oxygen concentrations, $O_{C\text{-}O}$ and $O_{S\text{-}O}$, are related to the carbon, $C_{C\text{-}O}$, and sulfur, $S_{S\text{-}O}$, concentrations of the adspecies by the oxygen to carbon, $\alpha_{O\text{-}C}$, and oxygen to sulfur, $\alpha_{O\text{-}C}$, ratios:

$$O_{C\text{-}O} = \alpha_{O\text{-}C} \times C_{C\text{-}O}, \qquad [5]$$

$$O_{S\text{-}O} = \alpha_{O\text{-}S} \times S_{S\text{-}O}. \qquad [6]$$

The C-O adspecies are taken to be carbon dioxide, since carbon monoxide reacts readily with rare earth oxides to produce surface carbonates or carboxyl groups (6) and carbon dioxide is strongly adsorbed on lanthanum oxide (4). The S-O adspecies are taken to be sulfur dioxide, since sulfur monoxide is too reactive and sulfur dioxide is unlikely to be oxidized to trioxide in a reducing environment. Hence, both $\alpha_{O\text{-}C}$ and $\alpha_{O\text{-}C}$ are taken to be two.

To allow direct comparison among the samples, the atomic concentrations of oxygen and sulfur are normalized to the concentration of lanthanum of the same sample to give the oxygen to lanthanum and sulfur to lanthanum atomic ratios (Table 4). The atomic ratios are then normalized to the corresponding ratio of lanthanum oxysulfide to give the compositional change in term of the comparison standard. The completely sulfidized Samples H1 and H2 have compositions closest to lanthanum oxysulfide. But Sample H1, which was not reduced, has slightly more sulfur in the lattice and the reduction by carbon monoxide removed a portion of the sulfur. Hence, reducing the sulfidized lanthanum hydroxide lowers the sulfur content of the material. On the other hand, Samples O1 and O2 were not completely sulfidized and further sulfidization increased the amount of lattice sulfur more than taken away by the reduction.

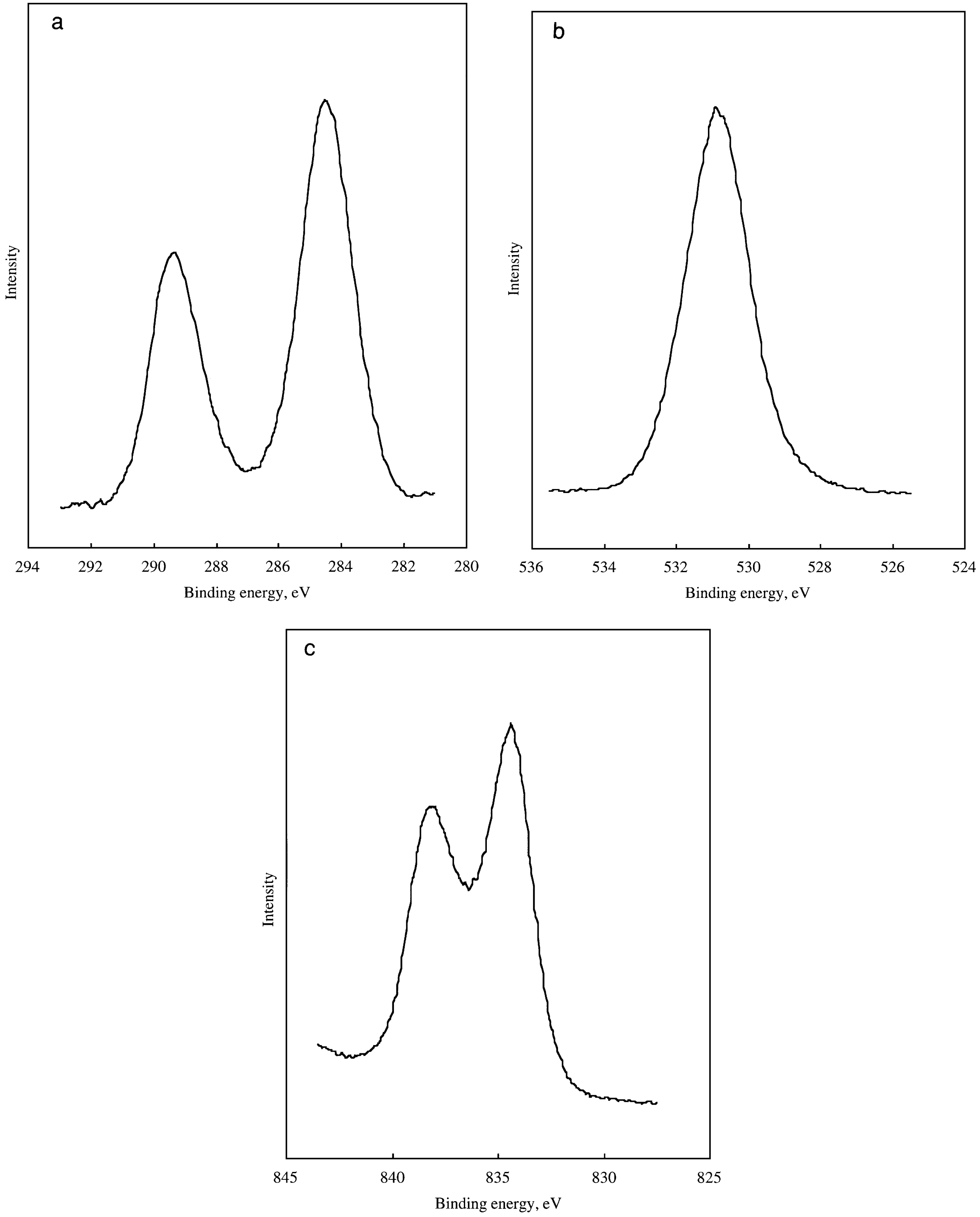

FIG. 1. (a) XPS of lanthanum hydroxide: C1s. (b) XPS of lanthanum hydroxide: O1s. (c) XPS of lanthanum hydroxide: La3$d_{5/2}$.

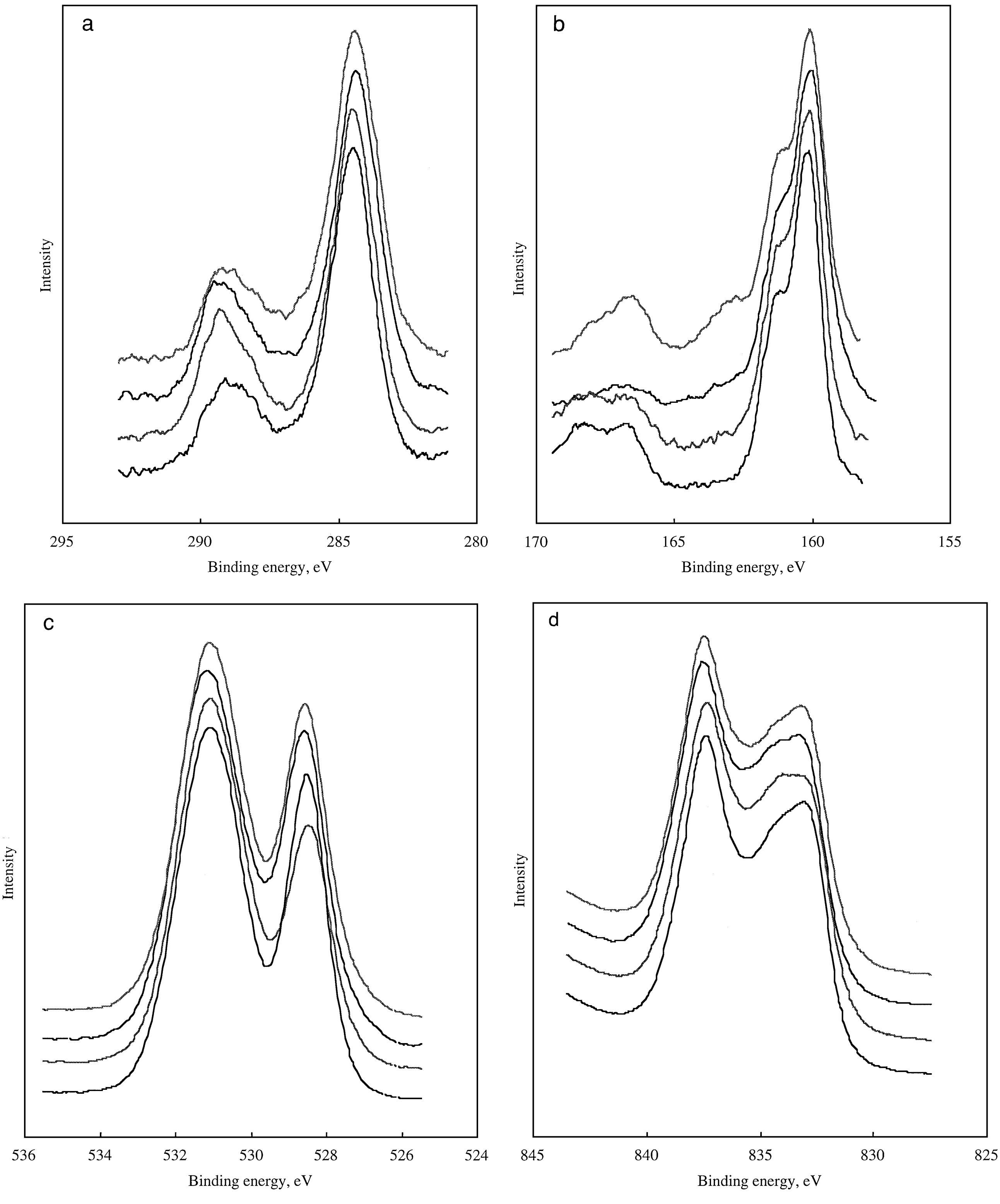

FIG. 2. (a) XPS of lanthanum oxysulfide and sulfidized lanthanum hydroxide: C1s. Note: From top to bottom: sulfidized lanthanum hydroxide (Sample H1), sulfidized and reduced lanthanum hydroxide (Sample H2), lanthanum oxysulfide and lanthanum oxysulfide exposed to atmosphere. (b) XPS of lanthanum oxysulfide and sulfidized lanthanum hydroxide: S2p. Note: From top to bottom: sulfidized lanthanum hydroxide (Sample H1), sulfidized and reduced lanthanum hydroxide (Sample H2), lanthanum oxysulfide and lanthanum oxysulfide exposed to atmosphere. (c) XPS of lanthanum oxysulfide and sulfidized lanthanum hydroxide: O1s. Note: From top to bottom: sulfidized lanthanum hydroxide (Sample H1), sulfidized and reduced lanthanum hydroxide (Sample H2), lanthanum oxysulfide and lanthanum oxysulfide exposed to atmosphere. (d) XPS of lanthanum oxysulfide and sulfidized lanthanum hydroxide: La3$d_{5/2}$. Note: From top to bottom: sulfidized lanthanum hydroxide (Sample H1), sulfidized and reduced lanthanum hydroxide (Sample H2), lanthanum oxysulfide and lanthanum oxysulfide exposed to atmosphere.

TABLE 4

Oxygen to Lanthanum and Sulfur to Lanthanum Atomic Ratios

Sample	H1	H2	O1	O2	Oxysulfide
$(O/La)_{overall}$	2.76	2.76	3.61	2.96	2.65
$(S/La)_{overall}$	0.83	0.69	0.61	0.64	0.81
$(O_{core}/La)_{normalized}$	1.0	1.0	1.4	1.1	1
$(S_{core}/La)_{normalized}$	1.1	1.0	0.7	0.9	1
$(C_{C\text{-}O}/La)_{normalized}$	1.3	1.5	1.4	1.6	1
$(S_{S\text{-}O}/La)_{normalized}$	0.8	0.3	1.1	0.5	1

Note. The overall ratios are ratios of the overall converted areas of O 1s and S 2p to La $3d_{5/2}$. The normalized ratios are the respective atomic ratios, divided by the corresponding atomic ratios of lanthanum oxysulfide. $C_{C\text{-}O}$ and $S_{S\text{-}O}$ refer to carbon and sulfur of carbon-oxygen and sulfur oxygen adspecies while O_{core} and S_{core} refer to oxygen and sulfur not accounted for by C-O and S-O and are taken to be in the solid core.

TPR/MS

When the sulfidized lanthanum hydroxide sample was reduced with carbon monoxide, carbonyl sulfide was found in the effluent (Fig. 3). On the other hand, when the sulfidized sample was heated in a helium stream, no carbonyl sulfide was detected but elemental sulfur was found to deposit at the cooled exit of the reactor cell. Hence, carbonyl sulfide is a product of the reaction between the sulfidized sample and carbon monoxide and not the adsorbate left behind from the prior sulfidization reaction, and heating the sample in helium stream releases the elemental sulfur from the sample into the gas phase.

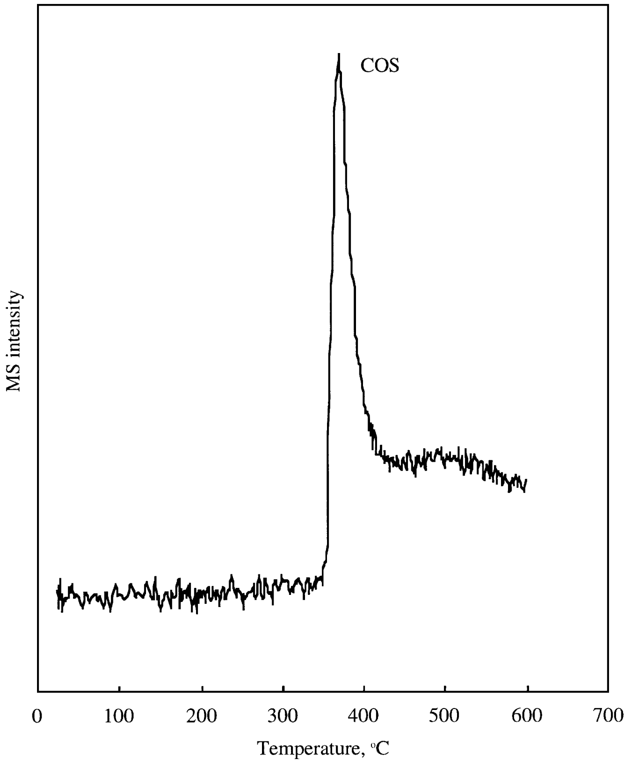

FIG. 3. TPR/MS of sulfidized lanthanum hydroxide.

In the reduction of the sulfidized sample by carbon monoxide, carbonyl sulfide started to appear as a huge surge at about 360°C. The duration of this startup surge was short and the concentration of carbonyl sulfide fell back quickly to a low and slightly decreased level. Besides, no elemental sulfur was depositing at the reactor exit during the reduction. Reducing the sample previously heated in helium also produced carbonyl sulfide but the surge and the fall-back level of carbonyl sulfide were much smaller. Hence, preheating the sulfidized sample in helium not only releases sulfur from the sample but also suppresses the formation of carbonyl sulfide in the subsequent reaction with carbon monoxide. The sulfur species which reacts with the carbon monoxide to form carbonyl sulfide is later released from lanthanum oxysulfide when the oxysulfide is heated. Furthermore, the formation of carbonyl sulfide can be related to two distinct processes: (1) the lower temperature process associated with the startup surge, and (2) the higher temperature process associated with the fall-back level. The lower temperature process probably involves the sulfur species which is readily available and easily accessible to carbon monoxide such as adsorbed sulfur atoms, and the higher temperature process probably involves the more tightly held sulfur species such as the sulfur in the lattice. It should be noted that heating the sample did not remove all the low temperature sulfur and, as a result, a small but significant carbonyl sulfide surge peak was produced in the subsequent reduction. However, it is believed that heating at 600°C, a temperature much higher than the temperature at which the surge appeared, for 2 h probably removes all the low temperature sulfur. This suggests that there is a mechanism for the sample to "regenerate" the low temperature sulfur species and the regenerated sulfur probably comes from the sulfur in the lattice of lanthanum oxysulfide; this is the only known reservoir of sulfur for the solid.

Sulfur Vacancy and Reactive Sulfur

Summarizing the XPS and TPR/MS results, we have:

1. The sulfidized lanthanum hydroxide, which is either completely or partially converted to lanthanum oxysulfide, can retain elemental sulfur in the material.
2. Reducing the sulfidized lanthanum hydroxide removes the retained sulfur and lowers the concentration of sulfur in the surface.
3. Heating the sulfidized lanthanum hydroxide in a helium stream releases the sulfur in the material to the gas phase.
4. Reducing the sulfidized lanthanum hydroxide by carbon monoxide produces carbonyl sulfide which starts to appear initially as a startup surge and then falls back to a low but steady level.

It can be concluded that there is some sulfur species in lanthanum oxysulfide, which is released to the environment and is able to react with the carbon monoxide to form carbonyl sulfide when the oxysulfide is heated. Besides, the sulfur species is probably released at a temperature lower than that for the formation of carbonyl sulfide. The sulfur species comes from the lattice of lanthanum oxysulfide and therefore it is lattice sulfur. The elemental sulfur detected with XPS in Sample H1 was probably the lattice sulfur released to the environment when the sample was still hot, condensed, and trapped in the sample when the sample was cooled down in the reactor in nitrogen. The direct interaction of carbon monoxide with the lattice sulfur of lanthanum oxysulfide, as described by Ma *et al*., (2) in Eq. [1] can be one of the ways to form carbonyl sulfide. Carbonyl sulfide can also be formed by the reaction of released sulfur with carbon monoxide.

Analogous to the oxygen vacancies in lanthanum oxide and other rare earth oxides, we postulate that sulfur vacancies are generated in the lanthanum oxysulfide crystals and the generation starts at a temperature lower than the carbonyl sulfide formation temperature, 360°C, and lattice sulfur is released,

$$^*S = {}^* + S, \qquad [7]$$

where $^*S$ is a sulfide ion in the lattice and * is a sulfur vacancy having two negative charges. The generation is a thermally activated process and heating the lanthanum oxysulfide crystals promotes the generation of sulfur vacancies and the release of sulfur atoms from the crystal lattice. The released sulfur atoms can either remain in the adsorbed state on lanthanum oxysulfide or enter into the gas stream and leave the oxysulfide. In the presence of carbon monoxide, the atomic sulfur is also available for the reaction with carbon monoxide to form carbonyl sulfide:

$$S + CO = COS. \qquad [8]$$

At the time when carbonyl sulfide starts to form, there are already plenty of atomic sulfur on the oxysulfide ready to react with carbon monoxide so that there is a huge startup surge of carbonyl sulfide. When the atomic sulfur is nearly used up, the formation rate of carbonyl sulfide drops and is limited by the rate of supply of atomic sulfur which comes from the lattice volume farther away from the surface and is hindered by the diffusion of lattice sulfur through the lattice. Besides, it is expected that when more lattice sulfur leaves, the rest of the sulfur is held more tightly in the lattice.

To complete the reaction cycle for the reduction of sulfur dioxide and maintain the integrity of the lanthanum oxysulfide catalyst, the oxysulfide has to be replenished for the sulfur it has released, probably via the reaction of carbonyl sulfide with sulfur dioxide, which is the subject of another paper.

This study also provides a possible clue to account for why Baglio's lanthanum oxysulfide catalyst had only minimal activity for the catalytic reduction of sulfur dioxide and produced no carbonyl sulfide. A lengthy high temperature treatment to the oxysulfide in an inert gas stream such as helium could drive out most of the lattice sulfur in the surface of the oxysulfide while the remaining lattice sulfur is either more tightly held or deep in the crystal lattice. The treated oxysulfide would have nearly no sulfur available for the formation of carbonyl sulfide thus no catalytic activity for the reduction of sulfur dioxide. This kind of high temperature treatment is a commonly employed sample pretreatment technique.

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