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SHORT COMMUNICATION

Selective oxidation of hydrogen sulfide over $LaCoO_3$ and $LaSrCoO_4$ mixed oxides

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Abstract−Perovskite $LaCoO_3$ and perovskite-like $LaSrCoO_4$ mixed oxides were prepared by polyglycol gel method, and their catalytic performance was compared for the selective oxidation of hydrogen sulfide in a stream containing excess amount of ammonia and water for the first time. These samples were investigated by using XRD, BET, O_2-TPD and XPS. The catalytic activity and the selectivity to solid products (ammonium thiosulfate and elemental sulfur) of $LaCoO_3$ were better than those of $LaSrCoO_4$, and this is explained in terms surface contents of oxygen and cobalt, oxidation state of cobalt, and BET surface area.

Key words: Selective Oxidation, H_2S, $LaCoO_3$, $LaSrCoO_4$, Mixed Oxide

INTRODUCTION

A large amount of hydrogen sulfide is released from crude oil, natural gas refineries and metal smelting process in steel production. For many years, most of the hydrogen sulfide in petroleum refineries and natural gas plants has been removed by the well-known Claus process [1,2]. However, due to thermodynamic limitations, 3-5% of H_2S is typically not converted to sulfur. Therefore, tail gas clean-up processes have been developed using dry solids or wet absorption methods to improve the overall sulfur recovery efficiency from Claus plants. Commercially developed procedures include titanium-based catalysts in MODOP process [3,4], and iron-based catalysts in Super Claus process [5-7]. Some binary metal oxides, such as Bi-V-O [8] or Fe-Cr-O [9], have also been reported as catalysts for the gas phase conversion of H_2S to sulfur. Li et al. [10,11] reported V-Mo, V-Bi, V-Mg, Fe-Sn and Fe-Sb mixed oxide catalyst systems. Zeolites have also been reported as catalysts for the gas phase conversion of H_2S to sulfur [12,13].

At present, perovskite-type metal oxide catalysts have been widely used in hydrocarbon combustion and NO reduction [14-16]. However, they have not been studied for the selective oxidation of hydrogen sulfide to elemental sulfur; furthermore, no information is available about the use of these catalysts for the selective oxidation of H_2S containing NH_3 and excess water. The perovskite and perovskite-like mixed oxides showed high redox property in many reactions [17-20].

We reported a new vapor phase catalytic process for the selective conversion of H_2S in the stream containing both ammonia and water [21-28]. Vanadium oxide based catalysts showed good catalytic activities in the selective oxidation of the H_2S to ammonium thiosulfate (ATS) and elemental sulfur.

In this paper, Co-based mixed oxides $LaCoO_3$ and $LaSrCoO_4$ were prepared and characterized. Their catalytic activities were determined for the selective oxidation of H_2S in the stream containing both ammonia and water for the first time.

EXPERIMENTAL

1. Preparation and Characterization of Catalysts

$LaCoO_3$ and $LaSrCoO_4$ were prepared by polyglycol gel method [29]. Briefly, lanthanum, strontium, and cobalt nitrates in a desired molar ratio were dissolved in a citric solution at 80 °C with constant stirring. The polyglycol 20000 was added in when the solution was evaporated to 40 mL. Stirring was continued until a viscous gel was formed. The resulting gel was evaporated to dryness, and the obtained precursor was calcined at 650 °C for 6 h, followed by pelletization (precursor of $LaCoO_3$ need not be pelletized) and calcination once more at 850 °C in air for 12 h. The synthesized pellet was pulverized. Powder X-ray diffractometer (XRD type D/max-3B) patterns were recorded at room temperature, operating at 40 kV and 10 mA, using Cu Kα radiation combined with the nickel filter. The specific surface areas of catalysts were determined by a BET apparatus. X-ray photoelectron spectroscopy (XPS) was performed with a Perkin-Elmer PHI 5000C ESCA system using Al Kα radiation to determine the surface electronic states and surface compositions. The sample was dried in situ in pure Ar atmosphere to minimize the surface oxidation. All the binding energy values were calibrated by using C1s equal to 284.6 eV as a reference. Temperature-programmed desorption of O_2 was carried out in an in-house apparatus over 0.3 g catalyst. The samples were first treated at 850 °C in oxygen for 1 h and cooled to room temperature in the same atmosphere, then swept with helium at a rate of 30 mL/min until the base line on the recorder remained unchanged. Finally, the samples were heated at a rate of 10 °C /min in He for recording the O_2-TPD spectra.

2. Catalytic Activity Test

Reaction tests were carried out in a continuous flow fixed-bed reactor. The reactor was made of a Pyrex® tube with an i.d. of 0.0254 m. A condenser was attached at the effluent side of the reactor, and its temperature was held at 110 °C to condense only solid products (sulfur+ammonium thiosulfate). A line filter was installed after the condenser to trap any solid mist which had not been captured by the condenser. Water vapor was introduced to the reactant stream by an evaporator filled with small glass beads, and its amount was

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controlled by a syringe pump. The content of the effluent gas (H_2S, SO_2, and NH_3) was analyzed by gas chromatography (HP 5890) equipped with a thermal conductivity detector and a 1.83 m Porapak T column (80-100 mesh) at 100 °C. The conversion of H_2S (X) and the selectivity to a special product (SO_2, S, ATS) (S) are defined as follows:

$$X\,(\%)=\{([H_2S]_{inlet}-[H_2S]_{outlet})/[H_2S]_{inlet}\}\times 100$$

$$S\,(\%)=\{[product]_{outlet}/([H_2S]_{inlet}-[H_2S]_{outlet})\}\times 100$$

For the calculation of ATS selectivity, moles of ATS was multiplied by a factor of 2 because 1 mol of ATS can be obtained from 2 mols of H_2S.

RESULTS AND DISCUSSION

1. Characterization of Catalysts

XRD patterns of $LaCoO_3$ and $LaSrCoO_4$ mixed oxides are presented in Fig. 1. The results of phase analysis obtained by XRD clearly showed that $LaCoO_3$ was ABO_3 perovskite mixed oxide, and $LaSrCoO_4$ was tetragonal K_2NiF_4-type A_2BO_4 perovskite-like mixed oxide. The BET surface areas of $LaCoO_3$ and $LaSrCoO_4$ were 7.0 and 3.2 m^2g^{-1}, respectively.

Table 1 indicates binding energies of the main elements in the $LaCoO_3$ and $LaSrCoO_4$ catalysts. The XPS results demonstrated that the binding energy of Co $2p_{3/2}$ in $LaSrCoO_4$ was higher than that in $LaCoO_3$. Since higher binding energy of cobalt oxide corresponds lower oxidation state, it means that Co^{3+} ions in $LaCoO_3$ were more than those in $LaSrCoO_4$, which was advantageous in catalytic oxidation of hydrogen sulfide for $LaCoO_3$. Table 2 shows surface composition of La, Sr, Co and O for $LaCoO_3$ and $LaSrCoO_4$. The surface content of O in $LaCoO_3$ was more than that in $LaSrCoO_4$.

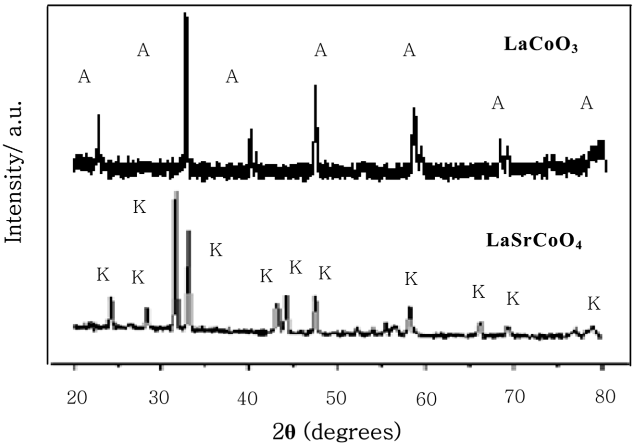

Fig. 1. XRD patterns of $LaCoO_3$ and $LaSrCoO_4$ catalysts (A: ABO_3, K: K_2NiF_4-type A_2BO_4).

Table 1. Binding energies of the main elements for $LaCoO_3$ and $LaSrCoO_4$ catalysts

Samples	Binding energy (eV)			
	La $3d_{5/2}$	Sr $3d_{5/2}$	Co $2p_{3/2}$	O1s
$LaCoO_3$	833.4	-	779.7	528.8
$LaSrCoO_4$	835.1	133.1	780.1	530.9

Table 2. Surface contents of the main elements in the $LaCoO_3$ and $LaSrCoO_4$ catalysts

Samples	Mol percent (%)			
	La $3d_{5/2}$	Sr $3d_{5/2}$	Co $2p_{3/2}$	O1s
$LaCoO_3$	16.71	-	6.94	76.35
$LaSrCoO_4$	9.98	6.63	11.82	71.57

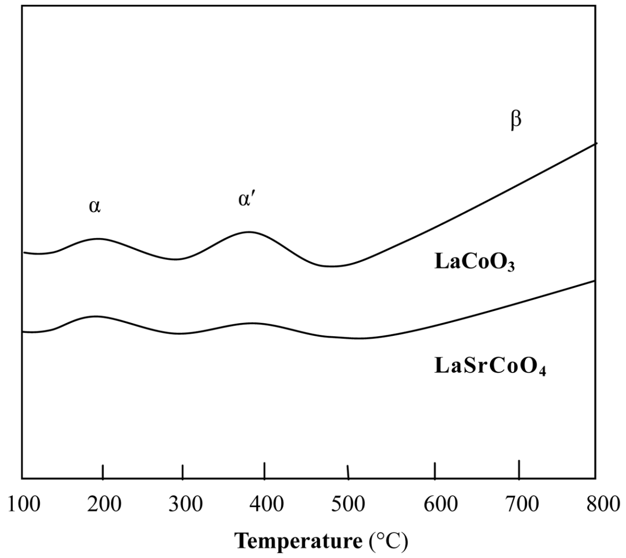

Fig. 2. O_2-TPD profiles for $LaCoO_3$ and $LaSrCoO_4$ catalysts.

Table 3. Conversion of H_2S versus reaction temperature over $LaCoO_3$ and $LaSrCoO_4$

Temperature (°C)	Conversion (%)	
	$LaCoO_3$	$LaSrCoO_4$
220	80.7	52.9
240	95.8	92.8
260	100	100
280	100	100
300	100	100

Reaction condition: $H_2S/O_2/NH_3/H_2O/He=5/2.5/5/60/27.5$, GHSV=30,000 h^{-1}, reaction time=2 h.

Fig. 2 shows O_2-TPD curves for $LaCoO_3$ and $LaSrCoO_4$. There are three O_2-desorption peaks (α, α' and β). The α peak (at ~200 °C) could be attributed to the ordinarily chemically adsorbed oxygen (O^2). α' peak (at ~385 °C) corresponding to the desorption of the oxygen chemically adsorbed on oxygen vacancies [20], namely, the oxygen was released by reduction of Co^{3+} according to the following reaction:

$$2\,Co^{3+}+O^{2-}\rightarrow 2\,Co^{2+}+Vo+1/2\,O_2 \qquad (1)$$

where Vo is oxygen vacancy. The β peak (~470-800 °C) might be attributed to the lattice oxygen. $LaCoO_3$ showed higher peak areas of α' and β than those of $LaSrCoO_4$.

2. Catalytic Activity in the Selective Oxidation of H_2S

The selective oxidation of hydrogen sulfide containing excess water and ammonia to elemental sulfur and ammonium thiosulfate [$(NH_4)_2S_2O_3$, ATS] was carried out in a continuous fixed-bed reactor. Table 3 shows conversion of H_2S versus reaction temperature for $LaCoO_3$ and $LaSrCoO_4$ at the standard reaction condition: $H_2S/O_2/NH_3/H_2O/He=5/2.5/5/60/27.5$, GHSV=30,000 h^{-1}, reaction time=2 h. Table 4 shows conversion of H_2S and product selectivity (SO_2, S, ATS) at 260 °C after 6 h of reaction. By comparing the experimental results, we found that the conversion of H_2S of $LaCoO_3$ was higher than that of $LaSrCoO_4$, and the selectivity to solid products (S and ATS) of $LaCoO_3$ was much better than that of $LaSrCoO_4$.

Table 5 shows H_2S conversion and selectivities to S and SO_2 without the presence of ammonia and water: $H_2/O_2/He=5:2.5:92.5$. One can also observe that $LaCoO_3$ showed higher H_2S conversion and higher selectivity to S than $LaSrCoO_4$ did.

Table 4. Conversion of H_2S and product selectivities at 260 °C after 6 h reaction.

Catalysts	X-H_2S (%)	S-SO_2 (%)	S-S (%)	S-ATS (%)
$LaCoO_3$	99.4	0.0	28.2	71.8
$LaSrCoO_4$	99.1	87.8	6.4	5.8

Reaction condition: $H_2S/O_2/NH_3/H_2O/He=5/2.5/5/60/27.5$, GHSV=30,000 h^{-1}.

Table 5. Conversion of H_2S and selectivities to S and SO_2 without the presence of ammonia and water

Catalyst	Temp. (°C)	X-H_2S (%)	S-SO_2 (%)	S-S (%)
$LaCoO_3$	240	92.4	1.4	98.6
	260	97.0	1.6	98.4
	280	98.1	1.8	98.2
$LaSrCoO_4$	240	58.9	2.5	97.5
	260	78.4	2.8	97.2
	280	92.5	3.1	96.9

Reaction condition: $H_2S/O_2/He=5/2.5/92.5$, GHSV=30,000 h^{-1}, reaction time=6 h.

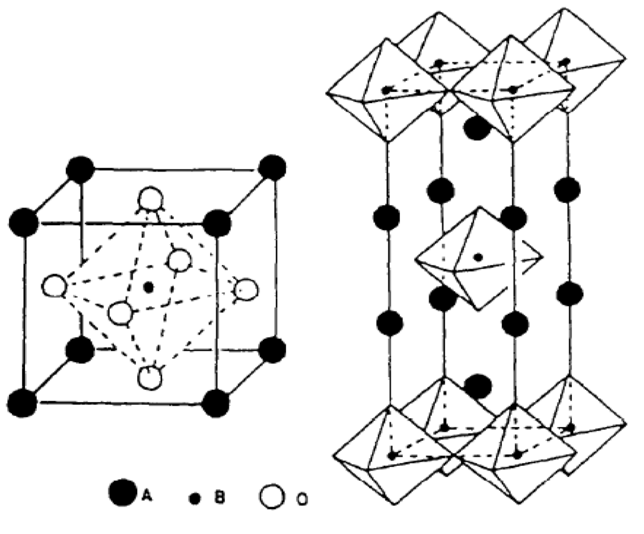

Fig. 3. Structure of $LaCoO_3$ and $LaSrCoO_4$ catalysts left to right: $LaCoO_3$ (ABO_3) and $LaSrCoO_4$ (A_2BO_4).

The oxidation mechanism over $LaCoO_3$ and $LaSrCoO_4$ can be proposed as reported previously [30]. Reactants are adsorbed on Co^{3+}, then react with lattice oxygen, whereas chemisorbed oxygen transforms into the lattice oxygen to reinforce consumed lattice oxygen. We can therefore deduce that Co^{3+} is active center, and lattice oxygen is active oxygen species.

The content of Co^{3+} and surface content of O in $LaCoO_3$ were more than those in $LaSrCoO_4$, which was caused by their structure as shown in Fig. 3 (A_2BO_4 mixed oxide consists of alternating layers of ABO_3 perovskite and AO rock salt), and it was confirmed by XPS. The amount of lattice oxygen was also high for $LaCoO_3$ as observed by O_2-TPD. In addition, the BET surface area of $LaCoO_3$ was larger than that of $LaSrCoO_4$. Therefore, higher oxidation state of Co, higher surface content of O, and higher amount of lattice oxygen combined with higher surface area were favorable for the good H_2S conversion and high selectivity to selective oxidation product, elemental sulfur and ATS over $LaCoO_3$ catalyst.

CONCLUSION

The perovskite $LaCoO_3$ and perovskite-like $LaSrCoO_4$ mixed oxides were prepared by the polyglycol gel method, and were used successfully for the selective oxidation of H_2S in the stream containing both ammonia and water for the first time. These samples were investigated by using the XRD, BET, O_2-TPD and XPS. The catalytic activity and the selectivity to solid products of $LaCoO_3$ were better than those of $LaSrCoO_4$, and this was explained by higher content of surface oxygen, higher oxidation state of cobalt, higher amount of lattice oxygen, and higher BET surface area of $LaCoO_3$ compared to $LaSrCoO_4$.

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