Simultaneous catalytic reduction of sulfur dioxide and nitric oxide

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The present work reports a catalytic system for the simultaneous reduction of SO_2 and NO using CO as a reducing agent. The catalyst contains lanthanum oxysulfide and cobalt sulfides. Experimental results showed that at temperature above 450 °C, SO_2 and NO conversions are greater than 98 and 99%, respectively.

Keywords: simultaneous reduction, sulfur dioxide, nitric oxide, carbon monoxide, carbonyl sulfide, lanthanum oxysulfide, cobalt disulfide

1. Introduction

Sulfur dioxide and nitrogen oxides are regulated air pollutants. They are usually emitted from industrial, transportation and domestic activities and in many occasions simultaneously. In addition to scrubbing processes, there are also catalytic as well as non-catalytic technologies to control these emissions. Prominent examples in the catalytic technology are the removal of sulfur dioxide by oxidation to form sulfuric acid and the selective catalytic reduction (SCR) of nitrogen oxides to nitrogen. However, none of these catalytic technologies can simultaneously remove these oxides, and in reality, sulfur dioxide is usually a chemical poison to the SCR catalysts. To remove both oxides, a combination deNOx and desulfurization technology is required. Noyes [1] gave an extensive review of commercially available processes for the removal of sulfur dioxide and NO_x. Usually, these combination technologies produce sufficient amount of solid/liquid wastes that require further disposal. Thus, a simultaneous removal technology, especially one which converts both oxides to their respective elemental forms, is highly desirable in terms of economics, design, and operation.

Our previous work [2–5] showed that lanthanum oxysulfide-based catalysts are active in the reduction of sulfur dioxide to elemental sulfur. It is also known that some transition or rare earth metal sulfates are able of catalyzing the reduction of NO_x [6–8]. Thus it seems possible to intricately balance the reactions between sulfur dioxide, nitric oxide and the reducing agent, using lanthanum oxysulfide-based catalysts, to simultaneously reduce the acid oxides to their respective elemental forms.

2. Experimental

The catalysts used in the present work were prepared by sulfidizing either lanthanum-containing perovskite-type oxides or lanthanum oxide according to the methods described in our previous work [2–5].

The structure of the catalysts before and after reaction was characterized using powder X-ray diffraction (Philips MPRD-1880 I X-ray diffractometer, Cu Kα radiation, $\lambda = 1.542$ Å). The surface area of the catalysts was measured using the BET method (Micromeritics ASAP2000).

The catalytic reaction was carried out in a fixed-bed flow reactor made of a 2 cm diameter, 50 cm long quartz tube. The reactor was externally heated using an electric furnace. The temperature of the catalyst bed was controlled to within 1 °C. A gas mixture containing sulfur dioxide (5.0%), nitric oxide (1.0%), carbon monoxide (11.0%) and nitrogen (balance) was diluted using nitrogen to make a feed containing 5000 ppm SO_2, 1000 ppm NO, and 1.1% CO. The flow rate of the feed was 180 ml/min measured at atmospheric pressure. The composition of the feed and effluent streams were monitored continuously using three Horiba non-dispersive infrared gas analyzers: a CFA-321 A unit for SO_2 and NO_x, a VIA-510 unit for CO, and another for CO_2. In addition, an HP 5890 Series II gas chromatograph with two columns and two TCD detectors was used in parallel to determine any of the by-products, such as COS, H_2S and CS_2, formed, as well as CO, CO_2 and SO_2 as a double check. Elemental sulfur was removed from the product gas stream by passing the gas through a sulfur trap and a filter with an average pore size of 2 μm. Catalytic activity was measured using 0.5 g of catalyst with a space velocity of 21,600 ml g^{-1} h^{-1}.

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3. Results and discussion

3.1. Reduction of NO by CO over sulfidized perovskite

The perovskite-type oxide, $La_{0.8}Sr_{0.2}CoO_3$, was sulfidized to catalyze the reduction of NO by CO (figure 1) and the conversion was greater than 90% above 550 °C. The major phases found in the catalyst were La_2O_2S and CoS_2. However, the NO reduction reaction could not be sustained (figure 2); the conversion decreased from 95 to 67% in 2 h. Elemental sulfur was found at the exit of the reactor; this sulfur could only have originated from the catalyst, which was the only possible sulfur source in the reactor system. XRD found that the CoS_2 was converted to lower cobalt sulfides such as $CoS_{1.097}$ and Co_3S_4 in the catalyst after reduction. This is consistent with our earlier study on the reduction of SO_2 by CO [2,5]; CO readily reacts with CoS_2 to form COS and lower cobalt sulfides. The elemental sulfur could be the decomposition product of COS or the reaction product of COS with other intermediates.

On the other hand, when the feed gas contained SO_2 in addition to NO and CO (figure 2), the reduction of NO was sustainable. This shows that the reduction of NO consumes sulfur in the catalyst and the replenishment of this sulfur species is essential for the sustainability of the catalytic reduction. If sulfur is not supplied from an appropriate source such as SO_2 in the feed, the catalyst will be gradually depleted of sulfur and deactivated.

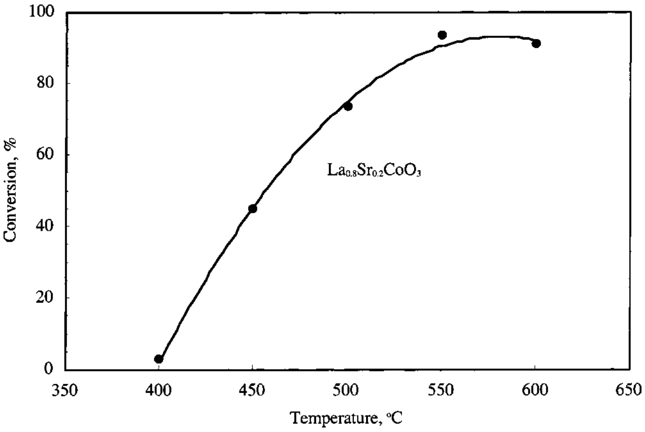

Figure 1. Reduction of NO over sulfidized perovskite by CO. The reaction temperature was increased stepwise from 400 to 600 °C. Conversion data was taken half an hour after the reaction temperature had been reached.

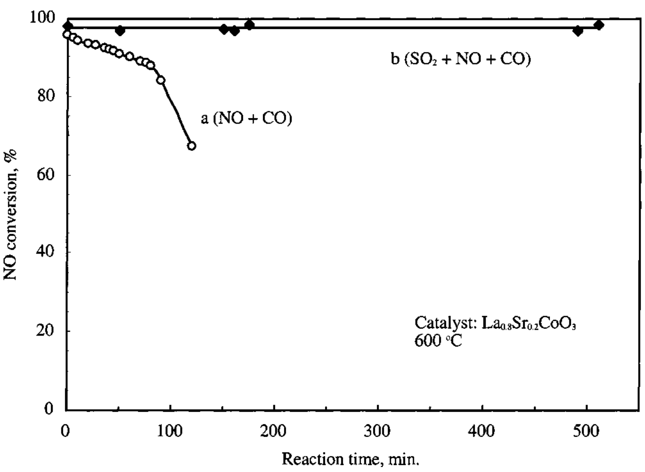

Figure 2. Sustainability of NO reduction.

3.2. Reaction of NO with COS

Figure 3 shows the high reactivity of COS towards NO. The reaction started at about 150 °C and the conversion of NO was almost completed at 450 °C. The NO reduction reaction was carried out with a feed containing 920 ppm NO and 920 ppm COS in nitrogen and La_2O_2S as the catalyst. It has been shown that COS reacts readily with SO_2 over La_2O_2S and is the crucial intermediate in the reduction of SO_2 by CO [3]. The reaction between CO and La_2O_2S produces COS [9]. Analogous to the reduction of SO_2 by CO on the La_2O_2S catalyst, it is expected that COS is also an intermediate in the reduction of NO by CO. The mechanism of the reduction of NO will be examined in detail in another paper.

3.3. Simultaneous reduction of NO and SO_2 by CO

3.3.1. Over CoS_2 or La_2O_2S

The results of the simultaneous reduction of SO_2 and NO by CO over CoS_2 are shown in figures 4 and 5. There was no conversion in NO and SO_2 before the temperature reached 400 °C; steady increases were observed as temperature rose to 600 °C. The CoS_2 catalyst gradually lost its desulfurization activity as the concentration of COS in the gas slowly dropped. This is because cobalt disulfide readily reacts with CO to form COS but is unable to catalyze the further reaction between SO_2 and COS [3]. On the other hand, high conversion of NO was maintained. The NO–CoS_2 interaction mechanism is unknown, but it seems that the interaction may be related to the vacancies formed after the CO reaction.

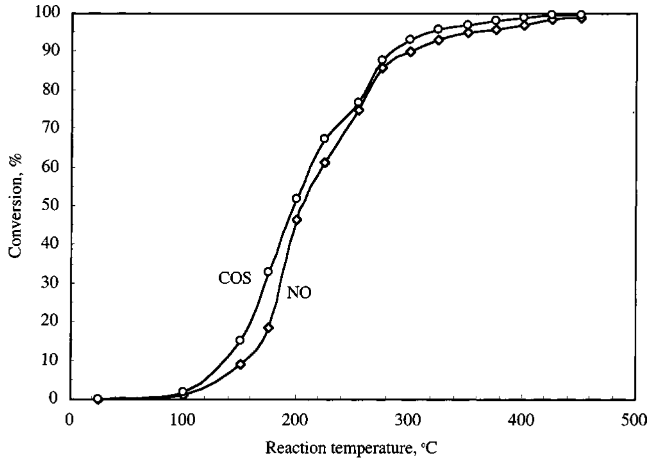

Figure 3. Catalytic reduction of NO by COS at steady state. The reaction temperature was increased stepwise from room temperature to 450 °C.

Unlike CoS_2, using La_2O_2S it was possible to maintain a steady simultaneous reduction of SO_2 and NO by CO. The conversion of SO_2 and NO at 600 °C was 84 and 95%, respectively. It is known that La_2O_2S is bifunctional due to its ability to deliver sulfur for the formation of COS and to catalyze the subsequent reaction between SO_2 and COS [4].

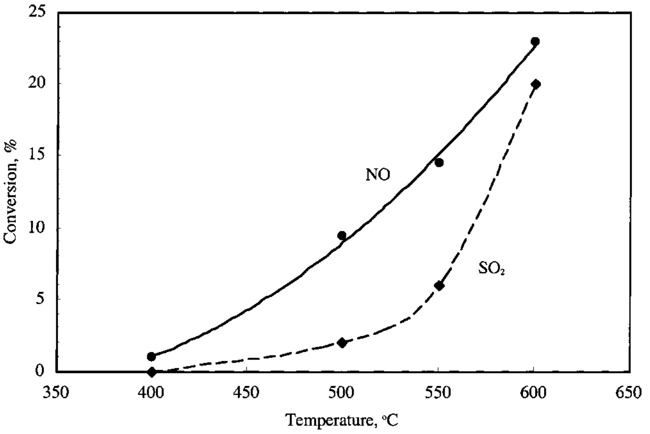

Figure 4. Simultaneous reduction of NO and SO_2 over CoS_2. The reaction temperature was increased stepwise from 400 to 600 °C. Conversion data was taken half an hour after the reaction temperature had been reached.

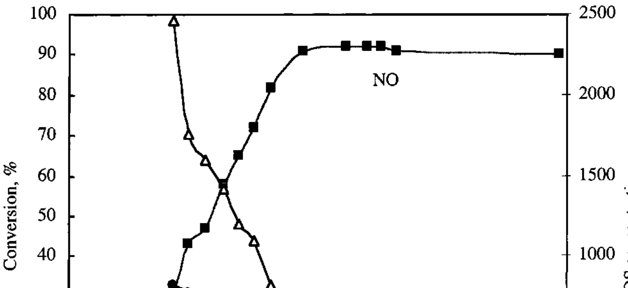

Figure 5. Time-on-stream conversion of NO and SO_2 over CoS_2. The reaction temperature was 600 °C.

3.3.2. Over a mixture of CoS_2 and La_2O_2S

The catalytic reduction of SO_2 and NO by CO over a mechanical mixture of CoS_2 and La_2O_2S (metal molar ratio Co : La = 7 : 3) is shown in figure 6. There was no conversion below 350 °C but it rapidly increased to over 80% in the 350–450 °C range; once over 500 °C more than 90% conversion was maintained. The concentration of COS in the gas phase increased abruptly when the reduction reactions began and also dropped abruptly to a low steady level at 450 °C.

3.3.3. Over sulfidized perovskites

The sulfidized perovskites $LaCoO_3$, $La_{0.8}Sr_{0.2}CoO_3$ and $La_{0.5}Sr_{0.5}CoO_3$ were found to be active in the simultaneous reduction of SO_2 and NO. The conversion of SO_2 and NO, and the concentration of COS residue in the gas phase between 400 and 600 °C are shown in table 1. In general, the conversion of NO and the concentration of COS increased with increasing temperature while conversion maxima for SO_2 over $LaCoO_3$ and $La_{0.8}Sr_{0.2}CoO_3$ were observed at 550 and 500 °C, respectively. The $La_{0.5}Sr_{0.5}CoO_3$ catalyst, which has the highest A-position substitution, had the lowest activity for both reduction reactions. The sulfidized catalyst contained CoS_2 and La_2O_2S, which are active com-

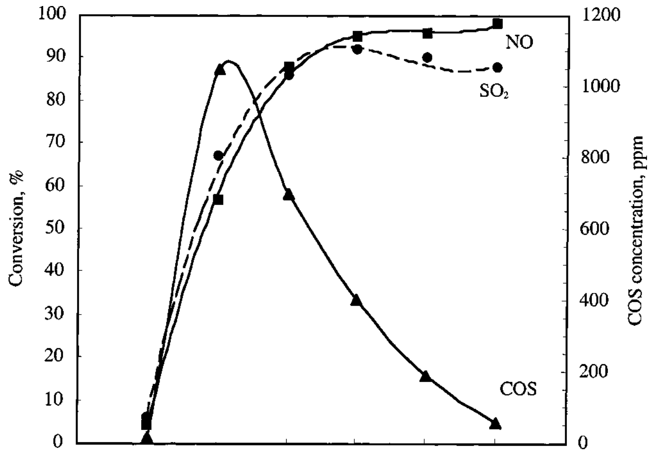

Figure 6. Simultaneous reduction of NO and SO_2 over a mechanical mixture of CoS_2 and La_2O_2S at steady state. The reaction temperature was increased stepwise from 350 to 600 °C.

Table 1
Conversion of SO_2 and NO, and concentration of COS in the gas for the simultaneous reduction of SO_2 and NO over Sr-substituted and non-substituted $LaCoO_3$.[a]

T	$LaCoO_3$			$La_{0.8}Sr_{0.2}CoO_3$			$La_{0.5}Sr_{0.5}CoO_3$		
(°C)	SO_2	NO	COS	SO_2	NO	COS	SO_2	NO	COS
400	46	30	1700	67	57	1060	48	39	1520
450	79	84	440	87	88	700	68	73	870
500	89	95	110	92	94	410	71	81	280
550	92	99	70	91	96	190	73	87	200
600	90	100	50	89	98	60	78	94	130

[a] Conversion in % and COS concentration in ppm.

ponents for the reduction of SO_2 [3], as well as some lower cobalt sulfides and strontium sulfide. Excess substitution by strontium made the active La_2O_2S less available and thus rendered the catalyst less active. Since the catalytic reduction of NO and SO_2 closely follows each other, the two reactions are probably interrelated, and the active catalytic components are likely to be the same.

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