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Catalytic properties of novel La–Sr–Cu–O–S perovskites for automotive C_3H_6/CO oxidation in the presence of SO_x

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Abstract

A La–Sr–Cu–O–S system with K_2NiF_4 perovskite-type structure has been studied as a novel SO_x-resistant combustion catalyst. The XRD result implied that sulfur is incorporated into the structure as non-sulfate-type cations. An introduction of sulfur with highly positive valence (S^{6+} or S^{4+}) into the lattice requires the charge compensation by decreasing the oxidation number of Cu. This is accompanied by the creation of more reducible Cu species, which would achieve the light-off of catalytic C_3H_6 oxidation at lower temperatures. More important feature of sulfur-containing compounds is that the catalytic C_3H_6 oxidation was significantly accelerated by addition of SO_2 to the gas feed. The catalytic performance for the oxidation of C_3H_6 and CO and the reduction of NO was finally evaluated in a simulated automotive exhaust in the presence of SO_2.

Keywords: Perovskite; Sulfur; Oxidation; Redox; Cu; C_3H_6

1. Introduction

Metal oxides with perovskite-type structure have extensively been studied as alternatives to noble metal catalysts for automotive emission control since 1970s [1]. The compounds which contain Mn or Co in the B-site of the perovskite structure are known as one of most active catalysts for the oxidation of hydrocarbons as well as CO. However, a serious problem is deactivation due to sulfur (SO_2) poisoning, because solid–gas reactions between SO_2 and perovskites are inevitable at high temperatures. Because many perovskite oxides contain alkaline earth or rare earth metals with a high basicity, the formation of sulfates from oxides is thermodynamically favorable in a wide temperature range. Several attempts have been made so far to overcome this problem by introducing Ru or Pt oxide less sensitive to SO_2 poisoning [2–4] and MgO as preferential adsorption site for SO_2 [5], or by seeking for sulfur bearing catalyst compositions [6–8]. Nevertheless, the development of SO_2-resistant perovskite catalysts remains unsolved even in the present stage. For the reason, a novel approach to design SO_x-resistant perovskite catalysts is strongly requested. In the present study, K_2NiF_4-type perovskite-related compounds, La–Sr–Cu–O–S, have been studied as a novel SO_2-resistant catalyst material. The effect of SO_2 in catalytic C_3H_6/CO oxidation was evaluated not only in a microreactor but also in an automotive-simulated reactor.

2. Experimental

$La_{2-x}Sr_xCuO_4S_y$ $(0 \leq x \leq 0.3,\ 0 \leq y \leq 0.3)$ compounds were synthesized by calcining stoichiometric mixtures of La_2O_3, $SrCO_3$, CuO, and $CuSO_4$ at 950 °C in air. The characterization was done by XRD, XRF, IR, XPS, TG, and TPR. The TPR measurement was conducted in a conventional flow reactor connected to a differential evacuation system. After evacuation at ambient temperature, the sample was heated in a flowing gas mixture of 10% H_2 and He (20 $cm^3\ min^{-1}$) at a constant rate (10 $°C\ min^{-1}$) up to 950 °C. Effluent gas from the sample was analyzed by a quadrupole residual gas analyzer mass spectrometer. Catalytic oxidation of C_3H_6 was examined in a conventional flow reactor at atmospheric pressure. The light-off characteristic was evaluated in a microreactor by heating the catalysts (0.2 g) from room temperature to 800 °C at constant rate of 2 $°C\ min^{-1}$ in a gaseous mixture of C_3H_6

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(0.2%), O_2 (0.5 or 5%), and N_2 (balance) supplied at 100 $cm^3\ min^{-1}$ (W/F = 0.002 g cat. min cm^{-3}). The sensitivity to SO_2 poisoning was evaluated during isothermal catalytic oxidation of C_3H_6 at ca. 400 °C by adding 20 ppm SO_2 to the gas feed and monitoring the change in C_3H_6 conversion to CO_2. Catalytic reactions were also carried out in a simulated automotive exhaust; 0.1% C_3H_6, 0.65% CO, 0.15% NO, 3% H_2O, 10 or 0.7% O_2, at space velocity (SV) of 200,000 h^{-1}.

3. Results and discussion

Perovskite oxides containing sulfur can be found in a series of studies directed toward high-temperature superconducting materials in 1990s. One example is the K_2NiF_4-type cuprate system, $La_{1.85}Sr_{0.15}Cu_{1-x}O_{4-x}(SO_4)_x$, in which sulfur is considered to be present in the form of sulfate ions (SO_4^{2-}) substituting ca. 10% of Cu site [9]. Another compound, $Ba_4YCu_xO_9(SO_4)_y$, which was also reported to contain SO_4 units substituting part of the Cu site in the structure, can accommodate larger amounts of sulfur up to $y = 0.8$ [10]. Although these materials are thermally stable, the catalytic property, chemical state, and stability of sulfur species in the perovskite structure have not been studied so far.

Fig. 1 shows the XRD patterns of $La_{2-x}Sr_xCuO_4S_{0.2}$ ($0 \leq x \leq 0.3$). As prepared compounds contained almost stoichiometric sulfur, but part of sulfur was deposited as $La_2O_2SO_4$ at lower x and as $SrSO_4$ at higher x. The composition with minimal impurities were determined to be $x = 0.3$. The diffraction pattern of the main phase is very similar to that of the $La_{1.85}Sr_{0.15}Cu_{1-x}O_{4-x}(SO_4)_x$ [9], but our X-ray structural analysis by means of the Rietveld method led to a different conclusion [11]. Fig. 2 shows the crystal structure model of the product with $y = 0$ and 0.2. The structural parameters for $y = 0$ is very similar to that reported for this material [12], in which La and Sr are distributed randomly in the A-site. For $y = 0.2$, sulfur is located in the interstitial site between adjacent two perovskite layers. Sulfur in this site is surrounded by four oxygens, but the S–O bond length (0.21 nm) is larger than that (0.15 nm) in a tetrahedral SO_4^{2-} ion. The compound contained about 50% of sulfur in the site in the K_2NiF_4 lattice, whereas other sulfur would be deposited as impurity ($SrSO_4$).

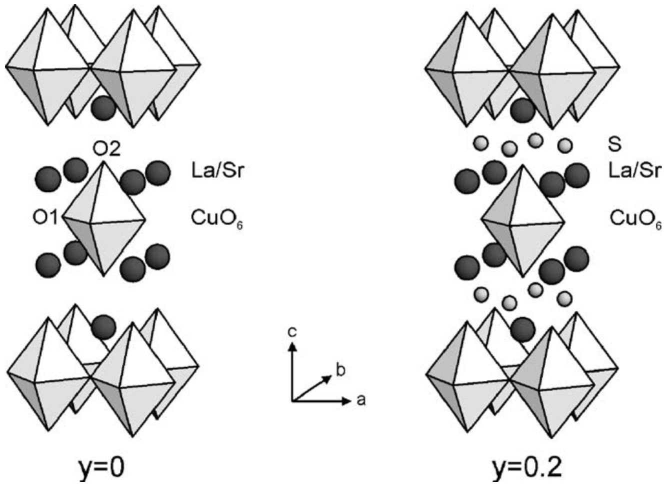

Fig. 2. Crystal structure of K_2NiF_4-type $La_{1.7}Sr_{0.3}CuO_4$ ($y = 0$) and $La_{1.7}Sr_{0.3}CuO_4S_{0.2}$ ($y = 0.2$).

The XRD analysis of the present study suggests that sulfur in the K_2NiF_4-type cuprate is not a sulfate. This is consistent with FT-IR results with no obvious absorption due to SO_4 groups. The XPS measurement showed the S 2p signals (E_B = 169 and 167 eV) similar to S^{6+} and S^{4+}. Although part of the S^{6+} signal comes from a $SrSO_4$ impurity, sulfur species in the structure should have highly positive valences. The TG analysis of $La_{1.7}Sr_{0.3}CuO_4S_y$ in a flowing H_2 showed that the oxidation number of Cu was decreased with increasing the S content. This is reasonable because the positive valence of sulfur in the lattice would be compensated by the oxidation number of Cu.

Thermal evolution of lattice oxygen as O_2 was very small from as prepared cuprates. Thus, the reduction behavior was studied by means of H_2-TPR technique as shown in Fig. 3.

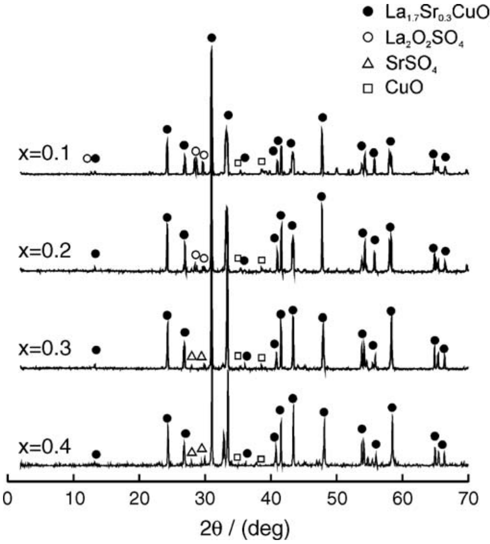

Fig. 1. XRD patterns of $La_{2-x}Sr_xCuO_4S_{0.2}$ after calcination at 950 °C in air.

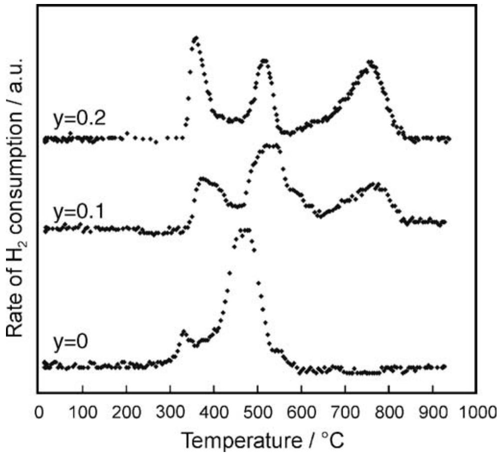

Fig. 3. TPR profiles of $La_{1.7}Sr_{0.3}CuO_4S_y$ in a stream of 5% H_2/He. Heating rate: 10 °C min^{-1}.

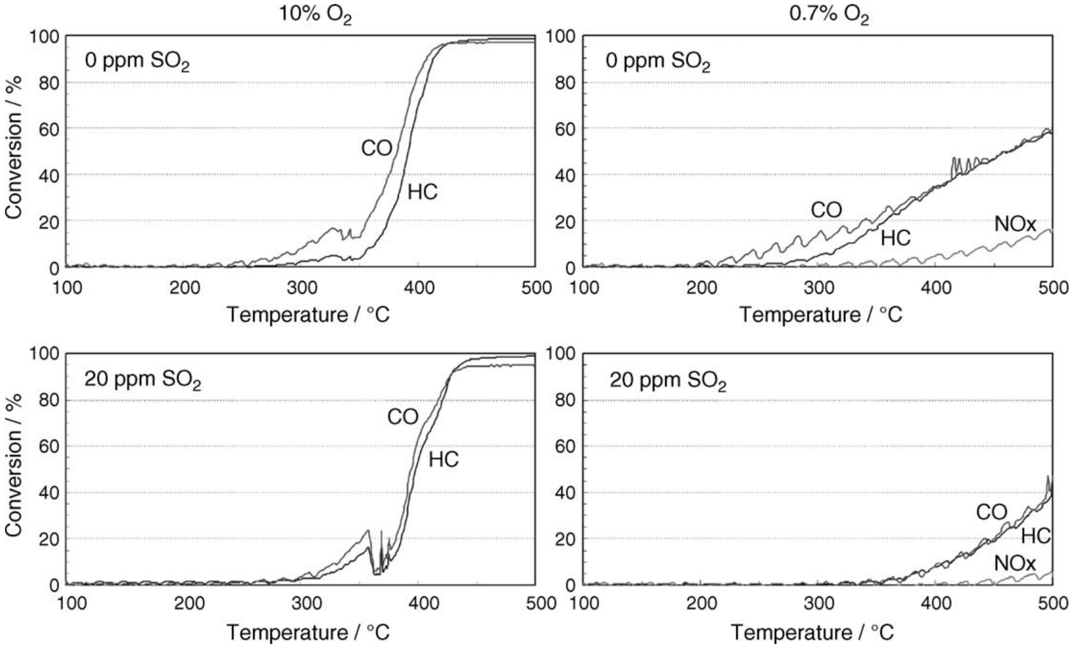

Fig. 4. Catalytic activity of the sulfur-containing phase ($y = 0.2$) for simulated automotive exhaust. 0.1% C_3H_6, 0.65% CO, 0.15% NO, 3% H_2O, 10 or 0.7% O_2, 0 or 20 ppm SO_2; SV = 200,000 h^{-1}.

When the pristine sample ($x = 0$) was heated in the stream of 10% H_2/He, two peaks due to H_2 consumption were observed at ca. 320 and 470 °C. A small peak at 320 °C is ascribable to the reduction of Cu^{3+} to Cu^{2+} and a large peak is due to the reduction of Cu^{2+} to Cu^0. The parallel XRD measurement indicated that the second peak was accompanied by the decomposition of K_2NiF_4-type perovskite to a mixture of La_2O_3, SrO, and Cu. On the contrary, the reduction peak split into two peaks at ca. 380 and 500 °C with an increase of the S content. This means that two Cu species with different reducibility were generated by introducing sulfur. Unlike the pristine compound, the sulfur-containing compound was decomposed into a mixture of La_2O_3, $SrSO_4$, and Cu. This is the reason why another reduction peak appeared at higher temperature of ca. 760 °C. The third peak can be assigned to the reduction of $SrSO_4$ (S^{6+}) to SrS (S^{2-}).

The catalytic activity of the sulfur-containing catalyst for the oxidation of C_3H_6 was carried out in a fixed bed microreactor. No significant change in the activity was observed irrespective of the sulfur content ($y \leq 0.2$). Nevertheless, the response to SO_2 was very interesting; the C_3H_6 conversion at 400 °C over sulfur-containing catalyst ($y = 0.2$) increased from 60 to more than 98% by supplying 20 ppm SO_2 in the presence of 5% O_2. The activity was very stable so that the conversion was kept almost constant during 50 h. Considering the concentration of SO_2 (20 ppm) much less than C_3H_6 (0.2%), direct interaction between these two reactants unlikely occurred. The XPS analysis showed that the amount of SO_2 adsorption onto the sulfur-containing phase was less than that onto a pristine phase ($y = 0$). However, the SO_2 adsorption onto sulfur-containing compounds may produce the adsorption species effective in enhancing the conversion of C_3H_6 in an excess O_2. A similar catalytic activation caused by SO_2 was reported for propane oxidation over supported Pt catalysts and was explained by increased chemisorption of propane [13]. The effect of SO_2 on the chemisorption in the present system is now under investigation.

The catalytic performance was also evaluated in a simulated automotive exhaust at a high velocity of SV = 200,000 h^{-1}. Fig. 4 exhibits conversions of C_3H_6, CO, and NO_x under lean (10% O_2) as well as stoichiometric (0.7% O_2) combustion conditions. Under a lean condition (10% O_2), steep rise in the conversion of C_3H_6 and CO occurred at >300 °C, whereas the reduction of NO_x was scarcely observed. The deactivation in light-off characteristics was not caused by introducing 20 ppm SO_2. In particular, the conversion of C_3H_6 in excess O_2 at ≤350 °C was rather gained by introducing SO_2, which is consistent with the result in a microreactor. Under a stoichiometric condition (0.7% O_2), the conversions increased very gradually with an increase of temperature and the reduction of NO took place at ≥400 °C. In this case, however, SO_2 caused the serious deactivation especially on the NO_x conversion.

4. Conclusions

The catalytic activity of sulfur-containing K_2NiF_4-type cuprates was studied in the presence of SO_2. The cationic sulfur in the lattice affected the oxidation state of Cu via the charge compensating mechanism. The activity of the sulfur-containing catalysts for C_3H_6 oxidation was found to be increased by SO_2 in an excess O_2, whereas the effect disappeared at low O_2 concentrations. In a simulated automotive exhaust at a high velocity, however, the effect of sulfur in the perovskite structure became less obvious.

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