Study on the poisoning mechanism of sulfur dioxide for perovskite $La_{0.9}Sr_{0.1}CoO_3$ model catalysts

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The reaction and poisoning mechanism of SO_2 with $La_{0.9}Sr_{0.1}CoO_3$ model catalysts have been investigated. The structure and the chemical states of the model catalysts have been studied by using AES, XPS and XRD techniques. The results indicated that SO_2 diffused into the $La_{0.9}Sr_{0.1}CoO_3$ film during poisoning. $La_2(SO_4)_3$ species was formed on the surface of the film and $La_2(SO_4)_3$, $La_2(SO_3)_3$, $La_2O_2SO_4$ and CoO species were found in the interior. The perovskite structure of $La_{0.9}Sr_{0.1}CoO_3$ was destroyed by invasion of SO_2. The concentration of sulfur in the film layer was related to the reaction temperature and time. After the sample was poisoned for a fairly long time, the distribution of sulfur in the $La_{0.9}Sr_{0.1}CoO_3$ layer became homogeneous, suggesting that a dynamic equilibrium was achieved between the poisoning reaction and the decomposition of the sulfates. XRD and catalytic activity test results proved that the destruction of perovskite structure and the formation of sulfates were the main causes of deactivation.

KEY WORDS: $La_{1-x}Sr_xCoO_3$; SO_2-poisoning; perovskite.

1. Introduction

The traditional noble metal catalysts are widely used for the purification of automotive pollutants. Although these catalysts are very effective in redox reactions for automotive exhaust gases, they are rare, expensive and easily lose activity. Non-noble metal catalysts such as the perovskite-based catalysts ABO_3 have attracted the attention of many researchers recently [1–3]. They are called three-way catalysts because they are effective for CO oxidation, HC complete oxidation and NO reduction at the same time. $La_{1-x}Sr_xCoO_3$ is one of the most promising perovskite catalysts. A major limitation for wide use of perovskite catalysts is sulfur poisoning [4].

SO_2 can severely inhibit NO reduction and reduce the oxygen storage capacity of the catalyst. Sulfates and sulfite are formed in catalysts after the catalysts were poisoned by SO_2. Based on the temperature and the composition of the catalysts, the sulfur species SO_2, SO_3, SO_3^{2-}, H_2SO_4, SO_4^{2-}, S^{2-} or H_2S have been reported [5,6]. However, the poisoning mechanism and process are not very clear, especially for perovskite oxide catalysts.

The sulfur-resistant property of the perovskite catalyst can be improved in a few ways, such as adjusting its components. It is believed that a thorough study of the sulfur poisoning mechanism will provide a good guide. In this work, $La_{1-x}Sr_xCoO_3$ film and powder model catalysts were used as simplified samples to investigate the poisoning mechanism. The $La_{0.9}Sr_{0.1}CoO_3$ model catalyst with perovskite structure was obtained using an amorphous complex of $La_{0.9}Sr_{0.1}Co(DTPA)\cdot 6H_2O$ as a precursor [7,8]. The poisoning species and structure were studied by using AES, XPS and XRD.

2. Experiment

2.1. Preparation and treatment

$La_{0.9}Sr_{0.1}CoO_3$ film was deposited on TiO_2/Si substrate using spin-coating of 15% $La_{0.9}Sr_{0.1}Co(DTPA)\cdot 6H_2O$ solution as a precursor. TiO_2 substrate layer was deposed onto a silicon wafer by spin-coating using 10% $Ti(OBu)_4$ sol as a precursor. The rate of spin-coating was 3000 rpm. The perovskite structure of $La_{0.9}Sr_{0.1}CoO_3$ was formed even after the precursor was calcined at as low as 600 °C for 1 h in air.

The $La_{0.9}Sr_{0.1}CoO_3/TiO_2/Si$ film with perovskite structure was obtained after calcination at 700 °C for 1 h in air. The thickness of $La_{0.9}Sr_{0.1}CoO_3$ film was about 100 nm by the analysis of the AES depth profile spectrum. The film model catalyst was poisoned with 0.01% SO_2 (the base gas is N_2). The purity of SO_2 and N_2 gas was 99.99 and 99.999%, respectively. The film was poisoned at 500, 600 and 700 °C for 8 h and also at 600 °C for 1, 4, 8, 12 and 20 h in order to study the effects of poisoning temperature and time.

The $La_{0.9}Sr_{0.1}CoO_3$ powder catalyst was obtained from the precursor after calcination at 700 °C for 2 h in air. The average grain size of the powder was about

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20–30 nm based on the results of TEM. The powder model catalyst was poisoned with 1% SO_2 at 700 °C for 0.5 and 3 h.

Catalytic activity tests were performed on fresh and poisoned catalysts. A gas mixture of 50 ml/min (composition: 1.8% CO, 0.9% O_2, balance Ar) was fed to a fixed bed of 0.1 g catalyst particles. The reactor temperature was increased from room temperature to 600 °C, and meanwhile the CO concentration was analyzed by using a GC analyzer. The starting temperature (T_0), half-conversion temperature (T_{50}) and complete conversion temperature (T_{100}) were measured.

2.2. Analysis techniques

The AES spectra were obtained using the PHI 610 SAM system. A coaxial electron gun with a single-pass cylindrical mirror analyzer (CMA) was used. The energy resolution of the CMA was set at 0.3% to obtain a good energy resolution. For AES analysis, the electron beam energy and the beam current were 3.0 keV and 0.5 μA, respectively. The electron beam was incident at an angle of 60° with respect to the specimen surface. The base pressure of the chamber was better than 3×10^{-9} Torr. During the depth profile analysis, the energy and beam current of the Ar ion beam were 3.0 keV and 6 μA, respectively. The beam diameter was 1 mm, and the sputtering rate was calibrated to be 30.0 nm/min using thermal oxidized SiO_2 thin film. The electron charge effect was not found for the film sample.

The XPS spectra were obtained using the PHI 5300 ESCA system with an Al K_α X-ray source. A power of 250 W and a pass energy of 37.5 eV were used during the experiment. The base pressure of the analysis chamber was better than 5×10^{-9} Torr. All spectra were calibrated using the binding energy of C 1s (285.0 eV) as a reference. The sputtering rate was calibrated to be 4 nm/min for thermal oxidized SiO_2 film. XRD experiments were carried out in a Rigaku DMAX-2400 diffractometer with Cu K_α radiation.

3. Results and discussion

3.1. Diffusion and reaction of SO_2 in $La_{0.9}Sr_{0.1}CoO_3$ film catalyst

The diffusion and reaction of SO_2 in film catalyst of $La_{0.9}Sr_{0.1}CoO_3/TiO_2/Si$ was studied using AES. Figure 1 shows a typical AES depth profile spectrum of $La_{0.9}Sr_{0.1}CoO_3/TiO_2/Si$ model catalyst, which was poisoned at 600 °C for 20 h. The thickness of the $La_{0.9}Sr_{0.1}CoO_3$ layer was about 100 nm. The interface between the $La_{0.9}Sr_{0.1}CoO_3$ layer and the TiO_2 layer was very wide, implying that the active component of $La_{0.9}Sr_{0.1}CoO_3$ had diffused into the TiO_2 substrate and reacted with the layer during thermal treatment. Some $La_2(TiO_3)_3$ species were formed on the surface. After the film catalyst was poisoned at 600 °C for 20 h, sulfur diffused into the $La_{0.9}Sr_{0.1}CoO_3$ layer and the TiO_2 substrate. The concentration of sulfur decreased gradually in the $La_{0.9}Sr_{0.1}CoO_3$ layer. The maximum concentration of sulfur in the $La_{0.9}Sr_{0.1}CoO_3$ layer was about 3.0%.

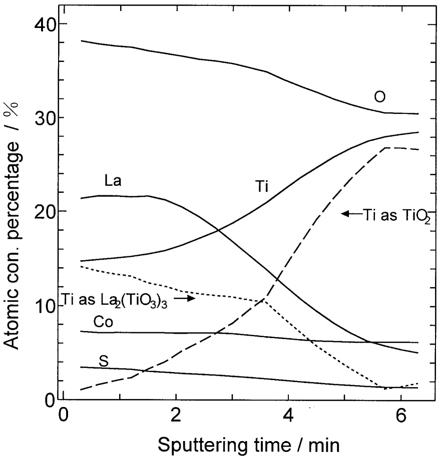

Figure 1. The AES depth profile spectrum of the film model catalyst after being poisoned at 600 °C for 20 h.

The chemical states of La in various depths of the poisoned sample were also studied using AES line shape analysis. Figure 2 shows the La MVV spectra in various depths of this model poisoned catalyst. On the surface, the kinetic energy of La MVV was 75.1 eV, which can be attributed to the $La_2(SO_4)_3$ species. With increasing depth, the kinetic energy shifted from 75.1 to 73.9 eV. This can be explained as the formation of $La_2(SO_3)_3$ species in the layer.

The above results indicate that SO_2 diffused into the $La_{0.9}Sr_{0.1}CoO_3$ layer and reacted with $La_{0.9}Sr_{0.1}CoO_3$

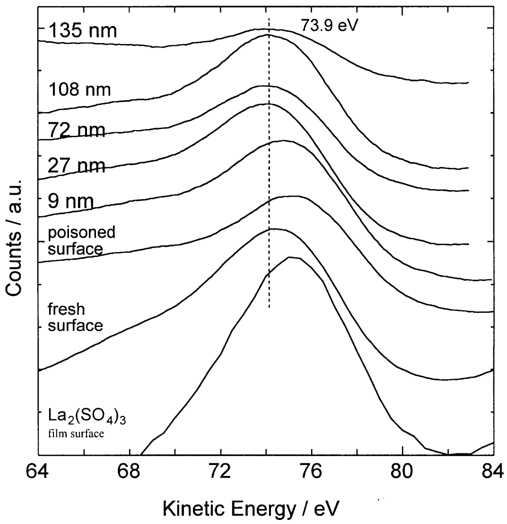

Figure 2. The La MVV line shapes of the film model catalyst poisoned at 600 °C for 20 h at various depths.

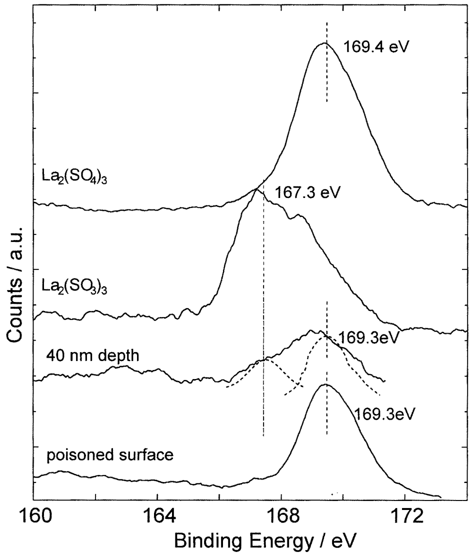

Figure 3. The S 2p spectra of the surface and 40 nm depth in the poisoned sample with 0.01% SO_2 at 600 °C for 20 h.

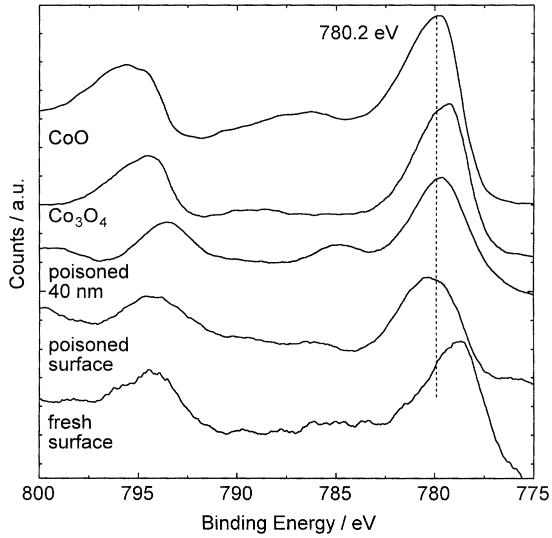

Figure 4. The Co 2p spectra of the surface and 40 nm depth in the poisoned sample with 0.01% SO_2 at 600 °C for 20 h compared with the fresh $La_{0.9}Sr_{0.1}CoO_3$ film surface.

to form sulfates and sulfites. The invasion of sulfur destroyed the $La_{0.9}Sr_{0.1}CoO_3$ complex oxide catalyst.

3.2 *Chemical states of $La_{0.9}Sr_{0.1}CoO_3$ film catalyst after the poisoning*

Figure 3 shows S 2p spectra of the film model catalyst, which was poisoned with SO_2 at 600 °C for 20 h. On the poisoned surface, the binding energy of S 2p was about 169.3 eV, which can be attributed to sulfate. At a depth of 40 nm, the peak of S 2p became broad. Two peaks can be distinguished after fit. The binding energies were 167.3 and 169.2 eV, which can be attributed to sulfite and sulfate, respectively [9]. The sulfate was the main product on the surface and the mixture of sulfite and sulfate was formed in the layer after SO_2 poisoning.

The Co 2p spectra of $La_{0.9}Sr_{0.1}CoO_3$ film poisoned at 600 °C for 20 h are shown in figure 4. The binding energies of Co $2p_{3/2}$ in Co_2O_3, Co_3O_4 and CoO oxides were 779.6, 779.8 and 780.4 eV, respectively [10]. The binding energy of Co $2p_{3/2}$ in $La_{0.9}Sr_{0.1}CoO_3$ fresh film was 778.8 eV, which was lower than that in simple cobalt oxides, implying that Co did not exist as simple cobalt oxides. The shake-up peaks were very weak, indicating that Co existed in $La_{0.9}Sr_{0.1}CoO_3$ film as a low-spin Co(III) compound [11]. After the model catalyst was poisoned with SO_2 at 600 °C for 20 h, the binding energy of Co $2p_{3/2}$ increased to 780.2 eV, which can be attributed to CoO species. A strong shake-up peak appeared and the line shape was similar to that of CoO species. The appearance of strong shake-up peaks implied that the Co existed as high-spin Co(II) species, which may exist as CoO species.

The binding energy of La 3d in the $La_{0.9}Sr_{0.1}CoO_3$ film was 832.2 eV (figure 5). After the film model catalyst was poisoned at 600 °C for 20 h, the binding energy of La 3d on the surface shifted to 834.2 eV, which resulted from the formation of $La_2(SO_4)_3$ species. At a depth of 40 nm, the binding energy of La $2d_{5/2}$ decreased to 833.2 eV, which can be attributed to the formation of $La_2(SO_3)_3$ species. The sulfates and CoO were formed on the surface, while the main products in the layer were sulfates, sulfites and CoO species.

3.3. *Effect of temperature and time on the poisoning of SO_2*

Figure 6 shows the AES depth profile spectra of S in the film model catalyst poisoned at 600 °C for different

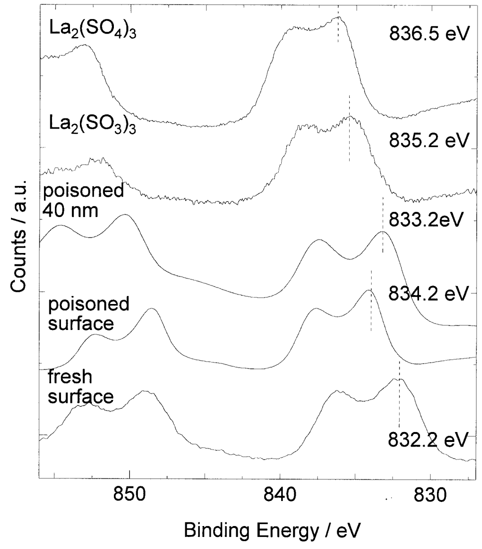

Figure 5. The La 3d spectra of the surface and 40 nm depth in the poisoned sample with 0.01% SO_2 at 600 °C for 20 h compared with the fresh $La_{0.9}Sr_{0.1}CoO_3$ film surface.

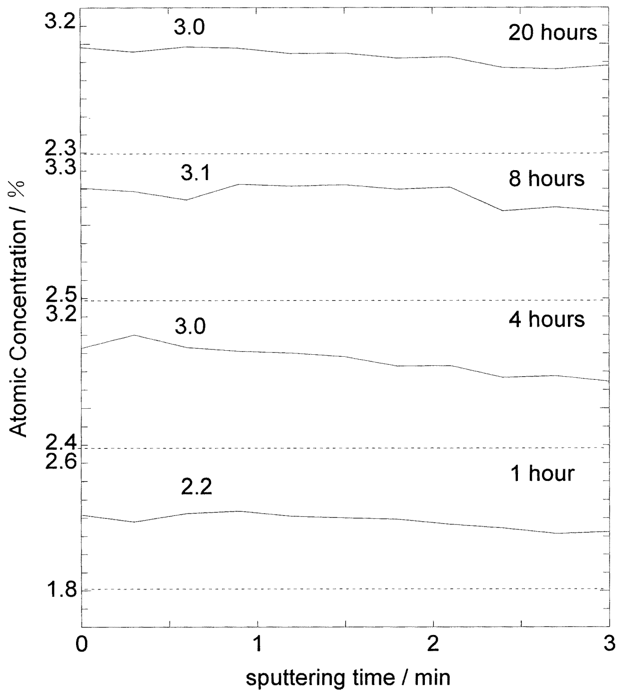

Figure 6. Atomic content of S as a function of sputtering time (*i.e.*, depth) for various poisoning times with 0.01% SO_2 at 600 °C.

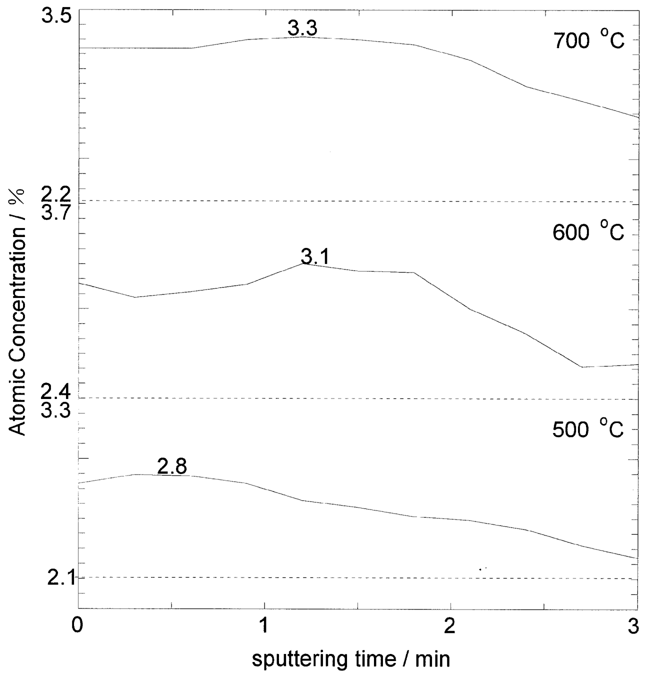

Figure 7. Atomic content of S as a function of sputtering time (*i.e.*, depth) at various poisoning temperatures with 0.01% SO_2 for 8 h.

times. When the poisoning time was 1 h, the atomic concentration of the sulfur element in the catalyst layer reached 2.2%. After the reaction time increased to 4 h, the maximum concentration of sulfur increased to 3.0% and the highest concentration of sulfur was at a depth of about 20 nm. When the poisoning time increased to 8 h, the maximum increased to 3.1% and the diffusion depth also increased. The maximum was at a depth of 30 nm. As to 20 h, the maximum concentration of sulfur decreased to 3.0%, while the distribution became more homogeneous. It was related to the dynamic equilibrium between the poisoning reaction and the decomposition reaction.

The effect of temperature on the poisoning reaction was also studied. The catalyst was poisoned at 500, 600 and 700 °C for 8 h. Figure 7 shows the distribution of sulfur at various poisoning temperatures. The maximum concentration of sulfur was about 2.8% after being poisoned at 500 °C for 8 h. When the model catalyst was poisoned at 600 °C for 8 h, the concentration of sulfur increased to about 3.0%. After being poisoned at 700 °C, the maximum concentration of sulfur reached 3.3%. It can be concluded that the concentration of the sulfites and sulfates increased with rising reaction temperature.

3.4 *Effects of SO_2 poisoning on the structure and performance of model catalyst*

The XRD patterns of $La_{0.9}Sr_{0.1}CoO_3$ perovskite film catalyst are shown in figure 8. After the sample was poisoned with 0.01% SO_2 at 600 °C for 12 h, the perovskite peaks became much lower and smaller, implying that the perovskite structure of $La_{0.9}Sr_{0.1}CoO_3$ was partly destroyed by SO_2. Several impurity diffraction peaks appeared, which can be attributed to lanthanum oxide sulfate. Based on the above results, it can be concluded that the poisoning product of $La_2(SO_4)_3$ in the film decomposed to $La_2O_2SO_4$ at the atmosphere of SO_2 at 600 °C.

Figure 9 shows the TEM of the fresh $La_{0.9}Sr_{0.1}CoO_3$ powder. It can be seen in the figure that the grain size of obtained fresh powder was homogenous and fairly small. But after poisoning, the particles grew larger and began to gather. The XRD patterns (figure 10) also

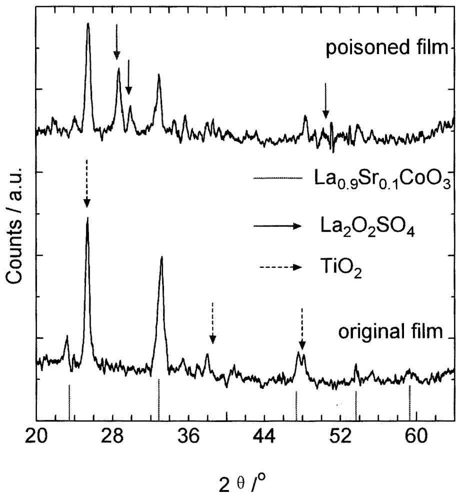

Figure 8. The XRD patterns of $La_{0.9}Sr_{0.1}CoO_3$ film catalyst before and after poisoning by 0.01% SO_2 at 600 °C for 12 h.

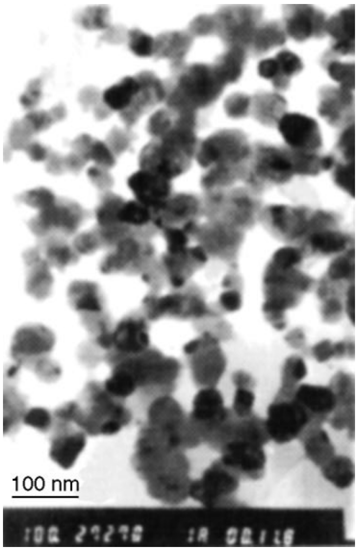

Figure 9. TEM image of the fresh $La_{0.9}Sr_{0.1}CoO_3$ powder catalyst.

demonstrate that the perovskite was partly destroyed and some new species ($La_2O_2SO_4$ and CoO) were found after the powder catalyst was poisoned with 1% SO_2 at 700 °C for 0.5 h. After being poisoned for 3 h, the peaks of the perovskite almost disappeared and the peaks of $La_2O_2SO_4$ and CoO were stronger. The perovskite structure was almost completely destroyed and some products such as $La_2O_2SO_4$ and CoO were obtained after being poisoned, consistent with the results of film catalyst.

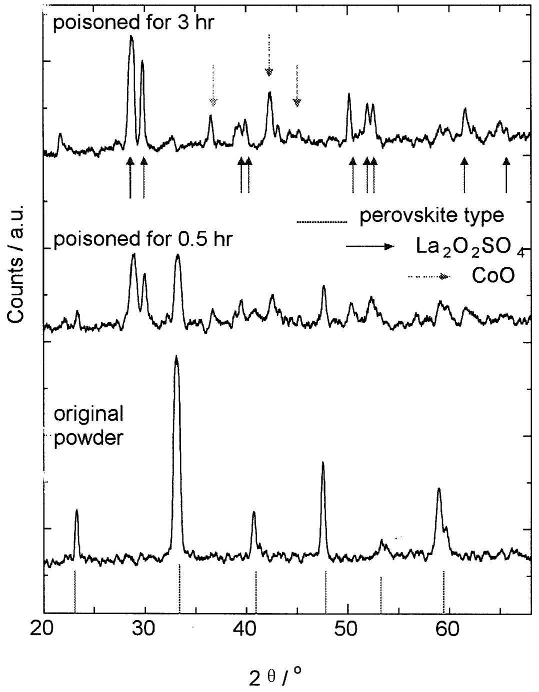

Figure 10. The XRD of $La_{0.9}Sr_{0.1}CoO_3$ powder before and after being poisoned with 1% SO_2 at 700 °C for different time.

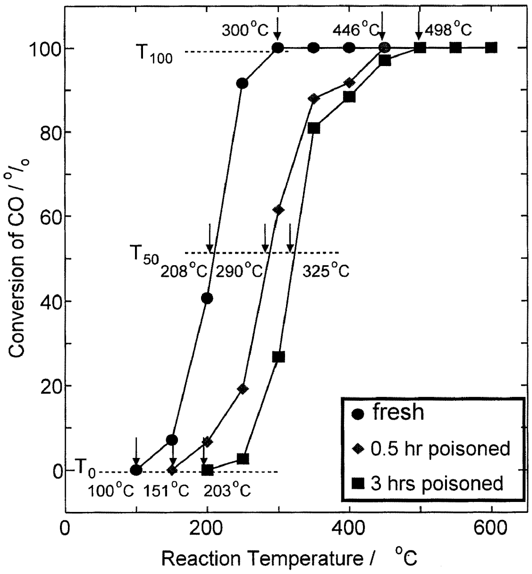

Figure 11. Catalytic activity test results for CO combustion in the $CO + O_2 \rightarrow CO_2$ reaction of fresh and poisoned $La_{0.9}Sr_{0.1}CoO_3$ powder catalyst.

The catalytic activities for the CO combustion reaction ($CO + O_2 \rightarrow CO_2$) of the fresh and poisoned $La_{0.9}Sr_{0.1}CoO_3$ powder catalyst were measured. The results are shown in figure 11. The meanings of T_0, T_{50} and T_{100} are defined as follows.

T_0 is the temperature at which a noticeable amount of CO disappeared (about 1% conversion). T_{50} is the temperature at which half of the amount of the concentration of CO has reacted. T_{100} is the temperature at which the CO was completely converted into CO_2

The fresh catalyst showed a comparable good catalytic activity (T_0 value of 100 °C, T_{50} of 208 °C and T_{100} of 300 °C) [12]. After being poisoned at 700 °C for 0.5 h, the T_0 (151 °C), T_{50} (290 °C) and T_{100} (446 °C) increased, implying the activity decreased. After the catalyst was poisoned for 3 h, the T_0, T_{50} and T_{100} increased to 203 °C, 325 °C and 498 °C respectively. The above results showed the deactivation became more serious with the prolonging of poisoning time.

It can be concluded from XRD and catalytic activity test results that the perovskite structure of $La_{0.9}Sr_{0.1}CoO_3$ was destroyed after SO_2 poisoning. The main product is $La_2(SO_x)_3$, $La_2O_2SO_4$. The mechanism of poisoning reaction may be explained as

$$La_{0.9}Sr_{0.1}CoO_3 + SO_2 \rightarrow La_2(SO_x)_3 + CoO + SrSO_4 \text{ (or } SrSO_3\text{)} \tag{1}$$

$$La_2(SO_4)_3 \rightarrow La_2O_2SO_4 + SO_3. \tag{2}$$

The destruction of the perovskite structure and the formation of some new phases led to the deactivation. The perovskite structure was destroyed more seriously when the poisoning time became longer.

Based on the results of AES, XPS and XRD, it can be concluded that SO_2 reacted with $La_{0.9}Sr_{0.1}CoO_3$ catalyst to form $La_2(SO_4)_3$, $La_2(SO_3)_3$, $La_2O_2SO_4$ and CoO species. High temperature can promote the decomposition of sulfates and sulfites, but the perovskite structure of $La_{0.9}Sr_{0.1}CoO_3$ cannot recover. SO_2 poisoning of $La_{0.9}Sr_{0.1}CoO_3$ catalyst was not reversible.

4. Conclusions

1. SO_2 diffused into $La_{0.9}Sr_{0.1}CoO_3$ model catalyst and reacted with $La_{0.9}Sr_{0.1}CoO_3$ to form $La_2(SO_4)_3$, $La_2(SO_3)_3$, $La_2O_2SO_4$ and CoO species during the SO_2 poisoning process.
2. The diffusion of sulfur increased with reaction temperature and time. The distribution of sulfur in the film became more homogeneous after a long reaction time of about 20 h.
3. The perovskite structure of $La_{0.9}Sr_{0.1}CoO_3$ was destroyed by the invasion of sulfur. Sulfates and a CoO phase were formed. Sulfates and sulfites would decompose at high temperature, but the perovskite phase cannot reform. Catalytic activity decreased due to the destruction of the perovskite structure.

Acknowledgments

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