

# Poisoning mechanism of perovskite $\text{LaCoO}_3$ catalyst by organophosphorous gas

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## Abstract

The reaction and poisoning mechanism of organophosphorous gas with  $\text{LaCoO}_3$  model catalyst have been studied. Organophosphorous gas diffused into  $\text{LaCoO}_3$  model catalyst and reacted to form some new species such as  $\text{LaPO}_4$ ,  $\text{La}_4(\text{P}_2\text{O}_7)_3$  and  $\text{CoO}$ , which resulted in the distortion and destruction of perovskite structure. The residual concentration of phosphorus in the catalyst layer reached a maximum after the catalyst was poisoned at  $600^\circ\text{C}$  for 2 h. The diffusion depth of phosphorus in  $\text{LaCoO}_3$  layer increased with poisoning temperature and time. After the model catalyst was poisoned at a high temperature above  $700^\circ\text{C}$  or for a longer period, the distribution of phosphorus in the  $\text{LaCoO}_3$  layer became homogeneous and the distribution peak of P concentration shifted into the layer. The catalytic performance test for oxidation of CO indicated that the formation of phosphate and the destruction of the perovskite structure in  $\text{LaCoO}_3$  catalyst layer resulted in the deactivation of the perovskite catalyst.

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**Keywords:**  $\text{LaCoO}_3$ ; Phosphorous poisoning; Perovskite structure

## 1. Introduction

Perovskite oxides based on  $\text{ABO}_3$  type, especially with rare earths, have been considered the most promising three-way catalysts as the substitute of the traditional noble-metal catalysts and catalytic combustion catalyst for the purification of automotive pollutants [1–4]. However, there are still many unsolved problems with perovskite-based catalysts, such as catalytic activity, thermal stability and resistance to potential poisons in fuel or from oil additives such as S and P.

Lubricating oil is indispensable for wear protection of the mechanical parts of engines. However, it has deleterious phosphorous poisoning impact on catalyst activity. The essential additive of engine lubricant is organophosphate such as tri-*o*-cresyl phosphate [5,6]. Not much information has been presented on the retention of phosphorous poisons. Some investigations about phosphorous poisoning were carried out for noble-metal catalysts [7–9]. General

consensus is that deactivation occurs mainly by pore mouth poisoning of the catalyst particles. The  $\text{La}_2\text{O}_3$  promoted Pt or Pd catalysts have exceptional thermal stability while poisoned by 1–5 wt.% phosphorus. The significant activity loss was expected, depending upon the degree of phosphorus accumulation. Ford Research and Advanced Engineering Laboratory has studied the phosphorous poisoned products of Pd catalyst [10,11]. The phosphate covering the noble-metal particles hinders the flow of gases through the catalytic converter. Recently, some studies have confirmed the presence of cerium phosphate in aged automotive catalysts [12,13]. The extended study of Ford Research and Advanced Engineering Laboratory provided the direct evidence of a decrease in oxygen storage capacity associated with the irreversible conversion of  $\text{CeO}_2$  to  $\text{CePO}_4$ , and identified  $\text{CePO}_4$  formation as a high-temperature mode of catalyst deactivation [14]. Until now, there are few reports on the poisoning mechanism of perovskite oxides by phosphorous.

The poisoning effect of phosphorous on perovskite structure and catalytic activity of  $\text{LaCoO}_3$  was confirmed in

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this report. LaCoO<sub>3</sub> film model catalyst was used in this research, which has comparability with real catalysts and has been adopted in our previous work about SO<sub>2</sub> poisoning and the interface interaction between LaCoO<sub>3</sub> active layer and Al<sub>2</sub>O<sub>3</sub> substrate. Such method is efficient and explicit to characterize the chemical structure of catalysts [15,16]. It is much easier and clearer to study the extent of the poisoning and the chemical nature of the poisoning species. The LaCoO<sub>3</sub> model catalyst with perovskite structure was prepared using an amorphous heteronuclear complex of LaCo(DTPA)·6H<sub>2</sub>O as a precursor [17] prepared with the complexing reagent of diethylenetriaminepentaacetic acid (H<sub>5</sub>DTPA). The phosphorous poisoning in the active layer was studied by using Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). The mechanism of poisoning of phosphorous on LaCoO<sub>3</sub> model catalyst was revealed.

## 2. Experimental

### 2.1. Preparation and treatment

Al<sub>2</sub>O<sub>3</sub> layer was deposited on silicon wafer using spin-coating of Al(BuO)<sub>3</sub> as a precursor. LaCoO<sub>3</sub> film was deposited on Al<sub>2</sub>O<sub>3</sub>/Si substrate using spin-coating of LaCo(DTPA)·6H<sub>2</sub>O as a precursor [17]. The LaCoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>/Si film model catalyst was obtained by calcining at 700 °C for 1 h in air. The thickness of LaCoO<sub>3</sub> film was about 70 nm.

The powder and model film catalyst of LaCoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> were poisoned in a saturated vapor of tri-*o*-cresyl phosphate diluted in N<sub>2</sub>. The purity of N<sub>2</sub> gas was 99.999%. The vapor pressure of tri-*o*-cresyl phosphate at 293 K was estimated using method 2 provided by Grain [18]. The vapor pressure of tri-*o*-cresyl phosphate at 293 K was about 2.325E–5 mmHg. The partial pressure of N<sub>2</sub> was 760 mmHg. So the concentration of phosphorous poison in the feed gas is about 0.03 ppm. In order to show the effect of temperature and time on the poisoning reaction, the model film catalysts were poisoned at 500, 600 and 700 °C for 2 h and also at 600 °C for 1, 2, 4 and 8 h, respectively.

The LaCoO<sub>3</sub> powder catalyst was obtained from precursor by calcining at 600 °C for 2 h in air [17]. The average grain size of the powder was about 20–30 nm. The powder model catalyst was poisoned by 0.03 ppm phosphorous gas at 600 °C for 2 h.

Catalytic activity tests were performed on unpoisoned and poisoned catalysts for carbon monoxide oxidation. A gas mixture of 50 ml/min (composition: CO = 1.8%, O<sub>2</sub> = 0.9%, Ar = balance) was fed to a fixed-bed of 0.1 g catalyst particles. The reactor temperature was increased from room temperature to 400 °C, while the CO concentration was analyzed by using a gas chromatograph analyzer in order to determine the conversion. The starting temperature ( $T_0$ ), half-conversion temperature ( $T_{50}$ ) and complete

conversion temperature ( $T_{100}$ ) of CO oxidation were considered index of the catalytic activity. The blank tests showed that the CO concentration did not obviously decrease below 400 °C without catalyst.

### 2.2. Instrumental

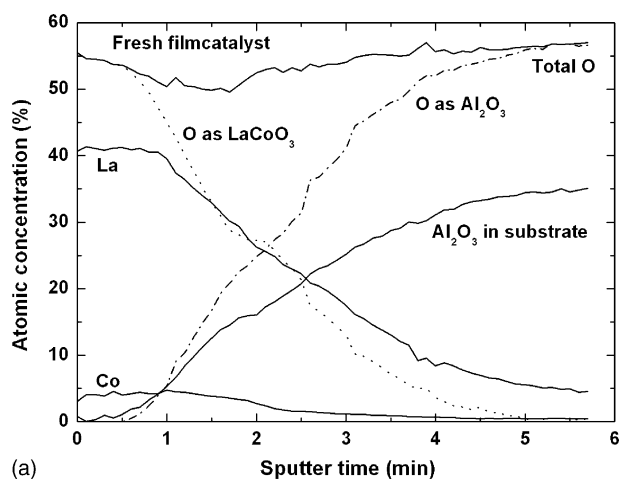
The AES spectra were obtained using a PHI 610 SAM system. A coaxial electron gun with a single pass cylindrical mirror analyzer (CMA) was used. The energy resolution of the CMA was set at 0.3% to obtain a good energy resolution. For AES analysis, the electron beam energy and the beam current were 3.0 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 analysis chamber was better than  $3 \times 10^{-9}$  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 diameter of the beam was 1 mm, and the sputtering rate was calibrated to be 30.0 nm/min using thermal oxidized SiO<sub>2</sub> thin film. No electron charge effect was found for the film sample during AES analysis. The concentration of element is obtained according to the following equation:  $C_x = (I_x/S_x) / (\sum_i I_i/S_i)$ ,  $C_x$  is the atomic concentration of element  $x$ ,  $I_x$  the relative peak area of photoelectrons from element  $x$ ,  $S_x$  the atomic sensitivity factor (ASF) of element  $x$ . The AES ASFs of the elements involved in this paper are: La MNN (0.090), Co LMM (0.270), P LVV (0.525), O KLL (0.500) and Al LVV (0.240), respectively [19].

The XPS spectra were obtained using PHI 5300 ESCA system with Al Kα 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  $5 \times 10^{-9}$  Torr. All spectra were calibrated using the binding energy of C 1s (285.0 eV) as a reference. The XPS ASFs of the elements involved in this paper are La 3d (9.122), Co 2p (3.590), P 2p (0.486), O 1s (0.717) and C 1s (0.296), respectively [20]. XRD experiments were carried out in Rigaku DMAX-2400 diffractometer with Cu Kα radiation.

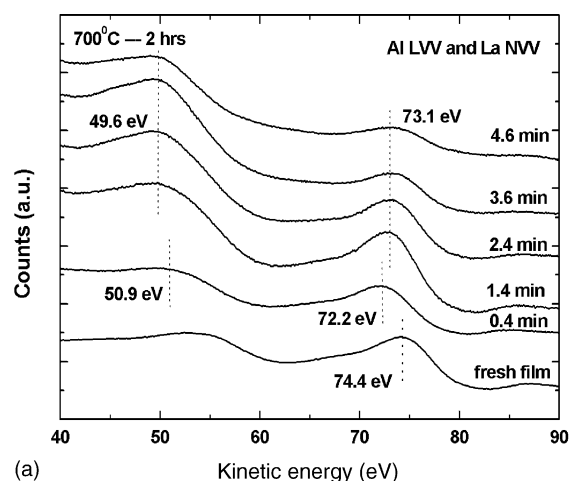
## 3. Results and discussion

### 3.1. Reaction and diffusion of phosphorous in LaCoO<sub>3</sub> film catalyst

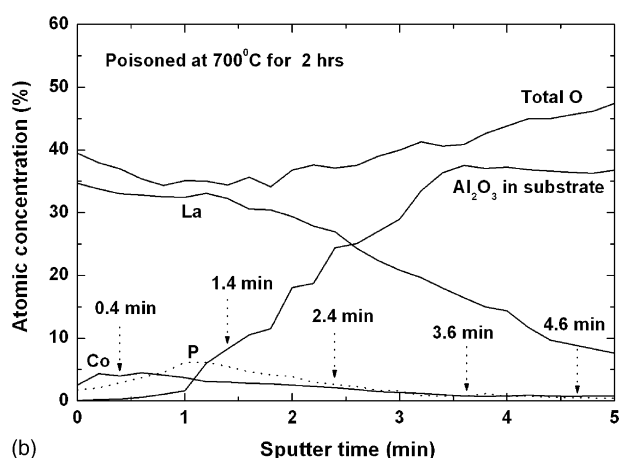
The diffusion and reaction of phosphorous in a model film catalyst of LaCoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>/Si were studied using AES. Fig. 1(a) shows a typical AES depth profile spectrum of the fresh LaCoO<sub>3</sub> film on Al<sub>2</sub>O<sub>3</sub>/Si substrate prepared at 700 °C. Fig. 1(b) is the AES depth profile spectrum of LaCoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>/Si model film catalyst, which was poisoned at 700 °C for 2 h. The thickness of the LaCoO<sub>3</sub> layer was about 70 nm. The interface between LaCoO<sub>3</sub> layer and Al<sub>2</sub>O<sub>3</sub> layer was very wide, implying that the active component of LaCoO<sub>3</sub> had diffused into Al<sub>2</sub>O<sub>3</sub> substrate during thermal treatment.



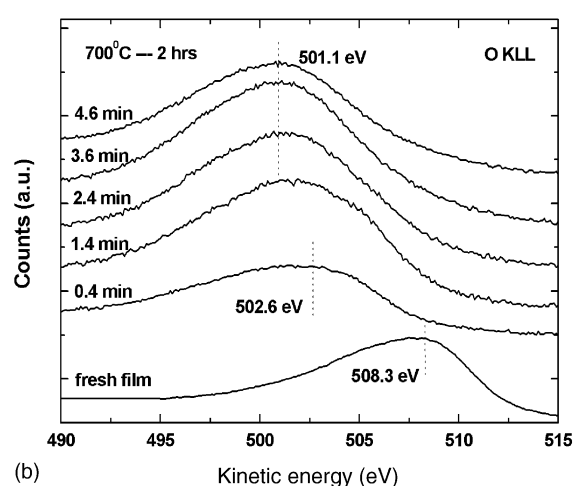
(a)



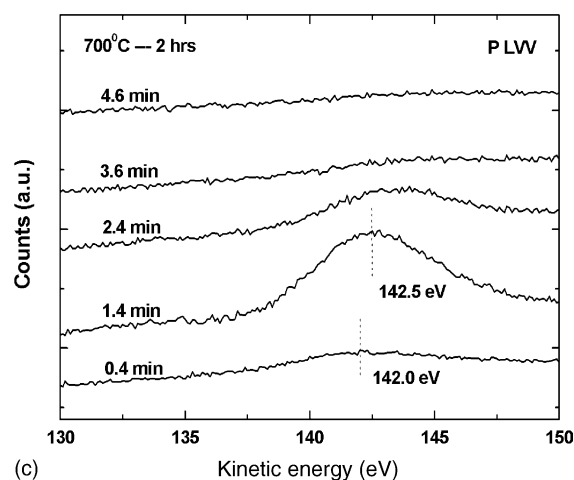
(a)



(b)



(b)



(c)

Fig. 1. The AES depth profile spectrum of the film model catalyst: (a) the typical fresh film; (b) the film poisoned at 700 °C for 2 h.

After the film catalyst sample was poisoned at 700 °C for 2 h, phosphorus diffused into LaCoO<sub>3</sub> catalyst layer. The concentration of phosphorus existed as a peak distribution in the LaCoO<sub>3</sub> model catalyst layer. The maximum concentration of P in the LaCoO<sub>3</sub> layer was about 6.1%.

The chemical states of La and Al in various depths of the sample were studied using AES line shape analysis [21]. Fig. 2(a) shows the Al LVV and La NVV spectra in various depths of the model film catalyst poisoned at 700 °C for 2 h. On the surface (sputtered for 0.4 min), the kinetic energy of La NVV was 72.2 eV. This was different from that of fresh LaCoO<sub>3</sub> film (74.4 eV). It was deduced that La reacted with some higher electronegativity element after the treatment with organophosphorous gas. With increasing the depth, the kinetic energy of La NVV shifted from 72.2 to 73.1 eV. This was attributed to the interaction between LaCoO<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> substrate. The kinetic energy of Al LVV in Al<sub>2</sub>O<sub>3</sub> species was 49.0 eV [19]. It can be seen from Al LVV spectra that the peaks on surface and at the depth of 12 nm (sputtered for 0.4 min) did not correspond to Al LVV peaks. They were produced by La NVV. Even after the film was sputtered for 4.6 min, the La NVV peak still existed and the kinetic

energy of Al LVV was 49.6 eV, implying that the interaction between LaCoO<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> substrate was significant [16]. Fig. 2(b) shows the O KLL line shapes in various depths of the model film catalyst including the standard line shape of O KLL in fresh LaCoO<sub>3</sub> species (508.3 eV). On the

energy of Al LVV was 49.6 eV, implying that the interaction between LaCoO<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> substrate was significant [16].

Fig. 2(b) shows the O KLL line shapes in various depths of the model film catalyst including the standard line shape of O KLL in fresh LaCoO<sub>3</sub> species (508.3 eV). On the

surface (sputtered for 0.4 min), the kinetic energy of O KLL was only 502.6 eV, which can be partly attributed to the presence of some new species. The kinetic energy shifted slightly to low direction in depth of 42 nm (sputtered for 1.4 min), where the concentration of P reached the maximum. The peak was so broad that it could be fitted into several species. The kinetic energy of O KLL was 501.1 eV while the depth increased to about 138 nm (sputtered for 4.6 min) where the concentration of P was very low. The kinetic energy of O KLL of sample was lower than that of pure  $\text{Al}_2\text{O}_3$ , which also implies the interaction of  $\text{LaCoO}_3$  with  $\text{Al}_2\text{O}_3$  substrate [17,19].

The P LVV line shapes in various depths are shown in Fig. 2(c). It was observed that there was only little amount of P on the surface (sputtered for 0.4 min). The kinetic energy was about 142.0 eV. The concentration of P reached a maximum when the film was sputtered for 1.4 min and the kinetic energy shifted to 142.5 eV. It was supposed that P reacted with the perovskite oxide and obtained some electrons from other element.

It can be concluded from the above that the saturated vapor of tricresyl phosphate diffused into  $\text{LaCoO}_3$  catalyst layer and reacted with  $\text{LaCoO}_3$  to form some new species. The invasion of phosphorus destroyed the  $\text{LaCoO}_3$  complex oxide to some degree.

### 3.2. Chemical states in $\text{LaCoO}_3$ catalyst layer after poisoning

The chemical states of each element in the catalyst layer were measured using XPS technique. Fig. 3 shows P 2p spectra on the surface (poisoned for 2 and 8 h, respectively) and in the catalyst layer ( $\text{Ar}^+$  sputtered) of film model catalyst which was poisoned with the saturated vapor of tricresyl phosphate at 700 °C. On the surface of the sample poisoned for 2 h, the binding energy of P 2p was about 133.3 eV, which could be mainly attributed to phosphate or pyrophosphate [20]. After the sample was etched about 4 nm by  $\text{Ar}^+$  ion beam, the peak of P 2p became narrower. The broaden of P 2p peak on the surface was mainly due to the superficial contamination. The P 2p peak of the sample poisoned for 8 h was the same as the former. It can be concluded that some phosphate or pyrophosphate was formed in the surface of the  $\text{LaCoO}_3$  catalyst layer.

The Co 2p spectra of  $\text{LaCoO}_3/\text{Al}_2\text{O}_3/\text{Si}$  poisoned at 700 °C for 2 and 8 h are shown in Fig. 4. The binding energies of  $\text{Co } 2p_{3/2}$  in  $\text{Co}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$  and  $\text{CoO}$  oxides were 779.6, 779.8 and 780.4 eV, respectively [20]. The binding energy of  $\text{Co } 2p_{3/2}$  in  $\text{LaCoO}_3$  fresh catalyst 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  $\text{LaCoO}_3$  film as a low spin Co(III) compound. After the model film catalyst was poisoned with organophosphorous gas at 700 °C for 2 h, the binding energy of  $\text{Co } 2p_{3/2}$  increased to 779.7 eV. After the sample was etched about

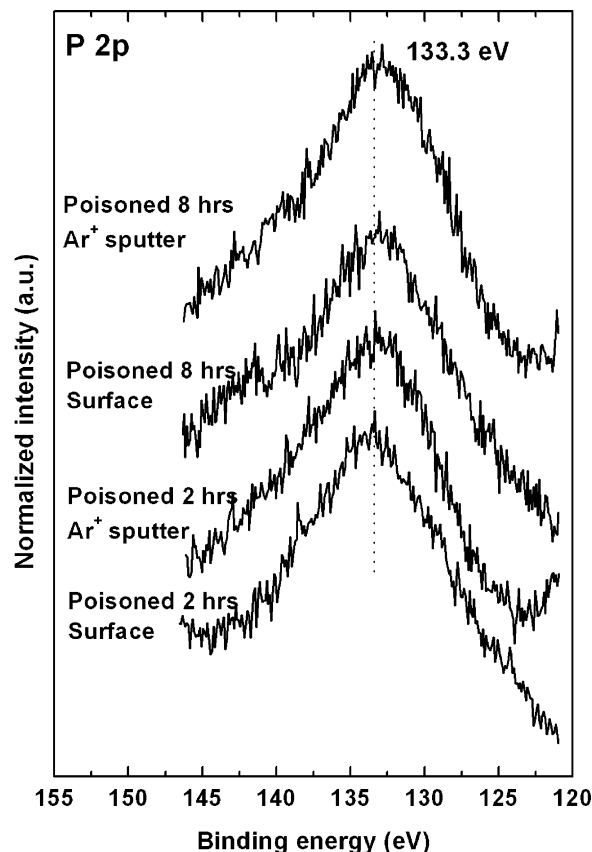


Fig. 3. The P 2p spectra in the poisoned sample at 700 °C for 2 and 8 h.

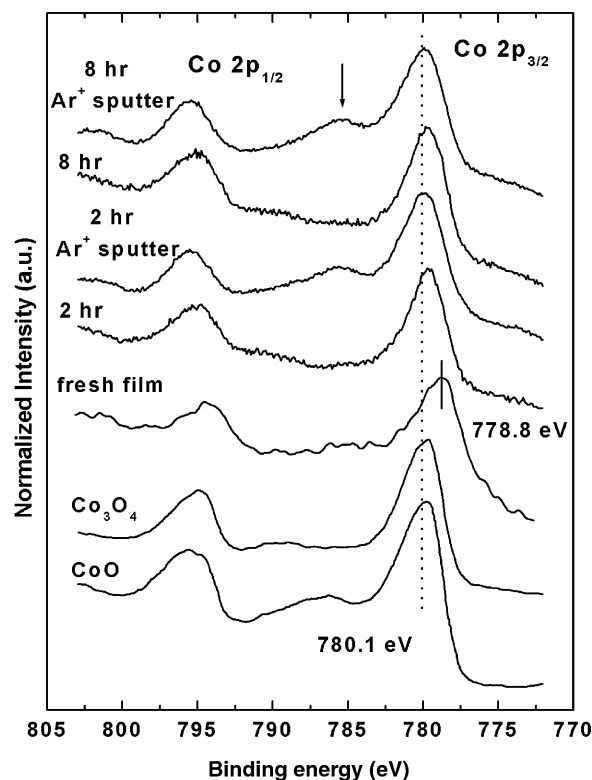


Fig. 4. The Co 2p spectra in the poisoned sample at 700 °C for 2 and 8 h.

4 nm, the binding energy shifted to 780.1 eV and two strong shake-up peaks appeared. The shake-up peaks could be attributed to high spin cobalt(II) compounds and the weak shake-up peaks to the low spin cobalt(III) compounds [22]. The appearance of strong shake-up peaks implied that the Co existed as high spin Co(II) species, which may exist as CoO species. It was the same for the sample poisoned for 8 h. It could be concluded that there was some new cobalt species formed on the surface after the film was poisoned and LaCoO<sub>3</sub> decomposed into CoO in the catalyst layer.

The binding energy of La 3d in the LaCoO<sub>3</sub> film was 832.2 eV (Fig. 5). The chemical environment of La element in the poisoned sample was very complicated. After the film model catalyst was poisoned at 700 °C for 2 h, the binding energy of La 3d on the surface shifted to 834.4 eV. It was inferred that this was partly due to the formation of the new lanthanum species. It could be deduced that La combined with some element which has larger electronegativity. After the film was etched about 4 nm with Ar ion beam, the binding energy of La 3d<sub>5/2</sub> decreased to 833.7 eV. When the film was poisoned for 8 h, the binding energy of La 3d<sub>5/2</sub> was the same. This phenomenon was consistent with the results of Co.

There were mainly two chemical states of oxygen in LaCoO<sub>3</sub> catalyst layer. They can be fitted into two oxygen species (Fig. 6). Peak 1 with a low binding energy (529.2 eV) was contributed to the oxygen in the crystal lattice of LaCoO<sub>3</sub>. The higher one, Peak 2 (about 531.3 eV) was contributed to the absorbed oxygen in this kind complex oxide with oxygen deficiency. It was observed that Peak 2 was much lower than Peak 1 in the poisoned catalyst films compared with that in the fresh LaCoO<sub>3</sub> species.

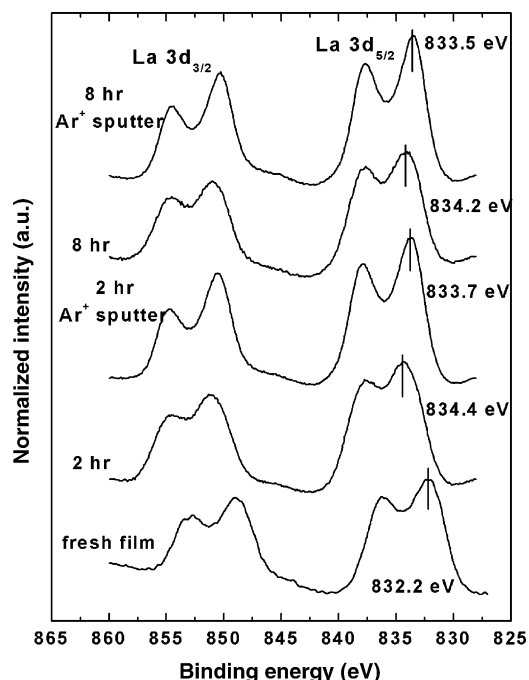


Fig. 5. The La 3d spectra in the poisoned sample at 700 °C for 2 and 8 h.

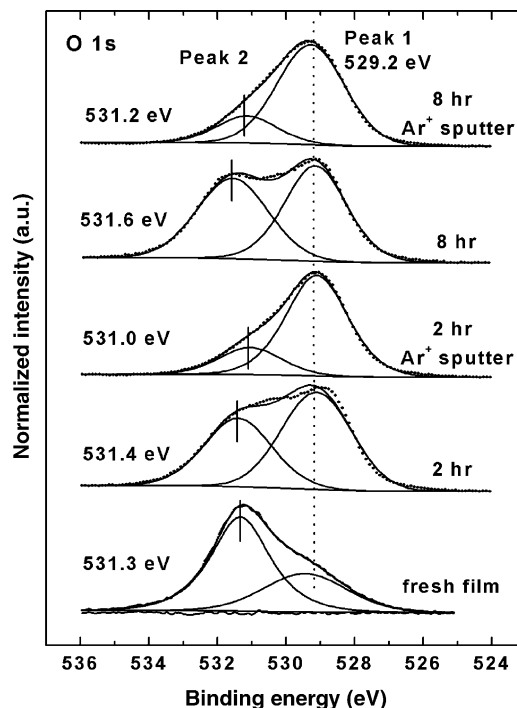


Fig. 6. The O 1s spectra in the poisoned sample at 700 °C for 2 and 8 h.

This resulted from the destruction of perovskite structure in LaCoO<sub>3</sub> oxide after the organophosphorous gas poisoning. After the poisoned catalyst films were sputtered for about 4 nm, Peak 2 was weakened due to the decomposition of LaCoO<sub>3</sub> and the Ar<sup>+</sup> etching.

From the above, it can be concluded that phosphate or pyrophosphate and CoO were formed in the surface of the LaCoO<sub>3</sub> catalyst layer due to organophosphorous gas poisoning.

### 3.3. Effects of poisoning temperature and time

Temperature has a serious effect on the poisoning reaction between organophosphorous gas and LaCoO<sub>3</sub> film model catalyst. The catalyst was poisoned at 500, 600 and 700 °C for 2 h, respectively. Fig. 7(a) shows the AES depth profile spectra of phosphorus at various poisoning temperatures. The peak concentration of phosphorus was about 8.4% at the depth of 25 nm in the catalyst layer after it was poisoned at 500 °C for 2 h. When the model film catalyst sample was poisoned at 600 °C for 2 h, the maximum concentration of phosphorus increased to 9.6% and phosphorus diffused into the film more deeply. The peak concentration of phosphorus decreased to 6.1% when the temperature was increased to 700 °C, while the distribution peak of P concentration shifted deeper to 35 nm. Because the decomposition temperature of phosphate is always higher than 1000 °C, the decrease of P concentration was not a result of decomposition of phosphorous compound. It could be explained as the equilibrium of the diffusion of P into layer and the accumulating of P due to reaction in LaCoO<sub>3</sub>

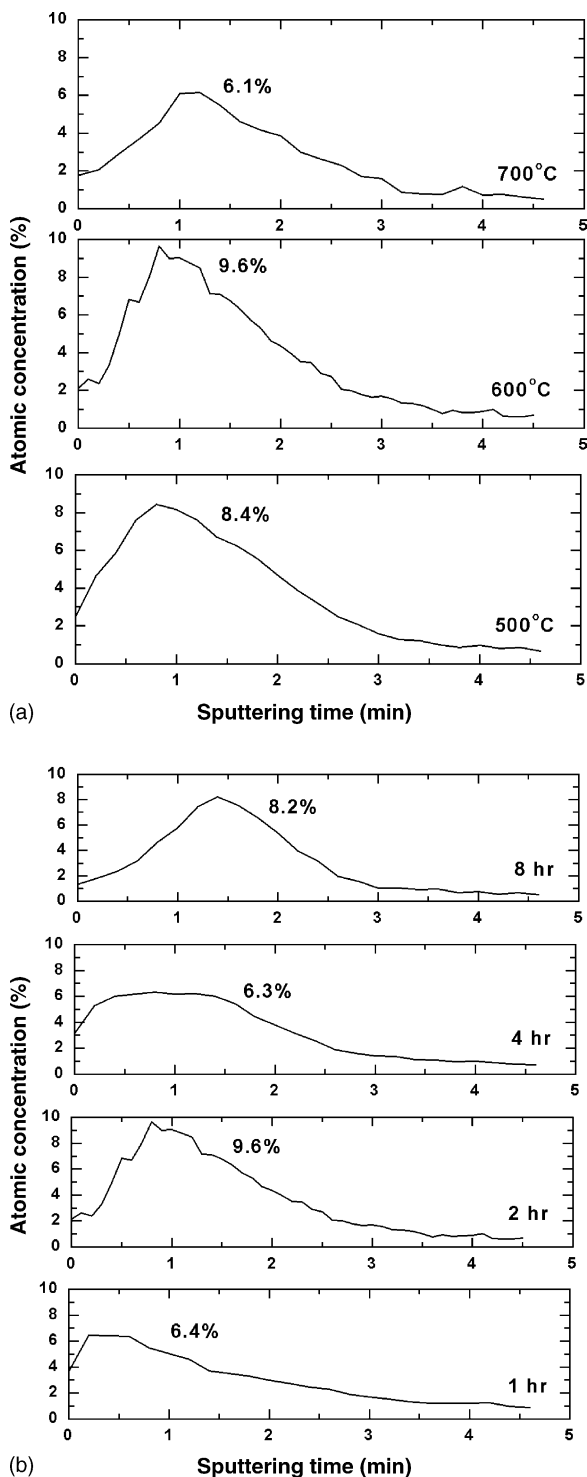


Fig. 7. The effects of reaction temperature (a) and reaction time (b) on the distribution of P with depth.

layer. When the poisoning temperature is below 600 °C, the accumulating of P due to reaction in LaCoO<sub>3</sub> layer was dominant. With increasing poisoning temperature, the concentration of peak distribution of P in LaCoO<sub>3</sub> layer increased. After the poisoning temperature reached 700 °C, the diffusion of P into layer was dominant. The diffusion rate

was faster than the accumulation rate of P in layer. Thus, the peak concentration decreased and the distribution of P was much deeper. The results of the line shape analysis also indicated that the reaction depth increased at higher temperature. Above results imply that the accumulating of phosphorus increased with temperature in the lower range from 500 to 600 °C. At high temperature above 700 °C, the diffusion of phosphorus and the chemical reaction in the layer between LaCoO<sub>3</sub> and organophosphorous gas increased greatly.

The reaction time is also an important factor for the poisoning reaction. Fig. 7(b) shows the distribution of P in film model catalyst poisoned at 600 °C for 1, 2, 4, and 8 h. When the poisoning time was 1 h, the concentration of phosphorus in the catalyst layer reached 6.4% on the surface of the film. After the reaction time increased to 2 h, the maximum concentration of phosphorus increased to 9.6% at the position of 25 nm. The peak concentration of phosphorus decreased to 6.3% but the distribution was more uniform when the poisoning time was prolonged to 4 h. When the poisoning time reached 8 h, the concentration of phosphorus reached 8.2% at a deeper position of 45 nm. It is concluded that the depth of diffusion and the reaction between P and the active layer increase with the exposure time.

#### 3.4. Effects of phosphorous poisoning on perovskite structure

The structures of LaCoO<sub>3</sub> perovskite film catalyst during phosphorous poisoning were determined by XRD. Fig. 8 shows the XRD patterns of LaCoO<sub>3</sub> film model catalyst poisoned at 700 °C for 2 and 8 h, respectively. The main peak at 28.6° (2θ) is related to silicon substrate. The XRD pattern of the pure LaCoO<sub>3</sub> showed the perovskite structure (2θ: 23.2°, 32.5°, 40.7°, 47.4°, 58.9°) with no other phases. After the sample was poisoned at 700 °C for 2 h, some new diffraction peaks (2θ: 43.0°, 66.1°) appeared, implying the formation of some new species. The new diffraction peaks could be attributed to La phosphate or pyrophosphate and CoO, respectively, although the strongest diffraction peak of phosphate or pyrophosphate overlapped with that of the Si substrate [10,11]. After the sample was poisoned at 700 °C for 8 h, these two new diffraction peaks sharpened while the characteristic peaks of the perovskite structure weakened obviously. It was also observed that the characteristic peaks of the perovskite structure shifted about 1° (2θ) to higher direction in the poisoned films, implying the distortion of the pure LaCoO<sub>3</sub> perovskite structure.

The grain size of the fresh powder obtained was homogenous and fairly small (about 20–30 nm). However, after poisoning, the grain size became larger and the powder began to gather. The fresh powder formed a perfect perovskite type structure, as shown in Fig. 9. The XRD patterns also demonstrated that the perovskite was partly destroyed and some new species (La phosphate or pyrophosphate, La<sub>2</sub>CoO<sub>4</sub> and CoO) were found after the

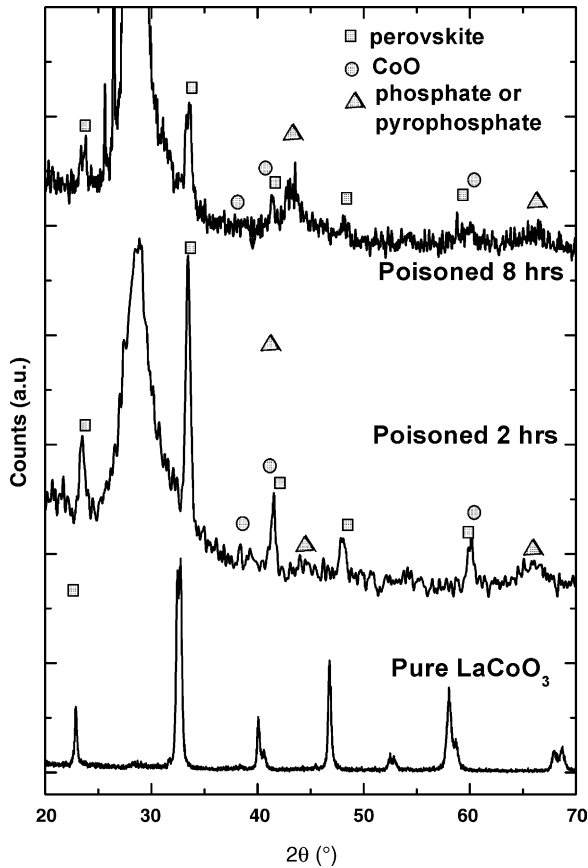


Fig. 8. The XRD patterns of LaCoO<sub>3</sub> model film catalyst before and after being poisoned by organophosphorous gas at 700 °C.

powder was poisoned by organophosphorous gas at 600 °C for 2 h. It was consistent with the results of film catalyst.

It can be concluded from XRD results that the perovskite structure of LaCoO<sub>3</sub> was destroyed after phosphorous

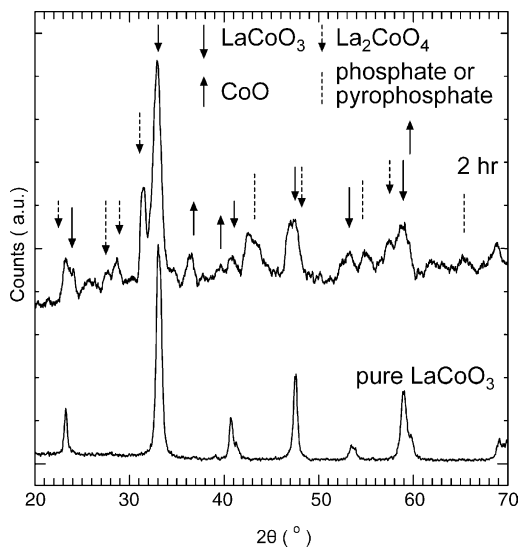


Fig. 9. The XRD patterns of LaCoO<sub>3</sub> powder before and after poisoned by organophosphorous gas at 600 °C for 2 h.

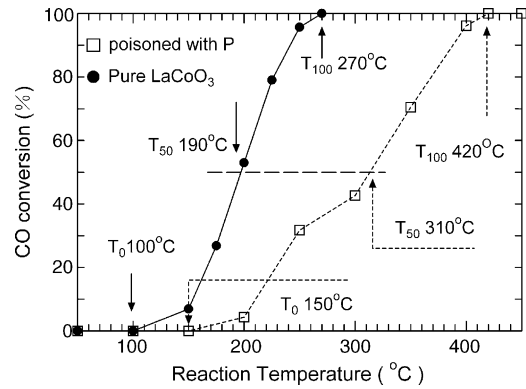


Fig. 10. Catalytic activity test results for CO combustion in the CO + O<sub>2</sub> → CO<sub>2</sub> reaction of fresh (a) and poisoned (b) LaCoO<sub>3</sub> powder catalyst.

poisoning. Some new crystalline phases attributed to LaPO<sub>4</sub> or La<sub>4</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>3</sub> and CoO were produced after the sample was poisoned by organophosphorous gas.

### 3.5. Effects of phosphorous poisoning on catalytic performance

The catalytic performance for CO + O<sub>2</sub> → CO<sub>2</sub> reaction were adopted to investigate the poisoning effects of P on LaCoO<sub>3</sub> powder model catalyst. Fig. 10 shows the results of the catalytic activity tests for carbon monoxide combustion performed with LaCoO<sub>3</sub> powder catalyst in fresh state, poisoned by organophosphorous gas at 600 °C for 2.0 h. The fresh catalyst showed good catalytic activity at T<sub>0</sub> of 100 °C, T<sub>50</sub> of 190 °C and T<sub>100</sub> of 270 °C, comparable with those reported by Simonot et al. [23]. After poisoned for 2 h, the T<sub>0</sub> (150 °C), T<sub>50</sub> (310 °C) and T<sub>100</sub> (420 °C) increased, which implying the activity of the powder catalyst decreased after poisoning reaction. The surface area of LaCoO<sub>3</sub> sample decreased from 17.07 m<sup>2</sup>/g to 15.23 m<sup>2</sup>/g after poisoned by organophosphorous gas at 600 °C for 2.0 h, implying the decrease of surface area was not the main factor. The decreasing of activity came from the destruction of LaCoO<sub>3</sub> perovskite structure.

It can be concluded that the destruction of the perovskite structure and the formation of phosphate after poisoning with P result in the deactivation of the perovskite catalyst.

## 4. Conclusion

- (1) Organophosphorous gas diffused into LaCoO<sub>3</sub> model film catalyst and reacted with LaCoO<sub>3</sub>. The phosphorus entered into the crystal lattice of the LaCoO<sub>3</sub> perovskite structure, which resulted in the distortion of perovskite structure. LaPO<sub>4</sub> or La<sub>4</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>3</sub> accompanied by CoO formation during the poisoning process. The catalytic activity of the powder catalyst decreased after the destruction of the perovskite structure.

- (2) The distribution of phosphorus in the  $\text{LaCoO}_3$  layer became homogeneous after it was poisoned at a high temperature above  $700\text{ }^\circ\text{C}$  or for a long period of time.

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