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Effect of thermal treatment on catalytic properties of $La_{0.9}Ce_{0.1}CoO_3$

KENJI TABATA*, IKUO MATSUMOTO
Matsushita Housing Products Co. Ltd, Housing Products Research Laboratory, Yamato-Koriyama, Nara, 639-11, Japan

SHIGEMI KOHIKI
Matsusita Technoresearch Inc., Moriguchi, Osaka, 570, Japan

The effect of thermal treatment on the catalytic properties of methane oxidations and the surface chemical states of $La_{0.9}Ce_{0.1}CoO_3$ have been investigated using X-ray photoelectron spectroscopy (XPS). The catalytic activity reached a maximum in the sample calcined at 1123 K. With further increase in the calcination temperature, the surface chemical states of cobalt seemed to shift from perovskite phase to CoO, and the catalytic activity decreased.

1. Introduction

Voorhoeve *et al.* reported that cerium-doped lanthanum cobalt oxides ($La_{1-x}Ce_xCoO_3$) with perovskite-type structure showed high activities as oxidation catalysts [1]. In our previous paper, we investigated the effects of cerium substitution for lanthanum in $LaCoO_3$ on catalytic activity [2], and reported that the catalytic activity had a peak at $x = 0.1$ for the both oxidation of methane and carbon monoxide. In this study we investigated the effects of calcination temperature on the oxidation activity of $La_{0.9}Ce_{0.1}CoO_3$. The relationships between the catalytic properties and the surface chemical states are also reported.

2. Experimental procedure

$La_{0.9}Ce_{0.1}CoO_3$ was prepared from mixtures of metal acetates of each component [3]. First, a solution of mixed acetates was evaporated to dryness in a rotary evaporator (343 to 363 K) and the solid obtained was decomposed in air at 673 K for 1 h, and then calcined in air at each temperature (873 to 1573 K) for 5 h.

The phases of the products were determined by X-ray diffraction (XRD) using Cu$K\alpha$ radiation (Philips APD-10). The surface areas of the samples were measured by the BET method (nitrogen adsorption).

XPS spectra were recorded on a V.G. ESCA LAB5 spectrometer with Al$K\alpha$ or Mg$K\alpha$ radiations. No shift due to charging was observed. The binding energies (BE) were corrected using the value of 285.0 eV for the C1s level resulting from the contaminated carbon. Then, the core-level BE of lead, silver and gold foils were measured. The $Pd3d_{5/2}$, $Ag3d_{5/2}$ and Au $4f_{7/2}$ BEs were, respectively, 335.4 ± 0.1 eV, 368.3 ± 0.1 eV and 84.0 ± 0.1 eV, relative to the Fermi level [4]. The experimental errors were within ± 0.1 eV. The normal operating vacuum pressure was less than 3×10^{-8} Pa. The spectra from X-ray photoelectron spectroscopy (XPS) were measured at room temperature without additional surface treatment.

The bulk composition of $La_{1-x}Ce_xCoO_3$ was measured by X-ray fluorescence spectroscopy (XRFS) using a glass bead method (Rigaku model 3370).

Catalytic activity for oxidation of methane was measured with the conventional flow system. Prior to the reaction, the catalysts (0.2 g) were heated in a stream of air for 1 h at 473 K. A mixed gas (methane 1.0% air balance) was fed at a flow rate of $300\,cm^3\,min^{-1}$. The reaction temperature for methane was 873 K. Products were analysed by gas chromatography (Shimazu GC-R1A) (activated charcoal column 1 m, kept at 363 K).

3. Results and discussion

3.1. Catalytic activity

Fig. 1 shows the effects of thermal treatment on the relative activity per unit weight of $La_{0.9}Ce_{0.1}CoO_3$ and Co_3O_4. The Co_3O_4 was the reagent (Kojundo Chemical LAB, 99.9% pure). For all the calcination temperatures, $La_{0.9}Ce_{0.1}CoO_3$ showed higher resistance than Co_3O_4.

Fig. 2 shows the catalytic activity per surface area of $La_{0.9}Ce_{0.1}CoO_3$. The catalytic activity exhibited a peak in the sample calcined at 1123 K. With further increase of calcination temperature, the activity decreased monotonically.

3.2. Surface area and atomic composition by XRFS

As shown in Table I, the surface of $La_{0.9}Ce_{0.1}CoO_3$ decreased gradually with increasing calcination temperature. The bulk composition of $La_{0.9}Ce_{0.1}CoO_3$ is also shown in Table I. In all samples, the average composition agreed with the stoichiometric ratio.

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*Author to whom all correspondence should be addressed.

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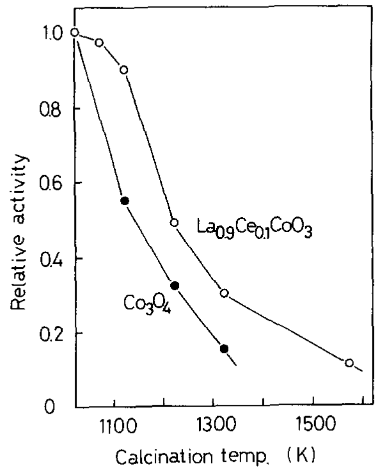

Figure 1 Effects of thermal treatment on the relative activity per unit weight of $La_{0.9}Ce_{0.1}CoO_3$ and Co_3O_4 in the oxidation of methane at 873 K. (Space velocity, S.V. 7500 h^{-1}.)

TABLE I Surface area obtained by BET method and bulk compositions obtained from X-ray fluorescence spectroscopy (XRFS) of $La_{0.9}Ce_{0.1}CoO_3$

Calcination temperature (K)	Surface area (m^2g^{-1})	XRFS (atomic ratio)		
		La	Ce	Co
873	14.0	0.90	0.10	1.00
1023	4.7	0.90	0.10	1.00
1073	4.0	0.90	0.10	1.00
1123	3.5	0.90	0.10	1.00
1223	2.1	0.90	0.10	1.00
1323	1.5	0.90	0.10	1.00
1573	0.6	0.90	0.10	1.00

3.3. X-ray measurement

Fig. 3 shows XRD patterns of $La_{0.9}Ce_{0.1}CoO_3$. The sample, calcined at 873 K, showed peaks due to CeO_2, Co_3O_4 and La_2CO_5 phases, but did not show the perovskite phase. However, in other samples, the perovskite-type compound was the dominant phase.

3.4. Surface states of $La_{0.9}Ce_{0.1}CoO_3$

The surface chemical states of these samples were measured by XPS at room temperature. Fig. 4 shows $Co2p_{3/2}$ spectra of $La_{0.9}Ce_{0.1}CoO_3$. With increasing calcination temperature, the spectrum of the peak became fine up to 1123 K. The peak of the sample calcined at 1123 K agreed quite well with the value of Co^{3+} in $LaCoO_3$ (779.6 eV) reported by Lombardo *et al.* [5]. The value of spin-orbit splitting of this sample was 15.3 eV and this value also agreed well with that of Co^{3+} in $LaCoO_3$ [6].

The peak of the spectrum at 1223 K apparently had a shoulder besides that of perovskite structure. This shoulder may be due to CoO (780.3 eV) [7]. With further increase of calcination temperature, the peak of the perovskite structure gradually diminished and seemed to shift to CoO. The value of spin-orbit splitting of the sample also increased slightly, to 15.6 eV at 1573 K. This value agreed with the reported values 15.5 eV [8] to 16.0 eV [6] for CoO.

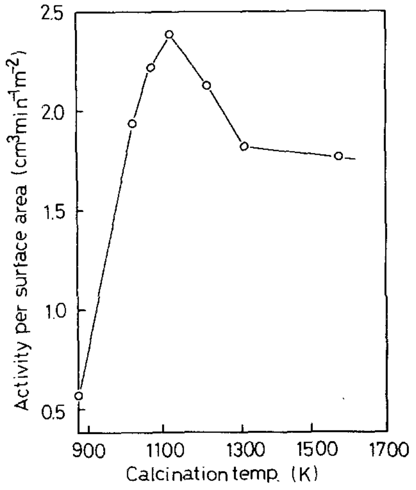

Figure 2 Effects of thermal treatment on the activity per unit surface area of $La_{0.9}Ce_{0.1}CoO_3$ in the oxidation of methane at 873 K. (Space velocity, S.V. 7500 h^{-1}.)

Fig. 5 shows the O1s spectra of $La_{0.9}Ce_{0.1}CoO_3$. The O1s spectrum of each sample became a doublet with increasing calcination temperature as reported by Yamazoe *et al.* [9] for $La_{1-x}Sr_xCoO_3$ [9]. According to them, the peak with lower BE was assigned to the lattice oxygen (O^a). The assignment of the other peak (O^b) is controversial. It may possibly be due to oxygen weakly bound on the surface [9], surface hydroxyls or oxygen bound to basic element (La_2O_3) [10].

3.5. Surface atomic ratio of $La_{0.9}Ce_{0.1}CoO_3$

As shown in Table I, the chemical composition in these samples agreed well with the stoichiometric ratio. However, the surface atomic ratio of cobalt changed drastically, as shown in Fig. 6. It increased with calcination temperature, and had a peak at 1223 K.

As shown in Fig. 7, both the atomic ratio of lanthanum to cobalt and cerium to cobalt on the surface decreased with increasing calcination temperature. The surface ratio of cerium to cobalt decreased monotonically, but that of lanthanum to cobalt increased slightly above 1223 K.

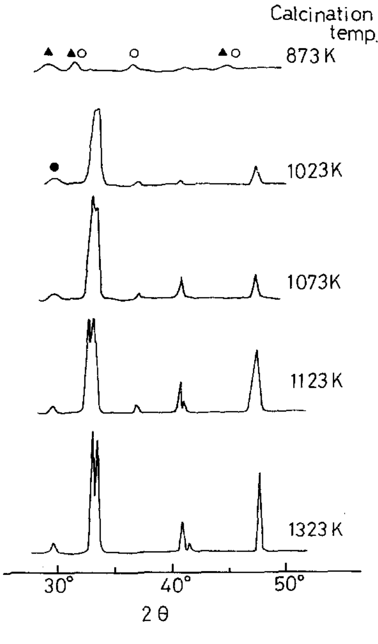

Figure 3 XRD patterns of $La_{0.9}Ce_{0.1}CoO_3$. (○) Co_3O_4, (▲) La_2CO_5, (●) CeO_2.

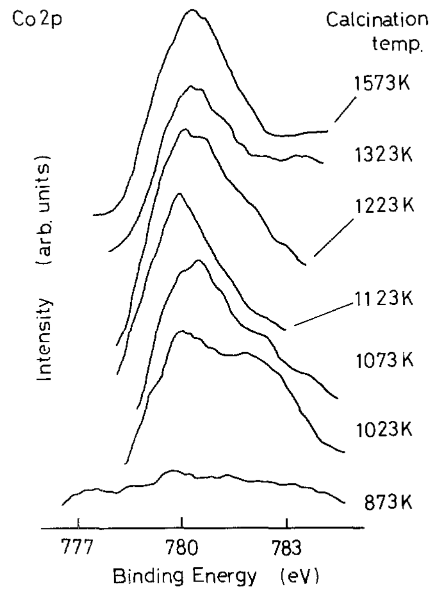

Figure 4 XPS spectra of the Co2p for $La_{0.9}Ce_{0.1}CoO_3$.

Overbury *et al.* [11] indicated that the surface tensions of the components were important to determine the surface composition. The Gibbs' free energies (ΔG) for La_2O_3, CeO_2 and Co_3O_4 are -1254.2, -1390.0 and $-769.3\,kJ\,mol^{-1}$, respectively. Consequently, lanthanum oxide and cerium oxide seemed to be formed first and to rise to the surface during calcination. With increasing calcination temperature, the surface composition was almost in agreement with the matrix composition. This may be because of the high diffusibilities of atoms in the higher temperature region.

As shown in Figs 2 and 6, the catalytic activity of $La_{0.9}Ce_{0.1}CoO_3$ per surface area was very similar to the surface atomic ratio Co/La + Ce. Because the reaction rate of both La_2O_3 and CeO_2 of reagents at the same temperature (873 K) were nearly zero, the catalytic activity seemed to depend on the cobalt on the surface. However, there is a difference in peak positions between Figs 2 and 6. This result may be understood by considering that the surface chemical states of cobalt, as shown in Fig. 4, changed gradually from the perovskite phase to CoO above 1223 K.

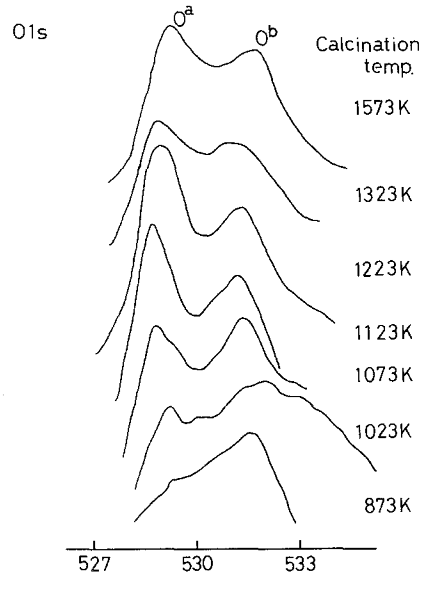

Figure 5 XPS spectra of the O1s of $La_{0.9}Ce_{0.1}CoO_3$.

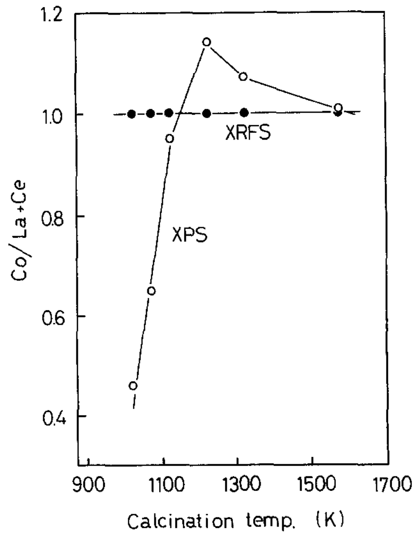

Figure 6 Surface atomic ratio (Co/La + Ce) of $La_{0.9}Ce_{0.1}CoO_3$.

From these results, the catalytic activity seemed to depend not only on the surface concentration of cobalt but also on the chemical states of cobalt.

Acknowledgements

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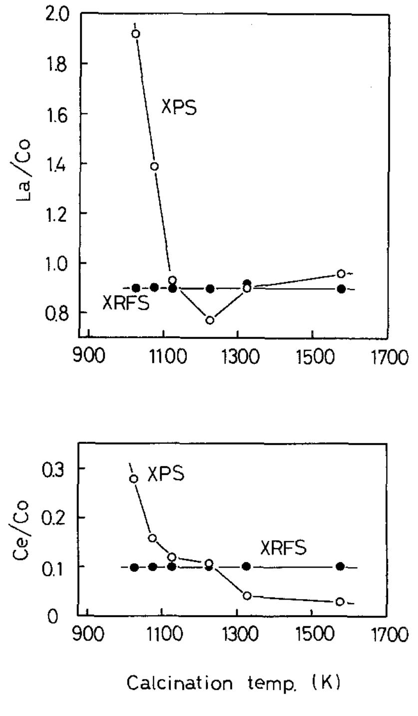

Figure 7 Surface atomic ratio (La/Co and Ce/Co) of $La_{0.9}Ce_{0.1}CoO_3$.

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