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X-Ray Photoelectron Study of the Methane Interaction with $LaCoO_3$

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The interaction of CH_4 with $LaCoO_3$ has been studied at room temperature with the use of an X-ray photoelectron spectroscopy (XPS) analyzer. CH_4 dissociated on the surface of $LaCoO_3$, and new carbonaceous products were detected at 10^4 langmuir exposure on the spectra for C1s. Since the intensities of the adsorbed oxygen on the spectra for O1s gradually decreased in proportion to the increase in the amount of CH_4 exposure, methane reacted with adsorbed oxygen of $LaCoO_3$ at room temperature in an XPS analyzer.

Perovskite-type mixed oxides (ABO_3) have been widely investigated concerning their catalytic properties, owing to their high activities for oxidation reactions.$^{1-3)}$ Since perovskites have a well-defined structure, they are suitable materials for studying the relations between catalytic properties and their structures. The surface states of perovskites have been intensively studied using X-ray photoelectron spectroscopy (XPS) or ultraviolet photoelectron spectroscopy (UPS).$^{4-6)}$ We have reported that the catalytic activities of La_{1-x} (Ce, Sr)$_x$-CoO_3 for CO oxidation could be related to changes of the surface states, that is, the surface atomic ratio or their chemical states of the surface cobalt.$^{6,7)}$

Recently, some studies have been carried out concerning the interaction of methane with nickel surfaces.$^{8-10)}$ Krishnan and Wise indicated that oxygen adatoms could greatly promote the dissociative chemisorption of methane on Ni (111) surfaces, and that the dissociated methane reacts immediately with the adsorbed oxygen atoms.$^{8)}$ It is very interesting to study the interaction of methane with the surface of $LaCoO_3$, since the peaks of the photoelectron spectrum of O1s for $LaCoO_3$ can be divided into lattice oxygen and adsorbed oxygen; it is thus a good sample for examining the states of chemisorption under coexistent oxygen. We therefore studied changes in the surface states of $LaCoO_3$ by exposing CH_4 inside of an XPS analyzer.

Experimental

Catalysts. $LaCoO_3$ was prepared from mixtures of the metal acetates of each component. First, a mixed acetate solution was evaporated to dryness in a rotary evaporator (343—363 K); the obtained solid was then decomposed in air at 1123 K for 5 h. The X-ray powder diffraction pattern of $LaCoO_3$ was purely indexed on the basis of its perovskite-type structure; no other phases were found. The crystal structure of $LaCoO_3$ was rhombohedral.

Apparatus and Procedures. CH_4 (UHP grade, Seitetsu Chemical Co., Ltd.) was introduced to XPS at room temperature from a leak valve. The quantities regarding the exposure of CH_4 were given by a langmuir (1 L=10^{-6} Torr s, 1 Torr=133.322 Pa) study.

The photoelectron spectra measurements were made on a V.G. ESCA LAB-5 electron spectrometer using unmonochromatized Al $K\alpha$ or Mg $K\alpha$ radiation. The binding energies were corrected using 285.0 eV for the C1s level, resulting from contaminated carbon as an internal standard. The XPS spectra were measured at room temperature without any additional surface treatment. No shifts due to charge-up effects were observed.

Results

Changes in the C1s spectra measured by XPS are shown in Fig. 1. No notable peak, except for the contaminated carbon (285.0 eV), can be seen before methane exposure (0 L). Hamlin et al. reported that the C1s spectrum for CH_4 is included in the contaminated carbon.$^{11)}$ A shoulder peak about 286 eV and another broad peak near 287.3 eV were made clear at 10^4 L. Another small peak, also at about 288.3 eV, can be seen at 10^4 L. Since Holm and Storp$^{12)}$ reported that the

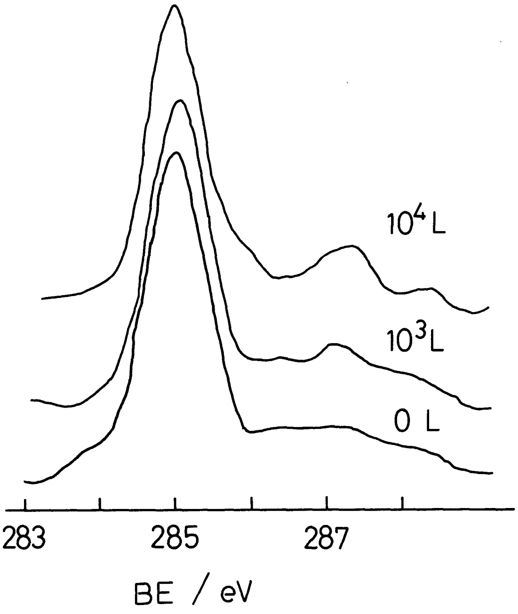

Fig. 1. XPS spectra of the C 1s for $LaCoO_3$.

carbon atoms of the C–O ether groups exhibiting a shift of 1.5 eV led to an asymmetric slope of the main C1s line, the shoulder peak at about 286 eV may be assigned as being carbonaceous products which include a C–O bond. Furthermore, the C1s binding energies of the sp^2 carbonyl carbon, such as CH_2O and $(CH_3)_2CO$, were reported as being separated for 2.9 and 3.1 eV, respectively, to the higher binding-energy side from 285.0 eV.[13] Since these values are near to those of the obtained broad peaks (287.3, 288.3 eV), these peaks also may result from carbonaceous products which include a C–O bond.

The Co2p spectra are shown in Fig. 2. The peak position of $Co2p_{3/2}$ of $LaCoO_3$ was reported to be at 779.6 eV by Lombardo et al.,[14] agreeing well with our experimental results (0 L). The value of the spin-orbit splitting and that of the full width at half-maximum (FWHM) for $LaCoO_3$ were reported as being 15.3 and 3.2 eV[15] respectively; they agree with our results. The oxidation state of the surface cobalt atoms at 0 L thus seemed to be Co^{3+} in $LaCoO_3$. Although the shift of the main peak was not clear, the value of the FWHM slightly increased with an increase of CH_4 exposure, as is shown in Table 1. The shoulder peak in the vicinity of 782 eV can be clearly obtained under 10^4 L exposure. This peak may be assigned to $CoCO_3$ from our experimental results (782.0 eV) for a commercial reagent. The small broad peak at around 786 eV is clear at 10^4 L. Okamoto et al. reported that a satellite peak of CoO appeared at 5.5 eV higher than the main peak (780.3 eV).[16] CoO should be included in the main peak at a 10^4 L exposure. Since the peak position of CoO is 780.3 eV, the increase of the FWHM of the main peak may result from an increase in CoO on the surface. The surface cobalt of $LaCoO_3$ seemed be reduced under this type of CH_4 exposure.

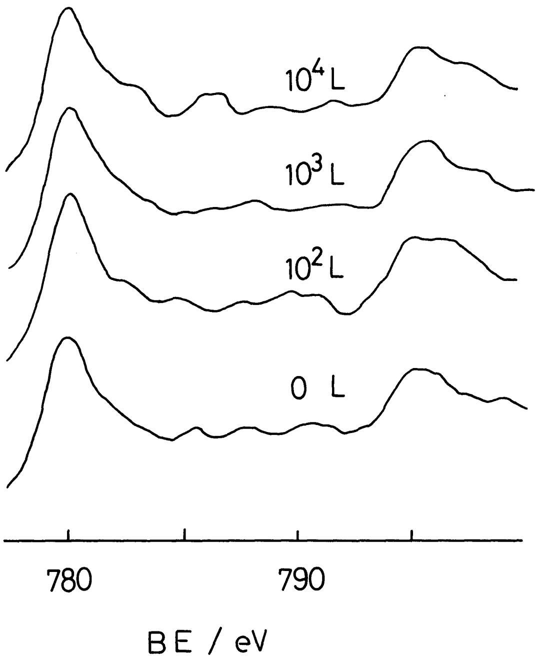

Fig. 2. XPS spectra of the Co 2p for $LaCoO_3$.

Table 1. Full Width at Half-Maximum (FWHM) of $Co2p_{3/2}$ for $LaCoO_3$

Q[a)]	FWHM
L[b)]	eV
0	3.2
10^2	3.0
10^3	3.6
10^4	3.6

a) Q is the quantities of the exposure of CH_4. b) L is langmuir (1 L=10^{-6} Torr s).

The La3d spectra are shown in Fig. 3. The spectrum at 0 L is very similar to that studied by Lam et al.,[17] that is, the satellite line on the higher binding energy side of the 3d level is separated from the main peak by 4 eV. Since the multiplet splitting between the $3d_{3/2}$ and $3d_{5/2}$ levels was consistent with their reported value of 16.8 eV, the surface state of La at 0 L is La^{3+} in $LaCoO_3$. It is interesting that the La3d spectra did not change at all, even after a 10^4 L exposure. Since CH_4 exposure did not affect the spectra for La3d, the interaction between CH_4 and La seems to be weak.

The photoelectron spectra of O1s measured before and after CH_4 exposure are shown in Fig. 4. The O1s spectra for $LaCoO_3$ have been studied by many researchers.[4,5] Richter et al. reported that there were two peaks in the spectrum of O1s for $LaCoO_3$.[4] The lower binding energy peak (O^a) was assignable to a lattice oxygen; another peak (O^b) was an adsorbed oxygen. Our results concerning the O1s spectrum at 0 langmuir was a doublet, as reported by them. These two peaks

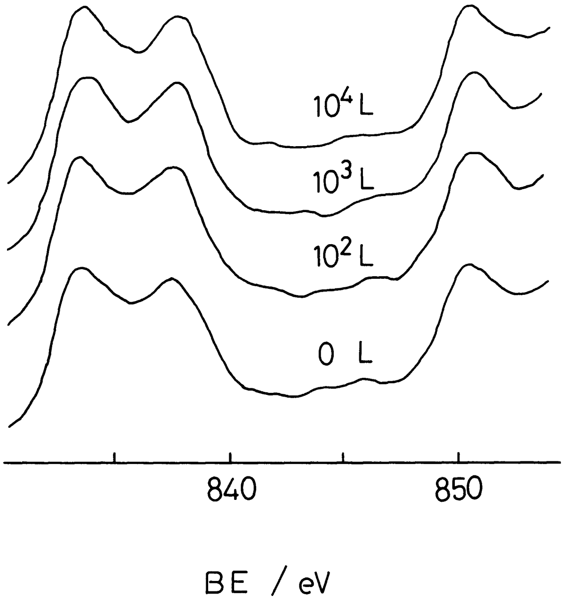

Fig. 3. XPS spectra of the La 3d for $LaCoO_3$.

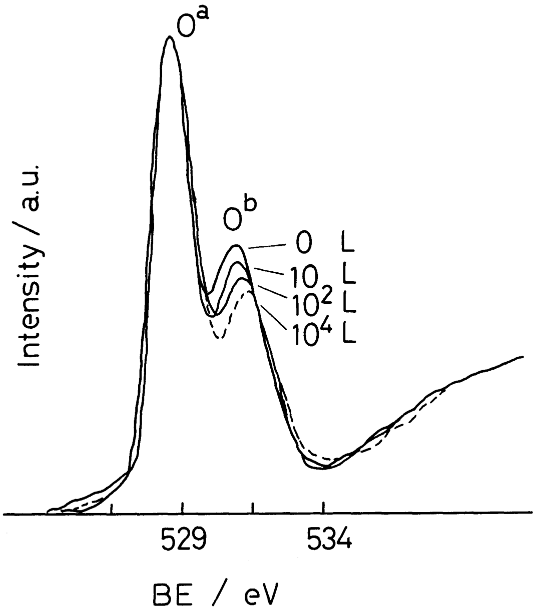

Fig. 4. XPS spectra of the O 1s for $LaCoO_3$.

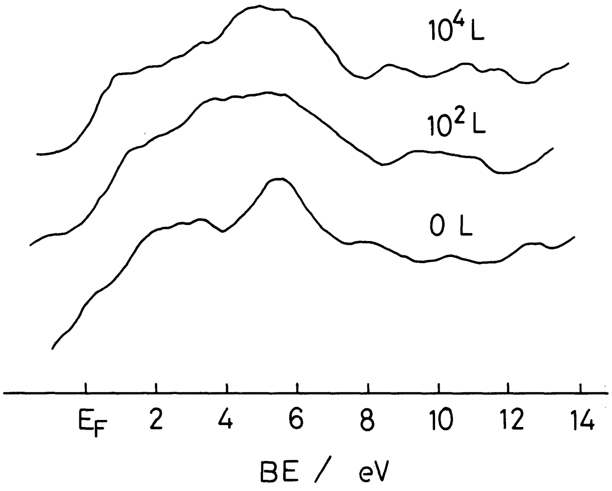

Fig. 5. Valence band spectra for $LaCoO_3$.

are indicated as O^a and O^b, respectively. These spectra show an interesting change with an increase in CH_4 exposure. Neither the peak position nor the intensity of the lattice oxygen changed at all as a result of CH_4 exposure, as shown in Fig. 4. However, the intensities of adsorbed oxygen (O^b) gradually decreased in proportion to the increase of CH_4 exposure. Namely, preadsorbed oxygen was decreased by CH_4 exposure. Furthermore, the peak positions of O^b shifted slightly to the higher binding-energy side. Regarding the slight shift of the binding energy of O^b to the higher binding-energy side, it can be explained as being the adsorbed oxygen are decreased in order of the weakness of the interaction with the $LaCoO_3$ surface. Since the increase in the value of the binding energy of O^b indicates that the chemical states of oxygen become more ionic,[18] the interaction between the surface cobalt and adsorbed oxygen becomes weaker. It can be seen from these results that CH_4 exposure did not affect the lattice oxygen of $LaCoO_3$, but did affect the adsorbed oxygen.

Figure 5 shows the valence band spectra for $LaCoO_3$ both before and after CH_4 exposure. The photoelectron spectra for the valence-band region of perovskite oxides have been studied intensively.[17,19] Especially, $LaCoO_3$ has been the subject of numerous experimental studies, since it shows temperature-dependent electronic instabilities associated with Co3d electrons. The valence-band spectrum comprises overlapping contributions due to Co3d and O2p emissions. This superposition complicates the analysis of the experimental spectra. Especially, the electronic states in the valence-band region of $LaCoO_3$ are even more complicated than those of other perovskites. Veal and Lam investigated the final-state multiplet structure of $LaCoO_3$ at both room temperature and 573 K, respectively.[19] From those results, they concluded that high-spin and low-spin trivalent cobalt ions coexisted in $LaCoO_3$ at room temperature. The energy difference between these two states is very small, as pointed out by Goodenough from magnetic measurements.[20] Therefore, the valence band spectrum for $LaCoO_3$ is quite complicated. From Our experimental results, we can observe changes of the spectra both before and after CH_4 exposure, as shown in Fig. 5. The peak near 5 eV clearly becomes broad after a 10^4 L exposure. This broadness is due to the accumulation of carbonaceous products on the surface.

Discussion

Krishnan and Wise[8] have reported that the effective activation energies on nickel surface were calculated to be 25 ± 2 kJ mol^{-1} for the reaction of surface oxygen with methane. Kuijpers et al. examined the interaction of CH_4 with a silica-supported nickel catalyst from 303 to 623 K.[21] Even at 303 K, chemisorption was observed: The apparent activation energy for the chemisorption was estimated at 25.1 kJ mol^{-1}. At temperatures above 448 K, methane, which was adsorbed on Ni catalyst, completely dissociated into adsorbed carbon atoms and hydrogen. From the results of the C1s spectra shown in Fig. 1, we concluded that CH_4 chemisorbed on the surface cobalt of $LaCoO_3$, and partly dissociated at room temperature. The dissociation of CH_4 may be enhanced to some degree by an increase in the temperature of a sample under X-ray irradiation.

Krishnan and Wise[8] pointed out that the reactive collision efficiencies for methane with adsorbed oxygen ($\theta < 0.25$) on nickel were many orders of magnitude greater than that for collisions with a clean surface. $LaCoO_3$ adsorbed oxygen on the surface, as shown in figure 4; these peak intensities decreased with an increase in the methane exposure. We therefore consider that methane reacted with adsorbed oxygen on the surface of $LaCoO_3$, thus causing a decrease in the peak intensities of O^b in the spectra for O 1s. The Eley–Rideal reaction mechanism was suggested, with a gaseous methane molecule interacting directly with an oxygen adatom.[8] They proposed an elementry step leading to the formation of a methane adspecies by the following reaction:

$$CH_4\ (g) + O\ (a) \rightarrow CH_3O\ (a) + H\ (a).$$

A subsequent reaction of CH_3O (a) was suggested to yield CH_2O (a), in analogy to the decomposition of CH_3O (a) formed during methanol adsorption. As shown in the C1s spectra (Fig. 1), the new broad peaks near 287.3 and 288.3 eV appear after 10^4 L CH_4 exposure. We consider that these new carbonaceous products resulted from a dissociation of CH_4; that is, chemisorbed methane reacted with adsorbed oxygen. The new carbonaceous products thus contain C–O bonds, such as CH_3O or CH_2O etc; they appeared in the C1s spectra. The effects of these new carbonaceous products can also be seen in the valence-band spectra given in Fig. 5. The broad peak at 3—7 eV in the spectra for both 10^2 L and 10^4 L can be ascribed to these new carbonaceous products.

Upon reacting methane and adsorbed oxygen, the surface cobalt of $LaCoO_3$ seemed to be reduced, as shown in Fig. 2. We consider that some adsorbed oxygen of $LaCoO_3$ reacts with methane; after it is removed from the surface, oxygen moves into new carbonaceous products. However, since the intensities of lattice oxygen for O 1s did not change at all as a result of CH_4 exposure, the contribution of lattice oxygen to the reaction with methane seems to be very slight at room temperature.

Finally, since we have not yet examined the exhaust components gas from the XPS analyzer, we cannot comment on the gaseous products.

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