JOURNAL OF CATALYSIS 80, 340–349 (1983)

XPS Characterization of Reduced $LaCoO_3$ Perovskite

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Received February 18, 1982; revised October 14, 1982

Three samples of $LaCoO_3$ were prepared by two different methods and calcined at 800 or 1000°C. They had BET areas of 1, 12, and 16 m^2/g and all of them showed pure perovskite X-ray diffraction patterns with identical unit cell dimensions. In a series of experiments the oxide, having larger surface area, was stepwise reduced in hydrogen at temperatures between 60 and 500°C. The XPS spectra, taken at room temperature after evacuation at 400°C at each reduction level, showed that the surface concentration of Co^0 was very low up to 300°C but increased sharply between 300 and 350°C (9–75%). This concentration further increased to 100% after 10 min reduction at 450°C, but upon heating in hydrogen for an additional 10 min at 500°C it decreased again to 75%. In another series of experiments the mixed oxide was reoxidized after each reduction. A fresh sample was reduced to 350 and 400°C by contacting with hydrogen for 1 hr and evacuated at temperatures between 400 and 500°C. Both high evacuation temperatures and reduction at 400°C during 1 hr produced a sharp decrease in Co^0 surface concentration. These results are consistent with the catalytic behavior of this perovskite reported earlier by E. A. Lombardo *et al.* (*4–7*). A model is proposed to interpret the reduction of $LaCoO_3$.

INTRODUCTION

Recently Yasumori *et al.* (*1–3*) and Lombardo *et al.* (*4–6*) have studied the hydrogenation and hydrogenolysis activities of $LaCoO_3$. The former group used $LaCoO_3$ evacuated at 600–800K for both types of reactions of C_2–C_5 hydrocarbons at reaction temperatures between 350 and 620K. Lombardo *et al.*, on the other hand, prereduced the mixed oxide in hydrogen under controlled conditions and then investigated the effect of its extent of reduction upon the catalytic activity for both ethylene hydrogenation at 253K (*4–6*) and cyclopropane hydrogenation and hydrogenolysis at 473K (*7*). They concluded (*6*) that the loci of catalytic activity were Co^0 sites formed upon reduction, but were unable to explain the maximum in activity that appeared at intermediate extents of reduction ($LaCoO_{2.25}$). Surface effects were thought to be responsible of this behavior.

The present XPS study was undertaken to investigate possible surface modifications occurring during catalyst pretreatment with the ultimate goal of relating surface chemistry to catalytic activity.

EXPERIMENTAL

Catalyst preparation. Three samples of $LaCoO_3$ were prepared, the first one by precipitating with tetraethylammonium hydroxide from an equimolar solution of

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0021-9517/83 $3.00

$La(NO_3)_3$ and $Co(NO_3)_2$ (analytical reagent grade). The precipitate was repeatedly washed with water till pH 7 and then dried under vacuum for 48 hr before being calcined under flowing oxygen at 800°C (*6*, *8*). The solid obtained had a surface area of 16 m^2/g (sample A). The other two samples were prepared by precipitation of $K_3[Co(CN)_6]$ with $La(NO_3)_3$. The precipitate was immediately filtered, washed, and dried at 120°C. Then it was heated under vacuum (1 Torr) by slowly raising the temperature up to 500°C and then calcined in flowing oxygen in a rotary quartz tube at 800°C for 4 hr. At this point an aliquot was removed from the oven. Its surface area was 12 m^2/g (sample B). The rest of the solid was calcined at 1000°C for an additional 4-hr period. This third preparation had a surface area of 1 m^2/g (sample C). Samples A and B were those used for catalytic studies. Sample C, of much lower surface area, was prepared to check if any difference could be detected by carefully studying the X-ray diffraction pattern. Note that this sample was similar to that used by Yasumori *et al.* (*1–3*), both in calcination temperature and surface area.

X-Ray measurements. The diffraction patterns were taken using a Rigaku Denki X-ray instrument with monochromatized $CuK\alpha_1$ radiation and a Ni filter.

XPS measurements. A VG ESCA 3 instrument with the $MgK\alpha$ source was used for this work. The pressure of both N_2 and O_2 in the pretreatment chamber was measured with a Pirani gauge. The hydrogen pressure was measured with a mercury manometer connected to the gas manifold through a liquid nitrogen trap. In order to heat the sample holder up to 500°C in hydrogen an infrared lamp was installed inside the pretreatment chamber to supplement the heating resistance of the sample probe. The sample was pressed onto the nickel sample holder on which a gold mesh was spot welded.

The gases used (H_2, N_2, and O_2) were 99.999% pure. Each new sample was treated in oxygen at 500 Torr and 400°C for 15 min and then evacuated at the same temperature to 2×10^{-8} Torr. After reduction up to 2 electrons/molecule[2] the sample was reoxidized in the same way, but at higher extents a mixture of 20% O_2 and 80% N_2 was used. In both cases the temperature was slowly raised from room temperature to 400°C. It has been shown that under these conditions the perovskite structure could be almost reversibly restored (*8*).

Two series of experiments were performed using samples A and B. In series I a fresh aliquot of sample B was reduced in hydrogen in successive steps between 60 and 500°C. At 60, 130, and 200°C the reduction lasted 1 hr. Between 250 and 350°C it lasted 30 min and at higher temperatures only 10 min. The hydrogen pressure was 250 Torr up to 400°C and 190 Torr at higher reduction temperatures. After each reduction the sample was evacuated for 30 min at 400°C and then cooled at room temperature to record the spectra. In series II a fresh aliquot of sample A was reduced and reoxidized several times to 350 and 400°C. Besides, in one experiment after reduction at 350°C the evacuation temperature was increased to 450 and 500°C. These experiments were done in this way because under the same conditions a sharp decrease in both catalytic activity and CO chemisorption was reported earlier (*4–7*).

All the spectra were recorded at room temperature, under a background pressure $<5 \times 10^{-9}$ Torr. Binding energies (B.E.) were always referred to C1*s* on the surface.

Treatment of data. To quantify the proportion of each oxidation state of cobalt the $Co2p_{3/2}$ spectrum was deconvoluted using a computer program which included a plotter subroutine. The B.E. and full-width at half-maximum (FWHM) values used for deconvolution are shown in Table 1. The

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[2] Extent of reduction is expressed as electrons/molecule according to the scheme $LaCoO_3 + xH_2 \xrightarrow{300-500°C} LaCoO_{3-x} + xH_2O$, $0 \leq x \leq 1.5$, $x = 1.5 \equiv$ 3 electrons/molecule.

TABLE I

Binding Energies and FWHMs Used to Deconvolute Cobalt Spectra

Species	$Co2p_{3/2}$ (eV)	FWHM (eV)
Co^{0}[a]	778.0	2.8
Co^{3+}[a]	779.6	4.3
Co^{2+}	780.3[b]	4.3[c]

[a] Experimental values from this work.

[b] Refs. (*2*) and (*9*).

[c] Adopted by comparison with Ref. (*10*). See text.

values for $Co^{3+}2p_{3/2}$ and $Co^{0}2p_{3/2}$ were determined in our instrument from spectra taken for the oxidized and completely reduced sample (La_2O_3 + Co^0). The $Co^{2+}2p_{3/2}$ B.E. was obtained from Okamoto *et al.* (*9*). Although its value is higher than the $Co^{3+}2p_{3/2}$ it is consistent with our experimental results (shift of this peak to higher B.E. at reduction temperatures up to 300°C). A similar trend could be observed in Fig. 4 of the paper by Yasumori *et al.* (*2*), where they show the Co2*p* spectra of several $LaCoO_3$ samples, prepared fresh and exposed several times to a mixture of H_2 and C_2H_4 at 300°C. It was also checked that the FWHM ratio for the three cobalt signals agreed quite well with that reported by McIntyre and Cook (*10*).

The deconvolution program operated as follows. The data shown in Table 1 was fed to the computer. For each spectrum to be deconvoluted a tentative value was given for each peak height (Co^0, Co^{2+}, and Co^{3+}) which was fed to the computer together with the experimental baseline drift. With this information the computer calculated each peak plus the composite curve with the same baseline slope as the original spectrum. It was usually necessary to make several trials until a good fit was obtained. This trial and error method stopped when the coincidence in both B.E. and FWHM was within ±0.1 eV and the peak height was within 5%. At this point a hard copy of the calculated spectra was obtained to allow a visual comparison with the experimental data. The method had a good sensitivity to deconvolute Co^0 from both Co^{2+} and Co^{3+}, but it was somewhat insensitive to evaluate the separate contribution of Co^{2+} and Co^{3+}. This was due to the close vicinity in B.E. of these two broad peaks.

RESULTS

X-Ray Diffraction Patterns

The three samples showed identical diffraction patterns (Fig. 1). They were coincident with the pattern reported in the literature for $LaCoO_3$ perovskite (*11*). No traces of segregated single oxide phases were observed. Sample C, calcined at 1000°C, showed a slightly higher crystallinity as indicated by somewhat sharper peaks and better resolution of the 110/104 planes (Fig. 1). To further investigate any possible differences in the bulk structure of these samples the cell parameters and unit cell volumes were determined. They were exactly coincident for the three samples within experimental error (Table 2).

XPS Data

The Co2*p* and C1*s* (30-eV span) and the Co2*p* + La3*d* (100-eV span) regions were always scanned at each reduction temperature. The O1*s* region (30-eV span) was also scanned in most cases. Besides, in a few cases a wide scanning was made (1253.6–253.6 eV) but no other peaks than those expected from pure $LaCoO_3$ were found. The very weak C1*s* signal always appeared at 284.7 ± 0.1 eV, indicating that no charging effects occurred in either sample A or B.

The B.E.s and FWHMs for Co2*p* peaks of series I experiments are shown in Table 3. The $Co2p_{3/2}$ peaks were deconvoluted and the percentage surface concentration of the three oxidation states was plotted vs bulk extent of reduction in Fig. 2. The bulk reduction, taken from previous work, was calculated by measuring the hydrogen uptake in a closed recirculation system and

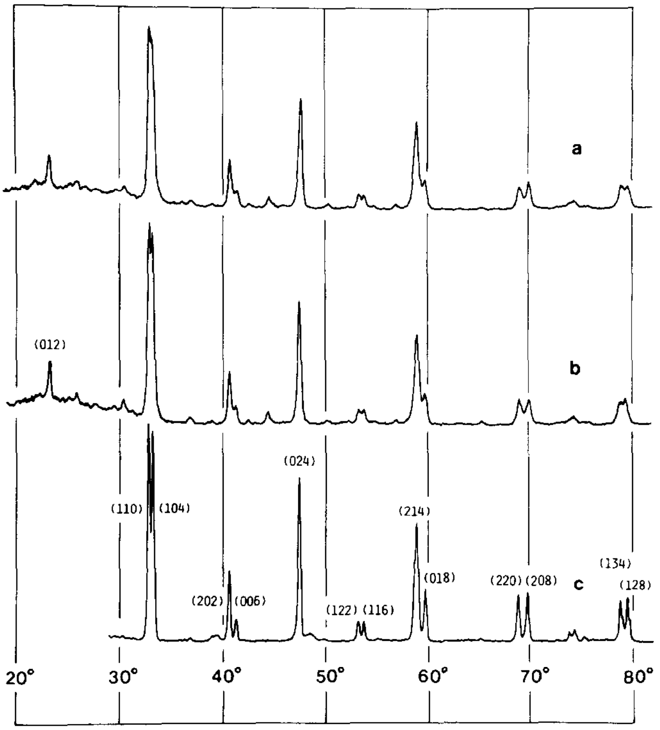

FIG. 1. X-Ray diffraction patterns of samples A, B, and C. Monochromatic Cu$K\alpha_1$ radiation, Ni filter.

further details were reported elsewhere (*4*, *5*). Note the large shift to lower B.E. and the narrowing of the Co2*p* spectrum that occurred between 300 and 350°C (Table 3), which correspond with a sharp increase in Co^0 concentration (Fig. 2). Besides, the sample was partially reoxidized between 450 and 500°C as denoted by the higher B.E. and a wider Co2*p* signal (Table 3 and Fig. 2).

The Co2*p* and La3*d* spectra were taken together in single scannings (774–874 eV) in order to ascertain any possible variation of Co/La ratio during reduction. The La3*d* doublets were ill defined when a fresh oxidized sample was introduced into the spec-

TABLE II

Cell Parameters of Various $LaCoO_3$ Preparations

Starting material	Sample	Calcination temperature (°C)	Surface area (m^2/g)	a_0[a] (Å)	c_0[a] (Å)	V_0[b] ($Å^3$)
$La(NO_3)_3$ + $Co(NO_3)_2$ + $(C_2H_5)_4N$	A	800	16	5.436 ± 0.003	13.091 ± 0.007	335.1 ± 0.5
$K_3[Co(CN)_6]$ + $La(NO_3)_3$	B	800	12	5.435 ± 0.003	13.088 ± 0.008	334.7 ± 0.6
	C	1000	1	5.434 ± 0.002	13.074 ± 0.006	334.3 ± 0.4

[a] Cell parameters.
[b] Unit cell volume.

TABLE III

Co2p Binding Energies and FWHMs of $LaCoO_3$ Reduced in Hydrogen (Series I)[a]

Sample	Reduction temperature (°C)	Bulk reduction (e/molec.)[b]	Co2$p_{3/2}$ B.E. (eV)	FWHM of Co2$p_{3/2}$ (eV)	Co2$p_{1/2}$ B.E. (eV)
A & B	Oxidized[c]	0.0	779.6 ± 0.1	4.3 ± 0.2	795.0 ± 0.2
B	60	0.0	779.6	4.7	795.1
B	130	~0.0[d]	779.5	4.9	795.0
B	200	0.2[d]	779.7	5.4	795.3
B	250	0.4	779.9	5.3	795.5
B	300	1.2	779.3	5.7	795.5
B	350	1.5	778.1	3.8	793.8
B	400	1.6	778.1	3.0	793.6
B	450	2.0	778.0	2.8	793.1
A & B	500[c]	3.0	778.4 ± 0.1	3.4 ± 0.1	793.4 ± 0.2

[a] P_{H_2} = 250 − 190 Torr. In all experiments the sample was heated using both the probe heating resistance and the ir lamp. See text.

[b] Obtained from previous experiments in which the hydrogen uptake was measured in a gas recirculating system (*4–5*).

[c] These values represent averages of five different aliquots of samples A and B.

[d] Up to 200°C the hydrogen uptake was too small to measure accurately.

trometer (Fig. 3a) and they remained the same after 4 hr of evacuation at 500°C. However, after reduction at 300°C the doublets were resolved (Fig. 3b). Furthermore, they stayed well resolved after reoxidation (Fig. 3c). Spectrum d in Fig. 3 shows the composite spectrum of La_2O_3 and $La_2(CO_3)_3$ obtained from the work of Jørgensen and Berthou (*12*), corrected for charging effect. Besides, in sample A, which apparently contained a higher concentration of carbonate on the surface, a second weak C1s peak appeared at 286.7 eV B.E., which compares well with the 286.0 value reported for $La_2(CO_3)_3$ (*12*). The O1s region also showed a behavior consistent with these observations. The fresh oxidized sample showed two O1s peaks at 528.5 and 531.5 eV. The first one corresponds to the reported B.E. for La CoO_3 (*12*), while the second one could be due to carbonate oxygen. This second peak steadily decreased as the sample was reduced at increasing reduction temperatures and was not restored by reoxidation with O_2. All these observations are thus consistent with the formation of a carbonate layer on the surface of these samples.

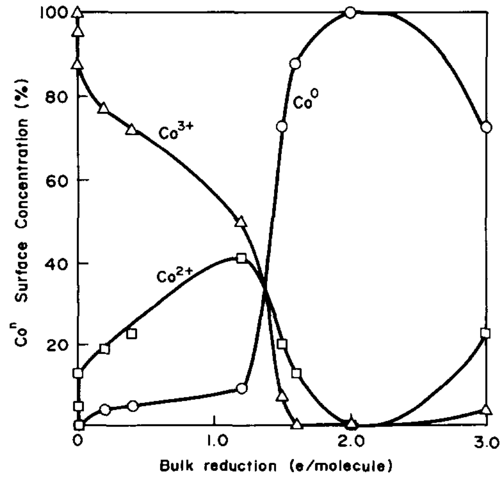

FIG. 2. Surface concentrations of Co^0, Co^{2+}, and Co^{3+} on reduced $LaCoO_3$. Points were obtained from deconvolution of Co2$p_{3/2}$ peaks (Table 3) using the data given in Table 1.

The Co2p/La3$d_{3/2}$ peak area ratio was used to evaluate any possible change in relative concentration with extent of reduction. This ratio decreased with higher re-

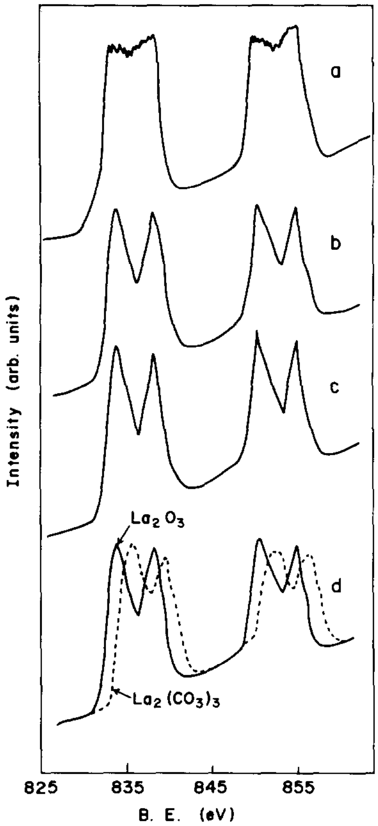

FIG. 3. La3*d* region in $LaCoO_3$. (a) Fresh oxidized sample, (b) sample reduced to 300°C in H_2, (c) reoxidized after (b), (d) La_2O_3 and $La_2(CO_3)_3$ spectra from Ref. (*12*). Analyzer energy 20 eV, 100 eV scanning in 1000 sec.

duction temperatures (Fig. 4). It should be noted, however, that the sharpest decrease occurred at low reduction temperatures and perhaps this reflected a change in sensitivity factors of the La peak due to the $La_2(CO_3)_3$ decomposition. Supporting this interpretation is the fact that upon reoxidation the Co/La ratio did not return to the original value (Fig. 4).

The results obtained in series II experiments are shown in Table 4. Experiments 1 and 2 were run to check that exposure to hydrogen for more than 1 hr at 350°C did not modify the extent of reduction. This indicated that a plateau value of reduction has been reached at this temperature. Comparing Exps. 1 and 2 (Table 4) with the 350°C data of both Table 3 and Fig. 2, it is concluded that B.E., FWHM, and cobalt surface concentration were essentially the same irrespective of whether the reduction process was conducted in one step or in successive steps at increasing temperatures. Besides, this comparison illustrates the close similarity in reduction behavior of samples A and B. This is consistent with the almost identical catalytic behavior of these preparations (*4–7*).

The spectra taken after Exps. 1 and 3-i (Table 4) were very similar. This means

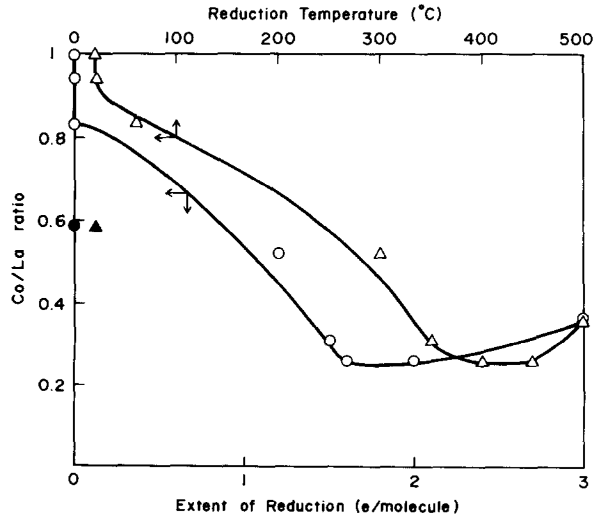

FIG. 4. Effect of reduction upon the Co/La ratio. (○,△) Stepwise reduction; (●,▲) after reoxidation.

TABLE IV

Co2*p* Binding Energies and Surface Concentration of Co^0, Co^{2+}, and Co^{3+} at 350–400°C Reduction Temperatures (Series II)[a]

Exp. No.	Reduction			Evacuation		B.E. (eV)		Surface concentration (%)		
	Temp. (°C)	Time (min)	Extent in bulk (*e*/molecule)	Temperature (°C)	Time (min)	$Co2p_{3/2}$	$Co2p_{1/2}$	Co^0	Co^{2+}	Co^{3+}
1	350	60	1.5	400	30	778.0	793.6	81	13	6
2	350	15	1.5	400	30	777.9	793.5	80	13	7
				Reoxidation (500 Torr O_2, 400°C)						
3-i	350	60	1.5	400	60	778.2	794.0	74	26	0[b]
ii				450	15	778.7	794.3	65	21	14
iii				500	60	778.7	794.0	74	26	0
iv				500		779.0	794.9	58	36	6[c]
v				500		779.9	795.6	5	17	78[d]
				Reoxidation (500 Torr O_2, 400°C)						
4-i	400	60	1.6	400	60	778.5	794.9	69	25	6
ii				400		779.5	795.3	45	33	22[d]

[a] Sample A, hydrogen pressure 250 Torr.

[b] No spectrum modification observed after changing the incidence angle of the X-ray beam.

[c] Lower penetration depth of X-ray beam (25° rotation of the sample holder).

[d] Lowest penetration depth of X-ray beam (33° rotation of the sample holder).

that the surface extent of reduction could be reproduced after reoxidation. It should be pointed out, however, that the deconvolution technique is not very sensitive for distinguishing between Co^{2+} and Co^{3+} due to the close vicinity of these broad peaks. This explains why Co^{2+} and Co^{3+} surface concentrations obtained from Exps. 1 and 3-i are different although its spectra are quite the same.

DISCUSSION

Since in several catalytic works $LaCoO_3$ perovskites have been used which were prepared by different methods and calcined at various temperatures (surface areas from 20 to 1 m^2/g), it was important to check the X-ray patterns of our three samples. The good agreement among the cell parameters of these samples is indicative of its close structural similarity. The only difference observed was the higher crystallinity of sample C, calcined at 1000°C, as expected from the lower surface area of this nonporous material (larger particle size).

The slow increase in ethylene hydrogenation activity up to a reduction temperature of 300°C (~1 *e*/molecule) and the sharp increase between 300 and 350°C (1–1.5 *e*/molecule), shown in Fig. 5a, can now be explained in terms of the XPS results shown in Table 3 and Fig. 2. Up to 300°C the amount of Co^0 formed was small (9%). This value is surprisingly close to the bulk concentration of Co^0 calculated by Sis *et al.* (*13*) from magnetic measurements. Between 300 and 350°C a sharp increase of the Co^0 concentration occurred (note the shift to lower B.E. and the sharp decrease in width in Table 3) reaching 75% at the last temperature (Fig. 2). The CO chemisorption data (*6*) are also consistent with these results (Fig. 5b). The difference between surface and bulk extents of reduction that could be calculated from Fig. 2 should be cautiously evaluated because the deconvolution of the Co^{2+} and Co^{3+} peaks, being wide and close in B.E., is not very precise. Instead the Co^0 peak is narrower and further away in B.E., therefore its deconvolution can be made with more confidence.

It should be noted that the quantitative uncertainty involved in the deconvolution of the cobalt spectra does not endanger the basic conclusions of this work since the main changes in oxidation states of cobalt are supported by significant variations of both B.E.s and FWHMs.

Neither Table 3 nor Fig. 2 give any clue to explain the sharp drop in both activity and CO adsorption beyond 1.5 *e*/molecule (Figs. 5a and b). One of the possible causes,

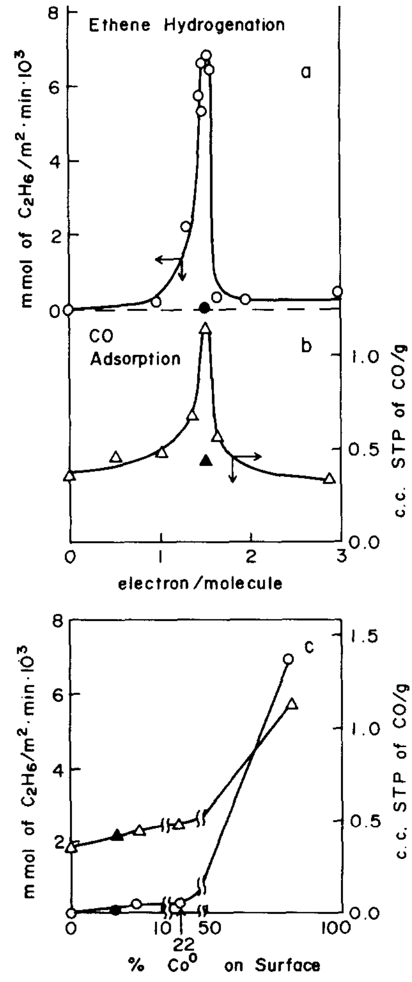

FIG. 5. Effect of reduction and evacuation temperature upon both catalytic activity and CO chemisorption. (a) and (b) from Ref. (*6*). (○,△) Catalyst evacuated at 400°C after reduction; (●,▲) evacuation temperature 500°C.

suspected in a previous paper, was the migration of Co^0 into the bulk of the solid. Figure 4 gives little support to this hypothesis. Most of the decrease in Co/La ratio occurred at low reduction temperature and this perhaps was due to the elimination of CO_2 from the surface layer, e.g., the La3*d* doublets that appeared at the beginning as carbonate have been transformed to La_2O_3 (Figs. 3a,b). Note that beyond 350°C the ratio was rather constant and this in turn is consistent with the disappearance of the carbonate bands from the spectra (compare Figs. 3a and b).

The data shown in Table 4 indicate that either evacuation temperatures higher than 400°C (Exps. 3-ii–v) or longer treatments with H_2 at 400°C or above (Exp. 4) produced a partial reoxidation of the surface. Besides, an incipient reoxidation process was observed when the sample was treated for only 10 min in hydrogen at 500°C (Table 3 and Fig. 2). The oxidation of Co^0 during evacuation could be produced by the hydroxyls still remaining on the surface at 500°C much in the same way as Mo^0 is reoxidized by alumina, as shown by Brenner and Burwell (*14*). They reported that upon heating $Mo(CO)_6$–Al_2O_3 above 200°C both CO and H_2 were detected in the gas phase and Mo^0 was oxidized, e.g., Mo^v E.P.R. signal steadily increased during heating in vacuum between 200 and 500°C.

The effect of hydrogen treatment at 400°C and above is not yet clearly understood. Although one could speculate about several possible causes for this behavior, for example, SMSI phenomenon (*15–17*), none of them could be substantiated with the available data.

In Fig. 5c both the activity and CO adsorption data were replotted against Co^0 surface concentration. In doing so the sharp maxima observed when the bulk reduction was represented in the abscissa have disappeared.

From these studies and related works a model can be proposed for the reduction of $LaCoO_3$. Reduction at relatively low temperatures ($\leq$300°C), up to ~1 *e*/molecule, produces a rather homogeneous reduction of the solid, with Co^{2+} being the predominant species and only a small amount of Co^0 being formed (<10%) (*8, 13*). Between 300 and 350°C the surface is much more rapidly reduced than the bulk: surface concentration of Co^0 reaches 75% when the average bulk cobalt oxidation state is 1.5. From here on the bulk reduction is much slower, e.g., heating to 500°C for 2 hr was needed to completely reduce the oxide to a mixture of La_2O_3 + Co^0 (*5*). At this point the reduction process is very likely diffusion limited. This is also supported by the higher temperatures (600°C) for total reduction reported by Sis *et al.* (*13*), who used a perovskite having a very low surface area (larger particle size). The behavior of the surface differs widely from the bulk at 400°C and above. Longer exposure to hydrogen at this point very likely produces additional oxygen vacancies and the Co^0 clusters already present can interact with electron-deficient metal clusters. In such a case the surface ability to chemisorb CO and to promote olefin hydrogenation would be impaired.

ACKNOWLEDGMENTS

Thanks are due to Professor Yu Hariya for the X-ray measurements, to Professor Iwao Yasumori for helpful discussion, and to Dr. Akiko Aramata for providing the computer program of XPS spectrum deconvolution. One of us (E.A.L.) is very grateful to Japan International Cooperation Agency for financial support of his stay in Japan. This research was also generously supported in part by Science Research Grant 343001 from the Ministry of Education (Japan) and by a Grant from Mitsubishi Foundation 1979 (I.T.).

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