

Characterization of Hydrogenation Active Sites on LaCoO₃ Perovskite

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LaCoO₃ becomes active for hydrogenation of ethene upon reduction in hydrogen at temperatures between 300 and 490°C. Several aspects of the reacting system were studied in order to ascertain the nature of the active sites generated in this manner. Catalyst deactivation was evaluated by comparing rates between two successive experiments. An upper limit was estimated for the amount of polymeric residues formed after a single run: $1.1 \pm 0.5 \times 10^{14}$ molecules of C₂ per square centimeter. Reduced LaCoO₃ also catalyzed the self-hydrogenation of ethene. When a mixture of C₂H₄:D₂ = 1:1 was reacted over LaCoO₃ reduced to varying extents multiple-exchanged ethenes and ethanes were formed. The exchange patterns were almost unaffected by the extent of reduction. The effect of pretreatment temperatures was also evaluated. The solid in its reduced form was particularly sensitive to high-temperature treatments. The amounts of CO chemisorbed when plotted vs extent of reduction gave curves that were almost identical to the activity plots. The results reported here, discussed in terms of the current literature, are consistent with a model in which finely dispersed Co⁰, formed in the oxide matrix upon reduction, is the locus of hydrogenation activity.

INTRODUCTION

Mixed oxides of the general formula ABO₃ with a perovskite structure have been thoroughly studied due to their many technological applications (1) and theoretical interest (2). However, their potential catalytic properties remained almost unexplored till the early seventies when a sustained effort began to try to use them as substitutes of noble metal-based automobile exhaust catalysts (1). Other possible catalytic applications have been forecasted, e.g., for coal liquefaction (3). Besides, these isomorphous oxides offer the possibility of varying their properties by cation substitution while still retaining their crystalline structure. This makes them very attractive for basic catalytic studies.

Crespin and Hall (4) have recently studied the reduction-oxidation cycle of several

mixed oxides. They have reported that LaCoO₃ could be reduced in hydrogen up to LaCoO_{1.5} (La₂O₃ + Co⁰) and reversibly oxidized back to the original structure with little loss in crystallinity. In two recent publications Lombardo and co-workers (5, 6) have reported that LaCoO₃ perovskite upon reduction at high temperature became active for ethene hydrogenation. When the catalytic activity was plotted vs extent of reduction the curve showed a sharp maximum. The goal of this work was to ascertain the nature of the active sites involved in hydrogenation reactions.

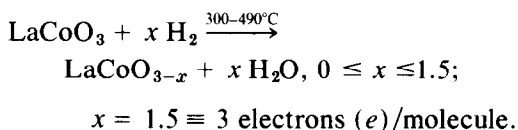
EXPERIMENTAL

Catalyst preparation and pretreatment. LaCoO₃ was prepared by precipitation from an equimolar solution of La(NO₃)₃ and Co(NO₃)₂ (analytical reagent grade) using tetraethylammonium hydroxide. The precipitate was repeatedly washed with water, till pH 7, and then dried under vacuum for 48 hr before being calcined under flowing

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oxygen at 800°C. This value was determined by increasing the temperature until the X-ray pattern of the perovskite phase was obtained and the patterns for the oxide phases had disappeared (4). The material obtained had a surface area of 16 m²/g.

The LaCoO₃ was reduced in hydrogen at the desired level before each run in a standard recirculation system. The extent of reduction could be followed volumetrically and controlled by selecting the reduction temperature between 300 and 490°C.



Reoxidation was carried out in air at 400°C. More details about this redox process have been given elsewhere (4-6). The standard pretreatment before either adsorption or activity measurements was as follows: oxidation with air for 2 h followed by evacuation for 1 h at 400°C, reduction at the desired level, and final evacuation at 400°C. After the first redox cycle, usually carried up to 1 *e*/molecule, the oxide showed approximately a 10% loss in surface area. From there on the surface area remained constant.

Gases. Hydrogen obtained from commercial sources was passed over copper wire thermostated at 300°C, anhydrous CaCl₂ and MgClO₄, and given a final cleanup with activated charcoal cooled at -195°C. Air was dried before contacting the catalyst. CO (research grade) was used as received. Deuterium was passed through a Pd thimble. Ethene, research grade, was used as received after having checked, by distillation between -78 and -195°C, that water was neither detected nor were other effects observed when ethene was used in kinetic experiments.

Adsorption measurements. They were done in a standard BET system to which a recirculation loop was added to reduce the catalyst *in situ* before CO adsorption.

Reaction procedures. The catalytic activity and tracer experiments were done in the same recirculation system used for reduction into which a bulb, containing most of the reaction volume (430 cm³), was incorporated through a bypass. The exit stream from the bulb could be sampled for glc analysis. Less than 1% of the circulating gas was removed for each analysis. The reactant mixtures were prepared volumetrically by introducing a measured amount of ethene first into the circulation system where it was frozen and outgassed before hydrogen or deuterium was admitted in the desired amounts. The reactants were mixed before contacting the catalyst. The average length of the hydrogenation run was 1 h.

Mass spectroscopy analysis. Provisions were made to trap the individual products at the exit of the glc column. Ethene was analyzed at low ionization voltage, 15 eV, but ethane was run at 70 eV; more details are given elsewhere (7).

RESULTS

Deactivation, Residue Formation, and Self-hydrogenation

To determine the extent of deactivation that occurred after the standard runs, in which C₂H₄:H₂ = 1:1 mixtures were used, the reactor was evacuated at 22°C for 1 h (10⁻⁵ Torr) and then a new load of reactants was admitted. The data obtained are shown in the first three rows of Table 1. A possible cause of the significant reduction in activity could be the formation of polymeric residues (coke) on the catalyst. To estimate an upper limit for this deposit the reactor was evacuated at 22°C for 1 h after a standard experiment and then oxidized in air in the circulation system. The amount of carbon dioxide collected in the cold trap (-195°C) was measured in the BET system. Results obtained from six runs done with the catalyst reduced between 1.0 and 3.0 *e*/molecule did not correlate with the extent of reduction; the average value obtained was 1.1 ± 0.5 × 10¹⁴ molecules of C₂ per square centimeter.

TABLE 1
 Deactivation and Self-hydrogenation Activity^a

Extent of reduction (<i>e</i> /molecule)	Reaction temperature (°C)	Reactants	Activity ($\frac{\text{m mol C}_2\text{H}_6}{\text{g cat min}}$)	Activity ratio
1.0	22	C ₂ H ₄ + H ₂ ^b	1.3 × 10 ⁻²	12.3
		C ₂ H ₄ + H ₂ ^c	1.1 × 10 ⁻³	
1.3	22	C ₂ H ₄ + H ₂ ^b	2.6 × 10 ⁻²	5.5
		C ₂ H ₄ + H ₂ ^c	4.7 × 10 ⁻³	
1.35	0	C ₂ H ₄ + H ₂ ^b	5.3 × 10 ⁻⁴	26.5
		C ₂ H ₄ + H ₂ ^c	2.0 × 10 ⁻⁵	
1.5	-20	C ₂ H ₄ + H ₂ ^b	6.1 × 10 ⁻²	11.0
		C ₂ H ₄ ^d	5.6 × 10 ⁻³	
1.5	0	C ₂ H ₄ + H ₂ ^b	1.1 × 10 ⁻¹	7.0
		C ₂ H ₄ ^d	1.5 × 10 ⁻²	

^a Batch reactor with recirculating gas system, 100 mg of LaCoO₃.

^b C₂H₄:H₂ = 1:1; total pressure, 170 Torr.

^c These experiments were done after evacuation of the catalyst at 10⁻⁵ Torr for 1 h at 22°C, following the previous run.

^d All conditions the same as in footnote *b* but without hydrogen. Ethene pressure = 85 Torr.

In the last two rows of Table 1 it is shown that reduced LaCoO₃ catalyzes the self-hydrogenation reaction, the rate of ethane formation being lower than in the presence of hydrogen. The only difference between these runs and hydrogenation experiments was the absence of hydrogen. In none of these runs or even in one experiment done at 50°C was it possible to detect acetylene in the gas phase.

Tracer Experiments

The previous results, particularly those of self-hydrogenation, seemed to indicate that the active sites were metallic in nature. To substantiate this behavior a series of experiments was performed in which ethene was reacted with deuterium. The region of low extent of reduction was carefully explored for in these cases it was more likely that an oxide-type behavior could be detected.

In Table 2 the raw data are presented for experiments in which mixtures of C₂H₄:D₂ = 1:1 were reacted over LaCoO₃ reduced to different extents. To cover a wide range

of conversions it was necessary to operate at 22 and 50°C and to use varying amounts of catalysts, 100 and 500 mg. An important isotope effect was observed when comparing hydrogenation with deuteration experiments. The data show that both ethene and ethane were multiply exchanged with deuterium. Note that different extents of reduction gave approximately the same product distribution at comparable conversions.

The experimental isotopic data have been compared to calculated binomial distributions. A good agreement between the experimental and calculated distributions was observed in all cases but those of ethane samples obtained at conversions below 5%. In these cases the experimental *d*₂ concentration was higher and the *d*₁ concentration was accordingly lower than the calculated ones. The important contribution of ethane-*d*₀ was due to the self-hydrogenation reaction. To illustrate this point the results obtained at low and high conversion over a slightly reduced catalyst (0.5 *e*/molecule) were plotted in Fig. 1.

In a separate experiment a C₂H₆:D₂ = 1:1

TABLE 2
 Ethene Deuteration over LaCoO₃ Perovskite^a

Extent of reduction (<i>e</i> /molecule)	Reaction temperature (°C)	Conversion (%)	Ethene					Ethane					
			<i>d</i> ₀	<i>d</i> ₁	<i>d</i> ₂	<i>d</i> ₃	<i>d</i> ₄	<i>d</i> ₀	<i>d</i> ₁	<i>d</i> ₂	<i>d</i> ₃	<i>d</i> ₄	<i>d</i> ₅
0.5	22	0.3	0.98	0.02	—	—	—	0.33	0.18	0.49	—	—	—
	22	0.5	0.99	0.01	—	—	—	0.35	0.28	0.37	—	—	—
0.5	50	5.1	0.94	0.06	—	—	—	0.42	0.25	0.33	—	—	—
	50	44.5	0.55	0.29	0.11	0.03	0.02	0.24	0.26	0.27	0.15	0.05	0.03
	50	54.0	0.40	0.36	0.16	0.05	0.03	0.23	0.30	0.28	0.12	0.05	0.02
	50	58.4	0.37	0.37	0.18	0.05	0.03	0.23	0.30	0.26	0.15	0.05	0.01
0.7	22	2.3	0.98	0.02	—	—	—	0.27	0.23	0.50	—	—	—
0.7	50	32.0	0.67	0.28	0.05	—	—	0.24	0.33	0.36	0.07	—	—
	50	42.0	0.55	0.34	0.08	0.02	0.01	0.20	0.34	0.37	0.09	—	—
1.25	22	9.0	0.94	0.06	—	—	—	0.14	0.37	0.43	0.04	0.02	—
1.25	50	56.5	0.52	0.33	0.11	0.03	0.01	0.14	0.36	0.38	0.10	0.02	—
	50	58.5	0.49	0.36	0.11	0.02	0.02	0.10	0.31	0.41	0.14	0.04	—
1.5	22	6.4	0.95	0.05	—	—	—	0.35	0.31	0.34	—	—	—
	22	6.8	0.97	0.03	—	—	—	0.33	0.27	0.36	0.04	—	—
1.75	50	2.9	—	—	—	—	—	0.45	0.17	0.38	—	—	—
	50	3.5	0.97	0.03	—	—	—	0.46	0.17	0.36	0.01	—	—

^a Batch reactor with gas recirculation. 100 or 500 mg of LaCoO₃. C₂H₄:D₂ = 1:1. Total pressure = 170 Torr.

mixture was contacted with the catalyst at 50°C for 2 h. The mass spectra showed no deuterated ethanes formed under these conditions.

Evacuation Temperature Effects upon Catalytic Activity

The experiments reported so far were run

following the standard pretreatment outlined under Experimental. In order to ascertain the effect of evacuation temperatures, both after oxidation and reduction, the set of experiments shown in Table 3 were run.

As could be expected from a structural point of view the evacuation temperature

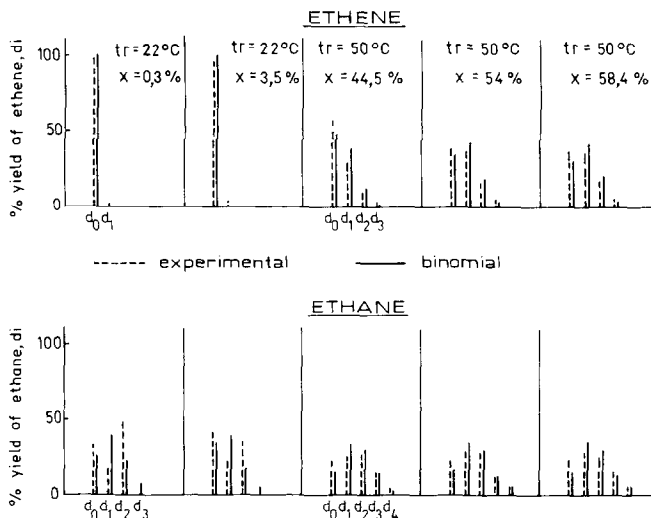


FIG. 1. Isotopic distribution of ethenes and ethanes produced by reaction of a C₂H₄:D₂ = 1:1 mixture over LaCoO₃ reduced at 0.5 *e*/molecule. Total pressure, 170 Torr; reaction temperature, *t*_r.

after reduction strongly influenced the catalytic activity of LaCoO_3 . By the same token evacuation temperatures after oxidation were not expected to affect the catalytic activity as shown in the last row of Table 3.

Adsorption Measurements

The previous results were consistent with a model of the reduced LaCoO_3 in which finely dispersed cobalt was supported in an oxide structure, the metallic sites being the loci of catalytic activity. However, according to this picture it is hard to explain the maximum in catalytic activity unless the concentration of exposed Co^0 is affected by other variables, e.g., temperature, besides extent of reduction. Hydrogen is the most convenient gas to estimate metal dispersions of supported catalysts. However, in this case it could not be used for it might penetrate within the lattice. The second-best choice for this purpose was carbon monoxide.

To determine the amount of CO chemisorbed the catalyst reduced at the desired level was contacted with carbon monoxide at a pressure of 300 Torr. The pressure was high enough to be located on the plateau of the adsorption isotherm. After the total amount of adsorbed gas was measured the

catalyst was evacuated at the adsorption temperature (-20°C) for 30 min. A second adsorption was done at the same pressure to measure the amount of physically adsorbed gas. The difference between the first and second adsorption gave the amount of CO chemisorbed which was plotted vs extent of reduction in Fig. 2a. Two curves are shown in this figure. Curve I corresponds to data points obtained with aliquots of the catalyst that have never been reduced to the highest possible extent, $3 e/\text{molecule}$. Curve II was obtained with aliquots that have been reduced at least once to maximum extent. Figure 2b (5, 6) has been included for comparison. It shows the effect of extent of reduction upon catalytic activity. Again two curves were obtained as in the adsorption case.

To check the connection between the adsorption and activity results (Fig. 2), experiments were done in which after the catalyst has been reduced to $1.5 e/\text{molecule}$ and CO chemisorbed an activity test was run. In these cases the activity dropped to zero both at 0 and -20°C . From the amount of CO chemisorbed an upper limit of active site concentration could be estimated. For the most active catalyst ($1.5 e/\text{molecule}$ on curve I) the maximum active site concentration calculated in this manner was 1.9×10^{14} sites/ cm^2 .

TABLE 3

Effect of Evacuation Temperature, after Reduction and Oxidation, upon Catalytic Activity^a

Evac. temp of oxidation ($^\circ\text{C}$)	Evac. temp. of reduction ($^\circ\text{C}$)	Activity ($\frac{\text{m mol C}_2\text{H}_6}{\text{g cat min}}$)
400	490	0
400	490	0
400	450	8.8×10^{-3}
400	400	6.1×10^{-2}
400	350	6.9×10^{-2}
490	400	8.0×10^{-2}

^a Batch reactor with recirculating gas system, 100 mg of LaCoO_3 , reduction temperature = 350°C , $1.5 e/\text{molecule}$, reaction temperature = -20°C , C_2H_4 : $\text{H}_2 = 1:1$, $P_T = 170$ Torr.

DISCUSSION

The three tests applied to investigate the nature of the hydrogenation active sites consistently supported a metallic behavior of reduced LaCoO_3 . In Table 4 the results obtained are summarized and compared with data reported in the literature for transition metals and their oxides. In the first row it is shown how the deactivation behavior resembles that of group VIII metals (8). Related metal oxides such as Co_3O_4 do not deactivate under similar conditions (9). Note that these data refer to short runs not to longer ones in flow systems where it is likely that oxides will also deactivate.

A stronger proof of metallic behavior is

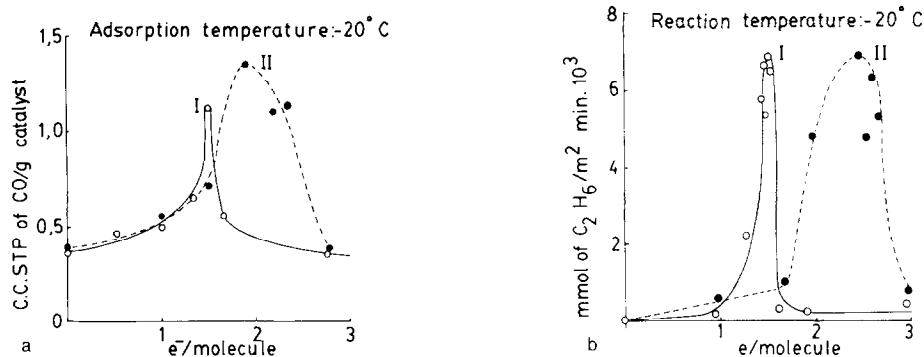


FIG. 2. Adsorption of carbon monoxide and hydrogenation activity over reduced LaCoO₃. ○, Catalyst aliquots never reduced to maximum extent. ●, Aliquots reduced at least once to 3 e/molecule. (a) CO chemisorption on reduced LaCoO₃. (b) Initial rates of ethene hydrogenation over reduced LaCoO₃. C₂H₄: H₂ = 1:1; total pressure, 170 Torr.

the ability to catalyze the self-hydrogenation reaction, Tables 1 and 4. This is characteristic of metals (10), while metal oxides are not known to be active for this reaction.

The ethene-deuterium reaction is another key test to decide between both alternatives. Group VIII metals catalyze the deuterium-olefin exchange. Therefore, multiply-exchanged ethene and ethane are obtained during the reaction (11-14). On the other hand metal oxides are more effective for hydrogenation than for exchange. The reaction products are then almost exclusively ethane-*d*₂ and unexchanged C₂H₄ at low temperature (9, 15-17). Reduced LaCoO₃ behaves very much the way metals do (Table 2).

In most cases there was an excellent

agreement between the experimental and the binomial distributions of deuterated ethanes and ethenes. However, when the conversion was below 5% the ethane distribution did not match the random pattern. Figure 1 shows that the ethane-*d*₂ concentration is higher and the *d*₁ lower than the values calculated assuming a binomial distribution. First, it could be concluded that a given contribution of oxide-type sites produced a higher *d*₂ concentration. But this conclusion is hard to sustain when almost identical results were obtained with a catalyst reduced at 1.15 e/molecule. This more likely is an artifact arising from the cracking pattern calculations for ethane which give multiple fragmentation strongly dependent on very many factors (18).

TABLE 4

Criteria for Differentiation of Ethene Hydrogenation Mechanisms over Metals and Metal Oxides^a

Criteria	Oxides	Metals	LaCoO ₃
Deactivation ^b	No (9, 16)	Yes (8)	Yes
Self-hydrogenation	No	Yes (10)	Yes
C ₂ H ₄ + D ₂	C ₂ H ₄ D ₂ ^c C ₂ H ₄ ⁺ (9, 15-17)	C ₂ H _{6-y} D _y ^d C ₂ H _{4-x} D _x (11-14)	Multiply-exchanged ethene and ethane

^a Numbers in parentheses correspond to references.

^b Applies to short runs at or below room temperature.

^c Low-temperature experiments.

^d Average deuterium exchanged depends on the metal considered.

Ichimura *et al.* (19), obtained similar tracer data for LaCoO_3 which has not been prerduced. However, their experiments were done at higher temperatures (80 and 300°C) at which it is expected that the oxide will be reduced to a certain extent. This possibility was not considered by the authors (19) and led them to conclude that Co(III) played an important catalytic role. The results shown here do not support their views.

If the locus of activity is Co^0 , formed upon reduction, how can the shape of the activity vs extent of reduction curves be rationalized, Fig. 2b? Part of the answer could be found in the work of Crespín and Hall (4). They claimed that Co^{2+} is selectively formed at the early stages of reduction, up to $1 e/\text{molecule}$. The results of Sis *et al.* (20) are also consistent with their views. This would explain the slow increase in activity up to this extent of reduction shown in Fig. 2b. From here on the activity went up very fast but it promptly reached a maximum (curve I, Fig. 2b). The question is why the activity did not steadily increase up to the maximum extent of reduction when all the cobalt has been reduced to the metallic form. Table 3 seems to give some clues. It shows a drastic drop in catalytic activity after heating the reduced perovskite under vacuum. Similarly, to reach the extents of reduction on the left-hand side of curve I it was necessary to heat the catalyst in hydrogen at or above 400°C for periods between 2 and 5 h (4-6). Heating at temperatures higher than 400°C , or perhaps even several hours in hydrogen at 400°C , could cause the migration of Co^0 to form small clusters, still not visible by X rays, but in any case producing a reduction in the concentration of exposed cobalt. As an alternative, migration of Co^0 into the bulk cannot be discarded.

To estimate the dispersion of Co^0 on the catalyst carbon monoxide was adsorbed for this should interact more strongly with metallic cobalt than with the oxide. Figure 2a shows this to be the case. Figures 2a and b

look very much the same. The differences in height of the maxima in the adsorption curves and the slightly different shape of the adsorption curve II compared with the activity curve II could be due to the dynamic character of both processes, i.e., slight variations of Co^0 migration rates could produce the effects observed. Besides, the fact that chemisorbed CO poisoned the catalyst clearly indicates that this is at least partially adsorbed on the active sites. The active site concentration estimate of 1.9×10^{14} sites/ cm^2 , obviously an upper limit, is close, although somewhat higher, than the density of Co^0 that should appear on the surface when LaCoO_3 was reduced to $1.5 e/\text{molecule}$.

In summary, a picture emerges from this work which is also consistent with the results of Crespín and Hall (4). The hydrogenation activity of reduced LaCoO_3 is almost exclusively due to the appearance of highly dispersed Co^0 (Tables 1 and 2). The slow increase in activity with extent of reduction up to $1 e/\text{molecule}$ and the sharp upturn beyond this point (curve I, Fig. 2b) are consistent with the relative stability of Co^{2+} reported by Crespín and Hall (4). The appearance of maxima in the activity curves (Fig. 2b) mirrored by the CO adsorption curves (Fig. 2a) seems to be due to changes in exposed Co^0 concentration. The maxima could develop as a consequence of two factors playing in opposite directions, the increased number of Co^0 produced by reduction and the decrease in exposed Co^0 due to heat effects (Table 3). To further substantiate this point more sophisticated techniques for surface studies will be used, e.g., ESCA-Auger spectrometry.

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