Ethylene Hydrogenation over $LaCoO_3$ Perovskite

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Summary $LaCoO_3$ is inactive for ethylene hydrogenation, but its activity sharply increases and goes through a maximum when the oxide, pretreated with hydrogen at temperatures between 300 and 490 °C, is reduced to different extents (up to 3 electrons/molecule).

PEROVSKITES, mixed oxides of the general formula ABO_3, have long been studied owing both to their theoretical interest and to their practical application. However, their potential use in catalysis was scarcely explored until the beginning of this decade, since when most of the published work has been concerned with their use as automobile exhaust catalysts.[1] We now report a novel application of $LaCoO_3$ as a hydrogenation catalyst, and a study of the relationship between the oxidation state of cobalt and catalytic activity.

$LaCoO_3$ was prepared by precipitation from an equimolecular solution of $La(NO_3)_3$ and $Co(NO_3)_3$ (analytical reagent grade) using tetraethylammonium hydroxide. The precipitate was repeatedly washed with water and then dried for 48 h *in vacuo* before being calcined under an oxygen stream at 800 °C, a temperature which 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.[2] The material obtained had a surface area of 16 m^2/g.

The $LaCoO_3$ was reduced under hydrogen 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. The reduction–oxidation cycle was almost perfectly reversible; the perovskite started to show a slight loss of crystallinity when the reduction reached its maximum level of 3 electrons/molecule.[2] The surface area dropped to 13 m^2 g^{-1} after the first reduction at 1 electron/molecule, remaining constant through the following redox cycles.[2] Plots of extent of reduction *vs.* time showed typical saturation curves at each temperature. The limiting values are shown in the Table.

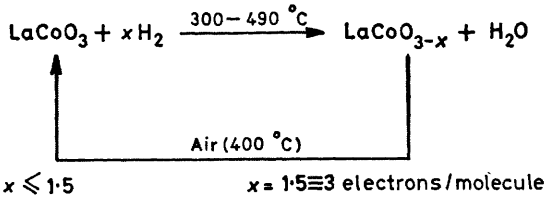

TABLE. Limiting extents of reduction of $LaCoO_3$[a]

Reduction temperature	300	350	400	450	490
Extent of reduction	1·2	1·5	1·6	2·0	3·0

[a] Recirculation system with cold trap, total volume 200 cm^3, initial hydrogen pressure 250 Torr, 100 mg of catalyst.

When the aliquot had been reduced once to the maximum extent (3·0 electrons/molecule) the second cycle of reductions was approximately five times faster at each temperature.

The catalytic activity was tested in the same recirculation system used for reduction into which a bulb, containing most of the reaction volume (430 cm^3), was incorporated through a by-pass. The standard pretreatment before reaction was as follows: oxidation with air for 2 h followed by evacuation for 1 h at 400 °C, reduction at the desired temperature, and final evacuation at 400 °C. A 1 : 1 mixture of C_2H_4 and H_2 was admitted to the reaction vessel and the initial rates obtained were plotted against extent of reduction as shown in the Figure. Curve I fits the data obtained when the catalyst, starting from the oxidized state, was progressively reduced to greater extents. Curve II fits the experimental points obtained when the catalyst was reduced for the second time at increasing extent of reduction.

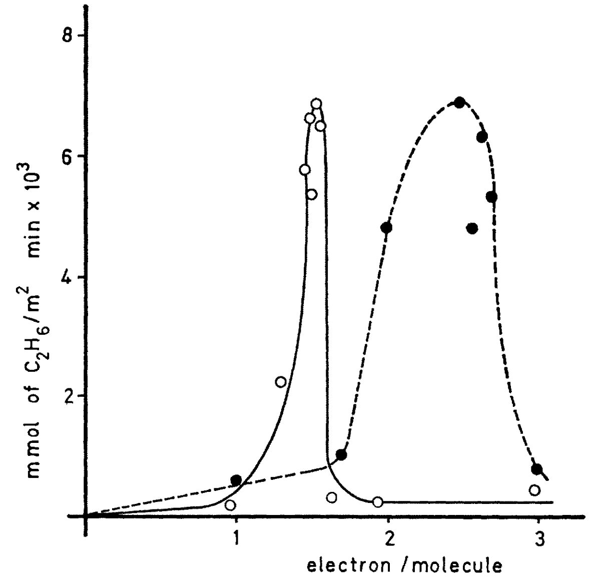

FIGURE. Effect of catalyst reduction upon initial rates of ethylene hydrogenation. Recirculation system; 100 mg of $LaCoO_3$ (13 m^2 g^{-1}); H_2 : C_2H_4 1 : 1; temp. −20 °C; total pressure 170 Torr; ○ first cycle, ● second cycle.

Both the decrease in reduction time and the shift in maximum activity to higher extent of reduction in the second cycle are symptomatic of structural changes when the catalyst has been subjected to severe treatment. There is little doubt, from *X*-ray studies, that at 3 electrons /molecule the perovskite has evolved into an almost atomic dispersion of Co^0 in a La_2O_3 matrix. At intermediate extents of reduction, however, it is not possible to ascertain, from the structural data available, the distribution of cobalt in different oxidation states, *e.g.* whether or not Co^{2+} is stable species. Tracer studies in progress indicate so far that the active sites are of a metallic nature, both at low and high extent of reduction. If this holds true the activity would be expected to increase monotonically with extent of reduction. Since this was not the case further studies are being performed trying to investigate the origin of this discrepancy. Phase segregation is a possible cause of this behaviour.

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[2] M. Crespin and W. K. Hall, personal communication.