Active State of the $LaCoO_3$ Catalyst. A Reply to the Comment, "Hydrogenolysis and Hydrogenation of Ethylene on $LaCoO_3$"

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The catalytic activities of mixed oxide perovskite, $LaCoO_3$, for oxidation as well as hydrogenation have been subjects of many researches because of this substance's peculiar valence-band structure, similar to those of transition metals. We have investigated this unique activity for ethylene hydrogenation and ethane hydrogenolysis,[1] and the hydrogenolysis of C_3–C_5 alkanes,[2] and have performed a comparative study of $LaCoO_3$, $LaAlO_3$, and $LaFeO_3$, in which the latter two perovskites showed only hydrogenation activity.[3] In our study, the activity of $LaCoO_3$ was stabilized by evacuation at 300 °C for 1 h prior to each kinetic run, and the catalyst exhibited a good reproducible activity for runs repeated several tens of times. After more than one hundred times, the catalyst was deactivated and an XPS analysis of the surface indicated that the Co^{3+} ions in the surface layer were reduced to Co^{2+} ions, which were characterized by the shake-up satellite peaks in the spectrum.[1]

Recently, Crespin and Hall have studied in detail the surface states of perovskite compounds, $BaTiO_3$, $SrTiO_3$, and $LaCoO_3$, and their changes during reduction.[4] They found that the Co^{3+} ions in their $LaCoO_3$ sample were easily reduced to the Co^{2+} by heating in hydrogen at 400 °C and that the compound was then decomposed to Co^0 and La_2O_3 by reduction at 500 °C. This reduced mixture was found to recover its original perovskite structure by reoxidation at as low a temperature 400 °C. By the use of $LaCoO_3$ prepared by the same procedure, Petunch *et al.* examined the change in activity for ethylene hydrogenation with an increase in the degree of reduction and proposed that the active state of $LaCoO_3$ was finely dispersed zerovalent Co particles on the La_2O_3 surface; a maximum activity for ethylene hydrogenation at −20 °C was observed on the $LaCoO_{3-x}$ catalyst at the $x=0.7$ composition for the first oxidation-reduction cycle and at $x=1.2$ for the second cycle.[5]

These results are quite different from ours, especially with regard to the stability of the catalyst in a reducing atmosphere; this difference may be attributed to the variation in the catalyst preparation and to the structure of the perovskite particles thus formed. The calcination of mixed hydroxides precipitates in the preparation of our catalyst was carried out by heating them at 900 °C for 3 h and then at 1100 °C for 12 h; a well-developed crystal of $LaCoO_3$ with a surface area of 0.33 m^2/g was thus obtained. The calcination temperature in their preparation was, however, lower than 800 °C, and the obtained compound had a large surface area of 16 m^2/g, about 50 times as large as that of ours, predicting that the difference in the average particle size between the two catalysts will be of the same order of magnitude.

This high reducibility of their compound and the recovery of the original structure by reoxidation at an extremely low temperature are surprising, as Crespin and Hall stated in their report; they ascribed those phenomena to the structure containing vacancies in the perovskite lattice and to the resultant high mobility of ions.[6] The fact that the surface area decreased from 16 to 13 m^2/g after the reoxidation, whereas the crystallite size decreased to some extent, supports this view. Such lattice imperfections may be exposed on the surface with a high concentration, so that some fraction of Co occupies "coordinatively unsaturated sites." The reported instability of hydrogenation activity which is seen from the drastic decrease in activity with an increased degree of reduction and the shift of activity maximum may reflect the labile nature of their catalyst. Moreover, it is amazing that the catalyst prepared by them is more reducible than that studied by Crespin and Hall, since their catalyst was reduced to some extent at 80 °C.[7]

It is not possible to compare the behavior of their catalyst for ethane hydrogenolysis with ours, since they examined the hydrogenation of ethylene only at temperatures up to 50 °C. As for the hydrogenolysis of ethane over our catalyst, the reaction orders with respect to ethane and hydrogen are 1.0 and −0.5 respectively, and the activation energy was estimated at 35 kJ/mol in the temperature range of 200—300 °C. These values of kinetic parameters are quite different from those for the reaction on metallic Co dispersed on carriers; the ethane and hydrogen orders are 1.0 and −0.8 respectively, the value of activation energy is 125 kJ/mol for Co/SiO_2.[8] The hydrogen order of −1.3 and the activation energy of 134 kJ/mol for Co/MgO were reported.[9] These results evidently show that the active state of our catalyst is far from that of metallic Co. By comparing the observed deuterium distributions of the reactant and the product molecules in the reaction of ethylene with D_2, Ulla and Lombardo insisted that our results were close to theirs and those obtained from the catalysis by "metal," and deviated from those observed in the reaction on "oxide," by illustrating the results of a reaction over Co_3O_4 at 23 °C.[10] It is, however, not reasonable to compare directly the properties of reactions which proceed in different temperature ranges and to classify the active state as simply "metal" or "oxide" without considering the variation in the character of oxides; in the cases of typical oxides, such as CaO[11] and MgO,[12] the most abundant species in the deuterium distribution of ethane, ethane-d_2, decreased its fraction with an increase in the reaction temperature and the distribution became broader. Even a comparison of our results (80 °C) with theirs (50 °C) shows that our distribution has a distinct maximum at ethane-d_2 and so is different from theirs.

It should also be noted that there is a limit to the amount of surface atoms detectable by means of XPS, a small percentage of the fraction of surface coverage, and that it is difficult to determine the oxidation state of a surface species when its amount is below this limit. Accordingly, a more sensitive method of surface analysis is needed to obtain a definite solution of this problem.

In conclusion, this reply does not detract from the results obtained by the use of their own catalyst, but we wish to point out that it is premature to generalize their view immediately on the basis of the conclusion deduced from a study using only a catalyst in a highly reducible state.

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