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COMMENTS

Hydrogenolysis and Hydrogenation of Ethylene on $LaCoO_3$

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Synopsis. The hydrogenation and hydrogenolitic activity of $LaCoO_3$ reported by Ichimura *et al.*1) can be rationalized in terms of the current literature by a model in which Co°, produced under reaction conditions, is the locus of catalytic activity. This interpretation disagrees with the model supported by the authors.

Recently, Ichimura *et al.*1) reported the results of a study of the hydrogenolysis of ethylene and ethane on $LaCoO_3$. Regarding the nature of the possible active sites they advanced a model that, we understand, does not take into account and to a certain extent contradicts the existing body of knowledge in the field. They concluded that the pairs of lanthanum and oxygen ions are mainly responsible for the hydrogenation activity while the Co^{3+} ions play a role in the rupture of the carbon-carbon bond. Opossing this view we have reasons to believe that the loci of both hydrogenation and hydrogenolytic activities are Co° atoms that appear on the surface as a consequence of the reduction of Co^{3+} by hydrogen at the reaction temperature. We will now review the pertinent literature that support our point of view.

Sis *et al.*2) have carefully studied the reduction of $LaCoO_3$ using various techniques. They were able to reduce the mixed oxide up to a mixture of La_2O_3+ Co° when the temperature reached 650 °C. However, they detected the appearance of Co° at temperatures as low as 300 °C. Similar results were reported by Petunchi *et al.*3) and Crespin *et al.*4) Furthermore, we have observed that at 80 °C $LaCoO_3$ could be rapidly reduced, under 170 Torr[†] of hydrogen pressure in a recirculating system, to $LaCoO_{2.9}$. Therefore, under the conditions Ichimura *et al.*1) did the experiments, $H_2/C_2H_4=10$ and temperatures between 80 °C and 300 °C, it is very likely they had a partially reduced perovskite.

Another important clue to ascribe a metallic behavior to their system was found within the data reported by Ichimura *et al.*1) The reaction between C_2H_4 and D_2 is a diagnostic tool to distinguish between metallic and metal oxide behavior. In the case of group VIII metals multiple exchanged ethylene and ethane are produced during the reaction.5—8) Oxides on the other hand, produce $C_2H_4D_2$ almost exclusively while the unreacted ethylene shows none or very little deuterium exchanged.9—12) This general trend also holds true for higher reaction temperatures (250—450 °C) in the case of a relatively inactive catalyst such as TiO_2.12) In the table it is shown for comparisson the data obtained by Ichimura *et al.*1) at 80 °C, our own data and a sample experiment reported by Tanaka *et al.*9) on Co_3O_4. In both cases in which $LaCoO_3$ was the catalyst either pre-reduced or not, the product hydrocarbons show similar exchange patterns, *e.g.* the calculated binomial distributions closely duplicate the experimental values. The typical Co_3O_4 data shows the selective addition of deuterium to the double bond while the ethylene remains virtually free of deuterium.

Ichimura *et al.*1) also reported tracer data obtained at 300 °C at which temperature there is no doubt Co° is already present in the solid.2,13) Both ethane and ethylene were multiple exchanged but the data show some deviation from binomial distribution. The deuterium distribution in methane formed by hydrogenolisis does not seem to fit in line with those reported for both ethylene and ethane. Additional data would

Table 1. Deuterated products from $C_2H_4+D_2$ reaction over $LaCoO_3$ and Co_3O_4

Catalyst	$LaCoO_{2.75}$a)				$LaCoO_3$b)				Co_3O_4c)	
Reaction temp	50 °C				80 °C				23 °C	
Conversion	54%				42%				50%	
Products	Ethane		Ethylene		Ethane		Ethylene		Ethane	Ethylene
	Exptl	Calcdd)	Exptl	Calcdd)	Exptl	Calcd	Exptl	Calcd	Exptl	Exptl
d_0	23.5	17.5	40.6	34.7	11	9.5	19.5	21.4	2.6	97.7
d_1	29.7	35.4	35.9	42.0	25	27	42.8	40.3	3.6	2.4
d_2	27.5	29.8	16.0	19.1	32	32.9	28.8	28.4	92.2	0.2
d_3	12.1	13.4	4.9	3.9	22	21.1	8.1	8.9	1.6	0
d_4	5.6	3.4	2.6	0.3	9	8	0.8	1.0	0	0
d_5	1.6	0.5			2	1.5			0	
d_6	0	0			0	0				

a) $LaCoO_3$ pre-reduced at 300 °C in hydrogen, Ref. 14. b) Ref. 1. c) Ref. 9. d) Calculated assuming a binomial distribution.

[†] 1 Torr≈133.322 Pa.

be needed to interpret the methane tracer results.

Ichimura *et al.*(1) argued that catalyst deactivation was due to the reduction of Co^{3+} to lower oxidation states. This is at variance with our finding(13) that the oxidized catalyst is inactive and its activity increases sharply going through a maximum with the extent of reduction of the oxide. Our experiments were conducted on two different aliquots of the catalyst that before each run received a standard re-oxidation and reduction pretreatment. The reaction temperature was 253 K. However, extrapolation of their results at this temperature fall within the activity range of our slightly reduced catalyst, *e.g.* $LaCoO_{3-x}$ ($x<0.2$). An alternative explanation for the deactivation process comes from the fact that most hydrocarbon reactions leave "residues" or "coke" on the surface which poison the catalyst. This system is no exception in this regard for we have measured the amount of strongly adsorbed molecules that remains on the surface after evacuation at reaction temperature, $2.2\pm1.0\times10^{14}$ atoms of C/cm^2.(14) This value is of the same order of magnitude as the maximum number of active sites estimated to exist on our catalyst by CO poisoning technique.(14)

In summary, the very likely reduction of even small amounts of Co^{3+} to Co° under reaction conditions and the tracer data that resemble those obtained over group VIII metals support a model in which finelly dispersed Co° on the matrix oxide is the responsible for both the hydrogenation and hydrogenolitic activity of $LaCoO_3$.

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