June, 1981] © 1981 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 54, 1787—1792 (1981) 1787

Catalysis by Mixed Oxide Perovskites. II. The Hydrogenolysis of C_3—C_5 Hydrocarbons on $LaCoO_3$

Kenji Ichimura, Yasunobu Inoue,* and Iwao Yasumori
Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

(Received September 25, 1980)

The catalytic hydrogenolysis of C_3—C_5 alkanes on $LaCoO_3$ perovskite oxide was found to show a highly selective formation of methane in the temperature range of 350—620 K. The reaction order with respect to the hydrocarbon pressure was unity in every hydrogenolysis, whereas the hydrogen order increased from zero for propane to 1.0 for butane and isobutane and to 2.0 for pentane, isopentane, and neopentane. The activation energies of the reactions ranged from 120 for propane to 32 kJ mol^{-1} for butane. The reaction of propane or butane with D_2 on $LaCoO_3$ provided large fractions of methane $[D_3]$ and $[D_4]$, but a negligible amount of deuterium-exchanged alkanes. An equilibrium among the gaseous H_2, HD, and D_2 was reached. These hydrogenolyses are described by a mechanism involving the almost concurrent repture of all the carbon-carbon bonds in the alkanes by the attack of adsorbed hydrogen atoms, and were proposed to be catalyzed by a synergetic effect; the CO^{3+} ion is effective in breaking the C–C bond, whereas the La^{3+} and O^{2-} ions serve to supply hydrogen atoms to the decomposed species. The reaction of propene or butenes with hydrogen produced the corresponding alkanes and methane. The kinetic analyses showed that the fractions of methane produced consecutively *via* the alkanes amounted to 16% for propene and to more than 93% for butenes. The observed pressure dependence and deuterium distributions in the alkene hydrogenation were interpreted in terms of the associative mechanism. The correlation between the structures of the reactant molecules and of the active sites present on $LaCoO_3$ was briefly discussed.

In the first paper of this series,[1)] we reported the noteworthy catalytic properties of $LaCoO_3$ for the hydrogenolysis of ethylene and ethane. This mixed oxide exhibited a stable and high catalytic activity and retained its original perovskite structure even after several runs in a reducing atmosphere. At reaction temperatures above 420 K, the ethylene hydrogenolysis to form methane was found to proceed in a consecutive way *via* ethane as a stable intermediate, accompanied by a minor side-reaction of the direct methane formation. The X-ray photoelectron spectroscopic studies emphasized the importance of the trivalent state of the cobalt ion in rupturing the C–C bond, and the active structures were proposed to be composed of the (110) plane.

The catalytic hydrogenolysis of C_3—C_{10} hydrocarbons has been extensively studied on transition-metal catalysts,[2-6)] but no detailed kinetic analyses have yet been done well because of complexities in the product distributions and because of the fast deactivation of the metal catalysts during the hydrogenolysis. In view of the remarkable selectivity and stable activity of $LaCoO_3$, it is of interest to examine the hydrogenolysis of alkanes and alkenes with longer carbon or side-carbon chains. Furthermore, we can expect that the employment of a variety of reactant molecules with different stereochemical conformations might be useful in obtaining information on the structure and distributions of the active sites exposed at the perovskite surface. In the present work, therefore, we investigated the hydrogenolysis of propene, butenes, and a series of alkanes from propane to pentane isomers by performing detailed kinetic studies, which were supplemented by a tracer work using D_2.

Experimental

The preparation of the mixed oxide perovskite, $LaCoO_3$, was described in the previous paper.[1)] This perovskite catalyst was activated by heating *in vacuo* in the temperature range of 600—800 K in order to obtain a constant catalytic activity; the activity was reproducible enough for more than ten successive hydrogenolysis runs of C_2—C_5 hydrocarbons, except for that of acetylene.

The reaction of hydrocarbons with hydrogen was studied in a closed circulating system at temperatures between 350 and 620 K in the pressure range of 5—30 Torr (1 Torr = 133.3 Pa) for hydrocarbons and in that of 50—150 Torr for hydrogen. The procedures of kinetic study and of the analysis of the deuterium-distributed reactant and products in the reaction with D_2 were much the same as those employed previously.[1)]

Reactant gases such as hydrogen (99.98% in purity), deuterium (containing less than 0.4% HD), propene (99.9%), propane (99.9%), butenes (99.0%), and butane (99.7%) were purchased from the Takachiho Shoji Co. and were used without further purification. Pentane and isopentane of an extra pure grade, obtained from the Wako Chemical Co., and neopentane from the Tokyo Kasei Co., were distilled and then subjected to several freeze-evacuation-thaw cycles to remove gaseous impurities.

Results

Hydrogenolysis of Alkanes. In the temperature and pressure ranges employed here, the hydrogenolysis of C_3 to C_5, *i.e.*, propane, butane, isobutane, pentane, isopentane, and neopentane, on $LaCoO_3$ produced only methane as a product. Neither the corresponding alkenes nor the fragmented hydrocarbons were detected in the gas phase.. The rates of hydrocarbon consumption fell within the same order of magnitude, 0.5—1.5×10^{13} molecule s^{-1} cm^{-2} at 573 K, irrespective of the alkanes, except for the case of butane, which gives a higher rate of 7×10^{13} molecule s^{-1} cm^{-2}. The kinetic analysis of the reaction showed that the reaction orders with respect to the hydrocarbon pressure, $P_{C_nH_{2n+1}}$, were unity for all the reactions. Figure 1 shows the dependence of the rate on the hydrogen pressure, P_{H_2}; the hydrogen orders increased with the number of carbon atoms involved in the reactant hydrocarbons and were found to be 0.0, 1.0, and 2.0 for the reactions of C_3H_8, C_4H_{10},

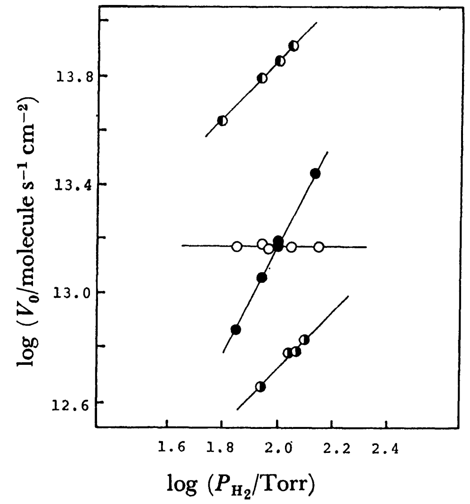

Fig. 1. Dependence of rate upon hydrogen pressure in the hydrogenolysis of C_3—C_5 alkanes.
○: C_3H_8, ◐: n-C_4H_{10}, ◑: i-C_4H_{10}, ●: n-C_5H_{12}, P_{HC} = 10 Torr, Reaction temperature = 573 K.

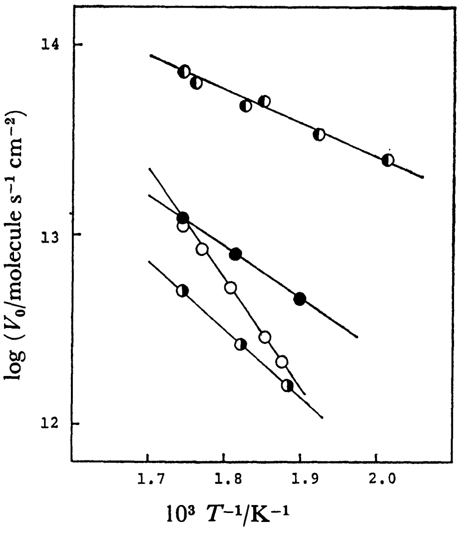

Fig. 2. Arrhenius plots of alkane hydrogenolysis.
○: C_3H_8, ◐: n-C_4H_{10}, ◑: i-C_4H_{10}, ●: n-C_5H_{12}, P_{HC} = 11 Torr, P_{H_2} = 100 Torr.

Table 1. Kinetic parameters in the hydrogenolysis of C_2 to C_5 alkanes on $LaCoO_3$

Reactions	Reaction order[a)] m	n	Activation energy[b)] kJ mol^{-1}	Rate[c)] molecule s^{-1} cm^{-2}
$C_2H_6 + H_2 \longrightarrow 2CH_4$	1.0	−0.5	35	1.0×10^{13}
$C_3H_8 + 2H_2 \longrightarrow 3CH_4$	1.0	0.0	120	1.5
n-$C_4H_{10} + 3H_2 \longrightarrow 4CH_4$	1.0	1.0	32	7.2
i-$C_4C_{10} + 3H_2 \longrightarrow 4CH_4$	1.0	1.0	71	0.5
n-$C_5H_{12} + 4H_2 \longrightarrow 5CH_4$	1.0	2.0	55	1.5
i-$C_5H_{12} + 4H_2 \longrightarrow 5CH_4$	1.0	2.0	38	1.0
$C(CH_3)_4 + 4H_2 \longrightarrow 5CH_4$	1.0	2.0	102	0.9

a) ±0.1, Rate$=k_e P^m_{C_nH_{2n+2}} P^n_{H_2}$ (573 K). b) ±3.
c) P_{H_2} = 100 Torr, $P_{C_nH_{2n+2}}$ = 10 Torr. d) See Ref. 1

and C_5H_{12} respectively. The Arrhenius plots of the reaction are demonstrated in Fig. 2. The values of the activation energy and other kinetic parameters are summarized in Table 1, together with the previous results on ethane hydrogenolysis. It should be noted that the activation energy was remarkably high for propane and neopentane, but low for ethane, butane, pentane, and isopentane hydrogenolysis. An intermediate value was obtained for isobutane hydrogenolysis.

Table 2 shows the deuterium distributions in the reactant and products in the reaction of propane and butane with D_2 at 573 K and compares them with the results for ethane hydrogenolysis. A common distribution pattern was observed in these three reactions; at conversions of 16—23%, an equilibrium among H_2, HD, and D_2 in the gas phase is established. The formation of the deuterium-exchanged ethane, propane, and butane was negligibly small, whereas the product, methane, consisted mainly of [D_3] and [D_4] species.

Hydrogenolysis of Propene and Butenes. The reaction of propene with hydrogen at 573 K produced a considerable amount of methane, together with propane at the initial stage of reaction. This behavior contrasts with the predominantly consecutive formation of methane which was observed in the case of ethylene hydrogenolysis.

The reaction of 1-butene, *trans*-2-butene, or *cis*-2-butene with hydrogen at 573 K underwent rapid isomerization, followed by the formation of butane and then methane; the ratio of the produced butene isomers, *R*(*cis*-2-butene/*trans*-2-butene), *R*(*cis*-2-butene/1-butene), and *R*(*trans*-2-butene/1-butene), were determined to be 1.0, 1.8, and 1.8 respectively. These ratios remained almost unchanged until the disappearance of the reactant butene. Table 3 shows the deuterium distributions of the reactant and products in the deuterogenation of propene and 1-butene at 573 K. There existed common features in the distributions for both reactions;

Table 2. Deuterium distributions in the reaction of C_2—C_4 alkanes with D_2 at 573 K on $LaCoO_3$

Reaction		$C_2H_6+D_2$[a)]			$C_3H_8+D_2$[b)]			n-$C_4H_{10}+D_2$[c)]		
Conversion/%		15			16			23		
Gases		C_2H_6	CH_4	H_2	C_3H_8	CH_4	H_2	C_4H_{10}	CH_4	H_2
Distributions	D_0	98	0	0.7	98	0	1	98	0	3
	D_1	1	0	14.7	2	0	17	2	2	27
	D_2	1	6	84.6		7	82		9	70
	D_3		21			20			34	
	D_4		73			73			55	

a) P_{D_2} = 117 and $P_{C_2H_6}$ = 10 Torr. b) P_{D_2} = 97 and $P_{C_3H_8}$ = 11 Torr. c) P_{D_2} = 97 and $P_{C_4H_{10}}$ = 11 Torr.

TABLE 3. DEUTERIUM DISTRIBUTIONS IN THE REACTION OF PROPENE AND 1-BUTENE WITH D_2 AT 573 K ON $LaCoO_3$

Reaction		$C_3H_6+D_2$[a]				$1\text{-}C_4H_8+D_2$[b]					
Gases		C_3H_6	C_3H_8	CH_4	H_2	$1\text{-}C_4H_8$	*cis*-2-C_4H_8	*trans*-2-C_4H_8	*n*-C_4H_{10}	CH_4	H_2
Distributions	D_0	27	4	0	0.1	37.6	44.6	45.6	17.5	0	0.2
	D_1	31	30	3	5.4	37.0	35.9	36.7	35.0	0	8.4
	D_2	27	44	10	94.5	19.0	14.0	13.7	32.5	0	91.4
	D_3	13	19	19		5.3	4.5	3.7	12.5	12	
	D_4	2	3	68		1.1	1.3	0.5	2.5	88	
	D_5—D_8		0			0	0	0	0		

a) $P_{C_3H_6}=11$ and $P_{D_2}=96$ Torr; conversion=11%. b) $P_{1\text{-}C_4H_8}=11$ and $P_{D_2}=97$ Torr; conversion=71%.

the gaseous composition of H_2, HD, and D_2 nearly reached equilibrium. Propene and 1-butene used as reactants gave rise to wide distributions of deuterium ranging from $[D_0]$ to $[D_4]$. The products involved deuterium-exchanged propane and butane distributed from $[D_0]$ to $[D_4]$. The subsidiary isomerization of 1-butene during hydrogenolysis gave *cis*- and *trans*-2-butenes possessing almost the same distributions of deuterium. Methane contained highly-exchanged methane $[D_3]$ and $[D_4]$, in which the fraction of the latter species amounted to as much as 70—90% of the total methane.

In the reaction of acetylene with hydrogen, ethylene was the only product, and the catalytic activity was drastically decreased during the course of reaction. The initial rate was about one hundredth that of ethylene hydrogenation at 473 K.

Discussion

The features of the hydrogenolysis of propene and butenes on $LaCoO_3$ are similar to those of ethylene hydrogenolysis in that there existed no products other than methane and the corresponding alkanes (except for the butene isomers). Thus, the change in the gaseous compositions of the reactant and products as a function of the time was analyzed by the same procedure as was used in the previous study of the ethylene hydrogenolysis:[1)]

$$\begin{tikzcd} & C_nH_{2n} \arrow[dl, "\mathrm{I}"', "H_2"] \arrow[dr, "nH_2", "\mathrm{II}"'] & \\ C_nH_{2n+2} \arrow[rr, "(n-1)\,H_2", "\mathrm{III}"'] & & n\,CH_4. \end{tikzcd} \qquad (1)$$

By assuming that the reaction order with respect to the partial pressure of respective hydrocarbons was unity, the following rate equation can be derived for the consumption of the alkene and alkane under the conditions of an excess of hydrogen:

$$\frac{dP_{C_nH_{2n}}}{dt} = -(k_1+k_2)\,P_{C_nH_{2n}} \qquad (2)$$

$$\frac{dP_{C_nH_{2n+2}}}{dt} = k_1P_{C_nH_{2n}} - k_3P_{C_nH_{2n+2}} \qquad (3)$$

$$\frac{dP_{CH_4}}{dt} = n(k_2P_{C_nH_{2n}}+k_3P_{C_nH_{2n+2}}), \qquad (4)$$

where k_i denotes the rate constant for Process i in Scheme (1). The values of k_i as parameters were determined by applying the non-linear least-squares method so as to give the curves best-fitting the experimental plots. For the reaction with propene, the determined values were $k_1=0.023$, $k_2=0.123$, and $k_3=0.167\ h^{-1}$ at 573 K ($P_{H_2}=100$ Torr), which indicates that the fraction of the direct hydrogenolysis *via* Process (II) is about 84%.

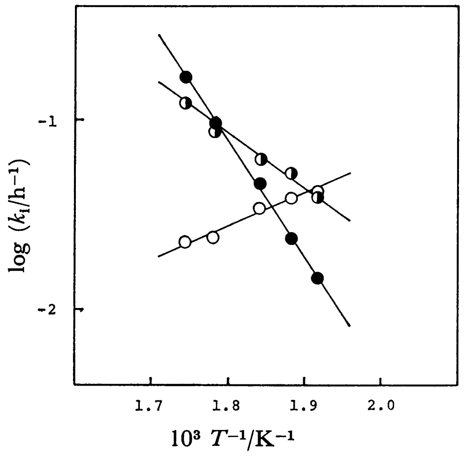

Fig. 3. Arrhenius plots of k_i.
○: k_1, ◑: k_2, ●: k_3.

Figure 3 shows the temperature dependence of k_i; the values of the activation energy, E_a, for Process (I), (II), and (III) were determined to be −33, 52, and 119 kJ mol^{-1} respectively. The analysis of the reaction with different initial hydrogen pressures provided the hydrogen order of unity for both Process (I) and (II) and of zero for Process (III). These results are summarized in Table 4. It should be noted that the rate, the activation energy, and the rate equation for Process (III) were in substantial agreement with the respective values in the propane hydrogenolysis (*cf.* Tables 1 and 4).

Since there was no marked difference in the observed rates of the hydrogenation of 1-butene, *trans*-2-butene, and *cis*-2-butene, the average of these rates could be employed as that of butene hydrogenation. The kinetic analysis gave the values of $k_1=0.040$, $k_2\approx0.003$, and $k_3=0.95\ h^{-1}$ at 573 K, indicating that the fraction of the direct formation of methane from butene was about 7%. As is demonstrated in Tables 1 and 4, there also exists a good agreement in the kinetic parameters and reaction rates between Process (III) and butane hydrogenolysis. These close coincidences give support to the analytical procedure employed here for

TABLE 4. KINETIC PARAMETERS IN THE HYDROGENOLYSIS OF PROPENE AND BUTENES

Reaction	Path[a)]	Rate[b)] molecule s^{-1} cm^{-2}	Reaction order[c)] m	Reaction order[c)] n[d)]	Activation energy[e)] kJ mol^{-1}
$C_3H_6+H_2$	I	0.18×10^{13}	1	1.0	−33
	II	0.96×10^{13}	1	1.0	52
	III	1.3×10^{13}	1	0.0	119
$C_4H_8+H_2$	I	0.31×10^{13}	1	1.0	−33
	II	$\approx0.03\times10^{13}$	1	—	—
	III	7.4×10^{13}	1	1.0	32

a) See text. b) Under the standard conditions; reaction temp=573 K, $P^\circ_{H_2}=100$ Torr, $P^\circ_{C_nH_{2n}}=10$ Torr, and $P^\circ_{C_nH_{2n+2}}=10$ Torr. c) Rate=$k'_e P^m_{HC} P^n_{H_2}$. d) ±0.1. e) ±4.

the propene and butene hydrogenolysis.

The previous kinetic study of the ethylene hydrogenation[1)] over $LaCoO_3$ revealed that the reaction proceeded mainly on the La and O ions *via* the associative mechanism and that, as the reaction temperature increased, the slow step varied from the dissociative adsorption of hydrogen to the hydrogenation of an ethyl radical. The reaction orders and the way of deuterium distribution in the present hydrogenation of propene and butene were quite similar to those observed in the ethylene hydrogenation in the high-temperature region. Thus, we can safely adopt the associative mechanism as well as the same active-site structure for both reactions, and the rate equation is given[1)] by:

$$R_h = k_h K_s K_a K_h\, P_{C_nH_{2n}}\, P_{H_2} = k\, P_{C_nH_{2n}}\, P_{H_2}, \qquad (5)$$

in a simplified form, where k_h is the rate constant for the hydrogenation of the half-hydrogenated species. The constants, K_h, K_a, and K_s, denote, respectively, the equilibrium constants for the adsorption of hydrogen, the adsorption of alkenes, and the surface reaction between adsorbed alkenes and a hydrogen atom. This equation accords well with the experimental pressure dependence.

Alkane Hydrogenolysis. The hydrogenolysis of alkanes has thus far been mostly confined to those catalyzed by transition-metal catalysts;[2)] these reactions are characterized by negative orders with respect to P_{H_2} and, generally, by a wide variety of products, coinsisting of fragmented hydrocarbons, except for the selective formation of methane in the case of Ni.[6,7)] The proposed mechanism involves the dissociative adsorption of alkanes, liberating a hydrogen atom on the surface, followed by the step-by-step scission of carbon-carbon bonds. The most striking features in the present hydrogenolysis on $LaCoO_3$ are the high reaction order with respect to P_{H_2} and the formation of only methane as the product. Neither the other fragmented nor dehydrogenated hydrocarbons were produced in the gas phase. Therefore, it is evident that the catalysis by this perovskite is essentially different from those by the transition metals, and so the above-mentioned mechanism can not be applied to the present reaction system.

The deuterium distributions in the reaction of the alkanes with D_2 showed a common feature irrespective of the alkanes employed: large amounts of methane [D_3] and [D_4] were produced even at the initial stage of hydrogenolysis, whereas the fractions of the deuterium-exchanged alkanes were negligibly small. These results clearly indicate that the adsorption of alkanes is irreversible, but the surface species thus produced undergo a rapid hydrogen exchange. Another important finding is that the reaction order with respect to the alkane pressure was unity in all cases, but the hydrogen order increased with the number of carbon atoms in the alkanes, independently of their molecular structure (*i.e.*, 0.0, 1.0, and 2.0 for the hydrogenolyses of C_3H_8, C_4H_{10}, and C_5H_{12} respectively). The value of −0.5 obtained previously for the ethane hydrogenolysis is also in line with this tendency.[1)] It should be noted that such a variation in the hydrogen order is not observed for the alkane hydrogenolysis on the transition-metal catalysts. These findings on the present hydrogenolysis indicate that the slowest elementary step involves not only the simultaneous rupture of the C–C bonds to produce monocarbon species, but also the attack of hydrogen atoms, the number of which is strongly related to that of the resulting monocarbon species.

A comparative study of hydrogenolysis by perovskite compounds, such as $LaAlO_3$, $LaFeO_3$, and $LaCoO_3$,[8)] and by component oxides, such as La_2O_3 and Co_2O_3,[1)] revealed that only $LaCoO_3$ and Co_2O_3 can accelerate the hydrogenolysis; this indicates that the cobalt ion plays an impotant role in breaking the C–C bond. The study also showed that La_2O_3 can effectively catalyze the H_2-D_2 equilibration reaction as well as ethylene hydrogenation, indicating the capability of adsorbing hydrogen dissociatively.[1)] These findings lead to the consideration that the peculiar activity of $LaCoO_3$ arises from the synergetic effect of La, Co, and O ions; the Co ion is responsible for the C–C bond rupture, whereas the La and O ions contribute mainly as sites for supplying hydrogen atoms to the decomposed species. Furthermore, the application of X-ray photoelectron spectroscopy to the active and deactivated $LaCoO_3$ catalysts showed that the presence of a trivalent cobalt ion rather than a divalent one is essential for the activity.[1,8)] Accordingly, we would like to propose the following mechanism as the most plausible pathway for the reaction of the C_3 to C_5 alkanes, which involves surface intermediates analogous to those suggested in the ethane hydrogenolysis:

$$H_2 \rightleftharpoons 2H(a) \qquad (6)$$

$$H_2 \rightleftharpoons 2H(a^*) \qquad (7)$$

$$C_nH_{2n+2} + 2(n-2)H(a) \longrightarrow 2CH_3(a^*) + (n-2)[H\cdots CH_2(a)\cdots H] \quad (8)$$

$$\left.\begin{array}{l} CH_3(a^*) \rightleftharpoons CH_2(a^*) + H(a) \\ [H\cdots CH_2(a)\cdots H] \rightleftharpoons CH_3(a) + H(a) \\ CH_3(a) \rightleftharpoons CH_2(a) + H(a) \end{array}\right\} \quad (9)$$

$$\left.\begin{array}{l} CH_3(a^*) + H(a) \longrightarrow CH_4 \\ [H\cdots CH_2(a)\cdots H] \longrightarrow CH_4 \end{array}\right\}, \quad (10)$$

where the symbols (a*) and (a) represent the adsorbed species on the Co^{3+} ion and those on the other sites respectively. The surface species, $[H\cdots CH_2(a)\cdots H]$, denotes a precursor of desorbing methane. The absence of deuterium-exchanged alkanes in the gas phase suggests that Step (8) is rate-determining, and the following rate equation is given to the hydrogenolysis by assuming that the requisite number of the site on the Co^{3+} ion is two for the selective adsorption of methyl groups in the alkane molecules:

$$R = k_8 P_{C_nH_{2n+2}}\, \theta_v^{*2}\, \theta_H^{2(n-2)}, \quad (11)$$

where $\theta_v{}^*$ denotes the fraction of the vacant Co^{3+} sites, and θ_H, the fractions of the La^{3+} and O^{2-} sites, occupied by hydrogen atoms. Provided that the fraction of the sites covered with hydrocarbon species is negligibly small, these fractions can be expressed, respectively, as;

$$\theta_v^* = 1/(1+\sqrt{K_h^* P_{H_2}}) \quad (12)$$

and

$$\theta_H = \sqrt{K_h P_{H_2}}/(1+\sqrt{K_h P_{H_2}}), \quad (13)$$

where $K_h{}^*$ and K_h are equilibrium constants. After introducing Eqs. 12 and 13 into Eq. 11, the rate equation is written as;

$$R = k_8 K_h^{n-2} P_{C_nH_{2n+2}} P_{H_2}^{n-2} / (1+\sqrt{K_h^* P_{H_2}})^2 (1+\sqrt{K_h P_{H_2}})^{2(n-2)}. \quad (14)$$

Under the conditions of a strong hydrogen adsorption on the Co^{3+} sites, $1 \ll \sqrt{K_h{}^* P_{H_2}}$, and a weak adsorption on the other sites, $1 \gg \sqrt{K_h P_{H_2}}$, Eq. 14 is simplified to;

$$R = k_8 \frac{K_h^{n-2}}{K_h^*} P_{C_nH_{2n+2}} P_{H_2}^{n-3}. \quad (15)$$

For normal and side-chain alkanes with the three to five carbon atoms, the observed pressure dependences of the rate are well represented by Eq. 15. Step (8) might proceed rapidly in a consecutive way involving the step-by-step C–C bond scission, but it is regarded as being a simultaneous step, as far as the kinetics is concerned, and the surface intermediates produced are not desorbed in the gas phase. In the above-mentioned mechanism, the surface Co^{3+} ion favors the adsorption of the methyl group rather than the methylene group. This is not unexpected, since a similar selective adsorption occurred on the Cr^{3+} ion in α-Cr_2O_3.[9] The formation of highly deuterium-exchanged methane is ascribable to the rapid hydrogen exchange between monocarbon species, such as methyl and carbene, as is shown in Step (9). The presence of surface carbene as an intermediate is possible, since this species was recently, by means of ultraviolet photoelectron spectroscopy, confirmed in the adsorption of C_2H_2 on the Ni (110) surface.[10]

The formation of methane *via* the direct hydrogenolysis of propene was expressed by a rate equation of the first order with respect to both the hydrogen and propene pressures (Table 4); the hydrogen order was different from that observed in the case of propane hydrogenolysis. One possible interpretation for this pressure dependence might be given by assuming the same surface intermediates as those described in Step (8). This assumption leads to this pathway;

$$C_3H_6 + 4H(a) \longrightarrow 2CH_3(a^*) + [H\cdots CH_2(a)\cdots H]. \quad (16)$$

Thus, it follows that the insertion of a stoichiometry number, $n=4$, of hydrogen atoms into Eq. 15 provides the same rate equation as the observed one.

The alkane hydrogenolysis showed a variety of activation energies, as is demonstrated in Table 1; E_a is high for propane and neopentane, intermediate for isobutane, and low for pentane, butane, isopentane, and ethane. It is difficult at present to give a clear interpretation for this variation, especially the extremely high value for propane. One might argue that the C–C bond between methylene groups in alkanes dissociates more readily than that between methylene and methyl group and that, thus, the number of the CH_2 group in the respective alkanes would govern the activation energy of reaction. This view, however, is unlikely, because the energy difference between those bonds (13 kJ mol^{-1})[11] is too small to explain the large variation in E_a, and no correlation between them exists. The following consideration of the conformation of alkane molecules and the $LaCoO_3$ surface appears to be useful. In previous studies,[1,8] the (110) plane of $LaCoO_3$ was supposed to be active for the hydrogenolysis because of the high density of the exposed Co, La, and O ions. The distance between the adjacent surface Co ions is 5.42 Å. The carbon-atom chain of butane or higher alkanes is long and flexible enough to interact with two Co ions in a bridged form, as shown in Fig. 4. Although the La^{3+} and O^{2-} ions fail to adsorb alkanes dissociatively, both ions are likely to accommodate the methyl and carbene groups formed as a result of the bond rupture. Thus, such bridged adsorption makes the nearby La^{3+} and O^{2-} ions effective in supplying hydrogen atoms to the decomposed species, thus lowering the activation energy. On the other hand, propane and neopentane can hardly take the bridged configuration because of their smaller size and less flexible shape. The adsorption

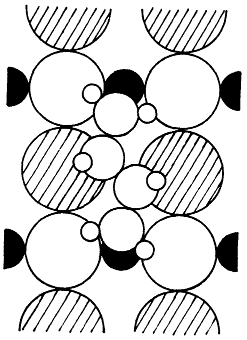

Fig. 4. Schematic representation of butane configuration on the (110) plane of $LaCoO_3$.

▨: La^{3+}, ○: O^{2-}, ●: Co^{3+}, ○: carbon atom, ○: hydrogen atom.

of these molecules on a single Co ion results in a larger steric hindrance, which makes the activation energy higher. In this regard, the small E_a in the ethane hydrogenolysis is exceptional, but presumably due to a lesser extent of the steric hindrance. As for the propane hydrogenolysis, the extremely larger E_a seems to be related to the specificity in the propene hydrogenolysis; *i.e.*, the direct methanation of propene was remarkably favored, compared to those of the ethylene and butene hydrogenolyses. This consideration is certainly supported by the fact that the E_a of the direct methane formation from propene was as low as 52 kJ mol^{-1}.

In order to reveal the peculiar behavior of propene and propane in the hydrogenolysis reaction, further information on the adsorbed states of the hydrocarbons on $LaCoO_3$ is needed; a thermal-desorption study is now in progress.

References

1) K. Ichimura, Y. Inoue, and I. Yasumori, *Bull. Chem. Soc. Jpn.*, **53**, 3044 (1980).

2) J. H. Sinfelt, *Adv. Catal.*, **23**, 91 (1973); *Catal. Rev.*, **3**, 175 (1970).

3) J. R. Anderson and B. G. Baker, *Proc. R. Soc. London, Ser. A*, **271**, 402 (1963).

4) J. R. Anderson and N. R. Avery, *J. Catal.*, **2**, 542 (1963); **5**; 446 (1966).

5) K. Kochloefl and V. Bazant, *J. Catal.*, **10**, 140 (1968).

6) H. Matsumoto, Y. Saito, and Y. Yoneda, *J. Catal.*, **19**, 101 (1970).

7) C. G. Myers and G. W. Munns, Jr., *Ind. Eng. Chem.*, **50**, 1727 (1958).

8) K. Ichimura, Y. Inoue, I. Kojima, E. Miyazaki, and I. Yasumori, *Proc. Intern. Congr. Catal., 7th*, 1980, *B*, 1281 (1981).

9) G. Pass, A. B. Littlewood, and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **82**, 6281 (1960).

10) J. E. Demuth, *Surf. Sci.*, **93**, 127 (1980).

11) "Kagaku Binran," ed by the Chemical Society of Japan, Maruzen, Tokyo (1975), p. 977.