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Catalysis by Alkaline Earth Metal Oxides. I. The Mechanism of Ethylene Hydrogenation on Calcium Oxide

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The mechanism of ethylene hydrogenation on a thermally activated CaO was studied in the overall temperature range of 197—623 K. The maximum in the reaction rate was observed around 320 K, while the activation energy was found to vary with the range of reaction temperatures, *i.e.*, 12.6 kJ/mol (197—273 K) and −16.7 kJ/mol (373—623 K). The partial pressure dependence of the rate was also different in these ranges; the reaction orders with respect to the hydrogen and ethylene pressures were 0.7 and nearly zero at 273 K respectively, whereas the orders shifted to 1.0 and 0.9 at 523 K in the pressure range from 6 to 40 Torr (1 Torr= 133.3 Pa). The reaction with deuterium at 523 K produced ethane containing widely distributed deuterium and was accompanied by the formation of highly-exchanged ethylene, HD, and H_2 molecules in the gas phase. On the contrary, the reaction at 273 K formed ethane [D_2] (>60%) selectively, and the hydrogen-deuterium exchange occurred to a lesser extent in both ethylene and deuterium. By the proposed associative mechanism, the variation in the kinetic behavior with the temperature was explained in terms of the change in the slow step from the reaction between the adsorbed hydrogen and surface ethylene to the hydrogenation of the ethyl radical. The poisoning of the hydrogenation by preadsorbed CO indicated that only 0.5% of the total surface atoms contributed actively to the reaction. On the basis of these results, the structures of active sites are briefly discussed.

Alkaline earth metal oxides have been known to become catalytically active in the H_2–D_2 equilibration reaction after irradiation with γ-rays.[1)] Recently, however, Boudart *et al.* found that the thermal treatment *in vacuo* at temperatures as high as 873 K can activate MgO to catalyze the same reaction.[2)] This finding has turned attention to the possibility of alkaline earth metal oxides as effective catalysts for other reactions. Tanabe and his co-workers found that the hydrogenation[3a,3b)] as well as the isomerization[4)] of olefins was catalyzed by BaO, MgO, CaO, and SrO when these oxides were evacuated at definite ranges of high temperatures. The mechanisms of such a generation of high activity and of the hydrogenation are of particular interest, but no precise information about them has so far been obtained.

In our series of work, we first studied the catalytic activity of calcium oxide in ethylene hydrogenation, since the reaction on CaO had not been investigated in detail, though extensive data on reactions over transition metals[5)] and their oxides[6)] had been accumulated. For a better understanding of the reaction mechanism, the kinetic study was carried out over a wide range of reaction temperatures and was supplemented by an analysis of deuterium distributions in the reaction of ethylene with deuterium. It is known that catalyses by transition metals and their oxides contrast remarkably with each other in terms of the deuterium distributions in the produced ethane;[6)] metal surfaces provide a wide distribution of ethane from [D_0] to [D_6], whereas such oxides as Cr_2O_3[7)] or ZnO[8)] are characterized by the selective formation of ethane [D_2]. These features are apparently attributable to the nature of the active sites on the catalysts; in this regard, an examination of the deuterium distributions in the reaction on CaO is interesting.

It is necessary to determine the portion of the surface which participates in the catalytic reaction. The poisoning by preadsorbed CO was, therefore, examined, and the quantitative relationship between the increased amount of surface CO and the extent of activity fall was obtained. On the basis of these results, we can provide a brief description of the structure of the active sites, the details of which will appear in a following paper.

Experimental

The calcium oxide used as a catalyst was prepared by decomposing calcium hydroxide of an extra pure grade, purchased from the Junsei Kagaku Co., Ltd., *in vacuo*. The oxide thus obtained was evacuated ($<1\times10^{-6}$ Torr) for 2 h at temperatures between 873 and 1273 K. Emission spectral analysis showed that CaO contained Mg (<3 ppm), Si (<80), Fe (<0.1), Cu (<0.5), and Mn (<10). Ethylene hydrogenation was studied at temperatures between 197 and 623 K over a pressure range from 6 to 40 Torr by using a closed circulating system with a volume of 610 ml which was directly connected to a gas chromatograph for the analysis of C_2-hydrocarbons. About 0.2 g of CaO was used for the kinetic runs. Since ethane was the only product under the present experimental conditions, the initial rate of ethane formation was employed as the measure of catalytic activity throughout the study. In the reaction of ethylene with deuterium, the product and reactants were separated gas chromatographically and analyzed on a Hitachi RMU-7M mass spectrometer at an ionization voltage of 70 V. Hydrogen, hydrogen deuteride, and deuterium were analysed by means of a gas chromatograph.[9)] The adsorption of CO on CaO activated at various temperatures was measured at room temperature and under pressures up to 40 Torr.

The hydrogen (99.99% pure), deuterium (containing less than 0.5% HD), carbon monoxide (99.5%), and ethylene (99.8%) were obtained from the Takachiho Chemical Co., Ltd., and were used without further purification.

Results

Figure 1 shows the variation in the surface area and the catalytic activity, V_e, represented by the ethane molecules produced per min and per m^2 of CaO as a function of the evacuation temperature. With an increase in the temperature, the surface area decreased monotonously, whereas V_e exhibited a max-

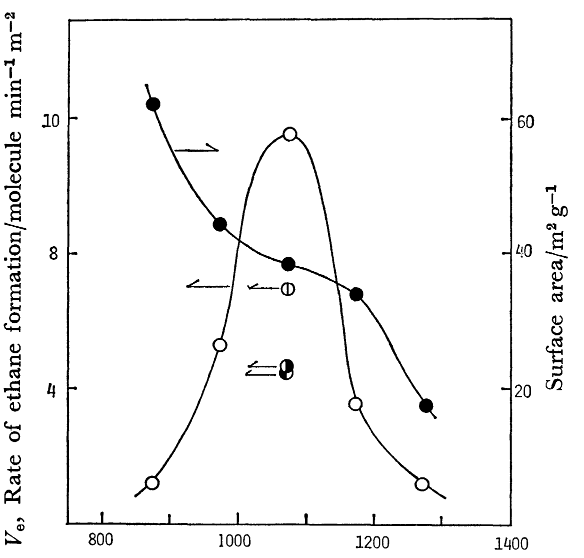


Fig. 1. Changes in surface area and catalytic activity of ethylene hydrogenation with evacuation temperature.
Reaction temp=573 K; P_h=20 Torr; P_e=10 Torr; ○; $Ca(OH)_2$ was decomposed *in vacuo*, followed by evacuation at respective temperatures, ⦶; $Ca(OH)_2$ was calcined in air at 873 K before evacuation at 1073 K. ◑; Calcined at 973 K, ◐; calcined at 1073 K.

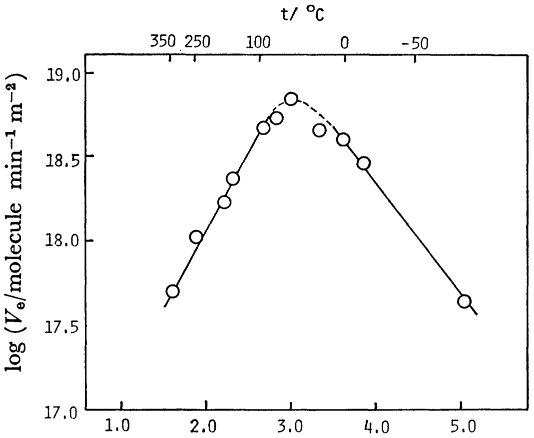


Fig. 2. Arrhenius plots of ethylene hydrogenation. P_h=20 Torr; P_e=10 Torr.

imum at 1073 K, which is larger by approximately one order of magnitude than the activity of the catalysts treated at 873 or 1273 K. This variation in the activity is similar to that previously reported by Hattori *et al.*,[3a)] although their results involved no correction for the change in the surface area. Figure 1 also shows V_e for the oxides which were prepared by calcining $Ca(OH)_2$ in air at 873, 973, or 1073 K for 2 h, followed by evacuation at 1073 K for 2 h. In this case the V_e's were smaller by 40 to 60% than those for the catalysts prepared by the decomposition *in vacuo*.

Since the CaO surface activated at 1073 K exhibited not only the maximum activity, but also the typical

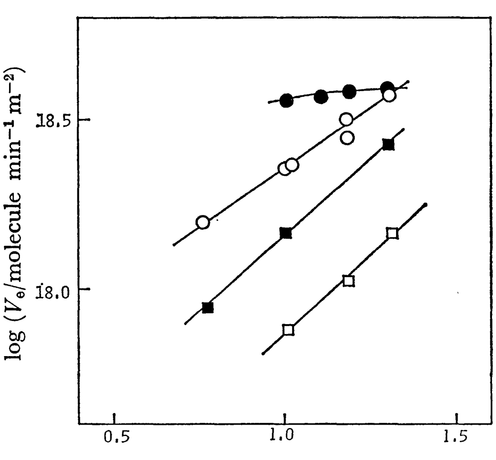


Fig. 3. Partial pressure dependence at 273 and 523 K. ○; 5.8<P_h<20 Torr, P_e=10 Torr at 273 K, ●; 10<P_e<20 Torr, P_h=20 Torr at 273 K, □; 10<P_h<20 Torr, P_e=10 Torr at 523 K, ■; 6<P_e<20 Torr, P_h=20 Torr at 523 K.

features of the catalysis, the kinetic study was carried out on the surface, unless otherwise stated. A gradual decay in the activity occurred during the course of the reaction at 533 K; the original activity was attenuated to almost 40% in the second run and to 10% in the third run. The activity thus reduced was, however, restored almost completely to the initial level after evacuation at 1073 K; hence, prior to each kinetic run, the catalyst was evacuated at that temperature for 30 min.

Figure 2 illustrates the Arrhenius plots of the hydrogenation in the temperature range between 197 and 623 K. The maximum in the rate appeared at around 340 K; the values of the apparent activation energy were determined to be 12.6 kJ mol^{-1} below 340 K and −16.7 kJ mol^{-1} above it. Such a complicated behavior suggests that the kinetics of the reaction is different in these regions. Thus, the reactions at 273 and 523 K were investigated as typical of the two regions. Figure 3 shows the partial pressure dependence of the rate. For the hydrogenation at 273 K, the reaction orders with respect to the hydrogen pressure, P_h, and the ethylene pressure, P_e, were, respectively, 0.7 and nearly zero, whereas at 523 K these orders shifted to 1.0 and 0.9. The deuterium distributions in ethylene and ethane at conversions of from 10 to 80% are summarized in Tables 1 and 2, together with the isotopic compositions of hydrogen in the gas phase. It should be noted that the differences in the distributions as well as the reaction orders between the reactions at these temperatures are striking. No isotopic exchange between D_2 and C_2H_6 occurred on CaO at reaction temperatures up to 523 K.

The adsorption of CO on CaO was examined at room temperature and in the pressure range up to 40 Torr. The amount CO adsorbed increased with the CO pressure and attained an almost saturation at the highest pressure employed. After the first run of adsorption the CO-covered surface was evacuated

TABLE 1. DEUTERIUM DISTRIBUTIONS IN THE REACTANT AND PRODUCT MOLECULES AT 273 K

Conv. (%)	Ethylene (%)					Ethane (%)							H_2	HD	D_2
	d_0	d_1	d_2	d_3	d_4	d_0	d_1	d_2	d_3	d_4	d_5	d_6		(%)	
12	97.7	0.5	1.5	0.2	0.1	0.6	16.0	72.3	9.9	1.2	0	0	0	5.7	94.3
26	94.6	0.9	4.0	0.4	0.1	1.3	18.5	62.8	11.7	5.0	0.7	0	0	12.9	87.1
52	88.6	1.6	9.2	0.5	0.1	2.5	20.4	58.3	15.5	2.9	0.4	0	1.0	17.6	81.4
74	69.9	8.7	17.2	3.9	0.3	1.0	20.8	54.4	19.8	3.4	0.6	0	1.1	23.0	75.9

P_D=20 Torr, P_e=10 Torr.

TABLE 2. DEUTERIUM DISTRIBUTIONS IN THE REACTANT AND PRODUCT MOLECULES AT 523 K

Conv. (%)	Ethylene (%)					Ethane (%)							H_2	HD	D_2
	d_0	d_1	d_2	d_3	d_4	d_0	d_1	d_2	d_3	d_4	d_5	d_6		(%)	
11	59.6	23.6	11.7	4.4	0.7	0	31.8	34.2	19.0	10.3	3.9	0.8	2.1	22.4	75.5
28													10.7	34.8	54.5
53	5.4	23.9	35.9	26.6	8.2	0	29.7	29.3	21.2	13.4	5.4	1.0	16.7	43.9	39.4
77													17.8	43.0	39.2
84	0	11.3	32.4	38.9	17.4	0	27.7	27.9	23.6	14.0	5.6	1.2	18.0	44.3	37.7

P_D=20 Torr, P_e=10 Torr.

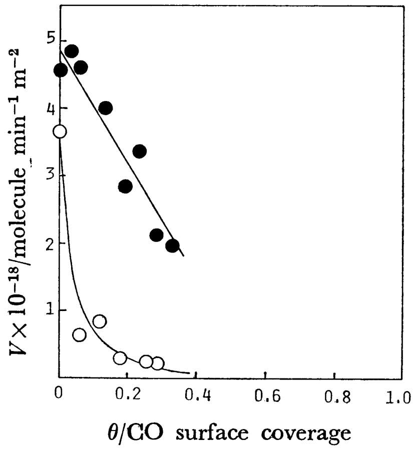


Fig. 4. Effect of preadsorbed CO on ethylene hydrogenation.
○; 273 K, ●; 373 K, P_h=20 Torr, P_e=10 Torr. CaO evacuated at 1073 K. The number of CO molecule at θ=1.0 is 1.48×10^{17} molecule m^{-2}.

at room temperature for 30 min and then exposed again to CO. In the second run, no significant adsorption occurred, indicating that the sites for the adsorption are saturated almost completely with the irreversibly bound CO. The amount at saturation was evaluated to be 1.6, 14.8, and 3.7×10^{16} molecules m^{-2} for CaO outgassed at 873, 1073, and 1273 K respectively. The evacuation temperature, after the first run of adsorption, was raised to 373 K, but the subsequent exposure to CO at room temperature gave rise to no detectable adsorption. Such a strong adsorption of CO accords with the preliminary results on thermal desorption; no gases were evolved from the surface with CO adsorbed on heating up to 423 K.

The effect of the irreversibly adsorbed CO upon the catalytic activity was examined at different reaction temperatures. Figure 4 indicates that the catalytic activity at 373 K decreased almost linearly with the increase in the coverage of CO, whereas the reaction at 273 K was characteristic in showing a drastic fall in the activity at the initial coverage of CO adsorption. The extrapolation of the plot showed that the activity is completely destroyed at the surface density of CO, 8×10^{16} molecules m^{-2}, which corresponds to about 0.5% of the total surface atoms.

Discussion

Reaction Pathway and Mechanism. The variation in the kinetic behavior of the reaction with the reaction temperature has been reported on the hydrogenation of ethylene[10] and 1-butene[11] over Ni metal catalysts. It is of interest that a similar phenomenon was observed in the present study of the reaction catalyzed by the calcium oxide surface. Such a similarity in the kinetic behavior is striking in the high-temperature region.

During the course of the reaction with deuterium in the high-temperature region, an equilibrium among the partial pressures of H_2, HD and D_2 in the gas phase was readily reached, and highly-exchanged ethylenes with deuterium were produced, even in a conversion as low as 11%. Thus, the following pathway of the reaction including the associative adsorption of ethylene can be proposed:

$$H_2(g) \rightleftharpoons 2H(a) \tag{1}$$

$$C_2H_4(g) \rightleftharpoons C_2H_4(a) \tag{2}$$

$$H(a) + C_2H_4(a) \rightleftharpoons C_2H_5(a) \tag{3}$$

$$H(a) + C_2H_5(a) \longrightarrow C_2H_6(g) \tag{4}$$

where (g) and (a) denotes, respectively, species in the gas phase and the adsorbed state. The observed deuterium distributions clearly indicate that Steps (1) and (2) are in a pseudo-equilibrium. The wide distributions of deuterium in the produced ethane further suggest that the forward and reverse processes of Step (3) are fast. Accordingly, the surface reaction (4) is assumed to be the rate-determining step in the reaction at high temperatures, and we can obtain the following rate equation for ethane formation:

$$V_e^h = k_4\theta_h\theta_{el}$$
$$= \frac{k_4K_hK_eK_3P_hP_e}{(1+\sqrt{K_hP_h}+K_eP_e+K_3K_eP_e\sqrt{K_hP_h})^2} \qquad (5)$$

where θ_h and θ_{el} denote, respectively, the fractions of the hydrogen atom and the ethyl radical, which occupy the surface sites. The k_4, K_h, and K_e constants are the rate constant and the adsorption constants of hydrogen and ethylene respectively. K_3 is an equilibrium constant in Step (3). When $1 \gg \sqrt{K_hP_h}+K_eP_e+K_3K_eP_e\sqrt{K_hP_h}$, Eq. 5 is reduced to

$$V_e^h = k_4K_hK_eK_3P_hP_e = kP_hP_e \qquad (6)$$

which agrees with the experimental pressure dependence. Equation 6 leads to the energy relationship, $E_a=E_t-Q_h-Q_e-Q_3$, where E_t is the activation energy of Reaction Step (4); Q_h is the heat of hydrogen adsorption; Q_e, the heat of ethylene adsorption, and Q_3, the heat of Reaction 3. The amounts of hydrogen and ethylene adsorbed on the CaO surface are so small that no reliable numerical data on the heat of adsorption are available at present, but the negative value of the apparent activation energy, $E_a=-16.7$ kJ mol^{-1}, is explicable if $E_t<Q_h+Q_e+Q_3$, as is seen in the case of Ni catalysts.

In the low-temperature range below 340 K, the characteristic features are the hydrogen order of 0.7, which was smaller than that, 1.0, for Ni and other transition metal catalysts, and also the selective formation of ethane[D_2] in the reaction with deuterium. Unlike Ni metal, no drastic rise in ethane[D_0] in the initial stage of the reaction was observed. The exchanged ethylene as well as hydrogen deuteride was produced in the gas phase, but their fractions were much smaller than those in the high-temperature range. These results predict that Step (3) is relatively slow compared to the other steps. In order to explain the kinetic order of 0.7 with respect to hydrogen, however, we have to introduce the assumption that a pair of dissociated hydrogen atoms on an isolated site is allowed to react with the adsorbed ethylene, because the contribution of hydrogen atoms in a randomly-mixed state to the reaction leads to a rate equation which cannot provide a kinetic order higher than 0.5. The assumption of an isolated site is supported by the results of CO posioning, which revealed that the fraction of the active site is less than 0.5% of the total surface. The selective formation of ethane[D_2] is also well accounted for by the nearly irreversible addition of the paired deuterium atoms on the site. Thus, the rate of ethane formation, V_e^1, is given by the following equation:

$$V_e^1 = k_3^1\theta'_h\theta_e$$
$$= \frac{k_3^1K_hK_eP_hP_e}{(1+K_hP_h+K_eP_e)^2} \qquad (7)$$

where θ'_h and θ_e are the fractions of coverage for the adsorbed hydrogen atom pair and for the adsorbed ethylene respectively. k_3^1 is a rate constant. Equation 7 was then transformed into

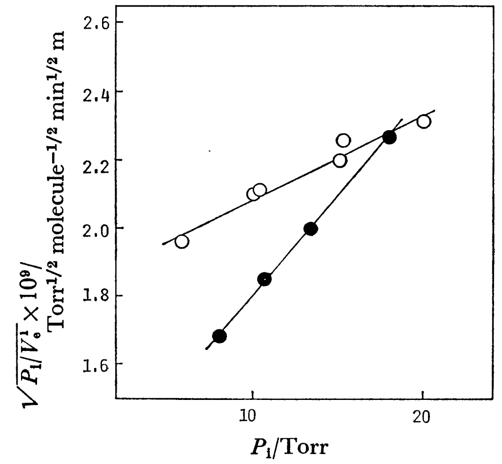


Fig. 5. Plots of $\sqrt{P_i/V_e^1}$ *vs.* P_i.
○; $P_i=P_h$ (P_e=10 Torr), ●; $P_i=P_e$ (P_h=20 Torr).

$$\sqrt{\frac{P_h}{V_e^1}} = \sqrt{\frac{1}{k_3^1K_hK_eP_e}}(1+K_eP_e+K_hP_h) \qquad (8)$$

or

$$\sqrt{\frac{P_e}{V_e^1}} = \sqrt{\frac{1}{k_3^1K_hK_eP_h}}(1+K_eP_e+K_hP_h). \qquad (9)$$

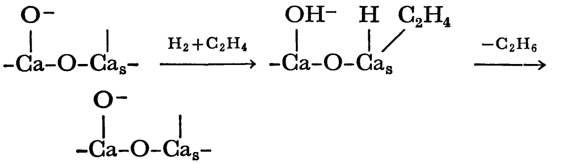
Figure 5 shows the plots of the $\sqrt{P_e/V_e^1}$ term against P_e (P_h=constant) and of the $\sqrt{P_h/V_e^1}$ term against P_h (P_e=constant). The linear relationships observed in the experimental results indicate the validity of the derived equation and, hence, the mechanism proposed.

It is of interest to compare the present data with those of others. The activation energy of 12.6 kJ mol^{-1} in the low-temperature range was smaller than those for such transition metal catalysts as Ni, Fe, and Pd,[5)] 30—40 kJ mol^{-1}. This is due to the fact that the slow step of the hydrogenation on CaO is the addition of the dissociated hydrogen atom pair to the adsorbed ethylene, whereas that on the metals is the dissociative adsorption of hydrogen. Another difference was observed in the deuterium distributions in ethane; the selectivity of ethane[D_2] formation in the present case was considerably higher than the earlier-reported values, 20% for Ni[10)] (363 K and 20% in conversion), 22% for Fe[12)] (173 K and 100%), and 17% for Pd[13)] (257 K and 5%). The selectivity, however, was much less than those, almost 100% for such oxides as Cr_2O_3[7)] (273 K), ZrO[8)] (298 K), and Co_3O_4[14)] (296 K). The CaO surface is also different from these metals in the infeasibility of the isotopic exchange between D_2 and ethane. Since the catalytic properties are different from those of the transition metals or their oxides, one can rule out the possibility that the catalytic activity of CaO might be ascribable to a trace of such components exposed at the surface.

As for the density of the active sites, the amount of CO which caused zero activity enables us to determine the fraction of the active part at be about 0.5%, which corresponds to 8×10^{12} surface ions cm^{-2}, provided that a CO molecule adsorbs on a surface ion. This result also shows that only specific sites are able to contribute to the catalytic reaction. By the use of this value, the turn-over frequency, N_t, was determined to be 0.75 s^{-1} at 273 K (P_h=20 and P_e=10

Torr). For a comparison of N_t, the data of others were corrected to the conditions of our work. N_t is given as 0.7—1.3 s^{-1} for the silica-supported Pt[15)] after calculation using the rate equation of $V_e = k'P_h^{1.0}P_e^{0.0}$. The value of N_t for the reaction on ZnO is evaluated to be 3×10^{-4}—6×10^{-4} s^{-1} by using the pressure dependence of a half-order with respect to the hydrogen pressure and by assuming that a reactive ethylene occupies an active site.[8,16)] These comparisons clearly show that the activated CaO is able to catalyze the hydrogenation of ethylene effectively.

Structure of Active Sites. A detailed study of the active sites will be published in a subsequent paper;[17)] thus, we will present here only a brief description of the plausible models of the structure of the sites and the pathway of the hydrogenation on them. The decomposition of $Ca(OH)_2$ caused the rearrangement of the structure from trigonal hydroxide to cubic oxide. A recent mass-spectrometric analysis of gases evolved during the thermal decomposition of $Mg(OH)_2$ to MgO showed that hydrogen is released together with H_2O by evacuation at high temperatures.[18)] This suggests that the desorption of hydrogen leaves oxygen atoms which are coordinatively unsaturated and negatively charged. The same processes presumably take place on CaO, since the oxide tends to form the peroxide more readily than does MgO. Thus, the electron-donating species, $-\text{O}-\overset{\overset{\text{O}^{\delta-}}{|}}{\text{Ca}}-\text{O}-$, are likely to participate in the catalytic cycle of the hydrogenation. The importance of this species, O_s^-, adjacent to an isolated OH^- group has also been pointed out in the case of the H_2–D_2 equilibration reaction on MgO.[2)] It is plausible that the active sites on CaO for the equilibration are analogous to those on MgO. It should be noted, however, that there existed a clear difference in the activation temperature of CaO for these reactions; CaO evacuated at 1273 K still possessed a high capability of catalyzing the equilibration reaction,[2)] but lost its activity for the hydrogenation of ethylene. These facts indicate that the active sites for the reactions are not identical and predict that the hydrogenation requires a contribution from the exposed Ca cations. This view is supported by the preliminary results on the structural rearrangement of CaO upon heat treatment.[17)] The fact that the active sites correspond to a small surface fraction, 0.5%, of the total surface atoms shows only a part of the surface in a specific conformation to be effective; thus, we tentatively propose a structure which is composed of the exposed Ca ion and the nearby O_s^- species. The hydrogenation of ethylene presumably proceeds as follows:



$$-\overset{\overset{\text{O}^-}{|}}{\text{Ca}}-\text{O}-\overset{|}{\text{Ca}_s}- \xrightarrow{H_2+C_2H_4} -\overset{\overset{\text{OH}^-}{|}}{\text{Ca}}-\text{O}-\overset{\overset{\text{H}\quad\text{C}_2\text{H}_4}{|\ \ /}}{\text{Ca}_s} \xrightarrow{-C_2H_6} -\overset{\overset{\text{O}^-}{|}}{\text{Ca}}-\text{O}-\overset{|}{\text{Ca}_s}-$$

where Ca_s denotes the exposed Ca ion.

The poisoning effect of CO on the hydrogenation of ethylene varied with the reaction temperature. The catalytic activity for the reaction at a high temperature decreased almost proportionaly to the CO coverage as a consequence of the homogeneous occupation of the active sites. This homogeneous character in the distribution of the active sites is probably achieved by the migration of hydrogen atoms from site to site at high temperatures. The presence of the hydrogen atom is consistent with the proposed mechanism that the rate-determining step is the surface reaction of a hydrogen atom with an ethyl radical. On the contrary, the poisoning effect at low temperatures was characterized by a marked fall in the activity in the initial coverage of CO. The presence of hydrogen-pair atoms together with ethylene in the low-temperature reaction puts more restrictions on the conformation of the active sites available for their adsorption than those for the reaction at high temperatures.

The adsorbed state of CO on CaO is not clear at present, but information from an infrared spectroscopic study of CO adsorbed on MgO[19)] is available; the exposure of MgO evacuated at 1273 K to CO at room temperature gave rise to two absorption peaks at 2100 cm^{-1}, in addition to complex bands in the region of 1450 cm^{-1}. The former absorption is characteristic of the stretching vibration of the CO molecule linked through the carbon atom to a single atom of the surface, whereas the latter might be associated with the CO molecule undergoing interaction with O^- and/or O^{2-} in the vicinity.[20)] A CO adsorption of a similar type is plausible in the case of CaO, and it appears likely that CO exists as a linear form on the exposed $-Ca_s-$.

A study is now in progress by the aid of X-ray Photoelectron Spectroscopy and ESR to clarify further the details of the structure and nature of the active sites.

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