Catalysis by Alkaline Earth Metal Oxides. II. The Mechanism of Ethylene Hydrogenation on Magnesium Oxides

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Synopsis. The kinetic study of ethylene hydrogenation on a thermally activated MgO was carried out. The slow step of the reaction changed from the irreversible addition of a hydrogen atom to adsorbed ethylene in the lower temperature range(373—423 K) to the hydrogenation of an ethyl radical in the higher temperature range (523—673 K).

In a previous paper, we reported the mechanism of ethylene hydrogenation on a thermally activated CaO.[1] The maximum in the reaction rate appeared around a reaction temperature of 340 K. Above this temperature, the kinetic behavior of the reaction resembled those on such transition metals as Ni, Fe, and Pd, whereas, below the temperature, they were rather similar to those on oxides, *e.g.*, ZnO[2] and Cr_2O_3.[3]

Tanabe and his co-workers[4] found that a pretreatment of MgO *in vacuo* at temperatures higher than 1200 K generated the catalytic activity for the hydrogenation of olefins and dienes. In order to establish catalysis by alkaline earth metal oxides, it would be constructive to extend the research into ethylene hydrogenation to other alkaline earth metal oxides. Thus, we undertook the present study to see whether or not the kinetic features described above exist on MgO and then to compare them with the previous results for CaO.

Experimental

Magnesium oxide catalysts were prepared by decomposing $Mg(OH)_2$ of an extra pure grade *in vacuo*. The DTA spectra of $Mg(OH)_2$ showed an endothermic peak in the temperature range of 590—720 K, which was due to H_2O evolution upon the structural rearrangement from trigonal to cubic; this indicated the development of the crystallite structure of MgO by treatment above this temperature range. The oxide thus obtained was subjected to evacuation at 1273 K for 2 h at a pressure lower than 2×10^{-6} Torr (1 Torr = 133.3 Pa). Emission spectral analysis showed that the oxide contained Cu (<0.5 ppm), Fe(<0.1), Mn(<10), Si(<80), and Ca(<0.5). The surface area of MgO after the treatment was 118 $m^2\ g^{-1}$. The apparatus, procedure, and reactant gases used were the same as those reported previously.[1] Ethane was the sole product under the present experimental conditions. The repetition of kinetic runs at 523 K decreased the catalytic activity to less than 50% of the initial value, but subsequent evacuation at 1273 K for 2 h recovered the deactivated activity to the original level.

Results and Discussion

As is shown in Fig. 1, the Arrhenius plot of the rate of ethylene hydrogenation on MgO gave rise to a maximum at around 490 K, and the activation energy, E_a, was determined to be 28.5 kJ mol^{-1} in the lower temperature range (373—423 K) and −36.8 kJ mol^{-1} in the higher temperature range (523—673 K). The reaction orders with respect to the pressure of hydrogen, P_h, and ethylene, P_e, were both 1.0 at 623 K, whereas the latter value decreased to nearly zero at 393 K. These variations were similar to those for the same reaction on CaO,[1] but the hydrogen order, 1.0, in the lower temperature range was different from 0.7. Table 1 shows the deuterium distributions in the reaction of ethylene with D_2. At 623 K and in conversions of 28 to 42%, there existed highly-exchanged ethylene ranging from $[D_1]$ to $[D_4]$, and the gaseous composition of H_2, HD, and D_2 nearly reached equilibrium. Ethane contained species from $[D_0]$ to $[D_4]$; the fraction

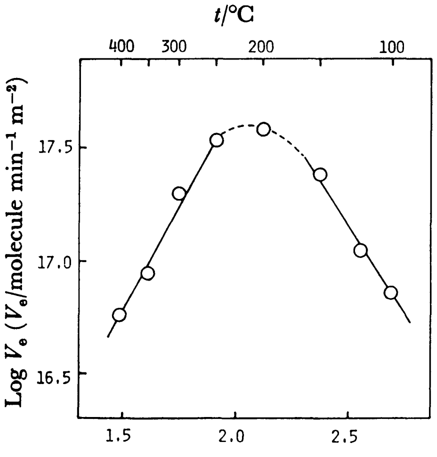

Fig 1. Arrhenius plot of rate in ethylene hydrogenation on MgO.
P_h = 20 Torr, P_e = 10 Torr.

TABLE 1. DEUTERIUM DISTRIBUTIONS IN THE REACTION OF ETHYLENE WITH D_2 ON MgO

Temp	Conv.	Ethylene(%)					Ethane(%)							H_2	HD	D_2
K	%	d_0	d_1	d_2	d_3	d_4	d_0	d_1	d_2	d_3	d_4	d_5	d_6		(%)	
393	27	96.1	3.9	0	0	0	1.4	6.9	84.4	5.4	1.9	0	0	0	2.8	97.2
	47	83.9	11.4	3.7	1.0	0	0	1.5	87.7	7.7	2.8	0.3	0	0	3.4	96.6
623	28	61.7	28.3	7.9	1.5	0.6	3.3	10.6	65.9	16.8	3.4	0	0	1.8	22.1	76.1
	42	21.5	42.0	26.4	4.8	5.3	1.9	9.0	61.6	20.9	6.4	0.2	0	—	—	—

P_D = 20 Torr, P_e = 10 Torr.

of ethane [D_2] amounted to about 65%. On the other hand, at 393 K and in similar conversions, small amounts of the deuterium-exchanged ethylene and HD were produced in the gas phase, whereas the fraction of ethane [D_2] was as high as 85%. No isotopic-exchange reaction between ethane and D_2 occurred up to 623 K.

The wide deuterium distributions in the higher temperature range indicated that the hydrogenation proceeds *via* the pathway described by the associative mechanism and that the reaction between the hydrogen atom and the ethyl radical was the rate-determining step, as has been proposed in the case of CaO.[1] Thus, we are able to employ the rate equation obtained before:

$$V_e^h = k_4 K_h K_3 K_e P_h P_e = k^h P_h P_e, \tag{1}$$

where k_4 is the rate constant of the reaction in the rate-determining step. K_e and K_h are the equilibrium constants for the adsorption of ethylene and hydrogen respectively, while K_3 is the equilibrium constant for the surface reaction between the hydrogen atom and the adsorbed ethylene to form the ethyl radical and its reverse reaction. Equation 1 is in agreement with the experimental rate equation.

The drastic fall in the catalytic activity during the course of a reaction at a higher temperature is probably due to the formation of strongly bound surface ethylene species, since the pre-exposure of a fresh catalyst to 10 Torr of ethylene at 523 K caused a decrease in the activity to as low as 15%. The species appears to remain after evacuation at the reaction temperature, but to be removed by evacuation at 1273 K. An analogous poisoning species, presumably polymerized ethylene, was observed in the ethylene hydrogenation on ZnO at 383—673 K.[5]

The reaction in the lower-temperature range provided very small amounts of the deuterium-exchanged ethylene and HD (with scarcely any H_2) in the gas phase, and resulted in the selective formation of ethane-[D_2]($\approx$85%). These findings indicate that the irreversible addition of a hydrogen atom to adsorbed ethylene is a slow step compared to the other steps. When one assumes that the hydrogen atoms adsorbed in a randomly-mixed state participate in the hydrogenation, the reaction order in P_h fails to become larger than 0.5; this contradicts the observed value, 1.0. However, the assumption that the reactive surface hydrogen is a pair of hydrogen atoms on an isolated site leads to the following rate equation:[1]

$$V_e^1 = \frac{k^1 K_e K_h P_h P_e}{(1+K_e P_e + K_h P_h)^2}, \tag{2}$$

where k^1 is the rate constant of the reaction between the hydrogen and adsorbed ethylene. This equation was transformed into the equations having a linear relationship between the $\sqrt{P_e/V_e^1}$ term and P_e or between the $\sqrt{P_h/V_e^1}$ term and P_h in the same way as has been described previously.[1] Figure 2 demonstrates the linearity in their relationships, which gives evidence for the validity of Eq. 2 and, hence, the mechanism proposed. The reaction of 1,3-butadiene with D_2 on MgO was proposed to proceed *via* the attack of a heterolytically split hydrogen atom on the adsorbed butadiene on the isolated sites;[6] this gives support to the assumption employed in deriving Eq. 2. The slightly higher kinetic order in P_h for the ethylene hydorgenation on MgO than for that on CaO suggested the weaker adsorption of hydrogen, in comparison with the ethylene adsorption, on the former oxide.

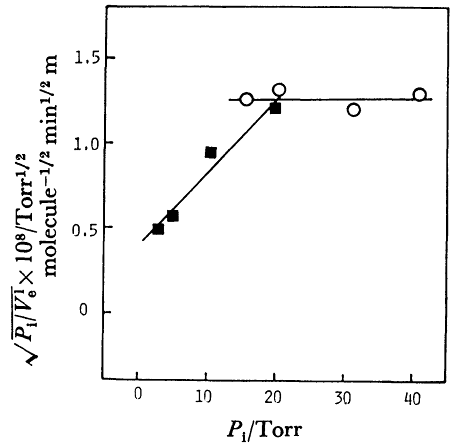

Fig. 2. Plots of $\sqrt{P_i/V_e^1}$ *vs.* P_i.
Reaction temp=393 K, ○: $P_i=P_h(P_e=10$ Torr), ■: $P_i=P_e(P_h=20$ Torr).

There existed a general similarity in the reaction behavior of the ethylene hydrogenation on MgO and CaO; it appears to arise from the common nature of these oxide surfaces. A study of the surface state of thermally-treated alkaline earth metal oxides is in progress using X-ray photoelectron spectroscopy.

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