[May, 1975] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (5), 1345—1348 (1975) 1345

The Catalytic Hydrogenation of Ethylene over Calcium Hydride and the Role of the Hydrogen of the Hydride

Masaru YAMAGUCHI, Yozaburo HIRAKI, Masatada WADA,* and Kimio TARAMA*

Faculty of Living Science, Kyoto Prefectural University, Sakyo-ku, Kyoto 606

* *Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606*

(Received July 20, 1974)

The catalytic hydrogenation of ethylene over the non-stoichiometric calcium hydride ($CaH_{2-\delta}$) prepared by means of high-temperature evacuation was studied. The order of introducing gases had no effect on the rate of ethylene hydrogenation. The rate expressions for the initial stage were $v=k\,P_H^{0.8-1.0}\,P_E$ and $v'=k'\,P_H^{0.8-1.0}\,P_E^0$ in the lower and higher pressure ranges of ethylene respectively. The amount of hydrogen bound initially to $CaH_{2-\delta}$ and participating in the reaction was estimated from the results of the D_2–$CaH_{2-\delta}$ exchange and H_2–D_2 equilibration reactions. From these results, the mechanism of ethylene hydrogenation over calcium hydride and the role of the hydrogen of the hydride were discussed. The poisoning caused by water and acetylene was also studied. Furthermore, the catalytic activity of calcium hydride was compared with that of three metallic hydrides.

It has been established that the non-stoichiometric calcium hydride prepared by means of high-temperature evacuation has an remarkable catalytic activity for hydrogenation,[1–3] whereas metallic calcium and stoichiometric calcium hydride are far less active as catalysts of the hydrogenation of olefins. Though it has been pointed out[4] that the electrons in s-, p-, and d-bands are overlapped with each other in metallic calcium, its electronic structure is remarkably different from that of the transition metals of the 8th group, known to be excellent catalysts for hydrogenation. The distance between calcium atoms in the hydride is unusually longer (minimum distance: about 3.4 Å) in comparison with that of the transition metals of the 8th group. Also, the hydride has a highly ionic character. Therefore, it may be said that the non-stoichiometric calcium hydride is a peculiar catalyst for hydrogenation.

When the catalytic activities of calcium hydride have been studied thus far,[1–3] the investigations have been limited to the qualitative aspect of hydrogenation, the detailed mechanism has been left unsurveyed. The present investigation was undertaken in order to obtain more detailed kinetic information concerning the mechanism of the ethylene hydrogenation on this catalyst and in order to determine the role of the hydrogen bound initially to the hydride during the catalytic reaction. The experimental results will also be compared with those of the previous works on palladium black,[5] tantalum powder,[6] and titanium hydride.[7]

Experimental

Materials. The calcium hydride was obtained from the Metal Hydride Co. (purity: 98—99 %). The major impurities in this specimen were nitrogen and oxygen. It was also contaminated with trace amounts of magnesium, manganese, sodium, strontium, and iron. Noble metals, which are known as excellent hydrogenation catalysts, were not detected by emission spectrographic analysis. The hydrogen was prepared by the thermal decomposition of titanium hydride.[6,7] The deuterium (purity: D_2 97.8 %, HD 2.2 %) and the acetylene (99.6 %) in a glass ampoule were obtained from the Takachiho Trading Co.; they were used without further purification. The ethylene was purified by the conventional procedure, followed by repeated fractionations at the temperature of liquid nitrogen.

Procedure. All of the experimental runs were conducted in a closed circulating system at a constant pressure or within a constant volume. The apparatus used in these experiments was similar to that reported in a previous paper.[6] Since calcium hydride is very sensitive to the moisture, each sampling manipulation was carried out carefully in a dry box. About two grams of the powdered catalyst was placed in the reaction vessel; as a standard pretreatment, it was evacuated at 200 °C for 1 hr and finally at 450 °C under 1×10^{-5} Torr for 1 hr. After the vessel has then been cooled to the predetermined temperature, all the runs were carried out. The rate of ethylene hydrogenation was measured in the temperature range between −78 and 450 °C and in the range of total pressure between 50 and 500 Torr. The relative concentrations of ethylene and ethane in the product were estimated by a micro gas-absorption method similar to that of a previous paper;[7] these concentrations agreed with the value calculated from the volume change, thus excluding any possibility of reactions other than ethylene hydrogenation occurring. The adsorption of reactant gases to the catalyst was negligible in the rate measurements. The hydrogen isotopes were analyzed by using a CEC-21-401 mass spectrometer. The spectrum of hydrogen isotopes was taken at an ionization energy of 70 eV and at an ion-accelerating voltage of 500 V. A Shimadzu GX-3B X-ray diffractometer with copper $K\alpha$ radiation was used to obtain the diffraction diagrams of calcium hydride.

Results and Discussion

Effect of the Pretreatments of Stoichiometric Calcium Hydride on Surface Area, the Amount of Hydrogen-Evolved, and the Initial Rate of Ethylene Hydrogenation. As is shown in Fig. 1, evacuation at temperatures below 200°C evolved only a slight amount of hydrogen, and the increase in the surface area was minor. No catalytic activity was observed for ethylene hydrogenation. As the temperature was raised above 250°C, the amount of hydrogen evolved and the surface area increased remarkably. The catalytic activity was considerably raised when more than ten percent of hydrogen was removed from the stoichiometric calcium hydride. Though an evaporated film of metallic calcium was formed on the wall of the evacuated reaction vessel above 450 °C,

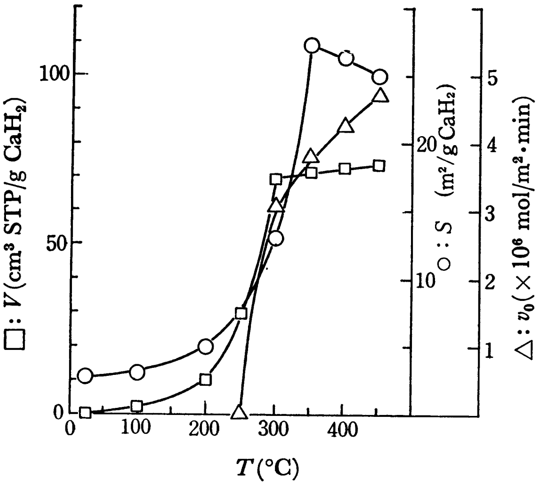

Fig. 1. Effects of the evacuation temperature (T) on the amount of hydrogen evolved (V), B.E.T. surface area (S) and the initial rate of ethylene hydrogenation (v_0).

the film revealed no catalytic activity.

It is thought that the increase in the surface area is caused by the loss of hydrogen from the crystal lattice, thus bringing about a higher porosity. Such a surface may contain many lattice defects, basic or base-like sites, metallic or metal like sites, and their interfaces.

Hydrogenation of Ethylene. Although the order of introducing gases significantly affects the rate of ethylene hydrogenation using palladium-, tantalum- and titanium hydride,[5–7] no significant differences were observed with the non-stoichiometric calcium hydride, $CaH_{2-\delta}$,* as is shown in Fig. 2. The reaction proceeds even at −40 °C; the maximum initial rate was observed at about 250 °C.

Figure 3 shows the dependence of the initial rate upon the hydrogen or ethylene pressure. From this figure, the initial rate of the ethane formation is expressed by:

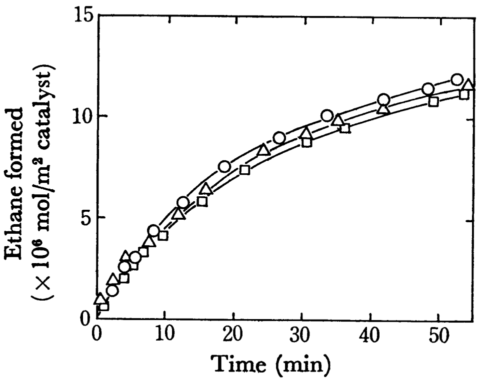

Fig. 2. Ethane formed—time plots at 0 °C (Effect of the order of introducing gases).

Each initial rate (v_0) was evaluated as follows:

Order of introduction	P_H Torr	P_E Torr	v_0 $\times 10^7 \cdot mol/m^2 \cdot min$
○: H+E	44.1	42.7	4.88
△: H→E	41.8	44.3	5.00
□: E→H	44.7	41.1	4.68

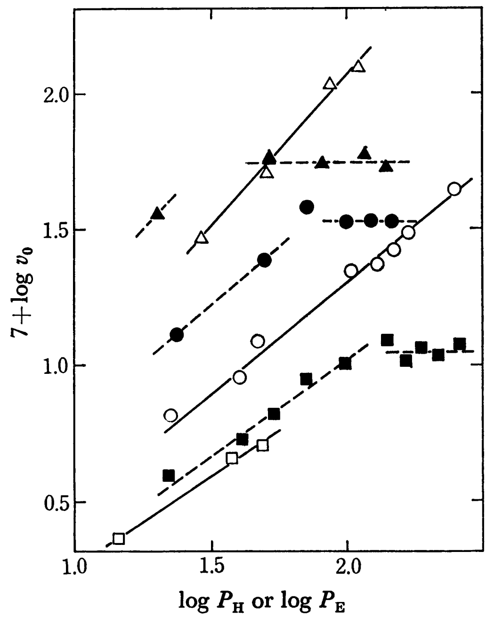

Fig. 3. Dependence of the initial rate of ethylene hydrogenation upon the pressures of ethylene and hydrogen. closed mark: dependencies upon ethylene (P_H= 48 Torr), open mark: dependencies upon hydrogen (P_E= 45 Torr), □, ■: 0°C, ○, ●: 50 °C, △, ▲: 100 °C.

$$v = kP_H^{0.8-1.0}P_E \text{ and } v' = k'P_H^{0.8-1.0}P_E^0$$

in the regions of lower and higher pressures of ethylene respectively. The apparent activation energies between 0 and 100°C were estimated to be 4.6 and 3.3 kcal/mol for k and k' respectively.

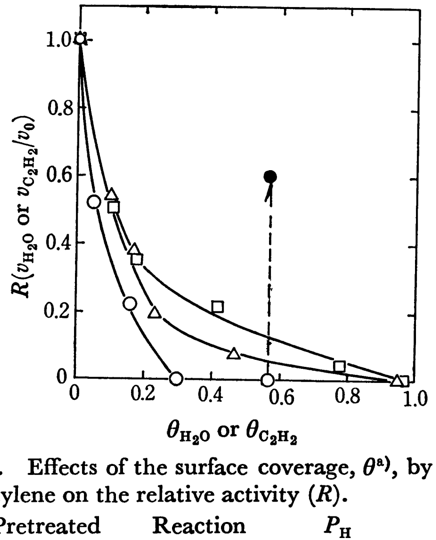

Fig. 4. Effects of the surface coverage, θ[a], by water or acetylene on the relative activity (R).

Pretreated substances	Reaction temperature	P_H Torr	P_E Torr
○: H_2O	100 °C	47.5	48.0
□: C_2H_2	100	52.5	49.3
△: C_2H_2	200	51.8	48.3

Closed circle shows restored relative activity after high temperature evacuation.

a) θ_{H_2O} (or $\theta_{C_2H_2}$) was estimated on the basis of the assumption that two molecules (or one molecule) of water (or acetylene) react with one atom of surface-exposed calcium: number of calcium atoms exposed on the surface was calculated from B.E.T. nitrogen surface area.

---

* δ=0.35 after the standard pretreatment.

The effect of the pretreatment by water or acetylene on the catalytic activity is shown in Fig. 4. The relative catalytic activity (R), which is defined as the ratio of the initial rate of hydrogenation with the catalysts after and before the pretreatment, decreased sharply, along with the surface coverage (θ_{H_2O}) by water, falling to zero at $\theta_{H_2O}=0.3$. When this deactivated catalyst was evacuated at 650°C and when the standard pretreatment was carried out after treating it with 300 Torr hydrogen at 400°C for 1 hr, the activity was restored to some extent. The poisoning by acetylene was similar to that of water up to about $\theta_{C_2H_2}=0.1$, though the relative activity fell to zero in the vicinity of $\theta_{C_2H_2}=1$. Contrary to the case of water, the poisoning by acetylene was perfectly irreversible, regardless of the kind of treatment thereafter. When a mixture of acetylene and hydrogen was introduced into the catalyst vessel, a considerable decrease in the pressure was observed. The analysis of the remaining gas, however, revealed that the pressure decrease was caused by the adsorption or by the reaction of the acetylene with the catalyst; it was not caused by the hydrogenation.

TABLE 1. H_2–D_2 EQUILIBRATION ON $CaH_{2-\delta}$ AND D_2–$CaH_{2-\delta}$ EXCHANGE REACTION[a]

(a) H_2–D_2 equilibration on $CaH_{2-\delta}$ (at 200 °C).
Initial gas composition (%) D_2: 51.6, HD: 1.2, H_2: 47.2
Total amount: 39.90 cm^3 STP

	V_{ph}[c] cm^3 STP	Final gas composition (%)[b] H_2	HD	D_2
Calcd	5.0	29.6	48.0	22.4
	6.0	30.6	48.1	21.3
	6.5	31.1	48.1	20.8
Obsd		28.9	49.5	21.6

(b) D_2–$CaH_{2-\delta}$ exchange (at 200 °C).
Initial gas composition (%) D_2: 97.8, HD: 2.2
Total amount: 38.29 cm^3 STP

	V_{ph}[c] cm^3 STP	H_2	HD	D_2
Calcd	6.0	2.4	24.2	73.4
	6.5	2.4	26.1	71.5
Obsd		2.8	25.4	71.8

(c) H_2–D_2 equilibration on $CaH_{2-\delta}$ (at 100 °C).
Initial gas composition (%) D_2: 49.7, HD: 1.1, H_2: 49.2
Total amount: 41.28 cm^3 STP

	V_{ph}[c] cm^3 STP	H_2	HD	D_2
Calcd	0	25.7	48.1	26.2
	0.2_5	26.0	48.1	25.9
	0.5	26.3	48.1	25.6
Obsd		24.1	49.9	26.0

(d) D_2–$CaH_{2-\delta}$ exchange (at 100 °C).
Initial gas composition (%) D_2: 97.8, HD: 2.2
Total amount: 39.91 cm^3 STP

	V_{ph}[c] cm^3 STP	H_2	HD	D_2
Calcd	0	~0	2.2	97.8
	0.2_5	0.0_3	3.4_2	96.5_5
	0.5	0.0_5	4.6_2	95.3_3
Obsd		0.4	3.3	96.3

a) $CaH_{2-\delta}$: *ca.* 2.2 g, reaction time: 30 min. The conversion of ethylene hydrogenation was about 95 % under the same condition. b) On the equilibrium constants K for $H_2+D_2 \rightleftharpoons 2HD$, the values of 3.59 and 3.43 were used for 200 and 100 °C, respectively.[9] c) The amount of hydrogen bound initially to $CaH_{2-\delta}$ and participated to the reaction.

$CaH_{2-\delta}$–D_2 Exchange and $CaH_{2-\delta}$–(H_2+D_2) Equilibration Reactions. In order to ascertain the role of the hydrogen of calcium hydride during the catalytic reaction, these two reactions were studied. The experiments were carried out when the equilibration reaction had almost been completed. The equilibrium compositions of the hydrogen isotopes, which must be composed of the hydrogen initially bound to $CaH_{2-\delta}$ and which participate in the reaction (V_{ph}), and the gas-phase hydrogen were calculated with respect to the temporal figure of V_{ph}. As is shown in Table 1 [(a) and (b), at 200°C], the observed equilibrium compositions are in good agreement with the calculated ones, in which 6.0—6.5 cm^3 STP of V_{ph} was assumed. This V_{ph} value corresponds to about 0.6% of the amount of the hydrogen initially bound to $CaH_{2-\delta}$, and it roughly corresponds to half of the hydrogen in the surface monolayer (12 cm^3 STP). The amount of hydrogen in the surface monolayer was estimated on the basis of the assumption that one molecule of hydrogen is attached to one atom of calcium. The V_{ph} value was very low at 100 °C compared with the values at 200 °C; it was estimated to be 0.1—0.3 cm^3 STP [Table 1. (c) and (d)]. These results suggest that only a minor amount of the hydrogen of calcium hydride participates in both reactions, contrary to the results by Wright and Weller.[2]

X-Ray Measurements. When calcium hydride of a stoichiometric composition is heated under a vacuum, the specimen is gradually changed with the rise in the heating temperature from greyish white to grey (400 °C) and to greyish black (500 °C), and a calcium mirror is formed above 450 °C at the cold parts of the vessel. These observations indicate that a part of the hydride is converted into metallic calcium. However, the X-ray diffraction analysis conducted on the powdered specimens which had been placed in a vacuum at 100, 250, 450 and 510 °C for 1 hr showed only the pattern of the stoichiometric hydride; that of metallic calcium was not detected. These results may suggest that metallic calcium is formed after the high-temperature evacuation, but it can not be detected

TABLE 2. INITIAL RATE OF ETHYLENE HYDROGENATION ON Pd-,[5] Ta-,[6] Ti-[7] AND Ca-HYDRIDE

Hydride	Reaction temp. °C	P_H Torr	P_E Torr	Initial rate of hydrogenation mol/g-cat·min	mol/m^2-cat·min
Pd (β-phase)	75	198	82	8.27×10^{-4}	6.3×10^{-5}
Ta	300	200	100	12.5×10^{-6}	12.5×10^{-5}
Ti	300	191	109	2.46×10^{-6}	0.3×10^{-5}
Ca	50	203	45	7.81×10^{-5}	0.3×10^{-5}
Ca	100	109	46	34.3×10^{-5}	1.35×10^{-5}

by X-ray measurements because of its extremely fine particle size.

Comparison with the Catalytic Activity of Other Metal Hydrides. The initial rates of ethylene hydrogenation on the non-stoichiometric calcium hydride are, in Table 2, compared with those of three metallic hydrides.[5-7] The catalytic activity of non-stoichiometric calcium hydride is slightly lower than that of palladium hydride (β-phase) under similar experimental conditions. It might be higher than that of tantalum- and titanium-hydride, however, because the rates of ethylene hydrogenation at 50—100 °C on non-stoichiometric calcium hydride are of the same magnitude as the rates at 300 °C on the two hydrides mentioned above.

The Mechanism of the Hydrogenation of Ethylene and the Role of Hydrogen Bound to $CaH_{2-\delta}$. From the results of the effect of the order of introducing gases and of the dependence of the initial rate upon the pressure, it was presumed that the rate-determining step of the ethylene hydrogenation on $CaH_{2-\delta}$ is the surface reaction between adsorbed ethylene and adsorbed hydrogen on different sites. The formation of HD during the H_2–D_2 equilibration reaction strongly suggests the dissociative adsorption of hydrogen and deuterium on the catalyst surface.

From the V_{Ph} values at lower temperatures ($<$ 100 °C) shown in Table 1, it can be said that the hydrogen which is initially bound to $CaH_{2-\delta}$ does not participate in the hydrogenation—only the hydrogen adsorbed from the gas phase does. At higher temperatures ($>$100 °C), on the other hand, both the hydrogen adsorbed from the gas phase and a part of the hydrogen loosely bound to calcium on the surface monolayer of $CaH_{2-\delta}$ participate in the hydrogenation. In both cases, the hydrogen in the bulk $CaH_{2-\delta}$ dose not participate. These interpretation are also supported by the results of the isomerization of butene over $CaD_{2-\delta}$.[8]

Although it is not yet certain what kind of site is catalytically active, the following suggestion may be made: the carbanion-type ethylene adsorbed on the basic or base-like sites may be able to associate with the hydrogen adsorbed on the neighboring metallic sites and may thus be converted to ethane.

The authors are grateful to Professor Shiichiro Teranishi of Osaka University and Professor Makoto Kumada of Kyoto University for their valuable suggestions. They are also thankful to Mr. Masataka Nakanishi of the Daiseru Co., Ltd., for his assistance. Thanks are further extended to Dr. Tsutomu Makita of Kyoto University for the mass spectrometric measurements.

References

1) R. N. Pease and L. Stewart, *J. Amer. Chem. Soc.*, **47**, 2763 (1925).

2) L. Wright and Sol Weller, *ibid.*, **76**, 5302, 5305, 5948 (1954).

3) E. Wiberg and E. Amberger, "Hydrides of the Elements of Main Group I—IV," Elsevier Publishing Co., Amsterdam (1971), p.69.

4) M. F. Manning and H. M. Krutter, *Phys. Rev.*, **51**, 76 (1937).

5) M. Yamaguchi, S. Teranishi, and K. Tarama, *Nippon Kagaku Zasshi*, **78**, 759 (1957).

6) M. Yamaguchi, *Sci. Rep. Kyoto Pref. Univ.*, *No.* 20, *Ser. A*, 5 (1969).

7) M. Yamaguchi, *ibid.*, *No.* 19, *Ser. A*, 11 (1968).

8) To be published.

9) S. Z. Roginsky, "Theoretical Principles of Isotope Methods for Investigating Chemical Reaction," U.S.A. A.E. C. tr-2873 (1956), p.155.