The Catalytic Activity of Barium and Calcium Hydrides. II. The Nature of the Catalyst

By SOL WELLER AND LEON WRIGHT

The optimum catalytic activity of calcium and barium hydrides for hydrogen-deuterium exchange and ethylene hydrogenation is developed by evacuation at temperatures in the range 200–300°. Exposure of the activated catalyst to hydrogen at elevated temperatures does not inhibit hydrogen–deuterium exchange at −78°, but it does deactivate the catalyst for ethylene hydrogenation at −78°. Exposure to hydrogen only at −78° does not affect the activity for either reaction. The catalytic activity is not attributable to oxide impurities. The catalytically active sites are believed to be dual metal–metal hydride sites occurring at an interface between free metal and metal hydride. Some of the problems are discussed which arise from the interpretation of this catalyst system in terms of the electronic and geometrical theories of catalysis.

Introduction

The alkaline earth metal hydrides have been found to catalyze a variety of reactions, resembling somewhat in their behavior transition metals such as nickel.[1] In view of the unexpected activity of these hydrides, it was considered highly desirable to try to determine the identity of the catalytically active sites. The problem was approached by consideration of the effects of possible impurities, and by study of the effects of pretreatment on the catalyst activity for low temperature hydrogen-deuterium exchange and ethylene hydrogenation.

Experimental

Materials.—Calcium and barium hydrides were obtained from Metal Hydrides, Inc. In order to maintain reproducible catalytic activity, these materials were stored under dry nitrogen and charged to reactors in a nitrogen-flushed dry-box.

Hydrogen was purified by passing over hot copper and then through dried silica–alumina (Houdry type S-45) at −195°. Deuterium of >99% purity was obtained from The Stuart Oxygen Company and was dried over anhydrous calcium sulfate at −195°.

A special blend of ethylene and hydrogen was obtained from the Matheson Company and used after drying by passage through anhydrous calcium sulfate at −78°.

Apparatus and Procedure.—All experiments were carried out in glass reactors using high vacuum technique. After the pretreatment period, during which a measured amount of catalyst was evacuated under 10^{-5} mm. usually at 200 or 300° for a fixed period, the reactor was cooled to some standard reaction temperature and charged with a known amount of ethylene–hydrogen or hydrogen–deuterium mixture. The gases were then circulated over the catalyst by an all-glass electromagnetic pump of approximately 10 cc. (STP) dead space; after various time periods gas samples were taken for analysis by mass spectrometer.

Results

Commercial calcium hydride is relatively inactive in catalyzing hydrogen–deuterium exchange, even at 100°, unless it is activated by high temperature treatment (Table I, run 1). As the data of Table I show, the activity increases with increasing temperature of evacuation, prior to testing, at least in the range 30–200°. Comparison of runs 4 and 5, Table I, indicates that for the sample of calcium hydride used, no further gain in activity is achieved by increasing the evacuation temperature from 200 to 400°.

Commercial barium hydride, activated by pumping at 300°, is active for hydrogen–deuterium exchange at −78° (run 1, Table II). The activity of the catalyst *for this reaction* is not poisoned by ex-

(1) L. Wright and S. Weller, THIS JOURNAL, **76**, 5305 (1954).

TABLE I

EFFECT OF EVACUATION TEMPERATURE ON HYDROGEN-DEUTERIUM EXCHANGE OVER CALCIUM HYDRIDE

1-hour evacuation

Run no.	Charge, mmoles CaH₂[a]	Charge, mmoles H₂-D₂	Evacuation temp., °C.	Conditions of exchange Temp., °C.	Conditions of exchange Time, min.	Gas anal. vol. % H₂	Gas anal. vol. % HD	Gas anal. vol. % D₂
1	34	0.17	30[b]	100	30	48.9	1.0	50.1
2	34	.17	100	100	30	44.0	8.1	47.9
3	34	.17	200	100	15	23.8	46.9	29.3
4	8.5	.17	200	0	30	37.3	18.6	44.1
5	8.5	.17	400	0	30	39.1	15.9	45.0

[a] Fresh catalyst sample in each run. [b] Evacuated only 30 seconds to remove air.

posure to hydrogen at elevated temperatures (run 2, Table II).

TABLE II

EFFECT OF HYDROGEN TREATMENT ON HYDROGEN–DEUTERIUM[a] EXCHANGE OVER BARIUM HYDRIDE AT −78°

Run no.	Pretreatment	React. time, min.	Gas anal., vol. % H₂	Gas anal., vol. % HD	Gas anal., vol. % D₂
1	Evac. 18 hr. at 300°, cooled in He to −78°	3	50.6	2.3	47.1
		10	48.9	6.2	44.9
2	After run 1, heated to 300° under vacuum, H₂ 1 hr. at 300°, cooled in H₂ to −78°	3	52.4	2.2	45.4
		10	50.2	5.5	44.3

[a] 1.8 mmoles BaH₂, 0.17 mmoles H₂-D₂.

Ethylene hydrogenation at −78° is also catalyzed by barium hydride activated at elevated temperatures. As the data of Table III indicate, barium hydride evacuated at −78 or 0° was inactive for ethylene hydrogenation at −78° (runs 1 and 2) even though considerable sorption of ethylene oc-

TABLE III

EFFECT OF EVACUATION TEMPERATURE AND TIME ON ETHYLENE HYDROGENATION[a] OVER BARIUM HYDRIDE[b] AT −78°

Run no.	Evacuation Temp., °C.	Evacuation Time, hr.	Reaction time, min.	Gas anal., vol. % H₂	Gas anal., vol. % C₂H₄	Gas anal., vol. % C₂H₆
1	−78	1	60	50.6	46.6	2.8
2	0	1	30	45.6	52.0	3.0
3	100	1	195	16.0	27.7	56.3
4	200	1	20	..	21.1	78.9
5	200	22	15	1.6	18.3	80.1
6	300	18	23	2.2	23.8	74.0

[a] 3.3 mmoles ethylene–hydrogen charged in each run. Charge analysis: 43.6% H₂; 53.6% C₂H₄; 2.8% C₂H₆. [b] 180 mmoles (10 cc.) of barium hydride charged in each run.

TABLE IV

EFFECT OF HYDROGEN TREATMENT ON ETHYLENE HYDROGENATION OVER BARIUM HYDRIDE AT −78°

Run[a] no.	Charge, mmoles BaH$_2$	C$_2$H$_4$–H$_2$	Temp., °C.	Pretreatment Time, hr.	Gas	Cooled in	Reaction time, min.	H$_2$	Gas anal., vol. % C$_2$H$_4$	C$_2$H$_6$
1a	90	3.3	{ 300	17	Vac					
			300	1	H$_2$	H$_2$	45	41.9	53.9	4.2
1b	90	3.3	300	65	Vac	He	50	1.8	24.8	73.3
2	180	3.3	{ 300	17	Vac	He	10	3.1	18.6	78.3
			−78	1	H$_2$					

[a] Fresh catalyst charged in 1a and 2. 1b followed 1a.

TABLE V

HYDROGEN-DEUTERIUM EXCHANGE OVER CALCIUM AND CALCIUM HYDRIDE AT 0°

(17.5 mmoles Ca, 0.17 mmoles H$_2$–D$_2$).

Run no.	Catalyst	Temp., °C.	Pretreatment Time, hr.	Gas	Cooled in	Reaction time, min.	H$_2$	Gas anal., vol. % HD	D$_2$
1	Ca	300	30	Vac	He	60	47.0	5.9	47.1
2[a]	CaH$_2$ 20%	300	1	Vac					
		300	1/2	H$_2$	He	60	27.0	45.8	27.0

[a] Sample after run 1 was hydrogenated at 300° to an extent equivalent to 20% CaH$_2$ and then used in run 2.

curred. Increasing the evacuation temperature to the range 100–200° resulted in an active catalyst (runs 3 and 4). Neither higher temperature nor increased time of evacuation (runs 5 and 6) resulted in a more active catalyst. The catalyst evacuated at −78 and 0° was subsequently shown to be active by evacuation at 200° and retesting at −78°.

In contrast to the results for hydrogen–deuterium exchange, ethylene hydrogenation at −78° is severely poisoned by exposure of the catalyst to hydrogen at elevated temperatures (Table IV, run 1). On the other hand, hydrogen treatment at −78° did not significantly affect the catalyst activity (run 2).

Table V shows the effect of partial hydriding on the activity of calcium metal for hydrogen–deuterium exchange. This experiment was done to establish the extent to which calcium oxide might be contributing to the activity (see Discussion). The metal was much more active after hydriding than before.

Discussion

Before any interpretation can be given to the catalytic activities observed for calcium and barium hydrides, it is necessary to demonstrate that the activity is not due to calcium or barium oxide present in the samples as impurities. Two lines of evidence indicate that oxides are not responsible for the catalysis. The first is shown in Table V. Contamination of the powdered calcium metal with water during transfer in the dry-box would have resulted in the presence of oxide in the metal after evacuation at 300° (run 1). No more oxide is introduced by the subsequent hydriding at 300°, prior to run 2; however, the activity after hydriding is higher by an order of magnitude than that before hydriding. The presence of any oxide cannot be responsible for the high activity of the hydrided sample.

The second point arguing against oxide as the catalyst is the relative inactivity of the pure oxides. It is necessary to pump the oxides at 450–500° in order to achieve the same activity for hydrogen-deuterium exchange as the hydrides show after pumping at much lower temperatures. Even with the high-temperature pumping, the oxides are almost inactive for ethylene hydrogenation, by comparison with the hydrides. We conclude, then, that while the oxides can have some catalytic effect, they are not primarily responsible for the phenomena described in this and the preceding paper.

The question then arises whether the catalyst is the hydride, metal produced by pumping the hydride, or a mixture of metal and hydride. Stoichiometric hydride appears not to be the catalyst, since if it were, no preliminary activation at high temperature would be necessary (Table I). Similarly, free metal alone appears not to be the catalyst. If it were, the large activity increase obtained on partial hydriding of the metal (Table V) would not have been observed.

It is significant that both metal and metal hydride are present in the catalysts under conditions of highest activity. Some decomposition of hydride to metal and hydrogen occurs on pumping at elevated temperatures. From the data of Johnson, et al.,[2] the dissociation pressure of bulk calcium hydride at 300° may be calculated to be 3×10^{-5} mm.; small amounts of hydrogen can probably be removed at even higher pressures. The dissociation pressure of barium hydride is somewhat greater; Schumb, et al.,[3] report it to be 10^{-2} mm. at 350°. It is thus reasonable to expect the formation of some metal sites by high temperature evacuation. Under the conditions of evacuation used in these experiments, only a very small fraction of the bulk hydride decomposes to metal. This is demonstrated by the fact that a barium hydride sample pumped for two days at 300° picked up only a small amount of hydrogen (0.02 mole %) on re-exposure to hydrogen at 300°. This amount may, however, be very significant in terms of the surface of the catalyst.

The interpretation given to these results is that the catalytic effect occurs at an interface between free metal and metal hydride, or, otherwise expressed, at points where neighboring metal and

(2) W. C. Johnson, M. F. Stubbs, A. E. Sidwell and A. Pechukas, THIS JOURNAL, 61, 318 (1939).

(3) W. C. Schumb, E. F. Sewell and A. S. Eisenstein, ibid., 69, 2029 (1947).

hydride surface sites occur. These points may be called "dual sites." There will certainly be a range of adsorption energies among the dual sites, corresponding to the range of dissociation pressures experimentally found to exist near the stoichiometric composition.[2] Putting back hydrogen at, say, 300° will destroy the dual sites of highest energy (lowest dissociation pressure) by reconstituting hydride, but dual sites of lower energy may persist through this treatment.

The mechanism of the hydrogen–deuterium exchange reaction is assumed to involve the reversible formation of hydride on dual sites of low energy. The necessity for dual sites in order to achieve highest activity can be understood on this basis. In the formation of hydride from "technical" calcium and barium catalysts (in contrast to evaporated films; cf. Trapnell[4]), the chemisorption of hydrogen is probably associated with an activation energy. The activation energy is less when the newly-formed hydride ions simply extend a pre-existing hydride nucleus than when a new nucleus has to be formed. That is, the activation energy is less when the chemisorption occurs on the metal part of a dual site than when it occurs on a bare metal surface. It is interesting, in this connection, that both Soliman[5] and Kawana[6] have reported induction periods in the formation of calcium hydride from calcium and that Kawana finds the rate of growth of hydride nuclei to be proportional to the boundary area of the nuclei.
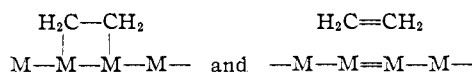
One complication exists in this interpretation. Hydride ion pre-existing in the catalyst does not participate in the hydrogen–deuterium exchange at −78° over barium hydride (Table II, ref. 1). If the low-temperature exchange involves the reversible formation of hydride, the hydride formed during the exchange must be different from the pre-existing hydride. This is consistent, of course, with the assumption made earlier that an intrinsic distribution of energy exists among the sites. The situation is closely analogous to that reported by Kummer and Emmett for iron catalysts[7] and by Voltz and Weller[8] for chromia catalysts; in both cases, hydrogen adsorbed at elevated temperatures did not participate in exchange reactions at low temperatures.

In contrast to hydrogen–deuterium exchange, which proceeds on dual sites of relatively low energy, ethylene hydrogenation requires higher energy sites, which can be destroyed by exposure to hydrogen at elevated temperatures (Table IV). This is consistent with general experience in catalysis that more severe conditions are required for olefin hydrogenation than for hydrogen–deuterium exchange. The failure of hydrogen at low temperature to poison ethylene hydrogenation (Table IV, run 2) demonstrates the existence of an activation energy for the reconstitution of hydride from dual sites of high energy.

The fact that the activity of the alkaline earth metal–metal hydride system is as high as it is for

ethylene hydrogenation and hydrogen activation raises some important questions for both the electronic and the geometric interpretations of catalysis. The activity of the transition metals has recently been explained in terms of "holes" in the d-band.[9,10] How is the activity of the alkaline earth metals to be understood in these terms? Theoretical work by Manning and Krutter[11] suggests that some overlap of s-, p-, and d-bands occurs in these metals. The overlap should be small, however, and should be smaller for barium than for calcium; this order is opposite to that of the catalytic activities.[1] Moreover, even cesium is reported to be moderately active for ethylene hydrogenation.[12] It seems doubtful, then, that the activity of these metals can be forced into a unitary theory of metal catalysis based only on d-band vacancies. This is not to deny the importance of this theory for the transition metals, but only to point out that other sources of catalytic activity can exist with other metals.

A comparable problem arises in considering the geometrical requirements for ethylene hydrogenation over hydride catalysts. Catalytic olefin hydrogenation is believed to usually involve two-point adsorption of the olefin on adjacent metal atoms or ions.[13] The metal–metal distance is much greater, however, for the alkaline earth metals and their hydrides than for the transition metals. For calcium and barium, the separations of nearest-neighbor atoms are 3.93 Å. and 4.34 Å., respectively; the corresponding ion distances in the hydrides are not well known, but they are probably about 3.7 Å. for calcium hydride and 4.3 Å. for barium hydride. If one assumes a carbon–carbon distance of 1.54 Å. for adsorbed ethylene and a metal–carbon distance equal to the sum of the metallic radius and 0.77 Å., two-point adsorption on adjacent calcium or barium atoms in the metal would require metal–carbon–carbon bond angles of 116 and 118°, respectively. (Substantially the same situation would prevail for the hydrides.) These values are appreciably larger than the expected tetrahedral value of 109°, suggesting that this structure is subject to considerable strain. A shift of the normal bond angle to these larger values would, however, be consistent with the assumption that resonance occurs between the normally-bonded and the "no-bond" structures

$$
\begin{array}{cc}
\text{H}_2\text{C}\!\!-\!\!\text{CH}_2 & \text{H}_2\text{C}\!\!=\!\!\text{CH}_2 \\
| \quad | & \\
\text{M}\!-\!\text{M}\!-\!\text{M}\!-\!\text{M}\!- & \text{and} \quad -\text{M}\!-\!\text{M}\!=\!\text{M}\!-\!\text{M}\!-
\end{array}
$$

considered as a variety of second-order hyperconjugation.

Two possibilities of single-point adsorption of ethylene should be considered. One of these, which may be written schematically as

$$\text{Ba}^{++}\text{H}^- + \text{H}_2\text{C} = \text{CH}_2 \longrightarrow \text{Ba}^{++}(\text{CH}_2\text{CH}_3)^- \quad (1)$$
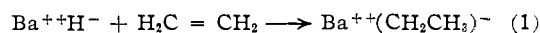
is an "associative" adsorption on a hydride site. It

(4) B. M. W. Trapnell, Proc. Roy. Soc. (London), **218A**, 566 (1953).

(5) A. Soliman, J. Appl. Chem., **1**, 98 (1951).

(6) Y. Kawana, J. Chem. Soc. Japan, **71**, 494 (1950).

(7) J. T. Kummer and P. H. Emmett, J. Phys. Chem., **56**, 258 (1952).

(8) S. E. Voltz and S. Weller. THIS JOURNAL, **75**, 5227 (1953).

(9) D. A. Dowden, J. Chem. Soc., 242 (1950).

(10) Disc. Faraday Soc., No. 8 (1950).

(11) M. F. Manning and H. M. Krutter, Phys. Rev., **51**, 761 (1937).

(12) D. G. Hill and G. B. Kistiakowsky, THIS JOURNAL, **52**, 892 (1930).

(13) R. H. Griffith, "Advances in Catalysis," Vol. I. Academic Press, Inc., New York, N. Y., 1948.

is equivalent to the formation of a barium alkyl, or a barium ion-carbanion pair. The second possibility involves "dissociative" adsorption on a barium atom and it may be schematically written as

$$Ba + CH_2 = CH_2 \longrightarrow (CH_2=CH)^- Ba^{++} H^- \quad (2)$$
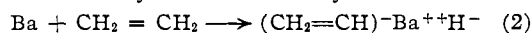
Reaction 1 can probably be ruled out, since it requires that exchange occur between hydrogen atoms in the ethylene and hydride ions in the catalyst, contrary to experiment (ref. 1). Reaction 2 does not imply such an exchange. Furthermore, since it

involves conversion of metal into a kind of hydride, it is likely to occur preferentially at the dual sites in the metal–hydride interface, as discussed above. In the absence of additional information, reaction 2 is favored as representing the manner in which ethylene is adsorbed.

The Catalytic Activity of Barium and Calcium Hydrides. I. An Exploratory Study

BY LEON WRIGHT AND SOL WELLER

A study has been made of the catalytic activity of barium and calcium hydrides. These hydrides are moderately active for ethylene hydrogenation, cyclohexane and isobutane dehydrogenation, pentene double bond isomerization, and hydrogen- and ethylene–deuterium exchange reactions. These catalysts show stable activity for the dehydrogenation of cyclohexane under elevated hydrogen pressure, and for the hydrogenation of ethylene at atmospheric pressure. Consideration of the types of reactions catalyzed indicates that the alkaline earth hydrides are typical hydrogenation–dehydrogenation catalysts, similar to transition metal catalysts such as nickel and platinum.

Introduction

The salt-like hydrides of barium and calcium have been little investigated from a catalytic viewpoint.

Pease and Stewart[1] have described the hydrogenation of ethylene over calcium hydride at 200°. The hydride appeared to be more active as a catalyst than metallic calcium; however, it was demonstrated that calcium hydride was relatively inactive toward ethylene in the absence of hydrogen.

Schmidt[2] stated that barium metal supported on quartz was moderately active for ethylene hydrogenation at 200°, but gave no experimental data.

In the present work the following reactions were found to be catalyzed by barium and calcium hydrides: (1) hydrogen–deuterium exchange; (2) ethylene hydrogenation and deuteration; (3) pentene double bond isomerization; (4) dehydrogenation of cyclohexene, cyclohexane and isobutane.

Experimental

Materials.—Calcium and barium hydrides were obtained from Metal Hydrides, Inc., as gray powder and lumps, respectively. They were obtained in 98–99% purity with oxygen and nitrogen said to be the chief impurities. Spectrographic analysis by the Houdry Laboratories indicated the absence of metals known to be hydrogenation catalysts, i.e., nickel, platinum, etc., and reported the following metals present in trace amounts: calcium, magnesium, strontium and manganese in the barium hydride; magnesium, manganese, sodium, strontium and iron in the calcium hydride. Surface area measurements by the BET method indicated that the surface areas of these materials were <1 m.²/gram.

Calcium hydride was also prepared from finely divided calcium metal of low "active metal" content supplied by the Ethyl Corporation.

Hydrogen was purified by passing over hot copper and then through dried silica–alumina (Houdry Type S-45) at −195°.

Deuterium of >99% purity was obtained from the Stuart Oxygen Company and used without further treatment.

A special blend of ethylene and hydrogen was obtained from the Matheson Company and used after drying by passage through anhydrous calcium sulfate at −78°.

Isobutene was obtained from the Phillips Petroleum Company (Research Grade, >99.5%) and was used after drying by passage through anhydrous calcium sulfate at 0°. Pentene-1, Phillips Technical Grade, 95%, was used as received.

Cyclohexene and cyclohexane were obtained from the Phillips Petroleum Company; after purification, infrared analysis indicated a purity of >99%.

Methylcyclopentene (the isomeric mixture) was prepared by the isomerization of cyclohexene over Houdry Type S-45 silica–alumina catalyst. Infrared analysis indicated that a product containing 97% methylcyclopentene was obtained by this procedure.

Apparatus and Procedure.—All static experiments were carried out by the use of high vacuum technique. Dynamic experiments were carried out with a procedure allowing evacuation of the catalysts during the pretreatment period. The general experimental procedure used was as follows: a measured amount of catalyst was evacuated under 10⁻⁵ mm. at 200 or 300° for a fixed period. The metered stream of hydrocarbon, and in some cases hydrogen or hydrogen and deuterium, was then passed over the catalyst at reaction temperature; after various on-stream periods, gas and/or liquid samples were taken for analysis by gas density, mass spectrometer, infrared spectrometer or silica gel adsorption.

High pressure experiments were carried out in an isothermal reactor previously described.[3]

Results and Discussion

Hydrogen–Deuterium Exchange.—In view of the results reported by Pease and Stewart it was anticipated that the alkaline earth hydrides would be able to activate molecular hydrogen. If this were the case, gaseous deuterium might also exchange with bulk hydride at elevated temperatures. It was found that no exchange occurred at 100° over calcium hydride, even after 17 hours. However, when the same sample of calcium hydride was pumped overnight at 200°, and then charged with an atmosphere of deuterium at 200°, considerable exchange occurred after one hour and appreciably more after six hours. From the data in Table I one can make the following observations: (1) only a fraction of the hydrogen in the calcium hydride

(1) R. N. Pease and L. Stewart, THIS JOURNAL, **47**, 2763 (1925).
(2) O. Schmidt, Chem. Revs., **12**, 363 (1933).

(3) H. Heinemann, G. A. Mills, J. B. Hattman and F. W. Kirsch, Ind. Eng. Chem., **45**, 130 (1953).