[CONTRIBUTION FROM GEORGE WASHINGTON UNIVERSITY AND THE U. S. DEPARTMENT OF AGRICULTURE, BUREAU OF CHEMISTRY AND SOILS]

The Hydrogenation of Ethylene by Iron Synthetic Ammonia Catalysts[1]

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The hydrogenation of ethylene in the presence of various metallic catalysts, notably nickel, copper, and some of the platinum metals, has been the subject of many investigations in recent years. Iron has been studied in this reaction only to a limited extent.[4] The present investigation was undertaken in order to ascertain the activity toward the ethylene hydrogenation of typical iron synthetic ammonia catalysts. It seemed probable that some very fruitful correlations would become evident between the activities of these iron catalysts for ethylene hydrogenation and their surface areas,[5] hydrogen adsorption[6] capacities, surface promoter concentrations,[7] and other properties that already have been studied intensively in the Fertilizer Division of the Bureau of Chemistry and Soils.

Experimental

The apparatus was the well-known static type, designed to serve both for adsorption measurements and rate of reaction measurements at constant volume. The essential parts consisted of a calibrated 125-cc. gas buret, a Toepler pump, a mercury manometer, and the catalyst bulb. These were sealed together through 2-mm. capillary tubing and appropriate stopcocks. The Toepler pump served the dual purpose of a mixing chamber for preparing reaction mixtures and of a pump for desorbing gas from the catalyst in taking desorption points after an adsorption run. An exit tube from the catalyst bulb was provided for the purpose of permitting reduction of the catalyst both initially and between runs. A U-trap was placed in the tubing leading to the catalyst bulb for freezing out traces of volatile matter which might be picked up by hydrogen from stopcock grease during reduction of the catalyst. A high vacuum system consisting of a McLeod gage and a single stage mercury diffusion pump backed by a Hy-Vac pump was sealed to a manifold connected with the catalyst bulb. Evacuation of the catalyst to a pressure of 5×10^{-5} mm. could be accomplished in about thirty minutes with this system.

Ethylene of anesthetic grade was repurified by condensing it in a liquid air trap, pumping it free of non-condensable gases, distilling it twice and rejecting all but the middle third of each distillation. Ethane was similarly repurified for adsorption measurements, its original purity being about 97%.

Tank nitrogen and commercial electrolytic tank hydrogen were purified in the usual manner with hot C. P. copper and dried with Dehydrite and phosphorus pentoxide.

Helium for "dead space" determinations and for use as a thermal conductor in cooling the catalyst to the desired temperature was freed of a trace of air by passage through a trap of thoroughly baked-out and degassed activated charcoal immersed in a liquid air trap.

The iron catalysts were prepared in 1926 at the Fixed Nitrogen Research Laboratory by the method of Larson and Richardson.[8] Catalyst 973 is an unpromoted iron catalyst containing 0.15% of aluminum oxide as an impurity; 931 is a doubly promoted iron catalyst containing 1.59% potassium oxide and 1.3% aluminum oxide as the promoters.

Ten cc. (17.9 g.)[9] of the pure iron catalyst in a 50-cc. bulb was reduced in a stream of 200 cc. of hydrogen per minute for sixty hours at 425–450° and was sintered for eight hours in this same flow of hydrogen at 525° to bring the surface to reproducible activity. This sample was used for nitrogen adsorption runs at −183°, for preliminary adsorption runs on ethylene, and for all reaction rate measurements. For the more detailed adsorption measurements on ethylene and hydrogen, 25 cc. (44.3 g.) of this catalyst was used in a catalyst bulb of the same volume. This larger sample was a composite of the smaller 17.9-g. sample with a 26.4-g. sample of 973 that had been freshly reduced. The 44.3-g. sample was considerably more sintered than the 17.9-g. sample. The preliminary adsorption measurements on the smaller sample of catalyst were made on ethylene between −79 and 150° at 50° intervals to ascertain the quantities of the gas adsorbed under the temperature–pressure conditions of the reaction rate measurements. The isotherms on this small sample are not shown in the present paper, however, since their general character was the same as that of the isotherms on the larger sample.

The promoted iron catalyst, 931, was reduced for eighty hours at 450–500° in 200 cc. of hydrogen per minute. For the reaction rate measurements 3 cc. (5 g.) was used in a 50-cc. catalyst bulb. These small quantities of both promoted and unpromoted catalysts were supported on a porous Pyrex disk about half-way up in the catalyst bulb in order to minimize diffusion effects.

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[1] From the thesis of Rowland C. Hansford presented to the Faculty of the George Washington University in part satisfaction of the requirement for the degree of Master of Arts, June, 1937.

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[4] Sabatier-Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Co., New York, N. Y., 1923, p. 506; Pease and Stewart, THIS JOURNAL, **49**, 2783 (1927); Klar, *Z. physik. Chem.*, **166A**, 273 (1933); Klar, *ibid.*, **27B**, 319 (1934); Klar, *ibid.*, **174A**, 1 (1935); Klar, *Z. Elektrochem.*, **43**, 379 (1937); Insley, *J. Phys. Chem.*, **39**, 623 (1935).

[5] (a) Brunauer and Emmett, THIS JOURNAL, **57**, 1750 (1935); (b) Emmett and Brunauer, *ibid.*, **59**, 1553 (1937).

[6] Emmett and Harkness, *ibid.*, **57**, 1631 (1935).

[7] Emmett and Brunauer, *ibid.*, **59**, 310 (1937).

[8] Larson and Richardson, *Ind. Eng. Chem.*, **17**, 971 (1925).

[9] The weights of catalyst given throughout the present paper are for the weights of the *reduced* iron rather than of the original oxide.

Between runs the following uniform procedure of reduction and degassing was adopted to maintain a reproducible catalyst surface. The catalyst was reduced in a stream of purified hydrogen flowing at the rate of 200 cc. per minute for one hour at 450°. It was then degassed at this temperature for two hours and for an additional hour while the furnace cooled to 100°. Both in the adsorption runs and with reaction rate runs thermal equilibrium between the catalyst and the surrounding constant temperature bath was ensured by admitting 100–200 mm. of purified helium to the catalyst after the above reduction and degassing treatment. After twenty to thirty minutes the helium was pumped out with the mercury diffusion pump for about twenty minutes, after which the catalyst was ready for the adsorption or reaction rate measurements.

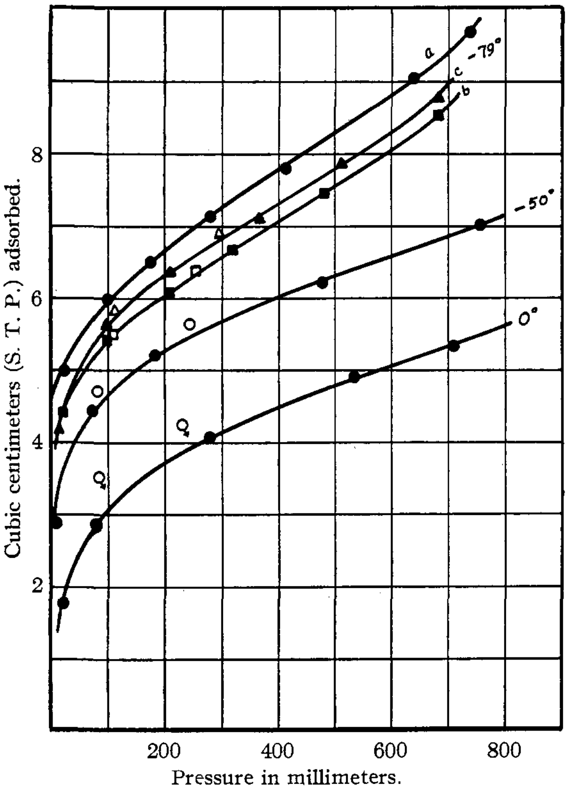

Fig. 1.—Adsorption of ethylene on 44.3 g. of catalyst 973: Curve (a), catalyst reduced and degassed at 450° before run; curve (b), catalyst degassed for one hour at 0° immediately after (a); curve (c), catalyst degassed for one hour at 125° immediately after (b).

Corrections for deviations from the perfect gas laws were applied to the nitrogen and carbon dioxide in the free space.[10] For ethylene and ethane corrections were not applied because no satisfactory data for the low temperature employed could be found in the literature. All manometer readings were corrected to the density of mercury at 0°.

Results

Surface Measurements.—The total surface area of each catalyst used in the reaction rate runs was determined by the method of Emmett and Brunauer[5] with purified nitrogen. The −183° adsorption isotherm on the pure iron catalyst (17.9 g.) indicated a surface area of 25 square meters, and that for the promoted catalyst (5 g.) 21 square meters. These values are in approximate agreement with 18 sq. meters and 20.1 sq. meters that one would calculate from the results reported by the above authors for catalyst 973 and for catalyst 931, respectively. The accumulation of promoter in the surface of the promoted catalyst previously reported by Emmett and Brunauer[7] was confirmed by determining carbon dioxide adsorption isotherms at −79°. These isotherms indicated that about 75% of the surface of the promoted catalyst was made up of promoter. Accordingly, the surface of iron in catalyst 931 was probably about one-fifth that of the pure iron catalyst 973, even though the total surfaces (iron atoms plus promoter molecules) of the samples of the two catalysts were about equal.

Adsorption of Ethylene on Pure Iron Catalyst 973.—Adsorption isotherms for ethylene on the 44-g. sample of catalyst 973 are shown in Fig. 1. The adsorption at −79° (curve a) was instantaneous throughout the run, no pressure drifts being observed at any adsorption point. At −50° a very slight drift was observed at about 175 mm., a pressure decrease equivalent to the adsorption of 0.03 cc. of the ethylene occurring in the ten minutes required for equilibrium to be established; in the same run at 480 mm. the total drift in ten minutes was equivalent to 0.05 cc. Desorption points at −50° were taken as indicated, a desorption drift equivalent to 0.03 cc. of ethylene occurring in five minutes at 80 mm. Somewhat larger drifts were observed at 0°, a total of 0.39 cc. of ethylene constituting the slow adsorption that occurred during the hour required for the adsorption run.

It should be mentioned that the adsorption made on the smaller sample of catalyst in a larger free space showed no perceptible drifts even at temperatures ranging up to 150°.

From isosteric pressures on the −79 and −50° isotherms for catalyst 973 corresponding to the adsorption of 5.0, 5.4, and 6.0 cc. of ethylene, heats of adsorption of 5200, 4300, and 4250 calories per mole were calculated; from the −50 and 0°

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[10] The percentage deviations used were as follows: nitrogen at −183°, 2.87%; carbon dioxide at −79°, 2.09%; carbon dioxide at room temperature, 0.58% (see ref. 5b).

isotherms at adsorptions of 3.6, 4.0, and 4.4 cc. the calculated heats of adsorption were 4725, 4200, and 4000 calories per mole, respectively.

No detailed adsorption measurements on ethylene were made on the promoted iron catalyst, but an estimate was made from the observed initial pressure in the reaction rate measurements as compared to the initial pressure calculated on the basis of the amount of gas admitted to the catalyst and the volume of free space in the system. At 200 mm. the adsorption of ethylene on 5 g. of this catalyst at −79° was approximately the same as that found on 17.9 g. of the pure iron catalyst, namely, about 4 cc.

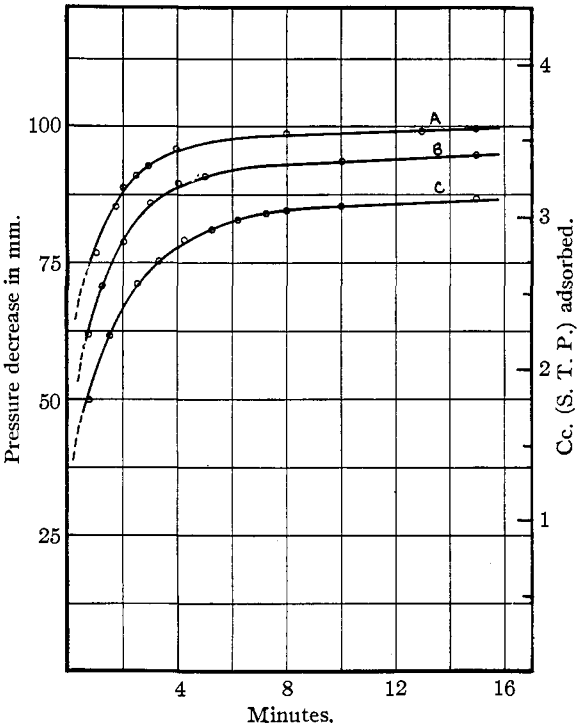

Fig. 2.—Rate of hydrogen adsorption at −79° on 44.3 g. of catalyst 973: curve (A), at 600 mm. initial pressure; curve (B), at 396 mm. initial pressure; curve (C), at 204 mm. initial pressure. The hydrogen used in these experiments was "unpoisoned."

Adsorption of Hydrogen.—The rate of hydrogen adsorption on 44.3 g. of pure iron catalyst at −79° was measured as a function of pressure. The results are shown in Fig. 2. The rate of hydrogen adsorption was also measured at 200 mm. initial pressure on the smaller samples of both promoted and unpromoted catalysts used in the reaction rate measurements in order to compare this with the reaction rate. These curves are shown along with those of the reaction rates in Fig. 3 and Fig. 4.

Adsorption of Ethane.—The adsorption isotherm of ethane was determined at −79° on the 17.9-g. sample of pure iron; at 200 mm. the volume adsorbed was found to be 4.6 cc. as compared to 4.2 cc. of ethylene at the same temperature and pressure.

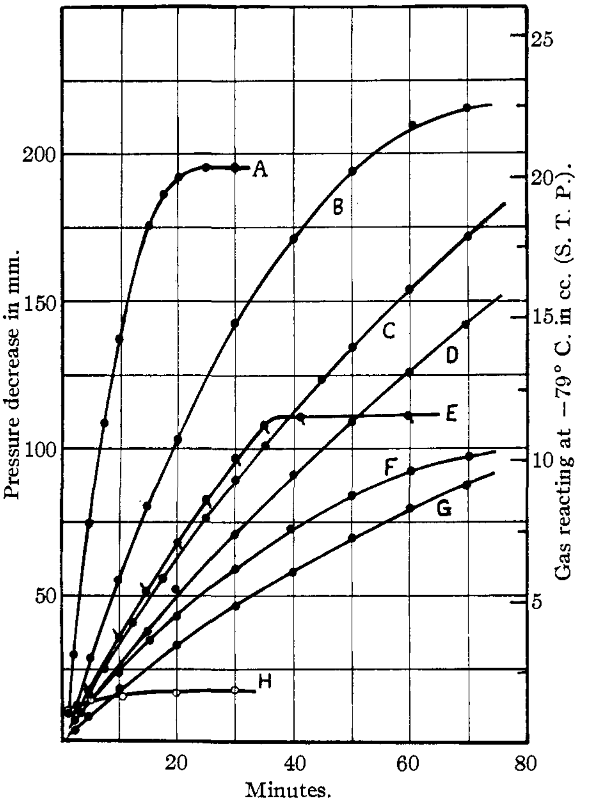

Fig. 3.—Reaction rates on 17.9 g. of catalyst 973:

Curve	Temp., °C.	Calculated[a] total initial pressure, mm.	Ratio $H_2 : C_2H_4$
A*	−50	455	1:1
B	−79	475	1:1
C*	−79	445	1:1
D	−89	485	1:1
E*	−79	465	3:1
F*	−79	800	1:6
G*	−79	450	1:3

H* Rate of hydrogen adsorption at 206 mm. initial pressure at −79°

* Runs marked with asterisk were made with hydrogen containing a trace of an undetermined poison which was not removed by hot copper.

[a] Total initial pressures were calculated from the volume of reaction mixture admitted to the catalyst bulb as compared to the same volume of helium.

Reaction Rate Measurements.—Reaction rate curves for various mixtures of hydrogen and ethylene at −89, −79 and −50° on pure iron are shown in Fig. 3. The rate curves obtained at higher temperatures (to 150° at 50° intervals) have been omitted because the reaction velocity was too great to obtain an accurate extrapolation of the curve at zero time.

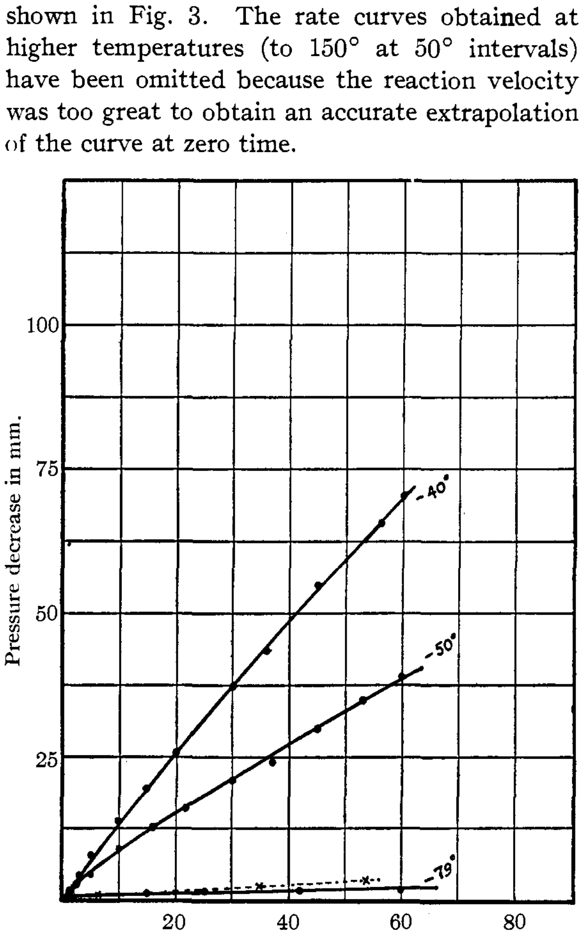

Fig. 4.—Rate of reaction on 5 g. of catalyst 931: 450 mm. total initial pressure. (Broken curve is the rate of hydrogen adsorption at 200 mm. initial pressure at −79°.)

From the reaction velocity during the first thirty minutes at −89 and −79° (curves B and D in Fig. 3) the average energy of activation for reaction on pure iron is found to be 5100 cal. corresponding to an average temperature coefficient of 2.06 per 10°.

In Fig. 5 is shown a plot of reaction velocities against calculated partial pressures of hydrogen in reaction mixtures of four different compositions. It appears that the reaction rate is proportional to a power of the hydrogen concentration intermediate between 0.5 and 1.0. Furthermore, it is nearly independent of the ethylene concentration, for a tenfold increase in the partial pressure of the latter produces at most a 30% increase in the reaction velocity (run A compared to run B, Fig. 5, at a hydrogen partial pressure of 90 mm.).

The reaction rate curves of Fig. 3, for the "poisoned" runs, require a word of explanation. The hydrogen used in these measurements contained a slight amount of an undetermined poison which in some way was getting through the purification system. This was not discovered until a fresh tank of hydrogen was put into service. However, since care has been used in taking cognizance of this fact in all comparisons made in the present paper it is believed that no serious errors in our conclusions have been introduced as a result of this poisoning. "Unpoisoned" hydrogen was used in the temperature coefficient runs on catalyst 973 and in the reaction rate runs on the promoted catalyst.

At −79° the reaction rate on the promoted iron catalyst was extremely slow, being approximately the same as the rate of hydrogen adsorption. Rate curves are shown in Fig. 4. The energy of activation for the reaction is found to be 5300 calories if calculated from the −50 and −40° rate

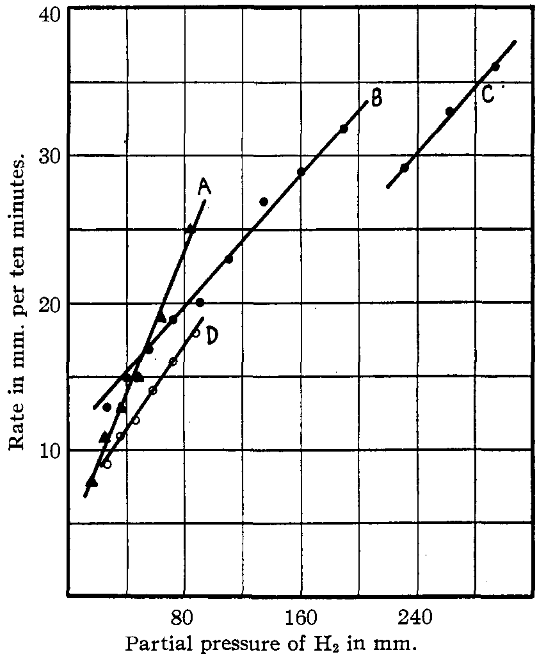

Fig. 5.—Reaction rate at −79° on catalyst 973 *vs.* partial pressure of H_2:

			Initial P_{H_2}, mm.	Initial $P_{C_2H_4}$, mm.
Curve (A)	Ratio H_2:C_2H_4	1:1	115	585
Curve (B)	Ratio H_2:C_2H_4	1:1	215	180
Curve (C)	Ratio H_2:C_2H_4	3:1	335	80
Curve (D)	Ratio H_2:C_2H_4	1:3	110	280

Initial partial pressures for this figure refer to the gas pressures *after* all instantaneous adsorption has occurred.

curves, and 7700 if calculated from the −40 to −79° curve. These values are approximately the same as found on pure iron.

Discussion

Klar[4] recently suggested that ethylene might be hydrogenated catalytically to ethane over iron without undergoing activated adsorption. The present experiments seem to constitute a confirmation of his hypothesis, for the hydrogenation reaction proceeds readily over the iron catalyst between −50 and −89°, a temperature range in which little if any activated adsorption of ethylene appears to be occurring. The ethylene adsorption on 17.9 g. of pure iron was instantaneous, readily reversible, and continually decreasing in amount with rise of temperature over the entire range from −79 to 150°, yielding no evidence of any activated adsorption. On the larger 44-g. sample on which the isotherms of Fig. 1 were obtained, the adsorption of ethylene at −79° had all of the characteristics of physical adsorption. The equilibration was instantaneous. At −50° a slight drift was noted and the desorption points were a little above the adsorption points. This drift was somewhat greater at 0° than at −50°. However, even at 0° it was certainly not marked, and the total adsorption was decidedly smaller than at either −50 or −79°. The heat of adsorption of ethylene as calculated from adsorption isosteres was about 4500 cal. compared to a heat of liquefaction of 3500 cal. The attempt to identify the adsorption occurring at −79° by pumping off the physical adsorption at a higher temperature and then making a new adsorption run is illustrated in Fig. 1, curves b and c. Pumping off the adsorbed ethylene for one hour at 125°, (curve c) is more effective than pumping it off at 0° (curve b). However, about 5% of the ethylene adsorbed at −79° was apparently not removed by one hour of pumping at even 125°. Whether this 5% is physical or activated adsorption cannot be decided with certainty from these experiments. Nevertheless, the combining evidence is, we believe, a very strong indication that no appreciable amount of activated adsorption of ethylene was occurring in the temperature range −50 to −79° at a sufficiently rapid rate to play a major part in the hydrogenation. It is realized, however, that a final answer on this point must await additional experimental work, for nothing in the present paper precludes the possibility that a rapid activated adsorption of ethylene on a very small fraction of the surface might be accounting for the catalysis.

It is interesting to note that at partial pressures of ethylene ranging from 200 to 500 mm. the catalyst is probably covered at −79° by between one and two layers of physically adsorbed ethylene if the conclusions previously reached[7] are correct relative to the point on a low temperature absorption isotherm corresponding to a monomolecular adsorbed layer. It is not so surprising, therefore, that the rate of reaction of ethylene and hydrogen appears to be practically independent of the partial pressure of ethylene, as pointed out above in connection with the curves of Fig. 5.

Experiments of Emmett and Harkness[6] have shown that on iron synthetic ammonia catalysts two types of activated adsorption of hydrogen occur. One type, called type A, occurs at a good rate above −100°, the energy of activation of the adsorption being about 10,000 cal. per mole. The other type, called type B, is negligibly slow below 0°, and occurs at a convenient rate only at or above 100°. There can be little doubt, therefore, that type A and not type B activated adsorption of hydrogen is involved in the hydrogenation of ethylene.

The rate of type A adsorption is sufficiently fast to account for the highest rate of hydrogenation observed in the present experiments. As a matter of fact the rate of hydrogenation appears to be intermediate between the initial and final rates of type A adsorption of hydrogen. The observed 5300 cal. energy of activation of the hydrogenation may easily be the energy of activation of the first part of the hydrogen adsorbed since the energy of activation ordinarily increases as the volume adsorbed increases and the 10,000 cal. value, found by Emmett and Harkness, for the energy of activation of type A hydrogen adsorption on catalyst 931 was calculated for fairly large adsorptions.

The mechanism by which a few per cent. of potassium oxide and aluminum oxide promoters enhance the activity of iron catalysts for ammonia synthesis is not well understood. It seems certain, however, that the action of the combined potassium oxide–aluminum oxide promoter on the ammonia synthesis does not arise entirely from the maintenance of a large surface area. Furthermore, it is now known that the promoter content of catalyst 931 covers 50 to 75% of the catalyst surface. Accordingly, if in the hydrogenation of ethylene this promoter combination has no specific effect one would expect that per unit total surface area the promoted catalyst would be at least 50 to 75% less active than the pure iron catalyst. This seems to be the case. Five grams of catalyst 931 was only about 1/60 as active at −79° as 17.9 g. of pure iron. The total surface area of the 5 g. of 931 is about the same as that of the 17.9 g. of pure iron. At −50° the rate on the 5 g. of catalyst 931 is about 1/15 of that on 17.9 g. of catalyst 973 in spite of the fact that the run on the latter catalyst was made with hydrogen containing some unidentified poison. The inhibitive effect of the promoter over the −50 to −79° range seems, therefore, to be definite. Its exact magnitude cannot be stated with certainty, however, until additional experiments have been carried out.

Throughout the present work it was noted that the total pressure decrease during an experiment corresponded invariably to that expected for the hydrogenation of ethylene to form ethane. There seemed to be little doubt, therefore, that the hydrogenation rather than the polymerization of ethylene was the principal reaction occurring. Nevertheless, in one reaction rate experiment on a 50:50 hydrogen: ethylene mixture the gas reremaining at the end of the run was freed of 2.6% ethylene which it contained and then passed into a trap at −100°. Complete condensation occurred, indicating that the product was ethane and that no free hydrogen remained. Accordingly, no appreciable amount of ethylene polymerization was occurring in the present experiments.

Summary

The hydrogenation of ethylene in the presence of pure and promoted iron synthetic ammonia catalysts has been studied between −40 and −89°. The reaction on the promoted iron catalyst in this temperature region was considerably slower than on unpromoted iron. The promoter of the synthetic ammonia catalyst appears to inhibit the hydrogenation of ethylene.

Evidence has been presented which indicates that the activated adsorption of hydrogen alone is involved in the reaction, ethylene being physically adsorbed. The lower temperature type of activated hydrogen adsorption plays the dominant part in the reaction.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Surface Electrification Due to the Recession of Aqueous Solutions from Hydrophobic Surfaces

BY IRVING LANGMUIR

Porter and Wyman[1] have shown that calcium stearate multilayers of X-type deposited on a metallic plate give contact potentials of about 70 mv. per layer. Thus with a film of 100 layers there is a potential difference of about 7 v. in the air between a point just above the stearate layer and another point in the air close to the bare metal surface. This potential in the air, which Porter and Wyman have measured, suggests that there is an internal polarization in the film.

If the plate bearing the film is immersed in water, the external field is short circuited by the water because of its relatively high conductivity and thus a current flows through the water until surface charges have been delivered to the film and the underlying metal which are sufficient to compensate for the original polarization.

Since the plate after being withdrawn from the water possesses the same contact potential as before dipping, it must follow that the act of withdrawal restores the original electric condition of the surface.

A contact potential such as that observed by Porter and Wyman may be due to one or more of the three following factors:

1. **Internal Dipoles.**—If the film is built up of layers of polar molecules all oriented in one direction, there should be a definite number of fixed dipoles per unit volume. Let m be the dipole moment per unit volume. If t is the thickness of the film, and D is the dielectric constant, the effect of the dipoles is to cause an apparent contact potential V equal to

$$V = (4\pi/D) \int m\mathrm{d}t \qquad (1)$$

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[1] E. F. Porter and J. Wyman, Jr., THIS JOURNAL, **59**, 2746 (1937).