[Contribution from the Department of Chemical Engineering, the Johns Hopkins University]

The Hydrogenation of Ethylene, Propylene and 2-Butene on Iron Catalysts

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The hydrogenation of ethylene, propylene and butylene on nickel catalysts has been extensively studied.[1] Very little work has been reported, however, on the hydrogenation of these gases over active iron catalysts. Hansford and Emmett[2] showed that the iron synthetic ammonia catalysts were capable of hydrogenating ethylene at an appreciable rate at as low as −100°. Furthermore, they obtained indications that the same promoter that enhances the activities of iron for ammonia synthesis actually decreases activity for ethylene hydrogenation. In the present paper are reported measurements on the kinetics, temperature coefficient, and influence of promoter on the hydrogenation of ethylene, propylene, and 2-butene over six different catalysts.

Experimental

The apparatus for making measurements of reaction rate was a constant volume type having a glass turbine rotated by magnets for eliminating diffusion effects in the gas phase. It was the type used by Beeck.[3] The details of the reaction rate vessel are shown in Fig. 1. The auxiliary apparatus for purifying and mixing the reactants is in Fig. 2.

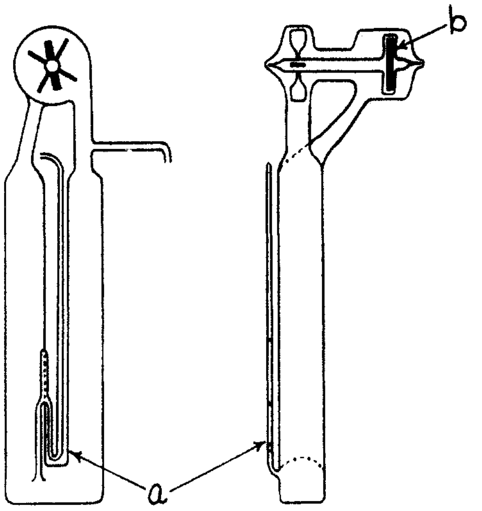

Fig. 1.—Reaction rate vessel: a, side tube for reducing catalyst; b, iron bar turned by magnets for driving glass turbine.

During a measurement of reaction rate the catalyst lay on the flat bottom of the reaction vessel. However, for reduction between runs the catalyst was moved by means of a small magnet to a U-tube on the side of the reaction vessel. The reduction was more effective with the catalyst in the U-tube than with it on the bottom of the reactor because of the greater rapidity with which traces of water vapor formed during reduction were swept out of the catalyst.

Conditions of constant temperature during a rate measurement were maintained as follows: all but the turbine of the reaction vessel was immersed in a Dewar flask. The bath was stirred by an air stream from a tube inserted in the bath fluid. The turbine was cooled to bath temperature by wrapping it with asbestos cloth and pumping the bath fluid to the top of the turbine by an air lift and allowing it to flow back over the asbestos to the Dewar. The bath fluid was maintained at the desired temperature ±0.1° by the addition of dry-ice at regular intervals.

The following uniform treatment of catalyst between runs was adopted. The catalyst was placed in the side tube and reduced for one hour (including a heating-up period of fifteen minutes) at 440 ± 10° in a stream of hydrogen flowing at a rate of 400 ± 20 cc./min. and passing first through U-tube B immersed in dry-ice. Next, the catalyst was evacuated for one hour at 440° to about 10^{-4} mm. using a mercury diffusion pump backed by a Nelson oil pump. After cooling under vacuum, the catalyst was transferred magnetically from the side tube to the base of the reaction vessel.

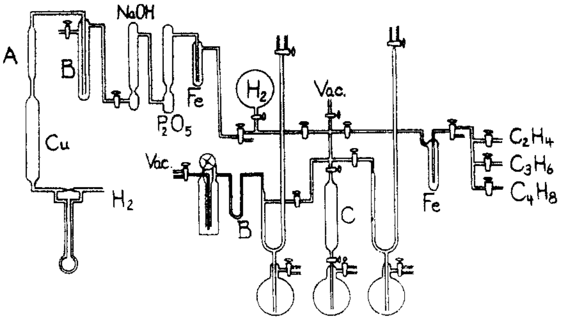

Fig. 2.—Reaction rate apparatus: A, platinized asbestos; B, dry-ice trap; C, mixing bulb for reactants.

Hydrogen for this reduction was obtained by passing commercial tank hydrogen through finely divided copper at 350° to remove oxygen, and then through platinized asbestos at 315° to remove any traces of oxygen that escaped the action of the copper. A trap immersed in dry-ice was followed by a phosphorus pentoxide drying tube to remove water vapor. Sodium hydroxide pellets were used to remove any traces of hydrogen chloride coming from the platinized asbestos as well as any carbon dioxide that might be present as an impurity. Hydrogen used for the reaction with olefins was further purified by being passed over iron (15 cc. of catalyst prepared by reducing iron oxide 973) kept at −195° and used to catch any final impurity that might poison the iron catalyst. The pure hydrogen was stored in a twelve-liter flask at a pressure greater than one atmosphere.

The olefins were obtained from the Ohio Chemicals Company. The ethylene was of anesthetic grade, 99.5% pure; the propylene, 99.5% pure; and the butylene, 85.8% pure. Each of these was further purified by fractional distillation in a vacuum-jacketed glass column having a wire spiral to increase the vapor-liquid contact area. The purity of the product was tested by measurement of vapor pressure. In this way the butylene was identified as 2-butene. The gases so purified were stored in glass flasks at slightly greater than atmospheric pressure.

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(1) (a) Sabatier and Senderens, *Compt. rend.*, **130**, 1761–1764 (1900). (b) Pease and Stewart, This Journal, **49**, 2783 (1927). (c) Klar, *Z. physik. Chem.*, **166A**, 273–284 (1933). (d) Klar, *ibid.*, **27B**, 319–320 (1934). (e) Klar, *ibid.*, **174A**, 1–14 (1935). (f) Insley, *J. Phys. Chem.*, **39**, 623–636 (1935).

(2) Hansford and Emmett, This Journal, **60**, 1185–1190 (1938).

(3) Beeck, Wheeler and Smith, *Phys. Rev.*, **55**, 601–602 (1939); also *Proc. Roy. Soc.* (London), **A177**, 62–90 (1940) Abst.

Between the storage flasks for the olefins and the mixing chamber for the reactants was placed 15 cc. of iron catalyst 973 to remove traces of impurities. For ethylene, this iron was immersed in a bath at −80°; for propylene, at −40°; and for butylene, at room temperature. After the iron clean-up catalyst had been used for about 500 cc. of olefin reactant, it was reduced at 450° for one hour at 800 cc./min. flow of hydrogen.

The type of apparatus used for adsorption measurements has already been described.[4] Before each adsorption experiment the sample of iron was reduced at 440 ± 10° for one hour at a hydrogen flow rate of 400 cc./min. This was followed by evacuating the catalyst at the same temperature for another hour. During reduction of the catalyst sample, the U-tube in the gas stream before the catalyst was immersed in a dry-ice-bath to condense mercury vapor or volatile matter from stopcock grease. An exit tube was provided on the catalyst bulb for use in reduction of the sample. This was opened prior to each reduction and sealed afterward.

Helium, purified by passing the gas at −195° through carefully degassed charcoal, was used for assuring temperature equilibration of the sample before adsorption measurements and for measuring the volume of the "dead space" in the sample bulb. The hydrogen for reducing the sample was purified as described above. Nitrogen for surface area measurements was passed through the purifying train normally used for hydrogen. The olefins used for adsorption were purified in the same manner as for the reaction experiments.

The catalyst samples for the reaction rate experiments were transferred, without exposure to air, from the large samples used for adsorption measurements. This was accomplished by means of small glass transfer tubes and a magnet.

With one exception the iron catalysts used in this investigation were prepared at the Fixed Nitrogen Research Laboratory by the method of Larson and Richardson[5]; they are designated by the numbers originally assigned to them. The exception was a catalyst prepared by reduction of ferric oxide from ignition of precipitated iron hydroxide.[1f] A list of all the catalysts with their treatment during preparation follows

(a) **973.**—37.6 g. of iron was prepared by reducing 14–28 mesh fused iron oxide for fifty-nine hours at 400–440° and eight hours at 515–532° in a hydrogen stream of 350–450 cc./min. This catalyst contained 0.15% alumina as an impurity.

(b) **983.**—19.8 g. of iron was prepared by reducing 14–28 mesh iron oxide for 75 hours at 450–486° in a hydrogen stream flowing at 370–450 cc./min. This ammonia catalyst contained 1.29% potassium oxide and 2.75 per cent. aluminum oxide as promoters.

(c) **652.**—0.5 g. of iron was prepared by reducing 28-mesh fused and promoted iron oxide for sixty hours at 390–550° and at a hydrogen flow rate of 430–490 cc./min. This catalyst contained 0.44% potassium oxide and 1.84% aluminum oxide.

(d) Iron from **Precipitated Fe_2O_3.**—200 g. of $Fe(NO_3)_3 \cdot 9H_2O$ was dissolved in four liters of distilled water and a slight excess of ammonia added. The precipitate was washed by decantation until neutral to litmus. The precipitate after filtering was dried for sixteen hours at 100°. The reduction was for twenty-four hours at 360–405° with a hydrogen flow rate of 470–580 cc./min.

(e) **954.**—2.57 g. of iron was obtained by the reduction of a fused promoted iron oxide. A hydrogen flow rate of 390–430 cc./min. and temperatures from 440 to 493° were used. This catalyst contained 10.2% aluminum oxide.

(f) **931.**—1.55 g. of iron was obtained by reduction of fused and promoted iron oxide for eighty-five hours at 469–520° and a hydrogen flow rate of 390–410 cc./min. This catalyst contained 1.59% potassium oxide and 1.3% aluminum oxide.

Results

Surface Measurements.—It is desirable to compare the activities of catalysts on the basis of unit surface area. In this investigation areas were measured using the low temperature van der Waals adsorption of nitrogen.[6] The surface areas of all catalysts used are listed in Table I.

TABLE I

Catalyst	973	983	652	Reduced from Fe_2O_3	954	931
Area (m.²/g.)	0.59	12.4	13.7	1.06	11.9	6.5

Some of these surface areas can be compared with previous work. Hansford and Emmett[2] obtained 1.40 m.²/g. for a previous sample of catalyst 973 reduced at 425–450° and sintered at 525°. Emmett and Brunauer[6] found 0.52 m.²/g. for catalyst 973 when it was reduced at 500° and 1.30 m.²/g. when reduced at 400°. Catalysts 954 and 931 were found[6] to have surface areas of 10.4 and 4.04 m.²/g., respectively.

Small amounts of aluminum oxide and potassium oxide in an iron synthetic ammonia catalyst may cover a large fraction of the total surface,[4b] as can be shown by measuring the relative amounts of chemisorbed and physically adsorbed carbon monoxide at −195°. Similar carbon monoxide adsorption isotherms were made on the promoted catalysts in the present investigation. The results are summarized in Table II.

TABLE II

Catalyst	Fraction of surface that is iron
983	0.46
652	.46
954	.69
931	.50[2]

Adsorption of Ethylene, Propylene and 2-Butene on Catalyst 973.—A knowledge of the fraction of the catalyst surface that is covered by adsorbed reactants is useful in a study of reaction kinetics. Adsorption isotherms can give such information.[6]

To determine the extent to which ethylene, propylene and butylene cover the catalyst surface under various conditions, physical adsorption isotherms of these gases were made.

Ethylene adsorptions were made at temperatures of −81, 0, 50 and 100°. Only for the isotherm at −81° was the adsorption instantaneous and reversible. The point V_m in Fig. 3 gives the volume of ethylene required to form a monolayer on the surface at −81°. This was calculated using the equation of Brunauer, Emmett and Teller[7] for low temperature van der Waals type adsorption.

Propylene adsorption (Fig. 4) at −40° was

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(4) (a) Emmett and Brunauer, THIS JOURNAL, **55**, 1783-1789 (1933); (b) Emmett and Brunauer, *ibid.*, **59**, 310-315 (1937); (c) Emmett and Harkness, *ibid.*, **57**, 1631-1635 (1935).

(5) Larson and Richardson, *Ind. Eng. Chem.*, **17**, 971 (1925).

(6) Emmett and Brunauer, THIS JOURNAL, **59**, 1553-1564 (1937).

(7) Brunauer, Emmett and Teller, *ibid.*, **60**, 309-319 (1938).

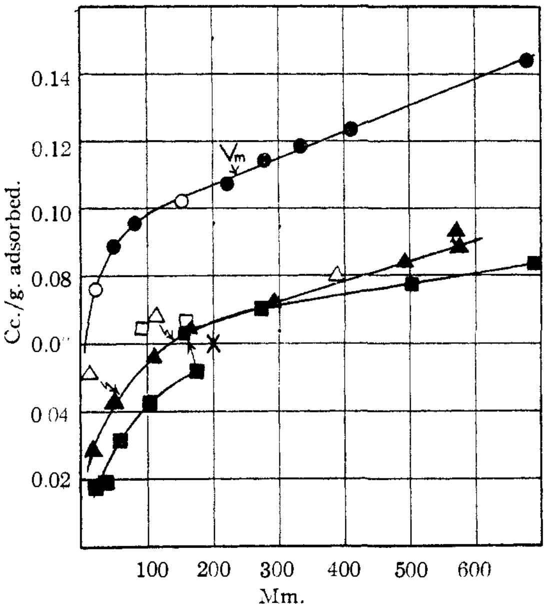

Fig. 3.—Adsorption of ethylene on catalyst 973: ●, at −81°; ▲, at 0°; ■, at 50°; ×, at 100°; O, △, □, desorption points.

likewise instantaneous and reversible. The adsorption at 23° was apparently instantaneous, and almost completely reversible.

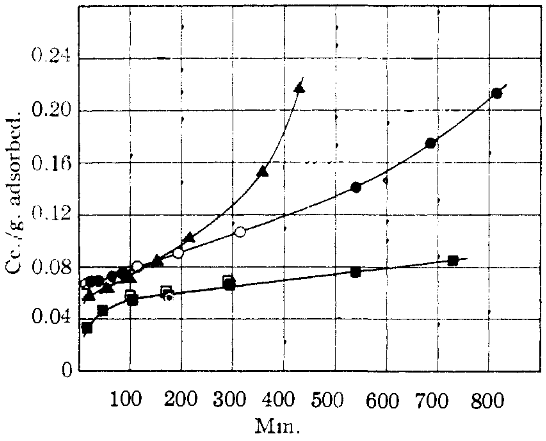

Fig. 4.—Adsorption of propylene and butylene on catalyst 973: ●, C_3H_6 at −40°; ■, C_3H_6 at 23°; ▲, C_4H_8 at −10°; O, □, △, desorption points.

Butylene adsorption was measured at −10° (Fig. 4). A desorption point lay slightly above the adsorption curve. It is not possible to state whether this slight irreversibility was due to a slow adsorption process on the iron or to solution in traces of grease on the walls of the adsorption apparatus. A glycerol–graphite mixture, "Glydag," was used as a stopcock lubricant to eliminate grease as much as possible.

The adsorption of hydrogen has already been studied on iron synthetic ammonia catalysts.[4c] Hence, no adsorption measurements on these catalysts were made in the present investigation. Nevertheless, it was of interest to repeat the adsorption of hydrogen on an iron prepared by reduction of ferric oxide Insley[1f] has claimed that the adsorption of hydrogen on such a catalyst at 0° was negligible. However, the present experiments show (Fig. 5) that this adsorption is appreciable. Slow drifts following an initial fast adsorption were noted for all points. An ethylene adsorption was made on this catalyst for comparison with the hydrogen adsorption (Fig. 5).

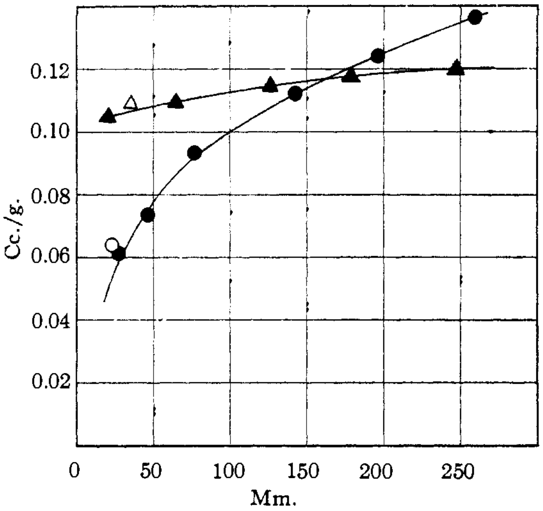

Fig. 5.—Adsorption of ethylene and hydrogen on iron from Fe_2O_3: ▲, hydrogen at 0°; ,● ethylene at 0°; O, △, desorption points.

Kinetics of the Hydrogenation of Ethylene, Propylene and Butylene.—The apparent energies of activation for the hydrogenation at low temperatures of ethylene, propylene and butylene are, respectively, 4200, 3200 and 2800 calories (Fig. 6). The values for propylene were deter-

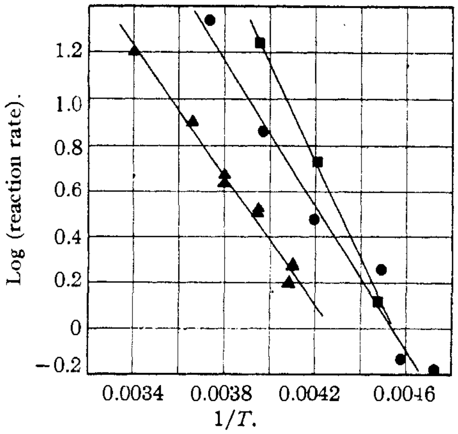

Fig. 6.—Apparent energy of activation for hydrogenation: ■, C_2H_4 4200 calories; ●, C_3H_6 3200 calories; ▲, C_4H_8 2800 calories. Initial partial pressures of hydrogen and of olefins were 200 mm.; 0.613 g. of catalyst 973 was used.

mined over the temperature range −5 to −61°; for butylene, −29 to +20°; and for ethylene, −20 to −50°

The relative rates of hydrogenation at −20° are 18.0, 8.5 and 2.9 mm. pressure drop per minute for ethylene, propylene, and butylene, respectively, at 200 mm. In these runs, as well as in those that follow, the initial reaction rate was determined by extrapolation to zero time which is the time at which the reactants were let into the reaction vessel.

A study of the effect of variations in the pressures of hydrogen and olefin is given in Figs. 7 and 8. The rate of hydrogenation varies approximately as the 0.6 power of the hydrogen pressures for the three olefins studied. As the pressure of ethylene was increased fourfold, the rate of hydrogenation increased somewhat. With propylene, the rate of hydrogenation fell off. The rate of hydrogenation of butylene did not change. Figure 9 shows the effect of the pressure of hydrogen on the rate of hydrogenation as it changes within a single run. The slopes of the lines indicate that the reaction rate is proportional to the first power of the hydrogen pressure for ethylene; to the 1.2–2.4 power of hydrogen for propylene; and to slightly more than the first power of hydrogen for butylene.

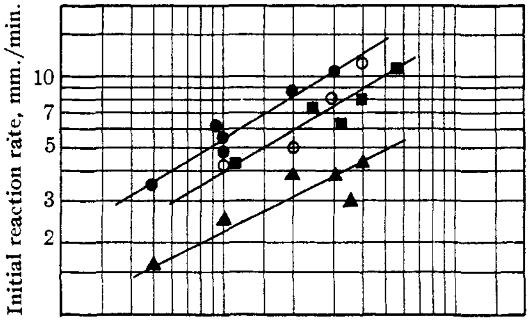

Fig. 7.—Effect of varying hydrogen partial pressure: hydrogenation using 100 mm. of olefin on 0.613 g. of catalyst 973: ●, C_2H_4 at −35°, slope = 0.6 (Batch 1 of C_2H_4); ○, C_2H_4 at −35°, slope = 0.5 to 1.0 (Batch 2 of C_2H_4); ▲, C_3H_6 at −35°, slope = 0.5; ■, C_4H_8 at −10°, slope = 0.6.

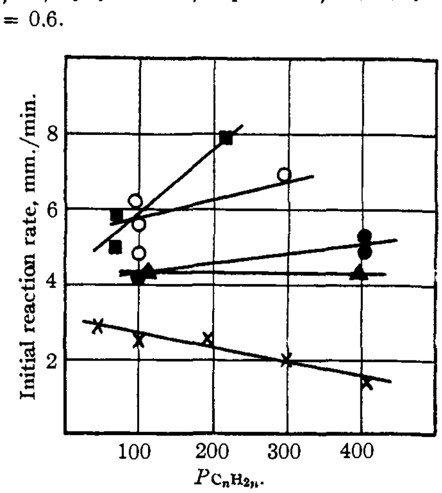

Fig. 8.—Effect of varying partial pressure of olefin: hydrogenation on 0.613 g. of catalyst 973 using 100 mm. of hydrogen: ●, ○, C_2H_4 at −35°; ×, C_3H_6 at −35°; ▲, C_4H_8 at −10°; ■, C_3H_6 at −35° using P_2O_5 for drying the C_3H_6.

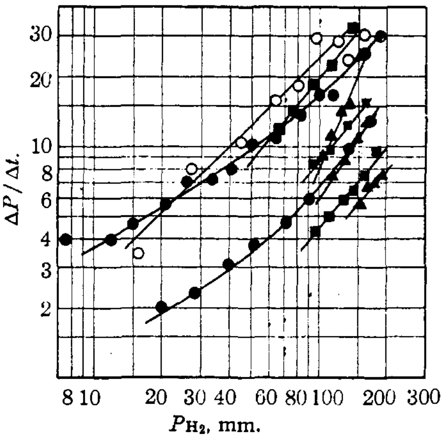

Fig. 9.—The change of the rate of hydrogenation with the change in the partial pressure of hydrogen during each run: ●, ○, C_2H_4, slope = 0.9–1.2; ▲, C_3H_6, slope = 1.2–2.4; ■, C_4H_8, slope = 1.2. It is assumed that the partial pressure of olefin has no effect on the reaction rate.

That the reaction taking place was hydrogenation with little if any polymerization was shown by condensing the reaction mixture in liquid nitrogen after the reaction had gone to completion. With butylene, the residual pressure was 7 mm.; for propylene, 2 mm.; and for ethylene, 2.5 mm. The total initial pressure in each case was about 400 mm. Part or all of this residual pressure may have been due to unreacted hydrogen in the exit and inlet tubes of the reaction vessel. In these experiments a slight excess of olefin over hydrogen was used so that there would be no residual pressure of hydrogen when the reaction was complete.

Hydrogenation of Butylene as Thin Liquid Films on Catalyst 973.—Since the rate of hydrogenation of butylene did not increase as the partial pressure of olefin was increased, it was thought of interest to investigate the influence of further increasing the thickness of the adsorbed layer of butylene.

At 0.8° small quantities of butylene were added to the reaction mixture consisting initially of 592 mm. of butylene and 298 mm. of hydrogen. The reaction rate as observed by the pressure change on the manometer was practically unchanged until saturation pressure (750 mm.) was reached. The falling off in the rate of hydrogenation due to the hydrogen being consumed was allowed for in comparing these rates of hydrogenation. Further addition of butylene resulted in a rapid decrease in hydrogenation rate as the thickness of the liquid layer increased. When the catalyst was covered with a 1-mm. layer of liquid, the reaction was very slow—approximately 0.1 as fast as when the saturation pressure was first reached.

The Effect of Al_2O_3 and K_2O on the Catalytic Activity of Iron.—Table III summarizes the data. The figures in the last column were calculated from the observed initial reaction rate, the weight of catalyst used, the surface area of the catalyst as measured by low temperature nitrogen adsorption, and the fraction of the total surface that is iron. The figures so calculated give a measure of the catalytic activity per unit surface area of iron.

TABLE III

Catalyst	Olefin	Temp., °C.	Initial reaction rate per sq. meter[b] Total surface	Iron surface
973	C_2H_4	−20	45.1	45.1
	C_3H_6	0.7	(78)[c]	(78)[c]
	C_4H_8	21	66.5	66.5
983	C_2H_4	−20	0.72[a]	1.57
	C_3H_6	0.7	20.0	43.5
	C_4H_8	21	13.4[a]	29.1
652	C_2H_4	−20	37.5	81.5
	C_4H_8	−20	28.2[a]	61.3
954	C_2H_4	−20	30.2[a]	43.8
931	C_2H_4	−20	0.33[a]	0.66
	C_3H_6	0.7	2.3[a]	4.6
	C_4H_8	21	4.4[a]	8.8

[a] Average of two or more runs. [b] Initial reaction rate is measured as mm. Hg pressure drop per minute. The initial partial pressures of hydrogen and of C_nH_{2n} were 200 mm. [c] Estimated from Fig. 6.

In Table IV are given the relative rates of hydrogenation of ethylene, propylene, and butylene using catalyst 973 as a basis for comparison.

TABLE IV

Catalyst	% Al_2O_3	% K_2O	Relative rates of hydrogenation per sq. meter of iron surface[a] C_2H_4	C_3H_6	C_4H_8
973	0.15	0.0	a	b	c
954	10.2	0.0	0.97a	..	..
652	1.84	0.44	1.81a	..	5.9c[b]
983	2.75	1.29	0.035a	0.56b	0.44c
931	1.30	1.59	.015a	.059b	.13c

[a] a = 45.1 mm. pressure drop per min. per sq. meter of iron surface at −20°; b = 78 mm. pressure drop, at 0.7°; c = 66.5 mm. pressure drop, at 21°. [b] The rate of hydrogenation of butylene on 652 shown here has been calculated by multiplying by six the rate of hydrogenation at −20°C. It was assumed for this calculation that the temperature coefficient of the hydrogenation was the same for 652 and 973.

To eliminate the possibility that the inhibition of ethylene hydrogenation by the promoter on catalyst 983 might have been due to a poisoning of the catalyst by an impurity in the reactants, a butylene hydrogenation was made immediately after an ethylene hydrogenation on catalyst 983 without the usual reduction and evacuation between runs. The rate of butylene hydrogenation was decreased only by a factor of one-half, whereas a 30-fold decrease in activity would have been expected if the catalyst had been poisoned during the ethylene hydrogenation as judged by the relative rates of hydrogenation of C_2H_4 on catalyst 973 and on catalyst 983.

Activity of Iron Prepared from Fe_2O_3 for Ethylene Hydrogenation.—A sample of iron catalyst prepared by reduction of Fe_2O_3 was taken from the large sample on which the adsorption of hydrogen and ethylene had been measured. A mixture of 200 mm. of ethylene and 200 mm. of hydrogen reacted at an initial rate of 7.3 mm. pressure drop per minute at 0.0° on 0.091 g. of iron. From Fig. 6 it may be estimated that 0.091 g. of catalyst 973 under the same conditions would have a reaction rate of 10.5 mm./min.

Discussion

Hansford and Emmett[2] ventured the opinion that the physical adsorption of ethylene is involved in its hydrogenation at low temperature on iron catalysts. In agreement with this there is no evidence that an activated adsorption of ethylene plays an important part in this hydrogenation. The same picture is believed true for propylene and β-butylene. This conclusion is based on the characteristics of the adsorptions of ethylene, propylene and β-butylene. Below 0° the adsorptions of ethylene and propylene were instantaneous and reversible. The same is probably true for butylene.

At −35° and pressures from 100 to 400 mm. of propylene the surface of the catalyst was covered by an amount of adsorbed gas sufficient to form more than one layer of molecules. This is based on the conclusion of Emmett and Brunauer[6] relative to the point on a physical adsorption isotherm at which a second adsorbed layer begins to be built up. The same is true for butylene at −10°. It is not surprising, therefore, that the rate of hydrogenation is nearly independent of the partial pressure of the olefins.

It seemed possible that the decrease in reaction rate observed with an increase in partial pressure of propylene was due to a poison present in the propylene. Since it was probable that this impurity was water, phosphorus pentoxide was placed in the line between the propylene storage flask and the 15 cc. of iron "clean-up" catalyst. The activity of the catalyst was considerably greater for the dried C_3H_6 than for the C_3H_6 before drying. Furthermore, the reaction rate now increased instead of decreased as the partial pressure of propylene was increased. Time did not permit similar drying experiments on ethylene and butylene; the low pressure-low temperature distillation used in preparing all three gases was assumed sufficient to remove moisture from them.

It is interesting to note in the case of butylene hydrogenation at −10° that the rate of reaction was nearly constant although the thickness of the layer of adsorbed butylene changed considerably. It is probable, therefore, that the diffusion of hydrogen through the layer of adsorbed butylene was fast relative to the rate of hydrogenation observed. On the other hand, a liquid phase experiment with butylene at 0° showed that the rate-controlling step of the hydrogenation here was the diffusion of hydrogen through the liquid surrounding the catalyst. The experiment was made in such a manner that the reaction rate could be observed as the adsorbed layer was increased in thickness until a liquid film was present. Not until an appreciable film thickness was reached did the rate of reaction decrease greatly. This can be explained by assuming that the liquid layer had been increased in thickness until diffusion through this layer became the slow step of the reaction.

The pressure dependencies shown in Figs. 7 and 9 indicate that the slow step of the hydrogenation is associated with hydrogen either in its adsorption or reaction with the olefin. If the rate controlling step of the hydrogenation were the activated adsorption of the olefin, it would be difficult to explain the observed dependence of the reaction rate on the partial pressure of hydrogen and its independence of the olefin pressure.

Table IV indicates that the inhibiting effect of the promoter of the promoted iron synthetic ammonia catalysts on the rate of olefin hydrogenation may be associated with the per cent. potassium oxide present. For all three gases for the three promoted catalysts containing potassium oxide the rate per unit iron surface area decreases as the potassium oxide content increases.

From Table IV one may also draw the conclusion that for ethylene more than for propylene and butylene the activities of the catalysts 983 and 931 (containing, respectively, 1.29 and 1.59% potassium oxide) per unit surface area of iron are low as compared to that of pure iron catalyst 973. Indeed, the activities of catalysts 983 and 931 are lower for ethylene hydrogenation than the activity of pure iron catalyst 973 even when the comparison is made on a per gram basis. This is true despite the fact that total areas of catalysts 983 and 931 are 21 and 11 times, respectively, as great as that of 973. This observation confirms that of Hansford and Emmett[2] on the relative activities of catalysts 931 and 973 for ethylene hydrogenation.

In Table IV catalyst 652 cannot be fairly compared with the other catalysts because it was reduced at a higher space velocity than the other catalysts and was used for only a few experiments. Since the molecular ratio of aluminum oxide: potassium oxide is 4 to 1, in catalyst 652, compared to 1.97 in 983 and 0.75 in 931, it is possible it contains little or no free potassium oxide.

The most that one can say from the results as regards the influence of the promoters on the iron catalysts for olefin hydrogenation is that the activity per unit iron surface is little changed by aluminum oxide promoter or aluminum oxide: potassium oxide promoter in which the aluminum oxide : potassium oxide ratio is 4 : 1; for catalysts with higher potassium oxide content a very marked inhibition of hydrogenation per unit iron surface (or even per gram of catalyst for ethylene hydrogenation) is found to exist. It is not clear why potassium oxide should manifest such an inhibiting effect nor why the inhibition should be relatively greater for ethylene than for propylene and butylene.

The presence of a small amount of undetermined poison in the hydrogen used for these experiments is indicated by the following facts: (1) The rate of hydrogenation increased according to the 0.6 power of hydrogen when the partial pressure of the hydrogen was increased in successive runs, whereas within a single run the rate was directly proportional to at least the first power of the hydrogen partial pressure. (2) There was a loss of reproducibility at high partial pressures of hydrogen. (3) If hydrogen were allowed to stand in contact with the catalyst prior to a run, the observed rate in that run was less than half what it should be. Very small amounts of hydrogen did not produce this effect.

It should be noted that the experiments were carried out in such a manner in this investigation that it is believed this trace of poison had no effect on the validity of the conclusions drawn.

In contrast to the negligible adsorption of hydrogen that Insley found on an iron catalyst reduced from ferric oxide, the present investigation shows an appreciable adsorption of hydrogen on a catalyst prepared in a similar manner. The adsorptions of hydrogen and ethylene were found to be nearly the same in amount. Insley found 0.5 cc. of ethylene adsorbed per gram at 100 mm., and no hydrogen adsorption. Figure 5 shows about 0.1 cc. of ethylene and hydrogen adsorption per gram at 100 mm. pressure.

After the completion of the present work the authors learned of the very extensive but still unpublished experiments of Beeck and his coworkers on the mechanism of ethylene hydrogenation on thin metal films. Apparently the hydrogenation mechanism on such films is very complicated. Accordingly, a more detailed discussion of the mechanism over these iron synthetic ammonia catalysts must await the publication of Beeck's work and probably the carrying out of additional experimental work.

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