and measurements have been made on aqueous solutions of barium chloride and of calcium chloride at 25, 35, and 45°. The activity of water in the barium chloride solutions changes only very slightly with temperature. The activity of water by vapor pressure measurement is in very good agreement with that calculated from electromotive force data, the maximum difference being 0.035%.

LAFAYETTE, INDIANA
RECEIVED FEBRUARY 16, 1940

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Hydrogenation of Ethylene at Surfaces of Certain Oxides. I. Zinc Oxide and Zinc Chromite

BY JOHN F. WOODMAN AND HUGH S. TAYLOR

The measurement of the activity of oxides as catalysts for the hydrogenation of ethylene was originally undertaken in the expectation of checking the results of Vaughen and Lazier[1] on zinc oxide. These authors had reported negligible amounts of ethane resulting from the passage of hydrogen and ethylene over zinc oxide and other oxides at 400°. It was hoped that this absence of activity would be confirmed by a few preliminary runs, after which it was planned to investigate possible activity of zinc oxide for deuterium substitution, with a view to developing a convenient method for the production of deutero-ethylenes free from overwhelming amounts of the ethanes.

Unfortunately for this program, the preliminary runs showed that the ability of zinc oxide to catalyze the hydrogenation of the double bond in ethylene is far from negligible, even at temperatures much below those used by Vaughen and Lazier. Since the latter authors had made their results the basis of a rather inclusive hypothesis regarding the specificity of oxide catalysts for the hydrogenation of organic compounds, it seemed worth while to investigate the discrepancy more closely, and, if possible, to determine the factors responsible for it.

Lazier and Vaughen[2] themselves soon discovered the high activity of chromium oxide for the hydrogenation of the alkene bond and stated that this property set chromium oxide apart from other oxides. Turkevich[3] showed that ethylene introduced to a mixed manganese–chromium oxide catalyst at temperatures of 184° and above, underwent activated adsorption accompanied by decomposition, the products pumped off at higher temperatures being largely saturated hydrocarbons. This indicated activity for hydrogenation at lower temperatures than had previously been reported for chromium oxide catalysts. As a consequence of his observations, Turkevich pointed out that the specificity of oxide catalysts must be regarded as a matter of degree.

The discovery of the activity of zinc oxide and its thorough study led to test of the activity of zinc chromite. In a later paper[4] we report work on compounds of molybdenum, chosen because of the well-known industrial applications of the oxides and sulfides of this element in hydrogenation and cracking of oils and tars.

Experimental Details

Apparatus.—The apparatus used consisted of the following units: (a) a catalyst tube, at controlled temperature, isolated from the system by a trap kept at −78° to keep out mercury vapor; (b) a mercury manometer; (c) a pump system for evacuation; (d) burets for gas mixing and measurement; (e) purification trains for the gases.

Catalysts.—Zinc oxide was prepared from the oxalate by the method of Taylor and Sickman,[5] zinc chromite according to the method of Taylor and Strother.[6]

Gases.—Electrolytic hydrogen and tank ethylene, carefully purified, were employed.

Procedure.—Originally the gaseous mixtures were circulated by means of a Toepler pump over the catalyst in a closed cycle. The later determinations were made in a static system of conventional design with the catalyst at the bottom of a Pyrex cylinder of 35 mm. diameter and 250 cc. capacity.

Experimental Results

Zinc Chromite.—A mixture of 357 mm. of hydrogen and 198 mm. ethylene was admitted to 5.5 g. of catalyst at 21° and slowly raised in temperature to 215°, with frequent gas circulation.

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[1] Vaughen and Lazier, THIS JOURNAL, **53**, 3719 (1931).

[2] Lazier and Vaughen, *ibid.*, **54**, 3080 (1932).

[3] Turkevich and Taylor, *ibid.*, **56**, 2254 (1934).

[4] Woodman, Taylor and Turkevich, *ibid.*, **62**, 1397 (1940).

[5] Taylor and Sickman, *ibid.*, **54**, 602 (1932).

[6] Taylor and Strother, *ibid.*, **56**, 586 (1934).

After thirty hours at 215° a decrease in pressure of 183 mm. was recorded. The final gas contained 53% C_2H_6, 44% H_2 and 2.2% olefins. A mixture of 222 mm. of H_2 and 403 mm. of C_2H_4 showed a slow pressure decrease at room temperature. After sixty hours at 250°, the gas contained 58% C_2H_6, 34.9% olefin and 7% H_2.

Zinc Oxide.—Qualitatively this catalyst behaved in the cyclic system at 200 and 300° like zinc chromite but was more active. With 333 mm. of H_2: 266 mm. of C_2H_4 at 200°, a pressure decrease of 256 mm. occurred in 2.5 hours, the product showing 77.2% C_2H_6, 20.4% H_2 and 2.2% olefin.

Static experiments showed that with evacuation at 450° of the air-ignited oxide the catalyst, weighing approximately 1 g., showed activity in the temperature range 0–80° with 56.5° (acetone vapor-bath) as a convenient working temperature. In successive experiments at 56.5°, with evacuation between experiments for intervals of two to twenty-one hours at the same temperature, a progressive decrease in velocity of reaction occurs, as shown by the following data for the period of half reaction, t_{50} = 19, 24, 35, 49, 68 minutes. In the succeeding experiment, after evacuation at 450° for twenty-nine hours, t_{50} fell once more to twenty minutes. Evacuation at 218° was not adequate to eliminate this progressive deterioration, as is shown by the following data for t_{50} at 56.6°, with intermediate evacuation at 218° for three hours: t_{50} = 74, 90, 100, 120, 140, 150 minutes.

Air activation of the surface by heating in a static system of air between each experiment to 450° for seventy-five minutes after evacuation of the catalyst for a few minutes at 56.5°, followed by a final three-hour evacuation at 450° immediately decreased the half-period of reaction of such deteriorated catalysts, as the following data with an initially inactive surface reveal: t_{50} = 170, 25, 23, 16, 19, 33, 44, 35, 29, 44, 44.

The decrease in reaction rate indicated by the final figures in the data just cited led to investigation of this secondary loss of activity. Since it would not appear to be due to inefficiency of removal of the primary agent of deterioration or its oxidation products, a test was made to ascertain whether the decrease might be due to strong adsorption of one of the components of the activating gas, most probably oxygen. This effect was tested thus: in a series of runs, activation with air for brief intervals at successively lower temperatures was tried, the conditions of evacuation, three hours at 450°, being maintained unchanged. The following data show that greater activity is obtained by using a shorter activation time. Further, lowering the activation temperature as far as 150° does not decrease the effectiveness of the activation. Activation with air at 56° is less effective.

TABLE I

INFLUENCE OF ACTIVATION CONDITIONS AT REACTION TEMPERATURE 56.5°

Activ. temp., °C.	450	450	400	345	305	250	200	150	56
Activ. time, min.	75	18	20	18	18	18	18	18	18
t_{50} min.	44	21	26	21	23	24	20	25	31

The increase in activity on decreasing the time and temperature of activation signifies that, with long activation, the primary effect of cleaning the surface, by removal of a deposit formed during reaction, is being partially nullified by a second effect, presumably oxygen adsorption, the resulting adsorbed layer not being completely removed by the evacuation procedure. To test this view, it was shown that admission of air, at 450°, for forty-five minutes to a surface of standard activity (t_{50} = 14–17 min.) followed by the standard evacuation at 450° for three hours gave a surface of lower activity, t_{50} = 29 minutes. The secondary film produced by air treatment is more tenaciously held than the primary poison, since evacuation at 250° of surfaces activated for eighteen minutes in air at 250° gave very slow reaction, t_{50} = 85 minutes. Evacuation, even at 450°, for less than twelve hours, does not clean an air activated surface completely. The highest and most reproducible activity was obtained by treating the catalyst with air at 250° for five to twenty minutes, then evacuating at 450° for twelve hours or longer.

Evacuation at 450° without activation with air was found to be undesirable practice since reduction of the catalyst by reactants may occur during the temperature rise after an experiment. Experiments at 218°, followed by evacuation at 450°, caused reduction of the surface and sublimation of metallic zinc. This does not occur after reaction at 56.5° if the system is thoroughly evacuated at 56° prior to raising the temperature to 450°.

The kinetics of the reaction on such surfaces, where the variability is great and not easily controlled, is difficult to study. A variation in the

H_2:C_2H_4 ratio from 5:1 to 3:1 ($p_{C_2H_4}$ = 50 mm.) gave no change in t_{50}. For H_2:C_2H_4 varying from 3:1 to 1:1 (for p_{H_2} = 160 mm.) the half-life varied from twenty-two to seventy-one minutes, and calculation from the initial slopes of the rate curves results in a dependence on the 0.1 power of the ethylene pressure. For equimolar mixtures with total pressures of 320 and 120 mm. the half-lives were seventy-one and forty minutes. Addition of 26 mm. of ethane to a 3:1 H_2:C_2H_4 mixture, $P_{C_2H_4}$ = 52 mm., did not change the half-life. Within these limits the reaction velocity appears to be independent of the reactant pressures.[7] The order of magnitude of the apparent activation energy of the reaction was determined, from two pairs of runs at 39 and 56°, as $\sim$ 18 kcal.

To study the influence of water vapor, experiments were carried out at 56 and at 400°, the latter being the temperature used by Vaughen and Lazier. Water vapor is known to be a strong reversible poison for zinc oxide catalysts[5,8] and its effect on the hydrogenation of ethylene is of interest because the experiments of Vaughen and Lazier, which failed to detect any activity in this reaction, were carried out with moist gases stored over salt solution. At 56° a hydrogen–ethylene mixture containing 3% water vapor or 7×10^{-5} moles per gram of catalyst, required a half period of reaction equal to seventy-five minutes, or three-fold the rate for dry gases. When the catalyst at 56° was equilibrated with water vapor from ice at 0° for two hours, the standard 3 hydrogen:1 ethylene mixture showed only a change of 1 mm. pressure in fifteen minutes. The catalyst was completely inactive.

At 400°, after the standard air activation and evacuation, the % reaction in fifteen minutes of a $3H_2$:$1C_2H_4$ mixture was negligible with 3.7 and 2% of water vapor in the gas, whereas the dry gas showed 72% reaction in the same interval. The 2% of water vapor present in the experiment corresponds to about 1.9 cc. at N. T. P. on the gram of catalyst used. Vaughen and Lazier used twenty grams of catalyst over which they several times passed samples of six to seven liters of gas stored over saturated salt solution. Thus, after the passage of 2.5 liters of gas, their catalyst would have been in contact with water vapor sufficient to stop reaction on our catalyst even if their technique had eliminated water vapor from the catalyst surface initially. Their failure to detect significant activity is thus completely explained. The greater effect of adsorbed water vapor at 400° compared to that at 56° is consistent with the known high temperature activated adsorption of water vapor on zinc oxide.[5]

Hydrogenation at 218° produced much more rapid decreases in velocity in successive runs; after three runs the velocity became almost negligible. Subsequent evacuation at 450° brought a tremendous increase in activity, to such an extent that diffusion became the rate-determining step, with t_{50} at 218° of the order of three minutes.

The evacuation process following reaction at 218° caused a grayish film of metal to appear on the cold walls of the reaction vessel, the deposit increasing with successive evacuations following later runs at 218°. The deposit could be sublimed. When the tube was heated after admission of air the color of the film changed to white. The film was evidently metallic zinc formed by reduction of the oxide surface by the reaction mixture at 218° or during the evacuation. Evacuation at 450° before access of the hydrogen–ethylene mixture produced no such deposit. The zinc was therefore not formed by thermal dissociation.

Pretreatment with 25 mm. of hydrogen for thirty minutes at 56° caused the adsorption of about 0.1 cc. at S. T. P. A mixture of hydrogen and ethylene added to make the total ratio a $3H_2$:$1C_2H_4$ mixture reacted slightly more slowly than normal. Exposure to hydrogen at 80° and 1 atm. pressure for five hours, with evacuation at 56° for fifteen minutes before the experiment, gave a retardation of the same order. Treatment with hydrogen at 218° turned the catalyst gray and the succeeding run at 56° after evacuation for fifteen minutes at 56° was very much slower. The change in color is a definite indication of reduction.

An atmosphere of hydrogen in contact with the catalyst at 218° for five hours changed the color to gray. After fifteen minutes of evacuation at 56° a run at this latter temperature showed very great retardation. Reduction of bulk zinc oxide by hydrogen has been shown not to occur below about 310°.[9] Reduction of active zinc oxide catalysts by hydrogen at lower temperatures has frequently been observed in this Laboratory[5,8,10]

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[7] *Cf.* Pease and Stewart, THIS JOURNAL, **47**, 2763 (1925).

[8] Burwell and Taylor, *ibid.*, **58**, 1753 (1936).

[9] St. John, *J. Phys. Chem.*, **33**, 1438 (1929); Schacherl, *Gazz. chim. ital.*, **62**, 839 (1932).

[10] Taylor and Kistiakowsky, THIS JOURNAL, **49**, 2468 (1927).

and the effect seems to be enhanced by hydrocarbons.[11]

Ethylene at a pressure of 320 mm. in contact with 5 g. of catalyst at 218° gave a pressure decrease of 53 mm. in one hundred hours. The gaseous product was completely condensable in liquid air, indicating that polymerization had taken place with no significant formation of hydrogen or methane. At 445°, 600 mm. of ethylene on the same catalyst gave first a rapid absorption of gas to 474 mm. in two hours followed by a slow pressure increase to 504 mm. in ninety hours. From 77 cc. of ethylene initially present, 11 cc. of hydrogen and 11 cc. of methane were recovered. Polymeric products also were formed. The ability of zinc oxide slowly to attack both C–H and C–C bonds at 445° is thus demonstrated.

General Discussion

Lazier and Vaughen[2] assumed a specific capacity in chromium oxide for the activation of alkenes leading to their hydrogenation, and the absence of such capacity in other difficultly reducible oxides. The accumulated chain of evidence, of which this article furnishes the latest link, shows definitely that this assumption is not in agreement with the facts now available.

Howard[12] observed that on chromium oxide at 218°, adsorbed hydrogen reacted readily with ethylene. Turkevich[3] found ethylene activated by adsorption on manganese–chromium oxides at 184°, and recoverable largely as ethane. The present work shows that, already at 56°, zinc oxide is activating ethylene for hydrogenation, and moreover suggests that, even at this temperature, there is activation of specific bonds leading to the formation of a hydrocarbon deposit which poisons the active centers. That this deposit is actually of hydrocarbon origin, and is not merely adsorbed hydrogen, is attested by its accumulation in successive runs, contrary to what one would expect from the known behavior of hydrogen, and by the failure to detect an inhibitory effect of hydrogen present in the reaction mixture.

With rising temperature, the parallelism in the cases of chromium oxide, manganese–chromium oxides, and zinc oxide is complete. On the last catalyst, hydrogenation is rapid at 218°, and activation of specific bonds is clearly established by the disappearance of ethylene alone in contact with the catalyst, forming probably $(C_2H_4)_n$, but no permanent gases. At higher temperatures, both C–C and C–H bonds are broken, with formation of methane and hydrogen, and deposition of carbon. These results for zinc oxide over the range from room temperature to 444° are entirely analogous, at the higher temperatures, to the behavior of chromium oxide,[12] and manganese–chromium oxides,[3] no attempt having been made, on these catalysts, to test the possibility of hydrogenation at lower temperatures. It is even more interesting that the behavior of zinc oxide parallels that shown by Morikawa, Trenner and Taylor[13] to be characteristic of nickel in the temperature range from −78° to about +130°.

Summary

1. Zinc oxide and zinc chromite have been shown to act as catalysts for the hydrogenation of ethylene with measurable velocity at and above room temperature. At 56° the reaction velocity on zinc oxide has been shown to be independent of hydrogen, ethylene and ethane partial pressures within a range of variation of these quantities.

2. On zinc oxide at 56° the number of active centers decreases because of the deposition of some substance probably arising from very slow polymerization or decomposition of ethylene at the surface. This poison can be oxidized by air at 150° and above, and the products removed by long pumping at 450°.

3. There is some evidence that oxygen is strongly adsorbed on the active centers of zinc oxide at 150° and above.

4. Reduction of zinc oxide to metallic zinc by the reaction mixture does not take place at 56°, but does so at 218° and above. The reducing effect of hydrogen alone at 218° has been confirmed.

5. Ethylene has been shown to polymerize slowly on zinc oxide at 218°, without appreciable formation of permanent gases. At 445°, polymerization is rapid, but accompanied by the formation of considerable amounts of hydrogen and methane.

6. Small amounts of water vapor have been shown to poison the surface of zinc oxide completely at 56° and even at 400°. This effect is responsible for the failure of Vaughen and Lazier[1] to observe the activity of this catalyst with their experimental procedure.

PRINCETON, NEW JERSEY RECEIVED MARCH 6, 1940

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[11] Smith and Taylor, THIS JOURNAL, **60**, 362 (1938).

[12] Howard and Taylor, *ibid.*, **56**, 2259 (1934).

[13] Morikawa, Trenner and Taylor, *ibid.*, **59**, 1103 (1937).