4.   The solubility curves of magnesium sulfate hexa-, penta- and tetra-hydrate have been studied at 85, 95 and 100°.

5.   The preparation of the hexa-, penta-, tetra-, di-, five-fourths and monohydrates of magnesium sulfate has been discussed, together with their identification with the aid of the petrographic microscope, and new optical data for the hexa-, penta-, tetra-, di- and five-fourths hydrates have been given.

6.   It has been suggested that there is a relation between the degree of crystallographic perfection exhibited by a salt and the rate at which it comes to equilibrium with its aqueous solution.

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# THE CATALYTIC ACTIVITY AND ADSORPTIVE POWER OF SUPPORTED IRON, COBALT, NICKEL, COPPER AND SILVER

BY ROBERT N. PEASE AND LELAND STEWART

This paper records the results of experiments on the activities of similarly prepared, supported iron, cobalt, nickel, copper and silver catalysts in the hydrogenation of ethylene.   The experiments were undertaken with the view to determine the true relative activities of these metals as hydrogenation catalysts and to obtaining preliminary results on reaction kinetics.

The specific activity of a contact catalyst depends ultimately on its chemical nature.   In addition, however, the catalytic effect as experimentally determined is conditioned by the area of surface exposed per unit volume of reactants and by its submicroscopic form, and these vary from one sample to the next.   If a comparison of two substances as catalysts is desired, therefore, some standardization relative to surface characteristics is required.   Bulk catalysts are out of the question, because the utmost care in preparation cannot ensure similarity of surface.   Supported catalysts are of greater promise.   The surface of a porous refractory will not change with any ordinary treatment and a film of the substance to be examined spread over the surface should assume the form of the latter. Consequently, if the catalysts to be compared are supported on average samples of the same refractory material, it may fairly be assumed that differences in activity are chiefly due to the specific properties of the substances under investigation.

We have prepared a uniform supply of crushed diatomite brick and have impregnated samples with such quantities of solutions of the nitrates of the metals as would correspond to 1 gram atom of metal per 1000 g. of dry brick.   These samples were then dried slowly, calcined and reduced. The amount of the metal is admittedly arbitrary.   It is approximately

that (10%) commonly used in preparing supported catalysts. We cannot say how thick a film it corresponds to, but we do know that the brick was not encrusted and appeared different only in color after treatment.

## Preparation of Catalysts

The catalysts were all prepared in the same manner except for the final temperature of reduction. Non-Pareil porous, diatomite brick (kindly furnished by the Armstrong Cork Co.) was broken up and screened to 5–10 mesh. The granules were boiled in 15% nitric acid, washed repeatedly with distilled water and finally dried at a low red heat. Twenty g. (about 70 cc. apparent volume) was used for each catalyst. This was weighed out and placed in a small flask. It was found that such a sample would absorb nearly its own weight of water without becoming definitely wet. Solutions of the nitrates of the metals were accordingly made up to contain the requisite quantity of metal (corresponding to 1 gram atom per 1000 g. of brick) in 15 cc. of solution. This amount of solution was then placed in a dropping funnel and allowed to flow drop by drop onto the brick granules while the latter were agitated. The granules were then transferred to a section of large (2 inch) glass tubing and warm, dry air was slowly drawn over them. The tube was occasionally turned. The catalyst was then transferred to the catalyst bulb, which was sealed to the apparatus. The catalyst was then further heated gradually to 350–400° in a stream of air to calcine it and was finally reduced in hydrogen. Temperatures of reduction were: iron, 450°; cobalt, 370°; nickel, 300° (to 420° at end); copper, 200°; silver, 150° (to 250° at end). In no case was there evidence of a loss of metal from the support at any point in the procedure.

The nitrates were all c. p., those of cobalt and nickel being sold as nickel-free and cobalt-free, respectively.

The apparatus, method and preparation of gases were the same as those used in earlier work on this reaction.[1] The apparatus consisted of a catalyst bulb, manometer, gas buret, Töpler pump and gas reservoirs, all sealed together through suitable stopcocks. Reaction rates were measured by the pressure decrease at constant volume. Adsorptions were obtained by comparing isotherms with that of helium.

## Results

Our measurements are summarized in the following tables. Initial rates of reaction, obtained by extrapolation, are compared with initial partial pressures. Determinations were made at such temperatures as would give appreciable rates. In the case of nickel and cobalt, the rates were immeasurably high even at 20°, so that no quantitative data were obtained. Reaction was practically complete in the time (a few seconds) taken to admit the gases. We can only say that these substances are of another order of activity than any of the others.

The data on copper are taken from the work of Dr. C. A. Harris.[2]

The results indicate that supported iron and silver are considerably better catalysts and supported copper is a somewhat poorer catalyst than the average corresponding unsupported materials. Schmidt,[3] for example, finds unsupported iron, prepared from the hydroxide, only moderately

[1] Pease, THIS JOURNAL, **45**, 1198 (1923).

[2] Pease and Harris, *ibid.*, **49**, 2503 (1927).

[3] Schmidt, *Z. physik. Chem.*, **118**, 208 (1925).

TABLE I

REACTION RATES

| Catalyst | Temp., °C. | Init. press., atm. | | Init. rate, mm./min. |
|---|---|---|---|---|
| Iron | 0 | $1/2$ | $1/2$ | 9.3 |
| | 0 | $1/3$ | $2/3$ | 6.9 |
| | 0 | $2/3$ | $1/3$ | 10.2 |
| | 0 | $1/2$ | $1/2$ | 7.5 |
| | 0 | $1/2$ | $1/2$ | 5.8 |
| | 10 | $1/2$ | $1/2$ | 9.0 |
| | 0 | $1/2$ | $1/2$ | 5.8 |
| | 20 | $1/2$ | $1/2$ | 12.7 |
| | 0 | $1/2$ | $1/2 r$ | 5.3 |
| Copper | 50 | $1/3$ | $1/3$ | 17.5 |
| | 50 | $1/3$ | $2/3$ | 11.8 |
| | 50 | $2/3$ | $1/3$ | 18.5 |
| Silver | 100 | $1/2$ | $1/2$ | 14.0 |
| | 100 | $1/3$ | $2/3$ | 9.7 |
| | 100 | $2/3$ | $1/3$ | 19.0 |
| | 50 | $1/2$ | $1/2$ | 1.8 |

TABLE II

ADSORPTIONS

| Subs. | Gas | Temp. °C. | Temp., 10 mm. | Absorption, cc. 760 mm. |
|---|---|---|---|---|
| Nickel | $H_2$ | 0 | 1.40 | 2.85 |
| Cobalt | $H_2$ | 0 | 0.50 | 1.26 |
| Iron | $H_2$ | 0 | <0.05 | 0.10 |
| Copper | $H_2$ | 50 | 0.10 | 0.15 |
| Silver | $H_2$ | 100 | <0.05 | 0.20 |
| Nickel | $C_2H_4$ | 0 | 0.95 | 9.00 |
| Cobalt | $C_2H_4$ | 0 | 0.80 | 8.20 |
| Iron | $C_2H_4$ | 0 | 1.95 | 12.70 |
| Copper | $C_2H_4$ | 50 | 0.20 | 3.05 |
| Silver | $C_2H_4$ | 100 | 0.10 | 1.15 |

active at 100°. Copper prepared from the carbonate is considerably more active than the iron, and silver has a very low and variable activity. Likewise Sabatier[4] finds unsupported iron active only above 180°. The same is reported of copper but the authors have regularly employed copper in several forms at 0°. Silver is not even mentioned. Our supported iron catalyst is active at 0°, the copper at 50° and the silver at 100°.

We interpret these results to mean that the advantage of using a support is to lend stability where this is needed. The high temperatures (400–500°) required to reduce iron oxide promote deactivation by sintering, while the extreme softness of silver renders it especially susceptible in this regard. Copper, on the other hand, can be reduced at low temperatures and is only

4 Sabatier, Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Company, New York, **1923**, p. 180.

moderately soft, so that a support is of no particular advantage. The fact that supported copper is actually less active than unsupported material is doubtless due to a smaller surface exposure. This is borne out by the uniformly low hydrogen adsorptions on all samples, even nickel adsorbing only 2.85 cc. at 1 atmosphere.

The adsorption of hydrogen by nickel and cobalt being considerably greater than by the other metals correlates with the high catalytic activity of the former. Adsorption of hydrogen by iron, copper and silver is small and probably the same within experimental error. Iron stands out with respect to ethylene adsorption and it is this apparently which places it above copper in catalytic activity.

As to reaction kinetics, the rate in the presence of silver at 100° is closely proportional to the hydrogen concentration and independent of the ethylene as was found for copper[1] at this temperature. Owing to the deactivation of the iron catalyst with use, the kinetics at 0° are not entirely clear. Excess of hydrogen undoubtedly increases the rate. The influence of ethylene is not great, but it is uncertain whether it is positive or negative. The kinetics in presence of copper are thoroughly treated in another paper.[1]

The temperature coefficients give for the heats of activation, 6200 cal. in the case of iron between 0 and 20°, 13,200 cal. in the case of copper between 0 and 100°[1] and 9800 cal. in the case of silver between 50 and 100°.

These comparative results serve anew to emphasize the marked superiority of nickel and cobalt as hydrogenation catalysts over their neighbors, iron and copper, in the periodic table. Reference to Sabatier,[4] reveals that the corresponding members of the two succeeding long periods stand in like relation. Thus, palladium and rhodium are considerably more active than ruthenium and silver and the same holds for platinum and presumably iridium, as compared with osmium and gold.

It is probably not without significance in catalytic theory that these highly active metals are those whose ions in solution enter into so great a variety of stable complexes. The tendency to form the latter seems to be traceable to electron sharing. Schmidt[5] would have it that the function of the metal in catalytic hydrogenation is to provide a medium wherein hydrogen may become ionized. Without accepting in full the somewhat elaborate analysis of this investigator, one can readily agree that the electron systems of hydrogen and the substance hydrogenated are profoundly disturbed when they come in contact with the metal. It would be difficult to show that complete ionization actually takes place. The important point is, perhaps, that the associative property of the metal brings the reactants together, and the metal, by its tendency to share electrons, renders both labile, whereupon they may settle down into a system characterized by lower free energy.

[5] Ref. 3, p. 193.

## Summary

1. Supported catalysts of iron, cobalt, nickel, copper and silver have been prepared by as nearly similar methods as possible and their activity in the hydrogenation of ethylene has been determined. Cobalt and nickel caused instantaneous action at $-20°$, iron was moderately active at $0°$, copper at $50°$ and silver at $100°$. The effect of the support appears to be to increase the effectiveness of all but copper. This is discussed.

2. Adsorption measurements show much more hydrogen adsorbed by nickel and cobalt than by the other metals, and more ethylene is adsorbed by iron.

3. Reaction kinetics in the presence of silver at $100°$ show that the rate is proportional to the hydrogen and independent of the ethylene concentration, as was found for copper. In the presence of iron at $0°$, excess of hydrogen increases the rate while excess of ethylene exerts little influence.

4. Attention is called to the periodicity among the metals in catalytic properties and the correlation with complex ion formation. An association rather than a dissociation theory of catalytic hydrogenation is indicated.

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## A SIMPLE TYPE OF FLOWING JUNCTION

BY E. J. ROBERTS AND F. FENWICK

In connection with a study of the relation of the potential of an antimony electrode in contact with a solution saturated with antimony trioxide to the acidity of that solution, the problem of obtaining a reproducible liquid junction potential between the antimony electrode and the reference electrode (Ag, AgCl, 3.5 $M$ KCl) became of prime importance. The electrode vessels used were modifications of the type described by Brönsted,[1] in which the solution flows slowly down through a deep layer of the saturating substance, past the electrode proper, to the junction; therefore, a flowing junction device requiring only small volumes of electrolyte and possessing an easy flexibility of adjustment to solutions of widely varying density was highly desirable. None of the arrangements previously described[2] meet these requirements. It was found, however, that by interposition of a thin mica plate vertically between the ends of the pair of horizontal exit tubes from the electrodes so that the streaming electrolytes flow slowly down opposite faces of the plate past a small hole, through which alone the solutions make contact, the resulting junction is satisfactory in all respects.

[1] Brönsted, *Kgl. Danske Videnskab. Selskab. Math.-fys. Medd.*, **3**, No. 9 (1920).
[2] Lamb and Larson, THIS JOURNAL, **42**, 229 (1920); (b) MacInnes and Yeh, *ibid.*, **43**, 2563 (1921); (c) Scatchard, *ibid.*, **47**, 696 (1925).