

[CONTRIBUTION FROM THE SANDERS LABORATORY OF CHEMISTRY, VASSAR COLLEGE]

The Adsorption of Hydrogen by Supported Nickel Poisoned with Carbon Monoxide¹

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Introduction

The inhibition of catalytic activity caused by minute quantities of poisons when placed upon various metallic catalysts probably always is accompanied by a definite change in the adsorptive power of the catalyst toward the interacting substances. The action of mercury² and of cyanogen³ as poisons on copper used in hydrogenation reactions furnish examples in which the sorption is decreased by the poisons at all pressures up to one atmosphere. The inhibitory action of carbon monoxide on certain catalysts⁴ has been known for over a century. Its effect upon the catalytic activity of massive copper employed in the hydrogenation of ethylene was shown by Pease and Stewart.⁵ A study of the sorptions of hydrogen and ethylene, so poisoned, revealing a low-pressure increase in the sorptions, was made by the author.⁶ When hydrogen adsorption measurements later were made on a supported copper catalyst,⁷ isotherms differing in character from those for massive copper were obtained. The use of an inert support for the copper was believed to confine the sorptive action to straight adsorption; that is, any secondary factor, such as solution of the hydrogen, was eliminated.

White and Benton⁸ have investigated the poisoning effect of carbon monoxide on massive nickel. This metal, an active hydrogenation catalyst, loses its catalytic activity to a great extent when poisoned with carbon monoxide.⁹ White and Benton found an increase in hydrogen adsorption due to 0.038 cc. of the poison which is maintained at all pressures up to one atmosphere, though there is a slight drawing together of the pure- and the poisoned-hydrogen isotherms at higher pressures. Thus, while their results differ considerably from those obtained with massive

copper by the author, there are two points common to nickel and copper; namely, at low pressure, a small amount of carbon monoxide increases the hydrogen adsorption and a larger amount of carbon monoxide causes little or no increase or even a decrease.

Since there seems to be practically no solubility of hydrogen in nickel it was believed unlikely that the contrast in hydrogen adsorption, such as was found to hold^{6,10} when massive copper and when supported copper were poisoned with the monoxide, would be found to exist also for massive and for supported nickel. The measurements here reported were made upon a quite active sample of supported nickel.

Experimental Part

The apparatus, preparation of gases, the limits of accuracy and the procedure for making a run have been described² (p. 1196). Helium was used as a reference gas. Between runs the catalyst bulb was evacuated at 250° for two hours. Diatomite brick from the same batch as was prepared for the supported copper of a previous study⁷ was employed as a support for the nickel. The brick particles were sized to 8–20 mesh, washed in nitric acid and dried. The brick itself was found to absorb no hydrogen. The granules were impregnated with nickel nitrate solution so as to obtain approximately two moles of nickel per thousand grams of brick. After wetting 50 g. of the brick particles with the nickel nitrate solution the brick was dried at 105° and then heated to 500°. The sample then was placed in a Pyrex bulb and sealed to the apparatus. Reduction in a stream of hydrogen followed. This reduction was carried out for forty-eight hours at 200°, after which the temperature was elevated to 300° and the process continued until the amount of water formed per hour was 1.9 mg. In making a poison run the monoxide was always introduced into the bulb at 0° a half hour before beginning the run.

Results

Runs are numbered in the order in which they were made and the curves of the figures are numbered to correspond to the runs. Three runs were first made on the unpoisoned nickel; these checked each other satisfactorily. Curve 1,2,3,5 of Fig. 1 gives the isotherm for these runs. The smallest amount of poison employed, 0.039 cc., was introduced before each of the runs 4, 6 and 7. The points secured in run 7 fall slightly below the

(1) Presented before the Division of Physical and Inorganic Chemistry at the Rochester meeting of the American Chemical Society, September 6, 1937.

(2) Pease, *THIS JOURNAL*, **45**, 1208 (1923).

(3) Griffin, *ibid.*, **36**, 845 (1934).

(4) Henry, *Phil. Mag.*, **65**, 269 (1835).

(5) Pease and Stewart, *THIS JOURNAL*, **47**, 1235 (1925).

(6) Griffin, *ibid.*, **49**, 2136 (1927).

(7) Griffin, *ibid.*, **57**, 1206 (1935).

(8) White and Benton, *J. Phys. Chem.*, **35**, 1784 (1931).

(9) Green, "Industrial Catalysis," Macmillan Co., New York, 1928, p. 365.

(10) Griffin, *THIS JOURNAL*, **49**, 2136 (1927).

curve established by runs 4 and 6; this was taken to mean that probably not all of the monoxide had been pumped off following the fourth and sixth runs and that therefore run 7 might have been made with slightly more than 0.039 cc. of carbon monoxide on the nickel. However, run 5, made with no poison and immediately following the first run with poison, gave a good check of runs 1, 2 and 3. Curve 8 shows the effect of adding 0.48 cc. of carbon monoxide a half hour before beginning the run and curve 9 the effect of 0.98 cc. of the poison. At this point in the study it was decided to make a run by adding the monoxide in small quantities until it gave a small but definite pressure and then following with hydrogen. After 1.90 cc. of carbon monoxide had been admitted a pressure of about 0.4 mm. was registered. (The smaller amounts of poison employed in the earlier runs never gave a measurable pressure.) The hydrogen adsorption following yielded curve 10. Finally, a hydrogen check run was made which is not shown in Fig. 1 but which gave points that fall between curves 8 and 9 instead of upon curve 1,2,3,5. Obviously it had not been possible to pump off all the poison during evacuations between runs.

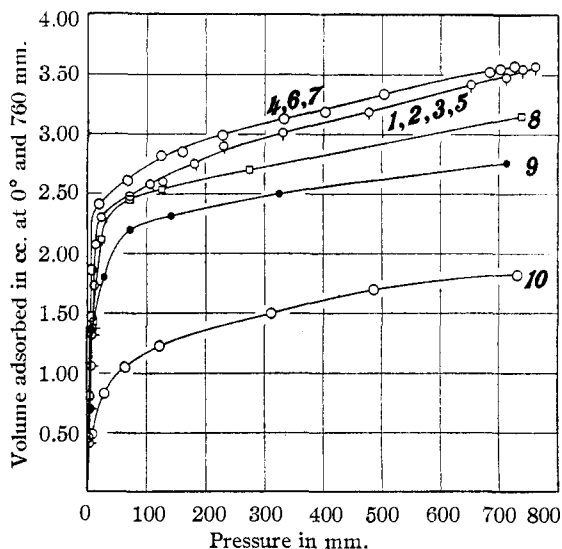


Fig. 1.—Adsorption of hydrogen on supported nickel, two moles of nickel per 1000 g. of brick, poisoned with carbon monoxide at 0°: curve 1,2,3,5, H₂ with no poison; 4,6,7, H₂ with 0.039 cc. CO; 8, H₂ with 0.48 cc. CO; 9, H₂ with 0.98 cc. CO; 10, H₂ with 1.90 cc. CO.

Discussion of Results

The effect of the smallest quantity of the poison on supported nickel is identical with that found by

White and Benton⁸ on massive nickel and with that of the poison on supported copper. That is, carbon monoxide, when used in small quantity, causes an increase in the adsorption of hydrogen. When larger amounts of the poison are employed the supported nickel still appears to give a very small low-pressure increase in hydrogen adsorption although at higher pressures there is a considerable decrease. Figure 2 is drawn on a larger scale than Fig. 1 and shows more clearly the conditions prevailing at lower pressures. It is

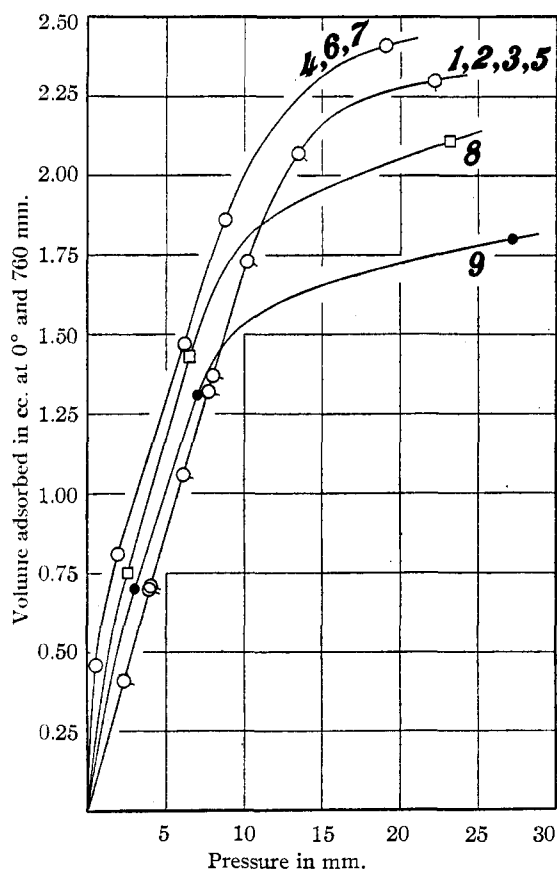


Fig. 2.—Adsorption of hydrogen on supported nickel, two moles of nickel per 1000 g. of brick, poisoned with carbon monoxide at 0°: curve 1,2,3,5, H₂ with no poison; 4,6,7, H₂ with 0.039 cc. CO; 8, H₂ with 0.48 cc. CO; 9, H₂ with 0.98 cc. CO.

true that these curves fall rather close together but examination shows, for example, that at a pressure of 5 mm. the increases in adsorption over that for unpoisoned nickel are as follows: for 0.039 cc. poison, 0.41 cc.; for 0.48 cc. poison, 0.30 cc.; and for 0.98 cc. poison, 0.13 cc. The smallest increase therefore is still above experimental error.

The higher-pressure decreases found for nickel

differ in some respects from the decreases found under similar conditions for hydrogen on supported copper. In the latter case the decrease was found to be equal to the difference between the volume of the poison employed and the low-pressure increase in adsorption. Such is not true for supported nickel. The isotherms show that, as a rule, the decreases in adsorption are not so great, even at atmospheric pressure, as the amount of poison used, though this was roughly so when 0.48 cc. of poison was used. It should be emphasized that at the beginning of run 8 there probably was more than 0.48 cc. of carbon monoxide due to inability to pump off some of the poison of previous runs. Likewise, just before making run 9 there probably was somewhat more than 0.98 cc. of poison on the nickel. It would seem from the "unpoisoned" run following run 10 which gave points falling between curves 8 and 9 that at this time there was between 0.5 and 1 cc. of poison present upon the nickel. Apparently then there is some carbon monoxide, less than 1 cc., which cannot be pumped off in two hours at 250° once larger quantities have contacted the nickel.

The behavior of the supported nickel may be accounted for in the following manner. On the surface there are only a few very active centers. These are the ones which have the strongest attraction for carbon monoxide, and thus when the smallest amount of poison is used it is they which attach the monoxide. In turn, it is this strongly adsorbed monoxide which is responsible for the later, indirect linking of several hydrogen units, thus accounting for the low-pressure increase in the hydrogen adsorption. In addition to these few centers of extraordinary activity there are upon the nickel surface many centers which are less active and which differ in activity among themselves. When a larger amount of poison is used many of them (insofar as carbon monoxide is available) also adsorb carbon monoxide, and, of them, a fraction is capable of causing the indirect linkage of one unit of hydrogen, thus slowly building up a second adsorbed layer as suggested by White and Benton.⁸ As a result, after the initial increase in adsorption, there follows a decrease, the decrease being more or less pronounced depending upon the proportion of centers, which, while able to adsorb a hydrogen molecule in the absence of monoxide, are of so small activity as to fail to build up a second layer consisting of hydrogen, once they have acquired a monoxide molecule.

(If *all* centers other than those of maximum activity had this power of contributing toward a second layer the result for all poisoned runs should be an adsorption greater than that for an unpoisoned run by a constant amount at all pressures. If *none* had this power the adsorption would be greater at low pressures and less at higher pressures, the decrease being equal to the volume of poison less the low-pressure increase. Thus it appears that a fraction of those centers other than those of maximum activity possesses the property of contributing to the second adsorbed layer.)

This view is substantiated by a study of the rates of adsorption observed. In the case of hydrogen adsorption on copper, either massive or supported, any change in rate due to the poison, has been to hasten the attainment of equilibrium, certainly not to slow down the process. In the present study, as in that of White and Benton⁸ with massive nickel, the effect of the poison upon the rate of adsorption was distinctly to decrease the rate. In runs with 0.039 cc. of poison on supported nickel it was found that equilibrium was established quickly after each addition of hydrogen. In runs employing greater amounts of poison this was not the case. On the contrary it was quite noticeable that though equilibrium followed quickly after the first two small additions of hydrogen in run 8 and after the one initial addition of hydrogen in run 9, thereafter in both cases the attainment of equilibrium was very much slower. This is taken as strong evidence that the use of larger quantities of poison had covered so many centers of less than maximum activity that the slower process of building up an adsorbed layer of hydrogen above the monoxide had begun early in these runs, and earlier in run 9, with its greater amount of poison, than in run 8. The rapid rate of equilibrium noticed throughout the runs employing 0.039 cc. of poison, and found also after one or two additions of hydrogen in runs employing larger amounts of monoxide, logically may be attributed (except for the low-pressure increase) to direct adsorption of hydrogen to metal. Thus, assuming that the decreased rate soon manifesting itself in runs 8 and 9 indicates that the adsorption of a second layer is in process, it appears that a second adsorbed layer is begun only after few if any unoccupied centers are left upon the nickel surface.

Numerous references¹¹ have been made to the

(11) (a) Maxted, *J. Chem. Soc.*, **119**, 1283 (1921); (b) Pease, *This Journal*, **46**, 2301 and 2303 (1923); (c) ref. 5, p. 1230; (d) ref. 6, p. 2144; (e) ref. 8, p. 1788.

relation of catalytic activity to adsorption of reactants. While mercury poisoning,^{2,11b} heat treatment^{11b} or cyanogen poisoning³ gives a decrease in both catalytic activity and in adsorption at all pressures, carbon monoxide, when used in small amounts on either copper or nickel, while decreasing the catalytic activity, increases the low-pressure adsorption. Obviously it is the condition of activation of the adsorbed reactants rather than the extent of the adsorption which is most important in regard to catalysis.

Summary

1. Adsorption measurements have been made

at 0° for hydrogen on a supported nickel catalyst poisoned with carbon monoxide.

2. A small quantity of poison causes an increase of hydrogen adsorption at all pressures up to one atmosphere.

3. A larger amount of poison gives a slight low-pressure increase and a higher-pressure decrease of adsorption.

4. Larger amounts of poison decrease the rate of adsorption.

5. An interpretation of the results has been outlined indicating a capacity for some but not all of the active centers of nickel to adsorb hydrogen as a second layer above the poison.

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Fluorinated Derivatives of Propane

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The papers previously published by this Laboratory¹ have reported the effects of fluorine atoms in derivatives of methane and of ethane. The extension of the study to the propane series was undertaken to see whether the previously reported effects could be generalized, to learn the behavior of fluorine in newly available positions, and to observe the effect of increased distances between the various groups in the molecule.

Previous experience suggested that it would be simplest to start the research by subjecting $\text{CCl}_3\text{CCl}_2\text{CCl}_3$, $\text{CHCl}_2\text{CCl}_2\text{CCl}_3$ and $\text{CCl}_3\text{CHCl}-\text{CCl}_3$, respectively, to fluorination with antimony fluoride. However, after successfully replacing from one to four atoms of chlorine by the same number of fluorine atoms, it was found that the position of the fluorine atoms could not be demonstrated and therefore the publication of this phase of the work was withheld until experimental proof (recently obtained) would confirm the formulas proposed for the new compounds.

Since the monofluoropropanes are known² and exhibit the customary poor stability of alkyl monofluorides, and since the fluorination of a terminal CHCl_2 or CCl_3 group would be little more than an extension of previous work, it was decided to synthesize a difluoride with a CF_2

group in the middle of the molecule, and to do it by subjecting $\text{CH}_2\text{CCl}_2\text{CH}_3$ to fluorination with antimony fluoride. The replacement of chlorine by fluorine in a CCl_2 group isolated in the center of the molecule is a new type of reaction. It proved faster and more complete than expected. The 2,2-dichloropropane and the antimony salt react, even without catalyst, at room temperature. A small amount of bromine accelerates the reaction enormously, and is recommended, while a small amount of antimony pentachloride is frequently enough to cause the reaction to escape control. The resulting product, $\text{CH}_2\text{CF}_2\text{CH}_3$, boils about 0°, and consequently leaves the reaction field as soon as it is formed, thus allowing the reaction to proceed rapidly to completion; it carries with it from 5 to 7% of intermediate product, $\text{CH}_3\text{CClFCH}_3$.

In its general behavior, this reaction is rather similar to the fluorination of CCl_3H_2 with antimony fluoride, and that of CH_3CHBr_2 with mercuric fluoride. It differs from the fluorination of CH_3CHCl_2 with antimony fluoride because CH_3CHCl_2 undergoes much decomposition when allowed to be fluorinated so rapidly.

The point was thus made that the ease and completion of the fluorination were due to the fact that all halogen atoms were gathered on a single carbon atom, in a group isolated within the molecule; this point was confirmed by three

(1) THIS JOURNAL, **56**, 1726 (1934); **58**, 402, 404, 882, 884, 887, 889 (1936); **59**, 1200, 1400 (1937).

(2) Meslans, *Compt. rend.*, **108**, 352 (1889); *Ann. chim.*, [7] **1**, 363 (1894).