molecules of coördination.[35] The atomic ions in long periods of the Periodic Table should then be considered as of the molecular type. Presumably magnetic influences on band spectra (Zeeman effect, Paschen-Back effect) should be invoked to study them and not the anomalous Zeeman effect on atomic ions as has been done heretofore.

The writer expresses with pleasure his deep obligation to Professor G. N. Lewis for his suggestions and interest in this research. He also wishes to thank Professor W. F. Giauque for his interest in this work.

Summary

1. A new method has been developed for measuring magnetic susceptibilities.

2. The magnetic susceptibilities of the positive quadrivalent, trivalent, and bivalent ions of vanadium have been measured.

3. It appears that: (*a*) the quadrivalent vanadium ion has 1 integral Bohr magneton; (*b*) the trivalent vanadium ion has 2 integral Bohr magnetons; (*c*) the bivalent vanadium ion has 3 integral Bohr magnetons.

4. The above results do not agree with any current theory based upon the quantum theory and anomalous Zeeman effect. A reason for this discordance is suggested.

5. Some measurements on diamagnetic substances are included.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

STUDIES OF METHANOL CATALYSTS. I

BY HUGH STOTT TAYLOR AND GEORGE B. KISTIAKOWSKY[1]

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During the past few years the technique of hydrogenation catalysis in industry has undergone a revolutionary development. Until recently, hydrogenation catalysts were confined practically exclusively to a very restricted series of metals, among which platinum, nickel, copper and iron were the most important. With the industrial development of methanol synthesis, this series of catalysts has expanded fundamentally in that it has been shown that a variety of hydrogenation processes may be carried out in contact with various oxides or mixtures of the same. This extension

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[35] Such a condition undoubtedly obtains among the ions having their outer electronic shells incompletely filled. On the other hand, among the ions of the rare earths the electrons responsible for the magnetic moments are far within the kernel and are surrounded by shells having their full complement of electrons. Under such conditions, the water molecules do not form an integral part of the ions and apparently their influence is slight, as is shown by the close agreement between the values calculated from spectroscopic studies and those observed in solution.

[1] International Research Fellow.

was an obvious development of the observations of Sabatier and succeeding workers on the activity of such oxides as dehydrogenating catalysts and on the conclusion from thermodynamic reasoning that a catalyst for a reaction in a given direction is a catalyst also for the reverse reaction.[2]

Thus far, the study of oxide catalysts for hydrogenation has been almost exclusively technical; little inquiry has been made into the fundamental aspects of the problem. The use of oxide catalysts for dehydrogenation processes has, on the other hand, been the object of a considerable amount of scientific study with a view to elucidating the mechanism of the catalytic action.[3] As yet, however, the problem of mixed dehydrogenation and dehydration is still a matter for lively discussion. We have accordingly ventured to initiate a systematic study of oxide catalysts as hydrogenation agents, along the lines that have proved successful in this Laboratory when applied to metal catalysts. It was hoped that something could be learned, by such studies, concerning the properties of oxide catalysts in general. The reason for their superiority over metal catalysts for methanol synthesis might also be elucidated. The present paper records the results of adsorption studies with two typical methanol catalysts, zinc oxide and a mixture of zinc and chromium oxides.

The adsorption of gases by oxide catalysts has already been the subject of some little study. Benton[4] measured the adsorptive capacity of various oxide oxidation catalysts for hydrogen and carbon monoxide. Lazier and Adkins[5] attempted to correlate the dehydrogenation-dehydration ratio of zinc oxide with the adsorption of this oxide and other catalysts but concluded that there existed no simple relationship between the two factors. Hoover and Rideal[6] studied the adsorptions of hydrogen and ethylene on thoria catalysts in order to learn something of the dehydrogenation-dehydration activity of thoria for ethanol. In our work, in ascertaining the adsorption of hydrogen and carbon monoxide on zinc oxide and on a mixture of zinc and chromium oxides, we were studying the capacity of a single oxide catalyst and of a well-known active methanol mixed oxide catalyst for the only two reactants of the methanol synthesis. We have also measured, in one case, the adsorption of carbon dioxide. Our results have abundantly justified the effort.

[2] See Rideal-Taylor, "Catalysis in Theory and Practice," 2nd edition, The Macmillan Company, New York, **1926**, p. 20.

[3] For a summary of this work see (a) Bancroft, Second Report of the Committee on Contact Catalysis; (b) Bischoff and Adkins, This Journal, **47**, 807 (1925); (c) Taylor, Fourth Report of the Committee on Contact Catalysis, *J. Phys. Chem.*, **30**, 185 (1926); (d) Taylor, Fourth National Colloid Symposium, Chemical Catalog Co., Inc., New York, **1926**, p. 25.

[4] Benton, This Journal, **45**, 887, 900 (1923).

[5] Lazier and Adkins, *J. Phys. Chem.*, **30**, 353 (1926).

[6] Hoover and Rideal, This Journal, **49**, 116 (1927).

Experimental Procedure

Apparatus.—The apparatus was essentially that used in the earlier experimental studies of adsorption on metal catalysts.[7] A vessel containing the catalyst was connected through three-way stopcocks with a manometer, gas buret and pump system for evacuation purposes. In the present experiments the latter consisted of two mercury vapor pumps in series with a high-vacuum oil pump as fore-vacuum. The free space in the catalyst vessel was determined by a series of measurements of volume and pressure of a non-adsorbed gas, for example, nitrogen, at a controlled temperature. From the volumes of hydrogen or carbon monoxide required to fill the vessel to a given pressure at the same temperature, the extent of adsorption at this pressure could be determined.

Catalysts Employed.—Three samples of a single preparation of zinc oxide and one of a mixed zinc oxide-chromium oxide were studied. The zinc oxide was prepared by ignition at 450°, special precautions being taken to ensure that the catalyst was entirely free even from traces of alkaline or acid ions, since these may both materially alter the characteristic of the catalyst.[3c,d] The mixed zinc oxide-chromium oxide was of the type described in patents of the Badische Company,[8] obtained by precipitating zinc chromate from a solution of the nitrate, thoroughly washing the precipitate, drying and igniting at 450°. It contained approximately two moles of ZnO to one mole of Cr_2O_3. With both these catalysts methanol can be readily made from mixtures of hydrogen and carbon monoxide; it is well known, however, that the mixed catalyst is far superior to the single oxide.[9] The zinc oxide samples were, respectively, 39, 39 and 32 g. The zinc oxide-chromium oxide sample weighed 25 g.

Experimental Results.—Our early experiments showed that the adsorptive capacity of a sample of the oxide was very sensitive to the cleanness of the surface. It was soon found that both zinc oxide and the mixed oxide catalyst showed no adsorption for either hydrogen or carbon monoxide even after evacuation for one hour at 300° in the high-vacuum system already described. Between 300 and 400°, however, a rapid evolution of adsorbed *water vapor* and *carbon dioxide* occurred, after which the surface of the catalyst immediately revealed pronounced adsorptive capacity for both gases.

Fig. 1 shows graphically the increase in adsorptive capacity for carbon monoxide of zinc oxide, No. 1, consequent on the increasing cleanliness of the surface, due to better evacuation. The curves 1a and 1b, etc., are corresponding runs at 100 and 0°. The initial runs with this gas,

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[7] See, for example, Pease, THIS JOURNAL, **45**, 1196 (1923).

[8] Brit. pat. 227,147; U. S. pat. 1,558,559.

[9] Patart, International Conference on Bituminous Coal, Carnegie Inst. Tech., 1926, p. 141.

after pumping off at 200°, showed identical values for nitrogen and carbon monoxide, indicating zero adsorption of the latter. The succeeding results, recorded in the order of their performance, show the progressive increase in the adsorptive capacity of the catalyst. Curves 3a and 3b were obtained after evacuation for three hours at 510°. One result with hydrogen, 4a and 4b, is also included for comparative purposes. We have found that portions of both gases are adsorbed very tenaciously and are only removed from the surface in the oxidized condition either as carbon dioxide or water vapor, partial reduction of the catalyst to a corresponding amount occurring. At first we were inclined to ascribe all of the increase in adsorptive capacity to this reduction process but we now have full evidence that even unreduced but clean surfaces of these catalysts show large adsorptive capacity for the two gases.

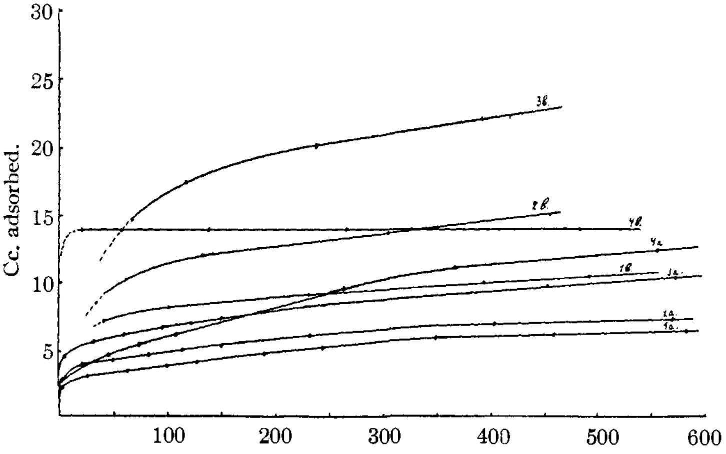

Fig. 1.

The reduction produces gray spots in the otherwise white zinc oxide. The reduction process is very probably an interface reaction as with copper oxide[10] since the gray spots grow with increased treatment. At first we considered the possibility that the dark spots might be due to catalytic decomposition of carbon monoxide by the reaction, $2CO = CO_2 + C$, carbon being deposited in the oxide. Our experiments on zinc oxide No. 2, carried out exclusively with hydrogen, disposed of this possibility since here again the gray specks formed. The adsorption of hydrogen on this catalyst is shown in Fig. 2, Curve I, after evacuation at 450°. Since we found that a treatment at 500° with oxygen partially destroyed the adsorptive capacity (Curve II) and since oxygen was partially consumed in the process, we asumed this to be evidence in favor of adsorption

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[10] Pease and Taylor, THIS JOURNAL, **43**, 2179 (1921).

by reduced zinc nuclei in the mass. An extended treatment with oxygen for 18 hours, followed by evacuation at 500°, gave a surface which subsequently showed (Curve III) high adsorption for hydrogen, thus discrediting the theory that adsorption is due *solely* to metal atoms.

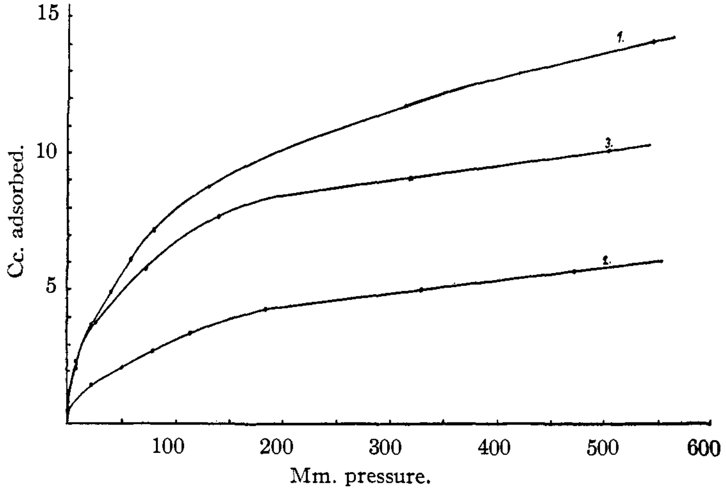

Fig. 2.

We disposed of this metal theory of adsorption by evacuating zinc oxide No. 3 thoroughly at 500° before bringing the sample into contact with any reducing gas. Curve I in Fig. 3 shows the high adsorptive capacity attained. With this catalyst we also showed the adverse effect of too high a temperature, since Curve II shows the diminished adsorption after evacuation at 600°. This sample was very dark in color after this treatment.

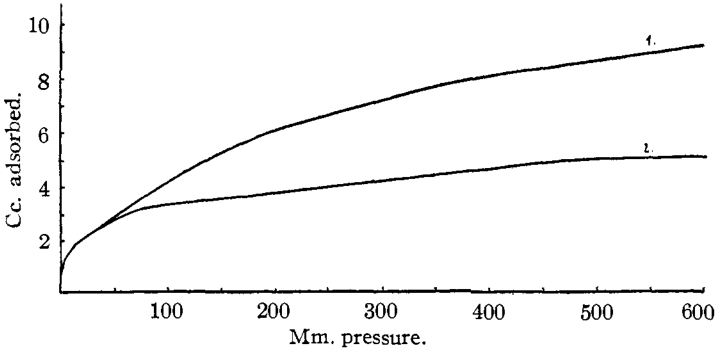

Fig. 3.

In order to compare adsorptions on zinc oxide and on the mixed oxides we next made measurements on the zinc oxide-chromium oxide sample.

This adsorbed neither gas after evacuation at 200 or 300°. After half an hour of evacuation at 400°, Curve I, Fig. 4, with hydrogen was obtained. A further half hour of evacuation at 400° gave with hydrogen the results in Curve II. Curve III records results with carbon monoxide after a further half hour of evacuation at 400°. Curve IV gave hydrogen adsorption after one further evacuation for half an hour at 400°. It is very definitely established from these results that the hydrogen adsorption is more marked than that of carbon monoxide on the mixed oxide catalyst, while the reverse is true on the single zinc oxide (Fig. 1).

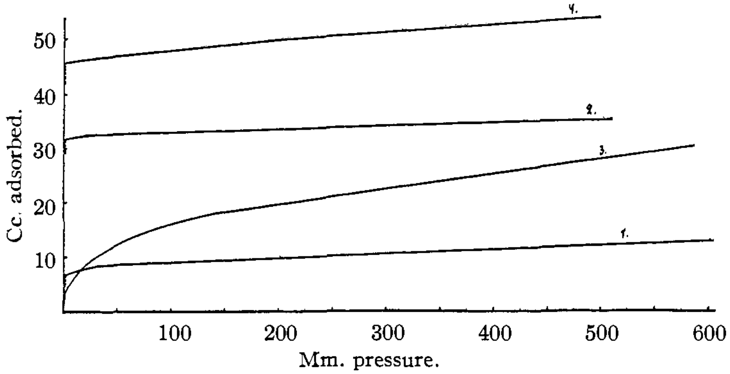

Fig. 4.

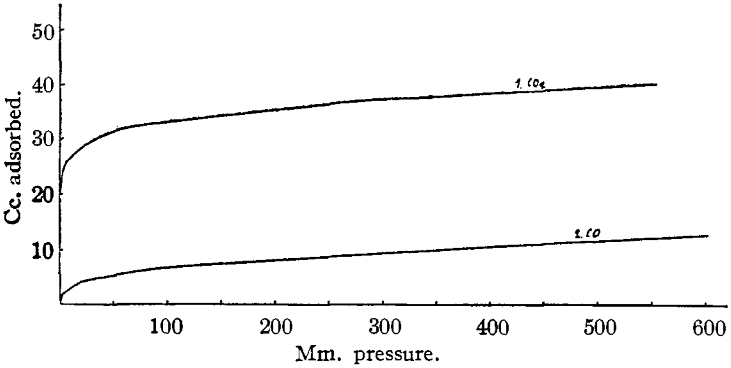

Fig. 5.

Fig. 5 shows the extraordinary adsorption of carbon dioxide by the zinc oxide catalyst. Thus the admission of 21.70 cc. of this gas to the catalyst at 100° produced a pressure of only 5 mm., and this pressure may be due in part to impurities, since tank carbon dioxide only was used; in the preceding runs with hydrogen and carbon monoxide the same amount of these gases had produced pressures of approximately 250 mm. This experiment confirms our observation in the evacuation process of the tenacity with which both carbon dioxide and water are adsorbed.

Discussion of Results

The experimental results demonstrate conclusively that zinc oxide and zinc oxide-chromium oxide catalysts show the same type of adsorption for the reactants of the methanol synthesis that is shown by metal catalysts in hydrogenation reactions. The type of adsorption isotherm is exactly the same in the two cases. There is strong adsorption at low pressures with relative saturation of the surface at these low pressures and little increase in adsorption with a many fold increase in pressure. This latter is readily appreciated by observing the nearly horizontal portions of the curves in the several diagrams.

The astonishing feature of the studies is, however, the extraordinary capacity of the catalysts for adsorption of the gases in question. They show many times the adsorptive capacity of the metal catalysts under the same conditions. This is readily seen from the appended Table I, which gives a few selected data of maximum adsorptions found in the earlier studies at Princeton on metal catalysts, under a variety of conditions, as well as some typical results from the present research.

TABLE I

ADSORPTIONS PER 100 G. OF CATALYST

Catalyst	Cc. H_2 adsorbed	Temp., °C.	Press., mm.	Author
Reduced copper	13.4	110	760	Taylor and Dew
Reduced copper	45	0	760	Taylor and Beebe
Reduced nickel	130	0	760	Taylor and Beebe
$ZnO-Cr_2O_3$	184	100	1	Taylor and Kistiakowsky
ZnO	50	0	20	Taylor and Kistiakowsky

The table shows that at 100° and 1 mm. pressure a zinc oxide-chromium oxide catalyst has a greater adsorptive capacity for hydrogen than the best nickel catalyst we have ever prepared possesses at 0° and 760 mm., and a 13-fold better adsorptive capacity than a very active sample of reduced copper at 110° and 760 mm. pressure. The extremely high adsorptive capacity at low pressures thus revealed implies a very considerable amount of active catalytic surface per unit weight of material. This implies a corresponding insensitiveness to poisons and foreign materials in the gas mixture for such oxide catalysts. It may be concluded that such catalysts will tolerate concentrations of reversible poisons many fold greater than those which, with metal catalysts, produce a given diminution in catalytic activity. This is a very important industrial consideration.

Both the curves and the table show that the active surface in a mixed zinc oxide-chromium oxide catalyst is far greater than that of a corresponding weight of zinc oxide catalyst. There is, therefore, no element of surprise in the statements in both patent and technical literature that such mixed oxide catalysts are preferable to the single zinc oxide. Whether the change in ratio of adsorption α_{H_2}/α_{CO}, with change from a single to a mixed oxide catalyst is significant in the synthesis of methanol cannot be deduced from these experiments. It will be noted that the ratio α_{H_2}/α_{CO} changes from approximately unity to approximately 0.5 at, for example, 100 mm. pressure. Whether this ratio change is significant may possibly be revealed by kinetic studies of the methanol process which are now in progress.

The very pronounced adsorption of carbon dioxide shown in Fig. 5, and the observation that both water vapor and carbon dioxide are so strongly retained by these catalysts that no measurable adsorptions were shown by samples evacuated at or below 300°, indicate that both gases are temporary poisons for these catalysts in methanol synthesis. It is significant that the activity of these methanol catalysts begins in the temperature range in which free evaporation of carbon dioxide and water vapor occur.

The rapid saturation of the surface at low pressures or the small change in total adsorption at higher pressures is characteristic of adsorptions involving high heats of adsorption. Rough calculations from the adsorption isotherms at 0 and 100° confirm this conclusion and indicate heats of adsorption of the same order of magnitude as are involved in adsorption of the gases on metal catalysts and considerably greater than the heats of liquefaction of the gases. We are attempting to measure these heats of adsorption directly to ascertain their precise magnitude and to discover whether they indicate special processes of activation.

The experiments recorded here are in complete harmony with the known activity of zinc oxide and zinc oxide-chromium oxide catalysts as agents for the synthesis of methanol. They suggest, however, a whole series of further investigations designed to ascertain why other oxides, for example magnesium oxide, cannot be utilized for such purposes with efficiency. The answer to such problems should promote a fuller understanding of the general problem of contact catalytic action. With some of these questions we are now engaged.

Summary

1. Adsorptions of hydrogen, carbon monoxide and carbon dioxide on two methanol catalysts, zinc oxide and zinc oxide-chromium oxide, have been measured at 0 and 100°.

2. It has been shown that, to obtain such measurements, the catalyst surface must be cleaned of adsorbed water vapor and carbon dioxide by evacuation at 400°.

3. It has been shown that both catalysts have adsorptive capacities per unit weight considerably greater than those of most metal catalysts.

4. The adsorption of both hydrogen and carbon monoxide is pro-

nounced at very low pressures and rapidly reaches saturation capacity independent of further pressure increase.

5. The experiments indicate that the heat of adsorption is considerably greater than the heat of liquefaction and attains values characteristic of heats of adsorption on metal catalysts.

6. The mixed oxide catalyst shows greater adsorptive capacity than the zinc oxide in harmony with its higher order of catalytic activity.

7. The experimental results generally are shown to be in agreement with the known facts concerning methanol synthesis on these catalysts.

PRINCETON, NEW JERSEY

THE STANDARDIZATION OF PROFESSOR T. W. RICHARDS'S THERMOCHEMICAL DATA

BY WOJCIECH SWIETOSLAWSKI AND J. BOBINSKA

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Professor T. W. Richards has authorized one of us to recalculate the values of the heats of combustion of organic compounds as examined by him, in order to standardize them and make them comparable with the standard unit now accepted in thermochemistry. As benzoic acid is established as this unit, the base for that comparison is the heat of combustion of 1 g. of benzoic acid weighed in a vacuum, 6319 cal. $_{15^\circ}$, or 1 g. of this acid weighed in air, 6324 cal. $_{15^\circ}$.

Discussing this question personally with Professor Richards, we accepted that, in the first column of each table containing the standardized thermochemical data, there must be cited the unchanged values, as given by the author in his original publication. Naturally, these values must be expressed in the same units used by the author. Therefore, we give in our two tables the values expressed in 18° calories or in kilojoules, respectively.

According to the different dates of publication, the measurements of Professor Richards are divided into two groups. The first series contains the determinations made with R. H. Jesse in 1910; the second one contains the rest, carried out after 1915, that is to say, after the appearance of Dickinson's investigations which established with great accuracy the heats of combustion of benzoic acid, cane sugar and naphthalene. This division is connected with the manner of determination of the heat capacity of the calorimetric system. In 1910, Professor Richards and R. H. Jesse carried out this determination using cane sugar as a standard substance. They accepted for the heat of combustion of this compound the value 16,545 kilojoules, proposed in 1909 by E. Fischer and Wrede. In the other papers, published after 1915, Professor Richards accepted the figures given by Dickinson.