[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Thermal Migration in Supported Copper Catalysts

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Development of a more sensitive magnetic susceptibility balance of the Faraday type has made possible extension of observations on supported cupric oxide, and of supported copper, on gamma alumina down to copper concentrations of less than 0.5%. It has been confirmed that thermal inactivation (sintering) of this system is not accompanied by copper partical aggregation. It has also been shown that supported cupric oxide is structurally different from a mechanical mixture of crystalline cupric oxide plus cupric ions at infinite magnetic dilution.

The word "sintering" is often used in discussions on contact catalysis. It implies a change brought about by heat, and attended with a loss of activity and of specific surface. Sintering is generally found to occur above the Tammann temperature, and far below the melting points of the catalyst components. Thus Shekhter, *et al.*,[2] have reported microcrystal growth in supported metal catalysts, such as platinum on asbestos, at temperatures of a few hundred degrees.

This kind of investigation lends itself to magnetochemical study because the magnetic susceptibility of many catalyst components is strongly dependent on particle size in the range of sizes often encountered in active catalysts. A preliminary study of supported copper by this method[3] failed to reveal any surface migration of copper atoms leading to aggregation. But the development of apparatus for measuring susceptibilities with a ten-fold increase of sensitivity, and for conducting reductions and oxidations *in situ*, suggested a reinvestigation of this problem.

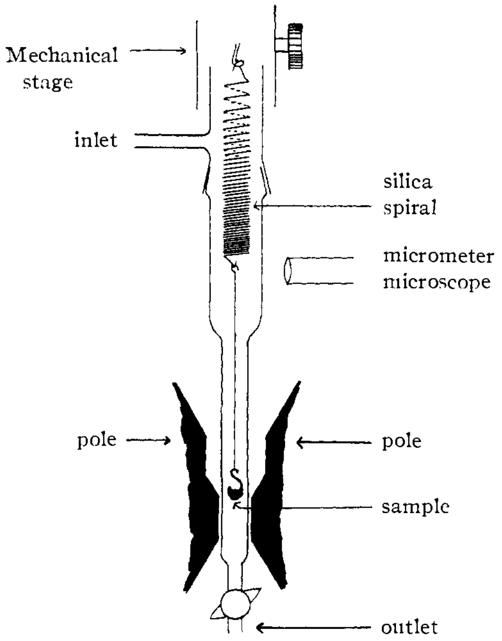

Fig. 1.—Faraday balance.

Experimental Methods

Magnetic Susceptibility Measurements.—The method used is essentially that of Faraday. The sample hangs in a strong field which possesses a gradient in the vertical direction. The sample is suspended from a silica spiral in a manner similar to a McBain–Bakr sorption balance. Deflection of the sample, on application of the magnetic field, is observed with a micrometer microscope. The silica spiral and the surrounding glass tubing are attached to the mechanical stage from a microscope. The stage is adapted for convenient vertical motion of the whole system relative to the magnet. The apparatus is shown diagrammatically in Fig. 1.

The field and gradient were obtained by an electromagnet with poles cut in the manner suggested by Sucksmith.[4] One pole face in profile is shown in Fig. 2. In an effort to increase sensitivity the angle ϕ shown as 15° was increased from the 5° recommended by Sucksmith. A compromise of 10° has since been found to give good sensitivity with more convenience. The minimum pole interspace was 1.1 cm. Maximum fields of 20,000 oersteds were obtained.

The force acting on the small sample in this apparatus is given by $f = m\chi H \, \partial H/\partial s$ where m is the mass of the sample, χ the susceptibility of the sample per gram, H is the field

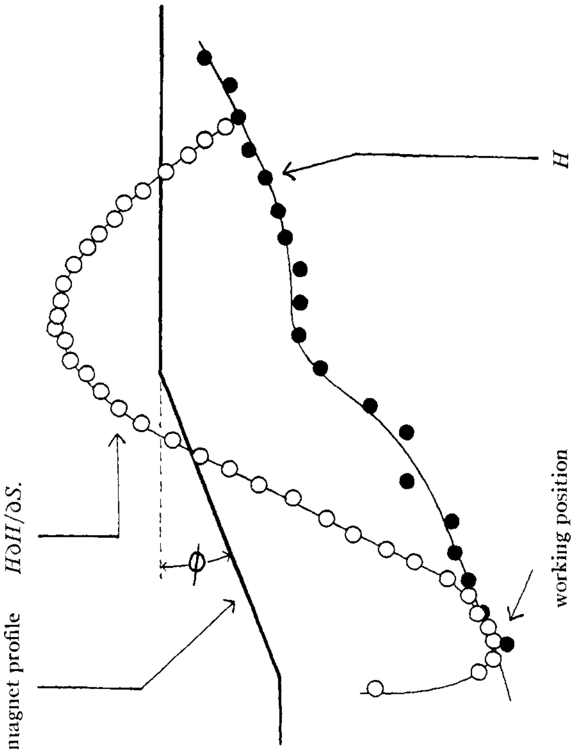

Fig. 2.—Magnetic field and product of field and gradient.

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[1] This work was initiated under contract with the Office of Naval Research and continued on the Union Carbide and Carbon Fellowship in Physical Chemistry, receipt of which is gratefully acknowledged. This is the fourteenth paper from this Laboratory on the susceptibility isotherm and related subjects. The thirteenth appeared in THIS JOURNAL, **76**, 346 (1954). Present address, Ketchikan Pulp Co., Ketchikan, Alaska.

[2] A. B. Shekhter, A. I. Echeistova and I. I. Tret'yakov, *C. A.*, **44**, 915 (1950); **45**, 3216 (1951).

[3] P. W. Selwood and N. S. Dallas, THIS JOURNAL, **70**, 2145 (1948).

[4] W. Sucksmith, *Phil. Mag.*, **8**, 158 (1929).

strength, and $\partial H/\partial s$ the field gradient. It is, therefore, necessary to obtain $H\,\partial H/\partial s$ in a region where this product is uniform and large. Most inorganic solids contain traces of ferromagnetic impurities. It is necessary, for this reason, also to obtain H as a function of current in the magnet, so that extrapolation may be made to zero reciprocal field.

The product $H\,\partial H/\partial s$ was obtained by calibration with pure cane sugar, the susceptibility of which was taken as -0.566×10^{-6} per gram.[5] Correction must, of course, be made for the diamagnetism of the glass or silica bucket used to hold the sample. The sample moves on application of the field, hence the procedure followed is to apply the desired field, move the sample to a fixed position as observed in the micrometer microscope, remove the field, and observe extension of the silica spiral. This operation, extended to complete vertical mapping of $H\,\partial H/\partial s$, is conveniently done with the aid of the mechanical stage referred to above. The results are shown in Fig. 2.

The field, H, alone may be obtained by the Quincke method, using nickel chloride solution as a calibrating agent. A glass or, better, silica rod mounted in the fashion of the Gouy method will also serve to obtain the field as a function of current as at the working position indicated in Fig. 2.

The samples used ranged in weight from 20 to 40 mg. The several silica spirals used averaged in sensitivity 0.2 mm. extension per mg. Over-all precision with the catalyst samples used was 0.1 to 0.6% of the measured susceptibility. All measurements, except a few noted below, were made at room temperature, near 25°. The surrounding atmosphere was nitrogen which had been passed over copper turnings at 600°, then dried over magnesium perchlorate.

This apparatus is convenient for carrying out reactions such as oxidation and reduction *in situ*. The mechanical stage permits horizontal motion of the sample. A small tubular furnace may be placed around the sample for such heat treatment as may be desired. The atmosphere surrounding the sample may readily be changed through flexible tubing attached to the apparatus as shown in Fig. 1.

Preparation and Analysis of Materials.—The substances investigated were alumina, cupric oxide and copper. So-called γ-alumina used throughout the study was prepared as described by Eischens and Selwood.[6] The specific surface area of this alumina as measured by nitrogen adsorption (B.E.T.) was about 250 m.^{2}. The apparent susceptibility of alumina is markedly dependent on the presence of paramagnetic and, especially, of ferromagnetic impurities. It also depends on the water content. For instance, an oven-dried alumina with a susceptibility of -0.378 ($\times 10^{-6}$) per gram was ignited at 500° for three hours. The susceptibility became -0.357, the change being roughly proportional to the water lost.

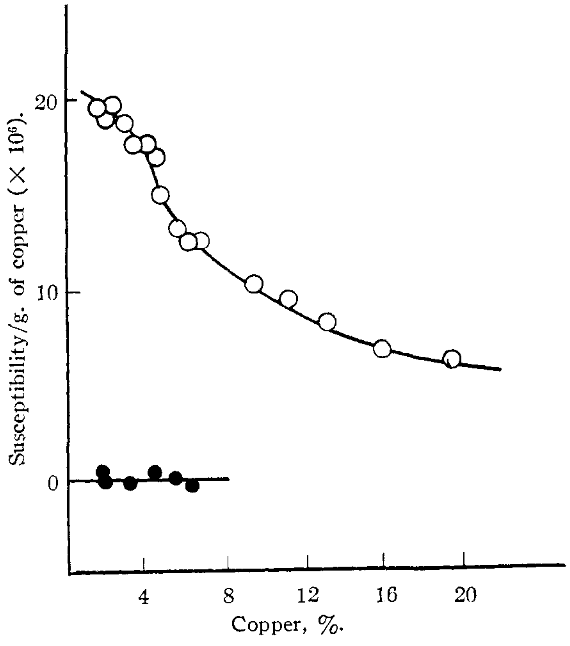

Fig. 3.—Susceptibility isotherm (25°) for supported copper on alumina: O, oxidized form; ●, reduced form.

In the interest of high precision it was necessary that the copper used in this study should be as nearly free from ferromagnetic impurity as possible. The expedient of quenching the sample from a high temperature, thus forcing the ferromagnetic impurity into solid solution, is obviously not practical here because the catalytically active surface would be destroyed.

C.P. copper generally shows strong evidence of ferromagnetism, and this may even be true of samples which seem to be spectroscopically free from iron, nickel or cobalt. Magnetically pure copper can sometimes be prepared directly from selected sheet copper, or it may be purified by repeated electrolysis.[7] A convenient alternative method[8] is to dissolve the copper in nitric acid, to form the tetrammine complex by the addition of excess ammonium hydroxide, and to add a dilute solution of aluminum nitrate. The aluminum hydroxide formed apparently coprecipitates ferromagnetic-forming impurities because, after the precipitate of aluminum hydroxide is filtered, the solution may be neutralized and the precipitate of cupric hydroxide filtered, washed, ignited and reduced to form magnetically pure copper.

Supported cupric oxide was obtained in the usual manner by impregnation of γ-alumina with cupric nitrate solution. The mixture was filtered, dried and ignited at 390° for 24 hours. The amount of copper present in the product could be varied at will by varying the concentration of the cupric nitrate solution.

Analysis of supported cupric oxide samples was done by dissolving the samples in sulfuric acid, then electroplating the copper on to weighed platinum electrodes.

The supported cupric oxide samples gave an X-ray diffraction pattern for cupric oxide, in addition to that for γ-alumina, at copper concentrations in excess of 7.5%. As previously reported, the sample colors ranged from yellow-green at the lowest concentrations studied ($\sim$0.5% Cu) through blue-green to gray at the highest concentrations ($\sim$20% Cu). Samples reduced in hydrogen were jet black at all copper concentrations except the highest.

Details concerning the procedure for reducing the supported oxides are given below.

Results

Results are reported first for the "susceptibility isotherm" of supported cupric oxide, then for reduced supported copper, then for samples which have been reduced, sintered and reoxidized. Finally, some data are given for lower temperatures.

A typical isotherm for the supported cupric oxide system on alumina at 23° is shown in Fig. 3. This is similar in general form to that previously reported for this system by Selwood and Dallas, but the copper concentration limit is extended down to 1.42%. The plateau of susceptibility per gram of cupric ion at low concentrations is confirmed. It should be emphasized that this is the only system, of some eight or ten studied in this Laboratory, in which a plateau suggesting infinite magnetic dilution is found. It also was found that the exact shape and height of the isotherm depend, as expected, on the purity and formulation of the support, and to some degree on the magnetic purity of the solution used for impregnation. The limiting susceptibility per gram of cupric ion at infinite dilution corresponds to a magnetic moment of 1.7 Bohr magnetons, in excellent agreement with the

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[5] This value is based on studies by Dr. Carl Pitha in this Laboratory, and is in agreement with the average of the three principal susceptibilities given in the "International Critical Tables."

[6] R. P. Eischens and P. W. Selwood, THIS JOURNAL, **69**, 1590 (1947).

[7] H. Morris and P. W. Selwood, *ibid.*, **62**, 2245 (1943).

[8] Developed in this Laboratory by Dr. Fred N. Hill.

spin-only moment for the one unpaired electron in the cupric ion.

Reduced copper–alumina samples were prepared by reduction with hydrogen at 550 to 650° for eight to ten hours. All reductions were carried out *in situ* in the magnetic balance. Figure 3 includes the susceptibility per gram of reduced copper supported on alumina down to a copper concentration of 0.488%. Most of these reduced samples gave susceptibilities which were independent of field strength. A typical sample containing 5.43% of copper had a susceptibility of 0.775($\times 10^{-6}$) per gram of catalyst sample in the oxidized state. This was changed to −0.334 in the reduced state. It was noted that the highest and, especially, the lowest concentrations of copper were more difficult to reduce than those of intermediate concentration. It also was noted that cooling the reduced samples in hydrogen produced the same final susceptibility as flushing and cooling in pure nitrogen after reduction had been completed in hydrogen. This suggests that adsorbed and dissolved hydrogen do not have a measurable effect on the susceptibility of reduced copper under the conditions of this experiment.

Before the results on thermal migration are presented, the theory of the method will be outlined. The cupric ions in highly dispersed cupric oxide have a magnetic susceptibility at room temperature of about 20($\times 10^{-6}$) per gram. The cupric ions in pure crystalline cupric oxide have a susceptibility of about 4($\times 10^{-6}$). Intermediate degrees of dispersion show intermediate susceptibilities, although the exact relationship between susceptibility and dispersion is not known.

If a highly dispersed copper system is "sintered" and if this brings about an aggregation of copper atoms, then the decreased dispersion of the copper will be revealed by a decrease of susceptibility. The observed relationship of susceptibility to dispersion occurs for copper only when the copper is in the form of cupric ions. Hence, attempts to detect thermal migration in the supported copper system involve the following steps: (1) measurement of susceptibility in the oxidized state, (2) reduction, (3) sintering, (4) reoxidation and (5) measurement of susceptibility in the reoxidized state. Any decrease of susceptibility occurring between steps (1) and (5) is evidence of thermal migration to form larger copper particles.

In the search for evidence of thermal migration there were tried a number of reduction and sintering conditions as indicated below.

Figure 4 gives the susceptibilities per gram, of samples at 23°, against reciprocal field. The samples contained 1.42% of copper. Reduction in hydrogen was for 90 minutes at 300°. No further "sintering" was done during this particular run. Reoxidation was performed by slowly heating the sample to 500° in oxygen over a period of one hour. Another trial, with reduction conditions changed to 16 hours at 400°, gave similar results. It will be noted that there is no evidence for migration. The susceptibility of the reduced phase, which is included in Fig. 4, is not necessary for the experiment, but it illustrates the ubiquitous trace of ferromagnetism as shown by some dependence of suceptibility on field strength.

Evidence of diffusion in copper–nickel systems has been obtained as low as 200°, but temperatures above the Tammann temperature were thought more likely to provide positive thermal migration. Figure 5 shows the data obtained on a sample containing 7.29% copper. This sample was reduced and "sintered" in hydrogen at 550° for 100 hours. Reoxidation was slow after this treatment. The progress of reoxidation was readily followed by the change of color and by the developing paramagnetism. Results similar to those shown in Fig. 5 were also obtained on samples containing 1.42 and 3.35% copper, when these were subjected to the 550° reduction and sintering treatment.

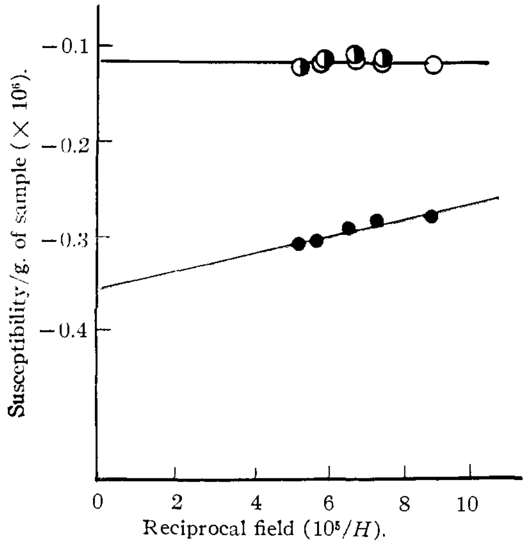

Fig. 4.—Oxidized (◑), reduced (●) and reoxidized (○) copper–alumina sample containing 1.42% copper; susceptibility *vs.* reciprocal field.

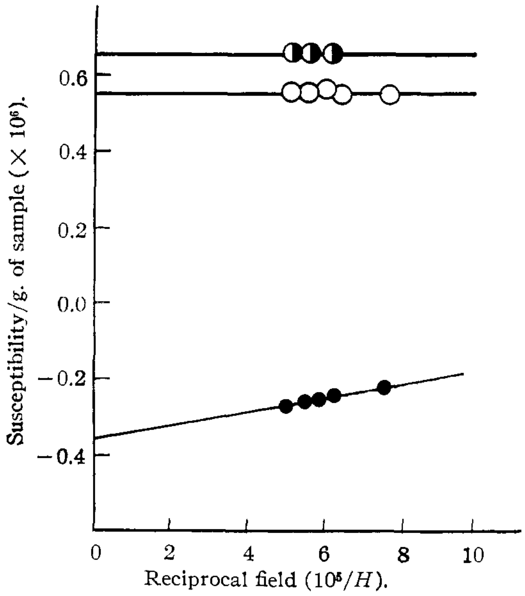

Fig. 5.—Oxidized (○), reduced (●) and reoxidized (◑) copper–alumina sample containing 7.29% copper; susceptibility *vs.* reciprocal field.

For reasons described below susceptibilities on several samples were obtained over a range of temperature. The results are given in Table I.[9]

TABLE I

SUSCEPTIBILITIES PER GRAM OF SAMPLE FOR SUPPORTED CUPRIC OXIDE ON ALUMINA

Wt. % Cu	$\chi \times 10^6$ 298°K.	195°K.	83°K.
1.42	−0.088	+0.104	+1.57
9.72	+0.811	+1.26	+5.23
79.9 (pure CuO)	+3.00	+2.43	+1.98

Two observations not directly related to the problem at hand will be mentioned.

The first is that some samples of supported cupric oxide on alumina on prolonged ignition at temperatures up to 900° gave definite evidence of ferromagnetism. This agrees with the contention that ferromagnetism may be found for certain phases of oxidation state and environment for almost any transition element in the periodic table.

The second observation is that some samples of supported cupric oxide on alumina undergo a spontaneous reduction when they are heated to about 500°. If this heating is done in air the reduction is rapidly followed by a reoxidation. The effect is apparently due to some adsorbed reducing gas, or may possibly be related to release of a trace of water from the γ-alumina at this temperature. The effect is not accompanied by a "glow phenomenon" or by significant loss of specific surface.

Discussion of Results

The plateau observed for the susceptibility isotherm of supported cupric oxide on alumina suggests that at low concentrations of copper in this system the cupric ions are effectively isolated from each other. Reduction might then be expected to yield isolated copper atoms, although these would doubtless be highly active chemically. Copper atoms have an odd number of electrons, and should be paramagnetic. It follows that reduction of a low concentration copper–alumina catalyst should produce little or no change of paramagnetism. Yet even at 1.42% copper, which is well up on the plateau, reduction lowers the susceptibility per gram of copper to zero. The conclusion previously reached, namely, that isolated copper atoms are not formed in these systems, is, therefore, confirmed and extended down to the lowest copper concentration which it is practical to reach with susceptibility apparatus at present available.

It has also been confirmed that there is no thermal migration leading to increased copper particle size in this system. "Sintering" as applied to low and moderate copper concentrations in a copper–alumina catalyst must have a different meaning. The fact that prolonged sintering leads to some increase of susceptibility (after reoxidation) suggests that solid solution or compound formation between cupric oxide and alumina is the more probable reason why ignition destroys the activity of this system. This is not to say that sintering in pure copper powder may not lead to increased particle size because in any pure, rather than supported, catalyst the system must be regarded as self-supported.

Another conclusion to be drawn from the data concerns the nature of the supported oxide phase. In earlier work from this Laboratory it has been assumed that supported oxides differ qualitatively from pure crystalline oxides by a continuous diminution of the paramagnetic neighborhood surrounding each paramagnetic supported ion. There is an alternative view that a supported oxide may consist of a mixture of ions at infinite magnetic dispersion together with massive crystalline oxide. According to this view, the susceptibility of, say, supported cupric oxide at any concentration on alumina should be the weighted average of the susceptibility of cupric ions at infinite magnetic dilution and that of cupric ions in massive cupric oxide. That this view is probably incorrect is shown by the following calculation.

Let χ_d be the susceptibility per gram of cupric ions in cupric oxide at infinite magnetic dilution, and let χ_m be the susceptibility per gram of cupric ions in massive cupric oxide. Then according to the view presented above, the observed susceptibility, χ_0, per gram of cupric ions in any catalyst sample should be given by $\chi_0 = \chi_d p + \chi_m(1 - p)$, where p is the fraction of total cupric ions present as infinitely dispersed ions. This fraction should be independent of the temperature at which the susceptibility measurements are made.

Taking as an example the sample containing 9.72% copper, we find the susceptibilities per gram of cupric ion to be as in Table II.

TABLE II

SUSCEPTIBILITIES ($\times 10^6$) PER GRAM OF CUPRIC IONS

Conditions	at 298°K.	at 195°K.	at 83°K.
Infinite magnetic dilution	20.5	34.2	137
9.72% catalyst	12.3	16.8	57.7
Pure cupric oxide[a]	4.13	3.42	2.86

[a] Pure cupric oxide is antiferromagnetic.

Substituting in the above equation and solving for p, we find that the apparent fraction of cupric ions present at infinite dispersion is: at 298°K., 0.50; at 195°K., 0.44; and at 83°K., 0.41. This deviation with temperature of the apparent degree of dispersion shows the fallacy of the view under discussion, namely, that supported cupric oxide may be considered as a mixture of infinitely dispersed cupric ions and of pure crystalline cupric oxide. Similar results are obtained with other catalyst concentrations. These results tend to support the view previously expressed that these supported catalyst systems, including copper and other paramagnetic elements, show a dependence of susceptibility on concentration because of a statistically varying paramagnetic neighborhood surrounding each paramagnetic ion.

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(9) These data were obtained in this Laboratory by Mr. Stephen Adler, to whom the authors are indebted for this assistance.