chemical bond between attractive and repulsive forces both of electronic nature. In first row elements the repulsive effects for single bonds arise principally in the valence shell whereas for heavier atoms the inner shells play a predominant role. The ideas are shown to account for several peculiarities in bonding behavior.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Susceptibility Isotherms for Supported Copper Oxide

BY P. W. SELWOOD AND NICK S. DALLAS

The purpose of this work was to examine the structure of supported copper catalysts by use of the magnetic methods previously described.[1] The present paper gives magnetic data on a series of copper–alumina catalyst systems, together with some X-ray and catalytic activity results.

Experimental

Preparation and Analysis of Samples.—Pure γ-alumina of surface area approximately 200 sq. m./g. and magnetic susceptibility -0.2×10^{-6} at −190°, was impregnated with copper nitrate solution, then filtered, dried, and ignited at 390° for twenty-four hours. Twelve samples of supported copper oxide were thus made, ranging in concentration from 0.60 to 34.7% copper.

The several samples were analyzed by dissolving them in nitric acid and titrating by the standard iodide–thiosulfate method. One catalyst sample was prepared by multiple impregnation. The copper nitrate impregnating solution was adjusted so as to give a catalyst containing about 1% copper. After ignition this catalyst was re-impregnated and ignited. The process was repeated until the copper concentration reached 5.2%.

Most of the catalyst samples were examined in the reduced condition as well as oxidized. Reduction was carried out in hydrogen at 300° for twelve hours. No change was caused by raising the reduction temperature to 400°.

It is of interest to record that the oxidized catalyst systems were bluish-green in color at all lower concentrations. The reduced catalysts were all jet black.

During the course of these studies it became necessary to prepare some supported silver oxide on alumina. This was obtained by impregnating γ-alumina with dilute silver nitrate solution, followed by drying and ignition at 390°. The sample contained approximately 2% silver. This sample was reduced in hydrogen at 200°. It may be mentioned that the oxidized silver supported on γ-alumina is rapidly changed from white to brown by mere exposure to hydrogen well below room temperature.

The reduced forms of all catalysts were readily reoxidized in air at room temperature. The lower concentrations were handled in the absence of air, although the reduced copper could be stabilized to a fair degree by exposure to carbon dioxide.

Catalytic Measurements.—Comparison of catalysts containing varying proportions of copper was made by mechanically mixing all samples, except the lowest in copper, with γ-alumina so that all samples contained 3.2% copper. The catalytic measurements were not extended below that concentration. The reaction chosen was the dehydrogenation of isopropyl alcohol.

A pelleted catalyst sample containing 0.32 g. of copper in 10 g. of catalyst was placed in the reaction chamber. The catalyst was reduced in hydrogen at 400° for two hours. The temperature was then lowered and held at 225°. Redistilled isopropyl alcohol was fed over the catalyst at the rate of 32 cc. (liquid) per hour. Tests were continued for one hour, and three successive such one hour activity runs were made for each catalyst.

The gaseous product was collected and the volume measured. The liquid product was fractionated in a simple column and a rough analysis was thereby obtained for acetone, unconverted isopropyl alcohol and higher boiling products.

The several catalysts used for the activity tests are conveniently described in the following manner. Catalyst 3.2/10.3 means a sample containing 3.2% of copper but that this was obtained by mechanically mixing appropriate amounts of γ-alumina and a CuO/Al_2O_3 impregnate which contained 10.3% of copper. Four such catalysts were tested. These are thus designated as 3.2/3.2, 3.2/10.3, 3.2/13.3 and 3.2/22.9.

Results

Table I shows the magnetic susceptibility at three temperatures for all the oxidized copper catalyst samples except that prepared by multiple impregnation. Samples containing less than 3% copper are discarded as being too dilute to permit accurate estimation of the susceptibility of the copper. Figure 1 shows the susceptibility isotherms calculated from the data of Table I.

TABLE I

MAGNETIC SUSCEPTIBILITY OF CuO/Al_2O_3 CATALYST SAMPLES

Weight per cent. copper	$\chi \times 10^6$ 25°	$\chi \times 10^6$ −80°	$\chi \times 10^6$ −190°
4.0	0.5 (±0.05)	0.9	2.4
7.2	0.9	1.8	4.4
10.3	1.4	2.5	5.6
11.9	1.3	1.8	3.8
13.3	1.0	1.4	3.1
16.5	0.9	1.2	2.6
22.9	1.0	1.4	2.6
28.4	1.3	1.5	2.6
30.6	1.4	1.7	2.6
34.7	1.7	1.7	2.5

Reduction of the copper in the samples in all cases caused the magnetic susceptibility to drop substantially to zero. The susceptibility isotherms at −180° for oxidized, reduced and reoxidized copper–alumina are compared in Fig. 2.

The magnetic susceptibility of the sample prepared by multiple impregnation was 2.45×10^{-6} at −170°. The susceptibility of the copper in this catalyst, which contained 5.2% copper, was, therefore, 51×10^{-6} at −170°.

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[1] This is the third paper on the susceptibility isotherm from this Laboratory. The second paper appeared in THIS JOURNAL, 69, 2698 (1947). Descriptions of magnetic, X-ray and surface area experimental methods will be found in the earlier papers.

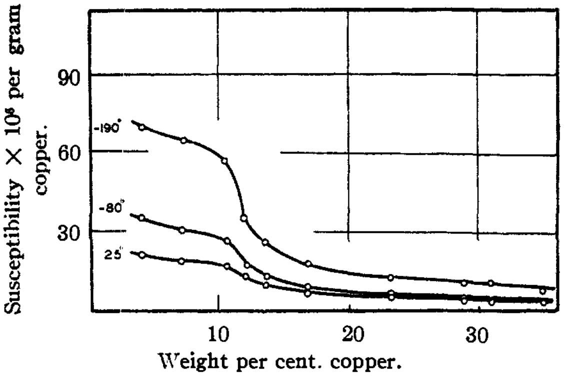

Fig. 1.—Susceptibility isotherms for supported copper oxide on γ-alumina.

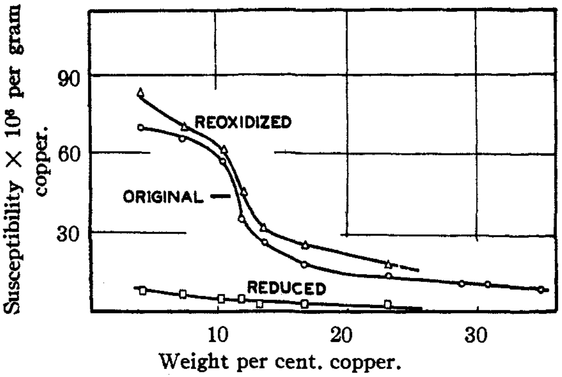

Fig. 2.—Susceptibility isotherms for copper and copper oxide on γ-alumina, all at −190°.

The single sample of supported silver on γ-alumina had a susceptibility of substantially zero both at 25° and at −170°.

The X-ray diffraction results showed clearly the principal lines of cupric oxide at 2.51, 2.30, 1.86, 1.58 and 1.50 Å. down to a concentration of 11.9% copper. But at 10.3% copper no cupric oxide lines, or any lines other than those of γ-alumina, were observed. There is, therefore, a parallelism between the disappearance of the cupric oxide lines and the region of maximum rise of susceptibility in the isotherm.

The results of the catalytic activity tests are summarized in Table II, which gives results for the second of three concordant runs in each case.

TABLE II

RELATIVE CATALYTIC ACTIVITY OF COPPER–ALUMINA CATALYSTS

Catalyst	% Acetone	% High boiling
Pure alumina	None	None
3.2/ 3.2	52	10
3.2/10.3	31	4
3.2/13.3	31	4
3.2/22.9	22	3

In addition, it should be stated that the more dispersed systems gave a relatively smaller volume of higher density gaseous product, and that these systems also lost activity much more rapidly during use than did the less dispersed systems.

Conclusions.—The susceptibility isotherm is generally characterized by a large increase of susceptibility at low concentrations. Copper shows this effect to a greater extent than any other element so far studied. The susceptibility of copper in supported cupric oxide at low concentrations is about twenty times larger than that of copper in massive (unsupported) cupric oxide.

Below about 10% copper the susceptibilities of the several samples accurately follow the Curie–Weiss law, from which it is possible to compute the Weiss constant and the magnetic moment. In this region the Weiss constant is small, but slowly rises, showing the normal effects of decreasing copper–copper distance. At the lower concentrations the magnetic moment is 1.8 Bohr magnetons. This corresponds exactly with the moment predicted from the "spin-only" formula for cupric ion. There is, therefore, no inductive effect of the support on the valence of the copper.

The most striking feature of the susceptibility isotherm for copper is the sharp rise in the neighborhood of 11% copper. The magnetic data, taken in conjunction with the X-ray results, suggest that this is the concentration region below which it is impossible to maintain extensive organization of the copper and oxide ions into unit cells. It might be said that cupric oxide crystallites do not exist below about 11% copper. Nevertheless, the copper can scarcely be considered as atomically dispersed even below 11%. This is shown by the gradual decrease of the Weiss constant and by considerations on the magnetic properties of the reduced copper.

Our general picture of the oxidized copper catalysts is, therefore, not dissimilar to that earlier obtained for the chromia–alumina system. The tendency in such supported systems is shown definitely to be toward inhomogeneity and formation of ionic assemblies, and not toward two-dimensional solid solution except at the greatest dilutions.

Turning now to the results on the reduced copper–alumina systems we are faced with a difficulty. The isotherm for the oxidized form strongly suggests that below 10% copper we are approaching infinite magnetic dilution because the susceptibility is not rising very rapidly. This is in contrast to the case for chromia–alumina.

It is well known that massive copper is slightly diamagnetic, but isolated copper atoms ought to be paramagnetic because they contain an odd number of electrons. It would be anticipated that the higher supported copper concentrations would become diamagnetic on reduction because the massive cupric oxide present is being converted to massive copper metal. But if the cupric ions were atomically dispersed at very low concentrations, then reduction should have no effect on the susceptibility.

Some very careful efforts were made to detect this effect. But the low susceptibilities and the ubiquitous trace of ferro-magnetic impurity combined to make it difficult to examine this region. We can say, however, that certainly no more than 10% of the copper atoms can be considered as atomically dispersed.

It was hoped that the multiple impregnation catalyst would lead to higher, more readily measureable, susceptibilities and to greater dispersion, but such was not the case. It was also hoped that dispersed silver might yield a more readily observable result. The reason for the choice of silver was that the oxidized form is here diamagnetic. But certainly no large fraction of the supported reduced silver became paramagnetic.

Our conclusion from all these negative results is that the tendency for aggregation is so strong that even when the support must be, of necessity, mostly unoccupied surface, still the supported atoms tend to cling together. It will be noted that the larger size of the reduced atoms may lead to greater exchange interaction as compared with the oxidized forms, even though the ion centers do not appreciably move during the oxidation–reduction cycle.

When reduced supported copper is reoxidized the susceptibility goes as high as or higher than in the original oxidized sample. This shows that no aggregation into crystallites occurs during the oxidation–reduction cycle. In fact the slight increase of susceptibility shown in Fig. 2 may be due to three-dimensional solution of cupric ions in the alumina.

The results on catalytic activity support in a general way this picture of the active surface. The more highly dispersed copper would normally be expected to show greater activity, and such is the case. It is somewhat surprising that no change of activity occurs in the anomalous 11% concentration region. This result must mean that the mere aggregation into definite cupric oxide crystallites has no effect on the activity. There is, of course, the possibility that in the *reduced* form there is no such obvious structural change occurring in this concentration region.

Summary

Susceptibility isotherms are given for copper oxide supported on γ-alumina, for the reduced catalyst, and for related systems. The magnetic data are related to X-ray diffraction studies, and to catalytic activity results on the dehydrogenation of isopropyl alcohol.

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[CONTRIBUTION FROM ARGONNE NATIONAL LABORATORY AND DEPARTMENT OF PHYSICS, UNIVERSITY OF CHICAGO]

Double Fluorides of Potassium or Sodium with Uranium, Thorium or Lanthanum

BY W. H. ZACHARIASEN

This paper summarizes the results of studies of the systems KF--UF_4, KF–ThF_4, KF–LaF_3, NaF–UF_4, NaF–ThF_4 and NaF–LaF_3. The investigations were carried out within the Manhattan Project during 1945.

The systems were studied by means of the X-ray diffraction method. The systematic survey extends over the entire composition range except for a gap between 35 and 65 mole per cent. ThF_4 in the NaF–ThF_4 system.

1. The Chemical Preparations.—All chemical preparations were made by the writer. The systematic studies were carried out by determining the phase compositions of solidified melts by means of X-ray diffraction patterns. Thermal analysis data were not taken, however. In the systems involving potassium fluoride precipitates from solutions were also examined.

The dry method preparations were made by melting together the component fluorides in a platinum crucible. The uranium tetrafluoride was from the Harshaw Chemical Company. Dr. Ralph Livingston had prepared the thorium fluoride by treating $ThF_4 \cdot xH_2O$ with HF. The Los Alamos Laboratory supplied the lanthanum fluoride.

The wet way preparations were obtained in the following ways:

1. Solutions of potassium chloride and uranium tetrachloride, of potassium nitrate and thorium or lanthanum nitrate were precipitated with hydrofluoric acid.
2. Solutions of uranium tetrachloride, of thorium nitrate or of lanthanum nitrate were precipitated with a potassium fluoride solution.
3. Solutions of $K_3UO_2F_5$ or of uranyl nitrate and potassium fluoride were reduced with formic acid and direct sunlight whereby precipitates were formed.

2. The Identification of the Phases.—The chemical identity of the various phases was deduced through interpretation of the X-ray diffraction patterns. This unorthodox method of analysis had to be used because the chemical analysts were busy with more important work. Direct chemical analyses of a few single phase preparations were, however, made. These direct analyses were rather unsatisfactory because the alkali content was not determined and because of the customary difficulty in obtaining reliable results for the fluorine percentage.

Because the method is unknown to most chem-