[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Susceptibility–Composition Isotherm for the Chromium–Aluminum Oxide Catalyst System

BY ROBERT P. EISCHENS[1] AND P. W. SELWOOD

A recent communication[2] described a new magnetic effect which gives promise of being useful in establishing the structures of catalytically active inorganic solids. This effect is, in brief, a large increase of magnetic susceptibility shown at low temperatures by transition group oxides supported on diamagnetic substances such as aluminum oxide.

The present paper reports further magnetic studies on chromic oxide supported on γ-alumina.

Experimental

Preparation of Catalysts.—The alumina used in all the work, except as later noted, was prepared through precipitation of the hydroxide by carbon dioxide from a solution of potassium aluminate.[3] Six moles of potassium hydroxide (U. S. P.) was dissolved in three liters of distilled water. Two moles of granular aluminum was dissolved in the base solution. The resulting solution was filtered to remove insoluble impurities. The filtrate was acidified with iron-free nitric acid until aluminum hydroxide just barely began to precipitate. Precipitation was then completed with a stream of carbon dioxide. The precipitation was carried out at room temperature. The precipitated hydroxide was washed with distilled water until the washings were neutral to litmus. The washed precipitate was dried overnight at 110°, then calcined at 350–360° for eighteen hours. The product was identified as γ-Al_2O_3 by X-ray diffraction. The magnetic susceptibility of the product was -0.3×10^{-6} and was independent of field strength, and of temperature in the range $-190°$ to 25°. The surface area of the γ-Al_2O_3 was found to be 423 square meters per gram. This was determined by low temperature nitrogen adsorption and the Brunauer–Emmett–Teller equation.

Catalyst samples were prepared by the method of impregnation. Anhydrous chromic acid was dissolved in water. To this solution the alumina was added and allowed to stand overnight. In an effort to obtain maximum uniformity, the chromic acid solution was present in three-fold excess over the maximum amount of solution which was adsorbed by the alumina. Different ratios of chromium to aluminum in the finished catalysts were obtained by modifying the concentration of the chromic acid solution. The alumina impregnated with chromic acid solution was then filtered, dried for eight hours at 350°, and reduced in a stream of hydrogen for five hours at 360°. In this way there were prepared samples of chromic oxide supported on γ-alumina in which the percentage by weight of chromium varied from about 0.1 to 40%. This more than covers the range of concentrations found in the industrial use of this catalyst. Analysis of each catalyst sample was carried out as follows: The samples were brought into solution by sodium peroxide fusion. The melt was dissolved in water and the solution was boiled to decompose the excess peroxide. A residue from the nickel crucible, used in the fusion, was removed by filtration. After acidification of the solution with sulfuric and phosphoric acids, an excess of ferrous ammonium sulfate was added, and the excess was titrated with dichromate solution, with the use of barium diphenylamine sulfonate as indicator. The analytical results so obtained were more accurate than the magnetic susceptibility results.

Magnetic Susceptibility Measurements.—The susceptibilities were measured as previously described.[4]

TABLE I

MAGNETIC SUSCEPTIBILITIES OF CHROMIUM–ALUMINUM OXIDE CATALYSTS

Wt. % chromium	Susceptibilities $\times 10^6$ 85°K.	190°K.	295°K.	370°K.
100	22.8	..	25.2	..
	33.3	..	36.8	..
41.4	25.5	20.5	15.8	..
	61.9	49.9	38.6	..
34.6	27.1	19.3	14.8	14.0
	78.9	56.3	43.3	41.2
30.1	24.9	18.2	14.3	12.6
	83.2	61.0	48.0	42.5
27.3	24.7	17.2	13.0	12.45
	91.3	63.6	48.3	46.4
25.7	24.3	16.8	13.6	10.9
	95.4	68.2	53.6	43.4
21.2	21.8	15.1	11.0	11.2
	104.3	72.4	53.0	53.1
17.6	18.8	12.8	9.1	..
	108.2	74.2	53.3	..
15.1	16.7	10.1	7.9	5.9
	113	68.9	54.3	41.4
12.3	15.9	9.7	6.8	..
	132	81.1	57.4	..
8.04	10.9	6.8	4.9	3.8
	140	88.5	64.7	51.2
5.74	8.4	4.85	3.7	2.9
	151	89	70	57
4.85	7.5	4.2	3.1	2.3
	160	93	70	55
4.61	8.4	4.4	3.2	2.9
	189	102	87	70
3.25	6.8	3.7	2.5	1.9
	218	122	85	68
1.86	4.3	2.2	1.3	1.0
	246	134	88	73
1.26	3.0	..	0.9	..
	260	..	91	..
0.84	2.2	..	0.5	..
	300	..	94	..
.42	0.95	..	0.10	..
	300	..	95	..
.11	0.00	..	−0.19	..
	300	..	95	..
0	−0.3	−0.3	−0.3	−0.3

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(1) Sinclair Refining Company Fellow in Chemistry.

(2) Selwood, Hill and Boardman, THIS JOURNAL, **68**, 2055 (1946).

(3) *Natl. Petroleum News*, **30**, 432 (1938).

(4) Selwood, THIS JOURNAL, **61**, 3168 (1939).

Results

Table I shows magnetic susceptibilities per gram of all catalyst samples at 25° and at −190°. Most samples were also measured at 100 and at −78°. The table also shows the calculated susceptibility per gram of the chromium in each sample. This is found by direct application of the Wiedemann additivity law. Justification for this procedure is indicated below. In each case, in the table, the first figure given is the susceptibility of the catalyst. Directly below this figure is given the calculated susceptibility of the chromium.

The most interesting results are those obtained at liquid air temperature. These are shown graphically in Fig. 1. We have chosen to call this curve a susceptibility–composition isotherm. The susceptibility–composition isotherm may be defined as the relation between susceptibility and concentration for a dispersion of a paramagnetic substance on a carrier as measured at one temperature. The term "susceptibility isotherm" has sometimes been used in magnetism for the relation between field strength and specific magnetization at constant temperature, but we doubt if any confusion may arise from this usage.

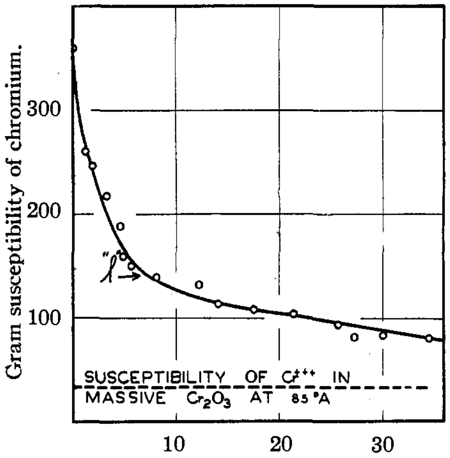

Fig. 1.—Susceptibility–composition isotherm for chromia impregnated on alumina.

It will be noted that the susceptibility–composition isotherm shows a critical point where the curve changes direction. It will be convenient to have a name for this point. We choose to call it "point *l*."

Discussion of Results

In the above computations leading to the susceptibilities of the chromium ion at different chromium concentrations, we have assumed that the susceptibilities of aluminum ions and oxide ions remained constant. This procedure is believed to be justified on the basis of previous experience. Diamagnetic susceptibilities seldom change more than a few per cent. during change of chemical environment, while paramagnetic substances, especially transition group ions, often suffer major changes. In brief, we have assumed that all the observed changes of susceptibility in the catalyst are due to changes in the susceptibility of the chromium ions.

An attempt will now be made to elucidate the shape of the susceptibility–composition isotherm in terms of the Curie–Weiss law, $\chi = C/(T + \Delta)$. Provided this law holds we can establish whether the effect is due to a major change in the Curie constant, *C*, in the Curie–Weiss law, or to a major change in the Weiss constant, Δ. In the first case the effect would be related primarily to a change of oxidation state, in the second to a change of environment.

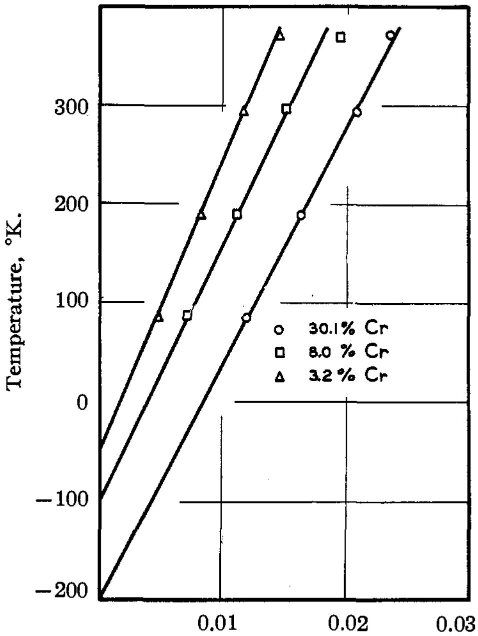

Fig. 2.—Determination of delta: $T = (C/x) - \Delta$.

That the Curie–Weiss law holds for these systems is amply proved by Fig. 2, in which reciprocal susceptibility is plotted against absolute temperature for a few representative chromium concentrations. Throughout the whole concentration range up to 30–40% chromium, and through the temperature range −190 to +100°, there is no perceptible deviation from the law. We may, therefore, calculate the Curie constant and the Weiss constant for each of our several catalyst samples. Instead of giving the constant *C* directly, we shall give the derived magnetic moment $\mu = 2.83 \sqrt{C}$, because this is more obviously related to the oxidation state of the chromium. Figure 3 shows both μ and Δ as a function of chromium concentration. It will at once be noticed that μ is almost constant, but that Δ is markedly dependent on chromium concentration.

We shall first consider the implications of μ and

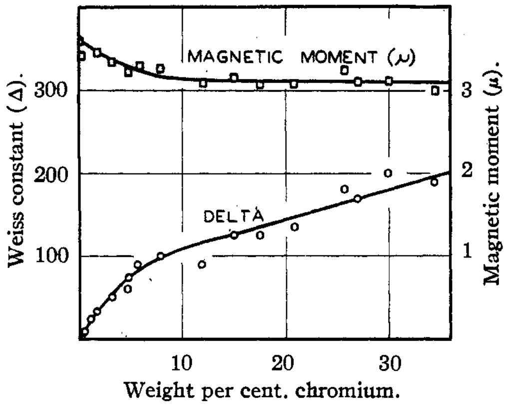

Fig. 3.—Relation of delta and magnetic moment to chromium concentration.

its relationship to the oxidation state of the chromium. It will be noted that the magnetic moment is independent of the chromium concentration except at quite low concentrations. The magnetic moment has a value of about 3.2 Bohr magnetons. According to the familiar "spin-only" formula $\mu = \sqrt{n(n + 2)}$, where n is the number of unpaired electrons, this corresponds to an oxidation state somewhat greater than +3, perhaps about 3.5. It is not clear whether this is a real effect, and that some chromium atoms may be considered to be in a state higher than +3, or whether the magnetic data are being misinterpreted. It should be pointed out that a belief sometimes expressed by catalytic chemists is that this catalyst is not active unless some higher valent chromium is present.

Some efforts have been made to detect chromium in an oxidation state higher than three by direct chemical analysis. But so far these efforts have been unsuccessful. Nevertheless, some confidence is placed in the magnetic determination of the chromium oxidation state. This confidence is based partly on the excellent agreement obtained between "magnetic" and "chemical" oxidation states as found for manganese oxide supported on alumina. This work on manganese will be presented in a forthcoming publication from this Laboratory.

An attempt has also been made to alter the apparent oxidation state of the chromium by changing the conditions of reduction. The results were completely negative as shown in Table II. The sample used for this series of tests contained 4.85% of chromium, and was identical with the starting impregnation mixture of the same concentration, shown in Table I. All reductions were in a stream of hydrogen.

TABLE II

EFFECT OF CHANGING REDUCTION CONDITIONS ON MAGNETIC PROPERTIES

Reduction conditions Temp., °C.	Hours	Susceptibility of chromium × 10^6 85°A.	196°A.	295°A.	370°A.	μ	Δ
350	5	160	92.6	70.3	55.2	3.3	70°
500	5	179	98.6	70.9	62.8	3.3	65°
190	5	161	..	66.1	..	3.2	63°
350	20	163	96.9	67.6	53.8	3.2	72°

At the lowest chromium concentrations the oxidation state apparently falls slightly, and almost approached +3. It will be noted that for chromium, but not necessarily for all transition group elements, a rise of magnetic moment implies a decrease of oxidation state.

These effects related to the oxidation state suggest that ions on the surface may have quite different relative stability from those in the interior of a crystal. This view is supported by the parallel magnetic and analytical studies which are being made in this Laboratory on supported oxides of manganese. Such changes in relative stability of various oxidation states are not unexpected in view of the great change in coördination of a surface ion as compared with one in the interior.

However, these "oxidation state" effects are all of small importance compared with the large changes which occur in the Weiss constant as the chromium concentration is changed. It is seen that nearly all the large changes in susceptibility of chromium are related to changes in Δ, and that the shape of the susceptibility–composition isotherm and the position of point l are accurately reflected in the plot of Δ against chromium concentration. In order to understand the susceptibility composition isotherm we must, therefore, examine more fully the nature of the Weiss constant.

The Weiss constant can be traced to three possible sources.[5] The first source is the existence of multiplet levels of about the same energy difference as kT. This actually occurs only in the elements samarium and europium, and to a slight degree in neodymium; the effect is absent in chromium. The second source of the Weiss constant lies in the crystalline field splitting of levels —the natural Stark effect. We choose to ignore this effect in the systems under consideration. Our justification for so doing lies in the approach of Δ to zero as the chromium concentration diminishes. If the field splitting were an appreciable factor in producing the Weiss constant, our observed values for Δ would asymptotically reach a value different from zero.

The third source of the Weiss constant is the Heisenberg exchange effect between neighboring chromium ions. This, we believe, is the source of the major changes in Δ with chromium concentration. Heisenberg has shown that, provided we neglect all sources of Δ other than the exchange interaction, the Weiss constant may be expressed as follows

$$- \Delta = 2JzS(S + 1)/3k$$

where J is the exchange integral, z is the number of equidistant paramagnetic neighboring ions, S is the vector sum of spin moments, and k is the Boltz-

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(5) Selwood, "Magnetochemistry," Interscience Publishers, Inc. New York. N. Y., 1943, p. 86.

mann constant. Our concern is with the quantity z.

Chromic oxide commonly adopts the corundum structure, consisting of a hexagonal close packed oxide ion lattice with chromic ions in two thirds of the octahedral holes. We are not certain that chromium oxide adopts this lattice in the supported catalyst, and the high apparent oxidation state for the chromium suggests that rather less than two-thirds of the octahedral holes are actually filled with chromium. However, we shall assume that the structure is actually not very different from the corundum lattice, until it can be shown otherwise.

A chromic ion situated in the interior of crystalline chromic oxide has nine nearest chromium neighbors; in other words, the value of z is nine. But as the thickness of a chromic oxide layer diminishes the value of z also diminishes. Examination of a crystal model show that z has the following values: for one layer, $z = 3$; for two layers, $z = 6$; for three layers, $z = 7$; and for four layers, $z = 7.5$. The relationship between z and the number of layers is shown graphically in Fig. 4. The reason that z first rises rapidly, and then slowly approaches a maximum, is because the relative importance of the surface layers rapidly diminishes as the number of layers increases. The most interesting feature of this relationship is that the graph of z against number of layers changes direction fairly sharply at about three layers.

We relate our experimentally observed Weiss constants in the catalyst systems to these changes of z with increasing number of layers of chromic oxide. We relate point l in the susceptibility–composition isotherm to approximately three layers of chromic oxide on the surface of the alumina. As our first conclusion we have, therefore, that the catalyst of such concentration as corresponds to point l in the susceptibility–composition isotherm consists of an alumina surface on which is deposited a layer of chromic oxide, and that this layer is about three oxide ion layers thick. Catalysts more concentrated in chromium have more layer of chromic oxide; those less concentrated have fewer layers, tending toward complete atomic dispersion.[6]

However, as we shall now see, this preliminary conclusion must be partially modified. In the system studied the surface area of the alumina as determined by low temperature nitrogen adsorption was 423 square meters per gram. We shall calculate the area which would be covered by a monolayer of chromic oxide in the catalyst corresponding to point l, namely, about 0.06 g. of chromium per gram of catalyst. One concept of a monolayer of chromic oxide is a single layer of close-packed oxide ions with chromium ions in two-thirds of the octahedral openings.

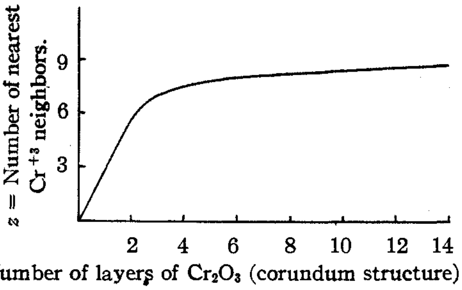

Fig. 4.—Relation of Δ to the number of layers of chromic oxide: $-\Delta = 2\,JzS(S + 1)/3k$.

The radius of an oxide ion is assumed to be 1.4 Å. The cross-sectional area is then $\pi(1.4 \times 10^{-8})^2$ sq. cm. = 6.15×10^{-16} sq. cm. The fraction of surface actually covered by close-packed spheres is approximately 90%. Hence the area effectively occupied by one oxide ion is $6.15 \times 10^{-16} \times 10/9 = 6.84 \times 10^{-16}$ sq. cm.

One gram of chromium oxide contains $1/152 \times 6.03 \times 10^{23} \times 3 = 1.19 \times 10^{22}$ oxide ions. The area covered by these ions will be $1.19 \times 10^{22} \times 6.84 \times 10^{-16} = 8.13 \times 10^{6}$ sq. cm. or 813 square meters. A sample of catalyst containing 6% of chromium contains 0.095 g. of chromium oxide per gram of aluminum oxide. The maximum area which could be covered by this weight of chromium oxide is 77 square meters.[7]

It is clear from this calculation that at a concentration corresponding to point l we have barely one-fifth as much chromium as would be required to cover the alumina with a monolayer of chromic oxide. We have, therefore, the apparent contradiction that the alumina is covered with about three layers of chromic oxide, yet is not covered with one layer. The explanation is, of course, obvious. Of the total "nitrogen" area of the alumina only a small fraction is actually covered by chromium oxide. But this small fraction is covered with an average of three atom layers thick. This refers to the catalyst of concentration corresponding to point l.

Two possible pictures of the surface of the catalyst now present themselves. In the first, the alumina surface is covered in spots. Each of these spots, which may possibly be related to active

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(6) It may be wondered why we ignore possible variations in J, the exchange integral. This quantity varies fairly rapidly with interatomic distance. The nearest approach of two chromic ions appears to be the diameter of one oxide ion, namely, 2.8 Å. This distance can obviously lead to strong exchange interaction as in massive chromic oxide. But as the chromium atoms become more dispersed on the surface of a support it is diffiult to see how the chromium–chromium distance can change by less than integral multiples of 2.8 Å. unless we imagine a chromic ion perched precariously in other than an octahedral opening. But even at a distance of 5.6 Å. the exchange interaction must be negligible because compounds with this degree of magnetic dilution always have modest values for the Weiss constant. Our conclusion with respect to the exchange integral is, therefore, that it has a constant value at the normal chromium–chromium distance of 2.8 Å., but that it drops to zero as the chromium ions become further dispersed.

(7) An alternative method for calculating the maximum surface which could be covered by a given weight of chromic oxide is based on the method applied by Emmett and Brunauer (THIS JOURNAL, **59**, 1553 (1937)) to molecular substances. This method gives an area somewhat smaller than that given above, but the general conclusions we reach would not be modified by use of this lower area.

centers of catalytic activity, is a crystal nucleus of chromium oxide. Each crystal nucleus is, on the average, three oxide ions thick. The nuclei are spread very far apart, most of the surface being exposed alumina. As the concentration of chromium increases, these crystal nuclei tend to grow until they finally overlap, but this does not occur until the chromium oxide layer is many atoms thick. As the concentration of chromium is decreased, the crystal nuclei shrink until they consist, at the limit, of a true two-dimensional atomic dispersion of chromium ions. A diagrammatic representation of the catalyst surface, as at point *l*, is shown in Fig. 5.

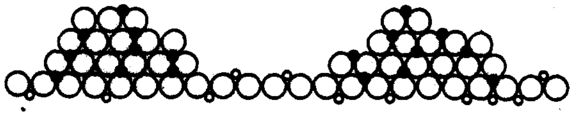

Fig. 5.—Possible structure of supported chromic oxide on aluminum oxide: O, O^{-2}; o, Al^{+3}; ●, Cr^{+3}.

In presenting Fig. 5 we do not imply that the alumina surface is flat. The representation is meant to be diagrammatic rather than pictorial. But the relationship shown of "nitrogen" area to chromium oxide is, we believe, a reasonable interpretation of the magnetic data. A second possible picture of the surface of the catalyst would have a large part of the "nitrogen" area in regions, such as pores, inaccessible to the chromium. We might, for instance, have the crystal nuclei of Fig. 5 actually touching or overlapping, with large fractions of the alumina surface free from chromium but concealed in "caves" and "pores." But, in any event, the thickness of the chromium oxide layer remains at about three oxide ions, as at point *l*. We see no reason for identifying point *l* with a monolayer of chromium oxide. Further experiments are being done to determine which picture of the surface is more nearly correct.

There is an alternative explanation for the suceptibility–composition isotherm. γ-Alumina has the structure of a spinel, with vacant places in the lattice corresponding to the missing ions. A possible structure has 21.3 aluminum ions present for every 24 possible positions for metal ions in the unit cell. The unit cell could, therefore, accommodate 2.7 chromic ions, which are only very slightly larger than aluminum ions. It might be thought that point *l* in the susceptibility–composition isotherm represented filling of all these vacant positions. It is, however, difficult to see how the isotherm would undergo anything but a very gradual change as the vacant positions became filled, and, furthermore, the positions are all filled at 9% chromium rather than at 6%, which is the actual position of point *l* in the system studied.

Acknowledgment.—It is a pleasure to acknowledge the support of the Sinclair Refining Company in connection with this work.

Summary

Magnetic susceptibilities have been measured for a series of catalysts of varying composition, but all containing chromium oxide supported on alumina. Variations in the susceptibility of the chromium in these catalysts is used to derive possible structures for the catalyst surface. The relation between magnetic susceptibility and concentration is named the susceptibility–composition isotherm.

EVANSTON, ILLINOIS RECEIVED JANUARY 27, 1947

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, THE OHIO STATE UNIVERSITY]

The Photovoltaic Effect. The Spectral Sensitivities of Cadmium, Zinc and Silver Electrodes; the Effect of *p*H and Oxygen

BY JOHN M. BLOCHER, JR., AND A. B. GARRETT

The present data extend to cadmium and zinc electrodes, the work[1] of Clark and Garrett on the spectral sensitivities of copper, silver, and gold electrodes in solutions of various electrolytes. Data are also presented for several silver and silver–silver chloride cells, for the effect of *p*H on certain silver cells and the effect of dissolved gases on various cells. The presence of dissolved oxygen is here shown to have a profound influence on the photopotentials of some cells, in certain cases to the extent of reversing the sign of the photopotential.

Experimental Procedure

The apparatus and procedure in the determination of the spectral sensitivities were essentially those used by Clark and Garrett,[1] with the exception that correction was made for the infrared transmission of the light filters.[2]

The electrodes were annealed in only a few cases since a comparison of the photopotentials developed by annealed and unannealed electrodes of silver, cadmium and zinc, indicated no differences which could be attributed to the presence or absence of annealing.

The metal and silver–silver halide electrodes were prepared as previously described.[1] Cu/"CuO" electrodes were prepared by heating cop-

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(1) P. E. Clark and A. B. Garrett, THIS JOURNAL, **61**, 1805 (1939).

(2) This has the effect of raising the points at λ = 4916 and 4358 Å. resulting in an increased sensitivity toward the ultraviolet generally without inflection.