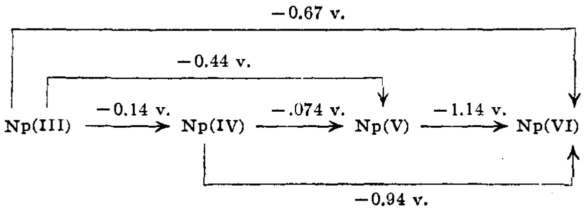

The Np(III)–Np(IV) and Np(V)–Np(VI) couples have been found to behave reversibly while the Np(IV)–Np(V) couple is irreversible. In the latter case measurements of the potential in a system in equilibrium with Fe(II) and Fe(III) have been used to obtain the value of the couple.

RECEIVED SEPTEMBER 20, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Supported Oxides of Manganese[1]

BY P. W. SELWOOD, T. E. MOORE,[2] MARYLINN ELLIS AND KATHRYN WETHINGTON

The applicability of the susceptibility isotherm method has already been described for supported oxides of chromium, and of copper. The present paper describes exploratory studies on the use of the method for supported oxides of manganese. Similar papers on nickel and on iron and other elements will shortly be forthcoming from this Laboratory.[3]

Experimental Part

X-Ray, magnetic susceptibility and surface area studies were made by standard methods previously described.[3]

One of the objectives of all this work is the relation of inorganic structure to catalyst activity. The various supported oxide systems are, therefore, referred to as catalysts, even though their applicability as catalysts may not be obvious.

Preparation of Catalysts.—Manganese oxides supported on alumina were prepared as follows: a water solution made from recrystallized manganous nitrate was impregnated in excess on γ-alumina. The area of the alumina was about 200 $m.^2$ $g.^{-1}$ (BET nitrogen). The susceptibility of the alumina was -0.3×10^{-6} and was independent of temperature. The impregnated alumina was filtered with suction, then dried and heated to 150–160° for forty-eight hours under slightly reduced pressure. The product was removed, ground, screened and reheated for twenty-four hours at 200°. This procedure would normally be expected to yield a layer of manganese dioxide in the *pyrolusite* structure covering the alumina. A series of catalysts was prepared in this way. Variations in manganese content was obtained by changing the concentration of the impregnating solution. Manganese concentrations ran from about 1 to over 20%. The color of all the finished catalysts ranged from pale tan to black. Analytical and other data are given below.

Prolonged heating of manganese dioxide results in the quantitative formation of the sesquioxide in the *bixbyite* structure. Some of the catalysts described above were subjected to thermal decomposition at 600°. The properties of this series are also described below.

During the course of this work it became obvious that manganese oxides supported on high-area *rutile* would be an interesting system for study. Considerable difficulty was experienced in obtaining this support, but finally a laboratory prepared sample was obtained from the National Lead Company, Titanium Division. This titania was all in the *rutile* structure, had a surface area of about 129 $m.^2$ $g.^{-1}$ (BET nitrogen), and had a susceptibility of -0.3×10^{-6}, which was substantially independent of temperature.

A series of supported manganese catalysts was prepared on the titania by procedures identical with those described for the alumina support, except that heating was not carried over 200°. Somewhat more concentrated impregnating solutions were found to be required to obtain equivalent concentrations of manganese on titania as compared with alumina.

One catalyst was made containing rhenium supported on alumina. γ-Alumina was impregnated with a hot saturated solution of potassium perrhenate. The mixture was kept hot for twenty minutes, then filtered and dried at 110°. The sample was then ignited in vacuum to 350°. After magnetic and other measurements had been made the sample was further heated in hydrogen at 350° for twenty-four hours. Before reduction the sample was white, and afterward gray. A few miscellaneous preparations are briefly indicated below.

Analytical Procedures.—The analytical data required were (1) manganese, and (2) "active" oxygen. For the manganese determination the sample was dissolved in sulfuric acid containing ferrous sulfate. The manganese was then oxidized with sodium bismuthate in nitric acid. The resulting permanganate was titrated with ferrous sulfate.

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[1] This paper describes, in part, work performed under contract with the Squier Signal Laboratory, Signal Corps Engineering Laboratories, as part of their program for the improvement of dry cells.

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[3] This is the fifth paper on the susceptibility isotherm from this Laboratory. The third and fourth appeared in THIS JOURNAL, **70**, 2145, 2271 (1948).

For "active" oxygen a known excess of standard ferrous ammonium sulfate was employed in dissolution of the sample. The excess was then titrated with standard permanganate.

The titania-supported samples were very slow to dissolve. In fact, direct solution in sulfuric acid probably would not have been possible had not the original ignition temperature been kept down to 200°. Fortunately, higher ignition temperatures were not necessary.

The single sample of supported rhenium on alumina was analyzed by the nitron acetate method.[4]

Results

The first series to be considered is that in which manganous nitrate is impregnated on γ-alumina and then ignited at not over 200°. The results are presented in Table I. Following plans used previously we give the weight per cent. of manganese in each sample, and the magnetic susceptibility per gram of sample at three temperatures. Directly below each measured susceptibility there is given the calculated susceptibility per gram of manganese in each corresponding sample. Thus the first catalyst sample had a susceptibility at 25° of 13.8×10^{-6} per gram of sample. This sample contained 23.4% of manganese, and the susceptibility per gram of manganese is then 60.4×10^{-6}.

TABLE I

SUSCEPTIBILITY OF MANGANESE OXIDE ON ALUMINA, IGNITED AT 200°

Wt. % manganese	Susceptibilities $\times 10^6$ 83°K.	195°K.	298°K.
63.1 (crystalline *pyrolusite*)	44	31	27
	69.8	49.1	42.8
23.4	27.5	16.8	13.8
	119	73.2	60.4
20.8	21.6	14.9	12.1
	105	73.2	59.7
19.8	20.4	14.0	11.2
	105	72.3	58.1
16.1	17.2	11.5	9.1
	109	73.1	58.5
11.9	10.1	7.6	6.0
	87.4	66.5	52.9
10.0	7.9 (102°K.)	6.2 (186°K.)	5.1
	82.0	65.0	54.1
8.5	6.8	5.1	4.1
	84.8	64.8	52.9
8.5	6.4 (102°K.)	5.7 (186°K.)	4.2
	80.0	71.7	54.2
8.3	6.1 (102°K.)	5.1 (186°K.)	4.1
	78.3	66.3	54.2
4.6	6.6	3.5	2.7
	152	84.8	67.3
3.1	5.4	3.5	2.6
	187	126	96.7
3.0	4.1	2.4	1.7
	150	93.3	70.0
2.4	8.1	3.7	2.7
	355	171	129
1.8	6.3	2.6	1.9
	371	167	128
1.3	4.8	2.2	1.3
	400	200	131
1.0	5.0	2.2	1.3
	540	260	170
0.6	2.6	1.0	0.6
	500	235	167

Table II shows similar data for the same system ignited at 600°, and Table III gives the corresponding data for the manganese oxide supported on high-area *rutile*.

TABLE II

SUSCEPTIBILITY OF MANGANESE OXIDE ON ALUMINA, IGNITED AT 600°

Wt. % manganese	Susceptibilities $\times 10^6$ 83°K.	195°K.	298°K.
26.3	66.7	45.7	34.0
	255	175	131
18.5	47.1	30.7	23.9
	255	168	131
16.6[a]	39.2	28.7	19.1
	238	175	118
8.9	23.6	15.9	11.2
	269	182	129
6.1[a]	18.8	10.3	7.1
	315	175	123
4.4	15.2	8.8	5.9
	353	209	143
4.0[a]	14.9	8.0	4.8
	383	200	130
3.0	13.1	6.5	4.5
	447	231	160
2.7[a]	12.8	5.3	3.4
	489	211	141
1.8	8.0	3.9	2.4
	462	240	156
1.1[a]	7.6	2.7	1.6
	727	282	182
1.0	4.6	2.1	1.2
	492	251	160

[a] Sample was prepared by direct decomposition of manganous nitrate on alumina at 600°. The other samples were derived from those of Table I by further heat treatment at 600°. There does not seem to be any difference in the two preparations.

The remaining experimental and derived data are more conveniently shown graphically. Figure 1 shows susceptibility isotherms for the three states of supported manganese, namely, low-temperature ignition on alumina, high-temperature ignition on alumina, and ignition on *rutile*.

Figures 2, 3 and 4 show, respectively, the concentration of manganese plotted against magnetic moment for each of the three series. The magnetic moment is given in Bohr magnetons as calculated from the usual formula $\mu = 2.84 \sqrt{\chi_M(T + \Delta)}$. On the same graphs there are

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[4] Furman, "Scott's Standard Methods of Chemical Analysis," 5th ed., D. Van Nostrand Co., Inc., New York, N. Y., 1939, p. 771.

TABLE III

SUSCEPTIBILITY OF MANGANESE OXIDE ON *Rutile*

Wt. % manganese	Susceptibilities × 10^6		
	102°K.[a]	186°K.	298°K.
18.8	15.1	12.7	10.2
	78.7	66.5	53.8
12.5	12.4	9.8	7.5
	96.8	76.7	59.2
7.9	9.7	7.1	5.7
	119	87.4	71.0
3.9	6.7	4.7	3.5
	167	115	87.2
3.1	6.1	...	2.9
	194	...	90.4
1.3	4.1	2.7	1.7
	292	192	123

[a] Note different temperatures caused by rebuilding of apparatus.

shown the apparent valences of the manganese obtained from the chemical analyses according to the following procedure: total gram-atoms of oxygen in a sample is equal to the sum of gram-atoms of active plus inactive oxygen, and this is equal to the sum of gram-atoms of active oxygen plus manganese. The valence of manganese is twice the gram-atoms of total oxygen per gram-atom of manganese.

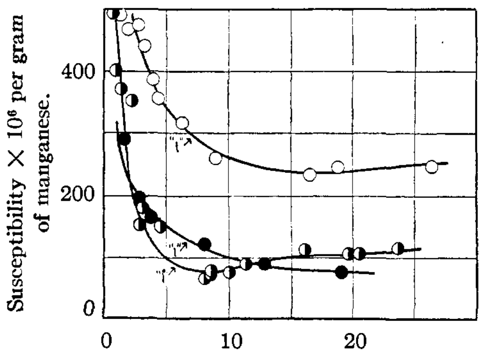

Fig. 1.—Susceptibility isotherms for supported manganese oxides at −171°: ○, high ignition on Al_2O_3; ◑, low ignition on Al_2O_3; ●, MnO_2 on TiO_2.

Figure 5 shows percentage of manganese plotted against the Weiss constant (Δ) for all three series of catalysts.

The single sample of supported rhenium on γ-alumina contained 4.8 per cent. of rhenium. The magnetic susceptibility before reduction was 0.3 × 10^{-6}, and after reduction it was −0.1 × 10^{-6}. Supported rhenium obviously does not show the magnetic dispersion effect.

Discussion of Results

Supported manganese shows the same magnetic dispersion effect first reported for chromium and now shown to apply to nearly all paramagnetic ions except molybdenum and rhenium. The effect will, for obvious reasons, probably not be found in the paramagnetic rare earths. Its failure to appear in molybdenum and rhenium is probably due to covalent bonds between adjacent positive ions.

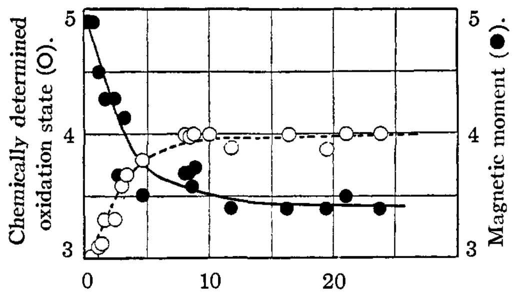

Fig. 2.—Oxidation state (○), and magnetic moment (●) for low-ignition series on alumina.

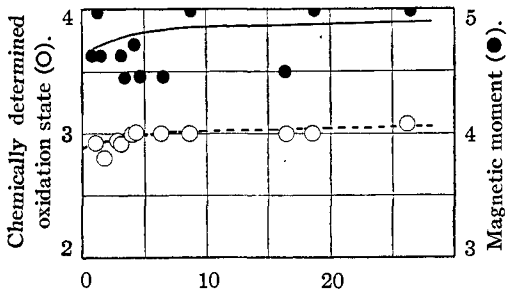

Fig. 3.—Oxidation state (○), and magnetic moment (●) for high-ignition series on alumina.

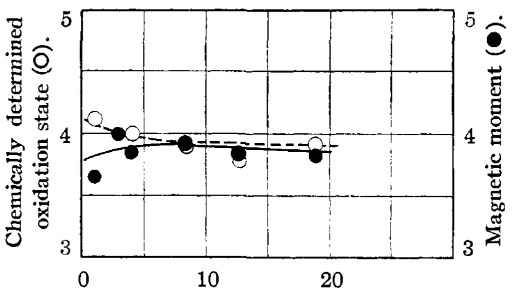

Fig. 4.—Oxidation state (○), and magnetic moment (●) for series on *rutile*.

The general shape of the susceptibility isotherm for supported manganese is the same as for the chromia–alumina system, except that the low-ignition series on alumina shows a very much sharper point "l" than anything heretofore observed. It is more convenient to discuss the high-ignition series on alumina first.

It would be expected that ignition of manganous nitrate at 600° would result in the formation of reasonably pure Mn_2O_3. The magnetic moment in the supported series ignited at this temperature is shown to be very close to the theoretical spin-only moment (4.9) for manganese in the plus three oxidation state. The conclusion that man-

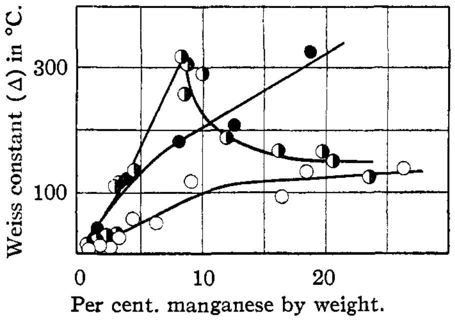

Fig. 5.—Weiss constants as a function of concentration: ○, high-ignition on Al_2O_3; ◑, low-ignition on Al_2O_3; ●, MnO_2 on TiO_2.

ganese has a valence of three throughout this series is amply verified by direct chemical analysis for total manganese and for active oxygen.

The shape of the susceptibility isotherm in this series is, therefore, in no way connected with changing oxidation state, and must be attributed to changing environment. The large change of the Weiss constant with manganese concentration is evidence that the number of nearest manganese neighbors possessed by each manganese ion changes rapidly at the lower manganese concentrations. Following the argument previously presented for chromium, with which this series is closely parallel, we conclude that the manganese ions are aggregated in microcrystals of Mn_2O_3, and that much of the alumina surface remains bare. Our conclusion is, again, that as at point "*l*" the manganese oxide layers are only three or four atoms thick. This general pattern seems to be the commonest susceptibility isotherm encountered.

The situation with respect to low temperature ignition of manganous nitrate on alumina is very different. Ignition at 200° would normally yield *pyrolusite*. The actual result, however, is that while the manganese clearly has an oxidation state of plus four at high concentrations, the oxidation state is definitely three at low concentrations. This result is shown both by the chemical analysis and by the magnetic moment, which are in excellent agreement with each other. (The theoretical spin-only moment for Mn^{+4} is 3.87). Simultaneous with this change in oxidation state, the Weiss constant shows an astonishing maximum in the neighborhood of 8% manganese.

We shall first consider the surprising change in oxidation state from four to three as the manganese concentration is lowered. It is well known that the Mn^{+3} ion has approximately the same radius as the Al^{+3} ion, and also that the γ-form of Mn_2O_3 is isomorphous with γ-Al_2O_3. It is suggested that the crystal lattice of the alumina exerts an inductive action on the manganese sufficient to cause a change of valence. It might be said that the manganese oxide attempts to imitate the crystal structure of the support, even to the extent of changing oxidation state. The effect described is somewhat related to the phenomenon of oriented overgrowth, and is reminiscent of a current theory of nucleoprotein synthesis.[5]

This effect apparently is of fairly general occurrence with transition group ions, provided the proper charge and radius may be assumed without too much difficulty. The effect does not occur with copper or silver supported on alumina, but it does occur with nickel on alumina and on *rutile*. It occurs with iron on *rutile* as will be described in forthcoming papers, and it occurs with manganese on *rutile* as shown in the results given in this paper. The effect may be expected to have a number of applications in the field of promoters, catalysts in general, corrosion, coprecipitation, crystallography and in the preparation of unique oxidizing agents.

It remains to explain the peculiar Weiss constant found in this series. It seems probable that the layers of manganese atoms in actual contact with alumina always are subject to the inductive action of the alumina and consequently always have the manganese in the plus three oxidation state. When large amounts of manganese are present these surface layers are negligible in their percentage contribution to the magnetic susceptibility. But as the concentration of manganese goes down the relative importance of the layers next to the alumina progressively increases until they ultimately account, at the limit, for all the manganese present.

Hence, according to this picture, the apparent change of oxidation state in the manganese is not so much an actual change in valence as a change in the ratio of manganese touching alumina and hence in the +3 state, to manganese merely touching manganese and hence reverting to the normal +4 state.

If the degree of exchange interaction in *bixbyite* were greater than that in *pyrolusite*, then the anomalous Weiss constants obtained would be easily explained. Actually the Weiss constants for supported +3 manganese are consistently lower than those for +4 manganese. This is clearly shown in Fig. 5. In order to further establish this point some Mn(III) on alumina was prepared by hydrogen reduction at 200° rather than by thermal decomposition at 600°. This also showed a lower Weiss constant than the +4 state.

In seeking an explanation of the anomalous Weiss constants in the MnO_2/Al_2O_3 series consideration was given to the fact that many solids show a variety of peculiar properties when metal ions of differing charges occupy adjacent positions in the lattice. It was thought that possibly the exchange interaction would increase if a +3 Mn ion were adjacent to a +4 ion, and that the large increase of the Weiss constant might be a measure of the number of manganese ions in this peculiar

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(5) A preliminary communication concerning this effect of valence inductivity was given in THIS JOURNAL, **70**, 883 (1948).

condition, namely, of being adjacent to manganese ions of different charge.

A further experiment was performed for the purpose of testing this idea. The experiment has some unusual features and will be described.

Slow Reduction of MnO_2/Al_2O_3.—A catalyst containing 20% manganese, substantially all in the +4 state, on alumina was slowly reduced in hydrogen at 180°. The reduction to the +3 state at this temperature took several weeks. At frequent intervals the sample was cooled, removed, and its susceptibility was determined. Figure 6 shows the Weiss constant of this sample plotted as a function of oxidation state.

In this experiment it was hoped that there would be produced a detectable proportion of +3 and +4 manganese ions in adjacent positions. The experiment is obviously one of some difficulty because of the tendency for heterogeneous reactions to proceed from discrete spots so that +3, +4 ion groups may occur only instantaneously at the reaction boundary. Furthermore, there is no reason to expect a maximum number of such groups at the point of 50% conversion from +4 to +3 manganese.

Under these circumstances the results are very gratifying. It is clearly shown that during the course of reduction the Weiss constant rises, but that when reduction is complete the Weiss constant is lower for the supported +3 state than for the +4 state. The erratic changes observed for the Weiss constant are not experimental error, but are probably a measure of the fluctuating proportion of +3, +4 ion groups present at the various stages of reduction.

The success of this experiment supports the view expressed concerning the anomalous Weiss constants found in this system.

The peculiar susceptibility isotherm found for the low-ignition manganese on alumina series is thus seen to be due to a combination of two changes both of which lead to greatly increased susceptibility at low manganese concentrations. These two changes are a change of oxidation state, and a change of environment. While both changes lead to an increase of susceptibility, the changing oxidation state alone at first produces an increase of the Weiss constant, but the increasing dispersion ultimately reduces the Weiss constant to zero. This is the first example we have encountered where the shape of the susceptibility isotherm is determined both by an oxidation state change and an environmental change.

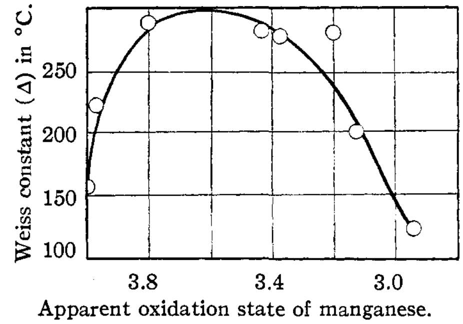

Fig. 6.—Weiss constants as a function of oxidation state during slow reduction of MnO_2 to Mn_2O_3.

The idea of supporting manganese on *rutile* was suggested by the considerations described above. It was clear that if our interpretation were correct then manganese on high-area *rutile* ought to yield all the manganese in the oxidation state of plus four. This proved to be the case and the susceptibility isotherm is a typical example of the type in which the whole change is due to change of environment and not to change of oxidation state. Titania seems to be the only diamagnetic solid isomorphous and approximately isometric with *pyrolusite*, of reasonable stability, and capable of being prepared in a high-area form.

It may be objected that manganous nitrate would give Mn(IV) even if ignited on low-area *rutile*. This is, of course, correct, but in that case the normal dispersion effect would be absent, the susceptibility of the manganese would be independent of concentration and the situation would resemble that previously reported for chromia supported on low-area corundum.

Summary

The susceptibility isotherm method has been extended to supported manganese. It has been found that in favorable cases supported transition group oxides may imitate the crystal structure of the support even to the extent of changing oxidation state.

EVANSTON, ILLINOIS RECEIVED AUGUST 9, 1948