double sulfates, each mole of the same will liberate one mole of the sulfate of bivalent metal and three moles of sulfuric acid. The electrical conductivity measurements were made of the solutions obtained after hydrolysis and these values were compared with similar values obtained from artificial solutions prepared on the above assumption.

TABLE II

SPECIFIC CONDUCTIVITY OF HYDROLYZED SOLUTIONS AND SYNTHETIC SOLUTIONS OF SAME CONCENTRATION

Solution	Wt. of $RSO_4 \cdot Sb_2(SO_4)_3$, g.	Sp. conductivity, mhos × 10^{-3}				
$MgSO_4Sb_2(SO_4)_3$	3.9	10.92	5.65	3.06	1.65	0.89
$MgSO_4 + H_2SO_4$		10.51	5.49	3.01	1.63	.88
$ZnSO_4 \cdot Sb_2(SO_4)_3$	3.88	8.61	4.82	2.61	1.39	.75
$ZnSO_4 + H_2SO_4$		8.32	4.63	2.55	1.36	.73
$CdSO_4 \cdot Sb_2(SO_4)_3$	3.7	7.52	4.35	2.45	1.32	.72
$CdSO_4 + H_2SO_4$		7.25	4.21	2.39	1.28	.69
$CoSO_4 \cdot Sb_2(SO_4)_3$	3.78	10.55	5.46	2.92	1.56	.81
$CoSO_4 + H_2SO_4$		10.28	5.30	2.85	1.51	.79
$MnSO_4 \cdot Sb_2(SO_4)_3$	3.9	9.51	5.11	2.94	1.55	1.82
$MnSO_4 + H_2SO_4$		9.36	5.01	2.87	1.51	0.79

A weighed amount (3.9 to 3.7 g.) of $RSO_4 \cdot Sb_2(SO_4)_3$ was boiled with distilled water (400 cc.), the hydrated antimony oxide was filtered off and the filtrate was made to 100 cc. The sp. conductivity of this solution was determined by the method of Kohlrausch; 50 cc. of this filtrate was made to 100 cc. with distilled water and the sp. conductivity was measured once again. This operation was repeated thrice. Similar measurements were made for the solutions containing the exact amount of sulfuric acid and the sulfate of bivalent metal calculated on the assumption that each mole of $RSO_4 \cdot Sb_2(SO_4)_3$ liberates on hydrolysis one mole of the sulfate of bivalent metal and three molecules of sulfuric acid. The data obtained are given in Table II.

From the above Table II it is observed that the values of sp. conductivity of hydrolyzed solutions and synthetic solutions of same concentration are very close to each other. This indicates that the compounds $RSO_4 \cdot Sb_2(SO_4)_3$ appear to be double sulfates.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Supported Oxides of Manganese: Influence of Support Modification[1]

BY P. W. SELWOOD AND LORRAINE LYON

The susceptibility isotherm method has been extended to a series of modified alumina supports—the supported oxides being those of manganese. It has been found that support phase modification has a negligible effect on the oxidation state or dispersion of the supported manganese, provided that the specific surface area is maintained large, and that no appreciable amounts of alkali are present. The presence of alkali in the support causes a large change in the susceptibility isotherm, reflecting substantial changes in oxidation state and degree of dispersion of the manganese.

Earlier papers from this Laboratory have been concerned with the possible influence of substrate modification on the susceptibility isotherm only to the extent of comparing low specific surface α-alumina with high area so-called γ-alumina, and with magnesia, rutile, anatase and silica as compared with alumina. The object of the present work was to examine the effect of phase modifications in alumina on the susceptibility isotherm. Supported oxides of manganese[2] were chosen for this study because this system has been shown to be sensitive to structural changes and to show large variations of magnetic susceptibility for relatively slight changes in oxidation state and degree of dispersion. Interest in this system was further stimulated by the appearance of a communication by Rodier and Rodier[3] in which it is stated that a major change takes place in the form of the susceptibility isotherm for supported manganese oxides on an alumina characterized only as "très actif."

The procedure adopted was to obtain magnetic susceptibility data for supported oxides of manganese on all the known phases of alumina, on alumina to which some alkali had been added and for samples obtained by various modifications of the preparation method.

Experimental Part

There will first be described the preparation of the several different substrates. Some of the starting materials were obtained from the Aluminum Company of America, Research Laboratories, through the courtesy of Dr. A. S. Russell. Several of the preparations were made by the methods described by Stumpf, Russell, Newsome and Tucker.[4]

α-$Al_2O_3 \cdot H_2O$ was made from Alcoa α-trihydrate by digestion in water at 200° at about 30 atmospheres pressure for 2.5 hours in a glass-lined nickel bomb. The X-ray pattern agreed in detail with that accepted. The magnetic susceptibility at room temperature was about 0.2×10^{-6}. This high susceptibility was doubtless due to a trace of impurity.

β-$Al_2O_3 \cdot 3H_2O$ was made by precipitation from "sodium aluminate" with carbon dioxide at 40°. The X-ray pattern agreed with the ASTM Index.

χ-Al_2O_3 was made from α-trihydrate by heating in dry air at 800° for one hour. The X-ray pattern agreed with Stumpf, *et al.* The susceptibility at −125° was -0.1×10^{-6}.

κ-Al_2O_3 was made by heating α-trihydrate in air at 1000° for one hour. The X-ray pattern agreed with Stumpf, *et al.*, and the susceptibility showed some temperature dependence, being 0.6 ($\times 10^{-6}$) at 28°, 1.2 at −125°, and 1.3 at −187°.

γ-Al_2O_3 was prepared from α-monohydrate by heating for one hour at 600° in a stream of dry air. The X-ray pattern

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[1] This is the tenth paper on the susceptibility isotherm from this Laboratory. The ninth, by Selwood, Lyon and Ellis appeared in THIS JOURNAL, **73**, 2310 (1951).

[2] P. W. Selwood, T. E. Moore, M. Ellis and K. Wethington, *ibid.*, **71**, 693 (1949).

[3] G. Rodier and G. Rodier, *Compt. rend.*, **230**, 93 (1950).

[4] H. C. Stumpf, A. S. Russell, J. W. Newsome and C. M. Tucker, *Ind. Eng. Chem.*, **42**, 1398 (1950).

agreed with Stumpf, *et al.*, and the susceptibility at −187° was 0.3×10^{-6}.

δ-Al_2O_3 was prepared from α-monohydrate by heating in steam at 1000° for one hour. The X-ray pattern agreed with Stumpf, *et al.*, and the susceptibility at −125° was 0.2×10^{-6}.

η-Al_2O_3 was prepared by heating β-trihydrate at 1100° in a stream of dry air. The X-ray pattern agreed with Stumpf, *et al.*, and the susceptibility at −187° was 0.1×10^{-6}.

α-Al_2O_3 (high area) was prepared by heating diaspore at 650° for one hour. The X-ray pattern agreed with the ASTM Index for corundum, but the susceptibility of 2.3×10^{-6} at −125° was obviously high owing to iron impurity in the diaspore. There appears to be no other known method for preparing high area α-alumina.

While all the above samples could properly be classed as "high surface area" materials, no adsorption isotherms were measured, reliance being placed on the surface data given by Stumpf, *et al.* That this was justifiable was seen by the strong adsorption of manganous nitrate solution shown by all samples.

SiO_2–Al_2O_3 was prepared by dissolving about 9.6 g. of sodium silicate in water, then adding 442 g. of aluminum sulfate which had been dissolved in 3 l. of water The milky mixture was treated with ammonium hydroxide, the final slurry being acid to litmus. The mixture, which was of course rich in alumina rather than in silica as in technical cracking catalysts, was washed, dried, sieved and calcined at 500° for one hour, then at 600° for five hours. It gave only a diffuse X-ray pattern. The susceptibility at −125° was zero.

Na_2O-Al_2O_3.—This sample of alumina containing some sodium was precipitated from sodium aluminate with carbon dioxide at room temperature. The usual washing step was omitted. The product gave a poor X-ray pattern with lines at 3.06, 2.30, 1.405 and 2.00 in order of decreasing intensity. The susceptibility at −125° was -0.2×10^{-6}. The *p*H of the suspension was 10.9.

Na-free Al_2O_3.—The so-called "γ"-alumina, used for nearly all earlier work on supported oxides in this Laboratory, was repeatedly washed with ammonium nitrate solution, calcined at 200° for 36 hours, then at 400° for a few hours. The *p*H of the suspension was 4.6, and the susceptibility -0.3×10^{-6} at −187°.

Na-free Al_2O_3, Acid-washed.—This was prepared as described immediately above except that the washing was done with 1:2 or 1:10 nitric acid.

Preparation of supported oxides of manganese on the above aluminas is given below. For convenience in reference to the data presented under Results the various samples are given short designations as indicated immediately below.

χ—prepared by impregnation of 5 g. of χ-Al_2O_3 with 25 cc. of 80% $Mn(NO_3)_2 \cdot 6H_2O$ solution for one hour, followed by filtering and calcining at 200° for 48 hours.
κ—similar to χ but on κ-Al_2O_3
γ—similar to χ but on γ-Al_2O_3
δ—similar to χ but on δ-Al_2O_3
η—similar to χ but on η-Al_2O_3
α—similar to χ but on high area α-Al_2O_3 from diaspore
Si—similar to χ but on the silica–alumina described above under SiO_2–Al_2O_3
Na—similar to χ but on alumina containing sodium ions described above under Na_2O-Al_2O_3. Various samples were prepared with various concentrations of manganese. This was done by changing the concentration of the manganous nitrate solution.
Na-PM—similar to Na but impregnated with potassium permanganate solution.
Na-free—similar to χ but on the alumina described above as Na-free Al_2O_3.
Na-free A—similar to χ but on the alumina described as Na-free Al_2O_3, acid washed.
Na-free, PM—similar to Na-PM but on Na-free Al_2O_3.
Na-W—impregnated from $Mn(NO_3)_2$ solution on Na_2O-Al_2O_3 but washed with water after impregnation.

A sample prepared like Na-free, but washed with water after impregnation but before ignition, proved to contain virtually no manganese.

The concentration of manganese in the finished samples varied widely, as expected, with nature of the support. Some idea of the concentration of impregnating solution required to obtain various samples is shown in Table I.

Table I

Concentration of Impregnating Solution Required to Yield Final Manganese Concentrations

Sample designation	Final Mn, %	$Mn(NO_3)_2 \cdot 6H_2O$ solution, %
χ	5.1	80
δ	11.7	80
Na	21.6	80
Na	7.9	4.8
Na–W	8.5	19
Na–W	5.3	80
Na-free	1.2	6

In general, for samples prepared by the usual impregnation method, the concentration of supported oxide in the finished sample is roughly proportional to the concentration of the impregnating solution. Thus for most samples described an increase in the concentration of the manganous nitrate solution resulted in a higher concentration of manganese in the ignited sample. The Na-W samples are interesting because here the reverse took place. For these samples, prepared by impregnation on alumina containing sodium ions and then washed before ignition, the more concentrated manganous nitrate solution yielded a lower manganese concentration in the finished sample. This effect is probably due to partial neutralization of the excess alkali by the nitrate solution and hence leaving less alkali on the surface to precipitate insoluble manganous hydroxide.

Total manganese, and average manganese oxidation state where required, were found by methods previously described,[2] as were determinations of magnetic susceptibility and X-ray diffraction pattern.

Results

Magnetic susceptibility results per gram of sample are given in Table II. Susceptibilities per gram of manganese are given in Fig. 1.

Table II

Susceptibility Data for Supported Manganese Oxides on Various Substrates

Sample designation	Mn, %	Susceptibility × 10^6 per g. sample at −187°	Sample designation	Mn, %	Susceptibility × 10^6 per g. sample at −187°
χ	5.1	5.4	Na	7.9	22.1
κ	8.3	8.9	Na	0.9	3.61
γ	12.4	14.4	Na-PM	1.6	4.0
δ	11.7	12.9	Na-PM	1.14	2.6
η	11.7	13.1	Na-PM	0.66	2.0
α	5.6	7.6[a]	Na-free	14.0	14.0
Si	3.1	5.1[a]	Na-free A	13.7	12.3
Na	22.1	40.5	Na-free A	12.6	12.5
Na	18.5	33.9	Na-free A	1.2	3.1
Na	18.0	33.6	Na-free PM	2.2	4.2
Na	17.1	32.1	Na–W	5.6	19.4
Na	14.5	32.8	Na–W	8.5	20.1
Na	12.9	29.4	Na–W	8.6	20.7
Na	11.3	26.1	Na–W	6.8	18.7
Na	11.0	27.2	Na–W	5.7	17.4

[a] At 125° K.

It will be noted from Fig. 1 that the only large influence of substrate modification occurs when alkali is present. More extensive susceptibility measurements were, therefore, made on some of the alkali-containing samples to determine, if possible, the cause of the large susceptibility increase found whenever alkali was permitted to remain in the support. In Table III there are given susceptibilities per gram-atom of manganese at several temperatures, together with the Weiss Constant, the magnetic moment and the oxidation state of the manganese as determined by chemical analysis. In every case the susceptibilities were found to be described by the Curie–Weiss law.

TABLE III

ADDITIONAL MAGNETIC DATA ON SAMPLES CONTAINING ALKALI

Sample designation	Mn, %	Δ	μ	Oxidation state
Na	22.1	155	4.4	3.6
Na	18.0	140	4.3	3.6
Na	14.5	100	4.3	3.6
Na	11.0	70	4.1	
Na–W	6.8	62	4.2	3.6
Na–W	5.7	42	4.4	3.5

Discussion

It may be concluded from this work that mere change of support phase has only a slight effect on the dispersion and oxidation state of manganese oxides supported on high area alumina. This is in contrast to the effects previously reported for the substitution of anatase for rutile and for the use of low specific surface corundum; but provided that the area is maintained high and that alkali concentrations are low, results obtained with the various known phase modifications of alumina are not sensibly different from those previously reported on so-called "γ"-alumina.

Similarly, the effect of adding small amounts of silica, of using permanganate as the impregnation agent, and of acid-washing the alumina had a negligible effect on the supported oxide although sometimes greatly modifying the amount of manganese which could be placed on the support.

The presence of alkali in the alumina has a marked effect on the position and form of the susceptibility isotherm. At moderate manganese concentrations the magnetic susceptibility per gram of manganese at liquid air temperature may be five times larger for a sample containing alkali as compared with one which is free from alkali. This is probably the reason for the effect noted by Rodier and Rodier.

The changes caused by alkali, which are often accompanied by major changes of catalytic activity, are due to a combination of circumstances. The marked inductive action of the support on the oxidation state of the manganese is greatly reduced. The oxidation state tends to remain about 3.6, namely, near the value expected from atmospheric oxidation of manganous hydroxide, while the dispersion of the manganese tends to be somewhat greater for equivalent concentrations when alkali is present.

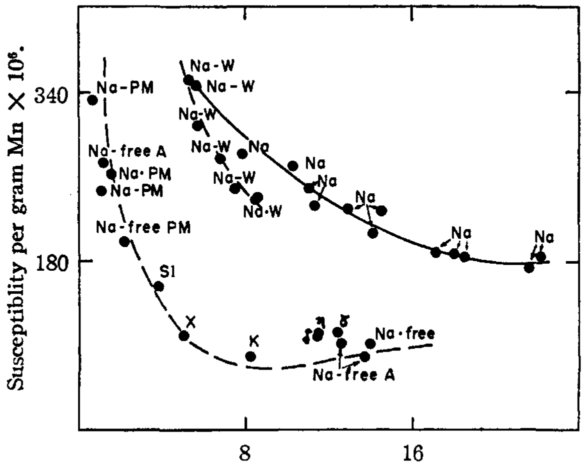

Fig. 1.—Magnetic susceptibility data at −187° for manganese on various modifications of alumina. The dashed line is the susceptibility isotherm previously reported for low temperature ignition of manganous nitrate on so-called γ-alumina. Identification of experimental points with the various samples is given in the text; thus Na–W refers to a sample impregnated on alumina containing alkali, then washed before ignition.

It is interesting to note that the presence of alkali makes the manganese much more resistant to washing out with water before the ignition step. For instance, if there were used for impregnation a manganous nitrate solution strong enough to yield a finished sample containing 15% manganese, then washing this sample with water after impregnation but before ignition would yield a product containing about 5% manganese. But in the absence of alkali virtually all the manganese would have been washed off. Furthermore, in the alkali-containing sample, that part of the manganese which is readily washed off is that which, if ignited, would have yielded a considerably less dispersed fraction of manganese in the finished sample. It is clear that the manganese most resistant to washing off is that which is more highly dispersed.

Catalytic activity data on these and related samples will be presented in a future paper.

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