[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Magnetic Properties of Titanium Sesquioxide[1,2]

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Magnetic susceptibility measurements over a range of temperature have been made on pure titanium sesquioxide, on the sesquioxide supported on γ-alumina, and on solid solutions of Ti_2O_3 and Al_2O_3. The pure sesquioxide is antiferromagnetic with a Curie point near 248°K. In supported and dissolved forms the tripositive titanium ion shows increasing susceptibility with increasing magnetic dilution. At infinite dilution the magnetic moment is approximately that expected for one unpaired electron spin. Some phases show a slight ferromagnetism.

Previous papers from this Laboratory have described magnetic susceptibility studies on the oxides of transition elements, with particular reference to elements and methods of preparation of interest in heterogeneous catalysis. It has, in general, been found that structural information concerning supported oxides is obtainable from the change of magnetic susceptibility which almost always occurs with changing magnetic dilution. The present work had as its purpose the extension of these observations to one of the few paramagnetic ions, of interest in catalysis, not hitherto studied. The low magnetic moment of the Ti^{+3} ion makes the results somewhat less accurate than those already reported.

Experimental Part

Preparation of Crystalline Titanium Sesquioxide.—This substance was prepared by the method of Friedel and Guérin.[3] Dried hydrogen was deoxygenated, dried again, saturated with titanium tetrachloride and passed over pure powdered rutile. The rutile was contained in an alundum boat held at 750°. After 48 hours the dark-violet crystalline product was removed from the furnace. X-Ray diffraction analysis gave only the lines for the sesquioxide. Quantitative analysis was done by heating in air a weighed sample until no further increase of weight occurred. The reaction is simply

$$2Ti_2O_3 + O_2 \longrightarrow 2TiO_2$$

For two samples the results were 99.2 and 99.4% Ti_2O_3.

Preparation of Supported Titanium Sesquioxide.—The usual impregnation procedure was not used for this preparation because it was felt that the high hydrogen ion concentration of stable Ti^{+3} solutions would alter the surface characteristics of the alumina support. It was found possible to prepare supported samples by the simple method of substituting γ-alumina for the rutile used in the preparation of crystalline sesquioxide. The alumina was magnetically pure and had a specific surface area of about 250 m.². Reaction times of from two to five hours were used to prepare samples of supported sesquioxide which were found to contain from 5 to 16% Ti_2O_3. The colors ranged from light to dark gray. Only a diffuse X-ray diffraction pattern was obtained from the samples in this concentration range. Quantitative analysis was based on a suggestion received from Dr. K. K. Kelley.[4] A weighed sample of supported oxide was placed in a flask with a small volume of 1:1 sulfuric acid. The flask was gently heated until the sample dissolved. The solution was then cooled, diluted with distilled water and passed through a Jones reductor. The reduced samples were treated with ferric ammonium sulfate, then titrated with a ceric solution.

Preparation of Ti_2O_3-Al_2O_3 Solid Solutions.—The solid solutions were prepared by heating portions of the several supported oxides in hydrogen at about 1050°, for five hours. Colors ranged from light to dark blue. Further analysis was not felt to be necessary. A sample of alumina was also heated at 1050° for five hours for reference in connection with the X-ray studies, and because the susceptibility of the support was to some degree dependent on the temperature to which it had been heated.

Magnetic Susceptibility Studies.—Measurements were made on a Faraday balance of a type to be described fully in a later communication. All measurements were made in an atmosphere of helium. A number of measurements were made over a considerable range of field strength in order to detect ferromagnetism.

X-Ray Measurements.—All X-ray work was done on the North American Phillips Recording Spectrometer.

Results

Pure Titanium Sesquioxide.—The magnetic susceptibility per gram of Ti_2O_3 at several temperatures is given below

T, °K.	83	195	248	273	298	350
$\chi \times 10^6$	0.854	0.874	0.921	0.888	0.874	0.821

Ehrlich[5] reports 0.94 at 293°K. and 0.88 ($\times 10^{-6}$) at 90°K. The susceptibility per gram of Ti^{+3} ion, corrected for the diamagnetism of oxide ions, is given as a function of temperature in Fig. 1. It will be clear from earlier work that these values will probably be dependent on particle size.

Supported Titanium Sesquioxide.—The pure alumina used in this work was found to have a susceptibility at room temperature of -0.386×10^{-6} per gram. Prolonged ignition at 1050° changed the (room temperature) susceptibility to -0.352×10^{-6}. Susceptibilities of supported titanium sesquioxide samples are given in Table I. The susceptibility isotherm for these samples at room temperature is shown in Fig. 2.

TABLE I

SUPPORTED Ti_2O_3 ON Al_2O_3. SUSCEPTIBILITIES χ PER GRAM OF SAMPLE AND $\chi_{Ti^{+3}}$ PER GRAM OF Ti^{+3}

Ti_2O_3, %	T, °K.	$\chi \times 10^6$	$\chi_{Ti} \times 10^6$
16.3	298	+0.031	3.6
16.3	195	+ .103	4.3
16.3	83	+ .648	9.3
14.3	298	− .008	3.8
8.02	298	− .081	5.5
8.02	195	− .037	7.7
8.02	83	− .683	19.8
6.67	298	− .082	6.7
5.33	298	− .100	7.8

Solid Solutions.—All but one solid solution showed some field strength dependence of susceptibility indicating the presence of ferromag-

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[1] This work was in part supported by the Signal Corps Engineering Laboratories.

[2] This is the thirteenth paper from this Laboratory on the susceptibility isotherm and related subjects. The twelfth, by Mooi and Selwood appeared in THIS JOURNAL, **74**, 2461 (1952). Inquiries should be addressed to P. W. Selwood.

[3] C. Friedel and J. Guérin, *Ann. chim.*, **7**, 38 (1876).

[4] Private communication.

[5] P. Ehrlich, *Z. Elektrochem.*, **45**, 362 (1939).

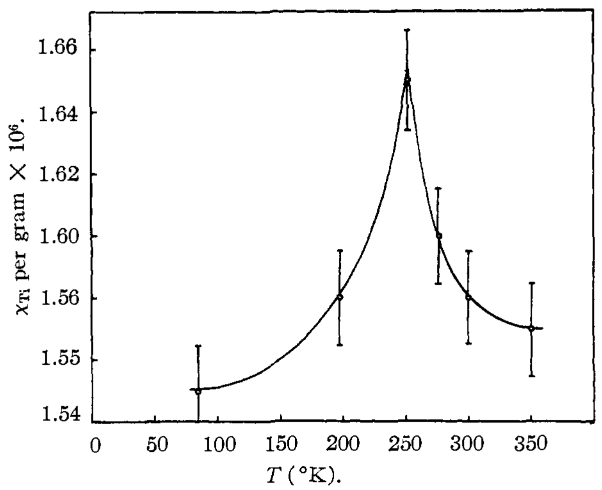

Fig. 1.—Susceptibility of Ti in Ti_2O_3 over a range of temperature.

netism. This parallels a recent observation of Weise[6] on some titanates. The one sample free from ferromagnetism, containing 14.3% of Ti_2O_3, gave the following susceptibilities

T, °K.	83	195	298
$\chi \times 10^6$	1.20	0.527	0.359
$\chi_{Ti} \times 10^6$	17.2	9.1	7.5

Discussion of Results

The existence of a Curie point for pure titanium sesquioxide shows that this oxide, as anticipated, is antiferromagnetic. The observed Curie point in the neighborhood of 248°K. is in agreement with the electrical and thermal anomalies reported[7-9] for this substance. The almost negligible slope of susceptibility with temperature above the Curie point makes it quite difficult to estimate the Weiss constant, although the Curie–Weiss law seems to be followed. The Weiss constant is certainly very large and may be roughly estimated at 2000°. Then the magnetic moment of the Ti^{+3} ion in the crystalline solid is about 1.2 Bohr magnetons. This large ratio of Weiss constant to Curie temperature is far greater than the maximum ratio calculated by Van Vleck.[10]

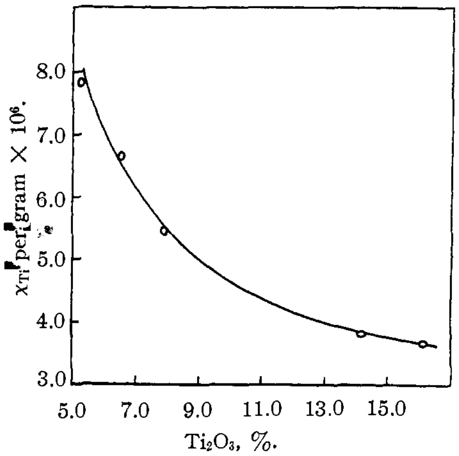

Fig. 2.—Susceptibility of Ti in supported titania on alumina.

The susceptibility isotherm for supported titanium sesquioxide follows the same general pattern shown by all paramagnetic transition elements except molybdenum and the rare earths. Increasing dilution is accompanied by increasing susceptibility, this being doubtless due to a reduction of the paramagnetic neighborhood around each Ti^{+3} ion. There appears to be some stabilization of the tripositive oxidation state of the titanium by the alumina; these supported oxides were stable in air. For a supported oxide containing 8.02% Ti_2O_3 (the lowest concentration for which precision is very satisfactory) the Weiss constant is 40° and the magnetic moment 0.9 Bohr magneton. This low moment parallels the case of supported ferric oxide.

A similar increase of susceptibility occurs in the solid solution. At 83°K. the susceptibility per gram of Ti^{+3} dissolved in alumina, at a concentration of 14.3% Ti_2O_3, is eleven times greater than that per gram of Ti^{+3} in pure Ti_2O_3 at the same temperature. For this solution the Weiss constant is 105° and the moment is 1.1 magneton.[11]

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(6) E. K. Weise and H. Katz, *Phys. Rev.*, **86**, 1046 (1952).

(7) B. F. Naylor, THIS JOURNAL, **68**, 1077 (1948).

(8) M. Foex and J. Loriers, *Compt. rend.*, **226**, 901 (1948).

(9) H. C. Shomate, THIS JOURNAL, **68**, 310 (1946).

(10) J. H. Van Vleck, "Colloques Internationaux du Centre National de la Recherche Scientifique," Vol. XXVIII, "Ferromagnetisme et Antiferromagnetisme," Grenoble, Paris, 1951, pp. 114–118.

(11) Complete experimental results are contained in the Master's Degree Thesis of Stephen F. Adler, Northwestern University, 1952.