

Experiments 4–7 were carried out in open platinum dishes and produced only polycrystalline $\text{BaFe}_{12}\text{O}_{19}$. *Anal.* Found: Ba, 12.35; Fe, 60.23; F, 0.02. Calcd. for $\text{BaFe}_{12}\text{O}_{19}$: Ba, 12.36; Fe, 60.29; F, 0.00.

Finally, Fe_2O_3 was introduced under completely non-stoichiometric conditions into a great excess of molten barium chloride. Exactly 300 g. of anhydrous barium chloride was melted in a platinum dish and oxygen was bubbled through a perforated platinum tube into the melt. At 1250° , 10.0 g. of Fe_2O_3 was introduced into the melt and reacted for 3 hr. The furnace then was cooled at a rate of 50° per hour. The cold reaction mixture was leached with water and 0.1 N HCl. The product consisted of lustrous platelets, most of which were transparent. Again it was shown, by means of an X-ray diffraction powder pattern, that even under these conditions $\text{BaFe}_{12}\text{O}_{19}$ was obtained as the only phase, which is further an indication for the high crystal energy of this particular barium ferrite. Finally, 10.00 g. of Fe_2O_3 reacted in 300.00 g. of molten SrCl_2 under conditions identical to those described above. As before, shiny, mostly transparent platelets of $\text{SrFe}_{12}\text{O}_{19}$ were obtained. (*Anal.* Found: Sr, 8.17; Fe, 62.89. Calcd. for $\text{SrFe}_{12}\text{O}_{19}$: Sr, 8.25; Fe, 63.12.) The d -spacings of the X-ray powder diffraction pattern of $\text{BaFe}_{12}\text{O}_{19}$ were in perfect agreement with ASTM File Card 7-276 and those of the isomorphous $\text{SrFe}_{12}\text{O}_{19}$ showed the same intensity variations with a correspondingly small shift in d -spacings.

X-Ray Analyses.—Powder samples of $\text{SrFe}_{12}\text{O}_{19}$ and $\text{BaFe}_{12}\text{O}_{19}$ were sealed in 0.3 mm. Lindemann glass capillaries and were mounted in a 114.6 mm. camera. Exposure times to copper K-alpha (λ 1.5418 Å.) radiation varied between 8 and 10 hr. Aluminum foil was placed over the film to minimize fluorescence effects.

Single crystal data were obtained by precession about the c -axis in a precession camera. 0 and 1 level photographs were taken with copper radiation and the elementary hexagonal cell dimensions were found to be $a_0 = 5.88$ Å., $c_0 = 23.20$ Å. for $\text{BaFe}_{12}\text{O}_{19}$; and $a_0 = 5.86$ Å., $c_0 = 23.00$ Å. for $\text{SrFe}_{12}\text{O}_{19}$. The space group is D_{6h}^4 ($P 6_3/mmc$.) With two formula weights per unit cell, the X-ray densities are 5.31 g. cc.⁻¹ for $\text{BaFe}_{12}\text{O}_{19}$ and 5.15 g. cc.⁻¹ for $\text{SrFe}_{12}\text{O}_{19}$ in excellent agreement with the pycnometric densities of 5.22 and 4.98 g. cc.⁻¹, respectively.

Domain Pattern.—The particular interest of the compounds prepared by the technique described lies in the fact that they are transparent at visible wave lengths. It must be assumed that for this special form of $\text{BaFe}_{12}\text{O}_{19}$ and $\text{SrFe}_{12}\text{O}_{19}$ all iron ions are 3-valent, since the presence of even small amounts of 2-valent iron would cause a significant absorption of light and make the crystal opaque.

In his paper, "Direct Observation of Weiss Domains by Means of the Faraday Effect," Kooy (ref. 4) shows pictures of internal domain patterns and also gives an explanation as to how these pictures come about. Figure 1 shows a virgin state domain pattern of a single crystalline platelet of

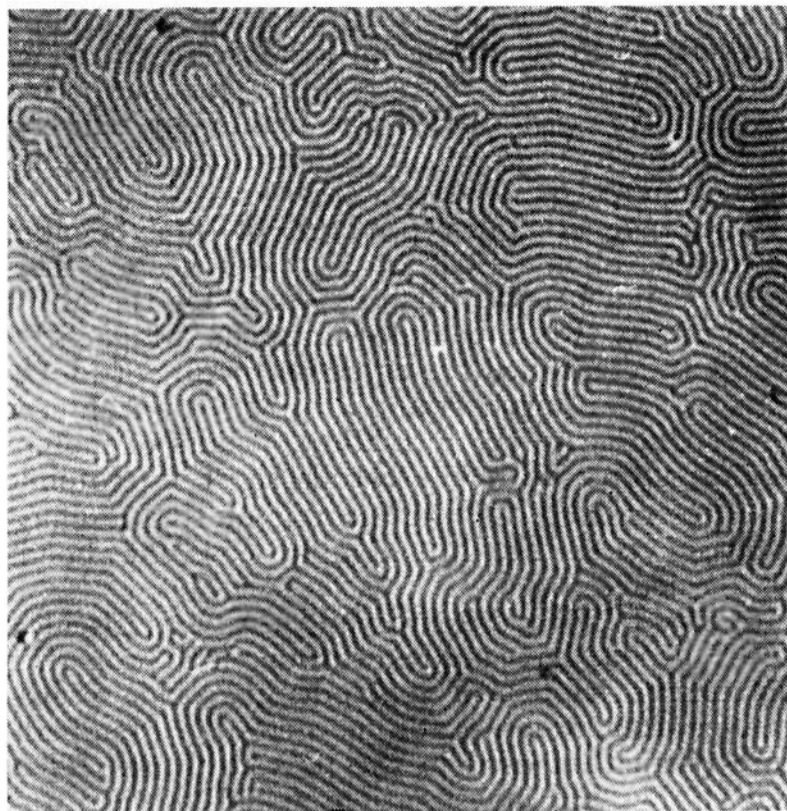


Fig. 1.—Domain pattern of $\text{SrFe}_{12}\text{O}_{19}$.

$\text{SrFe}_{12}\text{O}_{19}$ as obtained by the interaction of SrCl_2 and Fe_2O_3 . Transparent strontium-ferrite has not yet been reported in the literature. This pattern is practically identical with the pattern for $\text{BaFe}_{12}\text{O}_{19}$ as obtained by Kooy. Qualitatively, we also noticed that the domain pattern assumes a much more ordered form if it is observed after the crystal has been magnetized. With crystals of varying thicknesses, we furthermore found that the width of the domains depends on the thickness and that the domain size increases with temperature, which is in accordance with the decreasing crystal anisotropy with increasing temperature.

Quantitative observations on the domain pattern and its behavior in magnetic fields will be the subject of a forthcoming publication of F. J. Baum, H. S. Jarrett and M. S. Sadler.

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A Magnetic Investigation on Supported Molybdenum Dioxide

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The magnetic susceptibilities of a series of precipitated molybdenum oxide-alumina preparations have been measured in a hydrogen atmosphere after hydrogen reduction at 440 – 450° . Crystalline MoO_2 shows a temperature independent susceptibility of $+0.33 \times 10^{-6}$ per gram. By dilution of the molybdenum oxide on the alumina support, the susceptibility of MoO_2 increases considerably. For the highest diluted compound, with an atomic ratio of $\text{Mo}/\text{Al} = 1/99$, the MoO_2 susceptibility was determined as 27×10^{-6} at 78°K ., 9.8×10^{-6} at 195°K . and 6.5×10^{-6} at 295°K . The increase in paramagnetism on dilution probably is caused by an increasing number of unpaired electrons due to the decrease in number of Mo–Mo bonds present in the crystal lattice of MoO_2 . The susceptibility of the dispersed MoO_2 decreases considerably after exposure to air at room temperature, possibly due to chemisorption of oxygen. The investigation indicates close relationships between degree of dispersion and chemisorption efficiency of the supported MoO_2 .

Introduction

A number of transition metal oxides show an increase in magnetic susceptibility by dilution on a

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high-area diamagnetic support, such as $\gamma\text{-Al}_2\text{O}_3$. The usual explanation of this phenomenon is that exchange interaction covalent bonds exist between adjacent metal atoms in the crystal lattice. By

dilution of the oxide this interaction becomes weaker, which results in an increase in paramagnetism. Magnetic investigations on supported oxides have been carried out mainly by Selwood and co-workers. Selwood² has reviewed a number of such supported oxide systems.

The magnetic susceptibility of molybdenum dioxide is about $+0.3 \times 10^{-6}$ per gram. This value is much lower than expected for the Mo^{4+} ion with its two unpaired d-electrons. Magnéli,³⁻⁵ who has determined the crystal structure of MoO_2 , found alternating short and long Mo-Mo distances corresponding to the formation of pairs of molybdenum atoms with the rather short interatomic distance of 2.50 Å. On account of this Pauling⁶ suggests that Mo-Mo double covalent bonds are formed.

Selwood, Hill and Boardman,⁷ as well as Eischens and Selwood,⁸ have studied the magnetic properties of various supported molybdenum oxide preparations after reduction at somewhat higher temperatures than that used in the present work. They report that the investigations failed to yield any appreciable paramagnetism.

The present investigation shows that the susceptibility of MoO_2 , prepared by hydrogen reduction of a precipitated mixture of MoO_3 and Al_2O_3 at about 450°, increases considerably by lowering the concentration of molybdenum, at least when the oxide mixture is protected against air exposure.

Experimental

The supported MoO_3 samples used in the experiments were prepared by K. Søndergaard of this Laboratory. Solutions containing calculated amounts of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Baker's Analyzed) and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (Merck, pro analysis) were precipitated with concentrated ammonia. The slurry was well mixed and dried. After annealing for 3 hr. at 500° in the air, the samples were crushed in a mortar and sieved. The 60-80 mesh fraction was used. Measurements were carried out on preparations with these Mo/Al atomic ratios: 1/99, 2/98, 4/96, 8/92, 16/84, 32/68 and 50/50.

The supported molybdenum oxides were reduced in deoxidized and thoroughly dried hydrogen for about 17 hr. at 440-450° on a disk of fritted glass inside a Pyrex glass apparatus. The air was removed from the apparatus by several evacuations and purgings with hydrogen. During the reduction process a slow stream of hydrogen was passed through the sample. Afterwards, the reduced samples were transferred to a thin-walled Pyrex glass sphere, with a diameter of about 7 mm., connected to the apparatus through a capillary. The sphere was sealed by melting off the capillary.

The magnetic measurements were carried out by the Faraday method, and the balance was of the Sucksmith type. The magnet and balance were designed by O. Gram Jeppesen of this Laboratory. Calibrations were made against $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ as recommended by Selwood.⁹ At a pole piece distance of 25 mm., the product $H \times \partial H/\partial s$ has its maximum value of about 50×10^6 oersteds²/cm. and a field strength H of about 11,000 oersteds.

(2) P. W. Selwood, "Advances in Catalysis," Vol. III, Academic Press, Inc., New York, N. Y., 1951, pp. 27-106.

(3) A. Magnéli, *Arkiv Kemi, Mineral. Geol.*, **A24**, 1 (1946).

(4) A. Magnéli and G. Andersson, *Acta Chem. Scand.*, **9**, 1378 (1955).

(5) B.-O. Marinder and A. Magnéli, *ibid.*, **11**, 1635 (1957).

(6) L. Pauling, *Chem. Eng. News*, **23**, 2970 (1947).

(7) P. W. Selwood, F. N. Hill and H. Boardman, *THIS JOURNAL*, **68**, 2055 (1946).

(8) R. P. Eischens and P. W. Selwood, *ibid.*, **69**, 2698 (1947).

(9) P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 26.

The sphere was connected to the magnetic balance by means of deKhotinsky cement, and measurements were carried out at 78, 195 and 295° K. The apparatus was evacuated during the measurements. Afterwards the samples were weighed, and the magnetism of the empty containers were measured for the purpose of corrections.

Results

X-Ray powder photographs show that MoO_2 is formed in the molybdenum-rich samples by reduction with dry hydrogen for 17-18 hr. at 440-450°. Samples containing small amounts of molybdenum oxide gave no reflections from molybdenum compounds, possibly because of the crystallites of MoO_2 being too small. Herington and Rideal,¹⁰ as well as Moseman,¹¹ report that MoO_2 is stabilized when supported on γ -alumina. Accordingly, it is supposed that after the reduction also the most diluted samples studied here contain molybdenum in the form of MoO_2 . When precipitated, annealed and reduced in the same way as the supported MoO_3 samples, $\gamma\text{-Al}_2\text{O}_3$ showed a temperature independent susceptibility of $-(0.34 \pm 0.02) \times 10^{-6}$. The susceptibility of MoO_2 obtained by reduction of MoO_3 in the way described above was $+0.33 \times 10^{-6}$, independent of temperature. For samples reduced at 460-470° the susceptibility increased to $0.4-0.5 \times 10^{-6}$. A small amount of molybdenum metal could be detected in the X-ray photographs of such samples.

The susceptibilities of MoO_2 in the reduced, supported samples are listed in Table I.

TABLE I

Atomic ratio Mo/Al	Magnetic susceptibility, $\chi_M \times 10^6$ of supported MoO_2		
	78°K.	195°K.	295°K.
1/99	27	9.8	6.5
2/98	24	8.9	5.6
4/96	17	6.4	4.1
8/92	8.9	3.7	2.5
16/84	4.5	1.9	1.36
32/68	2.6	1.2	0.94
50/50	1.7	0.92	0.78

The reduced samples are pyrophoric and, after exposure to air at room temperature, their susceptibility decreases appreciably. This decrease is most marked during the first minutes of air exposure, and after a few days the susceptibility becomes constant. Due to water adsorption the weight of the samples increased 9 to 17%. The room temperature susceptibilities of MoO_2 , as measured in H_2 , and also after air exposure, are plotted *versus* composition in Fig. 1. The latter values are corrected for the water content using a susceptibility of -0.80×10^{-6} per gram adsorbed water. This rather low value was found for water adsorbed on pure γ -alumina. It corresponds, however, fairly well with Milligan and Whitehurst's¹² measurements for water adsorbed on silica.

By exposing reduced, supported molybdenum oxide to dry oxygen, oxygen-free water and ammonia, respectively, the susceptibility of supported MoO_2 decreases appreciably, whereas car-

(10) E. F. G. Herington and E. K. Rideal, *Proc. Roy. Soc. (London)*, **A184**, 434 (1945).

(11) M. A. Moseman, *THIS JOURNAL*, **73**, 5635 (1951).

(12) W. O. Milligan and H. B. Whitehurst, *J. Phys. Chem.*, **56**, 1073 (1952).

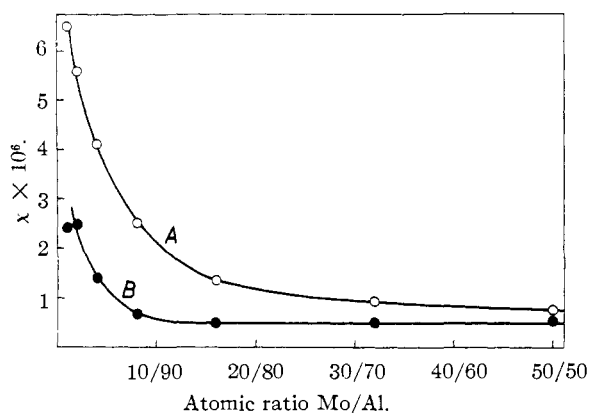


Fig. 1.—Gram susceptibility of MoO_2 at room temperature versus atomic ratio Mo/Al : A, measured in H_2 ; B, after air exposure.

bon monoxide treatment seems to lead to no such effect. Further measurements of the chemisorption effects of various gases on supported molybdenum dioxide are planned.

A sample of molybdenum oxide-titanium dioxide, prepared by precipitation, was reduced in the usual way. The magnetic behavior of MoO_2 on this support seems to be much the same as on $\gamma\text{-Al}_2\text{O}_3$.

A $\text{Mo/Al} = 4/96$ preparation was made by impregnation of $\gamma\text{-Al}_2\text{O}_3$ with a solution of ammonium molybdate. The susceptibility of the reduced sample, measured in hydrogen, was much lower than for a precipitated sample of the same composition.

Discussion

As mentioned above, the weak susceptibility of crystalline MoO_2 probably is due to covalent bonds between the metal atoms. By dilution on the support, the MoO_2 crystallites become smaller, and fewer molybdenum atoms can thus get their unpaired electrons engaged in Mo-Mo bonds. The increasing number of unpaired electrons formed will cause an increase in the susceptibility. The susceptibility of supported MoO_2 might be regarded as composed of two parts according to the equation

$$\chi_{\text{obsd}} = n \times \chi_1 + (1 - n) \times \chi_2 \quad (1)$$

where χ_{obsd} is the observed susceptibility, n is the weight fraction of MoO_2 not engaged in Mo-Mo bonds, χ_1 is the susceptibility due to unpaired electrons, and χ_2 the susceptibility of crystalline MoO_2 (0.33×10^{-6} per gram). Plots of $1/\chi$ versus absolute temperature show that the most highly diluted MoO_2 obeys the Curie law, whereas plots of the molybdenum-richer preparations show curvatures toward the temperature axis. All curves seem to pass through the origin. Such a temperature dependence of the susceptibility is just what is to be expected from equation 1.

A complete dispersion of MoO_2 would cause the formation of two unpaired electrons per metal atom, resulting in a "spin only" susceptibility of 26×10^{-6} , 40×10^{-6} and 99×10^{-6} at 295, 195 and 78°K., respectively. By inserting one of these values of χ_1 in equation 1, the value of n , which is assumed to be equal to the degree of dispersion, can be found. In Fig. 2 the amount of

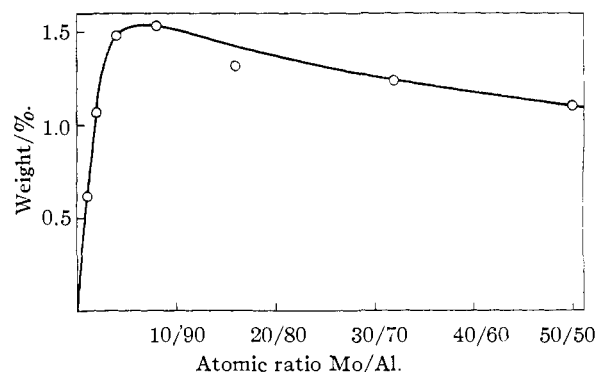


Fig. 2.—Amount of dispersed MoO_2 in weight % of total sample versus Mo/Al atomic ratio.

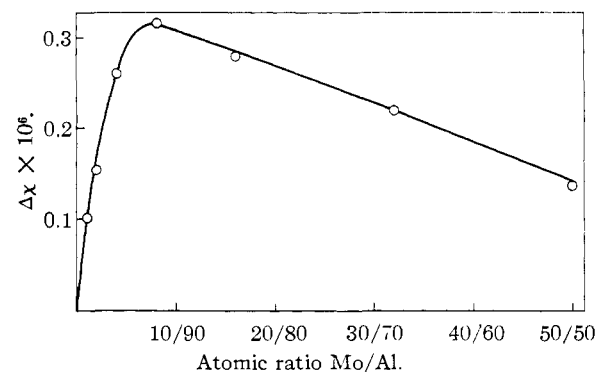


Fig. 3.—Decrease in susceptibility of total sample after exposure to air. Corrections are made for adsorbed water.

dispersed MoO_2 expressed in weight per cent. of the oxide mixture is plotted versus the atomic ratio Mo/Al . The calculations are made under the assumption that hydrogen does not seriously influence the susceptibility of the supported MoO_2 .

The decrease in magnetic susceptibility of MoO_2 during exposure to certain gases indicates that a great part of the unpaired electrons are engaged in chemisorption bonds. Figure 3 shows the decrease in susceptibility per gram sample after exposure to air. The similarity between Figs. 2 and 3 indicates close relationships between the degree of dispersion and the chemisorption efficiency of MoO_2 .

Russel and Stokes¹³ have determined the catalytic activity of molybdenum dioxides impregnated on alumina for the conversion of *n*-heptane to toluene. The curve showing the catalytic activity versus catalyst composition is rather similar to those in Figs. 2 and 3 of the present paper. This indicates a connection between degree of dispersion and chemisorption efficiency of supported molybdenum dioxide and its catalytic activity.

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(13) A. S. Russel and J. J. Stokes, Jr., *Ind. Eng. Chem.*, **38**, 1071 (1946).