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Preparation and Properties of Dispersed Iron (III) Oxide on Rutile

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Samples of 5 and 20 mole% α-Fe_2O_3 supported on rutile TiO_2 were prepared by incipient wetness. A temperature of 390°C was found to be necessary for complete decomposition of the nitrates. Below 400°C there appears to be little evidence for strong interactions between α-Fe_2O_3 and the support. However, ternary phase formation was observed at elevated temperature. Magnetic properties of bulk and supported α-Fe_2O_3 are compared and discussed.

Introduction

Morin in 1949 (*1*) showed that α-Fe_2O_3 is essentially antiferromagnetic as suggested by Néel (*2, 3*) with weak ferromagnetism superimposed upon antiferromagnetism above a transition temperature of 250 K. This transition is the so-called Morin transition. According to Dzyaloshinsky (*4*), between the Morin transition and the Néel temperature (T_N = 961 K), α-Fe_2O_3 shows a weak ferromagnetism caused by spin canting in the basal plane. At temperatures below 250 K (the Morin transition), the spins are aligned along the [111] axis and the oxide is a pure antiferromagnet. If the oxide is in the form of finely divided particles, the magnetic susceptibility becomes larger as the diameter of the particles becomes smaller (*5*) and the transition occurs at lower temperatures.

Finely divided α-Fe_2O_3 particles supported on high surface area supports such as silica were studied by Kündig *et al.* (*6*) by Mössbauer spectroscopy in order to examine the behavior of α-Fe_2O_3 as a function of temperature and particle size. It was indicated that silica interacts with α-Fe_2O_3 but the nature of this interaction was not discussed in their work.

Selwood *et al.* in 1949 (*7*) reported the magnetic properties of α-iron (III) oxide supported on rutile TiO_2. In their study, it was suggested that at low iron concentrations, the oxidation state of the iron approached four and that the rutile structure $M(IV)O_2$ was responsible for the induced stabilization of tetravalent iron. However, the existence of Fe(IV) was deduced for samples prepared at 200°C and there is evidence from TGA results reported in this study that supported samples do not decompose completely until 390°C. Hence, there is some question as to whether the nitrates were completely decomposed at 200°C.

In this study, α-Fe_2O_3 particles will be dispersed on rutile TiO_2 and the properties of the α-Fe_2O_3 will be studied as a function of temperature as well as concentration and

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size of the iron oxide particles. Furthermore, the interaction of α-Fe_2O_3 and the rutile TiO_2 will also be investigated and the degree and nature of the interaction will be ascertained.

Experimental

Preparation of rutile TiO_2 by hydrolysis of $TiCl_4$. A stock solution of 2 *M* $TiCl_4$ was prepared by adding 55 ml $TiCl_4$ (Matheson, Coleman and Bell, 99.5%) to the volume of 12 *M* hydrochloric acid necessary to give a final volume of 250 ml. A 50-ml aliquot of the stock solution was mixed with 50 ml of distilled water and refluxed for 12 hr. The solution was decanted and the white insoluble product, which adhered to the wall of the flask, was removed from the flask by means of a rubber policeman. The filtered precipitate was washed several times with distilled water in order to reduce the total chloride contamination.

The product was dried at 110°C for 12 hr and then suspended in 200 ml of distilled water and refluxed for 12 hr. The suspension was then transferred to a dialysis bag (Spectrapor Membrane; molecular weight cutoff 12,000–14,000) and dialysis was carried out for 24 hr. The resulting solution was filtered and dried at 110°C for 12 hr. The product gave a total concentration of 870 ppm of chloride as determined by neutron activation analysis (General Activation Analysis, Inc.).

Preparation of α-Fe_2O_3 on rutile TiO_2. Dispersed samples of α-Fe_2O_3 on rutile TiO_2 were prepared by incipient wetness. The weight of $Fe(NO_3)_3 \cdot 9H_2O$ (Fisher Scientific, Certified A.C.S.) to give the desired iron oxide loading was dissolved in 20 ml of distilled water. One gram of TiO_2 (rutile) was dispersed in the iron nitrate solution and then stirred for approximately 10 min. The resulting solution was placed in a drying oven at 150°C for 12 h to evaporate the water and dry the product. The sample was then ground and heated at 400°C for 24 hr. The final product was reground.

Pure α-Fe_2O_3 was prepared by dissolving $Fe(NO_3)_3 \cdot 9H_2O$ in 20 ml of distilled water. The solution was evaporated and the product dried at 150°C for 12 hr. The sample was then ground and decomposed at 400°C for 24 hr.

Temperature-programmed decomposition studies. In order to determine the minimum temperature for complete decomposition of supported iron nitrate, samples were heated in a predried (over P_2O_5) oxygen atmosphere at 60°C/hr and the weight change was recorded.

Characterization of products. X-ray powder diffraction patterns of the samples were obtained using a Philips diffractometer and monochromated high-intensity CuK_{α_1} radiation ($\lambda = 1.5405$ Å). The diffraction patterns were taken in the range of $12° < 2\theta < 72°$ with a scan rate of 1° 2θ min^{-1} and a chart speed of 30 inches per hour.

Crystallite sizes were calculated from the peak widths by using the Scherrer equation $D = k\lambda/(\beta \cos \theta)$, where D is the crystallite size, k is a shape factor (a value of 0.9 was used in this study), λ is the X-ray radiation wavelength (1.5405 Å for CuK_{α_1}), and β is the half-width (expressed in radians) of the peak at 2θ. β was determined from the experimental integral width by appyling standard corrections for the effects of $K\alpha_1$–$K\alpha_2$ separation and instrumental broadening.

The surface area was measured by the BET method using a Flow Sorb (II) 2300 (Micromeritics Instrument Corp., Norcross, GA). The samples were degassed at 250°C for 30 min and the adsorbate gas consisted of a mixture of 30% N_2–70% He.

Temperature-programmed reduction studies. The programmed temperature reductions were carried out using a Cahn 113 Thermal Balance. The sample was heated in a predried (P_2O_5) 85% Ar/15% H_2 atmosphere at a flow rate of 60 ml/min. The temperature was increased at 60°C/hr to 800°C and the weight change vs temperature was recorded.

Magnetic susceptibility. Magnetic susceptibilities were measured using a Faraday balance (*8*) at a field strength of 10.4 kOe. Honda–Owens (field dependency) plots were also made and all magnetic susceptibility data were corrected for core diamagnetism (*9*). Magnetic susceptibility measurements were made from liquid nitrogen to 300 K.

Electron microscopy. The samples were ultrasonically dispersed on grids and examined with a Philips EM420 scanning transmission electron microscope. The accelerating voltage was 120 kV and the magnification was 175×10^3. The degree of dispersion of iron oxide on rutile was examined in the transmission mode and the iron distribution was determined by EDAX.

Results and Discussion

Samples of α-Fe_2O_3 dispersed on rutile TiO_2 were prepared by decomposing $Fe(NO_3)_3 \cdot 9H_2O$ which was put onto rutile by incipient wetness. The low-temperature rutile was prepared by the hydrolysis of $TiCl_4$ in hydrochloric acid and separation of a large part of the chloride impurity was accomplished by dialysis. Complete decomposition of iron nitrate to bulk iron oxide occurs at 390°C. From TGA studies, it was observed that complete decomposition of the supported iron nitrate also occurred at 390°C. Therefore, samples of bulk iron oxide and products containing loadings of 5 and 20 mole% iron oxide were prepared at 400°C. X-ray analysis of the final products identified the phases as rhombohedral α-Fe_2O_3 and the tetragonal rutile form of TiO_2 (Fig. 1). It is evident that there is no apparent interaction below 390°C of iron nitrate or its intermediate decomposition products with rutile TiO_2 prepared at 110°C. However, samples prepared at 400°C show evidence of diffusion of Ti(IV) into the iron oxide. This is indicated by the disappearance of the Morin transition in the 5 mole% sample and is consistent with previous studies (*1*). At temperatures greater than 1000°C the formation of Fe_2TiO_5 was confirmed from X-ray diffraction analysis. The average surface area of the rutile-supported α-Fe_2O_3 particles was 11 m^2/g. From line-broadening measurements, the crystallite size of the segregated α-Fe_2O_3 particles was 230 Å and the average size of the rutile particles was 140 Å.

The existence of bulk α-Fe_2O_3, as indicated by the X-ray diffraction patterns of the supported samples, is consistent with the tendency of α-Fe_2O_3 to segregate under these preparative conditions. EDAX results for the sample with 20 mole% iron oxide loading showed the existence of both iron-rich and titanium-rich regions. For the 5 mole% sample, only titanium-rich regions were observed, but there was considerable variation in the concentration of iron oxide.

Temperature-programmed reduction studies were carried out in order to study the interaction between α-Fe_2O_3 and rutile TiO_2. The results are shown in Fig. 2. It was reported by Qian *et al.* (*10*) that bulk α-Fe_2O_3 reduces to magnetite in an 85% Ar/15% H_2 atmosphere between 280 and 305°C. The reduction proceeds completely to metallic iron at 480°C. In the initial reduction step, the supported samples show little difference from bulk α-Fe_2O_3. At higher reduction temperatures, the supported samples reduce more slowly than bulk α-Fe_2O_3. Complete reduction for supported samples does not occur until 700°C.

In order to identify the possible existence of phase formation between α-Fe_2O_3 and rutile above 400°C under reducing conditions, a 20 mole% α-Fe_2O_3/rutile was heated to 550°C at 60°C/hr in 85% Ar/15% H_2 and held at temperature for 2½ hr. X-ray analysis of the phases formed indicates the

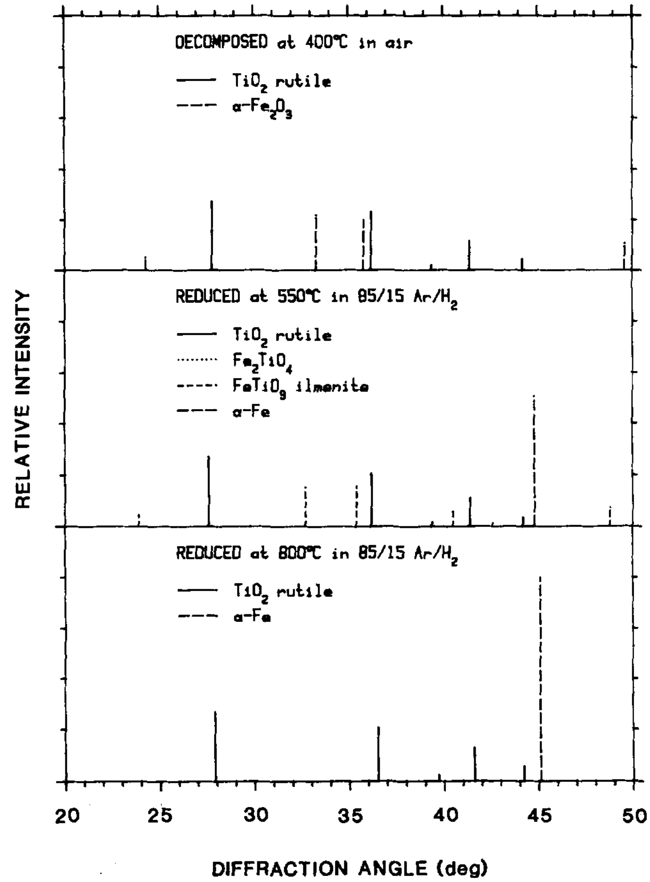

FIG. 1. X-ray diffraction patterns characteristic of 20 mole% α-Fe_2O_3 supported on TiO_2 rutile just after decomposition of the nitrate, after reduction in 85% Ar/15% H_2 at 550°C, and after reduction at 800°C.

presence of Fe, $FeTiO_3$, Fe_2TiO_4, and TiO_2 (see Fig. 1). The existence of the iron-rich phases $FeTiO_3$ and Fe_2TiO_4 indicates that the iron oxide must be segregated on the TiO_2 rutile support. The observed ternary phases form as a result of solid-state reactions at elevated temperatures. However, it will be seen from magnetic measurements of a TiO_2 sample containing 5 mole% α-Fe_2O_3 that there is some diffusion of titanium into α-Fe_2O_3 even at lower temperatures. Under more drastic reducing conditions, the phases observed in the product were only Fe and TiO_2.

For bulk α-Fe_2O_3, the measurement of susceptibility vs temperature indicates that at 240 K a transition is observed (Morin transition) as a result of a weak ferromagnetism superimposed upon the antiferromagnetic state (*1*). Field dependency measurements verify the existence of a spontaneous moment arising from the parasitic ferromagnetism of bulk α-Fe_2O_3 at room temperature, whereas the sample is purely antiferromagnetic at liquid nitrogen temperature. It was shown by neutron diffraction (*11*) that below the Morin transition the spins are antiparallel along the

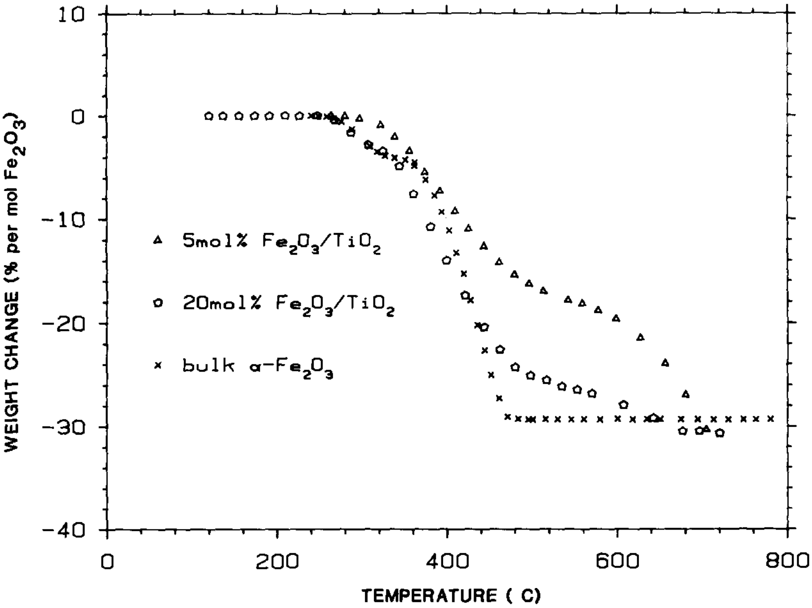

FIG. 2. Comparison of the relative weight change per mole α-Fe_2O_3 upon reduction of bulk and supported α-Fe_2O_3.

rhombohedral (111) direction, whereas above this temperature they lie in the basal (111) plane. The arrangement of the spins in the basal plane gives rise to a spin canting resulting in a spontaneous moment (*4*).

In addition to its parasitic ferromagnetism, finely divided α-Fe_2O_3 particles have been observed to show superparamagnetic behavior (*6*). Néel has described the latter phenomenon in finely divided antiferromagnetic compounds below their Néel points (*12*). The magnetic results obtained for bulk iron oxide in these studies are consistent with those reported by Morin (*1*).

The magnetic properties of the 20 mole% supported sample resemble those of the bulk α-Fe_2O_3. Parasitic ferromagnetism is observed above 240 K (Figs. 3 and 4) and the Morin transition occurs close to that of bulk α-Fe_2O_3. Below the transition temperatures (Fig. 3), the susceptibility increases with decreasing temperature unlike bulk α-Fe_2O_3. This indicates superparamagnetic behavior due to the presence of some finely divided particles.

For the 20 mole% α-Fe_2O_3 sample, the average crystallite size was determined as 230 Å. At the 5 mole% loading the α-Fe_2O_3

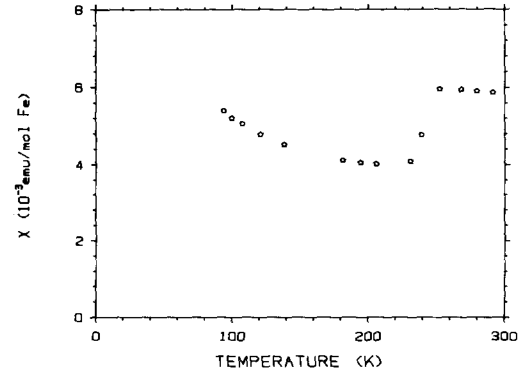

FIG. 3. Variation with temperature of the magnetic susceptibility of 20 mole% α-Fe_2O_3 supported on TiO_2 rutile.

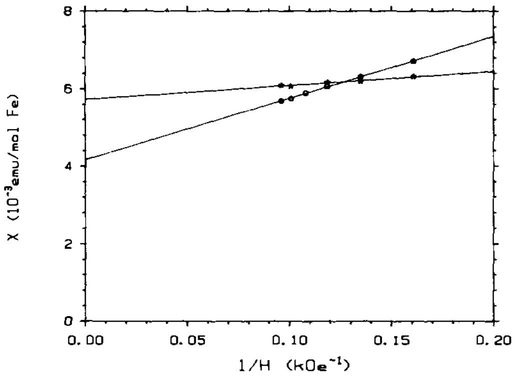

FIG. 4. Variation of the magnetic susceptibility of 20 mole% supported α-Fe_2O_3 on TiO_2 rutile with inverse magnetic field at 77 (*) and 298 K (○).

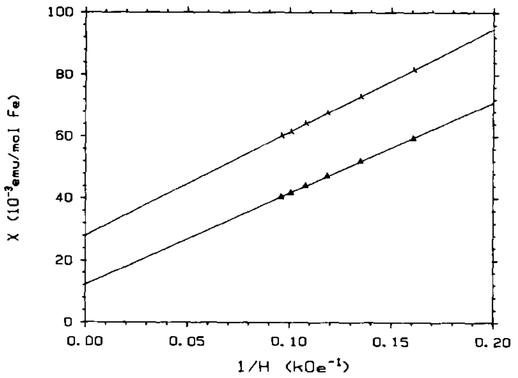

FIG. 6. Variation of the magnetic susceptibility of 5 mole% α-Fe_2O_3 supported on TiO_2 rutile with inverse magnetic field at 77 (○) and 298 K (△).

peaks were too weak to permit such a determination. However, the increased low-temperature susceptibility of the 5 mole% samples indicates a smaller particle size.

For the 5 mole% supported sample the transition temperature at 240 K is not observed. However, the larger increase in the susceptibility with decrease in the temperature (Fig. 5) indicates the presence of a larger percentage of finely divided particles which give rise to superparamagnetic behavior.

The field dependency at liquid nitrogen and room temperature, shown in Fig. 6, is also consistent with the existence of fine particles (*6*). The absence of an observable Morin transition (Fig. 5) and the persistence of field dependency to low temperature (Fig. 6) arise from a freezing in of the high-temperature canted spin configuration. This is probably due to the inclusion of small amounts of diffused titanium (*1*).

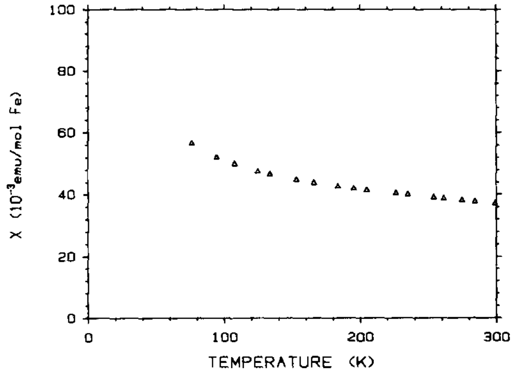

FIG. 5. Variation with temperature of the magnetic susceptibility of 5 mole% α-Fe_2O_3 supported on TiO_2 rutile.

Conclusions

α-Fe_2O_3 particles tend to segregate when supported on rutile TiO_2. At temperatures below 400°C, there appears to be little evidence for strong interactions between α-Fe_2O_3 and the support. However, ternary phase formation was observed during the reduction at elevated temperatures and the phases identified were Fe_2TiO_4 and $FeTiO_3$. The supported α-Fe_2O_3 gives rise to superparamagnetic behavior, which indicates the existence of some finely divided particles. In addition, these particles contain small amounts of diffused titanium as evidenced by the absence of a Morin transition.

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