CHEMISTRY LETTERS, pp. 723-726, 1986.

PREPARATION OF SiO_2 POWDER CONTAINING FINE γ-Fe_2O_3 PARTICLES

Tadashi AKIYAMA, Eiji TANIGAWA, Takashi IDA,
Hideyasu TSUIKI, and Akifumi UENO*

Department of Materials Science, Toyahashi University of
Technology, Tempaku, Toyohashi, Aichi 440

Fine γ-Fe_2O_3 particles dispersed in SiO_2 powder was prepared by simultaneous hydrolysis of mixed alkoxides solution composed of ethyl silicate and Fe-ethylene glycolate and the magnetic properties of this powder were discussed with an aid of TEM measurement.

Simultaneous hydrolytic decomposition of mixed alkoxides solution is one of the best methods for high degree of control over the purity and mixing uniformity,[1)] and has been widely applied in the field of inorganic synthesis expecting new and/or improved materials.[2)] The authors have often employed the technique to prepare fine metal catalysts supported over silica[3)] using metal glycolates and ethyl silicate. Fine metal particles are prepared by the reduction of tiny metal oxdes dispersed in silica, which are produced by the calcination of a gel obtained by the simultaneous hydrolysis of the corresponding mixed alkoxides solution. In the case of silica-supported iron catalyst the fine iron particles were prepared by reducing small particles of iron oxide dispersed in silica frame under hydrogen atmosphere.[4)] These iron oxide particles were readily magnetized in an ambient magnetic field, indicating the crystallographic structure of these iron oxide particles being Fe_3O_4 or γ-Fe_2O_3 although the most stable structure of iron oxide is α-Fe_2O_3. In the present communication the magnetic properties of these tiny iron oxide particles are discussed with the measurements by a transmission electron microscope (Hitachi H-800).

The preparation procedure of the silica powder containing tiny iron oxide particles is as.follows; iron(III) nitrate dissolved in ethylene glycol is mixed with ethyl silicate and vigorously stirred at 80 °C for a couple of hours. Then, an excess amount of water is added to the mixed alkoxides solution with stirring at 80 °C, resulting in the formation of a gel. The gel thus obtained is dried in an oven at 110 °C for 24 h, followed by calcination at desired temperatures for 4 h. These procedures are summarized in Table 1. The iron oxide particles thus prepared are incorporated in silica frame and are too small to be measured by X-ray diffraction even when the powder was calcined at 1000 °C in air for 4 h. The color of the calcined powder was brown, suggesting the iron oxide being γ-Fe_2O_3 but not Fe_3O_4 since the color of Fe_3O_4 is black. The particle size of the γ-Fe_2O_3 incorporated in silica powder was monitored by TEM and the size distribution curve was obtained by measuring the sizes of more than 500 particles in photographs enlarged by 4×10^5 times (Fig. 1). In Fig. 2 is shown the distribution curve of γ-Fe_2O_3 particle size in the silica powder calcined at 500 °C, iron concentration in the powder being 10 wt% measured by an atomic absorption spectroscopy. The mean particle size was estimated around 60 Å and can be varied with the iron concentration in the silica powder, as shown in Fig. 3.

The magnetization of the iron oxide was measured using a vibrating sample

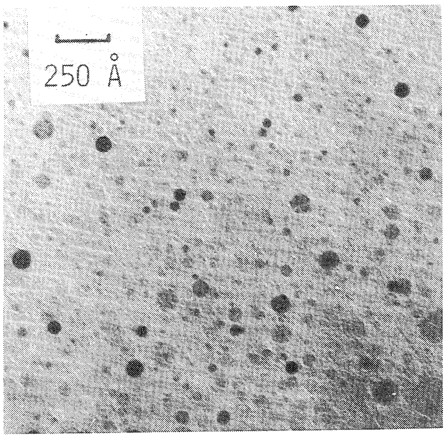
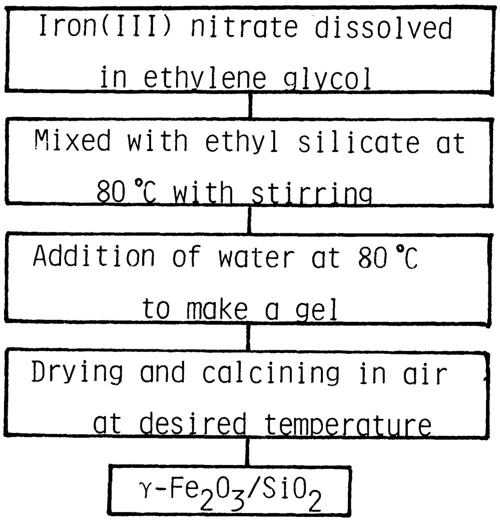


Fig. 1. TEM photograph of γ-Fe_2O_3 in silica containing 10 wt% of Fe.

Table 1. Preparation procedure



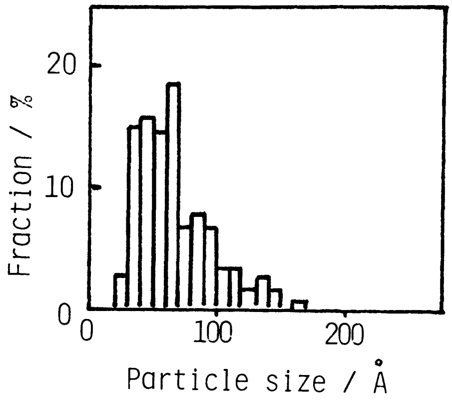


Fig. 2. Size distribution of γ-Fe_2O_3 in silica containing 10 wt% of iron.

magnetometer(VSM-2, Toei Kogyo) with the magnetic field, up to 20 koe(1.6×10^{6} Am^{-1}). In Fig.4 are given the magnetization curves of the silica powders containing 5, 10 and 30 wt% of iron as γ-Fe_2O_3, respectively. These magnetization curves are typical ones for super-paramagnetic materials since the coercive forces were as small as around 10 Oe(8.0×10^{2} Am^{-1}), also indicating the γ-Fe_2O_3 particles in silica powder are so small. The saturation magnetizations were varied with the iron concentration in the powder, as shown in Fig.5. The saturation magnetization decreased with the iron concentration and became almost zero when the concentration was less than 3 wt%.

The particle size of γ-Fe_2O_3 in the silica powder increased with the calcination temperature. The change in the particle size of the iron oxide with the calcination temperature is given in Fig.6. The saturation magnetization of the silica powder also changes with the calcination temperature, as is shown in Fig.7. The increase in the saturation magnetization with the calcination temperature up to 650 °C seems to be attributed to crystalline growth of γ-Fe_2O_3 and the decrease by the calcination at the higher temperature may be due to the phase transformation of the iron oxide to α-Fe_2O_3 which is an anti-ferromagnetic material. All the magnetic

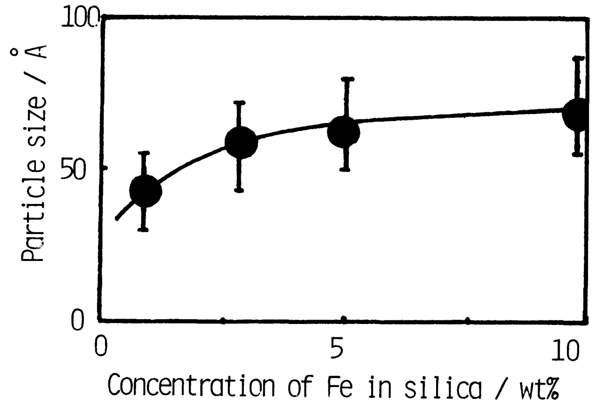


Fig. 3. Change in γ-Fe_2O_3 particle size with Fe concentration.

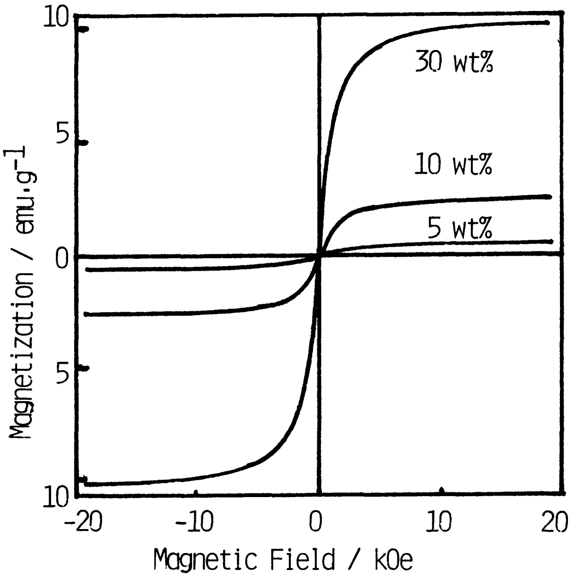


Fig. 4. Change in the magnetization of γ-Fe_2O_3 in silica with Fe concentration.

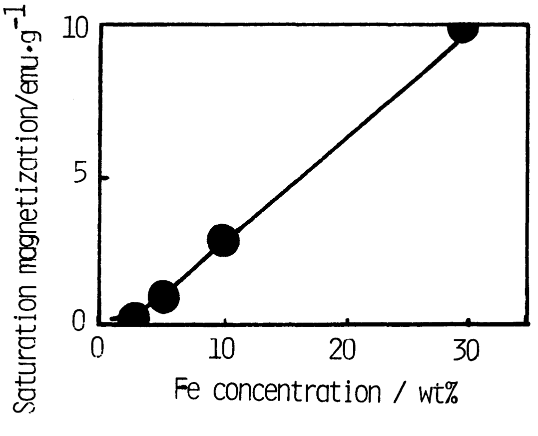


Fig. 5. Change in the saturation magnetization with Fe concentration in silica powder.

measurements were carried out at room temperature.

A question if the ethylene glycol employed as starting material might partially reduce the iron oxide during the calcination and the resulting iron metal may show the ferromagnetic property will arise. The powder, however, showed the ferromagnetic property even after the recalcination at 650 °C for prolonged hours, no metal being formed under the conditions. The role of the ethylene glycol is to produce iron-ethylene glycolate. If we start with iron isopropoxide($Fe(OC_3H_7)_3$) dissolved in propyl alcohol, instead of the iron-ethylene glycolate, and ethyl silicate, the iron oxide incorporated in the silica was α-Fe_2O_3 after the calcination of a gel obtained by the hydrolysis under the similar conditions. Ethylene glycol is an inevitable material for the preparation of fine γ-Fe_2O_3 particles dispersed in silica by the present preparation technique.

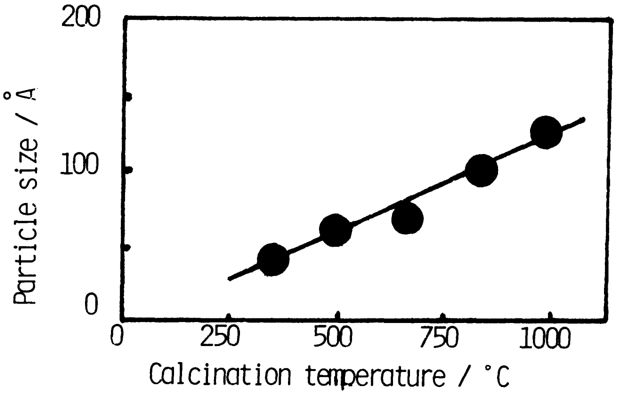


Fig.6. Increase in the particle size of γ-Fe_2O_3 in silica with calcination temperature.

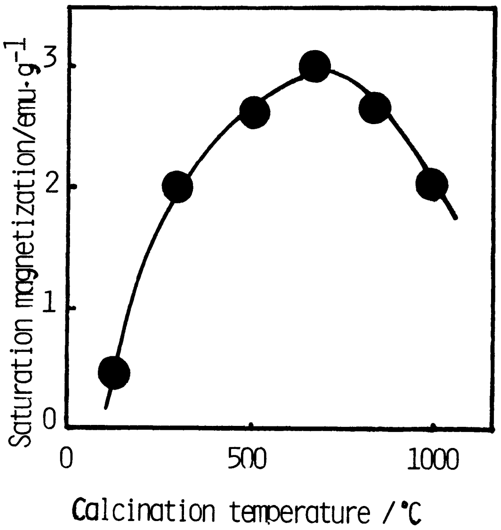


Fig. 7. Change in saturation magnetization of γ-Fe_2O_3 with the calcination temperature.

References

1) K.S.Mazditasni, C.T.Lynch, and J.S.Smith II, J.Am. Ceram. Soc., 50, 532 (1967).

2) A.L.Micheli, U.S. Patent, 3637505 (1972), 4286378 (1981).

3) S.Takasaki, S.Tanabe, K.Takahashi, H.Suzuki, A.Ueno, and Y.Kotera, J. Chem. Soc. Faraday Trans. 1, 79, 127 (1983); K.Tohji, Y.Udagawa, S.Tanabe, and A.Ueno, J. Am. Chem. Soc., 106, 612 (1984).

4) T.Ida, S.Tanabe, A.Ueno, K.Tohji, and Y.Udagawa, Chem. Lett., 1984, 1567.

(Received February 12, 1986)