

Structural Regulation of Iron Oxide supported on a Metal Oxide by Organic Compounds

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The structure of iron oxide supported on a metal oxide can be regulated by using different organic compounds at the impregnation step.

Most catalysts and sensors are composites in which certain active materials are supported on carriers. In such materials, performance is as much affected by the structure of a supported material as by its particle size. Thus, it is important to control the structure of a material supported on a carrier. Here we report a new and simple method for regulating the structure of iron oxide supported on other solid oxides.

Iron oxide was used as a model supported material because its properties vary with its structures.¹ There are roughly three kinds of structure, Fe_3O_4 (magnetite) and $\gamma\text{-Fe}_2\text{O}_3$ (maghemite), both being ferromagnetic and having a spinel structure and $\alpha\text{-Fe}_2\text{O}_3$ (hematite) which has a corundum structure and shows parasitic ferromagnetism.

It is generally accepted that sparingly soluble hydrated iron(III) oxide, $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$, is formed *via* oxo- and hydroxo-bridged oligomers by hydrolytic polymerization of ferric compounds,^{2,3} and several oligomers have been isolated in the form of complexes with organic ligands such as carboxylates and amines.⁴⁻⁷ All the oligomers have oxo-hydroxo iron(III) cores surrounded by the organic ligands, but the cores differ from each other in size and structure, depending on the organic ligands. This property allowed us to make the supported iron oxide specifically take a spinel or corundum structure.

The idea was to form precursors of a spinel or corundum iron oxide on the surface of a carrier by controlling the hydrolytic polymerization of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ with certain organic compounds and to transform the precursors into $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$, or Fe_3O_4 by a topotaxy reaction, or calcination. The conceptual procedure is shown in Figure 1. A metal oxide powder (carrier) was first impregnated with a solution of an organic compound (regulator) in acetone or ethanol. After drying at 50–110 °C, the powder was again impregnated with an ethanol solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The powder was dried again at 50–110 °C, and finally calcined at 400 °C for 1 h. In this procedure, the amounts of carrier and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ employed were generally 10 g and 7.3 g, respectively, and the iron oxide composites obtained mostly had a reddish-brown colour. The structure of the iron oxide in the composites was identified from their X-ray diffraction patterns and magnetic susceptibilities.

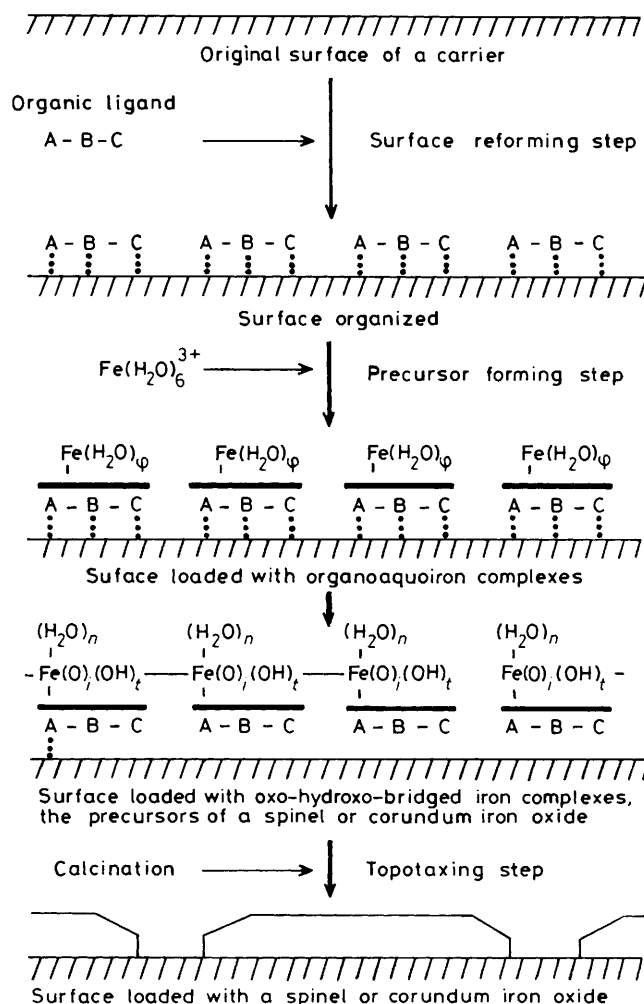


Figure 1. Conceptual procedure for the structural regulation of iron oxide supported on a carrier.

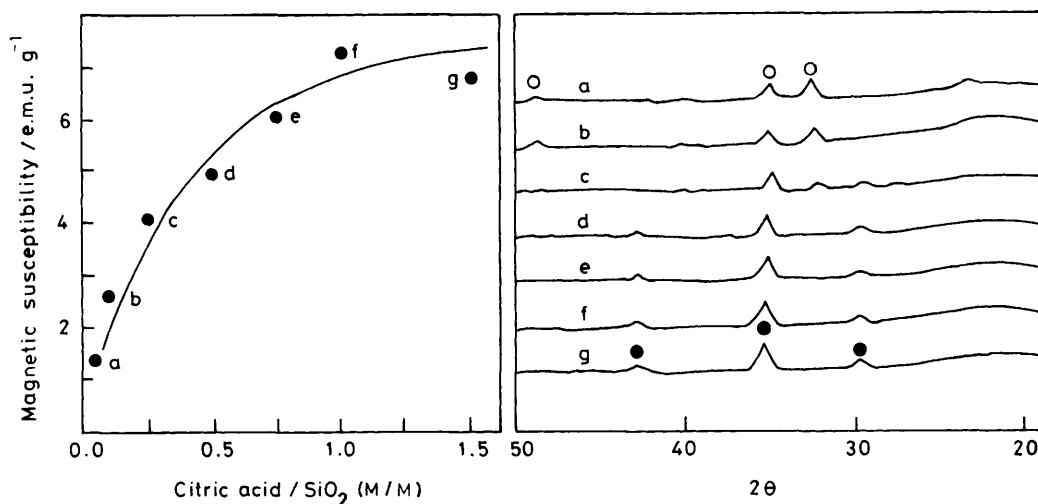


Figure 2. Magnetic susceptibilities and X-ray diffraction patterns of the iron oxide/silica composites. Citric acid:SiO₂ are the ratios used in the preparation of the composites. ○ = Corundum iron oxide; ● = spinel iron oxide.

When silica, alumina, titania, and zirconia were used as carriers, and only acetone and ethanol as regulators, all the composites obtained showed only very weak magnetic susceptibilities, <0.3 e.m.u./g. This suggests that the structure of iron oxide in the composites is corundum. Actually, the iron oxide/titania composite showed distinct X-ray diffraction peaks⁸ arising from a corundum iron oxide.

Figure 2 shows the effect of citric acid impregnated in silica as a regulator on the magnetic susceptibilities and X-ray diffraction patterns of the iron oxide/silica composites. The magnetic susceptibility of the composites initially increased as the amount of citric acid used in the preparation of the composites increased and then saturated at molar ratios of citric acid:SiO₂ >1. Similar phenomena on the magnetic susceptibility were also observed in the iron oxide composites of alumina, titania, and zirconia. These suggest that the structure of the iron oxide supported on the above carriers changes from corundum to spinel on increasing the amount of citric acid used in the preparation of the composites. The X-ray diffraction patterns in Figure 2 support this suggestion.

So far we have discovered that for the structural regulation

of supported iron oxide, citric acid, tartaric acid, ethylene glycol, ethanolamine and alanine show spinel preferences and acetone, ethanol, and diacetone alcohol show corundum preferences.

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References

- 1 R. B. Heslop and P. L. Robinson, 'Inorganic Chemistry,' Elsevier, Maruzen Asian Edition, Japan, 1960, p. 465.
- 2 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 4th edn., Wiley-Interscience, New York, 1980, p. 758.
- 3 C. M. Flynn, Jr., *Chem. Rev.*, 1984, **84**, 31.
- 4 K. Wieghardt, K. Pohl, I. Jibril, and G. Huttner, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 77.
- 5 S. M. Gorun and S. J. Lippard, *Nature*, 1986, **319**, 666.
- 6 S. J. Lippard, *Chem. Br.*, 1986, 222.
- 7 W. H. Armstrong, M. E. Roth, and S. J. Lippard, *J. Am. Chem. Soc.*, 1987, **109**, 6318.
- 8 J. Fukushima, K. Kodaira, and T. Matsushita, *Yogyo Kyokai Shi*, 1976, **84**, 529.