BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (8), 2423—2424 (1978)

Pore Structure of Iron Oxides

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(Received February 20, 1978)

Synopsis. The pore structure of iron oxides, subjected to oxidation into α-Fe_2O_3 as well as reduction into Fe_3O_4, was investigated by means of the *t*-method. The results show that the reduction is accompanied by the formation of slit-shaped pores, width 14 Å, open at both ends.

The mechanism of solid reaction is one of the most incomprehensible problems. The surface chemistry of intermediate and final products will shed light on this problem. de Boer and Lippens[1] investigated the process of thermal decomposition of boehmite and bayerite. They developed the *t*-method and applied it to the N_2-adsorption data, and found the formation of slit-shaped pores during the course of decomposition reaction. The *t*-plots are constructed by plotting the amount of adsorbed nitrogen on a sample against the statistical thickness *t* of the adsorbed layer of nitrogen on a nonporous reference solid. The choice of reference *t*-curve, therefore, is important. Cranston and Inkley[2] and Lippens *et al.*[3] each used a definite standard *t*-curve. Other researchers selected the reference curve from the data on specimens of the same substance.[4,5]

It is known that α-Fe_2O_3 can be reduced to Fe_3O_4 in a mixed gas of H_2 and H_2O, the reverse reaction taking place in O_2 at high temperatures.[6] The purpose of the present work is to investigate the surface chemistry of iron oxides produced by oxidation and reduction, by measuring the N_2-adsorption isotherms and converting them into *t*-plots.

Experimental

The sample of iron oxide was prepared by oxidizing iron rods (purity 99.99%) at 600 °C in an electric furnace. It was ground, heated at 1400 °C for 2 h and evacuated at 1100 °C for 2 h in a vacuum of 1×10^{-3} Pa (sample S). From this sample, four kinds of iron oxides with different compositions were prepared in the following way. Sample H was obtained by oxidizing sample S in O_2 at 300 °C for 48 h, during which time the amount of O_2 taken up was measured. Sample S was reduced with a mixture of H_2 and H_2O (4: 1), the ratio being selected to be suitable for the formation of Fe_3O_4 on the equilibrium phase diagram,[6] at 400 °C for 48 h ,the H_2-uptake being measured (sample M). The other two samples were prepared by reducing sample H as well as by oxidizing sample M under the same conditions as described above. The reactions were continued until the composition of the products gave α-hematite and magnetite in a 1: 1 ratio, from measurement of the amount of absorbed H_2 or O_2 (samples Ih and Im). X-Ray analysis showed that samples H and M are α-hematite and magnetite, respectively, samples S, Ih, and Im being mixtures of them. From the amounts of absorbed O_2 and H_2 when samples H and M were produced, the composition of sample S was found to be 70% α-hematite and 30% magnetite. α-Fe_2O_3 prepared by the calcination of iron(II) sulfate was used as a nonporous reference material.[7]

Prior to the adsorption experiments, *ca.* 20 g of the sample was degassed at 600 °C for 4 h in a vacuum of 1×10^{-3} Pa in order to remove surface impurities such as chemisorbed water and carbon dioxide. Nitrogen adsorption isotherms were measured volumetrically at −196 °C.

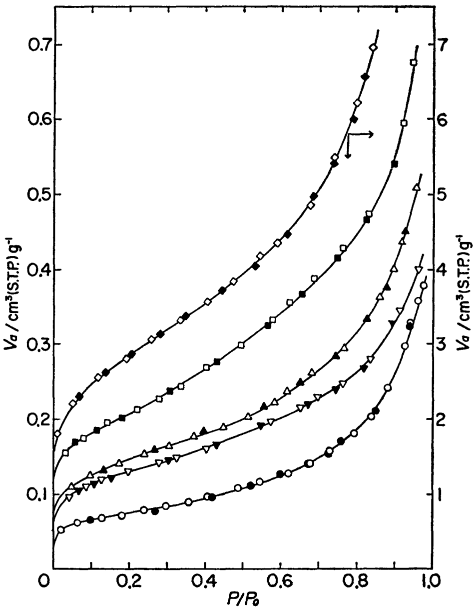

Fig. 1. N_2-adsorption isotherms on iron oxide samples. Sample S, ○; M, □; Ih, ▽; Im, △; preparation (II), ◇ (see the text). Filled points represent desorption.

Results and Discussion

Figure 1 shows the adsorption isotherms of N_2 on iron oxide samples. The isotherm for sample H was almost the same as that for sample S. Desorption isotherm was also measured, the result being consistent with the adsorption branch in the whole pressure range studied. The BET surface area (S_{BET}) is calculated as given in Table 1. It should be noted that oxidation and reduction treatment of iron oxide regularly alter the adsorbability of nitrogen molecules, *i.e.*, the specific surface area of the samples; the amount of adsorbed nitrogen increases in the course of the reduction of oxide, but decreases as the oxidation proceeds. This suggests that the reduction of iron oxide into Fe_3O_4 having the spinel structure is accompanied by the formation of pores in the products.

First, the *t*-plots were constructed on the basis of the standard *t*-curve of Lippens *et al.*[3] and that of Cranston and Inkley.[2] However, they did not give a straight line through the origin, showing disagreement with the BET area S_{BET}. The discrepancy between the *C*-value in the BET equation on a sample and that on the reference solid seriously affects the trend of

Table 1. Bet C-values and surface areas of iron oxide samples

Sample	C-value	Surface area ($m^2 g^{-1}$) S_{BET}	S_t	S_{out} a)
S	160	0.271	0.271	—
M	146	0.745	0.739	0.526
Ih	135	0.460	0.460	0.315
Im	140	0.518	0.518	0.397

a) S_{out} represents the outer surface area obtained from the t-plots ($t > 7$ Å).

t-plots.[8] In order to get an appropriate reference t-curve from the data on related substances, a nonporous α-Fe_2O_3 prepared by calcining iron(II) sulfate was treated as follows: evacuation at 600 °C for 4 h (I), followed by rehydration (II), calcination at 800 °C for 4 h and subsequent evacuation at 600 °C for 4 h (III), followed by rehydration (IV). The C-values in the N_2-adsorption isotherm on these preparations were found to be 124, 169, 243, and 253, respectively. We adopted the data on preparation (II) as the reference curve, because of the consistency of the C-value with that of the present samples (Table 1).

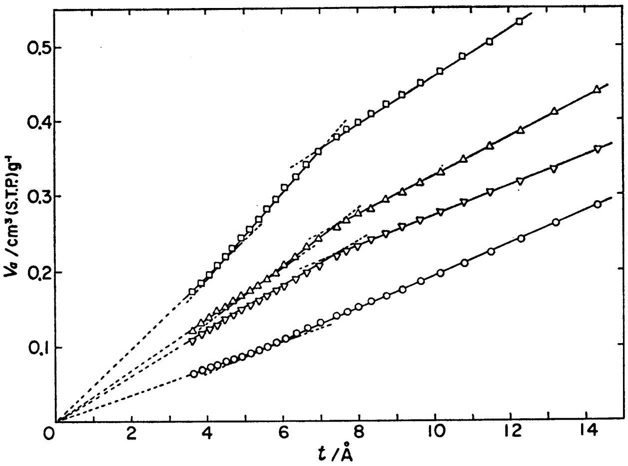

Fig. 2. t-Plots for N_2 adsorption on iron oxide samples. Sample S, ○; M, □; Ih, ▽; Im, △.

Figure 2 shows the t-plots for iron oxide samples subjected to oxidation or reduction treatment. In all cases the first part of the curves is in a straight line through the origin. The surface area S_t can be calculated from the slope of the straight line,[1] being in good agreement with S_{BET} (Table 1). Since S_t is a function of a particular t-curve employed, the agreement between S_t and S_{BET} is a good indicator for the validity of the reference t-curve.[8]

Sample S gives a straight line through the origin up to $t \approx 5$ Å, followed by a separate line with a greater slope. Although an upward deviation from the initial straight line represents a capillary condensation in pores,[1] no hysteresis appears in the isotherm of this sample. This might be due to reversible capillary condensation in wide and slit-shaped pores open at both ends.[9] A remarkable increase in surface area for sample M produced by reduction of sample S suggests the sample to be fairly porous. The t-plots for sample M consist of three straight lines: the first one up to $t \approx 4$ Å, the second one between 4 and 7 Å, and the last one beyond 7 Å. The former two of the three lines might correspond to the monolayer adsorption onto outer and inner surfaces, and the reversible capillary condensation in slit-shaped pores open at both ends, respectively, as on the sample S. Taking account of the density of liquid nitrogen at −196 °C, we obtain the monolayer thickness to be 3.54 Å.[3] Thus, since the pores would be filled when the thickness of the adsorbed layer is equal to half the width of pores, the width is found to be 14 Å. The last line indicates the adsorption in the wider pores as well as on the outer surface, the area calculated from this slope being 0.526 $m^2 g^{-1}$ (Table 1), which gives the inner surface area as 0.213 $m^2 g^{-1}$. The t-plots of sample Im obtained by partial oxidation of sample M have the same tendency as in the case of sample M. However, its surface area is less than the latter, because of partial closing of pores during the course of oxidation of Fe_3O_4. The inner surface of sample Im amounts to 0.121 $m^2 g^{-1}$, smaller than that of sample M. On the other hand, sample Ih shows a straight line with single break at $t \approx 7$ Å, indicating that the sample has pores accessible to nitrogen molecules in two statistical layers. This sample was obtained by partial reduction of sample H prepared by exhaustive oxidation of sample S having wide and slit-shaped pores. It appears evident that such pores were made in the course of reduction, since no change in S_{BET}-value was observed in the oxidizing process as stated above.

Thus, it is concluded that the reduction or oxidation of iron oxide is accompanied by the formation or closing of pores. The fact that the t-plots reveal distinct breaks at two definite t-values indicates the formation of pores of a regular size during the course of conversion into spinel structure. An increase either in the number or in the depth of such pores in the course of the reduction treatment will lead to an increase in surface area. The presence of pores might also lead to an elongation of the adsorption time of water.[10]

References

1) J. H. de Boer and B. C. Lippens, *J. Catal.*, **3**, 38, 44 (1964); **4**, 319 (1965).

2) R. W. Cranston and F. A. Inkley, *Adv. Catal.*, **9**, 143 (1957).

3) B. C. Lippens, B. G. Linsen, and J. H. de Boer, *J. Catal.*, **3**, 32 (1964).

4) R. F. Horlock and P. J. Anderson, *Trans. Faraday Soc.*, **63**, 717 (1967).

5) F. S. Baker, J. D. Carruthers, R. E. Day, K. S. W. Sing, and L. J. Stryker, *Discuss. Faraday Soc.*, **52**, 173 (1971).

6) K. Iwase, "Shinsei-Kinzoku-Koza, Tekko-Seiren II," Nippon Kinzoku Gakkai, Tokyo (1957), p. 206.

7) T. Morimoto, M. Nagao, and F. Tokuda, *J. Phys. Chem.*, **73**, 243 (1969).

8) K. M. Hanna, I. Odler, S. Brunauer, J. Haggymassy, Jr., and E. E. Bodor, *J. Colloid Interface Sci.*, **45**, 27 (1973).

9) J. H. de Boer, "The Structure and Properties of Porous Materials," Butterworth, London (1958), p. 68.

10) T. Morimoto, Y. Yokota, and M. Nagao, *J. Colloid Interface Sci.*, **64**, 188 (1978).