JOURNAL OF MATERIALS SCIENCE 19 (1984) 183–188

Effect of the partial pressure of water vapour on the thermal decomposition of γ-FeOOH and on the dispersity of the solid decomposition products

D. G. KLISSURSKI
Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1040 Sofia, Bulgaria

J. ŠUBRT
Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, Rez 25068, Czechoslovakia

V. N. BLASKOV
Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1040 Sofia, Bulgaria

J. LIPKA
Slovak Institute of Technology, Department of Electrical Engineering, Chair of Nuclear Physics, Bratislava, Czechoslovakia

P. HANOUSEK, K. BECHINE
Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, Rez 25068, Czechoslovakia

The thermal decomposition of pure γ-FeOOH in air flow has been studied at a water vapour partial pressure of 1×10^{-3} to 20 mm Hg. The specific surface areas of the decomposition products (γ-Fe_2O_3 and α-Fe_2O_3) have been found to decrease with increasing partial pressure. It has been also established that the increase in partial pressure of the water vapour accelerates the transformation of γ-Fe_2O_3 into α-Fe_2O_3.

1. Introduction

The thermal decomposition of γ-FeOOH is one of the methods used for the preparation of γ-Fe_2O_3 and α-Fe_2O_3. A number of factors such as temperature, reaction medium, purity of the initial compound, etc. [1–6] have a strong effect on the decomposition process. Investigations have been carried out on both the dehydration of γ-FeOOH to γ-Fe_2O_3 and the phase transformation γ-Fe_2O_3 → α-Fe_2O_3. In recent years additional factors affecting the mechanism of this transition have been found [7–10]. The purpose of the present paper was to study the effect of the water vapour partial pressure on the thermal decomposition of γ-FeOOH and the possibility of preparation of dispersed γ-Fe_2O_3. The influence of the water vapour on the phase transition γ-Fe_2O_3 → α-Fe_2O_3 was also investigated.

2. Experimental details

The initial pure γ-FeOOH was obtained by oxidative precipitation of a solution (0.36 M) of $FeSO_4$ according to the method of Šolcova *et al.* [11]. During the oxidative precipitation a constant pH = 7 was maintained, and the oxidation rate was 1.33×10^{-2} mol min^{-1} l^{-1}. According to elec-

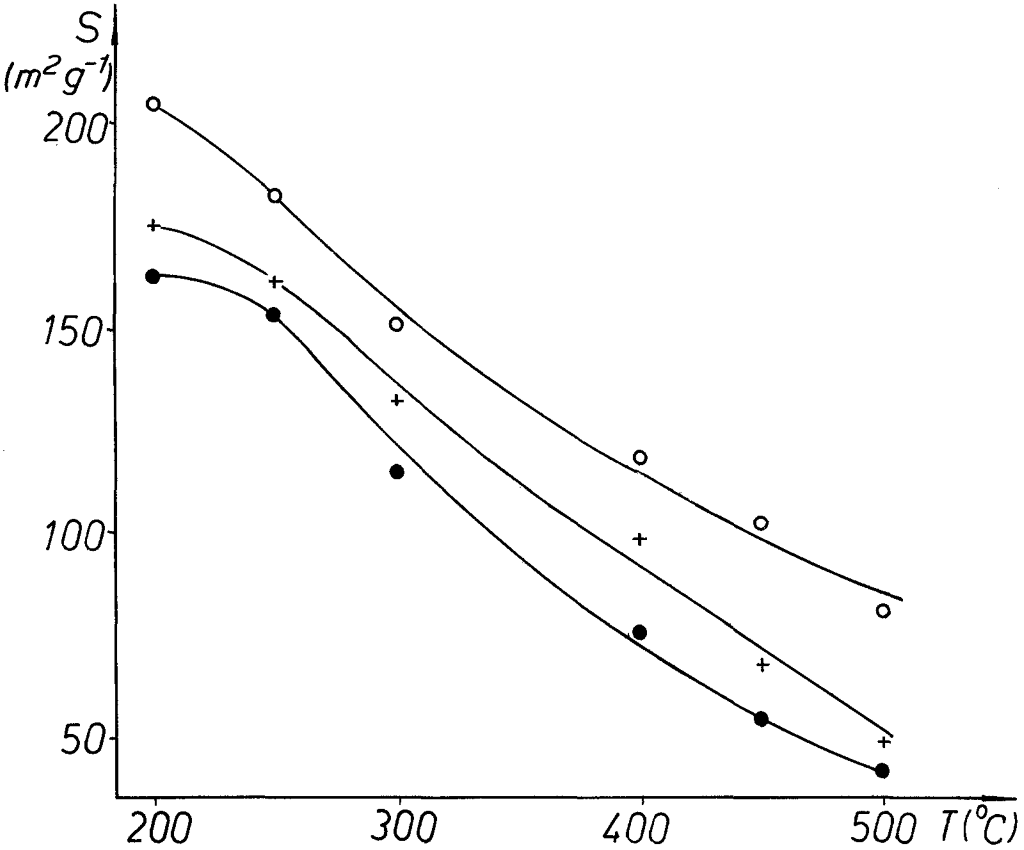

Figure 1 Change in the specific surface area of the oxides obtained by thermal treatment of γ-FeOOH for 3 h at high decomposition temperatures; ○, specific surface area of samples obtained in air flow at a water vapour partial pressure of 1×10^{-3} Hg; +, specific surface area of samples obtained in air flow at a water vapour partial pressure of 0.75 mm Hg; ●, specific surface area of samples obtained in air flow at a water vapour partial pressure of 17.5 mm Hg.

tron microscope data, the γ-FeOOH particles are needles with a mean size of 15.0 nm. The size of separate particles varied between 10.0 and 21.0 nm. The thermal decomposition of the oxyhydroxide proceeded at 200 to 500° C in air and a water vapour partial pressure of 1×10^{-3} to 0.75 to 17.5 mm Hg, respectively. The time of isothermal heating was chosen on the basis of preliminary experiments and was 3 h. The solid products of thermal decomposition were studied by infrared spectroscopy, Mössbauer spectroscopy, electron microscopy and magnetic measurements. The specific surface area was determined by a modified Brunauer, Emmett and Tellier (BET) method [14]. The infrared spectra were taken with a Beckman IR-20 spectrometer using TlBr as a matrix because of its higher refractive index and the fact that it is not hygroscopic. The Mössbauer spectra were obtained at room temperature using 512 and 256 channels, whereas at liquid nitrogen temperature 256 channels were utilized. The γ-radiation source was ^{57}Co in a rhodium matrix. The Mössbauer spectra obtained were processed by a computer. The magnetic measurements were made at room temperature by a Yokogama 3257 hysteresisograph.

3. Results and discussion

The present investigations showed that the temperature of thermal decomposition of the initial γ-FeOOH and the partial pressure of the water vapour in the reaction space effect the specific surface of the oxides obtained (Fig. 1). The specific surface area of the initial γ-FeOOH was 115 m^2 g^{-1}.

The curves in Fig. 1 illustrate a decrease in the specific surface area of the samples with increasing decomposition temperature. This is due to the proceeding of sintering and recrystallization reactions.

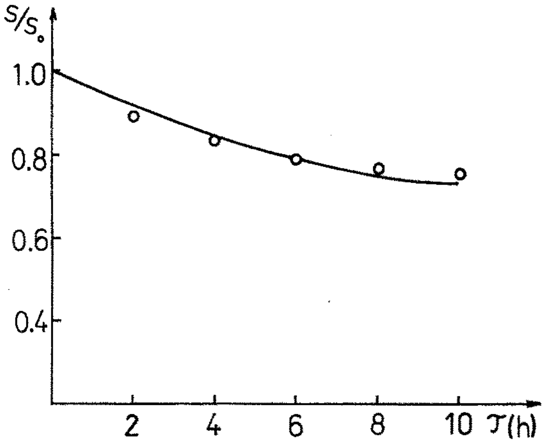

Figure 2 Relative change of surface (S/S_0) of γ-Fe_2O_3 during heating in air at a water vapour partial pressure of 17.5 mm Hg at 220° C.

TABLE I Data on the phase composition of the oxides obtained from the Mössbauer spectra

T (° C)	p_{H_2O} (mm Hg)	γ-Fe_2O_3 (%)	α-Fe_2O_3 (%)
250	1×10^{-3}	100	–
250	17.5	93	7
300	1×10^{-3}	88	12
400	1×10^{-3}	71	29
400	17.5	59	41
450	1×10^{-3}	–	100
450	17.5	–	100

Low-temperature sintering occurs at temperatures up to 300° C in an air flow at a water vapour partial pressure of 1×10^{-3} mm Hg as well as at 250° C and a water vapour partial pressure of 17.5 mm Hg. This process is favoured by the small size of the oxide and hydroxide particles and by their tendency to aggregation.

Fig. 2 shows low-temperature sintering of γ-Fe_2O_3 in air at a water vapour partial pressure of 17.5 mm Hg.

As is evident from Fig. 1, the thermal decomposition of γ-FeOOH is strongly affected by the water vapour present in the reaction space. With increasing water vapour partial pressure the specific surface area of the oxides obtained decreases. With rising temperature one observes an increase in the difference between the specific surface areas of the samples obtained in "dry" air (water vapour partial pressure, 1×10^{-3} mm Hg), on the one hand, and samples prepared in "humid" air (water vapour partial pressure 0.75 and 17.5 mm Hg), on the other. This is due to the different promoting effect of the water vapour interacting with the oxide surface:

(a) on the low-temperature sintering which proceeds at temperatures up to 250° C in a "humid" air flow and up to 300° C in a "dry" air flow;

(b) on the recrystallization of the X-ray amorphous γ-Fe_2O_3 which proceeds at 250 to 400° C in a "humid" air flow and at 300 to 400° C in a "dry" air flow.

(c) on the sintering of the α-Fe_2O_3 which proceeds at temperatures above 450° C.

The increase in the water vapour partial pressure in the reaction space at higher temperatures leads to an increase in the surface diffusion rate of the substance [12]. As a result, the rate of "coalescence" at the particle contact site increases and the specific surface area of the oxides rapidly decreases. The effect of the water vapour partial pressure on the crystallization process of highly dispersed γ-Fe_2O_3 is very strong. In this case the term "highly dispersed" is used for oxides with a particle size below 100 nm and a doublet unresolved Mössbauer spectrum at room temperature. A first order γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$ phase transition occurs within the temperature range of recrystallization. The obtained γ-Fe_2O_3 having a spinel type crystal structure passes into α-Fe_2O_3 with a corundum type crystal structure. The results from the Mössbauer studies showed increasing α-Fe_2O_3 amounts during decomposition of γ-FeOOH in air at a high water vapour partial pressure (Table I and Fig. 3).

The increase in amount of α-Fe_2O_3 with increasing water vapour partial pressure is associated with acceleration of the phase transition γ-$Fe_2O_3 \rightarrow$ α-Fe_2O_3 under the effect of the water vapour.

The infrared spectra of the samples gave qualitative information on the transition γ-$Fe_2O_3 \rightarrow$ α-Fe_2O_3 and on the accelerating effect of water vapour on the crystallization of the oxides (Table II and Fig. 4).

The results obtained by measuring the coercive force of the oxides obtained are given in Table III. The table shows that with increasing decomposition temperature within the range of 250 to 400° C the values of the coercive force increases. This is due to the increasing size of the oxide particles. This increase is associated with the decreasing superparamagnetism of the sample obtained. Simultaneously, γ-Fe_2O_3 passes into α-Fe_2O_3, and the amount of nonmagnetic α-Fe_2O_3 shows and increase at the higher temperatures. Obviously, the decrease in size of the γ-Fe_2O_3 particles more

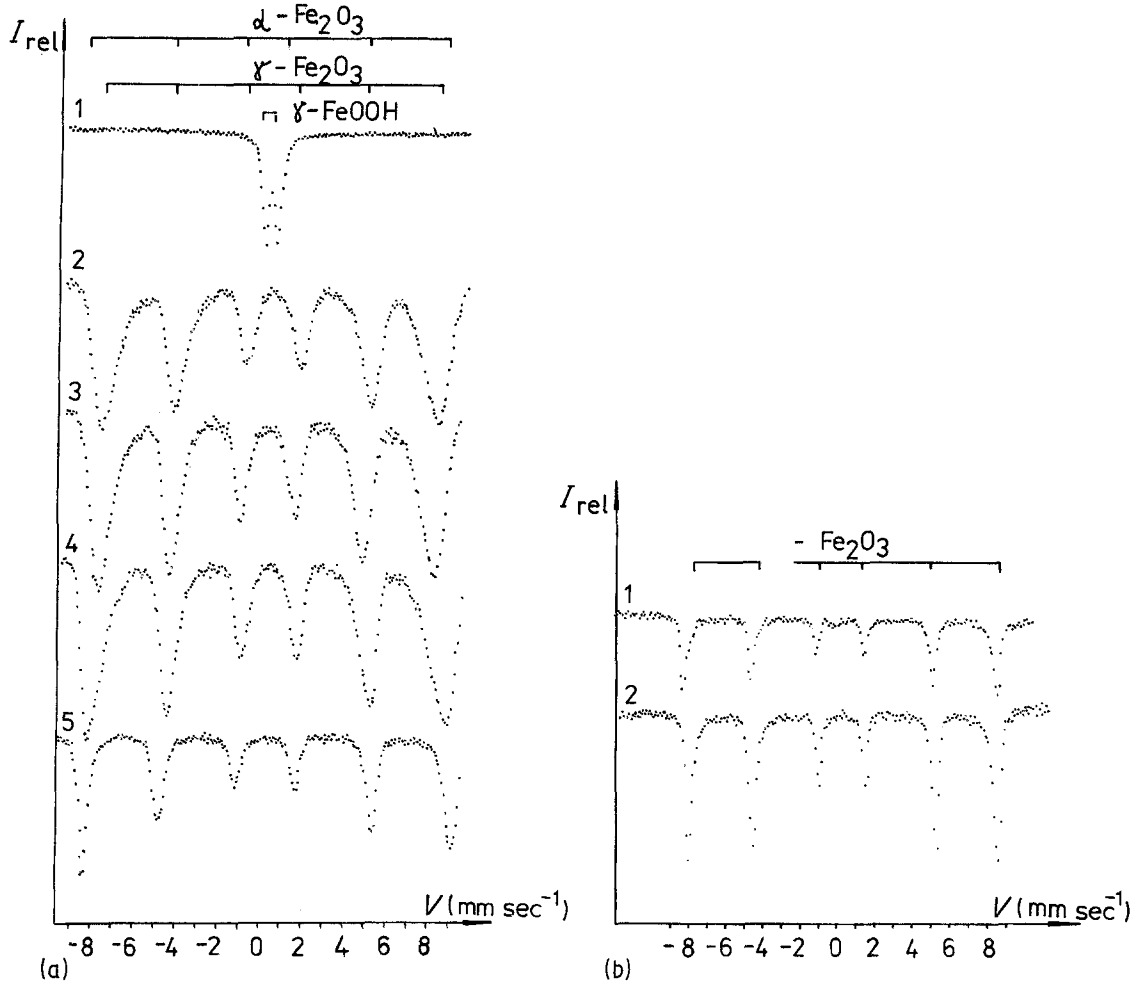

Figure 3 Mössbauer spectra of (a) 1. Initial γ-FeOOH at room temperature. 2. γ-Fe_2O_3 obtained by decomposition of γ-FeOOH at 250° C in air flow at a water vapour partial pressure of 1×10^{-3} mm Hg. 3. γ-FeOOH heated at 250° C in air flow and a water vapour partial pressure of 17.5 mm Hg. 4. γ-FeOOH heated at 400° C in air flow at a water vapour partial pressure of 1×10^{-3} mm Hg. 5. γ-FeOOH heated at 400° C in air flow at a partial pressure of 17.5 mm Hg. Spectra 2 to 5 were obtained at 78 K. (b) 1. α-Fe_2O_3 obtained by decomposition of γ-FeOOH at 450° C in air flow at a water partial pressure of 1×10^{-3} mm Hg. 2. α-Fe_2O_3 obtained by decomposition of γ-FeOOH at 450° C in air flow at a water partial pressure of 17.5 mm Hg. Spectra were obtained at room temperature.

strongly affects the coercive force than does its dilution by non-magnetic α-Fe_2O_3. The samples obtained at 450° C are nonmagnetic owing to the complete transformation of γ-Fe_2O_3 into α-Fe_2O_3.

Electron microscope observations showed the particles of initially formed γ-Fe_2O_3 to be needles. With advancing process of γ-$Fe_2O_3 \rightarrow$ α-Fe_2O_3 transition the particles become almost spherical. Table IV shows the mean particle size for the different samples as determined by electron microscopy.

TABLE II Infrared spectra of the oxides obtained

T (° C)	p_{H_2O} (mm Hg)	Absorption bands (cm^{-1})	
		γ-Fe_2O_3	α-Fe_2O_3
250	1×10^{-3}	400, 558, 1090, 1620	–
250	17.5	330, 400, 558, 1090, 1620	390, 445
300	1×10^{-3}	330, 558, 1090, 1620	390, 445, 615
400	1×10^{-3}	558, 1090, 1620	390, 445, 615
400	17.5	558, 1090, 1620	390, 445, 615

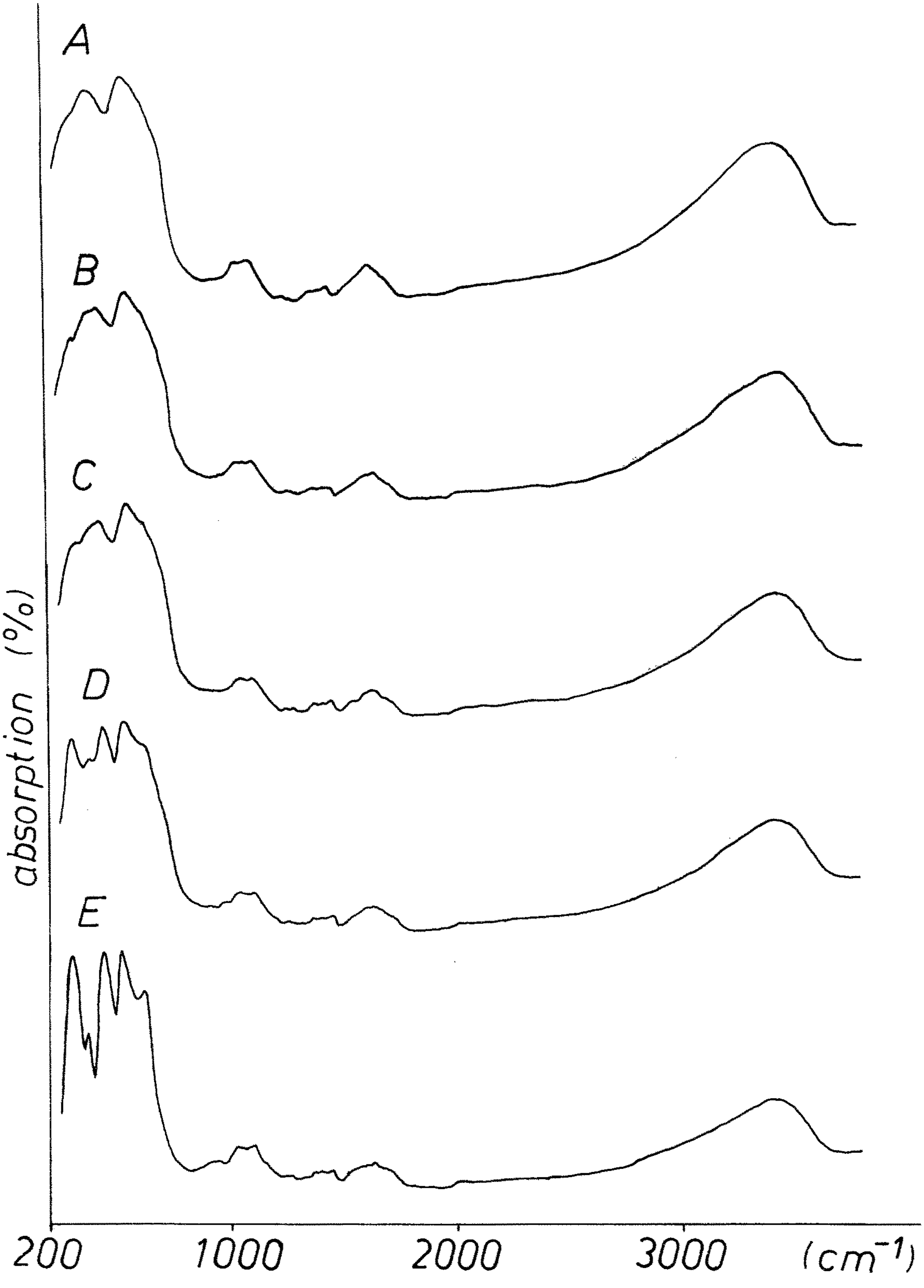

Figure 4 IR spectra of oxides obtained by decomposition of γ-FeOOH. (a), (c) and (d) In air flow at a water partial pressure of 1×10^{-3} mm Hg and temperatures of 250, 300 and 400° C, respectively. (b) and (e) In air flow at a water partial pressure of 17.5 mm Hg and temperatures of 250 and 400° C, respectively.

TABLE III Coercive force of the oxides obtained

T (° C)	p_{H_2O} (mm Hg)	H_c (oe)	Phase composition
250	1×10^{-3}	50	γ-Fe_2O_3
250	17.5	50	γ-Fe_2O_3 and α-Fe_2O_3
300	1×10^{-3}	62.5	γ-Fe_2O_3 and α-Fe_2O_3
300	17.5	62.5	γ-Fe_2O_3 and α-Fe_2O_3
400	1×10^{-3}	87.5	γ-Fe_2O_3 and α-Fe_2O_3
400	17.5	87.5	γ-Fe_2O_3 and α-Fe_2O_3
450	1×10^{-3}	–	α-Fe_2O_3
450	17.5	–	α-Fe_2O_3

The values of the coercive force given in Table III are lower than those available in the literature (400 to 500 oe) concerning γ-Fe_2O_3 obtained by oxidation of Fe_3O_4. The reason for this difference is, above all, in the superparamagnetism of γ-Fe_2O_3 with a small particle size. In his survey Morrish [13] also showed that magnetite obtained by decomposition of γ-FeOOH has weaker magnetic properties due to its bad morphology, i.e. its polydispersity and low density. However, improvement of these parameters can be expected if γ-FeOOH with a lower dispersity is used as an initial substance. The present investigations show a possibility of controlling the dispersity and phase composition of the system γ-Fe_2O_3/α-Fe_2O_3 by changing the partial pressure of water vapour during the thermal decomposition of γ-FeOOH.

References

1. J. ŠUBRT, P. HANOUSEK, V. ZAPLETAL and M. HUEL, *J. Thermal Anal.* **20** (1981) 61.
2. G. V. LOSEVA, N. V. MURASHKO and A. V. POLOZIN, *Izv. AN SSSR Neorg. Mater.* **10** (1974) 473.
3. G. V. LOSEVA, N. V. MURASHKO and G. S. SAKASH, *Ukrainski Fiz. Zhurnal* **17** (1972) 71.
4. R. GIOVANOLI, R. BRÜTSCH and W. STADELMAN, In Reaction Kinetics in Heterogeneous Chemical Systems, Proceedings of the 25th International Meeting of the Society Chimica Physica, edited by P. Barret, (Elsevier, Amsterdam, 1975) p. 302.
5. R. GIOVANOLLI and R. BRÜTSCH, *Thermochim. Acta* **13** (1975) 15.
6. G. S. SAKASH and N. P. TOPOR, *Vestnik Mosk. Univ.* **28** (1973) 99.
7. V. I. FADEEVA and L. A. REZNICKI, *Izv. AN SSSR Neorg. Mater.* **17** (1981) 828.
8. W. FEITKNECHT and U. MANNWEILER, *Helv. Chim. Acta* **50** (1967) 570.
9. J. BAND, M. KIJMA, T. TAKADA and J. KASHI, *Jpn. J. Appl. Phys.* **4** (1965) 240.
10. H. SENNO, Y. TAWARA and K. TIDA, *ibid.* **6** (1967) 509.
11. A. ŠOLCOVA, J. ŠUBRT, F. HANOUSEK, P. HOLBA, V. ZAPLETAL and J. LIPKA, *Silikaty* **24** (1980) 133.
12. V. A. DZISKO and D. V. TARASOVA, Katalizatory i kataliticheskie procesy, Sb. Nauch. trudy, Novosibirsk (1977) p. 57.
13. A. N. MORRISH, *Cryst. Growth Prop. Appl.* **2** (1980) 171.
14. J. M. THOMAS and W. J. THOMAS, "Introduction to the Principles of Heterogeneous Catalysis" (Academic Press, London, 1967) p. 45.

Received 6 January 1982
and accepted 12 May 1983

TABLE IV Oxide particle sizes as determined by electron microscopy

T (° C)	p_{H_2O} (mm Hg)	$\bar{d}$ (nm)
250	1×10^{-3}	55
250	17.5	62
300	1×10^{-3}	75
300	17.5	83
400	1×10^{-3}	116
400	17.5	125