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REACTIVITY OF FINELY DISPERSED IRON (III) OXIDES AND OXIDE HYDROXIDES IN SOLID-STATE REACTIONS

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The kinetics of the reaction of α-Fe_2O_3 (hematite) with K_2CO_3 was studied at 600–800 °C for hematite samples prepared in different ways. The results demonstrated that the hematite reactivity is not a simple function of the specific surface area (or particle size), but depends significantly on the sample preparation history, especially at lower reaction temperature. The effect of low-temperature sintering on the hematite reactivity is discussed.

Hematite (α-Fe_2O_3) is an important starting material for the synthesis of mixed oxides used as magnetic materials, catalysts, pigments, etc. It is well known that the rate of formation of the mixed oxides and the properties of the products depend on the properties of the starting iron oxide, e.g. the particle shape and dimensions, the presence of impurities, etc. Despite the efforts devoted to studies of the relations between the reactivity and history of the starting iron oxide preparation, this problem is still inadequately understood [1–5].

Experimental

Chemicals

Three types of α-Fe_2O_3 were used: 1) Hematite prepared by annealing of Fe_3O_4 with various particle sizes at 600° in air for 2 h. This kind of hematite did not contain structurally bound water. 2) Hematite prepared by oxidative precipitation of aqueous solutions of iron(II) sulphate. The resulting hematite contained structurally bound water and SO_4^{2-} ions [6]. Its average composition can be

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expressed by the formula $Fe_2O_3 \cdot 0.26H_2O$ (hydrohematite [6–8]). 3) Hematite prepared by the annealing of goethite (α-FeOOH) at 350° for 2 h. This kind of hematite also contained structurally bound water [8].

Potassium carbonate (analytical grade, Lachema, Brno) was dried at 110° for 24 h before use.

Thermal analysis

TG, DTG and DTA curves were recorded simultaneously on a derivatograph (MOM, Budapest). 100 mg of powdered sample was heated in a corundum crucible in the temperature range 20–800° at a constant heating rate of 10 deg min^{-1} in air or He (25 l h^{-1}). The ETA curves were recorded on a Netzsch ETA apparatus in the Institute of Nuclear Research.

Phase analysis

The starting samples and the reaction products were subjected to X-ray diffraction (XRD) and Mössbauer spectroscopic phase analyses. The XRD investigations were performed with a DRON 2.0 (USSR) diffractograph, using CoK_α radiation. Mössbauer spectra were taken on a 512-channel instrument (KFKI, Hungary) operating in a constant-acceleration regime. Specific surface area was determined by the thermal desorption method of Nelsen and Eggertsen, using a mixture of N_2 and H_2 containing 14% N_2.

Measurement of the reaction rate

The starting compounds were ground in an agate mortar. The mixture was annealed at constant temperature in corundum crucibles: it was withdrawn after chosen time intervals and quenched in a desiccator. The reaction products were stored over KOH. The phase analysis was performed in the absence of moisture, to prevent the hydrolysis of $KFeO_2$.

Results and discussion

Kinetics of reaction of K_2CO_3 with Fe_2O_3

The phase composition of the products of reaction of K_2CO_3 with Fe_2O_3 depends on the K : Fe ratio in the starting mixture. The results of investigations of the phase compositions of products of the reaction of K_2CO_3 and Fe_2O_3 at various K : Fe ratios were discussed in a previous paper [5]. At the ratio K : Fe = 1, the only product is $KFeO_2$. The kinetics of the reaction of K_2CO_3 with Fe_2O_3 was studied at this ratio as a function of temperature, surface area and the type of starting hematite. The kinetic curve has a distinct S-shape, and the reaction follows a rate law frequently used in the literature to describe solid-state reactions [9]:

$$\alpha = 1 - \exp(-kt^n)$$

where α is the degree of conversion defined as the molar ratio of $KFeO_2$ to Fe, k is the rate constant, n is the kinetic parameter, and t is the time in minutes.

Since the reaction rate is not a linear function of the constant k in Eq. (1), it is more convenient to characterize the reaction kinetics by the reaction half-life time $t_{0.5}$. The half-life is related to k by

$$t_{0.5} = (\ln(2)/k)^{1/n} \tag{2}$$

The values of $t_{0.5}$ measured at 600 and 800° for samples with different preparation histories are given in Table 1. The following conclusions can be drawn from this Table: The reactivity of α-Fe_2O_3 is not simple function of the specific surface area, but depends significantly on the preparation conditions. An increase in reactivity with increasing specific surface area was observed for samples prepared by the calcination of Fe_3O_4 (samples 1–2). For hematite prepared by the oxidative precipitation of $FeSO_4$ (samples 4–5), there was an opposite dependence. The preliminary 2 h heat treatment of samples 4–5 at 600° led to significant decreases in reactivity; on the other hand, such an effect was not observed for samples 1–2. The reactivity measured at 800° was nearly the same for all hematite kinds. The samples prepared by the calcination of Fe_3O_4 (samples 1–2) were slightly more reactive at this temperature. The changes in the reactivity of hematite at 600–800°, depending

Table 1 Variation of reactivity of α-Fe_2O_3 with temperature, method of hematite preparation, and specific surface area

Sample	Method of preparation	Specific surface area, m^2/g	Particle size, μm	$t_{0.5}$, min		n
				600 °C	800 °C	
1	A	12	0.1	114	8	1.7
2	A	2.6	0.45	240	11	1.7
3	B	30	0.6 × 0.1	120	12	1.8
4	C	15	0.08	240	16	1.8
5	C	5.6	0.2	137	16	1.8
6	D	2.3	0.5	2000	16	1.8
7	E	10.8	0.1	120	9	1.7
8	F	10	0.2	300	12	1.7

A – calcination of Fe_3O_4; B – thermal decomposition of α-FeOOH; C – oxidation-precipitation of $FeSO_4$ solution; D – sample 4 annealed at 600 °C for 2 h; E – sample 1 annealed at 600 °C for 2 h; F – sample 3 annealed at 600 °C for 2 h on the sample preparation history, indicate that these changes are related to processes occurring in hematite or hydrohematite during annealing in this temperature range.

Structural changes of hematite and hydrohematite during annealing

The changes in the specific surface area with temperature for hematite samples prepared by different methods are presented in Fig. 1. While the specific surface area changes for the hematite samples prepared by Fe_3O_4 calcination are negligible, the remaining hematite samples show significant increases in specific surface area, related to the loss of water and the formation of pores. The specific surface area rise is followed by a sharp decrease, resulting from the low-temperature sintering processes.

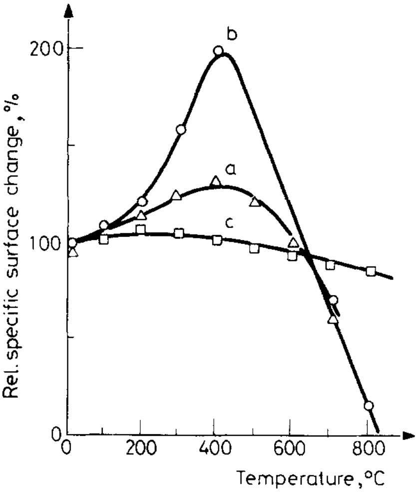

Fig. 1 Relative changes of the specific surface area of various hydrated iron (III) oxide samples with annealing
a – hydrohematite (sample 5, initial sp, surface area 5.6 m^2/g)
b – goethite (initial sp. surface area 12.1 m^2/g)
c – hematite (sample 1, initial sp. surfae area 12 m2/]

The changes in the specific surface area with temperature accord with the results of an electron microscopic study of the annealing products, where the formation of large particles resulting from the aggregation and sintering processes was observed at 600–900° for the precipitated hematite and also for the goethite dehydration products.

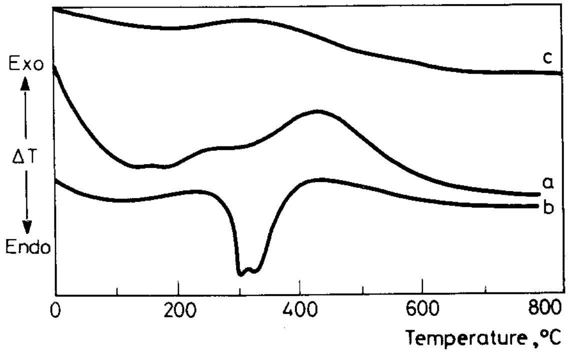

Fig. 2 DTA curves of hydrated iron oxides
a – hydrohematite (sample 5)
b – goethite
c – hematite (sample 1)

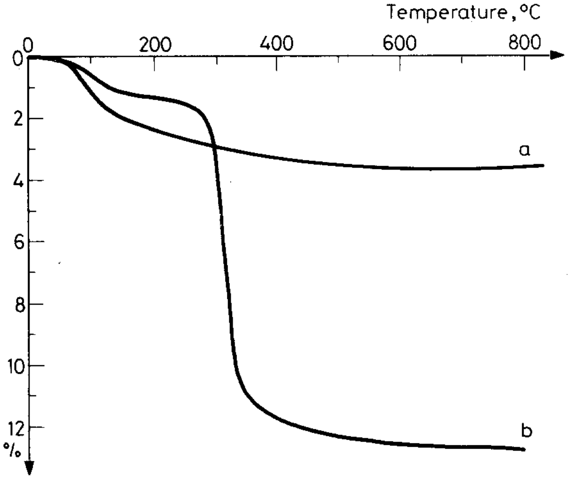

Fig. 3 TG curves of hydrated iron oxides
a – hydrohematite (sample 5)
b – geothite

An earlier study of the behaviour of hydrohematite and goethite during heating [6] revealed enhanced sensitivity of the particles of these phases to low-temperature sintering. The catalytic effect of water vapour on this process has been also described in the literature [10]. Therefore, it can be expected that the desactivation of α-Fe_2O_3 resulting from the low-temperature sintering phenomena proceeds simultaneously with the reaction with K_2CO_3, and this process can lower the reactivity of the hematite samples.

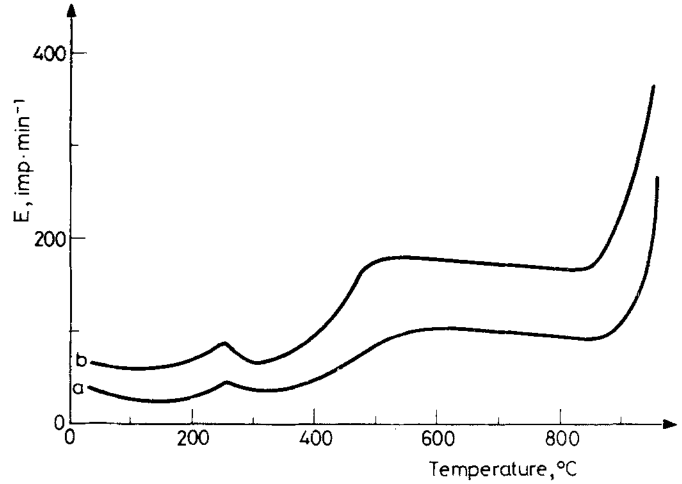

Fig. 4 ETA curves of hydrated iron oxides
a – hydrohematite (sample 5)
b – goethite

The changes occurring in the α-FeOOH thermal decomposition products and in hydrohematite during heating were studied by means of TG, DTA and ETA methods (Figs 2, 3 and 4). The loss of H_2O and a decrease in the emanation rate during heating of these samples were observed up to 800°. The decrease in the emanation rate was found in the temperature region in which the low-temperature sintering of the hematite particles occurs.

Conclusions

The reactivity of α-Fe_2O_3 is not a simple function of the specific surface area (or particle size), but depends significantly on the preparation process and on the preliminary heat treatment of the particular samples. During the heat treatment, the low-temperature sintering phenomena influence the reactivity, particularly of the samples more sensitive to such sintering. The most sensitive to these desactivation processes are the hematite samples containing structurally bound water, prepared from aqueous media at low temperature (hydrohematite).

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Zusammenfassung — Die Kinetik der Reaktion unterschiedlich präparierter α-Fe_2O_3- (Hämatit-) Proben mit K_2CO_3 bei 600–800 °C wurde untersucht. Die Ergebnisse zeigen, dass die Reaktivität des Hämatits keine einfache Funktion der spezifischen Oberfläche (bzw. Teilchengrösse) ist, sondern deutlich von der Vorgeschichte der Probe, insbesondere bei tieferer Temperatur, abhängt. Der Einfluss des Tieftemperatursinterns auf die Reaktivität des Hämatits wird diskutiert.

Резюме — При температуре 600—800° изучена кинетика реакции взаимодействия полученного различными способами гематита (α-$Ге_2O_3$) с карбонатом калия. Результаты показали, что реакционная способность гематита является не просто функцией его удельной площади поверхности (или размера частиц), а в значительной мере зависит, особенно при более низкой температуре реакции, от «истории» получения образца. Обсуждено влияние низкотемпературного спекания на реакционнуюспособность гематита.