REACTION OF α-Fe$_2$O$_3$ (HEMATITE) WITH POTASSIUM CARBONATE AT ELEVATED TEMPERATURES

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The kinetics of the reaction between α-Fe$_2$O$_3$ and K$_2$CO$_3$ have been investigated over the temperature range 600 to 800°C, and the phase composition of the products has been determined. The reaction follows the rate law $\alpha = 1 - \exp(-k\tau^n)$. At molar ratios K : Fe $\geq$ 1, KFeO$_2$ is the only product. At K : Fe $<$ 1, initially formed KFeO$_2$ reacts with hematite to yield K$_2$Fe$_4$O$_7$. The latter phase has been assigned a cubic structure with $a = 1\cdot681 \pm 0\cdot003$ nm. Based on X-ray powder diffraction patterns and Mössbauer spectra, the structure of K$_2$Fe$_4$O$_7$ is proposed to be a cubic close-packed array of oxygen atoms, part of these being replaced by potassium atoms, with Fe atoms occupying the octahedral interstices.

The dehydrogenation of ethylbenzene to styrene is carried out using Fe$_2$O$_3$-based catalysts and activating admixtures such as potassium oxide. In spite of considerable practical importance of the catalyst, information on the phases in the system Fe$_2$O$_3$--K$_2$O and on the kinetics of their formation is still incomplete.

The phase diagram of the system Fe$_2$O$_3$–K$_2$O has been published by Takahashi and coworkers[1]. The stable phase, KFeO$_2$, is formed, for example, by melting ferric oxide together with potassium oxide. The compound has a cubic structure[2,3] composed of arrays of FeO$_4$ tetrahedra with potassium ions occupying interstices in these arrays. Infrared spectra of products from the reaction of K$_2$CO$_3$ with iron oxides have been published by Eross and Klara[4].

Literature data on phases with molar ratios K : Fe $<$ 1 are fragmentary. Mention has been made of the compound K$_2$Fe$_4$O$_7$, but without any closer characterization[5]. Ischida[2] has studied Mössbauer spectra of products from thermal decomposition of K$_2$FeO$_4$; he found that at temperatures above 250 °C the decomposition product was KFeO$_2$, and at 170 °C he obtained an amorphous compound of trivalent iron which showed quadrupole splitting of Mössbauer line at 20 °C and magnetic six-line splitting at 4·2 K.

More detailed information is available on compounds that form on reaction of ferric oxide with sodium oxide. Besides NaFeO$_2$, the phase Na$_3$Fe$_5$O$_9$ with mono-

clinic lattice has been described[6]. The preparation and hydrolysis of the latter compound have been described by Voronin and coworkers[7,8]: hematite reacts with Na_2CO_3 to give cubic $NaFeO_2$ which on further reaction with excess Fe_2O_3 yields $Na_2Fe_5O_9$.

This paper presents results of a study on the kinetics of the reaction between hematite and potassium carbonate with hematite samples of different properties and on characterization of reaction products obtained for various K : Fe ratios in the starting mixture.

EXPERIMENTAL

Chemicals

Two types of α-Fe_2O_3 (hematite) were used: *1*) Commercial Bayer B 110 and B 160 iron pigments, *i.e.* pure hematite, with surface areas of 12·23 and 2·59 m^2/g, respectively. This type of hematite contains no structurally bound water. *2*) Hematite prepared by oxidative precipitation of aqueous solution of ferrous sulphate[9]. So obtained hematite contains structurally bound water and SO_4^{2-} ions. Its average composition can be expressed by the formula $Fe_2O_3.0.26\ H_2O.0.06\ SO_3$ (the so-called hydrohematite). Three samples with surface areas of 5·6, 9·87, and 15·02 m^2/g were used. The behaviour of hydrohematite on heating has been described by Šubrt and coworkers[10].

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

Procedure

Potassium carbonate was ground with a chosen amount of hematite in an agate dish. The mixture was annealed at a constant temperature in corrundum crucibles; these were withdrawn at chosen time intervals and quenched in desiccators. The reaction products were stored over KOH in order to prevent slow decomposition which occurs on exposure to moist air and CO_2.

Phase Analysis

The starting samples and reaction products were subjected to X-ray powder and Mössbauer spectroscopic phase analyses. X-ray powder diffraction patterns were recorded on a DRON 2·0 instrument (Burevestnik, Leningrad, U.S.S.R.) with Co(Kα)-radiation and Fe filter. Mössbauer spectra were taken on a 512 channel instrument (KFKI, Budapest, Hungary) operating in a constant-acceleration regime. The gamma radiation was obtained from ^{57}Co in Rh matrix. The adsorbent density was approximately 35 mg/cm^3. The specific surface area was determined by the thermal desorption method of Nelsen and Eggertsen on an instrument described by Mangel[11], using a mixture of nitrogen and hydrogen with 14% N_2.

RESULTS

Phase Composition of Products

A series of hematite (Bayer B 110) + K_2CO_3 mixtures with the molar ratio increasing

in steps of 0·1 from 0 to 2 were annealed at 900°C for 2 h. The reaction products were characterized by means of Mössbauer spectroscopy and X-ray powder diffraction method (Figs 1 and 2).

At $K : Fe \geq 1$, $KFeO_2$ was detected as the only product. At $K : Fe < 1$, K_2O . . xFe_2O_3 with variable composition appeared as an additional phase. Diffraction lines of the phase K_2O . xFe_2O_3, which are different from those of both hematite and $KFeO_2$, appeared already at $K : Fe = 0·1$, and at a ratio of 0·2 diffraction lines of hematite were no longer observed. First diffraction lines of the phase $KFeO_2$ appeared at $K : Fe = 0·6$, and K_2O . xFe_2O_3 disappeared at $K : Fe = 1$. Mössbauer spectra confirmed that a phase different from both hematite and $KFeO_2$ was formed at $K : Fe < 1$. This phase showed two sextets with parameters dependent on the $K : Fe$ ratio (see Table I). The parameters of magnetic splitting suggest that the arrangement of atoms about Fe is similar to that in hematite and varies continuously with increasing $K : Fe$ ratio.

Kinetics of α-Fe₂O₃ + K₂CO₃ Reaction

The kinetics of the reaction between Fe_2O_3 and K_2CO_3 were investigated over the temperature range 600 to 800°C. Potassium carbonate melts with decomposition at
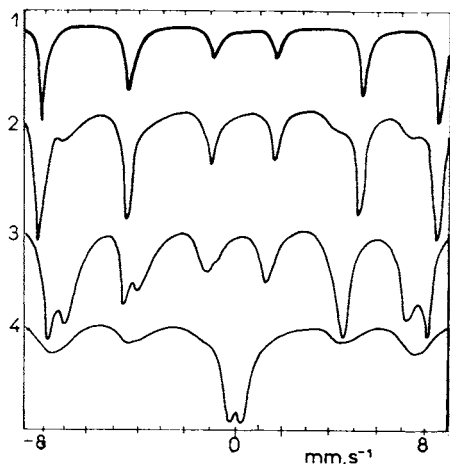
FIG. 1

Mössbauer spectra of products from α-Fe₂O₃ + K₂CO₃ reaction with various K : Fe ratios. K : Fe: *1* 0; *2* 0·2; *3* 0·4; *4* 0·6
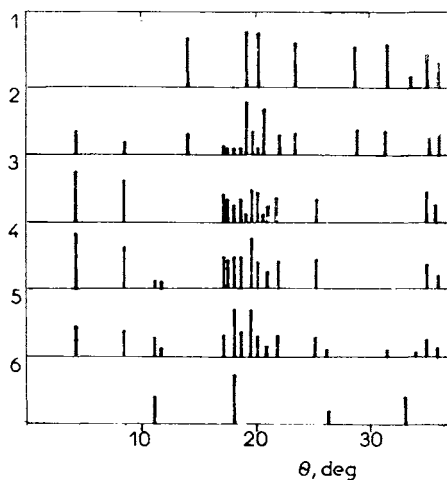
FIG. 2

X-ray powder diffraction patterns of products from α-Fe₂O₃ + K₂CO₃ reaction with various K : Fe ratios. K : Fe: *1* 0; *2* 0·2; *3* 0·4; *4* 0·6; *5* 0·8; *6* 1

TABLE I

Characteristics of Mössbauer spectra of products from α-Fe_2O_3 + K_2CO_3 reaction at various K : Fe ratios

K : Fe ratio	Components of Mössbauer spectrum[a]											
	I %	IS mm/s	Q mm/s	H MA.m^{-1}	I %	IS mm/s	Q mm/s	H MA.m^{-1}	I %	IS mm/s	Q mm/s	H MA.m^{-1}
0·0	100	0·18	—0·11	41·22	0	—	—	—	0	—	—	—
0·1	83	0·18	—0·10	41·22	17	0·13	—0·11	36·13	0	—	—	—
0·2	55	0·07	—0·02	40·03	45	0·11	—0·11	34·93	0	—	—	—
0·3	51	0·04	0·04	38·75	49	0·15	—0·10	35·25	0	—	—	—
0·4	53	0·00	0·03	38·59	47	0·11	—0·09	35·49	0	—	—	—
0·6	0	—	—	—	57	0·11	0·00	37·16	43	0·11	0·26	0
0·8	0	—	—	—	31	0·12	0·00	37·16	69	0·12	0·27	0
1·0	0	—	—	—	0	—	—	—	100	0·12	0·27	0

[a] I — relative intensity of a component of Mössbauer spectrum, IS — isomeric shift, Q — quadrupole splitting, H — intensity of internal magnetic field.

891°C. Its reaction with hematite occurs at a measurable rate already at 600°C, and at temperatures above 800°C it is complete within a few minutes.

The results for the phase composition of products in the course of the reaction between Fe_2O_3 and K_2CO_3 indicate that, at $K : Fe < 1$, $KFeO_2$ initially formed reacts with excess hematite according to the equations:

$$Fe_2O_3 + K_2CO_3 \rightarrow 2\,KFeO_2 + CO_2 \qquad (A)$$

$$2\,KFeO_2 + (x - 1)\,Fe_2O_3 \rightarrow K_2O.x\,Fe_2O_3 . \qquad (B)$$
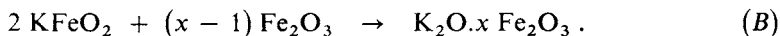
For $K : Fe = 1$, the reaction kinetics have been investitated in detail as a function of temperature, surface area and type of starting hematite. The kinetic curve has a distinct S-shape, and the reaction follows a rate law frequently used in the literature to describe solid phase reactions[12],

$$\alpha = 1 - \exp\left(-k\tau^n\right), \qquad (1)$$

where α is the degree of conversion defined as the molar $KFeO_2$ to Fe ratio, k is the rate constant, n is the kinetic parameter, and τ is the time in minutes. The magnitude of the parameter n depends on the variation in the degree of conversion with time. For $n < 1$, the initial reaction rate is infinitely high; this is typical of solid state reactions in which diffusion is the rate-controlling step[12]. For $n > 1$, the initial reaction rate is zero, and a plot of α against time has an S-shape. In the system under study, Eq. (1) was found adequate to describe the reaction kinetics for hematite samples of different origin and surface areas.

Since the reaction rate $d\alpha/d\tau$ is not a linear function of the constant k in Eq. (1), it is convenient to characterize the reaction kinetics by the reaction half-life $\tau_{1/2}$ rather than by the rate constant. The half-life is related to k by

$$\tau_{1/2} = \left[\ln\left(2\right)/k\right]^{1/n} . \qquad (2)$$

Equation (1) can now be written as

$$\alpha = 1 - 2^{-(\tau/\tau_{1/2})^n} . \qquad (3)$$

The parameters $\tau_{1/2}$ and n were evaluated by simultaneously correlating experimental data obtained at 600, 650, 700, 750, and 800°C for hematite samples of different specific surface areas. The parameter n has the same value for all hematite samples prepared by the same method.

The reaction kinetics for thermally prepared hematite (samples B 110 and B 160) followed Eq. (3) with the parameter n independent of both the reaction temperature

and the surface area of starting hematite. The results are summarized in Table II. The value of n is greater than unity $(n = 1.73)$, suggesting that the rate-controlling step is not diffusion but the actual chemical process coupled with generation and growth of $KFeO_2$ product nuclei.

The reaction of hematite prepared by oxidative precipitation shows more complex kinetics. The value of the parameter n increases with temperature. The evaluation was made by assuming n to be a linear function of temperature:

$$n = A + B(t - 700),\qquad (4)$$

where A and B are empirical parameters, and t is the reaction temperature (°C). Least-squares fitting to data given in Table II yielded $n = 1.82 + 0.0026(t - 700)$.

It is well known[9,10] that, at the temperature of the reaction with K_2CO_3, hematite prepared by oxidative precipitation undergoes changes such as sintering and loss of structurally bound water. Therefore, we also investigated the kinetics for this type of hematite pretreated thermally by heating at 600°C for 2 h. This treatment resulted in a strong reduction of the reaction rate, particularly at lower temperatures (see Table II).

DISCUSSION

The reaction of hematite with potassium carbonate always gives $KFeO_2$ as the first product. The reaction rate depends on temperature, the specific surface area and the method used in preparing the starting hematite. The reaction kinetics can be described

TABLE II

Variation of the reaction half-life (min) with temperature, method of hematite preparation and particle size

Reaction temperature °C	$\tau_{1/2}$ (min)					
	B 110[a]	B 160[b]	SH 127[c]	SH 128[d]	SH 118[e]	SH 128[f]
600	114	240	244	183	137	2 000
650	88	151	148	111	89	456
700	28.2	56.0	92	31.1	28.9	90
750	14.9	27.4	64.5	25.9	20.8	50.7
800	9.4	10.0	16.0	15.4	13.9	14.3

Values of parameter n in Eq. (3): samples a, b: $n = 1.73$; samples c—e: $n = 1.82 + 0.0026$ . . $(t - 700)$. Specific surface area (m^2/g): commercial iron pigments a 12.33; b 2.59; hematite prepared by oxidative precipitation: c 15.02; d 9.87; e 5.61; f annealed at 600°C for 2 h.

by Eq. (3). For thermally prepared hematite (samples B 110 and B 160), the kinetic parameter n is independent of temperature, and the reaction rate (reaction half-lives in Table II) increases with increasing surface area. Hematite prepared by oxidative precipitation loses the water bound in its structure and changes its surface area[10] when heated to temperatures at which its reaction with K_2CO_3 has been studied. These changes may result in a decrease of the reaction rate.

Fig. 3 shows a plot of the surface area against temperature for both thermally prepared hematite (sample B 110) and hematite obtained by oxidative precipitation (sample SH-118). The surface area of B 110 remains virtually constant up to about 600°C, and then slightly decreases. For hematite prepared by oxidative precipitation (sample SH-118), by contrast, initial increase up to a maximum at about 400°C is followed by decrease to a quarter of the maximum value, indicating initial surface activation followed by deactivation as the temperature is increased above 400°C. This may explain the low reactivity of thermally pretreated hematite precipitate, as well as higher reaction rates observed for samples of low surface area. Samples with high surface areas show higher rates of deactivation. These effects are pronounced at temperatures below 800°C; at 800°C, the reaction rate is practically the same for all samples of precipitated hematite.

At K : Fe $\geqq$ 1, $KFeO_2$ is the only product. At lower K : Fe ratios, reaction (B) between $KFeO_2$ and α-Fe$_2$O$_3$ yields a non-stoichiometric phase with an approximate composition of $K_2Fe_4O_7$. The X-ray powder pattern of this phase differs from that of the related sodium compound $Na_3Fe_5O_9$ to such an extent that the two compounds are unlikely to have analogous structures[7,8]. Miller indices were assigned to diffraction lines of $K_2Fe_4O_7$ on the assumption that the compound has a cubic symmetry with $a = 1 \cdot 681 \pm 0 \cdot 003$ nm (see Table III).
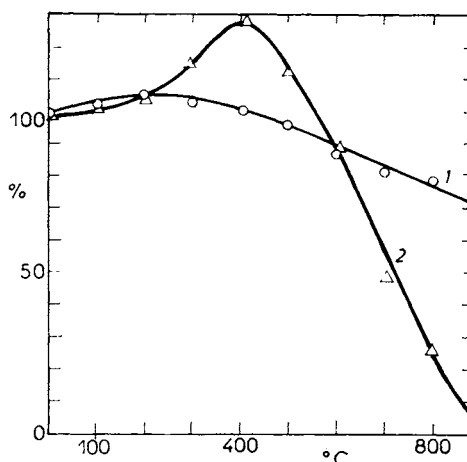

Fig. 3

Relative change in hematite surface area as a function of temperature. 1 commercial iron pigment (B 110); 2 hematite prepared by oxidative precipitation (SH-118)

Mössbauer spectra of the products of the reaction between Fe_2O_3 and K_2CO_3 (Fig. 1) vary considerably with the product composition. At K : Fe = 1, a doublet corresponding to $KFeO_2$ is observed. At K : Fe ratios between 0·5 and 1, a sextet characteristic of $K_2Fe_4O_7$ appears in addition to the doublet due to $KFeO_2$. At K : Fe ratios between 0·5 and approximately 0·2, the spectra show two sextets with parameters different from those characteristic of hematite. The intensity and the values of H_{eff}, IS, and Q of both sextets vary with composition.

Thus, it may be concluded that the non-stoichiometric phase $K_2Fe_4O_7$ involves a minimum of two non-equivalent positions of Fe atoms. The parameters of the

TABLE III

X-ray data for the phase $K_2Fe_4O_7$

d nm	I %	$h\ k\ l$	$2\,\theta_{exp}$	$2\,\theta_{calc}$
11·938	100	1 1 0	8·6	8·64
5·986	70	2 2 0	17·2	17·33
2·977	60	4 4 2	35·0	35·07
2·961	50	4 4 1 2 2 5	35·5	35·54
2·936	50	5 3 1	36·8	36·63
2·749	60	1 1 6	38·0	38·33
2·668	70	6 2 0	39·2	39·37
2·568	60	3 3 5	40·8	40·88
2·475	30	6 3 1	42·4	42·35
2·384	30	5 5 0 7 1 0 5 4 3	44·1	44·25
2·296	10	5 5 2 3 3 6	45·9	46·10
2·163	10	6 5 0 6 4 3	48·9	48·95
2·087	50	7 4 0 8 1 0 6 5 2	50·8	50·86
1·668	10	7 7 2	64·9	64·83
1·574	10	5 5 8 7 7 4 8 7 1	69·3	69·13
1·539	60	7 7 4	71·1	71·08
1·519	30	10 4 2	72·2	72·31

Mössbauer line splitting indicate the presence of octahedrally coordinated Fe^{3+} (Table I).

On this basis, the phase $K_2Fe_4O_7$ may be assumed to be a solid solution whose lattice is a cubic close-packed array of oxygen atoms. These are randomly replaced by potassium atoms (the ionic radii of O^{2-}, 0·132 nm, and K^+, 0·133 nm, are close to each other[13]), and the Fe atoms occupy the octahedral interstices. If the ionic radius of oxygen is 0·132 nm, then the interlayer spacing in the cubic close-packed structure is $4 \cdot 0\cdot132/\sqrt{2} = 0\cdot37$ nm. Thus, the unit cell of $K_2Fe_4O_7$ contains four layers; the theoretical figure $4 \cdot 0\cdot37 = 1\cdot49$ is in good agreement with the observed value $a = 1\cdot68$ nm. The structural model considered involves seven non-equivalent positions of Fe atoms. Assuming a random distribution of potassium atoms, the relative intensities of Mössbauer signals from the individual positions can be estimated from the equation

$$I_s = l_s p^s (1 - p)^{6-s}, \tag{5}$$

where I_s is the intensity of Mössbauer line due to an Fe-atom with s potassium atoms in its octahedral enviroment. The symbol p represents the probability that the lattice position at the octahedral vertex is occupied by potassium, and l_s is the number of possible arrangements of s potassium atoms in the octahedral environment of Fe atoms. The probability p can be calculated from balances for atoms and lattice positions and the requirement of crystal electroneutrality. For an entirely random arrangement, l_s is given by the binomial coefficient $\binom{6}{s}$. Taking account of the fact that potassium and oxygen atoms are oppositely charged and therefore are unlikely

TABLE IV

Relative intensities of the components of Mössbauer spectra of products from α-Fe_2O_3 + K_2CO_3 reaction, calculated from Eq. (5) for various K : Fe ratios

K : Fe ratio	$I_0{}^a$	$I_1{}^b$	$I_2{}^c$
0·1	71·45	27·66	0·89
0·2	55·65	41·74	2·61
0·3	45·66	49·81	4·53
0·4	38·79	54·77	6·44
0·5	33·79	57·93	8·28

[a] Fe atoms with no neighbouring K atom; [b] one K atom in the environment of Fe; [c] two K atoms in the environment of Fe.

to occupy nearest neighbour positions, we obtain $l_0 = 1$, $l_1 = 6$, $l_2 = 3$, $l_3 = l_4 = l_5 = l_6 = 0$.

Table IV lists values of relative intensities calculated from Eq. (5). It is apparent that only the first two terms $(I_0$ — Fe atoms with no neighbouring K atom; I_1 — Fe atoms with a single K atom in their environment$)$ should appear in the spectrum with sufficient intensity. This conclusion is in good agreement with experiment.

We can conclude that our picture of $K_2Fe_4O_7$ structure is in accord with the observed Mössbauer spectra and also explains the considerable variability of the composition of this phase, the only one that occurs over a wide range of K : Fe ratios from 0.2 to 0.5.

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