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REACTIVITY OF FINELY DISPERSED IRON OXIDES IN SOLID STATE REACTIONS

Jan Šubrt^x, Jaroslav Vinš, Institute of Inorganic Chemistry
Řež near Prague, Czechoslovakia
Igor S. Shaplygin, Alexander A. Zakharov
Institute of General and Inorganic Chemistry
Moscow, USSR

ABSTRACT

The reactions of α-Fe_2O_3 and γ-Fe_2O_3 with K_2CO_3 have been studied under dynamic and stationary conditions. The reaction course and the properties of the reaction products depend on the preparation and thermal treatment of iron(III) oxides. The starting γ-Fe_2O_3 yields ferromagnetic products with cubic structure while α-Fe_2O_3 gives non-magnetic products of different properties. In both cases, the reaction products are non-stoichiometric compounds of the composition $K_2O.x\ Fe_2O_3$ where $0.1 > x > 0.5$, $KFeO_2$ is additionally formed.

INTRODUCTION

Iron(III) oxides activated by potassium are among important dehydrogenation catalysts, used for example in making styrene from ethylbenzene. Nevertheless, data on the phases in the system Fe_2O_3-K_2O are too scarce to permit a satisfactory description of reaction that may take place in this system.

EXPERIMENTAL

Chemicals: α-Fe_2O_3 was prepared either by annealing and oxidation of Fe_3O_4 in air at 600 °C (Samples 1 and 2 with specific surface areas of 12.3 and 2.6 m^2/g, respectively), or by oxidative precipitation of aqueous solutions of $FeSO_4$ as described previously (Samples 3,4,5 with specific surface areas of 15.0, 9.9 and 5.6 m^2/g, respectively). Hematite obtained by the latter method contains water bound in its tsructure, the average composition being $Fe_2O_3 \cdot 0.25\ H_2O \cdot 0.06\ SO_3$. Sample 4 was additionally annealed at 600 °C for 2 h. Potassium carbonate was of analytical grade. γ-Fe_2O_3 (maghemite) was a single-phase, chemically pure commercial product (Pfizer Mo 2228).

Measuring techniques: Thermoanalytical curves were measured on a Q-derivatograph and an OD-103 derivatograph (MOM Budapest). X-ray powder analysis was performed by means of a DRON 2.0 diffractometer (KFK Budapest) with constant acceleration and ^{67}Co in

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an Rh matrix as the source. The specific surface area was measured by the thermal desorption method of Nelsen and Eggertsen.

Procedure: Potassium carbonate was ground with iron(III) oxide in an agate mortar, and the mixture was annealed under dynamic conditions or at constant temperature in a corundum crucible. When the reaction was complete, the mixture was quenched and stored in a desiccator over KOH.

RESULTS AND DISCUSSION

Phase composition of products of the reactions of K_2CO_3 with α-Fe_2O_3 and γ-Fe_2O_3.

A number of α-Fe_2O_3 (Sample 1) + K_2CO_3 mixtures with molar ratios K:Fe=0.0-2.0 were prepared and annealed at 800 °C for 2 h. The reaction products were characterized by X-ray powder diffraction analysis and Mössbauer spectroscopy.

At $K:Fe > 1$, the only product is $KFeO_2$. At $K:Fe < 1$, $K_2O.x\ Fe_2O_3$ with variable composition is additionally formed. Diffraction pattern of this phase differs from the patterns of α-Fe_2O_3 and $KFeO_2$. The phase apperas already at K:Fe=0.1, and at K:Fe=0.2 diffraction from α-Fe_2O_3 is no longer observed. At K:Fe=0.6, $KFeO_2$ appears, and diffraction from $K_2O.x\ Fe_2O_3$ disapperas at K:Fe=1.0. The formation of a phase different from α-Fe_2O_3 and $KFeO_2$ at $K:Fe < 1$ has been confirmed by Mössbauer spectra. The phase gives rise to two sextets, whose parameters depend on the ratio K:Fe (Table I). The splitting parameters suggest that the disposition of atoms about Fe is similar to that in hematite, varying continuosly with increasing ratio K:Fe.

Structural analysis results indicate that $K_2O.x\ Fe_2O_3$ has a closely knit structure of oxygen atoms with cubic symetry. Part of oxygen atoms in the oxygen sublattice are replaced by potassium atoms, and the Fe^{3+} ions occupy octahedral sites. Electroneutrality is provided by vacancies in the octahedral Fe^{3+} sites. Consistent with this picture are results of both Mössbaur spectroscopy and X-ray powder diffraction analysis.

The reaction of K_2CO_3 with γ-Fe_2O_3 follows a different course. Fig.1 shows DTA curves for the starting maghemite and a maghemite + K_2CO_3 mixture. Pure maghemite transforms at 500 °C into α-Fe_2O_3. In the presence of K_2CO_3, however, no exothermic effect due to the γ-$Fe_2O_3 \longrightarrow \alpha$-$Fe_2O_3$ transformation was observed even on increasing the temperature up to 800 °C.

X-ray diffraction patterns from products of K_2CO_3 + γ-Fe_2O_3 reaction show diffraction lines of maghemite, $KFeO_2$ and $K_2Fe_4O_7$. Mössbauer spectra of the products are different from those for products of reaction with hematite, showing a superposition of several sextets and at least one paramagnetic component.

Table I

Parameters of Mössbauer spectra of products of the reaction of K_2CO_3 with α-Fe_2O_3

K:Fe ratio			Parameters of components of Mössbauer spectra									
	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
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	35.48	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

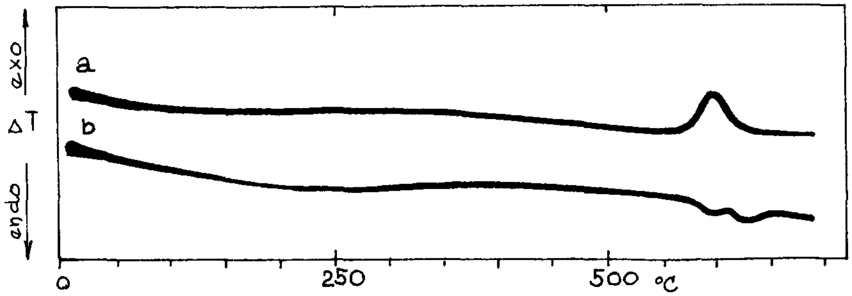

Fig.1. DTA curves of γ-Fe_2O_3 and mixture of γ-Fe_2O_3 with K_2CO_3.
a- DTA curve of γ-Fe_2O_3 (Pfizer Mo 2228)
b- DTA curve of the mixture of γ-Fe_2O_3 with K_2CO_3 1:1

Kinetics of the reaction between α-Fe_2O_3 and K_2CO_3

The reaction kinetics in the system α-Fe_2O_3-K_2CO_3 were followed over the temperature range 600-800 °C. Potassium carbonate melts while decomposing at 891 °C. Its reaction with hematite proceeds at a measurable rate already at 600 °C, and goes to completion in a few minutes at temperatures above 800 °C.

At K:Fe<1, $KFeO_2$ initialy formed reacts subsequently with excess hematite according to the equatıons

$$Fe_2O_3 + K_2CO_3 \longrightarrow 2\ KFeO_2 + CO_2 \qquad (1)$$

$$2\ KFeO_2 + (x-1)Fe_2O_3 \longrightarrow K_2O.x\ Fe_2O_3 \qquad (2)$$

The kinetics were found to comply with equation (3), comonly used for solid state reactions .

$$\alpha = 1 - \exp(-kt^n) \qquad (3)$$

The reaction rate was expressed in terms of the reaction half-life, $t_{1/2}$, which is related to the reaction rate constant k by

$$t_{1/2} = \left[\ln(2)/k\right]^{1/n} \qquad (4)$$

The reaction kinetics for the thermally prepared hematite (Samples 1 and 2) can be described by equation (3) where the parameter n is independent of both the temperature and the specific surface of the starting hematite. The results are given in Table II. The value n=1.73 suggests that the reaction proceeds in the kinetic regime. The reaction rate increases with increasing surface area of the starting hematite.

The reaction of hematite prepared by oxidadtive precipitation shows more complex kinetics. The parameter n increases with increase in temperature. The data (Table II) were least square fitted to the linear equation

$$n = A + B(T-700) \qquad (5)$$

The best fit was n= 1.82 + 0.026(T-700). (T:temperature in °C)

At such temperatures as used in reaction with K_2CO_3, hematite prepared by oxidadtive precipitation is known to undergo changes such as dehydration and sintering. Therefore, kinetics of this type of hematite pretreated thermally at 600 °C for 2 h have also been investigated (Sample 6). The thermal treatment markedly slows down the reaction, particularly at lower temperatures.

Table II

Dependence of the reaction half-life on temperature and type of the starting hematite

Temp. °C	$t_{1/2}$ /min/					
	1	2	3	4	5	6
600	115	240	244	183	137	2000
700	28.2	56.0	92	41.1	28.9	90
800	9.4	10.0	16	15.4	13.9	14.3