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ALKALI METAL DIFFUSION IN FERRITIC SYSTEMS

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Abstract. *The paper considers the mechanism of solid-phase interaction of potassium monoferrite with hematite. The authors assigned the role of iron oxide as a matrix for the creation of further structure of the catalyst.*

For the experiment the authors prepared pill samples of potassium monoferrite and haematite. The pills were placed in a special clamp and heat-treated. We investigate the mechanism of solid-phase interaction in the $KFeO_2$-Fe_2O_3 *system by the artificial mark method.*

We used the q parameters calculated from XRD data to assess the ratio of products of the solid-phase interaction between potassium monoferrite and haematite. The article presents a bar chart of the parameters $q[\beta''(0111)]$, $q[\beta(017)]$ *and* $q[Fe_2O_3(110)]$ *as a function of the depth of potassium penetration into the haematite volume. Analysis of the structures of haematite and potassium polyferrites suggests that alkali metal ions diffuse into the haematite lattice. In the polyferrite formed, the movement of cations continues between blocks of composition* $\{Fe_{11}O_{17}\}$. K^+ *ions occupy the correct positions in the lattice of the formed polyferrite. A layer rich in potassium β″-polyferrite is located closer to the pill contacts boundary. During the removing of the pills from the contact boundary, there is a formation of alkali metal polyferrites with β″-alumina and β-alumina structures. The distance from the contact boundary of the pills increases with decreasing of the content of β″-polyferrite following by increasing of the proportion of β-phase. The polyferrites formed are essentially solid electrolytes capable to ensure the transportation of alkali metal ions through specific channels in the polyferrite structure.*

The paper presents the dependence of the factor $f(\beta'')$ *on the degree of transformation of potassium monoferrite into polyferrites during heat treatment of* $KFeO_2+2Fe_2O_3$ *mixtures at 1150 K. It also describes the ratio of β- and β″-phases in the products of ferrite formation. As the degree of transformation is increasing, the* $f(\beta'')$ *decreases, reaching a certain ratio of β- to β″-polyferrites. In this case the energy of coherent coupling of the β- and β″-phases ensures rapid stabilisation.*

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Introduction

The promoted catalyst used for the process of dehydrogenation of ethylbenzene to styrene is a ferrite system. Potassium β''-polyferrite is one of the key components of this catalyst. It is in dynamic equilibrium with potassium monoferrite as well as magnetite [1-6]. Potassium polyferrite with a β''-alumina type structure (K-β''-Fe_2O_3) is a key component of the promoted iron-oxide catalyst for the dehydrogenation of ethylbenzene to styrene. Its properties make it a basic component of a catalytic system [1-3].

Potassium-promoted iron oxides are the most widely used catalysts for the catalytic dehydrogenation of ethylbenzene to styrene. In addition to potassium, other additives are also added to the catalyst for various purposes to enhance its catalytic properties and the stability of the catalyst. Chromium (Cr) and vanadium (V) are two traditionally used promoters. Chromium is widely used as a structure stabiliser. However, vanadium can increase the selectivity for styrene, but negatively affects the stability and activity of the catalysts. Since the effects of these two promoters are opposite, we studied the effect of these metals on the phase composition of the catalyst products [7].

Industrial catalysts have disadvantages such as chromium toxicity, deactivation due to potassium loss and coke deposition. In this study, the authors investigated the effect of magnesium on the properties of iron-oxide promoted catalyst. Magnesium compounds affect the crystal size, number of defects, and recoverability of iron oxides. These effects caused significant differences in the activity, selectivity, and stability of the catalysts. The catalyst with Mg/Fe = 0.09 ratio, consisting of hematite, MgO, and magnesium ferrite aggregates, showed high yield and is the most promising for industrial application [8].

The deactivation of an industrial Fe-K catalyst for the dehydrogenation of ethylbenzene to styrene was studied in [9]. The results showed that regeneration of the used catalyst by coke combustion can increase its activity. Nevertheless, after a short reaction time, the activity decreases to the level of the used catalyst. The analysis results showed that coke formation, catalyst sintering, and potassium loss were not the cause of catalyst deactivation. However, the main causes of deactivation were migration and uneven redistribution of potassium, as well as reduction of Fe^{3+} ions.

Researchers [10] examined the effect of neodymium, lanthanum, aluminium, and zirconium on the textural and catalytic properties of hematite – the main component of the catalyst for the dehydrogenation of ethylbenzene to styrene. The alloying elements increased the catalytic activity per unit area of hematite, except for aluminium, which acted only as a textural promoter. The selectivity was decreased by zirconium and lanthanum, while other alloying elements did not affect this parameter. The neodymium-containing catalyst showed high activity and selectivity and was able to operate up to 530 °C without deactivation.

The authors synthesised mixed polyferrites of the β''-alumina type containing dopants of rare earth elements. The authors examined the mechanism of alkaline promoter stabilisation upon doping of mixed potassium-cesium polyferrites with rare earth element oxides. The requirements for the alloying agent have been formulated [11].

Potassium-containing ferritic systems have a variety of applications. They are the active phase of promoted iron-oxide catalysts for the dehydrogenation of olefinic and alkylaromatic hydrocarbons, which are related to multiton petrochemical processes, and are also used as solid electrolytes. However, the mechanism of polyferrite formation, the direction and type of diffusion of components during solid-phase interaction are practically not studied.

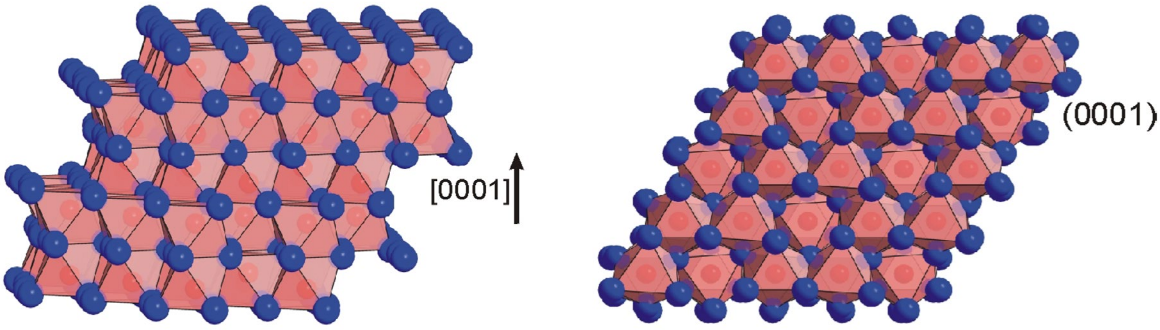
The purpose of this study is to determine the mechanism of solid-phase interaction of potassium monoferrite with hematite.

Main body

Potassium monoferrite was prepared by calcination of mixtures of potassium carbonate and hematite in a molar ratio of 1:1. We conducted the heat treatment in a muffle furnace at 700 °C for 4 h. We cooled the obtained monoferrite in the desiccator and then moulded it into tablets of 42 mm diameter and 12 mm height under 80-100 bar pressure. Haematite tablets were prepared in a similar manner. The horizontal surfaces of the hematite and potassium monoferrite tablets were polished and carefully aligned. The initial interface was fixed with an inert marker using a 0.2 mm silver wire. The tablets were pressed tightly together using a special device that provided a constant pressing force of 10 bar. The folded tablets were heat-treated at 750 °C for 6-8 h. After cooling, the sintered tablets were cut along the original contact boundary on a Secotom cutting device, which provides a high precision cut in thickness. Then, cuts were made on either side of the original contact boundary. The depth of potassium penetration into the haematite volume was estimated by atomic absorption spectroscopy. The phase analysis of the obtained slice samples was determined by X-ray diffractometry on a DRON instrument using CoCα radiation. The compounds were identified by peak intensities using PDF2 ICDD databases.

Hematite is the basis for the preparation of industrial catalysts for the dehydrogenation of olefinic and alkylaromatic hydrocarbons. The structure of iron oxide can be seen as a distorted NaCl structure; the each of the ions is replaced by a combination of Fe_2O_3. Oxygen forms the densest two-layer packing; Fe^{+3} ions occupy 2/3 of octahedral cavities.

The groups of three oxygen ions form a common surface of three adjacent octahedra, and each of these octahedra is bonded to the same iron couple (Fig. 1).



a b

Fig. 1. Hematite a) slightly angled side view of α-Fe_2O_3 (111), b) top view of two different sublayers of iron α-Fe_2O_3 (111).

The pairs of occupied octahedrons, interchanging with unoccupied one, create helical axes B1, characterising the so-called corundum packing moiety. Haematite crystallises in the

3m class of trigonal syngony. Their spatial group is R-3c. The layers of oxygen atoms are slightly closer due to the large electrostatic attraction between iron cations and oxygen anions compared to their arrangement in the ideal hexagonal densest packing. At the same time, iron ions are displaced towards the (0001) plane: they alternately occupy places approximately at heights equal to ⅓ and ⅔. Therefore, the ratio of c/a axes differs from the ideal one (1.33) and makes 2.72. The lattice parameter along the c-axis is 0.137 nm [12].

The plane (0001) has the highest packing density, where Fe^{3+} and O^{2-} ions are packed layer by layer. In particular, the packing density of Fe^{3+} and O^{2-} is 9.11 nm^{-2} and 13.8 nm^{-2}, respectively. The packing density in the (1010) plane for ions, on the contrary, is 2.89 nm^{-2} and 5.78 nm^{-2}. Figure 2 shows the detailed crystal structure of Fe_2O_3.

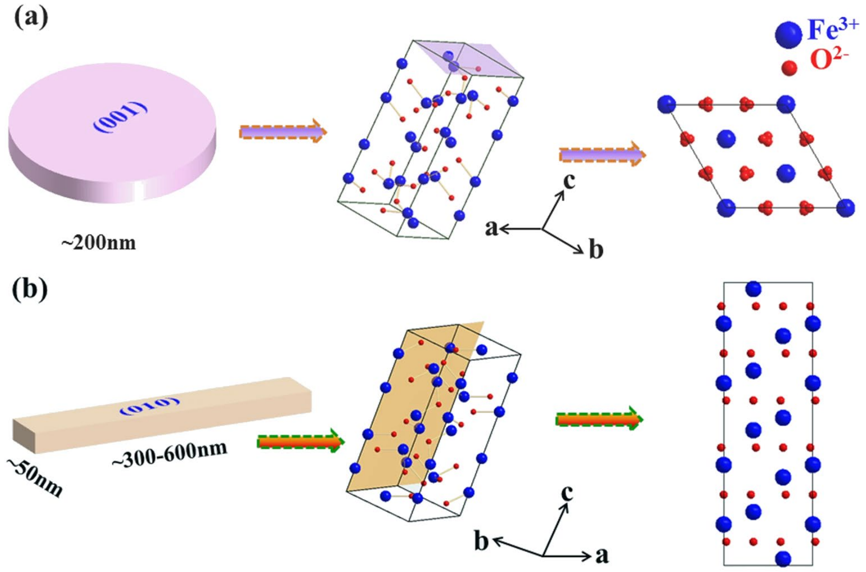


Fig. 2. Structure of hematite: (**a**) in plane (0001) and schematic structure of hematite projected along {0001}, (**b**) in plane (1010) and schematic structure of hematite projected along {1010}. Fe_2O_3 crystallographic information file (by the NIST/FIZ FindIt database) [13].

The study of the mechanism of solid-phase interaction in the $KFeO_2$-Fe_2O_3 system by the artificial labelling method indicates unilateral diffusion of potassium ions into the hematite lattice. It is coupled with the formation of potassium polyferrites K-(β+β')Fe_2O_3 in the layers close to the contact boundary of the tablets. Indeed, the ratio of β'- and β-phases decreases with distance from the contact boundary according to XRF data.

We used the q parameters calculated from XRD data to assess the ratio of products of the solid-phase interaction between potassium monoferrite and haematite according to the equations:

$$q[\beta"(0111)] = \frac{I[\beta"(0111)]}{I[\beta"(0111)]+\mathrm{I}[\beta(017)] + I[Fe_2O_3(110)]} \tag{1}$$

$$q[\beta(017)] = \frac{I[\beta(017)]}{I[\beta"(0111)]+\mathrm{I}[\beta(017)] + I[Fe_2O_3(110)]} \tag{2}$$

$$q[Fe_2O_3(110)] = \frac{I[\beta"(0111)]}{I[\beta"(0111)]+\mathrm{I}[\beta(017)] + I[Fe_2O_3(110)]} \tag{3}$$

Fig. 3 shows the bar diagram of parameters $q[\beta''(0111)]$, $q[\beta(017)]$ and $q[Fe_2O_3(110)]$ (heat treatment time 360 min, T=750 °C) as a function of the depth of potassium penetration into the haematite volume.

Moreover, no peaks related to the structure of monoferrite were detected in the diffractograms of the cuts. The experimental results confirm that the solid-phase interaction occurs due to one-way diffusion of alkali metal ions into the haematite structure. The diffusion seems to proceed as follows. First, alkali metal ions diffuse between coherent scattering regions (along interblock boundaries) in the hematite substructure.

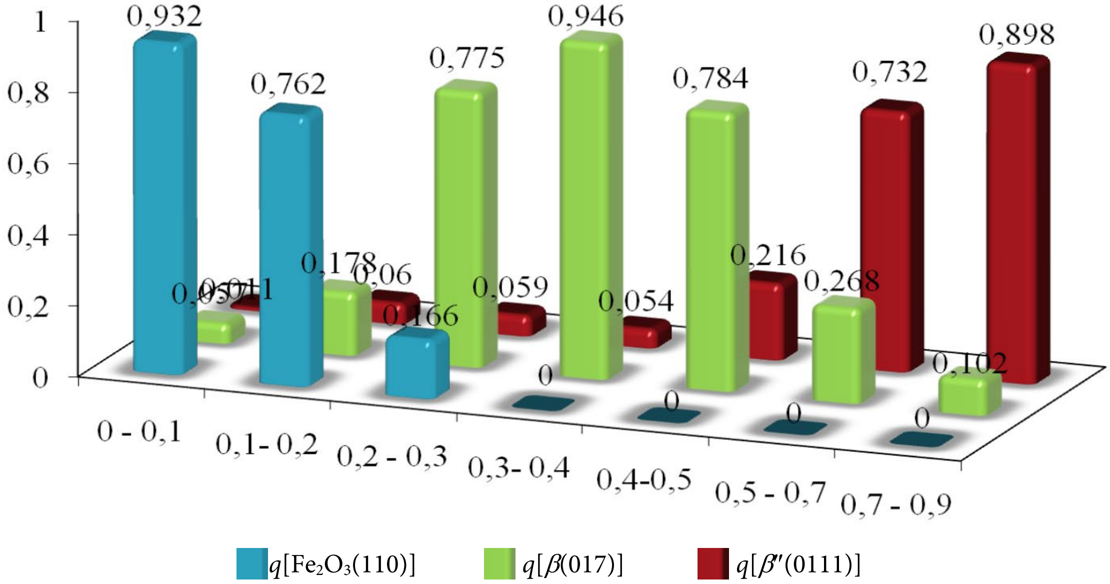


Fig. 3. Dependence of the cuttings composition (heat treatment time 360 min, T=750 °C) on the depth of potassium penetration into the haematite volume

However, this process does not lead to a solid-phase interaction proper. The diffusion of the same ions then proceeds at a deeper level into the hematite lattice. Considering the peculiarities of the Fe_2O_3 crystal structure, it can be assumed that the K^+ ion is introduced into the haematite structure in the (1010) plane. The density of Fe^{3+} and O^{2-} ions in it is 2.89 nm^{-2} and 5.78 nm^{-2}. It is the particular plane that is the least densely packed. The structure of haematite is rearranged into the structure of potassium polyferrite (Fig. 4).

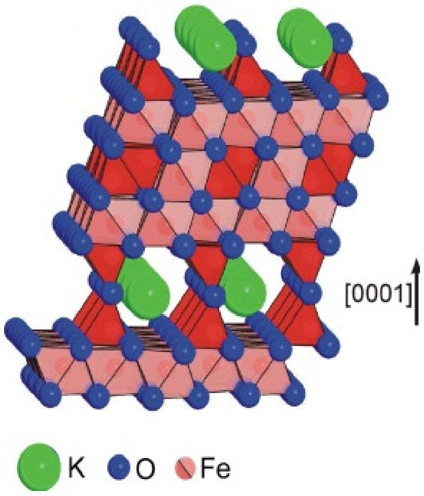


Fig. 4. Structure of potassium polyferrite

The unit cell of β''-polyferrite contains three spinel-like blocks of composition $\{Fe_1^{2+}Fe_{10}^{2+}O_{16}\}$ connected by a third-order helical axis. Each block is formed by four densely packed layers of oxygen ions. Some of the tetrahedral and octahedral voids in the block are occupied by Fe^{3+} ions. Fe^{2+} ions are located in octahedral voids adjacent directly to the planes separating the blocks.

Alkali metal polyferrites of the β''-alumina type crystallise in layered structures. The spinel-like blocks in β''-polyferrite are rotated 120° relative to each other.

The planes separating the blocks are not densely packed. They are only 70% filled with alkali metal ions and 82% filled with oxygen ions from the available positions. Such a low filling of the plane and a large width of the interblock space are the reason for the extremely high mobility of alkali metal ions. They can move freely in two directions within the conducting plane [14].

The analysis of the structures of haematite and potassium polyferrites suggests that alkali metal ions diffuse into the haematite lattice. In the polyferrite formed, the movement continues between blocks of composition $\{Fe_{11}O_{17}\}$. K^+ ions occupy the correct positions in the lattice of the formed polyferrite. A layer rich in potassium β''-polyferrite is located closer to the pill contacts boundary (Fig. 5).

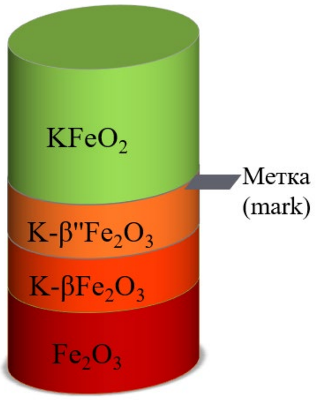


Fig. 5. Products of solid-phase interaction between hematite and potassium monoferrite

The chemical potential of potassium is high in the places of contact between monoferrite and haematite. It causes thermal dissociation of iron oxide. It is coupled with the formation of oxygen vacancies and an increase in the concentration of Fe^{2+} ions. Moreover, potassium ions have an ionising effect on the iron-oxygen bond. The lattice energy changes causing an increase in the chemical potential of oxygen in the solid phase. As a consequence, it causes the elimination of oxygen from the structure of iron oxide.

Polyferrites are formed in the process of solid-phase interaction in the potassium monoferrite-haematite system. They are essentially solid electrolytes and are able to provide transport of alkali metal through certain channels in the structure of polyferrite.

With increasing of the distance from the contact boundary of the pills, the content of β''-polyferrite decreases. It also increases the proportion of β-phase.

Fig. 6 shows the dependence of the factor $f(\beta'')$ on the degree of transformation of potassium monoferrite into polyferrites during heat treatment of $KFeO_2$+$2Fe_2O_3$ mixtures at 1150 K. It describes the ratio of β- and β''-phases in the products of ferrite formation,

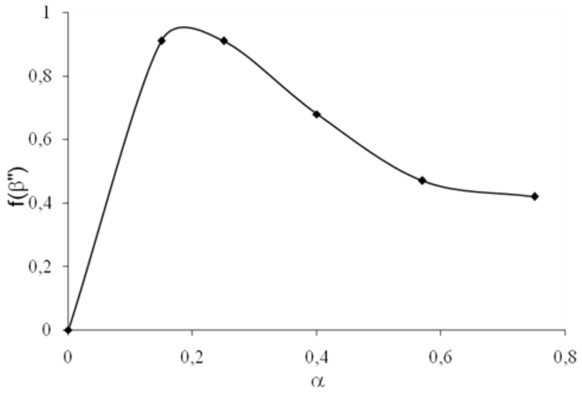


Fig. 6. Dependence of the factor $f(\beta')$ on the degree of transformation of potassium monoferrite at temperature 1150 K

The parameter $f(\beta')$ was calculated from the X-ray data according to Eq:

$$f(\beta") = \frac{I[\beta"(0111)]}{I[\beta"(0111)]+I[\beta(017)]} \tag{4}$$

According to Fig. 6, at the first stages of the reaction at low degree of monoferrite transformation a microheterogeneous mixture of potassium polyferrites with a high content of β'-phase is formed. An increase in the degree of transformation leads to a redistribution of the polyferrite ratio. At the same time, the complexity of the occurring structural-energetic interactions in the K-$(\beta+\beta')Fe_2O_3$ system does not allow us to unambiguously interpret β'-polyferrite as an intermediate product of β-polyferrite synthesis. Obviously, at the first stages β'-phase is stabilised in the zones of local thermodynamic equilibria by an excess of non-interacting monoferrite. As the degree of transformation increases, $f(\beta')$ decreases, reaching a certain ratio of β- to β'-polyferrites. In this case. the stabilisation is most rapidly achieved by the energy of the coherent coupling of the β- и β'-phases.

Conclusions

1. Solid-phase interaction in the system potassium monoferrite - haematite is performed as a result of one-way diffusion of potassium ions into the haematite lattice.
2. Polyferrites with the structure of β-alumina and β-alumina are formed as they distance from the initial boundary, respectively.
3. Polyferrites are formed in the process of solid-phase interaction in the potassium monoferrite-haematite system. They are essentially solid electrolytes and are able to ensure the transportation of alkali metal through certain channels in the structure of polyferrite.

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