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FORMATION OF THE ACTIVE STATE OF THE PROMOTED IRON OXIDE FOR CATALYTIC DEHYDROGENATION

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It was found that for K-β"Fe_2O_3 the maximum probability of realization of the active centers representing a cluster consisting of potassium ions, iron 3+ and 2+, and oxygen. The ability to self-reproduction and self-regulation in the reaction medium is an integral attribute of K-β"Fe_2O_3 as the main catalytically active component. This type of catalyst can be called a "catalyst with a permanently migrating promoter".

Polyferrite serves as a conductor of the alkaline promoter. The monoferrite concentrated in the depth of the catalyst granules, for example, on the inner surface of closed pores can be a source of potassium. Polyferrites are solid electrolytes with a cationic type of conductivity and provide not only the delivery of the promoter to a required location through channels embedded in the crystal structure, but also its regular placement in the composition of active clusters.

K-β"Fe_2O_3 is able to place the alloying additives in its structure. Only in this case, extremely small amounts of injected agent can greatly change the properties of the system. The rearrangement is not chaotic, if the K-β"Fe_2O_3 surface is chemically dispersed in the reaction medium to form a catalytically active short-lived substance - a nanoheterogeneous mixture of monoferrite and magnetite.

Introduction

Every stage of synthesis of the promoted iron-oxide catalyst for ethylbenzene dehydrogenation leads to changing of its chemical and phase composition, structure and properties. Most of the research in this field focused on either a freshly prepared contact or an already spent catalyst. In each case, the composition of the catalyst will not match the condition of the contact in service. This explains the lack of reliable data on the structure of catalysts in the reaction medium and the distribution of introduced components between the contact phases.

The series of publications of scientists from Germany is devoted to clarifying the nature of the active state of the catalyst. The evolution of the researchers' views is interesting. In earlier articles the authors point out the identity of the active centers for promoted and non-promoted iron oxide catalysts prepared in the form of films. According to [1], samples Fe_3O_4 (111) showed little catalytic activity in the dehydrogenation reaction because of the low Fe^{3+} content. There was an increase of the yield of styrene on Fe_2O_3 (0001) and the concentration of surface defects was also higher [1]. The authors define surface atomic defects as catalytically active centers. The active centers on the surface of $KFeO_2$ phase, the active phase of the industrial catalyst, should have similar properties as the atomic defects on the Fe_2O_3 (0001).

The catalyst is deactivated by the formation of carbon polymers and part of the catalyst surface is excluded from catalyst operation. Probably, the initial carbon deposits form on extended defects that do not coincide with the atomic defects on which styrene forms [1].

As the same authors stated later [2], potassium increases the activity of iron-oxide catalysts, although the dehydrogenation activation energy values are close for potassium-promoted and non - promoted catalysts. The increasing of activity is probably depending on potassium increasing the number of active centers [2].

Researchers [3] point to the distribution of potassium deep into the grain at elevated temperatures. It forms a non-stoichiometric structure consisting of $K_2O/K_2Fe_{22}O_{34}/Fe_3O_4$ (111) with gradually decreasing of potassium content as move deeper into the grain.

A comparative study of potassium-promoted and non-promoted catalysts [4] showed that the initial rate of the dehydrogenation reaction decreases and the active work time of the catalyst increases with increasing of potassium content. The authors [4] consider that introduction of potassium prevents catalyst deactivation and coking but at the same time blocks the active surface centers and reduces their concentration. As the potassium content increases, the surface is increasingly coated with $KFeO_2$, which is not a catalytically active phase. However, its presence can slow down deactivation.

The initial conversion values on potassium-promoted and non-promoted catalysts have similar values. On non-promoted Fe_2O_3 deactivation is rapid, and is caused by the reduction of Fe_2O_3 to Fe_3O_4 and coking. The water added to the reagent is responsible for gasification of the carbon deposits and limits their amount. In addition, it limits the reduction of Fe_2O_3 to Fe_3O_4 and prevents further reduction to metallic iron [4].

During the reaction there is a continuous loss of potassium, probably it is removed in the form of KOH. According to researchers [4], the loss of potassium occurs faster if the gas mixture contains only water without ethyl benzene. It is assumed that ethyl benzene, styrene and their decomposition products react with potassium to form potassium carbonate. We should avoid the catalyst steaming-out [4].

The authors [5-10] guess that the potassium monoferrite $KFeO_2$ is an active component of this class of contacts. As the catalyst in the active state, an equilibrium between the catalyst phases of $K_2Fe_{22}O_{34}$ and $KFeO_2$ is established. Hydrogen, formed as one of the products of the dehydrogenation reaction, reduces the contact activity and leads to the formation of KOH and magnetite Fe_3O_4 [5].

$K_2Fe_{22}O_{34}$ act as the generator of potassium ions, supplying into $Fe_3O_4$to form an active phase [6]. This requires a certain degree of matrix lattice imperfection, which depends on the method of preparation and the addition of promoters, which has effect on the iron oxide lattice more than the surface chemistry. The identification of $KFeO_2$ as the active phase was confirmed by independent synthesis of this phase and comparison of its activity with that of the commercial catalyst [6].

The real condition studies of the epitaxially grown catalyst model of the dehydrogenation reaction [11] showed that:

- the most active ions of Fe^{3+} are in Fe_2O_3 or KFe_xO_y;
- Fe_3O_4 is less active, probably about the strong reaction with ethyl benzene and styrene;
- deactivation of non - promoted catalysts occurs during the reduction of Fe_2O_3 to Fe_3O_4 and during the formation of coke. Consequently, deactivation can be prevented by supplying a small amount of oxygen;
- potassium is not active but suppresses reduction and catalyzes removal of carbon deposits;
- stable phases are $K_2Fe_{22}O_{34}$ and especially $KFeO_2$, they are also a reservoir for potassium;
- coke has notable catalytic activity;
- steaming-out (reaction in water vapor without ethylbenzene) significantly accelerates the loss of potassium [11].

The surface structure and composition of the potassium-promoted iron oxide catalyst prepared as epitaxial films of Fe_3O_4 (111) on Ru (0001), were investigated by X-ray photoelectron spectroscopy (XPS) combined with thermal desorption spectroscopy (TDS) and thermodynamic measurements, as well as by scanning tunneling microscopy (STM), low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) [12].

At 700 K, the $KFeO_2$ phase was identified, which at higher temperatures was converted to $K_xFe_{22}O_{34}$ ($0,67 < x < 4$). The formation of the monocrystalline layer of $K_xFe_{22}O_{34}$ ($x = 0,67$), bounded by a submonolayer of potassium, occurs at 970 K. This surface forms as a well - ordered phase with a superstructure for defining of a certain potassium content (2×2). Researchers point $KFeO_2$ as an active phase of the catalyst, while $K_2Fe_{22}O_{34}$ is only the reservoir for potassium storage. They argue that the structure of $KFeO_2$ is also formed on the film surface at normal calcination temperatures, corresponding to the mode of preparation of industrial catalyst samples. Treatment with water causes a loss of potassium from the surface of the sample even at reduced pressure. The deactivation, associated with the formation of Fe_3O_4 and KOH, is obvious. But the process is slow. By authors' opinions [12], carbon deposits on the contact surface serve as a protection against potassium loss.

The authors [13] showed that the atmosphere, in which the catalyst is formed and functions, has a great influence on the formation of the phase composition of the catalyst. $KFeO_2$ KFeO2 films were obtained in a vacuum and in an oxygen atmosphere at 870 K. Potassium loss and transformation to $K_xFe_{22}O_{34}$ (0001) was observed in vacuum, in an oxygen atmosphere $KFeO_2$ remained stable. The authors highlight that the stability ranges of ferrites depend on the partial pressure of oxygen.

Researchers [13] found that instead of large $KFeO_2$crystallites on the surface of $K_xFe_{22}O_{34}$ (0001) the $KFeO_2$thin films are forming. This confirms the assumption made by the XPS data that film thinning goes simultaneously with a decrease of potassium content in the volume, while the surface remains rich in potassium. There are both phases on the sample surface. These films simulate the catalytically active phase quite well. The data obtained are agree with the results of a study of an industrial catalyst consisting of $KFeO_2$ scales formed around of $K_2Fe_{22}O_{34}$core.

The proposed model is supported by Polish researchers [14, 15], who report that the main phases of catalysts for dehydrogenation of ethyl benzene to styrene are Fe_3O_4, $Fe_2O_3$and potassium ferrites $KFeO_2$, $K_2Fe_{22}O_{34}$. For each of the phases the activation energies of K and K^+

desorption at the dehydrogenation temperature were determined. It was shown that the active state of the catalyst as $K_2Fe_{22}O_{34}$ is responsible for the high potassium losses. The assumed optimal catalyst granules morphology consists of a $K_2Fe_{22}O_{34}$core, surrounded by a thin $KFeO_2$ scale, while the core and cracked shell model has been applied to calculate data on potassium desorption from the surface of real catalysts [14].

There is no doubt that the study of hematite or magnetite thin films oriented to the chosen crystallographic direction is one of the most promising ways to study the state of the catalyst in the reaction medium. The appending of alkali metal compounds into the film and subsequent treatment in hydrocarbon medium leads to the formation of metastable compounds corresponding to the composition of the catalyst surface in-service. We believe, the surface cannot be considered autonomously, in isolation from the internal contact structure, for this class of catalysts. This leads to an oversimplification of the approach. The resulting surface compounds or intermediates are unstable and short-lived. Continuous renewal of the surface layers, which is necessary to ensure the long-term functioning of the catalyst, maintaining the desired concentration of active centers, is only possible by using the resources of the deep layers or the entire volume of the granules.

We think, the model of the active center created by Chinese scientists, rarely mentioned in the literature, deserves special attention. In [16] the active center was modeled, and the reaction mechanism of ethylbenzene dehydrogenation to styrene on potassium-promoted iron oxide was considered in terms of these positions. The active center is a cluster consisting of one potassium atom (K_{27}), two iron atoms (Fe_{19} and Fe_{20}), and one oxygen atom (O_{23}), as shown in Fig. 1.

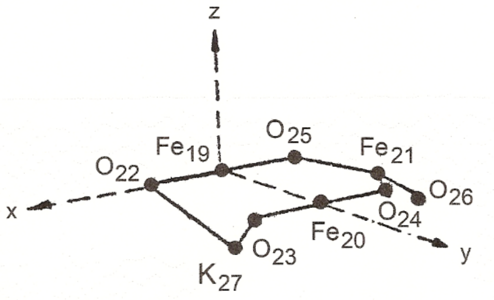

Fig. 1 Atomic cluster for the active phase on the 110 plane [16]

According to Chinese researchers [16], ethyl benzene forms σ-π - a coordination complex with Fe^{2+}, Fe^3+ ions with subsequent elimination of the αhydrogen atom of adsorbed ethyl benzene and formation of the benzene - phenol radical and OH-group by superconjugation. Then β the hydrogen atom attaches to the neighboring iron ion to form adsorbed styrene. In our opinion, it is quite remarkable that the active cluster includes differently charged iron. Potassium lowers the acidity of the catalyst, inhibiting side reactions. Moreover, the presence of potassium stabilizes the active phase and increases the number of active centers [16].

Questions of the mechanism of the catalytic process, the mechanism of formation of the active state of the catalyst, the nature of the catalytically active component, the phase and chemical composition of the contact in the dehydrogenation reaction, the mutual arrangement and interaction of the phases composing the catalytically active system, that is, the phase structure of the catalyst, the methods of transport of the alkaline promoter and its sources (reservoirs) remain a subject of discussion. At the same time, the answers to these questions are necessary for the correct formulation of the list of characteristics the desired product of solid-phase synthesis, the catalyst, should have.

Thus, the problems of modeling the phase and chemical state of the catalyst in an atmosphere with reduced oxygen partial pressure and quantitative interpretation of interactions in a complex heterogeneous ferritic composition remain highly relevant.

Experimental methods

The initial mixtures of potassium monoferrite, hematite, and metallic iron obtained by the carbonyl method were prepared by thorough grinding in an agate mortar under a layer of diethyl ether in a box filled with dried air. The resulting mixtures, without being taken out of the box, were tabulated using a laboratory press. The initial monoferrite was prepared by annealing a mixture of potassium carbonate with iron oxide in an equimolar ratio at 970 K for 4 hours. Initial substances for the preparation of tablets were taken in the proportions shown in Table 1.

Table 1. Quantity of substance (mol) in the initial mixtures (Fe_2O_3 + Fe + $KFeO_2$)

Sample N	Fe_2O_3	**Fe**	$KFeO_2$	u	t
1	0.793	0.023	0.230	0.230	0.070
2	0.760	0.040	0.280	0.280	0.120
3	0.740	0.060	0.320	0.320	0.180
4	0.720	0.080	0.360	0.360	0.240
5	0.640	0.110	0.470	0.470	0.330
6	0.607	0.127	0.520	0.520	0.380
7	0.560	0.140	0.580	0.580	0.420
8	0.583	0.033	0.450	0.450	0.100
9	0.333	0.033	0.700	0.700	0.100
10	0.467	0.067	0.600	0.600	0.200
11	0.500	0.100	0.600	0.600	0.300
12	0.833	0.033	0.200	0.200	0.100
13	0.867	0.067	0.200	0.200	0.200
14	0.900	0.100	0.200	0.200	0.300
15	0.833	0.133	0.300	0.300	0.400
16	0.633	0.133	0.500	0.500	0.400
17	0.767	0.167	0.400	0.400	0.500
18	0.900	0.200	0.300	0.300	0.600
19	1.000	0.200	0.200	0.200	0.600
20	1.100	0.200	0.100	0.100	0.600
21	0.910	0.010	0.100	0.100	0.030
22	0.967	0.167	0.200	0.200	0.500
23	0.933	0.133	0.200	0.200	0.400

Note: u and t – formula subscripts $K_uFe^{2+}_tFe^{3+}_{2-u}O_{3+t-u}$

The tablet mixtures were placed in quartz ampoules with an inner diameter of 12 mm. Ampoules with samples were evacuated using a laboratory vacuum station (pressure $1\cdot10^3$ Pa) and sealed. The sample ampoules were annealed at 870 K for 36 hours. After annealing, the samples were quenched by quickly transferring the ampoule with tablets from the muffle furnace into water. The ampoules were opened in a sealed box filled with dried nitrogen. After opening the ampoule, the tablets were transferred to an agate mortar, carefully rubbed with vaselene, and X-ray-phase analysis was performed. To prevent the sample from coming into contact with oxygen and air moisture the rubbing with vaselene was used.

X-ray analysis of polyferrite samples was performed by DRON-UM1; $Co_{K\alpha}$ radiation (λ = 0.17902 nm).

The catalytic activity of the model ferritic systems in ethyl benzene to styrene dehydrogenation reaction was tested in a laboratory flow reactor at atmospheric pressure and 600 °C. Volumetric feed rate of ethyl benzene (ϖ) was 1 h^{-1}, mass ratio ethyl benzene: water vapor is 1:3 [17].

Results and discussion

The formation of potassium polyferrite with a β″- alumina type structure (K-β″Fe_2O_3) during the reduction of the promoted iron oxide catalyst in an atmosphere of ethyl benzene and water vapor was first detected by X-ray diffraction method and Moessbauer spectroscopy [18]. It has been suggested that K-β″Fe_2O_3 acts as the main catalytically active component. Treatment of the ferritic system in an atmosphere of hydrocarbon vapor and water causes non-uniformity of the phase composition of the catalyst over the volume of the granules and accompanied by deposition of coke on the surface. These effects are the real problems for quantitative description of the phase composition of the catalyst.

The need to develop a new approach to modeling the phase composition of the catalyst in an atmosphere with low partial pressure of oxygen has become apparent. This method should overcome the above limitations, bring the recovery conditions closer to the equilibrium conditions, eliminate the influence of foreign impurities and provide an opportunity to operate the results, the reliability of which is not in doubt, i.e. to conduct X-ray measurements in air.

To achieve this goal, we first proposed a methodology involving the introduction of an internal restorer into the system [19]. Ultradispersed metallic iron obtained by carbonyl technique was used in this capacity. This component acts into the ferrite system organically. It is not a contaminant, is evenly distributed over the volume of the sample. During the heat treatment it interacts with hematite to form magnetite, simulating a reducing atmosphere. The annealing in conditions preventing the entering of oxygen system from the outside allows to set the content of double-charged iron in the system, which strictly corresponds to the amount of introduced metal.

The possibility of direct control of the composition, the ratio of the initial components, the analysis of the products of solid-phase interaction conducted in equilibrium conditions makes this method of modeling quite adequate for using.

The proposed approach was tested in a series of experiments carried out to obtain individual polyferrite with β"-type structure of alumina and to construct a phase diagram of the potassium - iron - oxygen system.

The X-ray data of K-β"Fe_2O_3 are the compounds obtained under conditions differ from those for the catalyst synthesis. β"-Polyferrites are produced by solid-phase synthesis at temperatures above 1400 K or grown from melt [20]. We faced the problem of synthesizing K-β"Fe_2O_3

at temperatures below 1000 K, which corresponds to the conditions of synthesis and use of the catalyst. It is necessary to determine the crystallographic X-ray parameters. They allow to identify the structure of future experiments more confident, to determine the composition of the individual phase and the area of its stability and chemical properties.

At the early stages of the experiment, tablet mixtures were annealed in vacuum sealed quartz ampoules. It is complicated the process and required the use of reagents, the interaction of which prevented the release of gaseous substances. In this regard, for the synthesis not alkali metal carbonate, but previously obtained monoferrite was used. A mixture of monoferrite, hematite, and metallic iron of a defined composition was calcined in an ampoule for time required to reach equilibrium. Subsequently, it was found that there was no need to use ampoules. The tablets were calcined in the same composition as the samples. This calcination was in the inert gas atmosphere.

The methodology based on a desired change in the composition of the studied samples makes it possible to find out the chemical composition and homogeneity area of the metastable component and to determine the optimal conditions for its synthesis. In this case, the main method of analysis is XRP analysis, which is guided by the principle: "X-ray phase analysis is not accurate enough to quantify the component of the multiphase system, but sensitive enough to make sure that the component is not in the system".

The phase diagram of the potassium - iron - oxygen system we constructed gives an answer to the question about the stability range of potassium polyferrites in an atmosphere with reduced partial oxygen pressure.

The interaction process in the potassium - iron - oxygen system can be represented by the following scheme:

$$K_2CO_3 + Fe_2O_3 = 2KFeO_2 + CO_2 \qquad \text{(I)}$$

$$xKFeO_2 + (1 - x)Fe_2O_3 = K_xFe_{2-x}O_{3-x} \qquad \text{(II)}$$

Thermal dissociation of sample composition $K_xFe_{2-x}O_{3-x}$ is described by equation

$$K_xFe_{2-x}O_{3-x} - \frac{\delta}{2}O_2 = K_xFe^{2+}_yFe^{3+}_{2-x-y}O_{3-x-\delta}, \text{ где } \delta = \frac{y}{2}. \qquad \text{(III)}$$

Thus, the product of the thermal dissociation of the system $KFeO_2$ - Fe_2O_3 can be shown as $K_xFe^{2+}_yFe^{3+}_{2-x-y}O_{3-x-y/2}$. To determine the value of δ, we usually use the heating of the studied substance in a gas stream with a fixed partial pressure of oxygen for the time required to reach equilibrium. The experiment is completed by quenching the samples, followed by phase and chemical analyses. However, this method requires a complex equipment design. In this regard, the following technique was used for the study of the composition of the potassium - iron - oxygen system: dissociation of the mixture $K_xFe_{2-x}O_{3-x}$ was modeled by introducing a certain amount of metallic iron into the initial samples, which interacted with hematite during annealing of the mixture in a sealed, evacuated ampoule:

$$4Fe_2O_3 + Fe = 3Fe_3O_4 \qquad \text{(IV)}$$

Consequently, the composition of the initial mixtures can be described as

$$uKFeO_2 + tFe_3O_4 + (1 - u - t)\ Fe_2O_3 = K_uFe^{2+}_tFe^{3+}_{2-u}O_{3+t-u} \qquad \text{(V)}$$

Transition to a formula that takes into account dissociation in the system of $KFeO_2$ – Fe_2O_3 is done by using the relations

$$x = \frac{2u}{2+t}. \quad (1)$$

$$y = \frac{2t}{2+t}. \quad (2)$$

Fig. 2 shows an isothermal projection of the phase diagram of the system Fe_2O_3 – Fe_3O_4 – $KFeO_2$ (T = 870 K).

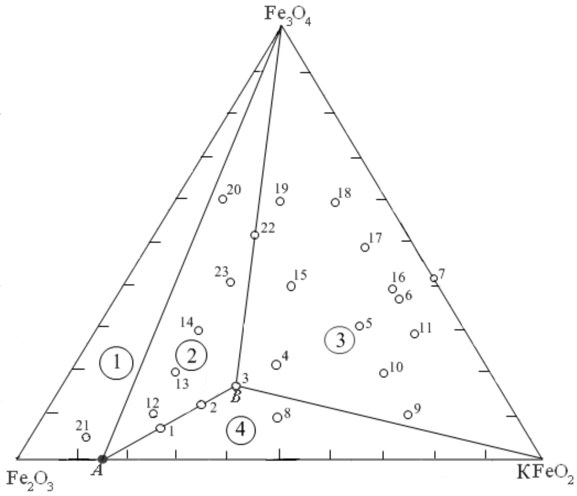

Fig. 2. Isothermal (T = 870 K) phase diagram section of the system $Fe_2O_3 – Fe_3O_4 – KFeO_2$

Point A *A* corresponds to the ideal composition of potassium polyferrite K-βFe_2O_3, i.e. $KFe_{11}O_{17}$; point *B* almost corresponds to the ideal composition of K-β″Fe_2O_3, $K_2O{\cdot}FeO{\cdot}5Fe_2O_3$. The segment connecting points A and B *A* и *B* characterizes the polyferrite system K-(β+β″)Fe_2O_3. Points *A* and *B* define the boundaries of the homogeneity region of the K-(β+β″) Fe_2O_3 system in an atmosphere with reduced oxygen partial pressure at 870 K. Due to the fact that the structure of polyferrites is characterized by layer-by-layer alternation of syntactically fused blocks β- and β″-phase, the general composition of polyferrite system samples can be described by the formula $K_{1+z}Fe^{2+}{}_zFe^{3+}{}_{11-z}O_{17}$. As can be seen from Figure 2, the phase diagram contains 4 fields.

1. Hematite + magnetite + β-polyferrite; the ratio of the components is calculated by the formula

$$K_xFe_y^{2+}Fe_{2-x-y}^{3+}O_{3\text{-}x-\frac{y}{2}} = (1 - 6x - 1{,}5y)Fe_2O_3 + yFe_3O_4 + xKFe_{11}O_{17} \quad \text{(VI)}$$

2. β-Polyferrite + magnetite + β"-polyferrite

$$K_xFe_y^{2+}Fe_{2-x-y}^{3+}O_{3\text{-}x-\frac{y}{2}} = \frac{2-5x-3y}{7}\ KFe_{11}O_{17} + \frac{2-12x+11y}{14}\ Fe_3O_4 + \frac{12x+3y-2}{14}\ K_2Fe^{2+}Fe_{10}^{3+}O_{17} \quad \text{(VII)}$$

3. Magnetite + β"- polyferrite + monoferrite

$$K_xFe_y^{2+}Fe_{2-x-y}^{3+}O_{3\text{-}x-\frac{y}{2}} = \frac{2x+9y-2}{6}\ Fe_3O_4 + \frac{2-2x-3y}{6}\ K_2Fe^{2+}Fe_{10}^{3+}O_{17} + \frac{5x+3y-2}{3}\ KFeO_2 \quad \text{(VIII)}$$

4. β-Polyferrite + β"-polyferrite + monoferrite

$$K_xFe_y^{2+}Fe_{2-x-y}^{3+}O_{3\text{-}x-\frac{y}{2}} = (0{,}2 - 0{,}2\,x - 0{,}9y)KFe_{11}O_{17} + y\,K_2Fe^{2+}Fe_{10}^{3+}O_{17} + (1{,}2\,x - 1{,}1y - 0{,}2)KFeO_2 \quad (IX)$$

It should be noted that temperature changes between 870 and 920 K had no appreciable effect on the phase composition of the ferrite-forming products.

Potassium polyferrite with a β″-alumina type structure of the ideal composition was obtained with the following molar ratio of the initial components: 0.65 mole of hematite, 0.05 mole of metallic iron, and 0.30 mole of potassium monoferrite.

The K-β″Fe_2O_3 elementary cell contains three spinel-like blocks of the composition $\{Fe^{II}{}_1Fe^{III}{}_{10}O_{16}\}$, connected by a third-order helical axis. It would be more correct to describe the composition of K-β″Fe_2O_3 by the formula $K_6Fe^{II}{}_3Fe^{III}{}_{30}O_{51}$, but we will stick to the designation $K_2Fe^{II}Fe^{III}{}_{10}O_{17}$, which describes the simplest composition. Each block is formed by four densely packed layers of oxygen ions. The part of the tetrahedral and octahedral voids in the block are occupied by Fe^{3+} ions. The Fe^{2+}ions are located in octahedral cavities adjacent directly to the planes separating the blocks. According to Mossbauer spectroscopy, there is an intense electronic exchange between Fe^{2+} and Fe^{3+} ions located near the potassium ions.

The planes separating the blocks are not densely packed and are filled with K^+ ions only 70% and oxygen ions 82% of the available positions. This small filling of the plane, as well as the large width of the interblock space is the reason for the extremely high mobility of K^+ ions in the direction perpendicular to the symmetry axis.

The diagram of the Fe_2O_3 – Fe_3O_4 – $KFeO_2$ system provides almost complete information about the phase and chemical composition of the catalyst in conditions of reaction medium. It is sufficient to analyze the selected contact sample for the content of alkali metal and divalent iron, determine the coefficients «*x*» and «*y*» in formula $K_xFe^{2+}{}_yFe^{3+}{}_{2\text{-}x\text{-}y}O_{3\text{-}x\text{-}y/2}$and calculate the ratio of compounds in the active ferrite system based on the data obtained. This allows to distinguish the content of potassium and divalent iron from the whole set of parameters as representative ones, on the basis of which the phase composition control scheme of the catalyst is built. The optimal modes of the catalytic process are selected by correlating representative parameters with dehydrogenation parameters.

The phase composition monitoring makes it possible to respond quickly to changes in the state of the catalyst and to control the technological parameters of the dehydrogenation process by changing the temperature, dilution with water vapor, varying the hydrocarbon feed rate. Moreover, monitoring of changes in phase and chemical composition makes it possible to avoid irreversible phase transformations, to prevent the formation of low-active catalyst components [21], to maintain an optimal concentration of dehydrogenation and coke annealing centers, to minimize the concentration of cracking and coke formation centers [22], to predict the deactivation dynamics and to calculate the catalyst service life.

We analyze the equation determining the ratio of components for field 3. In our opinion, this particular field describes the state of the catalyst in the reaction medium:

Magnetite + β"- polyferrite + monoferrite

$$K_xFe^{2+}_yFe^{3+}_{2-x-y}O_{3\text{-}x-\frac{y}{2}} = \frac{2x+9y-2}{6}\ Fe_3O_4 + \frac{2-2x-3y}{6}\ K_2Fe^{2+}Fe^{3+}_{10}O_{17} + \frac{5x+3y-2}{3}\ KFeO_2 \qquad (VIII)$$

1) If there is a loss of alkali metal in the system, for example, due to leaching of K - β"Fe_2O_3, this leads to a decrease in the parameter "*x*". In this case, the ferrite system begins to produce β"- phase from magnetite and monoferrite, which content will decrease. Thus, monoferrite not only prevents coke formation. $KFeO_2$ is a kind of buffer, a source of potassium that maintains a constant alkali metal content in the main catalytically active component.

2) Increasing the partial pressure of oxygen in the reaction medium will cause oxidation of the catalyst under quasi-equilibrium conditions, which will be accompanied by decrease in the parameter "*y*". The content of magnetite and monoferrite will decrease, but in a different proportion than in the first case. The main component will be practically unaffected; it will not change the most important ratios of K, Fe^{2+} and Fe^{3+}providing the catalytically active state.

3) Decrease of partial pressure of oxygen will lead to catalyst recovery, i.e. to increase of parameter "*y*". Magnetite will recover 3 times faster than the β"-phase will decrease. If the change in the reductive properties of the reaction medium is small, the catalyst will slightly decrease the activity, but the decomposition of the active phase will not occur.

Magnetite acts as a getter, a solid oxide maintaining the chemical potential of oxygen in the system. It should be noted that magnetite has a wide area of homogeneity $Fe_{3\text{-}\delta}O_4$, where δ takes a maximum value of 0.175. It can chemisorb oxygen or thermally dissociate with release of O_2independently, without disturbing the ratio of other solid-phase components. Usually there are other stabilizers in the composition of catalyst. For example, chromium compounds, which valence state changes in a wide range from +3 to +6. Probably, additives of molybdenum oxides have a similar effect.

The catalyst and the reaction medium establish a relationship in the process of activation development. When reaching the stationary operation mode, the temperature, feed rate of crude hydrocarbons, ratio of hydrocarbon and water vapor, which provides a certain partial pressure of oxygen, reach the set values. The catalyst and the reaction medium, the properties of which are determined by the dehydrogenation mode, should reach a complete "mutual understanding" by this period. Only in this case the effective functioning of the system is possible. This indicates that the iron - potassium oxide catalyst is a self-developing and self-regulating system capable of withstanding adverse external influences and confirms our assumption that the main active component of the considered class of catalysts is potassium polyferrite of β"-alumina type.

So, for the first time we experimentally proved that for the formation of K-β"Fe_2O_3 in a reducing atmosphere the temperature of 870 K, which corresponds to the temperature conditions of activation development and functioning of the catalyst, is sufficient. Later this fact was experimentally confirmed by German scientists [13]. It should be noted that the formula $K_2Fe_{14}O_{22}$ often attributed to potassium polyferrite actually reflects the composition of the polyferrite system in which there is a layer-by-layer alternation of β- and β"-phase blocks.

$$K\text{-}(\beta+\beta'')Fe_2O_3 : K_2Fe_{22}O_{34} + K_6Fe_3Fe_{30}O_{51} = K_8Fe_{55}O_{85}\ (\text{compare } K_2Fe_{14}O_{22}).$$

The individual phases were synthesized and their catalytic characteristics were determined (Table 2) to know the contribution of the components to the activity of the ferritic system.

Table 2. Styrene production rate and selectivity on individual compounds

Phase	$W \cdot 10^8$, моль·м$^{-2}$·с$^{-1}$	Selectivity, mol. %
$KFeO_2$	25.4	93
$KFe_{11}O_{17}$ (K-βFe_2O_3)	34.2	67
Fe_3O_4	32.5	48
$K_2Fe^{\text{П}}Fe^{\text{Ш}}_{10}O_{17}$(K-β"$Fe_2O_3$)	86.8	95.6

Single - phase β-polyferrite obtained at 1200 K showed a specific dehydrogenation rate lower than that of β"-alumina-type polyferrite. Magnetite catalyzes the dehydrogenation reaction with low selectivity, but its activity drops rapidly due to intense carbonization. Remarkably, the model mixture of monoferrite and magnetite showed a sufficient specific rate of styrene formation with high selectivity. The catalytic activity of individual monoferrite is low. It is noteworthy that he high selectivity of monoferrite and K-β"Fe_2O_3. In this case, polyferrite type β"-alumina (K-β"Fe_2O_3) has the greatest activity in the dehydrogenation reaction.

Based on the results of our studies and an analysis of data, we can conclude that for K-β"Fe_2O_3 the probability of realization of active centers representing a cluster consisting of K^+, Fe^{3+} and Fe^{2+}, O^{-2} [16] ions is maximum. A nanoheterogeneous mixture of potassium monoferrite and magnetite has a much smaller, but sufficient ability to form such clusters. Another inherent attribute of K-β"Fe_2O_3as the main catalytically active component is the ability to self-reproduction and self-regulation in the reaction medium. The type of catalyst under consideration can be called a "catalyst with a permanently migrating promoter". The speed of the promoter (transport) migration can be controlled [23, 24].

We believe that polyferrite can be neither a generator [6] nor a storage reservoir for potassium ions [13] (simple stoichiometric calculations refute this thesis), but it can be a conductor of the alkaline promoter [23, 24]. The monoferrite concentrated in the depth of the catalyst granules can be the source of potassium, for example, on the inner surface of closed pores [25]. Of course, diffusion of potassium from the volume to the surface can occur at interblock boundaries, but polyferrites are inherently solid electrolytes with a cationic type of conductivity. The assumption that β- and β"-type polyferrites serve as potassium conductors and ensure not only the delivery of the promoter to desired site via channels embedded in the crystal structure, but also its regular placement in the active clusters looks quite appropriate.

K-β"Fe_2O_3 is capable to place alloying additives in its structure. Only in this case, extremely small amounts of injected agent can greatly change the properties of the system. Additives forming an independent phase during catalyst synthesis are useless in terms of purposefully changing the characteristics of the doped system.

The rearrangement does not proceed chaotically, if the K-β"Fe_2O_3 surface is chemically dispersed in the reaction medium to form a catalytically active short-lived substance, a nanoheterogeneous mixture of monoferrite and magnetite ("cracked nutshell"). The initial matrix structure promotes the regular placement of nanoscale components that make up the catalytically active substance, which allows a high concentration of active centers to be maintained while the phase composition changes locally.

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