



FORMATION OF A CERAMIC STRUCTURE OF PROMOTED IRON OXIDE CATALYST

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Abstract. *The paper concerns with the mechanism of the promoters influence on the ceramic structure of the iron oxide catalyst for the dehydrogenation of olefin and alkylaromatic hydrocarbons. The research shows the dynamics of changes in the porous structure of alloyed and unalloyed catalysts as a result of heat treatment in air at several temperatures significantly exceeding the operating temperature. Moreover, the paper presents data on the mechanical strength of alloyed and unalloyed model catalysts. Indeed, the particles are sintered to each other at the contact points of the globules forming a mechanically strong and thermally stable framework. However, the particles are sintered to each other at the contact points of the globules forming. Supposedly, potassium performs the function of a kind of flux. It lowers the temperature of the melting phase formation, which ensures a strong sintering of the ceramic material (catalyst) particles to each other. Hereby, there is a formation of a stable framework without a noticeable reduction of the catalyst working surface. The addition of zirconium oxide as an alloying agent provides an increase in the depth and degree of annealing of imperfections during the restructuring of the catalyst structure. Additionally, it provides the redistribution of the released energy. This assumption is confirmed by increasing of the alloyed catalyst granules mechanical strength. The results of research can be used for development and modification of iron-oxide catalysts for dehydrogenation of olefinic and alkylaromatic hydrocarbons.*

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Introduction

Dehydrogenation of olefinic and alkylaromatic hydrocarbons is a multi-tonnage process. It is conducted with the use of promoted iron oxide catalysts [1-10]. The minimum set of parameters determining the effectiveness of the catalyst, in addition to the catalytic characteristics, always includes the size of the available pore surface, the thermal stability of the contact porous structure, and the mechanical strength of the catalyst granules.



In the promoted iron oxide catalysts for the dehydrogenation of alkylaromatic hydrocarbons, the mass content is: iron oxide – 60–70%; potassium compounds in terms of K_2O – 10–15%. There are also various additives providing the increased selectivity, thermal stability, mechanical strength, and durability [2-9].

The metal oxides of various nature have a significant effect on the properties of the catalyst, in particular, alkaline and alkaline earth – K, Rb, Cs, Ca, as well as transition elements such as Cr, Mo, Mn, Zn, Ce, La, Y, Sc, etc. [7-9].

Indeed, many researchers [11, 12] reported cerium, along with potassium, are effective promoters of iron-oxide catalyst activity for the dehydrogenation of olefinic and alkylaromatic hydrocarbons. Under the conditions of the reaction medium, the catalyst is a ferritic system consisting of potassium β -polyferrite, potassium and caesium monoferrites, and magnetite [13]. The main catalytically active component is polyferrite with the structure of β'' -alumina.

Some researchers [14-17] considering the composition of iron oxide catalysts for the dehydrogenation of ethylbenzene into styrene, indicate potassium monoferrite $KFeO_2$ as the active component of this class of contacts [14].

Commonly, the potassium promoter is introduced in the form of K_2CO_3 , KOH or K_2CrO_4 , with the main amount of alkali metal occurring in the starting mixture as K_2CO_3 [18].

The synthesis of the catalyst begins with the solid-phase interaction of individual components of potassium carbonate and iron oxide α - Fe_2O_3 , which results in potassium monoferrite.

The use of potassium carbonate for the promotion is provided by the relatively low temperature at the starting point of this compound interaction with hematite. Besides, potassium carbonate in the reaction of ferrite formation with iron oxide does not result in strong sintering of the catalyst, as it is the case in the use of other potassium compounds, for example, KOH. On the contrary, the release of the formed carbon dioxide has a positive effect on the formation of contact porous structure.

Solid-phase reactions in the $K_2CO_3 - Fe_2O_3$ and $KFeO_2 - Fe_2O_3$ systems represent the first and second stages of the potassium polyferrites formation. These processes are essential steps in the synthesis of promoted iron oxide catalysts [18].

At high temperatures, potassium polyferrite of the alumina type ($K-\beta Fe_2O_3$) is formed. An increase of the temperature of the samples calcination in air from 1020 to 1170 K is accompanied by the appearance of divalent iron as a result of thermal dissociation of hematite. The potassium content in the polyferrites varies symbatically with the concentration of divalent iron in the samples, and reflexes related to $K-\beta'' Fe_2O_3$ appear on radiographs. Fe^{2+} ions stabilize the β'' phase. This phase is catalytically active. Therefore, in samples calcinating at temperatures above 1150 K, a microheterogenic mixture of polyferrites with structures of the type β - and β'' -alumina $K-(\beta+\beta'') Fe_2O_3$ is formed [18].

The papers [19-21] considered a series of ferrites modified by metal ions (Cr, Mn, Co, Ni, Cu, Zn, and Ce). All modified ferrites showed high specific surface area, greater than for pure iron oxide (Fe_2O_3). According to the authors, the influence of additive ions on the increase of specific surface area may be related to the changes in the crystals growth rate. All modified ferrites showed a narrow pore size distribution in the range of 4.9–25.0 nm.



Nowadays, a large number of studies are aimed at establishing the relationship between the chemical and phase composition and the catalytic properties of the contact. However, the issue of the effect of promotion and alloying on the porous structure parameters, and as a consequence, such operational characteristics as thermal stability and mechanical strength, remains unresolved.

The purpose of the research is an investigation of the mechanism of promoters influence on the catalyst ceramic structure.

The main body

Model catalysts were prepared by conventional ceramic technology. The calcination temperature is 970–1170 K.

Zirconium was injected as an oxide. The mass content of the oxide did not exceed 1%.

Radiography was performed using $\text{Co}_{K\alpha}$ radiation ($\lambda = 0.17902$ nm) on a DRON-3 diffractometer.

The surface area was determined by thermal desorption of argon [22].

The porous structure of the samples was studied by mercury porometry on a Carlo-Erbeporosimeter according to the method [23, 24].

Thermal stability was determined by the dynamics of changes in the porous structure as a result of heat treatment of the catalyst in air in the temperature range of 830-1030 K.

Mechanical strength was determined by crushing [25].

When creating catalysts, it is necessary to predict their maximum productivity, selectivity, resistance to high temperatures used in the operation of the catalyst, the mechanical strength of contact granules, etc.

The main stages of the iron oxide catalysts synthesis are: mixing of the initial components with the addition of a solvent, extrusion, air drying, air calcination followed by heat treatment in water vapour and activation development.

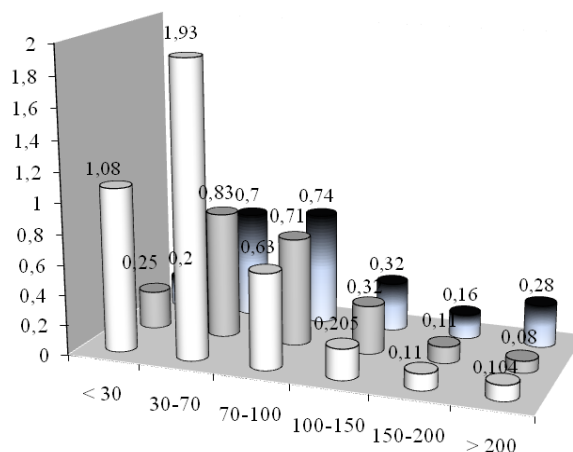
The porous structure of the catalyst formed under the calcination of the initial compounds in air [26]. The characteristics of the catalysts porous structure are influenced by various factors: the chemical and thermal background of the initial iron oxide [26], the temperature of catalyst synthesis, the rate of the removal of gaseous products from the reaction zone. For the experiment we take the samples of iron oxide obtained by decomposition of sulphate at a temperature of 910–920 K. A model catalyst was prepared at a temperature of 990 K. The initial components of an iron oxide catalyst are usually iron oxide and potassium carbonate. Some scientists indicate iron oxide as an active component of the catalyst [27-31]. However, our data correlate with the results obtained by many other researchers [32], and indicate a high carburisation of such catalyst surface and its low selectivity. The introduction of an alkali metal promoter into the system significantly increases the contact activity [1-4, 6-9].

Furthermore, alloying additives are usually introduced into the industrial catalyst, improving the performance properties of the final product - the catalyst [2, 4, 7, 11-12]. We selected zirconium as an alloying additive.

**Table 1.** Porous structure of model catalyst samples

R, nm	Catalyst Fe ₂ O ₃			Potassium-promoted catalyst			Potassium-promoted catalyst, alloyed with zirconium		
	S, m ² /g	V · 10 ² , cm ³ /g	V, %	S, m ² /g	V · 10 ² , cm ³ /g	V, %	S, m ² /g	V · 10 ² , cm ³ /g	V, %
>30	1.08	9.86	19.84	0.25	3.05	7.42	0.2	2.88	6.98
30-70	2.43	16.08	32.35	0.83	4.14	10.07	0.7	4.14	10.04
70-100	0.13	2.33	4.688	0.71	5.6	13.62	0.74	5.67	13.75
100-150	0.205	6.52	13.12	0.32	8.87	21.57	0.32	8.76	21.24
150-200	0.11	3.38	6.801	0.11	4.99	12.14	0.16	5.13	12.44
>200	0.104	11.53	23.2	0.08	14.99	36.45	0.28	14.85	36.01
Sum	4.059	49.7	100	2.3	41.12	100.00	2.4	41.24	100.00

Table 1 presents data on the porous structure of a catalyst sample obtained using only iron oxide. The initial components of a catalyst sample are iron oxide and potassium carbonate (promoted with potassium). The initial components of another catalyst sample are iron oxide and potassium carbonate alloyed with zirconium (promoted with potassium, alloyed with zirconium). Figure 1 shows the pore size distribution of the same samples

**Fig. 1.** Pore size distribution (m²/g) of model catalyst samples: □ – Fe₂O₃ catalyst; ■ – potassium-promoted catalyst; ■ – potassium-promoted catalyst alloyed with zirconium

As previously reported, the activity of the iron oxide catalyst is negatively affected by pores smaller than 70 nm [33]. The effective pore diameter of such a catalyst is limited within the range of 70 to 150 nm.

The analysis of the data in Table 1 and in Fig. 1 allows us to conclude that the alloying additive of zirconium has a negligible effect on the porous structure of the contact formation. At the same time, the use of a promotional agent leads to a significant decrease in the proportion of small pores and an increase in the proportion of effective pores. If the potassium promoter is introduced in the form of carbonate, then during the heat treatment of the catalyst there is a solid-phase interaction of K₂CO₃ with hematite, accompanied by the release of carbon dioxide, which loosens the structure of the granules.

Figure 2 shows the data of X-ray phase analysis of catalyst samples with the introduction of a potassium promoter into the system.

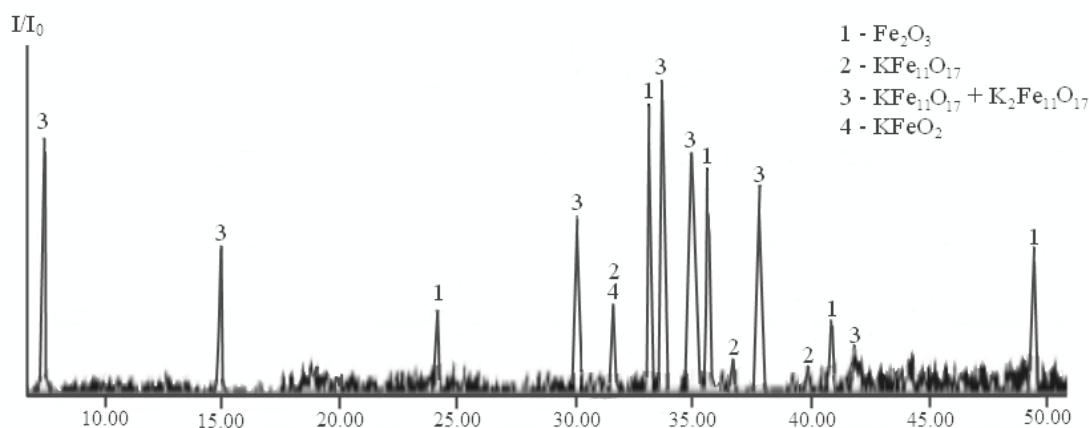


Fig. 2. Radiograph of an iron oxide catalyst sample promoted with potassium

In accordance with the data of X-ray diffraction analysis, a system including potassium – iron – oxygen contains potassium polyferrites, monoferrite, and residual iron oxide. In the contrary, the first sample radiographs contain only Fe_2O_3 peaks.

The introduction of potassium into the system leads to the formation of an optimal porous structure of the catalyst sample.

The catalyst is operated at high temperatures. The porous structure under such conditions can undergo significant changes. It seems appropriate to consider the effect of potassium promotion and zirconium alloying additives on the thermal stability of the catalyst porous structure.

To assess the thermal stability of the catalyst, a long exposure is usually used under the conditions of a dehydrogenation reaction with the measurement of the porous structure at certain time intervals. However, equally accurate results can be obtained by examining the catalyst after thermal exposure at temperatures significantly higher than operating ones.

Figure 3 shows the dependence of the surface formed by the pores of the samples of the model catalyst under study on the temperature of calcination in air.

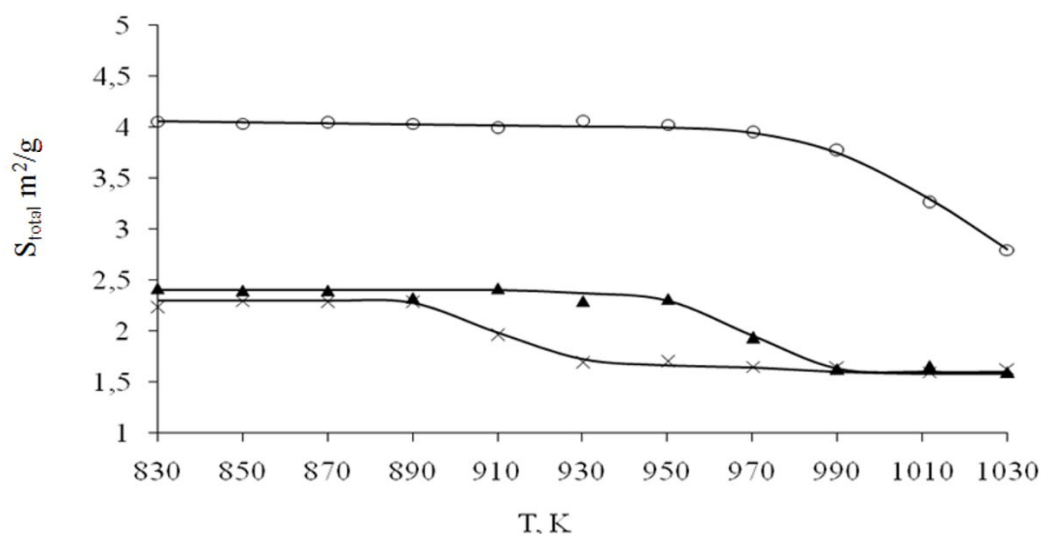


Fig. 3. Dependence of the specific surface area of the model catalyst samples on the calcination temperature in air: ○ – Fe_2O_3 catalyst; × – potassium-promoted catalyst; ▲ – potassium-promoted catalyst alloyed with zirconium



The iron oxide sample, as expected, is more thermally stable. The surface area of such a sample remains thermally stable up to a temperature of 970 K. The promoted samples have much less heat resistance. However, zirconium alloying increases heat resistance.

Figure 4 shows the dependence of the surface formed by the pores of effective size on the temperature of calcination in air for the promoted and non-promoted samples of the model catalyst.

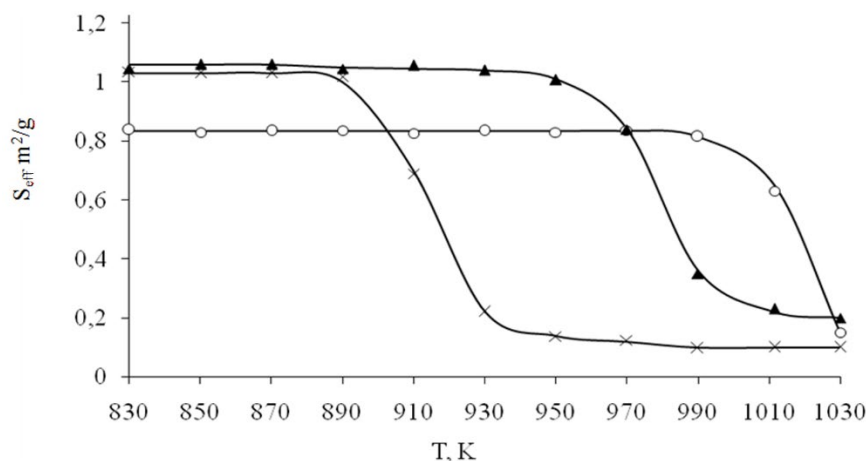


Fig. 4. Dependence of the specific surface area of the model catalyst samples on the calcination temperature in air: ○ – Fe₂O₃ catalyst; × – potassium-promoted catalyst; ▲ – potassium-promoted catalyst alloyed with zirconium

According to the studies, zirconium alloying results with a noticeable increase in the thermal stability of effective pores.

Freshly made catalyst is subjected to transport and reloading, it undergoes significant mechanical stresses, as the height of the catalyst bed in the reactor can reach several dozens of metres. It provides high demands on the mechanical strength of the contact granules.

Table 2 presents data on the mechanical strength of the catalyst samples under study.

Table 2. Mechanical strength of granules of the promoted and non-promoted model catalyst

Indicator	Catalyst Fe ₂ O ₃	Potassium-promoted catalyst	Potassium-promoted catalyst, alloyed with zirconium
Mechanical strength, kg/cm ²	1.8	5.2	5.85

The model catalyst unpromoted with potassium has obviously insufficient mechanical strength. The introduction of a promotional agent leads to occurring of a mechanically stable structure.

Conclusions and recommendations

Samples of powdered iron oxide are a system of corpuscular structure. The pores are formed by the space between the particles. The model catalyst, which does not contain a promoter, differs slightly in its structure from the initial iron oxide.

Indeed, the particles are sintered to each other at the contact points of the globules forming a mechanically strong and thermally stable framework. Sintering process can be compared to spot welding: a short-lived local thermodynamic equilibrium occurs in the contact zone of particles. The actual temperature in this zone may noticeably exceed the average



temperature of the granula. The source of additional energy required for spot welding is the energy of imperfections in the crystal lattice of hematite. Potassium performs the function of a kind of flux:

1. It lowers the temperature of the melting phase formation. Indeed, it ensures firmly sintering of the ceramic catalyst material particles together. The area of the sintering zone is small and slightly reduces the working surface area of the granules. However, sintering of the particles forming the framework is not accompanied by a significant increase in the bulk density of the granules, which would indicate the sintering of the granules, or the leakage of the pores.

2. Therefore, the granule acquires a strong and stable framework, while maintaining a developed porous structure.

The stability of the catalyst granules to the temperature effect is determined not only by the strength of particles sintering, but also by the lability of their crystalline structure, which is caused by the presence of residual dislocation mesh, microstresses, and non-equilibrium defects. The addition of zirconium oxide as an alloying agent 3 provides not only an increase in the depth and degree of annealing of imperfections during the restructuring of the catalyst structure, but also the redistribution of the released energy. There is not just a dispersion (dissipation) of stored energy, but its direction in a certain direction (sewerage), when most of the released energy goes to the zones of sintering globules.

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