Influence of structural-dimensional factor and catalytically active additives of Fe₂O₃/Cr₂O₃ in α-Al₂O₃-based membranes on hydrocarbon dehydrogenation

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1. Introduction

High-porous functional ceramics (membranes, filters) is one of the most intensively developing areas of modern materials science; there is an active development of new technologies for its production in many industrialized countries [1–3]. At the same time, the issues of increasing the efficiency of traditional processes for obtaining the most important petrochemical products and alternative energy carriers, as well as the search for new approaches and engineering solutions to create new breakthrough technologies for their production are acute [4,5]. Therefore, one of the most urgent tasks is to develop technologies for producing ultra-porous functional ceramics that are economically and environmentally efficient for deep processing of hydrocarbons.

The most widely used products of the petrochemical industry are low-molecular fractions of hydrocarbons containing monomers such as ethylene, propylene, isobutylene, 1,3-butadiene, styrene, alpha-methylstyrene, etc. [6,7]. But for industrial applications, monomers that are formed as by-products, e.g. in the production of ethylene and propylene, are also very important. This paper focuses on one of these by-products, isoprene, which is a very important monomer in industry.

Isoprene, along with 1,3-butadiene, is one of the most important raw materials for basic organic and petrochemical synthesis, with a continuing trend toward increasing demand for its consumption by modern industry. This semi-product is one of the basic monomers for the production of artificial rubbers, electrical insulating materials and some medical products [8]. In modern industry, isoprene production processes include many stages such as oil refining, organic synthesis, separation of hydrocarbon mixtures, etc.; that increase the environmental burden around its production sites [9].

The most common method for obtaining isoprene is extraction from C5 fractions of oil pyrolysis, but this fraction is usually a by-product of the synthesis of ethylene and propylene and is not higher than 20%. In addition, the extraction of isoprene from it also does not exceed 20% and is complicated by the fact that the components of the C5 fraction have close boiling points, which makes it difficult and economically unprofitable to separate them with traditional rectification [10]. Therefore, the separation of such closely boiling mixtures is more effective only with the help of extractive rectification or liquid-liquid extraction [11]. In this regard, all the methods proposed so far for obtaining isoprene are expensive and have significant environmental disadvantages.

A promising way to solve this problem is to use a hybrid membrane-catalytic technology for dehydrogenating a mixture of isoamylene to produce hydrogen and isoprene. Since isoamylene are a product of processing of isosamyl alcohol, that are an impurity in the production of biofuels and ethyl alcohol, the production of isoprene from this raw material is ecologically friendly.
Table 1. Dehydrogenation of isoamylene fraction in isoprene (mol.%) on Fe-Cr containing converter depending on excess water (600°C).

|                  | H₂O + isoamylenses |
|------------------|---------------------|
|                  | 12      | 24      | 36      |
| Isoamylene conversion | 84      | 46      | 43      |
| Synthesized isoprene/supplied isoamylanes, % | 3.6      | 9      | 8      |
| Isoprene Selectivity (synthesized isoprene/converted isoamylanes), % | 4.5      | 20      | 18      |

Dehydrogenation of isoamylenes by means of ultra-porous ceramic catalytic membrane converters will reduce the overall energy of the process by implementing the reaction stage in the channels of the catalytic converter. It will result in obtaining products with a high degree of purity and a higher yield in comparison with the process in a traditional reactor with a stationary layer of bulk catalyst.

The important problem to be solved in the development of high-performance catalytic membranes is to determine the role of structural-dimensional factors in the activity and thermal stability of catalysts. Establishing the relationship between the structural (material morphology, porosity, pore size, etc.) and catalytic properties of the developed oxide compositions will successfully solve the problem of creating effective catalysts that do not contain noble metals.

Also, it is evident that both macro- and micro-structures of the material depend on the properties of the original components (solid and liquid) as well as on the technological parameters of their production: the ratio of the filler and binder, the compaction pressure, the evolution of the phase composition at the synthesis temperature. A separate task is to impart catalytic properties to synthesized ceramic porous products; it is often associated with the complexity of introducing catalytically active components into the complex-structured volume of the entire pore space.

The aim of this work was to develop the scientific backgrounds for creating an effective one-stage technology to synthesize a porous ceramic material with the simultaneous addition of catalytic properties to the synthesized membrane.

To achieve this aim, we have to solve three related tasks:

1. Since the catalytic processes occur on the surface of the pore space, first of all, it is necessary to evaluate the most effective macro- and microstructural parameters of the porous material, based on analytical calculations of the free path of the substrate molecules.

2. To obtain a ceramic membrane with the required micro- and macrostructure, it is necessary to evaluate the influence of structural-dimensional factors on the physical and mechanical characteristics of the synthesized material and the product (membrane) based on it.

3. To assure that the synthesized membrane has the catalytic properties necessary for effective dehydrogenation of isoamylenes into isoprene.

To synthesize porous ceramics, a multicomponent mixture based on coarse alpha-Al₂O₃ with ultra-disperse magnesium and silicon additives was selected in this work. To impart catalytic properties, the additives of Fe₂O₃ and Cr₂O₃ of up to 10 mass % were introduced in a simple technological way; it allowed implementing a single-stage production of a porous catalytic converter.

2. Materials and methods

In order to ensure the formation of a porous structure in a ceramic material with the specified parameters for the most effective dehydrogenation of isoamylenes, first of all, it is necessary to estimate the required pore size of the membrane based on the average free path of the molecules of the dehydrogenated gas mixture.

The determination of the gas permeability coefficient and, consequently, the pore size in the range of 10–10⁶ nm is most easily performed by comparing the values of fluid flows corresponding to different modes of gas flow in a porous medium [12]. The total flow of gas G through a porous medium can be represented as a sum of two components – diffusive G₉ and viscous Gᵥ flows:

\[ G = G_9 + G_v \]  

The dependence of the gas flow regime through a porous medium on the average pressure is characterized by the intervals determined by the ratio between λ (the free path length of gas molecules in the channels of the porous medium) and d (the characteristic linear size of the porous medium).

To differentiate the diffusion mechanisms, the Knudsen number is used (the ratio of the average free path of gas molecules in the channels of the porous medium to the characteristic linear dimensions of the porous medium): \( Kn = \lambda/d \).

In the case of \( \lambda \leq 0.1d \), \( Kn \leq 0.1 \) (coarsely porous medium), a very small contribution is made by the diffusion flow, and the main transport of gas through the porous medium is carried out in a viscous flow regime.

At \( \lambda \geq 10d \), \( Kn \geq 10 \) (finely porous medium), the viscous (Poiseuille) flux Gᵥ practically disappears, and the diffusion flux G₉ acquires the character of Knudsen diffusion.

In the interval 0.1d \( \leq \lambda \leq 10d \), 0.1 \( \leq Kn \leq 10 \), both components of the flow in equation (1) make a significant contribution; therefore, it is assumed
that the diffusion flow is a slip flow \( G_s \), i.e. \( G_d = G_s \). In this interval, various intermediate regimes of gas flow are realized, and \( G_s \) is a constant addition to the viscous flow, which grows with an increase in the average pressure.

Since catalytic processes take place on the surface of the catalyst (pore surface), in order to obtain high-performance porous catalytic membranes, it is necessary to fulfill the condition \( \lambda = d \), which corresponds to the diffusion flow of the substrate through a porous medium [13]. This type of gas flow under the conditions of pressures and temperatures used in experiments for porous catalytic membranes is very effective.

According to the equation of the molecular kinetic theory of gases, the average free path of the gas mixture molecules was calculated using the formula:

\[
\langle \lambda \rangle_i = \frac{1}{\sqrt{2\sigma_i n_i + \mu \sigma_i n_i}}
\]

where \( \mu \) is the given mass, \( \sigma_i \) – gas-kinetic cross-section for collision of molecules of the mixture of isoamidens, \( \sigma_{in} \) – gas-kinetic cross-section for collision of molecules of isoamidens with water vapor molecules and \( n_i \) and \( n_n \) are the concentration values of molecules of the respective components of the mixture.

It is important to note that the process of dehydrogenation of the isoamylene mixture took place in the environment of distilled water vapor. The volume feed rates of substrates were set to ensure an equilibrium reaction mixture with the molar ratio of \( H_2O : isoamylene \) mixture being equal to 12/24/36. Thus, the partial pressures of isoamidens in the vapor-gas mixture were less than 0.01 MPa, which was taken into account in the calculations of the free run length.

During the experiments, the flow of the vapor-gas mixture was fed to the catalytic membrane reactor. Since the gas flow through the porous medium corresponds to the diffusion flow of the substrate (i.e. \( \lambda = d \)), it is possible to estimate the recommended value of open pores for efficient operation of the membrane in the production of isoprene. This value should be comparable to the calculated free run lengths of isoamidens according to the above-described technology of substrate supply as a vapor-gas mixture.

In the synthesized ceramic material, the pore size depends on several initial technological parameters, the main of which are the particle size of the initial powders, the ratio of the grain size of the filler and the binder in the initial mixture, as well as the compaction pressure of the material.

To achieve the target pore size, a coarse powder of \( \alpha-Al_2O_3 \) was used as a filler in the porous membrane material. The result of measuring the size distribution of the powder particles on the MicroSizer 201 laser particle analyzer is shown in Figure 1.

The particle size of the \( \alpha-Al_2O_3 \) filler varied from 1 to 150 \( \mu \)m, while the bulk of the particles (about 70%) had a size of about 100 \( \mu \)m. To intensify sintering and strengthen the bond between the filler grains, ultrafine components with a developed surface were added to the initial mixture as binders: MgO (<5 \( \mu \)m); SiC (~3 \( \mu \)m) obtained by SHS; SiO\(_2\) (~5 \( \mu \)m), SYLOID AL-1 FP brand). Ultrafine powders of Fe\(_2\)O\(_3\) and Cr\(_2\)O\(_3\) (~1–5 \( \mu \)m, grades K and OHP-1) of up to 10 mass % were used to impart catalytic properties to the membrane.

The powders were mixed dry in a ball mill using Al\(_2\)O\(_3\) balls at the rotation speed of 30 rpm for 2 hours. Then a double-side uniaxial compaction of the finished mixture at \( P = 70–100 \) MPa and its sintering at the maximum temperature of 1350°C in the air were performed.

After the high-temperature heat treatment, the X-ray phase analysis of the synthesized samples was carried out, as well as the analysis of the fracture

![Figure 1. Particle size distribution of initial Al\(_2\)O\(_3\) powder.](image-url)
microstructure of the experimental samples using electron microscopy to evaluate the dimensions and form factors of the structural components of the porous material.

The experimental method provided determination of the open porosity of the manufactured membranes by hydrostatic weighing and the size of the obtained pores by the bubble point method.

The bubble point method is one of the simplest methods for determining the maximum pore size (GOST R 50,516–93). This GOST applies to polymer ultra- and microfiltration hydrophilic and hydrophobic membranes and establishes a method for determining the bubble point of membranes with a maximum pore size from 0.1 to 15 µm in distilled water or alcohol. The method consists in determining the minimum gas pressure required for a gas bubble to pass through the pores of a flat hydrophilic membrane impregnated with water, or through the pores of a flat hydrophobic membrane impregnated with alcohol.

The pore size of the obtained membranes was determined using the Laplace formula for the “cylindrical pore model” and in accordance with GOST 26,849–86 (the pore size determination method) with due regard for the results of the slip pressure measurements using the bubble point method. The maximum pore size was calculated using the formula $2\pi R \cos \theta = \pi R^2 (\Delta p - h\gamma g)$, where $R$ was the capillary radius in cm; $\sigma$ was the surface tension of the liquid in dyn/cm; $\theta$ – the wetting angle, degrees; $h$ – the height of the liquid column above the sample surface, cm; $\gamma$ – the density of the liquid, g/cm$^3$; $g$ – the acceleration of gravity, cm/sec$^2$; $\Delta p$ – the gas pressure necessary to push the gas bubble through the pores of the membrane [14].

3. Results and discussion

To determine the required pore size, an analytical assessment of the average free path of gas mixture molecules was made according to the parameters of the technology for dehydrogenation of isoamylenes into isoprene. The average free path length ($\lambda$) of an isoamylene molecule (with the molecule gas-kinetic diameter of $d = 0.6$ nm) in the substrate flow, depending on the molar ratio (a mixture of isoamylenes $\div$ H2O = 1 $\div$ 12/24/36) was equal to 0.508 µm, 0.978 µm and 1.45 µm, respectively.

Taking into account the fact that for the efficient dehydrogenation, the free path of gas molecules in the channels of the porous medium must correspond to the characteristic linear dimensions of the porous medium with the diffusion flow of the substrate, we can conclude that the recommended value of the open pores of the membrane should be from 0.5 to 2 µm.

The structure of porous ceramics is known to depend on the size and shape of the filler grains, its ratio to the sintering strengthening fine-grained component, on the compaction pressure, presence and quantity of organic binders, plasticizers that facilitate the compaction, as well as on the heat treatment modes [15]. Using the obtained results of the calculation of the average free path length of the vapor-gas mixture molecules, it is possible to select the most appropriate ratio of the filler and binder grain size according to the method described in [7].

Figure 2 shows the literature data [16] and the results of the author’s experimental studies (curve 6) of the pore size dependence on the size of the components and their ratio in the initial mixture, compacted at the same pressure and subjected to identical heat treatment modes. It was determined that in order to obtain membranes with the target pore size of 0.5–2 microns, it was necessary to take a filler powder with the grain size of the base fraction of about 100 microns and the ratio of the filler grains to ultra-disperse binder powders of 65:35.

An important parameter affecting pore formation is the applied compaction pressure, which makes it
possible to regulate the density and, accordingly, the porosity of the material. So it allows adjusting the pore size within certain limits and obtaining a material with the preset properties.

The density of samples during cold pressing is known to increase non-linearly with increasing compaction pressure in molds, and the compaction curve of the powder material (Figure 3) includes three main stages.

At the first stage, the particles are laid, primarily due to their sliding, eliminating free spaces between the particles and increasing the contact area with the destruction of arches and bridges formed by the particles, but without deforming the particles themselves. The second stage, which is not always pronounced, is characterized by elastic deformation (repulsion), since the gaps in the bulk were eliminated at stage a, and the particles are in close contact with each other and resist compression. At the third stage, there is a brittle fracture or plastic deformation [17].

It is obvious that the porosity and pore size dependence on the compaction pressure will be the reverse of the density–pressure curve, since the pore space in the material decreases with the increasing density. To achieve the required strength and performance characteristics of the membrane, it is necessary to carry out the compaction in the pressure range within the elastic deformation. Also, at such compaction pressures, it is possible to achieve the necessary porosity and regulate the structural and dimensional factor in the material within certain limits. It was found experimentally that the optimal compaction pressure for the mixture under study was from 70 to 100 MPa (Figure 4). Within these values, it is possible to achieve the maximum porosity with the target pore size of the material as well as the optimal physical and mechanical characteristics.

The resulting sample (Figure 5) is a tube with one end plugged to ensure forced diffusion of gases through the working surface of the cylinder from the outer wall to the inner one, and on the other end there is a pressure nut for hermetical connection of the sample to the reactor through a graphite gasket.

The geometrical dimension of the synthesized membrane is 140 mm; the length of the working area is 130 mm; the outer diameter of the tube is 25 mm; the wall thickness is 7 mm.

The linear thermal shrinkage of the samples, estimated from the results of measurements before and after the heat treatment, did not exceed 1%; it indicated that there were no significant changes in the porous structure during the sintering.

The size of the open pores of the synthesized sample was determined using the results of measurements...
of the slip pressure by the bubble point method and was found to be equal to 1–3 µm.

The photos of the microstructure of the fracture of the ceramic membrane are shown in Figure 6. The material morphology allows us to conclude that it has a developed anisotropic porous structure, which is somewhat heterogeneous in size and the form factor of the main structural elements. It can be explained by the fact that in spite of the size of the filler powder grains of about 100 µm, the particles ranged in their size from 50 to 130 microns. Besides, the corundum particles in the sintering process with the addition of ultrafine MgO acquired a more isometric shape.

The corundum aggregates also have the edge fusion effects, and between them there are cast mellite-like structures enveloping them; they were formed during sintering in the liquid phase with the participation of the binding additives of MgO, SiC and SiO₂. These structures form a strong membrane framework with a developed porous structure. Their presence is also confirmed by the XRD data shown in Figure 9.

Various types of pores are found in the material: rounded, ellipsoid and slit-like, etc. Inside the pores, at high magnification, sub-nanoscale particles are clearly seen; they evenly cover the surface of the pores and appear to be catalytically active iron-chromium components.

The visible size of the pores in the photos varies from 0.5 to 30 µm, which is an order of magnitude smaller than the size of the filler particles (100 µm). However, determining the porosity and pore size of the samples from electron microscopy images does not provide accurate information, since the pores usually have a volumetric spatial structure of a variable diameter.

In this regard, the experimental method provided for the study of the open porosity of the material along the length of the membrane by hydrostatic weighing. The membrane was cut into washers of about 15 mm in thickness, and then the open porosity of each ring sample was determined.

The investigation results are shown in Figure 7. The open porosity of the samples is found to be maximal in the central part of the sample, where it reaches 42.5%. However, at the ends of the sample, the porosity decreases slightly, which is explained by the pressure gradient during the double-action uniaxial compaction of the initial mixture. The average open porosity of the sample is about 38%.

The elemental analysis of the sample microstructure was performed using an electron microscope LEO 1450.
VP with an EMF module INCA 300, its results are shown in Figure 8. According to the results presented in Fig. 8.1, points 1, 2 and 6 are mainly composed of α-Al_{2}O_{3}. Points 3, 4 and 5 fall into the area of the inner surface of the pores and include up to 15% of the total Cr and Fe, visually observed as ultradisperse particles covering the surface of the pores.

At higher magnification with localization on the inner surface of a separate pore (Fig. 8.2), the distribution pattern of catalytically active iron-chromium-containing components becomes even more obvious. In the places where they are concentrated, the content of Fe and Cr is 20% and higher.

The phase composition of the porous ceramic material fracture was studied using CuKα-radiation XRD. In the X-ray image, the reflex from α-Al_{2}O_{3} is clearly seen, and the reflexes of MgAl_{2}O_{4} aluminomagnesial spinel and Fe_{2}SiO_{4} compounds are also observed (Figure 9). They are formed in the pore surface as a result of partial interaction of the powders during liquid-phase sintering of the ultrafine SiO_{2} additives as well as oxides of magnesium and iron. The absence of reflexes of chromium-containing compounds and mullite structures in the presented X-ray pattern is explained by their merging with the background. The latter is explained by the insufficiently high sintering temperature of the sample and the small number of the synthesized mullite compounds. However, when the sintering temperature is above 1300°C, the formation of mullite structures increases quantitatively, and such structures as indialite – Mg_{2}Al_{4}Si_{2}O_{17} and clinoenstatite MgS_{2}O_{6} are detected.

In the experiments on the dehydrogenation of the mixture of isoamylenes on the synthesized membrane of α-Al_{2}O_{3} + MgO + SiC + SiO_{2} + Cr_{2}O_{3} (5%) + Fe_{2}O_{3} (5%), depending on the molar ratio of water-isoamylenes (table 1), it was found that the optimal conditions for obtaining isoprene were T = 600°C and 24-fold excess of water, when the maximum isoprene content was achieved with a reduced content of the

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**Figure 8.** Microstructure and elemental analysis of the sample.

**Figure 9.** Phase composition of membrane synthesized from α-Al_{2}O_{3} – α-Al_{2}O_{3}, Fe_{2}SiO_{4}, MgAl_{2}O_{4}.
reaction by-products. The yield of isoprene under the optimal conditions was ~9%, selectivity ~20%, and isoamylene fraction conversion ~46%.

In the most efficient granular model system of the composition γ-Al2O3 + Cr (5%) + Fe (5%) (with separate deposition of active components), the selectivity for isoprene reached about 13%, which correlates with the result obtained in a one-stage high-temperature process of dehydrogenation C5-fractions on multicompont industrial catalysts 1707 and Dow Type B [10,18–20]. The yield of isoprene at 24-fold dilution of the substrate with water reached ~5%, and at 36-fold dilution ~8%.

It should be noted that in addition to isoprene, the dehydrogenation products contained other valuable monomers (~15% of the total yield of the reaction products) formed in the side reactions of cracking, as well as very valuable hydrogen (~37%), alkanes and carbon oxides. It is important to note that for 6 hours of the experiment, a decrease in the catalytic activity of the system was not observed in comparison with the process realized in the traditional reactor with a granular catalyst layer, on which regeneration is carried out every 8–15 minutes. Thus, the use of the porous ceramic catalytic membrane allowed increasing the main characteristics in comparison with multi-component industrial granular catalysts.

4. Conclusions

(1) The nature of the substrate flow in pore channels, thermal stability and catalytic activity of the membrane are significantly influenced by the structural and dimensional factors of the synthesized porous membrane: its phase composition, porosity, pore size, uniform pore distribution by volume, etc.

In turn, the structural and dimensional factor and morphology of the material are directly influenced by the size and shape of the filler grains, its ratio with sintering fine-grained components, compaction pressure and heat treatment conditions.

(2) Using the results of the analytical calculations of the free path length of isoamylene molecules in the substrate, we established the effective pore size of the ceramic material for the catalytic dehydrogenation process (0.5–2 microns). In order to achieve it, the appropriate granulometric composition, the ratio of the filler and binder (65:35) and the compaction pressure (~70–100 MPa) were chosen.

(3) Dehydrogenation of the mixture of isoamylene into isoprene at a different level of isoamylene molar ratios shows that the optimal conditions for obtaining isoprene are the temperature of 600°C and 24-fold excess of water, at which the maximum isoprene content is achieved with a reduced content of the reaction by-products. The yield of isoprene under optimal conditions was ~9%, selectivity ~20%, conversion of isomylene fraction ~46% with a degree of hydrogen recovery ~37%.

Disclosure statement
No potential conflict of interest was reported by the author(s).

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