Application of catalytic systems containing iron in the process of propane cracking

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Composite catalysts containing various forms of metallic or oxide iron ((Fe^0 or Fe_xO_y, Fe^{3+}) in combination with an inert matrix (γ-Al_2O_3) were obtained and their catalytic ability in the propane cracking reaction was studied. It is shown that for pure aluminum oxide, no catalytic effect is observed in this reaction. The synthesis methods implemented in this work allowed us to obtain various catalytic centers that can effectively carry out electron transfer by changing the degree of iron oxidation during the transformation of the initial substances into the target reaction products. It is proved that the use of iron nano-particles for formation of catalytic centers does not lead to a noticeable improvement in the technological yield of propylene compared to the Fe^{3+}/Al_2O_3 material. Use of an inert oxide substrate (γ-Al_2O_3) and various iron compounds makes it possible to create a bifunctional catalytic center containing Fe(III) and Al(III) ions, which provides an energetically favorable interaction with the propane molecule and further breaking of the strongest C-H bond at a primary carbon atom. The synthesized catalytic systems can be used for thermocatalytic processes in natural gas processing instead of catalysts based on noble metals.
Keywords: dehydrogenation of propane, cracking, propylene, catalytic centres, aluminium oxide, carbon atoms, Fe^0, Fe_xO_y.
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Introduction

Examples of industrial use of iron and its different chemical compounds as reactants and catalysts in chemical and petrochemical production are known since rather old times. So, iron chips were used for a long time for aniline production via reduction of aromatic nitric compounds, and iron (III) chloride or iron scrap were often used in industrial organic synthesis of different compounds as well [1]. Scientific progress in chemistry and chemical technology was always accompanied by substantial variations allowing to implement industrial production more effectively. These variations are mainly stipulated by application of the new high-efficient catalysts [1, 2]. It is difficult today to imagine operation of oil and gas processing industry without modern catalytic systems, when iron-containing materials occupy important place among these systems.

Necessity of development of the new thermo-catalytic technologies for processing of gas raw material is determined by presence of enormous amount of natural and technological gas which contains ultimate hydrocarbons and which is not used in industrial production facilities for chemical and petrochemical synthesis [2]. Development and practical realization of thermo-catalytic processes of olefin production is one of the perspective directions in solving of this global problem. At the same time use of only high-temperature pyrolysis anf thermal cracking technologies doesn't lead to waiting results. Selectivity by olefin hydrocarbons leaves low without use of catalysts even at high transformation degree of initial raw material [3].

At present time selective dehydration of propane is one of the most required technologies for production of non-ultimate monomers which are used for synthesis of polymers. The main deficiency of this process is connected with necessity of use of high temperature of synthesis, which is needed for reaching the required propane conversion. However, high-temperature conditions needs use of specialized equipment and can have negative effect on technical and economical parameters of production process. Transition to use of thermo-catalytic technologies leads to apparent lowering of the temperature, but activity of a catalyst can decrease severely even in these conditions due to carbon deposition; output of finished product can reduce as well [4]. Thereby search of perspective catalysts, i.e. those based on Fe and its compounds, which have high operating parameters, is conducting by the scientists worldwide and is rather actual problem.

There are rather many catalysts and catalytic systems which are know at present time and can be used in catalytic cracking of propane [2-5].

Reaction of propane dehydration on platinum-tin catalysts, which were applied on various inert bases, was examined. It is shown that the catalyst is quickly deactivated by forming carbon depositions, and speed of this reaction rises with increases of specific base surface and Pt content [6].

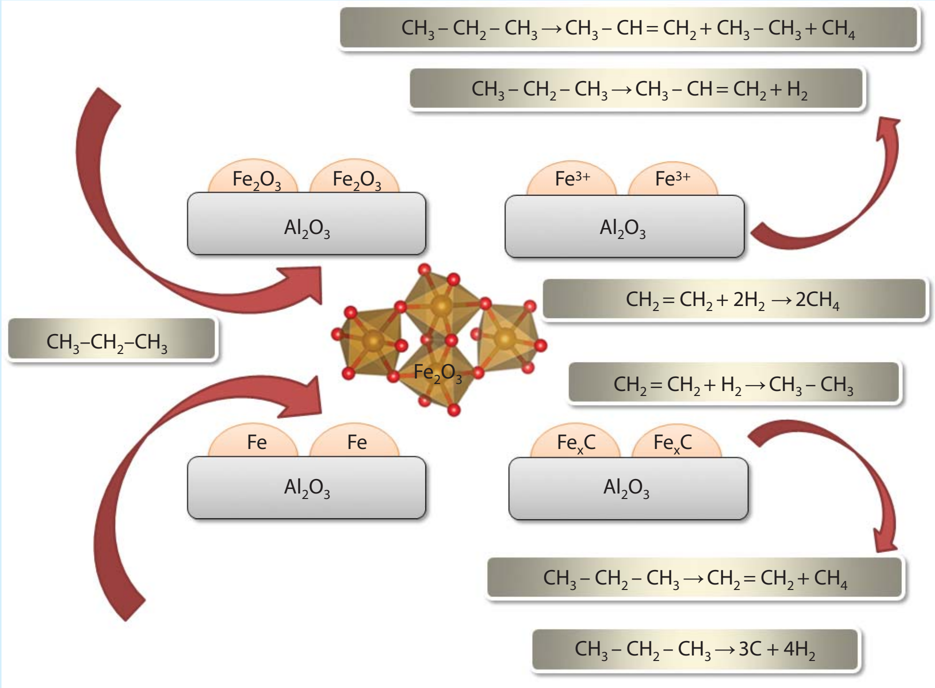

Fig. 1. The scheme of thermo-catalytic dehydration of propane with propylene forming on composite Fe-containing catalysts

The previously conducted researches displayed that composite catalysts which contain various forms of metallic or oxide iron (Fe^0 and Fe_xO_y) make the essential practical interest for intensification of this process [6-8].

The reason is that these Fe forms create catalytic centers, which can effectively provide transfer of electrons due to carrying of metal oxidation degree during transformation of initial substances in finished reaction products (**Fig. 1**). The nature of used carrier and the method of fabrication of the required composite catalyst play significant role in intensification of the considered interactions, which are connected with variation of technological output and process selectivity. Thereby the scientific novelty is presented by successful combination of a catalytic component and a carrier, which allow to decrease forming of carbon depositions on the surface and to provide large operating resource as well as improvement of strength parameters of the catalytic system.

The aim of this work is to synthesize Fe-containing composite catalysts, to examine their properties and to study efficiency of their use in the process of production of low molecular olefins via the method of thermal-catalytic dehydration of propane.

Experimental part

Pure aluminium oxide (γ-Al_2O_3) was used as a catalyst for examination of the process of catalytic cracking of propane; composite Fe-containing materials on the base of aluminium oxide, which was modified by Fe oxide (Fe^{3+}/Al_2O_3) and Fe nano-particles (Fe_{np}/Al_2O_3), ere synthesized also as catalysts. The results obtained with use of non-modified γ-Al_2O_3 as a catalyst (produced by Sigma-Aldrich) with content of the main substance 99.999 % (mass.) and specific surface 201.0 m^2/g (BET) were used for consequent comparative efficiency evaluation of Fe-containing composites.

To produce Fe nano-particles, the method of reduction of Fe ions in reverse micellar solution (RMS) on the base of bis-(2-dioctyl) sodium sulfosuccinate (AOT) and isooctane was used. Flavonoid quercetine was applied as complex forming agent and reducing agent [9]. To prepare the catalyst, γ-Al_2O_3 sample weight was put in the solution containing Fe nano-particles. After impregnation of a carrier, a sediment was filtered, washed by isooctane in a filter and dried in a vacuum box at the temperature 323 K. Fe amount in a synthesized sample was determined by increase of dry sample weight.

During synthesis of a catalyst, which was modified by Fe oxide (Fe^{3+}/Al_2O_3), the sample weight of aluminium oxide was dipped in concentrated aqueous solution of Fe nitrate. After impregnation a catalyst was dried in the air and then calcinated in nitrogen flow at the temperature 1000 K during 5 hours. As a result, the composition catalytic system on the base of γ-Al_2O_3 with Fe^{3+} applied on the surface was obtained. Content of oxide Fe form in a catalyst was determined by weight increase of a calcinated sample.

Fe_2O_3/Al_2O_3 catalyst was obtained using mechanical mixture of Fe_2O_3 and γ-Al_2O_3. The suggested Fe_2O_3 load made 10 % (mass.).

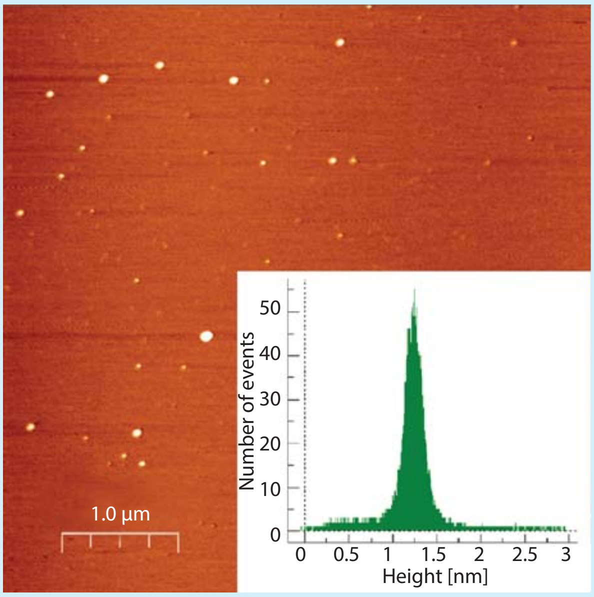

Fig. 2. Micro-pictures (Atomic-force microscopy - ACM) of Fe nano-particles in a composite catalyst on the base of γ-Al_2O_3 matrix and their distribution by dimensions

Specific surface of modified samples of Fe^{3+}/Al_2O_3 and Fe_{np}/Al_2O_3 catalysts was measured via the method of low-temperature nitrogen adsorption using the sensor Micromeritics ASAP-2020; it made 300.0 m²/g and 312.2 m²/g respectively.

Examination of the effect of catalysts properties on the process of propylene production via the method of propane catalytic cracking was conducted on the stand unit within the temperature range 750-1150 K (**Fig. 3**).

The reaction assembly for conduction of experiments was resented by the flow-through U-shaped quartzite reactor located in the furnace with electric heating. High-pure propane with content of the main substance as large as 99.98 % (mass.) was used as raw material. Flow speed of reaction gas made 1.25 ml/s. 0.125 ml of gas was collected for analysis after passing of reaction mixture through the reactor and then transferred to the chromatograph Kristall 5000M, which was supplied by the flame ionization detector and heat conductivity detector. Separation of the analyzed mixture was carried out in a standard column with 3 m length and 3 mm diameter, which was filled by "Porapak Q". The results obtained during catalytic conversion of propane were compared with the data of thermal cracking and literature data [10-13].

Degree of propane conversion was determined at the moment of reaching the stationary state by the amount of propane which participated in the reaction:

$$\alpha = \frac{n_{init} - n_{res}}{n_{init}} \qquad (1)$$

where n_{init} and n_{res} – initial and residual molar amount of propane respectively.

For calculation of propane conversion speed, the following expression was used:

$$w = \frac{K \times w_{out} \times s}{V_{loop}} [\mu Mol/g \times s] \qquad (2)$$

where K – correcting coefficient, w_{out} – output speed of the reaction mixture, s – peak square, V_{loop} – loop volume.

Selectivity by each component is calculated via the formula:

$$Sx = \frac{n_x}{n_{init} - n_{res}} \times 100\ \% \qquad (3)$$

where n_{init} – amount of propane participated in the reaction (µMol), n_{res} – amount of propane which didn't react (µMol).

Using the dependence between reaction speed and temperature, the observed values of process activation energy were calculated for all examined catalysts:

$$\ln w = \ln A - \frac{E_a}{RT} \qquad (4)$$

where E_a - observed process activation energy (kJ/mol).

Results and discussion

It was shown during conducted experiments that introduction of Fe ions and nano-particles in low-active aluminium oxide increases substantially the process efficiency in comparison with propane thermal cracking. As soon as the average stage of propane transformation in reaction products makes for non-catalytic process about 20 %, selectivity by propylene is about 1.0 % (**Table 1**). Use of pure γ-Al_2O_3 as a catalyst allowed to increase propane transformation degree up to 25.0 % and selectivity by propylene up to 4.6 %. However, this result can't be recognized as satisfactory one. Essential rise of efficiency parameters in propane catalytic cracking was achieved due to use of composite material on the base of modified γ-Al_2O_3. So, Fe^{3+}/Al_2O_3 catalyst showed transformation degree of initial reactant 72.2 %, while selectivity by propylene – 44.3 %. High result during use of this catalyst can't be explained only by observed increase of specific catalyst surface during transition from pure γ-Al_2O_3 to its modified forms. Perhaps the obtained result is explained by presence of Fe, Al and O_2 atoms in a composite, which are able to create bifunctional catalytic center Fe(III)-O-Al-, containing aluminium atoms in addition to Fe ions. Probably such material composition provides power-efficient interaction between active center and propane molecule, which leads to breaking of the most strong C-H bond for primary carbon atom (bond-breaking energy is equal to 418 kJ/mol). Molecular hydrogen which is emitted during dehydration can reduce iron of catalytic center from Fe^{3+} state to Fe^{2+} state, or to Fe^0 metallic Fe; their catalytic effect is various for the examined process. At the same time relationship between examined Fe forms is not constant and should vary during the reaction.

This suggestion is confirmed by the fact, that consequent transition to the catalytic system, modified by Fe nano-par-

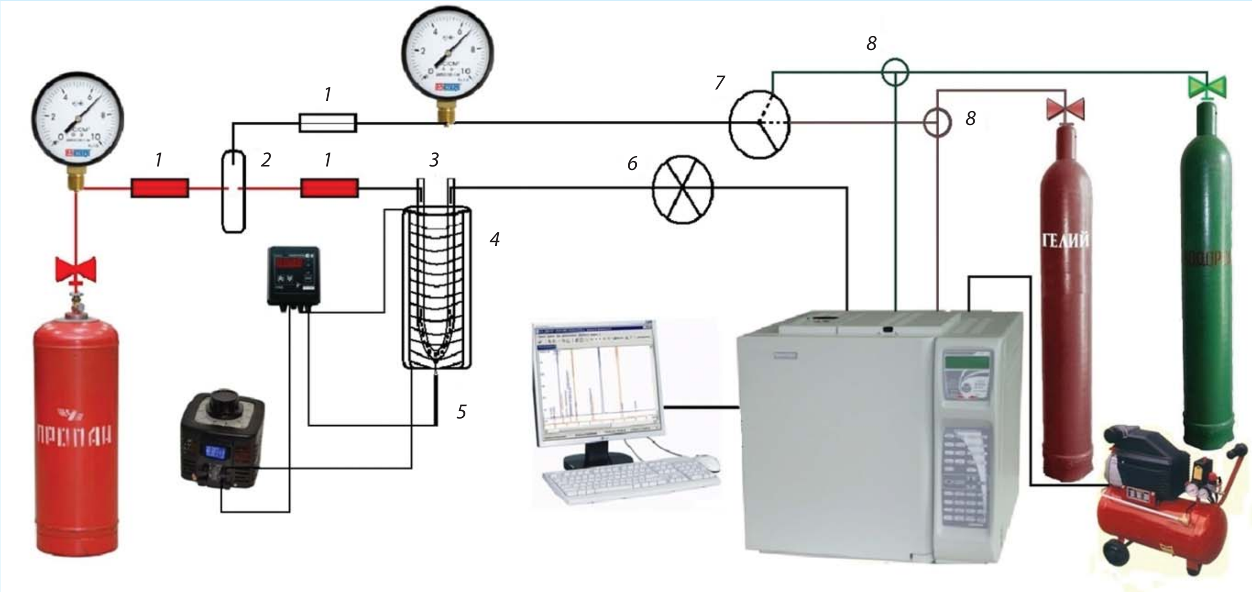

Fig. 3. Principal scheme of the catalytic unit for study of propane cracking process:
1 – capillary; *2* – mixer; *3* – U-shaped reactor; *4* – furnace; *5* – chromel-alumel thermocouple; *6* – six-way dosing tape; *7* – six-way dosing tape; *8* – T-shaped connector

ticles (Fe_{np}/Al_2O_3), was accompanied by increase of propane conversion up to 82.1 % with moderate lowering of selectivity by propylene (see Table 1).

Increase of the temperature above 950 K in all cases of catalytic cracking with use of synthesized catalysts led to rise of propane transformation degree with simultaneous decrease of selectivity by propylene. Thereby, consideration of propylene synthesis as the main reaction makes it possible to testify that transition from oxide form of modification to Fe nano-particles does not lead to substantial variation of the process technological efficiency. At the same time parameters of propane conversion and selectivity by polypropylene have high values in all cases, and these values exceed essentially similar parameters fir thermal cracking and catalytic reaction with use of pure γ-Al_2O_3 (see Table 1). These results display that propane conversion makes 30 % for industrial catalyst Pt/Al_2O_3 while propylene selectivity makes 40 %. Thereby total technological propylene output does not exceed 20 %, while use of Fe_{np}/Al_2O_3 and Fe^{3+}/Al_2O_3 rises technological output up to 25 % for increase of conversion up to 72 % and selectivity by propylene up to 44 %.

To confirm operating efficiency of the most effective catalysts, technological calculation was carried out and the main process parameters (such as speed of reactions and catalyst volume) were determined (**Table 2**).

It can be concluded mainly from the obtained results, that there is possibility of use of synthesized catalytic systems for thermal catalytic processing of natural gas with high efficiency, which can be compared with catalysts on the base of platinum, palladium and other noble metals [14, 15].

Undoubtedly, absence of significant influence of Fe nano-particles presence in composite on propylene technological output is an interesting fact. Increase of transformation degree of the initial component in reaction products, which was noted in this case, is accompanied by simultaneous decrease of selectivity by propylene. As a result, technological output of finished product does not differ from similar parameter for a catalyst (Fe^{3+}/Al_2O_3) in the case of use of composite with Fe nano-particles. Taking into account higher workability of manufacture of a composite catalyst with nano-particles, use of the catalyst which is modified by Fe ions (Fe^{3+}/Al_2O_3) is the most preferable.

Table 1. **Parameters of operating efficiency for examined catalytic systems at the temperature 750 K**

Catalyst	α, %	S (C_3H_6),%	w (C_3H_6), μMol/g×s	E_a, J/mol [14]
Without catalysis	20.0	1.0	17.5	209±1
Al_2O_3	25.0	4.6	23.4	190±1
Fe_2O_3	27.0	11.0	41.1	187±1
Fe^{3+}/Al_2O_3	72.2	44.3	159.3	119±1
$Fe_{нч}/Al_2O_3$	82.1	37,4	163.3	115±1
Fe_2O_3/Al_2O_3	27.0	15.0	61.1	175±1

where α – propane transformation degree; S – selectivity by propylene; w –propylene output speed; E_a – observed energy of process activation

Processing of the data about influence of temperature on speed of the catalytic conversion of propane in the coordinates of Arrenius equation allowed to calculate observed activation energy. It was lower by 2 times for catalytic processes than for thermal cracking (see Table 1), what correlates well with the results of researches of thermal catalytic transformations of various hydrocarbons [10].

Table 2. **Parameters of economical efficiency after putting into practice the results of conducted investigations.**

Catalysts	Content of Pt, Fe, %	Required volume of catalyst, m^3	Average annual expenses for catalyst, thou. rub./year	Average annual expenses for replacement of catalyst, thou. rub./year	Totally, thou. rub./year
Pt/Al_2O_3	0.55 Pt	0.03	317 900	11 500	329 400
Fe_{np}/Al_2O_3	0.20 Fe	0.03	132 000	11 500	143 500
Fe^{3+}/Al_2O_3	0.40 Fe	0.03	105 000	11 500	116 500

Conclusions

As a result of conducted experiments, high-efficient Fe-containing composite catalytic systems on the base of aluminium oxide were obtained. All produced catalysts were tested on technological stands for investigation of propane catalytic cracking, with obtaining of propylene as a finished product. It was shown that all synthesized catalysts are characterized by high catalytic properties and can be used in production processes of "light" olefins from natural and synthetic gas, which contains ultimate hydrocarbons. The best results were obtained during examination of the catalytic system Fe^{3+}/Al_2O_3. In this case, oxygen presence in inert substrate allows to create bifunctional catalytic center Fe(III)-O-Al-, which provides energetic profitable interaction with propane molecule and consequent bursting of the most strong C-H bond in primary carbon atom. Use of Fe nano-particles as a modifying additive didn't lead to apparent improvement of technological results in comparison with Fe^{3+}/Al_2O_3 material. Synthesized catalytic systems can be used for thermocatalytic processing of natural gas instead of the catalysts on the base of noble metals.

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