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Synthesis, Structure and Properties of Borate-Containing Oxide Catalysts for Petrochemical Processes and Synthesizing the Components of Motor Fuels

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Abstract

Results are presented concerning the studies on the formation of borate-containing aluminium oxide as a solid acidic catalyst system for the catalytic oligomerization of butenes. The possibilities of designing bi- and polyfunctional catalysts via modifying borate-containing aluminium oxide metals by metals and metal oxides from groups VI–VIII for the processes of oligomerizing ethylene, propylene, for single-stage production of ethylene, as well as for the processing of vegetable oil into diesel fuel components.

Key words: borate-containing aluminium oxide, polyfunctional catalysis, oligomerization of alkenes, alkene metathesis, hydrodeoxygenation

INTRODUCTION

The overwhelming majority of modern processing the natural gas, petroleum, plant material is based on the use of solid acidic and multifunctional catalysts [1]. The latter are usually characterized by the fact that alongside with the acid-base centres they have on the surface the centers, where specific reactions can effectively take place such as the activation of hydrogen molecules, unsaturated and heteroatomic compounds. The preparation of polyfunctional catalysts is most often carried out *via* the formation of metal or metal oxide dispersed particles immediately on the surface of a finished carrier matrix. In this case such a matrix can provide not only the necessary level of multifunctional catalyst acid-base properties, but also an influence upon the dispersion level and the structure, and hence on the activity and selectivity of the component applied due to the matrix textural properties and chemical nature of the surface.

To date, various systems based on anion-modified aluminium oxide are widely used in the industrial practice as carriers for the acidic polyfunctional catalysts due to the simplicity

of the synthesis, the possibility of a wide-range variation in acidic and structural properties, and their availability. As efficient anionic modifiers, one uses halide and sulphate compounds, less often oxygen compounds of phosphorus, tungsten, and boron.

Distinguishing boron compounds among others for anionic modification of aluminium oxide, it should be noted that as compared to the halide and sulphate containing aluminium oxide, the B_2O_3 – Al_2O_3 system can exhibit a high stability under hydrothermal conditions, within oxidizing and reducing atmospheres [2, 3]. This allows us to put forward an assumption consisting in the fact that a set of properties is inherent in borate-containing catalysts, such as environmental safety, the absence of corrosive activity, high stability, and regenerability. The average level of the Brønsted acidity and almost complete absence of the Lewis acid sites [4, 5], seems to determine the efficiency of using the borate-containing aluminium oxide as a catalyst for alkylation reactions [7], for the dehydration of alcohols [8, 9], for the isomerisation of alkenes [10, 11], for the cracking of vegetable oils [12]. Recently [13], we demonstrated the possibility of using this system for

the catalytic oligomerization of butenes. In addition, the borate-containing aluminium oxide is under active consideration as a carrier for the acidic polyfunctional catalysts, those find application for the metathesis of alkenes [4], especially for hydrorefining different petroleum fractions [14–16].

In this paper, we briefly discuss some of our results of the studies concerning the formation of $B_2O_3-Al_2O_3$ as an acidic catalyst for the oligomerization of butenes, as well as some possibilities for designing on this base bi- and polyfunctional catalysts containing metals or metal oxides from groups VI–VIII, for novel processes of ethylene oligomerization, for single-stage producing propylene from ethylene and refining vegetable oil into diesel fuel components.

OLIGOMERIZATION OF LIGHT ALKENES

The processes of the oligomerization of light C_2-C_4 alkenes are known for long as a possible basis for the components of gasoline, jet and diesel fuels with improved operation and environmental characteristics [17]. The current interest in the oligomerization is supported by the prospects of implementing the industrial methods of synthesizing light alkenes from natural gas *via* its oxidative dimerization or pyrolysis to create novel versions of “gas to liquid” technologies.

In the industrial processes of butene oligomerization there are solid silicon-phosphate catalysts mainly used, whose fundamental disadvantages include their destruction in the course of operation, impossibility to regenerate and reuse them. Sulphonic resins, amorphous aluminosilicates, zeolites, and various anion-modified zirconium and titanium oxides are under active consideration as promising systems for the oligomerization [1].

In our studies [1, 13] we described the oligomerization of butenes on the borate-containing aluminium oxide obtained *via* the treatment of $\gamma-Al_2O_3$ by an aqueous solution of orthoboric acid followed by drying and calcination stages. In order to increase the activity of aluminoborate oligomerization catalyst and to simplify its synthesis we used further a mixing method for obtaining the $B_2O_3-Al_2O_3$ system, which method was based on the calcination of pseudo-

boehmite previously modified with an aqueous solution orthoboric acid.

The studies concerning the effect of chemical composition and calcination temperature of the $B_2O_3-Al_2O_3$ system obtained by mixing demonstrated that the introduction of orthoboric acid into pseudoboehmite prevents alumina from crystallization in the course of subsequent thermal processing. To all appearance, this could be caused by a possible formation of aluminium borates.

According to X-ray diffraction phase analysis (Fig. 1, a), at the mass fraction of B_2O_3 amounting to 5 % (here and below we present the nominal content of B_2O_3 with taking into account anhydrous $B_2O_3-Al_2O_3$ system) the aluminium oxide borate-containing sample exhibits only traces of $\gamma-Al_2O_3$ after the calcination at 600 °C (for 16 h). According to the evaluation of the dispersion level of this phase from the coherent scattering region (CSR), the average particle size is less than 2.2 nm, which is

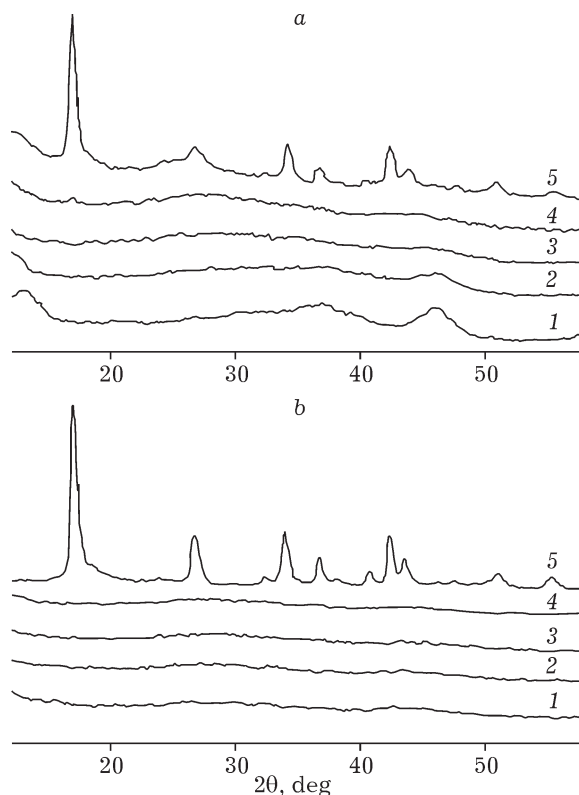


Fig. 1. Diffraction patterns of $B_2O_3-Al_2O_3$ samples with different mass fraction of B_2O_3 (a) and calcination temperature T_{calc} (b): a – $T_{calc} = 600$ °C; the mass fraction of B_2O_3 , %: $\gamma-Al_2O_3$ (1), 5 (2), 10 (3), 20 (4), 30 (5); b – the mass fraction of B_2O_3 equal to 20 %; T_{calc} , °C: 500 (1), 550 (2), 600 (3), 700 (4), 800 (5).

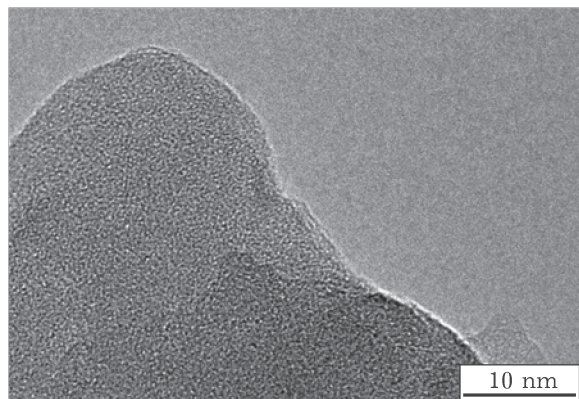


Fig. 2. Electron photomicrograph of $B_2O_3-Al_2O_3$ system with the mass fraction of B_2O_3 equal to 20 % after calcination at 600 °C.

almost two times less than the average particle size for the $\gamma-Al_2O_3$ obtained by calcination of unmodified pseudoboehmite. The growth of B_2O_3 content up to 10–20 mass % results in the formation of amorphous systems. The latter fact (Fig. 2) is directly confirmed by transmission electron microscopy.

With further increasing the mass fraction of B_2O_3 up to 30 % the diffraction pattern demonstrates the phase of aluminium borate with the composition such as $2Al_2O_3 \cdot B_2O_3$ with a particle size equal to 12 nm according to the CSR. From the diffraction patterns (see Fig. 1, b) one can see that the amorphous state of the $B_2O_3-Al_2O_3$ system (20 mass % of B_2O_3) can persist up to the calcination temperature of 700 °C. With increasing the calcination temperature up to 800 °C, both $2Al_2O_3 \cdot B_2O_3$ aluminium borate, and $\gamma-Al_2O_3$ undergo crystallization, but in a more coarse form with CSR approximately equal to 7.5 nm.

The data presented in Table 1 demonstrate the influence of the content of B_2O_3 upon the

textural characteristics of $B_2O_3-Al_2O_3$ samples synthesized. The dependences of the specific surface area and pore volume (determined according to the method of low-temperature nitrogen adsorption, BET model) on the chemical composition of the $B_2O_3-Al_2O_3$ system exhibit an extremum. The position of a maximum (270 m^2/g and 0.42 cm^3/g) corresponds to the mass fraction of B_2O_3 , equal to 20 %. These facts could be explained by the above-described changes in the phase state and in $B_2O_3-Al_2O_3$ dispersion level occurring with increasing the mass fraction of B_2O_3 . The presence of B_2O_3 even in small amounts prevents the crystallization and growth of $\gamma-Al_2O_3$ crystallite size in the course of high temperature treatment of the modified pseudoboehmite. As a result, the mixed oxide system $B_2O_3-Al_2O_3$ (the mass fraction of B_2O_3 equal to 5–20 %) is formed in the amorphous and/or highly dispersed state and has a large porosity in comparison with the $\gamma-Al_2O_3$ due to a smaller size of their primary particles. When the mass fraction of B_2O_3 increases up to 30 %, the system exhibit the formation of large aluminium borate crystallites $2Al_2O_3 \cdot B_2O_3$, and, to all appearance, also “melt” particles of unreacted B_2O_3 [3, 13], which just determines the effect of reducing the values of textural characteristics.

For the sample of $B_2O_3-Al_2O_3$ with the B_2O_3 mass fraction of 20 % that has the most developed surface area and pore volume, we studied acidic properties using the method of temperature-programmed desorption of ammonia molecules (Table 2). It is seen that in comparison with the $\gamma-Al_2O_3$, the borate-containing aluminium oxide can have 1.7 times more acidic sites amounting up to about 600 $\mu mol/g$. The character of acidic sites distribution with respect to

TABLE 1

Effect of chemical composition on the textural characteristics of $B_2O_3-Al_2O_3$ system (calcination temperature 600 °C)

Mass fraction of B_2O_3 , %	S_{sp} , m^2/g	V_{por} , cm^3/g	D_{av} , nm
0	184	0.26	52
10	238	0.35	53
20	270	0.42	64
30	189	0.16	35

TABLE 2

Acidic properties of $\gamma-Al_2O_3$ and $B_2O_3-Al_2O_3$ system (calcination temperature 600 °C, B_2O_3 mass fraction 20 %)

Systems	Desorption of ammonia, $\mu mol/g$ at the temperature values, °C			
	200–300	300–400	400–600	200–600
$\gamma-Al_2O_3$	0.15	0.12	0.06	0.33
$B_2O_3-Al_2O_3$	0.27	0.19	0.12	0.58

the acid strength (the temperature of ammonia desorption) is qualitatively identical for both oxide systems and indicates the dominance of surface acidic sites with medium acid strength (the desorption of ammonia at 200–300 °C).

The testing results for the samples of $B_2O_3-Al_2O_3$ in the butene oligomerization process (flow reactor, 40–200 °C, 8.0 MPa, industrial butane-butene fraction with the mass fraction of butenes about 60 % as a raw material, the mass flow rate of butenes equal to 1 h⁻¹) allow one to conclude that their level of activity for all the contents of B_2O_3 under study (5–30 mass %) principally (to a manifold extent) exceeds the level of $\gamma-Al_2O_3$ activity.

Figure 3 presents data concerning the effect of B_2O_3 content and $B_2O_3-Al_2O_3$ calcina-

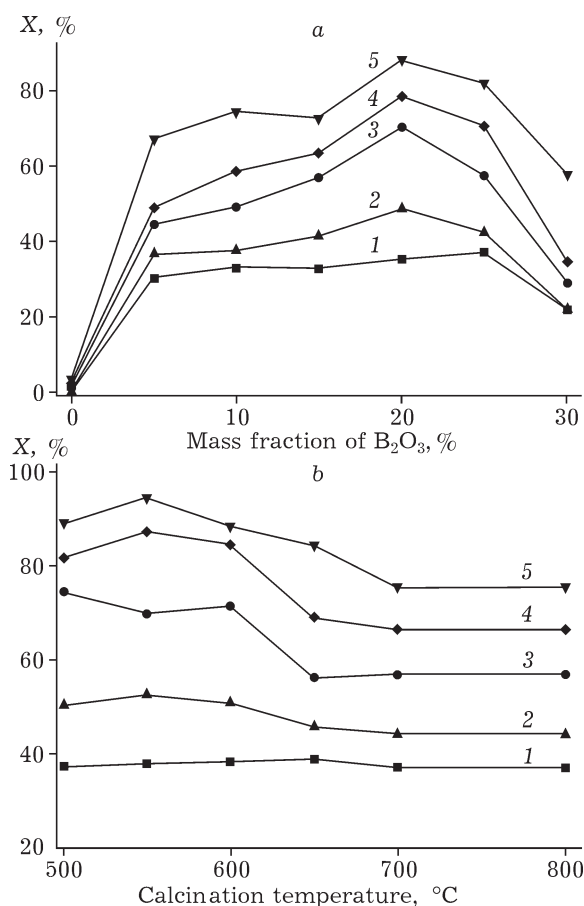


Fig. 3. Influence of $B_2O_3-Al_2O_3$ system chemical composition (a) and calcination temperature (b) upon the conversion level of butenes at different temperature values of the oligomerization process: a – the calcination temperature equal to 600 °C; b – the mass fraction of B_2O_3 equal to 20 %; T, °C: 40 (1), 80 (2), 120 (3), 150 (4), 200 (5).

tion temperature on the conversion level of butenes at different temperature values in the process of oligomerization. In all the cases, the oligomerization temperature increase within the range from 40 to 200 °C results in a more than twofold increase in the conversion level of butenes. This also demonstrates an extreme nature of the catalytic activity dependence on the chemical composition of $B_2O_3-Al_2O_3$. The highest conversion level of butenes in the course of oligomerization is achieved for the sample with the B_2O_3 mass fraction of 20 % that, as noted earlier, has the highest values of textural characteristics.

The effect of calcination temperature on the catalytic activity was less pronounced. Within the calcination temperature range 500–800 °C, the conversion level of butenes can always reach a level not less than 80 %. With the calcination temperature of 550 °C, the most active catalyst (20 mass % of B_2O_3) is formed which in the course of oligomerization at 200 °C provides a conversion level of butenes equal to 96.6 %.

The group composition of oligomerization products (Fig. 4) consisting of hydrocarbons C_5-C_{16} also depends on the chemical composition and calcination temperature of $B_2O_3-Al_2O_3$. However, this effect is, to all appearance, mediated to be associated with the conversion level of butenes achieved in this case. The fraction of light products C_5-C_7 is to the least extent dependent on changes in the mass fraction of B_2O_3 and the calcination temperature and varies within the range from 5 to 15 mass %. The main differences in the composition of liquid products of oligomerization, formed on different $B_2O_3-Al_2O_3$ samples are determined by redistribution between the C_8 and C_{9+} alkenes. In all the cases the following rule is observed: the higher the conversion level of butenes achieved, the higher is the fraction of C_{9+} hydrocarbons in the overall composition of the products resulted from C_{5+} . For the most active $B_2O_3-Al_2O_3$ sample (20 mass % of B_2O_3 , calcination temperature equal to 550 °C) the liquid products of oligomerization include C_5-C_8 hydrocarbons (45.3 mass %) and C_{9+} hydrocarbons (54.7 mass %). Thus, the catalyst could be used for simultaneous obtaining (*via* the oligomerization of butenes) the components of both gasoline, and jet as well as diesel fuels.

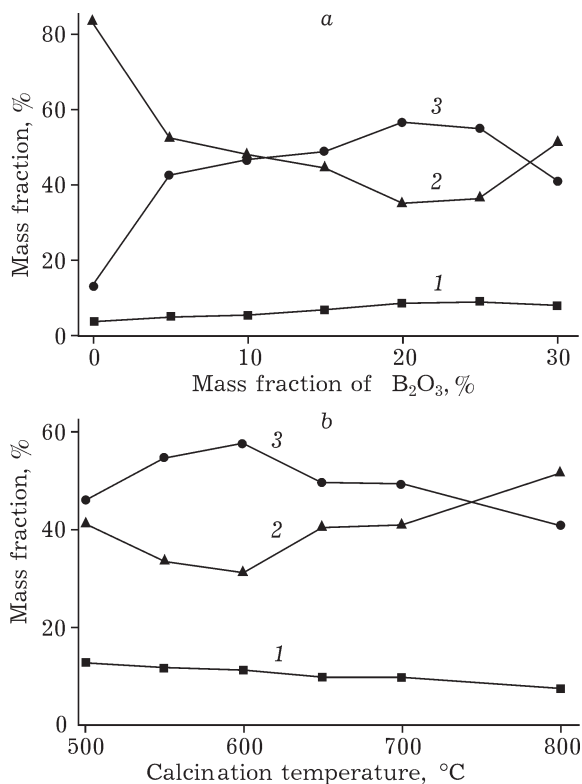


Fig. 4. Influence of B₂O₃-Al₂O₃ system chemical composition (a) and calcination temperature (b) upon the composition of oligomerization products at the process temperature equal to 200 °C: 1 - C₅-C₇, 2 - C₈, 3 - C₉₊.

Owing to the development of novel methods for producing ethylene from natural gas, the process of its oligomerization could now be considered an important step within the framework of technological concepts of “gas to liquid” being under development today [18]. At the same time the main focus in the improvement of ethylene oligomerization catalysts is to obtain isoalkenes C₅₊ as target products those could serve as a basis for environmentally safe motor fuels.

Solid bifunctional system, obtained *via* treating the acidic carriers (silica gel, amorphous aluminosilicates, zeolites, sulphate-, molybdate-, tungstate-containing aluminium, zirconium, titanium) with nickel salts followed by calcination are considered to be the most promising catalysts for the synthesis of isoalkenes from ethylene [19]. It is believed that the centers of ethylene activation on these catalysts are presented by Ni⁺ cations formed under the influence of the reaction medium in the course of oligomerization. The butene-1 resulting from the

dimerization of ethylene undergoes isomerisation on acidic sites, which further provides the formation of a wide range of alkenes C₅₊ with just isometric structure. The disadvantages of the known nickel-containing catalysts for ethylene oligomerization include either difficulty in obtaining, or high cost, and in most cases, a low selectivity of of ethylene oligomerization into liquid products.

We have attempted to develop a new efficient catalyst for the oligomerization of ethylene into C₅₊ isoalkenes based on NiO/B₂O₃-Al₂O₃ system [20]. As a result, for this system, obtained *via* impregnating the aluminoborate carrier (20 mass % of B₂O₃) with nickel nitrate solution and subsequent calcination at 500 °C, we revealed the extreme nature of the dependence of the catalyst activity in ethylene oligomerization on the content of NiO, most of which content ranges within 4.86–9.31 mass %.

According to the XRD phase analysis, the samples containing up to 23.2 mass % of NiO, exhibited no crystalline phase of nickel oxide. The study performed using TEM (Fig. 5) revealed the presence of NiO particles, localized in the amorphous regions of B₂O₃-Al₂O₃ carrier surface, with the size of 2–3 nm. The results of a simultaneously performed local chemical analysis demonstrated the presence of nickel also in those areas where the particles of NiO are invisible. This led us to the assumption that the catalyst involves cationic states of nickel,

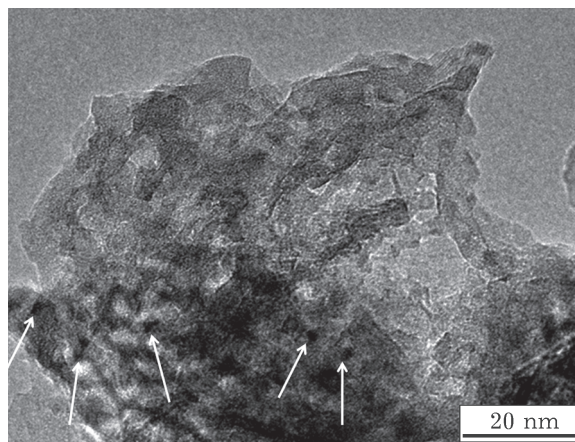


Fig. 5. Electron photomicrograph of NiO/B₂O₃-Al₂O₃ catalyst with the mass fraction of NiO equal to 4.86 %. The arrows indicate NiO particles.

caused by its interaction with the carrier and having a non-O²⁻ anionic environment (perhaps in the form of borate structures). The presence of cations Ni²⁺ being in chemical interaction with the carrier was directly confirmed by UV and IR spectroscopy.

The presence of this particular form of nickel was observed, especially in samples that exhibit the highest activity in the oligomerization of ethylene (the mass fraction of NiO being of 4.86–9.31 %). Consequently, these cations Ni²⁺ are the precursors of real ethylene activation centres Ni⁺, where into they are converted under the influence of the reaction medium at the beginning of the oligomerization process.

By varying the conditions of ethylene oligomerization within a wide range we established that the gas-phase mode of the process proceeds via a chain mechanism that is almost completely controlled by the active centers of nickel catalyst. At the same time, in order to describe the overall conversion level of ethylene, the first order kinetic equation is valid, whereas the molecular mass distribution of oligomerization products where butenes dominate is consistent with the Schulz–Flory distribution with parameter α , equal to 0.15.

Conducting the process in the liquid phase is characterized by a high contribution of secondary oligomerization processes, to all appearance, taking place with the participation of acidic carrier sites B₂O₃–Al₂O₃ providing the predominant formation of C₈₊ products. The latter determines the prospects of practical use of catalyst obtained (4.86 mass % NiO), that provides an almost complete conversion of ethylene is at the temperature of 200 °C, pressure of 4.0 MPa and the mass flow rate of ethylene 1.1 h⁻¹ with the yield of liquid oligomerization products up to 90.0 mass %, with the total content of C₈₊ alkanes amounting to 89.0 mass %.

SINGLE-STAGE PRODUCTION OF PROPYLENE FROM ETHYLENE

Propylene is mainly produced by the pyrolysis of liquid hydrocarbons. In this process, propylene is formed together with ethylene, the latter being formed in much larger quantities. On the other hand, the development of polymerization technology and the increased demand for products made of polypropylene already

lead to the emergence of commodity shortage in propylene, whose elimination requires for an active development of alternative methods for propylene pyrolysis, including from the gas raw [21]. These methods mainly include the processes of the catalytic cracking of petroleum fractions as well as, for example, butenes, propane dehydrogenation process and the metathesis of ethylene and butene-2.

When using the metathesis for obtaining propylene, ethylene most often is used as feedstock. Today's technologies used for transforming ethylene into propylene comprise three successive stages those implement the reactions of ethylene dimerization into butene-1, butene-1 isomerisation into butene-2 and, finally, the metathesis using three different catalytic systems.

The thermodynamic calculations demonstrate that at the temperature values up to 300 °C and at the atmospheric pressure an almost complete conversion is allowed for ethylene into the mixture of C₃–C₄ alkenes. In this case, the maximum possible yield of propylene is at least 20 mass %, which is comparable with the values attainable in practice in the multi-step catalytic obtaining of propylene basing on ethylene-based metathesis. It should be added that just within this temperature range an activity is exhibited by nickel traditional catalysts for the dimerization of ethylene, solid-acid catalysts for the isomerisation of alkenes, rhenium oxide catalysts for metathesis. In this regard, of particular interest may be one-step synthesis of propylene from ethylene, whose implementation requires for a multifunctional catalyst containing simultaneously active sites for dimerization reactions, isomerisation reactions and the metathesis of alkenes.

As such a catalyst for single-stage production of propylene from ethylene, we considered NiO–Re₂O₇/B₂O₃–Al₂O₃ system. The basis of the synthesis consist in the idea of “merging” the properties caused by applied Re₂O₇ (as an active component of the metathesis catalysts) with the properties of deposited NiO (as an active component of catalysts for ethylene dimerization) with the use of single aluminoborate acidic carrier.

The synthesis of NiO–Re₂O₇/B₂O₃–Al₂O₃ samples was carried out *via* impregnating the

TABLE 3

Effect of the chemical composition of NiO-Re₂O₇/B₂O₃-Al₂O₃ catalyst and of the temperature on the parameters of obtaining propylene from ethylene

Mass fraction, %		Process temperature, °C	Ethylene conversion level, %	Propylene yield, mass %	Selectivity of product formation, mass %		
NiO	Re ₂ O ₇				C ₃ H ₆	C ₄	C ₅₊
4.4	10.8	40.0	16.2	11.6	71.4	22.0	6.5
4.4	10.8	80.0	17.3	11.3	65.5	12.3	22.2
4.4	10.8	120.0	11.0	9.0	81.9	11.7	6.5
4.9	5.1	40.0	12.5	9.2	73.6	21.6	4.8
4.9	5.1	80.0	16.4	11.6	70.8	17.2	12.1
4.9	5.1	150.0	10.9	9.5	87.1	12.9	0.0
8.0	12.4	80.0	14.5	9.6	66.1	23.2	10.7

carrier (20 mass % of B₂O₃) with Ni(NO₃)₂ and HReO₄ solutions followed by drying and calcination at 550 °C. The mass fraction of NiO and Re₂O₇ was varied within the range of 4.4–8.0 and 5.1–12.4 %, respectively. Table 3 demonstrates the results of testing the samples synthesized in the course of concentrated ethylene conversion, which was conducted in a flow-through mode (40–200 °C, 0.1 MPa, the mass flow rate of ethylene amounting to 1 h⁻¹). One can see that under the testing conditions used the highest yield of propylene (11.6 mass %) at 40 °C is provided with the sample containing 5 mass % of NiO and 10 mass % of Re₂O₇, whereas at 80 °C with the sample containing 5 mass % of NiO and 5 mass % of Re₂O₇. In both cases, the selectivity with respect to propylene formation is higher than 70 %. In this case, the major by-products are presented by *n*-butenes formed with the selectivity level of 17–22 mass %. In the practical realization of the process, the *n*-butenes with ethylene could be directed to re-contacting with the catalyst.

HYDROOXYGENATION OF VEGETABLE OIL

The reduction of hydrocarbon reserves in conjunction with continuous deterioration in the world ecological situation already a long time ago determined trends towards the development and introduction into practice of the processes for producing motor fuels and valuable chemicals from renewable sources, primarily from plant biomass. At the same time, one of the most promising processes is presented by biodie-

sel fuel obtaining from vegetable oils basing on complete hydrodeoxygenation [22]. The hydrocarbon mixture formed as the result is extracted from a number of similar products with the prevailing content of C₁₅–C₁₈ alkanes and the absence of aromatic hydrocarbons, sulphur compounds, nitrogen and heavy metals.

As the catalysts for hydrodeoxygenation, till recently industrial Co(Ni)–Mo–S hydrorefining systems were actively considered. However, to provide stable operation of these systems one has to specifically introduce sulphur compounds into the reaction medium, which reduces to a considerable extent the advantages of biodiesel obtaining. In this context it becomes urgent to develop non-sulphide hydrodeoxygenation catalysts, primarily basing on applied Group VIII metals and oxide, or carbon carriers of different nature. Traditional systems of hydrogenation such as Pt, Pd, Ni/Al₂O₃ are not efficient as catalysts for hydrodeoxygenation.

Comparative tests we carried out for Pt-containing catalysts obtained basing on alumina and aluminoborate carriers in the course of sunflower oil hydrodeoxygenation demonstrated the advantages of using the system Pt/B₂O₃–Al₂O₃, connected, to all appearance, with a more pronounced bifunctional nature of its properties.

Fixing the platinum was carried out *via* impregnation of carriers γ -Al₂O₃, and B₂O₃–Al₂O₃ (20 mass % B₂O₃), with H₂PtCl₆ solution followed by the stages of drying, calcination in air and reduction in hydrogen at 500 °C. The content of platinum in the catalysts was equal to 0.5 mass %. Catalytic tests were carried out using a flow-through installation in a hydrogen

TABLE 4

Hydrocarbon composition of the diesel fraction produced as the result of sunflower oil hydrodeoxygenation on Pt/B₂O₃-Al₂O₃ catalyst

Component	Mass fraction, %
<i>n</i> -C ₁₂	0.03
<i>n</i> -C ₁₃	0.07
<i>n</i> -C ₁₄	0.08
<i>n</i> -C ₁₅	4.13
<i>n</i> -C ₁₆	3.07
<i>n</i> -C ₁₇	51.52
<i>n</i> -C ₁₈	38.28
<i>n</i> -C ₁₉	0.69
<i>n</i> -C ₂₀	0.30
Other	1.83
<i>Total</i>	100.00

atmosphere at the temperature of 350 °C and the pressure of 4 MPa, with the mass flow rate of raw material supply amounting to 1 h⁻¹. As a raw material we used refined sunflower oil. The duration of one testing procedure was equal to 5 h.

During the entire test duration a tested Pt/B₂O₃-Al₂O₃ sample provided the total hydrodeoxygenation of sunflower oil with the yield of liquid products amounting to 78.6 mass %, which products consisted of alkanes, isoalkanes, naphthenes, and water. The part of the diesel fraction (boiling range 200–350 °C) in the organic part of the liquid product was as high as 98 mass %, which diesel fraction consisted almost completely of C₁₅–C₁₈ *n*-alkanes (Table 4). The high mass fraction of *n*-octadecane (38.28 mass.%) indicates that to a considerable extent, alongside with the reactions of decarbonilation/decarboxylation, a “restoration” of carboxylic acids occurs formed during the decomposition of triglyceride molecules to give normal alkanes, including the acid-controlled dehydration of the molecules of saturated alcohols.

As against, Pt/γ-Al₂O₃ catalyst already after 1 h of operation is characterized by the presence of oxygen-containing compounds (saturated carboxylic acids, C₁₆–C₁₈ and C₁₈ saturated alcohols) among the liquid products of hydrodeoxygenation, as well as the formation of water in trace amounts only. To all appearance, the conversion toward the «restoration» of carboxylic acids in this case is not complete, most

likely due to a lower level of acidic properties of γ-Al₂O₃ compared to the system B₂O₃-Al₂O₃.

CONCLUSION

Alumina modified with mineral acid additives including orthoboric acid traditionally serves as a basis of catalysts for such basic oil refining processes as reforming and hydrorefining. The possibilities of a simple synthesis and a wide-range variation in acidic and structural properties, their availability determine the active using of the anion-modified metal oxides also in the future, despite notable successes connected with the development of the industrial applications of zeolite catalysts. It is hoped that the results presented in this paper could serve as a promise confirmation for oxide systems application, in particular borate-containing ones, not only for traditional hydrocarbon processing, but also for the new technologies of petrochemical synthesis, gas chemistry and for the production of motor fuels.

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