

PREPARATION AND TEST OF CATALYSTS DEPOSITED ON METAL BLOCKS USED IN SYNTHESIS OF DIMETHYL AND DIISOPROPYL ETHERS

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ABSTRACT

Effective selective catalysts deposited on monolithic metal blocks are developed and tested in reactions of dimethyl ether and diisopropyl ether production at atmospheric pressure from methanol and isopropyl alcohol, correspondingly. The catalysts active phase is based on compounds of Ni, Cu, Mo, W, V and zeolites. The presence of rare-earth elements in the catalysts composition stabilized their activity. The increase of the carrier acidity of the catalyst results in significant increase of iso-propanol transformation, whereas the selectivity in respect to diisopropyl ether decreases slightly. The optimum catalyst composition for diisopropyl ether synthesis is based on molybdenum and nickel compounds. Highly effective stable catalysts providing production of dimethyl ether from methanol with selectivity of 85 % - 97 % and that of diisopropyl ether from isopropyl alcohol with selectivity of 60 % - 69.4 % are developed.

Keywords: fuel additive, dimethyl ether, diisopropyl ether, metal block catalysts.

INTRODUCTION

According to the World Health Organization (WHO), the air pollution poses now a much greater health threat than Ebola or HIV and 80 % of all urban areas have air pollution levels above the standards accepted [1 - 3]. The atmosphere pollution leads to a decrease in oxygen and an increase in carbon dioxide, which entails a number of stable weather changes and creates real health hazard for people. The toxicity problem of the technogenic emissions into the atmosphere has particularly sharply risen

for the population of the big megacities. This concerns also Kazakhstan [4]. The Kazakhstan cities of Temirtau, Balkhash and Karaganda occupy the 4th to 6-th positions among the CIS cities, and the 1st to 3rd one in Kazakhstan in terms of gross emissions of harmful substances into the atmosphere. The southern capital of the Republic of Kazakhstan, Almaty, is a very unique city by its physico-geographical and natural climatic characteristics; the complex terrain and the climatic features create unfavorable conditions for impurities dispersion from low emission sources, as a result of which the harmful

substances accumulate in high concentrations. They participate in smog formation. The motor transport is the main source of atmospheric air pollution in Almaty. As a result, in the atmospheric air of Almaty, an increased content of formaldehyde, nitrogen dioxide, phenols, carbon monoxide is noted [5]. There are several ways to reduce engines toxicity, for example, an application of catalytic neutralizers, converters of exhaust gases [6 - 9], use of alternative fuels (methanol, ethanol, natural gas, biofuels) [10 - 14]. One of the promising methods refers to the application of dimethyl ether (DME). The latter is the only alternative of the diesel fuel for diesel engines [15 - 17]. The amount of the exhaust gases of the diesel engine working on DME is 6 times less than the standard EURO-4 referring to carbon oxide (CO) emissions, 4 times less than the hydrocarbons (CH) emissions, 4 times less than the emissions of particulates and 20 % less in respect to emissions of nitrogen oxides (NO_x). One of the ways of improving the operational properties of gasoline is use of oxygenates. The oxygen-containing compounds have become essential components of the motor fuels from the end of XX century. Oxygenates are oxygen-containing compounds such as low molecular weight alcohols, ethers, and mixtures thereof, which are known and widely used as octane enhancing components of the motor fuels [18, 19]. Gasolines with oxygenate additives are characterized by improved detergents properties and less carbon monoxide and hydrocarbons amounts emitted during the combustion. Diisopropyl ether (DIPE) is one of the most effective oxygen-containing additives. It has an advantage over the other ethers due to the much greater availability of olefin feedstock. It is a perspective substitute of meta-tert-butyl as it is non-toxic, has a lower volatility and cost of manufacture.

Today the catalysts deposited on blocks (metal or ceramic) are one of the preferable and the most suitable. All experiments described in this work are performed with the application of catalysts on metal block carriers.

The aim of this work is to create effective catalysts for synthesis DME from methanol and for DIPE production from isopropyl alcohol in the mild conditions.

EXPERIMENTAL

The reactions of DME and DIPE synthesis were carried out at a flowing catalytic installation at atmospheric pressure (Fig. 1(a)). The reactor was heated with an elec-

tric furnace. The temperature was varied from 150°C to 650°C and measured by a chromel-alumel thermocouple. An inert gas (argon) was used to prevent an explosion hazard in the system. A gas mixture (methanol-for DME synthesis and DIPE for that of DIPE) was directed to the reactor from corresponding cylinders by cranes of thin adjustment. The starting reagents in the mixtures with argon or air were directed to the reactor by a plunger pump. At the outlet of the reactor the reaction products were cooled, while the water vapor was removed. The temperature in the reactor was maintained according to the flow chart by introducing the cold initial compound to the second layer of the catalyst. The uniform feeding of the catalyst layer was achieved using nozzles placed along the circumference of the reactor. The purified dimethyl ether (diisopropyl ether) was cooled and condensed in a cold trap. The table below presents data on the composition of the feed mixture for DME synthesis.

The catalysts for the tests (Figs. 1(b), (c)) were prepared according to the methodology developed earlier [20 - 24]. A heat resisting foil of a thickness of 50 microns was used the preparation of the metal block carrier. The wash-coat was prepared from $\gamma\text{-Al}_2\text{O}_3$ with the addition of zeolite or from $\gamma\text{-Al}_2\text{O}_3$ modified by different compounds (on the basis of alkaline earth and rare earth metals). A wash-coat was deposited as a suspension on the metal block. The primary carriers (the metal blocks) were subjected to special treatment prior to the procedure just described. The active phase of the catalysts prepared

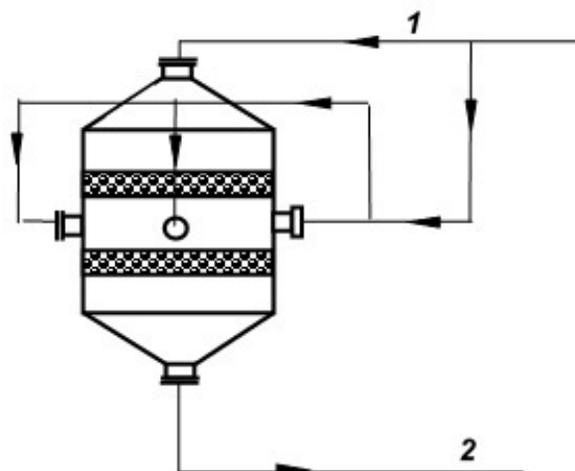


Fig. 1a. A scheme of the catalytic reactor for the synthesis of DME or DIPE: 1- the starting reagent (methanol or iso-propanol); 2- product of reaction (DME or DIPE).



Fig. 1b. A perspective view of the metal block for the laboratory sample of catalyst.



Fig. 1c. Full-sized catalysts on the metal blocks.

was based on the compounds of Ni, Cu, Mo, W, V and zeolites. For preparation of the zeolite – containing catalytic compositions a procedure of dealumination of the initial synthetic zeolites was carried out. The thermal and acid processing was alternated aiming to increase aluminium extraction from the zeolites. The heat treatment was conducted by heating the samples in a muffle furnace at 500°C - 550°C within 6 h - 8 h. The stage of dealumination was carried out to change the ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ for the purpose of stabilization of the hydroxylic groups and zeolites acidity increase. The specific surface of the synthesized catalysts deposited on block metal carriers was calculated by BET. It was found equal to 250 m^2/g - 320 m^2/g .

A powder of zeolite NaY of a module $\text{Si}/\text{Al} = 5.1$ transformed into its H-form by an ionic exchange of ammonia was used for DME synthesis from methanol. The specific surface of the prepared zeolite was defined by BET and was found equal to 420 m^2/g . The transformation of zeolites HY to a rare-earth form was carried out through impregnation with aqueous solutions of nitrates of Ce, La, Nd and mechanical mixing of zeolite HY and

the rare-earth oxides on IKA 11 C powder dispenser. According to the spectral analysis data the content of the rare-earth elements in zeolite was 1.8 wt. % - 2.1 wt. %. The optimum reaction temperatures were in the range of 250°C - 350°C.

The activity of the prepared catalysts was defined on the degree of transformation of iso-propyl alcohol (methanol). Their selectivity was determined on the concentration of DIPE (DME) in the product.

The chromatographic analysis of the initial compounds and the products of their transformation was performed on Chromatograph Crystal 2000M with a flame ionization detector and capillary column Zebron ZB-1 30 ml x 0,53 mm ID x 5,00 μm , 100 % dimethylsiloxane as a liquid phase, helium as a gas-carrier [25]. The total duration of the analysis was 15 min - 20 min.

The synthesized catalysts were investigated by different physical and chemical methods of investigation (XPA, EM, TPD). The specific surface of the catalysts was determined on the liquid nitrogen adsorption with the application of Accusorb. The samples were analyzed on EM-125K by the one-stage replicas method with extraction using microdiffraction (magnification of 160K), as well as on Jeol JSM-6610 (Japan) microscope.

RESULTS AND DISCUSSION

DIPE synthesis

DIPE synthesis from isopropyl alcohol was conducted using catalysts on the base of compounds of Ni and Mo. The reaction was carried out at temperatures which do not exceed 300°C. It is so because the selectivity of the created catalysts and DIPE yields decrease due to propylene formation at temperature higher than 300°C. It is found that the catalyst activity in iso-propyl alcohol transformation increases considerably, while the selectivity in respect to DIPE decreases slightly with carrier acidity increase. The data obtained is presented in Fig. 2. Most probably the acidity of the catalyst is an important factor in isopropanol conversion, and which is why the good yields of DIPE require a moderate acidity of the catalytic system based on metal oxides.

The addition of molybdenum oxide increases considerably activity the catalysts activity. The optimum composite of the catalysts for DIPE synthesis is on the basis of molybdenum- and nickel-containing compounds. The optimum temperature for DIPE maximum

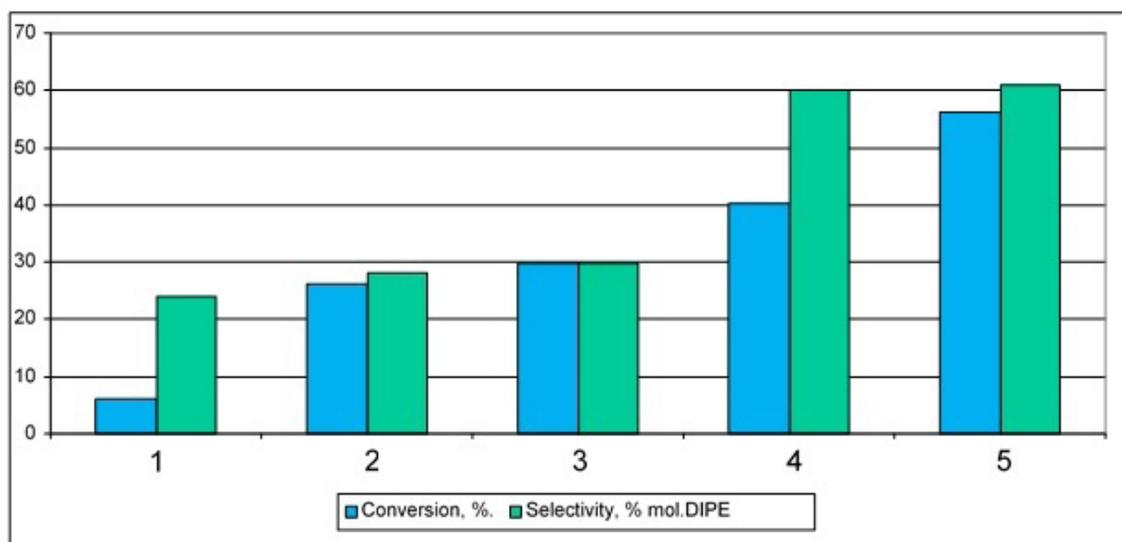


Fig. 2. The dependence of the activity and selectivity of the catalysts from their composition: 1 - NiO/Al₂O₃, 2 - NiO/Al₂O₃-NaY, 3 - NiO/SiO₂, 4 - MoO₃/Al₂O₃-SiO₂, 5 - MoO₃-NiO/Al₂O₃-SiO₂.

yield (69.4 %) refers to 300°C. DIPE yield increases with temperature increase. However, soot is formed on catalysts of a composition of NiO/Al₂O₃ and NiO/Al₂O₃-NaY and the catalyst activity decreases (Fig.3). On the catalyst Mo₃-NiO/Al₂O₃-SiO₂ at further increase of temperature up to 350°C the selectivity of the catalyst and DIPE yield decreased due to the formation of propylene. Thus, the optimal temperature for the DIPE yield of 69.4 % is 300°C.

DIPE was also synthesized by partial oxidation of propane by atmospheric oxygen at a ratio propane:air = 1:3 on La-containing catalysts in the temperature interval of 150°C - 650°C. It is found that the yields of propanol

and DIPE reach 81.5 % and 12.5 %, respectively, at temperatures up to 400°C. The maximum conversion of propane (94% - 95.1%) is obtained at 300°C. It decreases to 54.9 % with further temperature increase up to 650°C. The DIPE yield is 32.2 % at 600°C. Isopropyl alcohol is formed with yields of 80.3 %, 81.4 % and 82.4 % in case of partial oxidation of propane on the catalysts based on vanadium, nickel and molybdenum catalysts, correspondingly. The yield of DIPE was 2.3 %, 2.5 and 2.8 %, respectively. Propanol is formed with a yield of 59.6 % - 72.2 % on WO₃/ZrO₂ catalyst at 350°C - 550°C. It is found that the addition of 0.05 % - 0.1 % of Pd to a catalyst on the base of vanadium and molybdenum the

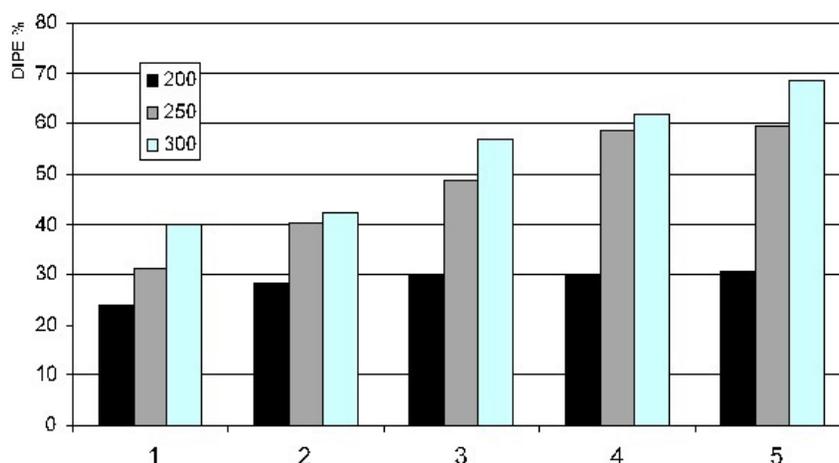


Fig. 3. Synthesis of DIPE on catalysts on the base of nickel: 1 - NiO/Al₂O₃, 2 - NiO/Al₂O₃-NaY, 3 - NiO/SiO₂, 4 - MoO₃/Al₂O₃-SiO₂, 5 - MoO₃-NiO/Al₂O₃-SiO₂.

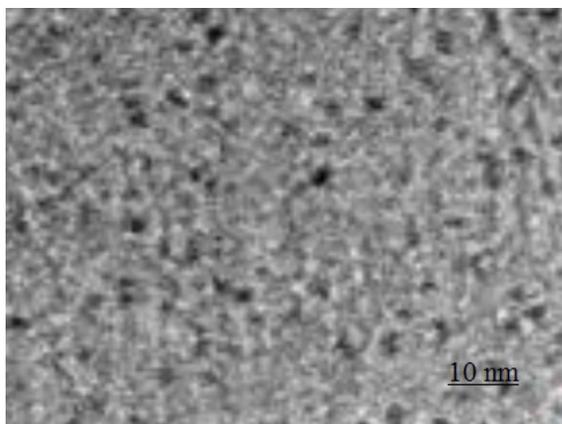


Fig. 4. TEM of $\text{WO}_3/\text{Al}_2\text{O}_3$ catalyst after calcination at 500°C .

conversion of propane to DIPE increases to 62.1 % - 67.3 % (0.05 % Pd) and to 75.2 % - 80.8 % at 450 - 550°C .

The XRD analyses of the catalysts carriers show peaks at 4.38 Å, 3.4 Å, 2.8 Å and an orthorhombic lattice [9, 25] in case of the catalyst on a metal carrier based on $\text{V}_2\text{O}_5\text{-WO}_3$. NiO-crystal lattice is not formed in the active phase. According to the TEM data of $\text{WO}_3/\text{Al}_2\text{O}_3$ sample calcined at 500°C , the tungsten compounds contain small particles of a size of ca 0.5 nm fixed on loose micro-block aggregates of Al_2O_3 . Fixed clusters of W of a size of ca 0.5 nm - 1.0 nm are found on Al_2O_3 . The presence of WO_3 phase is also confirmed by the XRD results. The diffractograms of the samples containing tungsten show WO_3 peaks and a wide peak at 28.7° (2θ), which can be attributed to mixed $\text{Al}_2(\text{WO}_4)_3$ oxide. The formation of the latter is possible because the ionic radii of W^{6+} and Al^{3+} are close and equal to 0.65 Å and 0.57 Å, respectively. Accumulations of solid particles which do not coalesce into aggregates are observed on Ni-W-V and Ni-Cu catalysts. Besides, metals are dispersed on the carrier surface. The particle size is ca 15 nm - 20 nm. The TEM data of Ni- and Mo-containing catalysts demonstrate the uniform distribution of the catalyst particles throughout the carrier block surface. It is found that a catalyst particle is composed of active ingredients - nickel and molybdenum, which are likely to form an alloy of the two metals. The particle size of the catalysts prepared from acetate solutions is equal to 50 nm - 60 nm, while that of the catalysts prepared from chloride solutions amounts to 200 nm - 300 nm (Fig. 4).

Fig. 5 presents the SEM images of $\text{NiO}/\text{Al}_2\text{O}_3$ and NiO/SiO_2 . Two types of nickel particles are revealed on

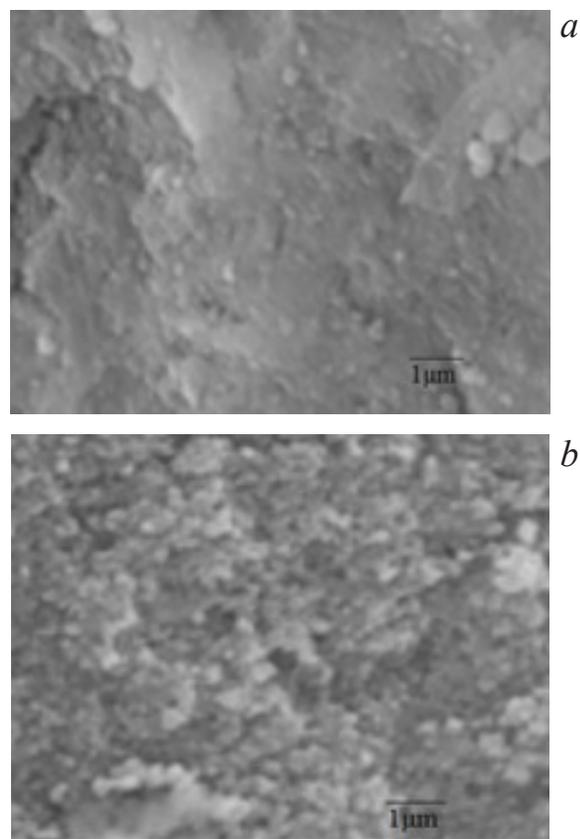


Fig. 5. SEM micrographs: a - $\text{NiO}/\text{Al}_2\text{O}_3$, b - NiO/SiO_2 .

the aluminum oxide surface in case of $\text{Ni}/\text{Al}_2\text{O}_3$ (Fig. 5(a)). The first type refers to almost spherical grains with a slight deformation and blurriness of the outlines. Their size is 120 nm - 600 nm. These are most probably NiO particles. The particles of the second type are smaller with a size of 25 nm - 75 nm. These are apparently Ni nanoparticles incorporated in the upper alumina. There are also NiO agglomerates reaching a size of up to 1 µm.

Catalysts development for DME synthesis

The studies on the effect of the volumetric feed rate of methanol on DME yield are carried out at NiNaY catalyst at constant temperature. The catalytic activity of synthetic zeolite NaY supported on a block carrier together with alumina with the mole ratio $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.1$ is investigated. The cationic zeolite forms are obtained by an ionic exchange from aqueous solutions of nitrates of the corresponding transitive metals and further decomposition of the nitrates within 4 h at 500°C . It is found that the catalysts on NaY basis promoted with

oxides of cobalt, copper and nickel are considerably more active in the reaction of methanol dehydrogenation than the starting NaY. The oxidized form of zeolite NiNaY is the most active – the DME yield reaches 79.7 % at 250°C - 260°C. It is connected, apparently, with the great mobility of the oxygen in the nickel oxide molecule. Methylformate and dimethylformate are also found at temperatures 150°C-200°C besides the target product, DME. The greatest amount is obtained using the initial NaY (up to 15 % - 20 % in total), while the smallest quantity is found in presence of NiNaY (up to 4 % - 5 %). The IR-spectroscopy analysis of the reaction products shows the presence of OH-groups at 3080 cm⁻¹, of C=C-groups at 1,600 cm⁻¹, and of CO₂ at 2,300 cm⁻¹.

Catalysts containing Cu, Ni and Cu-Ni are prepared. The most efficient and selective among them is that containing copper. A high selectivity of the process (100 % in case of DME) is already reached at 150°C. The catalysts containing Ni show activity and selectivity in respect to DME only at temperature increase to 400°C - 500°C. The process of methanol dehydration does not in general proceed on this catalyst at a temperature below 200°C - 300°C. The catalyst obtained by collateral im-

pregnation of Cu and Ni nitrates (i.e. the mixed catalyst of Cu-Ni) shows an average activity and selectivity on DME among the catalysts containing Cu and Ni. The Ni-Cu catalyst system has a high selectivity on DME production at reaction temperatures lower than 350°C. Also catalyst system on the base of Ni-Cu reduce the amount of coke formed on the surface of catalyst.

Fig. 6 shows the SEM images of Cu/ γ -Al₂O₃ and Ni-Cu/ γ -Al₂O₃ catalysts. A high distribution of particles of the active NiO-CuO phase on γ -Al₂O₃ (which presents clusters of a spongy type) is found for Ni-Cu/ γ -Al₂O₃ catalyst (Fig. 6(b)). It was revealed some sintering of prepared catalysts because range of particles sizes was in the limits of 5 - 500 nm. For Cu/Al₂O₃ (Fig. 6a), particles of alumina with copper particles (60 - 140 nm nanoparticles and agglomerates 1-1.5 μ m) with a morphology similar to Ni/Al₂O₃ (Fig. 5) were detected.

The revealed features of the catalysts prepared correlate with the literature data [26 - 30].

CONCLUSIONS

This work described the preparation of effective and selective catalysts deposited on monolithic metal blocks and the testing of their activity in the reactions of dimethyl ether production from methanol and diisopropyl ether production from isopropyl alcohol at atmospheric pressure. With increase of the carrier acidity in the conversion of iso-propanol the catalyst activity increased remarkably, whereas selectivity by diisopropyl ether decreased slightly. The optimum catalyst composition for diisopropyl ether synthesis is based on molybdenum and nickel compounds. It is found that catalysts on the basis of NaY promoted with oxides of cobalt, copper and nickel are considerably more active in the reaction of methanol dehydrogenation to DME than the starting NaY. The oxidized form of zeolite NiNaY is the most active providing DME yield of 79.7 % at 250°C - 260°C. It is probably connected with the great mobility of the oxygen in the nickel oxide molecule. Besides a target product, DME, at temperatures 150-200°C methylformate and dimethylformate were found out, in the greatest amount - on initial NaY (up to 15 - 20 % in sum), in the smallest amount - on NiNaY (up to 4 - 5 %). The presence of rare-earth elements in the composition of the catalysts stabilizes their activity. On the basis of La-Y catalyst selectivity on DME was

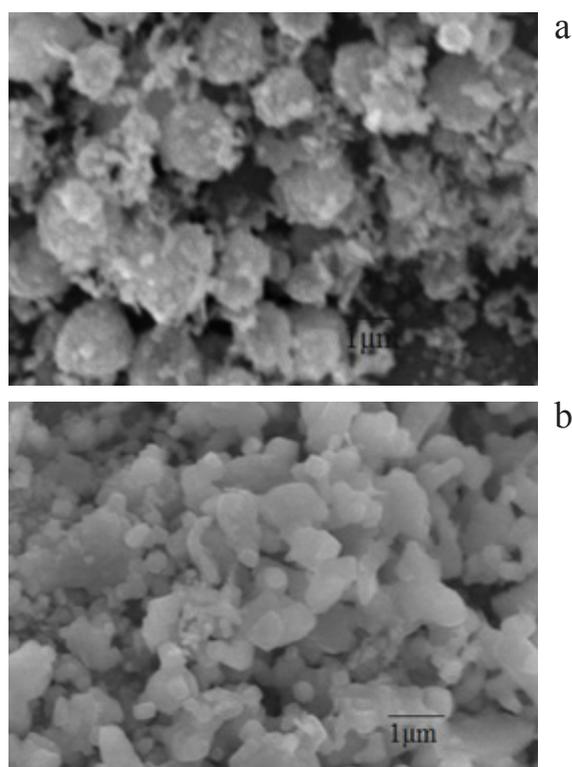


Fig. 6. SEM micrographs: a - Cu/ γ -Al₂O₃; b - Ni-Cu/ γ -Al₂O₃.

the greatest (97.4 %). Catalysts containing Cu, Ni and Cu-Ni are also prepared. The most efficient and selective catalyst is that containing copper. A high selectivity of the process (100% in respect to DME) is reached already at 150°C. Highly effective and stable catalysts on the basis of zeolites are developed. They provide synthesis of DME from methanol with selectivity of 85 % - 97 % and that of DIPE from isopropyl alcohol with selectivity of 60 % - 69.4 %.

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