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## THE BLOCK CATALYSTS FOR METHANOL AND THE DIMETHYL ETHER SYNTHESIS

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*The highly effective stable block catalysts on the basis of metals which will allow to receive DME from methanol and methanol from methane with a high yield are offered.*

Transport development leads today to progressing growth of the environmental contamination, especially in megacities. Last years this problem is more and more put in the forefront. The European Union struggles with a problem of pollution of atmosphere by introduction of special standards of norms of toxicity of exhaust gases. For the most widespread types of petrol engines with spark ignition the set alternative fuels is wide enough. It is natural gas methane, the condensed oil gas propane-butane, alcohols. As to diesel engines it is possible to consider as alternative to solar oil only the dimethyl ether (DME)! [1,2]. DME possesses a number of the surprising properties allowing it practically completely to displace the traditional diesel fuel – especially in large world megacities. First, exhausts of the diesel engine working on DME, in 6 times there is less than standard EURO-4 on emissions of the carbon oxide (CO), in 4 times it is less on emissions of hydrocarbons (CH), in 4 times it is less on emissions of firm particles (soot and a soot of the diesel cursors) and on 20 % less on emissions of the nitrogen oxides (NO<sub>x</sub>). Secondly, DME cardinally solves a problem of so-called cold start of diesel engines – working on DME the diesel engine can freely be got even at -50°C as the temperature of DME fusion is at -138.5 °C. We will notice, that some areas of Kazakhstan are in rather cold climatic zone that creates certain difficulties at cold start of the diesel engines. Thirdly, DME as the chemical substance is much more harmless some the same diesel fuel and gasoline. Fourthly, DME, except advantages of the fuel synthesized from natural gas, it is characterized by high cetane number (55-60, whereas at oil diesel fuel-40-55). Fifthly, results of the motor tests of diesel engines on DME have shown possibility of the considerable improvement of the following characteristics: ecological-decrease level of harmful emissions with the waste gases on the nitrogen oxides-in 3-4 times at practically smokeless exhaust on all operating rezhimes, economic-preservation or even improvement of profitability of a diesel engine in comparison with work on the diesel fuel, operational-decrease dynamics of a cycle and pressure of combustion that raises reliability of work and reduces noisiness on 10 dB (A), opening converting possibility in the diesel engines working on DME, petrol engines. Sixthly, it is possible to refer DME to the category of the renewed alternative fuels since the product for its manufacture can be received from a biomass. At the same time, the cheapest source for DME production there is a natural gas. In Kazakhstan there are the vastest resources of the natural gas which is used as a household fuel, and the basic quantity is transported in the form of the raw materials. Large-capacity manufacture of DME from the natural gas for the purpose of its use in a fuel direction as the final product – diesel fuel or a semi-product by gasoline manufacture is represented very perspective direction. Therefore working out of the catalytic systems and ways of the DME production represents scientific and applied value. It's most perspective to receive DME through methanol dehydration so it is received in Germany and Japan. Technology of the DME production it is direct from the synthesis-gas for today is one of advanced and promising. In the literature a number of ways of the methanol production from methane and the methane-containing gases is known. Now possibility of creation of the effective catalytic processes of direct oxidation of methane to methanol passing a stage of obtaining of synthesis-gas is intensively investigated.

In the work the block catalysts of synthesis of DME from methanol and for methane oxidation to methanol are developed and investigated at atmospheric pressure.

Researches on methanol production by direct partial oxidation of methanol and transformation of it to DME were carried out on the flowing installation. Reactions were studied at the atmospheric pressure. The

block metal catalyst was placed in a quartz reactor with internal diameter equal 10 mm. The reactor was heated with the electric furnace. Temperature was measured with the help of chromel-alumel thermocouples. For explosion hazard prevention in system the inert gas (argon or helium) was moved. A gas mix was submitted to a reactor from cylinders by means of the tapes of thin adjustment. Methanol (methane) in mixes with argon (or helium) or air was submitted to a reactor with the help of the plunger pump. The Chromatographic analysis of the initial compounds and products of their transformation was spent on the Chromatograph Crystal 2000M with capillary column Zebron ZB-1 30 ml x 0,53 mm ID x 5,00  $\mu$ m, a liquid phase – 100 % dimethylsiloxane (gas-carrier-helium, flame ionization detector). The total time of the analysis was 15-20 min.

Catalysts on a basis of oxides of titanium and vanadium-nickel in reaction of selective oxidation of methane by air oxygen to methanol were prepared and tested. As a synthesis method of the compound-oxidic nano-sized catalysts pyrolysis of the polymerous-salt compositions was used. The given method is universal, flexible, simple in realization, it allows to reduce the catalysts possessing a sufficient specific surface and adhesion. For introduction to composite of the compound-oxidic compounds of the metals were used the oxygen-containing ammonium salts: tungsten acid, metavanadate ammonium. As the polymeric components in the work the water-soluble nonionic polymers (polyvinyl alcohol, polyethylene glycol) which form the steady water solutions with the salt forms were used. The metal block carrier was impregnated by the polymerous-salt solutions with the subsequent heat treatment. As a result the nano-sized particles of oxides of vanadium, tungsten and nickel (20-15 nanometers) were obtained.

Series of the block catalysts on a basis of alumina, titanium dioxide, chrome oxide and vanadium oxide was prepared. As an active phase the nickel oxide, put on the block carrier by impregnation from the nitrate salts was used. The prepared catalysts were investigated at the various volume speeds and ratios gas – air in an interval of temperatures 400-700°C<sup>0</sup>. It was revealed, that the most active was the nickel-vanadium catalyst. At temperature 600°C<sup>0</sup> its activity was 98 %, and selectivity on methanol reached 92 %. Except methanol formic acids and, in insignificant quantities, acetic acid were formed. Presence of methanol was confirmed by IR-spectroscopy, occurrence of characteristic peaks in area 3400 cm<sup>-1</sup>. Series of the catalysts on the basis of Ni-V<sub>2</sub>O<sub>5</sub>, W-V was studied. It was established, that on the Ni-V<sub>2</sub>O<sub>5</sub> catalyst, as well as on titanium dioxide, degree of transformation of CH<sub>4</sub> to CH<sub>3</sub>OH with the increase of temperature was increased. The greatest degree of transformation of CH<sub>4</sub> to CH<sub>3</sub>OH (to 82.4 %) on NiO-V<sub>2</sub>O<sub>5</sub> catalyst was reached at 550°C. Optimum volume speed of transformation CH<sub>4</sub> to CH<sub>3</sub>OH on this catalyst, as well as on titanium dioxide was 400h<sup>-1</sup>.

For transformation of CH<sub>4</sub> to CH<sub>3</sub>OH the effective catalyst also was the nickel catalyst put on the vanadium-tungsten carrier. It was revealed, that introduction of tungsten oxide to the structure of the nickel catalyst led to the sharp growth of activity of the catalyst (to 89 %) and to decrease of temperature of the optimum transformation of CH<sub>4</sub> to CH<sub>3</sub>OH to 550°C<sup>0</sup>. Researches of the products of reaction by method of IR-spectroscopy were confirmed with formation of methyl alcohol on the investigated catalysts. So, presence weak intensity of the OH-groups was observed at 3460 cm<sup>-1</sup> on the titan-containing catalyst. On the vanadic catalyst were observed OH-groups of average intensity at 3450 cm<sup>-1</sup> were observed, and also CO and CO<sub>2</sub>. The most intensive peaks of OH-groups were observed on the vanadium – tungsten catalyst at 3480 cm<sup>-1</sup>, and also -CH<sub>2</sub>, -CH<sub>3</sub>-groups at 2800-2900 cm<sup>-1</sup>.

The carried out researches of the carriers and catalysts by the X-ray analysis method have shown the structure TiO<sub>2</sub>-anatase formation, reflexes 3,52; 1,89; 2,38Å<sup>0</sup>. The carrier on a basis of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub> – reflexes 4,38, 3,4, 2,8Å<sup>0</sup>, had trimetric a trimetric lattice. At an active phase NiO – the crystal lattice was not generated.

The catalysts have been investigated by means of an electronic microscope on device EM-125M by a method of one-stage remarks. On the nickel-vanadium-tungsten sample the congestions of the dense particles which didn't grow together in units were observed and dispersed on a carrier surface. The sizes of the particles were mainly 20-15 nanometers.

The catalysts on the basis of Cu, Ni-Cu for the purpose of selection of conditions of synthesis of DME in process of methanol dehydration were prepared and studied. The catalysts were prepared by deposition of compounds of the first metal, drying and calcination in the furnace at the need temperature regimens with the further impregnation of the blocks in a solution of the compounds of the second metal, drying and calcination in the furnace. The methanol dehydration was carried out in an interval 100-500°C. It was founded, that the copper-containing catalyst showed the high activity and selectivity (on DME) at 100-

150<sup>0</sup> C whereas on the nickel catalyst the main product was formed with a high yield (97-99 %) at rise in temperature of reaction to 500<sup>0</sup> C. The mixed catalyst (Ni-Cu) was active and selective on DME at temperature of reaction 150-200<sup>0</sup> C. It was established, that the most effective and selective catalyst was the sample on the basis of copper. High selectivity of process (on DME-100 %) was reached already at 150<sup>0</sup> C. The temperature increase above 200<sup>0</sup> C on this catalyst was not represented necessary. The catalysts on the basis of Ni have shown activity and selectivity on DME only at rise in temperature to 500<sup>0</sup> C. Yield of DME on this contact was 64-98 % (depending on temperature). Process of the methanol dehydration on this catalyst at temperature more low 200<sup>0</sup> C, 300<sup>0</sup> C didn't occur in general. At test of the catalysts obtained by the co-impregnation by nitrates of Cu and Ni (i.e. mixed catalyst Cu-Ni) it was established, that it had shown average activity and selectivity on DME among the catalysts on the basis of Cu and Ni, yield of DME was depending on temperature and a ratio of metals in an active phase, 62-88 %. On the catalysts on the basis of Mo activity was reached at ratio Mo of 3-5 % (in case of mixture with Ni in the ratio 1:1, and with copper 1:2) at temperature not more low 400 – 500<sup>0</sup> C, yield of DME at T=200-300<sup>0</sup> C did not exceed 40-45 %, and at increase of temperature to 550<sup>0</sup> C was 64-70 %. Thus, the structure on the basis of copper (at T=150-250<sup>0</sup> C) has appeared the most selective on DME. The prepared catalysts allow to synthesize DME from methanol to 90-98 %, at enough low temperature (150<sup>0</sup> C), and also at T=500-550<sup>0</sup> C with yield to 90-100.

#### REFERENCES

- 1 Rosovskii A.Ya. *Mezhd.shkola . Tr.3-ei sessii*, Kazan', **1997**, 110-133 (in Russ.).
- 2 Morozov L.N., Kostrov V.V., Lyakhin D.V., Burov A.V. *Izv.vuzov, Khim. i khim.tekhnologiya*, **2002**, 45, 6, C.111-113 (in Russ.).

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#### ДИМЕТИЛ ЭФИРІ МЕН МЕТАНОЛДЫ СИНТЕЗДЕУГЕ АРНАЛҒАН БЛОКТЫ КАТАЛИЗАТОРЛАР

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#### БЛОЧНЫЕ КАТАЛИЗАТОРЫ ДЛЯ СИНТЕЗА МЕТАНОЛА И ДИМЕТИЛОВОГО ЭФИРА

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Разработаны высокоэффективные стабильные блочные катализаторы на основе металлов, позволяющие получать ДМЭ из метанола и метанол из метана с высоким выходом.