Zeolite-containing catalysts for production of dimethyl- and diisopropyl ethers

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The air pollution environmental problem can be solved by 2 ways: improvement of quality of used fuel or improvement of work of an internal combustion engine and working out and introduction of neutralizers of exhaust gases.

The highly effective selective monolithic block catalysts with the honey comb structure of the channels, used for the decision of environmental problems were prepared in the work. It's known that the metal blocks are the preferable supports of catalysts since their properties: the developed surface, low pressure difference, high thermal and mechanical stability, ease of placing in a reactor. The secondary support was prepared on the base of the platinum metals which were translated to colloid condition that led to increase of activity of platinum catalysts in the researched reactions. The synthesized catalysts were used for obtaining of the ecologic pure fuel-dimethyl ether (DME) and of the component of additive to fuel for rising of octane number - diisopropyl ether (DIPE). Exhausts of the diesel engine working on DME, in 6 times there is less than standard EURO-4 on emissions of 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 and on 20 % less on emissions of nitrogen oxides (NO_x). At DME use a problem cardinally solves of so-called cold start of diesel engines - working on DME the diesel engine can freely be got even at -50°C and it's very actual for Kazakhstan because some regions are in rather cold climatic zone that creates certain difficulties at cold start of diesel engines. In work also reaction of synthesis of a component of the additives raising of octane number - diisopropil ether (DIPE) was studied.

Reactions of syntheses of DME and DIPE were carried out at the atmosphere pressure in the flowing catalytic installation on the block catalyst placed in the quartz reactor. A specific surface of catalysts defined on device Accusorb on adsorption of liquid nitrogen.

For preparation of zeolite-containing catalytic compositions at additive synthesis it has been spent dealuminizing of initial synthetic zeolites. For the purpose of extraction increase of aluminium from zeolites the alternated thermal and acid processings were carried out. Dealuminizing was spent for change of ratio SiO_2/Al_2O_3 for the purpose of hydroxyl groups stabilization and increase of acidity of zeolites.

The specific surface of the synthesized catalysts on the basis of block metal carriers makes on BET 250-320 m^2/g. Catalytic transformations of isopropyl alcohol were investigated on the catalysts of various acidity. Reaction was carried out in the range of temperatures 150-300^{o}C. There is no necessity to increase reaction temperature above 300^{o}C as selectivity of the catalyst and yield of DIPE decreases thanks to propylene formation. Activity of catalysts defined on degree of DIPE transformation from propanol, and selectivity - on concentration DIPE in a product. With growth of acidity of the support at DIPE transformation from propanol activity of the catalyst considerably increases, and selectivity on DIPE slightly decreases. Addition of Mo, Cu, Ni oxides in the support considerably raised activity of catalysts. Optimum composite of the catalysts for synthesis of DIPE in the conditions of experiment was on a basis of molybdenum and nickel compounds. On the catalysts with the content NiO/Al_2O_3 and $NaY\text{-}NiO/Al_2O_3$ soot was formed and activity of the catalyst decreased. The optimum temperature for DIPE formation with the yield 68.3 % was 300^{o}C.

For DME synthesis from methanol a powder of zeolite NaY with module Si/Al=5.1 was used which translated in the H-form by an ionic exchange of ammonia. The specific surface of the prepared zeolite was defined by method BET and was equal 420 m^2/g. According to data of the issue spectral analysis, that content of rare-earth metals in the zeolite was 1.9-2.0 weight %. The most suitable temperatures of reaction were in limits of 250-350^{o}C. There were carried the researches on influence of volume speed of methanol feed on yield of DME at the fixed temperature (340^{o}C) for determination of productivity of the catalyst with use of NiNaY catalyst. The increase in weight hour space velocity from 0.5 to 1.0 h^{-1} leaded to insignificant reduction of yield of DME - from 70 to 65 %, and at volume speed 2 h^{-1} the yield of DME sharply decreased. Thus, weight hour space velocity of the initial methanol 0.5-1.0 h^{-1} was optimum in the conditions of reaction. Presence of rare-earth elements at the catalyst stabilized its activity. At all catalysts the high selectivity in reaction was noted, and at the sample on the basis of La-Y selectivity on DME was the greatest (97.4 %).

Thus, the reactions of DME obtaining from methanol and DIPE from isopropanol at the flowing installation at atmospheric pressure were studied. As supports of the catalysts the block metal carriers with the honey comb structure of channels were used. The highly effective stable catalysts on the basis of zeolites which allow to receive DME from methanol with selectivity to 85-97 %, DIPE from isopropanol - to 60-65 % were developed.