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PRODUCTION OF ETHYLENE AND PROPENE FROM METHANOL AND DIMETHYLETHER ON ZEOLITE CATALYSTS

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Natural gas is an alternative source oil to obtain of synfuels and valuable products of the petrochemical synthesis. One of the most rational ways of converting natural gas is its conversion to syngas with the following conversion to the valuable hydrocarbons. Industrial processes of production of light olefins from non-oil raw build up by the Mobil (MTO), UOP and Norsk Hydro and Lurgi (GTP) on the basis of zeolite catalyst ZSM-5 and SAPO-34 type.

In the present work results of regular investigations of influence of active metal nature, method of metal adding, way of zeolite modification in ZVM, analogue of ZSM-5 (Nizhniy Novgorod's Sorbents, SiO_2/Al_2O_3=31,2), and SAPO-34 (Zeolyst) -based catalysts and conditions of methanol and dimethylether (DME) conversion on the catalytic activity and yield of light C_2-C_4 olefins are submitted.

The zeolite structure was characterized by XRD. Total acidity and zeolite acidity spectrum were investigated by NH_3-TPD in Chemical Faculty MSU. Catalytic properties of synthetic samples were studied on the pilot flowing setup of high pressure with fixed bed at atmospheric pressure.

It is shown, that yield of light olefins $C_{2=}$–$C_{4=}$ depends of zeolite type, metal nature and method of its adding to catalyst composition, and also conditions of experiments. Introduction of Zn, Fe and Co metal to catalyst composition leads to increasing of the olefins yield. Total yield of light olefins slightly increased with growing of the temperature, but then under 450°C decreased due to intensive cracking of products.

The study of the influence of zeolite modification by P and Zr has shown that yield of $C_{2=}$–$C_{4=}$ at 350-375°C most increased under P modification, as well as joint modification by P and Zr, $C_{2=}$ and $C_{3=}$ yield has formed near 20%, $C_{4=}$ yield - 10-12%. Yield of methane at the temperature before 400°C didn't exceed 3%. Conversion of DME equals 94-96% at the same time. Zeolite modification by P and Zr changes both general acidity of zeolites, spectrum of acidity and nature of acid sites that leads to changing of activity and selectivity of catalysts. Yield of $C_{2=}$–$C_{4=}$ olefins equals ~52-61%, ethylene ~12%, propylene ~23-32% and butenes ~16% in MeOH conversion accordingly. Introduction in the catalyst of promotors has led to substantial growth of $C_{2=}$ and $C_{3=}$ selectivity, C_{4+} - hydrocarbons practically are absent, an output of CH_4 insignificant. On Zn-zeolite catalyst with promotors conversion of DME in mix with water is achieved 96-98 % at 350-425°C, yield of $C_{2=}$–$C_{4=}$ olefins equals ~52 %, ethylene ~21-26 %, propylene ~18 % and butenes ~7-9 % accordingly.

SAPO-34 -based catalyst reached comparatively high yields of light olefins $C_{2=}$–$C_{4=}$ at 350-375°C: ~ 74–83%, of them $C_{2=}$ ~29-35%, $C_{3=}$ ~38-47%, $C_{4=}$ ~3-7% in MeOH and DME conversion ~96%. Yield of C_{5+} hydrocarbons doesn't exceed 1%, and yield of methane ~1% basically. Reduction of partial pressure of MeOH, and time of contact at simultaneous increase in temperature results in essential increase in $C_{2=}$–$C_{3=}$ yield, and to reduction of $C_{4=}$ yield. SAPO-34 - based catalyst are characterized by smaller stability in comparison with ZSM-5, however higher selectivity.

High selectivity of catalysts on basis SAPO-34 have allowed to offer bases for Russian process technology of $C_{2=}$–$C_{3=}$ production from MeOH and DME analogue of FCC processes for industrial applications.