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Conversion of ethyl acetate into benzene–toluene–xylene fraction over MFI zeolite-based catalysts

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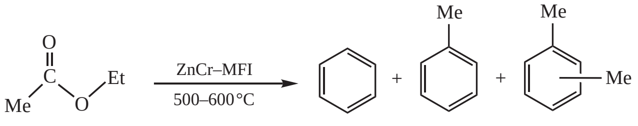
Ethyl acetate conversion over MFI zeolite-based catalysts synthesized by the hydrothermal-microwave method was investigated for the first time. MFI zeolites in the proton form and promoted with zinc and chromium catalyzed ethyl acetate conversion to liquid hydrocarbons with an almost 100% content of aromatic hydrocarbons. Moreover, the content of the benzene–toluene–xylene (BTX) fraction in aromatic hydrocarbons reached 92–93 wt%.



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The manufacture of petrochemicals from raw materials of plant origin not only helps to reduce the anthropogenic load on the environment but also expands the raw material base of the petrochemical industry. The development of eco-friendly processes for obtaining petrochemical intermediates from renewable raw materials is an urgent scientific and engineering task. One of the promising renewable sources of hydrocarbons are esters, in particular, ethyl acetate[1,2] which can be produced by processing renewable raw materials such as ethanol[3–5] and acetic acid.[6,7] Ethyl acetate is also considered as a biofuel.[8]

The use of renewable raw materials and catalysts complies with the principles of ‘green chemistry’. There are very few published data on the conversion of ethyl acetate over zeolite catalysts[9–11] when experiments were carried out at atmospheric pressure.

The study of ethyl acetate transformation over faujasite zeolites[9] (NaX, USY, HY) showed that in the temperature range of 300–450 °C the predominant products were ethylene, acetone, and acetic acid. The observed deactivation of the catalysts was attributed to the formation of aromatic hydrocarbons, the number of which was not specified. The conversion of a mixture of ethyl and methyl acetates (50:50, vol%) was carried out at 250–390 °C using the mordenite framework inverted (MFI) zeolite (SiO_2/Al_2O_3 = 18)[10] when condensed and monocyclic aromatic hydrocarbons with a noticeable content of oxygen-containing arenes were the main reaction products. The highest yield of monocyclic aromatic hydrocarbons (51 wt%) at a 97% feed conversion was achieved at 390 °C and a weight hourly space velocity of 4.6 h^{-1}. Under these conditions, the yield of the benzene–toluene–xylene (BTX) fraction composed mostly of xylenes was 22 wt% and the yield of xylenes was 16 wt%. It should be noted that the content of the BTX fraction in aromatic hydrocarbons did not exceed 43%, and a sharp growth in the yield of acetone and acetic acid occurred after 5 h of the experiment. However, insufficient data were available on the method of analysis of reaction products; probably, only the analysis of liquid organic products was reported.

The transformations of ethyl acetate over the MFI zeolite (SiO_2/Al_2O_3 = 50) were studied at 500 °C in a fluidized bed reactor.[11] The yields of the main products (in terms of carbon in the initial feedstock) were as follows: liquid organic products, 9.3%; coke, 5.7%; CO, 7.3%; CO_2, 5.8%; alkanes C_1–C_5, 21.6%, and gaseous olefins, 51.3%. In the liquid organic products, the content of phenols was 75% and the content of aromatic hydrocarbons did not exceed 10%.

In this work we studied for the first time ethyl acetate conversion over MFI zeolite (SiO_2/Al_2O_3 = 40) which was synthesized by the accelerated hydrothermal-microwave method. This method significantly reduces the synthesis time compared to the traditional hydrothermal method. The zeolite was used in the proton (HMFI) and Zn–Cr-promoted (ZnCr–MFI) forms. Zinc and chromium (1 wt% of each) were incorporated into the MFI zeolite by impregnation. Our previous studies showed that the co-promotion of high-silica zeolites with zinc and chromium had a synergistic effect and led to the formation of Lewis acid sites that differ in properties from those formed when promoters were introduced separately[12]. Use of zeolites synthesized by hydrothermal-microwave method and the presence of these active sites in MFI zeolite-based catalysts lead to an increase in selectivity of the formation of aromatic hydrocarbons in the processes of hydroconversion of rapeseed oil,[13,14] conversion of propane–butane fraction,[15] and conversion of isobutanol.[16] The synthesis of catalysts and their characterization is given in the Online Supplementary Materials.

In this study, high yields of arenes were attained only at 100% conversion of ethyl acetate. Therefore, we present only these results. Commonly, the yields of products can be calculated as the mass of the product divided by the mass of the feed (ethyl acetate). However, according to published data,[9–11] in the case of zeolites the first step of ethyl acetate conversion is its cracking into ethylene and acetic acid. The maximum theoretical yield of hydrocarbons from acetic acid is achieved through its dehydration to ketene which, in turn, is transformed into ethylene and carbon monoxide. Importantly, the maximum theoretical yield of C_{2+} hydrocarbons from ethyl acetate is 64%. Unless specifically stated, the yields of products are calculated (%) from this theoretical value. The description of catalytic tests is available in the Online Supplementary Materials. Catalyst characterization data confirm formation of the MFI structure. A greater part of the pore volume and specific surface area is provided by ultramicropores with pore sizes less than one nm. Catalyst characteristics change insignificantly after processing and oxidative regeneration. Our experiments showed that the MFI catalyst with a silica module 40 worked five cycles with regeneration (in total 10 h) without loss of activity and selectivity for aromatic hydrocarbons.

The yields of aromatic hydrocarbons in the course of ethyl acetate conversion over the non-promoted HMFI and ZnCr–MFI catalysts are shown in Figure 1. It is seen that the results obtained are ambiguous. As temperature is increased from 450 to 600 ºC, the yield of aromatics over HMFI steadily decreases from 30 to 16%, whereas the other byproducts are carbon monoxide, carbon dioxide, C_1–C_4 hydrocarbons, coke, and non-aromatic hydrocarbons C_{5+}. Acetone and acetic acid are detected among the products only at 450 °C (8% in terms of ethyl acetate feed). These results are inconsistent with the data on the transformations of other raw materials[12–15] when the arene yields grew with the reaction temperature. At the same time, in the presence of ZnCr–MFI the yield of aromatic hydrocarbons at 450 °C is as low as 14% (see Figure 1). As the temperature is raised from 450 to 500 °C, the yield of aromatic hydrocarbons grows to 25%. However, further raising the temperature to 600 ºC causes a reduction in the yield of aromatic hydrocarbons to 17%. Other byproducts are the same as in the case of zeolite HMFI. Acetone and acetic acid are observed among products at 450 and 500 °C (11 and 6%, respectively, in terms of ethyl acetate feed).

The temperature dependence of the content of aromatic hydrocarbons in liquid organic products is shown in Figure 2. For the HMFI sample, the content of aromatic hydrocarbons in liquid organic products increases from 83 to 90% as temperature is increased from 450 to 500 °C [see Figure 2(*a*)]. Upon further raising the temperature, the content of aromatic hydrocarbons in liquid hydrocarbons remains unchanged as 88–90% at 550–600 °C. The BTX content in aromatic hydrocarbons increases from 74 to 93% as the temperature is increased from 450 to 550 °C. In the presence of the ZnCr–MFI catalyst the content of aromatic hydrocarbons in liquid organic products sharply grows from 69 to 100% with raising the temperature to 600 °C [see Figure 2(*b*)]. At the same time, the BTX content in the aromatic hydrocarbons formed in the presence of ZnCr–MFI grows from 67 to 93% as temperature is increased from 450 to 550 °C. Thus, our studies have revealed that the HMFI zeolite synthesized by the hydrothermal-microwave method makes it possible to convert ethyl acetate into aromatic hydrocarbons, mainly into the BTX fraction. The co-introduction of zinc and chromium causes an increase in the content of aromatics in liquid organic products to 100%.

Note that the HMFI zeolite promoted with Zn and Cr unexpectedly provides lower yields of aromatic hydrocarbons. In our opinion, this result is consistent with the mechanism of ethyl acetate conversion to aromatic hydrocarbons according to which the reaction occurs through the formation of ethylene. According to reported data,[17] olefin aromatization over HMFI proceeds by the mechanism including hydrogen transfer from an oligomer to a lower olefin with the simultaneous formation of an aromatic component and paraffin. The key role of Brønsted sites consists in the oligomerization of alkenes and in the dehydrocyclization of oligomers.

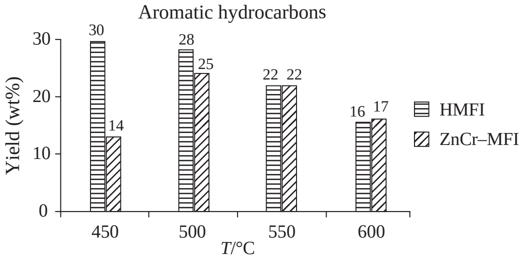

Figure 1 Yields of aromatic hydrocarbons produced by ethyl acetate conversion over HMFI and ZnCr–MFI catalysts at various temperatures. LHSV = 3.0 h^{-1}; time-on-stream, 2 h.

The mechanism of the action of promoted HMFI catalysts in the aromatization of lower alkanes relies on the assumption that strong L-sites, including metal ions, are involved in the dehydrogenation of saturated molecules. In our case, the stage of dehydrogenation is absent. The Brønsted sites of HMFI directly catalyze the oligomerization of alkenes and the dehydrocyclization of oligomers. Promoters such as Zn and Cr would significantly decrease the number of Brønsted sites and their aromatization activity. On the other hand, the Lewis sites of promoters can also participate in the formation of aromatic hydrocarbons through the interaction of allyl structures formed by olefins on the Lewis sites of promoters with the simultaneous release of hydrogen molecules. However, in the case of ethylene transformations this route to aromatic structures is hardly possible. Therefore, the use of the HMFI zeolite is more preferable for the production of aromatic hydrocarbons from ethyl acetate.

In the study of ethylene conversion over the HZSM-5 catalyst,[18] two mechanisms for the formation of arenes and paraffins depending on reaction temperature were proposed. The first mechanism provides the dehydrocyclization of C_{6+} olefins accompanied by the release of hydrogen into the reaction medium and the subsequent formation of paraffinic compounds *via* hydrogenation, while the second mechanism includes the hydrogen transfer between naphthenic compounds and olefins accompanied by the generation of arenes and paraffins. The experimental data[18] obtained under the conditions provide evidence for the occurrence of dehydrocyclization reactions, which are favorable at higher temperatures. Thus, our data on the conversion of ethyl acetate over HMFI are more consistent with the second mechanism controlling the formation of aromatic hydrocarbons. This assumption is confirmed by the fact that with

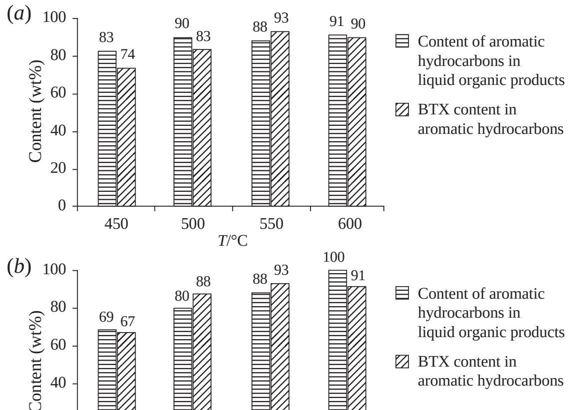

Figure 2 Content of aromatic hydrocarbons in liquid organic products and BTX content in aromatic hydrocarbons produced by ethyl acetate conversion over (*a*) HMFI and (*b*) ZnCr–MFI catalysts at various temperatures. LHSV = 3.0 h^{-1}; time-on-stream, 2 h.

an increase in temperature from 450 to 600 °C the yield of ethylene increases from 12 to 28% with the concomitant decrease in the yield of aromatics (see Figure 1).

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.07.017.

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