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

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Preparation of the catalysts. The MFI zeolite was synthesized by the hydrothermal-microwave method. Sodium aluminate, sodium chloride, tetra-*n*-propylammonium hydroxide, and tetraethyl orthosilicate were mixed in distilled water under vigorous stirring. The resulting gel was stirred for 2 h and aged at room temperature overnight. Then, the gel (20 ml) was placed in a Teflon autoclave and put in a Berghof SpeedWave 4 microwave system (maximum power, 1500 W; 2.45 GHz). The crystallization step was performed for 210 min at 210-215°C. MFI obtained in the sodium form was filtered, washed with distilled water, and dried at 190°C for 2 h. Afterwards, the material was calcined at 550°C for 5 h to remove the organic template. Finally, the Na-MFI was exchanged five times with ammonium nitrate (0.5 N) at 353 K and calcined at 773 K for 2 h and at 873 K for 2 h to obtain the MFI zeolite in the proton form (HMFI).

The zeolite was promoted by impregnation with aqueous solutions of zinc nitrate and chromium nitrate. Excess moisture was removed by evaporation at 100°C with subsequent drying at 190°C for 2 h and calcining at 500-600°C, which led to the transformation of zinc nitrate and chromium nitrate into oxides. In the resulting catalyst, the content of zinc and chromium was 1 wt % each.

Catalytic experiments. Conversion of ethyl acetate was carried out in a heated quartz flow-type fixed-bed reactor equipped with an axially located pocket for a thermocouple. The catalyst was loaded in the middle part of the reactor, and the free volume of the reactor before and after the catalyst was filled with crushed quartz. For both HMFI and ZnCr-MFI, the catalyst loading was 2.3 g; the particle size was 0.5-2 mm. The catalyst was heated to the reaction temperature in a stream of nitrogen (2 h^{-1}) for 1 h. When the nitrogen supply was stopped, ethyl acetate feeding was started.

The gas products were analysed by gas chromatography using steel packed columns (2 m × 5 mm). Helium was a carrier gas. A Porapak Q column was used for the separation of CH_4, CO_2, C_2H_4, and C_2H_6 at 70°C. H_2, O_2, N_2, CO, and CH_4 were separated at 30°C using a CaX zeolite-packed column. Hydrocarbons C_{3+} were determined at 70°C using a column packed with 5%Na_2CO_3/Al_2O_3. Liquid products were collected for 2 h in a cooled receiver at -80 °C and analyzed on a Crystallux-4000 gas chromatograph and a DB-PETRO column (100 m × 0.25 mm × 0.5 μm) according to ASTM D5134. The components were identified by GC-MS (Thermo Scientific Trace GC Ultra DSQ II) using an HP-5MS column (30 m × 0.25 mm × 0.25 μm).

The examples of products mass balance are given in Table S2.

Catalyst characterization. According to XRD (Rigaku MiniFlex 600, Japan, CuK_{α} radiation, λ = 1.54187 Å), the phase composition of the synthesized catalysts corresponded to the MFI structure (Figures S1, S2). The introduction of the promoters and catalytic tests did not cause significant changes in the phase composition.

The morphology of catalyst particles was studied by SEM (JEOL JSM-6390LA, Japan). The structure of the synthesized MFI is represented by typical prismatic crystals about hundreds nm in size which are stacked and agglomerated to larger polycrystals (Figure S3).

The texture properties of the catalysts were determined by low-temperature nitrogen adsorption-desorption on a Quantachrome AUTOSORB-1C/MS/TPR instrument. The results were processed with the help of the Quantachrome AS1Win software package using the BET, *t*-plot, and NLDFT methods (Table S1). The obtained adsorption-desorption isotherms are typical for microporous materials, such as MFI zeolites. According to the IUPAC recommendations and extensive working experience with microporous materials, calculations were made using the BET model in the low relative pressure range ($<0.02\ P/P_0$). Most of the pore volume and specific surface area is provided by ultramicropores with pore sizes less than one nm. The presence of micropores is evidenced by a dramatic absorption of N_2 in the adsorption isotherm at very low pressures. Therefore, information on the micropore size and micropore surface cannot be obtained with the use of nitrogen as an adsorbate. Only the volume of the micropores can reliably be estimated. In addition, the adsorption–desorption isotherms make it possible to suggest that the catalyst samples contain pores with a size of 2–5 nm. The volumes of micro- and mesopores of different sizes were determined by the NLDFT method. The shape of the adsorption–desorption isotherms indicates that the catalyst samples contain a small amount of mesopores. The hysteresis observed can apparently be attributed to the presence of poorly accessible micropores. This assumption is based on the finding that nitrogen absorption increases with decreasing pressure, as is seen from the desorption isotherms. In fact, the equilibrium adsorption isotherm cannot be obtained in this case; therefore, the additional ‘absorption’ of nitrogen is recorded during desorption. In general, it should be emphasized that for catalysts based on the MFI zeolite the total specific surface area and the specific surface area of micropores decrease after catalysis and regeneration. However, the ultramicroporous structure remains dominant in the composition of the used samples; in general, this finding indicates that the texture of the catalysts is stable.

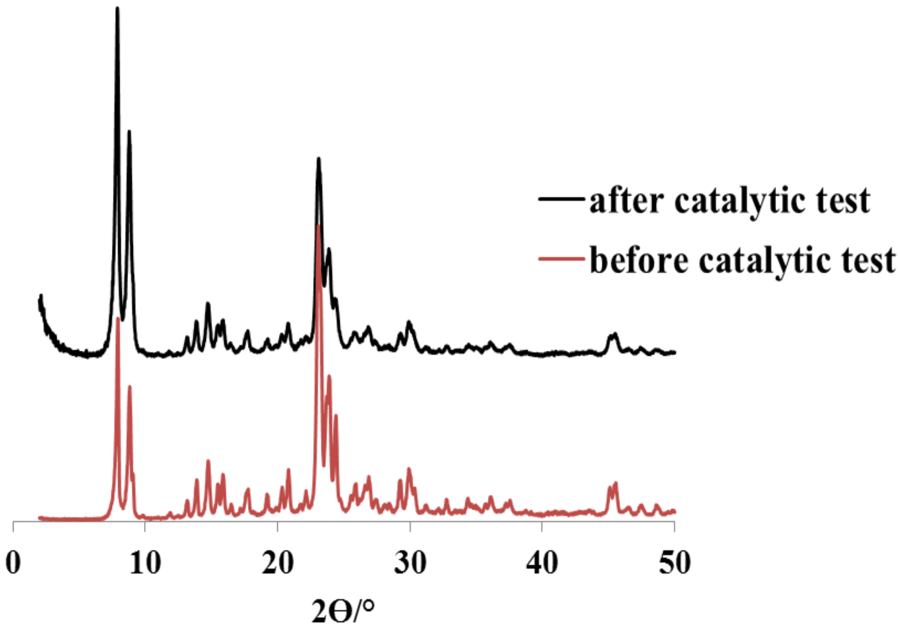

Figure S1 XRD patterns of the HMFI zeolite before and after catalytic test.

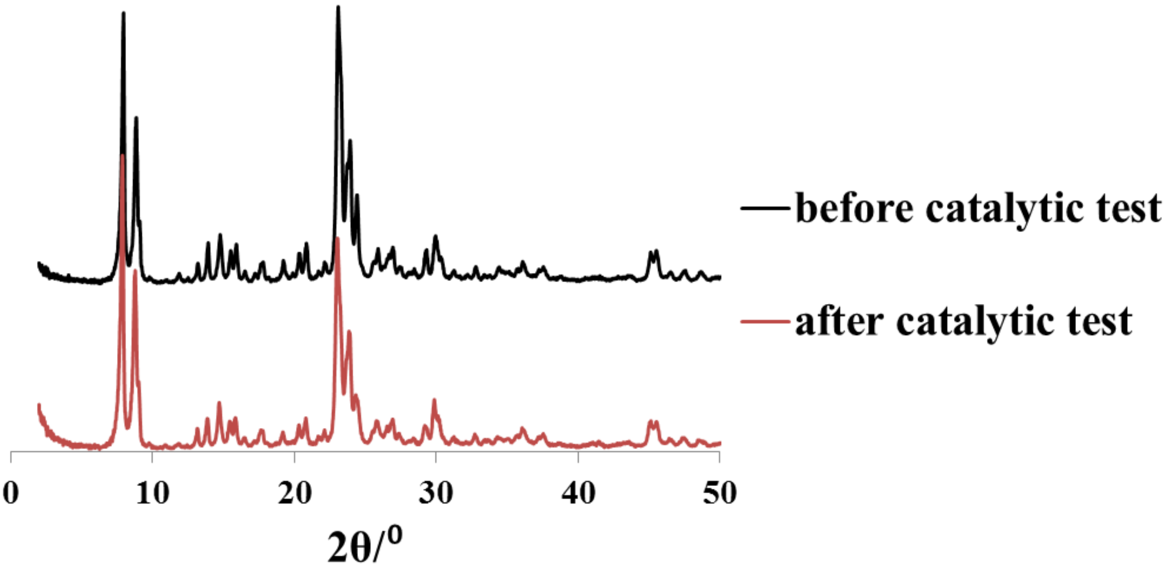

Figure S2 XRD patterns of the ZnCr-MFI zeolite before and after catalytic test.

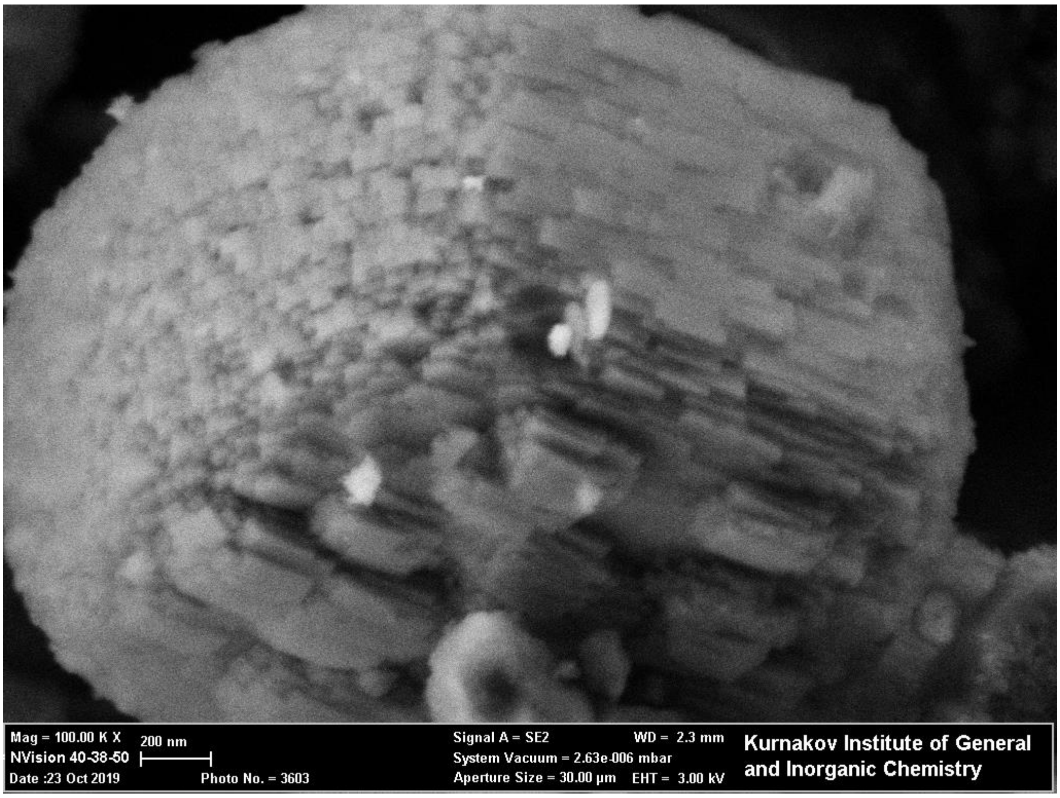

Figure S3 SEM picture of the ZnCr-MFI zeolite.

Table S1 Texture properties of ZnCr-MFI.

Catalyst	Surface area, $m^2\ g^{-1}$		Pore volume, $cm^3\ g^{-1}$		
	specific [a]	micropores [b]	total [c]	micro [d]	meso [d]
ZnCr-MFI (before catalytic test)	391	376	0.18	0.15	0.03
ZnCr-MFI (after catalytic test)	376	349	0.19	0.15	0.04

[a] Calculated by BET.

[b] Calculated by *t*-plot.

[c] Determined at $P/P_0 = 0.99$.

[d] Calculated by NLDFT.

Table S2 Product yields (weight balance) calculated in terms of ethyl acetate feed [a]

Products	**Yield, wt.%**	
	HMFI	ZnCrMFI
$CO+CO_2$	38	35
H_2O	13	10
Oxygenates	traces	4
Coke and heavy ends (residues)	5	6
Hydrocarbons	44	45
Total	100	100
Hydrocarbon yields, wt %		
Alkanes C_1-C_4	10	3
Ethylene	5	12
Propylene	5	7
Isobutylene	2	2
Other butenes	2	2
Benzene	2	1
Toluene	6	7
Ethylbenzene	1	1
p-Xylene	2	2
m- and *o*-Xylenes	4	3
Aromatic hydrocarbons C_{9+}	3	2
Other non-aromatic hydrocarbons C_5-C_{12}	2	3

[a] HMFI and ZnCrMFI-catalysts; $T = 500^{o}C$; LHSV, 3 h^{-1}; time-on-stream, 2 h; conversion of ethyl acetate, 100%.