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A novel direct catalytic production of *p*-xylene from isobutanol

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Catalysts synthesis

Micro-mesoporous composite MFI/MCM-41 was synthesized by new hydrothermal-microwave dual templating method which was developed by us [1]. The developed method involves the preparation of an aqueous solution containing aluminum isopropoxide, tetrapropylammonium hydroxide, and tetraethyl orthosilicate. The solution was subjected to microwaving in a Teflon autoclave of a Berghof SpeedWave 4 microwave digestion system, which provided uniform heating of the mixture to 115°C, for 110 min. After that, an aqueous solution of cetyltrimethylammonium bromide and sodium hydroxide was introduced into the autoclave, and the resulting mixture was microwaved at 190°C for 180 min. The resulting precipitate was washed with distilled water and dried in a muffle furnace at 110°C, and the organic templates were removed by annealing in air at 550°C. The Na-form of MFI/MCM-41 composite was converted into a hydrogen form by ion exchange with 0.5 N ammonium nitrate solution. The procedure was repeated 4 times. After that the composite was filtered, dried at 190°C for 1.5 h and then calcined at 550°C for 2 h and at 600°C for 2 h. The composite was obtained in hydrogen form. Promotion of the composite was carried out 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°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 % of each.

Catalytic experiments

Catalytic isobutanol conversion was carried out in a heated quartz flow type reactor with axially-located pocket for thermocouple. Catalyst was placed in the middle part of the reactor, the free volume of the reactor before and after the catalyst was filled with quartz nozzle. Catalyst loading was 2.5 g for MFI/MCM-41 and 2.1 g for ZnCrMFI/MCM-4, fraction 0.5-2 mm. The catalyst was heated to the reaction temperature in a stream of nitrogen (2 h^{-1}) for 1 h, and then, without stopping the nitrogen supply, isobutanol feeding was started. The gas and liquid products were

analyzed by GC method. A detailed description of the GC analysis is presented in the previous publication [2].

Characterization

It was shown by XRD (Rigaku MiniFlex 600, Japan, Cu – K_α radiation, λ= 1,54187 Å) that phase composition of synthesized catalysts corresponds to MFI/MCM-41 structure (Fig. S1, S2). The introduction of promoters and catalytic tests did not lead to the changes of phase composition.

The morphology of the catalyst particles was determined by the SEM (JEOL JSM-6390LA, Japan) and TEM methods (LEO912 AB OMEGA, accelerating voltage 120kV).

It is seen that the structure of synthesized MFI/MCM – 41 is represented by zeolite particles with characteristic form, which are surrounded by amorphous mesoporous silica matrix (Fig. S3, S4).

The texture properties of synthesized catalyst were determined by low-temperature nitrogen adsorption-desorption on Quantachrome AUTOSORB-1C/MS/TPR instrument. The results were processed using the Quantachrome AS1Win software package using the Brunauer–Emmett–Teller (BET), *t*-plot, Barrett–Joyner–Halenda (BJH) methods (Table S1).

The mass balance of the best experiment is given in Table S2.

References

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2. A. G. Dedov, A. S. Loktev, A. A. Karavaev, M. N. Kartasheva, S. V. Markin and I. I. Moiseev, *Dokl. Chem.*, 2016, **471,** 334.

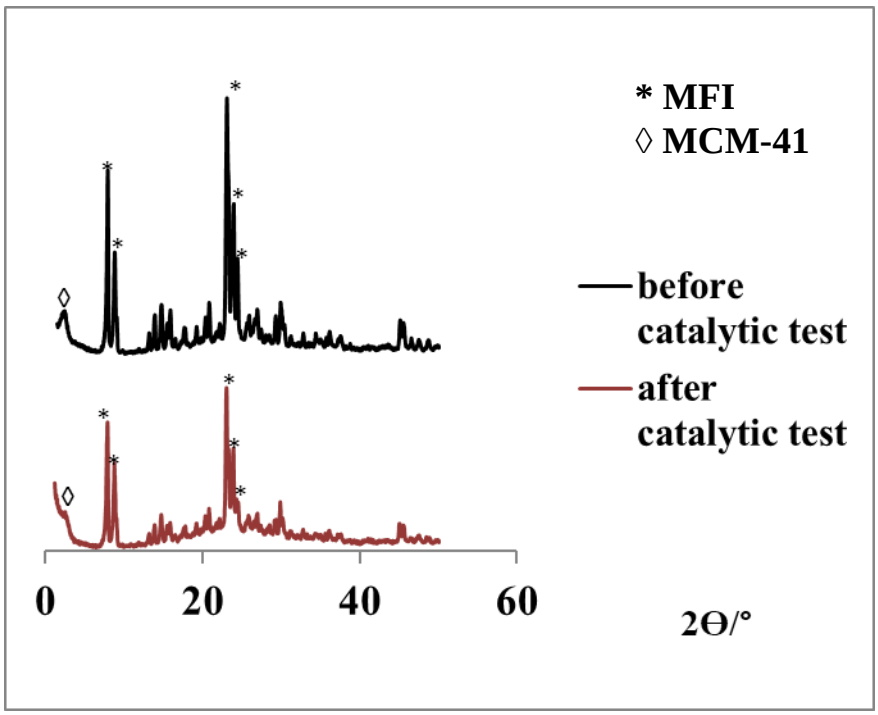

Figure S1 XRD patterns of micro-mesoporous MFI/MCM-41 composite before and after catalytic test.

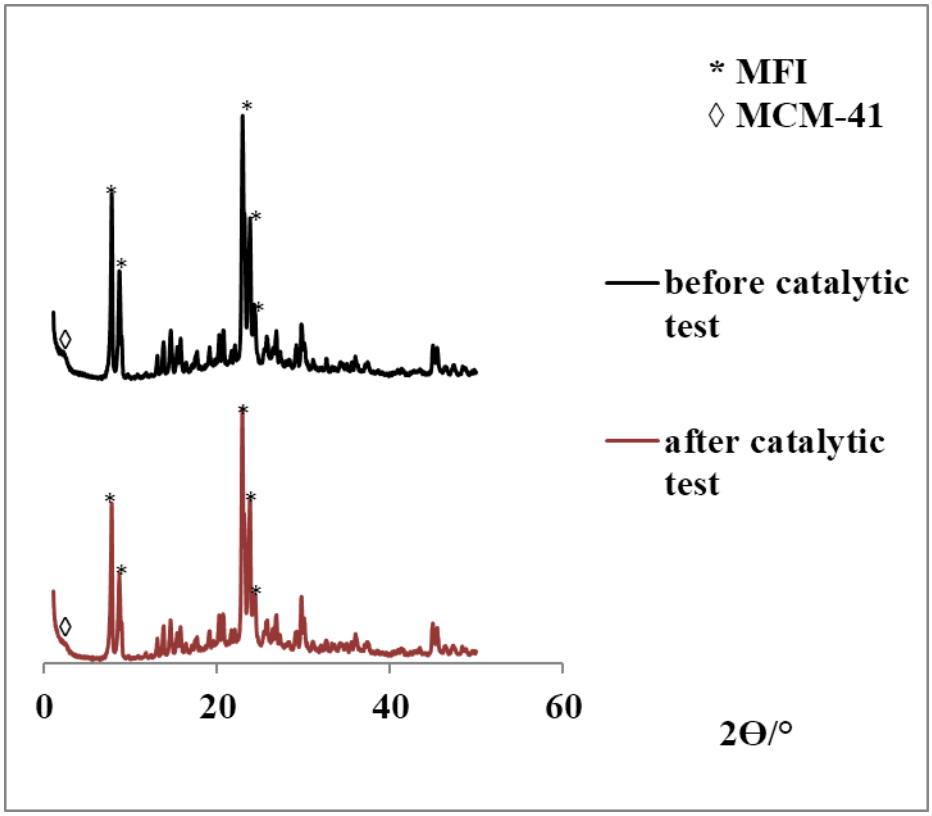

Figure S2 XRD patterns of micro-mesoporous MFI/MCM-41 composite promoted by Zn and Cr before and after catalytic test.

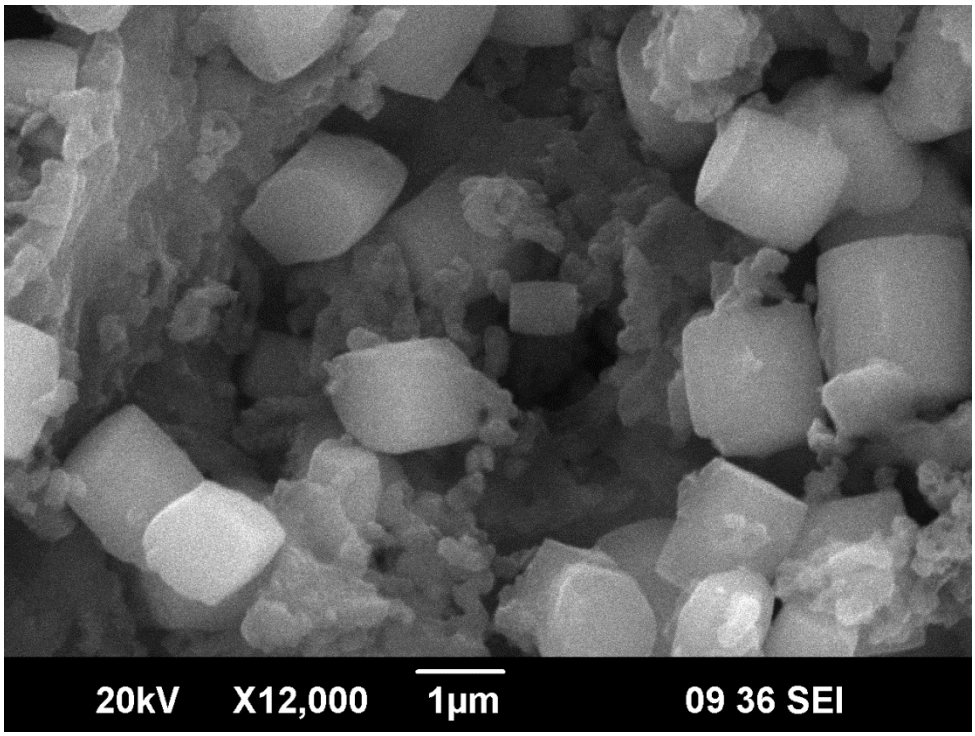

Figure S3 SEM picture of micro-mesoporous MFI/MCM-41 composite.

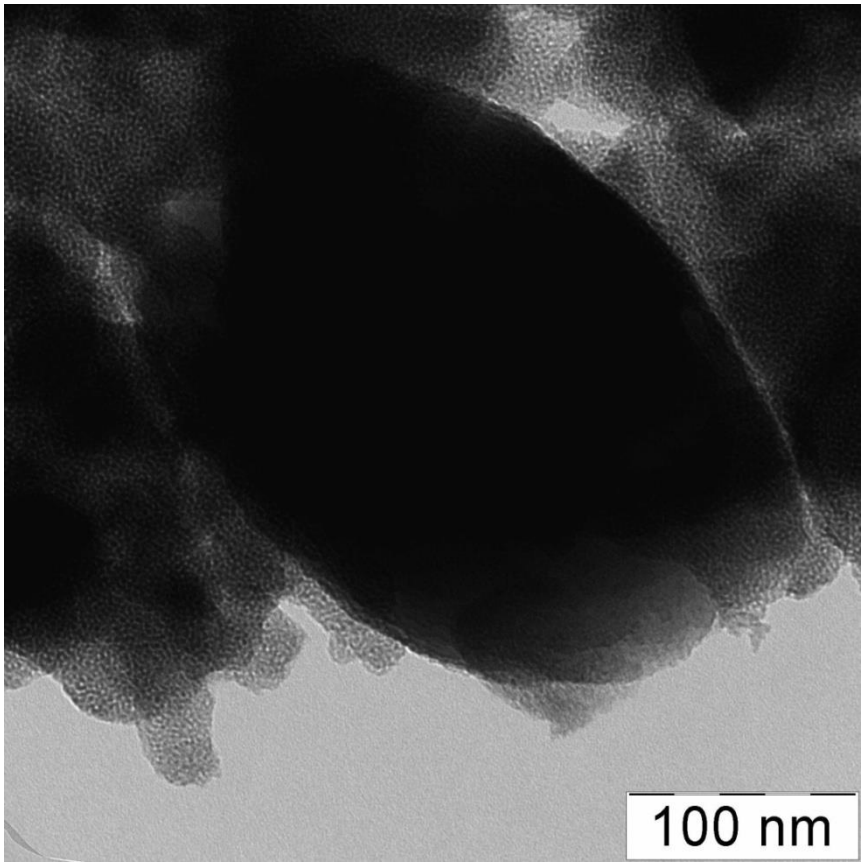

Figure S4 TEM picture of micro-mesoporous MFI/MCM-41 composite.

Table S1 Texture properties of ZnCrMFI/MCM-41 composite.

Catalyst	Specific surface area, $m^2\ g^{-1}$			Pore volume, $cm^3\ g^{-1}$		
	Total	Micropores	External	Total	Micro	Meso
ZnCrMFI/MCM-41	454	377	77	0,32	0,18	0,14

Table S2 Products yield (mass balance) calculated on the hydrocarbon part in isobutanol feed stock (without water), ZnCrMFI/MCM-41 catalyst, 450 °C, Weight Hour Space Velocity of isobutanol WHSV=2.3 h^{-1}, time on stream 2 h. Isobutanol conversion 100%.

Products	**Yield, wt. %**
H_2	1
Alkanes C_1-C_4	12
Ethylene	5
Propylene	14
Isobutylene	7
Other butenes	6
Benzene	2
Toluene	8
Ethylbenzene	2
p-Xylene	7
m-Xylene + *o*-Xylene	2
Other hydrocarbons C_5-C_{12}	17
Coke and heavy ends	17
Total	100