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Comparative study of methanol and dimethyl ether conversions to light olefins over a Mg–HZSM-5/Al_2O_3 catalyst in nitrogen and syngas atmospheres

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Catalyst used. In this study, we used a Mg–HZSM-5/Al_2O_3 zeolite-containing catalyst, which has previously proved effective in the synthesis of light olefins from DME and methanol in an inert medium. In order to prepare the catalyst, the following materials were employed:

– a high-silica commercial ZSM-5 zeolite (SiO_2/Al_2O_3 = 37) powder manufactured in an ammonium form by the Angarsk plant of catalysts and organic synthesis (Russia); the hydrogen form (HZSM-5) was obtained by calcination of the ammonium form at 500 °C for 4 h in air.

– an aluminum oxide (Al_2O_3) powder manufactured by the Promcatalysis (Russia);

– a magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$) powder;

– deionized water.

The catalyst was prepared by mixing the HZSM-5 zeolite with the Al_2O_3 slurry and subsequent molding of granules. Afterwards, the granules were dried in air and calcined at 500 °C for 4 h. Next, the granules were modified with magnesium by an incipient wetness impregnation with a $Mg(NO_3)_2 \cdot 6H_2O$ aqueous solution at room temperature followed by the drying and calcination at 500 °C for 4 h. The magnesium content in the as-prepared catalyst was 1 wt%.

Catalyst performance tests and product characterization.

The Mg–HZSM-5/Al_2O_3 catalyst (3 g) was loaded into the isothermal zone of the reactor as 5–10 mesh size fraction pellets mixed with quartz in a volume ratio of 1:2. During the experiment,

the inlet and outlet gas composition, gas flow rate, and WHSV were monitored. Gas and liquid products were collected and analyzed.

The gas and liquid products were analyzed by a gas chromatography on a Chromatech-Crystall 5000 instrument (Russia) using chromatographic columns in the programmed temperature rise mode from 50 to 280 °C in a 50 ml/min argon flow. A packed column filled with a SKT-4 activated carbon phase (1 m × 3 mm × 0.2–0.5 mm) was used to analyze inorganic gases. A Poraplot Q open-tubular column (25 m x 0.53 mm x 10 μm) was used to analyze methanol and organic gases. Inorganic and organic products were identified on a thermal conductivity detector and a flame ionization detector, respectively. The chromatogram peaks were obtained and processed using a «Chromatech Analytic» software.

Conversion (X) was calculated by Eq. (1):

$$X = \frac{n_0 - n}{n_0} \cdot 100\ (\%) \qquad (1)$$

where n_0 and n are amounts (mol) of reactants at the inlet and outlet of the reactor, respectively.

The product yield (Y) was calculated by Eq. (2):

$$\text{Yield} = X \cdot \frac{\mu_i \cdot N_i}{\sum \mu_i \cdot N_i}\ (\%) \qquad (2)$$

where μ_i is the molar fraction of product i, and N_i is the number of carbon atoms in a product molecule.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) *in situ* measurements of the catalyst used. *In situ* DRIFTS measurements were carried out using a high-temperature PIKE Diffus IR cell coupled to a Vertex-70 DRIFT spectrometer (Bruker, USA) at temperatures of 300, 320, 350, 400, and 450 °C. Prior to the experiment, the specimen was initially calcined at 450 °C in an argon flow. Then, the specimen was cooled to the experiment temperature, and argon was switched to a mixture of DME/N_2 or DME/syngas/N_2. The spectrum was continuously recorded for 5 min in the mode of 194 scans/spectrum with 2 cm^{-1} resolution in the range of 600–4000 cm^{-1}. The spectra were processed in an OPUS-7 software package.

Table S1 Specific surface area, pore volume, and acid site concentration of Mg–HZSM-5/Al_2O_3

Specific surface area[a]/$m^2 \cdot g^{-1}$	Pore volume/$cm^3 \cdot g^{-1}$		
	Total[a]	Micropores[b]	Mesopores[c]
286	0.214	0.133	0.081
Acid site concentration[d]/$mmol \cdot g^{-1}$			
Weak[e]	Strong[f]	Total	
256	278	534	

a) Determined by BET; b) determined by Horvath-Kawazoe; K; c) determined by BJH; d) determined by "total" – "micro" – "meso"; d) determined by NH_3-TPD; e) NH_3 desorbed at the peak temperature below 350 ºC; f) NH_3 desorbed at the peak temperature above 350 ºC.

Table S2 Alkane yield at different temperatures and reaction media (0.1 MPa, 1.6 h^{-1})

Reaction medium	Temperature/ºC				
	300	320	350	400	450
	Yield/%				
Methanol/N_2	3.0	11.8	28.3	31.1	22.7
DME/N_2	6.4	21.7	35.5	30.8	23.9
Methanol/syngas	3.1	10.8	32.3	34.2	28.5
DME/syngas	1.3	6.7	44.7	40.3	29.5

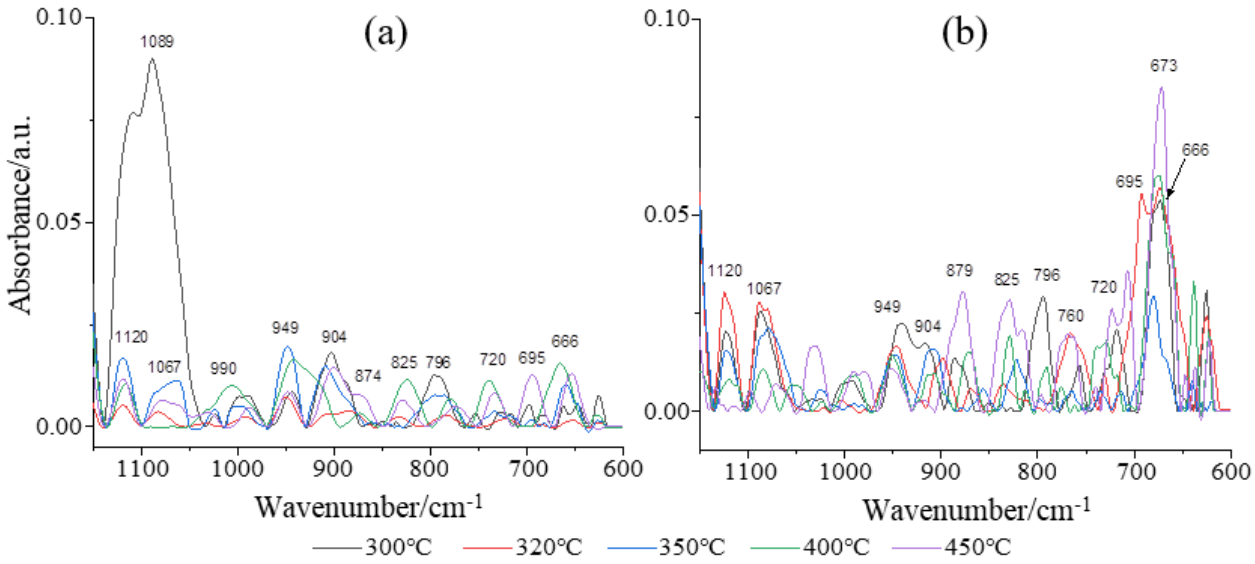

Figure S1 DRIFT spectra of the Mg–HZSM-5/Al_2O_3 surface in the flow of DME/syngas/N_2 (a) and DME/N_2 (b) collected after 10 min at different temperatures.