Dimethyl Ether to Olefins Conversion in a Slurry Reactor: Effects of the Size of Particles and the Textural and Acidic Properties of the MFI-Type Zeolite

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Abstract—Effects of the particle size of a suspended zeolite catalyst based on the commercial MFI-type (high modulus zeolite, HMZ) zeolite on its physicochemical characteristics and catalytic properties in the conversion of dimethyl ether (DME) in a three-phase system with a slurry reactor are studied. In order to gain insight into the relationships between the physicochemical characteristics of MFI-type zeolites and their catalytic properties, the textural, acidic, and catalytic properties of HMZ zeolites and synthesized nanocrystallites of the zeolite with the MFI structure are compared. It was found that, in the conversion of DME in the slurry reactor, the catalytic properties of the MFI zeolite are strongly affected by the size of particles of the suspended catalyst: on passage to nanosized suspensions, the activity of the catalyst grows by several times. Reduction in the size of catalyst particles leads to an increase in the yield of hydrocarbons C_5^+ and a decrease in the yield of lower olefins. At the same dispersity of suspensions, the catalytic properties of suspended catalysts are considerably affected by the distribution of acid sites over strength in the studied zeolite sample and the fraction of amphoteric sites in them.

Keywords: catalysis in the dispersed phase, zeolites with the MFI-type structure, physicochemical characteristics of MFI-type zeolites, nanosized zeolites, dimethyl ether conversion, lower olefins **DOI:** 10.1134/S0965544117070052

In recent years, the technologies of deep natural gas processing into lower olefins through methanol and/or dimethyl ether (DME) derived from syngas have been intensively studied and implemented all over the world [1–11]. These schemes are used for the synthesis of not only lower olefins but also higher boiling hydrocarbons [3, 5, 12–16].

The process of syngas conversion to olefins through methanol makes it possible to produce ethylene and/or propylene with yields at a level of 75–90 mol %. This process is being developed by a number of companies, is being brought to commercialization, and is being actively implemented in industry now [17].

Along with the methanol-to-olefins (MTO) technologies that have been implemented in industry, a new technology of obtaining of lower olefins from dimethyl ether has attracted considerable attention; this technology offers a way to manufacture lower olefins with high yield and selectivity (above 88 mol %), with the fraction of ethylene and propylene in the hydrocarbon product being above 80 mol % [8–11]. This process has not yet been brought to commercial use, but it has great potential, because its thermodynamic characteristics are more favorable than those in the scheme accomplished through methanol.

At the same time, all the studied technologies pertaining to the synthesis of lower olefins from methanol and/or dimethyl ether are based on the heterogeneous-catalytic gas-phase regime of the reaction.

Because the reaction in question is characterized by a marked heat effect, problems related to the technological design arise and a catalyst is usually deactivated rapidly. Therefore, the search is on for the transition from the conventional gas-phase catalysis to catalysis in the dispersed phase with the use of a slurry reactor, in which the process is conducted in a flow regime in a three-phase system (gas-liquid-solid catalvst). The continuous mode of the process (typical of gas-phase catalysis) is combined with the effective heat removal from the catalyst grain by the liquid medium (typical of catalytic liquid-phase processes). A catalyst is maintained in the state of a fine suspension, and in terms of its parameters and outcome, the process approaches homogeneous systems. As the size of catalyst particles decreases, the area of the active catalyst surface increases, the intradiffusion retardation declines, and the mass and heat transfer are improved; as a result, the rate of reaction grows and the deactivation processes decelerate. Ultrafine suspensions with nanosized catalyst particles exhibit the most promise.

This breakthrough technology has already been successively applied in a number of chemical, petrochemical, biochemical, and ecological catalytic processes [18–24]. For example, synthetic diesel fuel and higher alcohols are efficiently produced with the use of slurry reactors in the Fischer–Tropsch process technologies [25–28].

Recently, lower olefins have been synthesized from dimethyl ether in a slurry reactor using fine suspensions of zeolite-containing catalysts [29], and a technique for preparing ultrafine suspensions of nanosized catalysts from commercial MFI-type zeolite has been developed [30].

This paper presents the results of our research into the effect of particle size of the suspended zeolite catalyst formed from commercial MFI-type zeolite on its physicochemical characteristics and catalytic behavior in the conversion of DME in a three-phase system. The textural, acidic, and catalytic characteristics of a nanosized sample of this catalyst are compared with the analogous characteristics of specially synthesized MFI-type zeolite containing nanoparticles formed by nanocrystallites with the analogous crystal lattice structure.

EXPERIMENTAL

In this study, medium-pore zeolites with the MFI structure in the H form were used, namely, commercial high-modulus zeolite (HMZ) with a molar ratio of $SiO_2/Al_2O_3 = 37$ (OAO Angarks Plant KiOS) and laboratory-synthesized MFI zeolite with a molar ratio of $SiO_2/Al_2O_3 = 57$.

Nanoparticles were obtained from the commercial ultrasonically ground high modulus zeolite (HMZ) sample. Prior to ultrasonic treatment, the sample was calcined at a temperature of 500°C for 2 h to obtain its H form (HHMZ). The HHMZ powder was thoroughly ground in an agate mortar, placed in a Teflon glass, and drenched with distilled water at a ratio of 20 g of water per gram of catalyst. After mixing in water for 5 min, the zeolite aqueous suspension was ultrasonically treated in an Elmasonic P30 H ultrasonic bath (ultrasound frequency of 80 kHz and power of 130 W). The ultrasonic treatment of the HHMZ (HHMZ(0)) zeolite in water was performed for 60 and 90 min (HHMZ(60) and HHMZ(90)); the as-treated zeolite was dried and calcined at a temperature of 500°C for 2 h.

Zeolite MFI was synthesized as described in [31] and modified in accordance with [32]. The synthesized MFI zeolite was separated from the mother solution via centrifugation, washed off, dried, and calcined

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in a dry air steam of for 6 h at 550° C. After that, a threefold ion exchange using an ammonium nitrate solution with a concentration of 0.1 mol/L (10 g of solution per gram of zeolite) was conducted at a temperature of 80° C.

The particle size for the aggregates of crystallites of the synthesized MFI zeolite and the ground HMZ zeolite was measured at a temperature of 25°C by dynamic light scattering using a Malvern Zetasizer NANO SZ particle analyzer. A weighed portion of the powder was mixed with a hydrocarbon oil (DOWTHERM RP) at a ratio of 1 : 100 and ultrasonically dispersed for 20 min, and the size of zeolite particles was measured.

The morphology of zeolites was studied by scanning electron microscopy (SEM). After ultrasonic treatment in water, the sample was thoroughly mixed and 3 mL of the mixture was sampled. The sample was diluted with water by a factor of 200, deposited on a carbon strip fastened on a stage, and dried at room temperature. SEM images were taken on a Hitachi TM3030 microscope.

X-ray powder diffraction was applied to study the structural characteristics of the framework of original zeolite samples. XRD data were collected on a Bruker D2 PHASER X-ray diffractometer in the 2 θ geometry. The generator regime was as follows: 30 kW, 10 mA, and an X-ray tube with a copper anode ($\lambda \operatorname{Cu} K_{\alpha_1} = 1.5418$ Å). Diffraction patterns were recorded using rotation of the sample in the horizontal plane in a 2 θ angular range of 5°-50° in increments of 0.05°, with slit widths at the tube exit of 0.6 mm and before the detector of 1.15 mm, and an acquisition time at a point of 3 s.

The pore structure of the sample was studied by low-temperature molecular nitrogen adsorption desorption on an ASAP 2010 porosimeter (Micromeritics). Before measurements, all of the samples were evacuated at a temperature of 350°C to a pressure of 4×10^{-1} Pa. The adsorption of N₂ was conducted at a temperature of 77 K.

The acidic properties of the resulting samples were studied by temperature-programmed desorption of ammonia (TPD NH₃). Experiments were conducted on an USGA-101 universal gas sorption analyzer (Unisit). The sample (~0.1 g in the form of fraction 0.25–0.5 mm) was placed in a quartz reactor, heated in a helium stream to a temperature of 250°C at a temperature rise rate of 10°C/min, calcined at this temperature for 1 h in a helium stream, and cooled to 60°C. The saturation of zeolites by ammonia was conducted in a stream of the dried mixture of NH₃/N₂ (1 : 1) for 15 min. Physically adsorbed ammonia was removed at 100°C in a helium stream for 1 h. After the sample was cooled to 60°C in a dried helium stream at a feed velocity of

Zeelite	5:0 /41 0	C	Pore structure**				a ***
sample	mol/mol	Crystannity*, %	S _{BET} , m²/g	$S_{\text{outer surface}},$ m ² /g	$V_{\rm micro},$ cm ³ /g	$V_{\rm meso + macro},$ cm ³ /g	μ mol/g
HHMZ(0)	37	71	333	88	0.119	0.054	1469
HHMZ(60)	37	88	343	93	0.117	0.058	1305
HHMZ(90)	37	88	338	110	0.108	0.075	1317
HMFI	57	70	348	102	0.112	0.060	717

Table 1. Physicochemical characteristics of HHMZ samples with different UST times and synthetic zeolite HMFI

* Calculated from the signal/noise ratio for reflection 101. ** Surface area calculated by the Brunauer–Emmett–Teller method (S_{BET}), area of the outer surface calculated by the t-Plot method ($S_{outer surface} = S_{BET} - S_{micropores}$), and volume of micropores (V_{micro}) and the volume of meso- and macropores ($V_{meso + macro}$). *** The total number of acid sites according to the temperature-programmed desorption of ammonia (TPD NH₃).

30 mL/min, the linear temperature rise in the reactor was performed at a rate of 8° C/min to 800° C.

The diffuse reflectance infrared Fourier transform (DFIFT) spectra of the samples in Vaseline oil were measured in situ in an inert atmosphere (argon). The spectra were registered at a temperature 450°C in a Pike Diffus IR high-temperature cell combined with a Bruker Vertex-70 FTIR spectrometer. IR spectra were recorded with a resolution of 2 cm⁻¹ in the frequency range of 600–4000 cm⁻¹ in the continuous mode for 5 min (194 scans per spectrum). The spectra were treated using the Opus-7 software.

The synthesis of olefins from DME was accomplished using suspended zeolites. Before suspension preparation, magnesium (1 wt %) was deposited on the surface of zeolites via impregnation as described in [9]. The magnesium-modified zeolite was ground and dispersed in the high-boiling liquid in accordance with the above-described technique.

The catalyst suspensions in the DME conversion to olefins were tested in an autoclave with inlet and outlet fittings and equipped with a mechanical stirrer, a thermocouple (chromel/copel), a reflux condenser, and a dropping reflux condenser as a baffle. The reaction was run at a temperature of 300°C and atmospheric pressure under vigorous mechanical stirring in the continuous flow regime. Dimethyl ether was bubbled through the catalyst suspension layer. As a feedstock, dimethyl ether manufactured by AkzoNobel N.V. (DME weight fraction of 99.99%) diluted with molecular nitrogen was used. The concentration of DME in the feed gas mixture was 10 vol %. The gas flow velocity was 3.7 nL/h, and the weight load on the catalyst was 0.14 h^{-1} . The presented catalytic data refer to a catalyst operation time of 2 h.

The VHSV was varied within 400-1200 h⁻¹. To attain the desired feed gas velocity, the gas flow was controlled using Bronkhorst gas flow meters.

The gaseous product of DME conversion was analyzed by gas-liquid chromatography on a Kristal-

lyuks-4000M chromatograph equipped with a flameionization detector and a capillary column (27.5 m/0.32 mm) filled with a *CP*-PoraPLOT-Q liquid phase (10- μ m-thick adsorption layer). Helium was used as a carrier gas. The chromatograms were treated using the NetChromWin program.

RESULTS AND DISCUSSION

Figure 1 shows the SEM micrographs of the original HHMZ(0) sample and the same sample after ultrasonic treatment. Before SEM measurements, the HHMZ zeolite samples subjected to ultrasonic treatment for 60 and 90 min were diluted with water by a factor of 200 to prevent the aggregation of particles during drying of the sample. As is seen from the images, the original HHMZ(0) is composed of agglomerates of crystals (crystal size of $\sim 1-2 \,\mu m$) with a wide size distribution of agglomerates $(3-100 \ \mu m)$. Upon ultrasonic treatment (UST), the morphology of the sample changes appreciably. SEM images recorded for the HHMZ(60) sample also show coarse agglomerates of crystals (up to $100 \,\mu$ m); however, they are surrounded by both minute $3-5 \,\mu\text{m}$ agglomerates and HHMZ zeolite crystallites. An increase in the time of treatment to 90 min provides an even larger contribution of minute agglomerates and crystallites.

During water removal, zeolite crystals and minute agglomerates aggregate to coarse loose agglomerates; this finding may be attributed to their aggregative instability during drying of the sample.

Thus, the ultrasonic treatment of the zeolite in water causes an increase in the contribution of minute agglomerates and HHMZ zeolite crystallites; their content grows in the course of time. The drying of the sample is accompanied by the development of coarse, loose agglomerates composed of both zeolite crystallites and smaller agglomerates.

In accordance with the X-ray powder diffraction, during ultrasonic treatment, regardless of its duration,



Fig. 1. SEM images for HMZ zeolite samples with different UST times in water: (a) HHMZ (0 min), (b) HHMZ (60 min), and (c) HHMZ (90 min).



Fig. 2. Isotherms of low-temperature nitrogen adsorption for (a) the commercial HHMZ sample with different UST times and (b) the synthesized HMFI zeolite.

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Fig. 3. NH₃ TPD spectra of the HHMZ samples with various times of UST and the synthesized HMFI zeolite.

no marked changes in the crystalline structure of the HHMZ zeolite are observed (Table 1).

Figure 2 shows the isotherms of nitrogen low-temperature adsorption for HHMZ and HMFI samples.

For all of the HHMZ samples (Fig. 2a), regardless of the UST time, the adsorption isotherms display a well-defined hysteresis in the relative pressure (p/p_0) range of 0.4–1.0, indicating the presence of meso- and macropores connecting with the environment through micropores. As the time of ultrasonic treatment of the HHMZ zeolite increases, the volume of meso- and macropores tends to increase predominantly owing to the growth of macropores. This observation may be explained by the appearance of loose agglomerates formed via the aggregation of smaller particles during drying of the zeolite after treatment. These results are in good agreement with the data derived from the SEM images, because a change of dense agglomerates (Fig. 2a) for looser agglomerates (Fig. 2b) should be

 Table 2. Distribution of different types of acid sites in HHMZ and HMFI zeolites

Type of acid site	Fraction of acid sites on zeolite surface*, %			
on zeonte surrace	HHMZ(90)	HMFI		
1 + 2	60.0	24.0		
3	26.5	27.0		
4	13.5	35.0		
Total acidity a_0 , kmol/g	1317	690		

* The distribution of acid sites was estimated from the relative intensities of absorption bands in the DFIFT spectrum taking into consideration that the total amount of all OH groups is 100% (provided that the samples were prepared under the same conditions). accompanied by an increase in the contribution of meso- and macropores.

The isotherm obtained for the HMFI sample follows the pattern classical for zeolites having micron and submicron sizes of crystals with a small amount of mesopores (Fig. 2b). The presence of hysteresis in the range of $p/p_0 = 0.4-0.7$ and its absence in the range of high relative pressures provide evidence for the limited connection of the pore system with the zeolite crystal outer surface.

The detailed analysis of the pore structure of the samples indicates that the outer surface areas of HMFI and HHMZ(90) samples are similar (Table 1); however, in the case of HMFI, the volume of micropores is higher. This is evidence that the agglomerates of nanocrystals in the HMFI sample represent a densely intergrown structure rather than freely associated crystals. A considerable contribution of macropores for HHMZ(90) suggests a weak aggregation state of zeolite nanocrystals. The acidic properties of the zeolites were studied by the temperature-programmed desorption of ammonia (TPD NH₃) (Fig. 3, Table 1).

An analysis of the TPD NH₃ curves reveals that the HHMZ samples, regardless of the UST time, are characterized by close number and strength of acid sites, albeit ultrasonic treatment entails an insignificant reduction in the number of medium- and weakstrength acid sites. This finding may be attributed to zeolite amorphization under the UST conditions. Compared with HHMZ, the synthesized HMFI sample features a smaller number of acid sites, in agreement with a higher silicon/aluminum ratio. For the surface of zeolite samples, more detailed information about the origin, number, and strength of acid sites was obtained by DFIFT in situ used in combination with quantum-chemical calculations performed as described in length in [33]. The IR spectra of all of the zeolites show four absorption bands corresponding to the stretching vibrations of OH groups belonging to acid sites of different strengths. Bands with vibration frequencies at v = 3590 cm⁻¹ and v = 3614 cm⁻¹ indicate that two types of strong Brønsted acid sites occur on the surface of zeolites-with the end acidic group Al-OH(H) (type 1) and the bridging bond Al-O(H)-Si (type 2). The band in the range $v = 3665 \text{ cm}^{-1} \text{ cor-}$ responds to vibrations of two associated hydroxyl groups with weak acidic properties (type 3). In addition, the band at v = 3733 cm⁻¹ is assigned to vibrations of the isolated Al–OH bond belonging to the site with amphoteric properties (type 4).

Thus, four types of acid sites were identified on the surface of zeolites HHMZ and HMFI. The distributions of different types of acid sites on the surface of HHMZ and HMFI zeolites differ appreciably (Table 2). As opposed to the synthetic zeolite HMFI, the total acidity and the content of strong Brønsted

C. (. 1	Particle size	DME conversion, wt %	Selectivity for	Content of CH ₃ OH	
Catalyst sample*	in suspension, nm		$\Sigma C_{2=} - C_{4=}$	$\Sigma C_{2=} - C_{3=}$	in the product, wt %
Mg/HHMZ(0)	1530-1700	28.0	77.0	69.0	1.1
Mg/HHMZ(60)	600-813	89.0	55.0	47.7	2.5
Mg/HHMZ(90)	73-85	92.0	67.0	47.3	3.0
Mg/HMFI	61-74	81.0	59.8	52.5	16.6

 Table 3. Testing of suspended zeolite samples in the synthesis of lower olefins from DME under conditions of three-phase catalysis

* The content of magnesium on the zeolite surface is 1 wt %.

acid sites for the nanosized zeolite HMZ(90) are much higher (type 1 + 2), while the content of weak acid sites (type 3) is almost the same. As for the site with amphoteric properties (type 4), its content for zeolite HHMZ(90) is almost three times lower than that for the synthetic HMFI.

Using the zeolite samples, the magnesium catalysts of olefin synthesis were prepared [9]. The textural characteristics of MFI zeolites remained practically unchanged after deposition of 1 wt % magnesium on them, but the total acidity decreased.

After drying and calcination, magnesium-containing zeolite catalysts were ultrasonically dispersed in the high-boiling liquid Dowtherm for 20 min. The size of catalyst particles in the suspension was determined by dynamic light scattering.

The dispersing of HHMZ-based zeolite catalysts in the high-boiling liquid yielded suspensions with micron, submicron, and nanosized (after 90-min ultrasonic treatment) degrees of dispersion (Table 3). Using the catalyst based on the synthesized zeolite, a nanodispersed suspension was prepared: during ultrasonic dispersing, the agglomerates of the original MFI zeolite disintegrated into nanocrystallites.

The catalyst suspensions were tested in the conversion of DME in the slurry reactor (Table 3). As is seen, the time of preliminary ultrasonic treatment of the HMZ zeolite in water has a strong effect on the size of zeolite catalyst particles in the suspension: the longer the original HMZ sample was ultrasonically treated, the smaller the size of particles in the resulting suspensions. As the size of zeolite particles decreased, the conversion of DME increased. Note that, on passage from sample Mg/HHMZ(0) to sample Mg/HHMZ(60), the size of particles decreased by a factor of 2.3 and the conversion of DME increased by a factor of 3.2. Further almost 10fold reduction in the size of particles led to a small gain in the conversion of DME (from 89 to 92%). For the Mg/HMFI sample with a particle size of 61-74 nm, the conversion of DME was also high and it was much higher than that for the Mg/HHMZ(0) sample. The most probable reason for the experimentally measured

DME conversions is the intradiffusion retardation of the reaction in the pores of the primary crystalline structure of zeolite. This phenomenon is apparently observed at particle sizes above 500–600 nm.

As the size of Mg/HHMZ catalyst particles decreases, the rate of all reactions, including secondary transformations, grows; as a consequence, the product selectivity changes considerably (Fig. 4). Noteworthy is a somewhat higher selectivity for butenes and a lower selectivity for high-boiling hydrocarbons in the case of the Mg/HHMZ(0) sample with the largest sizes of particles. As the size of particles decreases, selectivity for butenes and hydrocarbons C₅ increases (Fig. 4). It appears that this finding may be explained by an increase in the contribution of the alkene cycle [34] to the formation of products. It is interesting that the selectivity for propane and butanes passes through a maximum. This fact indicates that the optimum sizes of particles can be found for the reaction of hydrogen redistribution.

At a close degree of dispersion of suspensions for the catalysts based on HHMZ(90) and HMFI, the conversion of DME is noticeably higher for (1%)



Fig. 4. Composition of hydrocarbon products of DME conversion under conditions of three-phase catalysis at different times of UST of HHMZ.

Mg/HHMZ (Table 3), which is due to a much high acidity of the original zeolite HHMZ (Table 2). Probably, the silicon/aluminum ratio in the samples under comparison plays a considerable role.

The selectivity for lower olefins is also different for the catalysts based on HHMZ(90) and the synthesized the HMFI zeolite. For example, the selectivity for olefins $C_{2=}-C_{4=}$ is higher for (1%) Mg/HHMZ(90) owing to the contribution due to butenes (Fig. 5). At the same time, selectivity for olefins $C_{2=}-C_{3=}$ is higher for contribution due to butenes (Fig. 5). At the same time, selectivity for olefins $C_{2=}-C_{3=}$ is higher for contribution due to butenes (Fig. 5). At the same time, selectivity for olefins $C_{2=}-C_{3=}$ is higher for contribution due to butenes (Fig. 5).

Mg/HMFI owing to formation of a higher amount of propylene. Probably, this is due to the fact that the methylation reaction over the Mg/HMFI zeolite is less intense. Moreover, the amount of methanol produced over the (1%) Mg/HMFI catalyst is much higher than that formed over systems (1%) Mg/HHMZ. This effect is possibly explained by a high content of type 4 acid sites in the original HMFI zeolite (Table 3). It is known [35, 36] that, over these amphoteric sites, the conversion of DME to methanol occurs to form e:



Scheme.

As a result, the conversion of DME shifts to the production of methanol rather than to the alkylation of ethylene and propylene with the concomitant changes in the composition of the products.

Thus, our studies have shown that, in the conversion of DME in the three-phase system in the slurry reactor, the catalytic properties of MFI zeolites are strongly influenced by the particle size of the suspended catalyst: on passage to nanosized suspensions, the activity of the catalyst grows by several times, in agreement with a change in the textural characteristics of the zeolites. An increase in the size of catalyst particles improves selectivity for olefins probably via the arenium ion mechanism but worsens selectivity for



Fig. 5. Composition of hydrocarbon products of DME conversion under conditions of three-phase catalysis over suspended Mg/HHMZ(90) and Mg/HMFI zeolites.

hydrocarbons C_5^+ . At the same degree of dispersion of suspensions, the catalytic properties of the suspended catalysts are considerably affected by the strength distribution of acid sites. An increase in the share of amphoteric sites provides a gain in selectivity for methanol, while selectivity for butenes decreases.

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