ZSM-5/γ-Al₂O₃ Catalysts for Methanol Dehydration: Tuning Pore Structure by Carbon Nanotubes as a Pore-Forming Agent

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1. Introduction

Zeolite ZSM-5 demonstrates high catalytic activity in many valuable chemical reactions, e.g., alcohols conversion to ethers and hydrocarbons [1–3], n-hexane conversion to aromatics [4], Claisen–Schmidt condensation [5], n-hexane cracking to light olefins [6], and 1-hexene oligomerization [7]. ZSM-5 typically consists of crystallite particles. The size of the crystallite particles may vary between 2 nm and 15 µm depending on the synthesis procedure [8, 9]. The smaller the ZSM-5 particles, the shorter the diffusion length traveled by a reagent molecule [10]. However, the use of so small particles in industrial heterogeneous catalytic reactors is sometimes discouraged due to several constraints limiting the maximum size of a catalyst particle that is suitable for use in industrial fixed-bed reactors [11]. Therefore, zeolite-based industrial catalysts typically contain binders to the extruded catalyst with an appropriate shape. γ-alumina is a commonly used binder for ZSM-5 zeolite-containing catalyst [12].

Adding alumina binder affects the catalyst acidity and catalytic activity, whereas zeolite crystallinity and porosity are preserved [13]. It has been shown that additional Bronsted acid sites are formed as a result of the Al atoms migration in ZSM-5/Al₂O₃ extrudates [14]. The yield of the products of a heterogeneous catalytic process over a ZSM-5/Al₂O₃ catalyst may also be affected by the dilution of strong acid sites by alumina binder [15]. Using a binder improves the mechanical stability of a catalyst, as well as enhances mass transfer through an extruded pellet because the pores formed in the binder matrix are usually considerably larger compared to pristine zeolite pores [16].

There are several approaches in improving the porous structure of a solid material. Pore-forming agents are often utilized to derive porous materials, e.g., alumina, with controlled pore size and morphology [17]. A recent approach to eliminate mass transfer limitations in zeolites is to introduce mesopores creating a hierarchical structure. For instance, mesoporous ZSM-5 zeolite crystals have been obtained by postsynthesis procedure [18]. A common pathway to create a hierarchical porous structure is template synthesis. The application of carbon nanotubes as a template during porous material synthesis has been reported in several works [19–21]. Zeolite crystals exhibiting the presence of mesopores have been prepared using the multiwall carbon nanotubes as a template [22]. Carbon nanotubes are used to modify textural properties, mainly by increasing surface area via introducing mesopores that are left after CNT removal.
In this paper, ZSM-5/alumina composites were synthesized using the MWCNTs as a pore-forming agent. The MWCNTs were completely removed by calcination and resulting voids act as mesopores. The physicochemical properties of the as-synthesized materials were investigated and found to differ significantly depending on the synthesis technique. The study on the methanol dehydration to DME over the as-synthesized composites revealed superior catalytic activity of the materials and allowed measurement of the effective kinetic parameters. The obtained results show utilization of MWCNTs may considerably affect both textural and acidic properties of zeolite/alumina composite.

2. Experimental

2.1. Synthesis. Al(NO₃)₃ (purity > 99.0%) was obtained from Donetsk Khimreactyv Plant, Ukraine. NaOH (purity > 99.8%) was supplied from BDC Group, Poland. ZSM-5 zeolite (Na-form, relative crystallinity = 70%, Si/Al = 35.1) was purchased from Nizhegorodskiy Sorbent Plant, Russian Federation. Multiwall carbon nanotubes (MWCNTs) were synthesized via ethylene decomposition over NiO/γ-Al₂O₃ catalyst using the routine procedure described in [23].

Hierarchically porous materials containing ZSM-5 zeolite and alumina (ZSM-5/Al₂O₃ = 3/1 by mass) were synthesized as follows. The MWCNTs were suspended in deionized water (0.5 g of MWCNTs per 100 ml of water). The obtained suspension was ultrasonicated by Bandelin Sonopuls 4100 ultrasonic homogenizer equipped with TS106 horn for 30 minutes at 40% of maximum ultrasonic amplitude to derive the homogeneous dispersion of the nanotubes. The as-prepared dispersion was utilized immediately.

The first sample (later referred to as ZA-1) was prepared using the following procedure. Al(NO₃)₃ was dissolved in deionized water to obtain a 1 M aluminum nitrate solution. The obtained Al(NO₃)₃ solution was mixed with the stoichiometric volume of the 3 M NaOH solution. The Al(OH)₃ hydrogel was washed from the electrolyte by repeated washing with deionized water and decantation. Aluminum hydroxide gel was mixed with the MWCNTs dispersion and ZSM-5 powder under constant stirring. The amount of the MWCNTs dispersion was 100 ml per 1 mole of the Al(OH)₃. The final ZSM-5/Al₂O₃/MWCNTs mixture was heated at 80°C to evaporate the water. After the ZSM-5/Al₂O₃/MWCNTs mixture became appropriate for extrusion, the granules were formed by extrusion through a die with a diameter of 2 mm. The obtained granules were dried at 80°C for 4 hours. Finally, the granules were calcined in an air atmosphere at 550°C for 4 hours. At this stage, the MWCNTs were removed and the final porous structure of the sample was formed. Thereafter, the molded granules were obtained.

Another sample (later referred to as ZA-2) was synthesized differently. 0.5 g of the MWCNTs were suspended in 100 ml of deionized water and mixed with 100 ml of 1 M Al(NO₃)₃ solution. The stoichiometric volume of 3 M NaOH solution and ZSM-5 zeolite were successively added to Al(NO₃)₃/MWCNTs mixture under constant stirring. The obtained suspension was washed from electrolyte with deionized water and by decantation. Afterward, the ZSM-5/Al₂O₃/MWCNTs mixture was heated at 80°C. After the water evaporation, the mixture was extruded, dried, and calcined following the procedure identical to ZA-1 synthesis.

A reference sample (referred to as ZA-0) was obtained for the same procedure as for ZA-1 sample, except the addition of the MWCNTs.

A sketch of the general sample synthesis procedure is shown in Figure 1.

2.2. Characterization. Textural properties of the samples were characterized by low-temperature N₂ adsorption-desorption isotherm. The latter was recorded by a Sorptomatic-1990 sorptometer. Surface area, micropore, and mesopore size distribution were evaluated from the adsorption branch of the isotherm according to BET, Saito and Foley, and Dollimore and Heal models, respectively.

To confirm the removal of the pore-forming agent from the composite matrix, the thermal stability of precursor MWCNTs was tested by thermogravimetric analysis using Shimadzu DTG-60H thermogravimetric and differential thermal analyzer.

The crystallinity of the samples was analyzed via the utilization of X-ray diffraction. The XRD patterns were recorded by Bruker D8 Advance diffractometer in the 2θ region between 5 and 80° at a scanning rate of 0.33°/min with Cu Kα radiation (λ = 0.154 nm).

Elemental analysis was estimated by X-ray fluorescence spectroscopy. The spectra were recorded using ElvaX XRF-spectrometer.

The morphology of the synthesized materials was characterized by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). SEM images were obtained using a Selmi TEM-125K transmission electron microscope at 100 kV acceleration voltage. SEM images were recorded with Tescan Mira 3 LMU scanning electron microscope at 10 kV acceleration voltage.

The Fourier transform infrared (FT-IR) spectroscopy was used to identify the characteristic chemical bonds. The spectra were recorded by Spectrum One (Perkin Elmer) spectrometer for KBr pellets in the wavenumber range between 400 and 4000 cm⁻¹ at a scanning rate of 0.5 cm⁻¹/min and 2 cm⁻¹ resolution.

The acidity of the materials (both Bronsted and Lewis) was evaluated using stepwise pyridine desorption at 150°C, 250°C, and 350°C. The amount of adsorbed pyridine was measured by FT-IR spectroscopy (Spectrum One (Perkin Elmer) spectrometer). The concentration of the acid sites was calculated using the integral intensity of the component according to the procedure described elsewhere [24].

2.3. Catalytic Test. The catalytic activity tests were conducted in a quartz tubular reactor. The catalyst particles were placed inside the reactor between the two layers of the quartz sand. 0.1 g of each sample was loaded into the reactor. The methanol was fed up by a syringe pump. Argon was used as
a gas carrier. The methanol and argon flow rates were kept at 25 and 45 cm³/min, respectively. This resulted in WHSV equal to 21 g/(g ⋅ h). The reaction temperature varied between 120 and 360°C. The reaction temperature was controlled by a controller with 0.1°C accuracies. The reaction products were analyzed online using a Chrom-5 gas chromatograph equipped with a Hewlett Packard DB-2 capillary column and a flame-ionization detector. To estimate the reaction order, the catalytic tests were performed at 150°C varying WHSV in the range between 13 and 30 g/(g ⋅ h).

Before acidity measurements and activity tests, each sample was activated by ion exchange with 3 M NH₄Cl solution at 50°C for 24 hours in total. After ion exchange, the samples were washed with deionized water and calcined at 550°C for 4 hours.

To investigate the catalytic activity, the catalyst granules were crushed and sieved to obtain particles with a size less than 0.5 mm. Small catalyst particles were used to eliminate the internal diffusion limitations, especially at lower temperatures.

The methanol conversion (X) was calculated as follows:

\[ X = 1 - \frac{C_{\text{MeOH}}}{C_{\text{MeOH}}} \]  

where \( C_{\text{MeOH}} \) and \( C_{\text{MeOH}} \) are the initial methanol concentration and the methanol concentration in the reaction mixture, respectively.

The methanol conversion rate (\(-r_m\), mol/(m² ⋅ s)) was evaluated using the following relation:

\[ -r_m = \frac{(C_{\text{MeOH}} - C_{\text{MeOH}}^0)}{m \cdot S \cdot 60 \cdot 22400} \]  

where \( V \) is the total feed flow rate, cm³/min; \( m \) is the catalyst mass, g; and \( S \) is the catalyst surface area, m²/g.

Equilibrium methanol conversion was calculated using the following equation:

\[ X = \frac{2 \cdot \sqrt{K}}{1 + 2 \cdot \sqrt{K}} \]  

where \( K \) is the dimensionless equilibrium constant. The equilibrium constants at various temperatures were computed following the algorithm presented in [25].

3. Results and Discussion

3.1. Characterization. Figure 2 shows the XRD patterns of the samples under investigation. The peaks at \( 2\theta = 8.00°, 8.95°, 20.95°, 21.85°, 23.30°, 23.95° \), and 24.55°, which are typical for the MFI structure of ZSM-5 zeolite and correspond to the spacing between the following zeolite crystallographic planes: (1 0 1), (0 0 2), (3 1 1), (3 2 0), (1 3 4), (3 3 0), and (3 1 3), accordingly [26]. The XRD patterns of the synthesized samples are characterized by small shoulders at around \( 2\theta = 5°, 23° \), and 65°. According to [27], these shoulders correspond to the \( γ \)-Al₂O₃. No additional peaks, except those that are attributed to ZSM-5 and \( γ \)-alumina, are observed on the XRD patterns.

Figure 3(a) presents N₂ adsorption and desorption isotherms for studied materials. The isotherms correspond to the H₃ type. This type is fairly typical for zeolite-alumina composites [28]. The shape of the hysteresis loop is almost identical for all three of the samples. The adsorption and desorption branches are quite close for the ZA-2 sample. Therefore, the porous structure of the ZA-1 sample is more heterogeneous compared to the ZA-2 sample. ZA-1 sample exhibits a considerably higher amount of the N₂ adsorbed. This indicated a higher surface area and improved porous structure compared to the ZA-2 sample. Textural properties estimated from the N₂ adsorption-desorption isotherms are presented in Table 1. ZA-1 sample is characterized by almost two times larger surface area, pore volume, micropore volume, and mesopore surface area compared to ZA-2 material. Figure 3(b) demonstrates the mesopore size distribution.
estimated from the isotherm data. Both samples are characterized by bimodal mesopore distribution centered at 3 nm and 7 nm. For ZA-1, the mesopore distribution is rather broad. This indicates that the pore structure is significantly inhomogeneous. A different situation is observed for micropore distribution (Figure 3(c)). ZA-2 sample exhibits broad distribution centered at approximately 0.9 nm, whereas the ZA-1 sample is characterized
by uniform distribution with the two peaks, both centered in a region around 0.9 nm. Porous structure of ZA-0 is significantly different compared to other samples. The values of surface area and pore volume are between ZA-1 and ZA-2, whereas the shape of adsorption hysteresis loop for ZA-0 shows less microporosity, which is confirmed by the pore size distribution. The obtained results demonstrate that the textural properties of the materials synthesized via the utilization of various preparation techniques are significantly different. The introduction of the MWCNTs as a pore-forming agent for the synthesis of the new porous solids considerably affects the porous structure of the as-prepared materials.

Figure 4 shows the TGA curve of the MWCNTs precursor. At 550°C, the weight loss equals approximately 80%. To this end, the calcination procedure provides satisfactory results in removing the pore-forming agent.

It is worth noting that the MWCNTs precursor contains nickel residues because the MWCNTs were obtained by thermal ethylene decomposition over Ni/CaO catalyst. Therefore, after MWCNTs removal during calcination, nickel is still present in the as-synthesized zeolite/alumina materials. The results of the elemental analysis demonstrated that the nickel content in both samples is approximately 0.33 ± 0.02% wt.

TEM (Figure 5) and SEM (Figure 6) images present the morphology of the samples. TEM image of ZA-1 (Figure 5(a)) demonstrates zeolite shells surrounded by alumina globes. For the ZA-2 sample, the TEM image (Figure 5(b)) reveals zeolite shells covered with alumina. SEM image of the ZA-1 surface (Figure 6(a)) shows coffin-shaped ZSM-5 zeolite crystallites embedded in the Al2O3 matrix. In contrast, ZA-2 material (Figure 6(b)) exhibits almost no visible zeolite crystallites on the surface of the massive sample. The MWCNTs residuals are not observed for both samples.

Figure 7 presents the FT-IR spectra of the samples. The characteristic band at 445 cm⁻¹ is associated with the bending mode vibrations of the Si–O and Al–O bonds in the SiO₄ and AlO₄ tetrahedra. The band at 545 cm⁻¹ is typically assigned to the symmetric vibrations of the five-membered rings in the zeolite framework. The band at 785 cm⁻¹ reflects the symmetric vibrations of Si–O–Si and Si–O–Al bonds. The band at 1050 cm⁻¹ is attributed to the internal vibrations of Si–O and Al–O bonds in the SiO₄ and AlO₄ tetrahedra. The band at 1090 cm⁻¹ may be assigned to the symmetric and asymmetric stretching vibrations of the Si–O–Al bonds of the zeolite framework. The shoulder at 1215 cm⁻¹ represents the asymmetric stretching of Si–O and Al–O bonds in the SiO₄ and AlO₄ tetrahedra. The band observed at 1410 cm⁻¹ may be attributed to the bending vibrations of C–O bonds of the carbon-containing residues that may be present on the surface of the samples. This observation may explain the deformation of the band for ZA-2. The latter is characterized as lower surface area compared to ZA-1. To this end, ZA-2 may contain a lower amount of carbon-containing residues. The band at 1540 cm⁻¹ may be assigned to the bending mode of the adsorbed water. The two small shoulders at 2400 cm⁻¹ are typically assigned to the adsorbed CO₂ molecules. The broad band between 3000 cm⁻¹ and 3650 cm⁻¹ reflects the vibrations of zeolite OH groups, OH bonds of the surface water, and Al–OH species in the zeolite framework.

The estimated concentrations of the Bronsted and Lewis acid sites are listed in Table 2. The ZA-1 sample is characterized by considerably higher acidity compared to the ZA-2 sample. This is not unexpected because the ZA-1 sample exhibits a significantly higher surface area compared to the ZA-2 sample. The activation procedure affects the concentration of the surface acid sites. Particularly, the concentration of Bronsted sites increases after activation. ZA-2 sample demonstrates an almost complete absence of Bronsted acid sites on its surface. This may be attributed to the morphology of the samples. γ-Al₂O₃ typically possesses no Bronsted acidity, whereas ZSM-5 zeolite is characterized by both, Bronsted and Lewis acidity. For the ZA-2 sample, zeolite crystallites are seemingly covered with the alumina matrix so that the adsorption of the pyridine molecules on the surface of zeolite crystallites is impossible.

Using various synthesis techniques provides different mechanisms for porous structure formation. Particularly, mixing ultrasonicated MWCNTs with Al(OH)₃ hydrogel (ZA-1 sample) gives the mesopores which are formed by the contacts between zeolite crystallites and alumina particles and by void spaces left by MWCNTs after calcination. In contrast, precipitation of Al(OH)₃ over ultrasonicated MWCNTs during ZA-2 sample synthesis leads to the derivation of the mesopores that are mainly formed by the contacts between alumina particles.
Figure 5: TEM images of (a) ZA-1 and (b) ZA-2.

Figure 6: SEM images of (a) ZA-1 and (b) ZA-2.

Figure 7: FT-IR spectra of the samples.
3.2. Catalytic Activity. The catalytic activity of the samples toward methanol dehydration to dimethyl ether was investigated in the temperature range between 120°C and 320°C. Figure 8 demonstrates the methanol conversion plotted against the reaction temperature, as well as equilibrium methanol conversion. Increasing the reaction temperature yields an increase in the methanol conversion as a consequence of an increase in the reaction rate (Figure 9). The methanol conversion is greater for the ZA-1 sample. The latter also exhibits a methanol conversion rate approximately two times higher compared to the ZA-2 sample. At 270°C, for ZA-1, the formation of hydrocarbons is observed. ZA-2 sample exhibits no activity toward hydrocarbons synthesis up to 320°C. Moreover, the methanol conversion over the ZA-2 sample reaches equilibrium at 320°C.

The effect of the NiO residues on the catalytic activity of the synthesized composites was verified by performing the catalytic experiment over pristine NiO at identical reaction conditions. No activity was observed up to 350°C. Therefore, we believe that NiO residues exhibit no effect on the catalytic activity of the studied solids.

The methanol conversion rate per unit of surface area is higher for ZA-2 compared to ZA-1 (Figure 9(a)). In contrast, reaction rate per unit mass is higher for ZA-1 (Figure 9(b)). The concentration of acid sites of Lewis-type per unit of surface area is higher for ZA-2 (Table 2). Lewis-type acid sites demonstrate higher activity in methanol dehydration to DME than that of Bronsted sites [29].

The activity of a catalyst may decrease with time-on-stream (TOS), as a consequence of deactivation. This may also affect the observed reaction rate. In this study, the methanol conversion was monitored with time-on-stream. The relevant tests were performed at harsh reaction conditions (270°C) to preserve the worst-case scenario. At this temperature, almost equilibrium methanol conversion is reached (X ≈ 80%). The methanol conversion remains stable for 4 hours (Figure 10) for both ZA-1 and ZA-2 samples.

The essential catalytic performance of the synthesized materials may be also governed by high surface area and broad mesopore size distribution. These two factors contribute to enhance the mass transfer of a reagent in the catalyst particle. The effect of the mass transfer phenomena is highlighted by calculations of the Carberry number (external diffusion) and Weisz–Prater criterion (internal diffusion). Supplementary Materials presents a detailed procedure of the diffusion criteria derivation. Figure 10 gives a pictorial representation of the Carberry number (Ca) and Weisz–Prater criterion (N_{WP}) at various reaction temperatures. In general, the reaction rate is limited by the external diffusion of a reagent provided Ca is greater than 0.05 [30]. Therefore, methanol conversion over the ZA-1 and ZA-2 samples is free of the external diffusion limitations in the investigated temperature range (Figure 11(a)). However, the situation is more complex for the internal diffusion limitations. The reaction rate over catalyst particles may be either affected or not by the internal diffusion limitations depending on the reaction order. The reaction rate is limited by internal diffusion if N_{WP} >0.3, 0.6, and 6.0 for a second-order, first-order, and zero-order reactions, respectively [31]. For a noninteger reaction order, the effect of the intraparticle diffusion may be evaluated using the following expression:

### Table 2: The acidity of the as-prepared materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation</th>
<th>Type</th>
<th>Temperature (°C)</th>
<th>Concentration (μmole/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZA-1</td>
<td>Inactivated</td>
<td>Lewis</td>
<td>150</td>
<td>0.46</td>
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<td></td>
<td></td>
<td></td>
<td>250</td>
<td>0.04</td>
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<td></td>
<td></td>
<td></td>
<td>150</td>
<td>0.04</td>
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<tr>
<td></td>
<td>Bronsted</td>
<td></td>
<td>250</td>
<td>0.02</td>
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<td></td>
<td></td>
<td>350</td>
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<tr>
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<td>0.17</td>
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<td></td>
<td>350</td>
<td>0.08</td>
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<td></td>
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<td>Bronsted</td>
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Figure 8: Methanol conversion versus temperature.

Figure 9: Temperature dependence of the methanol conversion rate (a) per unit surface area and (b) per unit mass of the catalysts.

Figure 10: The methanol conversion versus time on stream at 270°C and WHSV = 2.74 g/(g × h).
where \( n \) is the reaction order and \( \eta \) is the effectiveness factor. The latter is considered to be \( \eta \geq 0.95 \).

The reaction orders toward methanol are 0.9 and 0.7 for ZA-1 and ZA-2, respectively (Figure S1 in Supplementary Materials). Therefore, the boundary \( N_{WP} \) values are 0.66 for ZA-1 and 0.85 for ZA-2. If \( N_{WP} \) is below these values, the system is free of the internal diffusion limitations. Keeping this in mind, it may be concluded that the observed reaction rate is unaffected by the internal diffusion for both catalysts in the whole temperature range (Figure 11(b)).

The reaction rate in the absence of diffusion limitations may be approximated by the following equation:

\[
-r_m = k \cdot c_{\text{MeOH}}^n
\]

where \( k \) is the reaction rate constant. Knowing the values of \( k \) at various temperatures, the activation energy of the process (\( E_a \), kJ/mol) may be estimated using the Arrhenius plot:

\[
\ln k = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln k_0.
\]

Here, \( R \) is the universal gas constant (8.314 J/(K×mol)) and \( k_0 \) denotes the pre-exponential factor (mol\(^{1-n}\)/s×m\(^2\)).

Figure 12 presents Arrhenius plots for both catalysts. The log of the effective rate constant is fairly linear versus reciprocal temperature, as shown in Figure 10. The estimated activation energies are almost equal for both samples (Table 3). This situation is expected because both samples are of identical chemical composition with active sites of identical chemistry. The pre-exponential factor is considerably higher for the ZA-1 catalyst which is seemingly governed by the higher overall acidity of ZA-1 (Table 2). For ZSM-5/Al\(_2\)O\(_3\) catalyst with zeolite/alumina ratio = 3/2 by mass, \( k_0 \) in the order of 10\(^8\) mol/(g×s) has been reported [32]. The values of \( k_0 \) measured in the current study are several orders of magnitude different from those reported in the literature. The estimated activation energies coincide with the range of the existing data concerning methanol conversion to DME over ZSM-5 catalyst. Particularly, \( E_a \) of approximately 70 kJ/mol was obtained in [32, 33].
contrast, Yue et al. [30] and Grzesik et al. [34] obtained $E_a$ equal to 106 kJ/mol and 95 kJ/mol, respectively. It is worth noting that $E_a$ obtained in this study is smaller than that for ZSM-5/Al$_2$O$_3$ (104 kJ/mol) [35].

The obtained results demonstrate that using MWCNTs as a pore-forming agent allows the synthesis of the materials with significantly different textural properties. An increased porosity considerably affects the acidity of the material. Increasing acidity results in an increase in the pre-exponential factor. The pre-exponential factor determines the reaction rate over the synthesized catalyst. It has been shown that Bronsted acidity plays central role in the activity of a catalyst toward methanol conversion to DME [36, 37]. Therefore, higher $k_0$ for ZA-1 is seemingly defined by higher concentration of Bronsted acid sites compared to ZA-2. However, neither textural properties nor the acidity of the composite influences the activation energy. The latter indicates that the catalytic process occurs on the same active sites for both samples.

4. Conclusions

ZSM-5/$\gamma$-Al$_2$O$_3$ composites with significantly different physicochemical characteristics are synthesized using multiwall carbon nanotubes as a pore-forming agent. Varying the synthesis technique, the materials possessing a two-fold difference in surface area, pore volume, micropore volume, and mesopore surface area are obtained. The as-prepared composites demonstrate high catalytic activity in the process of the methanol dehydration to dimethyl ether. The methanol conversion over the as-prepared composites reaches equilibrium, and 100% selectivity toward DME is observed. Based on the catalytic activity tests, a link between the textural properties of the composites and the kinetic parameters of the process is provided. Tuning the textural properties does not affect the activation energy which is around 65–70 kJ/mol. However, this increases acidity resulting in increasing the pre-exponential factor and, as a consequence, increasing the activity of the catalyst.

Data Availability

The data supporting the findings of this study are available within the article and its supplementary materials.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors’ Contributions

I.P. and A.Z. wrote the main manuscript text and prepared the figures. V.G. performed the activity tests. P.S. supervised the work. All authors reviewed the manuscript.

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![Figure 12: Arrhenius plots for (a) ZA-1 and (b) ZA-2 samples. Points correspond to experimental data, whereas solid lines reflect theoretical fitting.](image-url)
**Supplementary Materials**

The additional information consists of experimental data, obtained during catalytic tests. Calculations of reaction order, mass, and heat transfer limitations criteria are present as well. The following is the detailed description of the Supplementary Materials presented. Figure S1: In $C_{\text{methanol}}$–ln $r$ plots for studied catalysts, where $r$ is the reaction rate. Also, fitting curves are shown. Table S1: values of diffusion limitations criteria for experimental conditions, performed to evaluate reaction order, are shown. Table S2: values of dimensionless parameter $\Phi_{ij}$ were used for Carberry number calculations. Table S3: density of gas mixtures, used in the experiments, at different temperatures. Table S4: gas flow rates in the channels between the catalyst particles at different temperatures. Table S5: values of mean velocity of the methanol molecules and mean free path of the methanol molecules at different temperatures. Table S6: obtained Sherwood number values. Table S7: observed reaction rates at different temperatures. Table S8: calculated Knudsen diffusion coefficient values. Table S9: calculated Mears criterion values. Table S10: calculated Damköhler’s number values. (Supplementary Materials)

**References**


