Ultrasonic Pretreatment as a Tool for the Preparation of Low-Defect Zeolite Mordenite

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ABSTRACT: The effects of the ultrasonic (US) pretreatment of synthesis gel for the preparation of mordenite zeolite were studied in comparison with the classical stirring method. Even though the US pretreatment was performed before the hydrothermal crystallization, it significantly affected the properties of the obtained mordenite crystals. The US-assisted procedure resulted in a material with improved textural characteristics, in particular, the micropore volume accessible for nitrogen molecules in the as-made form. On the other hand, mordenite prepared with the classical stirring method demonstrated comparable sorption properties only after a postsynthetic treatment. Moreover, in the case of US-pretreated mordenite, altered crystal shape and more homogeneous morphology were observed. 29Si magic-angle spinning nuclear magnetic resonance (MAS NMR) demonstrated that the US pretreatment introduced structural changes on the atomic level, resulting in fewer defects (reflected in the number of silanol groups) and less pore blockage (affected by Na+ cations) for the as-made sample.

INTRODUCTION

Zeolites are crystalline aluminosilicate materials featuring a unique combination of properties: (i) ordered microporosity giving rise to shape selectivity and (ii) well-defined proton and/or metal cation active sites, compensating the negative charge of the aluminosilicate network.1,2 These features create the setting for the exceptional performance of zeolites as selective sorbents and catalysts.3

Mordenite (three-letter code MOR for framework type4) can be used, in particular, as a sorbent for wastewater treatment.5,6 Yet, the most important application of this structure is industrial catalysis: hydro-isomerization of light naphtha (CS−C6 paraffins) and aromatic processing (e.g., cumene production, ethylbenzene isomerization, toluene disproportionation).3

Similar to other zeolites, the catalytic properties of mordenite are inextricably linked to the specific features of its pore system; moreover, this structure is remarkably stable upon catalytic reaction conditions, e.g., high temperature.

The MOR framework consists of ellipsoidal 12-ring channels of 6.5 × 7.0 Å² and 8-ring tortuous pores of 2.6 × 5.7 Å² parallel to the c-axis, both interconnected through 8-ring side (3.4 × 4.8 Å²) channels (forming so-called “side pockets”). Accessibility of the active sites, achieved by sorption through the size- and shape-selective channels, creates the basis for catalytic performance. In the theoretically assumed situation, all active sites are available, but only the molecules of a particular shape can move to or from the active sites through the specific micropore system. In practice, depending on the synthesis method or, in the case of natural zeolite, the origin of mineral, mordenites exhibit a nonideal channel structure and, therefore, different/limited sorption properties. On the basis of the sorption behavior, two types of mordenites are distinguished: small port (SP) and large port (LP).7 There are no established commercial applications of SP mordenite. The LP synthetic mordenite is applied, for example, in the conversion of linear paraffins in the light naphtha to branched paraffins with a higher octane number as a part of Pt-based bifunctional catalyst. The LP mordenite is modified by postsynthetic hierarchization to minimize diffusion limitations. In the presence of hydrogen, such catalysts optimize isomerization and minimize hydrocracking.8,9

According to Sanders,10 there might be three reasons for the inaccessibility of all pores in mordenites: blockage by amorphous material, blockage by inorganic cations, or crystallographic defects such as the presence of fault domains. To achieve the opening of pores and better transport of molecules, the range of postsynthetic treatments such as thermal treatment, ion exchange (IE), or dealumination may be applied.11 Yet, in many cases, side effects of the postsynthetic treatment include the partial destruction of the microporous system and the generation of structural defects that have a negative influence on selectivity.12

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Another important factor influencing the performance of zeolite catalysts is the presence of silanol groups (internal and surface SiOH), which is also connected with structural defects. An increased number of silanol groups are linked with the accumulation of coke on the catalysts, making them prone to fast deactivation.13,14

The importance of mordenite-based catalysts has led to a growing interest in facile synthesis procedures that allow us to prepare high-quality materials with accessible porosity, fewer structural defects, and improved textural properties in general. The application of ultrasound (US) in the zeolite synthesis has been proven to be an effective tool, in particular, to reduce the crystallization time, shorten the induction period, and provide a more uniform crystal size.15,16 The mechanism of ultrasonic (US) influence is still ambiguous, but supposedly it has a connection with the cavitation phenomenon, resulting from the formation, growth, and collapse of bubbles.17 Most probably, the modification of the synthesis gel is based on breaking down the complex sources of silica (or eventually alumina) by the locally generated high pressure, high temperature, and shockwaves during the bubble collapse.17

The advantage of the US pretreatment method, proposed for the zeolite production in the present work, is its simplicity and low cost in comparison to other novel effective strategies for zeolite synthesis (e.g., microwave and mechanochemical techniques). Ultrasonic bath applied for the pretreatment belongs to the standard laboratory equipment. Also, the US pretreatment can be introduced instead of the regular stirring of the standard synthesis gel, without altering its chemical composition and without additional installations in the hydrothermal synthesis equipment.

The present work describes how the application of US pretreatment may be used in the synthesis of mordenite. To the best of our knowledge, this is the first work on the application of the ultrasonic method for zeolite mordenite synthesis; moreover, the obtained 29Si magic-angle spinning nuclear magnetic resonance (MAS NMR) data showed that the US pretreatment of the synthesis gel induced structural changes in the resulting mordenite at an atomic level, which was not presented yet for zeolites originating from US-assisted syntheses. The practical aspect of the work lies in the improvement of zeolite properties (accessibility of the microporous system, fewer silanol defects, more homogeneous crystal morphology) achieved solely by the pretreatment of the synthesis gel on an ultrasonic bath, which may be realized with typical reagents and basic hydrothermal synthesis procedure and equipment.

# RESULTS AND DISCUSSION

According to the powder X-ray diffraction (XRD), both the prepared zeolites exhibited patterns characteristic for the MOR structure, without the presence of competing crystalline phases. The XRD patterns are presented in the Supporting Information (Figure S1). Scanning electron microscopy (SEM) studies, presented in Figure 1, demonstrated differences in the crystal morphology.

The reference material prepared with stirring (MOR-R)18 predominantly consisted of intergrown crystallites, 5–10 μm in size, with sharp edges. Additionally, some agglomerates of needles (up to 10 μm) were observed in MOR-R. Mordenite obtained with application of the US pretreatment (MOR-U) showed a more homogeneous morphology of intergrown pellets 10 × 5 μm2 and no signs of needle-like or fibrous formations. The observed differences in the crystal morphology might be attributed to dissimilarities in nucleation and the initial stages of the crystallization process, connected with ultrasonically driven changes in the gel.17,19

From the point of view of applicability as catalysts, the performance of zeolites is greatly influenced by their crystal size and shape.20,21 Besides, the homogeneous morphology is preferable rather than a mixture of different crystal types.20,21 Finding the parameters altering the crystal morphology or providing more control over the crystal size and shape is an essential direction toward tailoring the zeolite catalyst properties and improving the selectivity. Moreover, in the case of mordenite, the needle-like and fiber-like morphology (present in MOR-R) is undesirable because it is connected with the health hazard during material handling comparable to that of asbestos materials.22

To follow the crystallization process, additional syntheses were performed in the same way, but the crystallization was stopped after 12 and 18 h. The obtained samples were analyzed by XRD and SEM (relevant images are presented in the Supporting Information in Figure S2). The SEM studies showed a gradual growth of the same morphology crystals (and generally more homogeneous) for material MOR-U (Figure S2a–i), and the formation of few different morphologies for MOR-R (Figure S2g–j). Various morphologies (including the needle-like) were not observed by SEM studies in the case of MOR-U at different crystallization times and in the final sample. According to an estimation of crystallinity, calculated by dividing the integral area of peaks of the reference sample, the US-pretreated gels crystallize slightly faster. This observation agrees with the literature reports for the US-assisted zeolite synthesis.15 Yet, the SEM studies of morphology for all samples suggest that independent of the synthesis time and relative crystallinity, the sample MOR-U has a more homogeneous character. The presented results confirm that the US pretreatment might be recommended as one of the methods significantly influencing the crystal morphology and leading to more controllable crystalline phase formation due to its effect on initial crystallization steps.15

The differences in the chemical composition of the crystals, determined by the X-ray fluorescence (XRF) method, were not significant. Si/Al and Na/Al values can be found in Table 1,
together with a summary of other characterization data of the obtained samples. $^{27}$Al MAS NMR spectra of both materials (Figure S3, presented in the Supporting Information) contained only resonances centered around 56 ppm, demonstrating the exclusive presence of Al atoms in a tetrahedral framework environment and no undesirable octahedral extra-framework Al species. Results from $^{29}$Si MAS NMR, presented in Figure 2, show that both spectra are consistent with the previously published $^{29}$Si MAS NMR spectra of an Al-rich mordenite. However, there is a significant difference between the samples in the area below $-100$ ppm, where resonances reflecting terminal SiOH can be present. Thus, a detailed analysis of each spectrum was performed by its decomposition and simulation using Gaussian bands, which correspond to silica in different surroundings (see Figure 2). In the case of the US-pretreated sample (MOR-U), resonances at $-114$, $-113$, and $-110$ ppm represent Si$(4Si)$ atoms surrounded exclusively by silica atoms, whereas Si connected to one and two alumina atoms are present at $-106$ ppm Si$(3Si, 1Al)$ and $-99$ ppm and $-94$ ppm Si(2Si, 2Al), respectively. Framework Si/Al ratio was estimated from the single pulse $^{29}$Si MAS NMR spectrum using the formula

$$\text{Si/Al} = I_1/(0.25I_0 + 0.5I_2 + 0.7I_3)$$

(1)

where $I_1$ is the intensity of the NMR resonance of the Si$(3Si,1Al)$, $I_2$ is the Si$(2Si,2Al)$ atoms, $I_3$ is the Si$(1Si,3Al)$ atoms, and $I$ is the total $^{29}$Si intensity. $^{24,25}$

The NMR experiment does not allow the estimation of the unambiguous concentration of Al atoms in AlSiAl sequences in the zeolite due to the fact that these sequences can represent various types of Al organization. Limited cases represent isolated AlSiAl sequences (upper one) and (Al$_i$)$_n$ chains (lower one). To calculate the lower and upper limits of the concentration of Al in AlSiAl sequences, eqs 2 and 3 were used according to Sazama et al. $^{24,25}$

Table 1. Chemical Analysis and Sorption Properties of the Mordenites Prepared with US Pretreatment (MOR-U) and with Stirring (MOR-R)

| sample | Si/Al (XRF) | Si/Al (NMR) | Na/Al (XRF) | $V_{mic}$ (cm$^3$/g) | $S_{mic}$ (m$^2$/g) | $V_{mic}$ (cm$^3$/g) | $S_{mic}$ (m$^2$/g) | $V_{mic}$ (cm$^3$/g) | $S_{mic}$ (m$^2$/g) |
|--------|-------------|-------------|--------------|----------------------|---------------------|----------------------|---------------------|----------------------|---------------------|
| MOR-U  | 6.2         | 5.9         | 1.0          | 0.14                 | 267                 | 0.18                 | 359                 | 0.21                 | 415                 |
| MOR-R  | 5.4         | 5.6         | 1.1          | 0.001               | 3                   | 0.15                 | 309                 | 0.19                 | 391                 |

“Based on t-plot. $^{a}$NH$_4^+$ to H$^+$ partial conversion during the sorption measurement due to heating. $^{b}$Obtained by thermal treatment of NH$_4^+$ form prior to sorption measurement.”

Figure 2. $^{29}$Si MAS NMR of the mordenite prepared with US pretreatment (MOR-U, blue line) and with stirring (MOR-R, red line). Black lines show the spectra simulations and individual Gaussian bands of $^{29}$Si resonances.
\[ \text{AlSiAl} = \frac{I_2}{(I_2 + 1/4 \times (I_3 - 2 \times I_2))} \times 100\% \]  
\[ \text{Al(Ali)n} = \frac{(2 \times I_2)}{(2 \times I_2 + 1/4 \times (I_3 - 6 \times I_2))} \times 100\% \]

The framework Si/Al values obtained according to eq 1 are close to those received from the chemical analysis (see Table 1), which confirms the correct assignment of the observed resonances. Spectra of the reference sample (MOR-R) are more complicated and characterized by a greater abundance of various Si surroundings. The same three resonances for Si(4Si) at −114, −113, and −110 ppm are followed by resonances at −106, −97, and −90 ppm, representing silica atoms connected to one Si(3Si, 1Al), two Si(2Si, 2Al), and three Al atoms Si(1Si, 3Al), respectively. A significant fraction (16% of Si atoms) of new resonances at −100, −94, and −88 ppm can be attributed to terminal silanol groups or silanol nests, silica atoms with one (Q⁰) or two (Q¹) OH groups, i.e., Si(3Si, OH) and Si(2Si, 2OH). The latter assignment of Q² and Q³ units was confirmed by the cross-polarization experiment, which showed a strong signal in this area (see Supporting Information, Figure S4).

The framework Si/Al values also agreed with the chemical analysis data obtained by XRF for the studied sample, proving the right assignment of the resonances (see Table 1). These results clearly evidenced a negligible amount of silanol groups (i.e., defect sites) for the sample synthesized using the US pretreatment.

Al organization in Si-rich materials (distances between Al atoms) is a crucial parameter of a zeolite catalyst.¹⁸,²⁶,²⁷ The resonances reflecting the Si(2Si, 2Al) atoms demonstrate the presence of two close Al atoms in the AlSiAl sequences in the zeolite framework. Nevertheless, the exact concentration of Al atoms in the AlSiAl sequences cannot be estimated due to the fact that both isolated AlSiAl sequences and infinite (AlSi)₂ chains can be present in the framework. The upper and lower limits of Al concentration in these sequences were determined using equations eq 2 and 3²⁴ and represent 50−95% of Al atoms in AlSiAl for MOR-U and 70−100% of AlSiAl for MOR-R. Thus, on an atomic level, the application of ultrasound pretreatment of the synthesis gel affects not only the formation of silanol defects in the final product but also the Al organization in the zeolite framework with a presumable influence on its catalytic properties.²⁵ Noteworthy, the Na/Al values of both as-made forms were close to 1 (see Table 1). Considering that sodium cations can be accommodated only by the tetrahedrally coordinated Al, Na/Al = 1 is a direct confirmation that all Al is present in the structure as framework Al because the presence of extra-framework octahedral Al would lead to a Na/Al ratio lower than 1. This observation agrees with the absence of octahedral Al signals in ²⁷Al MAS NMR (Figure S3).

Textural properties of the samples, characterized by the nitrogen sorption at 77 K, exhibited the most apparent difference among the as-made MOR-R and MOR-U materials. Figure 3 shows the comparison of nitrogen sorption isotherms, confirming the accessibility of micropores for material originating from US-pretreated gel (MOR-U), whereas the reference material MOR-R demonstrated no significant sorption values.

All corresponding characterization data are collected in Table 1 (textural properties of various ion-exchanged forms, Si/Al, and Na/Al values). The respective t-plot analysis is presented in Figure S5 (Supporting Information). From the t-plot, values of micropore volume were calculated. The sample MOR-U demonstrated accessibility of 0.14 cm³/g of micropore volume, whereas in the case of the as-made reference material MOR-R, no significant sorption of nitrogen molecules occurred (0.001 cm³/g).

The situation changed after the ion exchange (IE) from the sodium form to the ammonium form. Following the initial thermal treatment (sample activation at 400 °C for 10 h for the nitrogen sorption studies) resulting in partial decomposition of the ammonium cation, the material NH₄⁺/H⁺-MOR-R exhibited 0.15 cm³/g of accessible micropores, whereas the US-pretreated sample showed 0.18 cm³/g.

The subsequent thermal treatment (450 °C overnight) led to the complete decomposition of ammonium cations and the formation of purely protonic forms of both materials, with further improvement in the micropore volume (0.21 and 0.19 cm³/g for H⁺-MOR-U and H⁺-MOR-R, respectively, see also Figure S6 in the Supporting Information). The differences in the sorption behavior of the as-made materials (which were purely sodium forms) might be attributed to different positions of Na⁺ cations, reflecting different Al organizations. This might explain why after the IE from sodium to ammonium forms, the materials started to demonstrate comparable sorption properties. Additional confirmation that it was not the thermal treatment alone, which led to pore opening in MOR-R, came from an experiment, where the as-made form was subjected to overnight thermal treatment at 450 °C without the preceding IE. For this case, sorption of N₂ did not occur as well (these results are not included in Table 1).

Other structural defects of MOR-R (reflected in silanol presence) did not strongly influence its sorption behavior as the sorption properties of both MOR-U and MOR-R became comparable after sodium cations were removed. Therefore, the different positions of Na⁺ cations seem to be the most influential factor in the sorption properties of the studied case.

CONCLUSIONS

In summary, the current study demonstrated that the ultrasonic pretreatment of synthesis gel affected the various properties of obtained mordenite, resulting in

1. more homogeneous crystal size and morphology, absence of undesirable fiber- and needle-like crystals;
2. fewer structural defects (reflected in negligible silanol groups resonances in the ²⁷Si MAS NMR spectra);
3. the consequent thermal treatment (450 °C overnight) led to the complete decomposition of ammonium cations and the formation of purely protonic forms of both materials, with further improvement in the micropore volume (0.21 and 0.19 cm³/g for H⁺-MOR-U and H⁺-MOR-R, respectively, see also Figure S6 in the Supporting Information). The differences in the sorption behavior of the as-made materials (which were purely sodium forms) might be attributed to different positions of Na⁺ cations, reflecting different Al organizations. This might explain why after the IE from sodium to ammonium forms, the materials started to demonstrate comparable sorption properties. Additional confirmation that it was not the thermal treatment alone, which led to pore opening in MOR-R, came from an experiment, where the as-made form was subjected to overnight thermal treatment at 450 °C without the preceding IE. For this case, sorption of N₂ did not occur as well (these results are not included in Table 1).
4. Other structural defects of MOR-R (reflected in silanol presence) did not strongly influence its sorption behavior as the sorption properties of both MOR-U and MOR-R became comparable after sodium cations were removed. Therefore, the different positions of Na⁺ cations seem to be the most influential factor in the sorption properties of the studied case.

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Al2O3/30SiO2/780H2O. The synthesized sample was desig-

The reduction of structural defects by ultrasonic pretreatment of the synthesis gel may be a feasible way to solve the common problem of “nonideal” structure in synthetic mordenites. Additionally, higher sorption capacity in this structure could be achieved by an easy and efficient US method applied before the synthesis, without time- and resource-consuming traditional postsynthetic treatment (which, on the contrary, leads to the generation of structural defects). Moreover, the lower number of silanol groups can contribute to a longer catalytic lifetime of the prepared mordenite.

**EXPERIMENTAL SECTION**

The standard mordenite synthesis was modified by the application of US pretreatment of the synthesis gel prepared using common industrial sources: NaAlO2 (technical grade, Sigma Aldrich), SiO2 (TIXOSIL 38A, Rhodia Silica Systems, Solvay), and NaOH (98%, Lach-Ner) in the molar ratio 6Na2O/A12O3/30SiO2/780H2O. The synthesized sample was designated as MOR-U. For comparison, the reference material (sample MOR-R) was synthesized without this modification. The parameters of ultrasonication were adjusted before the synthesis to prevent the heating of the gel, so the stirring and ultrasonication both were performed at RT (to avoid altering the kinetics of gel formation by temperature). Organic structure-directing agents (OSDAs) were not used, ensuring the “green route” of zeolite production. Hydrothermal crystallization of both gels was performed in Teflon-lined steel autoclaves (at 170 °C for 24 h). Both autoclaves were identical, and the synthesis was carried out in the same oven.

The prepared materials were characterized by powder X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM), 27Al and 29Si magic-angle spinning nuclear magnetic resonance (MAS NMR), and nitrogen sorption. Studies were performed for the various cationic forms of the samples: as-made Na+, NH4+, H+. Moreover, the reproducibility studies were performed (synthesis was repeated, with comparable results of XRD, XRF, SEM, MAS NMR, and N2 sorption analysis). A more detailed description of the synthesis, postsynthetic treatment, and characterization methods can be found in the Supporting Information.

**ASSOCIATED CONTENT**

- **Supporting Information**
  The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c05655.

Detailed synthesis, postsynthetic treatment, and experimental methods description; characterization of products by powder XRD, 27Al MAS NMR, 29Si CP MAS NMR, and SEM images following crystallization process after 12 and 18 h of the synthesis; and additional sorption data (t-plot, comparison of isotherms for materials after calcination and ion exchange) (PDF)

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**ABBREVIATIONS USED**

CP MAS NMR, cross-polarization magic-angle spinning nuclear magnetic resonance; IE, ion exchange; SEM, scanning electron microscopy; US, ultrasonic, ultrasound; XRD, powder X-ray diffraction; XRF, X-ray fluorescence

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