

Review

Recent Progress in Synthesis and Application of Nanosized and Hierarchical Mordenite—A Short Review

Yuri Kalvachev ^{1,*} , Totka Todorova ¹  and Cyril Popov ^{2,*} 

¹ Institute of Catalysis, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria; t.todorova@ic.bas.bg

² Institute of Nanostructure Technologies and Analytics, University of Kassel, 34132 Kassel, Germany

* Correspondence: kalvachev@ic.bas.bg (Y.K.); popov@ina.uni-kassel.de (C.P.); Tel.: +359-2-979-3989 (Y.K.); +49-561-804-4205 (C.P.)

Abstract: Zeolites with their unique properties find applications in various fields, including medicine, agronomy, ecology, production of detergents and drying agents, and in a number of industrial processes. Among zeolites, mordenite is particularly widespread because of its high silica/alumina ratio, which allows it to resist exposure to high temperatures and to acidic gases and liquids. Mordenite is commercially available as a natural mineral and as a synthesized material. This zeolite is mostly used in its synthetic form as an acid catalyst in the petrochemical industry for the isomerization of alkanes and aromatics. In this review, we consider the scientific literature on the structure, synthesis, and two main types of modifications that solve the diffusion difficulties during catalytic processes. The first type of modifications is related to a reduction of the size of the mordenite crystals obtained to submicron or nanometric range, whereas the second ones aim to obtain hierarchical mordenite samples by appropriate post-synthetic treatments. Both types of modifications find many other applications besides solving diffusion constraints in catalytic processes. Attempts to fine-tune and control the particle size in the first type of modifications or the pore size in the second ones by adjusting various parameters during the synthesis are described.

Keywords: zeolite; synthesis; nanosized mordenite; hierarchical material



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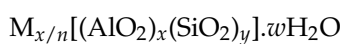
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1. Introduction

Zeolites are crystalline hydrated aluminosilicates. They possess right ordered structure containing one-, two-, or three-dimensional cavities and channels with sizes up to 2 nm through which a large number of molecules can pass. Their skeletons are built of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra (T), linked by a shared oxygen atom. The presence of aluminum atoms in zeolite structure determines the existence of negative skeleton charge, which could be compensated by numerous cations of alkali and alkaline earth metals or by some organic cations. Typical cations involved in the zeolite structure are K^+ , Na^+ , Ca^{2+} , Ba^{2+} , and H^+ [1–3]. The structural formula of a zeolite represents the smallest segment of the structure:



In the formula, n is the oxidation state of cation M , w the number of water molecule, and x and y are the numbers of aluminum and silicon atoms per unit cell. The ratio y/x varies for different zeolite structures [1,4]. The zeolite properties are determined by their chemical composition in combination with the specific channel system. Zeolites have been extensively studied and applied in different fields like oil refining, petrochemical industry, production of detergents and drying agents, separation of gas mixtures, in ecology, and also in many novel high-tech areas as electronics, optics, and sensor technology [5–9].

Due to its unique textural properties and strong acidity, mordenite has been widely employed as a heterogeneous catalyst in the petrochemical industry. Its superior acidic and shape-selective properties are used in numerous processes, such as toluene disproportionation, alkylation, m-xylene transformation, hydroisomerization, carbonylation, etc.

Soon after its discovery, mordenite became one of the most useful industrial zeolites. The reason is the high thermal and acidity stability in combination with a large channel system.

Despite the relatively large pores of mordenite, their size is often a drawback when the dimensions of the molecules subjected to transformations on the zeolites or that of the resulting products are large. There are two approaches to overcome this disadvantage and to provide improved diffusion of molecules—one is the synthesis of nanosized zeolite, the other the preparation of hierarchical material.

The goal of the present review is to summarize and systematize the data on the structure, modifications, characterizations, and applications of mordenite with a focus on various approaches for modifications that solve the diffusion problems. Synthesis methods for nanosized and hierarchical mordenite are discussed and their applications in the field of catalysis are presented.

2. Structure of Mordenite

The mordenite type of zeolite was discovered and named by Professor How in 1864. The name was introduced for a mineral found in region Morden, Nova Scotia in Canada [10,11]. This new-for-the-time mineral has high silicon content structure with approximate chemical composition $(\text{Na}_2, \text{K}_2, \text{Ca})_4(\text{Al}_8\text{Si}_{40}\text{O}_{96}) \cdot 28\text{H}_2\text{O}$. The zeolite mordenite belongs to pentasil family, typical for which are five membered rings as secondary building units [12–14]. The mordenite structure is composed of connected 5-membered rings forming a composite building unit “mor”. These building units are connected by 4-membered rings which determine the formation of 12-membered channels with a size of 0.7×0.65 nm and strongly compressed 8-membered channels with a size of 0.57×0.26 nm along the crystallographic direction [001] (Figure 1a). Only 8-membered channels (0.34×0.48 nm), referred as side pockets, are lined up in parallel to [010] direction (Figure 1b). The reason is that the channels, running staggered along the “b”-axis, intersect the other two types of channels arranged alongside the “c”-axis [11,15,16].

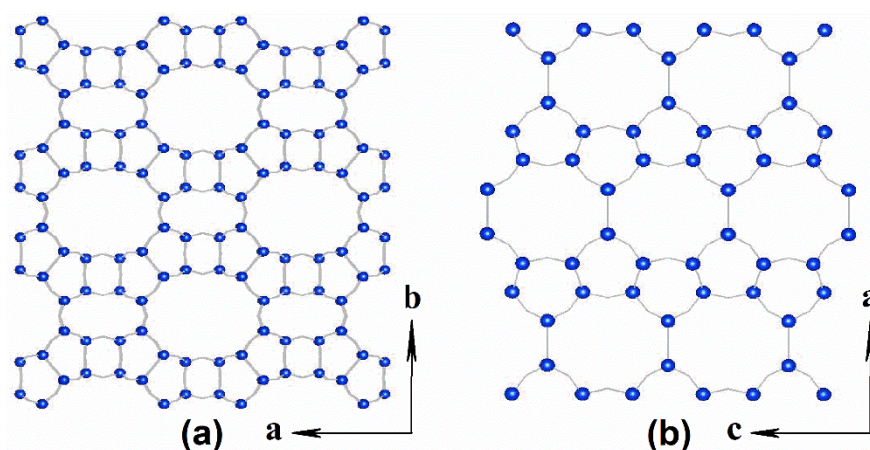


Figure 1. Skeletal structure of mordenite projected (a) perpendicular to axis “c” and (b) to axis “b”.

The mordenite structure possesses an orthorhombic unit cell of topological space-group of symmetry $Cmc2_1$. This space-group is very close to space-group $Cmcm$ ($a = 18.2560$ Å, $b = 20.5340$ Å, $c = 7.5420$ Å); the difference is due to the deviation of the T-O-T angle from 180° [15,17,18].

The most common arrangements of the tetrahedra in the mordenite structure are “Si-O-Si” or “Si-O-Al” as in majority of the zeolites. The hydroxyl group formed between two silicon atoms is called silanol group. Although these groups are located on the crystal surface, they possess low activity as a result of the greater strength of the O-H bond. The other type of OH groups contained in the zeolites are the so-called bridging hydroxyl groups. They belong simultaneously to silicon and aluminum tetrahedra, and therefore can easily separate a proton that allows them to act as Brönsted acidic centers (BAC). Figure 2

shows the possible and forbidden bonds in the zeolite structure, as well as the types of hydroxyl groups in it. In contrast to the silanol groups, the bridging hydroxyl groups are located in the zeolite pores and channels. The type, position, and strength of the active centers are essential for the zeolite properties in addition to the structure type [2,19].

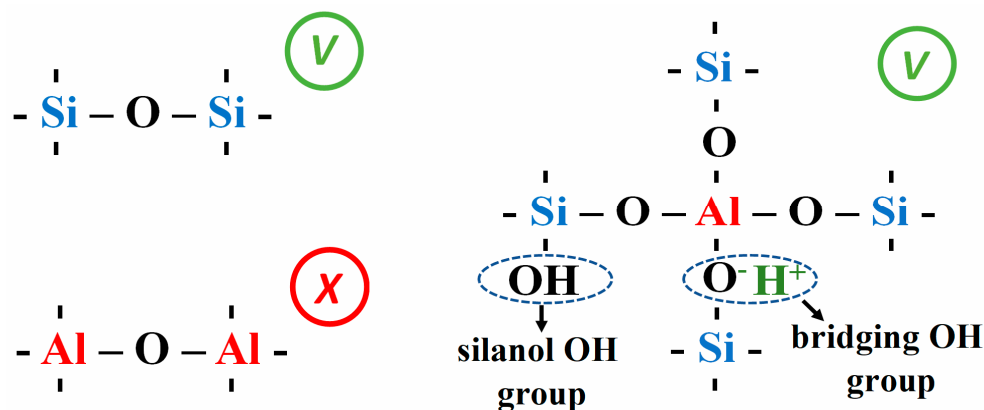


Figure 2. Schematic representation of possible bonds in zeolite structure.

The presence of wide and narrow channel systems with available Brönsted acidic centers defines the application of zeolites in catalytic reactions, adsorption, ion-exchange, oxidation, and reduction processes [20–23]. In order to study the mechanism of the flowing processes on the zeolite surface, it is especially important to know the number and positions of the aluminum tetrahedra (Brönsted acidic centers) in the mordenite structure [24,25]. D. Lukyanov et al. presented in their work data the distribution of the active centers between the individual positions [26]. Their results refer to a completely ion-exchanged acidic mordenite (H-Mor) sample and show that about 25% of BAC are located in the 8-membered channels, 13% are arranged between the 12-membered channels and the side-pockets, whereas the remaining 62% of the active zeolite sites are located in the center of the 12-membered channels. These values indicate equal acid distribution between the oxygen atoms in various crystallographic positions and demonstrate the complexity to determine accurately the positions of the aluminum tetrahedra. Earlier studies have reported high aluminum employment in the 4-membered rings connecting the 8- and 12-membered channels to direction [001], which is in agreement with the results of D. Lukyanov et al. [26].

3. Nanosized Mordenite

Recently, the number of zeolites synthesized as nanosized materials has significantly increased due to the new areas of applications such as preparation of zeolite films, membranes, other composite materials, and colloidal suspensions of nanosized zeolites. The size reduction of the zeolite crystals to submicrometric and nanometric scale plays an important role for their physical and chemical properties. The widespread employment of nanosized zeolites mainly in the fields of catalysis and adsorption applications is determined by their higher active surface area, high surface energy, and shorter channels. As a result of these features, they exhibit a number of properties, such as high catalytic activity, better selectivity, high resistance to coke formation, and better diffusion properties compared to the traditional “macro” materials. One of methods used to control the crystal size and morphology is the seed-assisted synthesis. Adding seeds (zeolite crystals from desired phase) into starting gel contributes to the formation of the predominant phase, increases the crystallization rate, and the crystal yield. The advantage of this method is the preparation of high-siliceous samples from systems free of organic structure-directing agents (OSDAs-free), providing new opportunities for ecological synthesis of a large amount of products [27–30]. Typical for the mordenite is the formation of long needle crystals along the “c” axis, where 12-membered channels with part of the active zeolite centers are located. In some reactions by which the diffusion of the reagents in the porous system

is decisive, the smaller crystal size enhances the reaction rate due to the reduced coke formation. During the synthesis of nano-mordenite, the formation of a large number of nuclei in the starting system is essential. By addition of mordenite crystals as seeds, a significant reduction of the induction period is achieved as well as a decrease of the following crystallization time from days to several hours. The small crystal size is a result of the large number of nuclei imported, around which the crystal growth takes place, causing a spatial limitation. Despite the addition of zeolite seeds and the strict control of the synthesis conditions (temperature, duration of synthesis, Si/Al ratio, OSDA free synthesis, etc.), it is difficult to obtain mordenite with crystal sizes below 5 μm . The reason is the mordenite morphology, built of stacked long nano-rods forming the crystals [31–33]. Successful synthesis of low-silica mordenite (Si/Al = 15) with particle sizes below 100 nm is reported by Hincapie et al. [34]. This size was achieved by a two-step gel preparation procedure, low synthesis temperature of 150 $^{\circ}\text{C}$, and reduced synthesis time.

The challenges of the new time require the introduction of novel methods and techniques for the synthesis of materials responding to modern requirements. K. Itabashi et al. [35] and H. Zhang et al. [36] offer an “exotic” method for production of mordenite by the addition of seeds from other zeolite phases such as Beta, ZSM-5, and ZSM-11. Their studies were based on the fact that all four structures (MOR, Beta, ZSM-5, and ZSM-11) contain *mor* composite building units. Moreover, the addition of Beta seeds to the starting gel has a serious effect on both the crystal size and the morphology of the resulting mordenite products. The presence of common *mor* composite building unit (CBU) between parent (BEA) and target (MOR) structures, as shown in Figure 3, helps to overcome the kinetic hurdles during transformations, especially assisting the nucleation. The preparation of homogeneous, dense, and efficient mordenite membranes by a seed-assisted method for separation of water–isopropyl alcohol mixtures has been also reported [28,37].

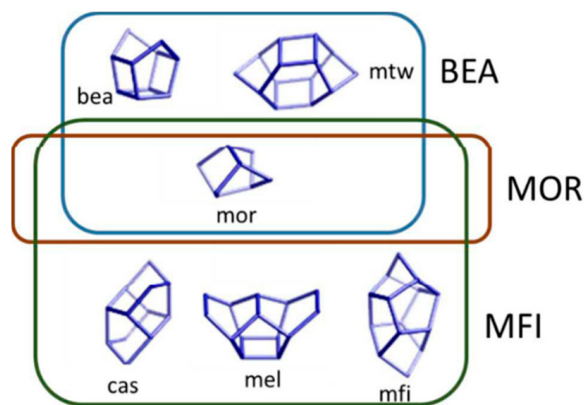


Figure 3. Correlation of the common composite building units between BEA, MOR and MFI. (zeolite framework type codes introduced by International Zeolite Association and approved by IUPAC). Reproduced from Ref. [36] with permission. Copyright 2016, Royal Society of Chemistry.

Our investigations showed that the size of the mordenite particles can be controlled [38]. The parameters, which influence the particle size of the synthesized mordenite, are the content of water in the initial gel and the amount of seeds. These factors have an effect also on the crystallization time and on the physicochemical properties of crystalline products. Six hours is the established shortest time for obtaining zeolite mordenite. X-ray diffraction patterns of the samples are shown in Figure 4. In all cases, mordenite of high crystallinity has been observed. By increasing the amount of seeds added to the initial gel, crystallization time is shortened. SEM images of synthesized mordenite crystals are shown in Figure 5.

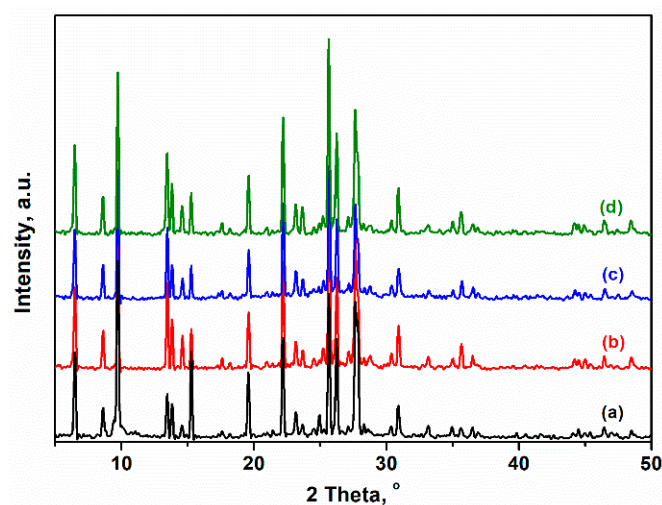


Figure 4. XRD patterns of samples prepared from gels with 280 moles of water (a) without seeds; (b) with 1% seeds; (c) with 2% seeds; (d) with 5% seeds.

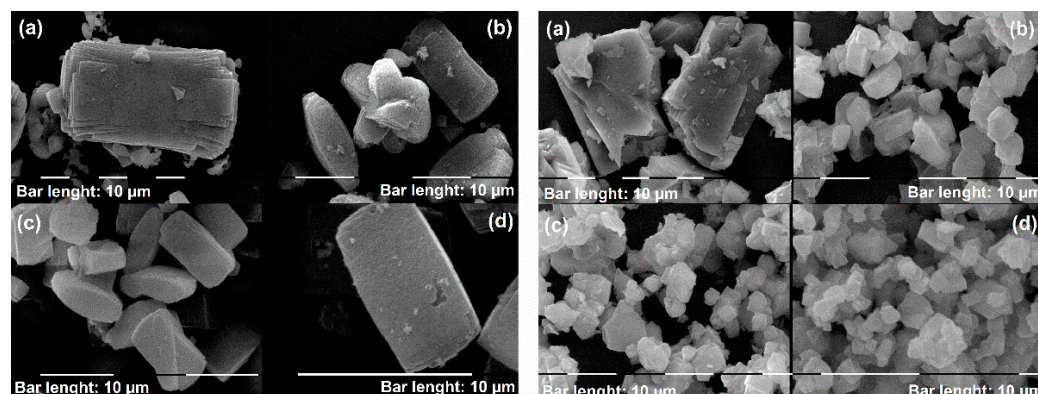


Figure 5. SEM images of mordenite crystals synthesized from gels with 280 moles (left) and 22.5 moles of water (right): (a) without seeds; (b) with 1% seeds; (c) with 2% seeds; (d) with 5% seeds.

The application of milled seeds with a crystal size of about 200 nm was found to be very efficient for increasing the crystallization rate of mordenite [39]. By using of a tubular reactor, further reduction of the mordenite synthesis time to 10 min was reached. In this case, a large amount of seeds was added to the synthesis gel—up to 30 wt.% on the basis of the initial SiO_2 amount.

In order to limit the crystal size of the synthesized zeolite materials, an often-used method is the space-confined synthesis applying a physical barrier. The systems with confined space minimize the dissolution of the small crystals or sol particles and their deposition onto the larger crystals (Ostwald ripening). There is a variety of materials used in the reaction mixture to achieve this effect such as a carbon matrix, polymers, and organosilanes [40,41]. One not very commonly used technique for synthesis of materials with predefined properties is dry gel conversion method. The crystallization of the dry aluminosilicate gel into appropriate zeolite forms is carried out in the presence of steam and volatile organic structure-directing agents. An advantage is the need of a smaller amount of OSDAs than by the standard hydrothermal synthesis [42,43].

Along with the reduction of the size of the zeolite materials, the type and transport properties of the materials must be taken into account. L. Zhang et al. combined macroscopic and microscopic diffusion measurements to perform a direct assessment of molecular transport in mordenite [44]. On considering mass transfer resistances in zeolite mordenite, the evidence is provided that there is a strong tendency towards the formation of transport resistances on the external surface of the crystals (of “surface barriers”). Since,

under barrier limitation, molecular uptake and release times scale with only the crystal size (and not with their square—as it is the case under diffusion limitation), this type of transport resistance reduces the benefit of transport enhancement by crystal size reduction in comparison with the situation under diffusion control.

4. Hierarchical Mordenite

Another way to solve the transport difficulties caused by the insufficient pore size and the coke formed during the catalytic reactions is applying post-synthetic methods, which aim to improve the accessibility to the active centers. An approach for modifying the crystals is their treatment with different solutions to form a hierarchical porosity by extracting skeletal elements (dealumination and/or desilication) as well as by passivation of the crystal surface [45–49].

The investigation of transport enhancement with hierarchically organized zeolites is well exemplified by L. Gueudre et al. [50] and by M.-O. Coppens et al. [51]. In a structural analysis of hierarchically organized zeolite, three key attributes, the crystal, the pore, and the active site structure, are indicated to dominate the design process [52].

4.1. Alkaline Treatment

To create additional meso and/or macro pores on the crystal surface, the zeolite materials are treated with alkaline solutions (NaOH, TEOH, Na_2CO_3 , and NaAlO_2) [53–56]. The alkaline treatment is characterized by the selective extraction of silicon atoms from the crystal lattice, which makes it suitable for application on high silicon-content zeolites with a Si/Al ratio above 30. Depending on the treatment time, the solution concentration and the temperature (from room temperature to 100 °C), a change in the crystallinity, and the Si/Al ratio was observed. There was a tendency that in solutions with low concentration, a larger change in the Si/Al ratio was observed, while in solutions with higher concentration, extraction of both Si and Al atoms from the skeleton was found. The reason is the aggressive action of the solution, leading to rapid amorphization of the zeolite structure as a result of its destruction [57]. Most commonly, mordenite was alkaline treated with aqueous solutions of NaOH with a concentration of 0.05–2.5 M (pH~10) in a temperature range from RT to 90 °C with duration from 10 min to 2 h [58–60]. The resulting formation of mesopores is due to surface hydrolysis and dissolution of the crystals, most likely in places with accumulations of crystal defects. This additional porosity makes mordenite a suitable catalyst for pentene oligomerization and major petrochemical processes [61,62]. In the process, a serious loss of crystal mass was observed while specific surface area and pore volume increased but prolonged processing led to complete crystal dissolution. The treatment of mordenite zeolite containing a one-dimensional channel system induces a significant increase in catalytic activity compared to structures with two- or three-dimensional channel systems. The silicon preference of alkaline solutions spares the acid centers, but the number of Lewis acid centers increases while the Brönsted acidity does not change. Despite the side effects of the method, its influence was studied on mordenite crystals, which show enhanced adsorption capacity and improved catalytic activity. The favorable effect of the alkaline treatment on mordenite catalyst was demonstrated by J.C. Groen et al. in the reaction of benzene alkylation with ethylene [63]. By controlled extraction of structural silicon, zeolite properties are preserved in combination with increased surface area, preservation of Brönsted acidity, suppression of ethylene oligomerization, and improvement of selectivity to ethylbenzene. Adri N.K. van Laak et al. studied the activity of mordenite in a similar reaction of alkylation of benzene with propene to form cumene [64]. In this work, the authors compared post-synthetic treatment of H-Mor and Na-Mor with sodium hydroxide solution. In both cases, additional crystalline porosity with preserved crystallinity is formed, but for obtaining of identical hierarchical materials, the Na-form of mordenite needs to be treated twice longer than the H-form. In other words, the step of transformation to H-form before treatment can be avoided, but on the other hand, the time for post-synthetic treatment should be longer. In order to find environmentally friendly

and industrially efficient catalysts, Je-Shian Lin et al. [65] investigated acid-treated, alkali-treated, and metal-loaded mordenite in alkylation of benzene with α -olefin. Hierarchically desilicated samples showed higher catalytic activity compared to the samples modified by other two treatment approaches (HCl treatment and Pt, Pd, and Zn loading). After careful selection of treatment parameters and parent samples, the NaOH-modified catalysts demonstrated stable dodecene conversions around 100% with linear alkylbenzene selectivity close to 98%. For the first time, hierarchical mordenite obtained by desilication was used in the reaction of selective synthesis of ethylenediamine (EDA) via condensation amination of monoethanolamine (MEA) [66]. A relationship was found between the higher concentrations of NaOH used during the treatment of mordenite and the improved diffusion properties of the catalysts with a decrease of the reaction temperature. The reduced reaction temperature favors the formation of EDA, which increases the selectivity to 93.6% (this is the highest achieved selectivity).

Recently, much attention has been paid to biomass as an alternative to petrochemical products. α -Pinene, which is a waste product from the softwood industry process, can be easily transformed by isomerization to products (limonene, camphene, and terpinolene) with a broad range of applications. For this purpose, Y. Liu et al. monitored the effect of alkaline treatment under the action of microwave radiation to form catalysts with a uniform distribution of mesopores [67]. The usage of a microwave oven during the post-synthesis mordenite treatment led to increased conversion of α -pinene to 94.7% as a result of the selective extraction of silicon atoms and the retention of aluminum atoms (responsible for Brönsted acidity) located in the 12-membered channels. Another work investigated the alkaline treatment of two types of mordenite samples: the first containing the synthesis template (organic molecule) and the second after high temperature calcination [68]. The catalytic efficiency of both types of samples regarding dimethyl ether carbonylation remained approximately the same but a difference was observed in the extraction of Brönsted acid sites in the mordenite. Apart from the preferential extraction of Si atoms from the samples subjected to pre-calcination, a certain amount of aluminum tetrahedra were separated. In the mordenites containing an organic template, the authors noted the preservation of strong acid sites in 8-membered channels and micropores, which prevented the occurrence of side reactions and coke formation.

Mordenites were also treated under moderate alkaline conditions at 180 °C in order to obtain membranes for mixture separations [69]. The prepared membranes were placed vertically in an autoclave, where processes of desilication and crystallization took place, forming products with increased pervaporation productivity. The combination of alkaline solution with various organic/inorganic compounds was tested in order to change the texture and chemical properties of mordenite without crystals decomposition.

One of the methods applied for formation of hierarchical mordenite is the recrystallization involving a mixture of an alkaline solution with a surfactant and subsequent addition of mordenite crystals [70,71]. A scheme of the recrystallization mechanism is presented in Figure 6. The mixture was subjected to hydrothermal treatment in an autoclave at 150 °C for 2–10 h. Detailed analysis of each stage of the process reveals a mechanism including:

- Rapid ion exchange of H^+ with Na^+ and extraction of skeletal silicon atoms, forming additional pores;
- Diffusion of hexadecyltrimethylammonium bromide (CTAB) in crystal spaces and ion exchange of CTA cations with sodium, which supports the formation of micelles;
- Condensation of silicon species separated during extraction.

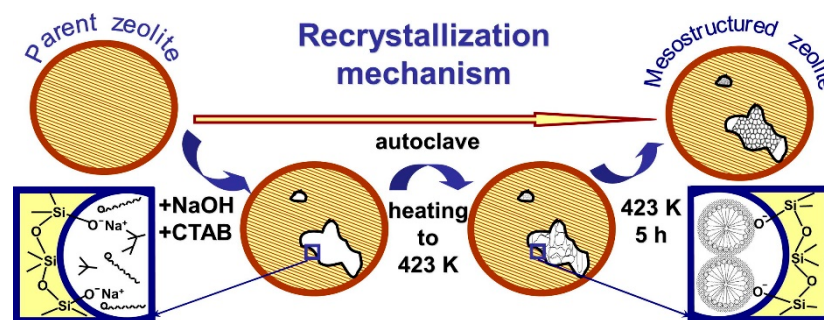


Figure 6. Presentation of recrystallization mechanism during the treatment of mordenite with an alkaline solution with a surfactant. Reprinted with permission from Ref. [71], Copyright 2016, Elsevier.

The mordenite structures obtained by this method possess high thermal and acid stability in combination with zeolite acidity and porosity through which bulky molecules can pass. A similar approach to recrystallization by replacement of the surfactant with pyridine was proposed by H. Issa et al. [72]. The authors concluded that pyridine interacts with external hydroxides which selectively directs the desilication towards small zeolite particles. The organic molecule remains in the structure of mordenite until the calcination process in which structural aluminum is released, forming extra-framework aluminum species. These two characteristics (smaller particle size and the presence of extra-framework aluminum) significantly improve the catalytic activity in reactions of *n*-hexane cracking and propene transformation. Another approach involved sequential treatment of the zeolite structure with acid and alkaline solutions [73]. Using this approach, hierarchical structure was formed with proper distribution of the mesopores due to basic interaction and less extra-framework aluminum as a result of acid attack, making the mordenite suitable for reactions of isomerization, alkylation, and adsorption of cationic dyes [74–76].

4.2. Acid Treatment

The acid treatment was first introduced by Barrer and Makki, using mineral acids to extract aluminum from the clinoptilolite structure [77]. The acid treatment with HCl, $C_2(OOH)_2$, H_2EDTA , Na_2EDTA , $SiCl_4$, $(NH_4)_2SiF_6$, etc. [78–81] extracts aluminum which leads to an increase in the Si/Al ratio in the zeolite lattice. Mordenite is a high silicon-content zeolite, which allows easy extraction of aluminum from its structure without loss of crystallinity. By treatment under mild acid conditions, catalysts with improved activity can be obtained due to the removal of the extra-framework aluminum and the amorphous phase located in the channel system. Modifications with acids that are more aggressive, have a longer processing time, and higher concentration lead to structures with secondary porosity. The catalytic behavior of hierarchical mordenite formed by various concentrations of HNO_3 and treatment durations was investigated in different reactions: *n*-hexane conversion [82], isomerization of *m*-xylene [83], dimethyl ether carbonylation [84], etc. The longer acid treatment leads to a decrease of the activity of the catalyst as a result of complete aluminum removal from the 4-membered rings into the zeolite frame, despite the improved diffusion properties and the increased active surface area. The results were also verified by a simulation model describing the multi-stage process of dealumination of the mordenite skeleton with HNO_3 [85]. Another example of acid extraction of Brönsted acid centers from the mordenite structure is with HCl, followed by HNO_3 treatments applied by G.S. Lee et al. [21]. The resulting structures were tested in the reaction of shape selectivity alkylation of biphenyl with propylene to produce 4,4'-diisopropylbiphenyl (DIPB), and with these catalysts, a very high yield up to 70% was reached. Comparative studies on the mordenite structure modified with nitric and oxalic acids demonstrated that aluminum was removed with a higher rate by oxalic acid even at lower concentrations [86]. The analyses showed that the extra-framework aluminum in the mordenite treated with nitric acid was almost absent and a well-formed meso-structure with pore diameters in the range 7–20 Å was formed. In contrast, the

treatment with oxalic acid resulted in the formation of structure defects and increased extra-framework aluminum content. By precise tuning of the treatment conditions (type of acid, duration, concentration, etc.), the properties of materials can be strongly affected. Alkane isomerization reactions such as n-hexane, n-pentane, and light naphtha isomerization play an important role in the modern oil refining industry. Commonly used catalysts combine two phases, one containing acid centers and the other being a highly active metal. One of the most widely used zeolite supports used for the aforementioned reactions is mordenite. A serious problem is the rapid deactivation of its one-dimensional channel system. To overcome this problem V.V. Bobik et al. [87] and P. Tamizhdurai et al. [88] investigated acid (HCl)-treated mordenite as support with deposited metal nanoparticles (Pd and Pt). In these investigations, special attention was paid to the study of the relationship structure (porosity, external acid centers) properties. It was proved that the metal-hierarchical mordenite catalyst is more active in the isomerization of n-hexane and light naphtha than the conventional one, and additionally, the reaction temperature was reduced to 200 °C. Mordenite treated with HCl under microwave radiation showed significant porosity, strong acid centers, and high catalytic activity in isomerization of styrene oxide [89]. Microwave heating not only affected the surface acid properties but also significantly reduced the treatment time.

In order to obtain effective membranes for water/ethanol separation, G. Li et al. [90,91] modified mordenite by a post-synthesis attack with oxalic and hydrochloric acid. It has been shown that by this approach of membrane modification, the efficiency for water/ethanol separation increased more than 200 times at appropriate conditions.

The most widely used method for aluminum removal from the crystal structure is steam treatment. In addition to extracting aluminum, the vapor causes redistributions of SiO_4 tetrahedra to form meso/macro pores. The aluminum separated by this method was re-deposited on the crystal surface, as a result of which no change in the ratio between the building elements was observed. On the other hand, this leads to an increase of the Lewis acid centers and to a partial clogging of the zeolite structure, independently of the additional pores formed [92,93]. To avoid the negative effect (partial clogging of the structure by the separated aluminum) during the steam dealumination, some research groups investigated a two-stage method combining steam leaching with subsequent acid treatment. During the vapor stage, the structural aluminum was gradually hydrolyzed and removed, while with the acid treatment, the deposited aluminum was extracted from the zeolite skeleton forming porous structures with very high Si/Al ratios. The structures formed by this procedure change their structural characteristics and the modified materials from hydrophilic become highly hydrophobic. However, the mordenite products retain their hydrocarbon adsorption and catalytic ability in reactions of benzene alkylation and isobutane conversion [94–96]. By wet application of metal salt (e.g., of Pt, Fe, etc.), an increase of catalytic efficiency in isomerization reactions of n-hexane and n-butane was achieved [97,98]. Another post-synthetic approach for zeolite structure modification combines high temperature steam treatment followed by treatment with SiCl_4 and acid attack (HCl, HNO_3 , $\text{C}_2\text{H}_2\text{O}_4$) [25,80]. The difference with the previous methods is that during the dealumination, the aluminum structural tetrahedra were directly replaced by silicon ones provided by SiCl_4 . The newly formed structures retain the high temperature stability inherent to the parent samples.

Ghosh and Kydd investigated the activity of mordenite crystals by treatment with HF acid [99]. The idea of their treatment was to replace O atoms or surface OH groups with F^- , which show higher reactivity. As a result, they found significant disturbance of the zeolite surface and a slight deviation in the Si/Al ratio after treatment with a more concentrated solution, while as the concentration of the solution decreased, removal of the aluminum atoms was observed. Despite this, the samples revealed increased catalytic activity. In cases with reduced content of active centers, faster deactivation of the catalyst activity was reported due to the coke formation.

Many efforts have been spent to find a controllable chemical approach to obtain hierarchical zeolites. V. Valtchev et al. [92] reported a new method for zeolite etching with hydrofluoric acid and ammonium fluoride as a buffer. Whereas F^- selectively etches aluminum from the crystal structure as mentioned above, the HF_2^- formed in the buffered solution exhibits a slightly higher reactivity and non-selectively extracts both framework elements (silicon and aluminum). This approach was initially applied on ZSM-5 zeolite with a Si/Al ratio of 19 and on a series of ferrierite crystals with a Si/Al ratio of 10, from which samples with chemical compositions very close to the initial ones were obtained [29,100].

In order to obtain catalytically active materials, we applied this approach on mordenite crystals [101,102], varying the time of treatment and the hydrofluoric acid concentration. Features resulting in the adsorption/desorption of nitrogen have been used to determine the specific surface area and pore size of the samples investigated (Table 1). The specific surface area of the treated samples is higher than that of the initial sample. There is significant difference in the pore size depending on the time of the acid treatment. By increasing the treatment time, the pore size increases. In sample 6 (20-min treatment), the pore size is almost two times larger than that of the parent sample.

Table 1. Textural properties of parent sample and treated samples.

Sample	Treatment Time (min.)	HF Concentration (M)	BET (M ² /G)	Pore Size (nm)
1	10	0.25	380	1.4
2	15	0.25	375	1.6
3	5	0.1	402	0.84
4	10	0.1	396	0.9
5	15	0.1	384	1.3
6	20	0.1	372	1.6
parent	-	-	372	0.86

The catalytic activity of the hierarchically treated samples in the reaction of m-xylene transformation was higher compared to that of the non-treated initial sample. The total conversion of m-xylene over parent and treated samples is shown on Figure 7.

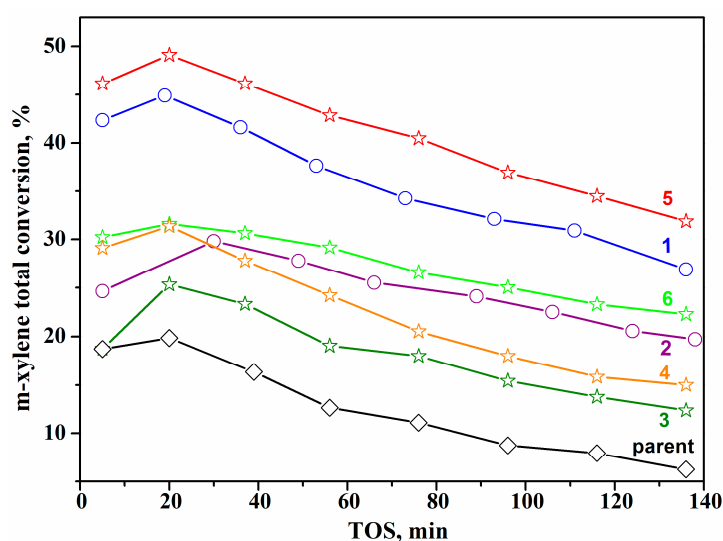


Figure 7. Total m-xylene conversion as a function of the time on stream (TOS) over parent sample and samples treated with buffered solution: 1 (10 min, 0.25 M HF); 2 (15 min, 0.25 M HF); 3 (5 min, 0.1 M HF); 4 (10 min, 0.1 M HF); 5 (15 min, 0.1 M HF); and 6 (20 min, 0.1 M HF). Reprinted with permission from Ref. [102], Copyright 2016, Springer.

This is an innovative way for the design of mordenite with improved accessibility of the active sites. Modification with zirconium of parent and hierarchical mordenite materials obtained by the above-described method was performed by incipient wetness impregnation [103]. The catalysts prepared by this method show high activity in glycerol esterification with acetic acid and selectivity to valuable triacetyl glycerol. Investigation of the acidic properties of the Zr-modified catalysts revealed that the presence of a sufficient number of Brönsted and Lewis acid sites with strong acidity is of crucial importance for their catalytic performance. Zr-modified hierarchical mordenite shows the best catalytic performance in the studied reaction, most probably due to the optimal ratio of Brönsted/Lewis acid sites and better access to them. It is a highly active, cost effective, stable, and reusable catalyst. H. Issa et al. applied several post-synthetic strategies for mordenite hierarchization [104,105] including HF etching (in various solvents or using additives) and they concluded that the best strategy in terms of catalyst activity (which defacto includes the preservation of the acidity) is the fluorine etching in the presence of pyridine. The authors concluded that the Brönsted centers located in the 8-MR side pockets are responsible for the toluene disproportionation reaction, whereas in the n-hexane-cracking reaction, the acid centers in both the 12-MR and 8-MR channels are considerably involved, as the centers in 8-MR channels are more reacting [106].

One interesting example for post synthesis modification of mordenite is air plasma treatment of mordenite-clinoptilolite materials performed to improve their water vapor capacity [107]. However, the results depend on the O/Si ratio in the parent samples in very narrow range and another disadvantage is the significant decrease of the specific surface area of the resulting materials.

It should be borne in mind that transport resistances are expected to occur at the interface between the space of micropores and the secondary obtained meso- and macropores (referred to as “transport” pores) in hierarchically organized mordenites, which is of crucial relevance for the “mechanism” of transport enhancement, namely in either the slow-exchange or the fast-exchange mode between the two pore spaces [108]. Knowledge about which of the two limiting cases is present is crucial for a knowledge-based transport optimization of the material, since the dependence of the time constants of uptake and release on, e.g., the particle texture and the diffusivities in the two pore spaces is notably different for the two limiting cases. It is true that a gain in knowledge in this field largely depends on a corresponding further development of the options of experimental observation.

5. Conclusions

The synthesis, modification, characterization, and application of mordenite are subjects of increasing research interest. It is a zeolite of special importance due to its thermal and acid stability as well as strong acidity, which demonstrates why mordenite is widely industrially employed in various processes including alkylations, isomerizations, dehydrations, and aminations.

In this review, we consider the scientific literature on the structure, synthesis, and two main approaches that solve the diffusion difficulties during catalytic processes. The first approach is the reduction of the size of the obtained mordenite crystals to submicron or nanometric range, whereas the second one is the formation of hierarchical mordenite samples by appropriate post-synthetic treatment. Attempts to fine-tune and control the particle size by the first approach or the pore size by the second one by adjusting various parameters during the synthesis or modification are described. Various synthetic methods for nanosized and hierarchical mordenite are discussed and their applications in the field of catalysis are presented. However, it should be noted that the treatment procedures can lead to the loss of the essential properties of mordenite such as its crystallinity, thermal and acid stability, and acid properties. Having this in mind, the future works should focus on procedures that are compliant with all aspects of application of the final material.

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