

Seed-mediated approach to size-controlled synthesis of a mordenite type zeolite from organic template free initial gel

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This study reports on the hydrothermal synthesis of mordenite crystals without an organic template and on the characterization of resulting crystals, as the ultimate goal has been to decrease the crystal size. Two synthesis approaches have been applied. The first one involved subjecting a standard initial gel $18\text{SiO}_2 : \text{Al}_2\text{O}_3 : 1.24\text{K}_2\text{O} : 1.21\text{Na}_2\text{O} : x\text{H}_2\text{O}$ to hydrothermal crystallization for a period of 2 to 7 days ($x=600, 280$ and 22.5). The second approach included the usage of seeds employing the same initial gel composition. The crystals growth kinetics of mordenite at a different seed content (1, 2 and 5 wt.%) has been studied. The seed-assisted process enabled us to synthesize mordenite crystals of submicrometric range. Particle size distribution of the resulting products strongly depends on the water content in the initial gel and on the amount of added seed. It has been found that seed concentration and water content in the initial gel are the key factors influencing the crystallization time and the physicochemical properties of crystalline products. All products have been characterized by X-ray, scanning electron microscopy (SEM), dynamic light scattering (DLS), and infrared spectroscopy (FTIR).

Key words: Nanozeolites, mordenite, hydrothermal synthesis, seed-mediated synthesis.

INTRODUCTION

Zeolites are crystalline hydrated aluminosilicates containing cavities and channels. Their structure consists of three-dimensional frameworks of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra linked through the shared oxygen atoms. Pure silicon structures are neutral. While isomorphic substitution of silicon tetrahedra with aluminum tetrahedra takes place the structure has a negative charge, which can be compensated by a number of cations – ions of the alkali and alkaline earth metals, protons, and certain organic cations. Being a combination of unique structure and composition of high efficiency makes zeolites useful in a wide range of areas. Due to the pore system zeolites may block various molecules and allow a smooth passage of the smaller molecules. Therefore they have also been referred to as “molecular sieves”. Many properties depend on Si/Al ratio in the framework of zeolites. With an increase in Si/Al ratio from 1 to infinity an increase

in the thermal stability of the zeolite framework is observed. The structural selectivity also changes and from hydrophilic becomes more hydrophobic, the acid stability enhances and the ion-exchange capacity is reduced within the zeolite structure. Some zeolites are found in nature as natural minerals, but the more widely used are synthetic materials due to the large number of application areas - chemical industry, cosmetics, building materials, purification and separation of liquids, gasses and many other fields. Another significant advantage of synthetic zeolite materials is their purity since parameters such as Si/Al ratio and purity of the phase can be controlled during the synthesis [1]. The shape-selectivity, the potential acidic properties and high active surface area are among the parameters which make zeolites widely applicable. Taking into account the industrial importance of zeolite materials many of scientists' efforts have been focused on the synthesis of new zeolite materials and on improving the characteristics of already existing zeolites. Size reduction of zeolite crystals to submicrometric and nanometric scale has a significant impact on their physical and chemical properties. The widespread use of nanosized zeolites, mainly in the applied fields of catalysis and adsorption, is due to their

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having a higher external surface area, a high surface energy and shorter channels. These surface properties provide new possibilities to explore adsorption and reaction of bulky molecules that do not normally interact with the micropore volume of the zeolites [2–4]. In the recent years, the number of zeolites synthesized as nanosized materials has increased significantly owing to the new areas of applications – preparation of zeolite films, membranes, other composite materials, hierarchical structures, etc. They are also used for obtaining colloidal suspensions of nanosized zeolites. New approaches to the synthesis and modification of zeolite materials have been implemented in order to achieve the desired size and morphology [5–7].

One of the widely used zeolite minerals mordenite has the chemical formula $[\text{Na}_8(\text{H}_2\text{O})_{24} | \text{Al}_8\text{Si}_{40}\text{O}_{96}]$. This high-silica representative was first found in Canada (Nova Scotia) and its crystal structure was reported by How in 1864 [8–10]. Mordenite has an orthorhombic structure with a space group symmetry Cmc m ($a = 18.3 \text{ \AA}$; $b = 20.5 \text{ \AA}$ and $c = 7.5 \text{ \AA}$). Its structure is composed of five-membered rings interconnected by four ring members, each corner of which is composed of silicon or aluminum shared tetrahedra forming properly arranged channels. The channel system is one-dimensional running parallel to [001]. There are two types of channels, namely, the twelve-membered channel system and the eight-membered channel system. In the direction (010) there is only a eight-membered channel system. Since the eight-membered channels are inaccessible for many molecules, it is often said that mordenite has a one-dimensional channel system taking into account only the twelve-member channels [11]. Because of the extensive channel system in combination with a high thermal and acidic stability mordenite is widely used as a catalyst in reactions such as hydrocracking, isomerization, hydroisomerization, alkylation, reforming, and for the production of dimethylamine [12]. In addition, mordenite is used for adsorption and separation of gaseous and liquid mixtures, in photochemistry, electrochemistry, as thin films and zeolite membranes. For its wide application in catalysis it has been a great challenge to obtain nanosized crystals possessing a high active surface area and facilitating both diffusion and an easy access to the active sites of the zeolite. Nanosized mordenite crystals are used preferably in the area of supramolecular catalysis, photochemistry, optoelectronics, for developing zeolite membranes as well [13, 14].

The synthesis of zeolite materials is carried out under hydrothermal conditions with the silicate or aluminosilicate gels at alkaline pH and at a temperature ranging from 40 to 200 °C. Basically there four sources for the formation of the gel, namely:

(i) reagents forming the frame and comprising SiO_2 , Al_2O_3 ; (ii) structure directing agents (SDA) – that are mostly organic molecules; (iii) mineralizing agents – OH^- or F^- and (iv) a synthetic medium, which is usually water. Although most of the applications of zeolites are aimed at protecting the environment, their synthesis is not fully ecological, due to the use of SDA during their synthesis. The usage of SDA facilitates the synthesis process, i.e. it aids/guides the polymerization and organizes the anionic building blocks that form the zeolite framework. To make the zeolite useful, SDA trapped in its crystal micropores should be removed via calcination at 500–550 °C. Besides, the organic templates used in the conventional synthesis of zeolites are often poisonous and expensive for massive industrially production. Moreover, removing them at high temperature induces inevitable energetic and environmental pollution [15]. That is the main reason for the scientists to focus their efforts on the synthesis of zeolites from starting gels without organic templates.

The aim of the work is to carry out a hydrothermal seed-assisted synthesis of pure mordenite from an initial gel free of organic template. Varying the water content in the initial gel and the amount of seeds used during the hydrothermal synthesis one can control the size of zeolite crystals.

EXPERIMENTAL

SDA-free synthesis of mordenite

Mordenite was prepared under hydrothermal conditions using seeds from the initial gel with molar composition: $18\text{SiO}_2 : \text{Al}_2\text{O}_3 : 1.24\text{K}_2\text{O} : 1.21\text{Na}_2\text{O} : x\text{H}_2\text{O}$ ($x = 600, 280$ and 22.5). The seed amount was adjusted to be 1, 2 and 5 wt % of the total silica amount in the gel. The initial gel was aged for 24 hours at room temperature and then the synthesis was carried out at 160 °C and 180 °C for a period between 6 and 168 hours.

The seeds were synthesized from a starting gel having molar composition: $18\text{SiO}_2 : \text{Al}_2\text{O}_3 : 1.24\text{K}_2\text{O} : 1.21\text{Na}_2\text{O} : 280\text{H}_2\text{O}$. The crystallization of seeds was performed under static conditions at 180 °C for 120 hours.

The starting reagents were: highly dispersed extra pure silicon dioxide – Merck; Aluminium 99.97% – Acros Organics; NaOH pellets 98% – Sigma Aldrich, KOH pellets 85% – Sigma Aldrich and distilled water. The suspension preparation procedure started with dissolution of sodium and potassium hydroxide into water, followed by adding of aluminium powder under constant stirring till a clear solution was obtained. After the silica source and seeds were added the initial suspension

was stirred at room temperature for 60 min and then aged at room temperature for 24 hours. In order to obtain a gel with low water content (22.5 moles H₂O) and have the water distributed evenly in the gel, a freeze-dryer and a desiccator were employed sequentially. The crystallization was performed in stainless steel Teflon-lined autoclaves under autogenous static conditions at two different temperatures of 160 °C and 180 °C for a period of 6–168 hours. After the synthesis the autoclaves were quenched in cold water. The solid was purified by four consecutive steps of centrifugation and re-dispersion in distilled water and then dried at 60 °C overnight.

Characterization

The X-ray powder diffraction patterns were recorded on a D2 Phaser (Bruker) diffractometer with CuK α radiation, working at 30 kV acceleration and 10 mA current. The 2 θ scanned range was 4–50 with a step of 0.05° and 1 s acquisition time. FTIR spectra were taken on a Bruker Tensor 37 spectrometer using KBr pellet technique. For each sample, 64 scans were collected at a resolution of 2 cm⁻¹ over the 4000–400 cm⁻¹ wavenumber region. The scanning electron microscope (SEM) analyses were obtained on a Philips 515 apparatus, working at 20 kV accelerating voltage. The samples were covered with gold before investigation. Dynamic light scattering (DLS) particle size distribution measurements were performed on a Brookhaven Instrument 90Plus by suspension of the samples in water.

RESULTS AND DISCUSSION

The results from the hydrothermal synthesis of mordenite from different molar composition of the initial gel are listed in Table 1. The crystallinity and purity of the phases has been investigated by X-ray at various amounts of water and seeds in the initial gel at two temperatures – 160 °C and 180 °C. In almost all systems synthesized from the initial gel containing a large amount of water (600 moles) the product is a mixture of two phases – mordenite and ferrierite. The presence of a ferrierite phase is evidenced by the appearance of peaks at 9.30 and 12.50 2 θ in X-ray diffraction patterns obtained. An exception is when the synthesis is carried out at 160 °C in the presence of 5 wt% mordenite seed crystals. In this case after 72 hours the product is a pure mordenite phase. SEM investigations show aggregates with slab morphology whose average size is about 8–10 μ m. Decreasing the water amount in the gel leads to an alkalinity increase. As a result, the crystallization time is shorter and the only product formed is mordenite.

Series of syntheses with starting gel 18SiO₂ : Al₂O₃ : 1,24K₂O : 1.21Na₂O : 280H₂O at two temperatures 160 °C and 180 °C has been carried out. X-ray diffraction patterns of the samples prepared from gels with 280 moles of water are shown in Fig. 1. In all cases mordenite of high crystallinity has been observed. With increasing the amount of seeds added to the initial gel, crystallization time is shortened. The same effect, but much less pro-

Table 1. List of used initial gel compositions, crystallization conditions and products of synthesis

Gel Composition	Seeds (%)	160 °C		180 °C	
		Time (hours)	Product	Time (hours)	Product
18SiO ₂ :Al ₂ O ₃ :1,24K ₂ O:1.21Na ₂ O:600H ₂ O	–	120 h	Mor. / Fer.	72 h	Mor. / Fer.
18SiO ₂ :Al ₂ O ₃ :1,24K ₂ O:1.21Na ₂ O:600H ₂ O	1%	96 h	Mor. / Fer.	48 h	Mor. / Fer.
18SiO ₂ :Al ₂ O ₃ :1,24K ₂ O:1.21Na ₂ O:600H ₂ O	2%	96 h	Mor. / Fer.	48 h	Mor. / Fer.
18SiO ₂ :Al ₂ O ₃ :1,24K ₂ O:1.21Na ₂ O:600H ₂ O	5%	72 h	Mor.	48 h	Mor. / Fer.
18SiO ₂ :Al ₂ O ₃ :1,24K ₂ O:1.21Na ₂ O:280H ₂ O	–	144 h	Mor.	96 h	Mor.
18SiO ₂ :Al ₂ O ₃ :1,24K ₂ O:1.21Na ₂ O:280H ₂ O	1%	96 h	Mor.	72 h	Mor.
18SiO ₂ :Al ₂ O ₃ :1,24K ₂ O:1.21Na ₂ O:280H ₂ O	2%	72 h	Mor.	72 h	Mor.
18SiO ₂ :Al ₂ O ₃ :1,24K ₂ O:1.21Na ₂ O:280H ₂ O	5%	48 h	Mor.	48 h	Mor.
18SiO ₂ :Al ₂ O ₃ :1,24K ₂ O:1.21Na ₂ O:22.5H ₂ O	–	96 h	Mor.	72 h	Mor.
18SiO ₂ :Al ₂ O ₃ :1,24K ₂ O:1.21Na ₂ O:22.5H ₂ O	1%	24 h	Mor.	48 h	Mor.
18SiO ₂ :Al ₂ O ₃ :1,24K ₂ O:1.21Na ₂ O:22.5H ₂ O	2%	24 h	Mor.	18 h	Mor.
18SiO ₂ :Al ₂ O ₃ :1,24K ₂ O:1.21Na ₂ O:22.5H ₂ O	5%	18 h	Mor.	6 h	Mor.

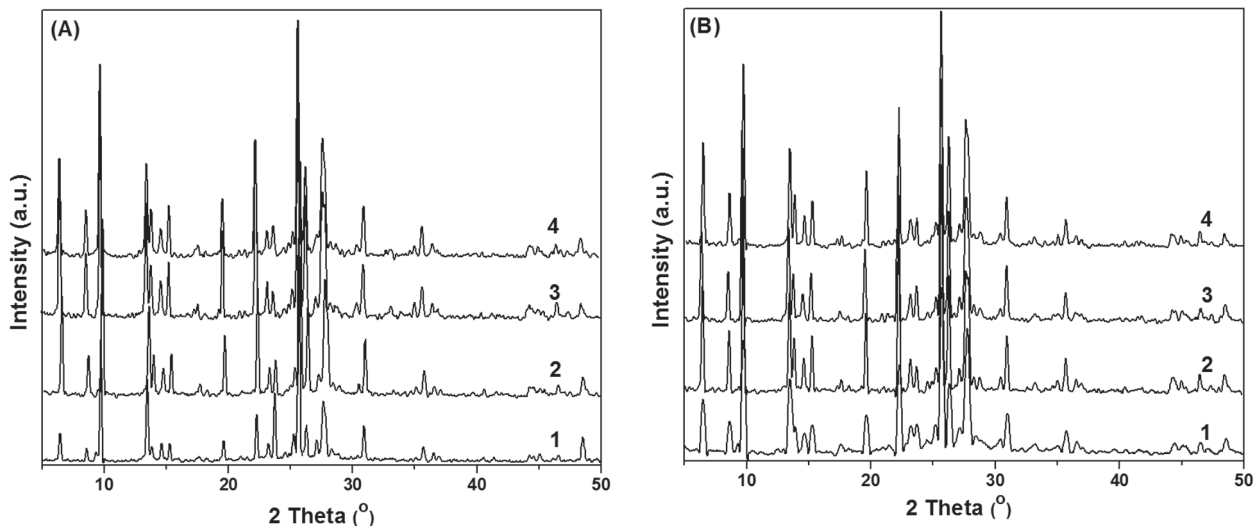


Fig. 1. XRD patterns of samples prepared from gels with 280 moles of water contents at 160 °C (A) and 180 °C (B) wherein: 1 – a gel composition without seeds, 2 – a gel composition with 1% seeds, 3 – a gel composition with 2% seeds and 4 – gel composition with 5% seeds

nounced has the increasing of temperature (Fig. 1, Table 1). Further extension of the crystallization time does not improve X-ray crystallinity of the material. The series of samples has been further examined by IR spectroscopy, thus complementing the information of the long-range (XRD) with short-range (IR) order analysis. Bands, characteristic for the zeolite framework at 1209, 1075, 806, 566 and 480 cm^{-1} have been observed in FTIR spectra what demonstrates the formation of the zeolite phase (Fig. 2). The shoulder at 1209 cm^{-1} and the band at 566 cm^{-1} are assigned to external linkage modes, i.e. their observation is associated with the presence of secondary building units in the mordenite structure.

The SEM inspection of mordenite has been performed to investigate the size and morphology of the crystals. The product is uniform in size (Fig. 3) comprising crystals of slab and slab-like morphology. As known, the increase in the synthesis temperature results into the formation of larger particles. However, in the presence of seeds this effect is less pronounced. Thus, the particles synthesized at 180 °C (Fig. 3B) are similar in size to those obtained at 160 °C (Fig. 3A). Obviously, the number of crystals in the systems is determined by the number of seeds per gel unit and the effect of other factors controlling zeolite crystal size is negligible. As seen from Fig. 3 the average size of the product synthesized without seeds is about 50 μm . The addition of seeds leads to a significant reduction of the crystal size. When 1 wt % of seeds (calculated as a percent of the total silica amount in the gel) is added, the size of the resulting crystals is about 15 μm , 2% seeds – 10 μm and 5% seeds – 7 μm , respec-

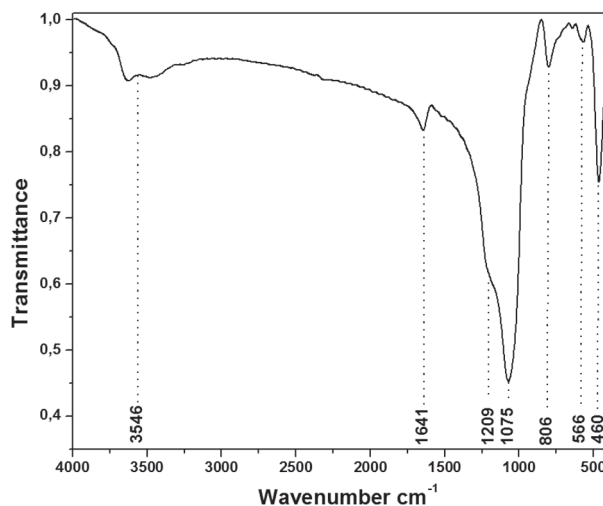


Fig. 2. FTIR spectrum of sample synthesized from gel containing 280 moles water at 160 °C without seeds

tively (Fig. 3). The results are confirmed by DLS investigations performed using a suspension of the samples in water. Crystal size distributions at both temperatures are similar. Increasing the amount of seed added to the initial gel results in shrinking the particle size of the product obtained.

Reductions of water content and seed-assisted methods are known for the synthesis of other zeolites and zeolite-like systems [16]. In order to obtain smaller mordenite crystals, water content in the initial gel has been further reduced up to 22.5 moles. That water amount has been achieved by sequential

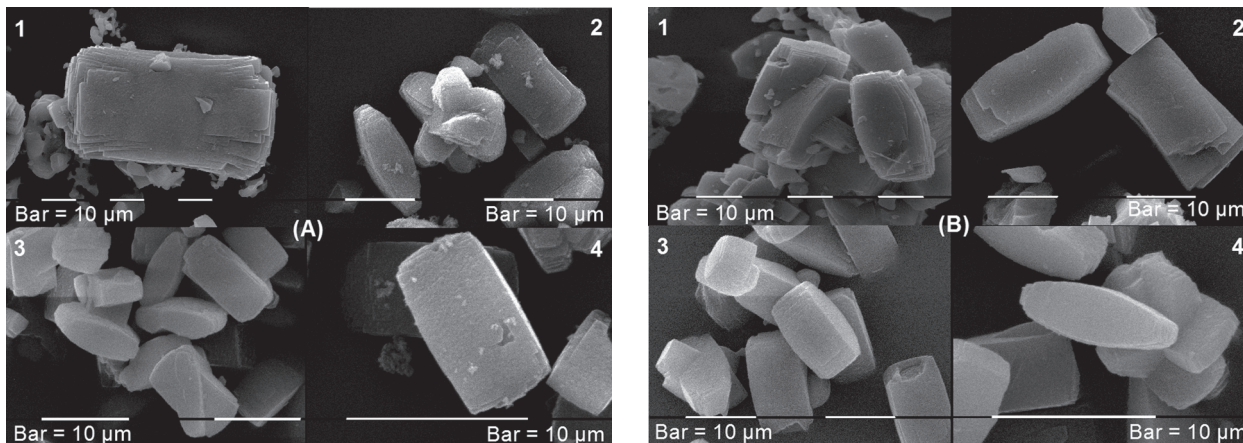


Fig. 3. SEM images of crystals synthesized from gels with 280 moles of water contents at 160 °C (A) and 180 °C (B) wherein: 1 is a gel composition without seeds, 2 is a gel composition with 1% seeds, 3 is a gel composition with 2% seeds and 4 gel composition 5% seeds

lyophilization of the initial gel and humidification in the desiccator, where together with the sample a plate with 1 M of NH_4Cl solution is placed. Thus the small amount of water is distributed evenly in the gel. The procedure then follows the conventional hydrothermal synthesis in an autoclave.

X-ray diffraction patterns of the products are shown in Fig. 4. Despite the large reduction of water in the initial gel, X-ray diffraction analysis indicates that the products are highly crystallized zeolite mordenite. The dependence of the yield on crystallization time at the two temperatures used – 160 °C

and 180 °C is presented in Fig. 5. The syntheses carried out at 160 °C show clearly the influence of seeds. The system without seeds gives a crystalline product for 96 hours while with the addition of 1% or 2% of seeds, the crystallization time is shortened to 24 hours. By increasing the seed content to 5%, the time for obtaining of pure zeolite phase mordenite is cut to 18 hours. Raising the temperature with 20 °C reduces the crystallization time. For the system without seeds it is 72 hours. The crystallization time is 6 hours for the system with 5% of seeds. Crystallization kinetics plotted in Fig. 5

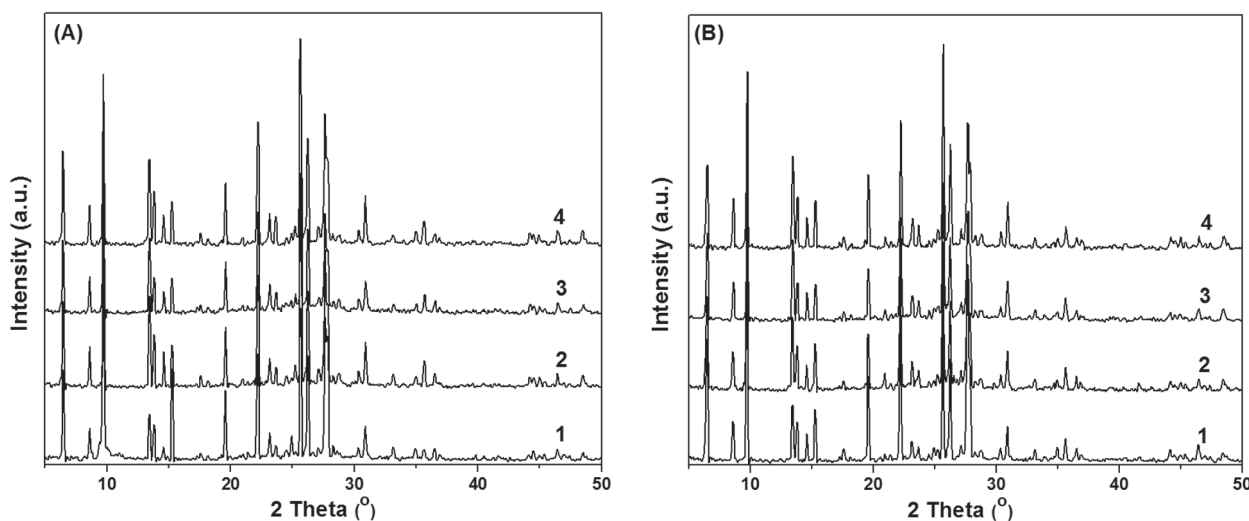


Fig. 4. XRD patterns of samples prepared from gels with 22.5 moles of water contents at 160 °C (A) and 180 °C (B) wherein: 1 is a gel composition without seeds, 2 is a gel composition with 1% seeds, 3 is a gel composition with 2% seeds and 4 gel composition 5% seeds

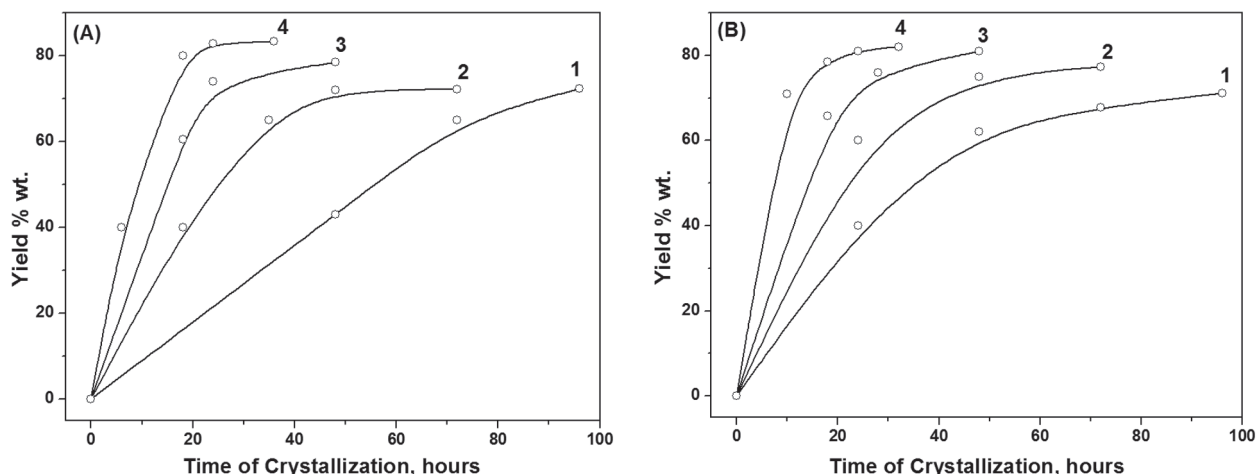


Fig. 5. Crystallization kinetics of samples prepared from gels with 22.5 moles of water contents at 160 °C (A) and 180 °C (B) wherein: 1 is a gel composition without seeds, 2 is a gel composition with 1% seeds, 3 is a gel composition with 2% seeds and 4 gel composition 5% seeds

shows clearly the effect that temperature and addition of seeds to the initial gel have upon the crystallization time.

SEM micrographs of the samples synthesized with 22.5 moles of water in the initial gel with a different amount of seeds in the system at two temperatures are presented in Fig. 6. The sample synthesized at 160 °C without seeds consists of large aggregates of slab morphology whose average size is 40 μm (Fig. 6 A1). The addition of seeds decreases the particle size, as seen from Fig. 6. The particle size of the sample synthesized with 1% of seed is 15 μm, of the

one with 2% – 6 μm. The particles synthesized with 5% of seeds are relatively uniform in size and shape with average crystals size of about 1–2 μm. The results concerning the size and morphology of the particles obtained at 180 °C (Fig. 6B) are similar, just uniformity is less pronounced because of the higher synthesis rate. The particle size distribution obtained by DLS analysis of all samples confirms these results. The narrowest distribution is for the samples synthesized with 5% of seeds. Thus, by adding a different amount of seeds to the synthesis system the size of the crystal particles obtained is controlled.

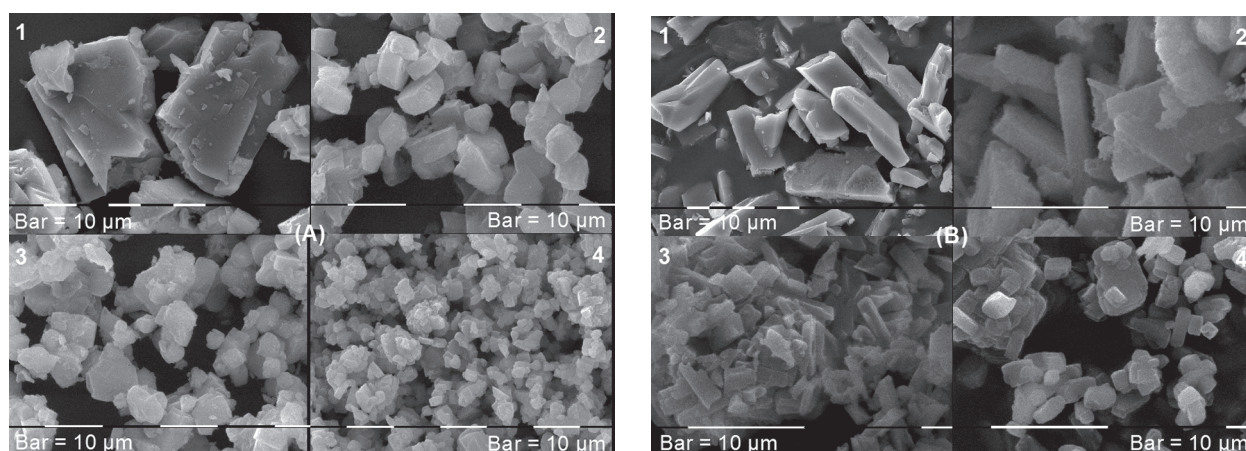


Fig. 6. SEM images of crystals synthesized from gels with 22.5 moles of water contents at 160 °C (A) and 180 °C (B) wherein: 1 is a gel composition without seeds, 2 is a gel composition with 1% seeds, 3 is a gel composition with 2% seeds and 4 gel composition 5% seeds

The seed crystals added to a synthesis system introduce crystallites into it and act as nuclei over which the crystals grow. The higher the number of crystallites in the initial gel is, the smaller is the size of the particles obtained. Adding seed crystals to a crystallization system has resulted in increased crystallization rates. The enhanced crystallization rate might be caused by an increase in the rate at which the solute is integrated into the solid phase of the solution due to the enlarged available surface area.

CONCLUSIONS

Hydrothermal syntheses of mordenite without using organic SDAs in the system $18\text{SiO}_2 : \text{Al}_2\text{O}_3 : 1.24 \text{K}_2\text{O} : 1.21\text{Na}_2\text{O} : x\text{H}_2\text{O}$ ($x=600, 280$ and 22.5) are reported. The resulting product has uniform particles of high crystallinity. Two synthesis approaches have been utilized. In the first one a standard initial gel is subjected to hydrothermal crystallization for a period ranging between 2 and 7 days. The second approach includes the use of seeds while the same initial gel composition is employed. The crystals growth kinetics of mordenite at different seed content (1, 2 and 5 wt.%) has been studied. Implementing the seed-assisted process we were able to synthesize mordenite crystals of sub-micrometric range. The water content in the initial gel and the amount of added seed are the parameters which strongly influence the particle size of the resulting products. Changing those parameters one can control the size of zeolite particles. It has been found the seed concentration and water content in the initial gel to be the key factors affecting the crystallization time and the physicochemical properties of crystalline products. Six hours is the established shortest time for obtaining zeolite mordenite of high crystallinity.

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КОНТРОЛИРАНЕ РАЗМЕРА НА ЧАСТИЦИТЕ НА МОРДЕНИТ ЧРЕЗ СИНТЕЗ С ИЗПОЛЗВАНЕ НА ЗАРОДИШИ И БЕЗ ОРГАНИЧЕН ТЕМПЛЕЙТ

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(Резюме)

Тази работа докладва успешен хидротермален синтез на морденит без използване на органичен темплейт, като крайната цел е да се получат кристали с намалени размери. При синтеза са приложени два подхода. При първия, се използва стандартен първоначален гел 18SiO_2 гел: Al_2O_3 : $1.24\text{K}_2\text{O}$: $1.21\text{Na}_2\text{O}$: $x\text{H}_2\text{O}$ ($X = 600, 280$ и 22.5) и време на хидротермална кристализация от 2 до 7 дни. Вторият подход включва използването на зародиши, добавени към същия първоначален гел. Проучена е кинетиката на растеж на морденитните кристали при използване на различно съдържание на зародиши (1, 2 и 5 %). Използването на зародиши прави възможен синтез на морденитните кристали с размери в субмикронния регион. Разпределението на частиците по размер силно зависи от съдържанието на вода в първоначалния гел и от количеството на добавените зародиши. Установено е, че концентрацията на зародишите и съдържанието на вода в първоначалния гел са основните фактори, които влияят върху времето на кристализация и физикохимичните свойства на кристалните продукти. Всички продукти се характеризирани с рентгенова дифракция, сканиращ електронен микроскоп, динамично разсейване на светлина и инфрачервена спектроскопия.