Synthesis and characterization of zeolites using phenyltrimethylammonium hydroxide (PTMAOH) as template by conventional hydrothermal and microwave assisted methods

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Abstract : A few sample of zeolites were synthesized using two different techniques, first by conventional heating method (hydrothermal) and another by exposing the hydrogel to microwave radiation assisted by hydrothermal heating (Microwave treatment). Microwave heating decreased the nucleation and crystallization time. These zeolites powder were prepared at temperature of 450 K and at presence of organic template and without it. Templates were organic species added to synthesis media to aid/guide in the polymerization of the anionic building blocks that form the framework. The crystalline zeolites samples obtained were characterized by X-ray diffraction (XRD), FT-IR spectroscopy and scanning electron microscopy (SEM) techniques. It was established that phase purity, morphology, and the size of crystals of crystalline products were affected by molar ratios of the substrate, such as (H_2O/Na_2O) and present of organic template. Amorphous silica powder (Zeosil) was the preferred as silica source. The size of crystals in the microwave treatment samples are 5–10 μm without template and 10–15 μm with template and for the conventional heating heated samples are 20–25 μm without template and 50–60 μm with template.

Keywords : Zeolite, conventional hydrothermal, microwave irradiation, crystallization period, template, PTMAOH.

Introduction

Zeolites occur in nature and have been known for almost 250 years as aluminosilicate minerals. Examples are faujasite, mordenite, offretite, ferrierite and chabazite. These and other zeolite structures are of great interest in catalysis, yet their naturally occurring forms are of limited value, because (i) they almost always contain undesired impurity phases, (ii) their chemical composition varies from one deposit to another and even from one stratum to another in the same deposit and (iii) nature did not optimize their properties for applications.

They are micro porous crystalline aluminosilicates with frameworks made of SiO_4 and AlO_4 tetrahedral units. Insertion of trivalent Al^{3+} in place of tetrahedral coordinated Si^{4+} creates negative charge on the lattice, which is compensated by extra framework cations. If the charge compensating cation is H^+ a bridged hydroxyl group (Si–O(H)–Al), is formed, which functions as a strong Bronsted-acid site. Due to these acid sites, zeolites are solid acids and are used as catalysts. Zeolites having both acidic and basic sites present in it act as a catalyst for many reactions[1], including side chain alkylation of toluene[2], condensation reaction[3] and selective alkylation of aromatic compounds containing oxygen and nitrogen[4].

Obviously, with their negatively charged porous framework and the small and mobile cations sitting in the pores, zeolites are widely used as softener in laundry detergents where their role is to take up calcium and magnesium ions in exchange for sodium ions, thereby softening the washing water. Obviously, a high possible cation exchange capacity and, hence, the highest possible aluminum content in the framework ($n_{Si}/n_{Al} = 1$) are desired for this application. The use of zeolites as ion exchangers in detergents represents their largest market in terms of tonnage with a worldwide production rate close to 1 million t/annum[5].

During zeolite synthesis, the pores in the nuclei are presumably occupied by solvent and other organic templating molecules or ions in much the same way as are the pores in the final crystal. If these species contribute to the stabilization of the nuclei to the same extent that they contribute to the stabilization of an equal volume of the completed crystal, their neglect in the above treatment is justified. This a reasonable assumption, bearing

in minds that only semi quantitative predictions can be expected from such a generalized theory[6].

Two sources were used for heating of batch, the hydrothermal and microwave irradiation methods. Zeolites are usually synthesized by hydrothermal treatment of the raw gels using autoclaves heated within convection ovens[10]. Recently, several reports about synthesis of zeolites by microwave heating have been presented[7–12]. The use of microwave radiation in the synthesis of zeolites offers advantages over the conventional synthesis including : a higher heating rate, due to volumetric heating, resulting in homogeneous nucleation, fast dissolution of precipitated gels, and eventually, a shorter crystallization time.

The effect of microwave radiation absorption in the synthesis could be due to the different mechanisms of heat transfer to the reagents or some specific activating effect (non-thermal) on the reagent molecules. The action of microwave heating is still under debate[7].

It is well established that certain cations such as $(CH_3)_4N^+$ or other solute species can promote the formation of particular zeolite structures as well as specific silicate or aluminosilicate rings and cages in solution, but there is often no obvious correlation between the structure of the synthesized zeolite and solute speciation in the supernatant liquor[13]. Already the kinds of ammine were used as templates, such as NBA (n-butylamine), TEABr (tetraethylammonium bromide), HMDA (1,6-hexamethylene diamine), TPAOH (tetrapropylammonium hydroxide), TPABr (tetrapropylammonium bromide).

In this work, we used microwave and hydrothermal heating methods and PTMAOH as organic template and two sources for aluminum content. Then XRD, FT-IR and SEM techniques used for characterization of zeolites were synthesized with this template and without it.

Experimental

Materials : Sodium hydroxide (Merck), aluminum foil, SiO_2 (synthesized in our laboratory), silicon tetrachloride (99.8%; Janssen Chemical Co.) and phenyltrimethylammonium bromide (PTMABr) (Fluka) were used in this work. Doubly distilled water was prepared in our laboratory.

Pure SiO_2 : Pure silica was produced by hydrolysis of silicon tetrachloride using doubly distilled water. Silicon tetrachloride reacts violently with water at room temprature to give white solid silicon dioxide and steamy fumes of

HCl. The produced silicon dioxide was filtered and washed many times with doubly distilled water to remove all acid. It was then dried at 105 ºC for 48 h. The chemical reaction is quite simple :

$$SiCl_4 + 2H_2O \longrightarrow SiO_2 + 4HCl$$
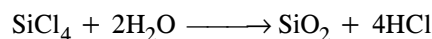
Silicate solution : Aqueous silicate solution was prepared by dissolving an appropriate of SiO_2 in 2 *M* sodium hydroxide solution at 70 ºC until the solution became clear. Dissolution of the silica was very slow at room temperature.

Aluminosilicate mixture : Aqueous sodium aluminate solution was prepared by dissolving an appropriate of aluminum in 2 *M* sodium hydroxide solution. Aluminosilicate mixtures were then obtained by mixing the aluminate and silicate solutions.

Procedure : Molar ratios of the synthesis mixtures have shown in Tables 1 and 2 for hydrothermal heating and microwave radiation respectively. These mixtures were placed in hydrothermal vessel and then emplaced in oven at 450 K for 48 h. Then the precipitate was filtered and washed with doubly distilled water to remove all base. Then they dried at 363 K for 15 h. In another method the hydrogel exposed to low power microwave radiation (100 W) for an hour, and then transfused to hydrothermal vessel and emplaced in oven as similar by past, then the

Table 1. Molar composition of the synthesis mixtures in conventional heating method

Sample No.	Gel composition
1	20 SiO_2 : Al_2O_3 : 24 Na_2O : 1800 H_2O
2	20 SiO_2 : $Al_2(SO_4)_3$: 24 Na_2O : 1800 H_2O
3	20 SiO_2 : Al_2O_3 : 24 Na_2O : 2 PTMAOH : 1800 H_2O
4	20 SiO_2 : $Al_2(SO_4)_3$: 24 Na_2O : 2 PTMAOH : 1800 H_2O

Table 2. Molar composition of samples[a] prepared by microwave assisted method[b]

Sample No.	Conventional heating time (h)
5	1.5
6	3
7	6
8	12
9	1.5
10	6

[a]The composition is [20 SiO_2 : $Al_2(SO_4)_3$: 24 Na_2O : 1800 H_2O] for Samples 5, 6, 7 and 8 and [20 SiO_2 : $Al_2(SO_4)_3$: 24 Na_2O : 2 PTMAOH : 1800 H_2O] for samples 9 and 10. [b]All sample heated by microwave for one hour.

obtained solid samples washed with pure water and dried at 363 K for 15 h.

Instrumentation : The crystallinity of the samples synthesized was tested by using X-ray diffractometer (GBC MMA Instrument) with Be Filtered Cu KL 1.5406 Å radiation operating at 35.4 kV and 28 mA. The scanning range of 2θ was set between 5° and 55° with a step size of 0.05 and scan rate 3°/min. The crystalline size and morphology were examined using a scanning electron microscope (SEM). The SEM photographs were obtained on a JEOL-JXA-840 scanning electron microscope. The IR spectra were recorded by Vector 22-Bruker spectrometer, using KBr pellet.

Results and discussion

XRD pattern : In zeolite systems, perturbations in the framework structure, crystal morphology, extra framework material, phase purity, crystallite size, and the setting and occupation of cation sites can produce differences in the X-ray diffraction patterns.

Zeolites were crystallized by conventional hydrothermal and microwaves treated methods have been analyzed by XRD. The XRD patterns of samples 1 and 2 were found to be similar as illustrated in Fig. 1. The results revealed that difference in aluminum source doesn't affect the structure of zeolites. The peak intensity at the 2θ equal 16° is increased at the present of the template (Samples 3 and 4).

The X-ray pattern of the zeolites which crystallized by using microwave are shown in Fig. 2. Regarding this figure, it can be concluded that the crystallinity of the samples is improved by increasing heating time. In this case, the XRD patterns are similar for samples 6, 7 and 8. The pattern of sample 5 shows an amorphous bulk that means the heating time (hydrothermal time) of 1.5 h is not enough for crystallization (see XRD pattern of sample 5 in Fig. 2). The XRD patterns of samples 9 and 10 are shown in Fig. 3. The same results have been obtained, for the samples synthesized in the presence of template using microwave.

SEM image : The scanning electron micrograph (Fig. 4) shows that the size of crystals of the microwave treatment samples are 5–10 μm and that of conventional heating heated samples are 10–40 μm. The zeolites have been crystallized in spherical particles morphology in both methods. However, the size of particle size in microwave treatment is smaller than that of conventional heating.
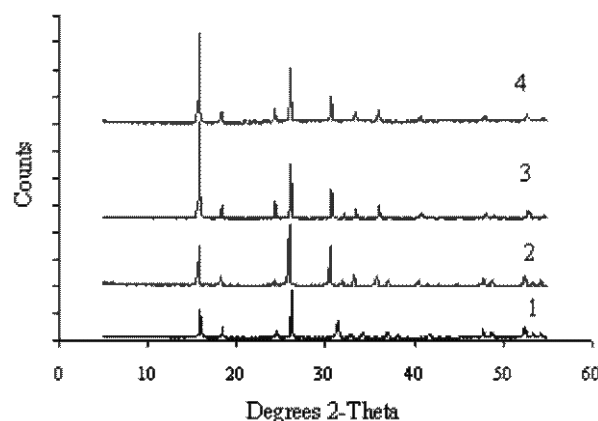

Fig. 1. XRD patterns of the synthesized samples by C–H. (1) and (2) without template; (3) and (4) at present of template.
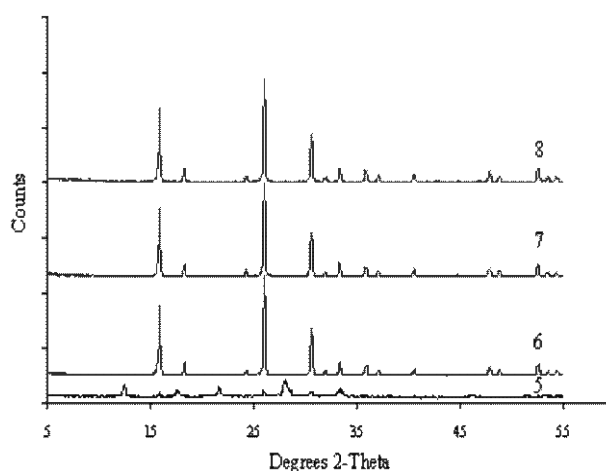

Fig. 2. XRD patterns of microwave treated zeolites, at different hydrothermal crystallization period : 1.5 h (5), 3 h (6), 6 h (7) and 12 h (8).
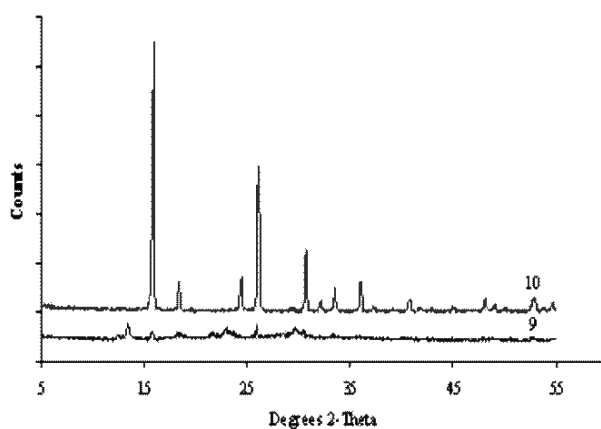

Fig. 3. XRD patterns of the samples which synthesized at present of template by microwave treatment : (9) 1.5 h and (10) 6 h.
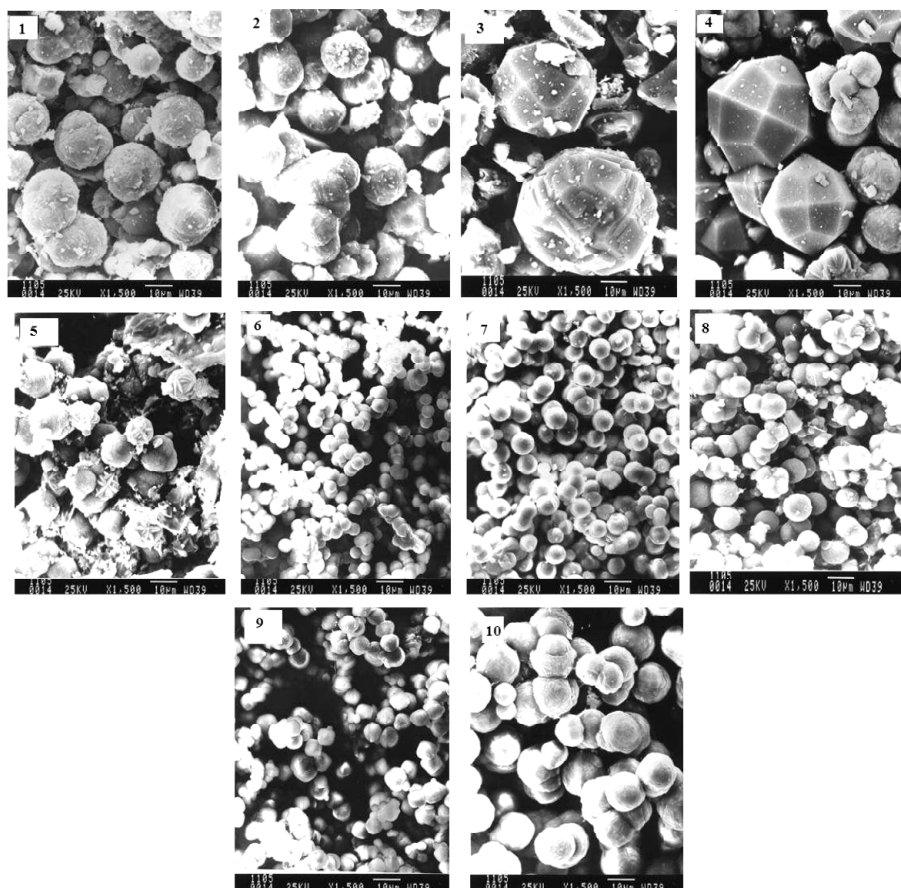
Fig. 4. SEM micrographs of the zeolites synthesized by : traditional heating (1–4), microwave heating (5–10).

The reason for different morphologies in microwave treatment system and conventional heating system has not well understood yet. Most zeolites exhibit different crystalline shapes and decreased crystal size in microwave treatment system[15,16] compared with those in conventional heating system. Comparison of the images 1 and 2 with images 3 and 4 show that, the crystals morphology can be affected by presence of the template in initial gel. Crystallization times in these samples are same; therefore, it can be concluding that the difference in morphology is due to the presence of template (comparison of the images 7 with 10 shows this too). Comparison of the images 6, 7 and 8 show a considerable increase in the size of crystals, due to long aging period. The size of crystals in image 8 is greater than image 6.

IR spectra : Supplementary information concerning the structure of the prepared zeolites was obtained by further studies using IR spectroscopy. The bands occurring in IR spectra of zeolites can be divided into two groups : bands connected with the internal vibrations of either SiO_4 and AlO_4 tetrahedra or Si–O–Si and Si–O–Al bridges; bands arising from the external vibrations of tetrahedra forming the fragments of aluminosilicate framework[18]. Each of the zeolites exhibits a typical IR pattern.

IR spectra were recorded in the frequency range 500–1300 cm^{-1}. Obviously, the results obtained by IR spectroscopy are in agreement with other data reported in the literature. The band at 635 cm^{-1} observed in the spectra of the minerals of the D6R group (double six-membered rings) can be related to the presence of six-membered rings in the three-dimensional zeolites structure. This band is also observed at about 640 cm^{-1} in the structure whose consists of the double six-membered rings.

According to the literature, increasing of ring member's could cause shifting of the ring band to the higher wave numbers[17]. Thus, we can expect that presence the 4-membered ring band in the region of 700–740 cm^{-1}. The spectra of framework silicates can be described using the model of Si_2O or SiAlO pseudo molecules[10]. Two bands, for

the Si–O–Si and Al–O–Si bridges are located in the region of 690–800 cm^{-1}.

The position of the most intensive band in the region of 950–1200 cm^{-1} arising from the Si(Al)–O stretching vibrations depends on the Al : Si ratio in zeolites. It shifts to the lower wave numbers with the increase of Al contents[18].

The infrared spectra of samples 1–4 were illustrated in Fig. 5. Obviously, the spectra of samples 1 and 2 are similar that means difference in the source of aluminum, does not affect at the structure of zeolite. In addition, synthesis of samples 3 and 4 were done in present of template and effect of presence of template observed in this figure (growing band at 640 cm^{-1}).

IR spectra of the microwave treatment samples (without the template) with varying period of crystallization were shown in Fig. 6. The spectra were recorded in the frequency range 500–2000 cm^{-1}. The bands near 1000 and 750 cm^{-1} were assigned, for the presence of Si–O–Si or Si–O–Al and Si–(Al)–O systems. It can be realized that by increasing intensity of the band located at 750 cm^{-1}, the crystallinity of the zeolite is improved. The IR spectra of the microwave treatment samples (at the present of template) are illustrated in Fig. 7. The template effect is the same for both conventional heating and microwave treatment.
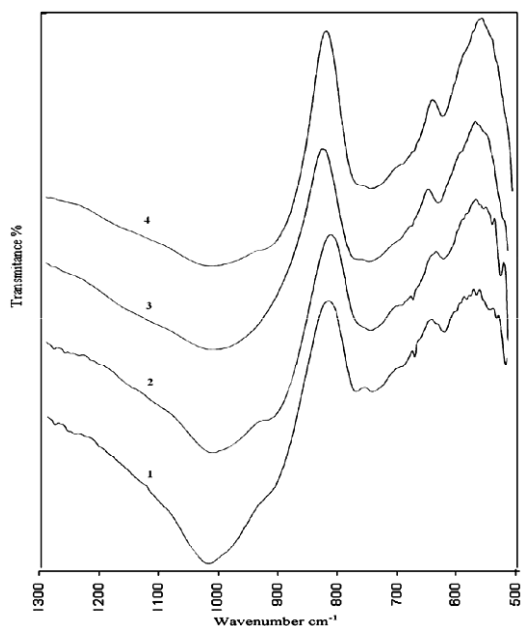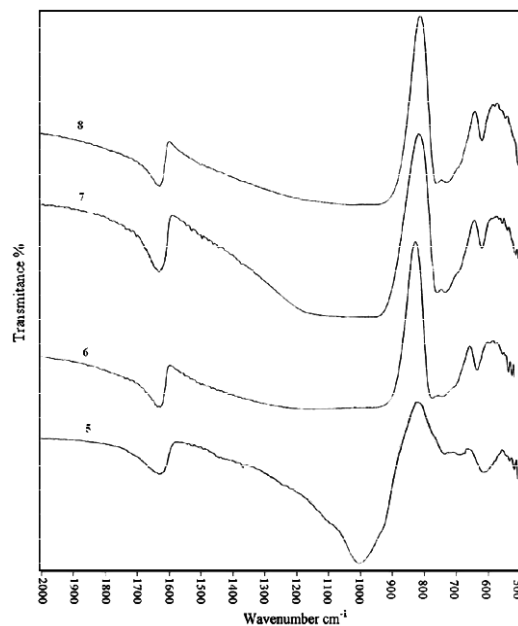

Fig. 6. Framework IR spectra of synthesized zeolites for M–H obtained at (5) 1.5 h, (6) 3 h, (7) 6 h and (8) 12 h.
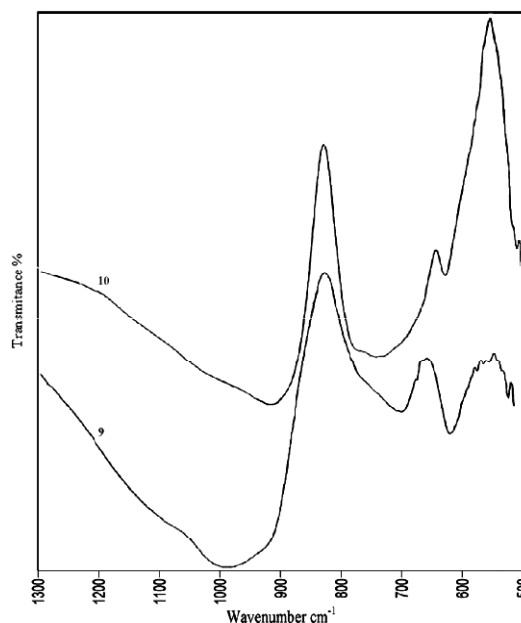

Fig. 7. IR spectra of the samples 9 and 10 which synthesized at present of template by microwave assisted method.

Conclusions

The capability of microwave irradiation to speed up zeolite crystallization has been already demonstrated by numerous authors. Although very similar crystallization mechanisms can be proposed for the two types of heating

Fig. 5. IR spectra of synthesized zeolites samples 1 and 2 (without template), 3 and 4 (at present of template).

methods here employed, it can be concluded that the microwave radiation increases the rate of the different steps of the crystallization mechanism. The use radiation generates a strong positive effect on the nucleation, due to the almost instantaneous heating of the synthesis medium, and on the last step solubility and mobility are enhanced. The zeolites can be synthesized employing microwave heating in a short period of time. The products obtained with microwave heating showed the same structural (crystallinity, silicon/aluminum molar ratio) than one synthesized with traditional heating but with lower particle size. Finally, the strong dissolution effect associated with the oscillating electromagnetic field can be used to reduce water content in zeolite formulation, increasing the yield and production capacity.

Acknowledgement

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