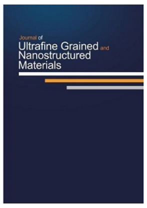

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Ultrafast synthesis of hierarchical zeolite FAU by microwave heating

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ABSTRACT

This work reports an ultrafast route for the preparation of hierarchical zeolite FAU by a combined templating-microwave heating method. An inexpensive and harmless cationic polymer polydiallyldimethylammonium chloride (PolyDADMAC) was used as a mesoporogen agent. Several characterization techniques such as X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), energy dispersive X-ray (EDX) spectroscopy and N_2 sorption analysis confirmed the successful synthesis of hierarchical zeolite FAU with both inter and intra-crystalline mesopores. The effects of microwave heating times and polymer quantities on the structural properties of the final product were evaluated. A crystallization time of 180 minutes and microwave radiation at 90°C proved to be adequate to obtain the best product. Microwave heating resulted in the formation of nanozeolite crystallites with mesopores between them and polymer removal through calcination created mesopores inside the zeolite crystals.

Keywords: *Hierarchical, Zeolite, Polymer, Microwave, Mesoporous.*

1. Introduction

Hierarchically-structured zeolites are considered as molecular sieves with at least bimodal (micro- and meso-pores) and in some cases multimodal porosity (micro-, meso- and macro-pores) described by IUPAC (International Union of Pure and Applied Chemistry) classification in their structures. There are various strategies such as demetallation, soft and hard templating, zeolitization, etc. to obtain hierarchical or mesoporous zeolite structures with different frameworks [1,2]. Despite development in producing mesoporous high silica zeolites, the efforts for the preparation of low silica ones such as LTA (Linde Type A) and FAU (faujasite) were not sufficient enough; whereas, their widespread applications in diverse industries like petrochemical and detergents are undoubtedly obvious [3,4]. Templating is a promising method to prepare a favorable zeolitic framework along with intra-crystalline mesopores. On the other hand, as a well-known process to acquire nanozeolites and a new inter-crystalline porosity gird in accordance with their aggregation, microwave heating has been established. In this case, Hu and co-workers [5] investigated the preparation of different nanozeolites as silicalite-1, ZSM-5, LTL, BEA, and LTA using a microwave-assisted two-step hydrothermal procedure. Moreover, zeolite ZSM-11 was prepared by a microwave method in a reduced synthesis time down to 3–4 days compared to a classical route with longer time (14 days), using seed crystals and pretreatment steps [6]. The preparation of hierarchical MFI zeolites (ZSM-5, TS-1, S-1) with intra-crystalline mesoporosity via a microwave-induced assembly between cetyltrimethylammonium bromide as a cationic surfactant and the anionic functionalized zeolite nanoparticles was a research fulfilled by Jin et al. [7]. They claimed that microwave powers and irradiation times could control the mesoporosity which gave rise to much higher catalytic selectivity and activity of the final product onto large molecules. In terms of metallurgical, mechanical, physical as well as saving time and energy during processing, the quality of materials is assumed to be improved by microwave heating. In the conventional method, heating the materials begins from the surface and then continues into the body through convection, conduction and radiations phenomena while in microwave radiation; heating at an atomic level resulting in volumetric heating of the component and the heat direction is from the center to outer parts of the substrate [8].

Considering a few reported studies dealing with the preparation of hierarchical zeolite FAU by applying templates during time-consuming processes (Table 1) and concurrently paying attention to the positive effect of microwave radiation in accelerating the crystal formation and growth, the present study focuses on applying microwave heating for a fast crystallization treatment to gain nanozeolites and utilizing a cationic polymer polydiallyldimethylammonium chloride (PolyDADMAC) as a mesoporogen agent to get a mesoporous low silica zeolite FAU (Meso FAU).

2. Materials and methods

2.1. Preparation and characterization of the samples

Hierarchical zeolite FAU was synthesized via a simple method as follows: firstly, 3.5 g NaOH (coarse powder from Ameretat Shimi) was dissolved in ca. 40 mL distilled water which was divided into two basic solutions afterwards. 2.7 g $NaAlO_2$ (Aldrich) and 9.5 mL Na_2SiO_3 (Nafis Silicate Sepahan) were added to each one and then mixed drop by drop. The obtained milky hydrogel was shaken for 60 minutes at room temperature (700 rpm) followed by addition of different amounts of PolyDADMAC polymer and subsequent stirring (24 h). After that, the final gel was transferred into an autoclave underwent microwave radiation (MILESTONE S.r.l. MICROSYNTH, MW output power: 1000W – 2450MHz) for various times at 90 ˚C (ultrasound power of 115 W). To determine the polymer effect on the zeolite structure, the same procedure was employed without polymer and calcination step (550 ˚C, 5 h). In addition, the mentioned process performed with the hydrothermal method for 20 h at 95 ˚C.

The structural characterization of obtained samples was recorded on X-ray diffractometer (JEOL-JDX 8030), Fourier transform infrared spectrometer (SHIMADZU-8400-s), nitrogen sorption analysis equipment (Micromeritics-ASAP 2020), scanning electron microscope (VEGAII TESCAN) and energy dispersive X-ray spectrometer (IDEFIX setup, SAMx company).

3. Results and discussion

The X-ray diffraction patterns of samples synthesized at different times at 90 ˚C under microwave radiation and one prepared hydrothermally during 20 hours at 95 ˚C are depicted in Fig. 1. As it is obvious, the characteristic peaks of the sample prepared at 3 h are deposited on 2θ degrees in a good agreement with those of reference structure with FAU framework topology (ICSD collection code: 066411) corroborating the successful synthesis of mesoporous zeolite FAU. However, amorphous products were obtained at shorter crystallization times (1 and 2 h); whereas, at a longer time (4 h) peaks assigned to zeolite LTA framework appeared. In fact, introducing mesopores in the zeolite structures should not damage their inherent microporous systems, because the highly desirable features of microporous zeolites such as their stability based on their crystallinity, their selectivity due to microporosity, and their defined acidity arising from a uniformly distributed aluminum sites in the crystalline network set them

Table 1- Different templates for the synthesis of hierarchical zeolite FAU

Heating method	Template	t (h)	T (˚C)	[Ref]
Hydrothermal	3-(trimethoxysilyl)propyl hexadecyl dimethyl ammonium chloride	96	75	[9]
Hydrothermal	Dimethyloctadecyl[3-(trimethoxysilyl)propyl] ammonium chloride	96	75	[10]
Hydrothermal	Polydiallyldimethylammonium chloride	16	100	[11]
Hydrothermal	Pluronic F127 (PEO_{106}-PPO_{70}-PEO_{106})	24	102	[12]
Hydrothermal	Sodium dodecylbenzenesulfonate	7	100	[13]
Hydrothermal	Spirulina	5	100	[11]

apart from the many other mesoporous compounds [14]. On the other hand, in order to favour the intracrystalline mass transfer phenomena in mesoporous zeolites which cause faster diffusion of the reacting and product molecules towards and from the active sites, respectively, the presence of an appropriate interconnected network of micropores and mesopores throughout the zeolite crystal is a main factor [15]. Here, the XRD patterns revealed that the crystal structure of the sample heated via templating-assisted microwave route (3 h) was desirably maintained.

Moreover, the assessment of FT-IR spectra of samples illustrated in Fig. 2 demonstrated the formation of zeolite FAU with characteristic infrared bands assigned to its framework; the symmetric and asymmetric stretching vibrational and bending ones were at wavenumbers 700-800, ca. 1000 and 400-500 cm^{-1}, respectively. The presence of double 6-membered rings (D6R) of FAU framework is shown at wavenumbers 500-600 cm^{-1} (563 cm^{-1}).

In fact, zeolite FAU possesses a 3- dimensional framework made from primary structural units of sodalite cages which are connected with each other by double-6-membered rings (D6R) [16,17]. Morales-Pacheco and co-workers [18] also reported that the presence of D6R in the framework of zeolite FAU resulted in the appearance of band at 560 cm^{-1}

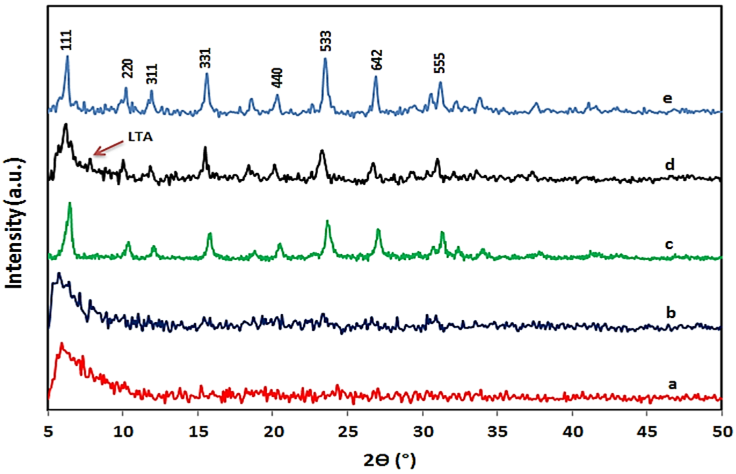

Fig. 1- XRD patterns of microwave-assisted prepared zeolites at different crystallization times with PolyDADMAC content: 2 mL, aging time: 24 h and crystallization temperature: 90 ˚C; (a) 1 h, (b) 2 h, (c) 3 h and (d) 4 h. (e) Sample hydrothermally synthesized with PolyDADMAC content: 2 mL, aging time: 24 h, crystallization time: 20 h and crystallization temperature: 95 ˚C.

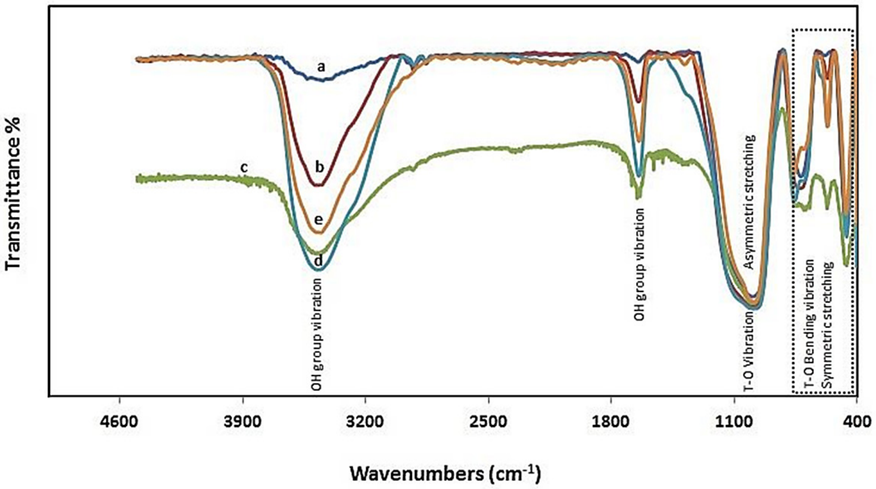

Fig. 2- FT-IR spectra of microwave-assisted prepared zeolites at different crystallization times with PolyDADMAC content: 2 mL, aging time: 24 h and crystallization temperature: 90 ˚C; (a) 1 h, (b) 2 h, (c) 3 h and (d) 4 h. (e) Sample hydrothermally synthesized with PolyDADMAC content: 2 mL, aging time: 24 h, crystallization time: 20 h and crystallization temperature: 95 ˚C; T is Si and/or Al.

in the FT-IR spectra which is very close to what we observed in this work (563 cm^{-1}). They believed that band was important as it confirmed the crystalline nature of the zeolite FAU. Moreover, vibration of water molecules appears at wavenumbers 1600-1700 and 3400-3700 cm^{-1}, respectively [17].

It has been recognized that the advantages of microwave heating in comparison with the conventional method, as a result of producing high pure tiny particles with narrow size distribution during short reaction time, makes it as an alternative choice for crystal growth and synthetic chemistry purposes [19]. Astonishingly, the thermal gradients appeared in conventional treatment is not allowed to occur in the case of microwave irradiation because of its special selective dielectric heating which conducts a uniform high-temperature reaction medium ending in particle size reduction down to the desired extent [5].

The average particle size and morphological properties of samples synthesized under microwave heating at various times are shown in Fig. 3.

Proportional to XRD data, the best-crystallized Meso FAU sample was obtained at 3 h under microwave radiation with a benefit of shorter time and lower temperature rather than the conventional route. Fig. 4 shows the SEM images of the optimum sample and those of hydrothermally-synthesized mesoporous zeolite.

Moreover, in order to investigate the effect of polymer addition on the formation of the final product, the synthesis method was carried out with

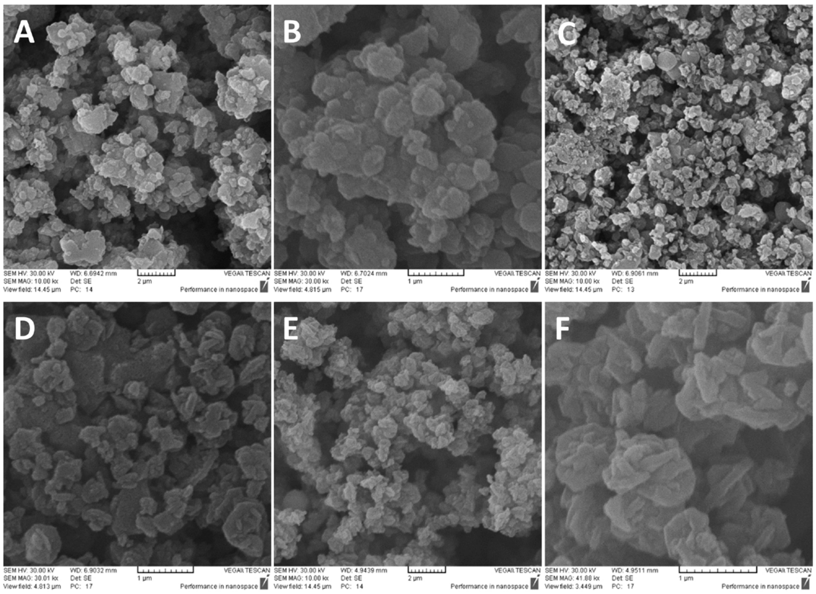

Fig. 3- SEM images of microwave-assisted prepared zeolites at different crystallization times with PolyDADMAC content: 2 mL, aging time: 24 h and crystallization temperature: 90 °C; (A,B) 1 h, (C,D) 2 h, and (E,F) 4 h. Samples synthesized at 1 and 2 h are shapeless while at 4 h, a mixture of zeolite FAU and LTA are formed.

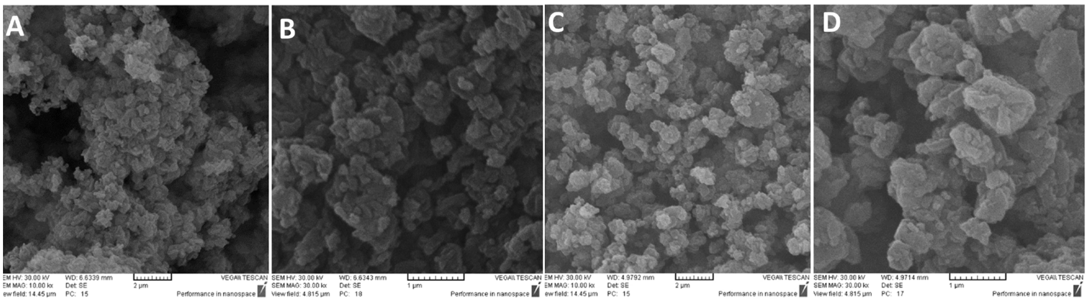

Fig. 4- (A,B) SEM images of microwave-assisted prepared zeolite at 3 h (PolyDADMAC content: 2 mL, aging time: 24 h, and crystallization temperature: 90 °C) and (C,D) sample hydrothermally synthesized at 20 h (PolyDADMAC content: 2 mL, aging time: 24 h, and crystallization temperature: 95 °C).

different amounts of PolyDADMAC as 0, 1, and 2 mL.

As it can be seen in the SEM images of all samples (Fig. 5), the fact of nanoparticle aggregation is upheld re-notifying the microwave heating effect on crystal size reduction and nanozeolite formation. In spite of nearly no clear distinct difference between SEM images and FT-IR spectra (Fig. 6); obviously, XRD patterns of the samples represent the successful formation of mesoporous zeolite FAU while adding 2 mL of the polymer as mesoporogen agent (Fig. 7).

In fact, the phase purity and crystallinity of the zeolites were maintained after polymer addition, because the position of the characteristic peaks was the same in all samples and the XRD peak intensities remained perceptibly unchanged which demonstrated the zeolite framework did not collapse. Similarly, preparation of hierarchical zeolite Beta (mesopore sizes of 5-40 nm) by use of the mesoscale cationic polymer PolyDADMAC was performed by Xiao et al. [20]. The authors believed that the presence of mesoporosity in the synthesized hierarchical zeolite Beta was

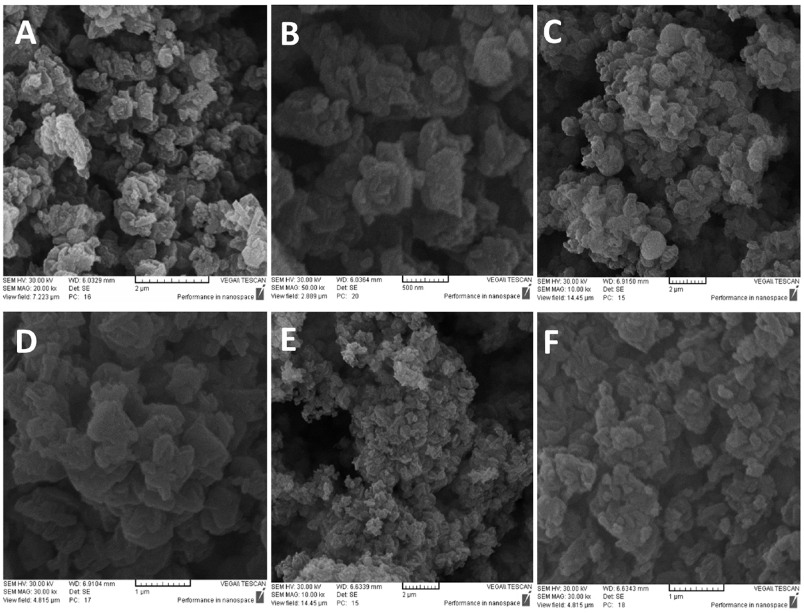

Fig. 5- SEM images of microwave-assisted prepared zeolites at different PolyDADMAC contents (aging time: 24 h, crystallization time: 3 h, and crystallization temperature: 90 °C); (A,B) 0 mL, (C,D) 1 mL and (E,F) 2 mL.

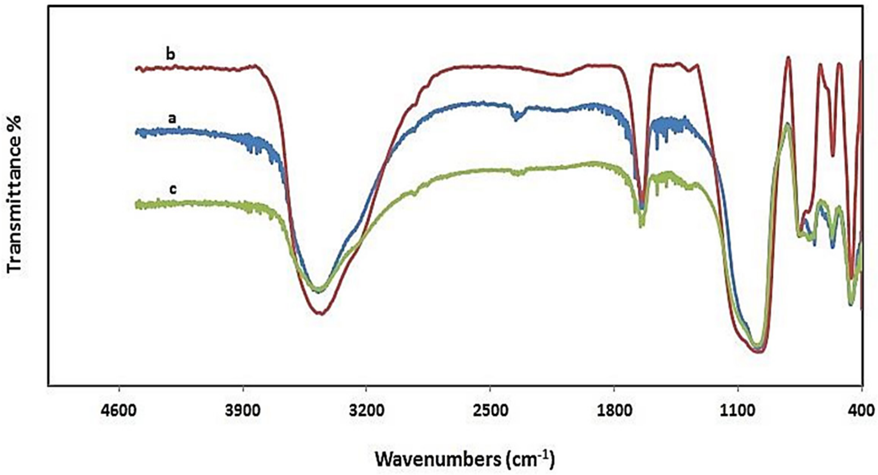

Fig. 6- FT-IR spectra of microwave-assisted prepared zeolites at different PolyDADMAC contents (aging time: 24 h, crystallization time: 3 h, and crystallization temperature: 90 °C); (a) 0 mL, (b) 1 mL and (c) 2 mL.

attributed to the use of molecular and aggregated PolyDADMAC. The size of the polymer is about 5-40 nm and its molecular weight is in the range of 1×10^5-1×10^6. This polymer can create mesopores as a result of effective interaction with negatively charged inorganic silica species in alkaline medium and the greater amount addition of the polymer yields zeolite with larger mesoporosity.

In addition, elemental analysis fulfilled by EDX technique (Fig. 8) indicated that the sample possessed Si/Al ratio of 1.0-1.5 designated as hierarchical low silica zeolite FAU type X. However, calcination has been recognized as a dealumination treatment so that some Al species could be extracted from the zeolite framework through hydrolysis of the Si–O–Al bonds; therefore, the ratio of Si to Al may become more than 1.5 and the Meso FAU sample is considered as Y-type zeolite FAU [14,21,22].

N_2 sorption analysis (Fig. 9) for both samples synthesized with 2 mL (Meso FAU-2) and without PolyDADMAC (Meso FAU-0) under microwave heating represents a new mesoporosity in the zeolite structures as hysteresis loops in relative pressures between 0.4 to 0.8 and isotherm type IV for mesoporous materials. Furthermore, sharp nitrogen uptake in low P/P_0 is ascribed to the filling of micro-pores inherently present in the zeolite FAU framework [21]. The textural features of the samples are collected in Table 2.

Considering the amounts of BET surface area and total pore volume, by taking ca. 5.3 percent reduction in the micropore area, and about 23.4 percent increase in the mesopore volume for Meso FAU-2 in comparison with Meso FAU-0 into account, the formation of intra-crystalline mesopores in the former sample would be rational. However, inter-crystalline mesopores are formed

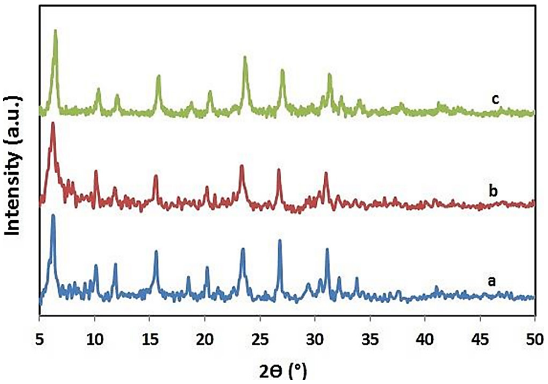

Fig. 7- XRD patterns of microwave-assisted prepared zeolites at different PolyDADMAC contents (aging time: 24 h, crystallization time: 3 h, and crystallization temperature: 90 °C); (a) 0 mL, (b) 1 mL and (c) 2 mL.

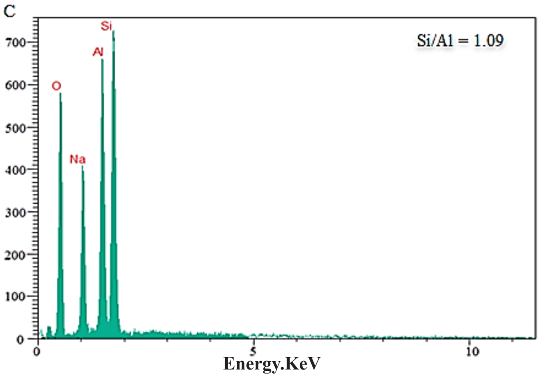

Fig. 8- EDX elemental analysis of sample synthesized using microwave heating method (aging time: 24 h, PolyDADMAC content: 2 mL, crystallization time: 3 h, and crystallization temperature: 90 °C).

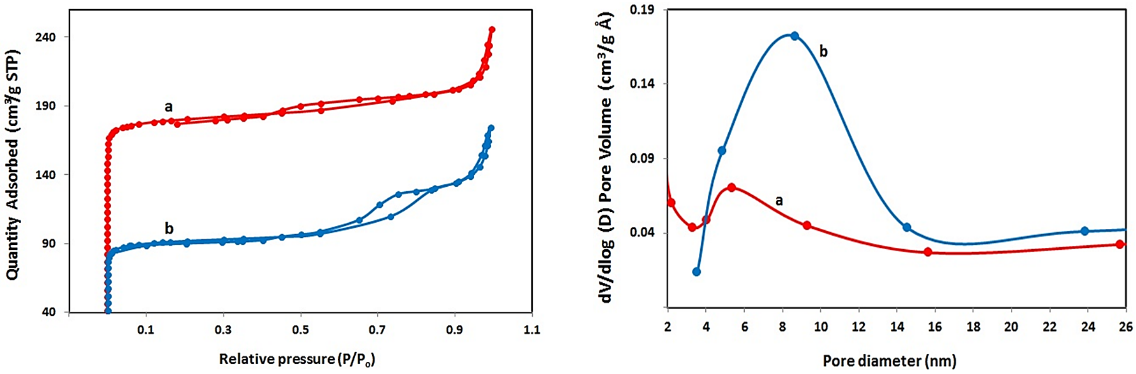

Fig. 9- N_2 adsorption-desorption isotherms (left) and pore size distribution curves (right) of samples synthesized using microwave heating method; (a) without (0 mL) and (b) with 2 mL PolyDADMAC (aging time: 24 h, crystallization time: 3 h, and crystallization temperature: 90 °C).

Table 2- Textural features of prepared zeolitic samples under microwave heating at crystallization time 3 h, and temperature 90°C without PolyDADMAC (Meso FAU-0) and with 2 mL PolyDADMAC (Meso FAU-2)

Textural feature	Meso FAU-0	Meso FAU-2
BET surface area (m^2 g^{-1})	513	262
Micropore area (m^2 g^{-1})	452	217
Total pore volume (cm^3 g^{-1})	0.35	0.25
t-Plot micropore volume (cm^3 g^{-1})	0.25	0.12
Mesopore volume (cm^3 g^{-1})	0.10	0.13
Pore diameter (nm)	7.3	9.3

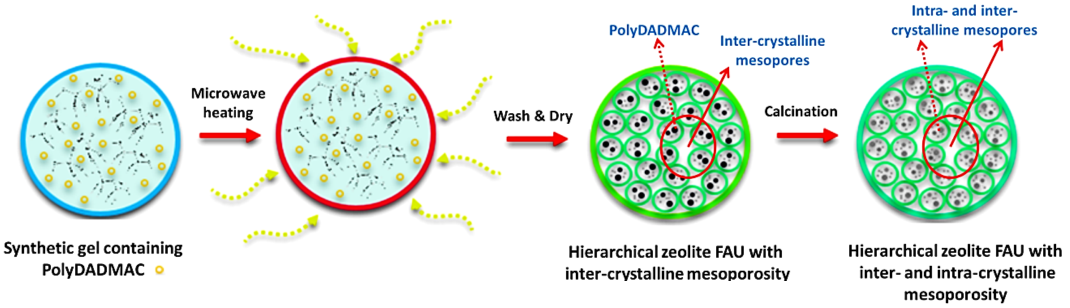

Fig. 10- The proposed mechanism for the formation of hierarchical zeolite FAU through a combined templating-microwave heating process.

in both samples due to the aggregation of zeolite crystals under microwave radiation; this type of structure makes a profit of being mechanically stable and sturdy.

Totally, as it has been made explicit, microwave radiation has a positive influence on crystal size reduction of zeolites, and subsequently their aggregation; this may result in inter-crystalline mesoporosity. On the other hand, soft templating strategy by using polymers can help the creation of intra-crystalline mesoporosity after the removal of template. Accordingly, a proposed mechanism is shown in Fig. 10 to explain what happens as hierarchical zeolite FAU is prepared by a combined templating-microwave heating method in the present study.

4. Conclusions

In this study, a combined templating-microwave heating synthesis method was used to prepare a hierarchical zeolite FAU. The effects of different synthetic conditions such as microwave heating time and polymer quantity on the structural properties of the end samples were investigated. Finally, a high-quality product was obtained within 3 h at 90 °C with inter- and intra-crystalline mesopores and an average pore size of ca. 9 nm. It was supposed that microwave radiation could produce inter-crystalline and polymer addition led to the formation of intra-crystalline mesopores. The results of this work promise an ultrafast and energy-efficient procedure to obtain a hierarchically-structured Al-rich zeolite framework in comparison with conventional hydrothermal heating method.

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