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Synthesis and Characterization of Aluminophosphate Zeolites with (2-hydroxyethyl) Trimethylammonium Using Microwave Assisted, Conventional Hydrothermal and Ultrasonic Technique

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Abstract: Different types of aluminophosphate zeolites were synthesized by conventional hydrothermal and microwave assisted hydrothermal using (2-hydroxyethyl) trimethylammonium as a template. The influence of the chemical composition of the starting sol-gel and the other parameters such as, aluminum source and time of microwave irradiation were studied. The effect of Al/P mole ratio was also investigated. Results indicated that the synthesized zeolite with Al/P = 1 contains more crystalline percentage than the others. Results specified that zeolites which synthesized without template have particles size of 112 μm but zeolite synthesized with 2-hydroxyethyl) trimethylammonium chloride was contained particles size of 33 μm. Aluminophosphate zeolites were also synthesized with ultrasonic as a mixer.

Key words: $AlPO_4$ zeolites · (2-hydroxyethyl) trimethylammonium · Ultrasonic technique · Microwave assisted hydrothermal

INTRODUCTION

A novel class of aluminophosphate ($AlPO_4$) was synthesized by Wilson and co-workers [1]. These zeolite-like molecular sieve AlPO-n (n denotes a structure type) contain framework oxide molecular sieves synthesized without silica. $AlPO_4$ is synthesized at low pH while aluminosilicate is obtained at high pH. Moreover, the solubility of $AlPO_4$ species in aqueous solution decreases with increasing temperature, but the solubility of silica increases by raising temperature [2]. Structure of aluminophosphates is typically contained from alternation of AlO_4 and PO_4 tetrahedral through corner sharing to form a neutral open-framework. Part of the aluminum and phosphorous sites can be replaced by some transition metal ions [3].

It is well-known that amorphous aluminum orthophosphates are solid bifunctional acid-bases that they can be used as catalysts. They are active in several chemical processes, such as isomerization, cracking, dehydration, alkylation, oxidative dehydrogenation, rearrangement, nucleophilic substitution, cetalization, condensation and decomposition of fluoro-and chlorofluorocarbons [4]. One of the important applications of AlPO-n is the aerial oxidations of linear and cyclic hydrocarbons [5]. Generally, zeolites are available in the growing field of solvent-free industrial reactions in the important area of clean technology [6-10].

Preparations of AlPO-n materials typically need hydrothermal treatment of an aqueous gel containing quaternary ammonium as a template. Some structures can only be obtained with a specific template, such as JDF-20, which can only be synthesized with triethylamine as template [11]. In contrast, $AlPO_4$-5 can be made in the presence of different amines [12]. Many of the frameworks contain a single channel system, in which the walls of the channel comprise six-rings of T atoms (T alternating Al and P centers, bridged by oxygen), analogous to the double-pyroxene chains of $AlPO_4$-tridymite. Recently a number of reports on new chain [13-18] and layer [19-27] aluminophosphate structures have increased steadily.

In the synthesis of phosphate-or silicate-based microporous molecular sieves (MMS), organic amines or quaternary ammonium ions are usually used as templates or structure directing agents. It is believed that these organic templates stabilize certain phases during the synthesis course via nonbonding interactions between the template and the host inorganic framework [28-32].

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It can be used one template for synthesis of different zeolites known "one template/multiple-structures" as in the case of di-*n*-propylamine that is used in the synthesis of more than 10 different AlPO structures, such as $AlPO_4$-11, $AlPO_4$-31, $AlPO_4$-39, $AlPO_4$-41, $AlPO_4$-43, $AlPO_4$-46, $AlPO_4$-47 and $AlPO_4$-50 [33]. Actually, the role of the organic template still remains an important issue that has not well understood yet. This difficulty of understanding the role of organic templates arises from the complexity of the hydrothermal crystallizations, the lack of information on the presence of different chemical species at different synthesis stages and the lack of complete understanding of the principles governing the formation of crystalline porous materials [34]. Also, synthesis of AlPOs molecular sieve was performed in the ionothermal media by microwave irradiation in eutectic mixture [35].

Recently, one of us (Samadi-Maybodi) synthesized aluminosilicates zeolites by conventional hydrothermal and microwave assisted hydrothermal using (2-hydroxyethyl) trimethylammonium hydroxide (2-HETMAOH) as a template [36]. To the best of our knowledge, no new topology of the aluminophosphate materials has been synthesized using a (2-hydroxyethyl) trimethylammonium. In this work, crystallization of the zeolite with conventional hydrothermal has been investigated using 2-HETMA cation as a template, different aluminum source such as aluminum sulfate, aluminum oxide and aluminum hydroxide was also studied. Crystallization of zeolites was performed by conventional hydrothermal (CH) method and microwave assisted hydrothermal (MAH). The effect of ultrasonic mixer was also investigated in this work. Zeolites were characterized by XRD and SEM techniques.

Experimental

Materials: Aluminum oxide (γ-Alumina), Aluminum hydroxide, 2-hydroxyethyl trimethylammonium chloride (2-HETMACl), tetramethylammonium chloride (TMACl), tetraethylammonium chloride (TEACl), triethylamine (TEA) and sodium hydroxide were obtained from Merck Company. Aluminum sulfate hexadecahydrate, ortho-phosphoric acid 85 wt?, tetrapropylammonium boromide (TPABr) and Amberlite resin CG-400(OH) were purchased from Fluka Company. Also, double distilled water was used throughout. (2-hydroxyethyl) tri-methylammonium chloride was converted to hydroxide form by dissolving it in minimum amount of water and passing down a column of Aldrich amberlite resin CG-400 (OH).

Chemical Preparation: Solutions containing aluminum, phosphorous and quaternary ammonium salts (as a template) were prepared with molar ratio of Al: P: 0.5 R: 20 H_2O (R= template). At the first, aluminum sulfate hexadecahydrate was added to the phosphoric acid 85% with stirring at *ca.* 60 °C until the solution became clear. Then an appropriate amount of templates (2-hydroxyethyl trimethylammonium chloride, tetramethylammonium chloride, tetraethylammonium chloride and triethylamine) and distillated water were added to above solution with stirring. The result mixture was introduced into 60 mL Teflon container, this vessel was put in stainless steel and heated at a constant temperature of 180 °C under autogenous pressure for 24 h. The mixing processing was also performed by ultrasonic tool.

In microwave assisted hydrothermal synthesis, the aluminophosphate solution was exposed to low power microwave radiation (100 W, operating at frequency of 2450 MHz) for various times and then it was transferred to an oven between 2 to 8 hours at temperature of 180 °C. The solid products were filtered off and washed several times with distillated water; subsequently, were dried at 110 °C for 3 h and calcinated at *ca.* 550 °C for 5.5 h.

Apparatus and Characterization: XRD patterns were recorded by X-ray diffractometer (XRD, GBC MMA Instrument) with Be Filtered Cu K_α radiation (1.5418 **E**) operating at 35.4 kV and 28 mA. The scanning range of 2θ was set between 2° and 50° with scan rate of 10 degree/min. SEM photographs were obtained on a VEGA2-TESCAN. A household microwave oven (2.45 GHz, 100 W) was used.

RESULTS AND DISCUSSION

The Influence of Aluminum Source: The effect of aluminum source was studied with compositions of, Al: P: 0.5 (2-HETMACl): 20 H_2O. The compounds of Al_2O_3, $Al(OH)_3$ and $Al_2(SO_4)_3$ were used as aluminum source for sample AP1, AP2 and AP3, respectively. Detail composition for above samples is shown in Table 1. Figure 1 shows the XRD patterns of the corresponding samples. Since no peaks were observed at $2\theta < 20°$, therefore all XRD patterns were cut off at $2\theta = 18°$. As can be seen, all XRD patterns have the same feature, however, for sample AP3 the intensity of reflection peak located at $2\theta = 26.4°$ is grater than the others. This specifies that percentage of the crystallization is more improved.

Table 1: Composition for the synthesis of the zeolites by conventional heating

Sample No.	Al[(a)](mol)	P (mol)	Template(mol)	H_2O(mol)	Heating time (h)	Temp.(°C)
AP1	1	1	2-HETMACl (0.5)	20	24.0	180
AP2	1	1	2-HETMACl (0.5)	20	24.0	180
AP3	1	1	2-HETMACl (0.5)	20	24.0	180
AP6	1	1	TEACl (0.5)	20	24.0	180
AP7	1	1	TEA (0.5)	20	24.0	180
AP8	1	1	TPABr (0.5)	20	24.0	180
AP9	1	1	TMACl (0.5)	20	24.0	180

(a) Al_2O_3 and $Al(OH)_3$ were used as aluminum source for samples AP1 and AP2 respectively but $Al_2(SO_4)_3.16H_2O$ was used as aluminum source for preparation of samples AP3, AP6-AP9.

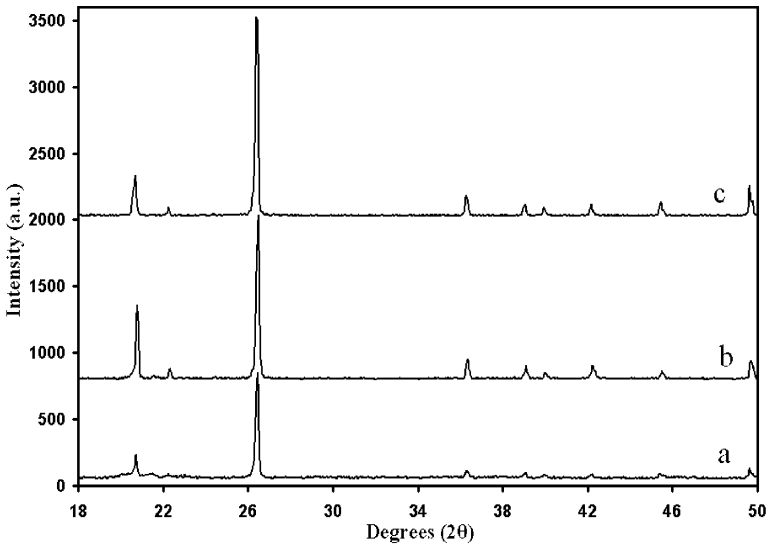

Fig. 1: XRD patterns for synthesized AlPOs zeolites by conventional heating and compositions of Al: P: 0.5 (2-HETMACl): 20 H_2O with different aluminum sources: a. sample AP1 with Al_2O_3, b. sample AP2 with $Al(OH)_3$ and c. sample AP3 with $Al_2(SO_4)_3$. No signals were found within range of 2-18 degree.

The Influence of Template: To determine the influence of the template, zeolites were synthesized with compositions of Al: P: 0.5R: 20H_2O that R is 2-HETMACl (sample AP3), 2-HETMAOH (sample AP5); no template was used for sample AP4. Aluminum sulfate hexadecahydrate was used as aluminum source. Figure 2 presents XRD patterns of the corresponding samples. As can be seen, the efficiency of crystallization for sample AP4 (i.e. sample without template) is very poor. The peak located at ca. $2\theta = 26.4$ is considerably enhanced for sample AP5 that indicates the crystallization of sample with 2-HETMAOH is highly improved.

Figure 3 presents SEM images of the above samples. Obviously, the particle sizes as well as shape of the crystals were affected by kind of the template. Results revealed that synthesized zeolite without template has larger particle size than that with template, i.e., the sizes of particles are 33 and 112 μm for samples with and without 2-HETMA, respectively. It is pertinent to mention that the size distribution for the synthesized zeolite with the 2-HETMACl is more regular than that with the 2-HETMAOH.

The effect of different templates was also examined for synthesis of aluminophsphate zeolite. In this experiment, templates such as 2-HETMACl, TMACl, TEACl, TPABr and TEA were used (Table 1). Figure 4 illustrates XRD patterns of the corresponding samples (AP3, AP6-AP9). Clearly, feature of the spectra are same but for sample AP9 the intensity of the signal located at 2θ equal 26.4° is much more intense than the others. As a result, crystallization is improved at the presence of TMACl.

The Effect of Al/P Ratio: The influence of Al/P mole ratio was investigated by studying the $AlPO_4$ molecular zeolite with Al/P mole ratios of, 0.50, 0.60, 0.72, 0.83, 0.92 and 1.0

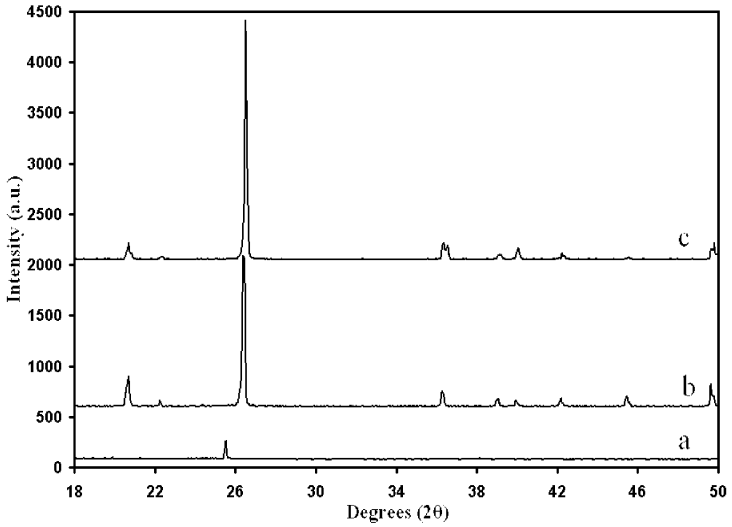

Fig. 2: XRD patterns for samples with compositions of Al: P: 0.5 R: 20 H_2O. a. sample AP4 without template, b. sample AP3 with R = 2-HETMACl and c. sample AP5 with R= 2-HETMAOH.

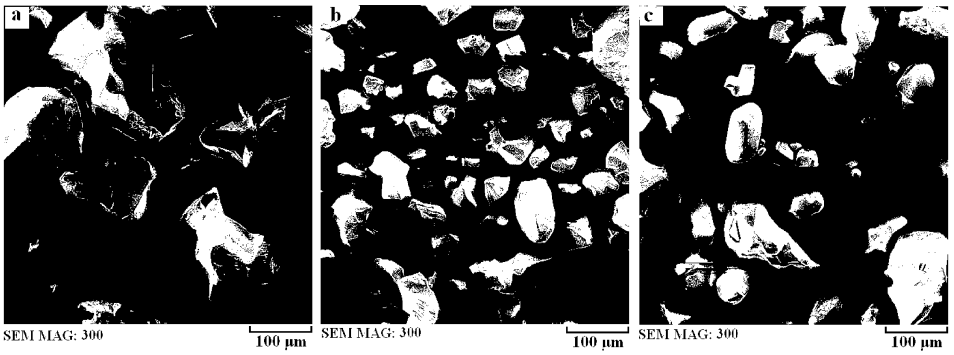

Fig. 3: SEM images for samples with compositions of Al: P: 0.5 R: 20 H_2O. a. sample AP4 without template, b. sample AP3 with R = 2-HETMACl and c. sample AP5 with R= 2-HETMAOH.

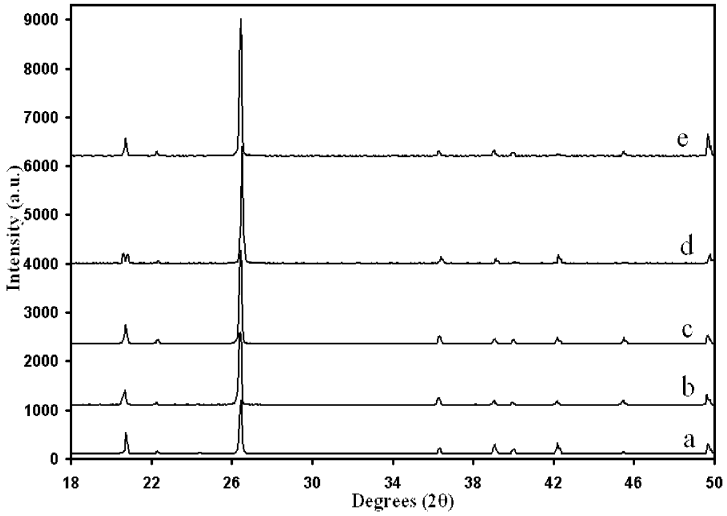

Fig. 4: XRD patterns for synthesized AlPOs zeolites by conventional heating and compositions of Al: P: 0.5 R: 20 H_2O with different template: a. sample AP6 with TEACl, b. sample AP3 with 2-HETMACl, c. sample AP7 with TEA, d. sample AP8 with TPABr and e. sample AP9 with TMACl.

Table 2: Composition for the synthesis of the zeolite with different Al/P mole ratios by hydrothermal synthesis

Sample No.	Al/P (mol ratio)*	2-HETMACl (mol)	H_2O (mol)	Heating time (h)	Temp.°C
AP10	0.50	0.5	20	24.0	180
AP11	0.6	0.5	20	24.0	180
AP12	0.722	0.5	20	24.0	180
AP13	0.833	0.5	20	24.0	180
AP14	0.923	0.5	20	24.0	180
AP 3	1.00	0.5	20	24.0	180

*$Al_2(SO_4)_3.16H_2O$ was used as aluminium source for preparation of all samples

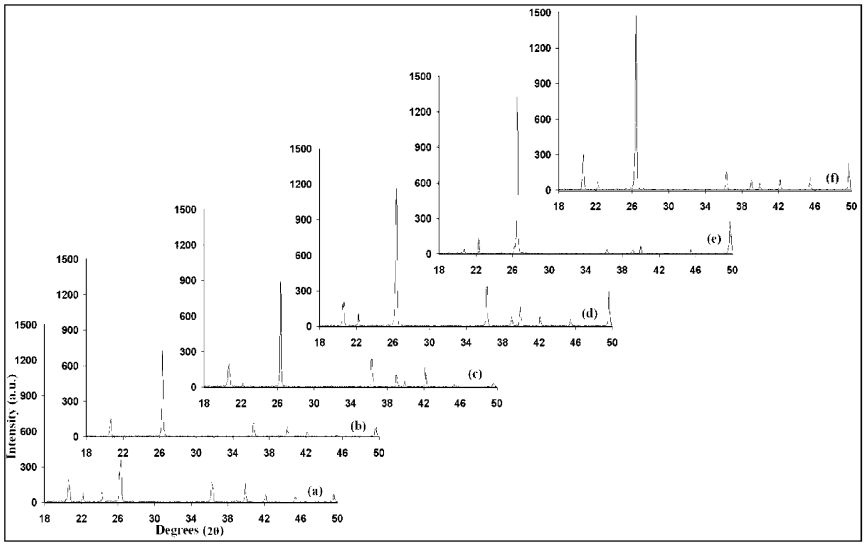

Fig. 5: XRD patterns of the AlPOs zeolites with different Al/P ratio: a. sample AP10 with Al/P = 0.50, b. sample AP11 with Al/P = 0.60, c. sample AP12 with Al/P = 0.72, d. sample AP13 with Al/P = 0.83, e. sample AP14 with Al/P = 0.92 and f. sample AP3 with Al/P = 1.0.

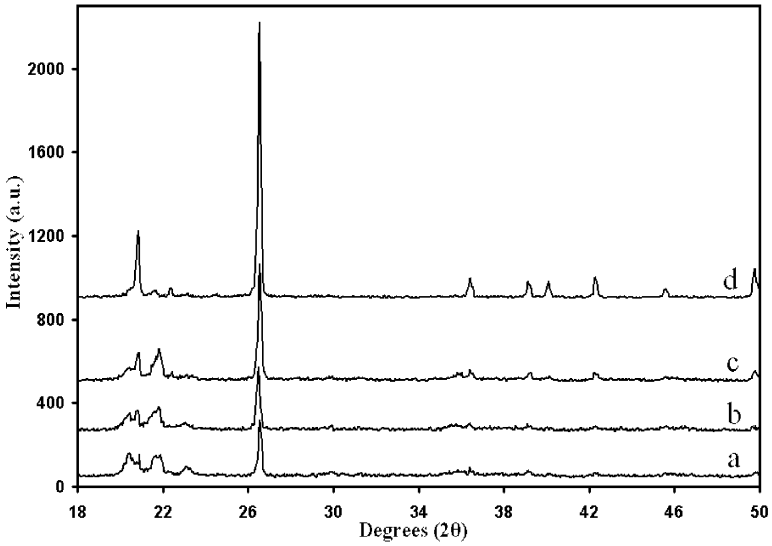

Fig. 6: XRD patterns of the zeolites with 30.0 min microwave heating times and different conventional heating (CH) time: a. sample AP15 with CH of 2 h, b. sample AP16 with CH of 4 h, c. sample AP17 with CH of 6 h and d. sample AP18 with CH of 8 h.

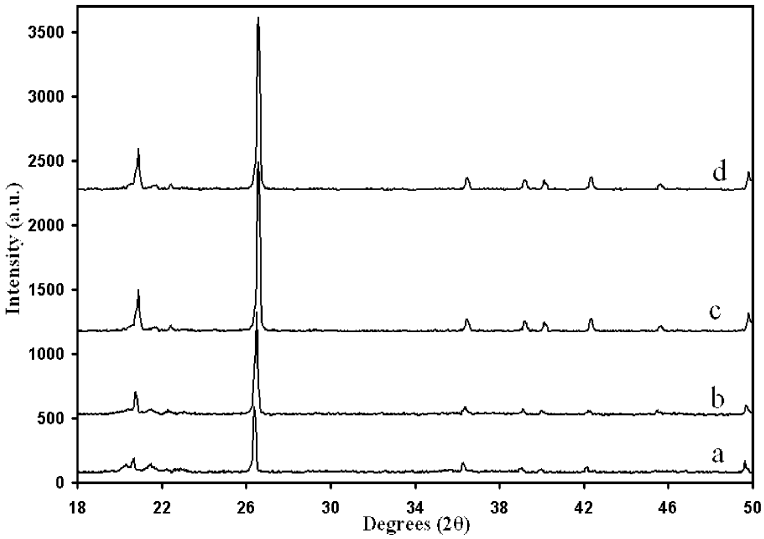

Fig. 7: XRD patterns of the zeolites with 8 h hydrothermal heating time and various microwave heating (MW) times: a. sample AP19 with MW of 5.0 min, b. sample AP20 with MW of 15.0 min, c. sample AP18 with MW of 30 min and d. sample AP21 with MW of 45 min.

(sample AP10-AP14 and AP3, respectively). $AlPO_4$ zeolite with Al/P = 1 has neutral framework, but the others framework are anionic (i.e. Al/P< 1). All samples were synthesized by conventional heating method. It should be noted that all samples contain the same phosphorous concentration but they have different aluminum concentration. Table 2 presents gel compositions of the samples. Figure 5 illustrates XRD patterns of the corresponding samples. Clearly, intensity of the peak located at 2θ equal 26.4 increases with increasing of Al/P mole ratio (i.e., improving crystallization).

The Effect of Microwave Irradiation: In this experiment, different $AlPO_4$ zeolites were synthesized with conventional hydrothermal assisted by microwave. $AlPO_4$ zeolites with composition of Al: P: 0.5 (2-HETMACl): 20 H_2O were synthesized with constant time of microwave irradiation (i.e. 30 min) and different conventional heating time (i.e., 2, 4, 6 and 8 h). To avoid evaporation of water, the solution was refluxed during microwave irradiation. Figure 6 shows the XRD patterns of the corresponding sample. Clearly, intensity of the peak located at 2θ equal 26.4 degree increases with increasing of heating time. As a result, conventional heating time of 8 hours is good enough to be crystallized the $AlPO_4$ satisfactorily. It is noticeable that no crystallization can be occurred with conventional heating time of 8 h without microwave irradiation.

In the other series of experiments, the exposing time of microwave irradiation was varied at 5.0, 15.0, 30.0 and 45.0 minutes meanwhile the conventional heating time (8 h) was held constant (sample AP19, AP20, AP18 and AP21, respectively). Figure 7 shows XRD patterns of the corresponding samples. Obviously, the peak located at 2θ=26.4 moderately enhances by increasing MW irradiation time. As Figure 7 shows no significant change can be observed between sample AP18 and AP21 that means MW irradiation more than 30 minutes has no further effect on crystallization of zeolite.

The Effect of Ultrasonic Technique: To find the effect of mixing rate on the synthesis of $AlPO_4$ zeolite, two separated experiments have been carried out. Sample AP22 was prepared using ultrasonic bath and sample AP1 was synthesized without ultrasonic by convectional hydrothermal. Sample AP23 was prepared using ultrasonic bath and sample AP18 was synthesized without ultrasonic by microwave assisted hydrothermal. Figure 8 shows the corresponding XRD patterns of above zeolites. By comparison figures 8(c) and (d), it can be deduced a dramatic change can be observed by ultrasonic. As a result, crystallization of $AlPO_4$ is improved by ultrasonic.

Figure 9(a and b) illustrates SEM images of the synthesized zeolite with (i) MW irradiation (30 min) plus CH (8 h) and (ii) MW irradiation (30 min) plus CH (8 h) using ultrasonic bath (1.5 h). Both samples have the same source of aluminum and composition. The images of the samples express that the shape and particle size of zeolites

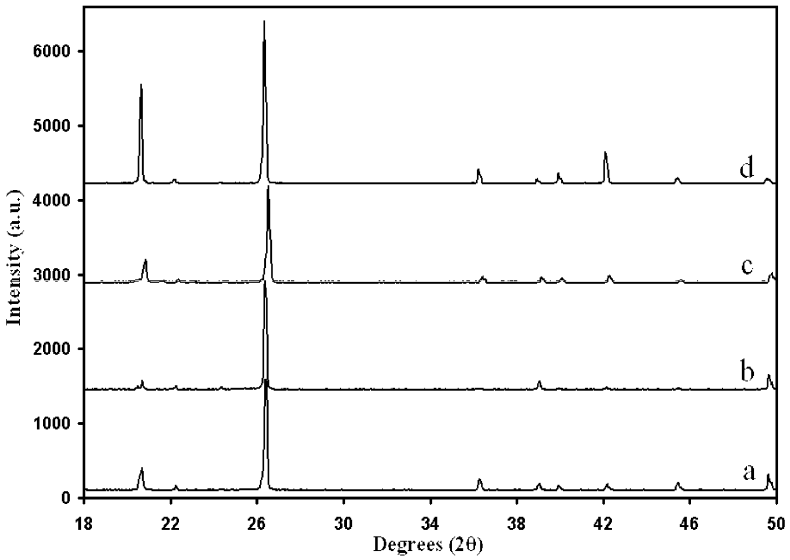

Fig. 8: XRD patterns of AlPOs zeolites without MW and with CH of 24.0 h at 180 °C: a. sample AP1 with stirring aging, b. sample AP22 with ultrasonic-assisted aging and with MW of 0.5 h and CH of 8.0 h: c. sample AP18 with stirring aging and d. sample AP23 with ultrasonic-assisted aging.

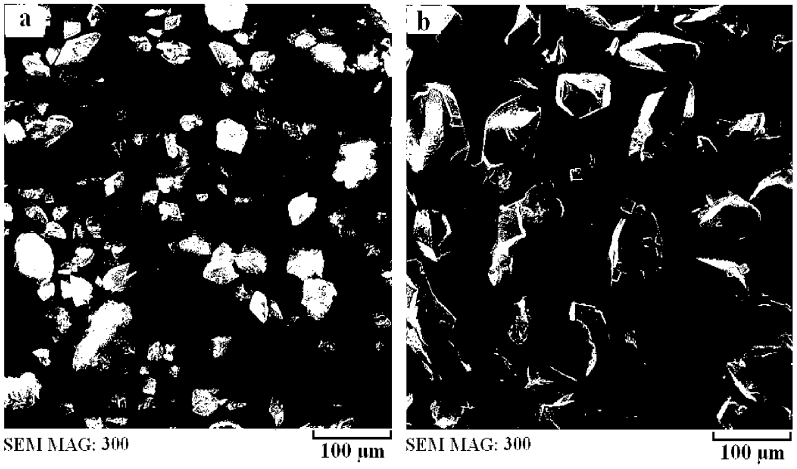

Fig. 9: SEM images for samples with compositions of Al: P: 0.5 2-HETMACl: 20H_2O with MW irradiation (a) without ultrasonic (sample AP18) and (b) with ultrasonic-assisted aging (sample AP23).

are related to the method of synthesis. Interesting result was obtained when ultrasonic used as a mixer. As can be seen in figure 9, the range of size distribution for both samples is similar but the crystal size of samples is considerably different. Sample without ultrasonic have lower particle size (22 ìm) than that sample using ultrasonic (53 ìm). Ultrasound is known to result in acoustic streaming providing enhanced mass transfer close to the crystal surface which is expected to increase the crystal growth rate [37]. However, increasing in the nucleation rate in the presence of ultrasound may also have contributed to the increase in the crystallization rate; nonetheless, crystal growth is generally dominant in this process.

CONCLUSIONS

Results obtained from a series of experiments indicated that synthesized zeolites by microwave assisted hydrothermal (MAH) have some advantages such as short synthesis times, small zeolite particle size and narrow particle size distribution. The presence of a template has a strong effect on the size of zeolite. Results revealed that synthesized zeolite with 2-HETMACl and

2-HETMAOH have small particle size. The crystallization of the $AlPO_4$ zeolites is highly improved by using ultrasonic bath.

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