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Synthesis and Characterization of Alumino Phosphate Zeolites with Tri Ethyl Amine as Template Using Microwave Assisted Technique

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ABSTRACT
Different types of aluminophosphate zeolites were prepared using aluminium hydroxide precursor as a source of alumina and TEA as the structure directing agent via microwave technique. The influence of the chemical composition of the starting sol-gel, agitation time, microwave power and heating time has been studied systematically.
Keywords: *$AlPO_4$ zeolites, aluminium hydroxide gel, triethyl amine, Microwave heating, aging, dynamic light scattering*

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INTRODUCTION

Porous materials are attracting increasing attention because of their applications, such as catalysis and gas separation[1], and development for new applications in membranes, sensors, optics, etc., is in progress [2] Natural zeolites contain tetrahedral SiO_4 and AlO_4 joined by Si–O–Al (Si) into 3D frameworks. The attractive and industrially useful zeolite architectures have fascinated generations of scientists and have shaped one of the most fruitful materials design strategies (called the 4-2 method here) based on tetrahedral nodes and bi coordinate (or ditopic) links. The alumino phosphates are usually synthesized using thermal heating conditions with a reaction time ranging from several hours to several days. A new synthesis method using microwave heating has been used for the preparation of microporous $AlPO_4$ zeolites due to a decline in the crystallization time. The microwave-assisted synthesis of molecular sieves is a relatively new area of research. It offers many advantages over conventional hydrothermal synthesis. They include speedy heating to crystallization temperature due to volumetric heating, resulting in homogeneous nucleation, and fast super saturation by the rapid dissolution of precipitated gels and ultimately a shorter crystallization time compared to conventional autoclave heating. It is also energy efficient and economical. This method has been successfully applied and reviewed for the synthesis of several types of zeolites namely zeolite A, Y, ZSM-5, MCM-41, metal substituted aluminophosphate, silico-aluminophosphate and gallophosphate [3–5]. Microwave-assisted heating is known to speed up the nucleation, thus results in rapid crystallization [5–7] as well as products with high purity and fine particle size distribution [8]. Microwave irradiation is more efficient for transferring thermal energy to a volume of material than conventional thermal processing which transfers heat to the material by convection, conduction and radiation. Microwave technique has been broadly applied in the synthesis of the zeolite and molecular sieves because of the reduced reaction time and better crystal quality. Microwave technique offers fast crystallization than conventional heating thus the growth of the crystals is homogeneous [9, 10].

In the present report by utilizing microwave techniques, we present the synthesis of $AlPO_4$-5 zeolites with various heating time. The effects of microwave power and heating time were investigated and explained by the combined results of XRD and IR.

EXPERIMENTAL

Synthesis

The preparation of aluminophosphate gel is very important in the synthesis of aluminophosphate zeolites. The basic requirements of the starting materials are that it should be taken in a desired molar ratio and composition and as homogeneous as possible. Preparation of the reactive gel differs in the

aging. The reactants used to synthesize zeolites are Phosphoric acid, Aluminium hydroxide gel and Triethylamine. The sample that contained alumina phosphates has been prepared from the starting mixtures with the molar compositions given in Table 1.

Solutions containing Aluminium, phosphours and an amine(as a template) were prepared with molar ration of Al:P:0.5R:20H_2O)(R=template). Aluminium hydroxide gel was first dispersed in water and then phosphoric acid, TEA added to the mixture drop wise into the reaction mixture while stirring and heating to 60^oC. After the addition of acid and amine, the gel was aged at R.T. for 2 hours. The suspension was transformed into a 250ml Teflon beaker closed with a lid after recording the pH. The beaker was placed in a CE 104VD-B model microwave oven according to the experimental parameters given in table 1. After exposing to microwave for certain duration, the products cooled to room temperature. The products were first cleaned in ultrasonic cleaner after recording the final pH, filtered, washed with distilled water several times and dried in an oven at 200^oC for 2h. The template species remain occluded in the as-synthesized products and it is essential to remove them in order to make the aluminophosphate framework porous for further use. This can be achieved thermally by calcination in air or oxygen, usually at400-600 ^oC.

Table 1: Parameters of the microwave synthesis of $AlPO_4$

Sample no.	Al/P (mol)	Template (mol)	H_2O	Aging time, h	Power, (W)	Heating time, Seconds
$ZTEA_1$	1	0.5	60 ml	2	300	300
$ZTEA_2$	1	0.5	30 ml	2	300	360
$ZTEA_3$	1	0.5	40 ml	2	300	600
$ZTEA_4$	1	0.5	40 ml	2	300	900
$ZTEA_5$	1	0.5	40ml	2	180	300
$ZTEA_6$	1	0.5	40ml	2	180	360
$ZTEA_7$	1	0.5	40ml	2	180	600
$ZTEA_8$	1.1	0.5	40ml	2	180	300
$ZTEA_9$	1.1	0.5	40ml	2	180	360
$ZTEA_{10}$	1.1	0.5	40ml	2	180	600
$ZTEA_{11}$	1.1	0.5	40ml	2	180	900
$ZTEA_{12}$	1.1	0.5	40ml	2	300	300
$ZTEA_{13}$	1.1	0.5	40ml	2	300	360
$ZTEA_{14}$	1.1	0.5	40ml	2	300	600
$ZTEA_{15}$	1.1	0.5	40ml	2	300	900

Characterization

The characterization describes those features of the composition and structure of a material that is significant for the preparation of desired $AlPO_4$ zeolites.

X-ray Diffraction

X-ray diffraction is a very important and absolutely essential technique to characterize zeolites. The products obtained in the present study were analysed by powder X-ray diffraction for qualitative phase identification. The patterns were indexed and compared with the JCPDS files and other literature data. The effect of organic amines, Al- and P-sources was studied by the XRD technique. The representative X-ray diffraction patterns of different $AlPO_4$ zeolite phases are depicted in figures 2.2.1(a) to 2.2.1(d). As evident from the XRD patterns, it is clear that the majority of the experiments yielded phases similar to $AlPO_4$-5. The shift in the 2θ and differences in indexes are due to the difference in heating time and power. A dense phase of alumino phosphate has been formed at 1h aging and 100W heating.

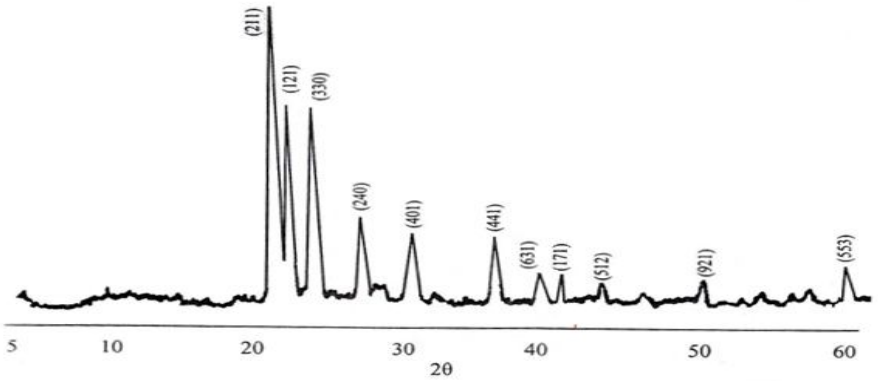

Fig.2.2.1(a): XRD pattern AlPO-5 obtained from $Al(OH)_3$,H_3PO_4,H_2O,TEA at 300 W,10 minute

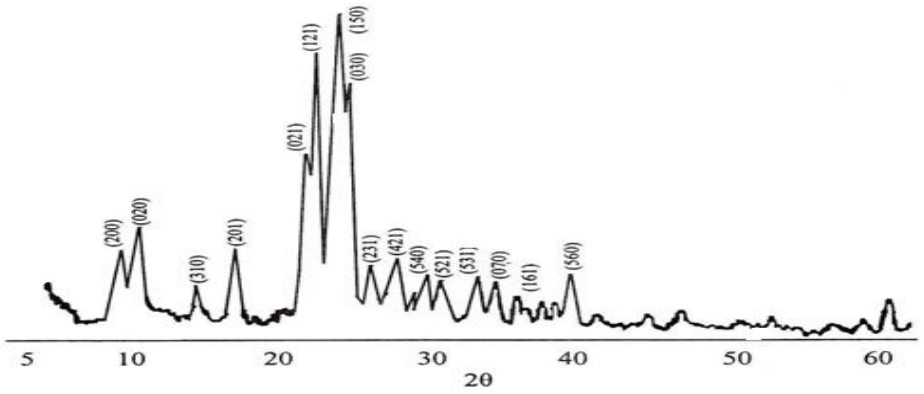

Fig.2.2.1(b):XRD pattern of $AlPO_4$ -5 obtained from $Al(OH)_3$,H_3PO_4,H_2O, TEA at 300 W, 15 minute

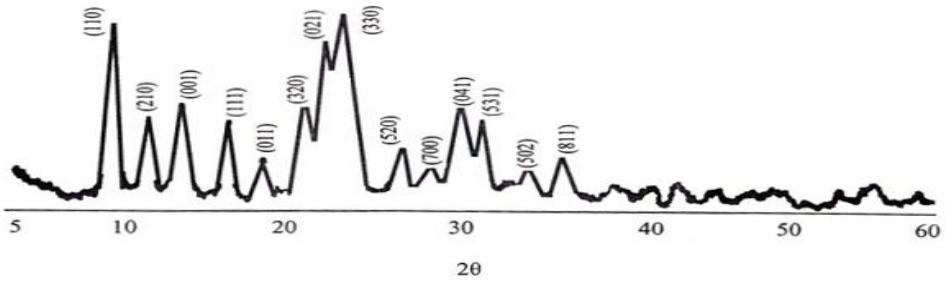

Fig.2.2.1 (c) : XRD pattern of $AlPO_4$-5 obtained from $Al(OH)_3$, H_3PO_4, H_2O, TEA at 180 W, 10 minute

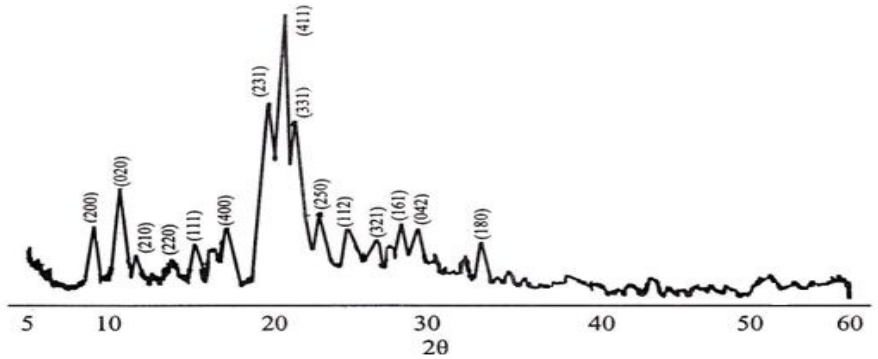

Fig.2.2.1(d) : XRD pattern of $AlPO_4$-5 obtained from $Al(OH)_3$, H_3PO_4, H_2O, TEA at 180

IR Spectroscopy

Infrared spectra of the synthesised zeolites were recorded on a SHIMADZU-8700 (Japan), FT-IR spectrometer. The spectra were measured in the solid state as pressed KBr pellets (13mm).

The mid-infrared spectra have been recorded for the AlPO4 zeolites obtained. The preliminary interpretation of the infrared spectra suggests specificity for zeolite structure type, group and for secondary building units like double rings and large pore openings. It is proposed that the major structural groups present in zeolites can be detected from their infrared patterns. The infrared spectrum in the region of 400 cm^{-1} to 1500 cm^{-1} is a finger print of the region indicating structural features of $AlPO_4$ zeolite frameworks.

The infrared spectra of $AlPO_4$ zeolites in the 1300cm^{-1} to 400 cm^{-1} region appear to consists of two classes of vibrations (i) those caused by internal vibration of the framework TO_4 tetrahedron, the primary building units(PBU) in all zeolite frameworks, which tend to be sensitive to variation in framework structure, (ii) vibration related to external linkage between tetrahedral units which are sensitive to the frame work structure and th the presence of secondary building units(SBU) and building blocks of polyhedral such as rings and pores.

The sharp peak around 1100cm^{-1} is usually for $AlPO_4$ zeolites. The exact position of the P=O varies with the sum of electronegative groups tend to pull electrons from the phosphorus, thus competing with the bond weakening tendency for the double oxygen to attract electrons(P-O), resulting in stiffer P=O bond and a higher frequency. The P=O frequency is sensitive to substitution. The presence of an OH or an NH group in the vicinity of a P=O group generally lowers the P=O stretching frequency by 50 to 80 cm^{-1} due to hydrogen bonding. The broad band around 1100 cm^{-1} has been assigned to the asymmetric stretching of PO_4 tetrahedra. The shift to higher wave number is due to the presence of large amounts of phosphorus, since the P-O bond distance is shorter than Al-O. The absorption peaks at 700 to 750 cm^{-1} corresponds to the symmetric stretching vibration of PO_4 groups. The bands around 649, 544 and 468 cm^{-1} are related to bending vibration of PO_4 groups or in the vibration modes of the 4-membered rings of $AlPO_4$ chains. The weak absorption at about 650cm^{-1} is due to the interaction between alumina tetrahedral of the zeolite structure and Al^{3+}. There is splitting of the peak at this region is due to higher O-P-O angles in the structure. The broad weak band around 3000 to 4000cm^{-1} is attributed to the stretching vibration of hydrogen group of water molecules and amines present in the pores of the $AlPO_4$ zeolites.

The weak and sharp peaks at 1700-1500 cm^{-1} resulted due to bending vibration of water. The OH stretching modes at wave numbers of 3626 cm^{-1} with a shoulder at 3600 cm^{-1} is due to two different bronsted sites as well as 3678cm^{-1}(P-OH) and 3743cm^{-1}(Al-OH). Various authors assign the band at 3660 cm^{-1} to the OH groups associated with extra frame work. Al species and the band at 3690 cm^{-1} to another type Al-OH species.

i. OH band around 3740cm^{-1} is due to occluded OH groups of hydroxyls on the zeolite crystal surface.
ii. OH band around 3650 cm^{-1} is due to non-acidic OH groups probably attached to [AlO]+ entities.
iii. OH band around 3610 cm^{-1} is due to the acidic OH groups.

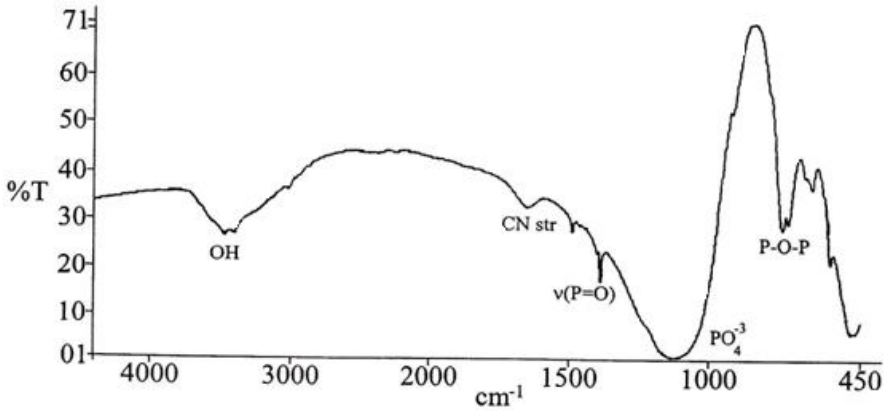

Fig 2.2.2(a): IR spectra of $AlPO_4$-5 obtained from $Al(OH)_3$,H_3PO_4,H_2O, TEA at 180W, 10 minute

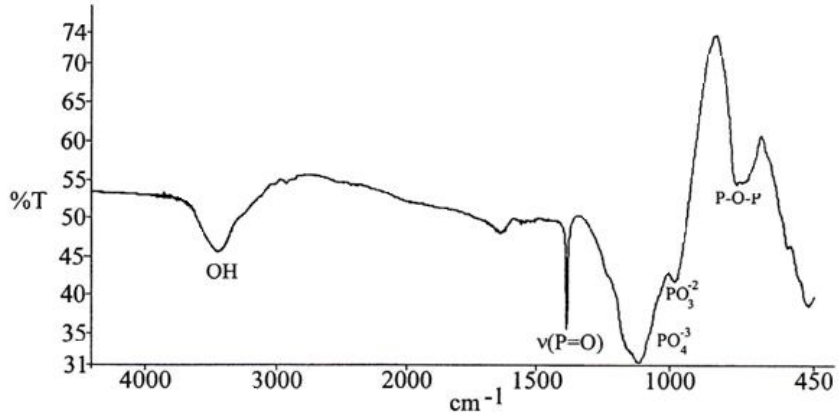

Fig 2.2.2(b): IR spectra of $AlPO_4$-5 obtained from $Al(OH)_3$,H_3PO_4,H_2O, TEA at 180W,15 minute

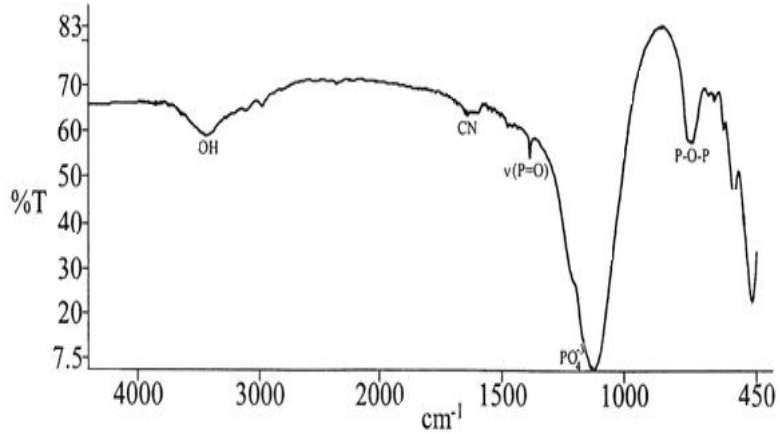

Fig 2.2.2(c): IR spectra of $AlPO_4$-5 obtained from $Al(OH)_3$,H_3PO_4,H_2O, TEA at 300W, 10 minute

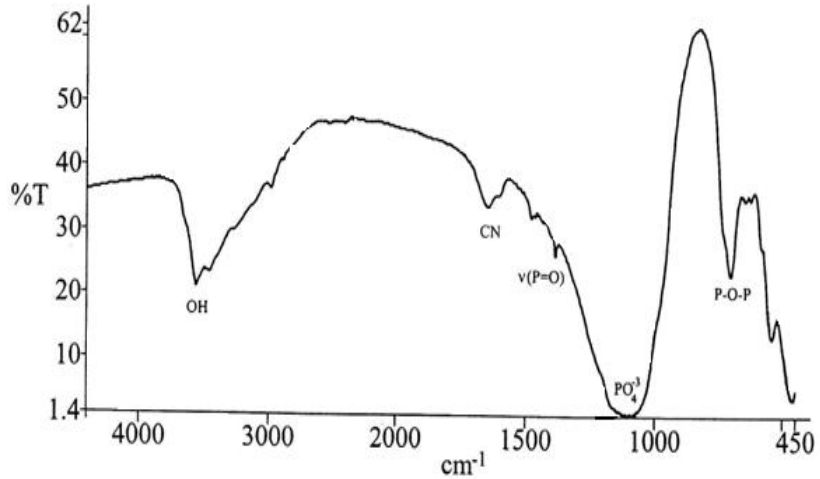

Fig 2.2.2(d): IR spectra of $AlPO_4$-5 obtained from $Al(OH)_3$,H_3PO_4,H_2O, TEA at 300W,15 minute

Dynamic Light Scattering

The dynamic light scattering (DLS) technique was used to measure the particle size analysis of the zeolites obtained in the present work.

The samples are initially dispersed in a suitable solvent like alcohol, acetone or ethanol, etc. The solvent was filtered using 0.23 µm syringe filters. The samples were ultrasonicated for 5 to 15 minutes to obtain a better dispersement. Then this homogeneous solution is diluted with the pure solvent in the ration 50:50, and ultrasonicated again to get a homogeneous solution, which was taken in a sample holder tube of the DLS instrument. The measurements are done using the microprocessor-based controllers. The values of average particle diameter, weight distribution, particle distribution and standard deviation are calculated using this DLS software. The histograms are constructed for the measured values. In the present work isoproponal was used as the solvent for dispersion. The values of refractive index=1.37983 and viscosity=2.39 were used in the measurements.

The average particle size for the AlPO is 0.8115µm. The distribution average is 0.9029µm. The standard deviation is 635. The weight distribution average is2414.2 and the standard deviation in the weight distribution is 1114.

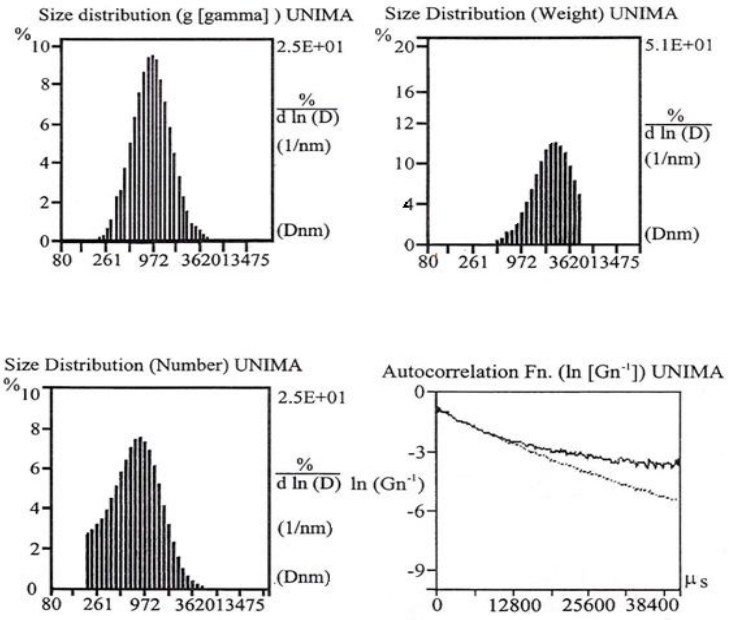

Fig.2.2.3(a) Dynamic light scattering of AlPO4-5 at 300W

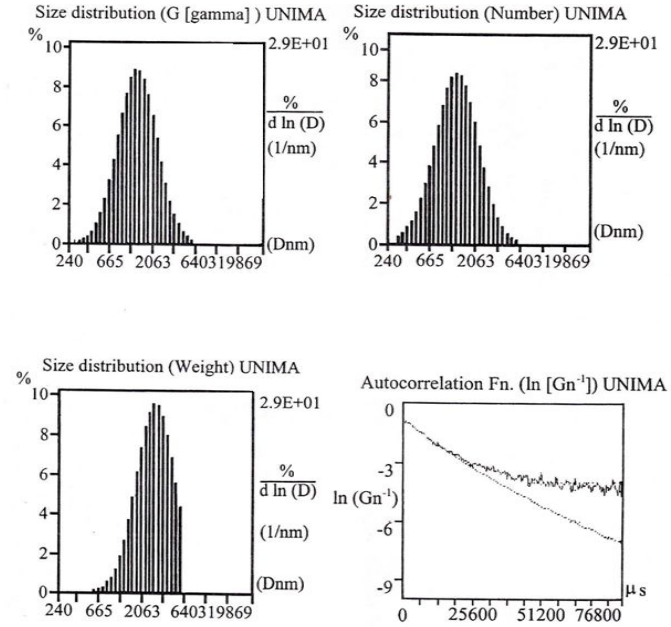

Fig.2.2.3(b) Dynamic light scattering of AlPO4-5 at 180W

CONCLUSIONS

A systematic study of the synthesis, structure and properties of aluminophosphate zeolites by microwave technique has led to the following conclusions:

Microwave synthesis is a promising method for the fast synthesis of zeolite membranes It has been shown that compared with conventional heating, microwave heating can remarkably reduce synthesis time.The choice of the Al and P sources plays a crucial role in the synthesis and phase purity of alumina phosphate molecular sieve zeolites.The role of organic additive is to provide the gel with a tetrahedral element required to build the framework in the form of useful species at a reasonable rate. The short duration of 2 to 3 hours of gel aging is very important for crystallization of different alumino phosphate zeolites. After very long period of aging the formation of a small amount of impurities was observed. The effect of organic amines, Al- and P- sources were studied by the XRD technique. The study of infrared spectra reveals that the presence of phosphate radicals and water molecule in the zeolite pores.

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