Synthesis and Characterization of Nanocrystalline Aluminophosphate $AlPO_4$-11 Molecular Sieves

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ABSTRACT:

Aluminophosphates molecular sieves ($AlPO_4$-11) were synthesized by hydrothermal reaction method. The syntheses were carried out using sealed stainless steel autoclave. Investigations of the effect of crystallization temperature, ratio of template to phosphoric pentoxide (R/P_2O_5), pH adjustment of gel solution and other parameters were studied. Characterization of products were carried out using powder X-ray diffraction (XRD), atomic force spectroscopy (AFM) , Fourier transform infrared (FTIR), N_2 adsorption-desorption BET surface , Differential scanning calorimetry-thermogravemetry analysis (DSC-TGA) and scanning electron spectroscopy (SEM). The XRD patterns revealed that the AEL structure is obtained with high crystallinity for $AlPO_4$-11 at crystallization temperature 190^o C. Type of template (R) and ratio of (R/P_2O_5) showed a great influence on XRD patterns and nano-level of particle size and optimum ratio of 0.95 was established for (R/P_2O_5) for $AlPO_4$-11. AFM results showed that a nano-level of 95 nm was obtained. Mapo-11 synthesized with 0.05-0.21 Mg substitution is successfully done but showed a negative effects on crystallinity, particle size and specific surface (BET).

Key words: Aluminophosphate, $AlPO_4$, Molecular sieve, Nanocrystalline, Template.

1. Introduction

Aluminophosphates ($AlPO_4$) molecular sieves family has variety of new structures, and has its potential application in catalytic processes. They are 10-membered ring channels, 6.3×3.9 Å **[1]**, the structure of $AlPO_4$-11 is orthorhombic and generated by eliminating of one-third of the 4-rings from the $AlPO_4$-5 structure with conversion of 12-ring channel into an elliptical 10 rings**[2]**. The templates used in synthesis of $AlPO_4$-5 are triethylamine (TEA) and tetrapropyl ammonium hydroxide (TPAOH), while for $AlPO_4$-11 structure di-n-propylamine (DPA)**[3].**$AlPO_4$s have very good hydrothermal and thermal stability comparable to what more stable zeolites have.AlPOs frameworks

have a neutral framework because of strict alternation of AlO_4^- and PO_4^+, their composition is expressed in an oxide formula ($\mathbf{xR.Al_2O_3.1.0\pm0.2P_2O_5.yH_2O}$),so they have weak acidic catalytic properties**[3]**, this led to limit their application as selective adsorbents. For Increasing their acidity and generation of bronsted acidity, an isomorphous substitution of Al^{+3} by divalent ions like Co, Mg, Mn, and Zn or tivalent like Fe **[3]**, can be incorporated. Mapo-11 which is the magnesium substituted version (or any divalent metal) of AlPOs and has the AEL structure could be a good catalyst for isomerization and aromatic reactions such as disproportion and alkylation **[4,5]**.

A.R.MacIntosh,**[6]** studied the synthesis of aluminophosphate molecular sieves $AlPO_4$-5 and -11 with AFI and AEL topologies respectively. He investigated two synthesis methods, hydrothermal synthesis (HTS) and dry-gel conversion (DGC) with different modifications.

Fernandes et al **[7]** synthesized Mapo-11 molecular sieves using pseudoboehmite, phosphoric acid, and magnesium acetate as sources for structural elements, their results revealed that a magnesium molar ratio of 0.3 in the reaction mixture as the highest levels, increasing this molar ratio will cause other phases formation. Zhu et al. **[8]** synthesized nanocrystals of $AlPO_4$-11 molecular sieve, they studied the optimization of P_2O_5/R, and HF content.

Song et al **[9]** investigated the synthesis of meso- sapo-11 (silicone substituted) by using citric acid in different temperature, they showed that dispersing of sapo-11 molecular sieve in 0.5M citric acid solution at 80 ^oC gave the best increase in specific area to about 269 m^2/g. they studied their efficiency in fluid catalytic cracking.

Many researchers investigated the ionothermal synthesis of aluminophosphate molecular sieves **[10-12]** using a series of imidazolium ionic liquids (ILs) as solvent and structure directing agent, owing to their good properties like low vapor pressure, strong solvent power, high thermal stability, and wide liquid range. The most favoured feature of ionothermal synthesis is the elimination of competition between solvent-framework and template-framework **[12]**.

Transition metal ions (TMI) substitution in crystalline aluminophosphate attracted many researchers **[13-19]** and large variety of zeotype structures have been synthesized.

Weckhuysen et al **[13]** investigated incorporation of TMI in microporous crystalline aluminophosphate, they concluded that its chemistry is complex and the synthesis conditions of the molecular sieves do not favour incorporation of TMI in the lattice and substitution introduce strain in the structure. They also concluded that even at low metal content, TMIs could be present under various geometries (a) truly isomorphous substituted TMI (b) defect sites-decrease crystallinity (c) extra framework.

Xu et al**[14]** studied the synthesis of Mg-substituted Mapo-11, they suggested that results of shape and size of crystal were influenced by presence of Mg, Mg/Al and type of template.

Hartmann and Elangovan**[19]** investigated n-decane isomerization over three bifunctional aluminophosphate molecular sieves. The catalysts studied are 0.5Pt/$MgAlPO_4$-11, 0.5Pt/$MgAlPO_4$-5 and 0.5Pt/$MgAlPO_4$-41 (AEL,AFI,AFO respectively), they showed that Pt/$MgAlPO_4$-11 exhibits a maximal isomer yield of 62%, while Pt/$MgAlPO_4$- 41 and -5 exhibit reduced selectivity of isomered products and a yield of 38% and 8% respectively. Gielgens et al **[20]** also showed that Me-$AlPO_4$-11's are active and stable catalyst for n-butene isomerization, where Me-$AlPO_4$-5's are not good for isomerization of n-butene, because the large pores are blocked irreversibly with n-butene reaction products.

In this research work, synthesis and characterization of nanocrystalline aluminophosphates ($AlPO_4$-11) were investigated by hydrothermal reaction. Substituted Mapo-11 was also studied and parameters of synthesis like process parameters and structural element sources and their compositions were investigated.

2. Experimental

2.1 materials and equipment

Aluminum isopropoxide (AIP, sigma Aldrich) and solution of phosphoric acid (85 wt.%, Merck) were used as alumina and phosphor sources respectively, di-n-propyleneamine as template, Magnesium chloride ($MgCl_2$, Merck) as magnesium source, and deionized water.

Hydrothermal reactions were carried out in polytetraflouroethylene (PTFE) sealed autoclave as described in Alnaama **[21]**.

2.2 Samples Syntheses

The procedures are as follows: 5g of aluminum isopropoxide (AIP) in 42g deionized water are stirred for 30min, 5.65g of phosphoric acid (85%) was added to AIP solution dropwise in half hour and stirred for 2h, amount of $MgCl_2$ needed was dispersed in 10 ml deionized water then added (in case of Mapo sample synthesis) to the solution. Finally the different amount of template (R) 1.74, 1.8, 2.35 and 3.1g of DPA added to get various molar ratio for R/P_2O_5 (0.7,0.73, 0.95, 1.25) respectively, and stirred for 1h. The gel composition then transferred into the autoclave and operated at the temperature and time of crystallization required (180, 190 ^oC) and 24h respectively, then washing and filtration. Calcination at 550 ^oC for 5h.

Table1 Molar compositions of samples

Sample	Molar composition
M4	$0.7R.Al_2O_3.P_2O_5.0.2MgO.95H_2O$
M5	$0.73R.Al_2O_3.P_2O_5.0.05MgO.95H_2O$
M6	$0.93R.Al_2O_3.P_2O_5.95H_2O$
M10	$1.25R.Al_2O_3.P_2O_5.95H_2O$

2.3 Characterization Techniques

The synthesized samples were analyzed by X-ray diffraction (XRD) using a 2D PHASER/Bruker (Germany 2010), with Ni-filtered CuKα radiation with $\lambda = 1.54$ Å (30 Kv, 10 mA) with a 0.02^o 2θ step and 0.5 s per step.

FTIR was conducted using sample diluted in KBr (1% in 99% KBr) and analyzed by IR-Prestige-21 (Shimazdu).

The particle size and topology were analyzed by atomic force microscopy (AFM), using scanning probe microscope AA3300, Angstrom Advance Inc. USA.

N_2-adsorption-desorption (BET) surface and t-plot micropore were analyzed by Micrometrics ASAP 2020 Accelerated surface area and porosimetry system.

Scanning electron microscopy (SEM) for morphology were conducted by Inspect S50, FEI (USA). DSC-TGA was conducted by Linseis Model STA PT-1000 (Germany) with sample weight 20 mg and temperature ramp 10 ^{o} C.

3. Results and Discussion

3.1 Characterization

XRD pattern with peaks positions for the AEL structure was obtained, and with 100% crystallinity for $AlPO_4$-11 and as shown in table 2 and Fig 1.

Table 2 XRD data of sample M6

hkl	2θ	d_s	I_{re1}
110	8.137	10.85	46
020	9.59	9.21	76.8
200	13.114	6.74	25.7
002	21.248	4.17	100

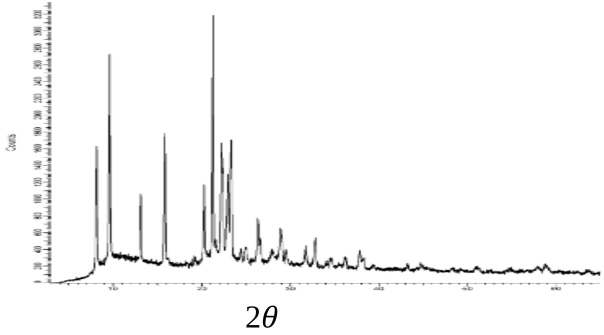

Fig 1 XRD Pattern for $AlPO_4$-11

Mg incorporation cause to a change in crystal surface growth direction, and formation of non-frame work species and lead to disturb crystal surfaces growth. This is noticed in Mg-$AlPO_4$-11 (Mapo-11) and as shown in fig.2. where the XRD main peaks intensities of MAPO-11 are lower than that of $AlPO_4$-

11 molecular sieve when comparing their XRD patterns in Fig 2 for M4 and M5. It revealed clearly that increasing MgO content influence the degree of crystallinity. M10 pattern showed that $AlPO_4$-5 (AFI) phase appeared and that is attributed to excess amount of template used R/P_2O_5 is 1.25.

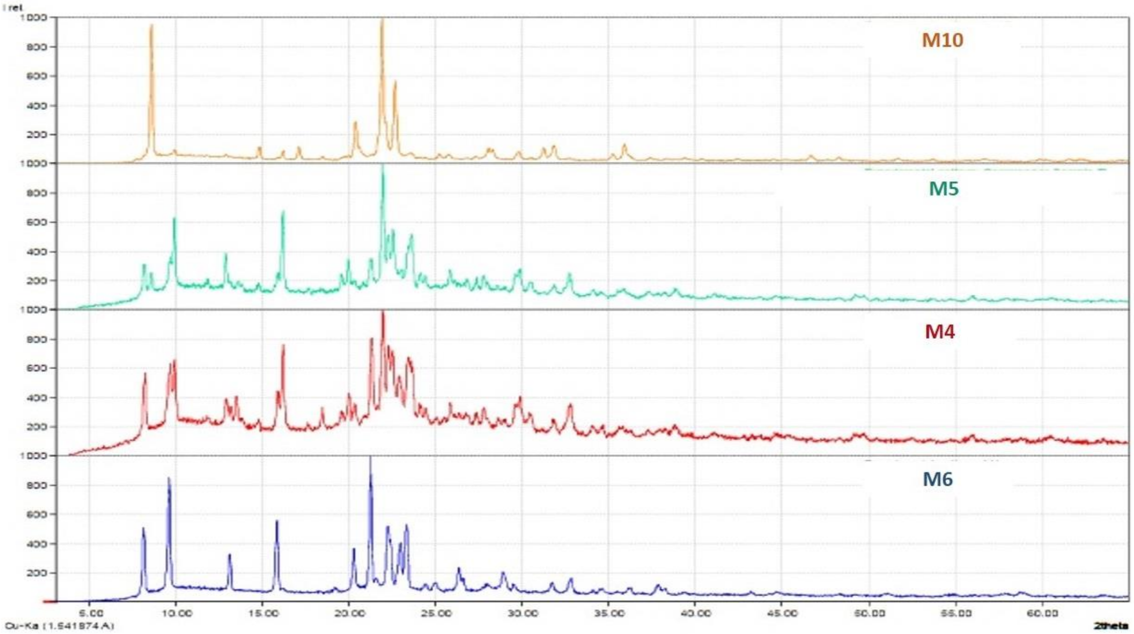

Fig 2 XRD-Patterns for M4, M5, M6, M10

Morphology of M6 sample investigated by SEM as shown in Fig 3, electronic image revealed that tight agglomeration of nanoparticles into microparticles, these tightly aggregated nanoparticles can lead to mesoporosity because of interparticle voids.

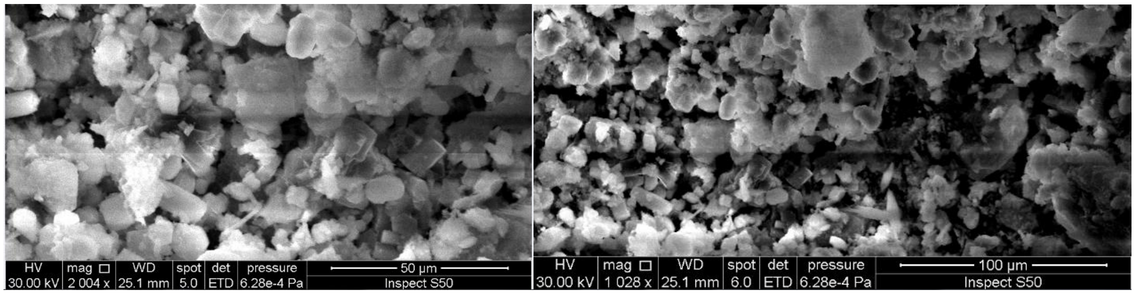

Fig 3 SEM images for M6 ($AlPO_4$-11)

Fig 4 displays the reflectance of infrared spectrum of synthesized $AlPO_4$-11. The spectrum shows the T-O-T assymetric stretching bands are located at 1184, 1157, 1107, and 1060 cm^{-1},The symmetric stretching bands (T-O-T) are located at 717, 702, 663 cm^{-1}.The bending (T-O-T) located at 480 cm^{-1} with shoulder at 501 cm^{-1}.Most of these bands results are in agree with reported data in **[7,22,23]**.

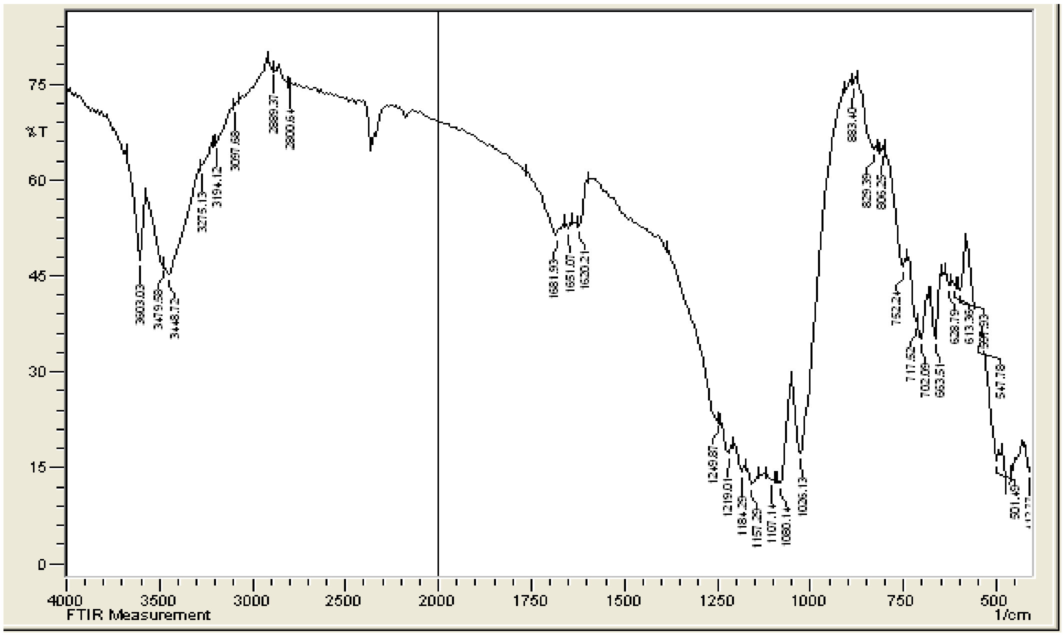

Fig 4 FTIR Spectrum for Aluminophosphate AlPO$_4$-11(M6)

AFM images in Fig 5 showed the detailed observation of nano-scale events at crystal surface, showing also the layer growth and height of terraces. These finding are well agreed with the work of Aghabozog, et al. **[24]**. Fig 5 is for two and three dimensional AFM image respectively showed some aggregation of crystals.

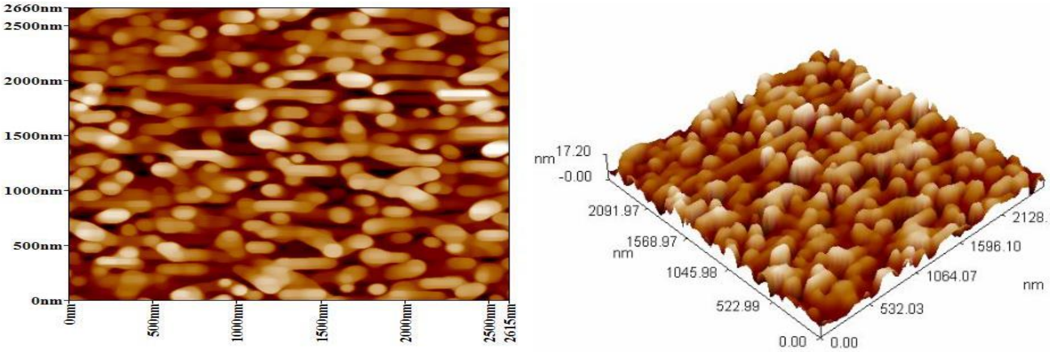

Fig 5 Two and Three dimensional AFM image for AlPO$_4$-11(M6)

Average particle size of 95 nm obtained. This result is confirmed, by comparing the crystallite size calculated by Scherer analysis through the results of XRD pattern and FWHM (measure of the broadening of the peaks) which gave an average of 29.2 nm (range of 11.2-49.3nm) for crystallite size, as shown in table 3 showing also sample details concerning MgO content and R/P_2O_5.

The data revealed that increased crystallite size which is attributed to induced strain in crystal lattice coming from isomorphous substitution of the metal (IMS) of Mg in the framework of the molecular sieve.

Table 3 Samples details with Particle and Crystallite size (AFM and Scherer)

Sample	xMgO	R/P_2O_5	Scherer crystallite size range,nm	Scherer Ave.Cryatllite size, nm	AFM particle size,nm
M4	0.21	0.7	28.4-100	70.1	NA
M5	0.05	0.74	14.7-100	45.2	NA
M6	0.0	0.93	11.2-49.3	29.2	95
M10	0.0	1.25	10.8-100	39	75

The N_2- adsorption-desorption isotherm of the calcined sample of $AlPO_4$-11 is demonstrated in Fig 6 below. It exhibits a hysteresis loop characteristic of mesopores. Fig 7 below show the pore size distribution curve.

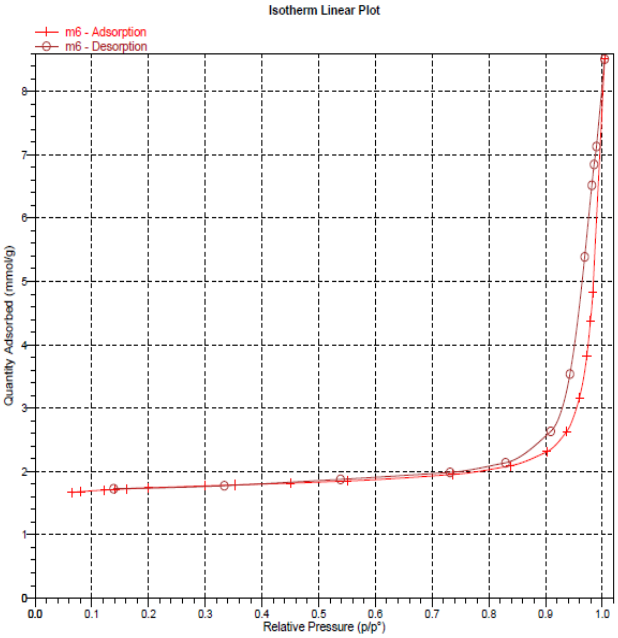

Fig 6 Isotherm Linear plot for $AlPO_4$-11

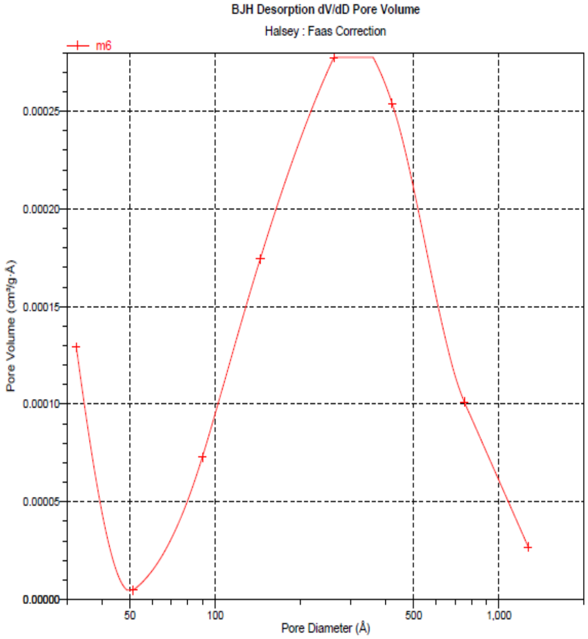

Fig 7 BJH Desorption pore volume for $AlPO_4$-11

Table 4 shows the results of BET analysis,and BET surface of 131 m^2/g was got for M6, while for M5 and M6 showed 51.5 and 72.8 m^2/g respectively, revealing the negative effect of Mg substitution on BET surface. The results are well agreed with reported data **[9,24]** concerning BET surface and pore volume. H.song et al **[9]** got 114 m^2/g, and for meso $AlPO_4$-11 got 268 m^2/g by dealumination using citric acid, while M.Choi**[24]** used organosilane surfactant-directed synthesis of mesoporous and got 112 m^2/g for $AlPO_4$-11 and 174 m^2/g for meso one.

Table 4 Results of BET Analysis for M6

BET Surface area (m^2/g)	131
Micropore surface area (m^2/g)	107
t-plot micropore volume (cm^3/g)	0.05
Pore size distribution (nm)	4.6-7.2
BJH adsorption-desorption cumulative volume of pores (cm^3/g)	0.117-0.198
BJH adsorption-desorption average pore diameter (nm)	22-32

DSC-TGA is shown in Fig 8 below, and revealed that the synthesized and calcined $AlPO_4$-11 is thermally stable with no mass loss indicating that there are no occluded water or/and template.

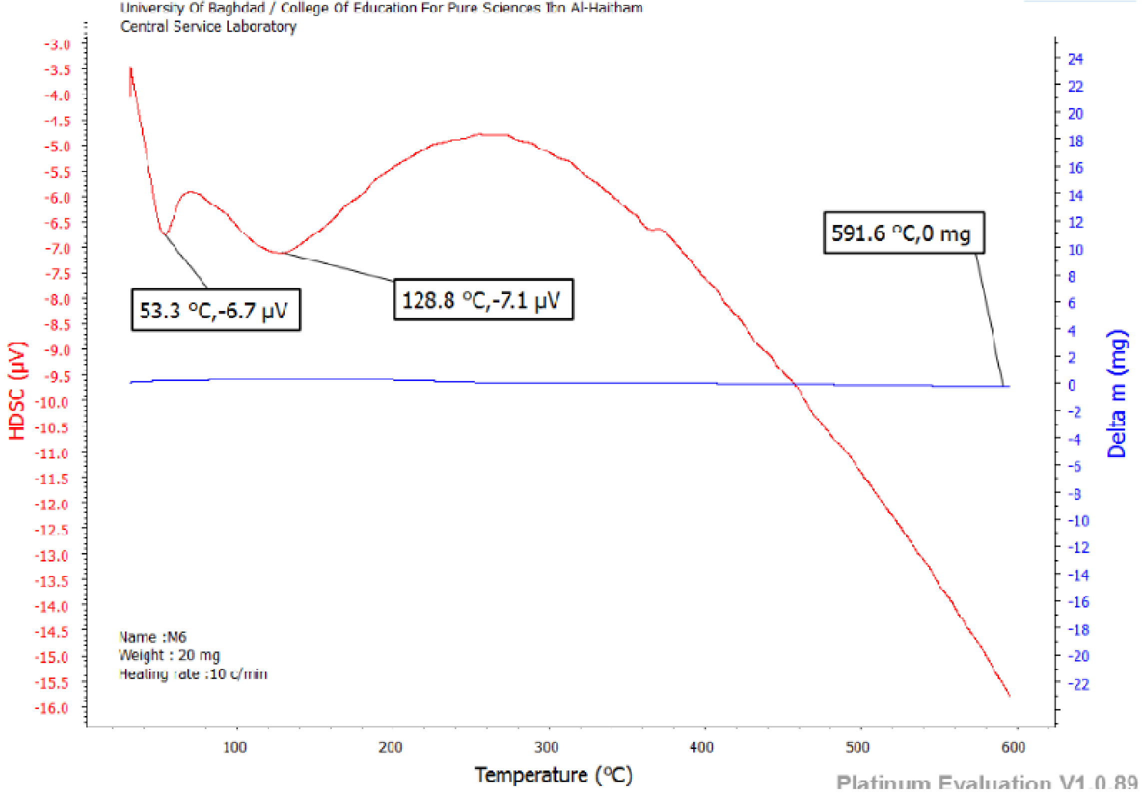

Fig 8 DSC-TGA for M6 ($AlPO_4$-11)

3.2 Effect of Synthesis Parameters

Temperature of crystallization of 180 and 190 °C were experienced and showed that good crystallization can be got at 180 °C, but at 190 °C gave best result concerning nano-level particle size (95 nm). This trend of decreasing the particle size with increased crystallization temperature was observed by other authors in synthesis of nanocrystalline zeolites, in other words aluminophoshates and zeolites have almost same behavior noticed for increasing crystallinity with temperature until optimum one**[8,20].**

Time of crystallization is one of the most important parameter in the synthesis of aluminophosphate ($AlPO_4$) molecular sieves, reported data **[26-28]** showed that optimum crystallization time is about 24h, in this research work all experiments were carried out at 24h.Q.Wang et al **[29]** investigated crystallinity of the hydrothermal reaction products at various reaction time intervals and observed that after 5h of a large amount of microspheres start to show and corresponding XRD pattern begins to reveal the diffraction peaks of $AlPO_4$-11, until 24h a complete crystallinity shows up and further reaction time will not be useful.

Template to phosphoric pentoxide mole ratio (R/P_2O_5) found to play crucial role in getting better crystallization and nano-level particle size. R/P_2O_5 equal to 0.95 found to be the optimum mole ratio in getting best results regarding crystallization and nanocrystalline molecular sieves, regarding $AlPO_4$-11 using DPA.

Ageing of gel-solution 2h and even more up to 24h is also found influencing the particle size decreasing. This phenomena is attributed for enough time given for the complex reactions and formation of nano-nuclie in the initial steps of induction and nucleation period to start taking place before propagation in crystallization process begins in the autoclave operation.

Adjustment of pH in gel-solution noticed to be very important, pH of 6-7 gave better properties and results concerning crystallization and decrease of particle size. $AlPO_4$ need weak acid or base medium in synthesis while aluminosilicate zeolite needs strong base medium (pH 12-14).

Calcination of $AlPO_4$ at 550 ^oC for 5h proved to be effective in getting the desired XRD pattern and removing the occluded template (DPA) in pore structure of the molecular sieve, knowing that the kinetic diameter of DPA (0.37) nm is lower than the pore size of solid $AlPO_4$-11 (0.39×0.63 nm) and has no difficulty in its removing **[30].**

Effect of water has a great influence on crystallization path of $AlPO_4$-11, Zhang et al **[31]** concluded in their research that in diluted conditions, an intermediate crystalline form of $AlPO_4$-5 formed first then co-existed with crystalline $AlPO_4$-11, and disappeared in last stage of crystallization and well-crystallized $AlPO_4$-11 formed, while in concentrated solution (low water content) there were no intermediate phase during crystallization and Raman spectra showed that formation of 10-membered rings was accompanied by transformation of octahedral Al to tetrahedral Al. Their final suggestion is that the pathway of crystallization of the $AlPO_4$-11 is influenced by the content of water, in this work a ratio $H_2O:Al_2O_3$ equal to 95:1 was used which is considered diluted composition of the liquid phase and may have formation of $AlPO_4$-5 in earlier stage of crystallization. Other researchers Zhu et al **[8]** concluded that decreasing water content leads to decrease the particle size and when the value of xH_2O goes from 200 to 35 the particle size decrease from $3 \times 10\mu m$ to $0.2 \times 0.7\mu m$, it seems that decreasing water content may decrease to some extent the competition between solvent-framework and template-framework in favour of template, and may decrease the behavior of particle agglomeration.

4. Conclusions

The results of this research showed the following:

-Substiuted aluminophosphate $AlPO_4$ molecular sieves can be synthesized by hydrothermal reaction methods using $MgCl_2$, AIP, phosphoric acid as percursors for Mg, Al, P respectively.

-Kind of template (R) and ratio of R/P_2O_5 play a vital role in getting the structure and XRD pattern required and always there must exist an optimum ratio for specific type of $AlPO_4$ molecular sieves.

-Optimum crystallization temperature is 190^oC for nano-level size of particle size.

-Favoured recommended research application for $AlPO_4$-11 is in isomerization of light naphtha in oil refinery.

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