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The Use of Ionic Liquids as Structure-Directing Agents and Solvents for Synthesis of Controlled Phosphate Based Materials Morphologies

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ABSTRACT

In this work, we report the effect of precursor gel preparation on the microstructural formation of Aluminophosphates (AlPOs) and Silicoaluminophosphates (SAPOs) molecular sieves prepared by ionothermal method using (1-ethyl- and 1-Benzyl-3-methylimidazolium chloride [EMIMCl], [BMIMCl]) as both structure-directing agent and solvent. SAPO-5, AlPO-11, AlPO-41 and AlPO-34 were the resultant molecular sieves. The variation of chemical compositions led to the differences in morphologies and crystal sizes. Their morphologies varied from like-needles shapes to cubic forms. The structures and morphologies were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), infra-red (IR) and thermogravimetric analysis (TGA).

Keywords: Ionic liquid, SAPO-5, AlPO-11, AlPO-41, AlPO-34

INTRODUCTION

Working on novel synthesis methods that lead to new structures and morphologies of molecular sieves always attract the interest of researchers all over the world.

In the early 1980s, the Union Carbide reported the synthesis of first Aluminophosphate (AlPO) as a new family of crystalline three-dimensional mineral frame molecular sieves [1]. Since then, different efforts to develop synthesis of novel microporous AlPO materials have been stimulated by using hydro, solvo and ionothermal methods [2-4]. Aluminophosphates have different large pore size compared to those of zeolites. In addition, the family of AlPO widens by adding Silicoaluminophosphates (SAPOs) and Metal-Substituted Aluminophosphates (MeAPOs) [5]. The successful synthesis of such materials is generally dependent on conditions and the synthetic parameters including the nature and relative ratios of source materials in the initial gel, the alkalinity of the solution (pH), the heating temperature and the heating time. The most important factor adding to these parameters is the nature of template or Structure-Directing Agent (SDA) and the gel chemistry [6,7].

The crystalline microporous materials, especially aluminosilicates and aluminophosphates, have been widely studied due to their variety chemical applications in catalysis processes, adsorption and ion-exchange and due to its advantages including large micropores and excellent thermal stabilities [8-10].

In general, these materials are prepared under hydrothermal conditions, with water in a sealed autoclave under autogenous pressure [5,10]. Other methods were also used, such as solvothermal synthesis [10], dry-gel conversion [11], microwave-assisted synthesis [12], solvent-free synthesis [13,14], or more innovative methods [15]. Moreover, in recent years, Morris and co-workers have developed ionothermal synthesis for preparing zeolitic and other porous materials [4,16-19], which involves the use of ionic liquids as both the solvent and structural directing agent. The properties of this ionic environment offer to us many advantages, avoid chemical hazards and limit pollution (ionic liquids have a low measurable vapor pressure and they are nonflammable).

In the present work, we reported the multifonction of ionic liquid as both SDA and solvent on the aluminophosphate molecular sieve products. The investigation on the effect of Ionic Liquid (IL) and its content on the nature, size and morphologies of crystals has been presented.

MATERIALS AND METHODS

Materials

All reagents were obtained commercially. Phosphor source: Orthophosphoric acid (85%, MERCK). H_3PO_4 (85 wt% in water), Aluminum source: Catapal B or pseudoboehmite alumina (hydrated alumina, Sigma-Aldrich), Silicon source: Ludox, and HF (40 wt% in water) were used as the reagent in the synthesis of aluminophosphates and silicoaluminophosphates molecular sieves. The 1-ethyl-3-methyl- and 1-Benzyl-3-methylimidazolium chloride was used as both structure directing-agent and solvent.

Synthesis

A glass beaker was charged with [Emim]Cl or [Bmim]Cl (3.77-15.12 g), hydrated Alumina (0.25 g), H_3PO_4 (0.54-1.23 g) SiO_2:(0.17-0.42 g), and HF (0.10 g). The reaction mixture was stirred electromagnetically for 90 min at 60°C in an oil bath throughout the synthesis. The final mixture was transferred and sealed into a stainless-steel autoclave (volume 25 mL) with Teflon liner then heated in an oven at 180°C for 7 days. The solid products were filtered, washed thoroughly with distilled water, and dried at 80ºC overnight.

The starting reagents composition and the synthesis method have been modified from those proposed in the recipe of Flanigen et al. [20]. The synthesis conditions are summarized in Table 1, in the presence of IL1 and IL2 respectively.

Characterizations

The solid products were characterized by powder X-ray diffraction (PXRD), measured on a Philips PW1140/90 diffractometer with 1.540598 Cu Kα radiation (25 mA and 40 kV) at a scan rate of 1°/min with a step size of 0.02°; by scanning electron microscopy (SEM): the images were taken with a JSM-6300F microscope (JEOL). The products were also characterized by Infra-red (IR) spectroscopy and TG-ATD analysis.

The Infrared absorption spectroscopy measurements were performed using an ALPHA FTIR Bruker spectrometer with Attenuated Total Reflectance mode (ATR). The samples were analyzed in the frequency range 400-4000 cm^{-1}. Thermogravimetric analysis (TG-DTA) was carried out on, LabSys evo analyzer under 100 $mL.min^{-1}$ airflow at a heating constant rate of 10°C/min to 800°C. TG-DTA analysis have been carried out using 17.3 mg for the sample FOR 44.

RESULTS AND DISCUSSION

Structure directing effect

The results shown in Table 1, reveal that the use of the two kinds of ionic liquid IL1 and IL2, lead to the formation of several phases: SAPO-5, AlPO-11, AlPO-41 and AlPO-34.

Table 1: Synthesis conditions and product phases

Sample	Molar ratio							Time	T (°C)	Phase(s)
	Al_2O_3	P_2O_5	IL	HF	SiO_2	H_2O[b]	IL[a]	(days)		
FOR 17	1	1	10	-	1	10	IL1	7	180	Quartz
FOR 18	1	1	10	0.5	1	10	IL1	7	180	Quartz+Trace of AFI
FOR 19	1	1	10	1.2	1	10	IL1	7	180	SAPO-5
FOR 20	1	1	10	1	-	10	IL2	7	180	AlPO-11
FOR 37	1	1	10	-	-	10	IL2	7	180	AlPO-11+Quartz
FOR 38	1	1	10	-	-	20	IL2	7	180	Quartz
FOR 39	1	1	20	-	-	10	IL2	7	180	AlPO-11
FOR 40	1	1	20	-	-	10	IL2	7	180	AlPO-34
FOR 41[c]	1	1	10	1	-	10	IL2	7	180	AlPO-34
FOR 42	1	1	40	1	-	10	IL2	7	180	AlPO-34
FOR 43	1	2,2	10	1	-	10	IL2	7	180	AlPO41+Amorphous
FOR 44	1	2,2	20	1	-	10	IL2	7	180	AlPO-34
FOR 45	1	2,2	40	1	-	10	IL2	7	180	AlPO-34+Amorphous
FOR 46	1	2,2	10	1	-	10	IL2	7	180	Quartz

[a] IL1: 1-Benzyl-, 3-methylimidazolium chloride; IL2: 1-ethyl-, 3-methylimidazolium chloride.

[b] All water in the reaction gel came from reagents and no extra water was added.

[c] the reaction mixture was aged under stirring for 30 min only.

The use of IL1 as structure directing-agent allowed the formation of the SAPO-5 pure and well crystallized using fluoride routes (FOR 19 sample).

The XRD pattern of the sample FOR 19 is given in Figure 1.

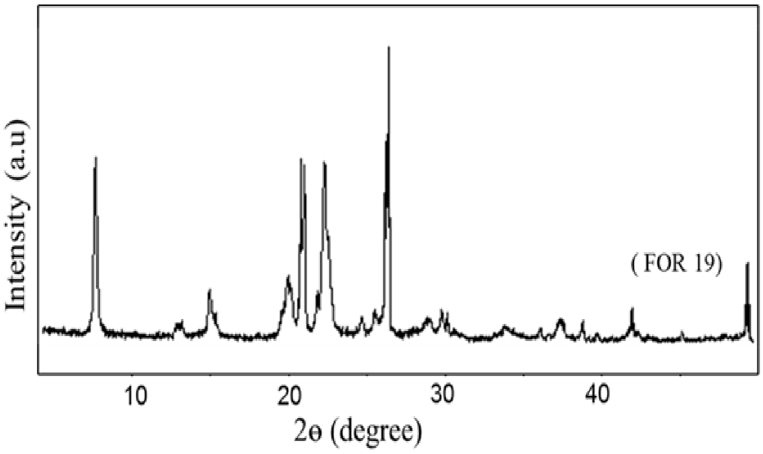

Figure 1: XRD pattern of the as-synthesized FOR 19 sample

It’s noted that an incomplete crystallization of the SAPO-5 (FOR 18) was obtained when the amount of silica was reduced. However, in the absence of silica, the reactants with similar composition, a few amount of $AlPO_4$-16 or quartz were obtained (not presented in the table of results).

Furthermore, using the structure directing agent IL2, several phases such as AEL, CHA and AFO structures topologies have been obtained.

The AlPO-11 phase (AEL topology) has been obtained in the cases of FOR-20; FOR-37 and FOR-39 samples, whose X-ray diffractograms exhibit the presence of this structure, as shown in Figure 2.

Indeed, in the absence of F- ions, traces of AlPO-11 were formed with presence of quartz phase (FOR 37). However, under the same conditions the pure AlPO-11 phase was formed (FOR 39). Moreover, the decrease of the amount of the IL2, leads also to pure AlPO-11 phase. The X-ray diffraction (XRD) patterns of FOR-20, FOR-37 and FOR-39 are given on Figure 2.

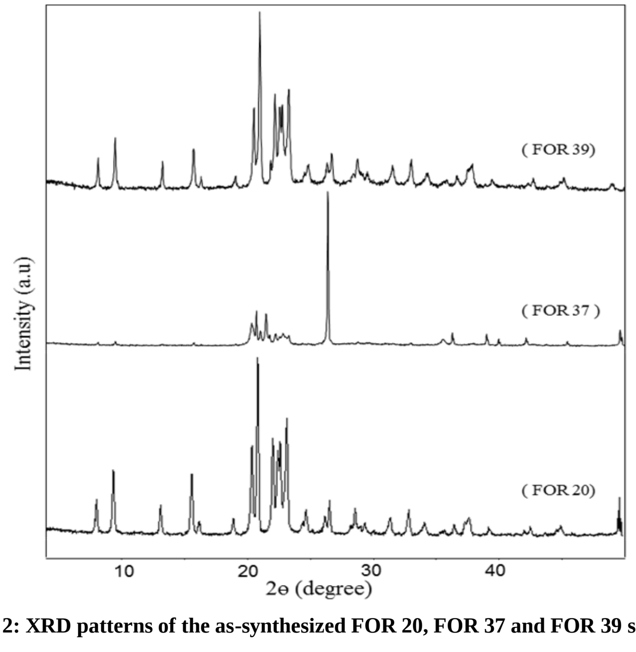

Figure 2: XRD patterns of the as-synthesized FOR 20, FOR 37 and FOR 39 samples

In addition, the duration of the reaction mixture affects the final structure, because instead of AlPO-11 (FOR-20) obtained after 90 mn of agitation, AlPO-34 like chabazite zeolite has been obtained after 30 mn of agitation (FOR 41). Indeed, these two samples have exactly the same molar composition but different duration of the reaction mixture (Table 1).

However, when increasing the amount of the ionic liquid (10-40 mol), after 90 mn of agitation, pure phase AlPO-34, has been obtained (FOR-42). In the absence of fluoride F-, AlPO-34 could be obtained even at low amount of IL2 (FOR 40). It is worth noting that AlPO-34 phase is rarely obtained in absence of fluoride ions whose form bridges Al-F-P in the framework of AlPO-34.

To the best of our knowledge, only J. Wu and coworkers claimed the first fluorine- free crystallization of AlPO-34 [21]. The XRD of FOR 40; FOR 41 and FOR 42, samples are given on Figure 3.

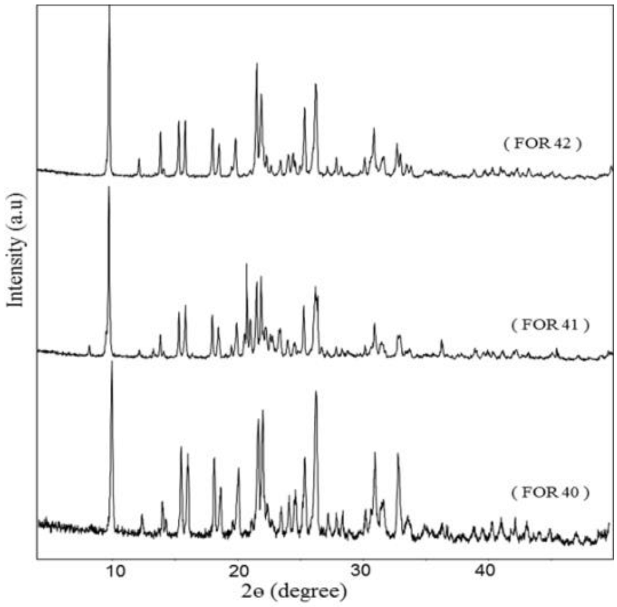

Figure 3: XRD patterns of the as-synthesized FOR 40, FOR 41 and FOR 42 samples

These results show that the amount of ionic liquid IL2 affects the nature of the final products and could be reduced in the absence of F-.

By increasing the amount P_2O_5/Al_2O_3 from 1 to 2.2 mol, AlPO-34 (FOR 44 and FOR 45) and AlPO-41 (FOR 43) phases have been obtained. The XRD patterns of these samples are given on Figure 4.

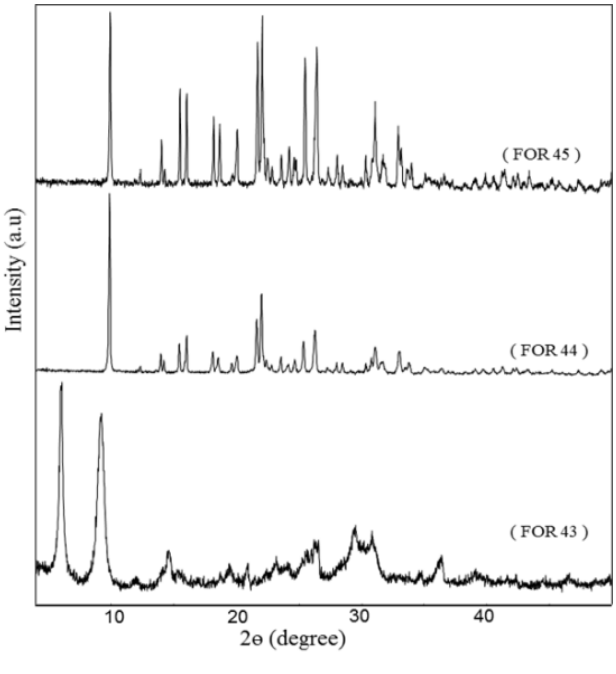

Figure 4: XRD patterns of the as-synthesized FOR 43, FOR 44 and FOR 45 samples

It's important to note that, since AlPO4-41 (AFO topology) and AlPO-11 (AEL topology) are built up from similar SBU "secondary building units", the intergrowth AFO/AEL is easily encountered. Indeed, they have several structure similarities: AEL and AFO are both medium pore molecular sieves having elliptical 10-ring channels, and their structures are built from 4- and 6-rings as secondary building units. Nevertheless, AEL and AFO topologies are rarely encountered with like-chabazite phosphates such as AlPO-34.

Morphologies

It is well-known that nature of the structure directing-agent affects the aluminophosphate molecular sieve crystal phase, size and morphology [22]. Indeed, crystals of the sample FOR 19 corresponding to SAPO-5 exhibit, as shown on Figure 5, microparticles of around 2.5 µm with hexagonal morphology consistently with the literature [23]. However, we note a slight decrease of the crystallites size from those usually appeared using other sources of structuring agents.

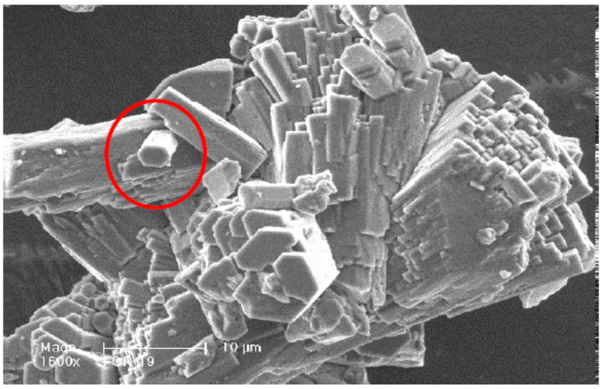

Figure 5: SEM image of the as-synthesized FOR 19 sample

In the other hand, it can be seen on Figure 6a and 6b, that FOR 20 and FOR 39 samples exhibit the well-defined needle-like morphology of AlPO-11 (AEL topology), with an almost regular and uniform morphology with almost 0,33 µm. Indeed, it's the smallest size of needle-like crystals ever seen, while spherical morphology of AlPO-11 is proposed by literature, when hydrothermal method synthesis was used [24]. In addition, crystals with cubic forms detected on FOR 37 sample characterize the quartz phase shown on Figure 6c, which was confirmed by XRD patterns.

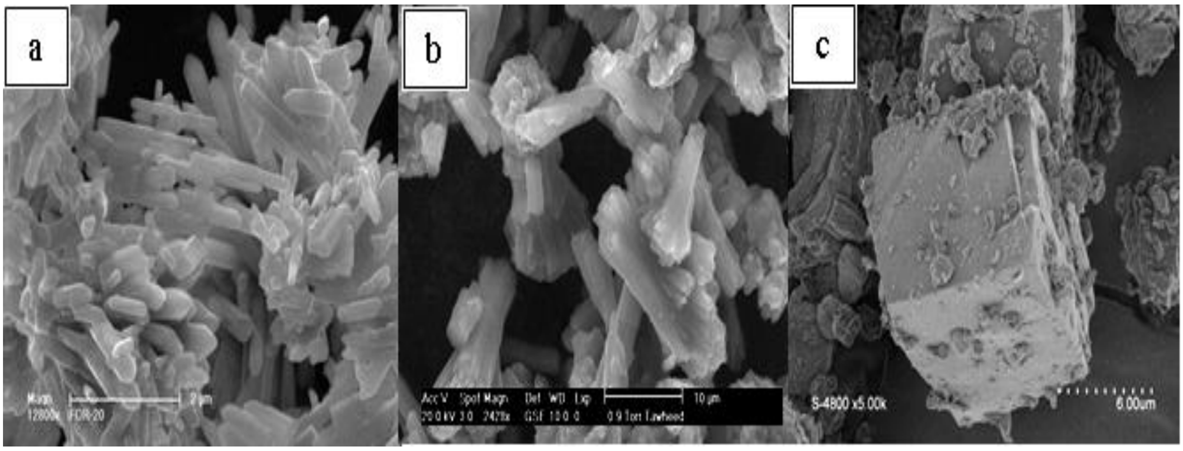

Figure 6: SEM images of the as-synthesized FOR 20 (a), FOR 39 (b) and FOR 37 (c) samples

Moreover, SEM images of samples FOR40; FOR41 and FOR42 corresponding all of them to the AlPO-34 phase (CHA topology) prepared with different amount of IL2 have been presented on Figure 7a-7c, respectively. Unexpected different morphologies of AlPO-34 (CHA topology) have been found. In fact, the crystals of the same AlPO-34 phase exhibits, layers agglomerate; needle-like or twinning crystals for, FOR40; FOR41 and FOR42 samples, respectively.

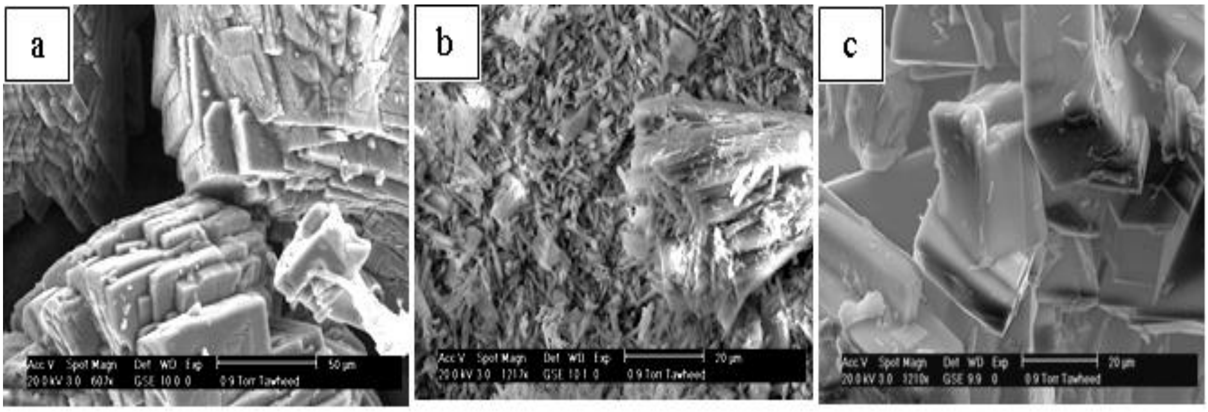

Figure 7: SEM images of the as-synthesized FOR40 (a), FOR41 (b) and FOR 42 (c) samples

However, by increasing the amount of P_2O_5/Al_2O_3 (FOR43 sample), unexpected AlPO-41 (AFO topology) phase was formed with large amount of amorphous phase that might be attributed to insufficient crystallization. Several attempts to get AlPO-41 pure were unsuccessful, whereas, the AlPO-34 (CHA topology) phase was obtained (FOR44 and FOR45 samples), rather than the AlPO-41(AFO topology). SEM images of FOR43; FOR44 and FOR45 samples corresponding to AlPO-41+amorphous and AlPO-34 phases, are given on Figure 8a-8c. The SEM photos show typical cubic-like rhombohedral shape of AlPO-34 with crystal size of 5 µm signaled by a circle on Figure 8b and 8c.

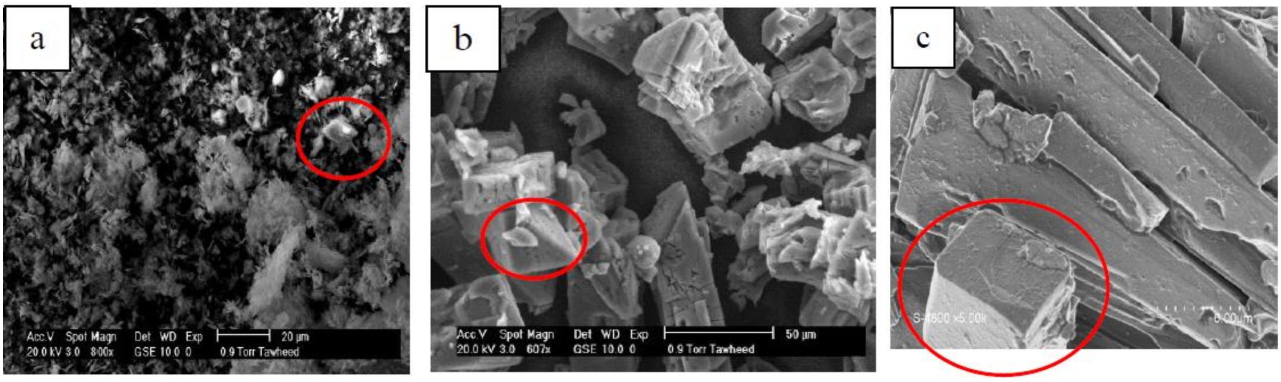

Figure 8: SEM images of the as-synthesized FOR43 (a), FOR44 (b) and FOR 45 (c) samples

Chemical analysis

The results of Table 2 show the percentage weight of Al, Si and P elements in some of obtained phases. SAPO-5, AlPO-11, AlPO-34 and AlPO-41 corresponding to FOR 19, FOR 20, FOR 41 and FOR 43 samples, are selected.

Table 2: Chemical analysis

Sample	Weight %						Atomic (%)					
	Al	Si	P	C	O	F	Al	Si	P	C	O	F
FOR 19	13.7	1.65	12.06	30.05	42.06	-	8.33	0.96	6.38	41.01	43.09	-
FOR 20	20.29	-	22.78	13.05	42.91	-	14.23	-	13.92	20.57	50.78	-
FOR 39	8.69	0.11	8.83	46.94	33.31	-	4.83	0.02	4.28	58.66	31.25	-
FOR 41	11.27	-	11.27	36.44	39.5	-	6.57	-	5.72	47.67	38.8	1.25
FOR 42	8.22	-	7.99	50.48	30.8	-	4.48	-	3.79	61.72	28.27	1.52
FOR 44	11.68	-	12.48	35.84	36.48	-	6.9	-	6.39	47.58	36.36	2.5

First of all, as expected, the atomic ratios Al/P and Al/Si+P of the products, are slightly close to 1, which is in accordance with the literature. The few amounts of chloride and nitrogen are not presented why it could be seen that total are not close to 100.

However, unexpected ratios of C are signaled on sample FOR 19 (SAPO-5) and FOR 20 (AlPO-11) prepared both by IL-1 molecule ($C_6H_{11}ClN_2$). Indeed, for FOR19, 8.33% atomic ratio correspond to 2 tetrahedron Al (P, Si)O4, whereas 41.01% of carbon correspond at only 1.7 molecule of IL-1. While the analysis of the sample FOR 20, show three tetrahedron AlPO4 for only 0.89 molecule IL-1. It could be assumed that a partial degradation of IL-1 molecule was held during the crystallization, as confirmed by the infrared spectroscopy.

In the other hand, the other samples prepared by IL2 molecule $C_{11}H_{13}ClN_2$, the correspondence of the inorganic framework and the organic molecule depends on the nature of the phase formed. In the case of AlPO-11 (sample FOR 39), the analysis shows, for each 1.6 AlPO4 tetrahedron, there is 1.7 IL2 molecule, this is in a good agreement. Whereas, for AlPO-34 corresponding to the other samples, FOR 41and FOR 44, two tetrahedron AlPO4 corresponding to 1.4 molecule IL2, are found, which is relatively accepted. Nevertheless, the analysis of FOR 42 corresponding to the same phase AlPO-34 shows a slight difference, because, only 1.4 tetrahedron AlPO4 corresponds to 1.8 molecules IL2. This could be attributed to an excess of extra-framework organic compound.

Infra-red analysis

Infrared spectroscopy of some samples reveals a degradation of ionic liquid IL1 molecule while IL2 has been conserved. As example, Infrared spectrum of FOR 19 and FOR 44, prepared respectively with IL1 and IL2, are given on Figure 9a and 9b. The infrared spectrum of pure IL1 and IL2 are also given.

As shown on Figure 9a, many bands characterizing IL1 molecule disappear in the spectrum of the as synthesized FOR 19 sample which confirms the degradation of this molecule. However, the bands characterizing IL2 molecule are present in the spectrum of FOR 44 and where detailed assignments is given below.

In order to study the role of ionic liquid in the formation of AlPO-34 molecular sieve, the pure [emim]Cl salt and as-synthesized AlPO-34 (FOR 44) were characterized with the FT-IR spectroscopy and superimposed on Figure 9b. As it can be seen, several IR absorption bands at 3370, 3100, 2926, 1638, 1539 and 1406 cm-1, which were found in the IR spectrum of pure [emim]Cl salt, were also observed in the IR spectrum of as-synthesized AlPO-34. The result indicated the presence of [emim]Cl bulk molecules incorporated in the inorganic matrix. On the other hand, the characteristic bands of CHA, which vibrate at 1100 (internal Al-O-P asymmetrical stretching) and 550 (double ring external linkage), were detected in the as-synthesized FOR 44 sample.

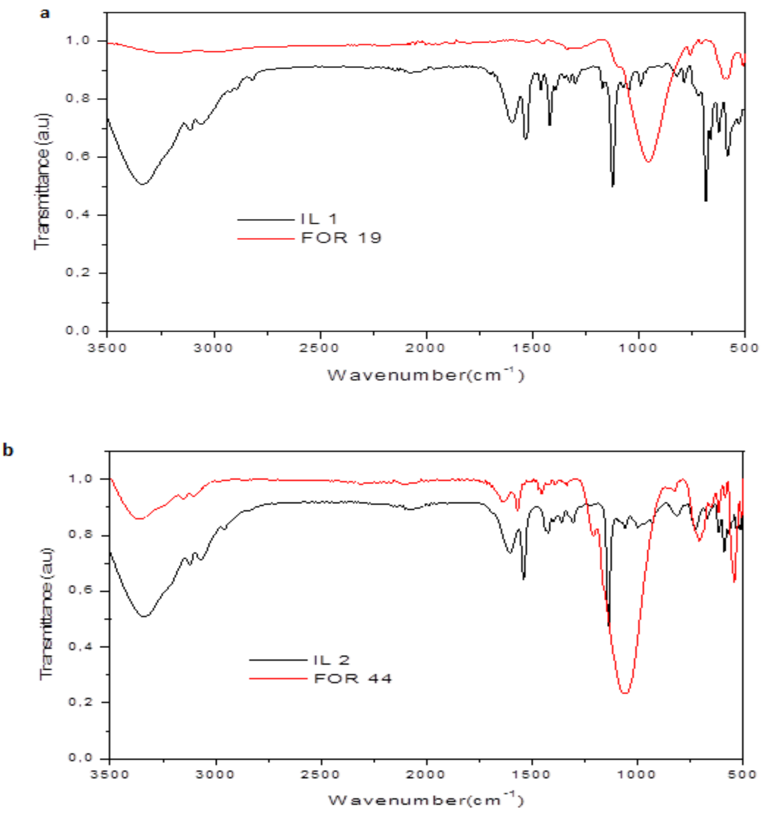

Figure 9: FT-IR spectra of superposed IL1/FOR19 (a) and IL2 / FOR 44 (b)

TG ATD analysis

All TGA curves have similar aspect. As example, the TG-DTA curves of as-synthesized FOR 44 are given on Figure 10.

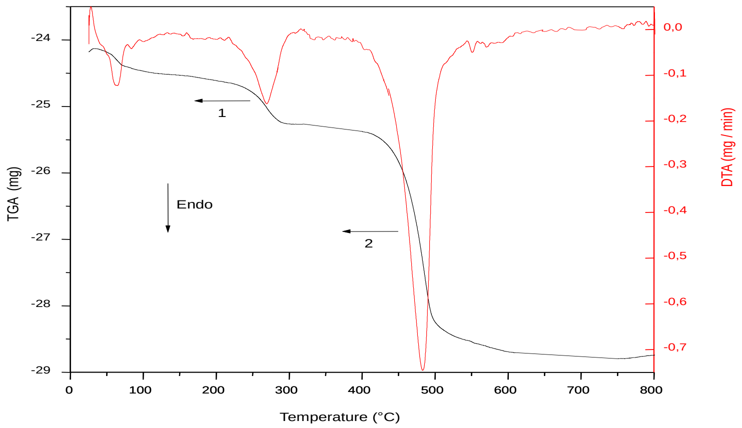

Figure 10: TG-DTA thermograms of as-synthesized FOR 44

These curves exhibit three-step weight losses which can be clearly observed before 120°C, 200-320°C and 400-550°C temperature ranges for the as-synthesized sample. The first step corresponds to the removal of physically adsorbed water from external surface of molecular sieve. The second weight loss (1) is due to the decomposition of alkyl part broken from ionic liquid. The last step (2) with a strongly endothermic process is likely related to the further removal of last part of organic resides and the release of about 17.7٪ of [emim]Cl occluded in the AlPO micropore framework.

CONCLUSION

In conclusion, the multifunctional ionic liquid is used as a solvent and a template simultaneously in synthesis of microporous materials with or without the addition of HF.

Despite the structural difference between SAPO-5 and AlPO-11 phases, they have been formed with the same ionic liquid IL1. In addition, the same ionic liquid IL2 lead to several phases such as AlPO-11, AlPO-34 and AlPO41. If AlPO-41 has structural similarities with AlPO-11, it isn’t the case of AlPO-34.

The ionothermal method affects also morphologies of the AlPO's formed. The morphology of AlPO-11 is needle-like crystals while it is spherical by hydrothermal environment and different morphologies of AlPO-34 are also seen.

The use of ionic liquids allowed reducing the crystallite size of microporous materials obtained by the conventional hydrothermal method.

The ionothermal synthesis was proved to be a safe method for molecular sieve preparation and Aluminophosphate could be successfully produced by ionothermal synthesis.

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