Isomorphous substitution induced ionothermal synthesis of magnesium aluminophosphate zeolites in fluoride-free media†

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Magnesium aluminophosphate zeolites (MgAPOs) with AEL, AFI and ATS structures were ionothermally synthesized in a fluoride-free system depending on the structure of the ionic liquids and the concentration of magnesium, where the incorporation of magnesium into the framework induced their crystallization, resembling that of fluoride ion in aluminophosphate analogues formation.

Crystalline microporous aluminophosphates (AlPOs) based on strict alternation of AlO4 and PO4 tetrahedra are known as a prominent family of zeolitic materials. Unlike aluminosilicate zeolite analogues, the framework of aluminophosphates is generally neutral, which limits their catalysis and ion-exchange functionality. Fortunately, the lattice Al and/or P can be isomorphously replaced by silicon and/or other metal atoms to form an anion zeolitic framework with Brønsted acid sites and/or catalytically active metal centers, i.e. silicon- or metal-substituted aluminophosphates, which are of great significance for their established and potential catalytic applications, for instance, paraffin isomerization and methanol to olefin process.

In recent years, ionothermal synthesis, a method that uses ionic liquid as both solvent and template, has exhibited unique features and potential advantages over traditional hydrothermal and solvothermal synthesis in preparing aluminophosphate-based zeolites, as well as metal–organic frameworks and inorganic–organic hybrids. For example, ionic liquid’s negligible vapor pressure allows the synthesis in atmospheric vessels and the safer use of microwave heating; ionic liquid’s different chemical and structural variety associated with the use of amines displays great potential to prepare zeolitic materials with novel structures and compositions. Till now, several heteroatom–, including Co-, Mg-, Fe-, Mn-, Zn-, substituted aluminophosphate zeolites have been obtained by this method. Remarkably, a new cobalt-substituted aluminophosphate named SIZ-7 (SIV structure) with 3-dimensional 8-membered ring channels of zeolitic structure was ionthermally prepared by Morris et al.. MgAPOs with AEL and AFI structures were successfully prepared by Wang et al. in fluoride-containing ionothermal media, exhibiting excellent catalytic performance in the isomerisation of long-chain paraffin.

During the ionothermal synthesis of these materials, HF is always used and considered as one of the very important synthesis variables. In addition to the role of promoting the crystallization kinetics, fluoride appears to be important in obtaining the full condensed structures of AlPOs without hanging P-O bonds, which is always stable for removal of the templates and thus to create the porosity. Furthermore, Ma et al. proposed that during the synthesis of AlPOs, fluoride could incorporated into the AFI structure and plays the role of structure-directing agent. However, fluoride in the synthesis media due to its toxicity and causticity is not desirable from an industrial viewpoint. Moreover, it was also reported that HF could catalyze the decomposition of some ionic liquids under the ionothermal synthesis condition.

Understanding the formation process of these materials is indispensable in the rational design of particular structure and composition for specific application. To gain more insight, it is pivotal to systematically investigate the synthesis parameters and study the corresponding effect. Herein, we report the ionothermal synthesis of MgAPOs with AEL, AFI and ATS structures in fluoride-free media with addition of different concentration of magnesium, where the ionic liquids 1-butyl-3-methylimidazolium bromide (BMIMBr) and 1-i-propyl-3-methylimidazolium bromide (iPrMIMBr) act as the templates without decomposition. We find that the isomorphous incorporation of magnesium into the framework induce the
crystallization of MgAPOs and contributes structure-directing effect together with ionic liquid cations, which is similar to that of fluoride in the crystallization of AlPOs analogues during ionothermal synthesis.

The MgAPOs were prepared as follow: a porcelain crucible was charged with ionic liquids (ILs), Al[OCH(CH3)2]3.H3PO4 (85 wt% in water) and Mg(CH3COO)2·4H2O. The initial gel molar composition was Al2O3:3P2O5:0.5MgO:40BMIMBr(iPrMIMBr). After stirred electromagnetically at 80 °C in an oil bath for 20 min, the crucible was moved into an oven and heated at 200 °C for required time. The white solid products were filtered, washed thoroughly with distilled water and ethanol, and dried at 110 °C overnight. For comparison, AlPOs were prepared with the procedure the same as described above for MgAPOs except with the addition of HF (40 wt% in water) instead of Mg(CH3COO)2·4H2O.

The product structures were dependent on the synthesis condition as summarized in Scheme 1. In the absence of magnesium and fluoride, it was difficult to obtain zeolitic materials, though the synthesis condition was carefully adjusted within a wide range, and the reaction always produced the dense phase AlPO-tridymite. On the addition of magnesium compounds, the MgAPOs mixture of AEL and AFI structures formed in BMIMBr, which were isostructures of the AlPOs mixture obtained when the fluoride was added instead of magnesium compounds. This result indicates that the addition of magnesium induced the crystallization of the MgAPOs mixture, which is similar to the effect of fluoride during the ionothermal formation of AlPOs mixture. Remarkably, when the ionic liquid was changed to iPrMIMBr, the MgAPOs mixture of AFI and ATS structures was obtained. However, in the presence of fluoride, AlPOs with CHA structure was obtained, the same structure as SIZ-10 as reported by Morris et al. SIZ-10 was also synthesized in iPrMIMBr and has been proved to be templated by dimethylimidazolium cations, which are derived from ionic liquid decomposition via transalkylation of the alkyl groups in the presence of fluoride.

The SEM images (Fig. 1) show that the AlPOs mixture of AEL and AFI structures displays two kinds of bundles of stick-like crystals. Compared with AlPOs, the MgAPOs mixture of AEL and AFI displays more irregular morphology of rod-like and cauliflower-like crystals, whereas the mixture of AEL and ATS structures displays rod-like crystals and fiber-like agglomerates. The structures of these products were further confirmed by the careful comparison of their diffraction peaks of XRD patterns with that of standard materials from PDF cards (Fig. 2 and S1 and S2†). All the three structures of MgAPOs consist of one-dimensional straight channels, with AEL structure containing 10-membered ring pores (4.0 Å × 6.5 Å), while both AFI and ATS structures containing 12-membered ring pores, but differently in size (AFI (7.3 Å × 7.3 Å), ATS (6.5 Å × 7.5 Å)). The difference in the product structure suggests the structure-directing effect of the ionic liquids as a result of their different size and shape.

To confirm the isomorphous substitution of magnesium in the structure, we performed XRF, NH3-TPD and NMR over these MgAPOs products. XRF results show that the contents of MgO/Al2O3 ratio for two MgAPOs mixtures were 0.141 and 0.150 respectively, which preliminarily prove that the presence of magnesium in the products. The NH3-TPD profiles (Fig. 3) of the MgAPOs mixtures present two obvious desorption region. The first one around 220 °C should be attributed to the weakly bounded ammonium, while the second one above 300 °C, which is absent in the profiles of AlPOs mixture, represents the strong acid site generating by the isomorphous substitution of magnesium into the framework.11 The 27Al MAS NMR spectra (Fig. 4) show an intense signal of tetrahedral coordinate aluminium in the framework at about δ = 38 ppm,12,13 and the disappearance of the five-coordinated aluminium peak indicates the absence of fluorine in the structure.7a The 31P MAS NMR spectra (Fig. 5) were deconvoluted into two individual peaks of Gaussian shape. The peak centered at about δ = −30 ppm is typically derived from the tetrahedral P(4Al) environment of AlPOs framework and the peak centered at about δ = −24 ppm should be assigned to the P(3Al, 1Mg) units in the

![Scheme 1](attachment:scheme_1.png)  
**Scheme 1** Representation of the synthesis condition and the corresponding product structures of the MgAPOs and AlPOs samples herein.

![Fig. 1](attachment:fig_1.png)  
**Fig. 1** SEM images of (a) AlPOs with AEL and AFI structures; MgAPOs with (b) AEL and AFI structures and (c) AEL and ATS structures.

![Fig. 2](attachment:fig_2.png)  
**Fig. 2** XRD patterns of (a) AlPOs with AEL and AFI structures; MgAPOs with (b) AEL and AFI structures and (c) AEL and ATS structures; topological structures viewed along their 1-dimensional channels.¹⁰
All the above results demonstrate that magnesium is isomorphously incorporated into the frameworks and no fluoride appears in the MgAPOs products. The TG/DSC profiles (Fig. 5) of both two MgAPOs mixtures show that there are two steps of weight loss. The first one between 30 °C and 200 °C about 2–3% with endothermic effect can be attributed to the removal of physically adsorbed water. The remaining weight loss about 6–8% takes place between 200 °C and 800 °C with exothermic peaks corresponding to the decomposition and combustion of the organic templates in the structures. From 13C CP/MAS NMR data, we can clearly see all the resonance peaks as marked in Fig. 6, which well in accordance with that of ionic liquids cations [BMIM]+ and [iPrMIM]+, respectively. This result further proves that the ionic liquid cations are occluded in the structures without decomposition and thus we deduce that ionic liquids act as structure-directing agent in the course of the crystallization of these MgAPOs.

Furthermore, the effect of crystallization time was comparatively studied on MgAPOs and AlPOs crystallization in BMIMBr. We found that MgAPOs crystallized after a short induction time and the crystallinity of the MgAPOs structures reached the maximum after about 12 h and did not vary even to 48 h. In comparison, the crystallization of AlPOs mixture showed a phase transformation where the AFI structure gradually transforms to AEL structure with increasing the crystallization time after about 80 min (Fig. 7). The phase transformation of zeolitic materials to denser structure observes Ostwald’s rule of successive crystallization. Our result suggested that MgAPOs was possibly dynamically more stable than AlPOs at the experimental condition herein. Moreover, we also investigated the effect of magnesium concentration in initial mixture on MgAPOs crystallization. The SEM images, XRD patterns of the products are shown in the ESI (Fig. S3 and S4†). The content of magnesium in the products linearly increased with that of magnesium in the initial gel, which also remarkably influenced the relative crystallinity of the structures in the final products (Fig. 8). In the absence of magnesium, the reaction exclusively produced the dense phase AlPO-tridymite. Increasing the concentration of magnesium, the AEL structure
pure phase could be obtained by choosing appropriate ionic reaction in sealed vessel. Though the products in the present phenomenon did not appear when we carried out the same time. An indirect proof is that the phase transformation well explained by the fact that transformation of AlPOs in the presence of magnesium content in the framework. In this context, the phase content of templates occluded in the structure increase with the di substituted AlPOs.

Generally, the crystallization of zeolitic materials involves a self-assembly of crystalline inorganic framework around the templates. In ionothermal system, one of the remarkable features is that the organic cations of the solvent ionic liquids always act as templates. According to the criterion of electroneutrality, it is difficult to obtain the neutral framework, e.g. AlPOs with condensed structure, and thus the reaction tends to form the dense phase without containing of the templates or sometimes the interrupted anion AlPOs frameworks (framework Al/P < 1) with hanging P–O or P=O bonds, e.g. SIZ-1, -6, RUB-A1, -A2 and JIS-1, . However, on the addition of magnesium compounds, the isomorphous substitution of Mg for Al in the framework, similar to the formation of F-Al in the presence of fluoride, will provide charge balance for the template ionic liquid cations and lead to the formation of the condensed structures. With excess of template ionic liquid cations during the ionothermal synthesis, the framework substitution concentration will control the template encapsulation concentration through the long-range electrostatic forces between the inorganic framework and the ionic liquid cations and direct the specific phase formation, which is in line with the previous studies on the hydrothermal synthesis of metal-substituted AlPOs. The TG profiles (Fig. S5†) of the samples with different magnesium concentration proves that the content of templates occluded in the structure increase with the magnesium content in the framework. In this context, the phase transformation of AlPOs in the presence of fluoride could be well explained by the fact that fluoride could gradually volatilize away from the open system with increasing the crystallization time. An indirect proof is that the phase transformation phenomenon did not appear when we carried out the same reaction in sealed vessel. Though the products in the present study are mixtures, we expect based on our experiments that the pure phase could be obtained by choosing appropriate ionic liquids and magnesium ion concentration. In fact, fluoride is absent in the study on the ionothermal synthesis of MnAlPO-5 nanocrystals in 1-ethyl-2,3-dimethylimidazolium bromide, which also further indicates the applicability of isomorphous substitution by other metals in fluoride-free media.  

Conclusions

In conclusion, MgAPOs with AEL, AFI and ATS structures were ionothermally prepared in fluoride-free media, where the ionic liquid cations acted as templates occluded in the structures without decomposition. The isomorphous substitution of magnesium into the MgAPOs framework induced their ionthermal crystallization and contributed the structure-directing effect through the interaction between inorganic framework and ionic liquid cations, which is similar to that of fluoride on the AlPOs analogues formation. This result helps us understand the ionothermal formation process of zeolitic materials and manifests the great potential of fluoride-free ionothermal synthesis for heteroatom-substituted aluminophosphate zeolites.

Acknowledgements

The authors thank the financial support from the Fundamental Research Funds for the Central Universities (No. bcuv201612 and No. ZY1603).

Notes and references


