

Highly efficient synthesis of LTA-type aluminophosphate molecular sieve by improved ionothermal method

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Abstract:

LTA-type aluminophosphate molecular sieve has been successfully synthesized by improved ionothermal method from a gel containing low-dosage ionic liquids. The optimum synthetic conditions of this material are refined. The resultant LTA molecular sieves were characterized by XRD, SEM, TG-DTA, CHN elemental analysis, solution ¹³C NMR, EDX, TEM and N₂ physisorption. The composition of the resulting LTA-type molecular sieves is determined to be (Al₁₂P₁₂O₄₈)(C₄H₉NO)₂(C₈H₁₅N₂⁺)₂(F⁻)₂, for which morpholine together with 1-butyl-3-methylimidazolium cations act as the structure-directing agent. The high zeolite yield, as well as the high specific surface area and micropore volume for the calcined LTA-type materials imply that these zeolitic materials have a high potential in applications.

Keywords: LTA; CHA; Solvent-free; Aluminophosphate molecular sieve; Ionothermal

1. Introduction

Aluminosilicate and aluminophosphate zeolites are two of the most important crystalline microporous materials, which have been extensively used as adsorbents, catalysts and ion-exchangers in diverse applications¹⁻³. Developing new synthetic methods to prepare zeolitic materials with various structures, compositions and morphologies is invariably one of the central tasks for the scientists in the zeolite community. According to the solvent used, the established synthetic methods of zeolites can be classified into three main categories, i.e. hydrothermal,

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solvothermal and ionothermal syntheses⁴. For the former two, the use of water or organic solvents as the reaction medium inevitably results in many drawbacks such as waste generation, low synthesis efficiency and high autogenous pressure. On the other hand, the ionothermal synthesis^{4, 5}, in which ionic liquids (ILs) with negligible vapor pressure are used as the solvent and template, can eliminate safety concerns associated with high pressure. In the past two decades, several other elegant synthetic strategies, such as high-throughput synthesis⁶, dry-gel conversion⁷, seed-assisted synthesis⁸⁻¹⁰, ultrafast synthesis¹¹⁻¹⁴, charge density mismatch approach^{15, 16} and rotational/sequential intergrowth¹⁷⁻¹⁹, have also been developed to fabricate zeolitic materials. Despite all this progress, synthesizing these materials in a high-efficiency and cost-saving manner is still the main challenge.

LTA-type aluminophosphate molecular sieve, which is isostructural with aluminosilicate zeolite-A, is composed of sodalite cages that are interconnected with D4R units to form large α cages. Recently, this zeolitic material received much attention due to its potential application in diverse areas^{20, 21}. Since 1994, a variety of structure-directing agents including organic and inorganic cations and anions have been attempted to synthesize AlPO₄-42 and SAPO-42 with LTA topology by several groups²¹⁻³¹, where ionic liquid was a peculiar chemical used as a recoverable solvent and template. Unfortunately, the heavy use of expensive ionic liquid makes its recycling process energy-intensive³².

Most recently, solvent-free synthesis has made great success in synthesizing aluminosilicate and aluminophosphate zeolites³³⁻³⁶. It is believed that this new route can improve the synthesis efficiency and reduce the waste production. In our previous work, AFI-type aluminophosphate molecular sieve has also been successfully synthesized by microwave heating under solvent-free

conditions³⁷. Inspired by these exciting results, we attempted to synthesize AlPO_4 -LTA material at a far lower $\text{ILs}/\text{Al}_2\text{O}_3$ ratio than the initial recipe of Bao's group^{25, 26}. This new developed synthetic route perhaps can combine the advantages of solvent-free synthesis and those of ionothermal synthesis. Here we termed it as improved ionothermal synthesis. In this contribution, the synthetic conditions, such as the ratios of $\text{F}/\text{Al}_2\text{O}_3$, $\text{amine}/\text{Al}_2\text{O}_3$ and $\text{ILs}/\text{Al}_2\text{O}_3$, crystallization temperature and time, were optimized to obtain pure LTA-type materials. The composition and structure of the resulting samples were analyzed by various techniques.

2. Experimental section

2.1. Synthesis of LTA-type aluminophosphate molecular sieve

In the present synthesis, all reagents were of reagent grade and used without further purifications: 1-butyl-3-methylimidazolium bromide ([bmim]Br, Lanzhou Kaite trade Co., Ltd), morpholine (Morp, Tianjin Kaixin Chemical Industry Co. Ltd), aluminum isopropoxide (Sinopharm Chemical Reagent Co. Ltd), phosphoric acid (85 wt% in water, Yantai Shuangshuang Chemical Reagent Co. Ltd), hydrofluoric acid (40 wt% in water, Sinopharm Chemical Reagent Co. Ltd), acetone (Beijing Chemical Plant) and deionized water.

General synthesis procedure of LTA-type structure was as follows: [bmim]Br, Morp, aluminum isopropoxide (0.012 mol), phosphoric acid and hydrofluoric acid were measured out in the molar ratio of $1\text{Al}_2\text{O}_3: 1\text{P}_2\text{O}_5: (0-4)\text{HF}: (0-4)\text{Morp}: (0-4)[\text{bmim}]\text{Br}$ and ground in a mortar for 20 min. The resulting quasi-solid mixture was transferred to Teflon-lined stainless-steel autoclaves and heated in an oven at designated temperature for 4-48 h. After crystallization, the solid product was recovered by centrifugation, washed with acetone and distilled water, dried in air at 110 °C. The structure-directing agents occluded within the as-made samples were removed by calcination

at 500 °C for 4 h. Detailed synthesis conditions are summarized in Table 1.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns of the synthesized materials were conducted on a D/Max-2400 Rigaku diffractometer with Cu K α radiation operated at 40 kV and 150 mA. Scanning electron microscopic (SEM) images were obtained from two microscopes, JEOL JSM-6700 and 6701F. CHN analysis was carried out on an Elemental Vario EL analyzer. Thermogravimetric (TG) and differential thermal analysis (DTA) (Netzsch, STA409) was performed in air at a heating rate of 10 °C/min. The solution NMR experiment was performed on an Agilent Technologies 600 MHz PremiumCompact+ Spectrometer. The as-synthesized LTA-type aluminophosphate molecular sieve was dissolved in a 36 wt% DCI solution at room temperature. After the solid sample was fully dissolved, the solution was collected and analyzed by liquid-state ^{13}C NMR. The chemical shifts were referenced to tetramethyl silane (TMS). Nitrogen adsorption/desorption studies were conducted on a Micromeritics ASAP 2020 surface area and pore size analyzer at -196 °C. **Samples were outgassed at 350 °C for 4 h prior to the measurements. Specific surface areas of the specimens were calculated from the adsorption data obtained at p/p_0 between 0.06 and 0.20, using the Brunauer-Emmett-Teller (BET) equation. The micropore volumes were determined by the t-plot method.** Transmission electron micrographs (TEM) were obtained on a JEOL JEM-2010 microscope equipped with an energy dispersive X-ray (EDX) detector. For TEM, the sample was ground, dispersed in acetone, and deposited on a holey carbon film supported on a copper grid.

3. Results and discussion

3.1. Optimization of synthesis conditions

For the synthesis of neutral aluminophosphate molecular sieve, the starting P_2O_5/Al_2O_3 ratio was generally fixed at 1.0. Therefore, the following initial molar composition, i.e. $1Al_2O_3: 1P_2O_5:$

Table 1 Initial compositions and crystallization conditions for the synthesis of LTA-type aluminophosphate molecular sieve

Sample	$Al_2O_3:P_2O_5:HF:Morp:$ ILs (molar ratio)	Temperature ($^{\circ}C$)	Time (h)
HF-0	1:1:0:2:4	150	24
HF-1	1:1:1:2:4	150	24
HF-2	1:1:2:2:4	150	24
HF-4	1:1:4:2:4	150	24
Morp-0	1:1:1:0:4	150	24
Morp-1	1:1:1:1:4	150	24
Morp-4	1:1:1:4:4	150	24
ILs-0	1:1:1:1:0	150	24
ILs-1	1:1:1:1:1	150	24
ILs-2	1:1:1:1:2	150	24
T170-24h	1:1:1:1:4	170	24
T190-24h	1:1:1:1:4	190	24
T170-4h	1:1:1:1:4	170	4
T170-12h	1:1:1:1:4	170	12
T170-48h	1:1:1:1:4	170	48

(0-4)HF: (0-4)Morp: (0-4)[bmim]Br, was attempted to make pure LTA-type aluminophosphate molecular sieve. In most previously reported cases, this material was only synthesized in the presence of F^- ions which served as co-template by structuring the D4R units of the framework^{22, 25, 26, 28}. In the present work, as shown in Fig. 1, the resulting product was amorphous when no F^- ions were added to the initial gels. When the F/Al_2O_3 ratio was in the range from 1 to 2, a minor LTA-type phase was detected. The stronger LTA-type diffraction peaks from HF-1 in comparison with those from HF-2 imply that lower F/Al_2O_3 ratio seems to favor the generation of LTA-type phase. Typical cubic crystals that belong to the LTA-type molecular sieve can be clearly observed from the SEM images of HF-1 (Fig. 1). When F/Al_2O_3 ratio was further increased to 4, large unknown rectangular crystals were produced. The EDX analysis showed that the ratio of P: Al

was 2 for this unknown crystal, which suggested that it may be a new open-framework aluminophosphate material. Based on the above analysis, it can be seen that the suitable F/Al₂O₃ ratio is 1 for the synthesis of the LTA-type phase.

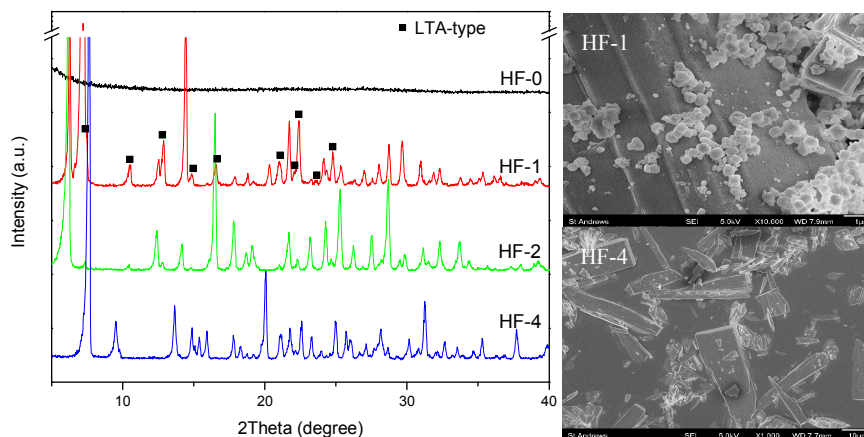


Fig. 1 XRD patterns of four samples under the conditions of different HF/Al₂O₃ ratios together with two typical SEM images

Bao's group first reported the ionothermal synthesis of AlPO₄-LTA material in the gel with a composition of 1Al₂O₃: 3P₂O₅: 0.5HF: 5.7Morp: 40[bmim]Br²⁵. On the basis of the results of in situ two-dimensional NMR and fluorescence measurements, they confirmed that the cooperative structure-directing effect between morpholine and ILs was the key for this synthesis. In this context, different amount of morpholine was introduced to the starting mixture to investigate its effect on the synthesis. As shown in Fig. 2 and Fig. S1, the product was a mixture of dense crystalline phase and ultra-thin unknown phase when no morpholine was added. Whereas when the Morp/Al₂O₃ ratio was 1, relatively pure LTA phase could be produced. As seen in the SEM image in Fig. 2, the crystals in the sample Morp-1 have different sizes but exclusively exhibit a typical cubic shape. On the other hand, when the Morp/Al₂O₃ ratio was further increased to 4, cubic LTA-type crystals with a size of about 300 nm could also be prepared successfully but accompanied by some very large impurity phase. Above results indicate that high-quality LTA

phase can only be synthesized in a narrow range of Morp/ Al_2O_3 ratio. This ratio was kept at 1 in the subsequent optimization.

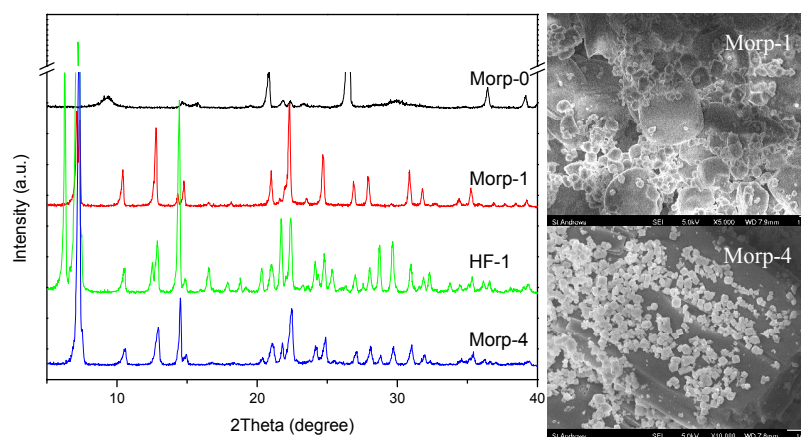


Fig. 2 XRD patterns of four samples under the conditions of different Morp/ Al_2O_3 ratios together with two typical SEM images.

Ionic liquids normally act as both solvents and structure-directing agents for the ionothermal synthesis of aluminophosphate molecular sieves. In a recent research, Morris's group obtained pure ZON zeolite under the condition of ILs/ SiO_2 ratio = 0.2 by ionic liquid assisted synthesis³⁸. This result together with the successful synthesis of zeolite-related materials in the solvent-free conditions implies that high ionic liquids dosage is not necessary for the so-called ionothermal synthesis. In the present work, the ILs/ Al_2O_3 ratio is restricted in the range of 0-4 to synthesize aluminophosphate molecular sieves in a reagent-saving manner. As exhibited in Fig. 3, only at the ratio of ILs/ Al_2O_3 = 4 can pure LTA structure (i.e. the sample Morp-1, see Table 1) be synthesized. When this ratio is below 4, various materials are produced, among which the sample ILs-2 is a triclinic AlPO_4 -34 molecular sieve (IZA code CHA), as verified by the characteristic triclinic-like shape (Fig. S2). The sample ILs-0 perhaps is a mixture of CHA and prephase (a layered crystalline precursor phase related with CHA)³⁹, in which the latter exhibits extremely irregular morphology (Fig. S3). To our surprise the XRD pattern of the sample ILs-1 reveals that it may contain three

phases, i.e. prephase, LTA and CHA, although cubic LTA cannot be clearly discerned in the SEM images (Fig. S4). Above results demonstrate the structure diversity and rich synthetic chemistry in the fluorine-mediated synthetic system⁴⁰. The optimum composition for the synthesis of LTA-type aluminophosphate molecular sieve is 1Al₂O₃: 1P₂O₅: 1HF: 1Morp: 4[bmim]Br. **It should be noted that a certain amount of water in HF and H₃PO₄ solution was not included in the initial molar composition of the synthesis gels. Water was considered to be vital for the ionothermal synthesis⁴,⁵. It may play a role of catalyst except the solvent in the present synthesis, since Tian's group had confirmed that the crystallization kinetics of aluminophosphate molecular sieves can be accelerated prominently by the addition of reagent quantities of water⁴¹.**

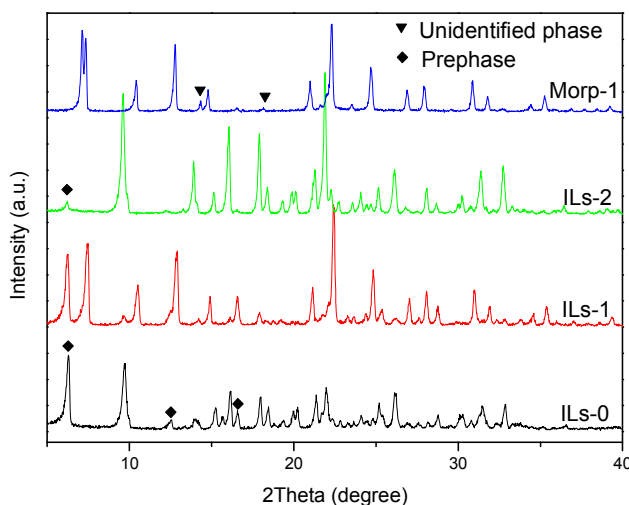


Fig. 3 XRD patterns of four samples under the conditions of different ILs/Al₂O₃ ratios. Note: Prephase is a layered crystalline precursor phase related with CHA

Crystallization temperature and time are two key factors in controlling the purity and crystallinity of the zeolite phase. According to the previous reports, the appropriate temperature is in the range of 150-190 °C in synthesizing the LTA-type phase. In the present work, the other two crystallization temperatures (170 °C and 190 °C) were investigated to further optimize the

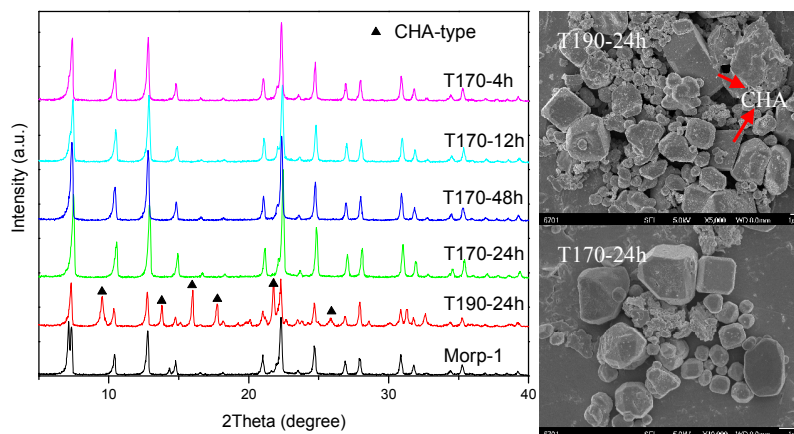


Fig. 4 XRD patterns of six samples under the conditions of different crystallization temperature and time together with two typical SEM images.

crystallization conditions. As shown in Fig. 4, compared with the sample Morp-1 synthesized at 150 °C, the diffraction peak intensity of the LTA phase in the sample T170-24h is prominently increased and minor impurity at $2\Theta = 14.2^\circ$ disappears completely when the crystallization temperature is elevated to 170 °C. However, at the crystallization temperature of 190 °C, the diffraction peaks attributed to triclinic CHA phase become very strong while those of the LTA phase significantly decrease in comparison with T170-24h. According to Davis et al. the relative stability of aluminophosphate molecular sieve is in proportion to their framework density⁴². The appearance of the CHA phase in the sample T190-24h may be accounted for by its high framework density (14.5 T/nm^3) relative to the LTA phase (12.9 T/nm^3). Furthermore, the cooperative structure-directing effect between morpholine and ILs that may be destroyed partly at elevated crystallization temperature is another reason. SEM images in Fig. 4 indicate that the crystals in the sample T170-24h exhibit two different shapes, one is cubic and the other is faceted octahedral. In the sample T190-24h, both cubic crystals and triclinic crystals are observed, verifying the coexistence of the LTA and CHA phase. On the other hand, it is seen from Fig. 4 that LTA-type aluminophosphate molecular sieve can be synthesized at 170 °C in the range of 4-48 h,

indicating that the synthesis of LTA phase seems not to be sensitive to the crystallization time. In the whole range of time investigated, the crystallization time of 24 h is the optimum one because the sample T170-24h reveals the highest crystallinity.

3.2. Composition and structural analysis

After performing a series of optimization, the appropriate conditions for the synthesis of LTA-type aluminophosphate molecular sieve are identified, and showed as follows: the initial composition is $1\text{Al}_2\text{O}_3$: $1\text{P}_2\text{O}_5$: 1HF : 1Morp : $4[\text{bmim}]\text{Br}$, the suitable crystallization temperature and time are in the ranges of $150\text{-}170\text{ }^\circ\text{C}$ and $4\text{-}24\text{ h}$, respectively. Three typical LTA samples, Morp-1, T170-24h and T170-4h, were selected for further investigations.

Solution ^{13}C NMR, TG-DTA experiment and CHN elemental analysis were used to determine the type and amount of organic amines occluded in the cavity of the sample Morp-1. TG-DTA experiment (Fig. 5) exhibits that three-step weight loss accompanied by exothermic effects can be clearly observed in the $250\text{-}320\text{ }^\circ\text{C}$, $320\text{-}387\text{ }^\circ\text{C}$ and $387\text{-}500\text{ }^\circ\text{C}$ temperature ranges for the sample Morp-1. The first one with a weak exothermic peak and $5.1\text{ wt}\%$ weight loss is ascribed to the combustion decomposition of organic species that is firmly adsorbed on the solid surface. The second one with $8.0\text{ wt}\%$ weight loss is related with the combustion of morpholine, whereas the last one with obvious exothermic peak and $11.1\text{ wt}\%$ weight loss is due to the combustion decomposition of ionic liquid according to the results of Bao's group⁴³. CHN analysis indicates that the contents of C, H and N are $16.0\text{ wt}\%$, $2.78\text{ wt}\%$ and $4.39\text{ wt}\%$ in this as-synthesized sample Morp-1. Then the molar ratio of C/N and the total weight of the three elements can be calculated and they are 4.2 and $23.17\text{ wt}\%$, respectively. Apparently, these data are in well agreement with the composition of organic amines and weight loss in TG curve.

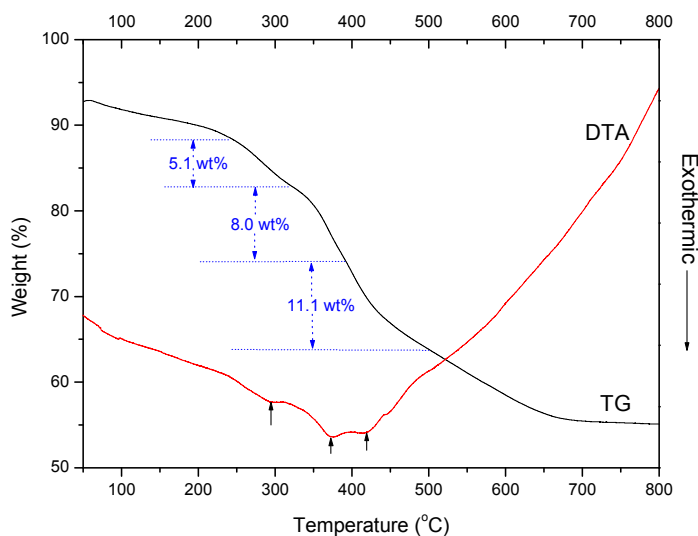


Fig. 5 TG-DTA curves of the as-synthesized LTA-type aluminophosphate molecular sieve (sample Morp-1)

Solution ^{13}C NMR of the sample Morp-1 was carried out to confirm the type of organic species occluded in the cavity of LTA. Before this test, this sample was washed numerous times with water and ethanol to remove the organic species adsorbed on the solid surface. As shown in Fig. 6, both morpholine and $[\text{bmim}]^+$ are observed in the cavity of LTA molecular sieve²⁵. The number of above two molecules per LTA cavity in the as-synthesized Morp-1 can be calculated from the TG results and the structural information of the LTA framework (i.e., each unit cell has one cavity and is composed of 24 T atoms). The value is 2.1 for morpholine and 1.8 for $[\text{bmim}]^+$, namely, almost two morpholine and two $[\text{bmim}]^+$ molecules per cavity are occluded in this material. The EDX analysis shows that the average ratio of F: Al: P is 3.72: 27.7: 29.3 in this sample, suggesting that each unit cell has about two F^- ions. On the basis of all information given before, an idealized chemical formula of the as-synthesized Morp-1 can be determined to be $(\text{Al}_{12}\text{P}_{12}\text{O}_{48})(\text{C}_4\text{H}_9\text{NO})_2(\text{C}_8\text{H}_{15}\text{N}_2^+)_2(\text{F}^-)_2$ (adsorbed water is not considered). **By comparing this chemical formula with the initial composition of the synthesis gels, it can be seen that ionic liquids**

is excessive relative to aluminum source. It can be anticipated that ionic liquids not only served as the structure-directing agent during the crystallization, but also as the solvent owing to its high solubility for the starting materials. The excessive ionic liquids can be recovered by rotational evaporation after the isolation of solid molecular sieve products.

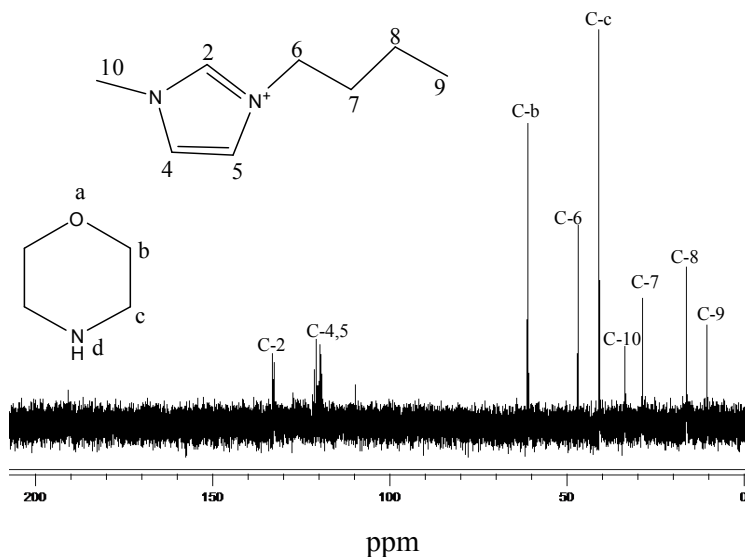


Fig. 6 Solution ^{13}C NMR of as-synthesized LTA-type aluminophosphate molecular sieve (sample Morp-1) dissolved in DCl solution

Fig. 7 exhibits a high resolution TEM (HRTEM) image and a selected area electron diffraction (SAED) pattern of the sample Morp-1. The view direction is along the $[-1\ 1\ 0]$ zone axis of the LTA structure. The d-spacings of the two marked spots in the SAED image are 1.13 and 0.83 nm, which can be indexed to (002) and (220) of the cubic LTA structure. The unit cell parameter is determined to be 2.26 nm, which is in consistent with previous XRD result and the data reported in literature²³.

Fig. 8 shows the nitrogen adsorption/desorption isotherms of the calcined T170-24h, Morp-1 and T170-4h. The type I isotherms of these three samples demonstrate that they are typical microporous materials. The appearance of hysteresis loops in the isotherms implies that these

materials have minor additional mesopore or macropore. The BET surface area and micropore volume of the three samples are in the ranges of 599-745 m²/g and 0.23-0.29 cm³/g, which are slightly higher than the data reported in the literature^{21,27,30}. As it is known, the LTA-type

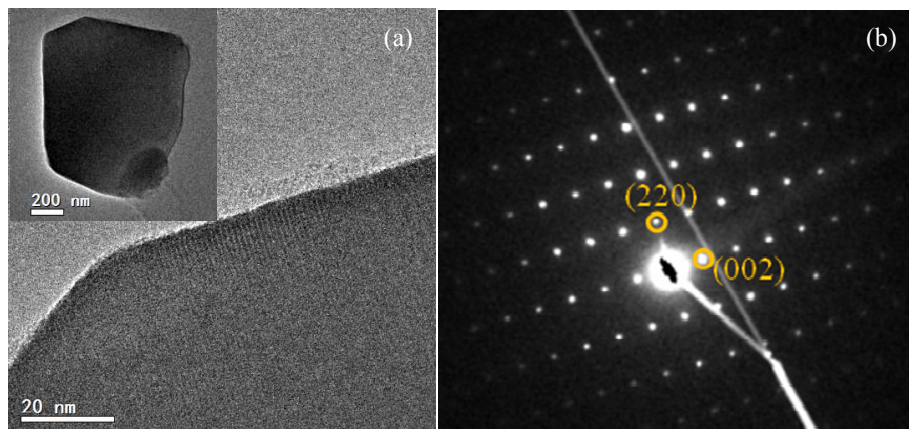


Fig. 7 (a) HRTEM image and (b) SAED pattern of typical crystal of sample Morp-1

aluminophosphate molecular sieve cannot resist severe calcination treatment. However, the materials reported here can preserve the majority of their micropores, which can be explained by the modest calcination temperature and short treatment time employed, although XRD patterns (Fig. S5) indicate that their structures have been partly damaged upon calcinations. The inorganic-sources utilizations of these three samples presented in Table 2 indicate that they are all beyond 86%, verifying the high efficiency of this improved ionothermal synthesis. The high zeolite yield, as well as the high surface area and micropore volume for these calcined LTA-type materials imply that they have potential to be used in zeolite-related applications, such as adsorption and separation. Recently, Corma's group reported the synthesis of SAPO-42 molecular sieve with LTA topology. This acidic material may be acted as a good catalyst in methanol-to-olefins and selective catalytic reduction relevant to industrial process. However, such work is still under consideration²¹.

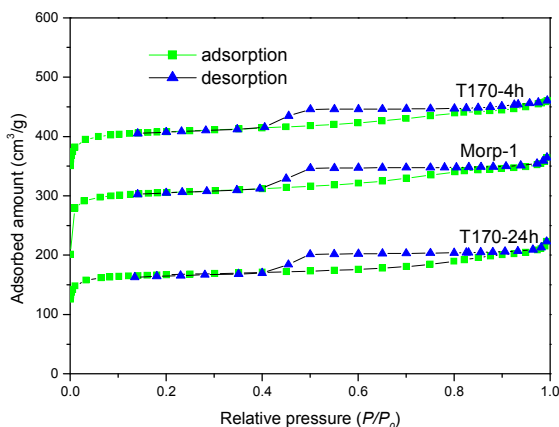


Fig. 8 N_2 adsorption/desorption isotherms of the calcined samples T170-24h, Morp-1 and T170-4h (The isotherms for Morp-1 and T170-4h were offset vertically by 100 and 200 cm^3/g).

Table 2 Calcined product yields, utilization of inorganic sources and textural parameters of three LTA-type samples

Sample	Calcined product yields (g)	Utilization of inorganic sources ^a (%)	BET Surface area (m^2/g)	Micropore Volume (cm^3/g)
Morp-1	1.261	86.1	729	0.27
T170-4h	1.353	92.4	745	0.28
T170-24h	1.320	90.2	599	0.23

a. The utilization calculated from the weight ratio of calcined product yield with total inorganic sources except for water and fluorine.

4. Conclusions

In conclusion, aluminophosphate molecular sieve with LTA topology has been synthesized by improved ionothermal method. The optimum starting composition for LTA structure is $1Al_2O_3:1P_2O_5:1HF:1Morp:4[bmim]Br$. The suitable crystallization temperature and time are in the ranges of 150-170 $^{\circ}C$ and 4-24 h, respectively. The characterization results indicate that the composition of the resultant LTA molecular sieve is $(Al_{12}P_{12}O_{48})(C_4H_9NO)_2(C_8H_{15}N_2^+)_2(F^-)_2$, for which morpholine together with 1-butyl-3-methylimidazolium cations act as the structure-directing agent. The BET surface area and micropore volume of the calcined LTA

material is as high as 745 m²/g and 0.28 cm³/g.

The present work demonstrates that high ionic liquid dosage is not necessary for the ionothermal synthesis of LTA- and CHA-type aluminophosphate molecular sieves. The rich structural diversity observed in this work implies that the newly developed methodology throws light on preparation of many other molecular sieves in a high-efficiency manner.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 21306072, 21203081) and Development Program of Lanzhou University of Technology for excellent teachers (Grant No. Q201113). WZ thanks EPSRC for financial support to upgrade the SEM facilities (No. EP/F019580/1). **We cordially thank the Reviewers and Editors for providing us with valuable comments and suggestions.**

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Supplementary Information for New Journal of Chemistry
Highly efficient synthesis of LTA-type aluminophosphate molecular sieve
by improved ionothermal method

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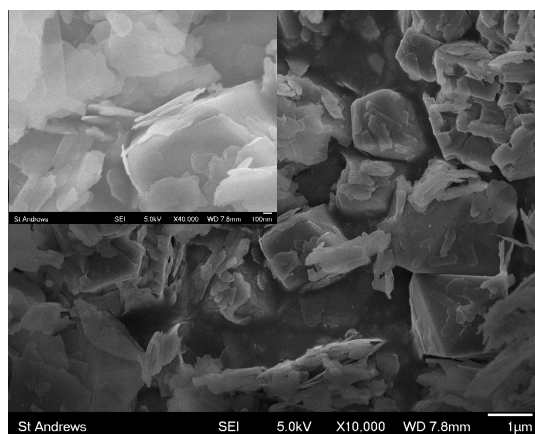


Fig. S1 SEM images of the as-synthesized sample Morp-0

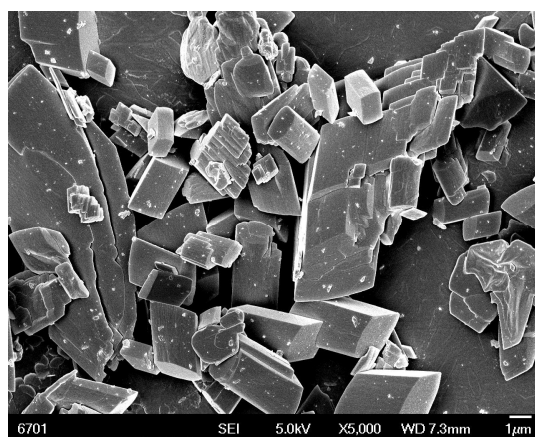


Fig. S2 SEM image of the as-synthesized sample ILs-2

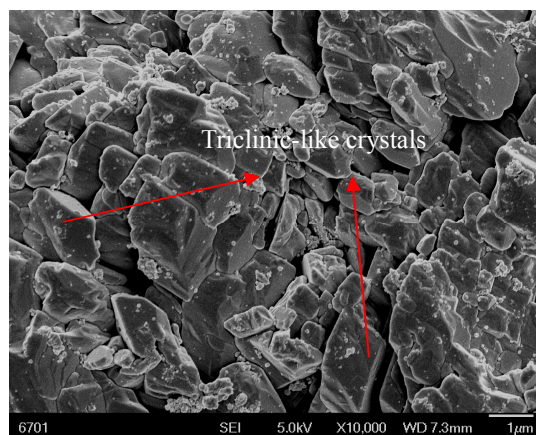


Fig. S3 SEM image of the as-synthesized sample ILs-0

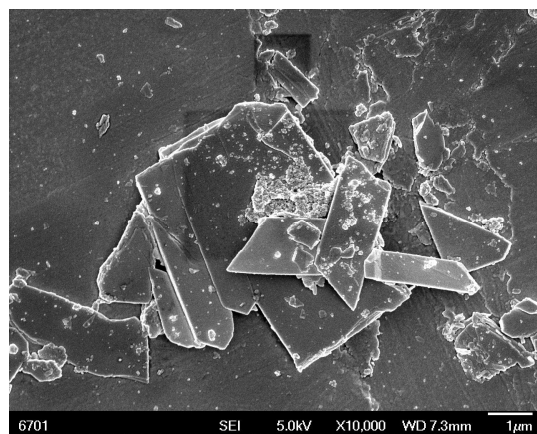


Fig. S4 SEM image of the as-synthesized sample ILs-1

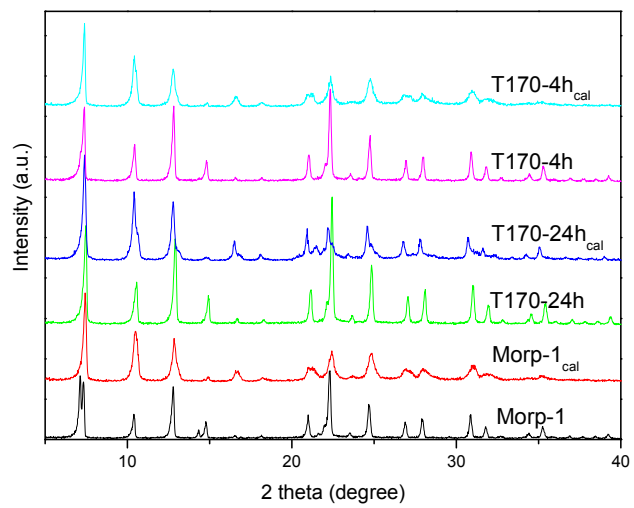


Fig. S5 XRD patterns of three calcined samples (T170-4h_{cal}, T170-24h_{cal} and Morp-1_{cal}) together with the corresponding as-synthesized samples as references.