

Ionothermal Synthesis of Magnesium-Containing Aluminophosphate Molecular Sieves and their Catalytic Performance

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Owing to their promising catalytic and adsorptive properties,^[1] microporous materials, often referred to as molecular sieves or open-framework materials, have attracted more and more attention in different research fields.^[2] Among them, microporous aluminophosphate molecular sieves (designated $\text{AlPO}_4\text{-}n$) have been extensively studied by many authors, owing to their wonderfully complex structures and broadly applications since their discovery in 1982.^[3] However, because the frameworks of these materials are neutral and lack of Brønsted acid sites,^[4] sometimes they can not be used in catalysis directly. Nevertheless, the lattice Al and/or P atoms in the $\text{AlPO}_4\text{-}n$ frameworks can be partially replaced by silicon (designated (SAPO- n)) and/or other metal elements (designated MeAPO- n), to form frameworks with Brønsted acid sites and/or catalytically active metal centers.^[5]

Commonly, $\text{AlPO}_4\text{-}n$ and MeAPO- n compounds are often crystallized from a gel under hydrothermal or solvothermal conditions.^[6,7] Recently, a novel synthetic route (ionothermal synthesis) provides a potential route to making these microporous materials. Ionothermal synthesis is the use of an ionic liquid^[8] or eutectic mixture^[9] as the reaction solvent and if necessary, the structure-directing agent in the synthesis of materials. Ionic liquids are special molten salts typically containing organic cations and inorganic anions.^[10] The

peculiar properties of ionic liquids endow the ionothermal synthesis many interesting features and potential advantages over the traditional methods of molecular sieve synthesis. For example, the ionothermal synthesis can take place at ambient pressure because of the vanishingly small vapor pressure of ionic liquids, which eliminates the safety concerns associated with high pressures. In addition, the excellent microwave-absorbing property of ionic liquids^[11] allows the ionothermal synthesis being carried out under microwave conditions,^[12] leading to the rapid crystal-growth rate and high product selectivity.

Although many AlPO_4 -based molecular sieves including some novel-framework topologies have been prepared using ionothermal method, the amount of the MeAPO- n structures synthesized ionothermally is relatively small. To date, only several SAPO- n ^[13] and CoAPO- n ^[14,15] structures could be obtained by using this new synthetic technique. Moreover, the research on the applications of these MeAPO- n compounds to catalysis or gas adsorption has not been reported in the literature.

Herein we demonstrate that the ionothermal synthesis method can be applied to the synthesis of MeAPO- n materials with excellent catalytic performance. In the present work, a magnesium compound was introduced into the reaction system of $\text{AlPO}_4\text{-}n$ and several Mg-containing aluminophosphate molecular sieves were successfully synthesized in 1-butyl 3-methylimidazolium bromide ionic liquid ([bmim]Br). Results are presented about the physical and chemical characterization (such as X-ray diffraction: XRD, X-ray fluorescence: XRF, scanning electron microscopy: SEM, Brunauer–Emmett–Teller: BET, NH_3 -temperature programmed desorption: NH_3 -TPD, thermogravimetric: TG, and NMR analysis) of the MAPO samples obtained with different Mg contents and amine as well as their catalytic evaluation in the hydroisomerization of n -docecane.

Table 1 summarizes the details of the synthesis conditions and the products obtained ionothermally. Only the AlPO_4 -tridymite dense phase could be obtained at 170 °C for 3 day without the addition of metal elements (Table 1, AlPO).

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Table 1. Synthesis details and conditions for the preparation of MAPO structures.

Sample ^[a]	$x(\text{MgO})$	$y(n\text{DPA})$	Time [d]	Structure	$\text{MgO}/\text{Al}_2\text{O}_3$ ^[c]
AlPO	0	0	3	T ^[b]	–
MA1	0.03	0	3	AEL + AFI + T ^[b]	0.011
MA2	0.06	0	3	AEL + AFI + T ^[b]	0.026
MA3	0.09	0	3	AEL + AFI + T ^[b]	0.065
MA4	0.03	0.3	7	AEL	0.003
MA5	0.06	0.3	7	AEL	0.018
MA6	0.09	0.3	7	AEL	0.032

[a] Molar composition of synthesis mixtures: $x(\text{MgO})$: $1.0\text{Al}_2\text{O}_3$; $3.0\text{P}_2\text{O}_5$; 0.6HF ; $20[\text{bmim}]\text{Br}$; $y(n\text{DPA})$ and the synthesis temperature is 170°C . [b] T represents AlPO_4 -tridymite dense phase. [c] Determined by elemental analysis.

However, after a magnesium compound was added to the reaction system in a range of ratios, MAPO mixture samples, which contained AFI,^[16] AEL,^[17] and dense structures, were prepared by using the same conditions (Table 1, MA1–MA3). This indicates that the magnesium compound added to the synthesis mixtures may contribute an additional structure-directing effect along with the ionic liquid, which is similar to the effect of cobalt hydroxide in the synthesis of CoAlPO_4 .^[14] When the same synthesis reaction was carried out in the presence of *n*-dipropylamine (*n*DPA), pure MAPO-11 samples (Table 1, MA4–MA6) with different Mg contents were formed after 7 days. This is another example of the structure-directing effect of amine, which affects the dynamics of the crystallization process and inhibits the transformation of MAPO frameworks to the ultimate dense phase.^[18]

The SEM images of the MAPO samples prepared ionothermally are shown in Figure 1. The MAPO mixtures display a block-like morphology and the particle size increases with the increase in the Mg content. In contrast, the crystals of the MAPO-11 samples are thin rods, which begin to agglomerate with increasing the Mg content. Such a significant difference in morphologies between the MAPO mixtures and the MAPO-11 samples should be attributed to the presence of the amine.

The results of characterization show that the addition of amine could also influenced the incorporation of Mg^{2+} ions into aluminophosphates, which is of great importance for the generation of the catalytically reactive sites.^[5,19] For MAPO samples with the same Mg content in the synthesis mixtures, the $\text{MgO}/\text{Al}_2\text{O}_3$ ratio in the MAPO mixtures (Table 1, MA1–MA3) is much higher than that in MAPO-11 (Table 1, MA4–MA6), suggesting that the amine may go against the incorporation of Mg element into the final products. Moreover, The MAPO mixtures present a drop in the BET surface area and micropore volume (Table 2, MA1–MA3) compared to the AlPO_4 -*n* products, and the drop is more pronounced with the increase in the Mg content. In contrast, in the hydrothermal synthesis of MAPO molecular sieves,^[20,21] the micropore volumes would not exhibit such a noticeable decrease. This is likely due to the poor solubility of Mg species in ionic liquid so that the excessive Mg mate-

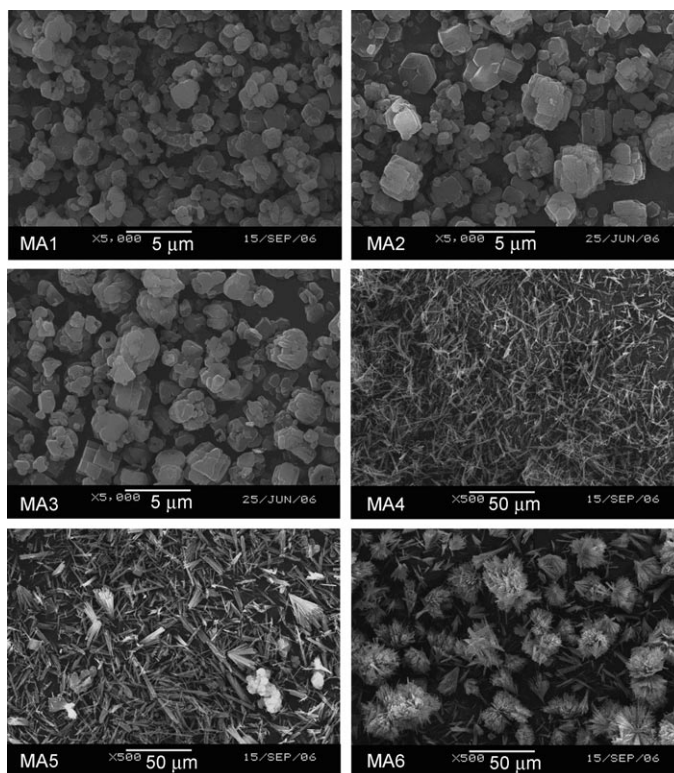


Figure 1. The SEM images of the MAPO samples.

Table 2. BET area, microporous volume and acidity of the MAPO samples.

Sample	BET area [m^2g^{-1}]	Micropore volume [cm^3g^{-1}]	Absorbed NH_3 [mmol g^{-1}]		
			Total acidity	Weak acidity ^[b]	Strong acidity ^[b]
AlPO_4 -11 ^[a]	196	0.070	–	–	–
MA1	103	0.050	0.051	0.013	0.038
MA2	73	0.035	0.148	0.064	0.084
MA3	47	0.021	0.410	0.141	0.269
MA4	185	0.085	0.356	0.192	0.164
MA5	143	0.062	0.623	0.327	0.296
MA6	81	0.036	0.345	0.151	0.194

[a] Synthesized at 170°C for 24 h with the composition: $x(\text{MgO})$: $1.0\text{Al}_2\text{O}_3$; $3.0\text{P}_2\text{O}_5$; 0.6HF ; $20[\text{bmim}]\text{Br}$. [b] Weak acidity = ammonia desorption in peak around 220°C , Strong acidity = ammonia desorption in peak around 330°C .

rials would not dissolved in the ionic liquid but formed extra-framework species probably located at the outer surface or occluded in channels. However, although a similar drop was observed in the case of MAPO-11 (Table 2, MA4–MA6), this decrease became less evident, indicating that the presence of amine may restrain the formation of the extra-framework species to some extent.

The NH_3 -TPD profiles of the MAPO samples showed two obvious desorption regions. The first maximum around 220°C was assigned to weakly bound ammonia and the second one at 330°C should be attributed to the ammonia desorbed from the strong acid sites originating from the substitution of Mg^{2+} for Al^{3+} in the framework.^[20] For the

MAPO mixtures (Table 2, MA1–MA3), the total number of acid sites increased with the Mg content, while the amounts of adsorbed ammonia from MAPO-11 synthesized with *n*DPA (Table 2, MA4–MA6) displayed a maximum. Moreover, for samples with Mg content in the synthesis mixtures in the range 0.03–0.06, the amount of ammonia adsorbed on the acid sites of the MAPO-11 samples is much larger than that of the MAPO mixtures. This may be ascribed to the larger amount of the extra-framework species on the MAPO mixtures which hampered the adsorption of ammonia on the Brønsted acid sites by blocking the pore. Nevertheless, because more Mg²⁺ ions may be incorporated into the framework, as the MgO/Al₂O₃ ratio in the MAPO mixture increases (Table 1), the amount of ammonia adsorbed on the strong acid sites of the MA3 sample is higher than that of the MA6 sample.

The typical ²⁷Al magic angle spinning (MAS) NMR spectra and the ³¹P MAS NMR spectra of the as-synthesized MAPO mixture (MA1) and MAPO-11 (MA4) is shown in Figure 2. The ²⁷Al MAS NMR spectra present an intense

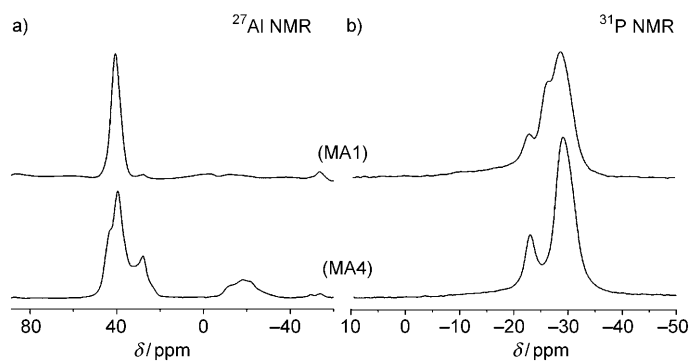


Figure 2. Typical ²⁷Al MAS NMR spectra (a) and ³¹P MAS NMR spectra (b) of the as-synthesized MAPO samples.

signal in the $\delta = 40.5$ and 39.6 ppm region for MA1 and MA4 sample, respectively, typical of Al in tetrahedral coordination.^[22,23] Two additional peaks: one at around $\delta = 28$ ppm assigned to the five-coordinated aluminum sites^[24,25] and the other broad resonance at around $\delta = -13$ ppm corresponding to octahedral aluminum environment^[26] were also observed for the MA4 sample, although undistinguishable in the case of the MA1 sample. For the MA4 sample, a shoulder appears at around $\delta = 42$ ppm, which may be caused by the secondary interaction of the framework Al sites with the template/water molecules.^[27]

The ³¹P MAS NMR spectra of the MAPO materials show a resonance at around $\delta = -29$ ppm attributed to the tetrahedral P(4Al) environment and a signal centered at around $\delta = -23$ ppm which can be assigned to P(3Al,1Mg) units in the framework.^[23,26] In the case of MA1, an additional resonance at $\delta = -26.7$ ppm can also be noticed. Similar result was obtained by Deng et al. in the study of the structure of MAPO and MAPSO molecular sieves synthesized hydrothermally.^[28] They have attributed this signal together with

the resonance at around $\delta = -23$ ppm to the two distinct P(3Al,1Mg) units.

The conversion and isomerization selectivity of *n*-dodecane over 0.5Pt/MAPO catalysts, as a function of the reaction temperature, is presented in Figure 3. For the Pt/

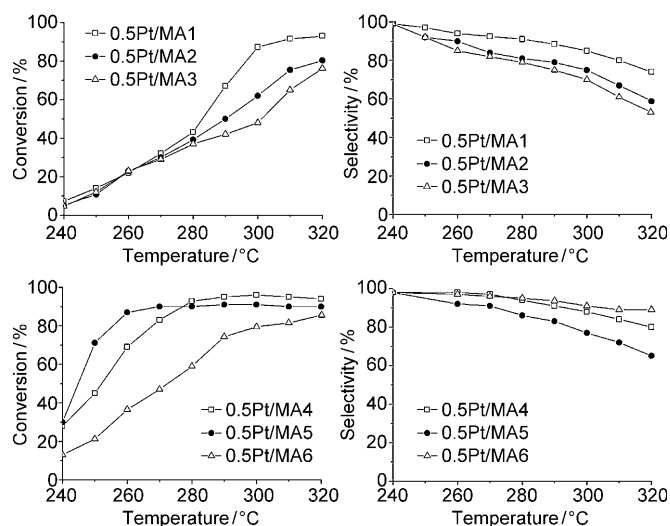


Figure 3. Conversion (left) and isomer selectivity (right) of *n*-dodecane as a function of reaction temperature over Pt/MAPO mixture (top row) and Pt/MAPO-11 (bottom row). Reaction conditions: $n(\text{H}_2)/n(\text{C}_{12}) = 15$ (mol/mol); WHSV = 0.3 h^{-1} (WHSV = weight hourly space velocity); $P =$ atmospheric pressure.

MAPO mixture catalysts, the activity and the isomer selectivity decreased gradually with the increase in the MgO/Al₂O₃ ratio, along with the number of acid sites of the samples. It has been considered that the hydroisomerization activity of *n*-alkane will increase with increasing the number of acid sites.^[29] However, the diffusional rate will decrease with the increase in the MgO/Al₂O₃ ratio of the MAPO mixture samples, owing to the fact that the micropore volume dropped remarkably (Table 2), which was caused by the formation of extra-framework species. This results the decrease in the activity and selectivity of the catalysts although the acidity increased.^[30] For the Pt/MAPO-11 catalysts, the Pt/MA5 exhibited the highest activity that the conversion of *n*-dodecane amounts to 90% at the reaction temperature of 270°C. However, the selectivity over this catalyst was the lowest. The MA5 sample possesses the largest number of acid sites (Table 2), which should be responsible for its highest activity.^[29] Nevertheless, the remarkable increase in the number of acid sites of MA5 sample may also influenced the balance between the acid and the hydrogenation function of the metal, therefore, reduced its isomer selectivity.^[32,33] Relatively speaking, the Pt/MA4 catalyst has the best hydroisomerization performance with the achievement of a conversion of 93% and a selectivity of 94% at 280°C.

By comparison, the catalytic performance of the Pt/MAPO-11 catalysts is much better than that of the Pt/

MAPO mixture catalysts. The large amount of the extra-framework species reduced the number of the acid sites accessible by the reactant and the diffusional rate on the Pt/MAPO mixtures by blocking the pore, which affected both the activity and selectivity of *n*-dodecane. The addition of amine may restrain the formation of the extra-framework species to some extent, which results an increase in the amount of acid sites accessible by the reactant and a weaker hindrance in the diffusion of isomerized products. Furthermore, the presence of amine may affect the incorporation of Mg²⁺ into the framework (Figure 2), leading to a change in the active sites on MAPOs. Accordingly, the higher activity and selectivity were achieved over the Pt/MAPO-11 catalysts. Notably, the hydroisomerization performance of *n*-dodecane over the Pt/MA4 catalyst has reached, or even surpassed, the optimum performance of *n*-alkane over the Pt/MAPO^[33] catalysts synthesized by using the conventional hydrothermal method. This result suggests that the ionothermal environment may lead to the unique sitting of the incorporated Mg²⁺ or novel distribution of the Mg²⁺ within the framework, which is worthy of further study.

In summary, Mg-containing aluminophosphate molecular sieves, with a range of Mg content, were synthesized ionothermally in [bmim]Br ionic liquid. The addition of amine could affect the physical and chemical properties of the MAPO materials and enhance the hydroisomerization performance of *n*-dodecane over the Pt/MAPO catalysts. The excellent catalytic result in this study shows that the ionothermal synthesis is a very promising method for the preparation of the microporous materials, which can be applied to catalysis.

Experimental Section

General synthesis procedure of MgAPO-11 samples: A round-bottom flask was charged with [bmim]Br (50 g, 0.228 mol), H₃PO₄ (3.35 g, 0.034 mol, 85 wt % in water), Al₂O(CH₃CO₂)₄·4H₂O (4.31 g, 0.011 mol), HF (0.15 g, 0.006 mol, 40 wt % in water), and an appropriate amount of Mg(CH₃COO)₂·4H₂O. Amine (0.003 mol) was added if required. Then the reaction mixture was heated to 170 °C for several days. After cooling to room temperature the products were washed thoroughly with distilled water and acetone.

Characterization: The XRD pattern was collected by using a PANalytical X'Pert Pro diffractometer with nickel-filtered Cu_{Kα} radiation. The sample morphology was examined by using SEM (JEOL JSN-6460LV model). Chemical composition analysis was determined with a Philips Magix X-ray fluorescence spectrometer. The acidity of the sample was characterized by using NH₃-TPD with a Micromeritics Autochem 2910 automated catalyst characterization system. The surface area and pore size distribution of the samples were measured by using the nitrogen adsorption-desorption method (ASAP 2010, Micromeritics). The thermal analysis was investigated by using a Perkin-Elmer Diamond analyzer. ¹H, ¹³C, ²⁷Al, and ³¹P MAS NMR experiments were performed by using a Bruker DRX-400 spectrometer.

Catalytic testing: The hydroisomerization of *n*-dodecane as a model reaction was conducted at atmospheric pressure in a fully automated stainless steel fixed bed continuous microreactor, loaded with 0.75 g of the catalyst powder. The products were collected and analyzed on-line using a Varian 3800 gas chromatograph equipped with a capillary column (PONA, 100 m in length). The reaction conditions used in this work are 0.3 h⁻¹

WHSV, H₂/hydrocarbon ratio of 15 mol mol⁻¹, and reaction temperatures ranging from 240 to 320 °C.

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