



# Ionothermal syntheses of transition-metal-substituted aluminophosphate molecular sieves in the presence of tetraalkylammonium hydroxides



Dawei Li <sup>a, c</sup>, Yunpeng Xu <sup>a</sup>, Huaijun Ma <sup>a</sup>, Renshun Xu <sup>a</sup>, Yasong Wang <sup>a, c</sup>, Hao Liu <sup>a, c</sup>, Bingchun Wang <sup>a</sup>, Zhijian Tian <sup>a, b, \*</sup>

<sup>a</sup> Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

<sup>b</sup> State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

<sup>c</sup> University of Chinese Academy of Sciences, Beijing 100049, China

## ARTICLE INFO

### Article history:

Received 6 January 2015

Received in revised form

16 February 2015

Accepted 16 February 2015

Available online 24 February 2015

### Keywords:

Ionothermal synthesis

Transition-metal-substituted

aluminophosphate

Tetraalkylammonium hydroxides

Structure directing effect

## ABSTRACT

Transition-metal-substituted aluminophosphate (MeAPO) molecular sieves with SOD and AEI framework types have been synthesized ionothermally in the ionic liquid 1-ethyl-3-methylimidazolium bromide with adding four tetraalkylammonium hydroxides, including tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide and tetrabutylammonium hydroxide. Detailed synthetic investigation shows that the nature and concentration of the tetraalkylammonium hydroxide, the Me/Al ratio in the reaction mixture and the metal sources greatly influence the phase selectivity of the reaction. The products have been characterized by PXRD, SEM, ICP, CHN, UV–Vis spectroscopy, <sup>13</sup>C, <sup>27</sup>Al and <sup>31</sup>P MAS NMR, and TG. The results reveal that the tetraalkylammonium cations compete with the ionic liquid cations to act as the structure directing agent. The templating ability of the tetraalkylammonium cations and the ionic liquid cations is closely related to their charge densities.

© 2015 Elsevier Inc. All rights reserved.

## 1. Introduction

Aluminophosphate (AIPO) molecular sieves and their silicoaluminophosphate (SAPO) and metalloaluminophosphate (MeAPO) analogs have been extensively investigated in the past decades, not only because of their structure variability and composition tunability but also because of their excellent catalytic properties in chemical processes [1–3]. These AIPO-based materials are conventionally synthesized under hydrothermal and solvothermal conditions where organic amines are added to act as templates or structure directing agents (SDAs) [4,5]. In recent years, ionothermal synthesis, using an ionic liquid (IL) as the reaction solvent and sometimes the SDA, has been developed for the synthesis of AIPO-based molecular sieves [6–9]. A number of AIPO-based molecular sieves with novel structures or new compositions have been synthesized by ionothermal method, such as SIZ-1 [6], SIZ-6 [7], SIZ-7

[10], JIS-1 [11] and DNL-1 [12]. In ionothermal synthesis, organic amines can be added to the IL in the same way that organic amines are normally added to water or organic solvent (e.g. alcohol) in hydrothermal or solvothermal synthesis [13]. It was found that the addition of organic amines to the IL can affect the dynamics of the crystallization process and result in better phase selectivity of the reaction. To date, many studies have focused on the synthesis of AIPO molecular sieves in alkyl imidazolium ILs with adding different organic amines or tetraalkylammonium cations [11–20]. Research results show that the added amines play different roles in the ionothermal synthesis of AIPO molecular sieves. The roles of the added amines can be broadly classified into three categories. They are as follows: i) the added amines replace ILs to play the role of SDA; ii) the added amines and ILs act as the co-SDAs; iii) the added amines cannot alter the original structure directing effect of ILs. In addition, it has been found that especially in the case of ii), the concentration of the added amines significantly affects the structure of the final product [15].

As is known, AIPO molecular sieves possess neutral frameworks without Brønsted acid sites, which limit their applications. Therefore, the incorporation of metal ions into the frameworks of AIPO

\* Corresponding author. Dalian National Laboratory for Clean Energy, State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China. Tel./fax: +86 411 84379151.

E-mail address: [tianz@dicp.ac.cn](mailto:tianz@dicp.ac.cn) (Z. Tian).

molecular sieves to yield MeAPO molecular sieves, which are useful for applications such as catalysis or gas adsorption, is of particular interest [3]. The ionothermal method has been proved to be suitable for incorporating the metal ions into the AlPO frameworks [10,21–26]. However, ionothermal synthesis often results in a mixture of MeAPO phases [10,21,22]. The problem associated with the synthesis of pure MeAPO molecular sieves from ILs can be attributed to the structure directing effect of the metal ions, which makes the crystallization process of MeAPO molecular sieves more complex than that of AlPO molecular sieves. To improve the phase selectivity in the ionothermal synthesis of MeAPO molecular sieves, a feasible way is to add organic amines to the IL. In our previous report on the synthesis of MgAPO molecular sieves, we attempted to introduce an organic amine (*n*-dipropylamine) into the IL and found that the addition of organic amine can not only improve the product selectivity but also has an effect on the physicochemical properties of the MgAPO materials, thus affecting the catalytic performance of the Pt/MgAPO catalysts in the hydroisomerization of *n*-dodecane [22].

Tetraalkylammonium hydroxides are frequently used as SDAs in the synthesis of silicate- and phosphate-based molecular sieves under hydrothermal conditions [4,27]. In the present work, we report the synthesis of MeAPO (Me = Co, Zn) molecular sieves in 1-methyl-3-ethylimidazolium bromide ([Emim] Br) with adding four tetraalkylammonium hydroxides, including tetramethylammonium hydroxide (TMAOH), tetraethylammonium hydroxide (TEAOH), tetrapropylammonium hydroxide (TPAOH) and tetrabutylammonium hydroxide (TBAOH). As a result, SOD-type MeAPO molecular sieves were obtained when TMAOH was added to the reaction mixture, while AEI-type MeAPO molecular sieves were formed when TEAOH, TPAOH or TBAOH was introduced. The structure directing effect of the IL cations and the tetraalkylammonium cations has been investigated by <sup>13</sup>C MAS NMR. The synthesis parameters that affect the product selectivity and the physicochemical properties of the products have been studied.

## 2. Experimental

### 2.1. Synthesis

The general synthesis procedure was as follows: Co(OH)<sub>2</sub> (or ZnO) and Al[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub> were first added to [Emim]Br with stirring at 90 °C in an oil bath for 30 min. Next, H<sub>3</sub>PO<sub>4</sub> (85wt% in water) was added and the mixture was stirred for 90 min. Finally, the tetraalkylammonium hydroxide (25wt% in water) was slowly added. After 30 min of stirring, the final mixture was sealed in a 100 ml Teflon-lined stainless steel autoclave and heated at 160 °C for 3 days, then cooled to room temperature. The resulting solids were recovered by filtration, washed with water and ethanol, and dried at 120 °C overnight. Details of the initial reaction mixture compositions and the corresponding product phases are listed in Table 1.

### 2.2. Characterization

Powder X-ray diffraction (PXRD) data were collected on a PANalytical X'Pert PRO X-ray diffractometer, operating at 40 kV and 40 mA, and using Cu K<sub>α</sub> radiation (λ = 1.5418 Å). The morphology of the samples was studied by scanning electron microscopy (SEM) on a JSM 7800F field emission scanning electron microscope. Inductively coupled plasma (ICP) analysis was performed on a Perkin–Elmer Optima 7300DV instrument. The organic content of the as-synthesized samples was determined by CHN analysis performed with a Thermo Scientific FLASH 2000 organic elemental analyzer. The solid-state diffuse reflectance UV–Vis spectra were

**Table 1**  
Synthesis conditions and resulting products.

Sample <sup>a</sup>	Gel compositions (molar ratio)					Product
	Me	Al	P	Amine	IL	
IL1	1.0Co	1	4	0.5TMAOH	20	SOD
IL2	1.0Co	1	4	0.5TEAOH	20	AEI
IL3	1.0Co	1	4	0.5TPAOH	20	AEI
IL4	1.0Co	1	4	0.5TBAOH	20	AEI
IL5	1.0Co	1	4	0	20	Cristobalite
IL6	1.0Co	1	4	0.1TMAOH	20	Cristobalite + SIZ-1 + SOD
IL7	1.0Co	1	4	0.3TMAOH	20	SOD + SIZ-1
IL8	1.0Co	1	4	0.1TPAOH	20	Cristobalite
IL9	1.0Co	1	4	0.3TPAOH	20	SIZ-1 + AEI
IL10	0	1	4	0.5TMAOH	20	Cristobalite
IL11	0.5Co	1	4	0.5TMAOH	20	SIZ-1
IL12	1.5Co	1	4	0.5TMAOH	20	SOD
IL13	0	1	4	0.5TPAOH	20	Cristobalite
IL14	0.5Co	1	4	0.5TPAOH	20	SIZ-1 + unknownphase
IL15	1.5Co	1	4	0.5TPAOH	20	AEI
IL16	1.0Co <sup>b</sup>	1	4	0.5TMAOH	20	SOD
IL17	1.0Co <sup>c</sup>	1	4	0.5TMAOH	20	Cristobalite
IL18	1.0Co <sup>b</sup>	1	4	0.5TPAOH	20	AEI
IL19	1.0Co <sup>c</sup>	1	4	0.5TPAOH	20	Cristobalite
IL20	1.0Zn	1	4	0.6TMAOH	20	SOD
IL21	1.0Zn	1	4	0.6TEAOH	20	AEI
IL22	1.0Zn	1	4	0.6TPAOH	20	AEI
IL23	1.0Zn	1	4	0.7TBAOH	20	AEI

<sup>a</sup> Reaction temperature: 160 °C; reaction time: 3 days.

<sup>b</sup> Co(OAc)<sub>2</sub>·4H<sub>2</sub>O was used as cobalt source.

<sup>c</sup> CoCl<sub>2</sub>·6H<sub>2</sub>O was used as cobalt source.

obtained on a Hitachi U-3900H spectrophotometer equipped with an integrating sphere with BaSO<sub>4</sub> as reference. Thermogravimetric (TG) analysis was conducted using a STA 449 F3 analyzer in air from 40 to 800 °C at a heating rate of 10 °C min<sup>-1</sup>. The solid-state MAS NMR experiments were performed on a Varian Infinityplus-400 spectrometer. <sup>1</sup>H → <sup>13</sup>C CP/MAS NMR spectra were recorded at 100.5 MHz with a spinning rate of 8 kHz. The chemical shifts were referenced to adamantane with the upfield methine peak at 29.5 ppm. <sup>27</sup>Al MAS NMR experiments were conducted at 104.2 MHz with a spinning rate of 12 kHz. The chemical shifts were referenced to 1% Al(NO<sub>3</sub>)<sub>3</sub> aqueous solution. <sup>31</sup>P MAS NMR spectra were recorded at 161.8 MHz with a spinning rate of 8 kHz. The chemical shifts were referenced to 85% H<sub>3</sub>PO<sub>4</sub>.

## 3. Results and discussions

### 3.1. Syntheses of MeAPO (Me = Co, Zn) molecular sieves

In this study, four tetraalkylammonium hydroxides, including TMAOH (N(CH<sub>3</sub>)<sub>4</sub><sup>+</sup> OH<sup>-</sup>), TEAOH (N(CH<sub>2</sub>CH<sub>3</sub>)<sub>4</sub><sup>+</sup> OH<sup>-</sup>), TPAOH (N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>4</sub><sup>+</sup> OH<sup>-</sup>) and TBAOH (N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>4</sub><sup>+</sup> OH<sup>-</sup>) were introduced into cobalt- and zinc-containing aluminophosphate reaction mixtures. As can be seen in Table 1, when TMAOH was added to the reaction mixture, the SOD phase was obtained (IL1, IL20). Interestingly, the AEI phase resulted from ionothermal syntheses in the presence of TEAOH, TPAOH and TBAOH (IL2–IL4, IL21–IL23). Besides the nature of the tetraalkylammonium hydroxide, there are several other synthesis parameters, such as the concentration of the tetraalkylammonium hydroxide, the Me/Al molar ratio and the metal sources used, which greatly affect the phase selectivity. The influence of these synthesis parameters on the synthesis of cobalt-containing SOD and AEI materials was investigated in detail.

In ionothermal synthesis, the amount of the added amines has been proved to be important in determining the phase selectivity of the reaction [15]. Consequently, the effect of the amount of tetraalkylammonium hydroxides (TMAOH and TPAOH) on the final

Download English Version:

<https://daneshyari.com/en/article/6533027>

Download Persian Version:

<https://daneshyari.com/article/6533027>

[Daneshyari.com](https://daneshyari.com)