

## Synthesis and Characterization of alkaline earth metal substituted aluminophosphates with AFI topology

Shyamal Kumar Saha, Suresh B. Waghmode, Yoshihiro Kubota, and Yoshihiro Sugi\*  
Department of Materials Science and Technology, Faculty of Engineering, Gifu University, Gifu 501-1193, Japan  
Tel/Fax: +81-58-293-2597; E-mail address: sugi@apchem.gifu-u.ac.jp (Y. Sugi)

Aluminophosphate type molecular sieves of AFI structure with isomorphous substitution of aluminum to alkaline earth metals: Mg, Ca, Sr, and Ba (M-AFI) were synthesized by conventional hydrothermal synthesis (HTS) and non-conventional dry-gel conversion (DGC including VPT and SAC), using triethylamine (Et<sub>3</sub>N) as a structure-directing agent (SDA). Systematic studies were carried out by varying gel composition, content of alkaline earth metals. MO/Al<sub>2</sub>O<sub>3</sub> (M: Mg, Ca, Sr, and Ba) ratios from 0.025 to 0.10 gave pure M-AFI, however, M-CHA was observed as an impurity with further increase of the MO content. Alkaline earth metals are isomorphously substituted in the framework of AFI judging from their unit cell parameters, NH<sub>3</sub>-TPD and ICP analyses.

**Keywords:** M-AFI; alkaline earth metal; dry-gel conversion; hydrothermal synthesis; isomorphous substitution

### 1. INTRODUCTION

Aluminophosphate molecular sieves are one of new types of microporous material, which were first reported by Wilson *et al.* in 1982 by hydrothermal synthesis.<sup>1</sup> Since then, aluminophosphates with different pore sizes and topology have been synthesized by changing the templates or crystallization condition. The main drawback of them as catalytic materials is low acidity because of neutral tetrahedral framework. The replacement of Al<sup>3+</sup> by divalent cations or P<sup>5+</sup> by tetravalent cations leads to Brønsted acid sites, which are key property for acid catalysis.<sup>2</sup> Silicoaluminophosphates (SAPOs)<sup>3</sup> and other metal substituted aluminophosphates (MeAPOs) were developed by Flanigen *et al.*<sup>4</sup> Recently, we have reported synthesis of AlPO<sub>4</sub>-5 (AFI<sup>5</sup>), AlPO<sub>4</sub>-11 (AEL), AlPO<sub>4</sub>-34 (CHA), and their derivatives with fine particle sizes by dry-gel conversion (DGC) method.<sup>6</sup> Their acidic property depends on amount of silica. However, there is a limitation to incorporate silica into the framework.<sup>6</sup> The addition of other elements expands the number and diversity of the aluminophosphate molecular sieves, and new properties of microporous materials.

Aluminophosphate molecular sieves are very promising materials from the application point of view. Mg-substituted aluminophosphate has strong Brønsted acidity<sup>7</sup> and they have been attracted by many researchers for solid acid catalysts.<sup>8,9</sup> In the present work, we describe the synthesis of AFI molecular sieves with isomorphous substitution of aluminum to alkaline earth metals, such as Mg, Ca, Sr, and Ba by conventional HTS and by DGC methods.

### 2. EXPERIMENTAL

#### 2.1. Synthesis.

The synthesis of M-containing AFI molecular sieves were carried out by hydrothermal synthesis (HTS) and DGC (including SAC and VPT) methods. In

every method, typical gel composition was as follows: 1.0Al<sub>2</sub>O<sub>3</sub>-0.10MO-1.0P<sub>2</sub>O<sub>5</sub>-0.76Et<sub>3</sub>N-45H<sub>2</sub>O (M: Mg, Ca, Sr, and Ba).

In a typical procedure of HTS for Mg-containing AFI synthesis is as follows: aluminum isopropoxide (2.05 g, 5.0 mmol) was slurred in water (1.85 g). To this slurry, 85% phosphoric acid (1.15 g, 5.0 mmol) diluted in water (2.00 g) was added drop wise over a period of 0.5 h with constant magnetic stirring. To the resulting solution, magnesium acetate (0.107 g, 0.5 mmol) was added and the stirring was further continued for 0.5 h. Finally triethylamine (0.384 g, 3.8 mmol) was added drop wise to the mixture and stirred for another 1 h. The resulting hydrogel was charged into a 23-ml Teflon-lined autoclave and statically heated at 175 °C for 24 h.

Vapor-phase transport method (VPT) and steam-assisted conversion method (SAC) were examined for the DGC method.<sup>10,11</sup>

In a SAC method, hydrogel was prepared in the same manner as the case of HTS. The hydrogel was dried at 80 °C in an oil bath with continuous stirring to remove water. When the gel became thick and viscous, it was homogenized manually using a Teflon-rod, and these procedures were continued until it dried. The drying period varied (*ca.* 0.75-1 h) with the gel composition. A white solid formed was ground to a fine powder, and finally transferred in a small Teflon cup (20 mm x 20 mm I.D.). This cup was placed in a Teflon-lined autoclave (23-ml) with the support of a Teflon holder. Small amount of water (*ca.* 0.30 g per 1.00 g of dry gel) was placed at the bottom of the autoclave in such a manner that the external bulk water never came into the direct contact with the dry-gel. The autoclave assembled for DGC method was shown in our previous paper.<sup>6</sup> The crystallization was carried out in steam in an oven with autogenous pressure at 175-200 °C for 24 h.

In VPT method, the initial gel was prepared and dried without the addition of SDA, and the SDA was finally mixed with the external bulk water and placed as the source of vapor in the bottom of the autoclave.

After the crystallization for all cases, the products were washed with distilled water, separated by centrifugation, and dried at 100 °C overnight. The as-synthesized sample was placed in a muffle furnace and heated it in a flow of air (flow rate: 50 ml/min). The temperature was raised from room temperature to 550 °C during 4 h. The sample was kept at this temperature for another 7 h, and finally, cooled to room temperature (in ambient condition) to give calcined sample.

## 2.2. Characterization

The phase purity and crystallinity of the molecular sieves were determined by powder X-ray diffraction (XRD-6000, Shimadzu) with CuK $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Elemental analysis was performed using inductively coupled plasma atomic emission spectroscopy (JICP-PS-1000UV, Leeman Labs Inc.). The crystal size and morphology of the samples were examined by scanning electron microscopy (SEM) using Philips XL30 microscope. Nitrogen adsorption measurements were carried out on a BELSORP 28SA (Bel Japan). Acidity measurements were performed by temperature programmed desorption of ammonia (NH<sub>3</sub>-TPD) on a BEL TPD-66 apparatus (Bel Japan). FT-IR spectra in the framework region were recorded by KBr pellet technique using 0.5 mg of the sample and 100 mg of KBr on a Thermo Nicolet Nexus 470. Unit cell parameters of the samples were calculated by using TREOR 90 program of Material Studio software supplied by Accelrys Inc. (U.K.) using Dell PC (Dimension 8250 series).

## 3. RESULTS AND DISCUSSION

### 3.1. Synthesis of AFI substituted with alkaline earth metals

Figures 1, 2, and 3 show XRD patterns of as-synthesized molecular sieves obtained by hydrothermal synthesis (HTS), and by two types of DGC methods: vapor-phase transport (VPT) and steam-assisted conversion (SAC) methods, respectively. The crystallization was carried out at 175 °C for 24 h for all samples although Ba-AFI by DGC method was done at 200 °C. All M-AFI molecular sieves synthesized by HTS consisted of relatively large crystals having high crystallinity without any impure phase.

Pure AFI phases were also obtained with small particle sizes by DGC method. In XRD pattern of the samples by HTS, the intensity was strongly enhanced in

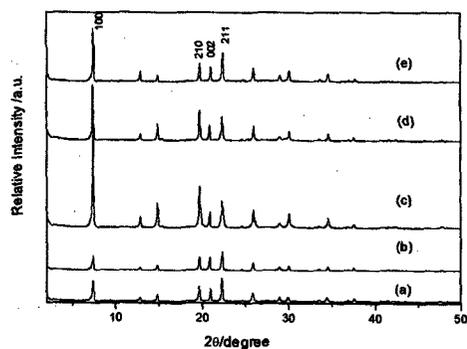


Fig. 1. XRD patterns of as-synthesized samples obtained by HTS method; (a) Mg-AFI, (b) Ca-AFI, (c) Sr-AFI, (d) Ba-AFI, (e) calcined samples of (a) as described in the text.

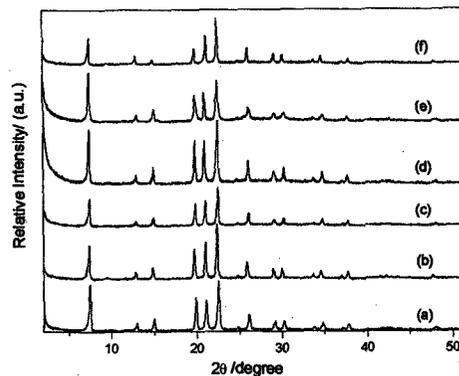


Fig. 2. XRD patterns of as-synthesized samples obtained by VPT method; (a) AFI, (b) Mg-AFI, (c) Ca-AFI, (d) Sr-AFI, (e) Ba-AFI, (f) calcined samples of (b) as described in the text.

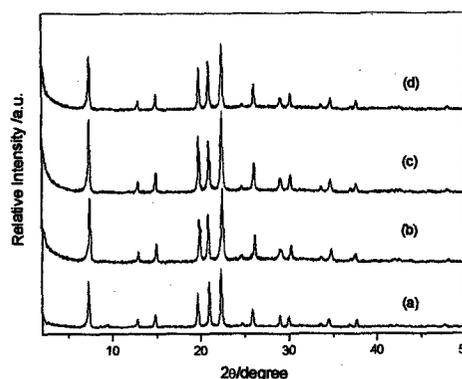


Fig. 3. XRD patterns of as-synthesized samples obtained by SAC method; (a) Mg-AFI, (b) Ca-AFI, (c) Sr-AFI, (d) Ba-AFI.

(002), (210) and (211) planes, which is due to the occurrence of preferred orientation of the crystal.<sup>11</sup> Further more the intensity of 100 plane is more enhanced for Sr and Ba containing AFI as compared to other planes. This means that the crystal growth is more prominent along *c* axis as compared to DGC method. It is noticed from the intensity of XRD that crystallization by HTS method was relatively faster among the three methods. VPT method shows lower intensity than corresponding SAC and HTS methods, and intensity decreases in the following order HTS > SAC > VPT.

Syntheses of M-AFI were performed by varying the starting gel compositions. MO/Al<sub>2</sub>O<sub>3</sub> ratio in the gel was influenced on the purity of AFI. The gel mixture with lower metal content enhances the formation of pure M-AFI, while higher metal content promotes the formation of M-CHA as an impure phase. Mg-AFI with good crystallinity was obtained at lower ratio of MgO/Al<sub>2</sub>O<sub>3</sub>. The ratios from 0.025 to 0.10 gave pure Mg-AFI, however, Mg-CHA phase was observed as an impurity with the further increase of the ratio. Similar phenomena were observed for the crystallization of Ca- and Sr-AFI. Ba-AFI was synthesized at slightly higher BaO/Al<sub>2</sub>O<sub>3</sub> ratio between 0.05-0.20, whereas crystallinity was low as compared to other alkaline earth metals.

Mg-AFI has been reported to be sensitive to the

calcination because the water vapor damages the structure.<sup>12,13</sup> However, Mg-AFI samples in our study are highly stable for the calcination at 550 °C, although some change in the intensity of XRD were observed as shown in Figs. 1e and 2f.

### 3.2. Characterization of M-AFI substituted with alkaline earth metals

Nitrogen adsorption measurement for pure M-AFI samples gave quite similar Type-I isotherms, indicating that every sample has micropores. A typical micropore volume for Mg-AFI is 0.111-0.122 ml. g<sup>-1</sup>, which are typical values of molecular sieves with 12-ring straight channels.<sup>14</sup> The BET surface area by DGC method was found to be slightly higher than that of HTS method.

According to scanning electron micrograms (Fig. 4), the Mg-AFI crystals have hexagonal morphology either as plate or long hexagonal prism. Average sizes of the hexagonal prism were around 10 μm for HTS (Fig. 4c), and small particles less than 1 μm and their agglomerates were observed for DGC method (Fig. 4a and 4b). In DGC method (SAC and VPT), particle size was almost similar with each other. In case of Mg-free AFI, aggregates of needle-like crystallites with the average size of ca. 2 μm were obtained by VPT method. SEM image of the sample did not show occurrence of any amorphous phases. Similar observation was found with other metals. However, crystal sizes decreased in the order: Mg > Ca > Sr > Ba both in HTS and VPT methods: differences of crystalline particles were significant in HTS method.

ICP analysis of the as synthesized samples obtained by VPT method in Table 1 shows that MO/Al<sub>2</sub>O<sub>3</sub> ratio is higher in products than in starting gel except Ba-AFI. These results suggest that alkaline earth metals cations participate in the frame work by the isomorphous substitution of Al<sup>3+</sup>. However, there is a possibility that a part of Ba are not in the framework because Ba<sup>2+</sup> is too large to substitute with Al<sup>3+</sup>.

NH<sub>3</sub>-TPD shows pure AFI has desorption peak (*l*-peak) at about 170 °C, which is due to the physical adsorption of ammonia. However, Mg-AFI has desorption peak (*h*-peak) around 250-350 °C in addition to *l*-peak. This peak is due to the acidity of Mg-AFI by isomorphous substitution of Mg<sup>2+</sup> with Al<sup>3+</sup>. However, no significant *h*-peak was observed for M-AFI except Mg-AFI. These results suggest that they have no appreciable strong acid sites characterized by NH<sub>3</sub>-TPD.

FT-IR spectra of pure AFI and M-AFI in the framework vibration range (800-1500 cm<sup>-1</sup>) were determined for calcined samples. Broad band in the region of 1000-1100 cm<sup>-1</sup> is characteristic of zeolitic materials, which are assigned to asymmetric stretching of tetrahedral Al-O and P-O.<sup>14</sup> Wavenumbers of M-AFI were higher than that of aluminosilicate. The presence of large amount of phosphorous is responsible for this shift.<sup>15-17</sup> Pure AFI and M-AFI exhibited similar pattern of IR spectra. However, the bands shift towards higher frequencies was observed on alkaline earth metals in AFI substituted with Al<sup>3+</sup> in the framework. FT-IR results indicate that strong vibration band around 1132 cm<sup>-1</sup> was shifted towards higher wave number. This shift is due to the concentration of alkaline earth metal in the framework.

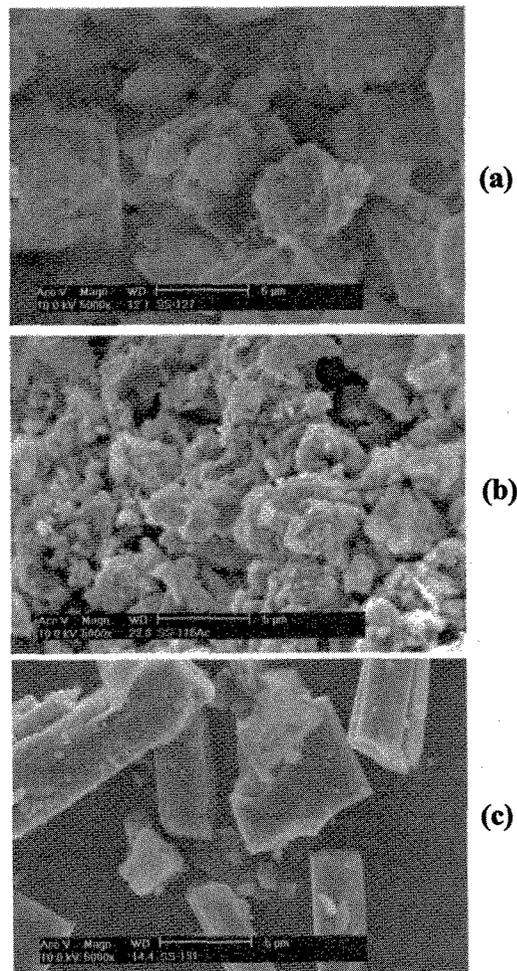


Fig. 4. SEM images of as-synthesized Mg-AFI obtained by (a) SAC, (b) VPT, and (c) HTS methods.

Unit cell parameters were calculated to confirm the isomorphous substitution of alkaline earth metals into the framework of AFI. Because of the difference in T-O bond distance [T=Mg (1.85), Ca (2.17), Sr (2.36), Ba (2.54), Al (1.73) and P (1.54)], an increase in cell volume is expected if Al or P is replaced by other metals.<sup>18,19</sup> If the variation observed in XRD could be taken as evidence that the metal was isomorphically incorporated the framework.<sup>19</sup> Hexagonal unit cell parameters, *a*, *c* and cell volume are shown in Table 2. In the case of the variation of the M-AFI, unit cell parameter *a* and unit cell volume increases as a function of types of metal,

Table 1. Alkaline earth metal in starting gel and products

Sample	MO/Al <sub>2</sub> O <sub>3</sub>	
	Starting gel	M-AFI <sup>a</sup>
AFI	-	-
Mg-AFI	0.1	0.128
Ca-AFI	0.1	0.170
Sr-AFI	0.1	0.174
Ba-AFI	0.1	0.083

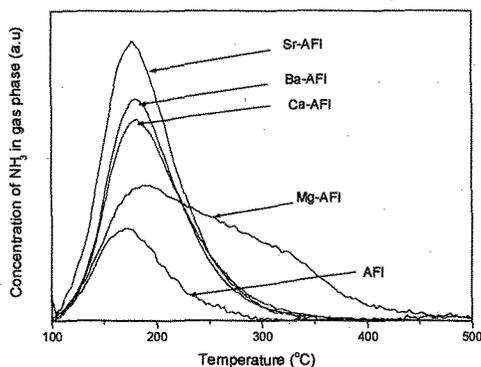


Fig. 5.  $\text{NH}_3$ -TPD profiles of AFI and M-AFI samples

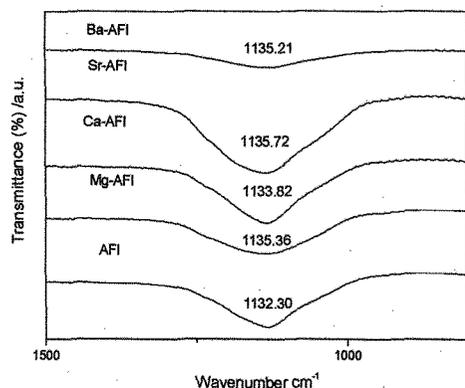


Fig. 6. IR spectra of calcined samples of AFI and M-AFI

Table 2. Unit cell parameters of M-AFI

Sample	Unit cell parameters (Å)		Unit cell volume (Å <sup>3</sup> )
	a=b	c	V
AFI	13.6630	8.4306	1362.96
Mg-AFI	13.7174	8.4645	1379.35
Ca-AFI	13.7133	8.4788	1380.86
Sr-AFI	13.7434	8.4701	1384.31
Ba-AFI	13.7147	8.4735	1381.23

whereas unit cell parameter *c* follows opposite trend. AFI shows lower unit cell parameters *a*, *c* and unit cell volume as compared to M-AFI. These results agree well with earlier work,<sup>18</sup> and support strongly that alkaline earth metals are incorporated in the framework of 12-membered ring AFI structure.

#### 4. Conclusions

M-AFI molecular sieves were successfully synthesized by conventional HTS and non-conventional DGC methods. Crystallization by HTS method was relatively faster as compare to DGC method. Surface areas of M-AFI molecular sieves by DGC method were slightly higher than that of HTS method. From  $\text{NH}_3$ -TPD, Mg-AFI has strong acidic sites, however, clear

acidic property was not found from TPD except Mg-AFI. Unit cell parameters study shows change of unit cell parameter *a* and unit cell volume from Mg to Ba. These results support that alkaline earth metals are isomorphously substituted into the framework.

Further aspects of M-AFI are under investigations, and will be described elsewhere.

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