

## Synthesis of $\text{AlPO}_4\text{-5}$ and $\text{AlPO}_4\text{-11}$ Molecular Sieves by Dry-Gel Conversion Method

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(Received June 7, 2000; CL-000549)

Synthesis of aluminophosphate molecular sieves  $\text{AlPO}_4\text{-5}$  and  $\text{AlPO}_4\text{-11}$  has been studied by dry-gel conversion method using triethylamine and dipropylamine as structure-directing agents (SDAs), respectively. Amount of SDAs and the bulk water as the source of steam played vital roles during the crystallization. SAPO counterparts of the  $\text{AlPO}_4$ 's were also synthesized by this method.

Since the first synthesis of aluminophosphate molecular sieves ( $\text{AlPO}_4\text{-n}$ ) by Wilson and co-workers,<sup>1</sup> these materials have shown immense applications as adsorbents and catalysts.<sup>2</sup> Moreover, having alternate  $\text{AlO}_4$  and  $\text{PO}_4$  tetrahedra and thus being electrically neutral, substitution in the aluminophosphate system by other elements such as Si (SAPO) and metals (MeAPO) gives rise to acidity, which could be utilized in ion-exchange as well as acid-catalysis processes.<sup>3,4</sup>

$\text{AlPO}_4$  molecular sieves are generally prepared by conventional hydrothermal method from the crystallization of an active aqueous aluminophosphate gel containing templating agents such as organic amine or quaternary ammonium ions.<sup>1</sup> However, some  $\text{AlPO}_4$  molecular sieves have also been synthesized in non-aqueous media using different organic solvents instead of water.<sup>5</sup> New and convenient method of synthesis of zeolites is a challenging part of research, and recently dry-gel conversion (DGC) method,<sup>6-9</sup> which was originally introduced as vapor-phase transport (VPT) method of crystallization,<sup>10-12</sup> has been utilized for this purpose. DGC method can be classified to two related but different methods; steam-assisted conversion (SAC, as used by Matsukata et al.<sup>13</sup>) and VPT (as used by Kim et al.<sup>11</sup>) methods. Unlike the hydrothermal synthesis (HTS) method, synthesis of zeolites by DGC allows nearly complete conversion of gel to zeolite, and involves minimization of waste disposal and reduction in reactor volume.<sup>6</sup> Although DGC method has been applied for the synthesis of aluminosilicate<sup>6</sup> and other element-substituted zeolites,<sup>7-9</sup> reports of synthesis of  $\text{AlPO}_4$  molecular sieves by this method are rather scarce. Only recently, Zhang and Gavalas<sup>14</sup> have reported the synthesis of  $\text{ZnAPO-34}$  molecular sieve by VPT method, although they used large amount of water in the liquid phase as the source of steam during the synthesis. Apart from this, mainly  $\text{AlPO}_4$ 's mixed with dense phase, and in some cases unknown or amorphous phase were obtained as briefly reported by Matsukata et al.<sup>13</sup> Here we report for the first time the synthesis of pure  $\text{AlPO}_4\text{-5}$  and  $\text{AlPO}_4\text{-11}$  molecular sieves by dry-gel conversion method. Silicon substitution of these materials to obtain their SAPO counterparts has also been partly investigated by this method.

The synthesis of  $\text{AlPO}_4\text{-5}$  and  $\text{AlPO}_4\text{-11}$  by dry-gel conversion method was performed by above-mentioned SAC and VPT methods. In SAC method, taking initial gel composition:  $1\text{Al}_2\text{O}_3\text{-xSDA-1P}_2\text{O}_5\text{-40H}_2\text{O}$  (SDA:  $0.3 \leq x \leq 1$ ), appropriate

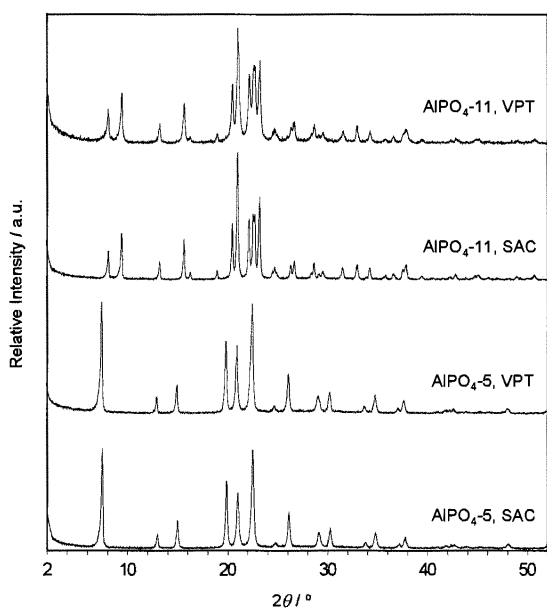
amount of aluminum isopropoxide was mixed with de-ionized water, followed by the dropwise addition of diluted  $\text{H}_3\text{PO}_4$  with continuous stirring. Afterwards, the SDA was added, and the homogeneous gel was dried at  $80^\circ\text{C}$  with constant stirring for about 1 h. Although the presence of very small water adhered in the dry gel could not be neglected, the gel was dried as much as possible. The dry gel was ground to a fine powder and transferred to a small Teflon cup (20 mm i.d.  $\times$  20 mm). This cup was placed in a Teflon-lined autoclave ( $23\text{ cm}^3$ ) with the support of a Teflon holder. Small amount (ca. 0.2–0.3 g per g of dry gel) of external water (which was the source of steam) was kept at the bottom of the autoclave in such a manner that the dry gel in the cup never came into the direct contact with external bulk water. The crystallization was carried out at  $175^\circ\text{C}$  for 24–72 h. In case of VPT method, the initial gel was prepared and dried without the addition of SDA, and the SDA was finally taken with the water at the bottom of the autoclave so as to be supplied as vapor. Finally, the sample was removed from the cup, washed with water, and dried in air at  $90^\circ\text{C}$ . The organic material was removed by calcination in air at  $550^\circ\text{C}$ . For comparison, the  $\text{AlPO}_4$  samples were also synthesized by conventional HTS method. In the case of SAPO synthesis by SAC method, colloidal silica (Ludox AS-40) was added prior to the addition of SDA. The samples were characterized by several physicochemical techniques such as XRD, SEM, TG-DTA, ICP and  $\text{N}_2$ -adsorption. The typical gel composition, crystallization conditions, and products are summarized in Table 1.

**Table 1.** Gel compositions, conditions and products

Method <sup>a</sup>	Dry gel				Liquid phase		Time /h	Product
	$\text{Al}_2\text{O}_3$	$\text{P}_2\text{O}_5$	$\text{SiO}_2$	SDA	$\text{H}_2\text{O}$	SDA		
SAC	1.0	1.0	0	1.0 <sup>b</sup>	1.5	0	24	$\text{AlPO}_4\text{-5}$
VPT	1.0	1.0	0	0	1.5	1.0 <sup>b</sup>	24	$\text{AlPO}_4\text{-5}$
SAC	1.0	1.0	0	0.3 <sup>b</sup>	1.5	0	24	$\text{AlPO}_4\text{-5}$
VPT	1.0	1.0	0	0	1.5	0.4 <sup>b</sup>	24	$\text{AlPO}_4\text{-5}$
SAC	1.0	1.0	0.3	1.0 <sup>b</sup>	1.5	0	24	SAPO-5
SAC	1.0	1.0	0.6	1.0 <sup>b</sup>	1.5	0	24	SAPO-5
SAC	1.0	1.0	0	1.0 <sup>c</sup>	1.5	0	72	$\text{AlPO}_4\text{-11}$
VPT	1.0	1.0	0	0	1.5	1.0 <sup>c</sup>	72	$\text{AlPO}_4\text{-11}$
SAC	1.0	1.0	0	0.3 <sup>c</sup>	1.5	0	72	$\text{AlPO}_4\text{-11}$
VPT	1.0	1.0	0	0	1.5	0.4 <sup>c</sup>	72	$\text{AlPO}_4\text{-11}$
SAC	1.0	1.0	0.3	1.0 <sup>c</sup>	1.5	0	24	SAPO-11
SAC	1.0	1.0	0.6	1.0 <sup>c</sup>	1.5	0	24	SAPO-11

<sup>a</sup>SAC and VPT denote steam-assisted conversion and vapor-phase transport, respectively. <sup>b</sup>Triethylamine was used. <sup>c</sup>Dipropylamine was used.

As revealed by the powder XRD patterns (Figure 1), the as-synthesized samples obtained by dry-gel conversion (both SAC and VPT methods) were well crystallized without any impure phase and resembled the samples synthesized by HTS method.



**Figure 1.** XRD patterns of the as-synthesized  $\text{AlPO}_4\text{-5}$  and  $\text{AlPO}_4\text{-11}$  samples made by SAC and VPT methods.

Pure  $\text{AlPO}_4\text{-5}$  and  $\text{AlPO}_4\text{-11}$  samples were obtained using triethylamine (TEA) and dipropylamine (DPA), respectively as SDA. We studied the synthesis by varying the amount of SDA in the starting gel. Although we usually used the SDA to  $\text{Al}_2\text{O}_3$  ratio ( $x$ ) of 1.0, it was found that there was minimum requirement of the SDA quantity. For both pure  $\text{AlPO}_4\text{-5}$  and  $\text{AlPO}_4\text{-11}$  syntheses, the minimum molar compositions ( $x_{\text{min}}$ ) were 0.3 and 0.4 for SAC and VPT methods, respectively. Below these lower limits,  $\text{AlPO}_4\text{-tridymite}$  contaminated the product in all cases.

When the synthesis was carried out in the absence of small amount of external bulk water at the bottom of the autoclave, amorphous phase was obtained in all cases. Thus the apparently adhered water in the dry gel could not contribute to the crystallization. It was interestingly observed that a minimal amount of external bulk water as the source of steam was necessary for the successful crystallization. To investigate this, the amount of external bulk water taken at the bottom was varied with a fixed amount of the dry gel. The threshold  $\text{H}_2\text{O}(\text{bulk})/\text{Al}_2\text{O}_3$  molar ratio for the successful synthesis of  $\text{AlPO}_4\text{-5}$  and  $\text{AlPO}_4\text{-11}$  was found to be 1.4 and 1.1, respectively. However, in our present study, increasing the amount of bulk water at the bottom did not show much change in the crystallinity of the outcoming product.

After calcination,  $\text{AlPO}_4\text{-5}$  samples made by SAC and VPT methods had BET surface areas of 277 and 273  $\text{m}^2\text{g}^{-1}$ , respectively, whereas  $\text{AlPO}_4\text{-11}$  samples made by SAC and VPT methods showed the surface areas of 170 and 188  $\text{m}^2\text{g}^{-1}$ , respectively. The micropore volumes measured by  $\text{N}_2$  adsorption method for  $\text{AlPO}_4\text{-5}$  samples by SAC and VPT were found to be 0.087 and 0.079  $\text{cm}^3\text{g}^{-1}$ , respectively, and for  $\text{AlPO}_4\text{-11}$  samples by SAC and VPT were 0.052 and 0.041  $\text{cm}^3\text{g}^{-1}$ , respectively. These adsorption results indicated that porosities were similar between samples made by two methods, and pores were not blocked by any occluded material. In the  $^{27}\text{Al}$  MAS NMR spectra of the as-synthesized samples obtained by both SAC and VPT methods, a major peak around 37.4 ppm and 35.4 ppm was observed for  $\text{AlPO}_4\text{-5}$  and  $\text{AlPO}_4\text{-11}$ , respective-

ly, which was consistent with the tetrahedral framework nature of the Al in the samples.<sup>15</sup> SEM images of  $\text{AlPO}_4\text{-5}$  showed spherical morphology formed by small plate like crystals. Average sizes of the spheres were 5  $\mu\text{m}$  (VPT) to 10  $\mu\text{m}$  (SAC) and that of the plates were 1  $\mu\text{m}$  (VPT) to 2  $\mu\text{m}$  (SAC).  $\text{AlPO}_4\text{-11}$  showed cluster of needle-like morphology, and the average size of the needles was 7.5  $\mu\text{m}$  in both VPT and SAC. ICP analysis of the as-synthesized samples showed  $\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5$  ratio near to 1 and the same as the initial gel. As summarized in Table 1, SAPO-5 and SAPO-11 could be also prepared by following DGC method using TEA and DPA as SDAs, respectively. The amount of silicon incorporated could be also varied.

From different physicochemical characterization techniques it was noticed that the DGC methods worked as effectively as HTS method. The yields of  $\text{AlPO}_4$  and SAPO samples made by DGC ranged 75–90% and were about 10% higher than that by HTS; otherwise the samples showed similar characteristics to that obtained by HTS method and there were no drastic differences. Our method of synthesis of  $\text{AlPO}_4$  molecular sieves is unique in the sense that the amorphous dry gel was directly converted into the crystals, and very small amount of water was enough for this conversion. Moreover, the syntheses were successful whether the SDA was mixed with the initial gel and dried as in SAC method, or taken as bulk at the bottom of the autoclave with water as in VPT method. Although DGC method has not been widely applied for the synthesis of  $\text{AlPO}_4$  molecular sieves so far, it should definitely contribute to the understanding of the gel chemistry and shed some light on the mechanism of nucleation and crystallization, and participation of the SDA during the synthesis. For the purpose of further use as catalysts, investigation of other metal-substituted  $\text{AlPO}_4$ 's is in progress.

This work was supported by the New Energy and Industrial Technology Development Organization (NEDO). R.B. thanks Japan Society for the Promotion of Science (JSPS) for a research fellowship.

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