GAM-3: A zeolite formed from AlPO₄-5 via multistep structural changes

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Abstract: The interzeolite conversion of AlPO₄-5 gave a new zeolitic material GAM-2 and the calcination caused further structural changes, forming a new zeolite GAM-3 with a 3-dimensional 12-8-6 rings pore system. This is the first synthetic example for zeolite formed through multistep structural changes in the metastable phase.

Experimental Procedures

Synthesis of aluminophosphate molecular sieve, AlPO₄₋₅

The typical synthetic procedure of AlPO₄-5 was as follows. To a mixture of H_3PO_4 (19.5 g, 85wt% in water, NACALAI TESQUE), Al[OCH(CH₃)₂]₃ (26.6 g, Aldrich) and triethylamine (10.5 g, NACALAI TESQUE) in distilled water (32.2 g) was added diluted HF (0.38 g, 55 wt% in water, Stella Chemifa Co.) in distilled water (2.0 g). The resulting mixture was stirred at room temperature for 2 h, and then transferred into a Teflon-lined autoclave (volume 110 mL). The hydrothermal synthesis was performed at 170 °C for 6 h. The product was filtered by suction, washed with distilled water and dried at 90 °C for 10 h. Then, calcination was performed at 600 °C (ramping rate 1 °C/min) for 6 h under air flow (100 ml/min) to yield the parent AlPO₄-5 zeolite (12.5 g).

Synthesis of GAM-2

The interzeolite conversion of AlPO₄-5 to GAM-2 was performed as follows. To a mixture of pyrrolidine (0.58 g, Aldrich) in distilled water (4.1 g) was added the parent AlPO₄-5 (1.0 g). The resulting suspension was stirred at room temperature for 1 h, and then transferred to a Teflon-lined autoclave (volume 30 mL). The hydrothermal treatment was carried out 170 °C for 7 days. The reaction mixture was cooled down, and the formed solid was filtrated by suction, washed with distilled water thoroughly and dried at 90 °C for 6 h to yield GAM-2 (0.35 g).

Preparation of GAM-3

The GAM-2 (0.17 g) was calcined at 550 °C (ramping rate 1.0 °C/min) for 6 h under air flow (100 ml/min) to yield a GAM-3 (0.14 g).

Characterization

Powder X-ray diffraction (XRD; Shimadzu XRD-6000) was measured using Cu K α radiation (λ = 1.5418 Å). Elemental analyses were performed using X-ray fluorescence spectroscopy (XRF; Bruker S8 TIGER). Nitrogen adsorption isotherm measurements were performed using an absorption analyzer (Bel Japan Belsorp 28SA). Thermogravimetric (TGA) and differential thermal analysis (DTA) were

conducted using an apparatus (Shimadzu DTG-50) with the ramp rate at 10 °C/min under an air stream. The crystallite size and morphology were measured using field emission scanning electron microscopy (FE-SEM; Hitachi High-Technologies Co. S-4800).

Solid-state ³¹P and ²⁷Al magic angle spinning (MAS) nuclear magnetic resonance (NMR) and ³¹P MAS NMR spectra were recorded at ambient temperature using a 4 mm diameter zirconia rotor with a spinning rate of 6 kHz (JEOL ECA-500 NMR spectrometer). Further 1D and 2D solid-state MAS NMR measurements took place by using an AVANCEIII 400WB spectrometer (Bruker Biospin K.K., Japan) and using a 3.2 mm VT-MAS probe with zirconia rotor. ²⁷Al 3QMAS NMR spectrum with z-filter was also measured with {¹H} decoupling and rotor spinning rate of 24 kHz. ²⁷Al→³¹P HETCOR 2D spectrum with a weak {¹H, ²⁷Al} double decoupling sequence was corrected at rotor spinning rate of 15 kHz. Pulse parameters were optimized by reference to a previous study [Ref. 1]. {¹H}-¹³C CP/MAS spectrum for GAM-2 was collected at 100.62 MHz with a spinning rate of 6 kHz for ¹³C. Furthermore, ¹H MAS spectra were also measured at 400.12 MHz with a spinning rate of 67 kHz for ¹H to reduce strong dipole-dipole interaction of ¹H–¹H using a 1.3 mm H-X very fast MAS probe. (NH₄)₂HPO₄, 1.0 M AlCl₃ solution, and adamantane powder were used as secondary reference materials of chemical shift for ³¹P, ²⁷Al, ¹³C, and ¹H nuclei.

Crystal structure analysis

The accurate XRD pattern for structure analysis was obtained using a D8-ADVANCE V α rio-1 powder diffractometer (Bruker AXS, Japan) with a modified Debye-Scherrer geometry using Cu K α 1 radiation. Samples were packed into a borosilicate glass capillary tube with an inner diameter of 0.5 mm ϕ . The diffractometer was equipped with a 1D position sensitive detector VANTEC-1 (Bruker AXS, Japan).

First, lattice constant and space group were determined by the indexing analysis using the program Conograph [Ref. 2]. Initial structure model of GAM-2 was determined by the direct space method using the program FOX [Ref. 3]. This analytical technique was referred to our previous study [Ref. 4]. In the direct space method, some molecular structure is introduced into the unit cell and their packing structure is analyzed. In this analysis, the local structure information obtained from the NMR measurement determines the appropriate number of virtual molecules. As a result, three AlO₄, three PO₄, one pyrrolidine were introduced into unit-cell. The packing structure was uniquely determined by the parallel-tempering algorithm. The obtained initial structure of GAM-2 was modified and refined by the Rietveld analysis using the program RIETAN-FP [Ref. 5]. In GAM-2, several small peaks were unindexed (observed at $2\theta = 12.26^{\circ}$, 14.26° , 15.89° , 16.41° , 16.85° , 22.66° , 23.67° , 25.22° , 26.72° , 32.97° and 34.06°), and these peaks were excluded from the Rietveld refinements.

During the structure refinement, we imposed restraints upon all the Al–O bond length $(1.63 \pm 0.07 \text{ Å})$, all the P–O bond length $(1.58 \pm 0.05 \text{ Å})$, and all the O–Al, P–O bond angles $(109.47 \pm 5.0^{\circ})$. As the *R* factor decreased, we gradually reduced the weight of restraint conditions. A soft-constraint of the molecular geometry of pyrrolidine was adopted in GAM-2. Site O10 in GAM-2 was assumed as OH⁻ group. In order to simplify the analysis, hydrogen atoms in both adsorbed water molecules and OH⁻ groups were omitted, and two virtual atoms (WO and Oh) were introduced. The virtual atom WO has the X-ray scattering amplitude corresponding to the summation of those of one O and two H atoms, and the other has that of one O atom and one H atom. The isotropic atomic displacement parameters,

B, were constrained as follows; B(A|n) = B(Pm), B(O1) = B(On), B(WO1) = B(WOm), and B(N) = B(Cn) = B(Hm) (*n* and *m* are site numbers). Obtained structure models were visualized by means of VESTA3 [Ref. 6].

The framework structure of GAM-2 has an isolated P–OH termination in micropore. NH moiety of pyrrolidine is close to –OH part and the distance of N1–O10 was 0.27 nm. Therefore, pyrrolidine would be stabilized by strong hydrogen bonding of N–H···O. The P–OH moiety is belong to *double zig-zag chain* (*dzc*) unit. Additionally, the Al1–O4–Al1 connectivity whose bond angle is close to180° is observed in the framework. When the position at O4 site is set in special position (0.5, 0.0, 0.90824), AlO₄ tetrahedron of Al1 site is largely distorted and the bond length of Al1–O4 is converged to an inappropriate large value. Therefore, a split atom model was adopted for the O4 site. A one WO site with site occupancy of 0.50(1) was detected near Al1–O4–Al1 connectivity (corresponds to 4-ring).

On the other hand, the lattice constants of *b* and *c* of GAM-3 are very similar to those of GAM-2, and space group of GAM-3 coincided with GAM-2 ($P2_12_12$). We consider the crystal structure of GAM-3 would be very similar to GAM-2. After calcination of GAM-2, P–OH group vanished, then a microporous structure composed of four-connected T atom only as shown Fig.4 was elucidated. It was found that the framework structure of GAM-3 is typical zeolite structure. 12-ring and 8-ring channels are visible along the *c*-axis. Both channels are connected to each other via a 6-ring pore window both in the *a*-axis direction and in the *b*-axis direction.

Six adsorbed water sites (defined as WO) were detected in micropores. The total amount of water is calculated to be 19.4 molecules per unit-cell which indicate 19.2 wt%. Actually, a weight loss of water up to 200°C was ca. 12 wt% and is smaller than the calculated value. This discrepancy is probably due to the presence of non-porous amorphous or unknown phases in the sample. In the indexing analysis of GAM-3, several broad peaks (observed at $2\theta = 7.87^{\circ}$, 9.40°, 12.43°, 13.37°, 15.00°, 22.07°, and 26.23°) were unindexed, indicating the formation of unknown byproduct phase. By omitting these peaks, the lattice constants close to that of GAM-2 could be obtained. Final structure analysis, these peaks were excluded from the Rietveld refinements also. Since the *B*(WO) value was converged a very large value (*approx.* 23), which indicates a highly positional disorder state, therefore, the *B*(WO) was fixed at 20.

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Table S3. Crystallographic Information File (CIF) of GAM-3.



Figure S1. Structure of AlPO₄-5 with **AFI** topology. FD is the framework density. The red and light green arrows represent the *a*- and *b*-axes. The black line represents the unit cell. Light blue stands for O atoms, orange for P and reddish pink for Al.



Figure S2. Powder XRD chart of the obtained product by *izc*AP using as-synthesized AlPO₄-5 in the presence of pyrrolidine.



Figure S3. Powder XRD patterns of AlPO₄-5 and the obtained products by the *izc*AP for different synthetic periods.



Figure S4. Powder XRD patterns of GAM-2 and GAM-3 prepared at different temperatures under airflow conditions.



Figure S5. FE-SEM images of AlPO₄-5 zeolite (a), GAM-2 (b) and GAM-3 zeolite (c).

AlPO₄-5 zeolite showed a typical hexagonal morphology. A tiny particle on the surface of GAM-2 was often observed as shown in image (**d**), which is most likely to be amorphous crystals. Due to the imcomplete structural change into GAM-3 zeolite, some large aggrigates were observed as impurity particles (by-product) corresponding to amorphous and/or an unknown crystals in the SEM image of GAM-3 (**e**). This observed finding suggests that, at the same time as the phase change from GAM-2 to GMA-3, a part of GAM-2 changed to aggrigates of unknown crystalline phase due to imcomplete structural change.



Figure S6. TG-DTA chart of GAM-2.



Figure S7. Solid-state ²⁷Al MAS NMR spectra of AlPO₄-5 (down) and GAM-2 (up).



Figure S8. Solid-state ³¹P MAS NMR spectra of AlPO₄-5 (down) and GAM-2 (up). Asterisks indicate spinning side band.



Figure S9. Solid-state ²⁷Al 3QMAS NMR spectrum of GAM-2.



Figure S10. Solid-state ²⁷Al \rightarrow ³¹P 3QHETCOR spectra with {¹H, ²⁷Al} double decoupling spectra of GAM-2. The projected F2 spectra of ²⁷Al 3QMAS and the ³¹P MAS spectra were overlaid for comparison.



Figure S11. Ultra-high-speed solid-state ¹H MAS NMR spectrum of GAM-2.



Figure S12. Solid-state ${}^{1}H \rightarrow {}^{13}C$ CP/MAS NMR spectrum of GAM-2.



Figure S13. Observed (red crosses), calculated (light blue solid line) and difference (blue) patterns obtained by the Rietveld refinement for GAM-2. Green tick marks indicate the peak position of possible Bragg reflections.



Figure S14. Framework structures of (b) GAM-2, the structurally similar zeolites (a) lithosite (**-LIT**) and (c) SSZ-61 (***–SSO**) and (d) GAM-3. FD is the framework density. Only the positions of the tetrahedrally coordinated atoms (T-atoms) are shown. The T-O-T moieties are represented by straight lines.



Figure S15. TG-DTA chart of GAM-3.



Figure S16. Solid-state ¹H MAS NMR spectrum of GAM-3.



Figure S17. Solid-state ²⁷Al MAS NMR spectrum of GAM-3.



Figure S18. Solid-state ³¹P MAS NMR spectrum of GAM-3.



Figure S19. Solid-state ²⁷Al 3QMAS NMR spectrum of GAM-3.



Figure S20. Observed, calculated and difference patterns obtained by the Rietveld refinement for GAM-3. Green tick marks indicate the peak positions of possible Bragg reflections. Several unindexed peaks (observed at $2\theta = 7.87^{\circ}$, 9.40°, 12.43°, 13.37°, 15.00°, 22.07°, and 26.23°) were excluded from the structure refinement.



Figure S21. FT-IR spectra of AlPO₄-5, GAM-2 and GAM-3.



Figure S22. N₂ adsorption isotherms of AlPO₄-5 and GAM-3 (left) and water adsorption isotherm of GAM-3 (right).

The obtained amount of water could be converted to 14.4 wt%, which is almost the same as the weight loss of TG-DTA shown in Fig. S15. According to the Ref.s7 (below), the water sorption capacity of AlPO₄-5 is 21.2 wt%, which is about 7 wt% larger than GAM-3. In their water adsorption isotherm of AlPO₄-5, two-step adsorption processes were reported, which is related to its structural characteristics and results from pore filling of 6-ring channels followed by the capillary condensation in 1D 12-ring straight channels. On the other hand, the water adsorption isotherm of GAM-3 is monotonically increased with increasing P/P_0 , such as the Freundlich type. In addition, argon gas adsorption measurement for GAM-3 was carried out for comparison with nitrogen adsorption, however, a specific surface area was only 11.5 m²/g.

Reference

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Figure S23. Speculative mechanism of *izc*AP, AlPO₄-5 \rightarrow GAM-2. (The red, light green and blue arrows represent the *a*-, *b*- and *c*-axes. The black lines represent the unit cell. Only the positions of the tetrahedrally coordinated atoms (T-atoms) are shown and the T-O-T moieties are represented by straight lines.)

The framework structure of GAM-2 includes a dzc structure composing by only 4-rings. In AlPO₄-5, when one of the three 6-rings at the 6^3 unit shared by their sides in the *afi* composite building unit (CBU) (6^26^3) dissociates and re-bonds at the 6-ring at 6^2 unit to form a new double 4-rings, the new unit structure gives two 4-rings and two 6-rings (4^26^2), and these 4- and 6-rings constitute a dzc and 6-rings facing at the *a-b* plane in GAM-2. Thus, it seems that the parent AlPO₄-5 and GAM-2 have local structural similarities. Upon this consideration, the 6-rings of the *afi* which constructs main 12-rings pore channel in AlPO₄-5 are facile to dissociate their bonds rather than structural rigid 4-rings, promoting the formation of nano-parts which consequently triggered off the *izc*AP.

Table S1. Conditions for the PXRD experiment and crystallographic information obtained therein for GAM-2 and GAM-3.

Compound name	GAM-2	GAM-3	
Estimated chemical composition	4(C ₄ H ₉ N) 0.99(H ₂ O)	19.4(H ₂ O)	
	$[Al_{12}P_{12}O_{46}(OH)_4]$	$[Al_{12}P_{12}O_{48}]$	
Space group	P2 ₁ 2 ₁ 2	P21212	
a / nm	1.67631(4)	1.50698(6)	
<i>b</i> / nm	1.74946(2)	1.79944(4)	
<i>c</i> / nm	0.497975(4)	0.503671(8)	
Unit-cell volume / nm ³	1.46038(3)	1.36581(6)	
2θ range / °	4.0-100.1	5.5-100.1	
Step size $(2\theta) / \circ$	0.016346	0.016346	
Profile range in FWHM	10	10	
Number of observations	5903	5965	
Number of contributing reflections	919	859	
Number of refined structural parameters	110	77	
Number of constraints	101	60	
<i>R</i> -factors obtained by Rietveld analysis			
R _{wp}	0.052	0.029	
R _p	0.039	0.022	
R_F	0.030	0.009	
R _{Bragg}	0.040	0.017	
R _{exp}	0.038	0.012	
χ^2	1.83	5.80	

#====						
# CRY #	STAL DATA					
data_	VESTA_phase_1					
			'GZ 16. 17. 90 90 90 90 18	M-2' 7631(2) 4946(2) 7975(4) 21 21 2'		
loop_ _spac 'x '- 'x	e_group_symop , y, z' x, -y, z' x+1/2, y+1/2, +1/2, -y+1/2,	o_operation_x -z' -z'	yz			
loop_ a a a a a a a a a _	tom_site_labe tom_site_frac tom_site_frac tom_site_occu tom_site_occu tom_site_wyck tom_site_ddp_ tom_site_U_is tom_site_type 0.5259(4) 0.7036(4) 0.1995(4) 0.8615(3) 0.6456(3)	el tt_x tt_y tt_z upancy tetry_multipl toff_symbol type 0.9080(3) 0.0357(3) 0.1198(4) 0.1231(4)	<pre>icity 0.828(1) 0.180(1) 0.756(1) 0.256(1) 0.675(1)</pre>	1 1 1 1	4 c Uiso 4 c Uiso 4 c Uiso 4 c Uiso 4 c Uiso	0.0092(4) 0.0092(4) 0.0092(4) 0.0092(4) 0.0092(4)
P2 P3 O1 O2 O3 O4 O5 O6 O7 O8 O9 O10 O11 O12 O13 N1 C2	0.6456(3) 0.6300(3) 0.5973(6) 0.6849(7) 0.5609(6) 0.514(2) 0.1438(7) 0.1729(8) 0.6487(6) 0.1831(7) 0.8041(6) -0.0510(6) 0.2998(7) 0.6813(7) 0.5591(6) 0.023(1) 0.142(1)	0.1231(4) 0.8741(4) 0.8911(7) -0.0597(6) 0.8656(8) 1.002(3) 0.8514(7) 0.8117(7) 0.0939(6) 0.6972(6) 0.0501(6) 0.1007(6) 0.8063(6) 0.1375(6) 0.116(1) 0.189(1)	0.675(1) 0.309(1) 0.589(2) 0.227(3) 0.111(2) 0.909(3) 0.559(2) 0.082(2) 0.384(2) 0.692(3) 0.227(3) 0.194(3) 0.711(3) 0.757(3) 0.714(3) 0.819(4)	1 1 1 1 0.5 1 1 1 1 1 1 1 1 1 1 1	4 c Uiso 4 c Uiso	0.0092(4) 0.0092(4) 0.0153(9) 0.027(3) 0.027(3)
C2 C3 C4 C5 H6 H7 H8 H9 H10 H11 H12 H13 H14 W01	0.142(1) 0.168(1) 0.054(1) 0.15(1) 0.174(9) 0.209(8) 0.18(1) 0.05(1) 0.02(1) 0.09(1) 0.09(1) -0.01(1) 0.5	0.109(1) 0.113(1) 0.194(1) 0.064(1) 0.228(7) 0.089(8) 0.12(1) 0.220(9) 0.04(1) 0.03(1) 0.11(1) 0	0.519(4) 0.706(4) 0.732(5) 1.01(3) 0.74(4) -0.19(4) 0.52(3) 0.56(4) 0.86(3) 0.52(4) 0.84(4) 0.57(3) 0.512(6)	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 0.50(1)	4 c Uiso 4 c Uiso	0.027 (3) 0.027 (3)

Al Al P P O O O O O O O O O O O O O

C C C H

H H H H H H H O

Table S2. Crystallographic Information File (CIF) of GAM-2.

Note: The WO site is a virtual atom site that simplifies adsorbed water molecules. Scattering amplitudes corresponding to the summation of those of one oxygen atom and two protons were applied at the WO site. Site O10 was assumed as OH⁻ group and its scattering amplitudes corresponding to the summation of those of one O and one H atom.

#======							
# CRYST	AL DATA						
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_chemica	al_name_com	mon	' GA	AM-3'			
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_cell_le	ength_b		17.	.9944(4)			
_cell_le	ength_c		5.0	03671(8)			
_cell_a	ngle_alpha		90				
_cell_a	ngle_beta		90				
_cell_a	ngle_gamma		90				
_space_q	group_name_	H-M_alt	'P	21 21 2'			
_space_q	group_IT_nu	mber	18				
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-x+. !v+1	$1/2, Y^{+}1/2,$	-2					
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ator	m site labe	1					
_ator	m_site_frac	+ + v					
_ator	m_site_frac	t_v					
_ator	m_site_frac	t_y					
_ator	m_site_occu	c_2 nancy					
	m_site_summ	etry multipl	icity				
_ator	m site Wyck	off symbol	rerey				
_ator	m site ado	tvne					
_ator	m sito II is	o or equiv					
	m_site_type	o_or_equiv					
	0 502(1)		0 801 (3)	1	1 0	Uico	0.016(1)
A12	0.352(1)	0.0001(0)	0.001(3)	1	4 0	Uiso	0.010(1)
AI2	0.700(1)	0.000(1)	0.100(3)	1	4 0	UISO	0.010(1)
ALS 1	0.200(1)	0.7204(0) 0.2295(7)	0.001(3)	1	4 0	UISO	0.016(1)
F T	0.0094(0)	0.2205(7)	0.50099	1	4 0	UISO	0.010(1)
FZ D2	0.010(1)	0.1333(0)	0.099(3)	1	4 C	UISO	0.010(1)
P 3	0.7033(9)	0.9117(9)	0.279(3)	1	4 C	UISO	0.016(1)
01	0.033(2)	0.092(1)	0.334(0)	1	4 C	UISO	0.025(2)
02	0.734(1)	-0.004(2)	0.233(9)	1	4 C	UISO	0.025(2)
03	0.635(2)	0.897(1)	0.064(5)	1	4 C	UISO	0.025(2)
04	0.209(2)	0.760(1)	0.619(6)	1	4 C	UISO	0.025(2)
05	0.263(2)	0./38(1)	0.124(7)	1	4 C	UISO	0.025(2)
06	0.620(2)	0.110(1)	0.382(5)	1	4 C	Ulso	0.025(2)
07	0.298(2)	0.636(2)	0.763(8)	1	4 C	Ulso	0.025(2)
08	0.805(2)	0.139(2)	0.245(8)	1	4 C	Ulso	0.025(2)
09	0.897(2)	0.267(2)	0.213(5)	1	4 C	Ulso	0.025(2)
010	U.381(2)	0.776(2)	U./51(6)	1	4 C	Ulso	0.025(2)
OII	0.6/6(2)	0.089(1)	0.886(4)	1	4 C	Ulso	0.025(2)
012	0.508(2)	0.1124(7)	0.793(6)	1	4 c	Ulso	0.025(2)
WOI	0.38(2)	0.70(1)	0.00(5)	0.18(5)	4 c	Ulso	0.2533
WO2	0.559(2)	0.446(2)	0.104(4)	1	4 c	Uiso	0.2533
WO3	0.425(2)	0.462(2)	0.686(7)	1	4 c	Uiso	0.2533
WO4	0.427(2)	0.611(1)	0.583(8)	1	4 c	Uiso	0.2533
WO5	0.472(4)	0.076(1)	0.22(1)	0.69(2)	4 c	Uiso	0.2533
WO6	0.571(3)	0.691(2)	0.489(7)	0.99(4)	4 C	Uiso	0.2533

Table S3. Crystallographic Information File (CIF) of GAM-3.

Note: The WO site is a virtual atom site that simplifies adsorbed water molecules. Scattering amplitudes corresponding to the summation of those of one oxygen atom and two protons were applied at the WO site. All U(WO) was fixed as 0.2533 (B(WO) = 20).

Al Al P P O O