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Location and orientation of the *N,N*-diisopropylethylamine template molecule in the $\text{AlPO}_4\text{-18}$ framework by X-ray synchrotron diffraction and molecular modelling

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ABSTRACT

Phase pure AlPO_4 with the $\text{AlPO}_4\text{-18}$ (AEI) structure was synthesised using *N,N*-diisopropylethylamine as a template. Using a combination of X-ray powder diffraction and computational methods, the location and orientation of the *N,N*-diisopropylethylamine molecules inside the cages of the AEI structure were determined. Thermogravimetric analysis confirmed that the number of template molecules per unit cell was consistent with the diffraction study. We unequivocally show that only one template molecule is present in each cage of the crystalline AEI material. Our work demonstrates that a combined approach enables accurate structure resolution of such complex materials.

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1. Introduction

Since the discovery of microporous aluminophosphates and their heteroatom substituted variants [1–3], many studies have been undertaken in the synthesis, *in situ* and *ex situ* characterisation, and application, including shape-selective catalysis, of these materials [4–14]. Small-pore systems, such as $\text{AlPO}_4\text{-18}$ (AEI) and $\text{AlPO}_4\text{-34}$ (CHA), have attracted considerable attention because of their ability to perform highly regioselective oxidation of alkanes and selective conversion of methanol to light olefins [15]. Recently, these materials have been targeted for application as catalysts in environmental control technologies [16,17]. One of the key factors in the preparation of such materials is the choice and concentration of organic bases that act as structure-directing agents (SDAs) during the synthesis. For the preparation of both AEI and CHA, the presence of a

specific SDA facilitates the formation of a cage structure. The cage in both materials is the same, but differences in the stacking of these cages give rise to crystallographically distinct phases (Fig. 1).

When small templates such as triethylamine (TEA) are used in the preparation of CHA structured materials, it has been suggested that two template molecules are necessary to template the cage, particularly during nucleation [18]. Competition between the AFI and CHA frameworks occurs in the presence of Co [18–20], which arises from the need for charge compensation by the template. Thus, it can be concluded that the AFI structure is less dependent on specific structure-directing agents and the template concentration. Recently, we showed that methyldicyclohexylamine exclusively produced the AFI structure without formation of any other competing phases [21]. While $\text{Me-AlPO}_4\text{-34}$ (*i.e.*, containing heteroatoms such as

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Fig. 1. Structures of $\text{AlPO}_4\text{-18}$ and $\text{AlPO}_4\text{-34}$. The pore dimensions and cage structure of $\text{AlPO}_4\text{-34}$ and $\text{AlPO}_4\text{-18}$ are identical but differ in the stacking of the double six-rings that form the framework.

Si or Mg) is readily formed with a number of templates (*e.g.*, tetraethylammonium hydroxide (TEAOH), triethylamine, cyclohexylamine, 4,4'-piperidinopiperidine, and morpholine) [22], pure aluminophosphate $\text{AlPO}_4\text{-34}$ requires HF-based synthesis [23], which is disadvantageous for scale-up. Although a variety of organic template molecules have been used to prepare CHA and AEI structures, both materials have been reported to be readily formed and stable when TEOAH is used as the SDA [24]. However, when TEOAH is used as the template molecule, it has been found that CHA structures are only formed when there is a heteroatom, while the AEI structure is only formed when there are no heteroatoms or a low concentration of heteroatoms in the system [19]. The structure and template positions of TEOAH in AEI were successfully resolved by Simmen *et al.* [9] using X-ray powder diffraction data with space group $C2/c$. However, it has been reported that synthesis of AEI using TEOAH can also produce CHA impurities in the presence of heteroatoms [25]. The template *N,N*-diisopropylethylamine (DIPE) was found to be effective in producing AEI without any evidence of CHA or AFI (the competing phases) [26] only when the pH was controlled at the starting gel composition [27], but no structure including the template location was reported. The use of DIPE to produce AEI structured aluminophosphate and heteroatom substituted analogues was verified and reported in the “verified synthesis of microporous materials” of the International Zeolite Association Synthesis Commission.

Obtaining complete information about the location of the template molecules in microporous materials is crucial to understand the chemistry behind the formation of small-pore materials, and hence in optimising the preparation of such catalysts. Many of these microporous solids are well-suited for analysis by X-ray powder diffraction methods, and in certain cases by single-crystal diffraction [28]. However, the long-range order in these systems is invariably dominated by the framework structure, and, because the organic molecules are usually disordered, it is difficult to determine their orientation and location by diffraction methods. In such situations, the application of molecular modelling techniques in conjunction with diffraction methods has proven to be advantageous, by identifying probable orientations that can then be used as input for the refinement of the experimental data [29,30].

Here, we report a combined computational and high-resolution powder diffraction (HRPD) study to determine the number and the final geometry of the DIPE template molecules located within the $\text{AlPO}_4\text{-18}$ material.

2. Experimental

2.1. Synthesis

The $\text{AlPO}_4\text{-18}$ samples were prepared using standard hydrothermal methods [26]. An appropriate amount of water (5.73 g) was added to 2.19 g of phosphoric acid followed by addition of 1.5 g of aluminium hydroxide (hydrate). The mixture was then stirred for *ca.* 30 min, and then 6.47 g of the structure-directing organic template (DIPE) was added to the mixture and stirred for another *ca.* 30 min. The final gel ratio was 1P:1Al:0.8R:30H₂O (R is the template) and the pH was 7. The gel was then placed in a Teflon-lined autoclave and heated in an oven at *ca.* 160 °C for *ca.* 96 h. The resulting white solid was washed and dried at 100 °C.

2.2. Characterisation

X-ray diffraction (XRD) data was collected on a standard laboratory X-ray diffractometer (Bruker D8, Germany) to confirm the phase purity of the material.

HRPD data was collected on station 2.3 of the Daresbury synchrotron radiation source, which operated at 2 GeV with a typical current of *ca.* 150 mA. The sample was placed in a capillary tube, which was rotated during data collection to reduce the influence of any preferred orientation. Because the intensity of data collection decays with time, the lower intensities (at the high angles) were scanned first. Thus, the sample was scanned in two phases: 55° to 80° and then 5° to 80°, both with a step size of 0.04 Å. The wavelength (1.300361 Å) was obtained from a monolithic double-bounce single crystal Si(111) channel-cut monochromator. The Rietveld analysis program GSAS [31–33] was then used to refine the data.

Structure refinement of the HRPD data was performed using GSAS software by taking the framework of the reported structure by Simmen *et al.* [9] and using the same $C2/c$ space group and reported framework model for as-prepared AEI. The diffraction peaks were modelled using a pseudo-Voigt peak profile shape. A number of constraints were introduced to achieve a stable refinement. In particular, the Al–O and P–O distances were restrained to *ca.* 1.74 Å and *ca.* 1.52 Å, respectively. A difference Fourier map was generated after including and refining only the framework atoms, and no template molecules were included in the model at this stage. The generated difference Fourier map was then used to assist assignment of the positions of the template atoms. Further refinement was performed after performing molecular modelling template docking calculations using the energy minimised structures as the starting model to obtain the final structure. Thermogravimetric analysis (TGA) data was collected on a Shimadzu TGA-50 thermogravimetric analyser, with the AEI material heated in N₂ (60 mL/s) from room temperature to 650 °C.

2.3. Molecular modelling

Computational methods (docking of template molecules) were used to provide a starting model for the template refine-

Fig. 2. XRD pattern of AEI prepared using the *N,N*-diisopropylethylamine (DIPE) template. The vertical lines represent the calculated 2θ positions for the given wavelength for a Cu $K\alpha$ radiation source.

ment. Using the procedure of Freeman *et al.* [34], Monte Carlo (MC) docking calculations were performed to generate an ensemble of possible template sites. The framework structure used was that determined by Simmen *et al.* [9]. These configurations were then energy minimised using Discover [35] with the *cff91_czeo* forcefield [36]. All of the atom positions and cell parameters were optimised.

3. Results and discussion

First, we discuss the XRD results followed by the results from computational modelling techniques. Finally, we show the structure derived by taking the coordinates of the structure obtained from molecular modelling as a starting point for refining the HRPD data.

The XRD pattern of as-synthesised $\text{AlPO}_4\text{-18}$ (Fig. 2) shows that it is phase pure and does not have any additional phases, and the pattern is the same as previously reported patterns [26,37].

3.1. Initial structure refinement

The detailed Rietveld refinement was performed taking the structure reported by Simmen *et al.* [9] (only the framework atoms because the reported structure contains tetraethylammonium hydroxide). Figure 3 shows the generated

Fig. 3. (a) AEI framework structure with TEOAH template positions and orientations derived from the crystallographic data reported by Simmen *et al.* [9] viewed from the (100) direction. (b) Conformation of TEOAH in the AEI framework from the (001) view. Note that there are four cages in the unit cell of AEI.

Fig. 4. High-resolution power diffraction (HRPD) patterns of the observed (1), calculated (2), and difference (3) of the AEI structure refined before including the template positions. The inset shows high-angle data because the intensity of the low-angle peaks dominates the data.

structure based on the reported data.

The experimental and calculated XRD patterns obtained from the Rietveld analysis using only the framework structure are shown in Fig. 4. In this figure, the difference is significant at low 2θ values because the structure of the template was not included at this stage. The inset shows the initial refinement for 30° – 80° , in which the template has very little effect. It is clear that it is not possible to obtain the best likely fit without considering the template. The difference Fourier map generated from the initial refinement without including the template molecule is poorly defined (Fig. 5). However, it was possible to identify some atoms of the template molecule, and it was most likely that there was only one template molecule per cage. However, for better refinement, a reasonable structural model for the template must be postulated. Thus, computational modelling methods were used to identify the likely energetically favourable geometries of the template molecule within the pores. The MC docking technique was used [34], which has previously been shown to provide excellent agreement with experiment when considering template geometries [38].

3.2. Molecular modelling

Firstly, the docking procedure was used to identify the low-

Fig. 5. Observed difference Fourier map for powder diffraction of DIPE in AEI.

est energy configuration of a single template molecule per cage at different loadings, and then when two template molecules are present in the cage (as was reported for triethylamine in $\text{AlPO}_4\text{-34}$ by Lewis *et al.* [18]). Although the docking methodology is capable of generating the later structures, the small void space of the cage makes such an automated procedure difficult and time-consuming, and hence the templates were placed manually as well.

Although about 50 starting configurations were generated for the single template molecule loading, minimization of these configurations resulted in only four different configurations. Similarly, only four different orientations of two template molecules per cage were found from an ensemble of approximately 20 initial configurations. We report the stabilization energy of the structure (Table 1) as the difference between the optimized templated structure and the optimised empty framework and isolated template molecule. The values reported are given relative to the most stable structure.

It is clear that two template molecules per cage is highly energetically unfavourable (Table 1), and thus no refinement using a structure with two template molecules was made. Previous studies have shown that the template molecules in the most energetically stable structure are located at sites that can be experimentally corroborated [28]. Thus, it is likely that the most stable structure found here is similar to that found experimentally. Nevertheless, we cannot completely discount the higher energy structures. However, we show below that the lowest energy configuration led to a successful refinement.

3.3. Final structure refinement

The four most energetically feasible configurations obtained from docking of one template molecule per cage (four replicates of the molecule were formed to give full occupation of the cages in the unit cell) were taken as starting points for detailed

Table 1
Relative stabilities of the templated unit cells.

Template molecules per unit cell	Relative stabilization energy (kJ/mol)	
	One	Two
0	0	119
33	33	120
39	39	142
39	39	154

Table 2
Crystallographic and experimental data for AEI.

Temperature (°C)	25
Wavelength (Å)	1.300361
Step size	0.04
Profile range in refinement (2θ)	5°–80°
<i>a</i> (Å)	13.5849
<i>b</i> (Å)	12.6106
<i>c</i> (Å)	18.5081
β	94.985
χ^2	3.017
R_{WP}	6.95%
R_p	5.25%
Al–O distance (Å)	1.74
P–O distance (Å)	1.52

Rietveld refinement of the synchrotron powder diffraction data. Each configuration was used to ensure that there was no bias and also to verify that the lowest energy structure from the calculations does indeed correlate with the experiment. Upon refinement, only the lowest energy configuration gave both acceptable bond distances and a reasonable *R* factor, suggesting that the MC docking method was successful. The crystallographic and experimental data for AEI are summarised in Table 2, and the final atomic parameters obtained from the refinement are summarised in Table 3. The final observed and calcu-

Table 3
Final atomic positions after refinement of as-prepared AEI (space group $C2/c$).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U^* (Å ²)
Al1	0.1277	0.0229	0.1566	0.0259
Al2	0.1080	−0.2270	0.9340	0.0259
Al3	−0.2169	−0.0971	0.0616	0.0259
P4	0.2270	−0.0936	0.0468	0.0259
P5	−0.1245	−0.2271	0.9353	0.0259
P6	−0.0936	0.0571	0.1781	0.0259
O7	−0.1514	−0.0453	0.1386	0.0329
O8	−0.1387	−0.1608	0.0060	0.0329
O9	−0.0132	−0.2691	0.9353	0.0329
O10	0.1404	−0.1601	0.0132	0.0329
O11	0.2104	−0.0622	0.1267	0.0329
O12	0.0039	0.0068	0.1615	0.0329
O13	−0.1251	0.1703	0.1494	0.0329
O14	−0.2947	−0.1878	0.0933	0.0329
O15	0.1411	0.0318	0.2497	0.0329
O16	0.1671	−0.3489	0.9328	0.0329
O17	−0.1587	−0.1516	0.8710	0.0329
O18	−0.2630	−0.0108	0.9921	0.0329
N20	0.5770	−0.0527	0.8154	0.0750
C21	0.6432	0.1245	0.7622	0.0750
C22	0.5738	0.0263	0.7495	0.0750
C23	0.5956	−0.0345	0.6836	0.0750
C24	0.4942	−0.2369	0.8148	0.0750
C25	0.5725	−0.1606	0.7826	0.0750
C26	0.5648	−0.1550	0.6933	0.0750
C27	0.4607	−0.1361	0.9019	0.0750
C28	0.4886	−0.0364	0.8630	0.0750

* Thermal parameters.

Fig. 6. HRPD patterns of the observed, calculated, and difference of the structure refined after including the template molecule positions. This refinement gives $\chi^2 = 3.017$, $R_{wp} = 6.95\%$, and $R_p = 5.25\%$.

lated powder patterns along with the difference are shown in Fig. 6. It is clear that the fit is now considerably better than that without including the template molecules (Fig. 4). The structural model obtained from the refined crystallographic data is shown in Fig. 7, where there is one DIPE molecule per cage and thus four template molecules per unit cell. The location of the template molecule is more central than that found in the calculations (the molecule is ~ 0.5 Å closer to the centre of the cage), but there is generally good agreement between the calculated and the final refined template geometry for refinement of the experimental data.

3.4. TGA results

TGA experiments were carried out to determine the number of template molecules per unit cell, and compared with the results obtained from the calculations and the structure refinement. The number of template molecules per unit cell was determined by considering the mass loss at various stages. Mass loss occurred in three stages (Fig. 8). The first stage at 35–120 °C was attributed to water, both within the structure and in intracrystalline regions. The remaining two stages were considered to be because of the breakdown of the template molecules. It is very difficult to identify a division between these two regions, but we assumed that the decomposition of

Fig. 8. TGA data for AEI prepared with the DIPE template.

the template molecules began at 150 °C. From TGA, we determined that the mass loss is equivalent to 3.99 molecules per unit cell, which is in excellent agreement with the occupancy obtained from the calculation and the positional occupation values found during the refinement. Thus, we can conclude that the material contains stoichiometric full loading of template molecules.

4. Conclusions

From XRD, we were able to determine that the as-synthesised material was phase pure. However, the aim was to determine the positions of the template molecules within the AEI structure. The docking procedure was used to identify the likely loading of template molecules and to provide suitable starting models for further structural refinement of the HRPD data. The calculations clearly showed that one template molecule per unit cell results in the most energetically favourable configuration. The Fourier transform map suggested the presence of a single molecule in each cage. Refinement of a number of models suggested by the calculations resulted in only one successful converged refinement, which (gratifyingly) was the most energetically favourable configuration. The TGA results confirmed that each cage within the structure was essentially full. A single template molecule per cage is consistent with the report by Simmen *et al.* [9] for tetraethylamine in AEI. The use of computer modelling enabled plausible models to be built and allowed full refinement of the HRPD data, without which it would have been difficult using only difference Fourier maps. Thus, MC docking calculations were used to provide a starting point for the refinement analysis. Determining the most energetically favourable configuration allowed successful structure refinement to be undertaken. This work demonstrates that the combination of different experimental techniques and modelling can lead to a more complete understanding of the complex structure of such materials.

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Fig. 7. Position and orientation of DIPE inside AEI obtained from the refinement of the crystallographic data viewed from the (001) (a) and (100) (b) directions.

Graphical Abstract

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Location and orientation of the *N,N*-diisopropylethylamine template molecule in the $\text{AlPO}_4\text{-18}$ framework by X-ray synchrotron diffraction and molecular modelling

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A combination of high-resolution powder diffraction and molecular modelling allowed determination of the as-synthesised structure of $\text{AlPO}_4\text{-18}$ templated with *N,N*-diisopropylethylamine.

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