The extremely high specificity of *N*-methyldicyclohexylamine for the production of the large-pore microporous AFI material

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We describe a highly efficient synthesis of microporous aluminophosphate $AlPO_4$-5 and its heteroatom-substituted variants, using *N*-methyldicyclohexylamine as a structure-directing agent that, in addition, does not result in the formation of any other microporous phase over the widest range of composition, temperature and pH conditions ever reported.

KEY WORDS: *N*-methylidicyclohexylamine; aluminophosphate; heteroatom-substituted variants.

1. Introduction

Since the discovery of microporous aluminophosphates and their hetero-atom (M) substituted variants [1–5], substantial progress has been made in the synthesis of several new microporous structures, their characterization and, more importantly, their catalytic applications [6–8]. The ease with which a variety of hetero-atoms (that introduce catalytic functionality to the otherwise neutral framework) can be incorporated into the $AlPO_4$ framework sites, as compared to the zeolite framework, has attracted considerable attention leading to the synthesis of several metal ion-substituted aluminophosphates (MAPOs, where M is a lower-valent hetero-atom). Amongst the $AlPO_4$ and MAPO structures, $AlPO_4$-5 (International Zeolite Association structure code AFI) has been the most extensively studied, for several reasons. Firstly, since it contains a large-pore channel system, it is suitable for processing not only small but also relatively large organic molecules. Secondly, the removal of the template does not lead to any structural collapse with the parent open-framework structure showing complete integrity [9,10]. Thirdly, this material may be synthesized using several structure-directing organic agents (SDAs) [11]. Finally, and most importantly, the incorporation of a large number of hetero-atoms is possible for this structure [5,6,12].

Although the preparation of $AlPO_4$-5 and its hetero-atom-substituted analogues are relatively easy compared to many other structures, it has been noted in the recently verified syntheses of zeolitic materials that the AFI structure can be formed only by employing specific conditions [13]. For example, it is interesting to note that the X-ray diffraction (XRD) patterns shown in reference [13], of both AlPO-5 and SAPO-5, contain extra reflections corresponding to tridymite and chabazite, respectively, in addition to the major AFI phase, demonstrating the difficulties in the preparation of pure AFI phase. In particular, for incorporating different M atoms in high concentrations (above *ca.* 4 at% of hetero-atoms in either framework Al(III) or P(V) sites), considerable effort is normally required to optimize the synthesis conditions to obtain a pure $AlPO_4$-5 phase, since other phases compete to form simultaneously [14–16]. In a recent systematic study, only two (triethylamine and diethylethanolamine) out of eight tested SDAs were found to direct the crystallization of pure AFI structure from gels containing high cobalt concentrations (10 at%), which was achieved only by using very narrow synthesis conditions [17]. Here we report a new structure-directing agent, *N*-methyldicyclohexylamine (MCHA), for the production of microporous AlPO-5 and its hetero-atom-substituted variants.

2. Experimental

Typical MAlPO-5 (M = Co or Zn) synthesis involves the addition of aluminum hydroxide over a phosphoric acid aqueous solution followed, after rigorous stirring for *ca.* 10 min, by the dropwise addition of respective acetate salts, dissolved in minimum amount of water. Once the gel attains homogeneity, the organic template, MCHA, is added to form the final gel. The general gel composition is $(1-x)\text{Al}:(1+y)\text{P}:x\text{Me}:z$ template: $25H_2O$, where x and z are the concentration of M and the amount of template, respectively, while y corresponds to the excess amount of H_3PO_4 added at the end to adjust the pH until the required value is achieved. Other conventional organic templates, such as triethylamine (TEA) and tetraethylammonium hydroxide

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(TEAOH), were also used employing identical conditions to that of the gel containing MCHA. After stirring the gel for *ca.* 1 h, it was transferred to a Teflon-lined autoclave that was heated in a preheated oven at temperatures between 398 and 473 K for *ca.* 3 to 24 h.

The solid extracted by the conventional filtering and drying procedures were investigated in detail by XRD technique employing Siemens D500 system. Co K-edge X-ray absorption spectroscopic data were collected at station 9.3 of the SRS, Daresbury, UK, which operates at 2 GeV with a typical current of *ca.* 150 to 250 mA. The data were collected in the transmission mode. The EXAFS data were processed using a suite of programs available at the Daresbury Laboratory, namely, EXCALIB, EXBROOK and EXCURV98.

3. Results and discussion

The phases obtained employing various precursor gel compositions, the pH of the starting gel and synthetic conditions are given in table 1. From table 1, it is clear that, irrespective of the composition, cobalt content, pH or temperature, we were able to synthesize phase-pure CoAPO-5 (AFI structure) material using MCHA as the structure-directing agent. When either TEAOH or TEA was used as the SDA, unless we used specific conditions such as lower amounts of cobalt, low pH and temperatures above 448 K, both AFI- and CHA-related phases were formed simultaneously. Although it is possible to prepare phase-pure CoAPO-5 materials over a small range of composition (up to *ca.* 4 at% of Co/Co + Al) using conditions such as pH of *ca* 5 and temperature of *ca* 453 K, using TEA or TEAOH as SDAs, it is very difficult to produce phase-pure zinc-substituted $AlPO_4$-5 material, under similar conditions. In figure 1, we show a few sets of typical XRD patterns of the solid obtained from the crystallization of the gels

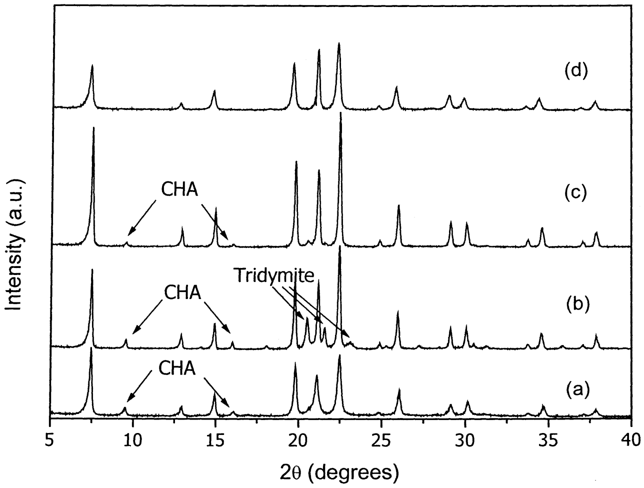

Figure 1. XRD patterns of the solid extracted from the hydrothermal crystallization of the zinc-substituted aluminophosphate systems employing TEAOH or MCHA as SDA. The major reflections correspond to the $AlPO_4$-5 (AFI) phase. The extra reflections are identified as being due to the microporous CHA phase and dense phase tridymite. (a) When typical composition used for MAPO-5 synthesis (pH of *ca* 6 and M/M + Al = 0.02 and a temperature of *ca* 175 °C) was employed for the zinc-containing gel, a mixture of AFI and CHA phases was produced. (b) and (c) Other typical conditions, for example, less TEAOH (to decrease the pH to *ca* 5) or more dilute gel (by increasing water content), which are known to suppress the formation of CHA resulted in the formation of both dense phase (tridymite) and small of amounts of CHA phase. (d) Note that even with a high zinc concentration of 10 at% (Zn/Zn + Al) with the new MCHA template it is possible to prepare phase-pure ZnAPO-5.

Table 1
Parameters employed for the synthesis of cobalt-substituted aluminophosphate using MCHA, TEA and TEAOH as SDAs

SDA	Composition[a]	pH	Phases
TEA	0.1 Co	5.9	AFI + CHA
TEA	0.1 Co, 1.18 P	5.0	AFI
TEA	0.04 Co	6.1	AFI + CHA
TEA	0.04, 1.19 P	5.0	AFI + CHA
TEAOH	0.1 Co	8.2	AFI + CHA
TEAOH	0.1 Co, 1.38 P	5.0	CHA + AFI
TEAOH	0.04 Co	7.8	CHA
TEAOH	0.1 Co, 1.41 P	4.9	AFI + CHA
MCHA	0.1 Co	7.4	AFI
MCHA	0.1 Co, 1.35 P	4.9	AFI
MCHA	0.04 Co	7.2	AFI
MCHA	0.04 Co, 1.32 P	5.0	AFI
MCHA	0.1 Co, 1.51 MCHA	9.0 [20]	AFI
TEA	0.1 Co, 1.24 TEA	8.0	Amorphous

Note: T: 448 K; Time: 3 h.

[a] Unless specified, the typical composition is $(1-x)$Al : 1.0P : xCo : 0.8 template : 25 H_2O.

containing zinc. Even with the use of 2 at% of zinc (Zn/Zn + Al), small amounts of SDA to maintain a low pH of *ca*. 4, not only the extracted solid contained small amounts of the CHA phase but also dense materials were formed under these conditions, clearly demonstrating the difficulties encountered in the production of ZnAPO-5 material. However, pure AFI phase is crystallized when MCHA is used as the SDA, even if the zinc content is *ca*. 10 at% (five times greater than the previous one) and over a wide range of pH conditions (see figure 1). Chemical analysis of MAPO-5 containing 10 at% of cobalt or zinc ions confirmed that the majority of the divalent ions are in the framework aluminum sites. In addition, we examined the incorporation of cobalt ions into the framework by Co K-edge X-ray absorption spectroscopy. Results of a typical Co K-edge EXAFS data and the associated Fourier transforms of CoAlPO-5 prepared at two extreme pH conditions are shown in figure 2. Both the coordination number and the Co–O distances obtained from the refinement of the EXAFS data suggest that the Co(II) ions are indeed present in the framework tetrahedral sites. In addition to pure $AlPO_4$-5, cobalt- and zinc-containing systems, we have successfully prepared several other hetero-atoms contained in $AlPO_4$-5 including Mn, Mg, Cr, Fe, Mn (in Al(III) sites), Ti and Si (in P(V) sites) for a typical gel composition of $0.96Al:1.0P:0.04Me:0.8MCHA:25H_2O$. In particular, the use of MCHA as the SDA for the production of a variety of hetero-atom-substituted $AlPO_4$-5, without forming any additional impurity phases, is one of the most significant aspects of this work.

In order to understand the structure-directing aspects of the MCHA molecule, we carried out Monte Carlo docking calculations for the MCHA molecule within the AFI and CHA structures (for simplicity we used the silica form for the calculations), since the CHA phase is the competing phase in the majority of the synthesis of $AlPO_4$-5 using other SDAs. The Monte Carlo docking [18] method was used to locate the thermodynamically preferred position of the MCHA template in these frameworks. The cff91-czeo force field [19] was employed in the calculations, which involved an exhaustive conformational sampling of the guest mol-

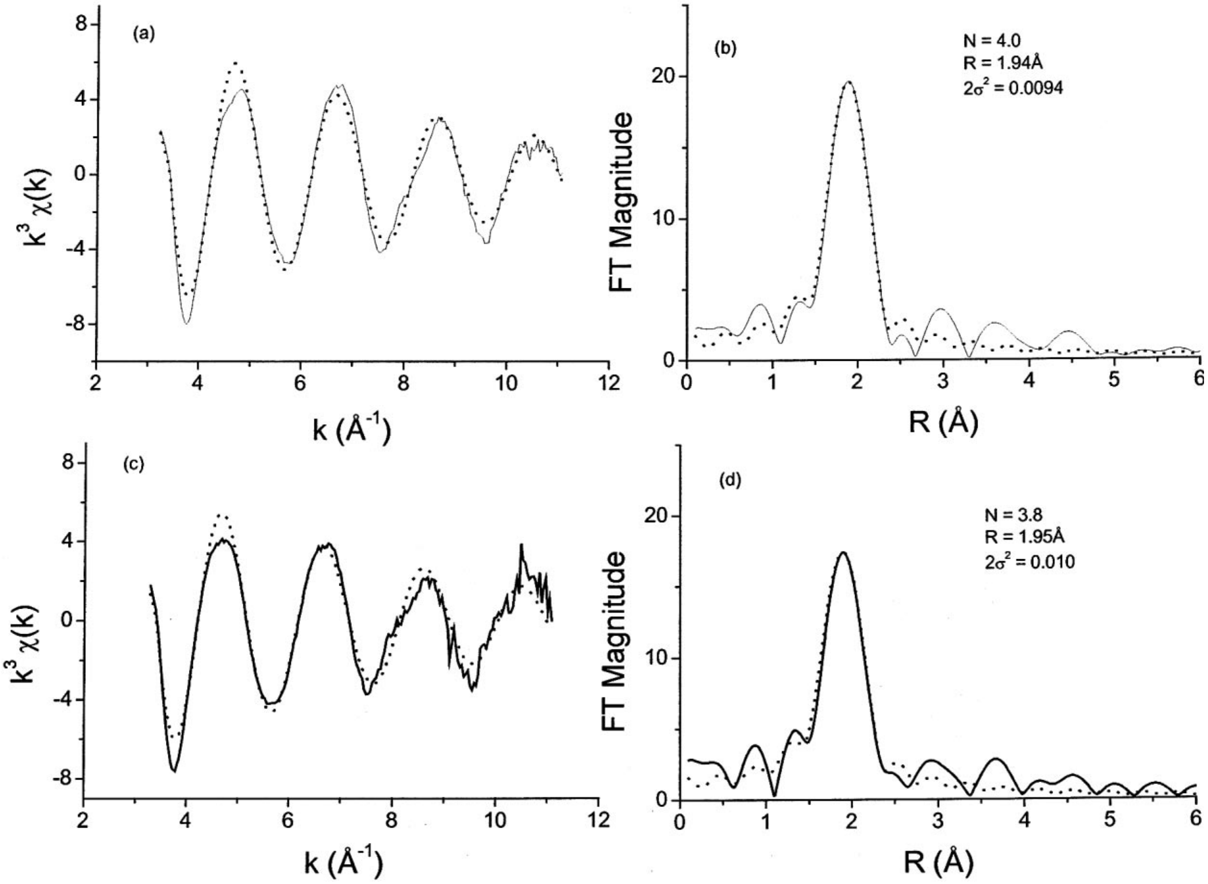

Figure 2. Typical Co K-edge EXAFS (in (a) and (c)) and the associated Fourier transforms of the as-prepared CoAlPO-5 material containing 4 at% of Co(II) ions in place of Al(III). The top set ((a) and (b)) corresponds to the sample prepared at pH of *ca* 5 and the bottom set ((c) and (d)) belongs to the sample prepared at pH of *ca* 8. The coordination number, bond distances and the Debye–Waller factors determined from the analysis of the EXAFS data are given in the figure. The solid line shows the experimental data and the dotted curve represents the calculated EXAFS.

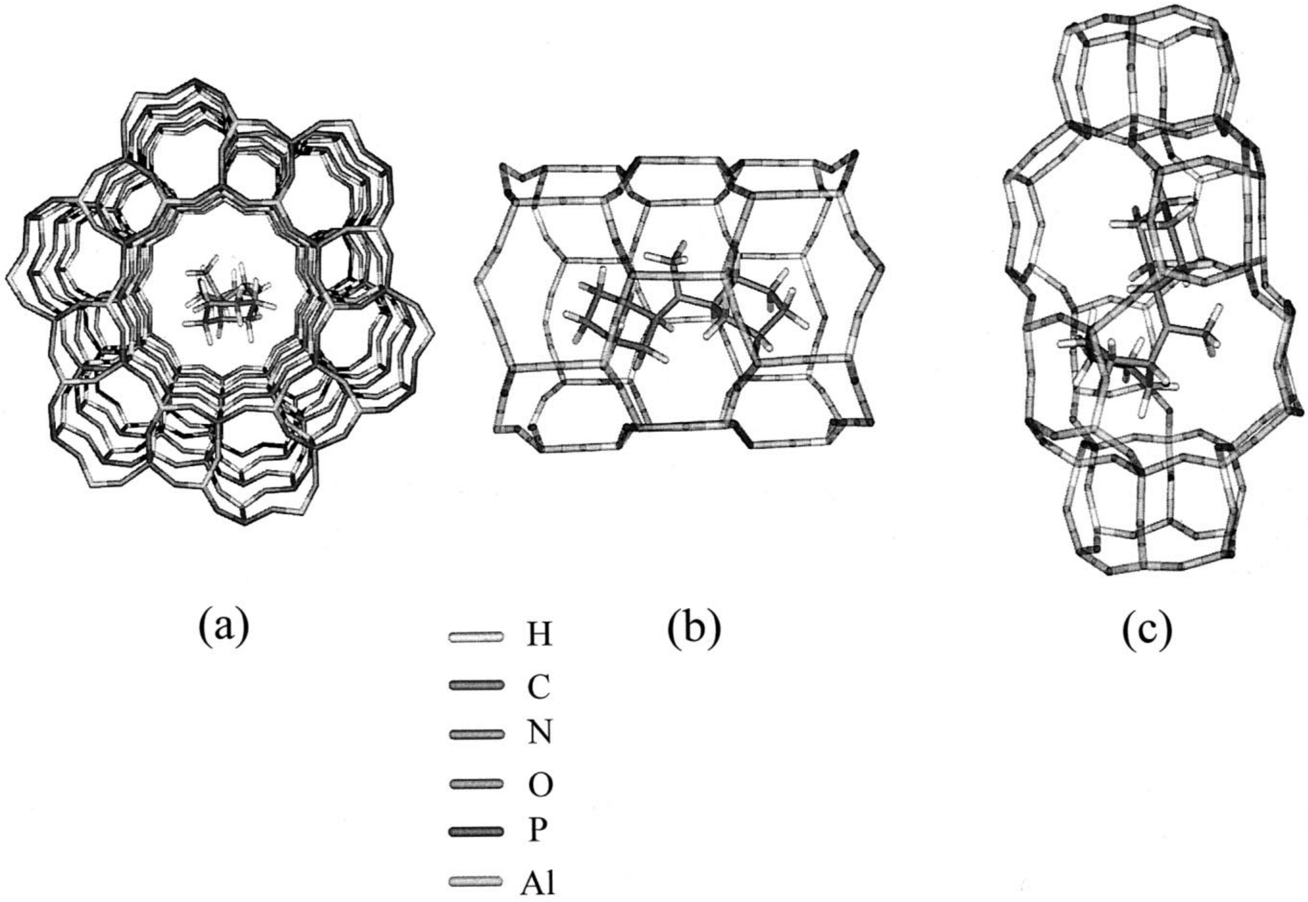

Figure 3. Energy-minimized structures of (a) and (b) $AlPO_4$-5 and (c) $AlPO_4$-34 containing *N*-methyldicyclohexylamine. (a) and (b) represent two different views of the one-dimensional channel showing the collinear alignment of the organic template molecule with the channel direction.

ecule, as well as full flexible framework minimization calculations using Discover was carried out subsequently to the Monte Carlo insertion stage. In AFI, the molecule was seen to adopt an elongated configuration (see figure 2(a) and (b)) in which both the cyclohexyl rings were oriented along the channel axis. In the CHA case, however, the template is found to take a more compact configuration with the two cyclohexyl rings orientated orthogonally to each other (figure 2). The calculated adsorption energies, E_{ADS} ($E_{\mathrm{ADS}} = E_{\mathrm{ZEO+TEMPLATE}} - E_{\mathrm{ZEO}} - E_{\mathrm{TEMPLATE}}$), were -277.44 kJ mol^{-1} (for CHA) and -344.05 kJ mol^{-1} (for AFI), suggesting that the formation of the AFI structure is more favorable compared to CHA, consistent with the non-competitive formation of phase-pure AFI structure for a wide composition range.

In summary, although synthesis of AlPO-5 is relatively straightforward, the preparation of phase-pure metal-substituted analogues of this microporous aluminophosphates is particularly difficult. Similar difficulties were encountered in the preparation of many other systems, such as MAPO-39, MAPO-31, *etc.* [20,21], in phase-pure form, unless specific conditions were employed. However, we have identified *N*-methyldicyclohexylamine as the most efficient organic template to direct the production of large-pore $AlPO_4$-5 containing one-dimensional channels and its metal ion-substituted variants over a wide range of synthetic conditions. Not only phase-pure AFI can be crystallized with excellent yields in a short period (in 3 h) but also, to our knowledge, MCHA has the highest specificity to direct a particular structure containing a one-dimensional channel system over a wide range of chemical composition ($M/M + Al = 0.0$ to 0.15), pH (5 to 9), and temperature (423 to 473 K), irrespective of the order of addition or the type of hetero-atom, implying the true structure-directing aspect of the MCHA. Thus, this study suggests that other new organic templates can be identified for the production of specific microporous structure which can avoid competitive formation of other phases that are normally encountered in the preparation of other one-dimensional channel systems. Furthermore, this structure-directing aspect of the MCHA template can be exploited to investigate the influence of other synthesis parameters such as pH on the morphology and catalytic performance of the hetero-atom-substituted microporous aluminophosphates.

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