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Microporous and Mesoporous Materials 88 (2006) 163–169

MICROPOROUS AND MESOPOROUS MATERIALS

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Solid state NMR investigation of the structure of $AlPO_4$-14A

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Received 5 May 2005; accepted 11 August 2005
Available online 2 November 2005

Abstract

The as-synthesized aluminophosphate framework material $AlPO_4$-14A has a number of unique structural features related to the connectivities in the network of Al and P atoms. One tetrahedral Al atom is present that is linked, via Al–O(H)–Al bonds to two octahedral Al atoms and, consequently to only two P atoms. However, an Al/P ratio of one is maintained as each of these octahedral Al atoms is connected to five P atoms in addition to the Al–O(H)–Al linkage. This connectivity network means that a framework made up of alternating Al and P atoms cannot be obtained by calcination. A variety of ^{1}H, ^{27}Al, and ^{31}P solid state NMR experiments have been employed to characterize the $AlPO_4$-14A structure. A fast ^{1}H MAS experiment showed that the template was in the protonated form and a $^{1}H\{^{27}Al\}$ TRAPDOR experiment identified the resonance of the 'framework' proton. The ^{27}Al and ^{31}P resonances were completely assigned by the $^{27}Al \rightarrow {}^{31}P$ INEPT heteronuclear correlation experiment and the quadrupolar parameters of the ^{27}Al signals determined from the ^{27}Al MQMAS experiment. Lastly, the complete assignment of both ^{27}Al and ^{31}P resonances made it possible to qualitatively determine the location and orientation of the template molecule within the framework from two-dimensional dipolar-based $^{1}H \rightarrow {}^{31}P$ cross-polarization and $^{1}H \rightarrow {}^{27}Al$ TEDOR heteronuclear correlation experiments. The data from these experiments confirm in detail the $AlPO_4$-14A structure and will be useful benchmarks for the investigation of other structures for which diffraction data are limited.

Keywords: Aluminophosphate; Zeolite; Solid state NMR; HETCOR; Structure

1. Introduction

A novel family of crystalline aluminophosphate molecular sieves, denominated as $AlPO_4$-*n* where *n* refers to a distinct structure, was obtained by Wilson et al. [1] by introducing structure-directing agents (SDAs) into the reaction mixtures. This family of materials has since been greatly extended [2]. In most cases, the neutral framework relies on a strict alternation of AlO_4 and PO_4 tetrahedra sharing their oxygen atoms but, in several examples, structural studies have revealed the presence of five- and six-coordinated Al atoms. The supplementary bonds may coordinate the Al atoms to water molecules, to hydroxyl groups, and to fluorides [3] but also to an oxygen atom in the SDA [4,5]. Very recently, coordination to the nitrogen atom of a templating amine has been observed in IST-1 [6]. These supplementary bonds do not prevent each Al and each P from being linked through oxygen to four P and four Al respectively. In these cases, a framework of alternating tetrahedra is observed after removal of water, hydroxyl groups, fluoride ions, and template molecules by calcination.

However, a noticeable exception to this alternation of Al and P sites is the case of $AlPO_4$-14A. According to Pluth and Smith [7], this material was obtained by Wilson et al. [1] as an impurity in an $AlPO_4$-14A synthesis. A single crystal X-ray diffraction (XRD) study [7] revealed a number of interesting structural features related to the connectivity network of the Al and P atoms. In the structure, there are Al–O(H)–Al bonds which involve a tetrahedral aluminum atom Al(1) that is linked, via the oxygen, to two

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1387-1811/$ - see front matter
doi:10.1016/j.micromeso.2005.08.035

octahedral aluminum atoms Al(4) and, consequently, to only two phosphorus atoms. However, an Al/P ratio of one is maintained, since for each Al(1), there exist two Al(4) which are linked to five phosphorus atoms. The full connectivity network of Al and P atoms is described in Table 1. The nature of this connectivity network means that a framework made up of alternating Al and P atoms cannot be obtained by calcination.

The particular feature described above is shown in Fig. 1a which shows an $Al_3P_2O_{18}H_2$ cluster containing two octahedral Al(4) species linked by one tetrahedral Al(1) and two tetrahedral P(4). Two such clusters are linked by two P(2) sites between each pair of octahedral Al(4) sites and directly by sharing the oxygen atoms between the tetrahedral Al(1) and P(4) sites. This forms a $[4^45^4]$ cage which has four 5-rings. Such odd-numbered rings of framework Al and P atoms cannot appear in $AlPO_4$s with a regular alternation of these atoms. A cluster belongs to two $[4^45^4]$ cage units, forming a chain parallel to the *c*-axis. Two such chains are linked by 6-rings to a twisted chain of 4-rings (P(3) and Al(3)), forming a sheet in the *bc* plane. The links between these sheets by a set of 4-rings (P(1) and Al(2)) generate a system of two-dimensional 8-ring channels which hosts the isopropylamine SDA (Fig. 1b).

Table 1
Relative site occupancies connectivities between the atoms[a] in the $AlPO_4$-14A structure [7]

		Rel. occ.[b]	Al				P			
			1	2	3	4	1	2	3	4
Al	1	1/2	0	0	0	2	0	0	0	2
	2	1	0	0	0	0	2	2	0	0
	3	1	0	0	0	0	1	0	2	1
	4	1	1	0	0	0	1	2	0	2
P	1	1	0	2	1	1	0	0	0	0
	2	1	0	2	0	2	0	0	0	0
	3	1/2	0	0	4	0	0	0	0	0
	4	1	1	0	1	2	0	0	0	0

[a] The element in row *i* and column *j* represents the number of atoms of type *j* in the X–O–X (X = Al or P) coordination environment of atom type *i*.
[b] Relative site occupancies of the atoms.

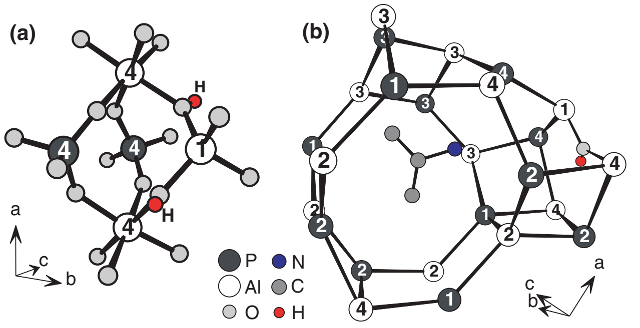

Fig. 1. Some aspects of the $AlPO_4$-14A structure [7]: (a) triple 4-ring unit ('cluster') containing the octahedral aluminums and the Al–O(H)–Al linkages. (b) Encapsulated isopropylamine molecule and surrounding 'cage' (Al and P atoms within 5 Å of the organic molecule).

The $AlPO_4$-14A material has subsequently been obtained in a pure phase by Goepper and Guth [8] by adding HF to the reaction mixture, although the fluorine is not incorporated in the material. Although their study presented ^{13}C, ^{31}P and ^{27}Al MAS NMR spectra, no detailed NMR study has been yet undertaken to fully investigate this complex structure by probing both through space interactions and through bond connectivities between the nuclei.

In general, structural characterization of zeolites and aluminophosphate framework materials is not straightforward since diffraction experiments are limited, in most cases, to microcrystalline powders. Single crystals of adequate dimensions for single crystal XRD, such as the $AlPO_4$-14A material investigated in this paper, are not normally available. Since the structural information obtained by solid state NMR is complementary to diffraction data, a more complete understanding of the structure usually emerges when the two techniques are used together, particularly when diffraction experiments are limited to powders.

Some of the interesting structural features of $AlPO_4$-14A may arise in other aluminophosphate framework materials for which only powder diffraction data is available. In particular, the presence of Al–O(H)–Al linkages and the location, orientation, and charge of the organic SDA molecule are difficult to characterize by powder XRD alone since H, C, and N atoms are weak X-ray scatterers relative to the aluminophosphate framework. Also, the non-alternating connectivity network of Al and P atoms is difficult to detect by powder XRD alone since Al and P atoms scatter X-rays with similar strengths. Since a reliable single crystal XRD structure of $AlPO_4$-14A is available, it is desirable to characterize this structure as well as possible by solid state NMR in order to serve as a benchmark study for the investigation of other structures for which the diffraction data are more limited. We therefore present the results of a selection of powerful ^1H, ^{27}Al, and ^{31}P solid state NMR experiments applied to $AlPO_4$-14A, including MQMAS, TRAPDOR, and various two-dimensional heteronuclear correlation experiments involving cross-polarization, TEDOR, and INEPT pulse sequences.

2. Experimental

2.1. Sample

The as-synthesized $AlPO_4$-14A sample was provided by Prof. J.L. Guth, Mulhouse. It was obtained from a gel of composition $1.0Al_2O_3/1.0P_2O_5/0.5HF/100H_2O/2i\text{-}C_3H_7\text{-}NH_2$. After aging for 1 h, the gel was heated in an autoclave at 200 °C for 24 h. The resulting crystalline product was filtered, washed and dried.

2.2. Solid state NMR

Solid state NMR experiments were carried out on a Bruker AVANCE DSX-400 spectrometer operating at