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Synthesis, structure and characterization of ZrPOF-DEA, a microporous zirconium phosphate framework material

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ABSTRACT

A microporous zirconium phosphate material with the chemical composition $|(C_4H_{12}N^+)_6(H_3O^+)_2(H_2O)_2|[Zr_{32}P_{48}O_{176}F_8(OH)_{16}]$ (ZrPOF-DEA) has been synthesized ionothermally using diethylammonium chloride and oxalic acid to form the deep eutectic solvent. It is closely related to the analagous ethylammonium material ZrPOF-EA, which has already been shown to discriminate very well between CO_2 and CH_4. The framework structures, with two different 8-ring channels running parallel to the *x*-axis, one of which intersects a 7-ring channel running parallel to the *z*-axis, proved to be identical. Only the positions of the non-framework cations and water molecules differ. The structure of ZrPOF-DEA (*Pbam*, $a = 20.03757(1)$ Å, $b = 37.19099(1)$ Å, $c = 6.62488(1)$ Å) was solved from synchrotron powder diffraction data using the charge-flipping algorithm in *Superflip*. Difference Fourier analyses were then used to locate the non-framework species in the channels. Rietveld refinement of the final structure converged with $R_F = 0.037$ and $R_{wp} = 0.138$. Although this material, like ZrPOF-EA, is stable up to 410 °C, it does not discriminate as well between CO_2 and CH_4. Thermogravimetric analysis shows that not all of the organic species have been removed at 410 °C, and this is presumably the reason for the poorer adsorption results.

1. Introduction

In the processing of low-quality natural gas, such as biogas, the separation of CO_2 from CH_4 is a key issue, because CO_2 not only reduces the energy content of the natural gas, but also causes corrosion in the storage tanks and pipelines. Unfortunately, the two molecules are quite similar in size (kinetic diameters for CO_2 and CH_4 are 3.3 and 3.8 Å, respectively), so finding a molecular sieve that can discriminate between them is not easy. Generally, microporous materials with 8-ring pore openings (*ca.* 3.8 Å), such as SAPO-34 (framework type CHA [1]), are used for this purpose. However, we recently reported the ionothermal synthesis of a microporous zirconium phosphate material, ZrPOF-EA, that can discriminate between CO_2 and CH_4 very well [2]. The structure analysis of that material showed that it has both 7- and 8-ring pore openings, and this clarifies why its adsorption capacity is markedly higher for the smaller CO_2 than for the larger CH_4.

During the course of those initial ionothermal syntheses, a second material with a very similar powder diffraction pattern was also prepared. In that case, however, diethylammonium (DEA) chloride rather than ethylammonium (EA) chloride was combined with oxalic acid to form the deep-eutectic solvent (DES). Although the similarity in the diffraction patterns of the two materials gave a strong indication that the basic zirconium phosphate framework structures were likely to be very closely related, the subtle differences showed that some of the details, such as the location of the organic species in the channels, would be different. To see where these differences lie, a structural analysis of this second material, ZrPOF-DEA, was undertaken.

2. Experimental

2.1. Synthesis

A Teflon-lined autoclave (total volume 23 mL) was charged with the eutectic mixture made from oxalic acid dihydrate ($H_2C_2O_4{\cdot}2H_2O$, 98 wt%, 2.5 g, 19.85 mmol) and diethylammonium chloride (DEACl, 99 wt%, 2.5 g, 30.63 mmol), zirconium(IV) oxychloride octahydrate ($ZrOCl_2{\cdot}8H_2O$, 99 wt%, 250 mg, 0.76 mmol), orthophosphoric acid (H_3PO_4, 85 wt% in water, 200 mg, 1.73 mmol) and HF (75 μL, 1.73 mmol). All chemicals were purchased from Aladdin Reagent (China) Co., Ltd. The autoclave was heated at 180 °C for 3 days and then cooled to room temperature. The solid product was washed thoroughly with acetone and water, and dried

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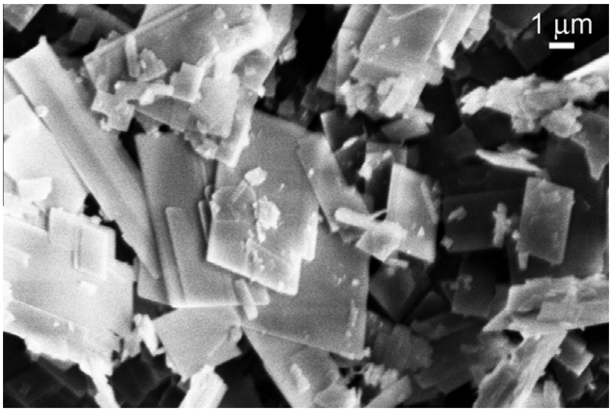

Fig. 1. Scanning electron microscopy image of ZrPOF-DEA showing the platelike morphology.

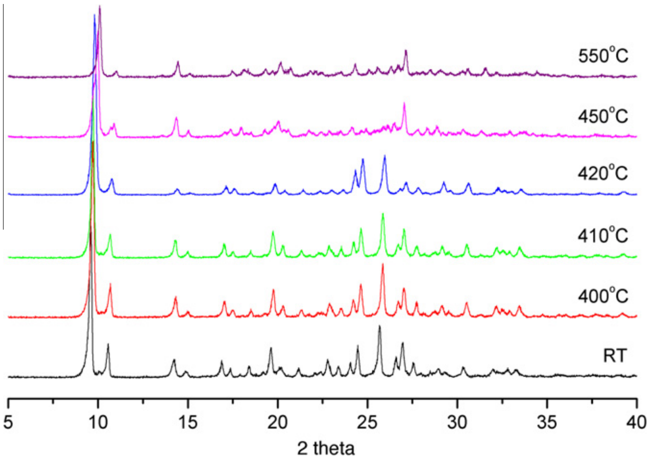

Fig. 2. X-ray powder diffraction patterns of ZrPOF-DEA taken after treatment at the temperature indicated for 5 h.

at room temperature. Scanning electron microscopy images of the material show crystals with a platelike morphology (Fig. 1).

2.2. Characterization

The thermal stability of the sample was determined by measuring the X-ray powder diffraction pattern after heating the sample in air for 5 h at several different temperatures (Fig. 2). Thermogravimetric analysis was performed in air with a heating rate of 10 °C/min (Fig. 3). CO_2, N_2 and CH_4 adsorption experiments were carried out on an intelligent gravimetric analyzer (IGA-001, Hiden Isochema) at 25 °C. Before each adsorption experiment, the ZrPOF-DEA was activated at 410 °C for 5 h and then outgassed at 300 °C under vacuum for 10 h.

2.3. Powder diffraction data collection

The X-ray powder diffraction data for ZrPOF-DEA were measured twice on the Materials Science beamline at the Swiss Light Source (SLS) in Villigen, Switzerland using the Mythen II Si-microstrip detector [3]. The first data set was collected on a sample loaded into a 0.3 mm capillary, but the refinement indicated that there may be a non-random orientation of the crystallites. Consequently, a second well-ground sample was prepared and a new data set collected. Details of the two measurements are given in Table 1.

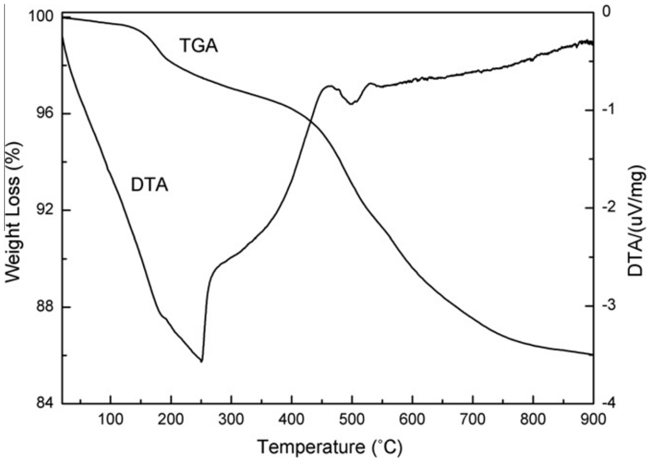

Fig. 3. TG-DTA curves for ZrPOF-DEA.

Table 1
Synchrotron powder diffraction data collection for ZrPOF-DEA.

	Data set 1	Data set 2
Synchrotron	SLS	SLS
Beamline	MS–X04SA	MS–X04SA
Detector	Mythen II	Mythen II
Diffraction geometry	Debye–Scherrer	Debye–Scherrer
Capillary	0.3 mm, rotating	0.3 mm, rotating
Wavelength (Å)	1.00044(1)	1.00036(2)
2θ range (2θ)	2.0–65.0	2.00–70.0
Step size	0.004	0.004

3. Results

3.1. Synthesis

The morphology of the ZrPOF-DEA crystallites (Fig. 1) is slightly different from that of ZrPOF-EA. While the ZrPOF-EA crystallites display a thin needle-like morphology (*ca.* $10 \times 1 \times 0.2$ µm^3), those of ZrPOF-DEA are more plate-like in form (*ca.* $10 \times 4 \times 0.2$ µm^3).

3.2. Characterization

The diffraction patterns measured as a function of heat treatment (Fig. 2) show that, like ZrPOF-EA, ZrPOF-DEA is stable up to *ca.* 410 °C. The TG analysis (Fig. 3) shows a total weight loss of 13.97% in four steps (RT-150 °C: 0.60%; 150–200 °C: 1.25%; 200–440 °C: 2.66%; 440–900 °C: 9.46%). At the activation temperature of 410 °C, the ZrPOF-DEA sample has lost slightly less weight than has the ZrPOF-EA sample, although the total loss for ZrPOF-DEA at 900 °C is significantly larger. For ZrPOF-DEA, the adsorption capacity for CO_2 is markedly higher than that for CH_4, with a CO_2/CH_4 adsorption ratio of 11.7 at 1 bar (Fig. 4).

3.3. Structure solution

The first data set could be indexed using an orthorhombic unit cell with $a = 20.035$ Å, $b = 37.164$ Å and $c = 6.625$ Å (for comparison, the cell for ZrPOF-EA is $a = 19.957$ Å, $b = 37.067$ Å and $c = 6.617$ Å). Systematic absences were indicative of the extinction symbol *Pba-* (space groups *Pbam* or *Pba*2), so centrosymmetric *Pbam* was assumed. Reflection intensities were extracted using the LeBail method [4] implemented in the program EXTRAC [5] in the XRS-82 suite of programs [6]. The extracted intensities were then used as input to the powder charge-flipping (*pCF*) algorithm