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Synthesis and structural characterisation of two new porous metal phosphonates: $Zn(O_3PCH_2CO_2H) \cdot H_2O$ and $Pb(O_3CH{=}CH_2)$

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Abstract

Changes in the synthetic procedures for making metal phosphonate materials can lead to whole new structure types. Using a eutectic mixture of urea and choline chloride as the reaction medium for a reaction between zinc acetate and diethylphosphonacetic acid gives rise to $Zn(O_3PCH_2CO_2H) \cdot H_2O$, which has a new porous structure. Replacing divalent transition metal cations with Pb^{2+} in the synthesis of a vinylphosphonate, $Pb(O_3PCH{=}CH_2)$, gives rise to a new porous structure that has not previously been observed for vinylphosphonates. In this case it is the ability of the Pb^{2+} ions to adopt co-ordination environments other than octahederal or tetrahedral that allows the structure to form.

Keywords: Zinc phosphonate; Layered; Microporous; Materials

1. Introduction

The desire for new functional materials has provided the impetus for a marked growth in the synthesis of new materials. Molecular sieves have enjoyed considerable interest over several decades and zeolites and aluminophosphates (AlPOs) are widely used in industrial applications, in which the high surface areas and selectivity exhibited by these materials can be exploited [1].

The nature of the internal surface of a porous catalyst is an important feature of the catalyst. In zeolites (and AlPOs) the internal surface is comprised of the van der Waal's surface of oxygen ions and charge balancing cations in low and asymmetric co-ordination environments. The result is that the internal surface is hydrophilic in all zeolites, excepting those with exceptionally high Si:Al ratios. The polar nature of the internal surface will hinder the migration of polar molecules in their movements to and from the catalytic site in the porous material, and as such the activity of the catalyst in reactions such as esterification, hydration or epoxidation will be affected. One of the major aims of the research in our group has been to investigate the synthesis of new porous inorganic–organic hybrid materials. In materials of this type it is thought that the nature of the internal surface may be tuned to some extent allowing the optimum environment for the migration of reactant, product and solvent molecules through the pores of the material to be achieved.

Metal phosphonates, i.e. materials containing $[O_3PR]^{2-}$ or $[HO_3PR]^{-}$ where R is an organic functional group, can be though of as derivatives of metal phosphates and have been known since 1976 [2]. These inorganic–organic hybrid materials offer the possibility of combining the structural properties of an inorganic matrix with the utility offered by the wide choice of organic functionality that is available. Attempts to synthesise porous M(IV) phosphonates have largely been based upon the inclusion of biphosphonate anions $[O_3P–R–PO_3]^{4-}$ [3]. In M(IV) phosphonates, these

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anions effectively form a bridge between two metal atoms. However, the resulting materials are often not porous due to the bulk of the R group located in the centre of the phosphonate anion. At best, the porosity is not uniform and broad pore size distributions are observed. Results from our own unpublished work suggest that the rates of reaction between metal and phosphonic acids vary with the functional group; in many cases two separate phases are formed which have appropriately different interlayer separations.

Since the first reported materials many different metal phosphonates have been synthesised and whilst they are mostly layered, they show a wide variety of structural architectures including chain, layer and three dimensional structures. The latter structure type has been known since 1994 when several porous materials were serendipitously synthesised; β-$Cu(O_3PCH_3)$ [4], β-$Al_2(O_3PCH_3)_3$ (known as AlMePO-β) [5,6], β-$Zn(O_3PCH_2NH_2) \cdot H_2O$ [7] and AlMePO-α [8]. There was however, no systematic synthetic method that could be employed in the synthesis of porous metal phosphonates. This is due, in part, to the fact that in the preparation these materials there is a fast reaction between the metal ions and the phosphonate anions in aqueous solution and the product is immediately precipitated. Subsequent hydrothermal treatment serves only to improve the crystallinity in many cases.

Over the past 5 years new synthetic methods have been developed which have given rise to porous materials. The approach used employs dialkylphosphonate esters in the synthesis rather than phosphonic acids. Under the hydrothermal reaction conditions the acidity of the transition metal solution ($pH = 4–5$) is sufficient to slowly hydrolyse the ester to yield the acid, which in turn reacts with the metal ions to form the metal phosphonate products. It has been shown that using this approach in syntheses, which have previously been carried out using the corresponding phosphonic acid, often leads to the formation of materials with completely different structure types [9,10] and in some cases polymorphs of existing materials [11]. Furthermore it has been shown that this method is well suited to producing series of isostructural materials that contain more than one metal ion [10].

The usual method of synthesising materials of this type involves hydrothermal or solvothermal methods, in which the reactants are placed in a sealed autoclave with water (or another solvent) and heated to 150–200 °C resulting in an autogenous pressure. A template or structure-directing agent is also often included which leads the synthesis to a particular structure type, particularly in the synthesis of zeolites and phosphates. The products produced in such reactions are highly dependent upon the conditions under which the reactions are carried out. Changes in the reaction temperature (and hence pressure), reactant concentration, pH and reaction time can have significant implications with regard to the final product obtained.

It has recently been reported that zeolite-like materials can be formed using imidazolium-based ionic liquids and urea/choline chloride eutectic mixtures as the reaction medium [12]. These media are commonly defined as salts, or mixtures of salts, whose melting points are lower than 100 °C. The high boiling points (and low vapour pressure) of these liquids means that even at temperatures typically used in the synthesis of porous materials, the pressure within the synthesis is essentially ambient, and in the ionic liquid reactions the reaction medium also plays the part of structure directing agent.

In this paper we report the synthesis of two new metal phosphonates with three dimensional frameworks; $Zn(O_3PCH_2CO_2H) \cdot H_2O$ and $Pb(O_3PCH{=}CH_2)$. The former was synthesised using a eutectic mixture of urea and choline chloride as a solvent. The latter was synthesised using the traditional hydrothermal method but demonstrates how new structure types can be synthesised when a diethyl phosphonate ester rather than a phosphonic acid is used in the synthesis.

2. Experimental

2.1. Synthesis

All reagents were used as received from the supplier (Aldrich) without further purification. All of the materials are synthesised by reaction between the relevant metal acetate, ($Pb(CH_3CO_2)_2 \cdot 3H_2O$ or $Zn(CH_3CO_2)_2 \cdot 2H_2O$), and the appropriate diethyl phosphonate ester. In a typical experiment 3.7 mmol of metal acetate are dissolved in 10 ml of solvent. The solution is stirred until the acetate has dissolved, after which 3.7 mmol of diethyl phosphonate are added. The reaction mixture is stirred for an additional 15 min, then transferred to a Teflon lined autoclave, which has a fill capacity of 23 ml. The autoclave is placed in an oven at 160 °C for 2 days, after which it is removed and allowed to cool. In the case of the $Pb(O_3CH{=}CH_2)$ distilled water was used as the solvent in a reaction between lead acetate and diethyl vinylphosphonate. In the synthesis of $Zn(O_3PCH_2CO_2H) \cdot H_2O$ however, the solvent used was a 1:1 choline chloride/urea eutectic mixture, and the solution containing zinc acetate was heated at 120 °C for 2 h to remove water prior to addition of diethyl phosphonoacetic acid. In both cases the products are recovered by filtration, washed with distilled water and allowed to dry in air. CHN contents were determined using a Carlos Elba 1011 analyser.

2.2. Sample characterisation

Single crystal data measurement of $Pb(O_3PCH{=}CH_2)$ was carried out using a Bruker Smart 6000 CCD diffractometer equipped with a copper tube radiation source (Cu K_α $\lambda = 1.54178$ Å). Data were collected at 23 °C for a crystal mounted on a glass fibre using an epoxy resin.

2.3. Synchrotron microcrystal diffraction data acquisition

The crystals of $Zn(O_3PCH_2CO_2H) \cdot H_2O$ were too small to be analysed using a laboratory diffractometer. Data were