



## Synthesis and crystal chemistry of the STA-12 family of metal *N,N'*-piperazinebis(methylenephosphonate)s and applications of STA-12(Ni) in the separation of gases

Michael T. Wharmby<sup>a</sup>, Gordon M. Pearce<sup>a</sup>, John P.S. Mowat<sup>a</sup>, John M. Griffin<sup>a</sup>, Sharon E. Ashbrook<sup>a</sup>, Paul A. Wright<sup>a,\*</sup>, Lars-Hendrik Schilling<sup>b</sup>, Alexandra Lieb<sup>b</sup>, Norbert Stock<sup>b</sup>, Sachin Chavan<sup>c</sup>, Silvia Bordiga<sup>c</sup>, Edder Garcia<sup>d</sup>, Gerhard D. Pirngruber<sup>d</sup>, Martin Vreeke<sup>e</sup>, Leszek Gora<sup>e</sup>

<sup>a</sup>EaStCHEM School of Chemistry, University of St. Andrews, Purdie Building, North Haugh, St. Andrews, Fife KY16 9ST, UK

<sup>b</sup>Institut für Anorganische Chemie, Christian-Albrechts-Universität zu Kiel, Max-Eyth-Straße 2, D-24118 Kiel, Germany

<sup>c</sup>Department of Inorganic, Physical and Materials Chemistry, INSTM Centro di Riferimento and NIS Centre of Excellence, Università di Torino, Via P. Giuria 7, I-10125 Torino, Italy

<sup>d</sup>JFP Energies Nouvelles – Lyon Site, Rondpoint de l'échangeur de Solaize, BP-3, F-69360 Solaize, France

<sup>e</sup>Agilent Technologies Netherlands B.V., P.O. Box 8033, 4330 EA Middelburg, The Netherlands

### ARTICLE INFO

#### Article history:

Available online 10 December 2011

#### Keywords:

Phosphonate MOFs  
Dehydration behaviour  
Adsorption  
Breakthrough curves  
GC PLOT column

### ABSTRACT

The crystal chemistry of divalent metal *N,N'*-piperazinebis(methylenephosphonates) of the STA-12 family,  $(M_2(H_2O)_2(O_3PCH_2NC_4H_8NCH_2PO_3) \cdot xH_2O)$ ,  $M = Mg, Mn, Fe, Co, Ni$ ) is compared. The different metal analogues are isostructural in the hydrated forms, possessing  $R\bar{3}$  symmetry, but their reversible dehydration behaviour and resultant porosity are strongly dependent on the metal cation. Whereas the Co and Ni forms change symmetry to triclinic upon dehydration, giving permanent porosity to  $N_2$  of  $0.14 \text{ cm}^3 \text{ g}^{-1}$  and  $0.27 \text{ cm}^3 \text{ g}^{-1}$ , respectively, the Mn and Fe forms remain rhombohedral but exhibit a strong decrease in unit cell volume (e.g. 23% for STA-12(Mn)). Structure determination of dehydrated STA-12(Mn) indicates a topotactic transformation with a change in coordination of the phosphonate O atoms. Negligible permanent porosity is observed in either dehydrated STA-12(Mn) or (Fe), suggesting the presence of non-crystallographic pore blocking. Dehydration of STA-12(Mg) results in loss of some long range order, preventing structural determination of the fully dehydrated form, but does give appreciable permanent porosity for  $N_2$  of  $0.20 \text{ cm}^3 \text{ g}^{-1}$ . Infrared spectroscopy (and for STA-12(Mg) solid-state NMR spectroscopy) have been used to follow the changes upon dehydration. Applications of the most porous and stable STA-12 structure, the Ni form, have also been investigated.  $CO_2$  adsorption selectivity over  $CH_4$  and CO has been measured via analysis of breakthrough curves, and a Porous Layer Open Tubular (PLOT) gas chromatographic column has been prepared and used to separate a mixture of low molecular weight alkanes.

© 2011 Elsevier Inc. All rights reserved.

### 1. Introduction

There is great current interest in porous metal organic frameworks (MOFs) because of the wide range of novel properties and potential applications that they possess [1,2]. Some of the most important structure types of MOFs can be prepared with more than one type of metal cation in their framework sites. Among those prepared with divalent metal cations, for example, the CPO-27/MOF-74 metal dihydroxyterephthalate framework has been reported to crystallise with Mg, Fe, Co, Ni, and Zn [3–8]. These different cationic forms show strongly different behaviour and properties, for example

in terms of their porosity upon dehydration and their stability in the presence of water vapour.

The family of divalent metal bisphosphonates derived from the linker *N,N'*-piperazinebis(methylenephosphonic acid) ( $H_4L$ ) of the structure type STA-12 (St. Andrews porous material No. 12 –  $M_2(H_2O)L \cdot xH_2O$ ,  $L = [O_3PCH_2NC_4H_8NCH_2PO]^{2-}$ ) represents the first-reported large-pore, fully-ordered, phosphonate MOF and shows some structural similarities with the CPO-27 family. Both structure types have been formed with a range of metal cations (earlier reports on STA-12 indicated that the Fe, Co, and Ni forms could be prepared [9,10]) and both contain chains of edge-sharing octahedrally coordinated metal centres, with chemisorbed water molecule included in the coordination sphere, which may be removed to generate a coordinatively unsaturated site. The structures differ in that the coordination environment of metal centres in CPO-27 is

\* Corresponding author. Tel.: +44 (0) 1334 463793; fax: +44 (0) 1334 463808.  
E-mail address: [paw2@st-andrews.ac.uk](mailto:paw2@st-andrews.ac.uk) (P.A. Wright).

provided entirely by O atoms (three from carboxylate groups and two from hydroxyl groups of the ligand, and one from a chemisorbed water molecule), whereas in STA-12 metals are coordinated by five O atoms (four from phosphonate groups of the ligand and one from the chemisorbed water molecule) and a N atom from the piperazinyll ring to form  $\text{MO}_5\text{N}$  octahedra. The piperazinyll groups link the chains to give a honeycomb array of channels filled with H-bonded water molecules. We have determined in detail the structural response to dehydration and the adsorption behaviour for small fuel-related molecules of the Ni form [10]. Loss of water (including that bound to the  $\text{Ni}^{2+}$  cations) results in a complex two-step structural reorganization involving rotation of two out of three phosphonate groups to become 3-fold rather than 2-fold coordinate, while the large pore character is retained. Single component adsorption isotherms at 303 K show higher uptake of carbon dioxide compared to methane, with ratios of uptake of 10 and 3 at 1 bar and 10 bar, respectively [10]. Furthermore, it has been possible via isorecticular synthesis to prepare a material with a topologically identical network but with pores of free-diameter approaching the mesoporous regime, using a bipiperidine analogue of the  $\text{H}_4\text{L}$  linker and  $\text{Co}^{2+}$  or  $\text{Ni}^{2+}$  [11].

In this work we report details of the synthesis, structural response to dehydration and adsorption behaviour of the previously reported Fe and Co versions of STA-12 [9,10,12]. In addition, we report for the first time the synthesis of the Mg form, prepared as CAU-2 (Christian-Albrechts-University) and its single crystal structure, dehydration behaviour and adsorption characteristics and also the synthesis of STA-12(Mn). The dehydration behaviour of these solids has been studied by X-ray diffraction and IR spectroscopy and the adsorption of  $\text{N}_2$  and  $\text{CO}$  at 77 K and  $\text{CO}_2$  at 195 K have been used to probe the permanent porosity. Remarkably, the structural transformations of these solids upon loss of chemisorbed water and the resultant accessible porosity differ strongly according to the type of metal cation in the structure, with the Ni form showing the highest available porosity for  $\text{N}_2$  and the strongest interaction with adsorbed molecules. We have therefore further explored the potential of STA-12(Ni) for applications in adsorption and separation.

Firstly, measurement of breakthrough curves has been used to examine gas separation behaviour in  $\text{CO}_2/\text{CH}_4$  and  $\text{CO}_2/\text{CH}_4/\text{CO}$  gas mixtures. The capacity and selectivity of adsorption of  $\text{CO}_2$  in such mixtures is important in determining the potential utility of porous solids in such applications as the removal of  $\text{CO}_2$  from synthesis gas mixtures produced by steam reforming, or in the purification of biogas, a mixture of  $\text{CO}_2$  and  $\text{CH}_4$  [13]. Previously, the analysis of breakthrough curves has been widely used to investigate the selectivity of adsorption of  $\text{CO}_2$  from mixtures with  $\text{CH}_4$  and  $\text{CO}$ , for example by the flexible MOF MIL-53(Al) [14,15] as well as the rigid MOF HKUST-1 (Cu-BTC) [13].

Secondly, a Porous Layer Open Tubular (PLOT) column of STA-12 has been tested in the separation of low boiling point alkanes by gas chromatography. PLOT columns find widespread application in analytical gas chromatography of permanent gases, light hydrocarbons and volatile solvents, where they are the state-of-the-art [16–18]. The large surface areas and readily tuned surface chemistry of MOFs, together with the ability to prepare them as small crystals suitable for coating the internal surfaces of columns, suggest that they could offer advantages in separation efficiency and selectivity as stationary phases. PLOT columns coated with pre-prepared nanoparticles of MIL-101(Cr) by deposition have shown promising properties for the separation of xylenes and ethylbenzene [19] and the *in situ* deposition of thin layers of MOF-5 within capillaries has given columns that show performance in the separation of light alkanes that is at least as good as observed for commercial alumina-based PLOT columns [20]. Most recently, columns with ZIF-8 have been used for selective micro-extraction and GC of linear alkanes in petroleum mixtures, utilising their size selectivity [21]. Here we report the preparation of a PLOT column

with STA-12(Ni) as the stationary phase, and its performance in the separation of a mixture of low boiling point alkanes, as commonly found in natural hydrocarbon gas.

## 2. Experimental

### 2.1. Synthesis

*N,N'*-Piperazinebis(methylenephosphonic acid) ( $\text{H}_4\text{L}$ ) was prepared by the method reported by Mowat et al. [22]. All other reagents were obtained from Sigma–Aldrich and were used without further purification. STA-12(Ni) was prepared for breakthrough curve measurement and GC column preparation using a gel of composition 2:1:1000 ( $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}:\text{H}_4\text{L}:\text{H}_2\text{O}$ ) on a 50 ml scale using a 100 ml Teflon<sup>®</sup> lined autoclave. The gel was then heated for 100 h at 493 K. For the other divalent metals, an initial series of experiments with reaction compositions 2:1:900 ( $\text{M}(\text{AcO})_2 \cdot x\text{H}_2\text{O}:\text{H}_4\text{L}:\text{H}_2\text{O}$ ) was performed on a 20 ml scale using 40 ml Teflon<sup>®</sup> lined autoclaves. The initial pH was raised to 6 (Mn, Fe) or 7 (Co, Mg) by dropwise addition of 1 M KOH and the resulting gels were heated hydrothermally at 433 or 493 K for 18–72 h. It was found that whereas STA-12 crystallised under these conditions with Mn, Fe, Co, (and Ni), a different phase was prepared in the presence of Mg ( $\text{Mg}_2\text{L} \cdot 1.6\text{H}_2\text{O}$  – Supplementary data). Optimised conditions for hydrothermal syntheses are given in Table 1. Additional work was performed that led to the successful synthesis of the Mg-version of STA-12, both by high-throughput (HT) methods and by microwave syntheses. With this information, it was possible to modify the hydrothermal synthesis to give either of the two new phases, STA-12(Mg) or  $\text{Mg}_2\text{L} \cdot 1.6\text{H}_2\text{O}$ . The final successful conditions for hydrothermal synthesis of the Mg form of STA-12 are also given in Table 1. Diffraction and analytical results for the various solids were consistent with the phase pure STA-12.

HT reactions were performed under hydrothermal conditions in a custom-made stainless steel HT reactor, containing 24 PTFE inserts each with a maximum volume of 2 ml [23,24]. For all reactions,  $\text{H}_4\text{L}$  was loaded directly into each PTFE insert. Standard solutions of metal salt ( $0.1\text{--}0.4\text{ g ml}^{-1}$ ) and KOH ( $2\text{ mol dm}^{-3}$ ) were transferred to each insert by micropipette. Each reaction was made up to a total volume of 1.5 ml by addition of distilled water. Reactions were then heated by conventional heating to 388–433 K for 24–52 h. The reaction system  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}/\text{H}_4\text{L}/\text{KOH}$  was investigated systematically by HT methods. Mg:L ratios of 1:1 and 2:1 were selected, with the amount of base varied between 0 and 10 M equivalents and the overall concentration of reagents kept constant at  $0.18\text{ mol dm}^{-3}$ . Reactions were heated at 413 K for 52 h, followed by slow cooling ( $0.2\text{ K min}^{-1}$ ). A summary of the results of the HT reactions is included in the Supplementary data.

Microwave syntheses were performed using a Biotage Initiator microwave system, using 5 ml glass microwave vials fitted with magnetic stirrer bars. In all reactions a total solvent volume of 3.5 ml was used. Initial syntheses used reaction ratios which had been found to be successful in the HT synthesis (1:1:3.5:1700 –  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}:\text{H}_4\text{L}:\text{KOH}:\text{H}_2\text{O}$ ). Toluene was added to the reaction to reduce the pressure of the reaction without reducing the reaction volume. In combination with rapid stirring, addition of toluene was found to produce a fine white powder characterised as phase pure CAU-2. The molar ratio 1:1:3.5:366:15.5 ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}:\text{H}_4\text{L}:\text{KOH}:\text{H}_2\text{O}:\text{toluene}$ ) heated at 413 K for 4 min and with rapid cooling, was found to produce the highest purity STA-12(Mg)/CAU-2.

### 2.2. Analytical methods

Powder X-ray diffraction (PXRD) patterns of hydrothermally prepared samples were collected for as-prepared and dehydrated

Download English Version:

<https://daneshyari.com/en/article/73946>

Download Persian Version:

<https://daneshyari.com/article/73946>

[Daneshyari.com](https://daneshyari.com)