

NEW ZINC-BASED METAL ORGANIC FRAMEWORK MATERIAL

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ABSTRACT

We have synthesized and structurally characterized new crystalline porous zinc benzene-1,3,5-tricarboxylate (Zn-MOF). The material was prepared in water/ethanol solution at 448 K after 1 day. Its structure was solved from synchrotron powder X-ray diffraction data (R3c, a=30.1003(3), c=6.9141(2) Å). The framework of the structure is built up from chains of ZnO₄ and ZnO₆ polyhedra that are further connected through the carboxylate anions into a 3-D porous structure. Free water molecules are disordered in the pores. Thermal analyses of the material, made by TG and HT-XRD and hydrothermal tests in boiling water, revealed its reversible water adsorption/desorption properties.

Keywords: metal-organic framework, zinc carboxylate, structure determination, hydrothermal stability

INTRODUCTION

Metal Organic Frameworks (MOFs) represent a new group of porous crystalline materials. MOFs are built up of metal atoms or clusters connected to multifunctional organic ligands (linkers), which possess different complexing groups (typically polycarboxylates or N-containing compounds) [1]. Main advantages of MOFs are their low density (down to 0.2 g cm⁻³), high surface area (up to 5900 m² g⁻¹) and large pore volume (up to 2 cm³ g⁻¹) [2]. The MOFs have attracted much attention in recent years, because of their unique chemical and structural characteristics, which enable a variety of applications [3]. MOF materials are suitable for adsorption and storage of many different gases [4], like hydrogen for energy applications [5], environmentally important gases CO₂ and SO₂ [6], and physiological important gases such as NO. These materials are also promising candidates for applications in heterogenous catalysis and drug delivery [7,8]. Recently, the potential of MOF adsorbents in heat transformation and storage applications has been pointed out [9].

Polydentate ligands, like benzene-1,3,5-tricarboxylate ions, are suitable for constructing porous solids, since carboxylates have a great ability to coordinate metal centers in different bonding modes: unidentate, bidentate and bridging. A great success of some porous zinc carboxylates (e.g. MOF-5, MOF-177) as potential gas storage materials raised the interest in designing new zinc-based coordination polymers [6,10]. Here we report on the synthesis and structure investigations of new hydrothermally stable porous zinc benzene-1,3,5-tricarboxylate (Zn-BTC).

EXPERIMENTAL

Needle-like shaped crystals of Zn-BTC crystallized from the gel with molar ratios of reactants Zn(ac)₂·2H₂O : BTC : 93.8 H₂O : 72.4 EtOH after solvothermal treatment at 448 K for 1 day in Teflon-lined autoclaves (Figure 1). The size and morphology of the crystals in the product were studied with scanning electron microscope Zeiss Supra™ 35VP.

Crystal structure was solved using synchrotron powder diffraction data collected at Soleil synchrotron facility at CRISTAL beamline. Infrared spectra recorded in the range of 500 in 4000 cm^{-1} by KBr containing pellets on Perkin-Elmer Spectrum 100 FT-IR 1720X spectrometer were studied to confirm some structural components and energy dispersive X-ray microanalyzer (EDX) connected to a scanning electron microscope was used for elemental analysis.

Thermogravimetric analysis was performed on thermal analysis system SDT 2960 thermal analysis system (TA Instruments, Inc.). The measurements were carried out in a nitrogen stream (flow rate - 100 mL/min) with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ from room temperature to 750 $^{\circ}\text{C}$. The thermal behavior of material was also studied by high temperature X-ray diffraction (HT-XRD) in a nitrogen flow employing a PANalytical X'Pert PRO MPD diffractometer ($\text{CuK}\alpha$ $\lambda = 1.5406$ \AA radiation) in the temperature range from RT to 600 $^{\circ}\text{C}$. The XRD patterns were collected using continuous scanning mode in 2θ range 5 - 70 $^{\circ}$ with a scanning speed of 0.013 $^{\circ}$ at a counting time of 100 s per step. Hydrothermal stability of Zn-BTC was evaluated by boiling in distilled water for different periods of time up to 16 hours

under refluxing. The reversibility of water sorption was checked by XRD analysis of the sample first heated for three hours at 200 $^{\circ}\text{C}$ and then left in humid air for 24 hours.

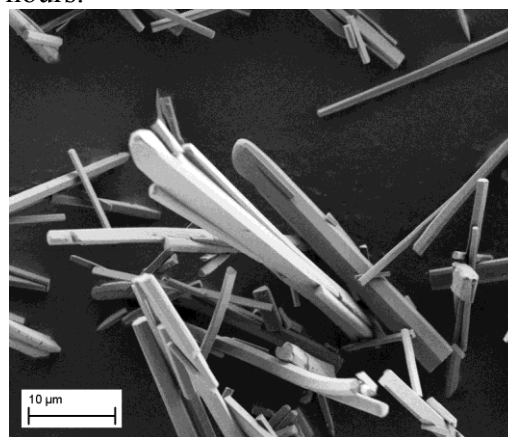


Figure 1. 10-20 μm needle-like crystals of Zn-BTC.

RESULTS AND DISCUSSION

The framework, shown on Figure 2a, with hexagonal $R3c$ symmetry and unit cell parameters $a = 30.1003(3)$ \AA , $c = 6.9141(2)$ \AA is built up from the chains of ZnO_4 and ZnO_6 polyhedra (Figure 2b), that are further connected through carboxylate anions into a 3-D porous structure. Free water molecules are disordered in the pores (omitted in Figure 2a for clarity).

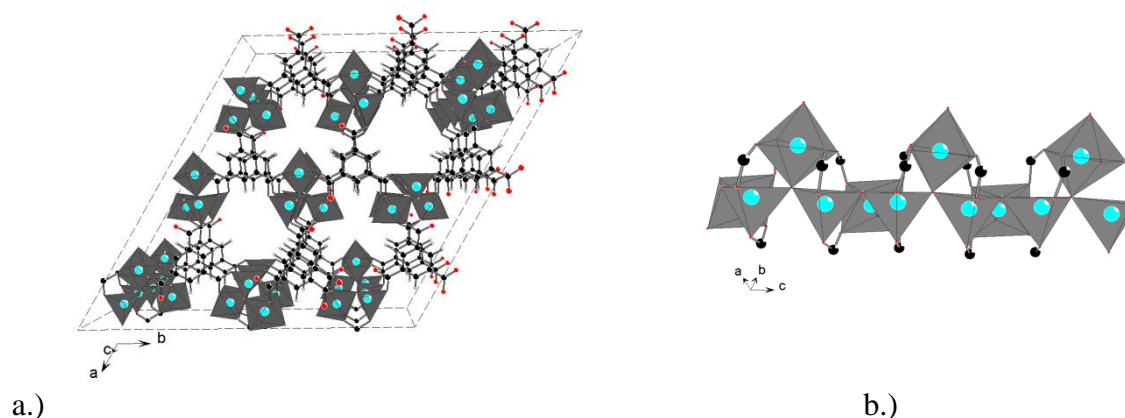


Figure 2. (a) Framework structure of Zn-trimesate along c axis with unit cell edges; (b) chain of Zn-centered corner-sharing tetrahedra and octahedra.

Thermal properties of the material were investigated by TG and HT-XRD. TG measurements (Figure 3) show weight loss in four major steps. The first step up to 363 K corresponds to the loss of physisorbed water on the surface of the crystallites, the second up to 473 K to desorption of water from the pores, the third one up to 623 K is due to desorption of water bonded to the framework Zn-atoms and the fourth one up to 773 K to framework degradation to ZnO phase. The indicated structural changes by TG were confirmed by HT-XRD.

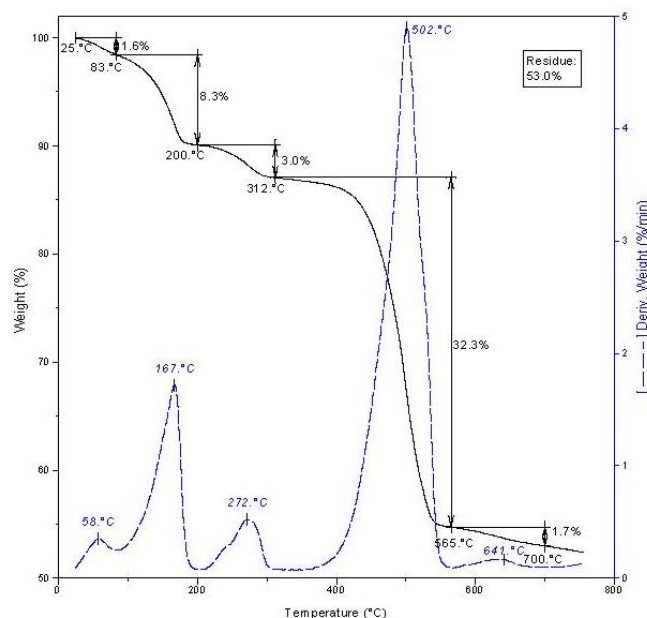


Figure 3. TGA data for zinc benzene-1,3,5-tricarboxylate (Zn-MOF) heated to 750°C in nitrogen at a rate of 10°C min⁻¹.

Figure 4a shows the investigation of dehydration-rehydration process (RT - 200°C - RT) of the structure made by X-ray powder diffraction. The treatment of materials at 200°C leads to a phase change. However, the dehydration is reversible and the XRD pattern of the rehydrated powder (bottom) corresponds to that of the initial compound (top).

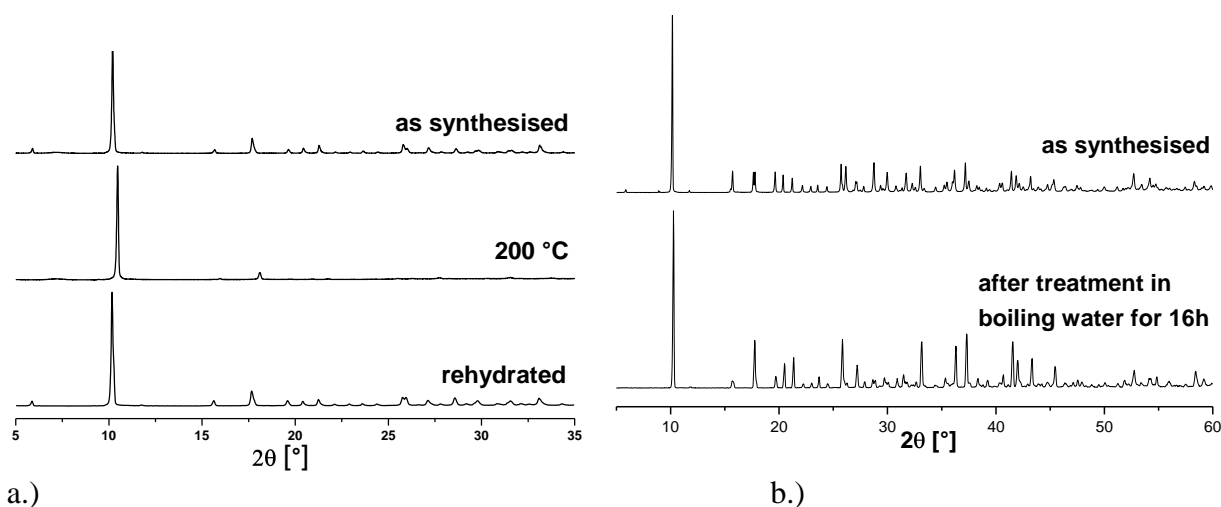


Figure 4. (a) XRD analysis of three patterns (as synthesised, treated at 200°C and rehydrated materials) confirmed reversible water sorption properties; (b) X-ray powder diffraction patterns of as synthesised Zn-MOF (top) and hydrothermally treated Zn-MOF (bottom).

The comparison of XRD patterns (Figure 4b) of as-synthesized Zn-BTC material and the one treated in boiling water under refluxing shows that material exhibits hydrothermal stability.

CONCLUSION

A porous 3-dimensional metal-organic framework compound was prepared from a reaction mixture of zinc acetate and benzene-1,3,5-tricarboxylate. Its good hydrothermal and reversible water adsorption/desorption properties make this material a promising candidate for sorption applications in gas or heat storage systems.

REFERENCES

- [1] J.L.C. Rowsell, O.M. Yaghi, *Microporous Mesoporous Mater.*, 2004, **73**, 3-14.
- [2] G. Férey, *Chem. Soc. Rev.*, 2008, **37**, 191-214.
- [3] A.U. Czaja, N. Trukhan, U. Müller, *Chem. Soc. Rev.*, 2009, **38**, 1284-1293.
- [4] R.E. Morris, P.S. Wheatley, *Angew. Chem. Int. Ed.*, 2008, **47**, 4966-4981.
- [5] M. Hirscher, B. Panella, B. Schmitz, *Microporous Mesoporous Mater.*, 2010, **129**, 335-339.
- [6] A. Millward, O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, **127**, 17998-17999.
- [7] A. Corma, H. García, F.X. Llabrés i Xamena, *Chem. Rev.*, 2010 in press.
- [8] P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebrie, T. Baati, J.F. Eubank, D. Heurtaux, P. Clayette, C. Kreuz, J.-S. Chang, Y.K. Hwang V. Marsaud, P.-N. Bories, L. Cynober, S. Gil, F. Férey, P. Couvreur, R. Gref, *Nat. Mater.*, 2010, **9**, 172-178.
- [9] S. K. Henninger, H. A. Habib and C. Janiak, *J. Am. Chem. Soc.* 2009, **131**, 2776-2777.
- [10] A.G. Wong-Foy, A.J. Matzger, O.M. Yaghi, *J. Am. Chem. Soc.* 2006, **128**, 3494-3495.