

Gas Chromatography. XRD powder patterns were collected on zeolites before and after adsorption on a Bruker D8 Advance diffractometer. Thermal analyses (TG and DTA) were performed in air up to 900°C at 10°C/min.

The experimental results prove that the kinetic of adsorption of all components is fast and indicates that competition exists between the organic compounds at low cosolute concentrations.

Rietveld refinements indicate that the relevant incorporation of DCE, MTBE and TOL in the organophilic zeolites causes significant increase of all unit cell parameters in comparison to those of the untreated material as well as strong distortions of the channel systems where the contaminants are hosted. The very favorable adsorption kinetics along with the effective and highly irreversible adsorption of DCE, MTBE and TOL molecules into zeolite pores make this cheap and environmental friendly material a tool with interesting applications for the removal of hydrocarbons from wastewater.

[1] A.R. Gavaskar, B.C. Kim, S.H. Rosansky, S.K. Ong, E.G. Marchand, *Environmental Progress* **1995**, *140*, 33–40. [2] D.Z. Chen, J.X. Zhang, J.M. Chen, *International journal of Environmental Science and Technology* **2010**, *7*, 235–242. [3] L. Abu-Lail, J.A. Bergendahl, R.W. Thompson, *Journal of Hazardous Materials* **2010**, *178*, 363–369.

Keywords: organophilic zeolites, X-ray diffraction, adsorption

MS.25.2

Acta Cryst. (2011) **A67**, C68

Synthesis and structures of new layered and framework anion exchangeable hydroxides

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New anion exchangeable intercalation compounds with either lanthanide hydroxide layers or lanthanide oxyhydroxide cationic inorganic frameworks have been synthesised. The layered materials have the general composition $\text{Ln}_2(\text{OH})_2\text{X}\cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{Y, Gd} - \text{Lu}$; $\text{X} = \text{NO}_3, \text{Cl, Br}$) and have been shown to be flexible intercalation hosts undergoing anion exchange reactions with a wide range of organic carboxylates and sulfonates. [1], [2] Structural characterisation of the halide intercalates has shown them to comprise 8 and 9 coordinate lanthanide cations within the $[\text{Ln}_2(\text{OH})_2]^+$ layers with bridging hydroxide anions and coordinated water molecules making up the coordination sphere.

Time resolved in situ X-ray diffraction studies of the synthesis of these materials have shown that their mechanism of formation is complex with four distinct phases being identified and isolated.[3] Three of these phases are layered intercalation hosts with the layer composition $[\text{Yb}_2(\text{OH})_5]^+$ with differing interlayer separations controlled by the level of hydration. The fourth phase is $\text{Yb}_4\text{O}(\text{OH})_9\text{NO}_3$ which has a 3D structure with 1D channels which contain the nitrate anions and as such this system represents a rare case where a 2D material has been observed to transform to a 3D structure. For the halide materials a different framework material, $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl}\cdot 2\text{H}_2\text{O}$ which has much larger channels is formed.[4] In this material the chloride anions can be exchanged for a range of small organic and inorganic anions and is therefore the first anion exchangeable hydroxide framework material. Additionally the framework is stable up to 200 °C and can be reversibly dehydrated.

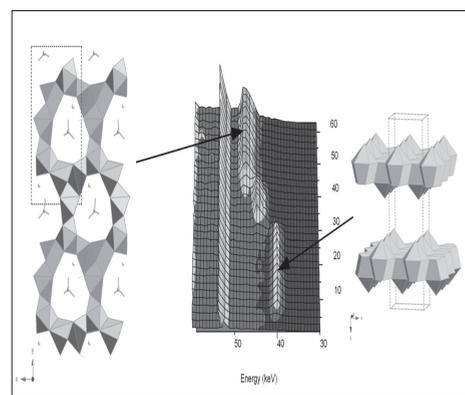


Figure 1 In situ diffraction pattern of the synthesis of $\text{Yb}_4\text{O}(\text{OH})_9\text{NO}_3$ showing the intermediate layered phases $\text{Yb}_2(\text{OH})_5\text{NO}_3\cdot n\text{H}_2\text{O}$.

[1] L. Poudret, T.J. Prior, L.J. McIntyre, A.M. Fogg *Chem. Mater.* **2008**, *20*, 7447. [2] L.J. McIntyre, L.K. Jackson, A.M. Fogg *Chem. Mater.* **2008**, *20*, 335. [3] L.J. McIntyre, T.J. Prior, A.M. Fogg *Chem. Mater.* **2010**, *22*, 2635. [4] H.V. Goulding, S.E. Hulse, W. Clegg, R.W. Harrington, H.Y. Playford, R.I. Walton, A.M. Fogg *J. Am. Chem. Soc.*, **2010**, *132*, 13618.

Keywords: framework, hydroxide, exchange

MS.25.3

Acta Cryst. (2011) **A67**, C68-C69

LHT-9: layered nano-material with reductive adsorption and exchange properties

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Layered hydrazinium titanate, LHT-9 for short, is a layered material with a lepidocrocite structure and $\approx 9\text{\AA}$ interlayer distance. It has been prepared by a simple one-pot synthesis at near ambient conditions. Its idealized chemical formula is $(\text{N}_2\text{H}_5)_{0.5}\text{Ti}_{1.87}\text{O}_4$, space group Immm, $a \approx 3.8\text{\AA}$, $b \approx 18.46\text{\AA}$, $c \approx 2.98\text{\AA}$. Under the correct conditions it forms as nano-crystalline material which, however, displays important non-periodic structural characteristics. It has been characterized by various methods, notably high resolution transmission electron microscopy, x-ray diffraction, IR spectroscopy with analysis of gas evolution upon heating, XANES and EXAFS. From the analysis it is clear that LHT-9 consists of bent and deformed nano-flakes with only a few layers thickness, a high concentration of titanyl-groups and Brønsted-sites at the surface, and chemically bound hydrazinium $(\text{N}_2\text{H}_5)^+$ in the interlayers. The reductive properties of the hydrazinium and the structural characteristics add to the remarkable properties of LHT-9 and make it a valuable tool kit for many applications. More than 50 elements of the periodic table have been shown to be reduced, adsorbed and/or ion exchanged by LHT-9. Several of these reactions have possible or even proved ecological or economical value, such as removal of toxic or radioactive species from industrial waste waters or combustion gases, or extraction of noble metals from solutions [1].

[1] S.N. Britvin, S.V. Krivovichev, W. Depmeier, O.I. Siidra, D.V. Spiridonova, V.V. Gurzhiy, A.A. Zolotarev, *PCT Patent Application PCT/EP2010/001864* filed March 25, 2010.

Keywords: layered titanates, adsorption, reduction

MS.25.4

Acta Cryst. (2011) A67, C69

Solid-State synthesis of mixed trihalides via reversible absorption of dihalogens by non porous onium salts

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1,6-Bis(trimethylammonium)hexane bis(trihalides) $1\cdot(\text{Br}_2)_2$ and mixed bis(trihalides) $2\cdot(\text{I}_2)_2$ and $2\cdot(\text{Br}_2)_2$ have been synthesized by treating the corresponding dihydrated halides $1\cdot(\text{H}_2\text{O})_2$ and $2\cdot(\text{H}_2\text{O})_2$ with molecular dihalogens (e.g., Br_2 and I_2) under gas-solid and solution conditions (Figure 1).[1] Despite the fact that the starting hexamethonium halides are non porous, the trihalides syntheses occur homogeneously, in quantitative yields, and reversibly. In all the cases the halogen bond [2] prevails over the hydrogen bond, and the hydrogen bonded water in the starting material is substituted by the halogen bonded dihalogens to form the crystalline trihalides. The stability of the trihalides is mainly due to cooperative halogen bond and cation templation effect [3]. Hexamethonium halides are proven effective solids for the clathration and storage of molecular dihalogens. While the starting salts are not isostructural, all the formed trihalides and mixed trihalides are isostructural. Single crystal X-ray diffraction, powder X-ray diffraction and Raman experiments have confirmed the formation of the solid trihalides. The method we describe is general and can be extended to the preparation of various uncommon trihalides species like interconversion of trihalides and mixed trihalides via solid-gas processes.

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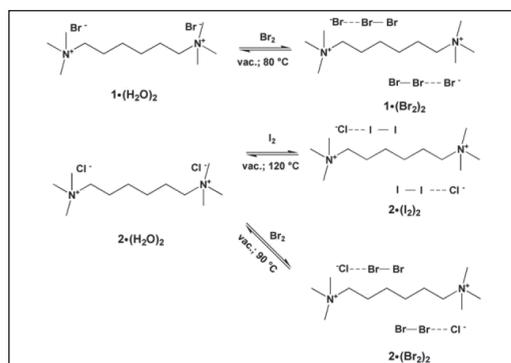


Figure 1. Synthesis of the complexes $1\cdot(\text{Br}_2)_2$, $2\cdot(\text{I}_2)_2$ and $2\cdot(\text{Br}_2)_2$ via reversible gas-solid reactions and their reversion to $1\cdot(\text{H}_2\text{O})_2$ and $2\cdot(\text{H}_2\text{O})_2$.

Keywords: gas-solid reactions, non porous salts, inclusion

MS.25.5

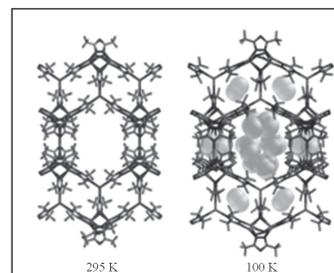
Acta Cryst. (2011) A67, C69

Experimental visualization of breathing in fluorinated metal-organic frameworks from single crystal diffraction - functionalized MOFs for gas storage and separation

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Fluorinated metal-organic frameworks (FMOFs) are a new class of advanced porous material with fluorine-lined pore surface and hydrogen-free. Reaction of silver(I) and 3,5-bis(trifluoromethyl)-1,2,4-triazolate in toluene/acetonitrile yields FMOF-1, the first example in the FMOF family, that shows high-density gas uptake and unique hysteretic sorption of H_2 [1]. Variable single crystal X-ray diffraction measurements reveals that FMOF-1 undergoes remarkable breathing and negative thermal expansion when the crystal is exposed to N_2 at ambient pressure [2]. Upon cooling a apparent negative thermal expansion takes place with very large changes in volume and unit-cell parameters during which multiple N_2 molecules are absorbed into channels and cages (see picture).

Details of the dynamic gas adsorption mechanism at the atomic level will be presented to illustrate the functional control and sequential filling of the multiple gas adsorption sites in both small and large pores within FMOF-1 and the consequent remarkable swelling of these framework cavities. Real-time 3D reciprocal space mapping technique employed at the SNS TOPAZ beam line for the analyses of guest-host interaction and structural transformation in MOFs will be introduced.



Work at ORNL was supported by UT-Battelle, LLC, under contract No. DE-AC05-00OR22725 with the US Department of Energy.

[1] C. Yang, X.P. Wang, M.A. Omary *Journal of the American Chemical Society* **2007**, *129*, 15454. [2] C. Yang, X.P. Wang, M.A. Omary *Angewandte Chemie-International Edition* **2009**, *48*, 2500-2505.

Keywords: gas storage, neutron diffraction, metal-organic framework

MS.26.1

Acta Cryst. (2011) A67, C69-C70

Understanding hydrogenation properties of various hydrogen storage materials from their local structure

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