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Stabilization of aluminium polycations by aminocarboxylic acid ligands to give Al_{15} clusters with zeotypic supramolecular structure

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Introduction

Aluminium-based materials find wide applications in the field of heterogeneous catalysis. *Barrer* and later *Vaughan*, for instance, investigated pillared clays where cations in the interlayer spaces of montmorillonite were replaced by aluminium *Keggin*-polycations. These systems are catalysts for the production of ethers and esters and show shape selectivity unlike their precursor acid-clays [1-3]. Of particular relevance for possible future applications is the ability to construct open-framework hybrid organic-inorganic materials from well-defined nanoscale alumina-derived building blocks.

Synthetic concept

In our scientific studies we succeeded in encapsulating $\{Al_7(OH)_{12}(H_2O)_{12}\}^{9+}$ polycation mineral fragments with four dimeric $\{Al_2$*hpdta*$\}$-units [4]. The three-dimensional order of the resulting Al_{15}-clusters in $(pipH_2)(H_3O)[Al_{15}(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{14}(hpdta)]\cdot pip\cdot 41H_2O$ (**1**) shows similarities to that of zeolites (Fig. 1). The clusters pack in the crystal in such a way that two different types of channels are created, which run parallel to the crystallographic *c*-axis. The larger channels (Ø ca. 11 Å), contain exclusively solvent molecules and the smaller channels (Ø ca 5 Å) the piperazinium ions. (H_5hpdta: $HOCH_2[CH_2N(CH_2COOH)_2]_2$.

Experimental, Results and Discussion

At beamline 18B we investigated new types of the above described compound where we exchanged the counterions in **1** with ethylenediamine or alkali metal ions (e.g. potassium ions). The materials crystallize from aqueous solution after the reaction of the organic ligand with four equivalent of aluminium nitrate under alkaline reaction conditions. The crystal analysis reveals that by substituting the counterions in **1** the packing of the clusters changes and we observe a transformation from the orthorhombic space group *Pccn* to the tetragonal, space-group $P4_2/ncm$. (in e.g. $(enH_2)(H_3O)[Al_{15}(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{14}(hpdta)_4]\cdot dioxane\cdot 19H_2O$ (colourless octahedral crystals: 0.2 mm x 0.2mm x 0.2mm, cell dimensions $a = 27.981(3)$, $b = 15.627(3)$, $Z = 4$, $T = 200$ K, $R_1(F) = 8.51$.). Similar results were also obtained with alkali metal ion substituted compounds.

In addition to these experiments, we exchanged the solvent in the larger channels of the structure with a series organic substrates (e.g. dioxane, acetone, ethylacetate, THF etc.). We investigated by measuring the crystal structures at a temperature of $T = 150$ K how these substrates interact with the framework of the zeotypic compound and how they bind to the mineral core in the cluster. In order to evaluate the potential of this hybrid organic-inorganic structure for hydrolytic activations or for catalysis, further investigations will be performed.

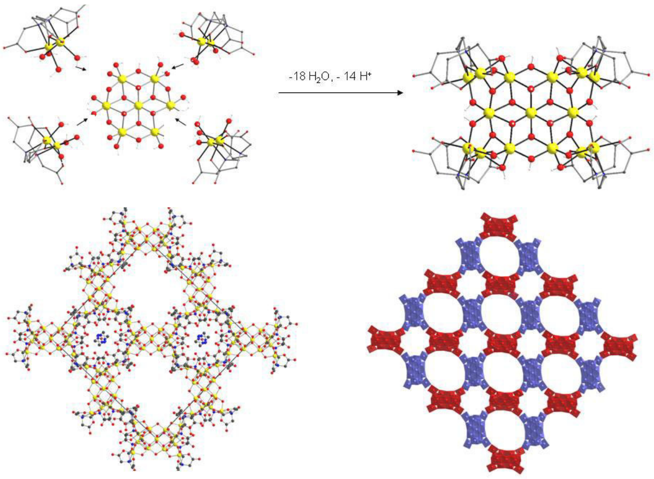

Figure 1. Encapsulation of $\{Al_7(OH)_{12}(H_2O)_{12}\}^{9+}$ -mineral fragments with four dimeric $[Al_2(hpdta)(H_2O)_4]^+$-units to form a $[Al_{15}(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{14}(hpdta)_4]^{3-}$ complex (Al: yellow, O: red, C: grey, N: blue). Lower Left: The supramolecular array of Al_{15} aggregates templated around the protonated base (piperazinium) in the smaller channels. Further solvent and base molecules have been omitted from the larger channels for clarity (view in [001]). Lower Right: Polyhedral representation. The blue Al_{15}-clusters are half a unit cell length below the plane containing the red clusters (view in [001]).

References

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