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Charge density matching in organic-inorganic uranyl compounds

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Organic-inorganic 2D nanocomposites is an emerging group of organic-inorganic materials that contain alternating organic and inorganic substructures. Here we will consider some examples of organic-inorganic nanocomposites consisting of inorganic (uranyl selenate) layers and organic 2D layers of long-chain amines and diamines. One useful concept to analyze structures of organic-inorganic nanocomposites has been the concept of charge density matching [1] at the organic/inorganic interface. The idea is that two different materials will self-organize to have similar charge densities at their surfaces and, therefore, achieve local electroneutrality. This concept has been successfully applied to a large number of organic-inorganic composites, including metal phosphates, vanadates and mesoporous silica. Application of this principle to uranyl compounds requires special attention since surface area of uranyl-based 2D units is higher than that of other inorganic oxysalts units (i.e. metal phosphates). The charge-density matching principle is, however, observed either through tail interdigitation (for long-chain monoamines) or incorporation of acid-water interlayers into organic substructure (for long-chain diamines). In some compounds, protonated amine molecules form cylindrical micelles that involves self-assembly governed by competing hydrophobic/hydrophillic interactions. The flexible inorganic complexes present in the reaction mixture could then form around cylindrical micelles to produce highly undulated 2D sheets [2] or nanotubules [3].

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A combined single crystal X-ray diffraction and FTIR study of CAL-1 a novel microporous silico-aluminophosphate

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Many AlPO and SAPO materials are isostructural with zeolites and have been prepared in the presence of amines as structure directing agents (SDA). The introduction of silicon ions into the AlPO framework leads to highly selective heterogeneous catalysts. For example, H-SAPO-34 is used for methanol-to-olefin (MTO). [1]
CAL-1, a silicoaluminophosphate with a chabasite-related structure was recently prepared by us [1] in the line of obtaining more efficient acid catalysts for MTO reactions. In this work, we present the fully solved structure of the novel CAL-1 material and a tentative to localize the SDA molecules within the zeolitic framework.
CAL-1 gels were prepared from AlPO-kanemite, a lamellar material [2], silica Aerosil 200 and hexamethyleneimine (HMI) as SDA. Syntheses were carried out at 190°C for 48 h.
The compound CAL-1 displays a chabasite-related framework with trigonal symmetry. The basic structural motif consists of an array of corner-sharing MO_4 (M = Al, P, Si) tetrahedra. The organic guest molecules are embedded within the cages of the inorganic porous host material in a disordered fashion. Calcination of CAL-1 leads to the removal of the SDA and results in the formation of H-SAPO-34 [3].
X-ray diffraction experiments on single crystals were performed using an Oxford Diffraction Xcalibur 2 single diffractometer at 120 K. FTIR spectroscopy of CAL-1 shows that, along with water molecules; protonated hexamethyleneimine and n-butylamine molecules are present in the cavities.

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