

## **MOF MATERIALS FROM DESIGN TO APPLICATIONS: CASE STUDIES OF CALCIUM- AND MAGNESIUM-BASED CARBOXYLATES**

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### **ABSTRACT**

In this contribution we present the study of Ca- and Mg-based MOF materials from rational design to application opportunities. In the case of Mg-benzene-1,3,5-tricarboxylate system we demonstrate how the solvent composition involved in the synthesis procedure plays the crucial role for the dimensionality of the final crystal structure. In the case of Ca-benzene-1,4-dicarboxylate we present the detailed spectroscopic study of its structural dynamics upon heating and elucidated the mechanism of crystal-to-crystal transformation. Finally, we show the degradation study of Ca- and Mg-based aliphatic dicarboxylates (succinates, glutarates and pimelates) in body fluid conditions and discuss the possibility employ those materials for bio-applications.

Keywords: MOFs, structural dynamic, rational design, bio-applications

### **INTRODUCTION**

The development metal-organic frameworks (MOFs) is one of the most intensively investigated topics in the field of nanoporous materials.[1] The number of new MOF structures is increasing rapidly, because their frameworks with the targeted applicative properties can be developed by rational design.[2] This however requires proper knowledge of interaction behavior between metal cations and functional groups of organic linkers in different synthetic conditions. The pores within synthesized metal-organic frameworks are often filled with solvent or template molecules and crystalline structure is usually significantly changed after removal of those moieties. In fact, majority of MOF networks are flexible and respond intensively also upon other external stimuli (temperature or pressure changes, solvent exchange).[3] The knowledge of structural dynamics of flexible frameworks is important to predict their behavior in different conditions. Framework flexibility is also one of the most interesting characteristic of metal-organic structures which can be exploited for various applications, such as sensing, separation and adsorption.[4] Majority of the research based on the design and structural characteristics was done on transition-metal MOFs. On the other hand Ca- and Mg-based MOFs are poorly explored. The investigations of Mg- and Ca-MOFs however deserve special attention. They are advantageous for implementation and industrial application due to their nontoxicity and relatively low-density frameworks. In this contribution we focused on the case studies of the design, structural dynamic investigations and application opportunities of Mg- and Ca-based MOFs.

## EXPERIMENTAL

In order to investigate the effect of solvent composition on dimensionality of Mg-MOFs, Mg(ac)<sub>2</sub>·4H<sub>2</sub>O and trimesic acid (BTC) were solvothermally treated at 150 °C for 1 to 3 days using solvents with different H<sub>2</sub>O/EtOH molar compositions (∞, 2, 1.4 and 0).

Structural dynamic upon heating was performed on the case of Ca-terephthalate, which was solvothermally treated at 125 °C for 3 days using Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, and terephthalic acid (BDC) in the mixture of DMF and water using as solvent.

In order to investigate degradation process of biocompatible Ca- and Mg-MOFs, various materials containing aliphatic ligands (succinic acid, glutaric acid, pimelic acid) were synthesized hydrothermally. Materials were put in aqueous solutions with pH values of 7 and 3 at 37 °C. At certain times of degradation aliquots were taken from solution and concentration of the released metal was measured by AAS analysis.

X-ray powder diffraction patterns were recorded on a PANalytical X'Pert PRO high-resolution diffractometer with Alpha1 configuration (CuKα1 λ = 1.5406 Å) in 2θ range from 5 to 60° using step of 0.016° per 100 s. Thermogravimetric (TG/DTG) analysis was performed on a SDT 2960 Thermal Analysis System (TA Instruments, Inc.). The measurement was carried out in static air with the heating rate of 10 °C min<sup>-1</sup>. Fourier-transform infra-red (FT-IR) measurements were performed on a Perkin Elmer Spectrum One FTIR spectrometer with resolution of 1 cm<sup>-1</sup> from self-supporting KBr pellets. <sup>1</sup>H and <sup>1</sup>H-<sup>13</sup>C CPMAS NMR spectra were recorded on a 600 MHz Varian NMR system equipped with a 3.2 mm Varian probehead. X-ray absorption (EXAFS and XANES) spectra of Ca-terephthalate materials were measured in the Ca K-edge energy region (4039 eV) in the transmission detection mode at the XAFS beamline at the ELETTRA synchrotron facility in Basovizza, Italy. Atomic absorption spectroscopy (AAS) was performed on a Perkin Elmer Analyst 200 spectrometer.

## RESULTS AND DISCUSSION

Four new Mg-based 1,3,5-benzenecarboxylates were obtained using H<sub>2</sub>O/EtOH mixed solvents with volume ratios 1:0, 1:1.6, 1:2.2 and 0:1, respectively, keeping Mg/BTC ratio constant. We found that the solvent composition has a strong influence on the formation of crystal structures and their dimensionalities can be controllably tuned with the variation of H<sub>2</sub>O/EtOH ratios in the synthesis procedure. When the synthesis is performed hydrothermally (with only water present) 0-D complex with the formula Mg(H<sub>2</sub>btc)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub> is crystallized. When using the mixture of water and ethanol as the solvent with the H<sub>2</sub>O/EtOH volume ratio of 0.63, one-dimensional, chain-like Mg<sub>3</sub>(btc)<sub>2</sub>(H<sub>2</sub>O)<sub>12</sub> material is formed. The further increase of ethanol amount (H<sub>2</sub>O/EtOH = 0.45) leads to the formation two-dimensional, layered structure with formula Mg<sub>2</sub>(Hbtc)(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>, while the synthesis in pure ethanol yields three-dimensional Mg<sub>3</sub>(btc)<sub>2</sub> structure. The influence of solvent composition on the dimensionality of the formed Mg-trimesates is schematically shown on Figure 1.

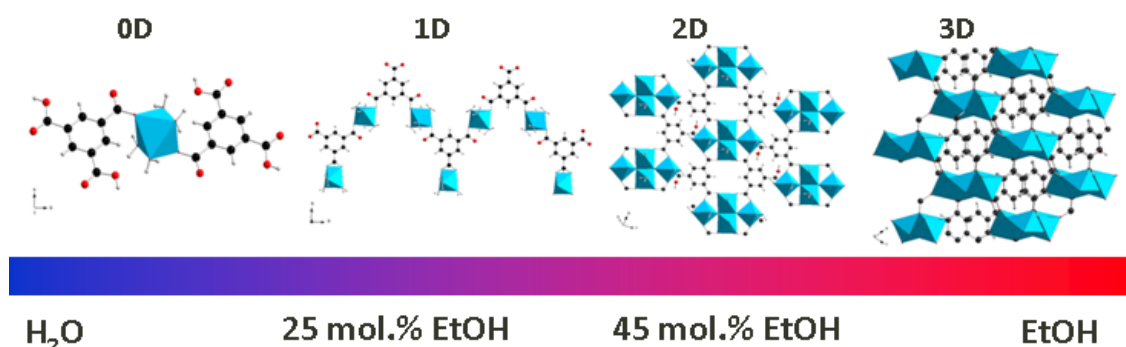


Figure 1: Schematic representation of solvent composition influence on Mg-BTC dimensionalities.

Structural dynamics of Ca(BDC)(DMF)(H<sub>2</sub>O) with rhombic-shaped channels upon heating were elucidated using complementary methods of diffraction (XRD) and spectroscopy (FT-IR, MAS NMR, EXAFS, XANES). During heating the Ca(BDC)(DMF)(H<sub>2</sub>O) framework underwent structural changes in two steps. First change at 150 °C includes breaking of Ca-O bonds with H<sub>2</sub>O and DMF molecules. In this step DMF is removed from the surface or near the surface of the crystals. The affected parts of the crystals are transformed to a new non-porous Ca-BDC(400) phase which prevents the diffusion of DMF from the cores of the crystals. Second transition at 400 °C led to the complete transformation to Ca-BDC(400). We proposed mechanism of Ca-BDC(RT) → Ca-BDC(400) transformation which includes breaking of the bonds between Ca<sup>2+</sup> and carboxylate groups, rotating of BDC ligand and re-coordination of COO<sup>-</sup> groups to Ca<sup>2+</sup> centers. The crystal-to-crystal transformations are driven by the tendencies to change the bonding modes between COO<sup>-</sup> and Ca<sup>2+</sup> with the change of Ca<sup>2+</sup> coordination number. Thus the decrease of Ca<sup>2+</sup> coordination number, which is usually a consequence of activation, does not lead to the expansion or contraction of the pores, but it leads to the pronounced structural rearrangement. The scheme of the crystal-to-crystal transformation mechanism is presented on Figure 2.

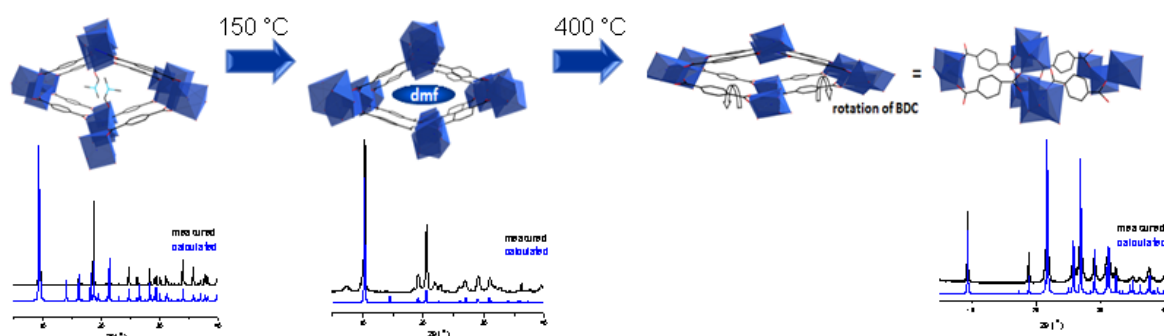


Figure 2: Scheme of structural dynamic of Ca(BDC)(DMF)(H<sub>2</sub>O) upon heating along with the corresponding measured and simulated XRD patterns.

Finally, biocompatible Ca- and Mg-based MOFs with succinate, glutarate and pimelate ligands were investigated for degradation processes in aqueous media at pH values of 7 and 3 at 37 °C. It was clearly shown that degradation rate is mostly dependent on the type of the ligand, present within the MOF structure. Succinates and glutarates possessing more hydrophilic nature and lower polarizability degrade more rapidly, while pimelates with higher polarizability and more hydrophobic nature degrade slower. Figure 3 shows the release of Mg<sup>2+</sup> and Ca<sup>2+</sup> cations from different materials at pH of 3.

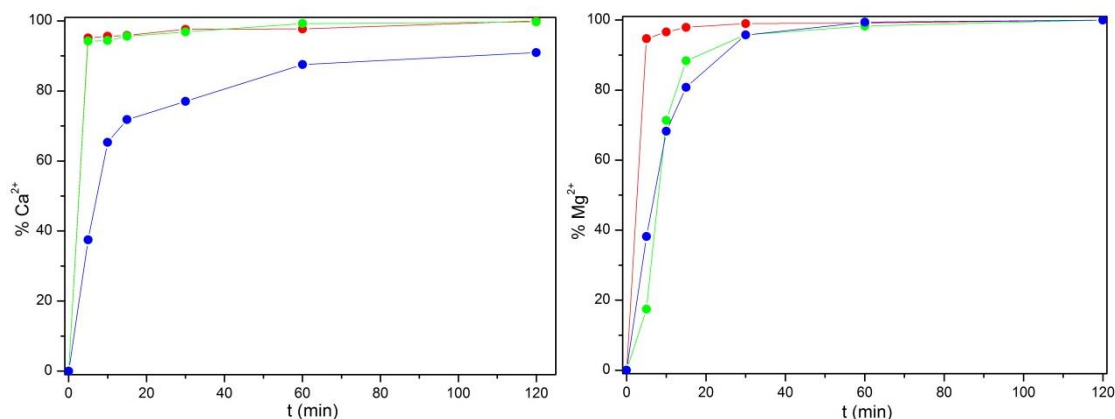


Figure 3: Amount of released cations ( $\text{Ca}^{2+}$  left,  $\text{Mg}^{2+}$  right) at  $\text{pH} = 3$  at given times for succinates (red), glutarates (green) and pimelates (blue)

## CONCLUSIONS

In this contribution we have focused on the case studies of design, structural dynamic and application opportunities investigations for Mg- and Ca-MOFs. We showed that the structure dimensionalities of Mg-trimesates can be tuned by solvent composition. In the case of Ca-terephthalate we showed that spectroscopic techniques are indispensable support to XRD analysis for investigation of structural dynamic. Finally, Ca- and Mg-based aliphatic MOFs were investigated for potential bioapplications. We showed that degradation rate of MOFs is strongly dependent on hydrophilic and polarizability nature of ligands.

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