

MS24-O4

Topotactic transformations during thermolysis of Mg-Ga(Al) LDHs: structure of disordered nanocrystalline phasesSvetlana Cherepanova¹, Nataliya Leonteva²

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Layered double hydroxides (LDHs) have hydrotalcite structure, which consists of the Mg(OH)₂-like layers formed by the closest packing of oxygen ions from OH groups. Octahedra are filled with divalent and trivalent cations. The latter create an excess positive charge compensated by the interlayer anions. The interlayer spaces also contain H₂O. It was shown that initial carbonate-containing Mg-Ga (Mg:Ga=2–4) and Mg-Al (Mg:Al=2–4) LDH's structure represents the mixture of 3R₁ (AC=CB=BA=...) and 2H₁ (AC=CA=...) polytypes. At ~200°C Mg-Ga and Mg-Al LDHs loose water and form metastable dehydrated phases. It was shown that both dehydrated phases consist of 3R₂ (AC~BA~CB~...) and 1H (AC~AC~...) polytypes. So this topotactic reaction leads to the transformation of prismatic interlayers into octahedral ones that can be related to the change of orientation of CO₃²⁻ anions. Calcination at ~400°C leads to the transformation of the dehydrated phases to the mixed Mg-Ga or Mg-Al oxides. It was shown that at low Mg content the mixed oxides consist of MgO-like octahedral layers and Mg-Al or Mg-Ga octahedral-tetrahedral spinel-like layers. MgO-like layers inherit the structure of Mg(OH)₂ ones; spinel-like layers are formed in the LDH interlayers due to diffusion of cations. TEM evidences that the oxide structure is 3D disordered. At high Mg contents the formation of partially inversed Mg-Al and Mg-Ga spinels along with layered oxides takes place. Rehydration of layered mixed oxides leads to the formation of three types of hydroxides having 1) hydrotalcite structure; 2) interstratified structure consisting of hydrotalcite and brucite layers; 3) brucite structure. The higher is Mg content, the lower is hydrotalcite structure reconstitution degree of rehydrated phase. Investigation of structures of initial, dehydrated, oxide and rehydrated phases was carried out with use of simulation of PXRD patterns on the basis of the models of 1D disordered structures of nanocrystalline materials with use of softwares [1] and [2]. PXRD patterns for 3D disordered layered mixed oxides were calculated with use of Debye scattering equation realised in self-developed program.

References:

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MS24-O5

Unraveling 2D polymerization: A topochemical reaction studied via total scatteringGregor Hofer¹, Florian Grieder², Martin Kroeger³, A. Dieter Schlueter², Thomas Weber¹

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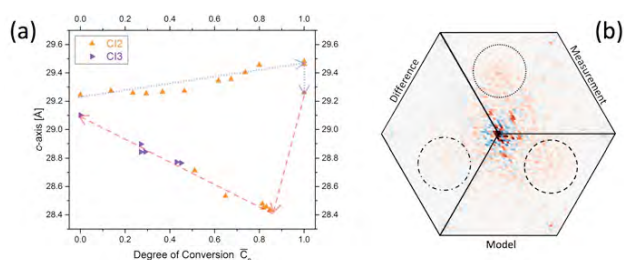
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Recently, the concept of single-crystalline photo-dimerization has been extended to create two-dimensional (2D) networks in the single-crystalline state [1]. To obtain these novel 2D polymers, the monomer is crystallized in a layered arrangement and afterwards photo-irradiated. This causes continuous formation of covalent bonds between adjacent monomer molecules, resulting in a single crystal of 2D-polymer sheet stacks. Heat treatment reverses the bond formation and the original monomer crystal is recovered. Polymerization and depolymerization can be suspended at any time by removing the crystals from the triggering source, allowing for detailed ex-situ structural investigations of any intermediate state

The 2D polymer developed by Kory et al. [1] was studied to understand the propagation of 2D polymerization via single-crystal total X-ray scattering experiments. Measurements were done at several increasing and decreasing degrees of conversion. The average structure revealed, inter alia, a hysteresis in the lattice parameter evolution during the polymerization-depolymerization cycle. The most notably change is a phase transformation and abrupt decrease of the *c*-axis (Figure 1a) by almost 1 Å during depolymerization. The time-dependent conversion was analyzed with the *Johnson-Avrami-Mehl-Kolmogorov* equation and combined with Monte-Carlo simulations as well as observations from the average structures. These results revealed that polymerization propagation proceeds in a partially self-impeding fashion [2]. The real structure is studied in detail via the 3D-ΔPDF method [3]. The measured three-dimensional diffuse scattering patterns and refined ΔPDF maps are dominated by displacive disorder (Figure 1b), but substitutional disorder contributions from the partially polymerized monomer can be identified. This information is used to describe the molecular correlations and further quantify the propagation mechanism. Polymerization and depolymerization are associated with substantial molecular movements which do not break the crystal. Breaking is prevented by several strain compensation mechanisms within the crystal itself. For example, the incorporated solvent molecules act not only as buffers but also as lubricant in-between sheets. Identifying strain sources and how they are compensated is of importance to engineer structurally perfect sheets. Only these can be used in potential applications such as membranes.

Figure 1: (a) Changes of the *c*-axis during polymerization and depolymerization [2]. (b) 3D-ΔPDF refinement of the *uv*0.08 layer highlighting observed (dotted circle) and modeled (dashed circle) PDF densities associated with displacive

cive disorder between neighboring molecules within the same layer. Image contrast modified for better visualization.



References:

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MS25 Combined approaches for the structure determination of new materials at the nanoscale

Chairs: Prof. Artem Abakumov,
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MS25-O1

Zeolite SSZ-70: new understanding of a successful catalytic material

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Understanding the regular arrangement of atoms within the zeolite structure is key to why and how these materials function, and to improve on the characteristics that make them useful. However, most zeolites, and many other industrially and commercially important materials, are used and produced in polycrystalline form, and not suitable for standard single-crystal structure analysis. Therefore, we have been developing methodology to uncover and characterize zeolite framework structures using X-ray powder diffraction (XRPD) data, often by making use of information gleaned from complementary characterization methods such as electron microscopy (HRTEM), electron diffraction and/or MAS NMR. This will be demonstrated on the basis of a recent example, the structure of calcined high-silica zeolite SSZ-70 [1].

The synthesis of the zeolite SSZ-70 was first reported over 10 years ago [2], but its structure proved to be difficult to characterize, because its framework structure is highly disordered. HRTEM images, synchrotron XRPD data, and DNP-enhanced 2D NMR spectra, each providing crucial and complementary insights, were used to probe different structural aspects of calcined SSZ-70, ranging from the long-range average structure (> 500 nm) to short-range stacking sequences (*ca.* 50 nm) to local atomic-level compositions and structures (< 1 nm). This combination is particularly well suited to the investigation of materials with complex partially disordered structures that cannot be resolved with conventional X-ray diffraction analysis alone. With these insights, the novel catalytic behavior of SSZ-70 can be better understood and opportunities for enhancement recognized.