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Insight into crystallization of Mg-substituted malachite - a precursor to Cu/MgO catalyst for methanol synthesis

Mixed metal hydroxycarbonates are widely used as precursor materials for tailormade catalysts and can easily be prepared by constant-pH co-precipitation.[1] Precipitation and phase evolution during ageing of mixed Cu,Mg hydroxycarbonates, which are candidates for precursors to Cu/MgO catalysts for CO hydrogenation, have been studied in detail by various methods. The synthesis starts with the co-precipitation of mixed metal nitrate solutions and Na2CO3 at basic pH. An amorphous magnesian georgeite precursor is formed and ageing is needed to yield a crystalline magnesian malachite. With powder X-ray diffraction and pair distribution function (PDF) analysis (measured at ESRF ID31) we were able to track the structural changes during the ageing process of a Cu/Mg 90:10 at.% Cu,Mg hydroxycarbonate. In combination with further methods like atomic absorption spectroscopy and infrared spectroscopy we draw a conclusive picture of the ageing process. We identified the initial precipitation product as magnesian georgeite. Minor side phases of Mg(OH)2, chalconatronite and Na2Zn3(CO3)4 • 3H2O isomorph persist during the ageing process and act as a Mg reservoir until fast crystallization to malachite takes place. Mg is successively built into the amorphous structure, as observed by AAS, pH trend, integral intensity of the (001) reflection of a Mg(OH)2 layered structure and Pearson correlation of the PDFs. PDF refinements (Fig. 1) showed a general match to the georgeite phase, while the short-range order resembles malachite with differently distorted MO6 octahedra for different stages of the crystallization process. Difference-PDFs (dPDF) calculated in between different reaction time intervals allowed us to pin down the structural changes, that seem to be necessary for crystallisation. These includes the built-up of medium-range order in the M (M=Cu,Mg) coordination sphere and inter-connection of MO6 octahedra.

We further studied the calcination of the Mg-substituted malachite to Cu/MgO precatalyst.

With laboratory based XRD and PDF, we found out that the degree of Mg-substitution highly influenced the structure of the formed Cu/MgO precatalyst. Mg-rich samples yielded disordered Cu nanoparticles with amorphous Mg-containing phases. With in-situ synchrotron PDF we now aim to get more insight into the pre-catalyst formation and the underlying mechanisms.

References:
[1] G. Behrendt, B. Mockenhaupt, N. Prinz, M. Zobel, E.J. Ras, M. Behrens, ChemCatChem. 2022, 14, e202200299.

Primary author: MANZONI, Fabio (Institute of Crystallography, RWTH Aachen University)

Co-authors: PRINZ, Nils (Institute of Crystallography, RWTH Aachen University); BEHRENDT, Gereon (Institute of Inorganic Chemistry, University of Duisburg-Essen); Prof. BEHRENS, Malte (Institute of Inorganic Chemistry, Christian-Albrecht University of Kiel); Prof. ZOBEL, Mirijam (Institute of Crystallography, RWTH Aachen University)

Presenter: MANZONI, Fabio (Institute of Crystallography, RWTH Aachen University)