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Trash to treasure: Recovery of transition metal phosphates for (electro)catalytical applications

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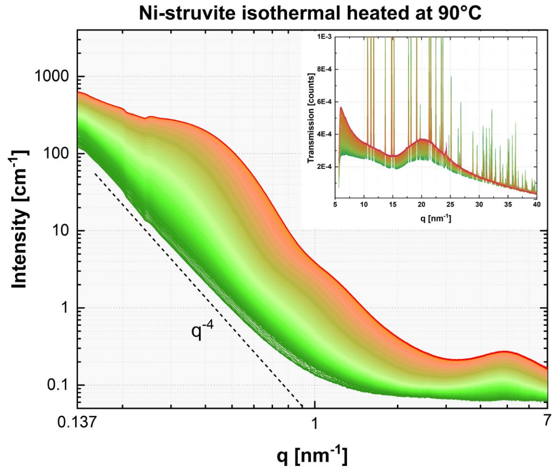
Wastewaters containing high concentrations of NH_4^+, PO_4^{3-} and transition metals are environmentally harmful and toxic pollutants. At the same time phosphorous and transition metals constitute valuable resources. Here, we report the synthesis routes for Co- and Ni-struvites ($NH_4MPO_4{\cdot}6H_2O$, M = Ni^{2+}, Co^{2+}) out of aqueous solutions resembling synthetic/industrial waste water compositions, and allowing for P, ammonia and metal co-precipitation. Furthermore, the as-obtained struvites were further up-cycled. When heated, these transition metal phosphates (TMPs) demonstrate significant changes in the degree of crystallinity/coordination environment involving a high amount of amorphous phases and importantly develop mesoporosity (**Figure 1**). In this regard, amorphous and mesoporous TMPs are known to be highly promising (electro-)catalysts.

Amorphous phases do not represent a simple "disordered" crystal but more a complex system with a broad range of compositions and physicochemical properties, which remain mostly unknown. Consequently, we investigated the recrystallization and amorphization process during thermal treatment and a resolved the complex amorphous/crystalline structures (**Figure 2**). As a proof-of-principle for their applicational use, the as-obtained TMPs demonstrate significant proton conductivity properties similar to apatite-like structures from room to high temperatures (>800°C).

Hence, we have developed a promising recycling route in which environmental harmful contaminants like PO_4^{3-}, NH_4^+ and 3d metals would be extracted out of waste waters in the form of precursor raw materials. These raw materials can be then further up-cycled through a simple thermal treatment for their specific application in electrocatalysis.



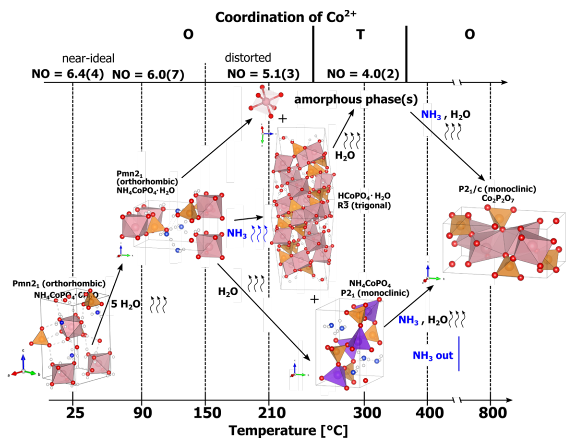


Figure 1: in-situ SAXS patterns from heating of the Ni-struvite at 90°C from t = 0 – 5490 s;10 s time steps per pattern; black dashed line: q^{-4} ; inset: in-situ WAXS diffractograms in transmission [counts].

Figure 2: Schematics of the thermal history of Co-struvite to its final crystallization of $Co_2P_2O_7$ based on XRD and XAS data; On the upper horizontal axis the main coordination of Co^{2+} in the distinct phases is shown; NO = calculated degeneracy of oxygen; coordination polyhedron: pink = octahedron (O), purple = tetrahedron (T).