Elucidation of Crystal Structures and Structural Changes using X-ray Powder diffraction

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Abstract

In the process of understanding the properties and behaviour of a compound, and designing improved materials, probing the atomic-level structure is a decisive step. Single crystal X-ray diffraction, a widespread, non-destructive technique, can certainly satisfy this requirement. However, suitable single crystals cannot always be obtained, especially in cases where compounds are synthesised in situ or investigated while they are subjected to external stimuli that can compromise the integrity of the crystal. In these cases, X-ray powder diffraction (XRPD) can be used. This method allows for analysis of the bulk material, regardless of the degree of the structural order in the compound (crystalline or amorphous), and delivers information about the crystal structure, local structure, microstructure, and phase composition.

In the present PhD thesis, several compounds belonging to different classes of materials such as organic molecules, coordination compounds, inorganic compounds, and polymers have been analyzed with the main aim of extracting structural details and determining structural changes. XRPD was used as the main technique, and complementary analyses such as thermal analysis (TGA, DTA, DSC), scanning electron microscopy (SEM), and vibrational spectroscopy (IR) supported the results.

This PhD thesis is divided in six main chapters. In the introduction and in the second chapter, a brief overview of techniques, methods, and instruments, extensively used in this PhD, is given. An illustration of the devices for in situ and operando experiments, designed and built during this thesis, is also provided.

The third chapter discusses the characterization of two compounds: ferrous glycine sulfate pentahydrate, currently used as an iron supplement, and glycolaldehyde ammonia, recently synthesized in the lab of BASF SE in Ludwigshafen am Rhein (Germany). In both cases, a careful characterization of the morphology by SEM, and the structural details by XRPD and IR were performed. For the first case study, the use of the SEM coupled with BSE and EDX, confirmed the stoichiometry (Fe:S:N ratio) and showed the presence of heavily scattering particles, attributed to by-products of the synthesis. IR revealed the denticity of the glycine is in the zwitterionic form, and the crystal structure of the iron compound was determined by XRPD analysis. Upon heating, the compound transforms to the anhydrous coordination complex, through a less hydrated crystal form, as observed by TGA/DTA analysis and temperature dependent in situ XRDP measurements. In the second case study, after extracting the molecular structure information through IR, the crystal structure was determined by XRPD analysis. Additionally, pair distribution function (PDF) analysis was used to confirm the molecular conformation and the crystal structure.

The fourth chapter is focused on the anisotropic thermal expansion analysis of two different organometallic systems: three isotypical copper complexes showing photosalient behaviour and two isotypical interpenetrated MOFs. The anisotropic thermal expansion was measured and visualized helping to explain the phenomenon through the development of structural motifs in the compounds. These studies showed the variation in the anisotropic thermal expansion as a function of the different positions of fluorine atoms on the benzene ring in the three isotypical photosalient crystals. In addition, temperature-dependent in situ measurements in vacuum on one of the two MOFs revealed a phase transition, which influences the optical properties.

The fifth chapter presents the investigation of the synthetic process of Chabazite zeolite with two different approaches (solvent-free and solvent-based), monitored through in situ XRPD and PDF measurements. In the first approach, trends on reactants and products were followed, and the concurrent formation of sodium sulfate was identified. In the second approach, the co-existence of the precursor and product was observed for a long period of time before the reaction completed at 190 °C. Additionally, the kinetic study revealed the possible presence of two reaction mechanisms.

The sixth chapter presents the crystal structure of a polymer, poly(p-dinitrosobenzene). Although structure solution of polymers from XRPD can be complicated, in this case, the comparatively high crystallinity of the

studied compound allowed for structure solution through XRPD. In addition, TGA/DTA/DSC analysis and temperature-dependent in situ XRPD measurements showed thermal stability until circa 150 °C.

The last chapter details an extensive structural study of different forms of metal thiocyanate coordination compounds and their thermal behaviour by temperature-dependent in situ XRPD. The crystal structures and thermal behaviour were determined for coordination compounds of cadmium, iron, nickel, and manganese with 4-methoxypyridine, 4-picoline, 4-cyanopyridine, and 3- ethylpyridine as co-ligands.

Overall, various XRPD methods were applied to extract structural information and enhance the understanding of the thermal behaviour and the formation processes of compounds without any limitation on the class of materials and the aggregation state.