MS44 Operando and in-situ crystallographic studies using powder diffraction

Chairs: Prof. Simona Galli, Dr. Gavi Vaughan

MS44-O1

Functional hybrid materials: Contribution of in situ powder X-ray diffraction

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Some functional hybrid materials can be obtained only as polycrystalline samples and in that case, powder diffraction is essential to characterize them. The aim of this talk is to show how in situ powder diffraction is significant for a better understanding of their structure-property relationships. In order to synthesize "tailor made" compounds, they are crucial in the understanding of Metal Organic Frameworks (MOFs) crystallisation processes.[1] In situ diffraction is also used to follow their "breathing" effect, or the adaptability of the pore opening to accommodate guest species with drastic changes in unit cell volume, without any loss of crystallinity or bond breaking. This second aspect will be illustrated by the uptake of CO_2 in MIL-53(Fe).[2] The use of a gas cell which allows samples contained in glass capillaries to be dosed with gas up to 60 bars on the ID31 beamline (ESRF) allowed the precise localization of the guests. Finally, the last part of this talk will be dedicated to in situ ball milling diffraction experiments carried out recently on the ID15A beamline (ESRF) on Phase Change Coordination Polymers (PCCPs), which allow high quality data collection for both PDF and Rietveld analyses.[3]

References:

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MS44-O2

New insight into nanoparticle nucleation mechanisms from X-ray total scattering

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Despite decades of research into nucleation processes, very little is known on how nanoparticle formation during solvothermal synthesis takes places on the atomic scale. We have developed methods which allows using *in situ* synchrotron X-ray Total Scattering and Pair Distribution Function analysis to follow nanoparticle nucleation and growth in situ.[1-2] In contrast to conventional crystallographic studies, PDF analysis gives structural information from non-crystalline species, allowing obtaining structural information on the atomic scale, all the way from precursor to the final nanoclusters during synthesis. We have furthermore shown how PDF allows obtaining detailed information on nanocluster structures with no long-range order on nanoclusters fundamentally different from bulk materials.3 Here, we use *in situ* PDF to study the formation of metal oxides in solvothermal synthesis. Metal oxide nanoparticles are used in numerous applications in e.g. energy conversion and storage, and synthetic control over structure, particle size and morphology is required in order to tailormake materials for new applications. Solvothermal synthesis in organic solvents, i.e. amines or alcohols, are known to give high control over particle size. However, despite the very broad range of applications, the chemical processes involved in the formation of metal oxides are not well understood. Several nucleation mechanisms have been proposed, such as the existence of pre-nucleation clusters and oriented attachment, however none of the current models take the actual chemical processes into account. Using X-ray total scattering, we deduce the *atomic structure* of prenucleation clusters, present in the processes just before the crystalline nanoparticles have formed. We show that the solvent and synthesis conditions have large influence on the nucleation parthway and the structure of the nano-scale clusters in the synthetic pathway.

Keywords: In situ, nanoparticles, Total Scattering