NMR assisted structure determination of coordination polymers

Brijith Thomas[1,3], Boyce S. Chang[2,3], Martin Thuo[2,3], Aaron Rossini[1,3*]

[1]*Department of Chemistry, Iowa State University, Ames, IA 50010 USA,*

[2]*Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011 USA,*

[3]*US DOE Ames Laboratory, Ames, Iowa, 50011, USA.*

arossini@iastate.edu

Structural analysis by XRD still remains a considerable challenge for materials that can't be isolated as single crystals. In NMR crystallography structural constraints are extracted from the modern solid-state NMR techniques, and along with DFT (density functional theory) calculations.[1-4] NMR crystallography has been used to derive de novo structures and to aid the refinement of Xray powder diffraction data.[1-4] In this work, computational integration of advanced solid-state NMR with PXRD (powder X-ray diffraction) and modelling is used to understand the structure of metal coordination polymers that are produced by the etching of metal nanoparticles in acidic solution.[5-7] Notably, these coordination polymers have some structural disorder which gives rise to broadened diffraction peaks. Solid-state NMR was applied to determine the number of molecules in the asymmetric unit and give insight into the geometry at the metal center. Then, the PXRD pattern of the coordination polymers was partially indexed to find probable unit cells. The position of heavy atoms was then optimized within the unit cell using the Free Objects for Crystallography (FOX) software. Finally, Rietveld refinement and DFT optimization was used to obtain a final structural model. The final NMR and PXRD derived structure is validated by comparing the experimental and simulated PXRD pattern and NMR parameters. This protocol was verified on scandium acetate which has a known single crystal structure from the literature. The protocol was then successfully applied to microcrystalline gallium and aluminum coordination polymers. We anticipate that this methodology could be extended to similar kind of coordination polymers with inherent heterogeneous character.

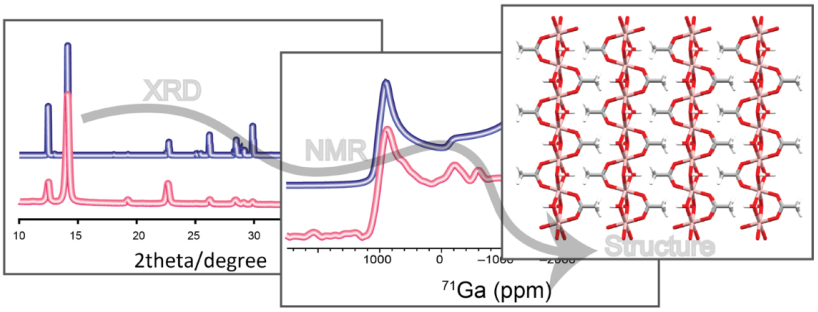

Figure 1. Schematic representation of the NMR crystallography approach used for finding the crystal structure of the coordination polymer.

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