

<p>1. Title of Case Study: Applications of Solid-state NMR Spectroscopy for the Study of Mechanisms in Inorganic Materials</p>
<p>2. Grant Reference Number: EPSRC EP/L504749/1, MR/T043024/1, EP/S022953/1, EP/M022501/1, EP/S023755/1; 2017 ERC-COG MISOTOP project</p>
<p>3. One sentence summary: High-field solid-state NMR enables a wide range of mechanistic processes in inorganic materials to be understood using a wider range of nuclei than is typically accessible at lower magnetic fields.</p>
<p>4. One paragraph summary: The high sensitivity of NMR to the local chemical environment makes it a powerful probe of mechanistic processes where short-range interactions and structural properties can be very important, but are difficult to probe by diffraction-based structure determination methods. For inorganic materials, the wide range of nuclei present can offer opportunities to probe mechanistic processes from different perspectives to the more commonly studied nuclei such as ^1H, ^{13}C, ^{15}N in organic materials, potentially increasing the amount of information that can be obtained. However, this can simultaneously present challenges in the observation and interpretation of experimental data due to e.g., low natural abundance, low gyromagnetic ratio, large quadrupolar interactions, or a combination of these. This case study illustrates how high-field NMR offers significant advantages in the observation of challenging nuclei and/or complex processes to enable a wide range of phenomena to be characterised.</p>
<p>5. Key outputs in bullet points:</p> <ul style="list-style-type: none"> • <i>Atomic-level mechanistic insight into a range of systems of technological and industrial insight</i> • <i>Training of early career researchers from multiple UK institutions in state-of-the NMR instrumentation</i> • <i>Demonstration of solid-state NMR spectroscopy for low receptivity nuclei</i> • <i>Publications in leading international journals</i>
<p>6. Main body text</p> <p>Metal-organic frameworks (MOFs) represent a diverse class of porous materials that are widely used and studied across chemistry and materials science. Despite this, many mechanistic aspects of their formation and function are difficult to characterise. One such question is that of the initial crystallisation process which remains poorly understood. Jones <i>et al.</i> used high-field <i>in situ</i> NMR to characterise the crystallisation mechanism of the model MOF MFM-500(Ni). The so-called “CLASSIC” NMR technique was used, where alternate liquid and solid-state NMR spectra are acquired as a solution begins to crystallise. ^1H NMR spectra revealed changes in the local environments of the organic linker groups as aggregation started to occur. Here, the high magnetic field was critical to allow resolution of liquid-like sharp components and broader components associated with aggregation of the linker. Using variable-temperature measurements, it was possible to extract activation energies for both nucleation and initial growth of the MOF crystallites. Crucially, this information is not possible to obtain by other methods such as diffraction which is only sensitive to long-range ordering which occurs after the initial aggregation. In another study, Berge <i>et al.</i> used ^{17}O NMR to probe the adsorption mechanism of ^{17}O-enriched CO_2 in a prototypical MOF for CO_2 capture and storage. ^{17}O MAS NMR measurements at 23.5 T revealed distinct oxygen environments that could be assigned to carbamate formation within the amine group upon CO_2 adsorption. For this study, it was important to perform experiments at the highest possible magnetic field to minimise the large ^{17}O quadrupolar broadening to allow accurate fitting and deconvolution of the experimental data. By screening experimental data for a set of 22 amine-functionalised MOFs against calculated NMR</p>

parameters, it was possible to confidently distinguish carbamate and carbamic acid species and provide evidence for a mixed acid-carbamate adsorption mechanism.

The sensitivity advantages of high-field NMR make it possible to study nuclei with large quadrupolar interactions that are difficult to observe at low magnetic field. Dawson *et al.* used high-field ^{71}Ga MAS NMR to characterise an unusual low-temperature dehydrofluorination process in a gallium-phosphate zeolitic framework. The ^{71}Ga nucleus is very informative but has a very large quadrupole moment making it very challenging to observe. By combining high magnetic field (20.0 T) with fast MAS (60 kHz), it was possible to observe both four- and five-coordinate Ga sites which could be linked to environments in a DFT model for the dehydrofluorinated structure. Fan *et al.* used static ^{93}Nb NMR at 20.0 T to probe the Nb environments in a Nb,Al-doped mesoporous silica catalyst. A very broad signal consistent with a tetra-coordinated environment was observed for the pristine catalyst, whereas a much narrower penta-coordinated resonance was observed after adsorption of a bio-derived reactant target molecule.

Mechanistic processes have also been studied in non-porous solids via nuclei which hold significant structural information but which are challenging to observe. Chen *et al.* used ^{17}O MAS NMR at 20.0 T to probe the ^{17}O enrichment process of silica surfaces via the cost-effective approach of grinding with H_2^{17}O . The high-field enabled observation of weak SiOH surface group resonances resulting from the enrichment process which could not be seen at lower field without DNP enhancement. Kilpatrick *et al.* used static ^{91}Zr NMR to study catalytic zirconene complexes developed for olefin polymerisation. Using frequency-stepped experiments combined with CPMG for signal enhancement, it was possible to obtain full lineshapes for four zirconenes studied, opening up new possibilities for the future study of this important class of materials.

Jones *et al.*, *Chem. Sci.* 2021, 12, 1486. Berge *et al.*, *Nature Commun.* 2022, 13, 7763. Dawson *et al.*, *J. Phys. Chem. C* 2021, 125, 2537. Fan *et al.*, *Angew. Chem.* 2022, 61, e202212164. Chen *et al.*, *Chem.-Eur. J.* 2021, 27, 12574. Kilpatrick *et al.*, *Mater. Chem. Frontiers* 2020, 4, 3226.

7. Names of key academics and any collaborators:

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9. Who should we contact for more information?

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