

Exploiting Solid-State NMR to Understand Microporous Materials

Microporous materials are an important class of inorganic and inorganic-organic hybrid solids, that include aluminosilicate zeolites, phosphate frameworks and metal-organic frameworks (MOFs). Each of these contain pores and channels of similar sizes to small molecules, and when coupled with their high internal surface area leads to applications in catalysis, drug delivery and in gas storage and separation. A detailed knowledge of the atomic-scale structure is vital to understanding the chemical reactivity of these materials; however, this is challenging owing to the varied type and levels of static and dynamic disorder present. Owing to its sensitivity to the local environment NMR presents an ideal tool for this job, complementary to the diffraction-based approaches that can inform on long-range or average structure. Isotopic enrichment is often used to improve the sensitivity of NMR measurements, but changes in the level and position of enrichment can provide important insight into chemical reactivity and mechanism.

In recent work at the Facility, ^{17}O NMR has been used to understand the distribution of cations in a mixed-metal MOF, (Al,Ga)-MIL-53 (see also Fig. 1).^{1,2} This material is particularly interesting owing to its “breathing” behaviour, where it can change its pore volume by up to ~33% upon the interaction with a guest molecule, or with a change in temperature. MIL-53 materials were enriched in ^{17}O either using a cost-effective dry gel conversion reaction, which reduces the amount of water required or a novel steaming approach where a pre-prepared MOF is placed in a Teflon cup inside an autoclave lined with 130 μl of $\text{H}_2^{17}\text{O}(\text{l})$ and heated at 150 $^\circ\text{C}$. High-resolution ^{17}O MQMAS spectra were able to show that although the cations were intimately mixed in the material, there was some preferential clustering of like cations. This led to the formation of a material with both larger and smaller pores sizes present, and the potential opportunity to control average pore volume using compositional changes in the future. In other work,³ Blanc and co-workers used ^{109}Ag NMR (with ^{13}C and ^{15}N experiments) to explore the ability of a Ag-based MOF to reversible capture perchlorate. By following the structural changes as a function of time, NMR provided information on the timescale of the process (complete within 70 mins), and measurements of the ^{15}N - ^{109}Ag J coupling showed the chemical bonds that were formed and the nature of the binding at the Ag centre.

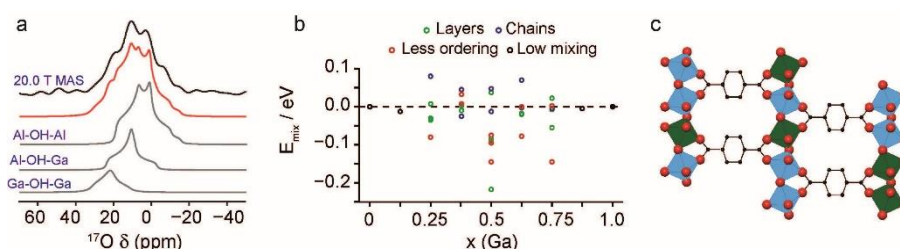


Figure 1. (a) ^{17}O MAS NMR (20.0 T) spectrum of $(\text{Al}_{0.5}\text{Ga}_{0.5})\text{-MIL-53}$ and fit, showing the decomposition into signals resulting from Al–OH–Al, Al–OH–Ga and Ga–OH–Ga species. (b) Calculated mixing energy for the NP form of mixed-metal $(\text{Al}_{1-x}\text{Ga}_x)\text{-MIL-53}$, plotted as a function of composition. (c) Proposed structure mixed-metal MIL-53.^{1,2}

Although NMR has been widely used to study zeolite structures in the past, work at the Facility has demonstrated its use for studying chemical reactivity in these systems. In 2019, Ashbrook and co-workers demonstrated the very surprising lability of zeolite frameworks at room temperature when exposed to water.⁴ Simply mixing a small amount of the zeolite with 100 μl of $\text{H}_2^{17}\text{O}(\text{l})$ showed ^{17}O enrichment of the Si–O–Si and Si–O–Al framework oxygens in a CHA zeolite on rapid timescales (1–24 hours) suggesting that the bonds were reversibly and rapidly breaking and reforming, challenging the widely-held notion that zeolites behave largely as inert scaffolds. This investigation built on previous work carried out at the Facility, which also exploited isotopic enrichment (of ^{29}Si and ^{17}O), to explore the mechanism of the ADOR (Assembly, Disassembly, Organisation and Reassembly) process, where new zeolites are produced by disassembling a known parent zeolite into its constituent parts, then organising these in a different way before reassembling to form a new structure.^{5,6} Blanc and co-workers also used isotopic enrichment to investigate the intermediates formed in zeolite catalysis.⁷ The reaction of zeolite H-ZSM-5 with ^{13}C enriched methanol allowed ^{13}C NMR spectroscopy (including challenging ^{13}C - ^{13}C correlation experiments) to probe the mechanism of the methanol-to-olefin reactions, widely used in industry for the production of olefins (mainly ethylene and propene) from non-petrochemical resources such as coal or natural gas. In addition, ^{13}C - ^{27}Al and ^{29}Si - ^{13}C experiments were able to probe the interactions between the confined carbon species and the framework of the zeolite, confirming the presence of supramolecular reaction centres that are highly efficient for methanol activation.

Work at the NRF in 2020 investigated disorder in a novel gallophosphate framework using multinuclear NMR spectroscopy.⁸ This material, GaPO-34A, was shown to form under the same synthesis conditions as GaPO-34, but at shorter gel aging times.^{8,9} Diffraction showed a complex average structure, but an NMR crystallographic approach, combining ¹³C, ¹⁹F, ³¹P and ⁷¹Ga NMR spectroscopy with extensive first-principles calculations on a suite of structural models, was able to show that the structure contains at least three distinct types of disorder (occupational, compositional, and dynamic). NMR confirmed the preferential substitution of F onto 3 of the 5 possible anion sites, and also demonstrated ms dynamics of the structure directing agent that balances this charge. This is a particularly challenging structure to solve and this work clearly demonstrated the need to combined different techniques to provide information on the time-scales and length-scales required.

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