1. Title of Case Study: Exploiting NMR Spectroscopy for the Investigation of Microporous Materials

2. Grant Reference Number: Contract: PR140003

3. One sentence summary: ^{17}O and ^{29}Si NMR spectroscopy of isotopically-enriched microporous solids provides information on their structure, disorder and reactivity.

4. One paragraph summary:

Microporous materials are an important class of inorganic and inorganic-organic hybrid solids. One of the most important members of this family are silica-based zeolites. By using advanced synthesis techniques, we can prepare isotopically-enriched zeolite materials that allow us to exploit the advantages in sensitivity and resolution afforded by the high-field 850 MHz solid-state NMR facility. This provides insight to the mechanism of a new approach to the synthesis of novel zeolites.

5. Key outputs in bullet points:

- *New insight into the mechanism of the ADOR process for obtaining zeolites with unconventional structures, and publication in high-impact journals*
- *Training of a PhD student (Giulia Bignami, EPSRC DTA St Andrews) in a wide range of skills, including synthesis, XRD and NMR spectroscopy.*
- *Dissemination of work to different communities: International Zeolite Association (Brazil), British Crystallographic Association (UK), NE Corridor Zeolite Meeting (USA), Workshop on layered materials (Czech Republic), EuroAsia Zeolite Conference (Indonesia), European Solid State Chemistry Meeting (UK), raising the profile of solid-state NMR spectroscopy*
- *Public dissemination (public lecture and open access general science article)*

6. Main body text

Microporous solids are one of the most exciting classes of materials in modern chemistry, with pores of similar sizes to small molecules and high internal surface areas. This leads to applications as molecular sieves or nanosize reaction vessels, in catalysis and in drug delivery. The structure of these materials is intimately connected with any application, and a detailed atomic-level knowledge is vital to controlling properties and developing new uses. The sensitivity of NMR spectroscopy to the local environment, at the atomic level, makes it an ideal tool for studying these complex materials. In some cases, the natural abundance of the NMR-active isotope is low, and experiments can be time consuming. One answer is to develop cost-effective and atom-efficient synthetic methods to enrich the solids, improving sensitivity and providing information on mechanism and reactivity.

Silica-based zeolites play a vital role in a wide range of industrial processes. There is a very large number of hypothetical zeolite structures, however, many cannot be prepared using traditional hydrothermal synthesis. The recently developed ADOR (Assembly, Disassembly, Organisation and Reassembly) process overcomes this by disassembling a known silicate-based parent zeolite into its constituent parts, then organising these differently before reassembling them to form a new material. An important goal is to understand exactly how the process occurs at the molecular level. By enriching different parts of the initial parent solid with, e.g., ^{29}Si and then by using an ^{17}O-enriched reactant to start the disassembly process we can increase the sensitivity of the NMR

experiments significantly, enabling new experiments that would not be possible otherwise. Figure 1 shows a schematic of the ADOR process using a ^{29}Si-enriched starting zeolite. This can be disassembled using ^{17}O-enriched acid to produce layers that are eventually reassembled to produce a new material. NMR experiments then give insight into the reactions involved. For example, by following the ^{17}O NMR signal we can understand how much the ADOR process alters the structure of the material on disassembly, see where the ^{17}O oxygen atoms end up in the material, and see how dynamic these processes are. By exploiting the high field and high sensitivity at the 850 MHz Facility, and combining this with *in situ* studies carried out in St Andrews, we have gained considerable insight into how the process develops. As shown in Figure 1, ^{17}O NMR spectra of a disassembled germanium-containing UTL zeolite reveal unexpectedly high levels of ^{17}O in the bulk zeolitic layers, and a much more extensive hydrolytic rearrangement than previously thought. *In situ* monitoring of the Q^4/Q^3 ratio using ^{29}Si NMR spectroscopy enables the changes to the local structure and the formation of different zeolitic products to be followed. This work sheds new light on the role played by water in the ADOR process and provides insight into the detailed mechanism of the structural changes involved.[1,2]

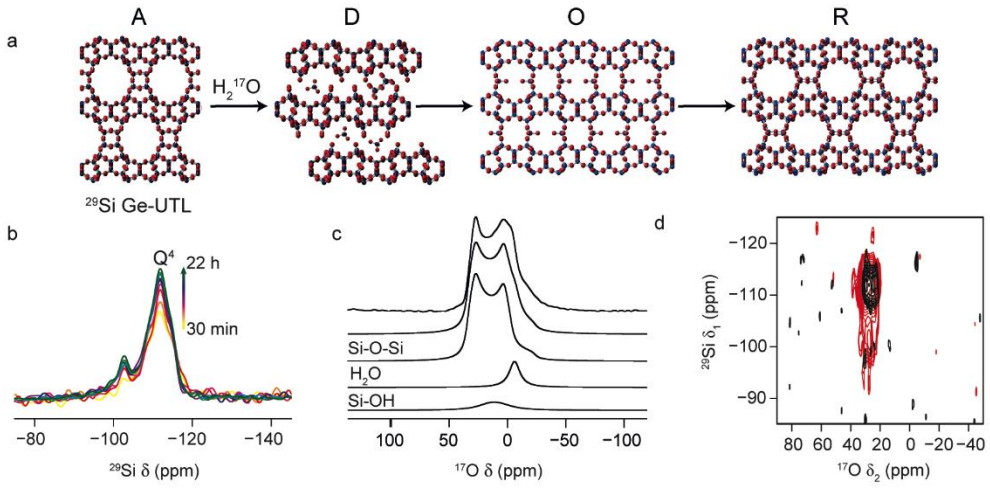

Figure 1. (a) Schematic showing the ADOR process for ^{17}O- and ^{29}Si-enriched zeolites. (b) *In situ* ^{29}Si (9.4 T) MAS NMR spectra during the disassembly step. (c) ^{17}O (14.1 T) MAS NMR spectra. (d) ^{29}Si-^{17}O (20.0 T) correlation spectra confirming the unexpected presence of ^{17}O within the bulk zeolite layers.

1. G.P.M. Bignami *et al. J. Am. Chem. Soc.* **139**, 5140 (2017). 2. S.A. Morris *et al.*, *Nature Chem.* **9**, 1012 (2017).

7. Names of key academics and any collaborators:

Professor Sharon Ashbrook and Professor Russell Morris (University of St Andrews)

8. Sources of significant sponsorship (if applicable):

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9. Who should we contact for more information?

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