Experimental report

13/09/2023

Proposal: **5-22-804**

Council: 10/2022

Title: Investigation of stable intermediates and reassembly step of the ADORmechanism in zeolites

Research area: Chemistry

This proposal is a new proposal

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Samples: ICP-1P (germanosilicate zeolite intermediate)
ICP-2P (germanosilicate zeolite intermediate)
ICP-2 (OKO, Germanosilicate zeolite)
ICP-4 (PCR, Germanosilicate zeolite)

Instrument	Requested days	Allocated days	From	To
D2B	2	2	23/06/2023	26/06/2023
D20	2	0		

Abstract:

Zeolites are a family of porous aluminosilicate materials that have found applications in many different technologies. Simulations predict the possibility of millions of zeolite topologies but only hundred of zeolite frameworks of all compositions are known so far. Some zeolite structures have been deemed as 'unfeasible' through classical synthesis methods. The ADOR (assembly¿disassembly¿organisation¿reassembly) process is an important tool to access zeolite structures, where a 3D parent zeolite materials is disassembled into 2d zeolite layers to then be reassembled into new structures through condensation. UTL is a key parent zeolite as it has produced multiple high-silica products through the ADOR method. Two final product formations of interest are that of IPC-2 and IPC-4 formed from UTL parent zeolite, with the mechanism of formation of great interest. Two slightly different intermediates, IPC-2P and IPC-1P, need to be investigated further to better comprehend the reassembly step as well as the role of disorder in the structures.

Investigation of stable intermediates and reassembly step of the ADOR mechanism in zeolites

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Introduction

Zeolites are an important class of porous materials with a wide range of uses, including heterogenous catalysis and water softening. They compose of tetrahedral TO_4 units with silicon being the main T atom. Key to the future of zeolite production is control over the porosity of the samples however traditional synthesis routes do not allow this, and some proposed structures are deemed ‘unfeasible’ through the tradition hydrothermal route. The ADOR method was developed to prepare new zeolite materials which over comes the barriers of hydrothermal routes and allows pore size manipulation[1].

ADOR stands for a four-step procedure, consisting of assembly, disassembly, organisation, and reassembly. A parent zeolite (UTL in this case) is prepared with germanium in the structure, as germanium preferentially occupies the double four ring units within zeolitic structures. The 3D zeolite can be ‘un-zipped’ through hydrolysis as germanium allows for selective dissolution out of the sample. Once two-dimensional layers are formed, they can be organised into new orientations so a final calcination at high temperatures condenses the material to a new zeolite with a highly predictable structure.

The purpose of the study is to better understand the reassembly step, to hopefully in future allow more control over the production of new zeolites. With understanding of the reassembly step we could design zeolites with specific pore sizes for specific applications.

Preparation and Analysis at University of St Andrews

The samples were all prepared in deuterated solvents to reduce background from protonation for the neutron experiments. Parent UTL was prepared through the usual hydrothermal route, with ratio 0.8 SiO_2:0.4 GeO_2:0.4 SDAOH:30 H_2O added to a Teflon-lined autoclave and heated to 150 ^oC for 7 days. The product was collected through filtration before calcination at 575 ^oC to remove the organic SDA. The UTL was hydrolysed into the two intermediates using deuterated hydrochloric acid, with IPC-1P made using 250 mg and 40 mL 0.1M DCL and IPC-2P using 250 mg and 5 mL 0.1M DCl. Both hydrolysis’ occur at 90^{o}C under reflux for 16 hours. The intermediates are collected through vacuum filtration and dried overnight in an 80^{o}C oven before calcination at 575^{o}C for 6 hours to IPC-4 (from IPC-1P) and IPC-2 (IPC-2P).

The samples were checked in house using capillary powder x-ray diffraction, with the change in d spacing of the 200 Bragg reflection key to identifying the structures formed. All samples were determined to be phase pure through the XRD patterns and dried thoroughly before transportation to the ILL.

Experiments at ILL

We performed 8 experiments on beamline D2B at room temperature using two wavelengths (for 4 samples). The samples have been loaded into vanadium containers 9 mm in diameter to reduce absorption effects in the measurements. The sample changer was used to maximise experiment time by shortening changeover time. Both wavelengths were required as the 200 peak occurs at high d spacing, the measurements at 1.594 Å miss this initial peak. The lower wavelength measurements are better at capturing data at lower d spacing, so both wavelengths cover all regions. Counting times were around 9 hours at the higher wavelength and around 5 hours for the lower wavelength.

Results

The raw data from the measurements can be seen in Figure 1, compared with calculated patterns generated using the CrystalDiffract package of CrystalMaker from cif files of proposed structures. The peak positions generally seem to fit but these model systems don't appear to fit the recorded data fully, the proposed IPC-4 structure does not appear to be a suitable match for the neutron data obtained as no peaks are expected above 60 2θ.

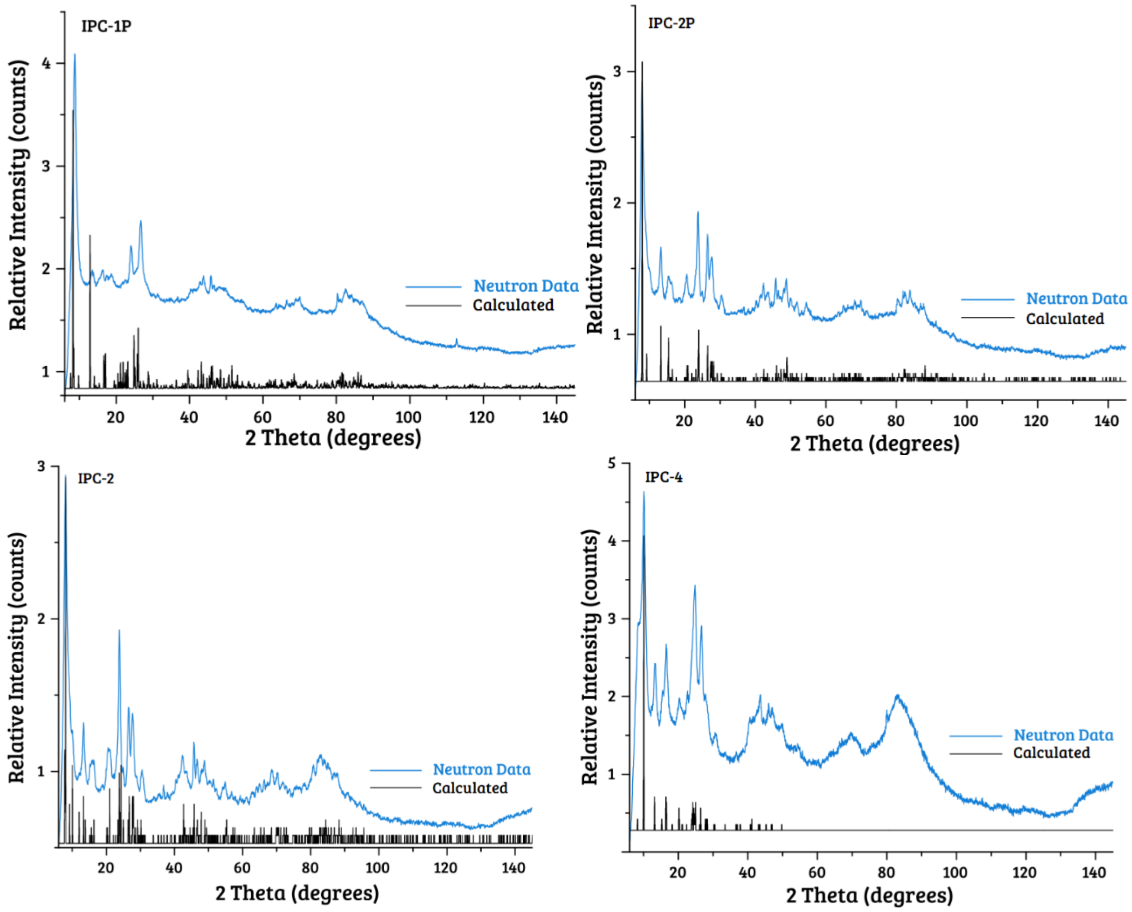

Figure 1: Recorded neutron diffraction patterns at 1.594 Å with the calculated theoretical patterns used as a comparison.

Rietveld refinements are to be carried out on all measurements to determine the structure of the samples using the FullProf Suite package. Some preliminary refinements have so far been performed on the IPC-2 and IPC-2P samples with relatively low χ^2 being reached (Figure 2). There is some agreement with the previously proposed IPC-2 and IPC-2P structures, as the core silicon structure is not changing significantly. There is however a clear difference between the intermediate and final product structures as expected with a larger unit cell for the IPC-2P material.

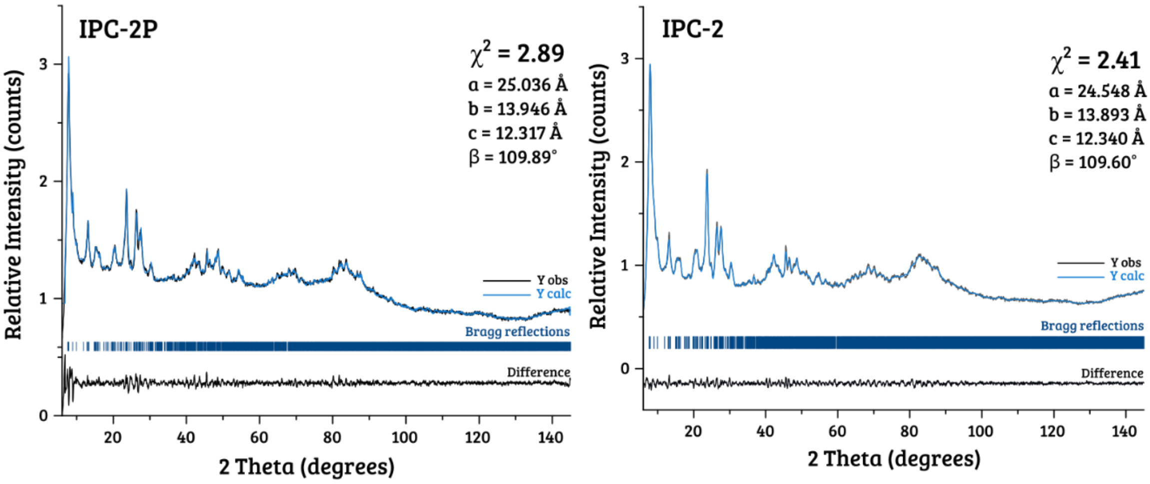

Figure 2: Rietveld refinements of the neutron diffraction data recorded with 1.594 Å wavelength for IPC-2P and IPC-2 samples.

The oxygen atoms are too free to move in the refinements, so the structures being produced have large bond lengths unexpected within the materials. As there are not many peaks from the diffraction experiments and large unit cells with numerous atoms (50+), some bond constraints need to be added in future to improve the quality of the data output. It is known that the oxygens will remain bonded to the silicon in the porous structures so they should only be allowed to move around the atoms within a bond distance of around 2 Å.

The 6 other sets of data need to be analysed in a similar way, taking into consideration the mobility of oxygen atoms. The refinements for IPC-2P will also be tried using different starting models as this sample structure is unknown thus far.

References

[1] Henkelis, S., Mazur, M., Rice, C., Bignami G., Wheatley, P., Ashbrook, S., Cejka, J., Morris, R., *Nature Protocols,* **14**, 781–794 (2019).