Tailoring the Flexible Zeolite Molecular Sieve Merlinoite for Carbon Capture

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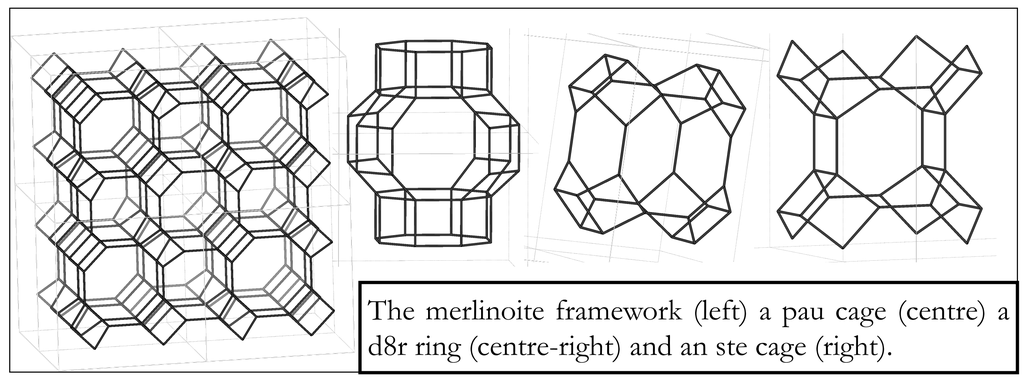
Introduction

Merlinoites are a subclass of zeolites showing strong and highly selective adsorption of carbon dioxide and other gases.[2] Merlinoites with a specific framework makeup, incorporating potassium and strontium cations, have been identified as showing promise for industrial gas separation and carbon capture processes.[1,3]

This project seeks to synthesise a series of merlinoites for use in these processes via a new scaled-up synthetic route, and analyse merlinoite adsorption kinetics.



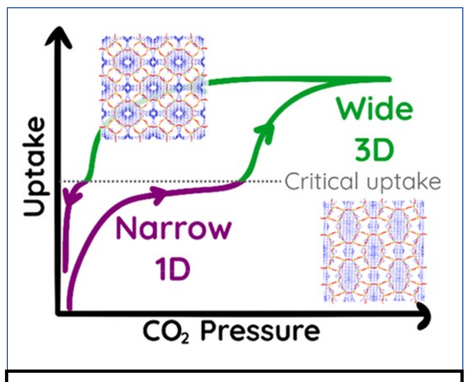
The merlinoite framework (left) a pau cage (centre) a d8r ring (centre-right) and an ste cage (right).

Selective Adsorption Mechanisms in Merlinoite Zeolites

Selectivity can arise from steric or kinetic effects. Steric selectivity arises as the size and shape of the pores within the material impose limits on the size and shape of molecules which can be adsorbed.[4]

Kinetic selectivity is where the rates of adsorption of gas components differ due to their particle sizes, and as such one component is preferentially adsorbed. This is termed a *sieving effect*.[4]

In both cases, the pore size is the determining factor. Control of the pore size is achieved by controlling the Si/Al ratio of the aluminosilicate framework and controlling the extraframework cations.[1] The shape of the pores is fixed by the framework topology (merlinoite).



Uptake schematic for a merlinoite with expected/ desirable adsorption characteristics. Reproduced from (3).

Note the asymmetry of adsorption and desorption – often stepped isotherms have significant hysteresis.

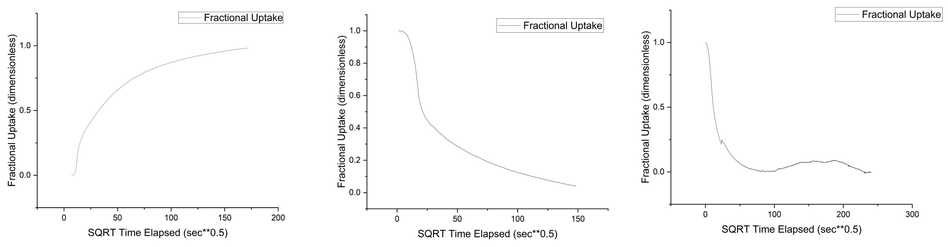
Structure of Merlinoite

Zeolites are based around TO_4 tetrahedra, where T is Si or Al in a given ratio (the Si/Al ratio). This ratio, in conjunction with distortions caused by extraframework cations, determines the T-O bond length and so the pore size.

The merlinoite framework topology is built from three distinct cage structures: pau, ste and d8r. These combine to create pore channels through the material. The size and connectivity of these pores controls the adsorption behaviour.

Four distinct cation sites exist within the structure (I, IIa, Iib and III). The effect of migration of cations between these sites is crucial to merlinoite's adsorptive behaviour changes.[2]

Carbon Dioxide Uptake Data



Fractional uptake against square root time for wide pore adsorption, wide pore desorption and narrow pore desorption (left to right). Wide pore adsorption data was not analysable. These curves can be fitted to a quadratic to yield the diffusivity.

Dynamic Adsorption Behaviour Changes

One feature of the carbon dioxide adsorption behaviour of merlinoites particularly suited to gas separation is that their uptake capacity (and potentially their kinetics) change as you raise the partial pressure of carbon dioxide. This is seen by their stepped (non type-1) adsorption isotherms.

Controlling the incorporated extraframework cations can create a sharp change in uptake behaviour at a critical pressure, which can be exploited for pressure-swing adsorption used for gas separation.[3]

This structural change can occur due to expansion of the framework or due to *gating effects*, where a critical level of adsorption causes cations to migrate through the structure, opening up new pores and increasing uptake. This can connect the pores across more dimensions, for example from 1D to 3D connected channels.

Results and Discussion

XRD data showed that five of the attempted syntheses made merlinoites as intended. The sixth synthesis made zeolite beta with unusually sharp diffraction peaks, pictured using SEM on the right below. This showed SLA 6.x consisted of large crystals of zeolite beta, with some crystals approaching 2.75 μm in diameter. The seventh synthesis returned the product, zeolite STA-30. EDX (Energy Dispersive X-Ray Spectroscopy) was used to determine the cation content and Si/Al ratios of the products (see essay for table).

Kinetic data was analysed, and a marked difference in the slope of the fractional uptake plots is apparent between the wide and narrow pores. Analysis of these values and optimal fitting of the curves remains an ongoing process, due to the potential complication of concurrent adsorptions with different diffusivities.

The most consequential result is the clear demonstration of the feasibility of the scaled-up merlinoite synthesis used, which was successful in five out of seven instances.

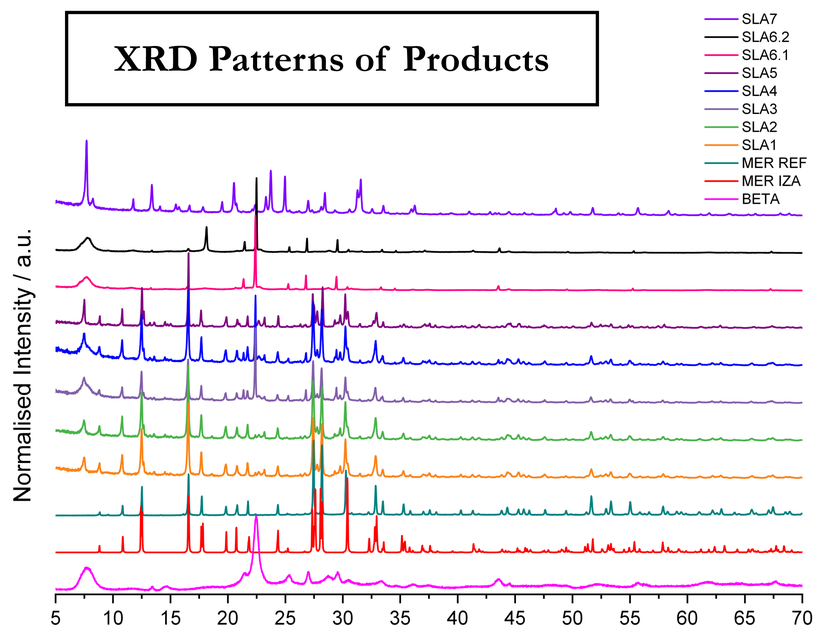
Conclusions and Future Work

The method used may prove to be a reliable way of producing beta with large crystal sizes when using the corresponding precursor CBV-720, although this requires further investigation.

The feasibility of the synthesis was demonstrated, and five of the seven attempted were successful. Minor tweaks were made to the synthesis. The products produced demonstrated that the precursor topology has a determining effect on the product, thereby suggesting that the colloid produced in the synthesis is a colloid of framework structures and isn't a simple silica / aluminium colloid. (See essay for details).

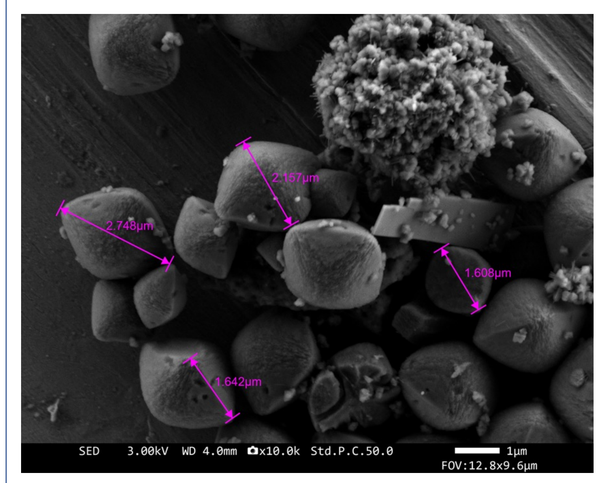
Examination of the adsorption kinetics reveals two distinct curve parameters for narrow and wide pore phases. Refinement of this analysis and final determination of values is ongoing, but it looks promising that the analysis will reveal two distinct diffusivities for the two phases.

XRD Patterns of Products



XRD patterns of all products shown with reference MER and BETA patterns for comparison.

SEM Image of Impurity (Beta)



SEM images of the zeolite beta produced revealed large crystal sizes as larges as ~ 2.75 μm. Image Credit: Ruxandra G. Chitac.

References

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