A Structural Study of Zeolite MER: Cations, CO_2 and Cooperativity

Elliott L. Bruce[1]

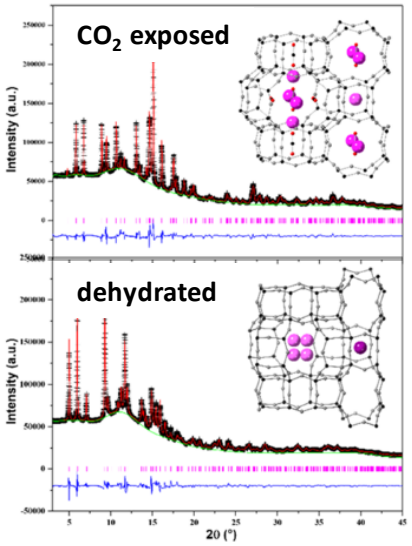
Additional Author(s): Veselina M. Georgieva[1], Ruxandra G. Chitac[1], Magdalena L. Lozinska[1], Anna M. Hall[1], Claire A. Murray[2], Ron I. Smith,[3] Alessandro Turrina[4], Paul A. Wright[1]

Institution(s): [1]School of Chemistry, University of St Andrews; [2]Diamond Light Source; [3]ISIS Neutron and Muon Source, [4]Johnson Matthey Technology Centre, Chilton.

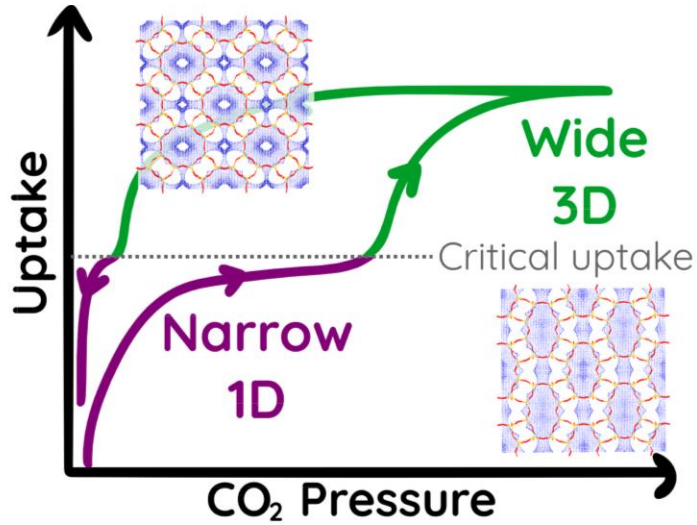
Funder(s): EPSRC, Johnson Matthey

Abstract

Zeolites are porous materials which can distort upon dehydration. Li-MER is one such material, decreasing unit cell volume by 13%. This narrow-pore phase (1D diffusion) expands to a wide-pore form (3D) upon CO_2 adsorption at critical uptake, accompanied by kinks in adsorption isotherms. Expansion occurs cooperatively via an intermediate phase. Varying cation content alters the distortion and inflection point.



Narrow- and wide-pore structures dictate maximum CO_2 uptake at low and high pCO_2 regimes



Project Description

- X-ray and neutron diffraction studies and subsequent Rietveld refinement allows structures of materials to be found.
- Extra-framework Li^+ causes the MER framework to distort greatly upon dehydration. Li^+ was exchanged for larger cations (Na^+, K^+, Cs^+) to give binary cation series. This increases unit cell volume and shifts the inflection point seen in the CO_2 adsorption isotherm to lower pressure.
- Variable pressure experiments examines structural change upon adsorption. These studies suggest that expansion proceeds via an intermediate phase. Expansion from the intermediate- to wide-pore form is cooperative, and is responsible for the step in adsorption isotherm.

Key Results)

- Li^+ greatly affects zeolite MER framework
  - Causes 1D channel connectivity for CO_2 percolation
  - Expands to 3D connectivity with sufficient pCO_2
- Introducing larger cations shifts transition to lower pCO_2
- Critical uptake occurs at with cooperative intermediate → wide-pore transition

This paper: Georgieva, V. M.; Bruce, E. L.; Chitac, R. G.; Lozinska, M. M.; Hall, A. M.; Murray, C. A.; Smith, R. I.; Turrina, A.; Wright, P. A. Cation Control of Cooperative CO_2 Adsorption in Li-Containing Mixed Cation Forms of the Flexible Merlinoite Zeolite. *Chem. Mater.* **2021**, *33*, 1157–1173.

Or click here: https://doi.org/10.1021/acs.chemmater.0c03773