Electronic Supplementary Material (ESI) for Faraday Discussions.
This journal is © The Royal Society of Chemistry 2022

Simulating Intergrowth Formation in Zeolite Crystals: Impact on Habit and Functionality

Mollie Trueman,*[a] Duncan Akporiaye,[b] Michael W. Anderson [a]

Electronic Supporting Information

Methods and Materials

The reagents used in synthesis of samples for this work were sodium hydroxide (Alfa Aesar $\geq$ 97%), potassium hydroxide (Sigma Aldrich $\geq$ 85%), colloidal silica (Ludox HS-40 and Ludox AM-30), sodium aluminate (Sigma Aldrich), tetramethyl ammonium chloride (Sigma Aldrich $\geq$ 99%), tetraethyl orthosilicate (Sigma Aldrich $\geq$ 98%) and tetraethyl ammonium hydroxide solution (Alfa Aesar 35 wt. %). All chemicals were used as received, with no further purification.

Synthesis of T-ERI sample

Zeolite T was prepared through a procedure based on that proposed by Cichocki *et al.*[1,2] A solution of sodium hydroxide (4.7g, 117.5 mmol) and potassium hydroxide (3.2 g, 57.0 mmol) in deionised water (30 cm^3) was combined with Ludox HS-40 colloidal silica (50.10 g, 333.5 mmol SiO_2). Sodium aluminate (3.275 g, 40.0 mmol) was added to the resultant gel over a period of 10 minutes with stirring. The mixture was stirred at room temperature for 24 hours, then 10 g of gel was transferred to a stainless steel autoclave fitted with a 20 ml Teflon liner, and transferred to a preheated oven for 6 days. The mixture was then cooled to room temperature, filtered, washed in deionised water (100 cm^3) and dried for 12 hours at 70°. The product was characterised using PXRD and SEM, and was found to crystallise as hexagonal prisms.

Gel composition: 16.70 SiO_2 : 1 Al_2O_3 : 3.98 Na_2O : 1.45 K_2O :1 72 H_2O

Synthesis of T-OFF sample

Ludox AM-30 colloidal silica (20.9 g, 104.2 mmol SiO_2) was added to a solution of potassium hydroxide (1.30 g, 23.2 mmol), sodium hydroxide (2.63 g, 65.7 mmol) and sodium aluminate (0.77 g, 9.39 mmol) in deionised water (21.3 cm^3) with vigorous stirring. Tetramethyl ammonium chloride (0.76 g, 4.19 mmol) was added to the resultant gel, and the mixture was stirred for 15 minutes until homogeneous. 8 g of this mixture was transferred to a stainless steel autoclave fitted with a 20 ml Teflon liner, and transferred to a preheated oven for four hours at 190°C. On removal, the product was cooled to room temperature, filtered, washed in deionised water (100 cm^3) and dried for 12 hours at 70°C, yielding 0.18 g of hexagonal prismatic crystals of average dimension (11.5 x 4.7 µm).

Gel composition: 22.2 SiO_2 : 1 Al_2O_3 : 7.99 Na_2O : 2.47 K_2O : 434 H_2O : 0.89 TMA^+

Synthesis of zeolite beta

Zeolite beta samples were prepared using a method based on that proposed by Egeblad *et al.*[3] Tetraethyl orthosilicate (3.47 g, 167 mmol) and deionised water (0.55 cm^3) were added to an aqueous solution of tetraethyl ammonium hydroxide (8.00 g, 19 mmol). The mixture was stirred for six hours to allow for evaporation of the ethanol formed, then concentrated hydrofluoric acid (0.95 g, 48 wt. %, 22.8 mmol) was added with stirring. The resultant gel was transferred to a 20 cm^3, Teflon lined, stainless steel autoclave and heated at 140°C for 5 days. Crystalline zeolite beta was recovered through vacuum filtration.

Gel composition: 1 SiO_2 : 1.14 TEAOH : 1.37 HF : 18.83 H_2O

Characterisation

Powder X-ray diffraction was used to check the phase purity of the zeolite beta, T-ERI and T-OFF samples. Diffraction data was collected using a Panalytical X-Pert diffractometer at 45 kV and 40 mA using Cu-Kα radiation (λ = 1.54060 Å, 1.54439 Å) with a step size of 0.008° and a scan rate of 3.85° min^{-1}. Samples were prepared for analysis by grinding gently in a pestle and mortar and were placed on a zero-background silicon plate. Crystal habit was studied using scanning electron microscopy (SEM). Images were acquired on a Quanta 200 SEM operating in high vacuum mode. All images were taken in secondary electron mode, with a working distance of 10 mm and an accelerating voltage of 10 kV. Prior to imaging, samples were sputter coated with platinum.

Atomic force microscopy (AFM)

AFM images were collected using a JPK NanoWizard II AFM operating in contact mode with Si_3N_4 cantilevers of nominal force constant 0.350 Nm^{-1} (Bruker DNP-10 A-tip). Scans were obtained at a scan rate of 2 Hz, with a set point of 1V. Samples were held in place by fixing in thermoplastic. Images were processed by flattening height traces using a line-by-line fitting followed by a plane fit.

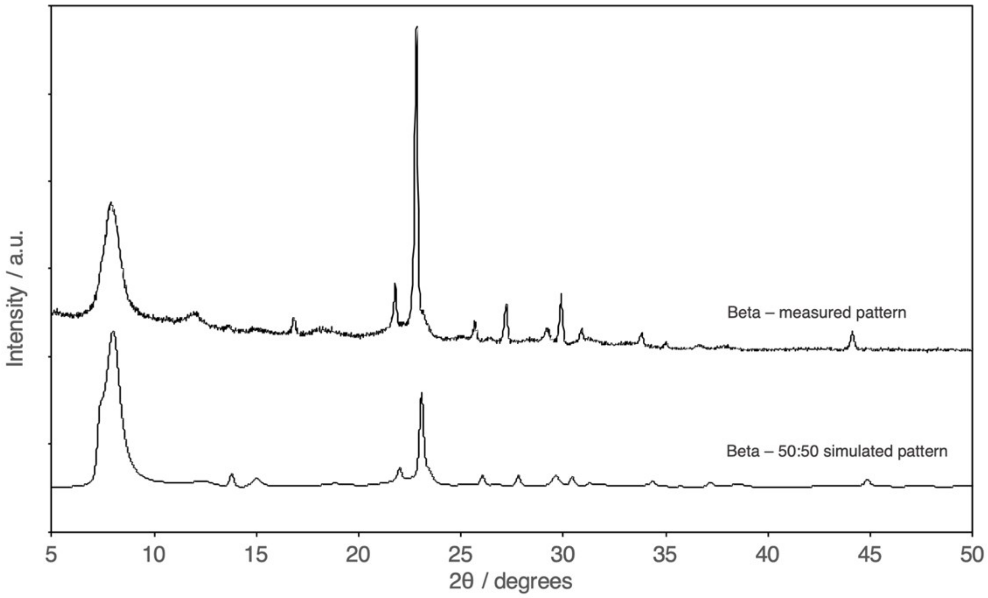

Figure S1: Powder X-ray diffraction pattern for zeolite beta sample. Simulated pattern, shown for comparison was generated using DIFFAX software,[4] for a 50:50 mixture of polymorph A and polymorph B.

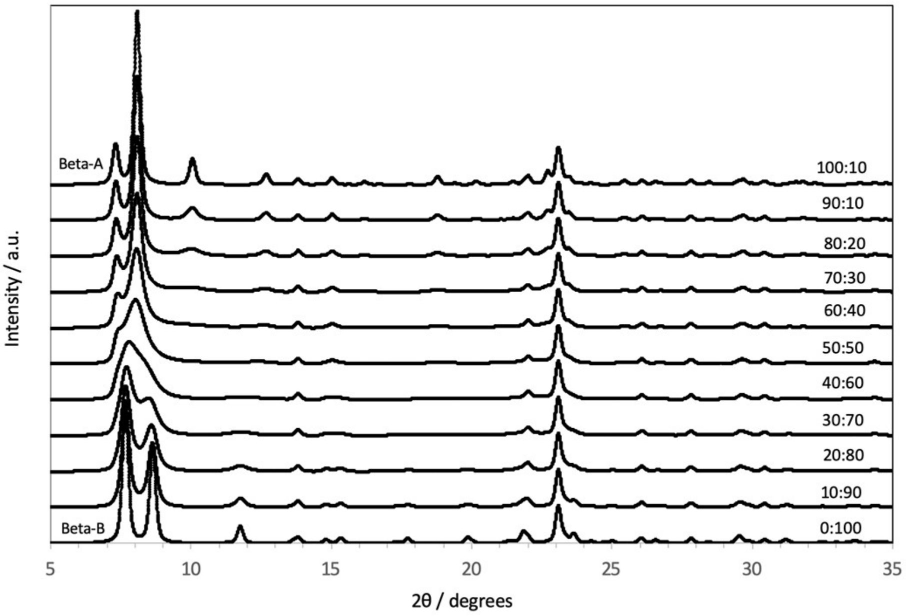

Figure S2: Simulated DIFFAX powder X-ray diffraction patterns for intergrowths of polymorph A and B of zeolite beta.[4]

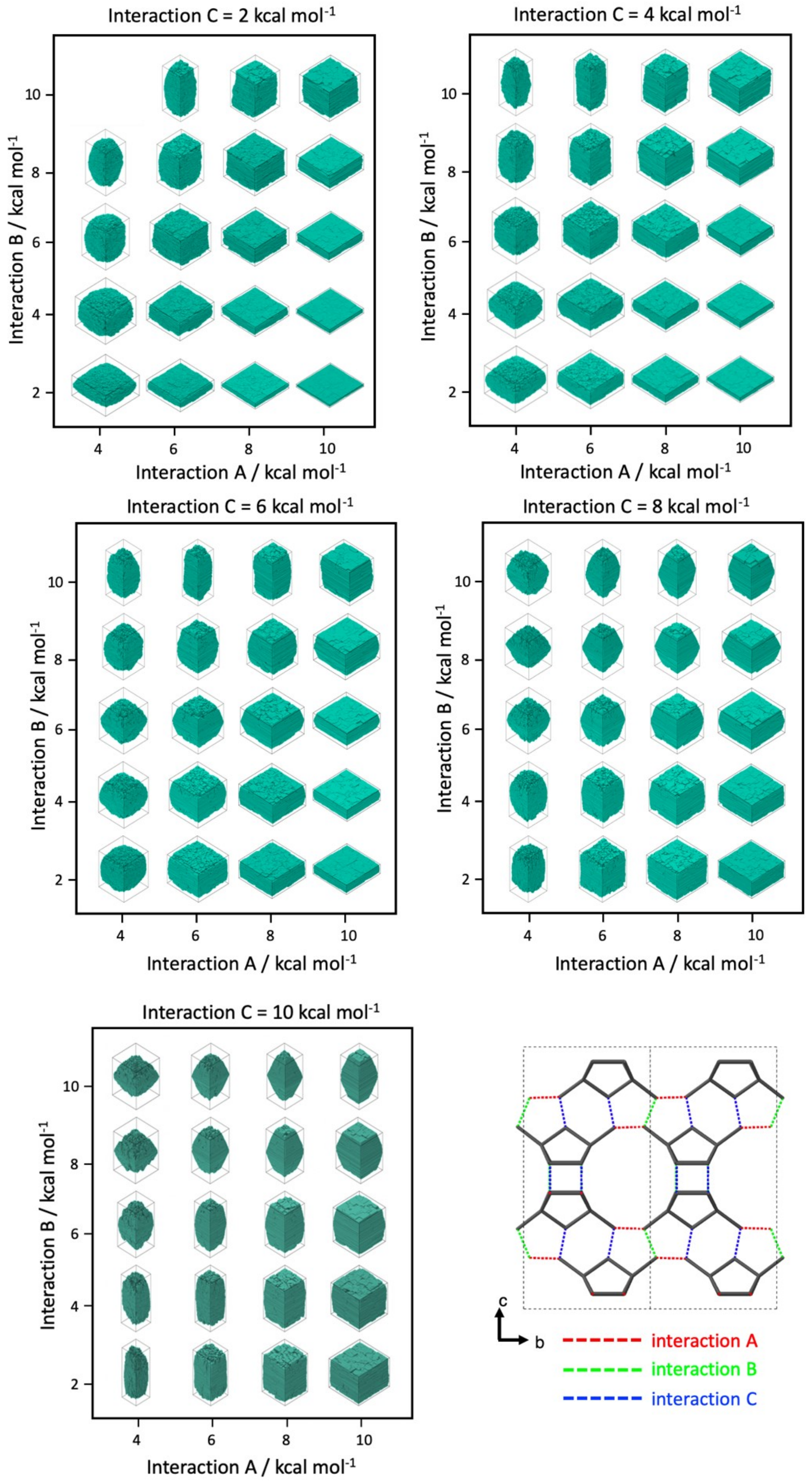

Figure S3: Three-dimensional data set showing the dependence of crystal habit on the value of three crystallisation free energies associated with three types of interaction in zeolite beta. The bond diagram in the lower portion of the screen indicates the labelling of each interaction type.

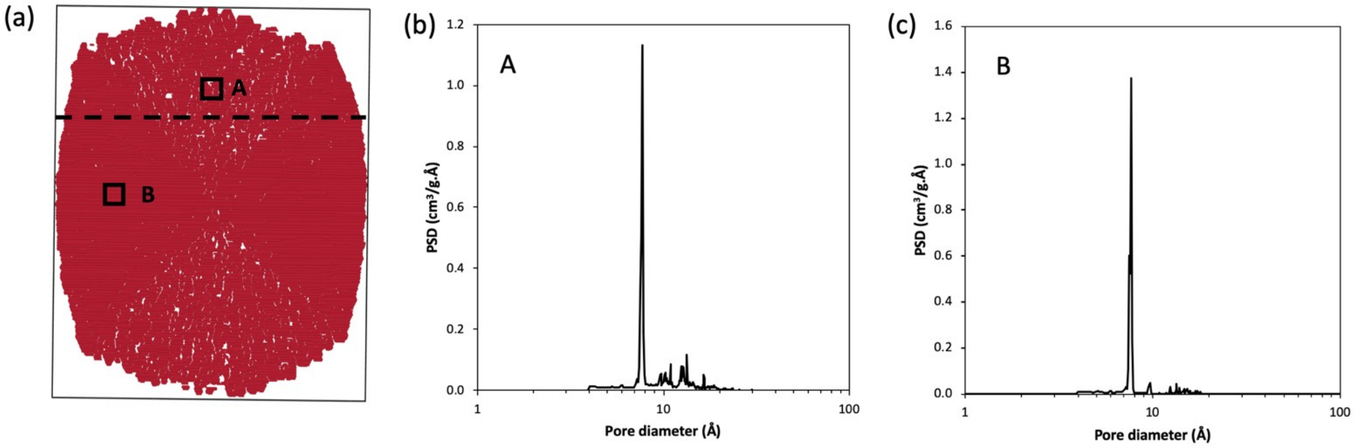

Figure S4 : Pore size distributions (PSDs) for two distinct zones in zeolite beta crystals. (a) Cross section of a simulated zeolite beta crystal, through the (100) plane at the centre of the crystal, showing regions of crystal where pore size distributions were calculated (b) Pore size distribution at position A as indicated in (a) (c) Pore size distribution at position B as indicated in (a). Note PSD at position B shows fewer large pores in the region 10-20 Å.

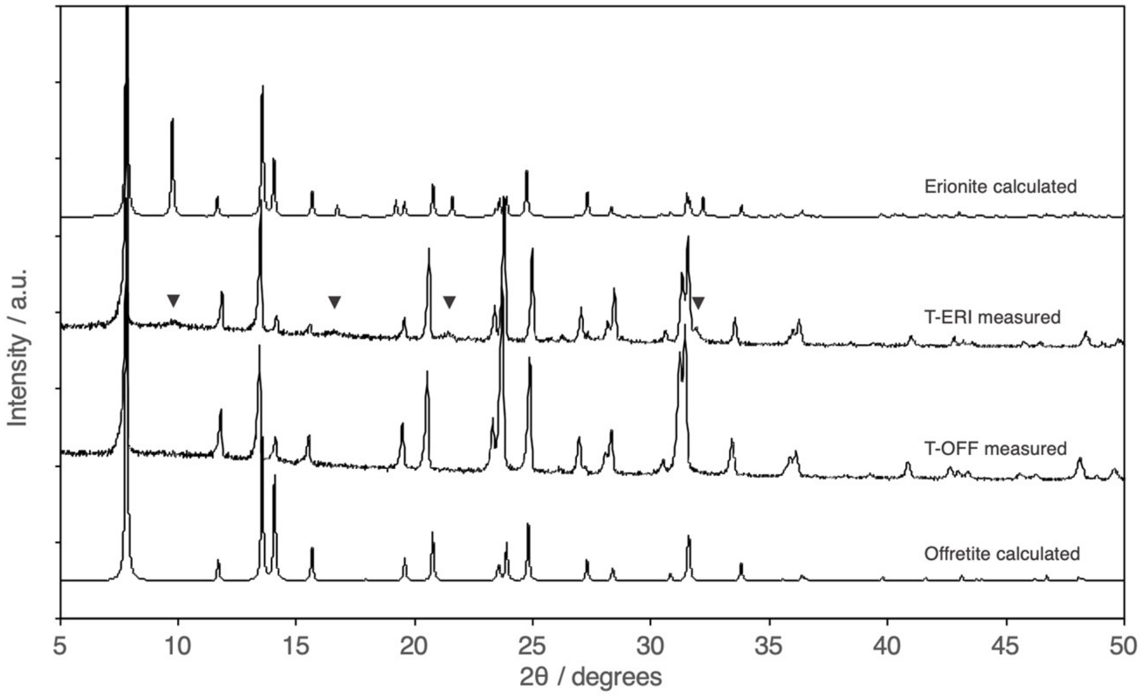

Figure S5: PXRD patterns of the products formed in the synthesis of T-ERI and T-OFF. Triangles above T-ERI pattern indicate positions of distinguishing peaks for erionite. Upper and lower patterns are calculated from the known crystal structures of erionite and offretite respectively.

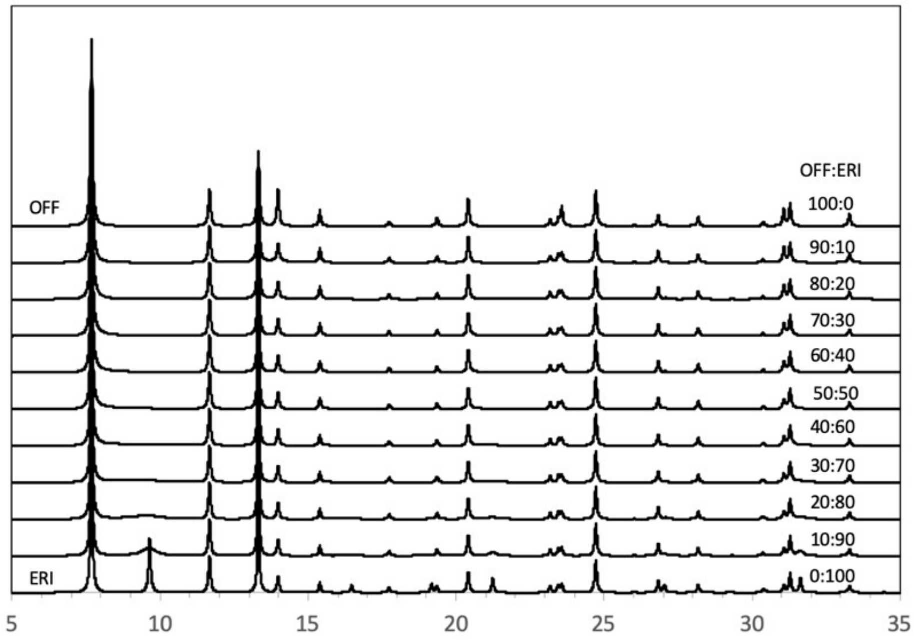

Figure S6 – Simulated DIFFAX powder XRD patterns for intergrowths of erionite and offretite.[4]

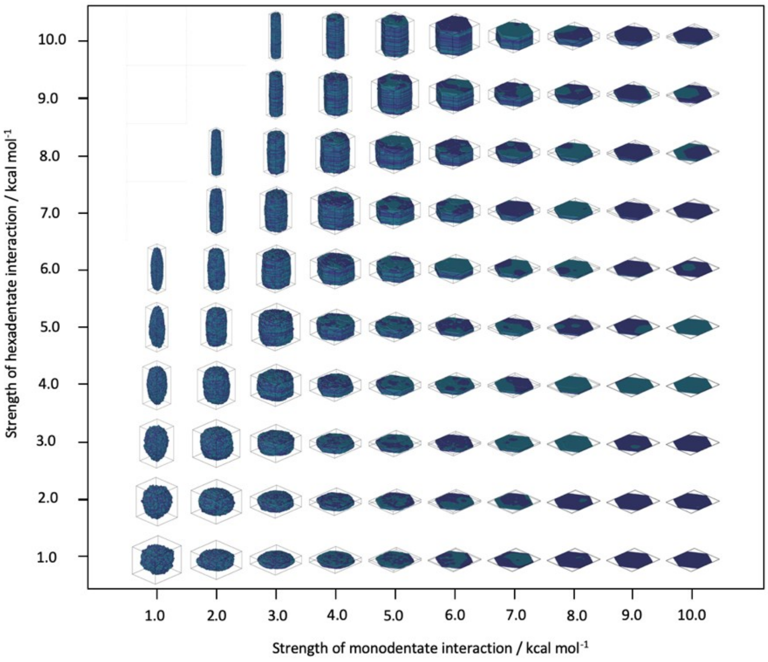

Figure S7: Graphical representation of the effect of the value of the two crystallisation free energies on the simulated crystal habit of zeolite T.

References

1 A. Cichocki, P. Kościelniak, M. Michalik and M. Buś, *Zeolites*, 1997, **18**, 25–32.

2 A. Cichocki and P. Kościelniak, *Microporous Mesoporous Mater.*, 1999, **29**, 369–382.

3 K. Egeblad, M. Kustova, S. K. Klitgaard, K. Zhu and C. H. Christensen, 2007, **101**, 214–223.

4 M. M. J. Treacy, 2010, http://www.public.asu.edu/~mtreacy/DIFFaX.html.