Microporous and Mesoporous Materials 255 (2018) 261–270

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Systematic approaches towards template-free synthesis of EMT-type zeolites

A. Nearchou*, P.R. Raithby, A. Sartbaeva**

Department of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY, UK

ARTICLE INFO

Article history:
Received 15 February 2017
Received in revised form
7 July 2017
Accepted 21 August 2017
Available online 24 August 2017

Keywords:
Zeolite
EMT
EMC-2
FAU
Synthesis
OSDA
PXRD
SEM
NMR

ABSTRACT

Presently it is understood that 18-crown-6 ether is necessary as an organic template to synthesise pure and well crystalline EMT-type zeolites. This is problematic for optimisation of organic-free synthesis of zeolites. We report a new method to synthesise pure zeolite EMC-2 using a lower amount of 18-crown-6 ether than previously reported. At these low 18-crown-6 ether concentrations, FAU-type zeolites were not seen to co-crystallise. We observe that the crystallinity of the EMT-type zeolite is proportional to the amount of 18-crown-6 ether added in the synthesis. The as-synthesised zeolites were characterised using X-ray powder diffraction, scanning electron microscopy and solid state nuclear magnetic resonance. These findings are a crucial step towards understanding template roles and designing syntheses for zeolites without the use of toxic organic templates.

1. Introduction

Zeolite EMC-2 has an EMT topology and is a hexagonal analogue of the cubic FAU framework [1–3]. Intergrowths of the two topologies have been observed widely in zeolite materials such as ECR-30, ZSM-20 and ZSM-3 [4–7]. It was not until 1990 that Delprato et al. [8] reported the successful synthesis of the pure EMT-type polymorph. This was achieved by using 18-crown-6 ether as an organic structure directing agent (OSDA).

Both the EMT and FAU framework consist of β-cages and D6R units, however the β-cages are orientated differently across the D6R units. In the EMT framework the cages are related by a mirror plane whereas in the FAU framework it is an inversion centre, as shown in Fig. 1 [1,2]. The two topologies are often described as hexagonal and cubic arrangements of faujasite sheets respectively. The FAU framework only contains one spherical supercage (*t-fau cage*) which has an internal diameter of 13 Å. Two different sized elliptical supercages are present in the EMT framework. The larger hypercage has an internal diameter of 13 Å by 14 Å and the smaller hypocage has a maximum diameter of 12 Å [1]. All three supercages are shown in Fig. 2.

The common appearance of intergrowths of the two polymorphs is believed to be due to stacking faults between these faujasite sheet layers. Treacy et al. [6] studied the distribution of stacking faults in different intergrowth FAU-EMT zeolite materials. It was concluded that the faults in these materials are not random, but rather segregated into discrete topological blocks. Ohsuna et al. [2,12] have also observed the appearance of discrete blocks of either FAU or EMT-type topology in intergrowth materials.

Due to this difference in porosity, EMT-type zeolites show enhanced catalytic potential compared to FAU-type zeolites [7,13]. However, the possibility of using zeolite EMC-2 as a catalyst is hindered by the necessity of OSDA in the synthesis process. The 18-crown-6 ether template is toxic and requires removal via calcination. Therefore, from a synthetic standpoint it is appealing to optimise the synthesis process to require less or no organic template [13–15]. This is of interest not just for zeolite EMC-2, but all zeolites synthesised using OSDA [16–18].

Previously, pure well-crystalline zeolite EMC-2 has been synthesised using conventional hydrothermal methods with a 18C6/

* Corresponding author.
** Corresponding author.
E-mail addresses: a.nearchou@bath.ac.uk (A. Nearchou), a.sartbaeva@bath.ac.uk (A. Sartbaeva).

http://dx.doi.org/10.1016/j.micromeso.2017.08.036
1387-1811/

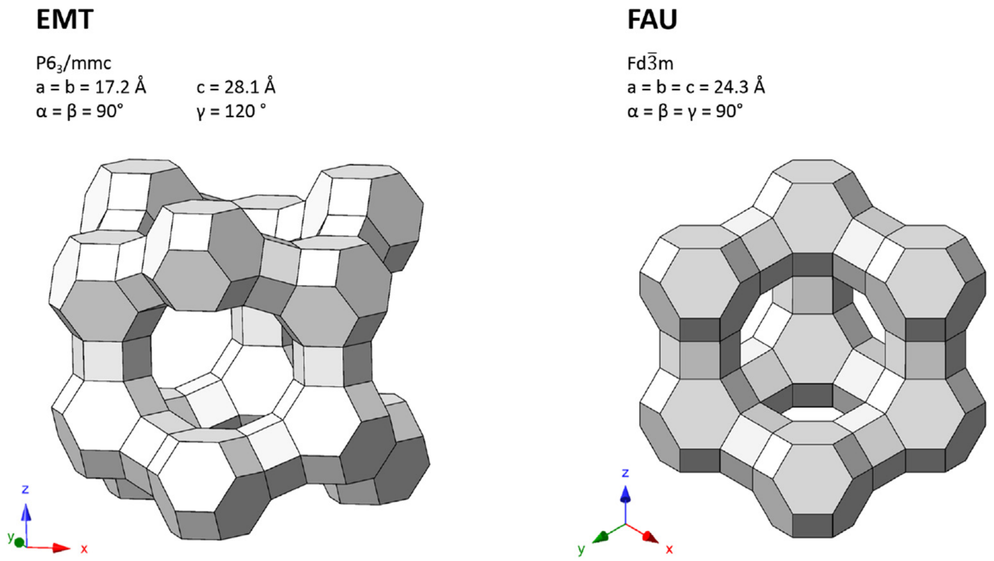

Fig. 1. Idealised cell parameters [9–11] and structures of the EMT (left) and FAU (right) frameworks, with the β-cages and D6R units shaded.

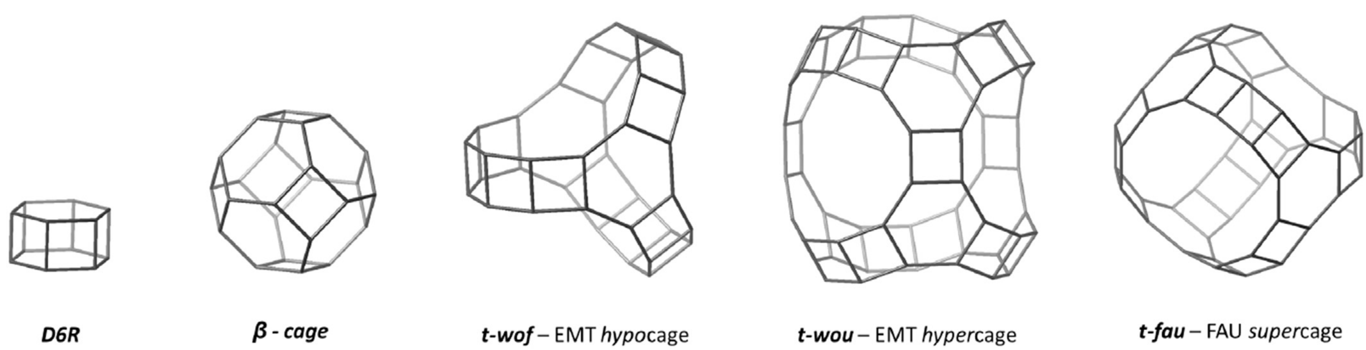

Fig. 2. Structures of the building units and supercages present in the EMT and FAU frameworks.

Al_2O_3 ratio as low as 0.3 [1]. This ratio has been reduced to 0.14 by using the SINTEF method where the hydrothermal vessel is rotated [19]. In 2012 Ng et al. [14,15] reported the successful synthesis of ultrasmall EMT-type nanocrystals without OSDA or organic additives. This was achieved by kinetically controlling the nucleation at ambient conditions. However the product was predominantly amorphous and the nanocrystals 6-5 nm in diameter.

We report a successful new synthesis of pure zeolite EMC-2 with a 18C6/Al_2O_3 ratio as low as 0.059 using conventional hydrothermal methods.

2. Synthesis mechanism

Concerning the synthetic formation of the EMT framework it is agreed that the [(18-crown-6)Na^+] macrocation complex is an integral feature. The 18-crown-6 ether molecule size, shape and ability to complex to sodium cations, are argued to be essential properties [5,8].

$$\frac{Na+}{[(18-crown-6)Na^{+}]} \tag{1}$$

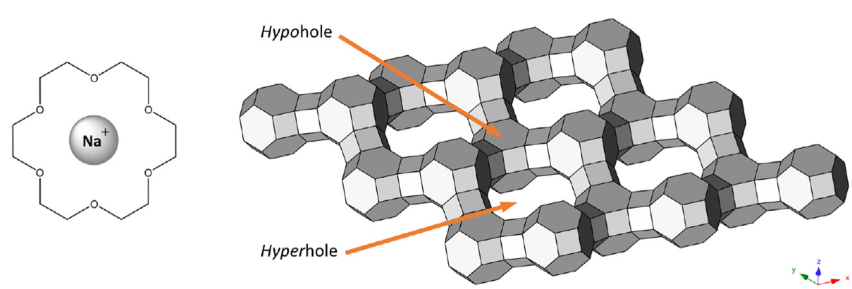

Fig. 3. Diagram showing the two pockets in the faujasite sheet that the [(18-crown-6)Na^+] macrocation can occupy to form hypo- and hypercages.