Microporous and Mesoporous Materials 174 (2013) 117–125

Contents lists available at SciVerse ScienceDirect

Microporous and Mesoporous Materials

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

Synthesis of FAU and EMT-type zeolites using structure-directing agents specifically designed by molecular modelling

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ARTICLE INFO

Article history:
Received 14 December 2012
Received in revised form 27 February 2013
Accepted 9 March 2013
Available online 16 March 2013

Keywords:
Molecular modelling
Zeolite
EMT
FAU
High throughput experiment

ABSTRACT

Molecular modelling is a growing science which allows to calculate short range forces between zeolite frameworks and organic compounds. By using a steric approach, it is possible to design templates matching closely with an inorganic framework. Herein, the design, synthesis and successful application of several di(azacrown ether) templates to direct the formation of FAU- and EMT-type zeolites are reported. Following a high throughput experiment design, the synthesis gel composition was optimized to obtain well-crystallized materials. Taking into account their respective crystallization rates, their textural and morphological properties were comparable to their counterparts, typically structured by 15-crown-5 and 18-crown-6 ethers. This work is the first step toward a further design of structure- and shape-directing templates, in order to control the properties of FAU- and EMT-type zeolites aiming specific catalytic and separation applications.

1. Introduction

Zeolites are well-defined microporous aluminosilicate materials obtained by the polymeric combination of TO_4 tetrahedra. Their unique design promotes the creation of multidimensional channels and cavities, responsible for their interesting adsorption and diffusion properties [1–3]. Combined with their intrinsic Brönsted acidity and high thermal stability, zeolites are nowadays widely used in petrochemistry and oil refining processes [4–8]. Particularly, FAU-type zeolites are one of the main components of cracking catalysts at the industrial scale due to their structure, one of the most open among zeolites: its porosity is composed of supercages, with a free diameter of 11.6 Å, interconnected through circular 12-member-ring (MR) apertures with a diameter of 7.4 Å [9].

Conventional Y zeolite (FAU-structure type), with a silicon-to-aluminum molar ratio between 1.5 and 2.5, lacks of thermal and hydrothermal stabilities [10]. Nowadays, high silica ultra-stable Y zeolite, with silicon to aluminum molar ratio generally above 4, is used for cracking applications, allowing good thermal and hydrothermal stabilities [11,12]. Mainly, ultra-stable Y zeolite is produced from dealumination of a conventional Y zeolite by hydrothermal or chemical treatment [13–16]. Unfortunately, these methods require several post-treatments such as calcination under steam (steaming), acid leaching, filtration, washing and drying: this explains the strong interest of a direct “one step” synthesis of high-silica FAU-type zeolites for industrial applications [10].

High silica FAU-type zeolite, with a silicon to aluminum molar ratio between 3 and 5, can be synthesized directly by using specific structure-directing agents (SDA) in a synthesis hydrogel. Thus, Guth and co-workers reported the crystallization of a high silica FAU-type zeolite commonly named EMC-1 (Elf Mulhouse Chemistry One) by using the 15-crown-5 ether as SDA [17–19]. While using the 18-crown-6 ether as SDA, they also obtained for the first time a pure hexagonal analogue of FAU, the EMC-2 zeolite (EMT-type structure) [17–19]. In fact, the true SDA correspond to the association of the sodium cation with the crown ether [20–22]. Additionally, intergrowth of the two structures can be observed when a mixture of both crown ethers is used [19,20,23,24]. While FAU structure results from the stacking through double six-rings of faujasite sheets with an inversion center symmetry operation, the EMT structure results from a mirror plane operation between the same sheets [20,21,23]. This latter stacking allows the formation of two different types of cage: the larger hypercage, having a free diameter of 14 Å, and the smaller ellipsoïd hypocage, with inner dimensions of 13 × 7 Å, connected through 12MR apertures [20,21]. Moreover, in the EMT-type structure a straight channel with 12 MR openings parallel to the *c* direction is observed.

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1387-1811/$ - see front matter
http://dx.doi.org/10.1016/j.micromeso.2013.03.006

The catalytic performances of these two zeolites have been widely studied. Compared to a EMC-1 zeolite with the same Si/Al molar ratio, EMC-2 zeolite allows to reach an higher conversion in terms of n-alkane isomerization and n-heptane cracking [19,25]. This improved catalytic activity comes from the heterogeneous repartition of aluminum atoms in the framework, and the presence of hypercages [25]. For vacuum gas-oil cracking, very close performances were obtained between EMC-1 and USY zeolites in terms of cracking selectivities and activity, the latter being increased when using EMC-2 zeolite [26].

In order to reduce the cost of these zeolites, attempts to search for less expensive SDA to direct the formation of high-silica FAU- and EMT-type zeolites were conducted, but did not afford pure EMT phase [27,28]. This might arise from a low fit between the SDA and the zeolite structure.

Molecular modelling is an emerging technique in the field of zeolite synthesis [29,30]. This method is based on mechanical and molecular dynamics techniques, along with Monte–Carlo methods. Particularly, a steric approach was applied to the design of SDA which directs the synthesis of specific frameworks such as ZSM-48 (*MRE), NU-87 (NES), DAF-4 (LEV), DAF-5 (CHA) and $AlPO_4$-21 (AWO) zeolites [31–35].

Herein, using a similar steric approach new di(azacrown ether)-based templates were designed to favor the formation of FAU and EMT-type zeolites. Following a high throughput experiment (HTE) design, the synthesis gel composition was optimized to obtain well-crystallized FAU and EMT-type zeolites. The obtained products were fully characterized by XRD (X-ray Diffraction), SEM (Scanning Electron Microscope), TGA/DTA (Thermogravimetric Analysis/Differential Thermal Analysis), ^{1}H liquid NMR and nitrogen sorption.

2. Experimental

2.1. Molecular modelling

Templates geometry optimization was performed in purely siliceous EMT and FAU frameworks using Materials Studio 5.5 software following a similar steric approach described elsewhere [31,34]. Fig. 1 shows the optimized geometry of the AC5-4 template in purely siliceous FAU framework. The energy minimized locations of SDA within theoritical purely siliceous EMT and FAU type structure were obtained by molecular modelling. Energy minimization was performed using Monte carlo-Simulated annealing runtines in the program Discover (implemented in MS Modelling 5.5 by Accelerys Inc.). Van der Waals interactions were calculated using the universal forcefield [36]. In this work, the "host–guest" interaction energy (bonding energy) is defined as the difference between the total energy of a system where a template is occluded inside a zeolite framework, and the sum of energies of the template in the vacuum and the zeolite in vacuum.

$$E_{\text{Host Guest}} = E_{(\text{Zeolite with template occluded})} - (E_{\text{template}} + E_{\text{Zeolite without template}})$$

The deformation energy is defined as the difference between the energy of a template sterically constricted inside a zeolite framework, and the energy of the template in vacuum.

2.2. Preparation of di(azacrown ether) templates ($ACn - m$)

During this study three templates (AC5-4, AC5-5, AC6-4), designed by molecular modelling, have been synthesized in order to study both the influence of the macrocycle diameter and the spacer length between the macrocycles upon zeolite formation. A schematic representation of those templates is given in Fig. 2. They were synthesized in two steps: the first one consists in a diacylation of the aza-crown ether by a diacyl chloride, followed by the reduction of the diamide with lithium aluminum hydride ($LiAlH_4$). The experimental conditions of all these syntheses being similar, only the preparation of AC6-4 (Mw = 580 g/mol), molecular formula $C_{12}H_{24}O_5N–C_4H_8–NO_5H_{24}C_{12}$) will be detailed thereafter.

2.2.1. Synthesis of AC6-4 compound

In a typical synthesis, 1.1 g (4.17 mmol, 2.5 eq) of 1-aza-18-crown-6 ether (molecular formula $C_{12}H_{25}NO_5$, Alfa Aesar) and 0.93 mL (6.72 mmol) of triethylamine (Alfa Aesar) were dissolved in 11 mL of freshly distilled dichloromethane (Alfa Aesar). The mixture is first maintained at 0 °C in an ice bath during dropwise addition of 0.187 mL (1.69 mmol, 1 eq) of succinyl chloride (Alfa Aesar), and then stirred at room temperature for 15 h. The solvent is removed under reduced pressure and the residue is mixed in 15 mL of ethyl acetate (VWR Intl) and then filtered. The filtrate, containing the desired diamide and the residual 1-aza-18-crown-6 ether, is purified by column chromatography on silicagel (acetone/triethylamine elutent, 95:5 v/v). Then 0.86 g (1.4 mmol, 1 eq) of the desired diamide and 0.109 g (2.8 mmol, 2 eq) of $LiAlH_4$

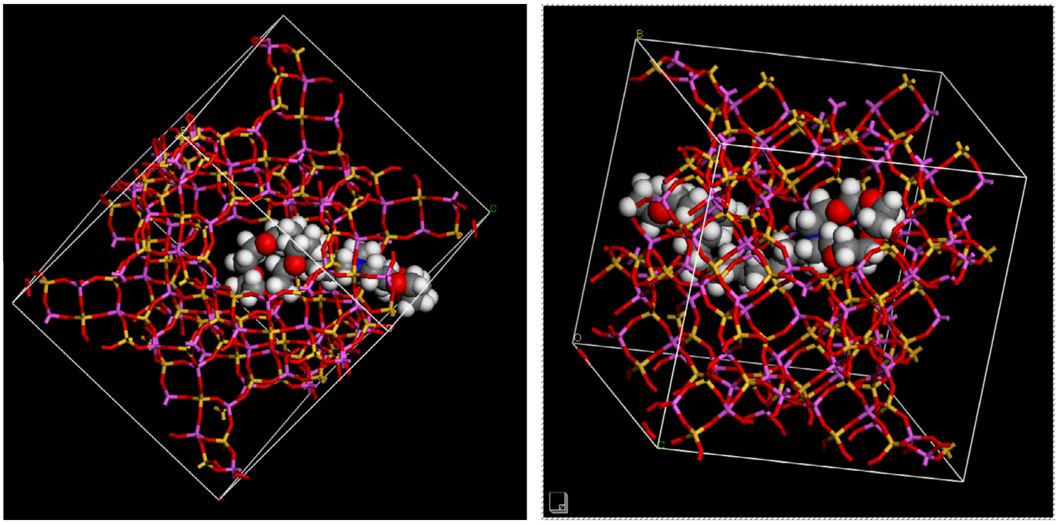

Fig. 1. Optimized geometry of the AC5-4 template in purely siliceous FAU framework.