Microporous and Mesoporous Materials 227 (2016) 176–190

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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

Size control of self-supported LTA zeolite nanoparticles monoliths

Bilel Said [a], Thomas Cacciaguerra [a], Franck Tancret [b], Francois Fajula [a], Anne Galarneau [a, *]

[a] *Institut Charles Gerhardt Montpellier, UMR 5253 CNRS-Université de Montpellier-ENSCM, ENSCM, 8 rue de l'Ecole Normale, 34296 Montpellier Cedex 05, France*

[b] *Université de Nantes, Institut des Matériaux de Nantes – Jean Rouxel (IMN), CNRS UMR 6502, Polytech Nantes, Rue Christian Pauc, BP 50609, 44306 Nantes Cedex 3, France*

ARTICLE INFO

Article history:
Received 16 November 2015
Received in revised form
22 February 2016
Accepted 23 February 2016
Available online 27 February 2016

Keywords:
Hierarchical zeolite
LTA nanocrystal
Nanozeolite
Macroporous monolith
Mesoporous zeolite

ABSTRACT

LTA zeolites are used in many applications as diverse as chemistry, physics, medicine, agriculture. By exploiting the concept of pseudomorphic transformation, i.e. using silica monoliths featuring macro- and mesopores as silica source, we manage to shape LTA zeolites as centimetric monoliths (6 mm diameter, 5 cm length) with trimodal hierarchical porosity (micro-, meso- and macropores). The skeleton of the monolith is formed by an aggregation of LTA nanocrystals of ca. 100 nm leading to mesopores due to voids between the nanocrystals. Diverse LTA nanocrystal shapes and sizes were realized by controlling aging time and crystallization temperature. These unique self-standing monoliths of LTA nanozeolites feature flow-trough macropores of 3–4 microns highly suitable for high mass transport of liquids, homogeneous distributions of mesopores for high diffusion of molecules and ions and therefore a high accessibility to zeolites active sites. Together with an easy handling, these materials offer the possibility to intensify many processes using classical LTA zeolite crystals.

1. Introduction

Due to its high cation-exchange capacity and its ability to trap water and small polar molecules, LTA zeolite has found many applications and is intensively used commercially in domains as diverse as chemistry, physics, medicine, agriculture.

As a sorbent, LTA zeolite is widely used as dessicant, for instance in the drying of industrial streams, or in purification and separation processes, such as propane/propene [1] and n-/iso-alkane separation technologies, or the removal of CO from hydrogen produced by alcohol hydrocarbon reforming [2] or the removal of CO_2 from exhaust air [3].

Cation-exchange properties of LTA zeolite are commercially exploited in water softening to trap Ca^{2+} and Mg^{2+} cations, and are at the basis of the largest use for LTA zeolite for the laundry detergent market [4]. LTA zeolite is also used for the removal of heavy metal ions present in process water at oil fields, the purification of drinking water, the desalination of aqueous solutions or the pre-concentration of heavy metals [5]. LTA zeolite has also great potential as radionucleide traps [6] as humidity microsensors [7] and as UV to visible light wavelength converters [8,9].

The unique properties of zeolites in separation and selective sorption result from the closeness between the size of their pores and that of the guest species, allowing molecular sieving and optimal interaction between the guest sorbent and the host surface. This situation however adversely affects mass transport in the pores, which is often constrained by diffusion, responsible for performance limitation. In order to overcome this drawback two strategies can be envisaged, either the production of small, nano-sized crystals, or the production of crystals with multimodal distributions of meso- and micropores pores, both allowing to increase the surface to volume ratio of the crystals and to decrease the diffusion path, thus favoring the access to the active surface. In the case of LTA synthesis, the latter approach has been described by the groups of Ryoo [10] and Zhao [11] for instance, who used long chain alkylammonium siloxanes or salts as mesoporogens. Syntheses of LTA nanocrystals in the presence of tetramethyl ammonium [12–14] or using quite complex emulsion-based [15] or two-phase segmented fuidic microreactor [16,17] methodologies have been reported as well. Organic template free synthesis of LTA nanocrystals appears as a more sustainable method. This type of synthesis is widely documented in the literature [18–26]. Gel

---

* Corresponding author.
E-mail address: anne.galarneau@enscm.fr (A. Galarneau).

http://dx.doi.org/10.1016/j.micromeso.2016.02.048

composition, aging time and crystallization temperature are the main parameters allowing to tune crystal size and distribution.

Regardless of their mode of production, shaping zeolite nanocrystals into usable macroscopic bodies or devices remains an open challenge. This is generally achieved by using inorganic binders, possibly in the presence of organic additives, a process, which may not be neutral in view of the very high surface to volume ratio. In order to overcome this limitation we have explored the possibility of preparing LTA nanocrystals as self-supported macroporous monoliths of 6 mm diameter and 5 or 10 cm length, using silica monoliths featuring open meso- and macroporous networks as starting material. The starting silica monoliths exhibit unique hydrodynamic characteristics and lead to remarkable productivities as catalyst supports [27–31] or sorbents [6,32] in continuous flow processes.

The synthesis is based on the concept of pseudomorphic transformation [33–36], a method where the dissolution rate of the silica precursor in alkaline medium is limited and controlled within the porosity of the silica source and adapted to the rate of crystallization of the desired zeolite in order to preserve the morphology of the parent silica material. This procedure has been successfully applied for the preparation of millimeter size binderless particles of SOD, LTA and FAU-X aggregates [37,38] and to SOD [39] and LTA-monoliths featuring micronic crystals [40]. The main challenge of the present work was to preserve the integrity and the stability of the parent monolith while scanning the experimental conditions allowing to produce LTA nanocrystals.

2. Experimental

2.1. Silica monolith synthesis of 6 mm diameter and 10 cm length

First, tetraethylorthosilicate (TEOS, Aldrich) (20 g) is left at −19 °C for 1 h. In parallel, water (24.560 g) and then (2.313 g) nitric acid (68%) are added in a 100 mL Erlenmeyer. The mixture is stirred 5 min at room temperature. Polyethylene oxide (PEO 20 kDa) (2.534 g) is added to the mixture and stirred at room temperature until having complete dissolution of the polymer. The mixture is left 10 min at −19 °C in the freezer to cool down the solution without freezing. The flask is then placed in an ice bath and stirred. TEOS (coming from the freezer) is directly added to the slurry and the solution is stirred for 30 min. The final composition of the mixture in molar ratio is: 1 Si/0.60 EO unit/0.26 HNO_3/14.21 H_2O. Polyvinyl chloride (PVC) tubes of 8 mm diameter and 10 cm length are closed on one side with a cap, sealed with parafilm and kept at −19 °C in the freezer. The tubes are taken from the freezer and filled with the mixture of the ice bath. The tubes are then closed by caps and sealed with parafilm and left in water bath at 40 °C for 3 days. The phase separation and the sol–gel process take place during this time. Monoliths are then removed from the tube molds and placed in 1 L water bath at room temperature. Water is changed every 30 min until reaching a neutral pH. The monoliths are then immersed in 1 L aqueous ammonia (0.1 M) in a polypropylene bottle and left in an oven at 40 °C for 1 day. Resulting monoliths are placed in a water bath and water is changed every 30 min until neutral pH. The monoliths are then dried at room temperature during 4 days and calcined at 550 °C for 8 h under air to totally remove remaining PEO. The resulting monoliths feature 6 mm diameter, 10 cm length and weight 80 mg/cm and a density of 0.28 g/cm^3. They can be cut at the desired length with a knife.

2.2. Synthesis of templated-free LTA monoliths

The synthesis composition is given for a calcined silica monolith of 5 cm length (400 mg). First, a seeding-gel is prepared. 0.46 g of NaOH is dissolved in 47.46 g of water. 3.9 g of tetrapropylammonium hydroxide (TPAOH 20 wt%) is added, and the mixture is stirred for 10 min at room temperature. Then the magnetic stirring bar is removed and the mixture is stirred vigorously at 1000 rpm. 5.3 g of Aerosil is added gradually and the agitation is kept 1 h. Then, the solution is put on an autoclave and aged at 100 °C for 16 h. The obtained solution is kept at 4 °C. Secondly, a solution is prepared under stirring with 0.037 g of NaOH, 1.389 g of sodium aluminate ($NaAlO_2$) and 3.828 g of water. After dissolution, 0.251 g of the previous seeding-gel is added and the mixture is stirred until dissolution of the gel. A calcined silica monolith is placed on the bottom of an autoclave and is totally impregnated with the solution. The molar composition of the system is: 1 SiO_2/0.14 NaOH/2.54 $NaAlO_2$/32 H_2O/0.004 TPAOH. The autoclave is placed in an oven at 100 °C 18 h or for synthesis with aging time first at 40 °C for 20 or 48 h and then at different temperature from 70 to 100 °C for 18–48 h. Monoliths are then recovered and put in a water bath at room temperature. Water is changed every 30 min until reaching a neutral pH. Monolith is then dried at 80 °C for 1 day and calcined at 550 °C for 8 h under air.

2.3. Synthesis of organic-templated LTA monoliths

The same synthesis protocole of LTA monoliths as in section 2.2 was performed using organic modified monoliths (amino- or phenylamino-Monoliths, MCM-41 Monoliths containing cetyltrimethylammonium in the mesoporosity) or by adding a surfactant organosilane during the synthesis. The different protocoles of organic-modified Monoliths are presented below.

2.3.1. Synthesis of amino- and phenylamino-grafted monoliths

A silica monolith (10 cm, 0.800 g) is activated under vacuum at 150 °C during 4 h. Then, the monolith is immersed in 50 mL of ethanol and 1.030 g of 3-aminopropyltriethoxysilane (APTES, Sigma Aldrich) for amino-grafting and 1.188 g of phenylaminopropyltrimethoxysilane (PHAPTMS, Aldrich) for phenylamino-grafting. The solution is gently stirred with a small bar magnet in order to preserve the monoliths shape, and heated to reflux at 80 °C for 18 h. Grafted-Monoliths are then washed with 50 mL of ethanol, then 50 mL of acetone and dried at 80 °C overnight.

2.3.2. Synthesis of MCM-41 monolith

The synthesis of MCM-41 monolith was adapted from previous work [35]. Silica monoliths obtained after the phase separation and sol–gel process (first step in acidic medium) are taken from the neutral water bath and reacted in an alkaline solution containing water, NaOH (Aldrich) and cetyltrimethylammonium bromide (CTAB, Aldrich). In a typical synthesis, two wet monoliths of 10 cm (corresponding to 0.80 g each of dried and calcined SiO_2) are taken and placed at the bottom of an autoclave. An aqueous solution is prepared by dissolving 0.213 of NaOH in 192 g of water. Then, 5.831 g of CTAB are added and the mixture is stirred for 1 h at room temperature. The alkaline solution is poured on the autoclave containing the monoliths and let in an oven at 115 °C for 6 days. The final composition in molar ratio is: 1 Si/0.60 CTAB/0.2 NaOH/400 H_2O. Monoliths are then removed from the autoclave and placed in 1 L water bath at room temperature. Water is changed every 30 min until reaching a neutral pH (around 3 washings). Monoliths are then dried at 80 °C for 1 day.

2.3.3. Synthesis of LTA monoliths with addition of surfactant organosilane

A calcined silica monolith (5 cm, 400 mg) is placed on the bottom of an autoclave. 0.037 g of NaOH and 1.389 g of sodium aluminate ($NaAlO_2$) are dissolved in 3.828 g of water. 0.251 g of