

Exceptionally stable and hierarchically porous self-standing zeolite monolith based on a solution-mediated and solid-state transformation synergistic mechanism



Manh Huy Do ^{a, b, c}, Dang-guo Cheng ^{b, *}, Fengqiu Chen ^{a, b}, Xiaoli Zhan ^b

^a Key Laboratory of Biomass Chemical Engineering of Ministry of Education, Zhejiang University, Hangzhou 310027, Zhejiang, China

^b College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, Zhejiang, China

^c Institute of Chemical Technology, Vietnamese Academy of Science and Technology, 01 Mac Dinh Chi, District 1, Ho Chi Minh, Viet Nam

HIGHLIGHTS

- Hierarchical self-standing MFI zeolite monoliths were synthesized via a facile method.
- Na⁺ and OH⁻ are used as counterions for breaking and remaking of T–O–T (T = Si or Al) bonds.
- Hierarchical self-standing MFI zeolite monoliths result from zeolite crystal intergrowth.
- Self-standing zeolite monolith has an excellent mechanical stability with tunable intracrystalline meso-/macropores.

ARTICLE INFO

Article history:

Received 14 December 2014

Received in revised form

22 October 2015

Accepted 2 November 2015

Available online 12 November 2015

Keywords:

Microporous materials

Crystallization

Mechanical testing

Nuclear magnetic resonance

ABSTRACT

Although many strategies exist for fabricating hierarchical zeolite monolith, it is still challenging to synthesize pure hierarchical zeolite monolith with intracrystalline meso-/macropores and stability suitable for industrial application in a general and efficient process. Here we describe a simple quasi-solid gel crystallization route to prepare hierarchical self-standing ZSM-5 zeolite monolith via the use of Na⁺ and OH⁻ as counterions to modify the breaking and remaking of T–O–T (T = Si or Al) bonds. X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), laser scan confocal microscopy (LSCM), N₂ adsorption–desorption, mercury porosimetry, solid-state nuclear magnetic resonance (NMR), and compression mechanical testing were applied to elucidate the structure and mechanical stability of the obtained monolith. The self-standing monolith is composed of self-interconnected meso-/macroporous MFI crystals with tunable intracrystalline meso-/macropores and possesses an unusually mechanical stability with a crushing strength of 5.01 MPa. Combined with controllable structure of the defect-free membrane layer on the monolith top, the self-standing zeolite monolith should widen their potential applications.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Hierarchical zeolite monoliths and monolith reactors are current of great interest because they offer a number of advantages as high geometric surface area, efficient mass and heat transfer, low pressure drop, enhanced thermal stability and mechanical strength, high effectiveness factors, and ease of handling [1,2]. To solve diffusion and transfer limitations of microporous zeolites, meso-/macropores are introduced in the zeolite crystal through

demetallation processes [3,4] or multifunctional single- [5,6] or dual-template [7–10] strategies or high energy ion irradiation [11]. However, the resulting hierarchical zeolites are usually in powder form. For industrial applications, the final zeolite materials are typically extruded with inorganic binders. Unfortunately, these binders often block the channels of zeolite partially, resulting in the unaccessibility to the active sites. To overcome these disadvantages, the shaped meso- and/or macroporous inorganic skeletons such as silica [12–18], aluminosilicate [19–21], silicoaluminophosphate [22], glass [23], aluminum [24] were used for growing zeolite crystals on their amorphous wall. Nonetheless, the presence of the amorphous supports, which exhibit low hydrothermal stability and

* Corresponding author.

E-mail address: dgcheng@zju.edu.cn (D.-g. Cheng).

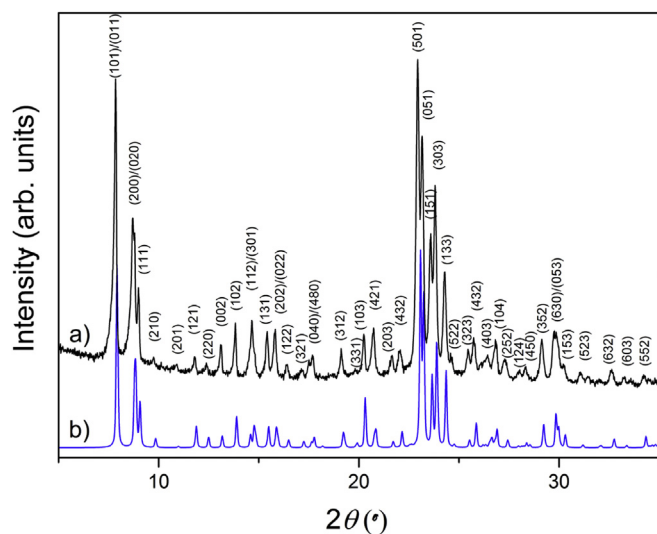
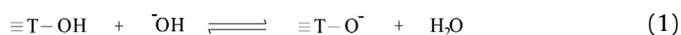


Fig. 1. XRD pattern of a) the as-synthesized ZSM-5-A before calcination, b) simulated pattern of ZSM-5 (JCPDS no. 39-0225).

acidity compared with crystalline zeolites, may cause the reduction of catalytic reaction efficiency. Recently, attempts have been made to achieve pure hierarchical zeolite monoliths via forming negative replicas of hard template structures [25–30]. However, the complexity in the preparation of hard templates, the difficulty in tuning the meso-/macropores and low mechanical stability of the resulting monolith limited their practical application. Furthermore, the hierarchical zeolite monoliths with intracrystalline meso-/macroporosities, which are critical for overcoming diffusion and mass transfer issues in zeolite crystalline microporous frameworks, are difficult to obtain through these above approaches. Very recently, to facilitate the preparation of the specimens for studying zeolite growth mechanism, we developed simple method of preparing zeolite monolith via the use of Na^+ and OH^- as counterions to modify the breaking, and remaking of T–O–T (T = Si or Al) bonds. In which, we mainly focused on explaining the mechanism, a synergistic growth between a solution-mediated process and a solid-state transformation, for the formation of a monolith framework composed of the intergrowth hierarchical crystals [31]. Here we show unusually stability and tunable hierarchical porosity of self-standing zeolite monolith composed of self-interconnected meso-/macroporous MFI zeolites obtained from the above quasi-solid gel crystallization method, namely, the use of Na^+ and OH^-

as counterions to modify the breaking, and remaking of T–O–T bonds. The processes can be described by the following reactions:



2. Experimental section

2.1. Materials

Tetrapropylammonium hydroxide (TPAOH, 25 wt% in water) was purchased from Wuhan Chifei Chemical Co., Ltd. All other chemicals were purchased from Sinopharm, Chemical Reagent Co., Ltd and used without further purification.

2.2. Synthesis of hierarchical self-standing MFI zeolite monolith

To illustrate our approach, we chose zeolite ZSM-5 as a model system, because it is one of the most important and widely used zeolite types. Hierarchical self-standing ZSM-5 zeolite monoliths were synthesized according to the procedure reported in our previous work [31]. Typically, at room temperature, 5.13 g tetraethylorthosilicate, 3 g of a sol containing 3.3 wt% boehmite obtained by hydrolysis of aluminiumisopropoxide at 85 °C for 24 h, 4 g tetrapropylammonium hydroxide (TPAOH, 25 wt% in water) was mixed with 2 g of deionized water and vigorously stirred. After 4 h under stirring, 3.5 mL of a solution of sodium hydroxide (6%) was added dropwise and the mixture was kept under vigorous stirring for about 10 min, the resultant quasi-solid gel was transferred to a Teflon-coated stainless-steel autoclave, and heated at 175 °C for 24 h in static condition. After crystallization, the resulting zeolite monolith was washed with deionized water, then with 0.1 M HCl and repeatedly with deionized water till the pH reached 7 and dried at 60 °C for 24 h. The dried product was calcined in flowing air (90 mL/min) for 6 h at 600 °C with a ramp rate of 1 °C/min and denoted as ZSM-5-A.

2.3. Characterization

Powder XRD pattern in the region of 2θ from 5 to 50° was

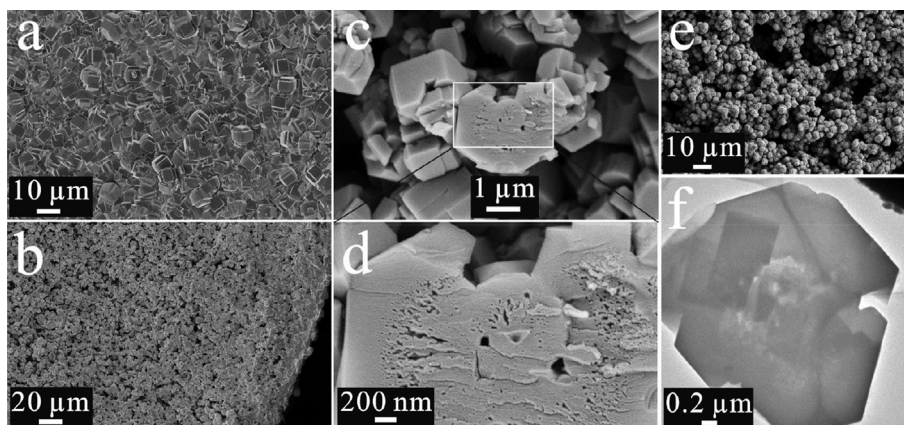


Fig. 2. SEM (a–e) and TEM (f) images of ZSM-5-A. (a) Top-view, (b) Cross-sectional view, (c) Interior-view, (e) Bottom-view.

Download English Version:

<https://daneshyari.com/en/article/7922604>

Download Persian Version:

<https://daneshyari.com/article/7922604>

[Daneshyari.com](https://daneshyari.com)