Microporous and Mesoporous Materials 139 (2011) 197–206

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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

Controllable and SDA-free synthesis of sub-micrometer sized zeolite ZSM-5. Part 1: Influence of alkalinity on the structural, particulate and chemical properties of the products

Nan Ren [a,*], Josip Bronić [b], Boris Subotić [b], Xin-Chun Lv [a], Zhi-Jian Yang [a], Yi Tang [a]

[a] Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials and Laboratory of Advanced Materials, Fudan University, Shanghai 200433, People's Republic of China
[b] Ruđer Bošković Institute, Division of Materials Chemistry, Laboratory for the Synthesis of New Materials, Bijenička 54, 10000 Zagreb, Croatia

ARTICLE INFO

Article history:
Received 31 August 2010
Received in revised form 12 October 2010
Accepted 26 October 2010
Available online 31 October 2010

Keywords:
TPA-free synthesis
Zeolite ZSM-5
Seeding
Mechanism
Product properties

ABSTRACT

In this work, the influence of alkalinity, $A = [Na_2O/H_2O]_b$ (b = batch), of the reaction mixture on structural, particulate, morphological and chemical properties of the crystalline end products obtained by hydrothermal treatment (heating at 483 K for 2 h) of the TPA-free reaction mixture: $1.0Al_2O_3/100SiO_2/xNa_2O/4000H_2O$ seeded by silicalite-1 nanocrystals (260 nm, 4 wt.% of silica in gel mixture), was investigated by different characterization methods such as powder X-ray diffraction (XRD), scanning-electron microscopy (SEM), particle size distribution (PSD) measuring by laser light scattering (LLS) and X-ray fluorescence (XRF). The obtained results showed that, when silicalite-1 having the size of 260 nm was used as seed, fully crystalline product (silicalite-1/ZSM-5) having the size in the range of 400–600 nm and Si/Al ratio of 10–18 can be obtained for $0.006 \leqslant A \leqslant 0.01$, in less than 2 h. However, the product obtained at low ($A \leqslant 0.005$) or high ($A \geqslant 0.011$) alkalinities possess amorphous and/or phillipsite impurities, respectively. The influence of alkalinity, *A*, on the mentioned properties of the crystalline end product was discussed in relation to the influence of alkalinity on the relevant critical process of zeolite ZSM-crystallization in the absence of organic templates.

1. Introduction

Due to successful application of zeolite ZSM-5 both as efficient catalysts for catalytic cracking, dewaxing, alkylation, isomerization and aromatization [1–3] and as molecular sieves for separation of organic compounds with different sizes and shapes [4], the efforts are continuously made to optimize its synthetic procedures for the purpose of either improving its properties to meet the demands of specific applications or reducing the production costs [5].

Zeolite ZSM-5 is conventionally synthesized by hydrothermal treatment of the reactive gel containing aluminosilicate as well as the tetrapropylammonium ions (TPA^+) as structure directing agent (SDA) [6,7]. To make the zeolite useful in catalysis and adsorption, calcination at 400–500 °C is necessary for the removal of the SDA trapped in its crystal micropores [8]. Besides, the organic templates used in conventional synthesis of ZSM-5 are often poisonous and expensive for massive industrially production, and removing them at high temperature induce the inevitable energetic consumption and environmental pollution. In addition, in the case of ZSM-5 membranes, the thermally treatment often results in the formation of microcracks or pinholes in the zeolite film [5,9–12].

These difficulties may be eliminated by adoption of TPA^+-free synthesis that not only renders calcinations unnecessary, but also employs cheaper, less toxic reactants and allows easier waste disposal [11]. Starting by Grose and Flanigen [13], there have been many investigations into crystallization of zeolite ZSM-5 from TPA^+-free reaction mixtures [3–5,8,11,12,14–26]. However, in difference to the case with TPA^+-containing reaction mixtures, the crystallization of zeolite ZSM-5 from TPA^+-free batches often occur under the relatively narrow ranges of SiO_2/Al_2O_3 (40–70) and Na_2O/SiO_2 (0.13–0.20) [8]. The batches having compositions out of these ranges often yield impurity phases, such as un-reacted amorphous solids [23], quartz [17], mordenite [18] or analcime [20]. In addition, a significant concern in the synthesis of zeolite ZSM-5 without organic template is about its crystal size which has appreciable influence on the catalytic properties [3]. Finally, the long crystallization time and low yield [16], respectively, is also suffered in industrial production of zeolite ZSM-5 from organic template free system.

The above mentioned disadvantages make that hardly any result of the synthesis of zeolite ZSM-5 without organic template

* Corresponding author. Tel.: +86 21 55664125; fax: +86 21 65641740.
E-mail address: nanren@fudan.edu.cn (N. Ren).

1387-1811/$ - see front matter © 2010 Elsevier Inc. All rights reserved.
doi:10.1016/j.micromeso.2010.10.043

has been satisfactory [24,25]. They however, can be overcome by addition of small amount of seed crystals (ZSM-5 and silicalite-1) in the TPA^+-free reaction mixture [4,5,12,14,16,21,26]; addition of seed crystals results in the formation of zeolite ZSM-5 with high degree of crystallinity and a narrow size distribution at short synthesis times [14,16].

On the basis of numerous experiments in the synthesis of zeolite ZSM-5 from TPA^+-free system [3,8,11,15,17–20,22–25] and considering positive effects of seeding on the formation of zeolite ZSM-5 crystals [5,12,14,16,21], recently we reported a controllable and low-cost procedure for the synthesis of zeolite ZSM-5 with adjustable submicron crystal size and the specific structure with all-silica core and aluminum containing shell [26]. The synthesis follows the seed surface crystallization (SSC) mechanism and the products with all the sizes can be accomplished within 2.5 h. The products with various morphologies and sizes in the domain of 270–1100 nm can also be facilely obtained depending upon the characteristics of silicalite-1 seeds, while their thickness of aluminum-containing zeolite ZSM-5 shells can be tuned by changing the ratios of silicalite-1 seed in the synthetic mixture.

Since the small-sized ZSM-5 zeolites have promising advantages such as large external surface area, easily accessible acid sites and high coke resistance ability, their synthesis and application in many important catalytic reactions including fluid catalytic cracking [27], methanol to propylene transformation [28], gas phase dehydration of glycerol to acrolein [29], propanal to alkyl–aromatics conversion [30] and intermolecular condensation of ethylenediamine to 1,4-diazabicyclo(2,2,2)octane [31] become a hot topic in such field in coming these years [32]. Based on the above works, the obtained submicron-sized ZSM-5 zeolites from our SSC approach will have many chances of applications. Although such approach was proved effective, there are some important factors which play decisive role either on the kinetics of crystallization or on the properties of product. These factors must be understood so that the large scale synthesis and further applications of the products can be performed repeatedly and steadily.

Thus, a series of the works is carried out to clarify the detailed effects of these crucial synthesis parameters on the structure and composition of products in the SSC synthesis system. In this work, the influence of batch alkalinity, $A = [Na_2O/H_2O]_b$, (b = batch) in the reaction mixture on the structural, chemical and particulate properties (size, morphology) of the products of crystallization is reported and discussed as the first part of this series. The critical process occurring during crystallization at different batch alkalinities are clearly revealed.

2. Experimental

2.1. Materials

The reagents used for the preparation of ZSM-5 zeolite are sodium hydroxide (NaOH, AR, Shanghai Chemical Co., China), aluminum sulfate ($Al_2(SO_4)_3{\cdot}18H_2O$, AR, Shanghai Chemical Co., China), tetraethyl orthosilicalite (TEOS, AR, Shanghai Chemical Co., China), silicon(IV) oxide, 40% in H_2O colloidal dispersion (SiO_2, AR, Alfa Aesar), tetrapropylammonium hydroxide, 40% w/w aqueous solution (TPAOH, AR, Alfa Aesar). All chemicals were used without any purification.

2.2. Synthesis of silicalite-1 nanocrystals as seed

The silicalite-1 seeds with crystal size of 260 nm were synthesized from clear solution method as reported previously [26]. Typically, the TEOS was added into the mixture of aqueous solution of TPAOH and NaOH. The system was stirred at ambient temperature for 24 h. Then, the mixture ($4.4TPAOH/0.1Na_2O/25SiO_2/1048H_2O/100EtOH$) was transferred to a polypropylene bottle and hydro-

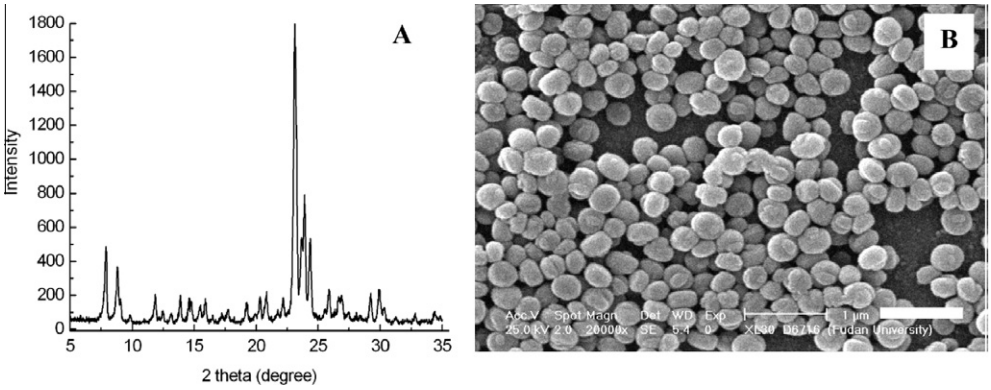

Fig. 1. The XRD pattern (A) and SEM image (B) of silicalite-1 seed (the scale bar in B represents 1 μm).

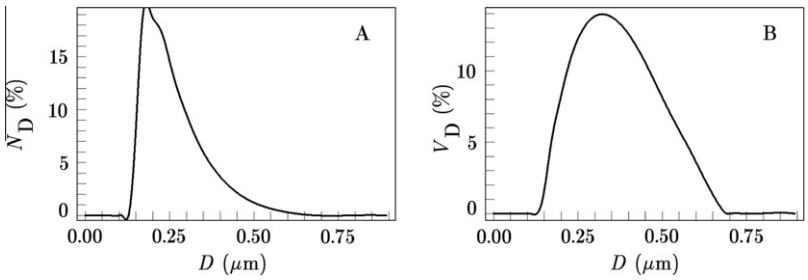

Fig. 2. Particle size distribution by number (A) and by volume (B) of silicalite-1 nanocrystals used as seed. N_D is number percentage and V_D is volume percentage, respectively, of crystals having the spherical equivalent diameter D.