Controllable synthesis of hierarchical beta nanozeolites from tailorable seeds

Wenjuan Sun, Li Wang, Xiangwen Zhang, Guozhu Liu *

Key Laboratory of Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

ARTICLE INFO

ABSTRACT

Hierarchical beta nanozeolites were controllably synthesized by tailoring seeds (or protozeolitic units, nanocrystals) grafted with phenylaminopropyltrimethoxysilane (PHAPTMS). The investigation of beta zeolite crystallization reveals that it proceeds through condensed-step mechanism, gradually growing in size along two populations of particles and evolving in internal structure. Based on the zeolitic seeds formation process, there were two roles of organosilane: the more-like mesoporogen agent in short pre-crystallization time and the growth inhibitor after the formation of secondary particles with significant amounts of terminal silanol groups. It was also found that both the mesopore properties and the crystal size of the prepared hierarchical beta nanozeolites were also strongly dependent on the properties of seeds. Moreover, the mechanisms for the formation of hierarchical beta nanozeolites, including size of the nanoseeds as well as its nature on the final crystal size, pore characteristics, crystallinity, and morphology were proposed and discussed in detail.

1. Introduction

Beta zeolite with a three-dimensional network of 12-ring channel system [1] combined with strong acidic sites [2] is one of most important zeolites and has been widely used in the petroleum refining and fine chemical industries exhibiting excellent properties in a series of catalytic reactions such as ethylene-benzene alkylation [3], isobutane-n-butene alkylation [4], aromatic acylation [5,6], and methyl tert-butyl ether synthesis [7], etc. Recently, hierarchical beta nanozeolites have received much attention for its remarkable external surface area and short diffusion channel length. The larger external surface area makes it possible to expose more reactive surface or acid sites, especially for the diffusion-limited reactions involving bulky molecules, which is preferred in the processes requiring a higher reaction rate and catalytic activity [8,9]. Another advantage is the decreased diffusion path length relative to micrometer-sized zeolites [10,11]. This makes it relatively easy for the molecules to diffuse in or out the zeolite and, thus, brings higher efficiency and a lower deactivation rate to catalytic processes.

Several synthetic methods have been reported for the preparation of nanocrystalline zeolites. A number of nanozeolites (ZSM-5, beta, etc) could be synthesized using a clear solution or gel of aluminosilicates by careful control of the gel composition and crystallizing conditions [12–16]. The clear solution method generally favors the nucleation rather than crystal growth in the system (low temperature, strongly basic medium, and high supersaturations), but with low yields of nanocrystals. Confined-space synthesis method has also been used to synthesize zeolite nanocrystals with the aid of an inert matrix such as mesoporous carbon matrices [17,18], polymer matrix [19], or microemulsions [20] to hinder zeolite crystal growth. During this process, the cationic surfactants have to be used to protect the zeolite precursors and subsequent steaming in an autoclave to achieve a completed crystallization. Recently, a novel strategy based on the organofunctionalization of protozeolitic units, i.e., so-called seed silanization, has been proposed by Serrano and coworkers to synthesize a series of nanozeolites with hierarchical pores, such as ZSM-5, ZSM-11, beta, TS-1, etc [21–24]. The organosilanes grafted onto the external surface of protozeolitic nuclei play a crucial role in hindering the growth of zeolite nanocrystals and their aggregations in the crystallization. The space initially occupied by the organosilane is released giving rise to the formation of mesopores after calcination. In this view, both the nanounit size and the mesopores could be controlled to some extent by changing the organosilanization agents and their amounts anchored to the protozeolitic units during the synthesis. For instance, beta zeolite organosilanized using 8 mol% of phenylaminopropyltrimethoxysilane (PHAPTMS) as seed organosilanization agent (SSA) has higher increase of the BET surface area of

---

$857 \, \mathrm{m^2 \, g^{-1}}$ and external surface area of $145 \, \mathrm{m^2 \, g^{-1}}$ compares to samples obtained using isobutyltriethoxysilane, and this is because the PHAPTMS has higher molecular size [23]. Moreover, the incorporation of increased amounts of SSA causes a further reduction of crystalline nanodomains. Since the precrystallization of the gel is one of the most important steps for producing zeolitic unclei in silanizing zeolite method, they synthesized silanized zeolites by precrystallizating for 20 h [24]. Therefore, amount of experimental works have to be done to establish the corresponding synthesis parameters. Inspired by this, we attempted to controllably synthesize nano-zeolite (for instance, beta) by grafting organosilane onto protozeolite units with different sizes, in which seeds evolution process should be carefully studied as a primary step for given zeolites.

The researches based on the mechanism of beta zeolite formation show the practicability of the above idea. Lobo and coworkers detected three precursor particles of beta zeolite in the Al-containing synthesis solution based on their dimensions and heating time: primary particles (<3 nm), secondary particles (6–50 nm) and tertiary particles (beta zeolite, <200 nm) [25–28]. The primary particles, formed spontaneously at room temperature, would aggregate to form the secondary particles with a density and composition similar to beta zeolite, and the size of secondary particles gradually grow larger up to 50 nm with the extension of heating time. Beta zeolite structure firstly evolves within the partial secondary structures (seeds) which preferentially aggregate to form the tertiary particles with well-ordered beta structure. Therefore, it is practical to controllably synthesize hierarchical beta nanozeolites by grafting organosilanes on the different-sized secondary seeds rather than on the primary seeds, which provides an easy way to tailor their crystal sizes and hierarchical structures without changing organosilanization agents and concentrations. Moreover, it also helps to elucidate the crystallization mechanism of nanoseeds grafted with organosilanes, especially their role in hindering crystal growth and tailoring mesopores structures.

The basic aim of this work is therefore to synthesize hierarchical beta nanozeolites through organosilanizing nano-seeds with different size to controllably tailor the crystal size and mesopores structures of hierarchical beta nanozeolites. By kinetic control over the zeolitic seeds formation, we report the direct synthesis of hierarchical beta nanozeolites with controllable crystal size and mesopores structures by using PHAPTMS as organosilanization agent. A systematically study was first performed to understand the crystallization mechanism and show the seeds growth with extension of crystallization time using SAXS, TEM, XRD and NMR measurements. After then, the hydrothermal crystallization of the nanoseeds grafted with organosilanes was performed to obtain the hierarchical beta nanozeolites with controllable size and mesoporous structures. Attempts were also made to the relationships between the sizes of grafted seeds (protozeolitic units) and as-prepared crystals, based on which a possible mechanism of controllable synthesis of hierarchical beta nanozeolites with organosilanes seeds was also proposed.

2. Experimental

2.1. Materials

The following raw materials were used as received: AEROSIL 200 (SiO_2, industrial grade, Evonik Degussa) as silica source, aluminite powder (analytical reagent, Tianjin Guangfu Chemical Reagent Co. Ltd.) as aluminum source, tetraethylammonium hydroxide (TEAOH, 25 wt% in water, J&K Scientific Ltd.) as structure-directing agent. PHAPTMS (98.0 wt%, J&K Scientific Ltd.) was used as organosilanization agent.

2.2. Zeolite preparation

Hierarchical beta nanozeolite was synthesized from the mixtures of composition 2 Al: 20 TEAOH: 70 SiO_2: 1000 H_2O. The synthesis mixture was placed in a Teflon-lined stainless-steel autoclave and precrystallized at 115 °C. Autoclaves were quenched to room temperature after various heating times for functionalization and characterization. The obtained zeolite prozeolitic units were functionalized by reaction with PHAPTMS (5 mol% in regards to the silica content in the gel) at 90 °C for 6 h. Subsequently, the resulting solution was subjected to crystallization in the autoclave at 115 °C for $(72 - x)$ h. The solids were collected by centrifugation, washed with ethanol and water until PH $\approx$ 7. The product was then dried overnight at 110 °C and calcined at 550 °C for 6 h. These synthesized organosilanized zeolites were named as Beta-Sx, wherein x stands for the precrystallized time. Additionally, a conventional beta zeolite, denoted as Beta (0), was synthesized for comparison following an identical procedure but without the precrystallization and organosilanization steps.

2.3. Characterizations

X-ray diffraction (XRD) data in the 2θ range of 5°–50° were collected on a Rigaku D-max 2500 V/PC X-ray diffractometer (Rigaku Corporation) using Cu Kα radiation source (40 kV, 200 mA). Transmission electron microscopy (TEM) images were obtained at room temperature on a Tecnai G2 F20 field-emission transmitting electron microscope (Philips). Dynamic light scattering (DLS) measurements were performed at 25 °C and 514 nm using a BI200SM dynamic light scattering apparatus (Brookhaven). The hydrodynamic radius distribution was determined from the Laplace inversion of the measured intensity time correlation function using the CONTIN program on the basis of the Stokes–Einstein equation. N_2 adsorption–desorption isothermals were measured with a Micromeritics ASAP 2020 system at 77 K. The samples were outgassed at 573 K for 24 h under 10^{-4} Pa. The specific BET surface area was calculated using adsorption data acquired at a relative pressure (P/P_0) range between 0.06 and 0.20 by Brunauer–Emmett–Teller (BET) method and the total pore volume was evaluated at $P/P_0 = 0.99$. The external surface area and micropore volume were determined from t-plots in the P/P_0 range between 0.12 and 0.5 [29,30]. The mesopore volume (V_{meso}) was calculated from the difference between the V_{tot} and V_{mico}. Pore size distributions were performed with the DFT method using the nitrogen on silica, cylindrical pore NLDFT equilibrium model. Solid-state nuclear magnetic resonance (NMR) was conducted on a Varian Infinity plus 300 MHz spectrometer (Varian Inc.) under condition of magic angle spinning. ^{29}Si solid-state CP/MAS NMR spectra were collected at room temperature with a frequency of 59.6 MHz, a pulse delay of 5.0 s, an acquisition time of 20.0 ms, a spin rate of 3.0 kHz, and a contact time of 5.0 ms. ^{27}Al solid-state MAS NMR spectra were collected at room temperature with a frequency of 78.1 MHz, a pulse delay of 2.0 s, an acquisition time of 6.4 ms, and a spin rate of 8.0 kHz.

Small Angel X-ray Scattering (SAXS) experiments were performed using a NanoSTAR-U (BRUKER AXS INC) with Cu Kα radiation ($\lambda = 0.154$ nm). The generator was operated at 40 kV and 650 μA. Two-dimensional SAXS patterns were obtained using a HI-STAR detector. The sample to detector distances were LSD = 1074 mm. The effective scattering vector q ($q = 4\pi\sin\theta/\lambda$, where 2θ is the scattering angle) at this distance ranges from 0.044 to 2.0 nm^{-1}. Water was used as the reference solvent for background subtraction. The scattering data were analyzed using the program GNOM [31] and the Guinier approximation [32] to determine the particle, which was also used in other papers [33,34]. The pair distance distribution functions (PDDFs) obtained