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Article

# Synthesis of ZSM-5 monoliths with hierarchical porosity through a steam-assisted crystallization method using sponges as scaffolds

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ABSTRACT

Self-supporting ZSM-5 crystals with hierarchical porosity were prepared through a steam-assisted crystallization method using sponges as rigid scaffolds. The synthesized materials were characterized by X-ray diffraction, nitrogen sorption, scanning electron microscopy, transmission electron microscopy, solid-state nuclear magnetic resonance spectroscopy and ammonia temperature-programmed desorption. The ZSM-5 monoliths exhibited high crystallinities, hierarchical porous structures and strong acidities. They showed superior catalytic performance in the liquid-phase esterification reaction between benzyl alcohol and hexanoic acid.



## 1. Introduction

Hierarchically structured porous materials have triggered extensive research because of their fascinating features such as high surface areas, interface-facilitated transport and advanced mass transport kinetics [1–3]. Recently, there have been successful attempts to synthesize hierarchically porous zeolites. For example, post-synthesis treatments can be used to generate hierarchically porous zeolites through selective leaching of aluminum (dealumination) or silicon (desilication) from the zeolite framework [4,5]. The major disadvantage of such a process is the partial degradation of the crystalline nature of the zeolite, and consequently, a reduction in the catalytic activity. More recently, other processes to create zeolites with a hierarchical porosity using a hard sacrificial templates have also been examined; carbon materials [6–8], mesoporous silica spheres [9,10] and aerogels [11,12] have been investigated. However, these processes were somewhat expensive and time consuming. Cationic polymers have also been successfully employed to produce hierarchical zeolites [13,14], but the synthetic zeolites were not suitable for industrial catalysis.

In the case of industrial catalysis, a certain amount of binders, such as alumina, silica or clay, is generally used for cementing zeolite crystals into large sticks or granules that are mechanically stable. However, the inorganic binders may dilute the active zeolite and partially block the pore system, which results in diffusion limitations and inaccessibility of the active species [15]. To overcome these problems, continuous progress has been made on the development of mechanically stable zeolite monoliths with uniform shapes and hierarchical structures. Such monolithic zeolite materials facilitate the diffusion of the reactants and products as well as the reaction efficiency and

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can be used in practical application. For example, Shi et al. [16,17] have reported the preparation of HSZs by using ordinary mesoporogens such as triethanolamine (TEA), P123, F127 and even sucrose as in situ carbonaceous templates. Ryoo et al. [18] designed several bifunctional templates, combing the features of both structural guide agent (SDA) and mesoporogens within one molecule, and successfully synthesized zeolite nanosheets with hierarchical structures. However, the reported synthesis of the hierarchically structured zeolites by massive mesoporogens was neither cost efficient nor friendly because most of the template agents were difficult to make and nocuous. Novel synthesis routes using few mesoporogens are highly desirable and have become a promising research field.

In this study, we prepared high-quality zeolite monoliths with hierarchical porosity through a steam-assisted crystallization (SAC) method using sponges as rigid scaffolds. X-ray diffraction (XRD) and nuclear magnetic resonance (NMR) spectroscopy analysis showed the ZSM-5 monoliths were highly crystalline. Because of their hierarchical porous structure, the zeolite monoliths had a higher surface area, stronger acidity, and showed better catalytic activity than that of traditional ZSM-5 in the liquid phase esterification reaction.

## 2. Experimental

### 2.1. Reagents

Tetraethylorthosilicate (TEOS, 98 wt%), tetrapropylammoniumhydroxide (TPAOH, 25 wt%), hexanoic acid (98.8%), benzyl alcohol (98.8%), ammonium nitrate (98.5%), toluene (99.5%), 4-methylbenzyl alcohol (98%), 4-nitrobenzyl alcohol (98%), 4-methoxybenzyl alcohol (98%) and 3-phenylpropan-1-ol were purchased from J&K Corporation. Aluminum isopropoxide (AIP, 97%) was obtained from Beijing Chemical Reagent Corporation (Beijing, China). Aqueous ammonia solution (28% in $H_2O$), sodium hydroxide and ethanol (99.9%) were purchased from Beijing Chemical Company. All the reagents were used without further purification. Nanosponges were purchased from Henan.

### 2.2. Preparation of zeolite monoliths

The sponges were cut into small cubes that were suitable for the size of the autoclave. To synthesize M-ZSM-60 (M indicates monolith, ZSM represents ZSM-5 zeolite, 60 represents the synthesized materials with Si/Al molar ratio of 60), 0.275 g of AIP was dissolved in 16 mL of ethanol at room temperature for 2 h and then added to 14 g of TEOS. The solution was stirred for 5 h and then the sponge was immersed in the solution. The impregnated sponge was then placed into a Teflon-lined autoclave containing 2 mL of 30% aqueous ammonia solution. The autoclave was then closed and treated at 80 °C for 12 h in a hot air oven. The autoclave was then quenched to room temperature and the sponge was once again impregnated with the ethanol solution containing AIP and TEOS. This procedure was repeated three times to ensure efficient loading of the silica source and aluminum source into the sponge. The finally loaded sponge was adsorbed with appropriate quantity of TPAOH. The TPAOH/Si molar ratio was maintained as 0.27. The dried sponge containing silica, aluminum and TPAOH was placed inside a Teflon-lined autoclave containing 2 mL of distilled water for steam-assisted crystallization. The autoclave was closed and placed in a hot air oven at 130 °C for 36 h. After the crystallization period, the autoclave was taken out and quenched to room temperature. The product was collected, dried at 80 °C for 8 h and then calcined at 550 °C for 8 h in air to remove the TPAOH and the sponge. The synthesis of M-ZSM-40 and M-ZSM-90 with different Si/Al ratios were similarly conducted by accordingly changing the AIP content in the precursor solution while keeping the addition of TEOS constant. For comparison, traditional ZSM-5 (denoted as ZSM-5(60)) was synthesis with a molar ratio of $28Na_2O{:}1Al_2O_3{:}120SiO_2{:}4000H_2O$.

### 2.3. Catalysis conditions

Prior to the catalytic tests, all the materials were exchanged to the H-form with an aqueous solution of $NH_4NO_3$ (1.0 mol/L) at 90 °C for 4 h and then converted to the $H^+$ form through calcination at 550 °C for 5 h. Esterification of the alcohol with an acid was carried out in a double-necked round bottom flask fitted with a reflux condenser. The alcohol (15 mmol), acid (18 mmol) and toluene (15 mL) were added to the round bottom flask, as well as *n*-nonane, which is an internal standard. The solution was heated to 110 °C using a silicone oil bath and then 250 mg of the catalyst was added. The reaction mixture was stirred using a magnetic stirrer and the stirring speed was maintained at 1200 r/min to avoid external mass transfer limitations. The reaction products were analyzed by GC (Agilent 6890 N) with a capillary column (DB-5, 30.0 m × 320 mm × 0.25 mm) and FID, and the products were further identified by GC-MS (Shimadzu, GCMS-QP 2010S) with a capillary column (DB-5 ms, 30.0 m × 320 mm × 0.25 mm).

### 2.4. Characterization

The morphology and size of the resultant powders were characterized with a field emission scanning electron microscope (FESEM JEOL-6701F). Transmission electron microscopy (TEM) images were taken using a JEM-2100F (JEOL) operated at 100 kV. Power XRD patterns were collected on a Rigaku-2500 in the $2\theta$ range of 5°–55°. The relative crystallinity (RC) of the synthesized M-ZSMs was calculated from the ratio of the sum of the intensities of the four most intense reflections in the $2\theta$ range of 22.5°–24° and the corresponding sum of the parent ZSM-5, which was purchased from the Catalyst Plant of Nankai University. $N_2$ adsorption isotherms were measured at −196 °C on a Quantachrome Autosorb AS-1 instrument; the samples were outgassed at 120 °C for 12 h prior to testing. Pore size distributions were evaluated from the adsorption isotherms using the Barret-Joyner-Halenda (BJH) formula and the microporous volume was evaluated by nonlocal density functional theory. $^{27}Al$ and $^{29}Si$ solid-state NMR spectroscopy experiments were performed on an AVANCE III 400WB spectrometer. The spectra were collected at a frequen-