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Original Research Paper

Hierarchically porous MFI zeolite synthesized by zeolite seeding and alkaline steaming-mediated crystallization

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ABSTRACT

A new strategy, zeolite seed-mediated alkaline steaming treatment, has developed for synthesizing hierarchically porous zeolite. This approach involves successive transformation from an initially amorphous mesophase to a crystallized mesophase with zeolite framework under alkaline steaming. This is the first demonstration that single-crystallized hierarchically porous MFI zeolite particles could be simply synthesized under alkali steaming assisted by a small amount of zeolite seeds. The mesoporosity and particle morphology of the obtained hierarchically porous zeolites can be well tuned by changing the composition of alkaline steaming. Steaming in alkaline vapor containing TBAOH and EDA, the synthesized hierarchically porous single crystalline MFI zeolite particles show an interlamellar sheet-packed oriented structure and highly developed mesoporosity with hierarchy factor (HF) of as high as 0.25 in comparison with most previous reports where HF values are lower than 0.20. This hierarchically porous zeolite shows capacious adsorption for heavy metal ions, such as Cu (II).

1. Introduction

Zeolites are crystalline, microporous materials with strong acidity and high hydrothermal stability that have found numerous applications in catalysis, separations, ion exchange, etc. Their small micropores, however, make diffusion of bulky molecules difficult [1,2]. Fabrication of hierarchical zeolite, such as integrating mesoporosity into zeolite crystals, is a proven solution to circumvent the diffusion limitation [3–5]. Similar to most of other hierarchical porous material with well defined pore dimensions and topologies [6–8], hierarchical porous zeolites minimize diffusive resistance to mass transport by mesopores and offer high surface area for active site dispersion over micropores. Considerable efforts have been devoted to the synthesis of hierarchical zeolites, including acid/base leaching [9,10], confined synthesis by hard templating [3], meso/micro-soft templates-directed co-assembly (one-pot route) [11–14] and using dual-function templates [15,16].

In meso/micro-template-directed co-assembly, since mesoporous structure can be formed through self-assembly in as short as minutes while crystallization of zeolites usually takes much longer time [17], hierarchically porous structure could be obtained only under the delicate balance between thermodynamic and kinetic processes. Therefore, the synthesis becomes difficult to control and sometimes, phase separation would take place, which results in the formation of single microporous zeolitic phase, or single amorphous mesoporous silica, or a mixture of them. Until now, synthesis of ordered and hierarchically porous zeolites by self-assembly is one of major challenges in chemical sciences [5].

In a previous work [18], we found alkaline condition is indispensable to crystallize zeolite MFI, which easily resulted in phase separation from the beginning of mixing mesoporogen with microporogen. As a result, it is important to carefully control pH value within a narrow range to obtain mesoporous zeolites, which made it difficult to synthesize the material in large quantity. On the other hand, from the viewpoints of kinetics, zeolite crystals grew too rapid to control once it reached critical high temperature, which often results in the blockage in mesopore by those grown-up zeolite crystallites and unavailability of mesostructure in the final product. In order to keep mesoporous structure, low temperature treatment with nanocrystalline zeolites as precursor became one of main approaches [2,3]. Such hierarchically porous frameworks were composed of the aggregated and poorly crystallized zeolite nanocrystals which resulted in weak acidity unfavorable for catalytic applications [19].

Considering the importance of minimizing the interaction between mesoporogen and microporogen, it would be simple and controllable to obtain hierarchical porosity if it is possible to

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separate alkaline condition (zeolitization) from the formation of mesostucture. Based on this hypothesis, we propose a new route to synthesize hierarchically porous single-crystalline zeolite: Crystalline-seed-mediated synthesis under alkaline steaming treatment (Fig. 1). Instead of alkaline used in the solution of mesoporogen (SDA) with microporogen, alkaline steaming was employed after the formation of amorphous aluminium-silicate mesophase with small amount of zeolite seeds. Under co-operation between alkaline steaming and crystalline seeding, highly crystallized mesoporous zeolite has been successfully obtained.

2. Experimental

2.1. Preparation of zeolite seeds

$NaAlO_2$ (0.11 g), tetrabutylammonium hydroxide (TBAOH, 10 wt.% aqueous solution, 21.9 ml) were dissolved into deionized water (16.5 ml) at room temperature. Then, tetraethylorthosilicate (TEOS, 99%, 12.4 ml) was added to the solution under vigorous stirring. After being stirred for 2.5 h, the solution was left to statically stand overnight after the mixture became transparent. Then, the solution was statically hydrothermal-treated in a sealed 100 ml Schott-Duran bottle under 110 °C for 4 h.

2.2. Preparation of crystalline-seed-mediated amorphous mesophase aluminium-silicate

Cetyltrimethylammonium bromide (CTAB, 3.64 g), NaOH (0.54 g) and $NaAlO_2$ (0.15 g) were dissolved in deionized water (92.3 ml) to form a transparent solution. Then, TEOS (17.16 ml) was added to the solution with stirring for 30 min. Then, zeolite seeds solution (10 ml) was added to the mixture above drop by drop. The molar ratio of the resulting sol was 0.019:1:0.09:0.01:62.82:0.11, $TBAOH:SiO_2:Na_2O:Al_2O_3:H_2O:CTAB$. After stirring for another 2 h under room temperature, the mixture was filtered directly. The resultant gel was dried at 55 °C for another 18 h.

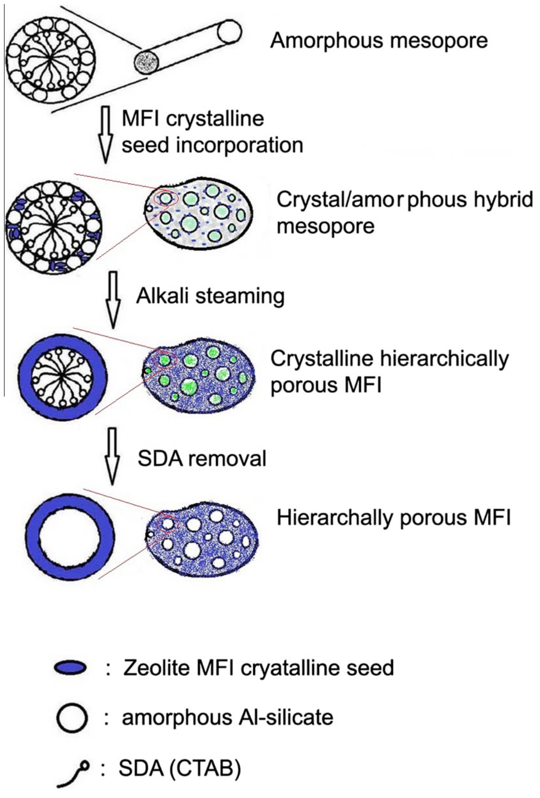

Fig. 1. Schematic of formation of hierarchically porous single-crystalline zeolite.

2.3. Preparation of alkaline solutions

A series steaming solution was prepared as shown in Table 1.

2.4. Preparation of mesoporous single-crystalline zeolite

The dried Crystalline-seed-mediated amorphous mesophase aluminium-silicate (1 g) was transferred into a small Teflon container, which was then put into a larger autoclave, similar to the steam-assisted crystallization approach as previously reported [12]. Various alkaline solutions (1 ml) were dropped into the bottom of the autoclave, and then the autoclave was heat-treated. Afterwards, the product was washed repeatedly with distilled water, dried in air and then calcined at 550 °C for 8 h to remove the organic agents. The Si/Al molar ratio of powder obtained was around 43. The final obtained powder was labeled as $C(A)T-t^*$, here, 'C' refer to crystal zeolite seed and 'A' for alkaline solution while 'T and t' correspond to the temperature and duration of steaming treatment, respectively, and * represents the type of alkaline solution in Table 1. For example, sample CA155-48b, both crystal zeolite seed and alkaline solution (solution b) were used and steaming condition is 155 °C for 48 h. In order to comparison, crystal zeolite seeds are used in place of TEOS and $NaAlO_2$ as reactant to prepare sample and then are aqueous steaming treated under 155 °C for 48 h, such sample was named as 'Z155-48d'; and also, same composition of ZSM 5 (without CTAB) are synthesized under hydrothermal treatment under 155 °C for 3 days. Detailed synthesis conditions are also given in Table S1.

2.5. Heavy metal ion, Cu^{2+} adsorption studies

The adsorption of Cu^{2+} was investigated in batch equilibrium experiments. Stock solutions of $Cu(NO_3)_2$ (150 mg/L) has the pH value of 6.0 at 25 °C. The pH value of solution was adjusted to the desired value with hydrochloric acid solution. 100 mg powder samples were mixed with 100 ml stock solutions of $Cu(NO_3)_2$ under continuous stirring for a given period, followed by filtration of the adsorbent. After filtration, the concentration of Cu(II) in the aqueous phase was determined by inductively coupled plasma mass spectrometry (ICP-MS).

2.6. Characterization

Powder XRD patterns were recorded by using a Rigaku D/Max 2200PC diffractometer with CuKa radiation (40 kV and 40 mA) with a scanning rate of 0.6 min^{-1} for small-angle testing and 10 min^{-1} for large-angle testing. The N_2 sorption isotherms were measured using Micromeritics 3H-2000PM2 porosimeters at 77 K. The mesoporous specific surface area, pore-size distribution, and pore volume were calculated using the Brunauner–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. The micropore specific surface area and volume were calculated by the t-plot method and DFT method, respectively. FE-SEM (field-emission-scanning) electron microscopy analysis was performed on a Hitachi SU8010 electron microscope. TEM (transmission electron microscopy) images were obtained on a JEOL-2010F electron microscope operated at 200 kV. Sample for TEM used embedded thin section technology. Temperature-programmed desorption of ammonia (NH_3-TPD) was performed by using PCA-1200 (chemical adsorption recorder) loaded with 100 mg of sample. The sample was pretreated at 323–923 K with