



# Synthesis method for introducing mesoporosity in a faujasitic-like zeolite system from a sodium aluminosilicate gel composition



Bo Wang, Prabir K. Dutta\*

Department of Chemistry and Biochemistry, The Ohio State University, 100 West 18th Avenue, Columbus, OH 43210, USA

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## ABSTRACT

We report a facile synthesis method of hierarchical faujasitic structures from a sodium aluminosilicate composition. The critical experimental variable was the removal of water via heat from the aluminosilicate gel during the synthesis process. These gels were used as starting materials for synthesis. With these partially dehydrated gels, extensive zeolite nucleation did occur, and the extent was varied both with the degree of dehydration and the temperature at which the dehydrated sample was maintained. Nanoparticles of FAU and EMT were formed that pack together resulting in external surface areas of 249–259 m<sup>2</sup>/g. In addition, under certain conditions of crystal growth, sheet like-structures arising from FAU-EMT intergrowths were observed. The interpenetration packing of the nanosheets lead to zeolitic particles with external surface areas in the range of 127–199 m<sup>2</sup>/g. The pore size distribution varied with sample preparation and ranged from 2 to 100 nm. These samples were characterized by N<sub>2</sub> adsorption, X-ray diffraction and electron microscopy. The thermal and hydrothermal stability was also studied. In order to evaluate the role of the higher external surface area on a chemical reaction, the dealkylation of 1,3,5-triisopropylbenzene was examined and the product distribution did reflect the mesoporous nature of the sample.

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## 1. Introduction

Microporous crystalline zeolitic materials find applications in catalysis, separation, adsorption and ion exchange [1]. Mass transfer limitations, inaccessibility of bulky molecules and coke formation are some of the drawbacks with reactions on conventionally prepared micropore zeolites. The combination of both micro and mesopores leads to a hierarchical structure, where mesopores can enhance the reactivity of bulky molecules, followed by reactions within the micropores of the zeolite framework. Hierarchical structures favor novel product distributions. Synthesis of hierarchical zeolites is an active research area, as exemplified by numerous review articles just in the past year on the synthesis, characterization and catalysis applications [2–9]. These articles provide a good background on the extensive effort in this field, and cite relevant literature references.

Mesopores in zeolites are typically generated by using hard-template, soft-template and template-free methods [2–9].

Mesopores can also be generated by packing of nanoparticles [10–12], as well as selective twinning [13]. Dealumination and desilication by post synthetic methods also generate mesoporosity [14], as do recrystallization methods [15]. Majority of synthesis studies focus on organic-templates, and requires the added step of removal of organics after zeolite synthesis by calcination.

There are many studies on synthesis of hierarchical faujasites (FAU), the structure of interest in the present study, and summarized well in a recent review [16]. Three-dimensional ordered mesoporous carbon has been used as hard template for confined growth of FAU [17]. Cetyltrimethylammonium bromide was also used to prepare FAU fragments [18]. Organosilanes have been employed to generate mesoporosity [19–21]. 3-(trimethoxysilyl)propyl hexadecyl dimethyl ammonium chloride was used to generate hierarchical zeolite X (Si/Al 1.2) with intergrowth of FAU nanosheets [22]. Nanosheets of FAU in these studies has been shown to be a mixture of major FAU and EMT phases [23]. A purely inorganic system using Li<sup>+</sup> and Zn<sup>2+</sup> in the aluminosilicate composition has also been reported to generate layer-like morphology of FAU structure [24].

In the present study, a synthesis method of faujasitic-zeolite with both microporous and mesoporous nature from an 8.3

\* Corresponding author.

E-mail address: [dutta@chemistry.ohio-state.edu](mailto:dutta@chemistry.ohio-state.edu) (P.K. Dutta).

Na<sub>2</sub>O: 1 Al<sub>2</sub>O<sub>3</sub>: 6.4 SiO<sub>2</sub>: 483.9 H<sub>2</sub>O composition was developed. The synthesis strategy involves creating conditions for extensive zeolite nucleation by removing water during reflux of the gel. The concentrated gels were the subject of this study. Nutrient transport in these concentrated gels can be modified by temperature, or by viscosity (controlled by the extent of water removal). Specific conditions for growth of numerous nanocrystals, as well as nanosheets of FAU-EMT intergrowths were discovered. The particles can pack to form a zeolitic structure with both meso and microporosity. This growth process has been characterized by X-Ray diffraction, N<sub>2</sub> adsorption and electron microscopy. Reactivity of proton-exchanged forms of the zeolites for dealkylation of a bulky molecule, 1,3,5-triisopropylbenzene (1,3,5-TIPB) indicates the influence of the mesoporous structure.

## 2. Experimental method

### 2.1. Chemicals

Aluminum hydroxide (Al(OH)<sub>3</sub>, 76.5%) was purchased from Alfa Aesar. Ludox SM-30 colloidal silica (SiO<sub>2</sub>, 30%) was bought from Sigma-Aldrich (Milwaukee, WI, USA). Sodium hydroxide pellet (NaOH, 99.0%) was ordered from Fisher Scientific. All chemicals were used as received. H<sub>2</sub>O used in this study was purified by a Millipore ultrapure water system.

### 2.2. Zeolite synthesis procedure

Zeolite synthesis gel preparation follows the method reported in literature [25], with composition of 8.3 Na<sub>2</sub>O: 1 Al<sub>2</sub>O<sub>3</sub>: 6.4 SiO<sub>2</sub>: 483.9 H<sub>2</sub>O. Al(OH)<sub>3</sub> (2.208 g) and 7.29 g NaOH were completely dissolved in 85.24 g H<sub>2</sub>O, forming a clear solution. Then, 13.85 g Ludox SM-30 was slowly added into the solution, which turns opaque immediately. The opaque gel was then sealed in a polypropylene bottle with stirring for 4 h at room temperature, resulting in the aged gel (AG). From AG, 2 types of gel were prepared: refluxed gel (RG) and concentrated gel (CG). Synthesis apparatus is shown in Fig. S1, a round bottom flask connected with a constant pressure funnel and condenser at the top. RG was prepared by heating AG for 1 h with the switch of constant pressure funnel “on”, which is the reflux process. To prepare CG, AG was introduced into the same apparatus with the switch of constant pressure funnel “off” and heated to boiling, and evaporated water was collected in the funnel. Twenty, 40 and 60 mL of H<sub>2</sub>O was removed from ~100 mL of the gel in an hour, resulting in CG<sub>20</sub>, CG<sub>40</sub> and CG<sub>60</sub>. RG and CG were then heated under different conditions. Synthesized zeolite powder product was washed with deionized water by repetitive centrifugation (2500 rpm) until pH 7 and freeze dried.

### 2.3. Yield calculation

Yield of zeolite samples were calculated as follows: In a typical batch, 100 mL AG was obtained after mixing all chemicals. From AG to CG<sub>40</sub>, 40 mL of water was removed, and content of other chemicals were still the same. There was 2.208 g Al(OH)<sub>3</sub>, 7.29 g NaOH and 4.16 g SiO<sub>2</sub> in 60 mL of CG<sub>40</sub>. For a batch of 20 mL CG<sub>40</sub> which contains 4.6 g (SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> + NaOH), 1.6 g of zeolite product was obtained. So, the yield of zeolite was 35%. In a batch of 20 mL CG<sub>40</sub>, there was 0.023 mol Si in the gel. Elemental analysis showed that about 65% of Si in the gel was incorporated in the zeolite

framework and 35% of Si stayed in the supernatant (Si analysis on supernatant done by Galbraith Laboratories).

### 2.4. Zeolite characterization

Bruker D8 Advance X-Ray Powder Diffractometer (XRD) was used to study the crystallinity of zeolite samples. Relative amounts of EMT and FAU were obtained from the high resolution XRD pattern (2θ from 5 to 7°) by calculating peak intensity with deconvolution and amount ratio using Reference Intensity Ratio (RIR) [26]. In this study, RIR values of 13.06 and 7.60 were used for FAU and EMT (relative to corundum), as obtained from PDF cards of 01-074-2394 and 00-046-0566, respectively. Calculation was done with software PDXL 2.0 from Rigaku. Equation used for calculation is shown below.

$$\frac{x_{FAU}}{x_{EMT}} = \frac{I_{FAU}}{I_{EMT}} \times \frac{RIR_{EMT}}{RIR_{FAU}} \quad (1)$$

In equation (1), x is the relative mass of FAU and EMT; I is peak intensity obtained from XRD peak deconvolution (Fig. S7); RIR is the relative intensity of the chosen peak and RIR values of FAU and EMT were obtained from the pdf files.

Si/Al ratio of zeolite samples was calculated from <sup>29</sup>Si Solid State Nuclear Magnetic Resonance (SSNMR) spectrum collected with Bruker 300 MHz DSX NMR equipped with a dual channel (H-X) MAS probe. Surface morphology of zeolite particles was studied with FEI Helios Nanolab 600 Scanning Electron Microscope (SEM). Particle morphology, crystallinity and composition analysis was obtained with FEI Probe Corrected Titan3™ 80–300 S/TEM.

### 2.5. N<sub>2</sub> adsorption isothermal experiments and calculations

Nova 2200e BET Surface Area Analyzer from Quantachrome was employed to collect the N<sub>2</sub> adsorption isotherm of zeolite samples. Surface area and pore size distribution was calculated with Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) theories, respectively. T-plot method was applied in relative pressure (p/p<sub>0</sub>) range of 0.21–0.42 to calculate external surface area and micro pore volume.

Before N<sub>2</sub> adsorption/desorption isotherm collection, zeolite samples were outgassed under vacuum at 400 °C for 24 h. After cooling down to room temperature, a full isotherm was collected with 30 points in adsorption process and 17 points in desorption process.

BET surface area, external surface area, micropore volume and pore distributions were obtained from the isotherm. For microporous materials, like zeolites, a linear relationship between 1/[W(p/p<sub>0</sub>)-1] and p/p<sub>0</sub> is expected in p/p<sub>0</sub> range of 0–0.05. External surface area of zeolite materials were calculated by the t-plot method, which is most suitable for oxide surfaces. In t-plot method, a t-plot was obtained from the isotherm using de Boer equation, which is most accurate in the range of p/p<sub>0</sub> 0.25–0.6. On the t-plot, a linear range was picked between 0.25 and 0.6 for external surface area calculation, (typically 0.2–0.42). Linear fitting in this range was employed to calculate external surface area (slope) and micropore volume (intercept). In this study, pore-size distribution analysis was obtained from each isotherm with 2 methods: Non-Linear Density Functional Theory (NLDFT) and Barrett–Joyner–Halenda (BJH). In NL-DFT method, full isotherm was employed for the calculation, while in BJH method, only desorption data was used. Detailed calculations of different methods employed in this study is found in the manual of Nova 2200e BET Surface Area Analyzer from Quantachrome.

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