Synthesis of Hierarchical ZSM-5 Zeolites by Solid-State Crystallization and Their Catalytic Properties

Yuxin Wang¹, Jianjun Song², Nathan C. Baxter¹, Guan-Tsein Kuo¹, Shengnian Wang^{1*}

¹ Chemical Engineering, Institute for Micromanufacturing, Louisiana Tech University, 911 Hergot Avenue, Ruston, LA, 71272, USA.

² Key Laboratory of Fine Chemicals of Universities in Shandong, School of Chemistry and Pharmaceutical Engineering, Qilu University of Technology, Jinan 250353, PR China.

Corresponding Author: Shengnian Wang, 318-257-5125, swang@latech.edu

KEYWORDS: zeolites, mesoporous materials, solid-state crystallization, lignin depolymerization, hydrogenation

ABSTRACT: Hierarchically porous structure is important to promote mass transport and active site utilization of zeolites for many petrochemical reactions involving bulky molecules. Their conventional hydrothermal synthesis with meso-template materials is often complicated, expensive, and produces a large amount of aqueous pollute. We demonstrate here successful synthesis of mesoporous zeolites of MFI structure by solid-state crystallization without meso-template. Aluminosilicate nanogels are produced with only precursors and the dried nanoparticles are then transformed into nanocrystals in solid state using only their intrinsic water storage. After orientating with each other at edges, these nanocrystals joint into monolithic zeolites with connecting inter-lattice mesopores. The produced hierarchical ZSM-5 zeolites exhibit superior stability and excellent catalytic performance in reactions like Friedel-Crafts benzylation, lignin ethanolysis, and naphthalene hydrogenation. Compared with conventional synthesis routes, this new solid crystallization approach simplifies zeolite production, lowers the cost, and avoids toxic liquid waste, which may greatly benefit many energy applications.

1. Introduction

Zeolites are crystalline aluminosilicates widely used as heterogeneous catalyst in different crude oil upgrading and chemical refinery processes.[1-3] The strong acidity and uniform micropores (< 2 nm in diameter) defined by their unique crystal structure enables superior selectivity based on shape and/or chemical configuration of molecules in various chemical reactions including alkylation, aromatization, cracking, pyrolysis, and hydrodesulfurization.[4-6] However, when bulky reactants/products are involved, this is often accompanied with serious diffusion problem inside zeolite crystalline and consequent pore blocking issues in both traditional petrochemical processes and the emerging renewable bio-energy processes.[7-9] Introducing mesopores (2-50 nm in diameter) or staged hierarchical

porosity (i.e., connected macropores, mesopores, and micropores) is considered as a promising solution to such limited molecule transport and low active site utilization issues in zeolites.[10-13] Various synthesis routes, including both post-treatment and template assembly, have been developed to produce hierarchically porous zeolites.[14-34] The former (post-treatment approach) obtains mesoporous structure by selectively leaching Si or Al atoms out of the zeolite crystal framework,[17-19] while the latter (template synthesis approach) pre-reserves the hierarchical space with either hard nanomaterials or surfactant-like macromolecules during the assembly or crystallization.[20-28] Compared to the inevitable change on the acidity and crystalline framework of zeolites in post treatment approaches, these properties are well preserved in the template synthesis processes. However, the template synthesis approaches often suffer from issues like the availability or synthesis challenges of desired template molecules [29-31], as well as their compatibility with precursors.[32-34] No matter which strategy is adopted, traditional hydrothermal synthesis process is essential in zeolite production, which requires the use of a large quantity of solvent (e.g., water and ethanol) while often results in incomplete crystallization with a yield of ~80% or less zeolites. [35] This leaves a significant amount of toxic liquid waste containing alkali, silicates, and aluminates, which not only increases the total cost for post-synthesis separation, but also results in consequent healthy issues and environmental pollution. [36] Such issues become more serious in many emerging biomass-based renewable energy processes with their significantly high quantity demand of zeolites (with a catalyst-to-reactant ratio often larger than 1:1). [37] This could largely offset the potential benefits of these bioenergy routes considering the new pollution concerns or negative impact to environment initiated by the involved zeolite industry. All of these facts stimulate great desire to look for new, low-cost, and environmental benign strategies in hierarchical zeolite synthesis.

We report here a new synthesis route to effectively produce hierarchical zeolites with MFI structure that requires neither help of meso-template materials nor solvent-involved crystallization environment. The synthesis details are illustrated schematically in Figure 1. In this approach, aluminosilicate nanogels are firstly prepared by a sol-gel process at relatively low temperature, involving only precursor compounds. After evaporating the solvent (i.e., water and ethanol) at room temperature, the dry nanogels are transferred to a Teflon-lined autoclave and calcined without adding water or any other solvent. During this solid phase crystallization process, the amorphous aluminosilicates are transformed slowly using water stored in individual nanogels. Accompanied with hydrolysis and condensation of Si-Al tetrahedral, adjacent nanogels are brought together as large ensembles simultaneously by weak, solid-solid interactions. With the crystallization extending to the edge of nanogels, the new formed crystals over there align their crystalline patterns to the surrounding nanocrystals and eventually joint into a single piece, large crystalline zeolite. The stacking of these nanocrystals creates many inter-lattice mesoscale space and pathways inside the produced monolithic zeolites.

Stage I: Aluminosilicate Nanogels

Stage II: Solid-state Crystallization

Figure 1. Schematics of the meso-template free synthesis and solid state crystallization route towards hierarchically zeolites, Meso-ZSM-5.

2. Materials and Methods

2.1 Materials

Tetrapropyl ammonium hydroxide (TPAOH, 1 M in H₂O), sodium aluminate (NaAlO₂, ~8% H₂O, >99%), tetraethylorthosilicate (TEOS, >99%), benzene (>99%), benzyl alcohol (>99%), lignin (alkali), ethanol (C₂H₅OH, >99.5%), naphthalene (C₁₀H₈, >99%), n-hexadecane (n-C₁₆H₃₄, >99%) were purchased from Sigma-Aldrich and used as received without further purification.

2.2 Zeolite Synthesis

Meso-ZSM-5 zeolites were synthesized by mixing TPAOH, NaAlO₂, TEOS, and H₂O with a molar ratio of 0.25TPAOH: 0.03Al₂O₃: SiO₂: 80H₂O. TPAOH and NaAlO₂ were first dissolved in H₂O, followed by adding TEOS under strong agitation (i.e., 600 rpm). The mixture was kept at 80 °C until a clear solution was obtained, which was left in hood overnight at room temperature allowing for solvent evaporation. The dry gel was then collected and ground into

powders and the as-prepared dry gel powders were further transferred to a Teflon-lined autoclave for crystallization at 140 °C for 12 h without adding any water. Note: autoclave or other high-pressure vessel is not mandatory in this solid-state crystallization process as no significant pressure is generated, unlike the traditional hydrothermal or steam-assisted crystallization in which 1-4 MPa steam pressure presents in autoclave, depending on the filling volume. [38, 39] Here, containers that are capable of tight seal at elevated temperature (e.g., air-tight glass or plastic lab bottles) and resistant to basic liquid can be used. Autoclaves were used here for the comparison convenience with the hydrothermal synthesis of microporous ZSM-5 (e.g., considering the consistence on internal temperature, the heating and cooling rates). Without washing, the fully crystallized zeolites were dried at 100°C for 4 h to remove the adsorbed water and calcined at 500°C for 6 h (at a heating rate of 1 °C /min) for structure stabilization and the removal of TPAOH. Conventional ZSM-5 zeolites with a similar Si/Al ratio (i.e., 33) were synthesized via traditional hydrothermal method at 140 °C for 48 h.

All zeolite samples were ion-exchanged three times with a 0.1 M NH₄NO₃ solution at 90 °C for 90 min with a liquid/solid ratio of 10 cm³/g under magnetic agitation (500 rpm). After that, samples were filtered, extensively washed with distilled water, and dried at 100 °C for 4 h. The H-type zeolites were obtained by calcined at 500°C for 6 h. The hydrothermal stability of zeolites was tested at 150 °C for 72 h in autoclave with a water/zeolite ratio of 50.

2.3. Pt/Zeolite Catalyst Preparation

Pt/ZSM-5 and Pt/Meso-ZSM-5 catalysts were prepared by conventional incipient wetness impregnation. In brief, an H₂PtCl₆.6H₂O (99%, Sigma-Aldrich) aqueous solution (10mL, containing 26.6 mg H₂PtCl₆.6H₂O) was added dropwise to wet H-type zeolite powder (1.0g) at room temperature and the suspension was further diluted with DI water to a total volume of 50 mL under agitation (200 rpm). After 3 hour of stirring, the suspension was left still, allowing for solvent evaporation. The dried catalyst were then transferred to a furnace for further drying at 120 °C for 12 h and calcined at 500 °C for 4 h (with a heating rate of 1.5 °C/min). Dried catalyst was reduced in a flow of H₂ for 3 hr at 450 °C, using a heating rate of 2.5 °C/min prior to use.

2.3 Characterization

X-ray diffraction (XRD) analysis was done on a Bruker D8 diffractometer, using Cu-Kα radiation at room temperature and instrumental settings of 40 kV and 40 mA. Data were recorded in the 2θ range of 5–60° with an angular step size of 0.02°. The crystallinity of the synthesized zeolites was quantified by taking the value of the integrated area from the XRD peaks in the 2θ range of 22.5–25°. These peaks appeared early during the crystallization process with clear peak boundary for accurate calculation. The relative crystallinity of Meso-ZSM-5 was calculated by comparing their integrated peak area with that of purely microporous zeolite ZSM-5 as:

$$\% \text{Crystallinity} = \frac{\text{Peak Area (sample of Meso-ZSM-5)}}{\text{Peak Area (Reference ZSM-5)}} \times 100\%.$$

1 Solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) spectra were
2 recorded with a single pulse experiment on a 9.4T (400 MHz ^1H) wide bore magnet using
3 Bruker AV console and 4 mm probe. The ^{29}Si experiments were done with single 4- μs pulse, a
4 relaxation delay of 60 s, and a MAS spinning rate of 8 kHz. Each ^{29}Si spectrum was collected
5 with 256 scans. The ^{27}Al experiments were done with a pulse length of 0.33 μs , a recycle delay
6 of 0.1 s, and 14 kHz MAS rate. Each ^{27}Al spectrum was collected with 4096 scans. The ^{29}Si and
7 ^{27}Al spectra were reported relative to tetrakis (trimethylsilyl)silane (TTMSS) and $\text{Al}(\text{NO}_3)_3$,
8 respectively. Some NMR spectra were deconvoluted using Gaussian function.

9 Scanning electron microscopy (SEM) images were taken on a Hitachi S-4800. Samples
10 were prepared by dusting the zeolite powder onto double sided carbon tape, mounted on an
11 alumina stub. All samples were subsequently sputter coated with a thin gold film to reduce
12 charging effects. Transmission electron microscopy (TEM) and selected-area electron diffraction
13 (ED) measurements were carried out on a JEOL 2010F instrument, operating at 200 kV. The
14 samples were suspended in ethanol and dispersed on a copper grid coated with lacey carbon film
15 before TEM analysis.

16 Nitrogen adsorption isotherms were obtained at $-196\text{ }^\circ\text{C}$ on a Micromeritics ASAP 2020
17 Surface Area and Porosity Analyzer in a relative pressure range from 0.05 to 0.99. Before
18 measurement, samples were degassed at $300\text{ }^\circ\text{C}$ for 6 h. The pore size distribution was calculated
19 using the Nonlocal Density Functional Theory (NLDF) method from the adsorption branch.

20 The ammonia temperature programmed desorption (NH_3 -TPD) was used to measure the
21 acidity of zeolites on a Micromeritics AutochemII Chemisorption Analyzer. Zeolite materials (50
22 mg) was pretreated at $300\text{ }^\circ\text{C}$ for 1 h and then cooled down to $50\text{ }^\circ\text{C}$ in an Ar flow of $20\text{ cm}^3/\text{min}$.
23 Pure NH_3 (at a flow rate of $20\text{ cm}^3/\text{min}$) was injected until adsorption saturation, followed by Ar
24 purging for another 1 h. The desorption of NH_3 was monitored in the range of $50\text{--}700\text{ }^\circ\text{C}$ with a
25 ramp of $10\text{ }^\circ\text{C}/\text{min}$ by a TCD detector.

26 Thermo-gravimetric analysis (TGA) was used to quantify water carried by dry nanogel
27 powder to the second solid-state crystallization step using a TGA 2050 Thermogravimetric
28 Analyzer (TA Instruments, Inc). To distinguish water left in dry nanogel from those through
29 adsorption, some dry nanogel powders were left in a high-purity argon-filled glove box (with
30 water content $<0.1\text{ ppm}$) for a week to remove the adsorbed water in nanogels. The weight loss of
31 nanogel samples was monitored through a thermal scanning from 30 to $110\text{ }^\circ\text{C}$ at a ramp rate of
32 $10\text{ }^\circ\text{C}/\text{min}$ in air atmosphere.

33 *2.4 Catalytic reaction tests*

34 The benzylation of benzene with benzyl alcohol was carried out at $80\text{ }^\circ\text{C}$, with 0.15 g
35 catalyst, 34 mL benzene, and 0.5 mL benzyl alcohol in a three-necked round-bottom flask
36 equipped with a reflux condenser. Samples were taken every hour and analyzed by gas
37 chromatography (VARIAN CP-3800 GC with an FID detector using a 30 m packed HP-5
38 column). The conversion was calculated based on benzyl alcohol quantity.

The catalytic conversion of Kraft lignin was carried out at 280 °C for 6 h in a high-pressure batch reactor (Col-Int Tech, 200 mL). For each run, 1.0 g lignin, 0.5 g catalyst, and 100 mL ethanol were first loaded in the reactor and the sealed reactor was then evacuated and purged with high-purity nitrogen gas for three times at room temperature. The reactor temperature was then risen to 280 °C with the reactor pressure reaching ~8 MPa. After the reaction was carried out for 6 h, the liquid was filtered and taken for product identification and analysis on a GC–MS instrument (Agilent 7890A-5975C). Benzyl alcohol (0.1 vol% in ethanol, 1.0 µL) was added in the product samples (1 mL) before GC-MS analysis, serving as the known internal standard in GC-MS spectra to normalize the peak area for each compound. Multiple-point internal standard plots were generated, covering the expected concentration range of major product compounds. For those commercially available compounds, such as 4-methyl phenol (i.e., cresol) and 2-methoxy-phenol (i.e., GUA), diluted solutions with known concentrations were prepared. For other commercially-not-available compounds like 3-methyl-1- adamantaneacetic acid, the lignin depolymerization product obtained from different catalysts were mixed and further concentrated by evaporating most ethanol using a rotary evaporator. The obtained liquid was then diluted with ethanol to get different concentrations of each compound using benzyl alcohol as the internal standard (0.8 mM). Plots of the peak area ratio of several major aromatic compounds in lignin depolymerisation products to the internal standard (benzyl alcohol) were made versus the concentration ratio (supplemental Figures 1 a&b). The original concentrations of those commercially-not-available compounds in the mother solution were determined by their area ratios to GUA whose concentration in samples were found through their own multiple-point internal standard curve (supplemental Figure 1a). The solid was collected and weighted to calculate the overall lignin conversion.

The hydrogenation of naphthalene on Pt/ZSM-5 and Pt/Meso-ZSM-5 catalysts was performed in a large high-pressure batch reactor (Col-Int Tech, 400 mL). As the hydrogenation of naphthalene and its intermediate product (i.e., tretalin) is exothermic, the generated heat can be quickly removed by the internal cooling coil of this bigger reactor to maintain the reaction temperature. It also allows taking samples while the reactor is in operation at elevated temperature and pressure conditions to obtain the reaction kinetics. For each experiment, 33 mg of naphthalene was dissolved in n-hexadecane (99%, Sigma-Aldrich) of 100 mL and the solution was loaded in the reactor, together with 0.5 g catalyst. After loading, the reactor was sealed tightly and the stirring speed was set to 1,000 rpm. The reactor was heated with an electric heating jacket to the desired temperature (~ 1hr) and the hydrogenation was studied at 200°C with a hydrogen pressure of 7.5 MPa. Samples were taken every hour of a total of 5 hour reaction period and were filtered through a syringe filter prior to GC-MS analysis.

3. Results and Discussion

3.1 Solid State Crystallization Evolution and Textural Properties

To reveal such solid-state crystallization evolution, aluminosilicate intermediates at different synthesis moments were examined with SEM, XRD and NMR. The nanogels collected after stage I synthesis have an average size of ~20-30 nm (Figure 2a) and are amorphous (Figure 3). After crystallizing in a solvent-free environment for 3 h, these nanogels started aggregating in some locations with unclear boundaries (Figure 2b) while the majority stayed amorphous (Figure 3). When the crystallization proceeded to 6 h, weak crystalline peaks appeared (Figure 3a) with a relative crystallinity of ~40% (Figure 3b). More aluminosilicate ensembles were found with defined boundaries (Figure 2c). All MFI peaks with strong, clearly defined pattern were first shown after 9-hour crystallization (Figure 3) with a relative crystallinity close to ~90% (Figure 3b). Large nanoparticle ensembles with clear boundaries and uniform size were seen everywhere (Figure 2d). With a total of 12-hour crystallization, the XRD pattern stayed the same without further increase on the intensity of individual peaks (Figure 3a). Further extending the crystallization time was found no change on the crystallinity degree (Figure 3b), indicating that fully crystallized zeolites are obtained after the 12-hour, solid-state crystallization. These large zeolites have similar spherical shape, uniform particle size (~400 nm in diameter), and very rough surface (Figure 2e). The high magnification SEM image (Figure 2f) further reveals that they are highly mesoporous, attributed to the assembly of many nanoparticles of 20-30 nm. The high-resolution TEM (HRTEM) image further tells that these are nanosized crystals (Figure 4a). Considering their similar size to the original aluminosilicates nanogels, we believe each monolithic zeolite nucleates simultaneously from many individual nanogels. The formed small nanocrystals exhibit lattice fringes of the same orientation (Figures 4a and 4b), suggesting that these nanocrystals have been grown and merged into a single, large monolithic crystal rather than randomly packed nanocrystal aggregates. The electron diffraction spot pattern of a selected-area in HRTEM image (inset of Figure 4a) evidences this fact. The jointed nanocrystals create many inter-lattice mesopores in zeolite crystalline frameworks (Figures 4a and 4b). With the XRD pattern of these zeolites matching that from a conventional microporous ZSM-5 sample and in good agreement with the database MFI structure (Figure 4c), we conclude the successful synthesis of mesoporous ZSM-5 with this new solid-state crystallization approach (denoted as Meso-ZSM-5 in later discussions). Although slightly broader XRD peaks were seen in these Meso-ZSM-5 samples to the microporous ZSM-5 due to the small individual crystallites (Figure 4d), their jointed framework as single, monolithic pieces of crystallites of 400 nm largely offsets any pronounced peak broadening effect often seen in physical aggregates of nanosized zeolites. Therefore, identical XRD patterns with similar peak width are found in Meso-ZSM-5 and microporous ZSM-5 of similar crystal sizes (400-500 nm).

Although these unique textural features are clearly shown by SEM and TEM, quantifying such properties is not trivial due to its staged hierarchical porosity (i.e., connected macropores, mesopores, and micropores). [40] The N₂ adsorption-desorption isotherm of the Meso-ZSM-5 zeolites sample was obtained, which exhibits features of both type I and type IV(a) profiles with two steep uptake steps, one at $P/P_0 < 0.02$ and the other at $0.45 < P/P_0 < 0.90$ locations, responding for micropore filling and mesopore capillary condensation, respectively (Figure 4e).

1 In contrast, the conventional ZSM-5 shows a typical type-I isotherm with only one high uptake at
2 low relative pressures ($P/P_0 < 0.02$) and a long plateau at high relative pressures ($0.4 < P/P_0 <$
3 0.9), indicating that the material is a purely microporous phase with negligible mesoporosity.
4 Together with this additional high uptake of the type-IV(a) profile, the appearance of a typical
5 H4 hysteresis loop on the isotherm of typical mesoporous materials at high relative pressure
6 further confirm the existing of both microporosity and mesoporosity in our synthesized Meso-
7 ZSM-5. This H4 loop with more pronounced uptake at low P/P_0 than H1 or H2 is in consistence
8 with the adsorption–desorption isotherms of aggregated nanocrystals of zeolites. [41] In the
9 NLDFT pore size distribution plot, a very sharp peak centered at 3.0 nm, followed by a weak,
10 broad peak centered at 9 nm is found for this Meso-ZSM-5 sample (Figure 4f). The long tail of
11 the second peak could be the result of mismatching between the actual pore structure and the
12 available model pore shapes. Nonetheless, it endorses the existing of mesopores in Meso-ZSM-5.
13 In contrast, only the first peak centered at 2.0 nm is shown in the NLDFT plot for traditional
14 ZSM-5 sample, in consistence with its sole microporous structure. Although the use of
15 traditional BET approach to extract surface area and pore volume information from these N_2
16 adsorption–desorption isotherms is known inappropriate for most zeolites, such results are
17 provided as a table in the supplemental document for general reference purpose, considering its
18 popular use for textural property measurement of zeolites in history and in case, some
19 comparisons with data from other researchers are needed.

20

Figure 2. SEM of the aluminosilicate particle samples that have been crystallized for (a) 0 h, (b) 3 h, (c) 6 h, (d) 9 h, and (e, f) 12 h.

Figure 3. (a) XRD patterns of the aluminosilicate particle samples that have crystallized for 0 h, 3 h, 6 h, 9 h, and 12 h and (b) the relative crystallinity kinetics.

1
2 **Figure 4.** (a, b) HRTEM images of Meso-ZSM-5. The inset in (a) is the corresponding electron
3 diffraction pattern of a selected area. (c, d) XRD patterns, (e) N₂ sorption isotherms, and (f) the
4 NLDFT pore size distribution plots of Meso-ZSM-5 and conventional ZSM-5. (d) is the
5 amplified XRD pattern of Meso-ZSM-5 between 7-10° of 2θ .

Figure 5. Solid-state MAS NMR spectra of Meso-ZSM-5. (a,b) ^{29}Si and ^{27}Al NMR patterns of samples during solid-state crystallization; (c-f) Comparison of ^{29}Si and ^{27}Al NMR patterns of Meso-ZSM-5 (d, f) and microporous ZSM-5 (c,e).

The solid-state ^{29}Si and ^{27}Al MAS NMR spectra (Figure 5) were employed to further investigate such framework formation dynamics of Meso-ZSM-5 through local bonding environment changes. ^{29}Si MAS NMR provides information about silicon atoms with different bonding environments in the zeolite framework with silicon atoms connected to silicon, aluminum, or other atoms via oxygen bridges named Q_{a+b} (bAl) or $\text{Si}(\text{OSi})_a(\text{OAl})_b(\text{OH})_{4-(a+b)}$, where a and b are the number of adjacent $-\text{OSi}$ and $-\text{OAl}$ units attached to Si , respectively. At the beginning of the crystallization, the ^{29}Si NMR chemical shift spectra shows one weak but very broad peak between -80 and -120 ppm due to its amorphous state with silicon atoms connected with multiple hydroxyl group (Figure 5a). With the crystallization ongoing, this peak becomes narrower and its intensity increases, indicating the formation of Si-O-Si and Si-O-Al bonds. Further extending the crystallization time results in peak split with one centered at -113 ppm identified as $\text{Q4}(\text{OAl})$ species and the other at -105 ppm identified as $\text{Q4}(\text{1Al})$ species. ^{27}Al MAS NMR was also collected to reveal the bonding environment around the aluminum atoms in the

framework (Figure 5b). The spectra feature a chemical shift between 40 and 60 ppm (designated as tetrahedrally coordinated Al) and similar peak evolution (i.e., intensity increases, accompanied with a decrease in the full width at half maximum (FWHM)). A well-defined peak is found at a chemical shift of 54.5 ppm on ^{27}Al MAS NMR of the fully crystallized sample, confirming the isomorphous substitution of Al in the SiO_4 structure. Further comparisons with the ^{29}Si and ^{27}Al spectra with microporous ZSM-5 samples show similar chemical shift pattern, except sharper and better resolved Q4(0Al) and Q4(1Al) peaks in ^{29}Si spectra (Figures 5c-5f). This further confirms their similar local bonding environment and the successful formation of ZSM-5 framework by this solid-state crystallization process.

3.2 Discussion on Synthesis Mechanism and Criteria

In this approach, though most transformations occur in the second solid-state crystallization stage, stage I synthesis is equally critical as it prepares dry, amorphous aluminosilicates nanogels so that precursors could self-assemble into nanoparticle aggregates of appropriate size without initiating crystallization. If these nanogels grow too fast and already start crystallizing in stage I, they would eventually turn into conventional microporous zeolites in later thermal treatment, just like those obtained in traditional hydrothermal synthesis (Figure 6a). This occurs if the original mother solution is too basic (i.e., high pH) or the chosen synthesis conditions are very harsh (e.g., high assembly temperature). Besides their amorphous feature, appropriate size is also important for nanogels collected after stage I growth. Nanogels of 50 nm or less (i.e., maintaining a clear sol in stage I before drying) are appropriate for stage II solid-state crystallization. Unlike most reported mesoporous zeolite synthesis approaches where organic and organosilane mesoporegen as mesotemplate help modulate both the precursor assembly and the hierarchically porous structure construction in the final crystal product, only a structure-directing agent (or so-called microtemplate), TPAOH, is involved in our approach. Besides its main role as governing crystallization of the MFI framework within the building blocks (i.e., amorphous nanogels), TPAOH also creates and maintains a high pH environment for the dissolution of sodium aluminate. As no substantial liquid water or steam is available for traditional dissolution-addition growth in the solid-state crystallization stage, the dried nanogels obtained from stage I assembly decide their own particle-particle interactions, accumulation, and the later solid crystallization in stage II solid crystallization. The buildup of large ensembles of uniform size from many adjacent nanogels is believed to initiate these transformations. Considering the range of available forces, small nanogels are therefore preferred for particle interactions and attachments. Along with nanogel assembly, such unique supply of needed solvent (i.e., water molecules stored in nanogels) also triggers the nucleation and further crystallization in the confined space of each individual nanogels. With the solid crystallization gradually extending to edges of nanocrystals, neighbouring nanocrystals orient their lattice pattern to each other and merge into a monolithic crystal. Simultaneously, hierarchical inter-lattice pores are built up between nanocrystals during their periodic piling. Such growth evolution is likely similar to a new aggregative growth model that is found in silicate-1 growth at

ambient conditions [42, 43] or more generally, the particle attachment crystallization mechanism seen in natural mineral formation. [44, 45] But unlike these classical assembly and crystallization in geologic or synthetic environments, nanoparticle powders, not an aqueous suspension of nanoparticles, are involved in our synthesis approach instead. Only water stored in those amorphous nanogels participates and mediates the assembly dynamics and crystallization kinetics. In fact, we found that such format of water and its quantity is the key to successfully build up the shown unique hierarchically porous zeolites with jointed crystal framework in this solid-state crystallization process. If substantial free liquid water or steam was introduced in the solid-state crystallization stage, some nanogels would nucleate earlier than others, consume aluminosilicate precursors from surrounding nanogels, and eventually transform into large piece, single crystal zeolites. As a result, a physically mixture of large, microporous zeolites and aluminosilicate nanoparticles would be obtained (Figure 6b).

Figure 6. SEM images of samples by preparing (a) aluminosilicate nanogel at high pH value, followed by stage II solid-state crystallization and (b) aluminosilicate nanogels prepared under appropriate stage I synthesis conditions, followed by traditional hydrothermal treatment.

Due to the critical role of water pre-stored in nanogels to the success of this solid-state crystallization, TGA was used to quantify the water content in nanogel powders obtained from stage I synthesis. Water available for later crystallization comes from two different sources: (1) water encapsulated in nanogels by their thick skin after the overnight evaporation process and (2) water adsorbed from environment as a consequence of significant increase of the total surface area after aluminosilicate gel was ground to powders. To distinguish the amount of water from each source, part of the nanogel sample was kept in an ultra-dry glove box (with water content $<0.1\text{ppm}$) for a week to eliminate the surface adsorbed water. As shown in Figure 7a, the total weight loss of nanogel sample without being further dried in glove box is nearly 20% while the

one deeply dried shows only ~10% loss of weight. This suggests that in solid-state crystallization, water stored in nanogels occupies ~20% of the total gel weight and is sufficient to fully transform aluminosilicates nanogels to zeolite framework. This is way less than the steam-assisted crystallization route, in which a water/gel ratio of 10 is commonly used [38, 39]). In addition, as such stored water is fully utilized in nanogel assembly and transformation, no pressure is built up during synthesis, unlike the traditional hydrothermal or steam-assisted crystallization route in which >1.0 MPa steam pressure is generated and high-pressure vessels like autoclave are required.

Figure 7. (a) TGA results of nanogels after stage I synthesis with and without further drying; (b) NH₃-TPD results of Meso-ZSM-5 and ZSM-5 zeolites.

3.3 Evaluation of Surface Acidity and Stability

The NH₃-TPD analysis was conducted to evaluate the surface acidity of both Meso-ZSM-5 and microporous ZSM-5 samples. As depicted in Figure 7b, the two profiles are almost identical, with two separated desorption peaks centered at ca. 140 °C and ca. 410 °C, which correspond to the weak and strong acid sites of zeolites, respectively. This confirms the similar acidity of Meso-ZSM-5 and microporous ZSM-5, attributed to their similar Si/Al ratios.

Unlike mesopores in physically aggregated nanosized crystals, the hierarchical structure from fused nanocrystals in Meso-ZSM-5 shows excellent stability after being further hydrothermally treated at 150 °C for 72 h: the same XRD and NMR patterns and peak intensity are preserved (Figures 8a, 8c & 8d), so do their size, morphology (Figure 8b), and the later catalytic activity (Figure 9b). These results indicate that the monolithic Meso-ZSM-5 synthesized by our approach has good hydrothermal stability. It also proves that the solid-state crystallization process is completed after the 12-hour calcination and the produced Meso-ZSM-5 zeolites indeed

1 reach their stable crystalline structure, not just some intermediates collected from the middle of a
2 slow crystallization process.

3
4 **Figure 8.** Hydrothermal stability tests. (a) XRD patterns and (b) SEM image of Meso-ZSM-5
5 after additional hydrothermal treatment; (c) ²⁹Si and (d) ²⁷Al MAS NMR patterns of Meso-ZSM-
6 5 before and after hydrothermal treatment.

7 3.4 Evaluation of Catalytic Performance

8 Although having similar overall acidity, the unique textural features of Meso-ZSM-5
9 zeolites synthesized by our approach are expected to promote the utilization of active sites and
10 diffusion of zeolites with bulky reactants and/or products from two different aspects: (i) its
11 nanocrystal building units help expose more accessible active sites of zeolites to bulky
12 molecules; (ii) the connected mesoscale pathways among these jointed nanocrystals reduce the
13 diffusion barriers for these large reactant molecules to reach them and for possible bulky product
14 molecules diffuse out to avoid pore blocking.

3.4.1 Catalytic Performance in Friedel-Crafts alkylation

Such catalytic performance improvement of Meso-ZSM-5 was first evaluated with the Friedel-Crafts alkylation of benzene with benzyl alcohol, a typical diffusion-constrained reaction with both bulky reactants and products (Figure 9a). As shown in Figure 9b, Meso-ZSM-5 shows a much higher catalytic conversion of benzyl alcohol than the conventional ZSM-5 after a 6-hour reaction at 80 °C (71% for Meso-ZSM-5 versus 11% for ZSM-5). Considering their similar Si/Al ratio (Si/Al=33) and acidity (Figure 7b), this suggests that the outstanding catalytic activity of Meso-ZSM-5 is mainly attributed to its mesoporous structure. The connected mesoscale pathways allow bulky reactants (e.g., benzyl alcohol) and products (e.g., diphenylmethane) to transport to the active sites easier. Such unique hierarchical configuration also provides more accessible active sites on the jointed nanocrystals. Unlike mesopores in physically aggregated nanosized crystals, the hierarchical structure from fused nanocrystals in Meso-ZSM-5 shows excellent stability after being further hydrothermally treated: the same catalytic activity in Friedel-Crafts alkylation (Figure 9b).

Figure 9. (a) Schematics of Friedel-Crafts alkylation of benzene with benzyl alcohol and (b) benzyl alcohol conversion over Meso-ZSM-5 and conventional ZSM-5.

3.4.2 Catalytic Performance in Lignin Depolymerization with Supercritical Ethanol

Considering the large quantity demand of zeolites in biomass conversion processes and the environment-friendly synthesis advantage of our Meso-ZSM-5, the catalytic performance of Meso-ZSM-5 was further checked in lignin depolymerization for its effective promotions for the transport of giant reactants and/or products. As the second most abundant natural polymer, lignin has long been a high-volume major byproduct and environmental hazard of the paper and pulp industry. Depolymerization of lignin recently drew great attentions, not just for its environmental benefits on eliminating such major pollution waste, but also for its promising potentials in producing high-value aromatics as renewable chemicals and fuels.[46] However, cracking lignin fragments to release the rich phenol-type aromatics is not trivial, considering the difficulty on effective cleavage of the many C-O-C and C-C linkages in its molecular structure and diffusion barriers to its truly gigantic fragments. Processes like hydrolysis, oxidation, and reduction of lignin have been investigated with the help of noble metal and/or hydrotreating catalysts.[47-49] Among these processes, ethanolysis under supercritical conditions (Figure 10a) is favourable with its high conversion and no char formation benefits. The ethanolysis of Kraft lignin was carried out in a batch reactor after purging with N₂ under operation conditions s to some other research work (i.e., at 280 °C under a pressure of 8 MPa for 6 h. [50]). Similar to benzylation reactions, Meso-ZSM-5 exhibited a higher conversion of lignin (72.5%), when compared to that of ZSM-5 (62.6%) and no tar or char was found. A total of 22 molecules with a mass weight of more than 1.0% of all products were detected by gas chromatography-mass spectrometry (GC-MS), as shown in Figure 10b. Some products eluted early in the GC-MS spectrum, particularly the three different types of short-chain ether, are mainly derivate of ethanol reforming reactions at the presence of zeolites. This is verified when comparing the GC-MS spectrum of lignin ethanolysis products with that from reactions involving only ethanol and zeolites at the same conditions (Figure 10b). Mass spectrum peaks of other 17 products including different types of alcohol, acetal, and aromatics appeared only when lignin was added. The early eluted ones in lignin depolymerization samples, with short chains of C₄-C₆, such as butanol, acetate, and acetal, show similarly peak intensity in the GC-MS spectrums for ethanolysis products using Meso-ZSM-5 and microporous ZSM-5. But signals of the later eluted compounds of C₈-C₁₁, most as aromatics, increases greatly for samples depolymerized by Meso-ZSM-5 than that using microporous ZSM-5 (Figures 10b-10d). The high-yield of overall aromatics (49.3% for Meso-ZSM-5 versus 32.6% for ZSM-5) with more diversified individual compounds suggests deeper breakdown of lignin fragments over Meso-ZSM-5 (Figure 10d). More small, high-valued aromatics, especially desired phenols such as guaiacol (~20%) and alkane substituted guaiacols such as ethylguaiacol and methylguaiacol (~15%), have obviously high yield over Meso-ZSM-5 catalyst, as shown in Figures 10b and 10d. As comparison, the major aromatic product in ethanolysis over traditional microporous ZSM-5 is 1,2-Dimethoxy-4-(1-methoxyethenyl) benzene (~25%), a relatively large intermediate aromatic fragment, together with quite limited phenol-type, small fragments (~6.2%). Similar to what occurs in Friedel-Crafts alkylation, the high phenol selectivity observed in ethanolysis over Meso-ZSM-5 is attributed to their more

exposed active sites on their nanosized zeolite building units and the mesoscale connecting channels to them in the monolithic crystal. Large fragments of lignin such as 1,2-Dimethoxy-4-(1-methoxyethenyl)benzene can readily reach the active sites of zeolites for further cracking into smaller fragments (e.g., phenols) before leaving the catalyst surface. Although the reactions occurred in supercritical ethanol, Meso-ZSM-5 zeolites still kept their original size and morphology with no sign of crystal broken after the 6-hour high-temperature, high pressure reaction (supplemental Figures 2 a&b). This evidence again endorses the superior stability of Meso-ZSM-5 obtained by our template-free assembly and solid-state crystallization approach. It also further supports the conclusion that the edges of nanocrystals in Meso-ZSM-5 are indeed fused together as single monolithic crystal, rather than some physical aggregates of many nanocrystals of zeolites.

Figure 10. (a) Schematics of lignin ethanolysis, (b) GC-MS spectrums of lignin ethanolysis over Meso-ZSM-5, conventional ZSM-5, and only ethanol and zeolites, and (c-d) the product distribution (c: overall; d: among aromatics) in lignin ethanolysis over Meso-ZSM-5 and conventional ZSM-5.

3.4.3 Catalytic Performance in Hydrogeneation of Naphthelene

Deep hydrogenation of aromatics is one of the most important unit operations in modern oil-refinery and coal liquefaction industries. [51–53]. The produced cycloalkane can significantly increase the cetane number (CN) of fuel, improve its combustion performane, and enhance its thermal stability even in some critical environments (e.g., for jet fuel) [53]. Because of its exothermic reaction feature, aromatics hydrogenation is thermodynamically favored at low temperature, for which noble metal supported catalyst is desired. Some recent studies found that when supported on acidic materials such as USY or Beta zeolites, noble metal catalyst such as platinum (Pt) showed much improved catalytic activity and sulfur tolerance in deep hydrogenation of aromatics. [54-56] However, the sole microporosity of these zeolites often makes these reactions less effective when bulky aromatic hydrocarbons such as naphthelene (a major compound of light cycle oil or coal tar) are involved due to the significant mass transfer limitation [57]. Here we investigate the catalytic performance of this new Pt/Meso-ZSM-5 catalyst in naphthalene hydrogenation. The reaction was performed in a batch reactor at 200°C with a hydrogen pressure of 7.5 MPa. Figure 11a shows the reaction network of naphthalene hydrogenation, with main compounds as partially hydrogenated tetralin and fully saturated cis- or trans-decalin. As shown in Figure 11b, the reaction rate of naphthalene is much faster over Pt/Meso-ZSM-5 catalyst than that over Pt/ZSM-5, with the conversion of naphthalene reaches to 100% within 3 hours. In contrast, only ~80% of naphthalene is consumed over Pt/ZSM-5 catalyst

at the end of a 5-hour reaction time. As demonstrated by other researchers, the hydrogenation of naphthalene to tetralin is much easier than the further hydrogenation of tetralin to decalin, with the reaction rate of the former about 30 times higher than the latter. [56, 58]. Hence decalin selectivity is often used as criterion to evaluate the performance of catalyst in naphthalene hydrogenation. From Figure 11c, no decalin is detected in the hydrogenation product over Pt/ZSM-5. The production of tetralin is also delayed for about an hour when enough naphthalene is converted and then goes up. This confirms the poor deep hydrogenation activity of Pt/ZSM-5 at such low hydrogenation temperature (200°C). But over Pt/Meso-ZSM-5, thanks to the quick consumption of naphthalene, both tetralin and decalin present in the hydrogenation product even at the early stage. The decalin selectivity continue going up when more naphthalene is converted and its selectivity exceeds that of tetralin after one hour. Among all decalin products, nearly equal quantity of trans- and cis-decalin presents.

Figure 11. (a) Schematics of hydrogenation of naphthalene, (b) kinetics of naphthalene conversion and (c) the product selectivity of in naphthalene hydrogenation over Pt/Meso-ZSM-5 and Pt/conventional ZSM-5.

Similar to the other two ZSM-5 catalyzed reactions involved bulky molecules, the improvement of such naphthalene hydrogenation performance over Pt/Meso-ZSM-5 is attributed to its unique mesoporous/microporous bimodal porous structure and strong acidity. Compounds involved in naphthalene hydrogenation have their molecular sizes between 0.50 and 0.71 nm, which could transport easily in mesopores of Meso-ZSM-5, while face significant resistance inside the 10-member ring of microporous ZSM-5. On Pt/ZSM-5, poorer hydrogenation capacity is attributed to such diffusion limitation of naphthalene and tetralin in their micropores. Such a result is in accordance with a previous report by Pawelec et al. [56]. In contrast, our staged hierarchical porosity (i.e., connected macropores, mesopores, and micropores) of Meso-ZSM-5 allows Pt particles to reach deep to the more exposed surface of zeolites during the wet impregnation. More electron-deficient Pt active centers attributed to effective hydrogenation could also be formed and become accessible in Pt/Meso-ZSM-5 during the partial electron transfer from Pt particles to acidic sites of zeolites, unlike in Pt/ZSM-5, some Pt active centers and the secondly spillover based hydrogenation pathway cannot be reached. The spillover hydrogen coming from connected micropores in Pt/Meso-ZSM-5 could further promote the hydrogenation of tetralin adsorbed on the acidic sites of zeolites to the saturated decalin before leaving those active sites. Based on these benefits (enhanced reactant/product diffusion and promoted hydrogenation pathways), it is not surprise to achieve much higher catalytic activity of naphthalene hydrogenation and selectivity to saturated decalin over Pt/Meso-ZSM-5 than that over Pt/ZSM-5. This not only proves the excellent deep hydrogenation performance of this new catalyst, but the high yield of decalin compounds (the saturated hydrocarbons) may also bring great profit to the fuel business of the oil-refinery and coal liquefaction industries from the perspective of producing high CN fuel like diesel (CN for naphthalene is 1, tetralin is 10, and decalin is 36) and fuel with superior thermal stability at extreme conditions like jet fuel.

3.5 Zeolite Processing Advantage of this Solid-State Crystallization Process

This new synthesis approach provides not only hierarchical zeolites of unique textural features (i.e., jointed nanocrystals with inter-crystalline mesovoids) and enhanced catalytic performance in multiple important operations in modern oil-refinery and coal liquefaction industries, but also solutions to some severe material, economics, and environmental issues associated with traditional hydrothermal zeolite production routes. First, our synthesis involves only solid crystallization. As no liquid is loaded and no pressure is built up during crystallization, the crystallization vessel could be fully loaded, which will significantly increase the zeolites yield. Moreover, as the crystallization is carried out at atmospheric pressure, any vessels that are capable of tight seal at elevated temperature and resistant to basic liquid can be used, unlike traditional hydrothermal or steam-assisted crystallization, high-pressure vessels like autoclave is mandatory. This will significantly save cost on the synthesis equipment as well as its operation. In addition, this largely reduces the liquid pollution generated in traditional hydrothermal zeolite synthesis, in which a large percentage of alkali, silicates, and aluminates are left in the post-synthesis solution. These unused chemicals not only lower the overall zeolite yield, but also

generate a large amount of waste liquid. With their recovery difficult and costly, this causes severe environmental pollution in zeolite industry. In contrast, our approach has all silicates and aluminates integrated in nanogels during stage I synthesis and carries out crystallization with only solid powders. This even eliminates the requirement for small amount of water that is critical in a different solvent-free synthesis route. [36] It helps increase zeolite yield, and more importantly, produces almost no liquid waste to the environment. Second, neither hard meso-template nor special soft meso-template materials are involved in our approach. This avoids aforementioned challenges for the common carbon or CaCO_3 hard meso-template (i.e., incompatibility of template and precursors) as well as cationic polymer or amphiphilic organosilane based soft meso-templates (i.e., synthesis difficulty for template macromolecule, their availability, and cost). It not only saves significantly the production cost, but also simplifies the synthesis procedures, even when comparing with the post-synthesis treatment methods. Although a structure directing agent (or so-called organic microtemplate), TPAOH, is used, they are encapsulated in nanogels and later produced zeolites during synthesis and are removed during zeolite calcination. Its air pollution concerns from the volatile toxic compounds released from TPAOH calcinations could be further minimized by drastically reducing its dosage during zeolite synthesis, which has been proved feasible for ZSM-5 by other researchers using a low-temperature hydrothermal synthesis or a steam-assisted crystallization process [38, 59]. Nevertheless, the advantages of this solid-state crystallization process could help promote the profit of hierarchical zeolites production and its environment-friendly synthesis.

4. Conclusions

In summary, hierarchical zeolites ZSM-5 is successfully produced in a new two-stage synthesis process with meso-template free assembly and solid-state crystallization. The resulting mesoporous zeolites show excellent hydrothermal stability and superior catalytic performance in reactions like Friedel-Crafts alkylations, lignin depolymerization in supercritical ethanol, and deep hydrogenation of naphthalene, all involve bulky aromatic molecules. Its unique meso-template free synthesis and solid crystallization conditions largely simplify the synthesis routes of zeolites, reduce its production cost, and avoid common liquid pollution issues in zeolite industry. Its superior catalytic performance and economically favourable synthesis route may stimulate further exploration interest for its large-scale production and wide effectiveness to a variety of applications requiring hierarchical zeolites.

Acknowledgments

This work was supported by National Science Foundation under Grant [1130468] and Louisiana Harrelson Family Professorship.

References

- [1] A. Corma, From microporous to mesoporous molecular sieve materials and their use in catalysis. *Chem. Rev.* 97 (1997) 2373-2420.
- [2] M. E. Davis, Ordered porous materials for emerging applications. *Nature* 417 (2002) 813-821.
- [3] A. Corma, State of the art and future challenges of zeolites as catalysts. *J. Catal.* 216 (2003) 298-312.
- [4] Y. Y. Sun, R. Prins, Hydrodesulfurization of 4, 6-Dimethyldibenzothiophene over Noble Metals Supported on Mesoporous Zeolites. *Angew. Chem. Int. Ed.* 47 (2008) 8478-8481.
- [5] M. Bejblova, D. Prochazkova, J. Čejka, Acylation reactions over zeolites and mesoporous catalysts. *ChemSusChem* 2 (2009) 486-499.
- [6] Y. N. Li, S. L. Liu, Z. K. Zhang, S. J. Me, X. X. Zhu, L. Y. Xu, Aromatization and isomerization of 1-hexene over alkali-treated HZSM-5 zeolites: Improved reaction stability. *Appl. Catal. A* 338 (2008) 100-113.
- [7] Y. Wang, Y. Fang, T. He, H. Hu, J. Wu, Hydrodeoxygenation of dibenzofuran over noble metal supported on mesoporous zeolite. *Catal. Commun.* 12 (2011) 1201-1205.
- [8] T. He, Y. Wang, P. Miao, J. Li, J. Wu, Y. Fang, Hydrogenation of naphthalene over noble metal supported on mesoporous zeolite in the absence and presence of sulfur. *Fuel* 106 (2013) 365-371.
- [9] Y. Wang, T. He, K. Liu, J. Wu, Y. Fang, From biomass to advanced bio-fuel by catalytic pyrolysis/hydro-processing: hydrodeoxygenation of bio-oil derived from biomass catalytic pyrolysis. *Bioresour. Technol.* 108 (2012) 280-284.
- [10] J. Jiang, J. Yu, A. Corma, Extra-Large-Pore Zeolites: Bridging the Gap between Micro and Mesoporous Structures. *Angew. Chem. Int. Ed.* 49 (2010) 3120-3145.
- [11] L. Chen, X. Li, J.C. Rooke, Y. Zhang, X. Yang, Y. Tang, F. Xiao, B. Su, Hierarchically structured zeolites: synthesis, mass transport properties and applications. *J. Mater. Chem.* 22 (2012) 17381-17403.
- [12] Y. Wang, J. Wu, S. Wang, Hydrodeoxygenation of bio-oil over Pt-based supported catalysts: importance of mesopores and acidity of the support to compounds with different oxygen contents. *RSC Adv.* 3 (2013) 12635-12640.
- [13] C. Herrmann, J. Haas, F. Fetting, Effect of the crystal size on the activity of ZSM-5 catalysts in various reactions. *Appl. Catal.* 35 (1987) 299-310.
- [14] Z. Wang, C. Li, H.J. Cho, S. Kung, M.A. Snyder, W. Fan, Direct, single-step synthesis of hierarchical zeolites without secondary templating. *J. Mater. Chem. A* 3 (2015) 1298-1305.
- [15] H. Wang, Z. Wang, L. Huang, A. Mitra, B. Holmberg, Y. Yan, High-surface-area zeolitic silica with mesoporosity. *J. Mater. Chem.* 11 (2001) 2307-2310.

- [16] P. Behrens, Mesoporous inorganic solids. *Adv. Mater.* 5 (1993) 127-132.
- [17] T. Wakihara, K. Sato, S. Inagaki, J. Tatami, K. Komeya, T. Meguro, Y. Kubota, Fabrication of fine zeolite with improved catalytic properties by bead milling and alkali treatment. *ACS Applied Materials & Interfaces* 2 (2010) 2715-2718.
- [18] Y. Wang, K. Liu, T. He, J. Wu, Y. Fang, Zeolite with trimodal porosity by desilication of zeolite nanocrystals aggregate. *J. Solid State Chem.* 194 (2012) 416-421.
- [19] C. Ju, Y. Wang, Y. Huang, Y. Fang, Design of mesoporous KA zeolite supported sulfur-tolerant noble metal catalyst for naphthalene hydrogenation. *Fuel* 154 (2015) 80-87.
- [20] J. Jiang, J. L. Jorda, J. Yu, L. A. Baumes, E. Mugnaioli, M. J. Diaz-Cabanas, U. Kolb, A. Corma, Synthesis and structure determination of the hierarchical meso-microporous zeolite ITQ-43. *Science* 333 (2011) 1131-1134.
- [21] Z. Yang, Y. Xia, R. Mokaya. Zeolite ZSM-5 with unique supermicropores synthesized using mesoporous carbon as a template. *Adv. Mater.* 16 (2004) 727-732.
- [22] J.E. Schmidt, D. Xie, M.E. Davis, Synthesis of the RTH-type layer: the first small-pore, two dimensional layered zeolite precursor. *Chem. Sci.* 6 (2015) 5955-5963.
- [23] W. Fan, M. A. Snyder, S. Kumar, P.-S. Lee, W. C. Yoo, A. V. McCormick, R. L. Penn, A. Stein, M. Tsapatsis, Hierarchical Nanofabrication of Microporous Crystals with Ordered Mesoporosity. *Nat. Mater.* 7 (2008) 984-991.
- [24] H. Wang, T. J. Pinnavaia, MFI zeolite with small and uniform intracrystal mesopores. *Angew. Chem. Int. Ed.* 45 (2006) 7603-7606.
- [25] S. Du, F. Li, Q. Sun, N. Wang, M. Jia, J. Yu, A green surfactant-assisted synthesis of hierarchical TS-1 zeolites with excellent catalytic properties for oxidative desulfurization. *Chem. Commun.* 52 (2016) 3368-3371.
- [26] M. Choi, D.-H. Lee, K. Na, B.-W. Yu, R. Ryoo, High Catalytic Activity of Palladium (II)-Exchanged Mesoporous Sodalite and NaA Zeolite for Bulky Aryl Coupling Reactions: Reusability under Aerobic Conditions. *Angew. Chem. Int. Ed.* 48 (2009) 3673-3676.
- [27] L. Emdadi, Y. WU, G. Zhu, C.-C. Chang, W. Fan, T. Pham, R. F. Lobo, D. Liu, Dual template synthesis of meso-and microporous MFI zeolite nanosheet assemblies with tailored activity in catalytic reactions. *Chem. Mater.* 26 (2014) 1345-1355.
- [28] B. Li, Z. Hu, B.o Kong, J. Wang, W. Li, Z. Sun, X. Qian, Y. Yang, W. Shen, H. Xu, D. Zhao, Hierarchically tetramodal-porous zeolite ZSM-5 monoliths with template-free-derived intracrystalline mesopores. *Chem. Sci.* 5 (2014) 1565-1573.
- [29] M. Choi, R. Srivastava, R. Ryoo, Organosilane surfactant-directed synthesis of mesoporous aluminophosphates constructed with crystalline microporous frameworks. *Chem. Commun.* 42 (2006) 4380-4382.

- [30] K. Na, M. Choi, W. Park, Y. Sakamoto, O. Terasaki, R. Ryoo, Pillared MFI Zeolite Nanosheets of a Single-Unit-Cell Thickness. *J. Am. Chem. Soc.* 132 (2010) 4169-4177.
- [31] G. A. Ozin, A. Kuperman, A. Stein, Advanced zeolite materials science. *Adv. Mater.* 1 (1989) 69-86.
- [32] A. Sakthivel, S. Huang, W. Chen, Z. Lan, K. Chen, T. Kim, R. Ryoo, A. S. Chiang, S. Liu, Replication of mesoporous aluminosilicate molecular sieves (RMMs) with zeolite framework from mesoporous carbons (CMKs). *Chem. Mater.* 16 (2004) 3168-3175.
- [33] D. P. Serrano, J. M. Escola, P. Pizarro, Synthesis strategies in the search for hierarchical zeolites. *Chem. Soc. Rev.* 42 (2013) 4004-4035.
- [34] D. Verboekend, J. Pérez-Ramírez, Towards a sustainable manufacture of hierarchical zeolites. *ChemSusChem* 7 (2014) 753-764.
- [35] R. Xu, W. Pang, J. Yu, Q. Huo, J. Chen, in *Chemistry of zeolites and related porous materials: synthesis and structure*, John Wiley & Sons (Asia) Pte Ltd, 2007, pp. 117-189.
- [36] L. Ren, Q. Wu, C. Yang, L. Zhu, C. Li, P. Zhang, H. Zhang, X. Meng, F. Xiao, Solvent-free synthesis of zeolites from solid raw materials. *J. Am. Chem. Soc.* 134 (2012) 15173-15176.
- [37] G. W. Huber, A. Corma, Synergies between bio- and oil refineries for the production of fuels from biomass, *Angew. Chem. Int. Ed.* 46 (2007) 7184-7201.
- [38] M. Rilyanti, R. R. Mukti, G. T. M. Kadja, M. O. Ogura, H. Nur, E.-P. Ng, Ismunandar, On the drastic reduction of organic structure directing agent in the steam-assisted crystallization of zeolite with hierarchical porosity, *Microporous and Mesoporous Materials*, 230 (2016) 30-38.
- [39] Y. Zhang, K. Zhu, X. Zhou, W. Yuan, Synthesis of hierarchically porous ZSM-5 zeolites by steam-assisted crystallization of dry gels silanized with short-chain organosilanes, *New Journal of Chemistry*, 38 (2014) 5808-5816.
- [40] J. Garcia-Martinez, C. Xiao, K. A. Cychosz, K. Li, W. Wan, X. Zou, M. Thommes, Evidence of intracrystalline mesostructured porosity in zeolites by advanced gas sorption, electron tomography and rotation electron diffraction, *ChemCatChem* 6 (2014) 3110-3115.
- [41] M. Thommes, K. Kaneko, A.V. Neimark, J. P. Oliver, F. Rodriguez-Reinoso, J. Rouquerol, K. S.W. Sing, Physiorption of gas, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report), *Pure Appl. Chem.* 87 (2015) 1051-1069.
- [42] T. M. Davis, T. O. Drews, H. Ramanan, C. He, J. Dong, H. Schnablegger, M.A. Katsoulakis, E. Kokkoli, A. V. McCormick, R. L. Penn, M., Tsapatsis, Mechanistic principles of nanoparticle evolution to zeolite crystals. *Nat. Mater.* 5 (2006) 400-408.
- [43] S. Kumar, Z. Wang, R. Lee Penn, M. Tsapatsis, A structural resolution cryo-TEM study of the early stages of MFI growth. *J. Am. Chem. Soc.* 130 (2008) 17284-17286.
- [44] E. Beniash, J. Aizenberg, L. Addadi, S. Weiner, Amorphous calcium carbonate transforms into calcite during sea urchin larval spicule growth. *Proc. R. Soc. B-Biol. Sci.* 264 (1997) 461-465.

- [45] Y. U. T. Gong, C. E. Killian, I. C. Olson, N. P. Appathural, A. L. Amasino, M. C. Martin, L. J. Holt, F. H. Wilt, P. U. P. A. Gilbert, Phase transitions in biogenic amorphous calcium carbonate. *Proc. Natl. Acad. Sci. U.S.A.* 109 (2012) 6088-6093.
- [46] A. J. Ragauskas, G. T. Beckham, M.J. Biddy, R. Chandra, F. Chen, M. F. Davis, B. H. Davison, R. A. Dixon, P. Gilna, M. Keller, P. Langan, Lignin valorization: improving lignin processing in the biorefinery. *Science* 344 (2014) 1246843.
- [47] A. K. Deepa, P. L. Dhepe, Lignin depolymerization into aromatic monomers over solid acid catalysts. *ACS Catalysis* 5 (2014) 365-379.
- [48] K. Staerk, N. Taccardi, A. Boesmann, P. Wasserscheid, Oxidative depolymerization of lignin in ionic liquids. *ChemSusChem* 3 (2010) 719-723.
- [49] Q. Song, F. Wang, J. Cai, Y. Wang, J. Zhang, W. Yu, J. Xu, Lignin depolymerization (LDP) in alcohol over nickel-based catalysts via a fragmentation–hydrogenolysis process. *Energy Environ. Sci.* 6 (2013) 994-1007.
- [50] R. Ma, W. Hao, X. Ma, Y. Tian, Y. Li, Catalytic Ethanolysis of Kraft Lignin into High-Value Small-Molecular Chemicals over a Nanostructured α -Molybdenum Carbide Catalyst. *Angew. Chem. Int. Ed.* 53 (2014) 7310-7315.
- [51] A. Stanislaus, B. H. Cooper, Aromatic hydrogenation catalysis: a review. *Catal Rev Sci Eng* 36 (1994) 75–123.
- [52] T. Tang, C. Yin, L. Wang, Y. Ji, F. Xiao, Good sulfur tolerance of a mesoporous Beta zeolite-supported palladium catalyst in the deep hydrogenation of aromatics. *J Catal* 257 (2008) 125–133.
- [53] H. H. Schobert, Development of an advanced, thermally stable, coal-based jet fuel. *Fuel Process Technol* 89 (2008) 364–378.
- [54] J. Park, J. Lee, J. Miyawaki, Y. Kim, S. Yoon, I. Mochida, Hydro-conversion of 1-methyl naphthalene into (alkyl)benzenes over alumina-coated USY zeolite-supported NiMoS catalysts. *Fuel* 90 (2011) 182–189.
- [55] H. Yasuda, T. Sato, Y. Yoshimura, Influence of the acidity of USY zeolite on the sulfur tolerance of Pd–Pt catalysts for aromatic hydrogenation, *Catal Today* 50 (1999) 63–71.
- [56] B. Pawelec, R. Mariscal, R. M. Navarro, S. Van Bokhorst, S. Rojas, J. L. Fierro, Hydrogenation of aromatics over supported Pt–Pd catalysts. *Appl Catal A* 225 (2002) 223–237.
- [57] A. H. Janssen, A. J. Koster, K. D. Jong, On the shape of the mesopores in zeolite Y: a three-dimensional transmission electron microscopy study combined with texture analysis. *J Phys Chem B* 106 (2002) 11905–11909.
- [58] A. Corma, A. Martínez, V. Martínez-Soria, Catalytic performance of the new delaminated ITQ-2 zeolite for mild hydrocracking and aromatic hydrogenation processes. *J Catal* 200 (2001) 259–269.
- [59] G. T. M. Kadja, R. R. Mukti, Z. Liu, M. Rilyanti, Ismunandar, I. N. Marsih, M. Ogura, T. Wakihara, T. Okubo, Mesopore-free synthesis of hierarchically porous ZSM-5 below 100°C, *Microporous Mesoporous Materials*, 226 (2016) 344-352.

Graphical Abstract

Hierarchical zeolites with MFI structure are synthesized by solid-state crystallization of aluminosilicate nanogels without the involvement of meso-template. After transforming within nanogels using only intrinsic water storage, the new formed nanocrystals further joint each other at edges into monolithic zeolites to create many inter-crystal mesopores. The produced mesoporous ZSM-5 zeolites exhibits superior stability and catalytic performance in benzylation, lignin ethanolysis, and naphthalene hydrogenation.

[60]