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

Bo Wang and Prabir K. Dutta*

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

* Author to whom correspondence should be addressed (dutta@chemistry.ohio-state.edu)

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 m²/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 m²/g. The pore size distribution varied with sample preparation and ranged from 2-100 nm. These samples were characterized by N₂ 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.

Keywords

Faujasite • Hierarchical • Template-free • Nanosheets • Catalysis

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^+ and Zn^{2+} 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 Na_2O : 1 Al_2O_3 : 6.4 SiO_2 : 483.9 H_2O 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_2 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

Chemicals

Aluminum hydroxide ($\text{Al}(\text{OH})_3$, 76.5%) was purchased from Alfa Aesar. Ludox SM-30 colloidal silica (SiO_2 , 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_2O used in this study was purified by a Millipore ultrapure water system.

Zeolite Synthesis Procedure

Zeolite synthesis gel preparation follows the method reported in literature[25], with composition of 8.3 Na₂O: 1 Al₂O₃: 6.4 SiO₂: 483.9 H₂O. Al(OH)₃ (2.208 g) and 7.29 g NaOH were completely dissolved in 85.24 g H₂O, 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 hours 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 Figure S1, a round bottom flask connected with a constant pressure funnel and condenser at the top. RG was prepared by heating AG for 1 hour 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 H₂O was removed from ~ 100 mL of the gel in an hour, resulting in CG₂₀, CG₄₀ and CG₆₀. RG and CG were then heated under different conditions. Synthesized zeolite powder product was washed with deionized water by repetitive centrifugation (2,500 rpm) until pH 7 and freeze dried.

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 CG₄₀, 40 mL of water was removed, and content of other chemicals were still the same. There was 2.208 g Al(OH)₃, 7.29 g NaOH and 4.16 g SiO₂ in 60 mL of CG₄₀. For a batch of 20 mL CG₄₀ which contains 4.6 g (SiO₂ + Al₂O₃ + NaOH), 1.6 g of zeolite product was obtained. So, the yield of zeolite was 35%. In a batch of 20

mL CG₄₀, 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).

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 5-7°) 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.

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

In equation (1), x is the relative mass of FAU and EMT; I is peak intensity obtained from XRD peak deconvolution (Figure S7); Ir 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 ²⁹Si 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.

N₂ Adsorption Isothermal Experiments and Calculations

Nova 2200e BET Surface Area Analyzer from Quantachrome was employed to collect the N₂ adsorption isotherm of zeolite samples. Surface area and pore size distribution was calculated with Brunauer–Emmett–Teller (BET) and Barrett-Joyner-Halenda (BJH) theories. T-plot method was applied in relative pressure (p/p_0) range of 0.21 to 0.42 to calculate external surface area and micro pore volume.

Before N₂ adsorption/desorption isotherm collection, zeolite samples were outgassed under vacuum at 400 °C for 24 hours. 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 $1/[W(p/p_0)-1]$ and p/p_0 is expected in p/p_0 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_0 0.25-0.6. On the t-plot, a linear range was picked between 0.25-0.6 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.

1,3,5-TIPB dealkylation

Catalytic performance of zeolites were studied with 1,3,5-TIPB dealkylation reaction. The acidic FAU was prepared by ion-exchanging zeolite samples with 0.2 M NH_4Cl solution for 1 h at 25 °C, washing and calcination at 500 °C to eliminate the NH_3 . 10 mg of acidic zeolite was placed in a gas phase downflow reactor catalysis setup shown in Figure S2. Initially, zeolite samples were dehydrated in dry air flow (50 mL/min) at 100 °C for 2 hours followed by 500 °C for 2 hours. Subsequently, dry nitrogen flow was applied (50 mL/min) and reactor temperature was dropped to the desired catalysis reaction temperature. Catalytic products as well as reactant samples were collected by bubbling through 40 mL dichloromethane and analyzed quantitatively with a Thermo DSQ II GC-MS system. Calibration curves of anticipated catalysis products (1,3-diisopropylbenzene, 1,4-diisopropylbenzene, cumene and benzene) are displayed in Figure S3.

Catalysis product calculation was performed as follows. Peak areas of reactant and product samples were obtained from the GC. Based on the calibration curves, concentrations of each component in the dichloromethane solution was calculated. Yield of each anticipated products was calculated by weight percent over reactant (1,3,5- TIPB). Conversion was calculated by 1 minus the weight percent of unreacted 1,3,5- TIPB in product samples. Other components were calculated by subtracting 1 with all recognized components, 1,3,5- TIPB, 1,3-diisopropylbenzene, 1,4-diisopropylbenzene, cumene and benzene, and the rest was considered propylene, coke and unrecognized products.

3. Results

3.1. Synthesis Strategy

The basic synthesis strategy of this study is outlined in Schemes 1 and 2. It involved the formation of

- An opaque aluminosilicate gel by aging the composition 8.3 Na₂O: 1 Al₂O₃: 6.4 SiO₂: 483.9 H₂O for 4 hours at room temperature, resulting in a material labeled the aged gel (AG).
- RG (refluxed gel) was prepared by heating AG under reflux for 1 hour in a round bottom flask connected with condenser (Figure S1).
- CG (concentrated gel) was prepared from AG by removing 20, 40 and 60 % of the H₂O from the reaction composition during reflux, and labeled as CG₂₀, CG₄₀ and CG₆₀, respectively.

These gels had significant water still left in the composition and used as such for further experiments. As shown in Scheme 2, the CG gels were aged for different times at different temperatures until crystallization was complete (as monitored by XRD). A heat treatment step at 100 °C for 2 hours was carried out on all samples to ensure complete crystallization, and in most cases resulted in improvement of the specific surface area. Samples in this study were named with the following rule, “gel type”-“aging temperature and time”-“heating at 100°C for 2 hours”.

3.2. Synthesis Results

3.2.1. Direct heating of gels

Figure 1a shows the TEM image of the as-synthesized RG, it has a coral-like structure. CG₄₀ has a similar coral-like morphology to RG, but with bright spots appearing on CG₄₀ as marked by arrows in Figure 1b (insert is a higher magnification TEM image). RG and CG₄₀ were both amorphous as characterized by XRD patterns (Figure S4).

RG and CG₄₀ were sealed in a Teflon bottle and heated at 100 °C for 2 hours. XRD patterns are shown in Figure 2a, only FAU peaks are observed. Particle morphologies of RG-100C and CG₄₀-100C are shown in Figure 2b and c. RG-100C particles are single crystals with well-defined octahedral morphology, whereas CG₄₀ has similar overall morphology, but with clear steps on these surfaces. The N₂ adsorption/desorption isotherm of RG-100C shown in Figure S5 is that of a Type I (microporous) material, whereas a slight hysteresis was observed with CG₄₀. Table 1 lists the equivalent specific surface area (measured by BET method, which includes the surface area of mesopores, micropores and the external surface), the external surface area (measured by t-plot method) and micropore volume (measured by t-plot method).

3.2.2. Aging of the gels followed by heat treatment

CG₂₀

The CG₂₀ sample was aged at 50 °C. Figure 3 shows the XRD and TEM images of CG₂₀-50C4d-100C sample. The choice of the aging time of 4 days at 50 °C was based on the time that crystallization appeared to be complete, based on the XRD. The XRD at earlier times are not being shown except for the CG₄₀ sample, which is presented below. Figure S6 is the adsorption-desorption isotherm for CG₂₀-50C-4d100C, and appears to be a Type I isotherm, with a slight hysteresis (external surface area = 63 m²/g).

CG₄₀

Four sets of samples were prepared with the CG₄₀ (Scheme 2), primarily involving aging at different temperatures. For the material aged at 2 °C, it took 247 days for crystallization to be complete. With the 25 °C aging, it took 72 days; at 50 °C, it took four days; and at 75 °C, it took

3 days. All samples after the aging step were heated at 100 °C for 2 hours to ensure complete crystallization (Scheme 2).

Figure 4 shows the XRD of the four CG₄₀ samples, and besides FAU, there was clear indication that EMT was also being formed (shoulder at $2\Theta = 5.8^\circ$). In order to estimate the ratio of FAU to EMT, high resolution XRD was obtained in the 2Θ region between $5-7^\circ$ (data shown as inserts in Figure 4). The FAU/EMT ratio was obtained by curve fitting with $2\Theta = 5.8^\circ$ and 6.1° for EMT and FAU, respectively. Relative amount of FAU and EMT were calculated as in equation (1) (an example is shown in Figure S7). Table 2 shows these ratios, and EMT amounts increase at the lower temperatures of aging.

Figure 5 shows the adsorption isotherms of the four CG₄₀ samples, and it is clear that the isotherms are a combination of Type I (microporous) and Type IV (mesoporous) adsorption. The external surface area is listed in Table 1. It appears that as the EMT amount is increasing, the mesoporosity is also exhibiting an increase (e.g. for CG₄₀-2C247d-100C, EMT= 16%; $S_{\text{ext}} = 249 \text{ m}^2/\text{g}$).

Figure 6 shows the pore size distribution calculated by the BJH method, and Figure S8 shows the pore size distribution calculated using NLDFT. They both indicate the same trends. As the aging temperature was lowered, there was a broader distribution of the pore size.

Figure 7 shows the TEM of the four samples. The sizes estimated for CG₄₀-2C247d-100C, CG₄₀-25C72d-100C, CG₄₀-50C4d-100C, CG₄₀-75C3d-100C are 51, 105, 450 and 850 nm, respectively, indicating that particle size was decreasing as the temperature of aging was lowered. The thicknesses of the sheets estimated from the TEM images are ~10 nm for the CG₄₀-2C247d-100C, 12 nm for CG₄₀-25C72d-100C, 48 nm for CG₄₀-50C4d-100C, and 88 nm for CG₄₀-75C3d-100C, respectively (Figure S9 shows the TEM's from which the sheet thickness was estimated).

CG₆₀

The *CG₆₀* took longer time to crystallize at 50 °C, about 10 days. Figure 8 shows the XRD, TEM, adsorption isotherms and pore size distributions. Of all the samples examined, this material has the largest amount of EMT (92%), and the smallest particle size (48 nm). It also has the largest external surface area (259 m²/g), along with a broad pore size distribution (2-30 nm).

3.3. Detailed Studies on *CG₄₀* System

In order to gain more insight on the synthesis process, we investigated the *CG₄₀*-50C system in more detail.

3.3.1. Dynamics of crystallization

The evolution of crystals in the *CG₄₀* system as it was aged at 50 °C was examined. The specific surface area and the external surface area of *CG₄₀* increases continually with time (Table 3). In particular, *S_{ext}* changes from 48 m²/g (*CG₄₀*-50C0d), 51 m²/g (*CG₄₀*-50C1d), 64 m²/g (*CG₄₀*-50C2d), 111 m²/g (*CG₄₀*-50C3d) and, 155 m²/g (*CG₄₀*-50C4d, 4 days). XRD indicates that *CG* starts to crystallize after 3 days, as shown in Figure 9a. Morphologies of *CG₄₀* heated at 50 °C for 1 to 4 days were characterized with SEM (Figure 9b) and TEM (figure 9c). From day 1 to day 3, loose coral-like structure shrinks into a core. Then, ~ 50 nm thick FAU nanosheets start to extend out from the core from day 3 to day 4. The nanosheets at the outer surface have sharp edges.

Yield of *CG₄₀*-50C4d-100C was 35%, with 98% of the Al being incorporated into the final product. Si/Al ratios of *CG₄₀*-50C4d-100C was 1.43 (Table S1, from ²⁹SiSSNMR spectra),

comparable to Si/Al of zeolite synthesized via conventional hydrothermal methods from the same composition [25].

3.3.2. High resolution TEM

Figure 10 shows the high-resolution TEM micrographs of CG₄₀-50C4d-100C. Figure 10a shows that the particles are about 400-500 nm in size. A FIB-SEM vertical cut through the particle results in Figure 10b, showing aggregates of nanosheets (there was some sample damage in FIB cutting process). Figure 10c, a higher resolution TEM image shows that the particle is made up of a collection of nanosheets. The larger nanosheets that extend out from the core appear fully crystalline, as evidenced by the TEM images in Figure 10de (insert shows discrete spots in Fast Fourier Transform (FFT) indicating single crystalline nature of each nanosheet). Figure 10f shows the presence of FAU-EMT intergrowths in the nanosheets.

3.3.3. Thermal/hydrothermal treatment

Morphology and crystallinity of CG₄₀-50C4d-100C after heat treatment at 600 °C for 24 hours was unchanged (XRD in Figure 11a), SEM and TEM images (Figure S10), with a specific surface area of 834 m²/g and external surface area of 183 m²/g, indicating the thermal stability of the mesoporous structure. If the acidic form (NH₄⁺ exchanged) was heated at 550 °C in the presence of steam for 24 hours, there was considerable degradation, as evidenced in the XRD (Figure 11b), and BET surface area of 346 m²/g and external surface area of 126 m²/g.

3.4. Catalysis Studies

The influence of the higher external surface area in CG₄₀-50C4d-100C on the dealkylation of 1,3,5-TIPB (9.5 Å, cannot penetrate the 7.4 Å zeolite pores) was compared with the microporous-only RG-100C sample. All samples used the acid forms of the zeolite, prepared via NH₄⁺ exchange and calcination, and carried out between 200-500 °C (without steam). Crystallinity and morphology of CG-50C4d-100C catalysts were maintained and confirmed by XRD patterns and TEM image in Figure S11. Si/Al ratio of acidic CG-50C4d-100C and RG-100C are shown in table S1. Table S2 details the product distributions. The products of the reaction at 200-400 °C are shown in Figure 12, and the trends for each class of material were similar. The overall conversion of 1,3,5 TIPB at 400 °C were higher for CG₄₀-50C4d-100C (95%) as compared to RG-100C (68%), and, the product distributions were very distinct with the two materials. For CG₄₀-50C4d-100C, dialkylated products, cumene and benzene is produced, whereas with RG-100C, there is much lower amounts of the dialkylated products, considerable isomerization of 1,3 to 1,4 TIPB, and coke is formed, as evidenced by the appearance of a brown catalyst after the reaction (Figure S12).

4. Discussion

The important observation in this paper is the generation of mesoporosity during the synthesis of microporous zeolites. This discussion focuses on the types of mesopores that develop, and the synthesis conditions that promote them.

The starting gel composition 8.3 Na₂O 1Al₂O₃ 6.4SiO₂ 483H₂O under typical hydrothermal conditions leads to well-defined microporous faujasitic zeolite with Si/Al = 1.5[25]. We have modified the treatment of this gel in ways outlined in schemes 1 and 2. RG was the solid isolated after refluxing the gel for an hour at 100 °C, and was still amorphous. CG was

prepared by permanently removing a certain portion of the water from the gel via distillation, and our focus here is on 20, 40 and 60% removal of the water (CG₂₀, CG₄₀, CG₆₀, respectively). All three CG samples were amorphous, and we have studied the CG₄₀ in most detail. Even though CG₄₀ was amorphous by XRD, the electron micrograph (Figure 1b) shows bright spots. Such bright spots in the electron micrograph of an aluminosilicate gel has been related to trapped liquids in a study on EMT [27]. Since such spots were not observed in the case of RG, we propose an alternative explanation, that these bright spots are indicative of small crystalline regions (could not be imaged by TEM at high resolution because of beam damage). The process of removing the water results in concentration of the gel and promotes nucleation. Both RG and CG₄₀ when heated at 100 °C for 2h results in well crystallized FAU with no mesoporosity.

The CG₂₀ sample crystallizes at 50 °C within 4 days. Only FAU crystals were observed, with minimal mesoporosity, and not investigated any further. Mesoporosity developed in the CG₄₀ and CG₆₀ samples, the extent depending on the aging temperature and time (Table 1). The size distribution of the mesopores also was influenced by these factors. The other important observation was the appearance of EMT, along with FAU (Table 2). As we describe below, these observations are interrelated.

For the CG₄₀ samples, low temperatures promoted EMT, with the aging at 2 °C for 247 days leading to the maximum amount of EMT (16%). With CG₆₀, even though the gel was more concentrated, it took 10 days for crystallization at 50 °C (as compared to 4 days for CG₂₀ and CG₄₀) and led to formation of mostly EMT (92%). Both the CG₄₀-2C and the CG₆₀-50C samples also produce the smallest crystals (48, 51 nm, Figure 7a, 8b, respectively), and the highest external surface area (249 and 259 m²/g, respectively). The nutrient transport during crystallization was slowed down either via decreasing temperature (CG₄₀-2C) or increasing gel

viscosity (CG₆₀-50C). As the crystal growth is slowed down by limiting mass transport, there was higher amounts of EMT formed (Table 2).

Previous studies have noted that limiting mass transport influences the mesoporosity. Vapor phase synthesis of ZSM-5 from an aluminosilicate gel resulted in mesopores between the nanocrystals[28]. Using a steam assisted conversion of a dense gel, 20 nm crystals of zeolite beta assembled to form a mesoporous structure [29]. Steam assisted transformation of a silica gel to hierarchical silicalite has also been reported[30].

We suggest that the high S_{ext} ($> 200 \text{ m}^2/\text{g}$) observed for the CG₄₀-2C247d-100c and CG₆₀-50C10d-100c samples arise from the extensively nucleated nanocrystals in the gel that connect to form the mesoporosity. The pore size distribution of the mesopores was also broad (2 -100 nm for CG₄₀-2C247d-100C and 2-30 nm for CG₆₀-50C10d-100C). Previous studies have shown that nanoparticles of ZSM-5 can aggregate to generate mesoporosity[31–33]. Nanocrystals of zeolite T aggregate with mesoporosity resulting from the interstitial voids [34]. Nano FAU crystals are also reported to pack in ways to generate mesoporosity[10].

On the other hand, the CG₄₀-50C samples were quite distinct. The particle size was larger, between 200 -500 nm, and each particle appears to be a collection of sheets with tens of nanometer thickness (Figure S9). These nanosheets are the result of FAU-EMT intergrowths (Figure 10f), and has been noted in several studies with different synthesis methods. Hierarchical FAU have been reported using organosilane surfactants[17–23]. Because [111] faces are the flat and slow growing faces of FAU[35], organosilane molecules bond to -OH groups on the zeolite framework and block the crystal growth perpendicular to [111] faces, so that nanosheets form [23]. In these nanosheets, mixed phase of FAU and EMT were observed [23]. With a Zn^{2+} and Li^+ aluminosilicate gel, similar layer-like morphologies arising from FAU/EMT intergrowths

was also observed [24]. The materials generated with the use of $\text{Zn}^{2+}/\text{Li}^{+}$ in a completely inorganic composition are most similar to CG₄₀-50C4d-100C, though the latter tends to be smaller in size by an order of magnitude (< 500 nm). The materials made with $\text{Zn}^{2+}/\text{Li}^{+}$ are also quite distinct in morphology from the nanosized CG₄₀2C and CG₆₀50C. Zinc salts are known to promote twinning [24] in MFI crystals, and Li^{+} also promotes twinning in EMT/ZSM-3 formation [36]. In a clear sol sodium aluminosilicate composition, FAU/EMT intergrowths were observed, and lead to mesoporosity, and cryo-TEM shows the coexistence of these crystals at early times of synthesis [37]. In the present study with only Na^{+} in a highly viscous gel composition, the mechanism was possibly different from the clear sol synthesis, since FAU was the preferred form with the present composition, and only by controlling kinetic aspects (slowing down the mass transport), the formation of FAU/EMT intergrowths was promoted.

The sheets in CG₄₀-50C4d-100C were about ~ 50 nm in width and tightly bonded to each other to generate a single particle. This is obvious from the SEM of the FIB cut along a vertical cross-section of the particle (Figure 10b). In addition, these nanosheets are held together firmly and are not broken apart by sonication (see TEM image in Figure S13). It is the packing and intergrowths of the nanosheets that generate the mesoporosity, as proposed in earlier studies[28]. The pore size distribution CG₄₀-50C4d-100C was considerably narrower (2-20 nm) as compared to the mesoporosity generated by the packing of nanoparticles in CG₄₀-2C and CG₆₀-50C samples (Figures 6c, 6a, 8d).

In all samples with mesoporosity, the micropore volume of $0.22\text{-}0.26\text{ cm}^3/\text{g}$ was maintained, with a slight decrease in micropore volume for the smallest crystals, and this decrease in micropore volume with size has also been noted for zeolite beta[38].

Though the thermal stability of CG₄₀-50C4d-100C sample was excellent, the hydrothermal stability of the acid form of the sample in the presence of steam was poor (though it was stable in the absence of steam). This is not surprising considering the Si/Al ratio is 1.5 for this sample. The surface area measurements indicate collapse of both the micropores and mesopores with high temperature steam (Figure 11, Table 1).

CG samples were prepared by distilling water out of the reaction mixture during reflux, and two control experiments provide mechanistic information. The first issue is the property of a gel composition that has water removed right from the start, and its comparison with CG₄₀. The following gel composition 8.3 Na₂O 1Al₂O₃ 6.4SiO₂ 290 H₂O was made, aged for 4 hours and then the gel was refluxed for an hour, followed by aging of the gel at 50 °C (labeled as CRG₄₀-50C4d-100C). With this material, the crystallization was complete in one day versus the four days it took for the identical CG₄₀-50C4d-100C composition to crystallize. The material was primarily FAU with minor EMT as measured by XRD (Figure 13a). From the TEM image (Figure 13b), it appears that the sheets were thicker (85 nm), the particle size was significantly larger (> 600 nm, compare Figure 13b with Figure 7c), and the mesoporosity was lower ($S_{\text{ext}} = 112 \text{ m}^2/\text{g}$). This suggests that removal of the water during the reflux results in a different pathway as compared to a more concentrated gel right from the start, both of the same composition.

The second issue is the effect of the rate of water removal from the gel on the crystallization pathway. Figure 14abc shows that removing 40% water in 30 min (as compared to 1 hour) results in more EMT (14%) with comparable external surface area ($162 \text{ m}^2/\text{g}$) and similar crystal growth dynamics to CG₄₀-50C4d-100C. Slower removal of the water (2 hr) results in rapid crystallization of FAU with no EMT and no mesoporosity (Figure 14def). Faster removal

of water results in a more viscous gel with lower mass transport that favors EMT. Slower removal also keeps the entire system under reflux conditions longer, directing the system to FAU.

There are several studies in the literature where water was removed from a composition by freeze drying, as compared to distillation as done in the present study. For a zeolite A composition, removal of water by freeze drying from the gel and adding it back did not influence the phase purity or morphology [39]. However, with a clear sol synthesis, freeze drying of an aged gel led to formation of nano FAU crystals, whereas adding the water back led to mixtures of EMT and FAU[10,37].

Thus, factors that change the composition mid-synthesis (freeze-drying or distillation) have different effects on the final products and their morphology. The advantage of removal of water by distillation is that it provides several routes of directing the crystallization process. These include the amount of water removed, as well as the rate of removal of the water, and the temperature of crystallization. These different routes result in materials with very distinct morphologies.

The mesoporosity of the CG₄₀-50C4d-100C sample leads to an altered chemical reactivity of 1,3,5-TIPB as compared to the microporous only sample RG-100C. Cracking of 1,3,5-TIPB has been extensively studied, and the major reaction pathway occurs via consecutive loss of propyl groups to form the dialkylated products, cumene, benzene and propylene, as well as coke[40–43]. The conversions increased as a function of reaction temperatures for both CG₄₀-50C4d-100C and RG-100C samples, though the conversion level was higher for CG₄₀-50C4d-100C (e.g. at 400 °C, the conversion for CG₄₀-50C4d-100C and RG-100C were 95 and 68% respectively, Figure 12 and Table S2). Both CG₄₀-50C4d-100C and RG-100C should have

comparable acidity (similar Si/Al ratio), thus the product distribution is a reflection of the textural properties. In CG₄₀-50C4d-100C, the mesopores provides the reaction site for the first dealkylation step of 1,3,5-TIPB, and the resulting 1,3 DIPB can react within the zeolite micropores to form cumene, and then benzene. With RG-100C, the reaction occurs on the zeolite surface and blocks the pores and results in coking of the sample (Figure S12). With this catalysis study, our goal was to demonstrate that the presence of mesopores leads to a different reactivity in the CG₄₀-50C4d-100C, with comparable results to mesoporous zeolites formed by packing of nanocrystals[10]. Because of the steam degradation shown in Figure 11, these materials will be limited as acid cracking catalysts at high temperatures, but there are definitely possibilities for base catalysis, which are typically done under milder conditions, as has been documented for low Si/Al zeolites, such as zeolites A and X [44].

5. Conclusion

In this paper, we report a synthesis method that involves removal of water from an aluminosilicate gel of composition 8.3 Na₂O: 1 Al₂O₃: 6.4 SiO₂: 483.9 H₂O during reflux. The amounts of water removed varied between 20-60% of the total volume. A CG₄₀50C4d100C sample is defined as removing 40% of the water, maintaining the resulting gel at 50 °C for 4 days, and then heating at 100 °C for two hours (all samples were subjected to the same 100 °C treatment, and typically resulted in slight improvement of surface area). Crystallization pathways of the resulting concentrated gels take various routes depending on the mass transport, which is controlled by temperature or gel viscosity (depending on how much water is removed). Resulting materials in all cases were microporous zeolite crystals with varying degrees of mesoporosity (external surface area ranging from 127-259 m²/g). Removing water while heating the initial gel

enhances both supersaturation and promotes nucleation via the added thermal energy. The final morphology of the crystals was dependent on the viscosity of the gel and the temperature, which influence nutrient transport. The smallest crystallites (~50 nm) were generated under the most constrained mass transport (e.g. CG₄₀-2C247d-100C and CG₆₀-50C10d-100C), and were more EMT rich. In these cases, the mesoporosity was produced via packing of the small crystallites, with a broad pore size distribution (2-100 nm). Another type of material as manifested in the sample CG₄₀-50C4d-100C had narrower mesopore distribution (2-20 nm), and formed by interpenetrating packing of nanosheets (which were FAU-EMT intergrowths). Cracking of 1,3,5-TIPB on the mesopore containing sample CG₄₀-50C4d-100C leads to higher conversion and dialkylated products, cumene and benzene whereas with the non mesoporous FAU zeolite, significant levels of coke were formed.

Acknowledgements

Authors would like to thank Hendrik Colijn for his help collecting TEM images.

This manuscript was based on the PhD thesis of Bo Wang, who did the bulk of the work. The paper was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources

This work was initiated with funding from the U. S. Department of Energy under Award Number DE-FE0007632. However, any opinions, findings, conclusions, or recommendations expressed herein were those of the author(s) and do not necessarily reflect the views of the DOE.

Notes

The authors declare no competing financial interest.

Reference

- [1] S.M. Auerbach, K.A. Carrado, P.K. Dutta, Handbook of Zeolite Science and Technology, in: Handb. Zeolite Sci. Technol., NY: Marcel Dekker, Inc., 2003.
- [2] S. Mitchell, A.B. Pinar, J. Kevlin, P. Crivelli, J. Kärger, J. Pérez-Ramírez, Structural analysis of hierarchically organized zeolites, *Nat. Commun.* 6 (2015) 8633. doi:10.1038/ncomms9633.
- [3] N.D. Shcherban, V.G. Ilyin, Preparation, Physicochemical Properties and Functional Characteristics of Micromesoporous Zeolite Materials, *Theor. Exp. Chem.* 51 (2016) 339–357. doi:10.1007/s11237-016-9435-0.
- [4] W. Schwieger, A.G. Machoke, T. Weissenberger, A. Inayat, T. Selvam, M. Klumpp, A. Inayat, Hierarchy concepts: classification and preparation strategies for zeolite containing materials with hierarchical porosity, *Chem. Soc. Rev.* 45 (2016) 3353–3376. doi:10.1039/C5CS00599J.
- [5] M. Hartmann, A.G. Machoke, W. Schwieger, Catalytic test reactions for the evaluation of hierarchical zeolites, *Chem. Soc. Rev.* 45 (2016) 3313–3330. doi:10.1039/C5CS00935A.
- [6] Y. Wei, T.E. Parmentier, K.P. de Jong, J. Zečević, Tailoring and visualizing the pore architecture of hierarchical zeolites, *Chem. Soc. Rev.* 44 (2015) 7234–7261. doi:10.1039/C5CS00155B.
- [7] K. Zhang, M.L. Ostraat, Innovations in hierarchical zeolite synthesis, *Catal. Today.* 264 (2016) 3–15. doi:10.1016/j.cattod.2015.08.012.
- [8] L.-H. Chen, X.-Y. Li, J.C. Rooke, Y.-H. Zhang, X.-Y. Yang, Y. Tang, F.-S. Xiao, B.-L. Su, Hierarchically structured zeolites: synthesis, mass transport properties and applications, *J. Mater. Chem.* 22 (2012) 17381–17403. doi:10.1039/C2JM31957H.

- [9] D. Verboekend, J. Pérez-Ramírez, Towards a Sustainable Manufacture of Hierarchical Zeolites, *ChemSusChem*. 7 (2014) 753–764. doi:10.1002/cssc.201301313.
- [10] H. Awala, J.-P. Gilson, R. Retoux, P. Boullay, J.-M. Goupil, V. Valtchev, S. Mintova, Template-free nanosized faujasite-type zeolites, *Nat. Mater.* 14 (2015) 447–451. doi:10.1038/nmat4173.
- [11] A. Petushkov, S. Yoon, S.C. Larsen, Synthesis of hierarchical nanocrystalline ZSM-5 with controlled particle size and mesoporosity, *Microporous Mesoporous Mater.* 137 (2011) 92–100. doi:10.1016/j.micromeso.2010.09.001.
- [12] Z. Wan, W. Wu, W. Chen, H. Yang, D. Zhang, Direct Synthesis of Hierarchical ZSM-5 Zeolite and Its Performance in Catalyzing Methanol to Gasoline Conversion, *Ind. Eng. Chem. Res.* 53 (2014) 19471–19478. doi:10.1021/ie5036308.
- [13] X. Zhang, D. Liu, D. Xu, S. Asahina, K.A. Cychosz, K.V. Agrawal, Y.A. Wahedi, A. Bhan, S.A. Hashimi, O. Terasaki, M. Thommes, M. Tsapatsis, Synthesis of Self-Pillared Zeolite Nanosheets by Repetitive Branching, *Science*. 336 (2012) 1684–1687. doi:10.1126/science.1221111.
- [14] M.-C. Silaghi, C. Chizallet, P. Raybaud, Challenges on molecular aspects of dealumination and desilication of zeolites, *Microporous Mesoporous Mater.* 191 (2014) 82–96. doi:10.1016/j.micromeso.2014.02.040.
- [15] I.I. Ivanova, E.E. Knyazeva, Micro–mesoporous materials obtained by zeolite recrystallization: synthesis, characterization and catalytic applications, *Chem. Soc. Rev.* 42 (2013) 3671–3688. doi:10.1039/C2CS35341E.
- [16] D. Verboekend, N. Nuttens, R. Locus, J.V. Aelst, P. Verolme, J.C. Groen, J. Pérez-Ramírez, B.F. Sels, Synthesis, characterisation, and catalytic evaluation of hierarchical faujasite

- zeolites: milestones, challenges, and future directions, *Chem. Soc. Rev.* 45 (2016) 3331–3352. doi:10.1039/C5CS00520E.
- [17] H. Chen, J. Wydra, X. Zhang, P.-S. Lee, Z. Wang, W. Fan, M. Tsapatsis, Hydrothermal Synthesis of Zeolites with Three-Dimensionally Ordered Mesoporous-Imprinted Structure, *J. Am. Chem. Soc.* 133 (2011) 12390–12393. doi:10.1021/ja2046815.
- [18] F.N. Gu, F. Wei, J.Y. Yang, N. Lin, W.G. Lin, Y. Wang, J.H. Zhu, New Strategy to Synthesis of Hierarchical Mesoporous Zeolites, *Chem. Mater.* 22 (2010) 2442–2450. doi:10.1021/cm903785r.
- [19] B. Liu, F. Chen, L. Zheng, J. Ge, H. Xi, Y. Qian, Synthesis and structural properties of hierarchically structured aluminosilicates with zeolite Y (FAU) frameworks, *RSC Adv.* 3 (2013) 15075–15084. doi:10.1039/C3RA41862F.
- [20] J. Jin, C. Peng, J. Wang, H. Liu, X. Gao, H. Liu, C. Xu, Facile Synthesis of Mesoporous Zeolite Y with Improved Catalytic Performance for Heavy Oil Fluid Catalytic Cracking, *Ind. Eng. Chem. Res.* 53 (2014) 3406–3411. doi:10.1021/ie403486x.
- [21] G. Rioland, S. Albrecht, L. Josien, L. Vidal, T.J. Daou, The influence of the nature of organosilane surfactants and their concentration on the formation of hierarchical FAU-type zeolite nanosheets, *New J. Chem.* 39 (2015) 2675–2681. doi:10.1039/C4NJ02137A.
- [22] A. Inayat, I. Knoke, E. Spiecker, W. Schwieger, Assemblies of Mesoporous FAU-Type Zeolite Nanosheets, *Angew. Chem. Int. Ed.* 51 (2012) 1962–1965. doi:10.1002/anie.201105738.
- [23] M. Khaleel, A.J. Wagner, K.A. Mkhoyan, M. Tsapatsis, On the Rotational Intergrowth of Hierarchical FAU/EMT Zeolites, *Angew. Chem. Int. Ed.* 53 (2014) 9456–9461. doi:10.1002/anie.201402024.

- [24] A. Inayat, C. Schneider, W. Schwieger, Organic-free synthesis of layer-like FAU-type zeolites, *Chem. Commun.* 51 (2014) 279–281. doi:10.1039/C4CC07947G.
- [25] M. Severance, B. Wang, K. Ramasubramanian, L. Zhao, W.S.W. Ho, P.K. Dutta, Rapid Crystallization of Faujasitic Zeolites: Mechanism and Application to Zeolite Membrane Growth on Polymer Supports, *Langmuir*. 30 (2014) 6929–6937. doi:10.1021/la5004512.
- [26] C.R. Hubbard, R.L. Snyder, RIR - Measurement and Use in Quantitative XRD, *Powder Diff.* 3 (1988) 74–77. doi:10.1017/S0885715600013257.
- [27] G. Melinte, V. Georgieva, M.-A. Springuel-Huet, A. Nossov, O. Ersen, F. Guenneau, A. Gedeon, A. Palčić, K.N. Bozhilov, C. Pham-Huu, S. Qiu, S. Mintova, V. Valtchev, 3D Study of the Morphology and Dynamics of Zeolite Nucleation, *Chem. – Eur. J.* 21 (2015) 18316–18327. doi:10.1002/chem.201501919.
- [28] B. Li, Z. Hu, B. 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. doi:10.1039/C3SC52779D.
- [29] K. Möller, B. Yilmaz, R.M. Jacubinas, U. Müller, T. Bein, One-Step Synthesis of Hierarchical Zeolite Beta via Network Formation of Uniform Nanocrystals, *J. Am. Chem. Soc.* 133 (2011) 5284–5295. doi:10.1021/ja108698s.
- [30] M. Klumpp, L. Zeng, S.A. Al-Thabaiti, A.P. Weber, W. Schwieger, Building concept inspired by raspberries: From microporous zeolite nanocrystals to hierarchically porous assemblies, *Microporous Mesoporous Mater.* 229 (2016) 155–165. doi:10.1016/j.micromeso.2016.04.012.

- [31] Z. Wang, C. Li, H.J. Cho, S.-C. Kung, M.A. Snyder, W. Fan, Direct, single-step synthesis of hierarchical zeolites without secondary templating, *J. Mater. Chem. A*. 3 (2014) 1298–1305. doi:10.1039/C4TA05031B.
- [32] B.T. Holland, Transformation of mostly amorphous mesoscopic aluminosilicate colloids into high surface area mesoporous ZSM-5, *Microporous Mesoporous Mater.* 89 (2006) 291–299. doi:10.1016/j.micromeso.2005.10.039.
- [33] A.A. Rownaghi, F. Rezaei, J. Hedlund, Uniform mesoporous ZSM-5 single crystals catalyst with high resistance to coke formation for methanol deoxygenation, *Microporous Mesoporous Mater.* 151 (2012) 26–33. doi:10.1016/j.micromeso.2011.11.020.
- [34] X. Yin, Z. Li, S. Wang, N. Chu, J. Yang, J. Wang, Hydrothermal synthesis of hierarchical zeolite T aggregates using tetramethylammonium hydroxide as single template, *Microporous Mesoporous Mater.* 201 (2015) 247–257. doi:10.1016/j.micromeso.2014.09.018.
- [35] T. Wakihara, A. Sugiyama, T. Okubo, Crystal growth of faujasite observed by atomic force microscopy, *Microporous Mesoporous Mater.* 70 (2004) 7–13. doi:10.1016/j.micromeso.2004.02.016.
- [36] G.T. KOKOTAILO, J. CIRIC, Synthesis and Structural Features of Zeolite ZSM-3, in: *Mol. Sieve Zeolites-I*, AMERICAN CHEMICAL SOCIETY, 1974: pp. 109–121. <http://dx.doi.org/10.1021/ba-1971-0101.ch008> (accessed September 20, 2016).
- [37] M. Khaleel, W. Xu, D.A. Lesch, M. Tsapatsis, Combining Pre- and Post-Nucleation Trajectories for the Synthesis of High FAU-Content Faujasite Nanocrystals from Organic-Free Sols, *Chem. Mater.* 28 (2016) 4204–4213. doi:10.1021/acs.chemmater.6b00588.

- [38] M.A. Camblor, A. Corma, S. Valencia, Characterization of nanocrystalline zeolite Beta, *Microporous Mesoporous Mater.* 25 (1998) 59–74. doi:10.1016/S1387-1811(98)00172-3.
- [39] T. Antić Jelić, J. Bronić, M. Hadžija, B. Subotić, I. Marić, Influence of the freeze-drying of hydrogel on the critical processes occurring during crystallization of zeolite A – A new evidence of the gel “memory” effect, *Microporous Mesoporous Mater.* 105 (2007) 65–74. doi:10.1016/j.micromeso.2007.05.023.
- [40] S. Al-Khattaf, H. de Lasa, The role of diffusion in alkyl-benzenes catalytic cracking, *Appl. Catal. Gen.* 226 (2002) 139–153. doi:10.1016/S0926-860X(01)00895-X.
- [41] J.R. García, M. Falco, U. Sedran, Impact of the Desilication Treatment of Y Zeolite on the Catalytic Cracking of Bulky Hydrocarbon Molecules, *Top. Catal.* 59 (2015) 268–277. doi:10.1007/s11244-015-0432-7.
- [42] P. Morales-Pacheco, J.M. Domínguez, L. Bucio, F. Alvarez, U. Sedran, M. Falco, Synthesis of FAU(Y)- and MFI(ZSM5)-nanosized crystallites for catalytic cracking of 1,3,5-triisopropylbenzene, *Catal. Today.* 166 (2011) 25–38. doi:10.1016/j.cattod.2010.07.005.
- [43] J. Qi, Q. Jin, K. Zhao, T. Zhao, Catalytic cracking of 1, 3, 5-triisopropylbenzene over silicoaluminophosphate with hierarchical pore structure, *J. Porous Mater.* 22 (2015) 1021–1032. doi:10.1007/s10934-015-9976-y.
- [44] D. Verboekend, T.C. Keller, S. Mitchell, J. Pérez-Ramírez, Hierarchical FAU- and LTA-Type Zeolites by Post-Synthetic Design: A New Generation of Highly Efficient Base Catalysts, *Adv. Funct. Mater.* 23 (2013) 1923–1934. doi:10.1002/adfm.201202320.

Table 1. N₂ adsorption characteristics of zeolite samples

Sample	S _{BET} m ² /g	S _{Ext} m ² /g	V _{micro} cm ³ /g
RG	48	48	-
RG-100C	760	43	0.27
CG ₄₀	48	48	-
CG ₄₀ -100C	689	88	0.23
CG ₂₀ -50C4d-100C	789	63	0.28
CG ₄₀ -2C247d-100C	801	249	0.22
CG ₄₀ -25C72d-100C	849	199	0.26
CG ₄₀ -50C4d-100C	806	189	0.24
CG ₄₀ -75C3d-100C	756	127	0.24
CG ₆₀ -50C10d-100C	812	259	0.22
CRG ₄₀ -50C1d-100C	802	112	0.27
CG ₄₀ -0.5h-50C4d-100C	811	162	0.25
CG ₄₀ -2h-50C1d-100C	791	45	0.28
Na ⁺ exchanged thermal stability CG ₄₀ -50C4d-100C	834	183	0.25
H ⁺ exchanged steam treated CG ₄₀ -50C4d-100C	346	126	0.09

Table 2. FAU/EMT ratio of zeolite samples

Sample	Relative Amount	
	FAU	EMT
CG ₂₀ -50C4d-100C	>99	<1
CG ₄₀ -2C247d-100C	84	16
CG ₄₀ -25C72d-100C	92	8
CG ₄₀ -50C4d-100C	93	7
CG ₄₀ -75C3d-100C	93	7
CG ₆₀ -50C10d-100C	8	92
CRG ₄₀ -50C1d-100C	95	5
CG ₄₀ -0.5h-50C4d-100C	86	14
CG ₄₀ -2h-50C1d-100C	>99	<1

Table 3. N₂ adsorption characteristics of CG₄₀-50C samples as a function of time

Sample	S _{BET} m ² /g	S _{Ext} m ² /g	V _{micro} cm ³ /g
CG ₄₀ -50C0d	48	48	-
CG ₄₀ -50C1d	51	51	-
CG ₄₀ -50C2d	64	64	-
CG ₄₀ -50C3d	301	111	0.08
CG ₄₀ -50C4d	581	155	0.17

Scheme 1. Scheme of gel materials used in this study

Scheme 2. Scheme of synthesis experiments with CG

Figure 1. Morphologies of gel particles. TEM images of (a) RG and (b) CG₄₀ (Insert: high magnification TEM image of CG₄₀)

Figure 2. Characteristics of zeolites crystallized at 100 °C (a). XRD patterns of (i) RG-100C and (ii) CG₄₀-100C and SEM images of (b) RG-100C and (c) CG₄₀-100C

Figure 3. (a) XRD pattern and (b) SEM image of CG₂₀-50C4d-100C

Figure 4. XRD patterns of (a). $\text{CG}_{40}\text{-2C247d-100C}$; (b). $\text{CG}_{40}\text{-25C72d-100C}$; (c). $\text{CG}_{40}\text{-50C4d-100C}$ and (d). $\text{CG}_{40}\text{-75C3d-100C}$ with high resolution XRD scan in the range of 2θ $5\text{-}7^\circ$ in the inserts

Figure 5. Adsorption/desorption isotherms of (a). CG₄₀-2C247d-100C; (b). CG₄₀-25C72d-100C; (c). CG₄₀-50C4d-100C and (d). CG₄₀-75C3d-100C

Figure 6. Pore size distribution analysis using BJH method of (a). $CG_{40-2C247d-100C}$; (b). $CG_{40-25C72d-100C}$; (c). $CG_{40-50C4d-100C}$ and (d). $CG_{40-75C3d-100C}$

Figure 7. TEM images of (a). CG_{40} -2C247d-100C; (b). CG_{40} -25C72d-100C; (c). CG_{40} -50C4d-100C and (d). CG_{40} -75C3d-100C

Figure 8. (a) XRD pattern; (b) TEM image; (c) Adsorption/desorption isotherm and (d) Pore size distribution analysis (BJH) of CG₆₀-50C10d-100C

Figure 9. Characteristics of materials obtained during $\text{CG}_{40}\text{-50C}$ reaction (a) XRD patterns of (i) $\text{CG}_{40}\text{-50C1d}$; (ii) $\text{CG}_{40}\text{-50C2d}$; (iii) $\text{CG}_{40}\text{-50C3d}$; (iv) $\text{CG}_{40}\text{-50C4d}$ and (v) $\text{CG}_{40}\text{-50C4d-100C}$; (b) SEM images and (c) TEM images of (i) $\text{CG}_{40}\text{-50C1d}$; (ii) $\text{CG}_{40}\text{-50C2d}$; (iii) $\text{CG}_{40}\text{-50C3d}$; (iv) $\text{CG}_{40}\text{-50C4d}$ and (v) $\text{CG}_{40}\text{-50C4d-100C}$

Figure 10. High resolution electron microscopy images of CG₄₀-50C4d-100C (a) Low magnification TEM image on multiple particles; (b) SEM images of one particle with Focused Ion Beam (FIB) cut; High resolution TEM images of (c) nanosheets packing; (d) entire particle; (e) nanosheet only and (f) showing an example of a FAU/EMT intergrowth (inserts: corresponding FFT of the TEM images)

Figure 11. XRD pattern of CG₄₀-50C4d-100C with (i) thermal treatment at 600 °C for 24 hours and (ii) acid form of CG₄₀-50C4d-100C (prepared by NH_4^+ exchange followed by calcination) at 550 °C with 100% relative humidity for 24 hours

Figure 12. Comparison of product distribution of dealkylation of 1,3,5-triisopropylbenzene at 200, 300 and 400 °C for RG-100C and CG_{40-50C4d-100C} (1,3-DiPBz: 1,3-Diisopropylbenzene; 1,4-DiPBz: 1,4-Diisopropylbenzene)

Figure 13. (a) XRD pattern; (b) TEM image; (c) Adsorption/desorption isotherm and (d) Pore size distribution analysis (BJH) of CRG₄₀-50C1d-100C (40% of water removed right from start of synthesis)

Figure 14. (a, d) XRD pattern; (b, e) Adsorption/desorption isotherms and (c, f) Pore size distribution analysis (BJH) of (a, b, c) CG₄₀-0.5h-50C4d-100C and (d, e, f) CG₄₀-2h-50C1d-100C

Hierarchical FAU/EMT

- Template-free
- External Surface Area of **189 m²/g**