Surname *et al. Chem Synth* Year;Volume:Number
**DOI**: 10.20517/cs.2021.xx

Chemical Synthesis

# Supplementary Material

# A Simple Strategy for Synthesis of *b*-Axis-Oriented MFI Zeolite Macro-Nanosheets

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## EXPERIMENTAL SECTION

### Chemicals and reagents:

Tetraethylorthosilicate (TEOS, 99%, Aladdin), tetrapropylammonium hydroxide solution (TPAOH, 25 wt.%, InnoChem Chemical Reagents Company), sulfuric acid ( 95%~98% , Tianjin Chemical Reagent ), hydrochloric acid ( 36%~38%, Tianjin Chemical Reagent ), Acetic acid ($C_2H_4O_2$, 99.5%, Shanghai Macklin Biochemical Technology Co., LTD ), Oxalic acid dehydrate ( $H_2C_2O_4·2H_2O$, 99.5%, Tianjin Guangfu Technology Development Co., LTD ), Lithium sulfate ( $Li_2SO_4$, 98.5%, Aladdin ), Sodium sulfate ( $Na_2SO_4$, 99%, Energy Chemical ), Potassium sulfate ( $K_2SO_4$, 99%, Aladdin ), Magnesium sulfate ( $MgSO_4$, 99%, Beijing Shiji ), tetrabutyl titanate ( TBOT，TCI (SHANGHAI) Development Co., LTD ), Sodium aluminate (NaAlO2, 45% $Al_2O_3$, Tianjin Guangfu Fine Chemical Research Institute).

### Synthesis of MFI (Silicalite-1, S-1) ZMNs:

To synthesize the S-1 ZMNs, the molar composition of 1.0 $SiO_2$: x TPAOH: 25 $H_2O$ was used, where x = 0.1 ~ 0.3. A typical experiment involved mixing 18.7 g TEOS, 14 g $H_2O$, and 10.85 g TPAOH with the molar composition of 1.0 $SiO_2$: 0.15 TPAOH: 25 $H_2O$ at room temperature. The mixture was then aged at 90 ℃ for 12 h while stirring. Next, 1.8 mol/L of $H_2SO_4$ and 18 g $H_2O$ were added to the mixture to adjust the pH of the gel, which was then vigorously stirred at 90 ℃ for another 12 h. Finally, the gel was placed into a Teflon-lined steel autoclave and kept at static conditions at 90 ~ 180 ℃ for 3 days (unless stated otherwise). The resulting solid products were collected through filtration

or centrifugation, washed with deionized water, and dried overnight at 80 ℃. Calcination was performed at 550 ℃ for 6 h in the air if needed.

**Synthesis of heteroatom-containing MFI ZMNs:**

MFI ZMNs containing heteroatoms have also been synthesized using 1.0 $SiO_2$: 0.15 TPAOH: 0.02 M: 25 $H_2O$ as the gel composition, where M is either $Al_2O_3$ or TBOT. Specifically, 0.61 g of TBOT was combined with 18.7 g of TEOS, 10.85 g of TPAOH, and 14 g of $H_2O$ at room temperature. The detailed procedures are similar to those used for the synthesis of S-1 ZMNs, except that the crystallization temperature was maintained at 150 ℃. In a similar manner, $NaAlO_2$ was introduced into the synthesis gel instead of TBOT, while keeping all the other procedures unchanged.

**Characterization:**

X-ray diffraction (XRD) patterns were recorded on a Rigaku Smart Lab 3kW diffractometer using Cu-Kα radiation (λ = 0.1541 nm) in the region of 2θ = 5° ~ 50°, and the degree of crystallinity was calculated by comparing the sum of the areas below the dominant peaks between 2θ = 22.5° ~25°.

Ar adsorption - desorption isotherms were obtained with a Quantachrome iQ-MP gas adsorption analyzer at -186 ℃ (87 K). The total surface area was calculated via the Brunauer-Emmett-Teller (BET) equation and the micropore volume was determined using the t-plot method.

Field-emission scanning electron microscope (FE-SEM) images were obtained on JSM-7800F.

High-resolution transmission electron microscopy (HR-TEM) images and the selected area electron diffraction (SAED) patterns were recorded on a JEOL JEM-2800 electron microscope.

Fourier transform infrared (FTIR) spectra were characterized by a Bruker Tensor 27 spectrometer with 128 scans at a resolution of 2 $cm^{-1}$, using KBr pellets.

$^{29}Si$ MAS NMR and $^{27}Al$ MAS NMR spectra were performed on Bruker Avance III WB 400 spectrometer at resonance frequency of 79.5 and 104.3 MHz. The $^{29}Si$ NMR spectra were recorded with a sample spinning rate of 5 kHz using a 7 mm MAS NMR probe.

Diffuse reflectance ultraviolet-visible (UV-Vis) spectra were recorded over the range of 200 to 800 nm with a blank sample as the reference, on a Perkin Elmer (Lambda 750) spectrophotometer.

**Kinetic Study:**

Kinetic study can be explored by plotting the crystallinity against the crystallization time, resulting in a crystallization curve. To investigate the kinetic behavior, the reaction was conducted using the optimum composition of 1.0 $SiO_2$: 0.15 TPAOH: 25 $H_2O$ crystallized for various reaction times at 90, 100, 110 and 120 ℃, respectively.

The Avrami-Erofeev equation (eq-1) was employed to describe the changes in MFI crystals over time during crystallization.[1]

$$\alpha = 1 - e^{-k(t-t_0)^n} \quad (1)$$

where $\alpha$ is the degree of crystallinity (0 to 1), $t$ is the crystallization time, $t_0$ is the induction time, $k$ is the kinetic constant for crystalline growth in $t^{-n}$ units, $n$ is the Avrami's exponent, which is related with the crystallization mechanism.[2]

The values of $n$ and $k$ can be obtained using the following equation,[2] which is expressed by taking the double logarithm of eq-1.

$$ln[-ln(1-\alpha)] = n\,ln(t-t_0) + ln\,k \quad (2)$$

The growth rate of MFI crystals was calculated using the first derivative of eq-1.

$$\frac{d\alpha}{dt} = kn(t-t_0)^{(n-1)} \cdot e^{-k(t-t_0)^n} \quad (3)$$

The inflection point of the crystallization stage, which corresponds to the steepest slope on the crystallization curve, was chosen as the crystallization rate ($v_c$).[3] The inflection point existing in the crystallization stage was obtained by setting the second derivative of eq-1 to zero.

$$\frac{d^2\alpha}{dt^2} = kn(n-1)(t-t_0)^{(n-2)} \cdot e^{-k(t-t_0)^n} - k^2n^2(t-t_0)^{(2n-2)} \cdot e^{-k(t-t_0)^n} \quad (4)$$

The transition period ($t_{tr}$) was determined by projecting the tangent line from the inflection point to the $x$ axis within the crystallization curve.[2]

The values of activation energy ($E$) and preexponential factor ($\ln A$) of three stages (induction, transition and crystallization) were determined based on Arrhenius equation.

$$ln(1/t_0) = ln\,A_0 - E_0/RT \quad (5)$$

$$ln\, v_{tr} = ln\, A_{tr} - E_{tr}/RT \quad (6)$$

$$ln\, v_c = ln\, A_c - E_c/RT \quad (7)$$

**Catalytic study:**

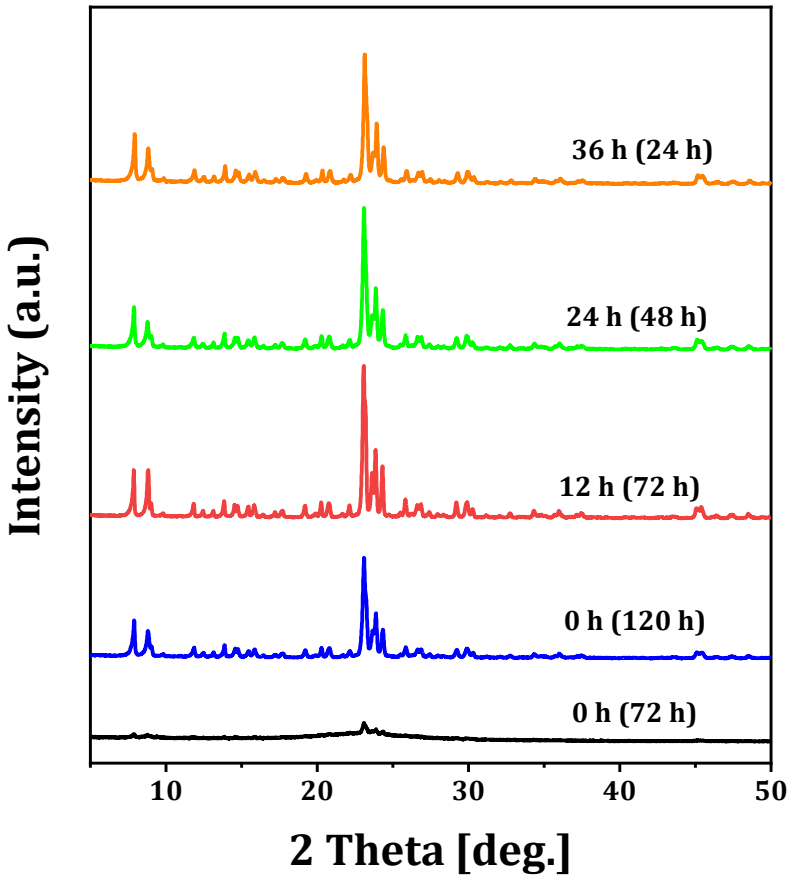
The methanol-to-hydrocarbons (MTH) reaction was performed in a fixed-bed reactor at atmospheric pressure. Typically, 0.4 g of the zeolite sample (sieve fraction, 0.25~0.5 mm) was placed in a quartz reactor (5 mm i.d.) and treated with flowing helium at 450 ℃ for 1 h. After cooling to the desired reaction temperature of 425 ℃, methanol was injected with a flow of 1 mL/h, corresponding to a weight hourly space velocity (WHSV) of 2.0 $h^{-1}$. The products were analyzed by an on-line gas chromatograph Shimadzu GC-2010 Plus with flame ionization detector (FID) and a Poraplot Q-HT column (40 m × 0.18 mm × 0.18 μm). The temperature of the column was kept at 40 ℃ for 7 min and then increased to 200 ℃ at a heating rate of 10 ℃/min, and then maintained at 200 ℃ for 4 min.

**Supplementary Table 1. Textual parameters from Ar adsorption-desorption tests of samples at different synthesis stages**

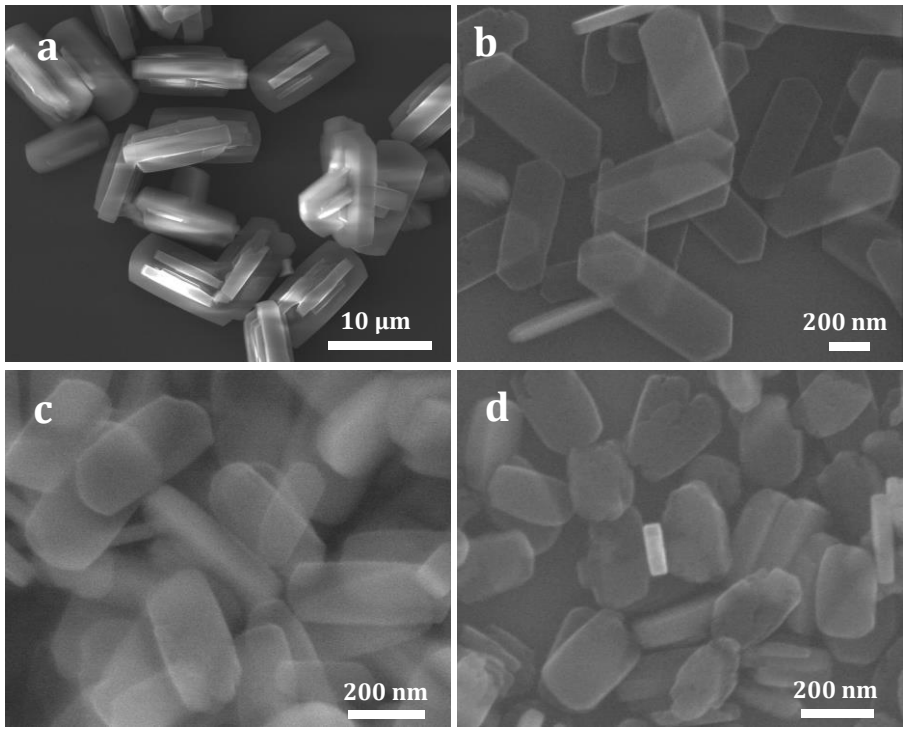
| Sample | $S_{BET}$[a] ($m^2/g$) | $S_{extra}$[b] ($m^2/g$) | $V_{Total}$ ($cm^3/g$) | $V_{micro}$[b] ($cm^3/g$) |
|---|---|---|---|---|
| As-synthesized representing S-1 ZMN | 426 | 71 | 0.23 | 0.14 |
| Solid product after aging for 12 h | 541 | 74 | 0.27 | 0.19 |
| Solid product after pH regulation and aging for another 12 h | 274 | 274 | 0.49 | 0 |

[a]: determined by the multi-point BET method

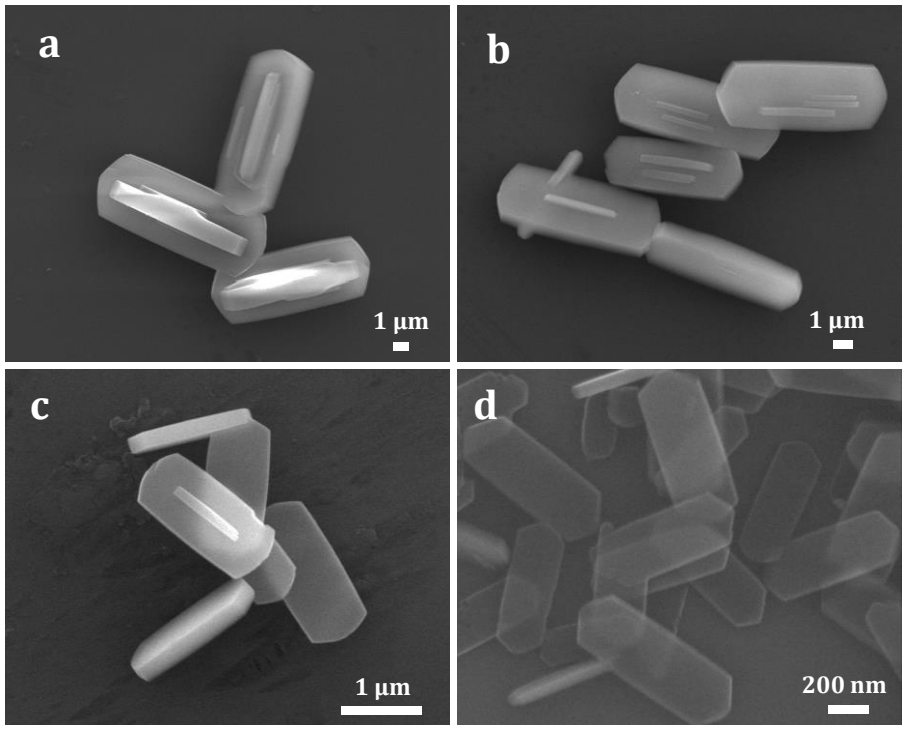
[b]: calculated using the t-plot method.



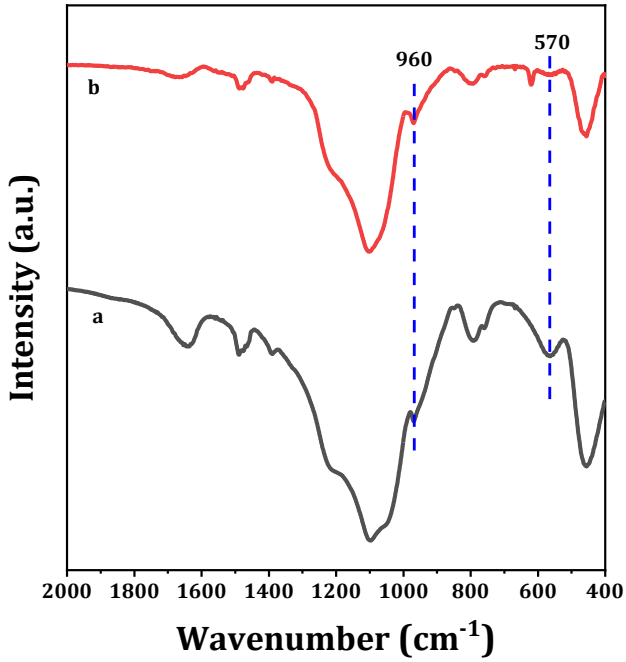

**Supplementary Figure 1**. XRD patterns of samples synthesized at aging temperature of 90℃ for different time and different crystallization time (crystallization time is shown in parentheses, crystallization temperature=120 ℃)



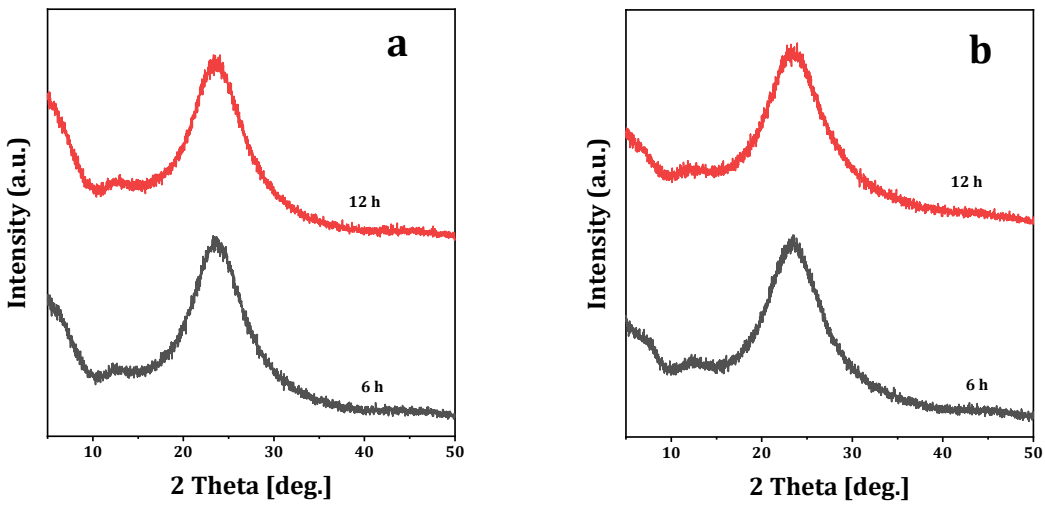

**Supplementary Figure 2.** SEM images of samples synthesized at aging temperature of 90℃ for different time and different crystallization time: (a) 0 h, 120h; (b) 12 h, 72 h; (c) 24 h, 48 h; (d) 36 h, 24 h (crystallization temperature=120 ℃).



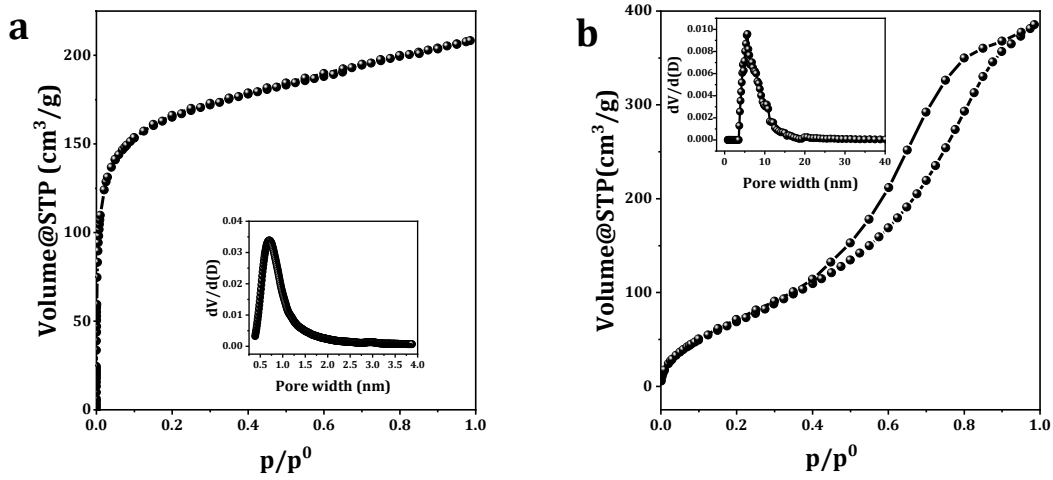

**Supplementary Figure 3.** SEM images of samples synthesized at different aging temperatures for 12 h and different crystallization time: (a) 30 ℃, 120 h; (b) 50 ℃, 72h; (c) 70 ℃, 72 h; (d) 90 ℃, 72 h (crystallization temperature=120 ℃).



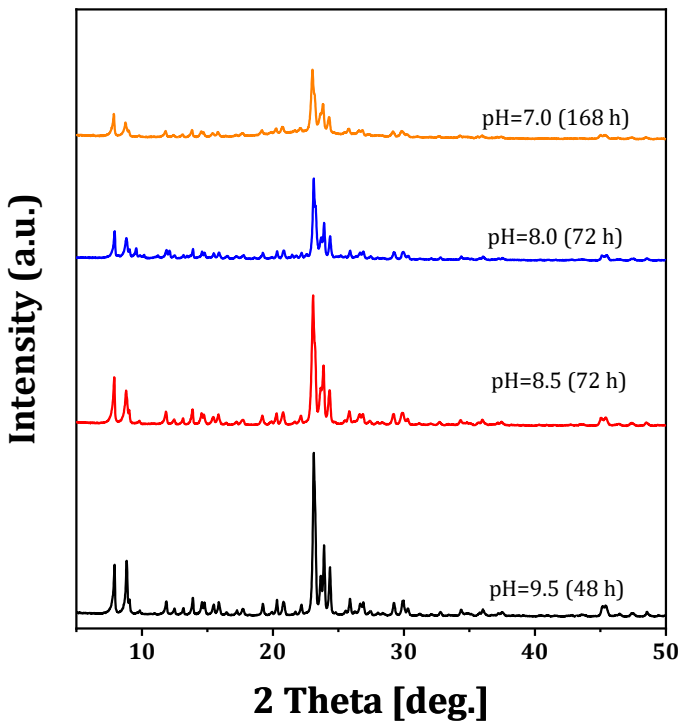

**Supplementary Figure 4.** The FTIR spectra of (a) the solid phase from the vacuum freeze-drying gel aging at 90℃ for 12h and (b) the solid phase from the vacuum freeze-drying gel after regulating the pH to 8.5 and aging at 90℃ for another 12h.



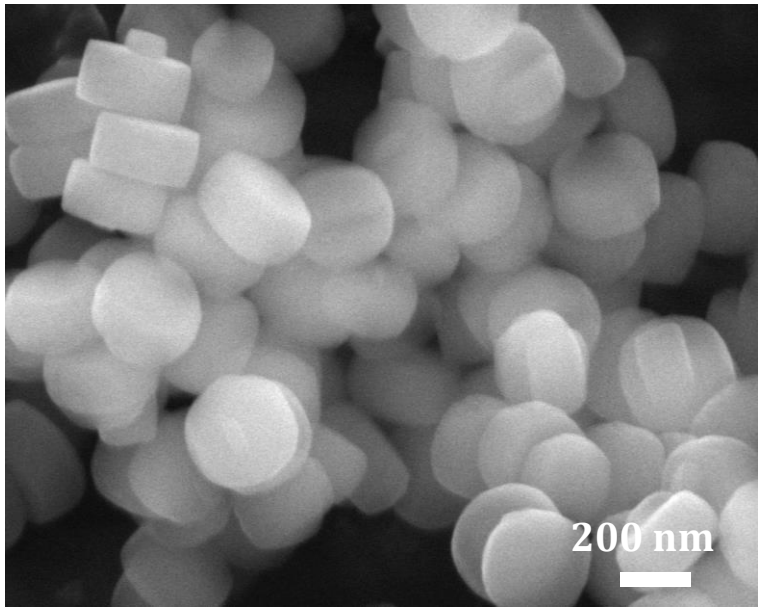

**Supplementary Figure 5.** XRD patterns of samples (a) after aging for 6 and 12 h, and (b) after regulating pH to 8.5 and aging for another 6h and 12h.



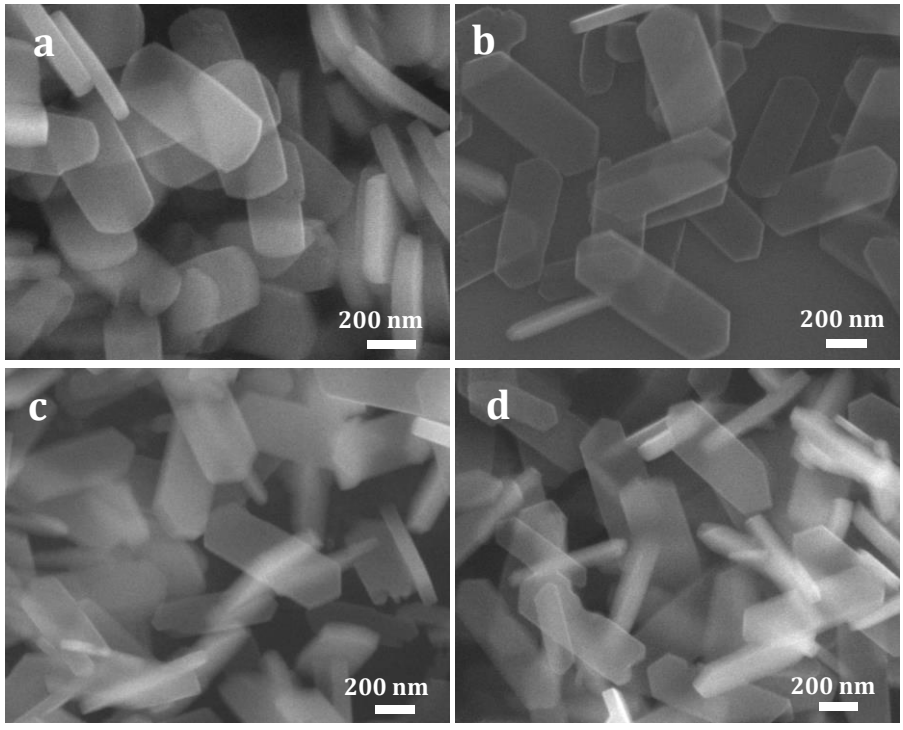

**Supplementary Figure 6.** Ar adsorption-desorption isotherms with pore size distribution shown as insets of (a) the solid phase from the vacuum freeze-drying gel aging at 90 ℃ for 12h and (b) the solid phase from the vacuum freeze-drying gel after regulating the pH to 8.5 and aging at 90 ℃ for another 12h.



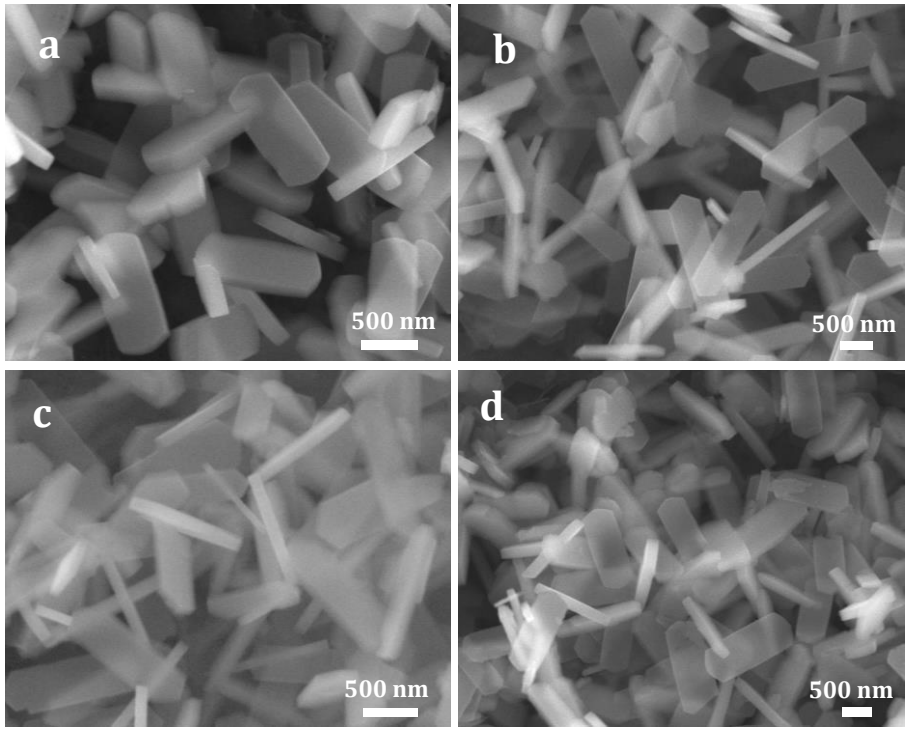

**Supplementary Figure 7.** XRD patterns of S-1 ZMNs synthesized at different pH of the aging gel and different crystallization time: (a) pH=9.5, 48 h, (b) pH=8.5, 72 h, (c) pH=8.0, 72 h, (d) pH=7.0, 168 h. Crystallization temperature: 120 ℃ (a, b) or 150 ℃ (c, d).



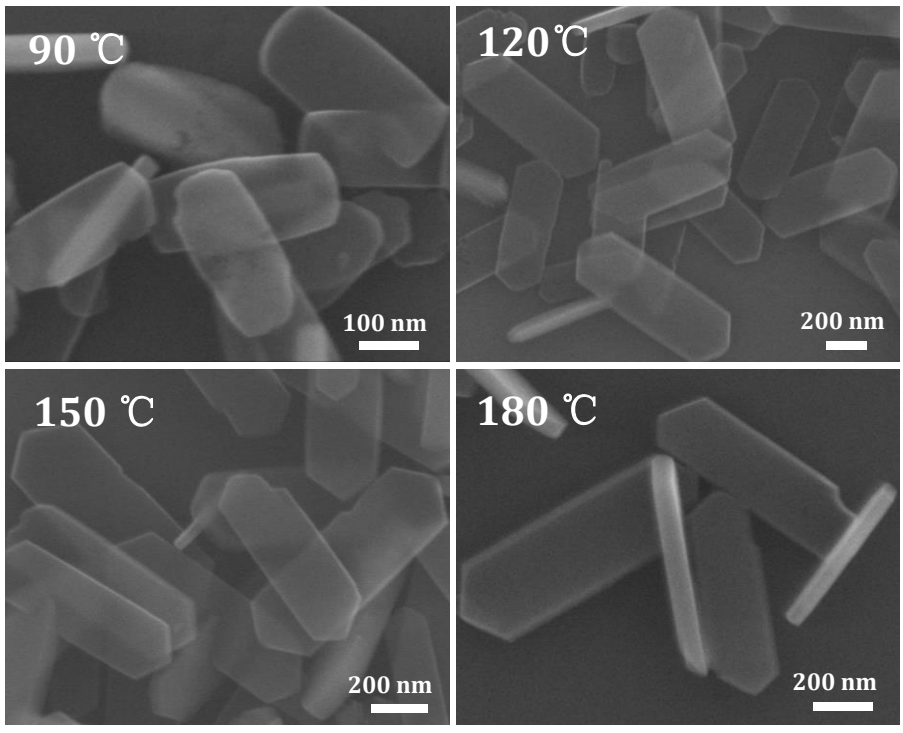

**Supplementary Figure 8.** SEM image of sample synthesized under the alkaline condition (pH = 11.4) without pH regulation at 120 ℃ for 48 h.



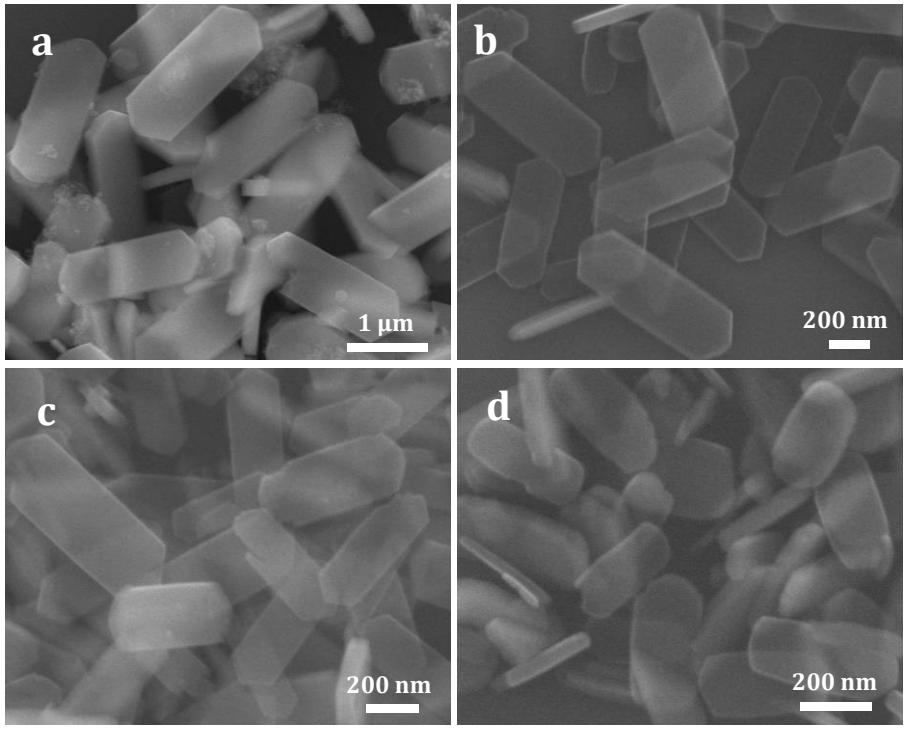

**Supplementary Figure 9.** SEM images of S-1 ZMNs synthesized under different anionic systems: (a) HCl, (b) $H_2SO_4$, (c) $CH_3COOH$ and (d) $H_2C_2O_4$. (crystallization temperature=120 ℃; crystallization time=72 h).



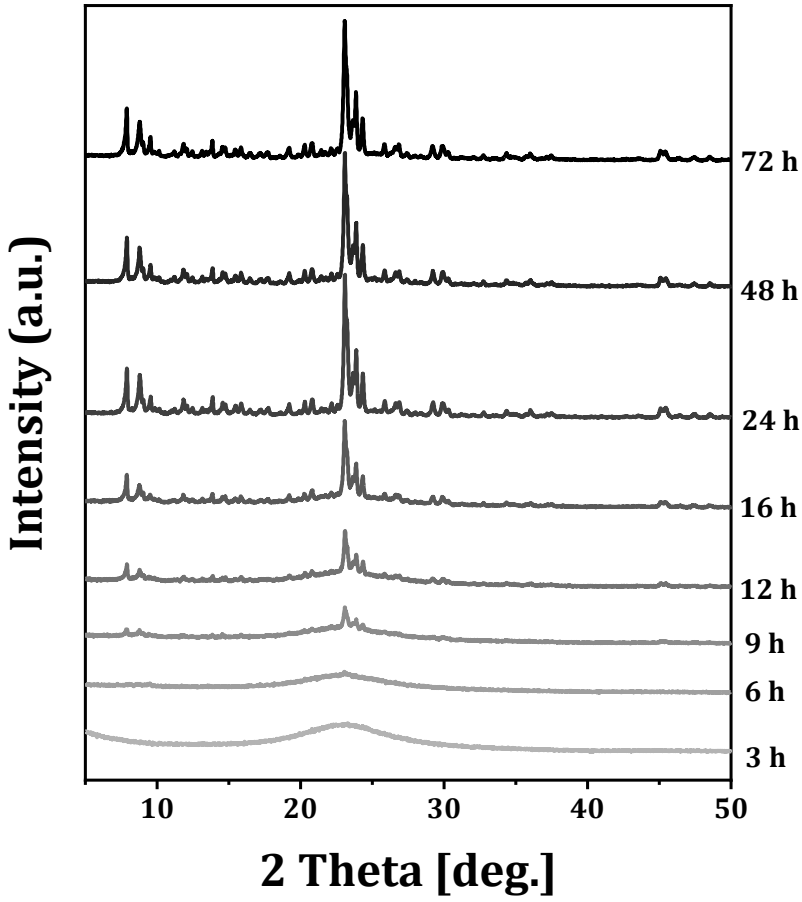

**Supplementary Figure 10.** SEM images of S-1 ZMNs synthesized from the system of $SiO_2$: 0.15 TPAOH: 25 $H_2O$: 0.025 $MSO_4$, M=(a) $Li_2$, (b) $Na_2$, (c) $K_2$ and (d) Mg.



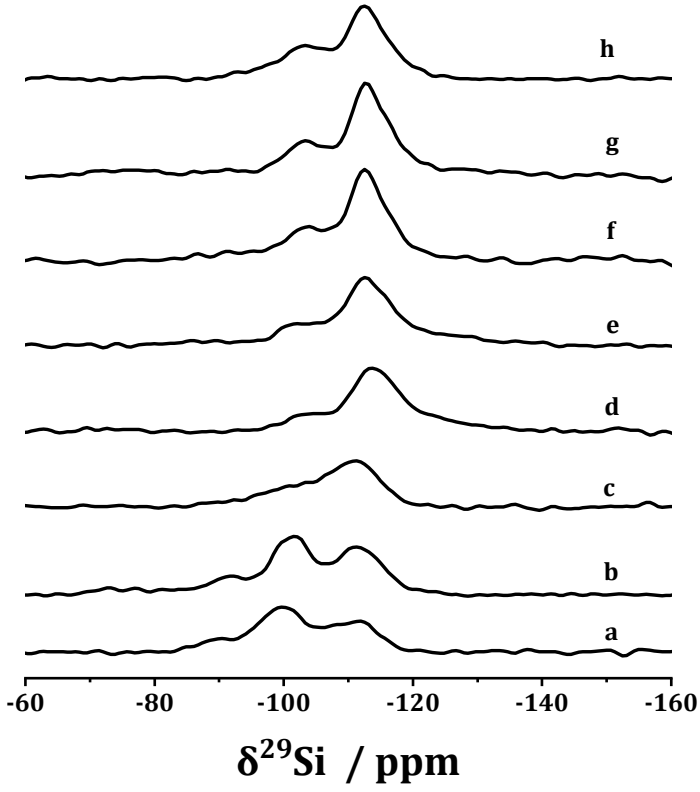

**Supplementary Figure 11.** SEM images of samples crystallized at 90 ℃ for 96 h, and 120, 150 and 180 ℃ for 72 h.



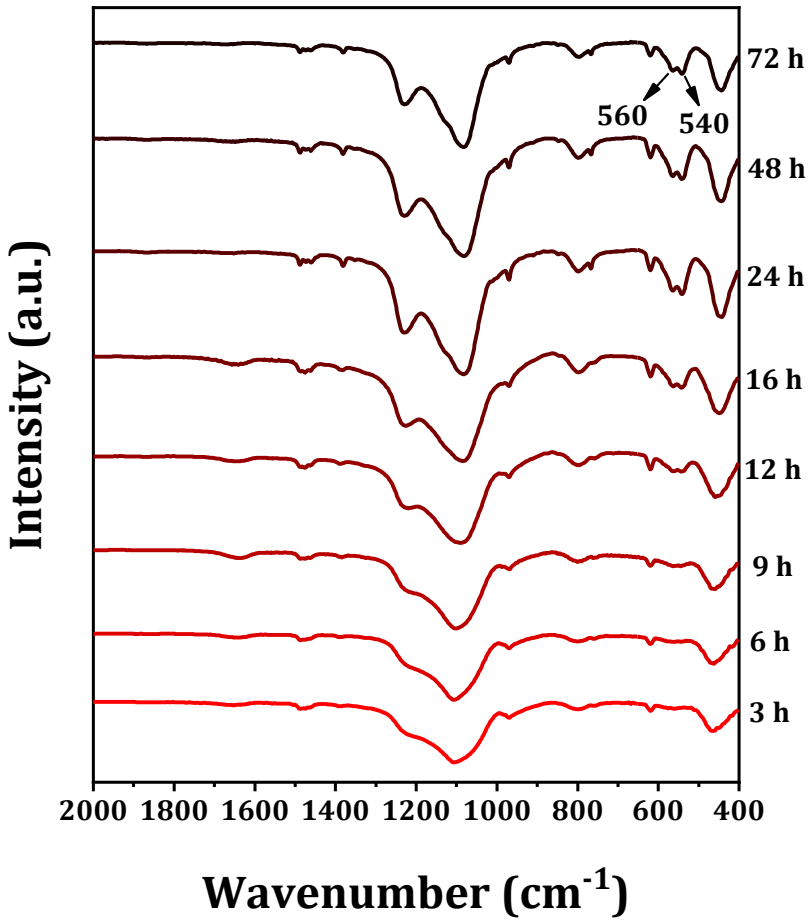

**Supplementary Figure 12.** SEM images of samples synthesized from the system of xTPAOH: 1.0 $SiO_2$: 25 $H_2O$, where x = (a) 0.1, (b) 0.15, (c) 0.2, and (d) 0.3 (crystallization temperature=120℃, crystallization time=72 h, pH=8.5).



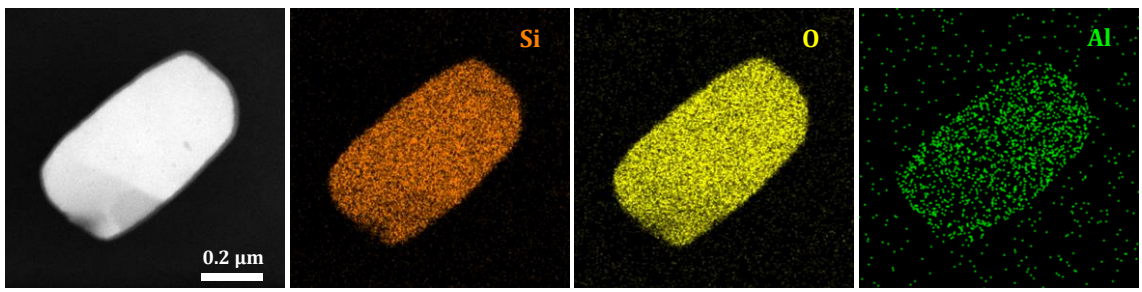

**Supplementary Figure 13.** XRD patterns of samples after hydrothermal treatment in the autoclave for 3, 6, 9, 12, 16, 24, 48 and 72 h.



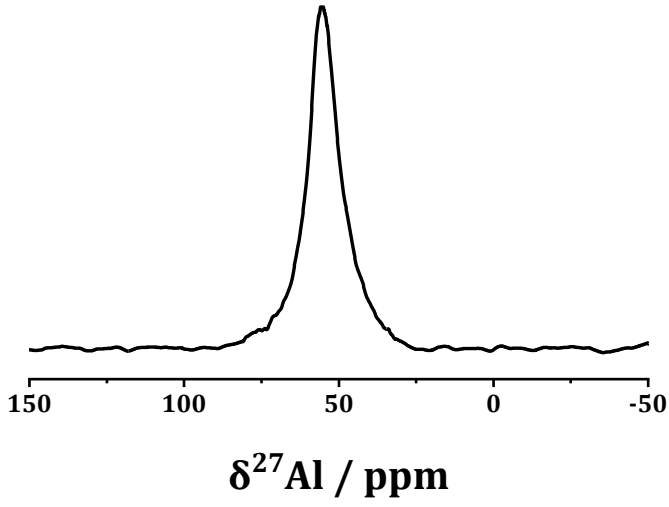

**Supplementary Figure 14.** $^{29}$Si MAS NMR spectra of samples at different stages of ZMN synthesis: (a) after aging at 90 °C for 12 h; (b) after regulating the pH to 8.5 and aging at 90 °C for another 12 h; after hydrothermal treatment in the autoclave for (c) 6, (d) 12, (e) 16, (f) 24, (g) 48 and (h) 72 h.




**Supplementary Figure 15.** The FT-IR spectra of samples after hydrothermal treatment in the autoclave for 3, 6, 9, 12, 16, 24, 48 and 72 h.




**Supplementary Figure 16.** TEM images of a single ZSM-5 ZMN crystal and the corresponding element mapping analysis.

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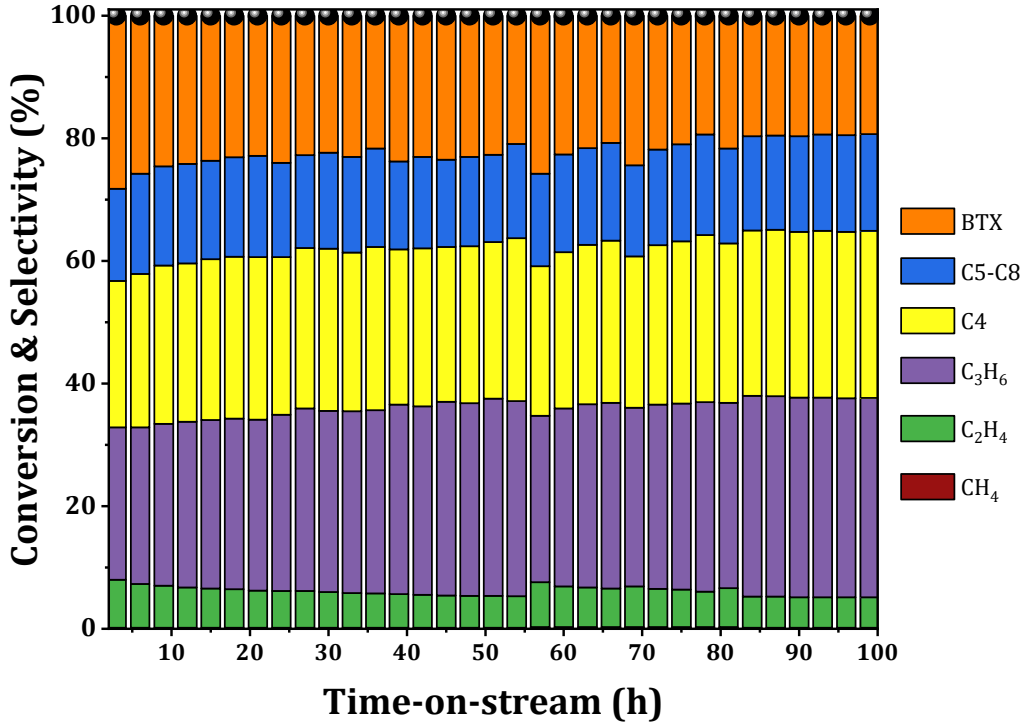
178 **Supplementary Figure 17.** $^{27}$Al MAS NMR spectrum of as-synthesized ZSM-5 ZMN.

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180 **Supplementary Figure 18.** Methanol conversion and product selectivity as a function

181 of time over ZSM-5 ZMNs in MTH reaction. Reaction conditions: 0.4 g catalyst, WHSV

182 = 2 $h^{-1}$, T= 425 °C, ambient pressure.

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