In Situ UV Raman Spectroscopic Studies on the Synthesis Mechanism of Zeolite X

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1. XRD patterns were obtained on a Rigaku MiniFlex diffractometer with a Cu Kα radiation source. Diffraction patterns were collected from 5° to 50° at a speed of 5°/min.

2. Magic-angle spinning (MAS) $^{27}$Al NMR spectra were recorded on a Bruker DMX500 spectrometer equipped with a 4 mm MAS probe head. The $^{27}$Al NMR frequency was 130 MHz. The sample rotation speed was 12 kHz. The chemical shifts and excitation angles were calibrated against a saturated Al(NO₃)₃ solution.

3. Figure S1. Equilibrium geometry of proposed model.
4. Figure S2. UV Raman spectra of the precursors of zeolite X a) experimental spectrum; b) simulated spectrum based on theoretical calculations.
<table>
<thead>
<tr>
<th></th>
<th>Experiment (cm⁻¹)</th>
<th>Theory (cm⁻¹)</th>
<th>Intensity*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ring breathing modes</td>
<td>500</td>
<td>530</td>
<td>33.09</td>
</tr>
<tr>
<td>Al-O-Si stretches</td>
<td>575</td>
<td>580</td>
<td>8.89</td>
</tr>
</tbody>
</table>

5. Table S1. The calculated and experimental vibration frequencies of proposed model in Figure S3

* The intensities are normalized to the strongest band in the calculated spectrum.

Equilibrium geometry of the proposed model has been determined in the gas phase and has evaluated vibrational frequencies (Figure S2). The theoretical calculation results are listed in Table s1. Figure S1f shows simulated Raman spectrum base on theoretical calculations. The calculated ring breathing modes of four-membered ring appears at 530 cm⁻¹ while experimental frequency at 500 cm⁻¹. The band at 580 cm⁻¹ corresponding to the experimental frequency at 575 cm⁻¹ (Figure S1e) attributed to the Si-O-Al stretches of side branch on the ring structure.
6. Figure S3. In situ UV Raman monitoring the reaction between the NaOH and zeolite X. The reaction temperature is 180°C and carried out in the in situ Raman cell for hydrothermal synthesis. The weight ratio of zeolite X / NaOH is 2:1.

In order to further understand the origin of the band at 575 cm\(^{-1}\). We use in situ Raman to monitor the reaction between NaOH and zeolite X. The treatment of zeolite X with NaOH can lead to the crack down and break up of the ring structures in the framework, and thus form some branched ring species. The band at 389 cm\(^{-1}\) originates from the solid NaOH. The band at 514 cm\(^{-1}\) has been assigned to the four-ring breathing vibrations in the crystalline framework. With increasing reaction time, the disappearance of the band at 514 cm\(^{-1}\) is accomplished by the instant appearance of the band at 490 cm\(^{-1}\) with can be assigned to the four-membered aluminosilicate ring. After reaction for 60 min, a band appears at 565 cm\(^{-1}\). Further increase the reaction time lead to the shift of the band at 565 cm\(^{-1}\) to 555 cm\(^{-1}\) and appearance of the band at 598 cm\(^{-1}\) due to the Si-O-Si stretches.\(^{[1]}\)
Figure S4. $^{27}$Al MAS NMR spectra of zeolite X reacted with NaOH after 80 min under 180°C.

The $^{27}$Al MAS NMR spectra of zeolite X reacted with NaOH after 80 min shows a broad band centered at 66.71 ppm. Mueller and coworkers reported the $^{27}$Al NMR spectra of tetramethylammonium aluminosilicate solutions and found that the chemical shift of $^{27}$Al correlated with the number of Si atoms surrounding the Al nucleus. According to their results, the band centered at 66.71 ppm are mainly composed of $Q^2$ (2Si) at 69.5 ppm and $Q^3$ (3Si) at 64.5 ppm. [2] This result suggest us that alkaline treatment of zeolite X lead to the break down of the framework $Q^4$ (4Si) Al to $Q^2$ (2Si) and $Q^3$ (3Si) Al, namely, breaking up of the ring structure.

Base on in situ Raman, $^{27}$Al MAS NMR spectra and DFT calculation, the appearance of the band at 565 cm$^{-1}$ may caused by the formation of some branched ring species and the slight difference of frequencies between 575 and 565 cm$^{-1}$ may arise from different coordination environment of Al atom on the branched chains.

References
