Synthesis of Zeolites with Controlled Defects by Understanding the Role of Charge Balance in Zeolite Crystallization

Song Luo

University of Massachusetts Amherst

Follow this and additional works at: https://scholarworks.umass.edu/dissertations_2

Part of the Materials Science and Engineering Commons

Recommended Citation
https://doi.org/10.7275/32930122 https://scholarworks.umass.edu/dissertations_2/2768

This Open Access Dissertation is brought to you for free and open access by the Dissertations and Theses at ScholarWorks@UMass Amherst. It has been accepted for inclusion in Doctoral Dissertations by an authorized administrator of ScholarWorks@UMass Amherst. For more information, please contact scholarworks@library.umass.edu.
Synthesis of Zeolites with Controlled Defects by Understanding the Role of Charge Balance in Zeolite Crystallization

A Dissertation Presented

by

SONG LUO

Submitted to the Graduate School of the University of Massachusetts Amherst in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

February 2023

Department of Chemical Engineering
Synthesis of Zeolites with Controlled Defects by Understanding the Role of Charge Balance in Zeolite Crystallization

A Dissertation Presented

by

SONG LUO

Approved as to style and content by:

______________________________
Wei Fan, Chair

______________________________
Scott M. Auerbach, Member

______________________________
T. J. Mountziaris, Member

______________________________
Neil Forbes, Graduate Program Director
Department of Chemical Engineering
ACKNOWLEDGMENTS

First of all, all of my Ph.D. work were supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division, under Award No. DE-SC0019170, and I would like to thank this funding source: without their generous assistance, nothing would be done. Next, I would like to acknowledge the Department of Chemical Engineering at UMass Amherst for enrolling me into its great Ph.D. program 6.5 years ago in 2016, and then helping me pursue my Ph.D. degree all the way till now in every aspect. I also would like to express my very great appreciation to my Ph.D. advisor, Prof. Wei Fan for his patient mentorship and support over the past 6 years. When coming across setbacks each time, his encouragement and guidance always helped me overcome all the barriers throughout the duration of my Ph.D. I am in particular grateful to the research freedom from him, which allowed me to try my own new ideas from even my 1st year. This process indeed practiced and developed my researching abilities and confidence as an independent researcher. I also would like to acknowledge my co-advisor, Prof. Scott M. Auerbach for the extensive help. The advice from him in each discussion and meeting, often from the theoretical perspective, was always fruitful, illuminating and inspiring, and just like Prof. Fan, I also learned lots of soft skills from him, such as good time management, efficient communication in English, and good presentation and writing abilities. I really enjoyed working with both professors for the past 6 years. I am thankful to have Prof. T. J. Mountziaris as part of my committee as well. His suggestions and comments during the prospectus and also the final thesis defense enriched my study and helped me improve my work to an even greater extent.
I am fortunate to have been able to carry out my research alongside the fantastic group members and also the smart undergraduate students once worked with me: Dr. Vivek Vattpalli, Dr. Xiaoduo Qi, Dr. Sanket Sabnis, Dr. Jason Gulbinski, Dr. Guangyue Xu, Dr. Huiyong Chen, Kaivalya Gawande, Muhammad Shah, Jonathan Chen, Alex Engstrom, Kirby Yen, and Taras Nagornyy. In particular, I want to thank my simulation collaborator, Tongkun Wang. We have been working together well and happily under the supervision of Prof. Fan and Prof. Auerbach for the past 5 years. Each time when coming up with some new ideas, we would immediately discuss about them with each other from different angles, to try to improve them before showing to the two advisors, and after each meeting with the professors, we would summarize and create the to-do list together. It is really a pleasurable and productive experience. Meanwhile, I also want to express my great appreciation to Prof. Feijian Chen, who worked as a visiting scholar at our group in the whole year of 2019. During that year, we had countless valuable discussions about zeolite synthesis, including the times when walking back home and having dinner at dining commons together. It is a time period when I made progress with the highest efficiency during my Ph.D. life. I want to thank Dr. Weiguo Hu (UMass Amherst), Dr. Long Qi (Ames Lab), Prof. Michael Timko (WPI), and Dr. Geoffrey Tompsett (WPI) as well for their help with NMR and Raman spectroscopy. By communicating with them, I not only mastered how to use those characterization techniques, but also learned the related proper underlying theories, which are even more important and definitely helped me with the data analysis and also the further experimental designs.

Finally, from a personal standpoint, I would like to thank all my friends and family members. Thank you all for supporting me through all the difficulties for so many years. Without you, I could not have achieved anything. In particular, I want to thank my
grandmother for her constant encouragement and love. She is 93 years old this year and
still in good health. Although we often talk by phone, I have not seen her in person since
August 29, 2017. I really miss her.
ABSTRACT

SYNTHESIS OF ZEOLITES WITH CONTROLLED DEFECTS BY UNDERSTANDING THE ROLE OF CHARGE BALANCE IN ZEOLITE CRYSTALLIZATION

FEBRUARY 2023

SONG LUO, B.S., SICHUAN UNIVERSITY
M.S., SICHUAN UNIVERSITY
Ph.D., UNIVERSITY OF MASSACHUSETTS AMHERST

Directed by: Professor Wei Fan

Zeolites are well-defined and ordered microporous crystalline materials constructed by the continuous linkage of corner sharing TO$_4$ tetrahedra (taking T atoms (e.g., Si or Al) as the tetrahedral center). Due to the structural and compositional diversities and superior hydrothermal stability, zeolites have been broadly utilized to many industrial fields, including gas separation and catalysis heterogeneous catalysis. However, understanding zeolite crystallization mechanisms remains a tantalizing challenge, which causes challenges in tailoring this material for advanced applications. Raman spectroscopy has emerged as a powerful tool for probing medium-range (0.35 - 1 nm) structures. Since this scale is consistent with the micropore size of zeolites, using Raman can shed light on the developmental process of rings or more complex building units during zeolite crystallization. However, despite this importance, rigorous assignments of Raman spectra of zeolites are not completely understood. Therefore, herein, we reported a systematic zeolite synthesis, spectroscopy, and periodic DFT study of several all-silica zeolites. We discovered that zeolite Raman bands should be assigned to “tricyclic bridges” — three zeolite rings that share a common Si–O–Si bridge. Furthermore, we have found that the vibrational frequency of a given Raman band can be correlated to the smallest ring of its tricyclic bridge and...
not to the ring that is actually vibrating. Finally, we have discovered a precise anti-correlation between Raman frequency and Si–O–Si angle.

Based on the new discoveries regarding the assignments of Raman bands of zeolites, the crystallization process, from amorphous gel to final crystals, of siliceous LTA zeolite synthesized with HF was investigated by Raman spectroscopy complemented with XRD and NMR. By integrating experimental Raman with periodic density functional theory (DFT) calculations, it was discovered that the F–-filled double four-membered ring (F–/D4R) and the empty D4R exhibit rather distinct Raman features, which opens a new window for studying defects in the D4Rs during zeolite formation. In particular, we have observed a variation in Raman intensities of F–/D4R and empty D4R bands during LTA crystallization. Periodic DFT calculations indicate that the observed Raman behavior is consistent with empty D4R units containing one or two Si vacancies surrounded by Q3 Si. These defects appear to heal during further crystallization, leading to the formation of defect-free LTA zeolite crystals. These results for the LTA crystallization process provide deeper understanding on the roles of F– in charge balancing and stabilizing intact D4R units during zeolite formation.

Controlling defects in zeolites is crucial for tuning their adsorption and catalytic properties. An integrated zeolite synthesis, spectroscopy, and density functional theory study was performed to investigate the minimum amount of F– as a charge-balancing agent that mitigates defects in siliceous zeolites. It was found that positive charges could be titrated into the resulting as-made siliceous LTA zeolite by varying the amount of tetramethylammonium cations (TMA+) introduced as the secondary organic structure-directing agent (OSDA). According to the results from 29Si solid-state MAS NMR, Raman spectroscopy, and density functional theory, those additional positive charges from TMA+ are balanced by framework defects of SiO– in the LTA crystals, rather than F–. In this way, the number of defects in the as-made LTA can be precisely controlled by the amount of TMA+ in the zeolite structures. A DFT thermodynamic analysis
explains that crowding of siliceous LTA pores by TMA\(^{+}\) impedes defect healing, leading to the formation of the controllable defects.

Based on all these discoveries, siliceous isolated D4Rs (synthesized without F\(^{-}\); to help the formation of D4Rs in LTA product) and an appropriate amount of Al (to balance positively-charged OSDAs) were added into the synthetic precursor, trying to increase the Si/Al ratio of LTA synthesized in a HF-free way. It was discovered that the Si/Al ratio could be increased to 7.55 (a progress of 37.2% compared to the previous highest one). \(^{29}\)Si NMR, \(^{13}\)C NMR, \(^{27}\)Al NMR, and TGA clearly shed light on the details of the picture of the charge balancing between OSDAs and tetrahedral Al in the LTA framework. The superior hydrothermal stability of this LTA sample was confirmed by an in-situ XRD experiment under temperatures as high as 1000 °C for 3 h. This research broadened the application scope for LTA zeolite in industry, and also provided inspirations in increasing the Si/Al ratios of other 37 zeolites featuring D4Rs synthesized in the absence of HF.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>i</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xi</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xiii</td>
</tr>
<tr>
<td>CHAPTER</td>
<td></td>
</tr>
<tr>
<td>1. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Zeolites Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Synthesis of Zeolites</td>
<td>2</td>
</tr>
<tr>
<td>1.3 Challenges in Understanding Zeolites Crystallization Mechanisms</td>
<td>6</td>
</tr>
<tr>
<td>1.4 Previous Studies about Zeolites Crystallization Mechanisms</td>
<td>8</td>
</tr>
<tr>
<td>1.5 Defects Control in Zeolite Synthesis</td>
<td>12</td>
</tr>
<tr>
<td>1.6 Si/Al Ratio Control in Zeolite Synthesis</td>
<td>16</td>
</tr>
<tr>
<td>1.7 Thesis Scope</td>
<td>19</td>
</tr>
<tr>
<td>2. CRITICAL ROLE OF TRICYCLIC BRIDGES INCLUDING NEIGHBORING RINGS FOR UNDERSTANDING RAMAN SPECTRA OF ZEOLITES</td>
<td>21</td>
</tr>
<tr>
<td>2.1 Background</td>
<td>21</td>
</tr>
<tr>
<td>2.2 Methods</td>
<td>21</td>
</tr>
<tr>
<td>2.2.1 Choice of Zeolite for the Study</td>
<td>22</td>
</tr>
<tr>
<td>2.2.2 Experimental Methods</td>
<td>23</td>
</tr>
<tr>
<td>2.2.3 Computational Methods</td>
<td>23</td>
</tr>
<tr>
<td>2.3 Results and Discussion</td>
<td>24</td>
</tr>
</tbody>
</table>
2.3.1 Comparisons between Experimental and Computed Raman Spectra ................................................................. 24
2.3.2 Normal Mode Analysis of Raman Spectrum of LTA ........ 26
2.3.3 Interpretation Using Triyclic Bridges ........................................ 28
2.3.4 Raman Frequency and Si-O-Si Angle .................................. 31

2.4 Summary ...................................................................................... 32

3. IDENTIFYING ORDER AND DISORDER IN DOUBLE FOUR-MEMBERED RINGS VIA RAMAN SPECTROSCOPY DURING CRYSTALLIZATION OF LTA ZEOLITE .......................................................................................................................... 34

3.1 Background ................................................................................. 34
3.2 Methods ........................................................................................ 37

3.2.1 Experimental Section .............................................................. 37

3.2.1.1 Synthesis of Zeolite (LTA-BULKY-F). .......................... 37
3.2.1.2 Synthesis of LTA Seeds .............................................. 38
3.2.1.3 Characterizations ......................................................... 39

3.2.2 Computational Section ............................................................ 41

3.3 Results and Discussion ............................................................... 42

3.3.1 Synthesis of LTA-BULKY-F .................................................. 42
3.3.2 Raman Signatures of the F/D4R and Empty D4R .............. 43
3.3.3 Structure and Dynamics of the F/D4R via Raman Analysis ................................................................. 45
3.3.4 Ordered and Disordered Fluoride Distribution in LTA ...... 46
3.3.5 Quantifying the Empty D4R and F/D4R in LTA ................. 49
3.3.6 Probing Si-LTA Crystallization Using Raman Analyses

3.3.7 Synthesis of Siliceous LTA with Reduced Fluoride

3.4 Summary

4. TITRATING CONTROLLED DEFECTS INTO SILICEOUS LTA ZEOLITE CRYSTALS USING MULTIPLE ORGANIC STRUCTURE-DIRECTING AGENTS

4.1 Background

4.2 Methods

4.2.1 Experimental Section

4.2.1.1 Synthesis of Zeolites (LTA-BULKY-xTMA)

4.2.1.2 Characterization Studies

4.2.2 Computational Section

4.3 Results and Discussion

4.3.1 Synthesis of Si-LTA Using BULKY and TMA as OSDAs

4.3.2 Raman Signatures of F⁻/D₄R and Empty D₄R in LTA-BULKY-xTMA

4.3.3 Identifying Defect Structures with Computational Spectroscopy

4.3.4 Thermodynamic DFT Analysis of Defect-Healing Processes in LTA-BULKY-TMA

4.4 Summary

5. NOVEL SYNTHESIS OF HIGH-SILICA LTA ZEOLITE IN HF-FREE WAY

5.1 Background
5.1.1 History in Synthesizing LTA Zeolite with Si/Al Ratio from 1 to Infinity ................................................................. 85

5.1.2 Synthesis of High-Silica LTA in Fluoride-Free Way .............. 91

5.2 Methods ......................................................................................... 94

5.2.1 High-Silica LTA (Si/Al = 7.55) Synthesis in HF-Free Way ................................................................. 94

5.2.2 Characterizations ........................................................................ 95

5.3 Results and Discussion .................................................................... 96

5.4 Summary ......................................................................................... 105

6. CONCLUSIONS .................................................................................. 106

6.1 Concluding Remarks ......................................................................... 106

6.2 Suggested Future Directions ............................................................ 106

REFERENCES ....................................................................................... 111
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 2.1 Assignments of main Raman bands to tricyclic bridges and their corresponding Si–O–Si computational angles.</td>
<td>30</td>
</tr>
<tr>
<td>Table 3.1 Elemental analysis of LTA-BULKY-F.</td>
<td>50</td>
</tr>
<tr>
<td>Table 4.1 Elemental analysis of LTA-BULKY-xTMA (x = 0, 0.01, 0.025, and 0.05).</td>
<td>72</td>
</tr>
<tr>
<td>Table 4.2 $Q_3/(Q_3 + Q_4)$ ratio of LTA-BULKY-xTMA collected from $^{29}$Si MAS NMR.</td>
<td>74</td>
</tr>
<tr>
<td>Table 4.3 $Q_3/(Q_3 + Q_4)$ ratios measured from $^{29}$Si MAS NMR of LTA-BULKY-TMA-0.050TMA synthesized at various temperatures.</td>
<td>83</td>
</tr>
<tr>
<td>Table 5.1 Overview of notable LTA zeolite synthesis conditions and results.</td>
<td>88</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1.1 Schematic showing how two T atoms are connected by a T-O-T bond to form linked TO4 tetrahedra, and how the linked TO4 tetrahedra combine together to form rings, cages, and continuous channels in a supercell of BEA. The composition of a 12-MR from the BEA zeolite is displayed in detail, and when a Si (IV) atom in the 12-MR is substituted by an Al (III), a proton will appear to connect with the neighboring O atom (shaded in red), to fulfill the charge balancing requirement and form a Brønsted acid site, which is catalytically active</td>
<td>2</td>
</tr>
<tr>
<td>Figure 1.2 Schematic representation of the two different mechanisms of zeolite BEA crystallization based on the solution-mediated crystallite formation and solid-solid transformation</td>
<td>10</td>
</tr>
<tr>
<td>Figure 2.1 Structures of (a) CHA, (b) LTA, (c) ACO, (d) GME, (e) AST, (f) SOD, (g) DOH, (h) ITH, and (i) ITW. CHA, LTA, AST, SOD, ITH, and ITW were synthesized in their pure-silica form, and then their experimental Raman spectra were compared to the simulations. Linkages shown in red provide examples of tricyclic bridges</td>
<td>24</td>
</tr>
<tr>
<td>Figure 2.2 Comparison between experimental and simulated Raman spectra of (a) Si-LTA and (b) Si-CHA</td>
<td>25</td>
</tr>
</tbody>
</table>
Figure 2.3 Parity plot comparing experimental and simulated Raman band locations, indicating that the theory consistently red-shifts by 20–25 cm$^{-1}$.

Figure 2.4 (a) Normal mode eigenvectors computed for LTA vibrations at 318 and 476 cm$^{-1}$; (b) LTA structure showing three different tricyclic bridges (4–4–6 in blue, 4–4–8 in red, and 6–6–8 in green).

Figure 2.5 Calculated Raman spectra of all the nine studied zeolites.

Figure 2.6 Correlation between computed main-band Raman frequency and Si–O–Si angle in simulation; the slope of the best-fit line is -3.64 and the correlation coefficient ($R^2$) is 0.88.

Figure 3.1 LTA zeolite structure and its three building subunits: one $\alpha$-cage, one $\beta$-cage, and three D4Rs per unit cell. Each subunit may contain species as shown in the figure. Synthesis with a dimer of BULKY cations would require 2/3 of D4Rs to be filled with $F^-$ according to charge balancing hypothesis. 4-4-6 and 4-4-8 tricyclic bridges in siliceous LTA are highlighted in green and red, respectively.

Figure 3.2 (a) Raman spectra of calcined LTA (experiment in green, DFT in red) and as-made LTA before calcination (experiment in purple, DFT in blue) showing excellent agreement between experiment and theory, with DFT exhibiting red-shifts from measured band locations. Raman bands for LTA vibrations are marked with black star; unmarked bands
are assigned by DFT to BULKY OSDA; yellow-shaded band is empty D4R symmetric breathing mode; black-shaded band is assigned by DFT to F-filled D4R (F/D4R). (b) Periodic DFT analysis of blue-shift of D4R Raman band from empty (green dot) to F-filled (blue dot): most of blue-shift explained by geometrical distortion of D4R (decrease in Si-O-Si angle, red dot); remaining blue-shift attributed to unique F/D4R bonding interaction. ................................................................. 44

Figure 3.3 Experimental Raman spectrum of fully crystalline LTA-BULKY-F (experimental 8 day sample) and calculated Raman spectra of LTA-BULKY-F with heterogeneous (blue) and homogeneous (red) distributions of F/D4R. The arrow points to a shoulder band in the heterogeneous model, which is absent in both the homogeneous model and the experimental spectrum. ................................................................. 49

Figure 3.4 (a) $^{19}$F MAS NMR and (b) $^{29}$Si MAS solid state NMR spectra of LTA-BULKY-F with peak deconvolution. The peaks marked with asterisk in the $^{19}$F MAS NMR spectrum are side bands from the peak at -39 ppm. Two peaks at -109 and -112 ppm in the $^{29}$Si MAS NMR spectrum are from Si (Q$_4$) in F/D4R and empty D4R, respectively. ............ 50

Figure 3.5 TGA of LTA-BULKY after intensive washing with acetone and ethanol. ........................................................................................................... 51
Figure 3.6 (a) Raman spectra at various stages of LTA synthesis with BULKY, and (b) XRD data for the same samples as (a). LTA crystals appear in XRD at 3 h, as do empty and F-filled D4R bands in Raman spectra. 

Figure 3.7 SEM images of LTA-BULKY-F at different times (A) 2.5 h, (B) 3 h, (C) 6 h and (D) 8 d.

Figure 3.8 $^{29}$Si MAS NMR spectra of LTA-BULKY-F at various stages of LTA synthesis. The 3 and 6 h samples show the presence of Q3 Si due to the partial crystallinity of the two samples.
Figure 3.9 (a) Experimental Raman spectra of fully crystalline LTA-BULKY-F (purple) and partially crystalline LTA-BULKY-F (blue), DFT-calculated Raman spectrum of LTA-BULKY-F composed of intact D4Rs (red), and (green) DFT-calculated Raman spectrum combining (i) LTA-BULKY-F only with intact D4Rs, (ii) LTA-BULKY-F with one point defect in an empty D4R in each unit cell, and (iii) LTA-BULKY-F with two point defects in an empty D4R in each unit cell in a 4:1:1 ratio, respectively. (b) Structures of four different D4Rs used for the combined spectrum. From left to right, from top to bottom: intact $F^-$/D4R; intact empty D4R; empty D4R with one missing Si; and empty D4R with two missing Si.

Figure 3.10 (a) Raman spectrum, (b) XRD and (c) $^{29}$Si MAS SS-NMR spectrum of LTA-BULKY-F synthesized using the gel with a composition of 1.00 SiO$_2$ : 0.083 HF : 0.50 BULKY OSDA-OH : 5.00 H$_2$O. The Raman band ratio of $F^-$/D4R to empty D4R is 0.73, which is similar to the conventional LTA-BULKY-F synthesized using the composition of 1.00 SiO$_2$ : 0.5 HF : 0.50 BULKY OSDA-OH : 5.00 H$_2$O, indicating around 2/3 of D4Rs in the sample are occupied with $F^-$. The $^{29}$Si MAS SS-NMR result also suggests the presence of two different Si ($Q_4$) of D4R.

Figure 4.1 LTA zeolite structure and its three building subunits: one $\alpha$-cage, one $\beta$-cage, and three double four-membered ring (D4R) per unit cell.
Each subunit may contain species as shown. Synthesis with a dimer of BULKY cations would require 2/3 of D4R to be F-filled; making LTA with two BULKY and one TMA would require 3/3 of D4R to be F-filled, according to a charge-balancing hypothesis.

Figure 4.2 (a) XRD patterns of LTA-BULKY-xTMA (x = 0, 0.01, 0.025, and 0.05) where x = TMA/SiO$_2$ molar ratios in synthesis mixtures. (b) Raman spectra of as-made LTA-BULKY-xTMA before calcination. Raman bands assigned by DFT to LTA vibrations are marked with a black star at the top; unmarked bands are for either BULKY or TMA; the yellow-shaded band is assigned by DFT to the empty D4R symmetric breathing mode and the cyan-shaded band is for the F$^-$/D4R; the green-shaded band is from the CN symmetric stretching of TMA. (c) Correlation between the Raman band intensity ratio of F$^-$/D4R to empty D4R and the TMA quantity in the precursor gel.

Figure 4.3 (a) $^{29}$Si MAS NMR spectra of LTA-BULKY-xTMA (x = 0, 0.01, 0.025, and 0.05); the peak locating around 98 ppm and the two peaks at 109 and 112 ppm are from Si (Q$_3$), Si (Q$_4$) in the intact F$^-$/D4R, and Si (Q$_4$) in intact empty D4R, respectively. (b) Peak deconvolution for the three peaks in the $^{29}$Si MAS NMR spectra.

Figure 4.4 (a) Calculated Raman spectra from DFT of individual defective systems and their components for combination. (b) Structures of defected D4Rs. Color coding: blue—Si, red—O, green—F,
highlighted—O\(^-\). (c) Comparison between calculated (black) and experimental (purple) Raman spectra. The calculated LTA-BULKY-TMA spectrum is from averaging spectra with weights in panel (a). (The calculated frequency axis is blue shifted by 20 cm\(^{-1}\), representing the known systematic shift of vibrational frequencies predicted by the PBE functional.) ........................................................................................................77

Figure 4.5 (a) Calculated \(^{29}\text{Si}\) NMR spectra of Si atoms in the individual defective systems shown in Figure 4.4b. (b) Comparison between calculated (black) and experimental (purple) \(^{29}\text{Si}\) NMR spectra. The calculated LTA-BULKY-TMA NMR spectrum is from averaging spectra with weights in Figure 4.4a..............................................................80

Figure 4.6 Energy changes of key reactions in defect healing for (a) LTA-BULKY and (b) LTA-BULKY-TMA. In both systems, neutral and charged defects are healed with Si(OH)\(_4\) and HF, respectively. All reactions are favorable except for healing charged defect in LTA-BULKY-TMA. Negatively charged oxygen is highlighted using a yellow cross...................................................................................................82

Figure 4.7 (a) \(^{29}\text{Si}\) MAS NMR spectra of LTA-BULKY-TMA-0.050TMA synthesized at 125, 150, and 170 °C to test for thermodynamic control of defect healing. (b) Peak deconvolution of the \(^{29}\text{Si}\) MAS NMR spectra...........................................................................................................83
Figure 5.1 Structure of LTA with its three composite building blocks.......................... 87

Figure 5.2 The hypothetical crystallization for the high-silica LTA (Si/Al = 7) synthesized in fluoride-free way using two silica sources (Si from isolated Si-D4Rs : Si from conventional TEOS = 1 : 1)........................................ 94

Figure 5.3 Scheme for the crystallization of high-silica LTA (Si/Al = 7.55) in HF-free way.......................................................................................................................................................... 95

Figure 5.4 XRD results of the high-silica LTA synthesized in fluoride-free way. The final ratio of composition of the precursor solution is 0.5 TEOS : 1/16 isolated Si-D4R·8TMA·64H$_2$O : 1/24 Al$_2$O$_3$ : 0.45 BULKY-OH OSDA : 205 H$_2$O, plus 1 wt.% seeds. The chosen temperatures and times for the synthesis are 120 °C (a), 135 °C (b), and 150 °C (c), 3 w, 4 w, and 5 w, respectively................................................................. 98

Figure 5.5 XRD results for the crystallization of the high-silica LTA with different water content in the precursor. The final ratio of composition of the precursor solutions is 0.5 TEOS : 1/16 isolated Si-D4R·8TMA·64H$_2$O : 1/24 Al$_2$O$_3$ : 0.45 BULKY-OH OSDA : X H$_2$O, plus 1 wt.% seeds. The temperatures and times for all the syntheses are 135 °C and 3 weeks, respectively................................................................. 99

Figure 5.6 XRD comparison between the high-silica LTA (using siliceous isolated D4Rs; synthesized under 135 °C for 3 weeks in HF-free way) and other LTA materials with different Si/Al ratios....................................................... 100
Figure 5.7 $^{29}$Si NMR (a), $^{27}$Al NMR (b), $^{13}$C NMR (c), and TGA (d) results for the high-silica LTA with an Si/Al ratio of 7.55 synthesized using isolated siliceous D4Rs in HF-free way, under 135 °C for 3 weeks. In (a), Peak 1, 2, 3, and 4 are assigned to different Si atoms of $Q_4(nAl)$ in the framework, in which $n = 0, 1, 2,$ and 3, respectively; In (b), the 2 small peaks marked by a star are the sidebands of the main peak; In (c), Peak e is assigned to the only C in TMA, while Peak a, b, and C are assigned to the 3 methyl groups in the BULKY molecule. Peak d is assigned to the methylene group in BULKY, but with inadequate relaxation in the NMR measurement; In (d), the sample loss before 200 °C is due to the water removal, while the the sample loss of 24.8% after 375 °C is attributed to the oxidation of BULKY and TMA.

Figure 5.8 SEM pictures for the high-silica LTA with an Si/Al ratio of 7.55 synthesized using isolated siliceous D4Rs in HF-free way, under 120 °C after 2 (a), 3 (b), and 4 weeks (c); the corresponding XRD results are shown in (d).

Figure 5.9 Raman spectrum of the high-silica LTA synthesized in fluoride-free way (using both TEOS and isolated Si-D4Rs as the silica source) compared with LTA-BULKY before and also after calcination.

Figure 5.10 (a) In-situ XRD results of commercial LTA (Si/Al = 1), LTA seeds (Si/Al = 2.2), LTA-BULKY (Si/Al = 66), and the novel LTA (Si/Al = 7.55). All the samples were first measured under room
temperature, and then measured again after being treated under 800 °C for 3 h, 900 °C for 3 h, and 1000 °C for 3 h.
1.1 Zeolites Introduction

Zeolites are well-defined and ordered microporous crystalline materials constructed by the continuous linkage of corner-sharing TO$_4$ tetrahedra, which take T atoms (e.g., Si or Al) as the tetrahedral center in the structure (Figure 1.1). Since the assembly and combination of the tetrahedra can be achieved in a wide variety of ways with different T-O-T angles and lengths, there exist numerous different frameworks of zeolites (e.g., MFI, CHA, LTA, BEA, and FAU zeolites; each zeolite framework is assigned to a three-letter code by the International Zeolite Association (IZA)) with distinct pore sizes (0.4 - 2 nm), channel shapes and surface areas. In addition, due to that the different T atoms, such as Al, Sn, Zr, et al., in TO$_4$ tetrahedra, the composition of zeolites is also various. Because of all those structural and compositional properties, and its excellent hydrothermal stability, zeolites have been broadly applied to many industrial fields, including molecular-sieving-based gas separation, ion exchange, catalytic chemical reactions (as heterogeneous solid acid catalysts). Recently, zeolites have been used in several emerging areas such as biomass conversion, carbon capture, and energy storage. Specifically, Cu-containing SSZ-13 zeolite with CHA structure (containing Al in the framework, and Cu cations for balancing charge from those Al), has been commercialized in treating NO$_x$ emission from vehicle exhaust (4NO + 4NH$_3$ + O$_2$ → 4N$_2$ + 6H$_2$O and 6NO$_2$ + 8NH$_3$ + O$_2$ → 7N$_2$ + 12H$_2$O, in which NH$_3$ is generated from the decomposition of urea under an elevated temperature around 150 °C; also named “DeNO$_x$” reaction). Owing to the small pore size (consisting of 4-membered rings (4-MRs), 6-MRs, and 8-MRs), other bulky molecules in vehicle exhaust, including unreacted fuels, cannot diffuse into the micropores of this zeolite, preventing the coke formation and catalyst deactivation. Another important example of zeolites is FAU zeolite (with 3-dimentional 12-membered ring channels and spherical super-cages ($\approx$ 1.12 nm diameter)), which has been commercialized for the fluid catalytic
cracking (FCC) in the petrochemical industry due to its large pore opening and strong acidity. By converting heavy oil into value-added lighter products, FCC using FAU zeolite not only becomes the most valuable reaction in zeolite catalysts, but also one of the most important processes in the petroleum refineries. Only in 2020 in the USA, 1.46 billion barrels of crude oil were processed in the FCC unit, accounting for about 40% of downstream processing of fresh feed input. In addition, Si atoms in zeolite frameworks can be replaced by heteroatoms. When Ti, Sn, and Zr are introduced into the framework, new catalytically active centers are created, leading to improved performance for many new reactions, including aromatic oxidation, ketone oxidation and Beckmann rearrangement, olefins epoxidation, and when Tin is incorporated into the framework, Baeyer-Villiger oxidation can be then catalyzed. Recently, it has been found the hydrophobic Sn-BEA catalyst is an outstanding catalyst for isomerization of glucose to fructose in aqueous phase, which is a critical step for converting lignocellulosic biomass into fuels and value-added chemicals.

Fig. 1.1: Schematic showing how two T atoms are connected by a T-O-T bond to form linked TO₄ tetrahedra, and how the linked TO₄ tetrahedra combine together to form rings, cages, and continuous channels in a supercell of BEA. The composition of a 12-MR from the BEA zeolite is displayed in detail, and when a Si (IV) atom in the 12-MR is substituted by an Al (III), a proton will appear to connect with the neighboring O atom (shaded in red), to fulfill the charge balancing requirement and form a Brønsted acid site, which is catalytically active.
1.2 Synthesis of Zeolites

Close to some volcanic areas on the earth, there are naturally formed zeolites, and it is the place where in 1756, the Swedish mineralogist A. F. Cronstedt first discovered this porous material. Inspired by the geologic characteristics of those sites and the composition of the zeolites found in nature, in the 1940s, Barrer and Sameshima et al. simulated the crystallization conditions and first attempted to artificially synthesize zeolites with a low Si/Al ratio (from 1 to 5) through a hydrothermal process, using natural reactants such as volcanic glasses and performing the crystallization in a well-sealed pressurized autoclave (> 10 MPa) under a high temperature (> 200 °C). Later on, by employing more reactive silica and alumina raw materials (e.g., aluminates and soluble silicates), Breck and Milton, from Dow Chemical Company, developed the hydrothermal synthetic pathway. In the synthesis method, a homogeneous synthetic solution/gel was treated under a significantly lower temperature (around 100 °C) with autogenous pressure. New zeolites, including zeolite Type L (LTL), and Type X and Y (FAU), all still with low Si/Al ratios, were then obtained. Apart from silicon and aluminum sources, the solution/gel involved here is also comprised of inorganic base (e.g., NaOH or KOH) and water. The inorganic base is utilized as the mineralizing agent to help dissolve and reassemble silica and alumina in aqueous media during zeolite crystallization, and water is considered generally as the solvent and also the medium to transfer the heat necessary for the crystallization. Meanwhile, water is also thought by some researchers to act as a catalyst (or “mineralizer”) for the breakage and/or formation of T-O-T bonds of zeolites.

In 1961, another milestone for the hydrothermal synthesis of zeolites was achieved by Barrer and Koktali et al., who introduced organic molecules into the precursor gel/solution for the hydrothermal crystallization. The first of such organic species was quaternary ammonium cations, and later imidazolium/pyrazolium cations, phosphonium cations, sulphonium cations, coordination complex cations, and neutral amines were also employed. With the addition of...
these organic cations, the Si/Al ratio of crystallized zeolites was increased to 5-10, and those high-silica zeolites displayed improved thermal/hydrothermal stability and wider catalytic applications, including FCC,\textsuperscript{40} selective catalytic reduction (SCR),\textsuperscript{41,42} alkylation and rearrangement,\textsuperscript{43} et al. Meanwhile, this new methodology also led to the syntheses of new zeolites, such as high-silica BEA\textsuperscript{44} and ZSM-5 (MFI)\textsuperscript{40,45} and from that time on, the number of synthesizable zeolites grew explosively, to 255 as of July 2022.

Because those organic cations reside in the micropores of as-made zeolites, it was believed that during crystallization, the zeolitic pores and channels, and then the zeolites themselves are formed around those cations. The organic cations were then considered as templates (named “organic templates”) for the formed zeolite frameworks, determining the size and shape of the pore system and hence of zeolites.\textsuperscript{46,47} Nevertheless, zeolite scientists realized a deficiency for this definition: it lacks a 1 to 1 correspondence of key-and-lock type between “organic templates” and zeolites. For example, zeolites with MFI framework can be prepared using 22 different organic cations as of 1988,\textsuperscript{48} and today this number has even further increased. As a result, the nomenclature of organic templates for the organic cations was abandoned. After understanding of the capability of the organic cations in directing crystallization toward to a particular zeolite, people noticed different roles of the organic cations, including various degrees of pore filling, from weak match to strong template effect, and stabilization of some zeolite cages and substructures via a host-guest interaction. Hence, another terminology, “organic structure-directing agent (OSDA)”, was adopted instead of “template”.\textsuperscript{30,33,49}

It was until 1978 that all the synthesized zeolites still relied on basic media, in which hydroxide anion (OH\textsuperscript{−}) performed as the mineralizing agent. Afterwards, Flanigen and Patton first used fluoride (F\textsuperscript{−}) as the mineralizer instead of OH\textsuperscript{−}. The corresponding pH of the synthesis environment changed from basic to neutral.\textsuperscript{50} From then on, this fluoride-mediated hydrothermal synthesis route has been extensively developed in the following four decades, and a large number of known and also unknown
zeolites were synthesized successfully with the addition of F$^-$.\textsuperscript{51} Since F$^-$ in the as-made zeolites can balance the positively-charged OSDAs, zeolites with a higher Si/Al ratio, or even siliceous zeolites were obtained. Due to the same reason and slow crystallization, the negatively-charged defects (Si-O$^-$), formed in basic condition, can also be reduced remarkably, causing low-defect or even defect-free zeolites.\textsuperscript{52} Moreover, research using $^{19}$F NMR has shown that F$^-$ is located in some small cages of zeolites after crystallization. Therefore it is considered that F$^-$ can play a structure-directing role for the formation of those cages.\textsuperscript{53} Consequently, some new small-cage-containing zeolites, or existing ones with notably higher Si/Al ratios, were synthesized with F$^-$ in the synthesis media. Among all the cases, double 4-membered rings (D4Rs) are the most well-known one. The role of F$^-$ on the stabilization and formation of the D4Rs is called “Zicovich-Wilson effect”.\textsuperscript{52} Even so far, F$^-$ is still indispensable in the syntheses of siliceous zeolites with D4Rs (e.g., siliceous LTA, ITH, and AST).\textsuperscript{54-56}

Besides the most common hydrothermal synthesis approach, there are other ways invented for synthesis of zeolites. The first one is the solvothermal synthesis, which can be regarded as a continuation of the hydrothermal method, since only water is replaced by organic solvents in this synthesis approach.\textsuperscript{57} Owing to the decreased potential energy on the surface of zeolite crystals formed in the organic solvents, zeolites with a larger size and less defects can be made.\textsuperscript{58} The first reported zeolite synthesized using this method was pure-silica SOD, where Bibby and Dale introduced ethylene glycol and 2-propanol as solvents.\textsuperscript{59} Similarly, ionic liquids are also utilized to replace water in the hydrothermal method and the zeolite crystallization is accordingly called “ionothermal synthesis”. Ionic liquids are made up of organic cations (e.g., imidazolium) and inorganic anions (e.g., BF$_4^-$). Due to their low melting points, they are in liquid state under room or relatively low temperatures.\textsuperscript{60} In 2004, Morris et al. exploited this method to first successfully crystallize new aluminophosphate zeolites, including SIZ-x (x = 1, 3, 4, and 5; 3 is for AEL, 4 is for CHA, and 5 is for AFO).\textsuperscript{61} The reason for these successes might be that most inorganic species involved in the zeolite synthesis have a superior
solubility in the ionic liquids, which can lead to a strong interaction among all the molecules in the gel and improve the homogeneity of the precursors.\textsuperscript{62,63}

Another continuation of the hydrothermal synthesis is called “dry-gel-conversion (DGC)” method, in which concentrated precursor gel with a little water is prepared first. The precursor is then treated under crystallization temperature in an autoclave where a small amount of water is added, but without directly contacting with the precursor gel. During the crystallization process, the precursor gel is converted into zeolite crystals by contacting water vapor. The method was reported by Xu et al. in 1990, who successfully made zeolites with MFI structure.\textsuperscript{64} Later, BEA zeolites, with an Si/Al ratio ranging from 30 to 370, were also successfully synthesized by Matsukata et al. using the DGC method.\textsuperscript{65,66} In 1990, Camblor and Villaescusa et al. further decreased the water ratio ($\text{H}_2\text{O}/\text{Si}$ less than 15) in precursor gel for the DGC method\textsuperscript{52,67} and successfully made a series of zeolites, such as BEA,\textsuperscript{68} ITQ-3 (ITE),\textsuperscript{69} ITQ-4 (IFR),\textsuperscript{70} ITQ-7 (ISV),\textsuperscript{54} ITQ-9 (STF),\textsuperscript{71} ITQ-12 (ITW),\textsuperscript{72,73} SSZ-23 (STT),\textsuperscript{74,75} et al. They also discovered that in the DGC method, the water to silica ratio heavily influences the final product. A tiny change of water in the precursor may lead to another totally different zeolite. Another interesting observation found in the comparison between DGC and the conventional hydrothermal method is that, when decreasing the water amount in the gel precursors, zeolites with more open frameworks (or lower framework density, defined as the number of tetrahedral atoms per 1000 Å\textsuperscript{3}) could be synthesized. Zeolite scientists summarized this as “Villaescusa's Rule”.\textsuperscript{52}

Recently, another interesting synthesis approach, called as “solvent-free crystallization”, was invented, in which no additional solvent is added in the synthesis, making the overall synthesis process more sustainable and environmentally friendly.\textsuperscript{76} Employing this method, MFI, MTN, SOD, MOR, BEA, and FAU were all synthesized successfully.\textsuperscript{77}
1.3 Challenges in Understanding of Zeolites Crystallization Mechanisms

Despite massive and considerable research efforts in exploring new methods for zeolite crystallization, all the synthetic approaches developed so far are somehow still based on empirical knowledge that has been accumulated by experimentalists. The time- and energy-consuming trial-and-error method is still the most commonly-used approach for zeolite research, which is mainly due to the lack of understanding of the zeolite crystallization mechanisms. Although many previous studies have focused on this topic using different characterization techniques (detailed in following chapters), we still have not yet comprehensively discerned and understood the whole picture at atomic-level of how the silica and alumina sources are used to grow around OSDAs to form microporous zeolites during the crystallization process. In addition, the roles played by other species in the media (such as F−) in synthesis and how to control zeolite properties during crystallization are still not fully understood. As a result, the rational synthesis of zeolites with desired structures remains a great challenge, and these barriers limit the development and further applications of zeolites.

The first specific example of this issue is reflected in synthesizing zeolites with new frameworks. By using Monte-Carlo computational approach, Deem et al. has built a database for theoretically possible hypothetical zeolites structures, which included more than 4 million of possible structures. In contrast, however, according to the IZA, to date the number of synthesizable zeolites is just 255. The huge difference restricts us in obtaining more new zeolites and applying them to new industrial fields. The huge difference between the theoretical and experimental studies clearly suggests that there is still no such a general mathematical model that we can refer to synthesize new zeolites.

Another example is reflected in the control zeolite compositions. Zeolite composition is a critical parameter which can greatly influence the catalytic performance of zeolites. For instance, in the DeNOx application (introduced in Section 1.1), Al-containing CHA zeolite should have a proper Si/Al ratio. High Si/Al ratio would lead to a reduced number of exchangeable sites and then a lower catalytically
active Cu content, causing a lowered catalytic efficiency. Low Si/Al ratio can help to promote the reaction rate and conversion due to the higher density of Cu sites, but meanwhile, too much Al will result in a poor hydrothermal stability for the zeolite catalysts.\textsuperscript{79} However, in spite of its importance, researchers still find difficulties in controlling the composition of many zeolites. A symbolic example is FAU zeolite: so far it is still challenging to synthesize high-silica FAU (with a better hydrothermal stability) in a one-step pathway. As a result, the further development of hydrocracking application (FCC, as introduced in Section 1.1) using FAU zeolites is restricted. In 2020, Zhongmin et al.\textsuperscript{80} developed a cooperative strategy involving the uses of FAU nuclei, a bulky OSDA (tetrabutylammonium hydroxide), and a gel system with low alkalinity to increase the Si/Al ratio of FAU up to 7.8, which was a great progress compared to the previous highest value of 4.5 achieved by using the OSDA of 15-crown-5 ether. However, this Si/Al ratio of 7.8 is still not high enough to satisfy the industrial requirement for FCC process, due to its relatively poor hydrothermal stability. The lack of synthesis approach for controlling the zeolite composition, again, is due to the poorly understood formation mechanisms of zeolites. In fact, crystallizing a targeted zeolite by designing an appropriate synthesis approach still has not been achieved, which is still the “Holy Grail” problem in this field.\textsuperscript{81,82}

My Ph.D projects are aimed to solve this problem, by mainly using Raman spectroscopy (with the correct assignments of zeolite Raman bands) to probe the assembly of building units and defect structures formed during zeolite crystallization processes. Inspired by the mechanistic study, I have developed different approaches to synthesize zeolites with targeted composition (Si/Al ratio) and defect properties.

1.4 Previous Studies about Zeolite Crystallization Mechanisms

In order to study the crystallization processes of zeolites, the characterization techniques have evolved from pure \textit{ex-situ} examinations to increasingly complex \textit{in-situ} or \textit{operando} methods on different length scales ranging from atomic subunit structures and molecules up to macroscopic objects.
in the millimeter or centimeter range. Solid-state NMR can be used to characterize short-range and local features less than 0.35 nm (e.g., adjacent atoms). Raman and/or IR spectroscopy can be used to observe medium-range structures within 0.35 - 1 nm (e.g., rings and composite building units in zeolites). X-ray diffraction can be used to characterize long-range periodic structures larger than 1 nm.\textsuperscript{83}

X-ray powder diffraction (XRPD) is the most common characterization method to study the crystalline structures of zeolites. It is a non-destructive technique providing information not only on crystal structures, but also on phase compositions and microstructures of a given phase (space groups and lattice parameters, crystallite size, and microstrain). However, since XPRD is limited to the samples possessing a long-range order, it is not suitable for the investigation of the nucleation and growth stages of zeolite crystallization. It is often employed with other short- and/or medium-range characterization techniques together to reveal the full picture of zeolite formation.

Solid-state NMR spectroscopy, as introduced, is a short-range probe and ideally suitable for researching nucleation and crystallization/growth processes of zeolite materials. Additionally, interzeolite conversion, another way for us to get desired zeolite frameworks, could also be monitored by using solid-state NMR. In order to study the AlPO\textsubscript{4}-5 zeolite crystallization process, Hu et al.\textsuperscript{84} designed and made a ceramic rotor with tight sealing, which could stand a pressure as high as 10 MPa and a maximum temperature of 250 °C. Then, time-dependent \textit{in-situ} \textsuperscript{27}Al MAS NMR measurements were performed: tracing the \textsuperscript{27}Al MAS NMR signals exhibited the existence of six-fold coordinated (Al\textsuperscript{[VI]}) at the initial crystallization stage (still amorphous monitored by XRD), and then it was changed into the four-fold coordinated form and incorporated into the zeolite framework, with which the amorphous phase was converted into a crystalline one. Hartmann et al.\textsuperscript{85} once used the solid-state \textsuperscript{27}Al NMR technique to study how VPI-5 transformed into AlPO\textsubscript{4}-8. It was revealed that there were 2 consecutive steps in the transformation: the 1\textsuperscript{st} one was relevant to the desorption of water, and the 2\textsuperscript{nd} was for the rearrangement of the framework. Ivanova et al.,\textsuperscript{86} by utilizing \textit{in-situ} \textsuperscript{13}Si MAS NMR
alongside $^{29}$Na and $^{27}$Al MAS NMR, first attempted to observe the formation processes of BEA zeolite, and they found that corresponding to the 2 different applied synthesis protocols (based on the solution-mediated crystallite formation and solid-solid transformation), there were two distinct crystallization mechanisms with completely different gel formation and aging plus crystal nucleation and growth (Figure 1.2). In addition, through monitoring the structure-directing behavior of tetraethylammonium cations (TEA$^+$) at the very early stage of the crystallization, TEA$^+$ in different forms were identified, and the mechanism of their interaction with other species has been established.

Fig. 1.2: Schematic representation of the two different mechanisms of zeolite BEA crystallization based on the solution-mediated crystallite formation and solid-solid transformation.
The dimension of zeolite precursor structures falls into a particular range (0.35 nm - 1 nm), which is too large for short-range techniques like IR and NMR specially designed for atomic-level structural analyses, and meanwhile also too small and disordered for other long-range characterizations such as X-ray diffraction (XRD). Therefore, understanding the full picture of the formation mechanisms of zeolites, such as the evolution of rings and composite building units during crystallization, still requires the techniques sensitive to their length scales.87,88 Raman signals are from inelastic scattering of photons, which are generated due to the density change of electron clouds often occurring in symmetrical molecular vibrations. Owing to this property, plus its sensitivity to medium-range structures, Raman spectroscopy has emerged as a powerful tool for investigating the developments of zeolitic rings and composite building units during zeolite crystallization.89 In order to better understand the charge density mismatch synthesis approach, Hong et al.90 applied Raman, 29Si NMR, and 13C NMR to investigate the formation pathway for high-silica LTA zeolite crystals in the simultaneous presence of TEA+, tetramethylammonium (TMA+), and Na+ ions as SDAs. They discovered that the nucleation began with the formation of lta-cages rather than the notably smaller sod-cages and D4Rs, with concomitant incorporation of TMA+ and Na+ into a very small amount of the solid phase, with a low Si/Al ratio of 2.5. Later, it was demonstrated that sod-cages were built around the pre-organized lta-cages and that D4R-cages were then constructed by the progressive addition of low-molecular-weight aluminosilicate species. Through this process, the formation and growth of embryonic LTA zeolite crystals were promoted. Matsukata et al.91 applied Raman and 29Si NMR to study the medium-range structures in BEA-type zeolite synthesized with TEA+. It was found that double three-membered silicate rings (D3Rs) stabilized by TEA+ were present in the mother TEA+-silicate solution. In the next course of crystallization, the D3R units transformed “4−2”-type secondary building units (SBUs) in the formed dry gel. Such “4−2”-type SBUs remained in the dry gel and played an imperative role in the crystallization of BEA-type zeolite. Okubo et al.,92 by using Raman from another perspective, observed
the change of Raman signals of TEA$^+$ in the hydrothermal synthesis for BEA zeolite, proposing a comprehensive scheme for its crystallization by focusing on the clustered behavior of TEA$^+$: (i) after heating, TEA$^+$–aluminosilicate composites formed; (ii) the aluminosilicate reorganized together with the conformational rearrangement of TEA$^+$, yielding the formation of the amorphous TEA$^+$–aluminosilicate species with zeolite BEA-like structure; (iii) zeolite BEA nuclei formed by the reorganization of the amorphous TEA$^+$–aluminosilicate species obtained in (ii); (iv) the crystals grew continuously. Dusselier et al. presented a cooperative OSDA blueprint between 15-crown-5 and trans choline for high-silica (Si/Al > 6) FAU zeolite synthesis. A mechanistic study, completed by a Raman tracking for the crystallization, pointed to a nucleation induced by the formation of sod-cages with trans choline (rather than D6R- or super-cages).

However, despite all these great progresses from Raman, one obstacle - the partially-understood and inductive- and comparative-reasoning-based assignments of zeolite Raman spectra - is still out there, which indeed restricts its application to the zeolite study, and even makes the previous results doubtful. In the past, it was often assumed that Raman bands of zeolites should be assigned to individual rings, but if this assignment methodology were valid, why would not LTA and CHA, the 2 zeolite cases both comprised of 4-MRs, 6-MRs and 8-MRs yet in different configurations, present essentially identical Raman spectra? For this discrepancy, another fundamental question was prompted: if Raman features cannot be assigned to the vibration of individual rings, what else should be? Should they be associated with other larger composite building units in zeolites? In order to answer this question rigorously, herein, we used an integrated method, trying to combine together zeolite synthesis, spectroscopy, and Raman simulation (based on periodic DFT modeling) to advance our understanding on the Raman vibrations of a range of well-defined zeolite frameworks. The relevant results are shown in the following chapters.
1.5 Defects Control in Zeolite Synthesis

Another critical aspect regarding the zeolite crystallization mechanisms is its defects control. Although zeolites are crystalline inorganic solids, their structures are actually imperfect and the presence of defect sites heavily influences their overall properties, including the thermal and chemical stabilities, as well as their performances in key areas such as catalysis, gas and liquid separations, and ion-exchange.\textsuperscript{99}

Zeolite defects are defined as a perturbation or irregularity in the periodic crystalline arrangement that will somehow break the perfect symmetry of the periodic association of \( \text{TO}_4 \) units. Specifically, zeolite defects can be categorized into three groups. The 1\textsuperscript{st} group is caused by heteroatoms in the framework: when Si\(^{4+}\) is replaced by Al\(^{3+}\), a negative charge will be created. The negative charge requires being compensated by an extra-framework positive charge. When the extra-framework positive charge is from a proton bound to one of the bridging oxygens in the Al tetrahedron [Si–O(H)–Al], a Brønsted acid site (also referred to “bridged hydroxyls”) will emerge.\textsuperscript{100} Such “defect” is responsible for the origin of the remarkable properties of zeolites in acid-catalyzed reactions. The 2\textsuperscript{nd} group is called “isolated external silanol defects” (Si-OH), which are formed on the crystal surface when the crystallization finishes (at crystal terminations).\textsuperscript{101} The 3\textsuperscript{rd} one, with similar Si-OH or Si-O\(^-\) structures, is named “internal silanol defects”, since they are distributed inside zeolites rather than on the surface.\textsuperscript{99,101}

Moreover, there are 2 subsets in the group of internal silanol defects: the 1\textsuperscript{st} one is called “connectivity defects”, which result from the disconnection at oxygen atoms of T-O-T bonds in zeolites; the 2\textsuperscript{nd} is “silanol nests”, which are caused by missing tetrahedrally coordinated T atoms (or “vacancy”) in the framework.\textsuperscript{102–104} Although both connectivity defects and silanol nests appear in multiple forms (for the former, it includes geminal, vicinal, and bridged silanol, while for the latter, it includes silanol triad and silanol tetrad), they all show a much weaker acid strength than the Brønsted acid sites,\textsuperscript{105} and it is them that I focused on in my Ph.D. studies.
For the interested defects of silanol species, first they are considered as reactive sites that are able to stabilize metals introduced into tetrahedral positions of zeolites via an isomorphous substitution.\textsuperscript{106,107} Furthermore, the existence of the defects will increase the hydrophilicity of zeolites.\textsuperscript{108–111} Finally, they act as (synergistically or on their own) as active sites in catalysis, influencing the selectivity,\textsuperscript{112,113} and also the formation of coke.\textsuperscript{114–117} Due to all these properties, defects-containing zeolites have been studied and applied to many directions.

In catalysis, many clean-energy catalytic applications of zeolites involve conversion of biomass-derived feedstocks into sustainable fuels and chemicals. Such conversions often involve oxygen-containing organic compounds. Recent research shows that the catalytic performance of zeolites for upgrading of oxygen-containing organics can be dramatically enhanced through the engineering of Si-OH/Si-O\textsuperscript{−} defects into otherwise hydrophobic materials. For example, in alkene epoxidation with H\textsubscript{2}O\textsubscript{2}, it was found that the most hydrophilic Ti-BEA (titanium-containing zeolite BEA) gives epoxidation turnover rates 100 times larger than those in defect-free Ti-BEA, and with the highest selectivities, which was attributed to a favorable activation entropy from the disruption of water clusters anchored at Si-OH defects at epoxidation transition states.\textsuperscript{118} Silanol defects in all-silica MFI zeolite (silicalite-1) improve both activity and selectivity in the conversion of cyclohexanone oxime to epsilon-caprolactam (Beckmann rearrangement).\textsuperscript{119} Propane dehydrogenation to propylene (120 million metric tons produced in 2018, projected to increase to more than 190 million metric tons by 2030), was enhanced by adding Si-OH defects in HZSM-5 (aluminosilicate MFI) zeolite catalysts, allowing the homogeneous dispersion of Zn/Sn/Pt particles as active sites throughout the acid catalysts.\textsuperscript{120}

In terms of gas adsorption, enhancing adsorption capacities of oxygen-containing organics and of CO\textsubscript{2} itself in zeolites are both important for clean-energy technologies. Several studies point to improved adsorption properties of zeolites when containing defects. For example, uptake of small polyols in silicalite-1 increased from adding defects, with propylene glycol adsorption increasing by a
factor of 20. CO₂ adsorption in ZSM-58 and silicalite-1 zeolites can be also increased when defects are introduced into the zeolites. In both cases, enhanced adsorption capacity was attributed to increased access to smaller cavities in the structures after introducing defects.

These recent findings all indicate the importance of controlling defects in zeolite catalysts, which can be critical for their catalytic and adsorptive properties. Researchers in the past have explored many ways to engineer defects in zeolites.

The first one is the synthesis of layered zeolites. Due to their high surface to bulk ratio, layered zeolites contain a high density of defects. The layered zeolitic precursor with a MWW structure was among the first zeolite precursors to be delaminated, producing zeolite ITQ-2, in which the stacking of the layered precursor was broken, separating the layers and forming a highly accessible house of cards structure. As a result, the ITQ-2 layers are rich in terminal silanols as confirmed by ²⁹Si NMR. Single-unit-cell MFI nanosheets, synthesized in the presence di-quaternary ammonium-type surfactant, also possess a high density of defects.

The 2nd approach, similar to the 1st, is to create mesopores in zeolites, since the addition of mesoporosity to the parent zeolite crystals also produce defects in zeolites. The OSDA of 3-(trimethoxysilyl)propyl]hexadecyldimethylammonium chloride was used to synthesize MFI zeolite with 3–8 nm mesopores and an increased number of defects. It was also discovered that using low temperature (100 °C) and well-distributed Si/Al (198), the propagation of defects was favored. An interesting strategy to create defects in FAU zeolite with tunable dimensions was proposed by Garcia-Martinez: after a partial dissolution of the zeolite in an alkali media, its recrystallization would occur around the introduced surfactant micelles, leading to the creation of well-defined mesopores.

Another method is to remove Al in the zeolite framework to cause silanol nests, which could be achieved by acid leaching or steaming processing. For the steaming treatment, it has been widely applied in industry for the production of ultra-stable zeolite Y (USY with FAU structure) for tens of
years, assisting FCC and hydrocracking of heavy crude oil fractions, including atmospheric and vacuum gas oils or residues. Similarly, water intrusion at high pressure could also be utilized to create defects in zeolites. This method was applied to a defect-free silicalite-1, and owing to the breaking of siloxane bridges, isolated external silanols and silanol nests were both created in this hydrophobic zeolite only after the first water intrusion cycle. Interestingly, it was also observed that, in this high-pressure water intrusion treatment, the silanol defects created in a defect-free silicalite-1 (fluoride-mediated synthesis) were lower than that synthesized in alkaline media without fluoride.

Finally, similar to the described layered zeolites, zeolite crystals with smaller sizes should contain more defects compared to large crystals, because they have more prominent external surface areas. Therefore, several synthesis methods have been developed for the synthesis of zeolite nanocrystals. Silica sources (e.g., fumed silica, tetraethyl orthosilicate, or colloid silica, et al.), impurities in silica sources (e.g., Al, Fe, Ca, et al.), different inorganic and organic OSDAs (also their quantities), and even growth modifiers (e.g., polyethylenimine for SSZ-13 synthesis) all have been known to affect the crystal size of zeolites, leading to the formation of zeolite nanocrystals.

Despite all the significant efforts in defects engineering of zeolites, the current synthesis methods are still either merely about increasing the external surfaces of crystals (only for isolated external defects) or using post-synthesis treatments to obtain defects in an uncontrollable way. To date, it is still difficult to control defects formed in the internal spaces of zeolites where shape-selectivity is conferred. Hence, it is highly desirable to develop synthetic strategies to exert control at atomic-level over the amount and type of defects in zeolites.

In my Ph.D. study, based on our understandings obtained in studying zeolite formation mechanisms of siliceous LTA, we developed a novel route to control the defects in zeolite formation – beyond what is possible from the traditional fluoride-free (basic pH) and fluoride-mediated (neutral pH)
routes—opening up new, atomic-level control of defects engineering during zeolite crystallization,133 which will be elaborated in the following chapters.

1.6 Si/Al Ratio Control in Zeolite Synthesis

The control of Si/Al ratio in zeolite synthesis is another attention-drawing aspect regarding zeolite crystallization mechanisms. As introduced in Chapter 1.3, Si/Al control is critical in zeolite applications: although a limited amount of Al could render a better hydrothermal stability for zeolites, the catalytic efficiency might be sacrificed to a large extent. Therefore, it is a trade-off problem between catalysis and stability. Also, the desired Si/Al ratio is also dependent on the specific application, indicating that synthesizing a particular zeolite with Si/Al ratio from 1 to infinity is important for a wide range of applications. For example, although siliceous zeolites cannot be used in catalysis, they have shown exciting potential in several conventional and also newly emerging areas, such as gas separation, drug delivery, and low-

6

As described in Chapter 1.2, before OSDAs were invented, it was difficult to synthesize zeolites with a high Si/Al ratio. This obstacle lay in the mismatch between the basicity requirement of nucleation/crystallization and high framework Si/Al ratio. The high basicity in gel facilitates the nucleation and crystallization processes, but meanwhile it would increase the solubility of silica sources, leading to a low Si/Al ratio in solid-state zeolites. On the contrary, a lower basicity of gel in theory could help with the formation of more siliceous polymeric intermediates and products, but in practice, due to the increased energy barrier for nucleation and crystal growth, the zeolite crystallization is difficult to complete.134

The emergence of OSDAs, with a much lower charge density than the inorganic cations (e.g., Na+, K+, and Li+) used in the zeolite synthesis, solved this problem and offered an effective way to improve the Si/Al ratio. The reason for the increase in the Si/Al ratio is straightforward. With a larger volume of the cations (OSDAs), zeolites could only contain a lower concentration of cations in the
pores, so the amount of negative charges in framework, arising from the substitution of Si (IV) by Al(III), was reduced. At the same time, unlike the synthesis without using OSDAs, the crystallization kinetics is even accelerated by virtue of the enhanced host-guest interaction and the stabilization effect of OSDAs on the internal pores and cages.

Consistent with the development history of zeolite synthesis, after Flanigen and Patton introduced fluoride into zeolite synthesis in 1978, Si/Al ratio was further increased, to even infinity for some zeolites (e.g., LTA, ITH, AST, and ITW). This further improvement was ascribed the ability of fluoride in charge balancing the OSDAs with positive charges, hence further reducing the Al number in zeolite framework. To date, this fluoride-mediated synthesis avenue has been indeed successful, since more than 90% of the siliceous zeolites were prepared in this way.

However, the use of fluoride, in particular HF, induced problems that hindered its industrial commercialization due to the cost and safety-related issues about the environment and people’s health. Therefore, it is required to develop fluoride-free routes for the synthesis of high- and pure-silica zeolites. For example, in 2018, Fan et al. used the DGC method, as described in Chapter 1.2, for the first time succeeded in synthesizing siliceous CHA and STT zeolites, and meanwhile siliceous BEA, MFI, and MRE were also made for obtaining a better insight into the crystallization processes. By using XRD and $^{29}$Si NMR, it was also discovered that instead of F$, defects of Si-O$, also possessing negative charges, were formed during the crystallization to compensate OSDAs and also inorganic cations (e.g., Na$^+$. They also quantified this phenomenon of charge balance by using a term of “OSDA charge/Silica ratio” of those as-synthesized zeolites, demonstrating that the DGC approach opens a new way for synthesizing high-silica or siliceous zeolite in fluoride-free way.

Nonetheless, the DGC method is not a broadly applicable. For example, when using the same DGC method to synthesize siliceous LTA, it is always failed. Moreover, in fact so far LTA synthesized in HF-free way has a Si/Al as high as 5.5. For other D4R-containing siliceous zeolites, to date they
are also impossible to be synthesized in a fluoride-free way. It is hypothesized that the difficulty is attributed to the “Villaescusa's Rule” as mentioned in Chapter 1.2: the stabilization and formation of pure silica D4Rs still do need the help from fluoride based on its size and electronic properties (or fluoride plays a structure-directing role in D4R formation). Therefore, in my Ph.D. study, we used Raman spectroscopy with correct assignments of zeolite Raman bands, which was complemented with other characterizations (e.g., XRD and NMR), to study the crystallization process of siliceous LTA. In the study, I tried to obtain solid evidence to test the hypothesis and confirm the exclusive roles of fluoride during the pure-silica LTA crystallization, especially its differences compared with the fluoride-mediated siliceous CHA and STT syntheses. Herein, LTA was chosen as the representative of the 38 zeolites featuring D4Rs, because, first, it is one of most-commonly used and researched zeolites in academia and also industry due to its large pore volume and ion exchange capacity (when Al in included); furthermore, the structure of zeolite LTA comprises one large cavity (α-cage), three smaller cavities (β-cages), and three connecting D4R units in each LTA unit cell, which makes LTA a fascinating nanoporous network because these building blocks can contain distinct chemical moieties that allow rigorous investigations of the structure-directing hypotheses for the fluoride-mediated synthesis. Hence, it is a unique opportunity to address fundamental questions concerning the roles of fluoride in zeolite formation.

Based on the information obtained in the study about siliceous LTA crystallization mechanisms, I tried to synthesize LTA possessing a high Si/Al ratio without using fluoride. In the study, isolated siliceous D4Rs, synthesized in the absence of fluoride, was introduced into a basic precursor used to crystallize LTA with a high Si/Al ratio in HF-free way. The isolated siliceous D4Rs may help the formation of Al-containing D4Rs during LTA crystallization. I also found that the Al content can be tailored to satisfy the charge balance requirement from the OSDAs, leading to the formation of LTA
with a Si/Al ratio of 7.55. All the related contents about this synthesis are detailed in the following chapters.

1.7 Thesis Scope

The remaining chapters of the thesis are structured as follows. The correct assignments of zeolite Raman bands to tricyclic bridges (three zeolite rings that share a common Si–O–Si bridge), which were evidenced by a systematic zeolite synthesis, spectroscopy, and periodic DFT study of nine all-silica zeolites, were presented in Chapter 2. Chapter 3 depicts our investigation on utilizing Raman spectroscopy and periodic density functional theory (DFT) calculations to observe and explain the crystallization process, especially the defects healing, of siliceous LTA in the presence of $F^−$, confirming with solid evidence the roles of $F^−$ in charge balancing and stabilizing intact D4R units during LTA zeolite formation. Based on these insights for the roles of $F^-$, the amount of $F^−$ required to synthesize defect-free, highly siliceous LTA was significantly reduced by a factor of 6. In Chapter 4, another integrated zeolite synthesis, spectroscopy, and density functional theory study to test the limit of $F^−$ as a charge-balancing agent that mitigates defects in siliceous zeolites was detailed; meanwhile, a novel approach (based on varying the quantity of the secondary OSDA (TMA$^+$) used in the siliceous LTA synthesis) used to precisely titrate the number of defects into zeolites at atomic-level during zeolite crystallization was displayed in detail. A DFT thermodynamic analysis was also used to interpret this phenomenon. In Chapter 5, another novel and also facile method (based on the application of isolated siliceous D4Rs and also a fine tuning for the charge balance between OSDAs and framework Al) employed to increase the Si/Al ratio in LTA synthesized in HF-free way was elaborated. Chapter 5 includes concluding remarks and some suggested future directions for the accomplished research work as part of this thesis.
CHAPTER 2
CRITICAL ROLE OF TRICYCLIC BRIDGES INCLUDING NEIGHBORING RINGS FOR UNDERSTANDING RAMAN SPECTRA OF ZEOLITES

2.1 Background

Understanding the formation mechanisms of nanoporous catalysts such as zeolites,\textsuperscript{139} which can open the door to tailoring materials for advanced applications in catalysis and separations,\textsuperscript{5,100} has remained a tantalizing challenge.\textsuperscript{7,140} Discovering how zeolites form is complicated by the fact that zeolite precursor structures fall into a nanoscale blind spot — too large for atomic-level and functional group structural analyses by methods like IR and NMR and too disordered for X-ray diffraction — necessitating characterization methods sensitive to medium-range structures such as rings and larger building units.\textsuperscript{87,88} Raman spectroscopy\textsuperscript{89} has emerged as a powerful tool for probing medium-range structures in a variety of materials including disordered silica,\textsuperscript{141} zeolites,\textsuperscript{96} MOFs,\textsuperscript{142} and zeolite precursor solutions.\textsuperscript{143–145} However, despite significant research into the Raman spectra of zeolites,\textsuperscript{94,146–150} the detailed assignments of such Raman spectra are not completely understood, though it is often assumed that Raman bands can be assigned to individual ring structures.\textsuperscript{95} For example, Suzuki et al. collected Raman spectra of amorphous gels leading to zeolites VPI-7, sodalite, and ferrierite\textsuperscript{151} and concluded that these amorphous gels contain high concentrations of 3-membered rings (3MR), 4MR, and 5MR, respectively, which correspond to rings found in the respective zeolite frameworks. This intriguing result raises a fundamental question: can Raman features really be assigned to individual rings or should they be associated with other, possibly larger building units? We answer this question rigorously through an integrated synthesis, spectroscopy, and periodic DFT modeling study.

Zeolites CHA and LTA (Figure 1a,b) present a fascinating test case, both comprising 4MR, 6MR, and 8MR, though in different arrangements. If assigning Raman features to individual rings were valid, then these zeolites would present essentially identical Raman spectra. Interestingly, previously
reported Raman spectra for CHA\textsuperscript{97} and LTA\textsuperscript{96} differ substantially in the key 200–700 cm\textsuperscript{-1} range associated with framework vibrations, with CHA exhibiting a doublet around 475 cm\textsuperscript{-1} assigned to 4MR vibrations,\textsuperscript{97} and LTA showing a singlet around 505 cm\textsuperscript{-1} assigned to the so-called $\nu_s$(T-O-T) mode, the symmetric stretch of T-O-T bridges (T = tetrahedral atom = Si or Al).\textsuperscript{96} The simple assignment of Raman features to single ring structures cannot explain this discrepancy. Unfortunately, extracting chemical insights from these Raman spectra is greatly complicated by the fact that these zeolites have different chemical compositions (i.e., Si/Al ratios). Advancing our understanding of nanopore framework vibrations requires a synthesis and Raman spectroscopy study on a range of well-defined zeolite frameworks that differ from one another in known, systematic ways, complemented by predictive theory for rigorous assignment of the key Raman features.\textsuperscript{152} We report such a study herein, finding that Raman spectra of zeolites can be understood in terms of rings embedded in “tricyclic bridges” as described below.

2.2 Methods

2.2.1 Choice of Zeolite for the Study

For systematic study of the effects of ring structures on Raman spectra of zeolites, we selected zeolite frameworks based on the following criteria: (i) synthesizable as all silica materials to remove ambiguities regarding distributions of framework heteroatoms such as Al, and mobile charge-compensating species such as Na; (ii) involving unit cells that are sufficiently small to allow accurate periodic DFT calculations of lattice energy, framework structure, normal modes, and Raman intensities; and (iii) containing 4MRs in various arrangements\textsuperscript{153} to allow direct comparisons of Raman features. Figure 2.1 shows the nine zeolite frameworks studied herein, ranging from the very simple SOD zeolite structure with only 4MR and 6MR to the relatively complicated ITH material with 4MR, 5MR, 6MR, 9MR, and 10MR. We computed DFT-based Raman spectra for each of these nine structures;
synthesized all silica SOD, AST, LTA, CHA, ITW, and ITH zeolites; and measured their Raman spectra
to compare with calculations.

2.2.2 Experimental Methods

Zeolite syntheses were based on previously reported methods. All-silica CHA\textsuperscript{154} was crystallized
using a commercial OSDA, while the all-silica zeolites AST,\textsuperscript{155} ITH,\textsuperscript{156} ITW,\textsuperscript{73} and LTA\textsuperscript{157} were
crystallized by fluoride-mediated methods after four different OSDAs were synthesized and confirmed
by NMR. All-silica SOD\textsuperscript{158} was synthesized by a phase-transformation pathway starting from silicates
with double 4MR. All zeolite syntheses were confirmed by X-ray diffraction (XRD), by comparing with
literature XRD data. Raman spectra were collected on calcined zeolite (to prevent the influence from
OSDAs and F\textsuperscript{−}) samples using an XploRa Raman microscope with a 785 nm laser line.

2.2.3 Computational Methods

Initial structural data for modeling all-silica zeolites ACO, AST, CHA, DOH, GME, LTA, ITH,
ITW, and SOD were downloaded from the IZA Web site.\textsuperscript{153} All calculations were based on periodic
density functional theory (DFT) with plane wave basis sets using the Vienna Ab initio Simulation
Package (VASP).\textsuperscript{159} We used projector augmented wave pseudopotentials\textsuperscript{160,161} and the
Perdew–Burke–Ernzerhof (PBE) exchange correlation functional for structural optimization, normal-
mode analysis, and Raman intensity calculations.\textsuperscript{162} Normal mode vibrations were visualized and
analyzed using the program VESTA, focusing on symmetric stretch \(\nu_s(T-O-T)\) modes of Si–O–Si
bridges following the previous work of Dutta et al.\textsuperscript{96}
2.3 Results and Discussion

2.3.1 Comparisons between Experimental and Computed Raman Spectra

The measured (blue) and predicted (red) Raman spectra of LTA and CHA zeolites are shown in Figure 2.2, panels a (LTA) and b (CHA). The main feature in the experimental LTA spectrum at 506 cm\(^{-1}\) corresponds with the band observed at 489 cm\(^{-1}\) by Dutta and Del Barco for Na-A.\(^{96}\) The slight blue shift is expected when replacing Si–O–Al bonds in Na-A with the slightly stiffer Si–O–Si bonds in Si-LTA. The doublet observed for Si-CHA in Figure 2.2b at about 475 cm\(^{-1}\) is the characteristic of the CHA structure, as reported in previous work.\(^{97}\)
Very good agreement between experimental (blue) and computed (red) Raman spectra is clearly visible for both LTA and CHA materials. In particular, Figure 2.2a, b shows that theory accurately reproduces most patterns in Raman band intensities. The main difference is the missing doublet in the computed CHA spectrum (Figure 2.2b). There are actually two Raman-active modes predicted by theory for CHA at $\sim 448$ cm$^{-1}$, but the splitting between these modes is underestimated by normal-mode analysis. Overall, the computed frequencies appear to be red-shifted from experiment by about 20–25 cm$^{-1}$. This red-shift was observed in all of the six zeolites (SOD, AST, LTA, CHA, ITW, and ITH), as summarized by the parity plot in Figure 2.3. A best-fit line through these data in the parity plot gives a slope of 1.02, intercept of 19.6 cm$^{-1}$, and $R^2 = 0.96$, indicating a regular pattern of systematic error. Such a red-shift is expected from the PBE density functional, which is known$^{163,164}$ to slightly overestimate lattice parameters by about 1%, and hence to slightly underestimate vibrational frequencies. The high degree of agreement between the experimental and simulated Raman spectra allows the assignment of Raman bands to particular vibrational modes in the silica zeolite structures, which can help pinpoint the role of rings in Raman spectra of zeolites.
If the Raman spectra were essentially identical for Si-LTA and Si-CHA — two zeolites with the same collection of rings (4MR, 6MR, and 8MR) — it would be justified to assign the bands to individual ring modes. However, while the spectra in Figure 2.2a, b are similar, they are sufficiently different to necessitate more rigorous assignments that go beyond associating bands to individual 4MR, 6MR, and 8MR. The previous assignments of the CHA doublet to 4MR vibrations and the LTA singlet to T-O-T bridges were made by comparative and inductive reasoning; here we report assignments based on normal-mode analysis by periodic DFT calculations.

2.3.2 Normal Mode Analysis of Raman Spectrum of LTA

Figure 2.4 shows the results of normal-mode analysis for the Raman spectrum Si-LTA. Images of the normal mode eigenvectors for the main LTA feature at 476 cm\(^{-1}\) and the smaller band at 318 cm\(^{-1}\) are shown in Figure 2.4a. These outcomes reveal that it is the ring breathing via symmetric oxygen stretching in the plane consisting of the 3 atoms from a Si–O–Si bridge (also bisecting the Si-O-Si bridge angle) that leads to the Raman bands, and during this process, those Si atoms stand still. These reveal ring breathing via oxygen motion in Si–O–Si bridges with surprising patterns. For example, the
normal mode for 318 cm$^{-1}$ appears to be an 8MR breathing mode because the normal-mode vectors show displacements in the plane of the 8MR. This would be a surprising and controversial assignment because Raman bands in this frequency range (300–350 cm$^{-1}$) are typically associated with 6MR vibrations (cf., the CHA band at 335 cm$^{-1}$ assigned to the double-6MR).\textsuperscript{97} However, on closer inspection, we see in Figure 2.4a that only the Si–O–Si bridges that also make up 6MR participate in this normal mode. As a second example, the normal mode for 476 cm$^{-1}$ appears to be a mixture of 8MR and 6MR breathing modes (Figure 2.4a). This would constitute another surprising assignment because Raman bands in this frequency range (450–500 cm$^{-1}$) are often associated with 4MR motions.\textsuperscript{96,97} Then again, on closer inspection, we see that only the Si–O–Si bridges which also make up 4MR contribute to LTA vibration at 476 cm$^{-1}$. These findings necessitate a new way to understand zeolite structures that takes into account both a given ring structure and its immediate environment.
2.3.3 Interpretations Using Tricyclic Bridges

The major new insight in this study involves understanding zeolite structure and vibrations in terms of so-called “tricyclic bridges.” These are defined as three zeolite rings that share a common Si–O–Si bridge, such as those shown in Figure 2.4a and highlighted in Figure 2.4b. Tricyclic bridges are general structural elements of all materials built from corner-sharing tetrahedra, because each bridge (-\(T \cdots X \cdots T'\)-, where \(T, T'\) = tetrahedral atoms, \(X\) = bridge atom) connects to three rings in the network (Figure 2.4b). Because each tricyclic bridge contains a given ring and its nearby environment, this new
notion can help explain the Raman assignments discussed above. In particular, the 8MR breathing mode in Figure 2.4a at 318 cm$^{-1}$, a frequency typically associated with 6MR vibrations, is assigned to a tricyclic bridge containing the 8MR and two 6MR. This observation suggests the following general principle: the vibrational frequency of a given Raman band can be correlated to the smallest ring of its tricyclic bridge and not to the ring that is actually vibrating.

We now test this principle on the mixed 6MR/8MR breathing mode in Figure 2.4a at 476 cm$^{-1}$ – a frequency often associated with 4MR vibrations. This normal mode involves two tricyclic bridges: the first is a 6MR with two 4MR; the second is an 8MR with two 4MR. As such, both tricyclic bridges have 4MR as the smallest ring, which comports with a Raman band at 476 cm$^{-1}$. Because of the apparent primary importance of the smallest ring in a tricyclic bridge, we name tricyclic bridges in increasing order of ring size. Thus, the normal mode for LTA at 318 cm$^{-1}$ is assigned to a 6−6−8 tricyclic bridge, whereas LTA motion at 476 cm$^{-1}$ is assigned to a mixture of 4−4−6 and 4−4−8 tricyclic bridges. We note that for the LTA structure, the 4−4−6 and 4−4−8 vibrations combine to yield a collective vibration of the double-4MR. An analysis of the Si−O−Si angle distribution in Si-LTA reveals three distinct angles, each corresponding to one of these tricyclic bridges. As such, these three tricyclic bridges account for the distinct structural building blocks of LTA as shown in Figure 2.4b, as well as the main features of its Raman spectrum.

We have assigned the main features of the Raman spectra in the ring-breathing region for all nine zeolites studied herein, using periodic DFT and normal-mode analysis along with the concept of tricyclic bridges, as described above for LTA. The tricyclic bridge assignments for all main bands are given in Table 2.1, along with the corresponding DFT-computed frequencies and Si−O−Si angles from DFT-optimized structures. In all cases, the main band is in the 400−500 cm$^{-1}$ region (see Fig. 2.5, for all the 9 zeolites simulated), consistent with the fact that each main band is assigned to one or more tricyclic bridges with the 4MR as its smallest ring. In most cases, this main band is assigned to a mix of
two or more tricyclic bridges, suggesting that the concept of assigning Raman bands to individual rings is overly simplistic.

Table 2.1: Assignments of main Raman bands to tricyclic bridges and their corresponding Si–O–Si computational angles

<table>
<thead>
<tr>
<th>zeolite</th>
<th>ITH</th>
<th>ACO</th>
<th>LTA</th>
<th>ITW</th>
<th>AST</th>
<th>CHA</th>
<th>GME</th>
<th>SOD</th>
<th>DOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>computed band (cm⁻¹)</td>
<td>487</td>
<td>477</td>
<td>476</td>
<td>468</td>
<td>465</td>
<td>448</td>
<td>446</td>
<td>417</td>
<td>408</td>
</tr>
<tr>
<td>tricyclic bridge assignment(s)</td>
<td>4–4–5</td>
<td>4–4–5</td>
<td>4–4–6</td>
<td>4–4–6</td>
<td>4–4–6</td>
<td>4–4–6</td>
<td>4–6–6</td>
<td>4–5–5</td>
<td></td>
</tr>
<tr>
<td>Si–O–Si angle⁴</td>
<td>138.5</td>
<td>146.7</td>
<td>147.9</td>
<td>144.5</td>
<td>148.3</td>
<td>148.6</td>
<td>150.1</td>
<td>158.9</td>
<td>162.0</td>
</tr>
</tbody>
</table>

⁴For assignments to several tricyclic bridges, reported Si–O–Si angle is averaged over relevant DFT-optimized angles.

Fig. 2.5: Calculated Raman spectra of all the nine studied zeolites.
2.3.4 Raman Frequency and Si–O–Si Angle

A simple trend arises when we consider the correlation of Raman frequency and Si–O–Si angle, as seen in Table 2.1. The possibility of such a dependence in the vibrational density of states was first theorized in 1977 for tetrahedral glasses such as silica, and then later observed empirically by Dutta et al. In their investigation of Raman spectra for zeolites with a relatively narrow range of angles. Our results put this relationship on a firm ab initio foundation and extend this to a much broader range of angles and framework structures. For Raman features that mix several tricyclic bridges (such as LTA 476 cm\(^{-1}\), mixing 4-4-6 and 4-4-8), Table 2.1 shows the average Si–O–Si angle. In almost all cases of tricyclic-bridge mixing, the participating Si–O–Si angles are very similar, which may explain the origin of such mixing.

To underscore our new approach for understanding the Raman spectra of zeolites, we show all the computed Raman spectra for the nine zeolites in Figure 2.5, which clearly shows the trend in the main band in the 400–500 cm\(^{-1}\) region. Band assignment by normal-mode analysis shows that each of these main bands is associated with one or more 4-x-y tricyclic bridges (see Table 2.1), where x and y vary with zeolite structure. Figure 2.6 shows the correlation of Raman frequency and Si–O–Si angle, with a correlation coefficient of 0.88 over a broad range of angles (24°).

Two outliers are included in Figure 2.6 for illustration purposes: a band for zeolite Si-ITW with a computed frequency of 374 cm\(^{-1}\) and a band for Si-LTA at 318 cm\(^{-1}\). Clearly neither of these points falls on the frequency-angle correlation line. These apparent outliers make perfect sense based on our notion of tricyclic bridges. All of the Raman bands that fit the line involve individual 4-x-y tricyclic bridges or mixtures thereof, and as such represent a generalized notion of 4MR systems. Instead of assigning Raman bands to individual zeolite rings, we now assign Raman bands to tricyclic bridges and group them together based on the smallest ring in the tricyclic bridge. Figure 2.6 shows such a grouping for 4-x-y tricyclic bridges, arising from our study of several zeolites, all with 4MR. The outlier point
for Si-ITW, assigned to a 5−5−8 tricyclic bridge, is predicted to lie on a different correlation line associated with 5−x−y tricyclic bridges; we will test that prediction in future work by studying a collection of zeolites containing 5MR. Furthermore, the outlier point for Si-LTA (6−6−8) is predicted to lie on a correlation line for 6−x−y tricyclic bridges obtained from studying zeolites with 6MR.

![Graph showing correlation between computed main-band Raman frequency and Si−O−Si angle in simulation; the slope of the best-fit line is -3.64 and the correlation coefficient (R²) is 0.88.](image)

**Fig. 2.6: Correlation between computed main-band Raman frequency and Si−O−Si angle in simulation; the slope of the best-fit line is -3.64 and the correlation coefficient (R²) is 0.88.**

### 2.4 Summary

We have engaged in an integrated synthesis, spectroscopy, and periodic DFT modeling study which has shown that assigning features present in the Raman spectra of zeolites to individual rings is overly simplistic. Instead, the new notion of making assignments based on tricyclic bridges is more robust. Such structures are collections of three zeolite rings that have common Si−O−Si (or more generally T-X-T’’) bridges. Tricyclic bridges are common elements of all zeolites and all materials built from corner-sharing tetrahedra. By organizing Raman bands according to the smallest ring of their assigned tricyclic bridges, we have shown a strong anti-correlation (for 4MR systems) of Raman vibrational frequency and Si−O−Si angle.
This discovery will be particularly important for investigating crystalline structures of zeolites affected by heteroatoms and organic structure-directing agents, as well as the formation of zeolite crystals from amorphous precursors. Despite the intense effort to understand the fundamental structures participating in zeolite crystallization, the lack of suitable analytical techniques makes atomic-level characterization of zeolite formation processes extremely challenging. Our approach could be used to reinterpret the data of Suzuki et al.,\textsuperscript{151} who collected Raman spectra of amorphous gels, in terms of tricyclic bridges and T-O-T’ bond angles present during zeolite formation. Overall, the findings reported herein enhance our ability to use Raman spectroscopy as an analytical tool for investigating zeolite structure and formation, using the new concept of tricyclic bridges.

Therefore, in the next chapter, we are going to utilize Raman as the analytical tool to research the crystallization mechanisms of siliceous LTA, aiming to obtain information about the exclusive role of fluoride during the siliceous LTA synthesis, and then attempt to synthesize high-silica LTA in fluoride-free way.
CHAPTER 3
IDENTIFYING ORDER AND DISORDER IN DOUBLE FOUR-MEMBERED RINGS VIA RAMAN SPECTROSCOPY DURING CRYSTALLIZATION OF LTA ZEOLITE

3.1 Background

Zeolites are crystalline microporous structures with pore sizes ranging from 0.3 to 2 nm with important applications in catalysis, separations, and several emerging areas.\textsuperscript{7,100,167} The great diversity of zeolite structures and compositions arises from an equally great collection of synthetic protocols that have been discovered over the last seven decades through laborious research.\textsuperscript{48,57,168} Despite these massive efforts, the atomic-level events involved in zeolite crystallization processes remain largely unknown.\textsuperscript{81,82,169} Better understanding of these events in zeolite assembly could help unlock a treasure trove of hypothetical zeolite structures,\textsuperscript{78,170} many of which show promise for emerging applications such as carbon capture\textsuperscript{5} and clean energy production.\textsuperscript{171} Herein, the crystallization of Linde type A (LTA) zeolite in the presence of $\text{F}^-$ was investigated using Raman spectroscopy and periodic density functional theory (DFT) calculations with the aim of probing the assembly of building units and defect structures formed during the crystallization process.

In general, zeolites can be synthesized in alkaline media at high pH or in fluoride media under more neutral conditions, with $\text{OH}^-$ and $\text{F}^-$ required as mineralizing agents for crystallization.\textsuperscript{50,52} The fluoride synthesis route, which was invented by Flanigen and Patton,\textsuperscript{50} has been extensively developed during the last three decades and has led to a variety of new, defect-free microporous materials—essentially high silica or even all-silica zeolites.\textsuperscript{52,172} Zeolite chemists have hypothesized that $\text{F}^-$ creates new zeolite structures via (i) a structure-directing effect of $\text{F}^-$ stabilizing small silicate rings and cages such as the D4R unit in zeolites\textsuperscript{53,173–175} and
(ii) a charge-compensating role, where F\textsuperscript− balances the positive charges from OSDAs, thus removing the need for negatively charged framework defects.\textsuperscript{52,176,177} To date, the synthesis of siliceous zeolites containing the D4R is possible only through the F-mediated route,\textsuperscript{54–56,156} with F\textsuperscript− inside the D4R\textsuperscript{175} or by a post-synthetic method called assembly−disassembly−organization−reassemble (ADOR).\textsuperscript{178–180} After crystallization, the F\textsuperscript− inside the D4R cannot be removed by ambient ion exchange,\textsuperscript{181,182} suggesting that the D4R may form around F\textsuperscript− in a kind of directed assembly process. Interestingly, it has also been found that the D4R in siliceous zeolites remains stable even after the removal of F\textsuperscript− by calcination.\textsuperscript{181,182} These intriguing observations prompt the following fundamental questions: how do F\textsuperscript−-filled D4R units (F\textsuperscript−/D4R) form and how do these units assemble to make zeolites? Can the echoes of this assembly process be discerned by discovering defects and disorder left behind in F\textsuperscript−/D4R units? How can such defects and disorder be probed during zeolite formation? In the following, we make a substantial step in answering these questions by integrating experimental zeolite synthesis and characterization by Raman spectroscopy with periodic DFT calculations.

Despite the long history of zeolite synthesis and characterization research, investigating zeolite crystallization processes remains challenging mainly due to the lack of characterization techniques that can examine medium-range structures including rings and cages formed during zeolite assembly.\textsuperscript{183} Raman spectroscopy has emerged as a critical tool for probing medium-range structures in a range of silica network assemblies,\textsuperscript{95,98,141,145,184} complementing shorter range techniques such as nuclear magnetic resonance (NMR) and longer-range information from X-ray diffraction (XRD).\textsuperscript{87,185} However, assignments of Raman bands to specific rings and cages have largely been made by inductive reasoning that must be confirmed by predictive calculations.
We have addressed the issue of Raman band assignments in our recent (as detailed in Chapter 2) work through a systematic synthesis, spectroscopy, and periodic DFT study of several siliceous zeolites with various frameworks. Normal-mode analysis (NMA) suggests that Raman bands should be assigned to tricyclic bridges — three zeolite rings that share a common Si–O–Si bridge, rather than to individual rings. For example, while Raman bands at ~ 500 cm\(^{-1}\) for zeolites have typically been assigned to four-membered ring vibrations, NMA applied to siliceous LTA indicates that the Raman band at 506 cm\(^{-1}\) results from vibrations of 4-4-6 and 4-4-8 tricyclic bridges (green and red, respectively, in Figure 3.1), where “x-y-z” denotes a tricyclic bridge connecting an x-ring, a y-ring, and a z-ring. These 4-4-6 and 4-4-8 tricyclic bridges in LTA come together to comprise the D4R, indicating that the LTA Raman band at 506 cm\(^{-1}\) corresponds to symmetric breathing of the D4R. We have also discovered, via the concept of tricyclic bridges, a strong anti-correlation between the Raman frequency and Si–O–Si angle. Rigorous assignment of Raman bands arising from specific zeolite structures provides new avenues for studying the role of structural defects in zeolite crystallization.

Here, we apply zeolite synthesis, Raman spectroscopy, and periodic DFT to investigate the effects of F\(^{-}\) on the structures of subunits formed during the crystallization of siliceous LTA zeolite. Our discovery of distinct Raman signatures of F\(^{-}\)-filled and empty D4R units has revealed detailed information on the evolution of these units during the crystallization process. Such insights are fundamentally important for understanding the hierarchical nature of zeolite crystallization mechanisms and may also assist in designing syntheses of zeolites with new structures and compositions.
Fig. 3.1: LTA zeolite structure and its three building subunits: one α-cage, one β-cage, and three D4Rs per unit cell. Each subunit may contain species as shown in the figure. Synthesis with two BULKY cations would require 2/3 of D4Rs to be filled with F⁻ according to charge balancing hypothesis. 4-4-6 and 4-4-8 tricyclic bridges in siliceous LTA are highlighted in green and red, respectively.

3.2 Methods
3.2.1 Experimental Section
3.2.1.1 Synthesis of Zeolite (LTA-BULKY-F)

Dimethyl-3-(4-methylbenzyl) imidazolium hydroxide (denoted as “BULKY-OH”) was synthesized by following the method previously reported. Aluminosilicate LTA nanocrystals with a size of around 200 nm were used as the seeds for the crystallization of siliceous LTA. Such seeds were prepared using a conventional hydrothermal synthesis method in the absence of F⁻ (detailed below). BULKY was used as an OSDA in the synthesis of LTA-BULKY-F by following a method reported previously. Briefly, 10.76 g of aqueous solution of BULKY-OH (0.1872 mmol/g in water) was mixed with 900 μL of tetraethyl orthosilicate (TEOS, 99 wt %, Alfa Aesar), and the obtained mixture was stirred overnight at room temperature to ensure the hydrolysis of TEOS. A total of 70 μL of hydrofluoric acid (HF, 48–52 wt % in water, Alfa Aesar)
was then pipetted into the mixture, followed by adding 398 μL of aqueous solution of LTA seeds (42.6 mg/mL; 7 wt.% with regard to the total silica source). Since HF is toxic and especially hazardous to handle, safety procedures should be strictly followed. Water was then evaporated from the suspension at 60 °C, until a final desired composition (1.00 SiO₂/0.50 HF/0.50 BULKY/5.00 H₂O) was achieved. Finally, crystallization was conducted at 170 °C for 1.5, 2.5, 3, 6 h, and 8 days in a 50 mL Teflon-lined stainless-steel autoclave. The synthesized product of about 250 mg was washed by dispersing in 50 mL of deionized (DI) water and separating using centrifugation. The washing procedure was repeated five times. A part of LTA-BULKY-F samples were calcined under flowing dry air in a tube furnace to remove the BULKY OSDA. The calcination temperature and time were 550 °C and 12 h, respectively, with a ramping rate of 1 °C/min.

3.2.1.2 Synthesis of LTA Seeds

Briefly, first, in a 50 mL centrifuge tube, 0.082 mL of NaOH (10 M, Thermo Fisher Scientific) was mixed with 6.65 g of tetramethylammonium hydroxide (TMAOH) (25 wt % in water, Alfa Aesar) and 3.45 g of DI water. Then, 0.60 g of silicic acid (99 wt %, Sigma-Aldrich) was added. Afterward, when a transparent solution was achieved at 70 °C and cooled down to RT, 0.50 g of aluminum isopropoxide (≥98 wt %, Thermo Fisher Scientific) was added in two steps (each with 0.25 g). After achieving a complete dissolution of the Al source by employing a sonicator and vortex oscillator, the obtained clear solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave for crystallization at 93 °C for 1 day. The obtained LTA seeds were washed through centrifugation using excess DI water until the pH of the supernatant approached neutral. Finally, the LTA seeds were dried at 80 °C in an oven.
3.2.1.3 Characterizations

The crystalline structure of the zeolite samples was characterized by XRD using a Rigaku SmartLab diffractometer, which was equipped with Cu Kα radiation produced at 40 mA and 45 kV, with a step size of 0.016°. All the LTA samples, including the corresponding precursor gel and BULKY-Cl, were characterized using Raman spectroscopy. Raman samples were prepared by dispersing several milligrams of each sample on a gold-coated silicon wafer, and then, Raman spectra were recorded by employing an XploRa Raman microscope (Horiba Scientific, USA) operated using a 785 nm laser line as the excitation light source, at □ 10 mW power. A 1200-line grating was set, and the laser light was focused on the sample through a 100× magnification lens from the Olympus. A scan time of 20 s and an accumulation of 20 scans were chosen for all the measurements. The laser focus was aimed at the smooth edge part of a particle to ensure favorable light scattering for an optimal Raman signal-to-noise ratio. Spectra of multiple particles were obtained to check for consistency. For the BULKY in the hydroxide form, its Raman spectrum was obtained in an aqueous solution (0.2 mmol/g). This Raman analysis was performed by employing an EZRaman-I series high-performance portable Raman analyzer (TSI Incorporated, USA) with a 785 nm laser. The measuring conditions included 170 mW laser power, 2 s averaging parameter, and 5 s integration time.

The structure of BULKY in the chloride form was characterized by liquid-state $^{13}$C NMR on a Bruker 400 MHz NMR spectrometer. Before the measurement, the BULKY in the chloride form was dissolved in D$_2$O.

To test whether fluoride ions were occluded in D4Rs of LTA-BULKY-F, $^{19}$F MAS SS-NMR spectra were acquired on a Bruker AVANCE 400 wide-bore spectrometer (9.4 T, 376.48 MHz for $^{19}$F), using a 4 mm double-resonance probe, operating at a spinning rate of 9.0 kHz. The
$^{19}$F direct polarization spectra were collected using the spin-echo sequence with 2.25 μs 90° pulse duration for a total of 32 scans. The chemical shift was calibrated using an external reference (sodium fluoride at −121.5 ppm). Data analysis was carried out using with a line broadening factor of 10 Hz.

$^{29}$Si MAS SS-NMR measurements were performed on a Bruker 600 MHz solid-state NMR spectrometer using a 4 mm MAS probe. The spectral operating frequencies were 600.1 and 119.2 MHz for $^1$H and $^{29}$Si nuclei, respectively, and the samples were spun at 5 kHz during the measurements. A recycle delay time of 200 s was found to be sufficient for the samples.

The amounts of C, H, N, and F in the as-made LTA-BULKY-F sample were measured by Atlantic Microlab at GA, USA, using a flask combustion method followed by ion chromatography. The amounts of Si and Al of the LTA sample after calcination were measured at Galbraith Laboratories at TN, USA, using inductively coupled plasma atomic emission spectroscopy. The samples were dried at 120 °C for 2 h before measurements to remove the adsorbed water.

TGA was conducted on a thermogravimetric analyzer (SDT600, TA). For each measurement, about 10 mg of the sample was used. The temperature was programmed from RT to 900 °C (with a ramping rate of 1 °C/min) and finally held for 2 h with an air flow of 10 mL/min.

SEM was utilized to determine the morphology of the LTA-BULKY-F samples at different crystallization times. The SEM images were collected using a FEI Magellan 400 XHR-SEM instrument, which is equipped with a field-emission gun operated at 3.0 kV. Prior to this characterization, all the samples were sputter-coated with platinum for a better imaging quality.
3.2.2 Computational Section

Zeolite LTA systems containing BULKY and fluoride ions (F<sup>−</sup>) were studied using periodic DFT via plane-wave basis sets with Vienna Ab initio Simulation Package (VASP).<sup>159</sup> The structure of zeolite LTA was adopted from our previous work.<sup>98</sup> For all DFT periodic simulations reported here, we applied the projector augmented wave<sup>160,161</sup> pseudo-potential and the PBE56 exchange–correlation functional with the D3 dispersion corrections<sup>188,189</sup> and non-spherical corrections, using an energy cutoff value of 480 eV, a 1 × 1 × 1 K-point mesh, and Gaussian smearing of which the width is 0.05 eV. Avogadro<sup>190</sup> was used to initially combine the LTA framework with BULKY and F so that two BULKY cations are inside the α-cage and two fluoride ions are inside D4Rs. Ab initio molecular dynamics (AIMD) simulations with the NVT ensemble (Nose–Hoover thermostat)<sup>191</sup> were then performed for 1 ps to identify stable configurations of the LTA-BULKY-F systems at 443 K, which is the experimental synthesis temperature of LTA-BULKY-F.<sup>157</sup> Such systems were optimized from initial conditions extracted at random from AIMD, to identify minimum-energy configurations for NMA until the energy of ionic steps varied within 10<sup>−4</sup> eV. The optimizations also relaxed unit cell lattice parameters. Initial structures of defected systems were made based on the optimized intact LTA-BULKY-F system. For Si-missing defects (point defects), selected Si atoms were deleted, and their surrounding O atoms were compensated by H atoms to form −OH terminals. For hydrolyzed defects, a water molecule was added across a Si–O–Si tricyclic bridge, leading to two OH terminal defects.<sup>98</sup> NMA was performed to determine vibrational frequencies and normal-mode vibrational coordinates. Density functional perturbation theory was used to compute intensities of Raman bands in the frequency ranges of interest. To better mimic experimental Raman spectra, Lorentzian line broadening was applied to the calculated spectral
lines using a full band width at half maximum of 5 cm\(^{-1}\). Visualizations of optimized structures and normal modes were performed on VESTA.\textsuperscript{191}

### 3.3 Results and Discussion

Here, we detail and discuss our results on the F-mediated synthesis of LTA using BULKY as the OSDA and the Raman spectroscopy of as-made LTA-BULKY-F distinguishing empty D4R and F\(^{-}/\)D4R units. Raman was used using Raman to study the crystallization process of LTA. The insights gained was applied to synthesize Si-LTA with substantially reduced hydrogen fluoride (HF).

#### 3.3.1 Synthesis of LTA-BULKY-F

Synthesis of siliceous LTA zeolite in the presence of F\(^{-}\) was pioneered by Corma et al.\textsuperscript{55} using dimers of bulky OSDA cations.\textsuperscript{55} This method was extended by Davis et al.\textsuperscript{157} who synthesized LTA using dimers of 1,2-dimethyl-3-(4-methylbenzyl) imidazolium (herein denoted as “BULKY”), which occupies the α-cage in a structural motif akin to two hands packing a snowball (Figure 3.1). Because the α-cage is occupied by two BULKY molecules and the β-cage is empty, only two out of three D4Rs per unit cell are theoretically occupied with F\(^{-}\) to achieve charge balance in the zeolite. As a result, we expect to find the presence of both the F\(^{-}/\)D4R and empty D4R in the LTA synthesized using BULKY, possibly with distinct Raman signatures.

LTA-BULKY-F was synthesized using a gel composition of 1.00 SiO\(_2\)/0.50 HF/0.50 BULKY-OH/5.00 H\(_2\)O with addition of 7 wt.% LTA seeds with regard to the silica source, following the literature method.\textsuperscript{157} Aluminosilicate LTA nanocrystals (Si/Al = 1.26) with a size of around 200 nm were used as seeds for the crystallization. Highly crystalline LTA crystals were obtained after hydrothermal synthesis at 170 °C for 8 days. The synthesized LTA exhibits a Si/Al ratio of 66. Strictly speaking, the LTA sample is not a siliceous zeolite. However, the aluminum
content is approximately one aluminum atom per three unit cells, indicating that the LTA zeolite is close to but not precisely a siliceous zeolite.

3.3.2 Raman Signatures of the F⁻/D⁴R and Empty D⁴R

Figure 3.2a shows experimental and DFT-computed Raman spectra of LTA synthesized using BULKY as the OSDA, including spectra obtained both before and after calcination. The Raman spectrum obtained from the sample after calcination (experiment: green; DFT: red) reveals a prominent band around 500 cm⁻¹ (shaded yellow) assigned by DFT to the combination of 4-4-6 and 4-4-8 tricyclic bridge vibrations, which as discussed in Section 3.1, come together to comprise the empty D⁴R symmetric breathing mode.⁹⁶ Figure 3.2a shows that periodic DFT using the Perdew–Burke–Ernzerhof (PBE) functional accurately reproduces this experimental Raman spectrum, with a consistent red shift of about ∆20 cm⁻¹, a characteristic of PBE (frequencies are left unscaled).⁹⁸
Fig. 3.2: (a) Raman spectra of calcined LTA (experiment in green, DFT in red) and as-
made LTA before calcination (experiment in purple, DFT in blue) showing excellent
agreement between experiment and theory, with DFT exhibiting red-shifts from measured
band locations. Raman bands for LTA vibrations are marked with black star; unmarked
bands are assigned by DFT to BULKY OSDA; yellow-shaded band is empty D4R
symmetric breathing mode; black-shaded band is assigned by DFT to F-filled D4R (F−/D4R).
(b) Periodic DFT analysis of blue-shift of D4R Raman band from empty (green dot)
to F-filled (blue dot): most of blue-shift explained by geometrical distortion of D4R
(decrease in Si-O-Si angle, red dot); remaining blue-shift attributed to unique F−/D4R
bonding interaction.

Periodic DFT was further used to simulate the Raman spectrum of LTA-BULKY-F
before calcination, with two molecules of BULKY in the α-cage and two F− ions in the D4R. As
shown in Figure 3.2a, comparing the experimental (purple) and simulated spectra (blue) shows
that periodic DFT using the PBE functional also reproduces most features of the Raman
spectrum of as-made LTA. NMA allows us to distinguish the Raman bands of the BULKY
OSDA and zeolite lattice, which is critical for utilizing Raman spectroscopy to investigate zeolite
samples synthesized in the presence of OSDAs. Raman bands in Figure 3.2a marked with a black
star correspond to the vibrations of the LTA lattice, whereas the unmarked bands in Figure 3.2a
are assigned to the vibrations of the BULKY OSDA. Interestingly, two Raman bands associated
with the D4R in the LTA-BULKY-F sample before calcination are observed in Figure 3.2a.
These Raman bands are shaded in yellow and black and are assigned by DFT to D4R symmetric
breathing modes (combining 4-4-6 and 4-4-8 tricyclic bridges) of the empty D4R (yellow) and F-/D4R (black). This assignment, relying on NMA, is in agreement with the previous Raman assignment (based on comparative and inductive reasoning) for tetramethylammonium fluoride octadecasil (AST) zeolite, in which the 491 and 524 cm$^{-1}$ bands were assigned to empty and F-filled D4R units of AST, respectively. The DFT-predicted bands appear at 490 cm$^{-1}$ (empty D4R) and 524 cm$^{-1}$ (F-/D4R) — a predicted band separation of 34 cm$^{-1}$ — while the measured Raman bands appear at 512 and 548 cm$^{-1}$ (observed separation of 36 cm$^{-1}$), indicating quantitative agreement on this band separation. The presence of the empty D4R in LTA-BULKY-F is intriguing since previous studies have suggested that siliceous D4R units in zeolites can only be formed in the presence of F$^-$ (unless using the post-synthetic ADOR method).

3.3.3 Structure and Dynamics of the F-/D4R via Raman Analysis

To better understand how the interaction between F$^-$ and the D4R influences the Raman signature of the F-/D4R unit, we investigated the frequencies of the empty D4R and F-/D4R bands in Figure 3.2a to reveal the interplay among the geometry, vibrational dynamics, and electronic structure of the F-/D4R building unit. Figure 3.2b displays a periodic DFT analysis of Raman frequencies associated with F$^-$ occupying the D4R. Our previous Raman study reported an anti-correlation between the Raman frequency and Si–O–Si angle for several zeolites containing 4-x-y tricyclic bridges (black dots in Figure 3.2b), suggesting that we should expect decreased Si–O–Si angles in the D4R upon including F$^-$ based on the observed blue shift. Indeed, our periodic DFT calculations indicate a decrease in D4R angles from 146.9 to 139.6° upon including F$, consistent with the expected anti-correlation and previous studies but insufficient to explain the full magnitude (34 cm$^{-1}$) of the calculated blue shift.
Figure 3.2b shows DFT-computed Raman band frequencies of the empty D4R (green dot), the F⁻/D4R (blue dot), and the D4R distorted to the F-filled geometry but still empty (red dot). Including the red point in Figure 3.2b provides a way to determine if geometrical distortion alone is sufficient to explain the magnitude of the blue shift. Figure 3.2b shows that most of the Raman blue shift (“Geometry” in Figure 3.2b) can be explained by the geometrical distortion. However, a significant portion of the blue shift (“Bonding” in Figure 3.2b) cannot be explained by D4R distortion alone, indicating a change in Si–O bonding in the F⁻/D4R. This result is consistent with previous calculations, finding a unique chemical interaction between F⁻ and the D4R involving donation of electron density from F⁻ to frontier orbitals of the D4R.53,193 Thus, the Raman blue shift in Figure 3.2a,b serves as an indicator of both geometrical distortion and charge transfer to the D4R upon inclusion of F⁻.

3.3.4 Ordered and Disordered Fluoride Distributions in LTA

Since not all the D4R units in LTA-BULKY-F are filled with F⁻, both homogeneous and heterogeneous F⁻ distributions are possible. In both cases, we assume two BULKY cations in each α-cage, which is consistent with elemental analysis and thermogravimetric analysis (TGA) data (vide infra). In the homogeneous case, each unit cell would contain two F⁻/D4Rs and one empty D4R, with the two negative F⁻ charges balancing the two BULKY positive charges. In contrast, a heterogeneous distribution is possible, for example, where one unit cell contains three F⁻ ions and an adjacent cell contains only one ion. Here, we investigate these cases by studying their predicted Raman intensities and band shapes for the F⁻/D4R and empty D4R, in comparison with experiments.

We simulated the homogeneous case with a periodic cell comprising a single LTA unit cell, which produces the calculated Raman spectrum shown in Figure 3.2a (blue). The ratio of
Raman intensities of $F^-$/D4R and empty D4R bands (denoted $I_F/I_E$) can shed light on $F^-$ distributions. The experimental data in Figure 3.2a give an $I_F/I_E$ value of 0.75, while DFT in the homogeneous case predicts 0.79 — excellent agreement that lends credence to the homogeneous model. Reflecting now on the origin of this intensity ratio, the fact that two D4Rs are F-filled while one is empty would seem to suggest an $I_F/I_E$ value closer to 2. However, we find that both experiment and the homogeneous model find $I_F/I_E$ values closer to unity. The apparent contradiction can be explained by vibrational symmetries in the homogeneous case. In particular, the breathing vibrations of the two $F^-$/D4Rs couple to make symmetric and anti-symmetric normal modes, but only the symmetric combination of the two $F^-$/D4R breathing motions exhibits significant Raman intensity. As such, the DFT-computed ratio $I_F/I_E$ is near unity because it compares Raman intensity from one mode of coupled $F^-$/D4Rs to one mode of the empty D4R. Therefore, the excellent agreement between experiment and DFT theory in the homogeneous case — as explained by the coupling of oscillators at high symmetry — seems to argue for a homogeneous fluoride distribution in the LTA-BULKY-F sample.

To test the homogeneous model, we considered the heterogeneous case using a supercell containing two LTA unit cells: one unit cell with two BULKY cations and three $F^-$ anions and the other unit cell with two BULKY and one $F^-$. After optimizing coordinates and lattice parameters, the energy of the heterogeneous model was found to be 1.2 eV = 116 kJ/mol greater than the energy of two homogeneous unit cells because of the charge separation between the heterogeneous unit cells. Normalizing this energy difference by the 48 SiO$_2$ units of the two LTA unit cells gives 2.4 kJ/mol Si — a value well within the normal range of zeolite framework energies, suggesting that the heterogeneous distribution is thermodynamically feasible.
The results of the Raman calculations for the heterogeneous case are shown in Figure 3.3 along with the homogeneous result and the experimental Raman spectrum for as-made LTA-BULKY-F. Careful analyses of the Raman spectra in Figure 3.3 reveal two discrepancies between the heterogeneous model and experimental data. First, the $F^-/D4R$ to empty D4R Raman intensity ratio ($I_F/I_E$) calculated from the heterogeneous spectrum is 0.61, which is 19% less than the experimental value of 0.75, while the homogeneous prediction (0.79) is within 5.3% of the experimental one. Second, the heterogeneous model Raman spectrum in Figure 3.3 shows a small shoulder band associated with slightly different vibrational frequencies of the $F^-/D4R$ in the unit cells containing one $F^-$ and three $F^-$ ions. In contrast, peak fitting of the experimental Raman spectra (Figure 3.3) shows no discernible shoulder band for the 8-day sample. Thus, we conclude from these experimental and simulated Raman spectra that fluoride is homogeneously distributed among the D4R in the as-made LTA-BULKY-F system.

Overall, the Raman bands for the empty D4R and $F^-/D4R$ in LTA zeolite are found to be rich with information about the $F^-/D4R$ structure, bonding, and spatial distribution, opening the door to investigate defects in crystallization, as we show below.
Fig. 3.3: Experimental Raman spectrum of fully crystalline LTA-BULKY-F (experimental 8-day sample) and calculated Raman spectra of LTA-BULKY-F with heterogeneous (blue) and homogeneous (red) distributions of F/D4R. The arrow points to a shoulder band in the heterogeneous model, which is absent in both the homogeneous model and the experimental spectrum.

3.3.5 Quantifying the Empty D4R and F/D4R in LTA

The F⁻ distribution and the amount of the empty D4R and F⁻/D4R in LTA-BULKY-F samples were studied by TGA, elemental analysis, and $^{19}$F/$^{29}$Si magic-angle spinning solid-state NMR (MAS SS-NMR) to shed light on the nature of charge balancing in the as-made zeolite.
The $^{19}$F NMR spectrum, as displayed in Figures 3.4a, consists of a single peak located at $-39$ ppm, indicating that $\text{F}^-$ exclusively resides in the D4R of as-made LTA-BULKY-F samples. This finding is consistent with that of previous studies, indicating a preferred distribution of $\text{F}^-$ in the D4R of LTA.\textsuperscript{157,175,182} The small anisotropy observed in the $^{19}$F NMR might be due to the non-uniform particle size and shape achieved in the synthesis. Elemental analysis indicates that

<table>
<thead>
<tr>
<th></th>
<th>C (wt%)</th>
<th>H (wt%)</th>
<th>N (wt%)</th>
<th>F (wt%)</th>
<th>F-filled D4R (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>LTA-BULKY-F</strong></td>
<td>17.37</td>
<td>1.93</td>
<td>3.13</td>
<td>1.84</td>
<td>61 ± 2%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Si (wt%)</th>
<th>Al (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>LTA-BULKY-F</strong></td>
<td>47.20</td>
<td>0.71</td>
</tr>
<tr>
<td>(After calcination)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
the amount of $F^-$ in LTA-BULKY-F is $1.84 \pm 0.04$ wt %, which corresponds to $61 \pm 2\%$ of the D4R filled with $F^-$ (Table 3.1). TGA weight loss of LTA-BULKY-F is 23.9\% (Figure 3.5), within 2\% of the theoretical loss of 23.4\% corresponding to two BULKY and two $F^-$ per unit cell of LTA, suggesting that two BULKY cations reside in each $\alpha$-cage of LTA-BULKY-F and that the $\beta$-cage is empty.$^{157}$

![TGA of LTA-BULKY after intensive washing with acetone and ethanol.](image)

The $^{29}$Si NMR spectrum in Figure 3.4b shows that there are two peaks located at $-109$ and $-112$ ppm for LTA-BULKY-F, indicating that Si atoms in LTA-BULKY-F exhibit two different local environments. Following Shayib et al.$^{175}$, the $-112$ ppm peak is assigned to Si (Q$_4$) in the empty D4R, and the $-109$ ppm peak is assigned to Si (Q$_4$) in the $F^-$/D4R. The difference in the chemical shift of the empty D4R and $F^-$/D4R is consistent with results from Shayib et al.$^{175}$ on $F^-$/D4R-containing ITW zeolite.$^{175}$ Because the LTA sample is not strictly a siliceous zeolite but contains small amounts of Al with a Si/Al ratio of 66 determined by elemental analysis, the sample contains some number of Si–O–Al linkages. Due to the negative charge caused by the
incorporation of Al into the D4R, the Al is more likely to be distributed in the empty D4R to avoid strong electrostatic repulsion with the F⁻ in the F⁻/D4R. Our DFT calculation and the previous literature¹⁹⁵ both suggest that incorporating Al into zeolite frameworks causes a peak shift to less-negative chemical shifts of around 5 ppm, meaning that the NMR peak for Si connected to one Al, Q₄(1Al), in the empty D4R will overlap the peak from the Si atom in the F⁻/D4R. As a result, we expect the actual ratio of the F⁻/D4R to the empty D4R to be less than the ratio obtained from the integrated Si NMR peak area at −109 and −112 ppm. No partially coordinated Si such as Q₃ or Q₂ is observed in LTA-BULKY-F, indicating that the sample is defect-free and that the positive charge from BULKY cations is balanced by the negative charge from F⁻ ions and the presence of framework Al from seeds. The molar ratio (F + Al)/BULKY, representing the ratio of the negative to positive charge, was found by elemental analysis to be 1.05 (Table 3.1), indicating a well-understood charge balance in the as-made LTA-BULKY-F sample. This finding lends further credence to the charge balancing role of F⁻ in zeolite synthesis.

### 3.3.6 Probing Si-LTA Crystallization Using Raman Analyses

Raman spectra and XRD patterns were collected at various stages of LTA synthesis using BULKY as the OSDA, to investigate the evolution of empty D4R and F⁻/D4R units during crystallization. Figure 3.6a shows Raman spectra for samples at the following stages/times of LTA synthesis: the precursor gel (red), 1.5 h (gold), 2.5 h (green), 3 h (teal), 6 h (blue), and 8 day (purple). Figure 3.6b shows XRD patterns of the same samples. No diffraction peaks from the LTA seeds were observed in the 1.5 and 2.5 h samples, and very weak diffraction peaks were observed in the precursor gel. For synthesis times less than 3 h, the XRD patterns consist of a broad, featureless signal in the range of 20–25°, a characteristic of amorphous silica and with no sign of crystal formation. Similarly, for synthesis times less than 3 h, the Raman spectra show no
evidence of D4R formation but do show characteristic bands of the BULKY OSDA. The concurrent absences of the D4R signal in the Raman and crystal diffraction peaks in the XRD may indicate that well-defined D4R units can be observed by Raman spectroscopy only when detectable LTA crystals are formed in the synthesis gel.

From 3 to 6 h of synthesis time, the XRD data in Figure 3.6b suggest a transition period of crystal growth. Scanning electron microscopy (SEM) imaging of the 2.5 h sample (Figure 3.7a) shows spherical particles with sizes of around 400 nm; these particles lack the long-range order, as shown by XRD (Figure 3.6b). SEM of the 3 h sample (Figure 3.7b) shows spherical particles in the size range of 400−700 nm; these are partially crystalline, as shown by XRD. The final crystal size of the 8 day sample (Figure 3.7d) is in the range of 1−2 μm. The question what the Raman spectra in Figure 3.6a can reveal about the evolution of D4R units during the formation of the LTA-BULKY-F sample remains.

Focusing now on the 3 h sample, we see the initial emergence of LTA crystals in the XRD data, alongside the early appearance of the empty D4R and F−/D4R bands in the Raman spectra. Although the empty D4R and F−/D4R band locations appear to be constant with time, their relative intensities ($I_F/I_E$) are seen to vary with time, with $I_F/I_E = 1.12$ at 3 h and decreasing to 0.75 at day 8. Several hypotheses can potentially explain the higher $I_F/I_E$ values at early crystallization times. The first involves possible zones of F− enrichment in growing LTA crystals, giving more F−/D4R units than seen at later times. Indeed, we reported above that only 61% of D4R units are F-filled for the fully crystallized sample (8 d); increasing this amount by a factor of 1.12/0.75 (the Raman intensity ratios) would give possibly 91% F-filled D4Rs. However, there are two problems with this hypothesis. The first involves difficulty with charge balance — additional BULKY cations cannot fit in LTA and there are no other obvious cations in the
synthesis mixture to balance the charge. The second problem involves $F^-$ ion mobility — once an $F^-/D4R$ unit fully forms, the $F^-$ becomes trapped at synthesis temperatures, precluding fluoride redistribution over time. Thus, the $F^-$ enrichment hypothesis fails to explain the Raman data, raising more questions than it answers.

Fig. 3.6: (a) Raman spectra at various stages of LTA synthesis with BULKY, and (b) XRD data for the same samples as (a). LTA crystals appear in XRD at 3 h, as do empty and F-filled D4R bands in Raman spectra.
Fig. 3.7: SEM images of LTA-BULKY-F at different times (A) 2.5 h, (B) 3 h, (C) 6 h and (D) 8 d.

A second possible origin for higher $I_S/I_E$ values at early crystallization times is related to the presence of defects associated with the LTA zeolite structure. As shown in Figure 3.8, $^{29}$Si NMR spectra of the 1.5, 3, and 6 h samples show two peaks from Q$_3$ Si species (i.e., Si atoms with three bridging oxygens and one terminal oxygen) and Q$_4$ Si species (i.e., Si atoms with four bridging oxygens). The presence of Q$_3$ and Q$_4$ Si species in the amorphous 1.5 h sample suggests that the silica species are partially condensed. The Q$_3$ Si species in the partially crystalline 3 and 6 h samples are possibly from both an amorphous phase and a defect-containing LTA crystalline phase. The Q$_3$/(Q$_4$ + Q$_3$) ratios for the 3 and 6 h samples are 39.2 and 35.1%, respectively, which are similar values. However, the crystallinity of the 6 h sample was found to be much higher than that of the 3 h sample, 80% versus 33%, which indicates that a part of the Q$_3$ Si species in the partially crystalline 6 h sample must come from Q$_3$ defects associated with the LTA crystalline
phase. With the crystallization time increasing to 8 days, the peak from Q$_3$ Si species completely disappears from the $^{29}$Si NMR spectrum, suggesting that the defects in the partially crystalline zeolite are healed. Such Q$_3$ Si species associated with the LTA crystals (6 h sample) can be attributed to either of the following: (i) D4R units with a missing Si atom as a point defect or (ii) hydrolyzed Si – O – Si bridges in the D4R giving Si – OH/HO – Si defects. Periodic DFT calculations were performed to determine the influence on Raman spectra of placing either a point defect or a hydrolyzed defect into F$^−$/D4R and/or empty D4R units. The calculation results suggest that the presence of hydrolyzed Si – O – Si defects in the D4R of LTA-BULKY-F is unlikely because the tightly filled pore space of the as-made zeolite forces the formation of high energy, pentavalent Si species, giving rise to the calculated $^{29}$Si NMR and Raman spectra that look entirely different from those found experimentally. As such, we can rule out hydrolyzed defects causing the varying Raman intensities in Figure 3.6a.

Fig. 3.8: $^{29}$Si MAS NMR spectra of LTA-BULKY-F at various stages of LTA synthesis. The 3 and 6 h samples show the presence of Q$_3$ Si due to the partial crystallinity of the two samples.
Point defects — missing Si atoms with near-neighbor oxygens capped by hydrogens — can be present in both the empty D4R and F⁻/D4R. Accordingly, Raman spectra of LTA-BULKY-F with a range of such point defects were calculated and compared with those in experiments. In general, our DFT calculations predict that the presence of point defects in the D4R influences both the Raman band frequency and intensity. Figure 3.9 shows that averaging the computed Raman spectra from the following three systems — (i) the defect-free LTA-BULKY-F system, (ii) LTA-BULKY-F with one point defect in an empty D4R in each unit cell, and (iii) LTA-BULKY-F with two point defects in an empty D4R in each unit cell — with a ratio of 4:1:1, respectively, reproduce the features of the 3 h experimental sample. In other words, the varying Raman intensities in Figure 3.6a indicate the presence and evolution of defects in the empty D4R but not in the F⁻/D4R. We thus arrive at the conclusion that an important component of zeolite LTA crystal growth involves the healing of point defects in the zeolite framework around otherwise defect-free F⁻/D4R units, giving strong support for the notion that F⁻ plays a structure-directing role in LTA synthesis. This result is consistent with the previous gas-phase electronic structure calculations, which demonstrate that small zeolite building units like D4R are stabilized by F⁻ based on its size and electronic properties.
Fig. 3.9: (a) Experimental Raman spectra of fully crystalline LTA-BULKY-F (purple) and partially crystalline LTA-BULKY-F (blue), DFT-calculated Raman spectrum of LTA-BULKY-F composed of intact D4Rs (red), and (green) DFT-calculated Raman spectrum combining (i) LTA-BULKY-F only with intact D4Rs, (ii) LTA-BULKY-F with one point defect in an empty D4R in each unit cell, and (iii) LTA-BULKY-F with two point defects in an empty D4R in each unit cell in a 4:1:1 ratio, respectively. (b) Structures of four different D4Rs used for the combined spectrum. From left to right, from top to bottom: intact F⁻/D4R; intact empty D4R; empty D4R with one missing Si; and empty D4R with two missing Si.

3.3.7 Synthesis of Siliceous LTA with Reduced Fluoride

Finding new synthesis procedures for making siliceous and high-silica zeolites with much less fluoride is a key target for zeolite chemists because of the expense and challenge of handling HF at industrial scales. The conclusions drawn above — that approximately 2/3 of D4Rs per unit cell in siliceous LTA-BULKY-F are filled with F⁻ and that F⁻ plays a structure-directing role in the formation of D4Rs — provide key insights that inform a new synthesis of Si-LTA with a substantially reduced amount of F⁻. In the conventional synthesis of LTA-BULKY-F, the molar ratio of F/BULKY is kept close to unity to provide a neutral-pH environment and sufficient F⁻ to balance the OSDA positive charge.
The results of our study suggest that tying the initial HF concentration in the synthesis mixture to the amount of BULKY used in the synthesis may be excessive. In fact, instead of linking the molar composition of F to BULKY, our results suggest linking the molar composition of F to SiO$_2$ in the ratio HF/SiO$_2$ = 1:12, based on the target of two F$^-$ ions per 24 SiO$_2$ in the LTA unit cell. We have found that highly crystalline Si-LTA can successfully be obtained with this approach, which reduces the HF/BULKY ratio in the synthesis gel from 1 in the conventional method to 0.17 in the new composition. The amount of F$^-$ in the synthesis gel when HF/BULKY is 0.17 equals the value needed to fill 2/3 of the D4Rs in the final LTA crystals, indicating that most of the added F was utilized for D4R formation. We also found that further reducing F$^-$ leads to partially crystalline zeolites under these synthesis conditions. The Raman, XRD, and $^{29}$Si NMR spectra of Si-LTA made with this reduced, stoichiometric amount of F$^-$ in the initial gel (Fig. 3.10) are very similar with those from the conventional LTA-BULKY-F synthesis, indicating that this sixfold reduction of F$^-$ in the synthesis can still lead to defect-free highly siliceous LTA zeolites.
Fig. 3.10: (a) Raman spectrum, (b) XRD and (c) $^{29}$Si MAS SS-NMR spectrum of LTA-BULKY-F synthesized using the gel with a composition of 1.00 SiO$_2$ : 0.083 HF : 0.50 BULKY OSDA-OH : 5.00 H$_2$O. The Raman band ratio of F$^-$/D4R to empty D4R is 0.73, which is similar to the conventional LTA-BULKY-F synthesized using the composition of 1.00 SiO$_2$ : 0.5 HF : 0.50 BULKY OSDA-OH : 5.00 H$_2$O, indicating around 2/3 of D4Rs in the sample are occupied with F$^-$. The $^{29}$Si MAS SS-NMR result also suggests the presence of two different Si (Q$_4$) of D4R.

3.4 Summary

Zeolite synthesis experiments, periodic DFT, Raman spectroscopy, and other characterization methods were applied to investigate the charge-balancing and structure-directing roles of F$^-$ in zeolite LTA synthesis. Raman spectra show that both the empty D4R and F$^-$/D4R can be observed in zeolite LTA synthesized using BULKY as the OSDA in the presence of F$^-$. The two different D4Rs show distinct Raman bands due to the geometrical distortion of the D4R and charge transfer to the D4R upon inclusion of F$^-$. The Raman spectra from the two different D4R units can be used to quantify their distribution in the formed zeolites. Studies on the crystal growth of LTA-BULKY-F suggest that LTA crystals initially emerge with both the empty D4R and F$^-$/D4R. We have observed variation in Raman intensities for empty and F-filled D4Rs during the early stages of LTA crystal growth. Periodic DFT has attributed this variation to the presence of defects in growing LTA crystals, namely, missing Si atoms in empty D4R units.
Upon further crystallization, these defects appear to become healed, leading to the formation of defect-free LTA zeolite crystals. Our results confirm both the charge-balancing and structure-directing roles of $\text{F}^-$ in zeolite synthesis. These insights were used to reduce the amount of $\text{F}^-$ required to synthesize defect-free, highly siliceous LTA by a factor of 6, which can benefit the industrial scale synthesis of high-silica zeolites. Such insights are also fundamentally important for understanding the hierarchical nature of zeolite crystallization mechanisms and may also assist in designing other syntheses of zeolites with new structures and compositions.

In addition, for the questions raised at the end of the 1st chapter, due to the newly-discovered Raman evidence, it is concluded that the exclusive role of $\text{F}^-$ in Si-LTA synthesis is stabilizing intact D4R units during crystallization. This is also why by using the HF-free DGC method, pure- or high-silica LTA is still difficult to be obtained: pure- or high-silica D4R formation does need $\text{F}^-$ participation. Therefore, in order to synthesize pure- or high-silica LTA without using fluoride, we should try to overcome this barrier and come up with ideas which can form D4R in the absence of fluoride.
CHAPTER 4

TITRATING CONTROLLED DEFECTS INTO SILICEOUS LTA ZEOLITE CRYSTALS USING MULTIPLE ORGANIC STRUCTURE-DIRECTING AGENTS

4.1 Background

Highly ordered and specific microporous structures of zeolites, with pore sizes ranging from 0.3 to 2 nm, have made zeolites the shape-selective materials of choice for many applications in catalysis\(^\text{167}\) and separations\(^\text{7,196}\) and in several emerging areas including carbon capture\(^\text{5}\) and clean energy production.\(^\text{171}\) Despite massive research efforts, the rational synthesis of zeolites with targeted framework structure, composition, and defect properties remains a grand challenge because of the complex interplay among synthesis parameters and our poor understanding of crystallization mechanisms.\(^\text{81,82,87,99,169}\) For example, zeolites can be hydrothermally synthesized in alkaline or neutral media using hydroxide or fluoride,\(^\text{50,52}\) respectively, as the mineralizing agent for crystallization. Under alkaline conditions, negatively charged framework defects are often formed in as-made zeolites to balance the positive charges from organic structure-directing agents (OSDAs) and/or inorganic cations.\(^\text{197}\) In contrast, the fluoride synthesis route has led to a variety of new, defect-free zeolite materials — essentially high-silica or even all-silica zeolites.\(^\text{52,172}\) In addition to being a mineralizing agent, fluoride is hypothesized to act as a structure-directing agent, stabilizing small silicate rings and cages such as the double four-membered ring (D4R) in zeolites.\(^\text{53,173–175,198}\) Fluoride is also hypothesized to play a charge-compensating role, where F\(^-\) balances the positive charges from OSDAs or inorganic cations used in zeolite synthesis, thereby producing low-defect or defect-free materials.\(^\text{52,176,177}\) But it remains unclear whether there is a limit to fluoride’s capacity for balancing positive charge. Such a limit would provide a useful design parameter in zeolite
synthesis and raises an important question about the nature of defects that arise when this limit is surpassed. In this article, we present an integrated synthesis, spectroscopy, and density functional theory study on the limits of fluoride as a charge-compensating agent in the crystallization of siliceous LTA zeolite.

Fig. 4.1: LTA zeolite structure and its three building subunits: one α-cage, one β-cage, and three double four-membered ring (D4R) per unit cell. Each subunit may contain species as shown. Synthesis with a dimer of BULKY cations would require 2/3 of D4R to be F-filled; making LTA with two BULKY and one TMA would require 3/3 of D4R to be F-filled, according to a charge-balancing hypothesis.

The range of synthetic pathways available for crystallizing siliceous LTA (Si-LTA) makes this an excellent system for investigating charge compensation by fluoride. To put these pathways into perspective, we note that the structure of LTA comprises one α-cage, one β-cage, and three connecting D4R units in each unit cell (Figure 4.1). It has been found that Si-LTA zeolite can be synthesized in the presence of F\(^{-}\).\(^{55,157,187}\) Similar to many other zeolites with D4R, the D4R unit in as-made Si-LTA zeolite (before calcination) is occupied by F\(^{-}\) based on its size and electronic properties.\(^{53}\) Boal et al. synthesized Si-LTA using dimers of 1,2-dimethyl-3-(4-
methylbenzyl) imidazolium cations (herein denoted as “BULKY”), which occupy the α-cage in a structural motif akin to two hands packing a snowball (Figure 4.1). In our previous work, we combined elemental analysis, Raman spectroscopy, and DFT to confirm that the positive charge of BULKY OSDA is balanced by \( F^- \) located within D4R. Two of the three D4R units in the LTA unit cell are filled with \( F^- \), resulting in two negative charges per unit cell that balance the two positive charges from the BULKY dimer. Because of the charge balance achieved by \( F^- \) and BULKY OSDA, a defect-free Si-LTA zeolite can be made from this pathway.

Interestingly, a range of different OSDAs can be used for the synthesis of Si-LTA zeolite, thus allowing various amounts of OSDA-positive charge to be incorporated into the zeolite. Boal et al. found that Si-LTA can also be synthesized using dimers of BULKY cations along with tetramethyl ammonium (TMA) as a secondary OSDA, which occupies the β-cage (Figure 4.1). In principle, this increased amount of OSDA positive charge must be balanced by additional negative charges. The question remains whether including additional fluoride in the synthesis mixture can balance this extra positive charge in as-made zeolites. If not, then negatively charged framework defects may be required to compensate the positive OSDA charge, meaning that the fluoride-mediated route to zeolite synthesis may still lead to significant defect densities.

Precisely characterizing defects in as-made zeolites can be a notoriously difficult problem. For example, incompletely networked silicon atoms — e.g., silicons with only three bridging oxygens, denoted as \( Q_3 \) silicon — can appear with the lone terminal oxygen either as a neutral OH or as a charged \( O^- \) species. It can be challenging for \( ^{29}\text{Si} \) solid-state nuclear magnetic resonance (NMR) to distinguish between Si-OH and Si-O\(^-\) species, both exhibiting broad features in the \( ^{29}\text{Si} \) chemical shift range of (−95, −105) ppm. Such speciation can be
accomplished by carefully controlling pH and characterizing by cross-polarization $^1$H-$^{29}$Si NMR methods.\textsuperscript{200,201} However, the pH usually changes during zeolite crystallization in ways that can be hard to control. As such, applying $^{29}$Si solid-state NMR alongside other characterization methods is an important avenue for determining the kinds and numbers of defects that may appear in fluoride-mediated zeolite synthesis. In the present work, we have applied a battery of characterization methods including Raman spectroscopy, elemental analysis, $^{29}$Si, $^{19}$F, and $^{13}$C solid-state NMR, and density functional theory to shed light on the nature of defects present in as-made LTA zeolites.

Below, we find that using multiple OSDAs in the synthesis of Si-LTA allows the controlled titration of positive charge into the as-made zeolite, exceeding the capacity of fluoride to balance charge and requiring anionic framework defects to make up the difference. We then present a thermodynamic analysis explaining the limited capacity for charge compensation by fluoride and corroborate the thermodynamic predictions with synthesis experiments.

4.2 Methods

4.2.1 Experimental Section

4.2.1.1 Synthesis of Zeolites (LTA-BULKY-xTMA)

The OSDA, dimethyl-3-(4-methylbenzyl) imidazolium hydroxide (denoted as “BULKY-OH”), used in this zeolite synthesis, was obtained by following the previously reported recipe.\textsuperscript{157,198} For the synthesis of LTA-BULKY-0.00TMA, briefly, first, 7.71 g of aqueous solution of BULKY-OH (concentration: 0.2613 mmol/g) was mixed with 900 μL of tetraethyl orthosilicate (TEOS, 99 wt %, Alfa Aesar) in a 50 mL beaker. After being capped by parafilm, the mixture was stirred continuously under RT for around 20 h, for the complete hydrolysis of TEOS. Then, 70 μL of hydrofluoric acid (HF, 48−52 wt% in water, Alfa Aesar) was carefully
pipetted into the clear solution (Caution! HF is extremely hazardous and toxic, and this step should ALWAYS be performed in a hood with special gloves and lab coat designed exclusively for handling HF), followed by adding 0.439 mL of aqueous solution of LTA seeds (38.6 mg/mL; 7 wt % with regard to the total silica source). LTA seeds used here, with a size of around 200 nm, are aluminosilicate LTA nanocrystals prepared by a conventional hydrothermal crystallization method in the absence of $F^-$. Afterward, a particular amount of water in the obtained suspension was evaporated in a 60 °C oven to achieve the desired ratio for the composition (1.00 SiO$_2$:0.50 HF:0.50 BULKY:5.00 H$_2$O, 7 wt % seeds) of the precursor gel. Finally, the gel was transferred into a 50 mL Teflon-lined stainless-steel autoclave and the zeolite crystallization was carried out under 150 °C for 8 days. The obtained zeolite product was purified by dispersing in 50 mL of DI water, followed by centrifugation, and removal of the supernatant. After repeating the washing process five times, the purified product was dried in a 70 °C oven overnight.

For the syntheses of LTA-BULKY-xTMA (x = 0.01, 0.025, and 0.05; x here should not be higher than 0.1; otherwise an impure phase that includes AST zeolite might appear, especially when there are no seeds) under 150 °C, the procedures are similar to LTA-BULKY-0.00TMA, except that during the step of mixing BULKY-OH with TEOS, tetramethyl ammonium hydroxide (TMA-OH, 25 wt % in water, Alfa Aesar) solutions of 14, 36, and 72 μL were added, respectively. When HF was added, its volume was also increased to 71, 74, and 77 μL accordingly, to keep the pH of the four precursor gels the same using different amounts of TMA-OH. The molar ratio of these four precursor gels is 1.00 SiO$_2$:(0.50 + x) HF:0.50 BULKY:xTMA-OH:5.00 H$_2$O with 7 wt % seeds, where x is 0, 0.01, 0.025, or 0.05. The crystallization of LTA-BULKY-0.05TMA was also carried out under 125 and 170 °C for 8 days.
4.2.1.2 Characterization Studies

The crystalline structure of all the synthesized LTA samples was confirmed by XRD on a Rigaku SmartLab diffractometer equipped with a Cu Kα X-ray radiation produced at 40 mA and 45 kV. The structure of BULKY in chloride form (before ion-exchange) was confirmed by liquid-state $^1$H NMR on a Bruker 400 MHz NMR spectrometer. The solvent chosen for this measurement was D$_2$O. For Raman measurements, several milligrams of the zeolite sample were dispersed on a silicon wafer coated by gold. The Raman spectra were recorded utilizing a XploRa Raman microscope (Horiba Scientific), which was operated using a 785 nm laser line as the excitation light source and its power was controlled at 10 mW. A 1200-line grating was set, and the laser light was focused on the sample through a $100 \times$ magnification lens (Olympus, Japan). A 20 s scan time and an accumulation of 20 scans were chosen for all the measurements.

$^{29}$Si MAS NMR measurements were performed on a Bruker 600 MHz solid-state NMR spectrometer employing a 4 mm MAS probe. For $^1$H and $^{29}$Si nuclei, the spectral operating frequencies were 600.1 and 119.2 MHz, respectively. All samples were spun at 5 kHz during the measurements. A recycle delay time of 200 s was found to be adequate for both Q$_3$ and Q$_4$ signals of every sample. The number of scans was set at 200 for all the measurements. $^{19}$F MAS NMR spectra of LTA-BULKY-0.000TMA and LTA-BULKY-0.050TMA were acquired on a Bruker AVANCE 400 wide-bore spectrometer (9.4 T, 376.48 MHz for $^{19}$F) operated under a spinning rate of 9 kHz, employing a 4 mm double resonance probe. $^{19}$F direct polarization spectra were collected by a spin-echo sequence for which the 90° pulse duration and the number of scans were set at 2.25 μs and 32, respectively. To calibrate the chemical shift of the results, an external reference of sodium fluoride (at $-121.5$ ppm) was used. A line broadening factor of 10 Hz was chosen to carry out the data analysis. $^{13}$C MAS NMR (DP) measurements were
performed on a Bruker 600 MHz solid-state NMR spectrometer using a 4 mm MAS probe. For 
$^1$H and $^{13}$C nuclei, the spectral operating frequencies were 600.1 and 150.9 MHz, respectively. 
All the samples were spun at 5 kHz during the measurements. A recycle delay time of 50 s was 
found to be adequate for the only carbon in TMA$^+$ and also the three carbon atoms of the three 
methyl groups in BULKY. The number of scans was set at 256 for all the measurements. $^{13}$C 
MAS NMR (CP) was also used to measure LTA-BULKY-0.000TMA and LTA-BULKY-
0.050TMA. The two samples were spun at 9 kHz during the measurements, and the number of 
scans was set at 2000. SEM was utilized to determine the morphology of all the samples. SEM 
images were collected with a Hitachi S-4800 field emission scanning electron microscope. Prior 
to this characterization, all the samples were sputter-coated with Au. The amounts of C, H, and N 
of all the LTA samples synthesized under 150 °C were measured at Galbraith Laboratories (TN) 
using a flask combustion method, followed by ion chromatography. The F amount of each 
sample was also measured at Galbraith Laboratories (TN) by pyrohydrolysis. The samples were 
dried under 120 °C overnight before measurements to avoid the influence from adsorbed water.

4.2.2 Computational Section

Intact and defected zeolite LTA systems containing BULKY, TMA, and fluoride ions (F$^-$) 
were studied using periodic density functional theory (DFT) via planewave basis sets with the 
Vienna Ab initio Simulation Package (VASP).\textsuperscript{159} We used the simulation parameters, structures, 
and Raman data of zeolite LTA and LTA-BULKY-F from our previous work.\textsuperscript{98,198} For all DFT 
periodic simulations reported here, we applied the projector augmented wave (PAW)\textsuperscript{160,161} 
pseudo-potential and the Perdew–Burke–Ernzerhof (PBE)\textsuperscript{162} exchange-correlation functional 
with the D$_3$ dispersion corrections\textsuperscript{188,189} and nonspherical corrections, using an energy cutoff 
value of 480 eV, a $1 \times 1 \times 1$ K-point mesh, and Gaussian smearing of which the width is 0.05 eV.
Avogadro\textsuperscript{190} was used to initially combine the LTA framework with BULKY, TMA, and F so that two BULKY cations are inside the α-cage, one TMA cation is inside the β-cage, and three fluoride ions are inside D4Rs. Ab initio molecular dynamics (AIMD) simulations in the NVT ensemble (Nose–Hoover thermostat)\textsuperscript{202} were then performed for 2 ps to identify stable configurations of LTA-BULKY-TMA-F systems at 400 K. Several configurations were extracted at random from the last 1 ps of AIMD and were then optimized for atomic positions and lattice parameters to identify minimum-energy configurations for normal mode analysis (NMA) until the energy variation of ionic steps fell below 10−4 eV. To find possible candidates explaining the $Q_3$ Si peak found in the experimental $^{29}$Si NMR, we made defects to initial intact structures based on the optimized LTA–BULKY-TMA-F system. The method of introducing defects into initial intact systems and calculating theoretical Raman spectra are the same with our previous work.\textsuperscript{198} If more than one defect presents, we calculated energy differences of possible configurations to find thermodynamically favored ones. Theoretical chemical shifts of intact and defected systems were calculated using the PBE exchange-correlation functional at an energy cutoff value of 800 eV based on the linear response method.\textsuperscript{203,204} CFCl$_3$ and TMS were set as the standards to calculate chemical shifts of $^{19}$F NMR and $^{29}$Si NMR, respectively, using the same method, functional and basis set. Calculated chemical shifts were broadened using Lorentzian curves of which the FWHM was 0.5 ppm, to mimic experimental NMR spectra. Multiple calculated Raman and NMR spectra of intact and defected systems were combined to fit the experimental results simultaneously. The best combination we found was considered to represent experimental samples of as-made LTA–BULKY-TMA-F. We also performed thermodynamic calculations for LTA-BULKY-F and LTA–BULKY-TMA-F to explain
experimental defect healing processes. We calculated energy changes between charged and neutral defects and configurations before and after possible defect-healing reactions.

4.3 Results and Discussion

4.3.1 Synthesis of Si-LTA Using BULKY and TMA as OSDAs

Si-LTA can be synthesized using one OSDA (BULKY-OH) or two OSDAs (BULKY-OH and TMA-OH), both in the presence of $\text{F}^{-}$ under hydrothermal synthesis conditions. To investigate the effects of a secondary OSDA on the charge balancing and structures of the formed zeolites, four Si-LTA samples (denoted LTA-BULKY-xTMA; $x = 0, 0.01, 0.025, \text{and } 0.05$) were synthesized with different amounts of TMA-OH using a gel composition of $1.00 \text{SiO}_2:(0.50 + x)\text{HF}:0.50 \text{BULKY-OH}:x\text{TMA-OH}:5.00 \text{H}_2\text{O}$ at $150 \degree\text{C}$ for 8 days. In the synthesis gel, the amount of HF was increased accordingly with increasing TMA-OH to maintain the same pH of the gels for all four samples. 7 wt % LTA seeds (with regard to the silica source), with a size of about 200 nm and an Si/Al ratio of 1.26, were used in the synthesis. It has been found that the synthesized LTA exhibits a Si/Al ratio of 66. Strictly speaking, the LTA sample is a high-silica zeolite, with approximately one aluminum atom per three unit cells of LTA. Our previous computational and experimental study found negligible effects on the Raman spectra from these very low Al contents.\textsuperscript{198} For this reason, we denote the resulting materials as Si-LTA.

As reflected by XRD results (Figure 4.2a), all of the four siliceous LTA samples are fully crystalline with the characteristic diffraction peaks from the LTA framework. The different intensity ratios of the first two diffraction peaks in the four samples indicate the presence of different amounts of TMA$^+$ located within LTA zeolites.
Fig. 4.2: (a) XRD patterns of LTA-BULKY-xTMA (x = 0, 0.01, 0.025, and 0.05) where x = TMA/SiO$_2$ molar ratios in synthesis mixtures. (b) Raman spectra of as-made LTA-BULKY-xTMA before calcination. Raman bands assigned by DFT to LTA vibrations are marked with a black star at the top; unmarked bands are for either BULKY or TMA; the yellow-shaded band is assigned by DFT to the empty D4R symmetric breathing mode and the cyan-shaded band is for the F$^-$/D4R; the green-shaded band is from the CN symmetric stretching of TMA. (c) Correlation between the Raman band intensity ratio of F$^-$/D4R to empty D4R and the TMA quantity in the precursor gel.

4.3.2 Raman Signatures of F$^-$/D4R and Empty D4R in LTA-BULKY-xTMA

Raman spectroscopy was used to study the structural differences in the four LTA-BULKY-xTMA samples, investigating the distribution of F$^-$/D4R and empty D4R. Through the integrated method combining DFT-simulated and experimental Raman spectra, our previous
studies have assigned the Raman bands of the siliceous LTA zeolite synthesized in the presence of $F^-$.$^{98,198}$ As shown by the Raman results for the four LTA samples (Figure 4.2b), the bands marked with a star at the top are assigned to Raman-active vibrations of the LTA framework, while those unmarked are assigned to the OSDAs (either TMA or BULKY). Of particular interest are the Raman bands in Figure 4.2b associated with the empty D4R (at about 512 cm$^{-1}$; shaded yellow in Figure 4.2b) and the F-filled D4R (at about 548 cm$^{-1}$; shaded cyan in Figure 4.2b). Interestingly, it was found that with increasing TMA concentration in the synthesis gel, the intensity ratio of Raman bands assigned to F-filled and empty D4R (denoted $I_F/I_E$) increases linearly (Figure 4.2c), suggesting that empty D4R may be filling with $F^-$ as the amount of TMA in the synthesis mixture is increased.

Table 4.1 Elemental Analysis of LTA-BULKY-xTMA (x = 0, 0.01, 0.025, and 0.05)

<table>
<thead>
<tr>
<th></th>
<th>C (wt%)</th>
<th>H (wt%)</th>
<th>N (wt%)</th>
<th>F (wt%)</th>
<th>TMA unit cell*</th>
<th>TMA unit cell**</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTA-BULKY-0.050TMA</td>
<td>19.32</td>
<td>2.56</td>
<td>3.54</td>
<td>1.69</td>
<td>0.94</td>
<td>1.00</td>
</tr>
<tr>
<td>LTA-BULKY-0.025TMA</td>
<td>18.87</td>
<td>2.35</td>
<td>3.46</td>
<td>1.52</td>
<td>0.80</td>
<td>0.76</td>
</tr>
<tr>
<td>LTA-BULKY-0.010TMA</td>
<td>18.59</td>
<td>2.16</td>
<td>3.30</td>
<td>1.55</td>
<td>0.53</td>
<td>0.47</td>
</tr>
<tr>
<td>LTA-BULKY-0.000TMA</td>
<td>17.37</td>
<td>1.93</td>
<td>3.13</td>
<td>1.76</td>
<td>0.25</td>
<td>0.23</td>
</tr>
</tbody>
</table>

*Values calculated from elemental analysis via N wt %.**Values calculated from $^{13}$C DP SS NMR.

The presence of TMA in LTA samples was confirmed by the Raman band at about 782 cm$^{-1}$ (shaded in green), assigned to the CN symmetric stretching vibration of TMA.$^{205}$ TMA is located within β-cages of the LTA structure.$^{90,186}$ The amount of TMA in the as-made LTA samples was quantified by elemental analysis (Table 4.1) and by $^{13}$C MAS NMR (Table 4.1). The TMA occupancy (molecules per unit cell) from elemental analysis was computed based on nitrogen weight % values. The amount of TMA in the as-made LTA was found to vary from 0.23 per unit cell (for LTA-BULKY-0.000TMA in which TMA$^+$ is from the low-silica seeds synthesized with TMA-OH) to 1.00 per unit cell in the high-concentration TMA case, indicating
that it is possible to titrate controlled amounts of positive charge into the as-made LTA zeolite. The question remains: what is balancing this charge — F\(^-\) or some other anion?

Surprisingly, the elemental analysis data indicate that the amount of F\(^-\) in the four samples does not change significantly with increasing amount of TMA (Table 4.1), suggesting that the additional positive charge from TMA is balanced by another source, e.g., negative charges from structural defects such as Si–O\(^-\). To investigate the presence of defects in the as-made LTA samples, the LTA-BULKY-\(x\)TMA samples were characterized using \(^{29}\)Si solid-state MAS NMR. As displayed in Figure 4.3 and Table 4.2, for the sample without TMA, no Q\(_3\) peak was found in the \(^{29}\)Si MAS NMR spectrum, implying a defect-free LTA structure with all positive charge from BULKY balanced by F\(^-\), consistent with our previous study.\(^{198}\) With increasing TMA, the ratio of Q\(_3\)/(Q\(_3\) + Q\(_4\)) grows accordingly, consistent with an increasing amount of anionic framework defects to balance charge. This correlation on the macroscale prompts the question: what are the atomic-level structures on the microscale responsible for this trend? We address this question through a computational DFT analysis in the next section.
Fig. 4.3: (a) $^{29}$Si MAS NMR spectra of LTA-BULKY-xTMA ($x = 0, 0.01, 0.025$, and $0.05$); the peak locating around 98 ppm and the two peaks at 109 and 112 ppm are from Si ($Q_3$), Si ($Q_4$) in the intact F/D4R, and Si ($Q_4$) in intact empty D4R, respectively. (b) Peak deconvolution for the three peaks in the $^{29}$Si MAS NMR spectra.

<table>
<thead>
<tr>
<th>LTA-BULKY-xTMA</th>
<th>$Q_3/(Q_3 + Q_4)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTA-BULKY-0.050TMA</td>
<td>$21.9 \pm 3.1%$</td>
</tr>
<tr>
<td>LTA-BULKY-0.025TMA</td>
<td>$19.3 \pm 2.4%$</td>
</tr>
<tr>
<td>LTA-BULKY-0.010TMA</td>
<td>$10.0 \pm 1.6%$</td>
</tr>
<tr>
<td>LTA-BULKY-0.000TMA</td>
<td>$0$</td>
</tr>
</tbody>
</table>

4.3.3 Identifying Defect Structures with Computational Spectroscopy

Raman spectra and $^{29}$Si NMR spectra, both computed with periodic DFT, were used to study possible defect structures in the as-made LTA-BULKY-TMA sample with TMA/SiO$_2$ = 0.050, the maximum amount studied herein. Based on our previous study, which investigated the healing of neutral defects in the LTA-BULKY system, we focus below on point defects in LTA-BULKY-TMA with missing Si atoms and with surrounding oxygens either capped by hydrogens or with negative charge.
An alternative defect structure considered in ref \textsuperscript{198} is hydrolyzed Si–O–Si bridges yielding Si-OH/HO-Si moieties, also considered by Davis and co-workers in MFI-type zeolites.\textsuperscript{200} However, the crowded nanopore spaces in as-made LTA-BULKY were found to make hydrolyzed bridges extremely energetically unfavorable — consistent with the recent DFT results of Hammond and co-workers for SOD-type materials,\textsuperscript{152} and with simulations by Sholl and co-workers on the framework flexibility.\textsuperscript{206} Because LTA-BULKY-TMA is even more crowded (incorporating TMA into β-cages) than Si-LTA, we expect that hydrolyzed bridge defects are equally or even more energetically unfavorable in this case. As such, we focus below on point defects involving missing Si atoms in LTA-BULKY-TMA.

Our goal in this computational study is to identify point defect structures and probabilities that reproduce key features of the Raman and \textsuperscript{29}Si NMR spectra of as-made LTA-BULKY-0.050TMA. In particular, for the Raman spectra, we seek to reproduce empty and F-filled D4R band locations, band shapes, and the F-filled-D4R to empty D4R band intensity ratio ($I_F/I_E$), which was found to be 1.2 for LTA-BULKY-0.050TMA (Figure 4.2c). For the \textsuperscript{29}Si NMR spectrum, we aim to reproduce locations and shapes of Q\textsubscript{3} and Q\textsubscript{4} bands, as well as the Q\textsubscript{3}/(Q\textsubscript{3} + Q\textsubscript{4}) ratio (21.9 ± 3.1\%, Table 4.2). For all calculations reported below, we assumed that each LTA unit cell contains two BULKY cations and two F\textsuperscript{−} anions, consistent with the elemental analysis data in Table 4.1.

In this work, one defective unit cell of LTA was considered having up to two point defects. To reasonably cover the complexity of all possible defected systems, we assumed that it is likely that the defect structures are controlled by thermodynamic stability. We performed optimizations to identify energetically preferred defect structures. For systems with one defect per unit cell, the defect location was found to be preferred in the empty D4R regardless of
whether it is a charged or neutral defect. This finding speaks to a structure-directing role played by $F^{-}$, stabilizing defect-free D4R units.

For systems with two defects per unit cell, we considered various structures with one neutral and one charged (Si−O$^{-}$) defect, where the Si−O$^{-}$ defect balances the residual charge from two BULKY$^{+}$, one TMA$^{+}$, and two F$^{-}$. For each defect structure found to be relatively stable, we computed its Raman and $^{29}$Si NMR spectra by periodic DFT. We then assumed that the Raman spectrum for the LTA-BULKY-TMA material with several kinds of defected and defect-free environments can be approximated by a weighted average of the Raman spectra over the various structures, with weights that reproduce experimental spectra.

The calculated Raman spectra and stable defect structures are shown in Figure 4.4a,b, respectively. The fractions in Figure 4.4a indicate the weights that give the best agreement between Raman calculations and experiments, as shown in Figure 4.4c, including both LTA-BULKY and LTA-BULKY-TMA-0.050 systems. In constructing Figure 4.4c, we have utilized the well-established fact that periodic DFT with the PBE functional systematically underestimates vibrational frequencies of zeolites, with computational red shifts in the 20 cm$^{-1}$ range.$^{98}$ As such, the top and bottom x-axes in Figure 4.4c have been shifted by this amount.
Fig. 4.4: (a) Calculated Raman spectra from DFT of individual defective systems and their components for combination. (b) Structures of defected D4Rs. Color coding: blue—Si, red—O, green—F, highlighted—O$^-$. (c) Comparison between calculated (black) and experimental (purple) Raman spectra. The calculated LTA-BULKY-TMA spectrum is from averaging spectra with weights in panel (a). (The calculated frequency axis is blue shifted by 20 cm$^{-1}$, representing the known systematic shift of vibrational frequencies predicted by the PBE functional.).

Figure 4.4c shows very good agreement between Raman calculations (black) and the experiment (purple) for the empty D4R and F-filled D4R band shapes and their intensity ratios, reproducing the experimental $I_F/I_E$ values of 0.79 (LTA-BULKY) and 1.2 (LTA-BULKY-0.050TMA). The agreement in Figure 4.4c shows that the most likely defect structures in the LTA-BULKY-0.050TMA sample are as follows: two point defects, one neutral and one charged,
in an empty D4R (denoted 8F-8F-6E-O⁻: blue spectrum in Figure 4.4a) and one charged defect in an empty D4R (8F-8F-7E-O⁻: green spectrum in Figure 4.4a). The blue spectrum in Figure 4.4a shows unchanged intensity for the F-filled D4Rs (as expected — they are defect free), while the empty D4R band exhibits substantially reduced intensity and is slightly red-shifted. As such, our calculations predict that defects localized in empty D4R units manifest as reduced Raman intensity for the empty D4R band. Taken together, these results indicate that the growth of the experimental Raman $I_F/I_E$ values in Figure 4.2b with increasing TMA concentration does not arise from increasing F⁻ loading in D4R, but rather from decreasing Raman intensity associated with the presence of defects in empty D4R units.

The defected structures and weights in Figure 4.4 guide our computational study of $^{29}$Si NMR solid-state MAS spectra of LTA-BULKY and LTA-BULKY-0.050TMA systems. The $^{29}$Si NMR MAS spectrum in Figure 4.3 for LTA-BULKY-TMA-0.050TMA gives a $Q_3/(Q_3 + Q_4)$ ratio of $21.9 \pm 3.1\%$ (Table 4.2). The defected structures in Figure 4.4b and weights in Figure 4.4a are consistent with a $Q_3/(Q_3 + Q_4)$ ratio of $25.7\%$, which is very close to the upper end of the experimental range of values (25%). The $^{29}$Si NMR spectra associated with the defected structures in Figure 4.4b, calculated by periodic DFT, are shown in Figure 4.5a, and the resulting weighted sum spectrum is shown in Figure 4.5b alongside the experimental spectrum. The calculated and experimental $^{29}$Si NMR spectra for LTA-BULKY-0.05TMA show very good agreement, perhaps surprisingly so, given that the weights for computing this averaged NMR spectrum are based on reproducing the Raman data and not the NMR data. Nonetheless, what emerges is a strikingly consistent picture from Raman spectroscopy, elemental analysis, $^{13}$C and $^{29}$Si solid-state NMR, and DFT, that adding TMA to the LTA-BULKY synthesis mixture goes
beyond the capacity of F⁻ to balance OSDA charge, causing Si–O⁻ defects to form, with Si–O⁻ defect densities increasing with TMA concentration.

Fig. 4.5: (a) Calculated $^{29}$Si NMR spectra of Si atoms in the individual defective systems shown in Figure 4.4b. (b) Comparison between calculated (black) and experimental (purple) $^{29}$Si NMR spectra. The calculated LTA-BULKY-TMA NMR spectrum is from averaging spectra with weights in Figure 4.4a.

While these results are encouraging in their ability to pinpoint defect structures in as-made zeolites, they also raise the important question: Why does adding TMA as a secondary OSDA lead to defect formation in LTA? We address this question with the following thermodynamic analysis.

4.3.4 Thermodynamic DFT Analysis of Defect-Healing Processes in LTA-BULKY-TMA

Our previous study\textsuperscript{198} on the crystallization of the LTA-BULKY system indicates that, while the process culminates in a defect-free, as-made LTA zeolite containing BULKY cations and F⁻ anions, it passes through early stages involving the presence of Q₃ defects that eventually heal over time. This previous study teaches us that defect formation and subsequent healing are likely ubiquitous features of zeolite crystallization. In the context of the present study on LTA-
BULKY-TMA, the lesson from the previous study is to avoid asking “why does adding TMA lead to defects?” and instead to ask “why does adding TMA inhibit defect healing?” We have addressed this latter question with a DFT-based thermodynamic analysis, considering a collection of defect healing reactions in both LTA-BULKY and LTA-BULKY-TMA systems, for comparison. We have pursued a thermodynamic approach because of its simplicity compared to kinetics.

We consider two kinds of defect-healing reactions: neutral defect healing of a Q₃ silanol nest of 4 Si-OH moieties reacting with Si(OH)₄ to give 4 H₂O as byproducts; and charged-defect healing of an Si–O⁻ with HF, placing an F⁻ in a D₄R.⁹⁹ For the LTA-BULKY system, the β-cage is empty, allowing this as swing space for reactants (Si(OH)₄ or HF) and byproducts (4 H₂O). In contrast, for LTA-BULKY-TMA, the β-cage is occupied with TMA, forcing reactants and byproducts to co-locate with BULKY cations in the crowded α-cage. This is a critical distinction that influences the results shown in Figure 4.6.

Figure 4.6 shows that neutral-defect-healing reactions are thermodynamically favored for both LTA-BULKY and LTA-BULKY-TMA systems, with reaction energies ranging from −44.3 to −126.6 kJ/mol. This is qualitatively consistent with our previous study on LTA-BULKY, which found early-stage materials (3 h) with neutral Q₃ defects, which then evolved to defect-free materials at later times (8 d), indicating that neutral defects had spontaneously healed. The charged-defect-healing reaction in LTA-BULKY is also thermodynamically favored (−20.4 kJ/mol), although less so than for neutral-defect healing (−126.6 kJ/mol). This result is also consistent with the fact that we do not see evidence of charged defects in the final LTA-BULKY zeolite (see lack of the Q₃ band in Figure 4.3a, green spectrum).
In contrast, the healing of charged defects in LTA-BULKY-TMA was found to be slightly endothermic (1.9 kJ/mol), indicating the lack of a strong driving force for this process and the possibility of an equilibrium between Si–O−/HF and Si–OH/F− species. Such an equilibrium would limit the ability of the next step in Figure 4.6, neutral-defect healing, from reaching completion, thus explaining why LTA-BULKY-TMA shows evidence for both charged and neutral defects in the final, as-made materials.

Fig. 4.6: Energy changes of key reactions in defect healing for (a) LTA-BULKY and (b) LTA-BULKY-TMA. In both systems, neutral and charged defects are healed with Si(OH)₄ and HF, respectively. All reactions are favorable except for healing charged defect in LTA-BULKY-TMA. Negatively charged oxygen is highlighted using a yellow cross.

This analysis predicts that adding TMA to LTA-BULKY imposes thermodynamic limitations on charged-defect healing due to substantial crowding in the LTA framework. If the prediction of a thermodynamic limitation (and not a kinetic one) were correct, then running synthesis experiments at higher temperatures would result in substantially the same defect-containing LTA-BULKY-TMA material. If, in contrast, unhealed defects result from kinetic
limitations, then running hotter syntheses could substantially heal defects (depending on the barriers involved).

We have tested these ideas by performing LTA-BULKY-TMA syntheses at various temperatures (125, 150, 170 °C) for 8 days each and then characterized the resulting zeolite samples with $^{29}$Si MAS NMR. The resulting NMR spectra are shown in Figure 4.7 and the $Q_3/(Q_3 + Q_4)$ ratios are given in Table 4.3. The $Q_3/(Q_3 + Q_4)$ ratios in Table 4.3 show weak and nonmonotonic variation, indicating the lack of a consistent trend with increasing synthesis temperature. Within an experimental error, the results in Table 4.3 are essentially constant, thus consistent with the notion of a thermodynamic limitation on defect healing in LTA-BULKY-TMA.

Fig. 4.7: (a) $^{29}$Si MAS NMR spectra of LTA-BULKY-TMA-0.050TMA synthesized at 125, 150, and 170 °C to test for thermodynamic control of defect healing. (b) Peak deconvolution of the $^{29}$Si MAS NMR spectra.
Table 4.3: \( Q_{3}/(Q_{3} + Q_{4}) \) ratios measured from \(^{29}\text{Si} \) MAS NMR of LTA-BULKY-TMA-0.050TMA synthesized at various temperatures

<table>
<thead>
<tr>
<th>LTA-BULKY-0.050TMA, 170 °C</th>
<th>23.0 ± 2.2%</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTA-BULKY-0.050TMA, 150 °C</td>
<td>21.9 ± 3.1%</td>
</tr>
<tr>
<td>LTA-BULKY-0.050TMA, 125 °C</td>
<td>29.3 ± 1.6%</td>
</tr>
</tbody>
</table>

4.4 Summary

We have performed an integrated zeolite synthesis, Raman and NMR spectroscopy, and density functional theory study to test the limit of \( \text{F}^- \) as a charge-balancing agent in making defect-free zeolites. We have investigated the fluoride-mediated synthesis of siliceous zeolite A (Si-LTA) with the cationic molecule denoted “BULKY” as the primary OSDA. We have also used tetramethyl ammonium (TMA) as a secondary OSDA, varying the amount of TMA in the synthesis mixture. By varying the TMA concentration, we endeavor to “titrate” positive charge into the resulting as-made Si-LTA. We wonder whether the additional positive charge of TMA, over and above that coming from BULKY, can be balanced by \( \text{F}^- \) in the final as-made Si-LTA zeolite. Although a naive interpretation of Raman spectra of the resulting materials might suggest that greater TMA concentration pulls more \( \text{F}^- \) into the zeolite, the elemental analysis tells another story, one of approximately constant \( \text{F}^- \) content. As a result, we suggest that this system has reached the capacity of \( \text{F}^- \) to balance OSDA charge (that coming from BULKY), and additional positive charge (from TMA) is balanced by Si–O\(^-\) framework defects along with other neutral \( Q_{3} \) Si defects. This picture is supported by \(^{29}\text{Si} \) solid-state MAS NMR and density functional theory interpretations of NMR and Raman spectra.

Interestingly, while the LTA-BULKY-TMA system forms with various defects, the same synthesis system without TMA forms without measurable defects. We performed a
thermodynamic analysis to explain why, considering various reactions that could lead to defect healing in both systems. We found that thermodynamics is indeed capable of explaining the observed trends through enhanced crowding of the LTA-BULKY-TMA system. This prediction of thermodynamic control of defect persistence was tested and corroborated by additional synthesis experiments at various temperatures.

Although not a focus of this project, in another work, we have found that adding TMA to the LTA-BULKY synthesis system speeds up LTA crystallization by as much as a factor of 3.\textsuperscript{207} We find it fascinating that adding a secondary OSDA can speed up the synthesis while forcing the persistence of defects. We wonder whether there is a correlation between crystallization speed and defect persistence in zeolite formation, which we will study in our forthcoming work.
CHAPTER 5

NOVEL SYNTHESIS OF HIGH-SILICA LTA ZEOLITE IN HF-FREE WAY

5.1 Background

5.1.1 History in Synthesizing LTA Zeolite with Si/Al Ratio from 1 to Infinity

LTA is a typical small-pore zeolite, which has been employed as a universal desiccant for gases as well as non-polar and polar liquids. Furthermore, it is also utilized as a widespread ion-exchanger and adsorbent in both industry and academia. Currently, there are 3 common commercially available LTA products, named “3A”, “4A” and “5A”: since the Al atoms in LTA framework can be charge balanced by either K\(^+\), Na\(^+\) or Ca\(^{2+}\), the resultant pore openings are 3, 4 or 5 Å accordingly.

As shown in Fig. 5.1, the structure of zeolite LTA comprises one large cavity (α-cage), three smaller cavities (β-cages), and three connecting D4R units in each LTA unit cell. From another perspective, the stereochemical structure of LTA could be also visualized as lots of independent double 4-membered rings (D4Rs) connected together in a particular way, forming 4-MRs, 6-MRs, and 8-MRs.

![Fig. 5.1: Structure of LTA with its three composite building blocks.](image-url)
In the past decades, researchers have tried lots of efforts to synthesize LTA with a Si/Al ratio ranging from 1 to infinity, as displayed in Table 5.1 from Davis et al.\textsuperscript{134} During this course, the very first pioneering synthesis\textsuperscript{134} led to LTA type zeolite (named “Linde type A”) with Si/Al ratio at 1 (Table 5.1, Entry 1). Then, Kerr\textsuperscript{208} and other scholars obtained an Si/Al ratio near 1.5 using tetramethylammonium hydroxide (TMAOH) and Na\textsuperscript{+} as the OSDA and charge-compensating ions (Table 5.1, Entry 2 and 3). By changing the ratios of TMAOH and Na\textsuperscript{+} in the precursor solution, researchers from Mobil company reported an Si/Al ratio increased to 3 (Table 5.1, Entry 4 and 5). However, the LTA with Si/Al ratio of 3 cannot provide a satisfying long-term catalytic activity for catalytic applications because of its low hydrothermal stability. In order to address this issue, Si/Al ratio of LTA needed to be further enhanced.
Table 5.1: Overview of notable LTA zeolite synthesis conditions and results

<table>
<thead>
<tr>
<th>E</th>
<th>material name / approach</th>
<th>OSDA</th>
<th>synthesis mixtures composition relative to Si</th>
<th>T, t °C, h</th>
<th>Si/Al prod.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Al</td>
<td>OSDA</td>
<td>Na⁺⁺</td>
</tr>
<tr>
<td>1</td>
<td>Linde type A</td>
<td>-</td>
<td>1.03</td>
<td>-</td>
<td>3.29</td>
</tr>
<tr>
<td>2</td>
<td>ZK-4</td>
<td>N⁺</td>
<td>0.49</td>
<td>2.03</td>
<td>0.72</td>
</tr>
<tr>
<td>3</td>
<td>ZK-4</td>
<td>TMA</td>
<td>0.51</td>
<td>2.11</td>
<td>0.79</td>
</tr>
<tr>
<td>4</td>
<td>zeolite alpha</td>
<td>TMA</td>
<td>0.09</td>
<td>0.89</td>
<td>0.09</td>
</tr>
<tr>
<td>5</td>
<td>zeolite alpha</td>
<td>TMA</td>
<td>0.20</td>
<td>0.48</td>
<td>0.21</td>
</tr>
<tr>
<td>6</td>
<td>UZM-9</td>
<td>TEA + DEDMA + TMA</td>
<td>0.12</td>
<td>0.4 + 0.1 + 0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>7</td>
<td>ITQ-29c</td>
<td>TMA + π-π-complex</td>
<td>0.02</td>
<td>0.25 + 0.25</td>
<td>0.5</td>
</tr>
<tr>
<td>8</td>
<td>as entry 7, different seed</td>
<td>TMA + π-π-complex</td>
<td>0.02</td>
<td>0.25 + 0.25</td>
<td>0.5</td>
</tr>
<tr>
<td>9</td>
<td>as entry 7, FAU + seeds</td>
<td>TMA + π-π-complex</td>
<td>0.02</td>
<td>0.25 + 0.25</td>
<td>0.5</td>
</tr>
<tr>
<td>10</td>
<td>pure Si-LTA seeds</td>
<td>DM3(4MB) + TMA + α</td>
<td>0.05</td>
<td>0.05 + 0.45</td>
<td>0.5</td>
</tr>
<tr>
<td>11</td>
<td>no seeds</td>
<td>TMA + DM3(4MB)</td>
<td>0.01</td>
<td>0.05 + 0.45</td>
<td>0.5</td>
</tr>
<tr>
<td>12</td>
<td>seeds</td>
<td>TMA + DM3(4MB)</td>
<td>0.02</td>
<td>0.02 + 0.50</td>
<td>0.49</td>
</tr>
<tr>
<td>13</td>
<td>no seeds</td>
<td>TMA + DM3(4MB)</td>
<td>0.13</td>
<td>0.10+ 0.50</td>
<td>0.49</td>
</tr>
<tr>
<td>14</td>
<td>no seeds</td>
<td>TMA + DM3(4MB)</td>
<td>0.01</td>
<td>0.01+0.50</td>
<td>0.49</td>
</tr>
<tr>
<td>15</td>
<td>HOU-2</td>
<td>-</td>
<td>0.43</td>
<td>-</td>
<td>0.56</td>
</tr>
<tr>
<td>16</td>
<td>metal/LTA</td>
<td>-</td>
<td>1.18</td>
<td>0.12</td>
<td>3.76</td>
</tr>
</tbody>
</table>

Na/Si, unless other element is explicitly mentioned; then element/Si ratio is tabulated, e.g., F/Si. By assuming use of pure NaAl₂O₃ where stated sodium aluminate. Seeded with 10 wt % pure-silica LTA. Two such OSDAs can form a π-π-complex. 1, 5, or 10 wt % of LTA (Si/Al = 2) seeds added, giving Si/Al of 110, 267, or 440. 10 wt % of FAU (Si/Al = 2.5) added, and 5 wt % of ITQ-29 seeds. 0.011 Pt/Si was also added. The organic is said to lose its methyl groups by hydrolysis, associate with 3 Na⁺ cations, and complex with the metal giving Pt(Na₃-OSDA-SH)₄.
In 2004, based on the principle of charge density mismatch (CDM), Lewis et al. from UOP LLC invented an interesting and creative methodology for zeolite synthesis, by which LTA with Si/Al ratio as high as 5.5 had been achieved under a basic medium (Table 5.1, Entry 6).\textsuperscript{209} Basically, in the first step of this brand-new approach, precrystallization gel is prepared in water by mixing silica source, aluminum source and OSDA (always with a relatively larger size). At this time, the crystallization will not start even under a high temperature after a long time, owing to the charge density mismatch between the negative charges (high charge density) from Al to be incorporated into zeolite framework and the positive charges (low charge density) from OSDAs. In order to overcome this barrier,\textsuperscript{210} small cations, such as TMA\textsuperscript{+} and Na\textsuperscript{+}, are added. Upon all the involved charges being balanced, the crystallization starts immediately. Specifically, for the CDM-based LTA synthesis,\textsuperscript{90} tetraethylammonium (TEA\textsuperscript{+}) or diethyldimethylammonium (DEDMA\textsuperscript{+}) is taken as the OSDA, while TMA\textsuperscript{+} and Na\textsuperscript{+} as the small cations to fulfill the charge balance requirement. In addition to LTA, through this CDM method, other existing zeolites with new compositions like ERI, or even some new zeolite topologies such as UFI were crystallized for the first time. Furthermore, the crystallization model and the CDM-based LTA formation mechanism were studied by Hong recently.\textsuperscript{210}

Application of F\textsuperscript{-} in the zeolite synthesis has been widely used to control the frameworks, compositions and defects. It has been known that F\textsuperscript{-} plays three different roles in zeolite synthesis, including as a mineralizing agent, stabilization of certain small building units, and balance of positive charges from OSDAs in zeolite structures. In 2004, Corma and his coworkers, via utilizing a large supramolecular dimer complex (self-assembled by π–π stacking interaction between two identical large aromatic cations) as the OSDA, successfully synthesized pure-silica and Ge-containing LTA under fluoride media for the first time (also called “ITQ-29”); Table 5.1,
After crystallization, the dimers were found to be appearing in α-cage of LTA. Moreover, they also found that by further adding extra TMA+ into this system, a small number of Al (Si/Al = 47) could be introduced into the LTA framework, and meanwhile TMA+ would be occluded into sod-cages. Soon afterwards, Valtchev et al. investigated and further optimized Corma’s synthetic method through adding nano-sized TMA-containing LTA (Si/Al = 2) as seeds, finally extending the Si/Al ratio range of the aluminosilicate version of LTA (Si/Al ratio ranging from 110-440; Table 5.1, Entry 8). An interesting phenomenon during this process was that, in the presence of F− and under this neutral condition, the used seeds here would be dissolved and decomposed into low-molecular-weight species, then participating in the “polymerization” process to form LTA framework in conjunction with other Si and Al raw materials. Recently Lobo and his coworkers replaced the conventional Al source (e.g., aluminum isopropoxide or aluminum hydroxide) with Al-containing FAU and discovered that it is possible to further expand the scope of the Si/Al ratio for LTA (63-420; Table 5.1, Entry 9). As with the LTA seeds used in Valtchev’s method, the FAU added in the synthesis approach will also decompose prior to the LTA crystallization. Beside, in terms of OSDA, other researchers found that other organics could also substitute the large aromatic cation, one of which is a large crown-ether named “Kryptofix K222” (C18H36O6N2).

The next milestone event in this fascinating history of covering the full range of Si/Al ratio for LTA is from Davis et al. (Table 5.1, Entry 10 and 11) by using 1,2-dimethyl-3-(4-methylbenzyl)imidazolium hydroxide to generate the dimer, pure-silica LTA can be obtained in the fluoride-mediated way with pH around 7. Both thermogravimetric analysis and molecular simulation showed that this new dimer, just like its “predecessors”, would emerge in the lta-cages of LTA and also stabilize them after crystallization. Furthermore, based on this new dimer
and with the help of TMA$^+$, they also successfully synthesized LTA with Si/Al ratio from 12 to 42 for the first time. Hong$^{187}$ and his coworkers demonstrated that in this new method, by fine tuning the compositional ratio of the precursor gel, the Si/Al ratio can be further extended to a wider range, from 8.3 to 56 (Table 5.1, Entry 12 and 13). Hence, till then (2016), the gap in the previous synthesizable Si/Al ratio range for LTA had almost been closed.

What should be emphasized here is that while pure-silica LTA can be synthesized in the presence of F$^-$ with either seeds or TMA$^+$, aluminosilicate LTA ($8.3 < \text{Si/Al} < 42$) can only be crystallized when both seeds and TMA$^+$ are present. Some researchers proposed that the reason for this difference is in the Al-containing sod cage of the aluminosilicate LTA: for this kind of LTA, not only the lta-cages need to be stabilized by the dimers, but also sod-cages by TMA$^+$ inside them.$^{134}$

5.1.2 Synthesis of High-Silica LTA in a Fluoride-Free Way

Zeolites, as solid Bronsted acid catalysts, their acid sites are derived from the protons associated with the bridging oxygen between the framework Al and Si in zeolite structures. Si/Al ratio in zeolite frameworks is a critical parameter for their catalytic property. As introduced, low Si/Al ratio provides higher acid site density, but often leads to low hydrothermal stability and hydrophobicity, which limits their catalytic performance. High Si/Al can improve their hydrothermal stability and hydrophobicity, therefore, is preferred for reactions involving hydrophobic molecules. Synthesis of zeolites with a wide range of Si/Al, thus, has been a key research topic for zeolite catalysts.

Particularly, in 2017, Hong et al. applied LTA zeolite with Si/Al ratio ranging from 16-23 (with divalent copper cations balancing Al sites) in DeNO$_x$ reaction, finding that this kind of material not only exhibited an excellent catalytic performance, but also maintained its
outstanding thermal durability even after being hydrothermally aged under 900 °C for a long time (simulating the practical working environment in vehicle exhaust pipe). The poor thermal stability actually has remained as one major technical hurdle for the current commercial SSZ-13 zeolite for this application, owing to its thermal structural decomposition under the same conditions. Deeper structure-related characterizations from Hong suggested that those Cu\(^{2+}\) cations, mainly located at the center of 6-MRs in LTA, not only acted as the catalytically active sites, but also was the main reason for the inhibition of dealumination, which would lead to the CuO\(_x\) species formation, catalysis deactivation or even structural collapse.

However, it is difficult to apply the high-silica LTA to the DeNOx application, mainly due to the use of hypertoxic F\(^-\) in the synthesis process, which poses severe environment and health concerns as what has been introduced above. Moreover, as shown in Table 5.1, to date LTA crystallized in fluoride-free way has the Si/Al ratio only as high as 5.5, which might be ascribed to the strain in pure- or high-silica D4R units: Formation of Si–O–Al in the D4R unit is required to relax the strain and favors the formation of LTA structures if F is not used in the synthesis.

In order to solve this problem in increasing the Si/Al ratio in LTA zeolite synthesized in HF-free way, we introduced isolated siliceous D4Rs as a part of the silica source into the crystallization. The details are displayed as follows.

Inspired by the observation in Chapter 3 and 4 above, we investigated the LTA synthesis using BULKY and TMA as the OSDAs in a hydroxide media. It was noted that in the presence of F\(^-\), two BULKY molecules are located in the α-cage and one TMA molecule is located in the β cage of the formed pure-silica LTA, leading to three positive charges per unit cell. Therefore, instead of F\(^-\), incorporating of three Al atoms per unit cell into the framework, meaning one Al
per D4R unit, will be able to balance the charges from OSDAs (Fig. 5.2). In addition, isolated pure-silica D4Rs (Si-D4Rs), as shown in Fig. 5.2, can be synthesized using TMA$^+$ in a basic aqueous solution without using F$^-$ as the structure-directing agent.\textsuperscript{158} We argue that it might be possible to use the preformed isolated Si-D4Rs as a silica source for the synthesis of high-silica LTA in the absence of F$^-$, during which, similar to F$^-$, they are able to assist the formation of aluminosilicate D4Rs in LTA. We demonstrated that by tailoring the synthetic parameters of the proposed crystallization involving isolated siliceous D4Rs, LTA with a Si/Al of 7.55 is successfully made in the absence of F$^-$, which increased the Si/Al ratio by 37.2\% for LTA obtained in a HF-free way.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.2.png}
\caption{The hypothetical crystallization for the high-silica LTA (Si/Al = 7) synthesized in fluoride-free way using two silica sources (Si from isolated Si-D4Rs : Si from conventional TEOS = 1 : 1).}
\end{figure}

5.2 Methods

5.2.1 High-Silica LTA (Si/Al= 7.55) Synthesis in HF-Free Way

For this synthesis, first 450 $\mu$L of TEOS was mixed with an appropriate amount of Al isopropoxide (dissolved in ethanol) and 7.51 g of BULKY-OH (aqueous solution, 0.2414 mmol/g). After hydrolyzing TEOS at room temperature overnight, a particular amount of isolated Si-D4Rs (dissolved in water beforehand; synthesized by using the previously-reported method\textsuperscript{158}) and 1 wt.% LTA seeds were added into the solution. The final ratio of composition of the precursor solution was 0.5 TEOS : 1/16 isolated Si-D4R·8TMA·64H$_2$O : 1/24 Al$_2$O$_3$ : 0.45
BULKY-OH OSDA : 205 H₂O, plus seeds (1 wt.% with regard to the total amount of Si source). After transferring the precursor solution into a Teflon-lined stainless-steel autoclave, the crystallization was carried out under a series of temperatures for different crystallization times. Herein, three temperatures (120 °C, 135 °C, and 150 °C) and three synthesis times (3 weeks, 4 weeks, and 5 weeks) were chosen to optimize the crystallization conditions. The whole crystallization processes were depicted in Fig. 5.3.

**Fig. 5.3: Scheme for the crystallization of high-silica LTA (Si/Al = 7.55) in HF-free way.**

### 5.2.2 Characterizations

The crystalline structure of the LTA samples with a high Si/Al ratio synthesized in HF-free way was confirmed by XRD on a Rigaku SmartLab diffractometer equipped with a Cu Kα X-ray radiation produced at 40 mA and 45 kV. In-situ XRD was also used to confirm its thermal stability, in which 800, 900, and 1000 °C were employed: after being treated under those temperatures for 3 h, the XRD was run for the samples. Apart from the LTA sample with a high Si/Al ratio made without fluoride, commercial LTA (Si/Al = 1), LTA seeds (Si/Al = 2.2), LTA-BULKY (Si/Al = 66) were used for a comparison.
For Raman measurements, several milligrams of the zeolite sample were dispersed on a silicon wafer coated by gold. The Raman spectra were recorded utilizing a XploRa Raman microscope (Horiba Scientific), which was operated using a 785 nm laser line as the excitation light source and its power was controlled at 10 mW. A 1200-line grating was set, and the laser light was focused on the sample through a 100× magnification lens (Olympus, Japan). A 20 s scan time and an accumulation of 20 scans were chosen for all of the measurements.

$^{29}$Si MAS NMR measurements were performed on a Bruker 600 MHz solid-state NMR spectrometer employing a 4 mm MAS probe. For $^1$H and $^{29}$Si nuclei, the spectral operating frequencies were 600.1 and 119.2 MHz, respectively. All samples were spun at 5 kHz during the measurements. A recycle delay time of 200 s was found to be adequate for Si-related signals of every sample. The number of scans was set at 200 for all of the measurements. $^{27}$Al MAS NMR spectra was acquired on the Bruker 600 MHz solid-state NMR spectrometer employing a 4 mm MAS probe (156.3 MHz for $^{27}$Al) operated under a spinning rate of 5 kHz. A recycle delay time of 2 s was found to be adequate for the fully relaxation of Al in the zeolite framework. $^{13}$C MAS NMR (DP) measurements were performed on the same Bruker 600 MHz solid-state NMR spectrometer using a 4 mm MAS probe. For $^1$H and $^{13}$C nuclei, the spectral operating frequencies were 600.1 and 150.9 MHz, respectively. All of the samples were spun at 5 kHz during the measurements. A recycle delay time of 50 s was found to be adequate for the only carbon in TMA$^+$ and also the three carbon atoms of the three methyl groups in BULKY. The number of scans was set at 256 for all of the measurements.

SEM was utilized to determine the morphology of all the samples. SEM images were collected with a Hitachi S-4800 field emission scanning electron microscope. Prior to this characterization, all the samples with different crystallinity were sputter-coated with Au.
The elemental analysis for Si and Al of all the LTA samples were completed at Galbraith Laboratories (TN) using pyrohydrolysis. The samples were dried under 120 °C overnight before measurements to avoid the influence from adsorbed water.

TGA was conducted on a thermogravimetric analyzer (SDT600, TA). For each measurement, about 10 mg of the sample was used. The temperature was programmed from RT to 800 °C (with a ramping rate of 1 °C/min) and finally held for 2 h with an air flow of 10 mL/min.

5.3 Results and Discussion

As shown in Fig. 5.4, after about 4 weeks of crystallization, the fully crystalline LTA was obtained at the crystallization temperature of 120 °C. At 135 °C, the crystallization kinetic was improved and fully crystalline LTA zeolite was obtained within 3 weeks. However, at an even higher temperature of 150 °C, the obtained samples showed low crystallinity. One possible reason for the low crystallinity obtained at 150 °C was that the BULKY OSDA was decomposed under the relatively high temperature. Another possibility might be that under this high temperature, the used isolated siliceous D4Rs can’t play the role for promoting the formation of Al containing D4R.
Fig. 5.4: XRD results of the high-silica LTA synthesized in fluoride-free way. The final ratio of composition of the precursor solution is 0.5 TEOS : 1/16 isolated Si-D4R·8TMA·64H₂O : 1/24 Al₂O₃ : 0.45 BULKY-OH OSDA : 205 H₂O, plus 1 wt.% seeds. The chosen temperatures and times for the synthesis are 120 °C (a), 135 °C (b), and 150 °C (c), 3 w, 4 w, and 5 w, respectively.

We also researched the effect of water content on the crystallization. As shown in Fig. 5.5, with the water ratio gradually decreasing in the precursor, the product would first become a mixture of SOD and LTA zeolites, and when the water/Si ratio is as low as 8, the product is pure SOD. The tendency suggests the importance of the amount of water on the crystallization of this high-silica LTA synthesized without F⁻. Since the SOD structure is a denser structure compared to LTA, the observation may suggest that the less amount of water might be favor for the formation of dense zeolite phase.
Fig. 5.5: XRD results for the crystallization of the high-silica LTA with different water content in the precursor. The final ratio of composition of the precursor solutions is 0.5 TEOS : 1/16 isolated Si-D4R·8TMA·64H2O : 1/24 Al2O3 : 0.45 BULKY-OH OSDA : X H2O, plus 1 wt.% seeds. The temperatures and times for all the syntheses are 135 °C and 3 weeks, respectively.

We compared the XRD result of this high-silica LTA synthesized in the absence of fluoride under 135 °C for 3 weeks with other LTA samples with different Si/Al ratios. As shown in Fig. 5.6, it is clear that, with Al content in zeolite framework decreasing, the LTA diffraction peaks shift to higher angle range. This is due to the longer length of Al-O bond compared to Si-O one. Therefore, for this high-silica LTA synthesized using no HF, its Si/Al ratio should be between 3.3 and 10. Elemental analysis revealed that the Si/Al ratio in this LTA is 7.55, which is consistent with the XRD analysis. As listed in Table 5.1, compared to the previous highest Si/Al ratio (5.5) for LTA made in fluoride-free way, our result leads to a progress by 37.2%.
Fig. 5.6: XRD comparison between the high-silica LTA (using siliceous isolated D4Rs; synthesized under 135 °C for 3 weeks in HF-free way) and other LTA materials with different Si/Al ratios.

$^{29}$Si NMR was used to better understand the structure of this high-silica LTA. As shown in Fig. 5.7a, according to previously-published paper, Peak 1, 2, 3, and 4 are assigned different Si atoms of $Q_4(n\text{Al})$ in the framework, in which $n = 0, 1, 2,$ and 3, respectively. Compared with the $^{29}$Si NMR result for LTA with an Si/Al ratio of 3.3, the percentages of integration areas for Peak 1 and 2 are larger (together accounting for 79.5%), consistent with that this high-silica LTA possessing a higher Si/Al ratio of 7.55.

Furthermore, in Figure 5.7b, there exists only one peak (located at 55 ppm) on the $^{27}$Al NMR spectrum of the high-silica LTA, suggesting tetrahedral Al in the zeolite framework. The weight loss in the TGA measurement (Figure 5.7d) is similar to the situation of LTA-BULKY.
(24.8% v.s. 23.9%) in Chapter 3, implying that 2 BULKY cations reside in the α-cage of LTA. In
Figure 5.7c, the integration area of Peak e, assigned to the carbon in TMA, is twice of Peak a, b,
and c (assigned to the 3 methyl groups in the BULKY OSDA). This indicates that there is also
one TMA (from isolated Si-D4Rs·8TMA·64H₂O; occupying the β-cages of the LTA product) in
each unit cell of this LTA. Combining together with the positive charges from the dimer of the
BULKY, there are 3 positive charges in each unit cell of this LTA sample.

Based on all the information from NMR and TGA, it was found that the charge balance
in this high-silica LTA (Si/Al = 7.55) is achieved by the negative charge from the framework Al
and positive charges from OSDAs: in each unit cell, the 3 positive charges from BULKY and
TMA are balanced by the 3 negative charges from the 3 tetrahedral Al atoms in the framework,
which caused the Si/Al ratio around 7 (corresponding to 21 Si atoms and 3 Al atoms in each unit
cell). This result (Si/Al of 7.55, a little larger than 7) may indicate that a few defects of Si-O−
were formed and participate in the charge balance.
Fig. 5.7: $^{29}$Si NMR (a), $^{27}$Al NMR (b), $^{13}$C NMR (c), and TGA (d) results for the high-silica LTA with an Si/Al ratio of 7.55 synthesized using isolated siliceous D4Rs in HF-free way, under 135 °C for 3 weeks. In (a), Peak 1, 2, 3, and 4 are assigned to different Si atoms of Q₄(nAl) in the framework, in which n = 0, 1, 2, and 3, respectively; In (b), the 2 small peaks marked by a star are the sidebands of the main peak; In (c), Peak e is assigned to the only C in TMA, while Peak a, b, and c are assigned to the 3 methyl groups in the BULKY molecule. Peak d is assigned to the methylene group in BULKY, but with inadequate relaxation in the NMR measurement; In (d), the sample loss before 200 °C is due to the water removal, while the sample loss of 24.8% after 375 °C is attributed to the oxidation of BULKY and TMA.

SEM was used to study the crystallization process of this LTA synthesis. In order to better observe the process, the crystallization was slowed down on purpose by lowering the synthesis temperature to 120 °C. As shown in Fig. 5.8, when at 2 weeks, the crystallinity is still low (Fig. 5.8d, the blue curve), and the intermediate product comprises thin layers of about 0.8 μm (Fig. 5.8a), still with irregular small particles on and between them, which are from amorphous silica; after 3 weeks, the crystallization is close to finish (Fig. 5.8d, the red curve),
and at this time the product is cube-shaped crystals with a size of 1 μm (Fig. 5.8b), which are still with a few irregular particles of amorphous silica; finally, after 4 weeks, the crystallization is complete (Fig. 5.8b), and all the remaining amorphous silica were converted to form the cube-shaped LTA crystals with a size of 1 μm (Fig. 5.8c).

Fig. 5.8: SEM pictures for the high-silica LTA with an Si/Al ratio of 7.55 synthesized using isolated siliceous D4Rs in HF-free way, under 120 °C after 2 (a), 3 (b), and 4 weeks (c); the corresponding XRD results are shown in (d).

Raman spectrum (blue) for the novel as-made LTA is shown in Fig. 5.9 and compared to LTA-BULKY (green). Interestingly, only one band associated with empty Al-containing D4Rs was observed within the D4R-related wavenumber range for the LTA with an Si/Al ratio of 7.55. Empty pure-silica D4R band was not observed in the same spectrum. Moreover, owing to the T-
O-T bond angle change from the presence of Al, there is a 15 cm\(^{-1}\) red-shift from the band assigned to empty siliceous D4Rs in LTA-BULKY. The sole presence of Al-containing D4Rs in the Raman spectrum of this high-silica LTA suggests that the as-made LTA sample synthesized with this method does not contain siliceous D4Rs. Then, it can be deduced that, although isolated Si-D4Rs are used as a silica source in the synthesis gel, they must be completely or partially decomposed during the zeolite formation process, and it might be the products from this decomposition that helped the formation of Al-containing D4Rs in the final LTA sample. Further study on the change of the isolated Si-D4Rs during the crystallization is also worth trying.

Fig. 5.9: Raman spectrum of the high-silica LTA synthesized in fluoride-free way (using both TEOS and isolated Si-D4Rs as the silica source) compared with LTA-BULKY before and also after calcination.
In-situ XRD was used to test the thermal stability of this LTA sample, by comparing to the commercial LTA (Si/Al = 1), LTA seeds (Si/Al = 2.2), and LTA-BULKY (Si/Al = 66). As shown in Figure 10, for the commercial LTA and LTA seeds, at 800 °C their frameworks start to shrink, causing the XRD peaks shift to higher angle range. At 900 °C, it was observed that the intensity of their XRD peaks decreased, indicating the lowered crystallinity led by the framework collapse. Finally, when the temperature reached to 1000 °C, the frameworks completely collapsed. In contrast, for LTA-BULKY with a much higher Si/Al ratio, as expected, it can keep its crystalline structure at all tested temperatures. Surprisingly, for the LTA sample synthesized using siliceous isolated D4Rs in HF-free way, although its Si/Al ratio is only 7.55, similar to LTA-BULKY, it can maintain its crystalline structure even when the temperature is 1000 °C, which confirms that it has an excellent hydrothermal stability. The in-situ XRD measurements show that the LTA sample with Si/Al of 7.55 has an improved thermal stability compared to lower Si/Al LTA samples.
5.4 Summary

The synthesis of high-silica (Si/Al $>5.5$) LTA zeolite in HF-free way is still a challenge in the field, which severely limits its industrial application. Herein, by introducing siliceous isolated D4Rs into the crystallization, and using Al to fine tune the charge balance, LTA with an Si/Al ratio of 7.55 was synthesized successfully for the first time. XRD results showed that apart from Al content and siliceous isolated D4Rs, water composition controlled in the precursor and temperature used in the crystallization are also important to obtain the LTA product with high purity and crystallinity. In addition, the information provided by NMR and TGA measurements clearly revealed the picture of charge balance in the sample: the 3 positive charges from two BULKY molecules and one TMA are balanced by 3 negative charges from 3 tetrahedral Al atoms in each unit cell of LTA zeolite. Raman spectrum of this novel LTA product indicated that the isolated siliceous D4Rs should experience some decomposition during the crystallization process, in which the species generated in the decomposition might help the formation of D4Rs in the final LTA zeolite. In-situ XRD also proves the thermal stability of this LTA sample, which suggests its potential for catalytic applications at a high temperature. This method of introducing isolated siliceous D4Rs into zeolite synthesis opens new ways to crystallize other 37 zeolite featuring D4Rs in high-silica form without using HF.
CHAPTER 6

CONCLUSIONS

6.1 Concluding Remarks

The first part of this thesis solved out the problem about assigning vibrational Raman bands to particular units in zeolites with solid physical evidence by utilizing an integrated synthesis, spectroscopy, and periodic DFT modeling study. Instead of assigning features present in the Raman spectra of zeolites to individual rings, we found that a new notion of making assignments based on tricyclic bridges is more robust. Tricyclic bridges are a kind of particular building unit in every zeolite, which are comprised of three zeolite rings sharing one common Si–O–Si (or more generally T-X-T’) bridges. By organizing Raman bands according to the smallest ring of their assigned tricyclic bridges, a strong anti-correlation (for 4MR systems) between Raman vibrational frequency and Si–O–Si angle was revealed. This discovery is of particular importance for investigating the formation mechanisms of zeolite crystals at atomic level, using the new concept of tricyclic bridges.

Therefore, after mastering the tool of Raman spectroscopy in the correct way, in the next part of the thesis we talked about the crystallization mechanisms of Si-LTA synthesized with F⁻, which were researched by Raman complemented with other characterization techniques. First by integrating experimental Raman with the simulation, two distinct bands from the LTA framework were observed and assigned to empty D4R and F⁻/D4R. The different locations of those two bands are interpreted by the geometrical distortion of the D4R and charge transfer to the D4R upon inclusion of F⁻. Then, using Raman to monitor the crystallization of siliceous LTA in the presence of F⁻; it was observed that initially both empty D4R and F⁻/D4R bands emerged; afterwards, as crystallization progressed to the end, the ratio of integration area of these two...
bands gradually changed. Periodic DFT has attributed this variation to the presence of point defects in empty D4Rs in growing LTA crystals. Upon further crystallization, these defects appear to become healed, leading to the formation of defect-free LTA zeolite crystals. These results combined together ensured the hypothetical roles of F\textsuperscript{−} in both charge-balancing and D4R-structure-directing during siliceous LTA crystallization. Finally, based on these insights, the amount of F\textsuperscript{−} in pure-silica LTA synthesis was reduced by 83%, which can benefit the industrial scale synthesis of not only LTA, but also other high-silica D4R-containing zeolites.

Next, we found that for those defects formed and then gradually healed during siliceous LTA crystallization, when TMA as the secondary OSDA is introduced, the results will be totally different, and we aim to elaborate those in Chapter 4 of the thesis. Specifically, by integrating zeolite synthesis, Raman and NMR spectroscopy, and density functional theory again, the limit of F\textsuperscript{−} as a charge-balancing agent in making defect-free zeolites was tested. It was discovered that with the TMA concentration varying, positive charges can be titrated into the resulting as-made Si-LTA. Using elemental analysis, Raman spectroscopy, \textsuperscript{29}Si solid-state MAS NMR, and density functional theory interpretations of NMR and Raman spectra, we found that those additional newly-introduced positive charges from TMA are balanced by defects of Si-O\textsuperscript{−}, rather than F\textsuperscript{−}, which has reached its maximum capacity in terms of charge balancing. As a result, the number of defects in siliceous LTA can be precisely controlled by varying the quantity of TMA in the precursor. This discovery is beneficial for this zeolite to be used in industrial applications based on its defects, and also inspiring in accurately controlling the number of defects in other zeolites. Finally, thermodynamic analysis was performed, and the defects-related trend was ascribed to the enhanced crowding of the LTA-BULKY-TMA system.
Based on all our discoveries and understandings regarding F⁻ roles in the LTA synthesis, in Chapter 5 of the thesis, we tried to increase the Si/Al ratio of LTA synthesized in HF-free way. In order to fulfill that, siliceous isolated D4Rs and an appropriate amount of Al were introduced into the LTA crystallization, which were employed to perform the jobs in assisting D4R formation and balancing the positively charged OSDAs once achieved by F⁻, respectively. Consequently, LTA with an Si/Al ratio of 7.55 was obtained (a 37.5% progress). ²⁹Si NMR, ¹³C NMR, ²⁷Al NMR, and TGA clearly reveal the charge balancing details between OSDAs and tetrahedral Al in LTA framework. In-situ XRD also proves the superior hydrothermal stability of this LTA. This research broadened the application scope for LTA zeolite in industry, and also provided inspirations in increasing the Si/Al ratio of other 37 zeolites featuring D4Rs.

6.2 Suggested Future Directions

According to Hong’s report, specifically, LTA with an Si/Al ratio of 16-23 (still synthesized with F⁻) is desirable to replace the commercial SSZ-13 zeolite in the DeNOₓ application, due to its better hydrothermal stability. Since so far only LTA with an Si/Al ratio of 7.55 was successfully crystallized by using isolated siliceous D4Rs in HF-free way, there is space for the improvement. One of the ideas for this objective is inspired by Kato:²¹⁶ in his previous report, it is mentioned that as long as 3 of the 4 arms of TMA are methyl groups, it is able to help to form and stabilize isolated Si-D4R cubes by locating at the 8 corners, regardless of the fourth arm. In fact, they successfully used trimethylbenzylammonium cations to prepare stable isolated siliceous D4R units. Therefore, if isolated Si-D4Rs stabilized by trimethylbenzylammonium, rather than TMA⁺, are introduced into the synthesis of the novel LTA as discussed in Chapter 5, due to the bigger size of trimethylbenzylammonium cation, after
crystallization, theoretically all the β-cages will keep empty, and then LTA with an Si/Al ratio as high as 11 might be obtained due to charge balance requirement.

As discussed in Chapter 3, siliceous LTA has been successfully synthesized by using only 17% of the conventional HF quantity, and also in Chapter 5, LTA with an Si/Al ratio as high as 7.55 has been obtained in HF-free way. Then, focusing on the same topic: if it would be an unprecedented achievement if the two results could be combined together for one ultimate objective: synthesizing siliceous LTA in one-step method without F⁻. Then inspired by the contents in Chapter 4 that defects of SiO⁻ could be used to balance the positive charges from OSDAs, and the discovery in Chapter 3 that the formation and stabilization of defective siliceous D4Rs do not rely on F⁻, a promising idea to synthesize siliceous LTA without F⁻ is to crystallize an LTA with every D4R possessing some defects, during which TMA could be employed to titrate a desired number of defects, while siliceous isolated D4Rs might be taken as a variable for the precursor “input”. Since pH for the crystallization is another important parameter to control the relative number of defects of Si-OH and Si-O⁻, finding a proper pH to obtain just enough Si-O⁻ to balance OSDAs and avoid forming too many defects (might lead to a failed crystallization) is expected to be critical.

For the controllable defects obtained in Chapter 4 for LTA zeolite, a further serious problem that needs to be addressed is that, when using conventional calcination (550 °C) to remove away OSDAs residing in the zeolitic micropores, those defects will be all healed. In order to solve this issue, O₃ treatment under a low temperature might be promising, since O₃, owing to its better oxidizability than O₂, can convert the OSDA into gases of NOₓ, CO₂, and H₂O under 200 °C. Meanwhile, due to the low temperature, the defects might be maintained, and then the barrier will be overcome. We have been trying this idea, and it has been found that the 2
objectives — keeping the defects and also making the accessible lta-cages open — were achieved. Meanwhile, it was also observed that TMA stays in sod-cages after the ozone treatment.

Finally, as mentioned in Chapter 5, the effect of water on the purity of the LTA product synthesized in HF-free way based on isolated siliceous D4Rs can be researched by NMR, XRD, and especially Raman, since Raman could provide information about D4R existence and quantity. Then by using Raman, we might answer the question why when water content in the precursor is decreasing, more SOD product (with no D4Rs) will emerge. This study may provide some insights for the long-lasting question in the field of zeolite synthesis: the exact role of water. In addition, how isolated siliceous D4Rs helped the formation of Al-containing D4Rs in the final LTA product can be studied in a similar way by utilizing Raman, and the information from this research might assist in using this special silica source to try to increase the Si/Al ratios for other more zeolites also containing D4Rs synthesized in the absence of HF.

Overall, all of these suggested future study directions, if achieved, could help us obtain LTA products with desirable structures (controllable defects in accessible zeolite) and compositions (ideal Si/Al ratio) via a methodology of rational synthesis mainly based on charge balance. They will further broaden the application potential and scope (e.g., DeNOₓ) of LTA in the zeolite industry, even establish a well-understood mathematical model of zeolite synthesis to inspire the structural and compositional controls of other zeolites. In addition, for the studies regrading the roles of water and isolated siliceous D4Rs in zeolite crystallization, if such secrets can be unlocked by Raman complemented by other techniques, the whole picture of zeolite crystallization at atomic level — the “Holy Grail” problem in this field — will be further revealed, which will help zeolite scientists take a solid forward step in mastering the rational
synthesis for zeolites, completely avoiding the conventional time- and energy- consuming trial-and-error method.
REFERENCES


(81) Lupulescu, A. I.; Rimer, J. D. In Situ Imaging of Silicalite-1 Surface Growth Reveals the Mechanism of Crystallization. Science 2014, 344 (6185), 729–732.


(86) Ivanova, I. I.; Kolyagin, Y. G.; Kasyanov, I. A.; Yakimov, A. V.; Bok, T. O.; Zarubin, D. N. Time-Resolved In Situ MAS NMR Monitoring of the Nucleation and Growth of Zeolite


