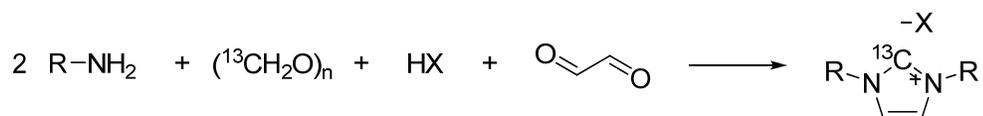


## Chapter Five: Conclusions and Future Considerations

The guest/host study presented in Chapter Two successfully expanded the SSZ-70 composition window to pure-silica and aluminum containing materials. Other phases observed in the study were TON, MFI, MTT, MTW, Beta, EUO, CFI, SSZ-16 (AFX) and STF. The aluminum-containing SSZ-70 materials were shown to be active catalysts for hydrocarbon cracking. One aspect that remained unsolved was the structure of SSZ-70. In particular, the physical characterization showed strong similarity to MWW materials but catalytic behavior was different. Additional catalytic investigations, such as methanol to higher hydrocarbons, could provide complementary information about possible structural features<sup>1</sup>. Recent advances in combining electron microscopy with high resolution XRD data might offer a path to structure solution. These techniques have been recently used to solve several complex structures from crystals too small for single-crystal analysis<sup>2</sup>. Successful application of these techniques requires sufficient long range order within SSZ-70. It is possible that disorder occurs throughout SSZ-70 making structure solution more difficult. If disorder is present, advanced two-dimensional NMR techniques might offer insight into local structure through  $^{29}\text{Si}\{^{29}\text{Si}\}$  2D experiments<sup>3, 4</sup>. Solid-state NMR measurements showed well resolved  $^{29}\text{Si}$  resonances indicating strong local order suggesting this approach holds promise. In addition, understanding where the SDA molecules are located might offer insight into the observed differences in catalytic behavior. One area of interest is the relative proximity of the charge center to the silicate framework. Again, 2D NMR techniques could offer valuable information although the

relatively weak  $^{13}\text{C}$  resonance associated with the imidazolium C(2) carbon could hamper investigations. This potential limitation could be overcome if an imidazolium SDA with  $^{13}\text{C}$  enrichment at the C(2) position was employed. Reports of 2- $^{13}\text{C}$ -4,5-diphenylimidazole using  $^{13}\text{C}$ -formic acid suggest this could be a viable strategy<sup>5</sup>. The proposed synthesis would employ  $^{13}\text{C}$ -labeled paraformaldehyde as shown in Scheme 5.1.



Scheme 5.1: Proposed synthesis of  $^{13}\text{C}$ -labeled imidazolium SDA

The proposed  $^{13}\text{C}$ -labeling could help understand organic/silicate interactions with 1,3-bis(1-adamantyl)imidazolium hydroxide. This SDA was able to produce three crystalline phases whereas the two other SDA with quaternary carbons adjacent to nitrogen were not nearly as successful. Information about the distance between the charge center and silicate species would help discriminate the structure direction mechanism.

The apparent similarity between SSZ-70 and MWW should be investigated further through layer manipulation experiments. MWW materials can be swollen, delaminated, pillared and exfoliated with enhanced catalytic properties towards larger molecules<sup>6-8</sup>. Investigations into MWW delamination have focused on aluminosilicate products. As demonstrated in Chapter Two, SSZ-70 can be synthesized as a borosilicate and aluminosilicate. Different delamination behavior might be observed between borosilicate and aluminosilicate materials.

The second guest/host study presented in Chapter Three investigated chiral imidazolium SDAs in the synthesis of polymorph A enriched Beta. Both 1,3-bis((S)-3,3-dimethylbutan-2-yl)imidazolium hydroxide and 1,3-bis((S)-1-cyclohexylethyl)imidazolium hydroxide produced Beta, and many of the XRD patterns were distinctly different than those for regular Beta. EUO was the only other crystalline phase observed in the study. The observed differences in XRD patterns did not correspond to simulated patterns for polymorph A enrichment. Molecular modeling suggested both SDAs occupied the straight 12MR pores. This arrangement did not project chirality across the [001] fault planes providing an explanation for absence of polymorph A enrichment. Modeling showed careful consideration must be given to efficiently filling the entire void space with large SDAs. This obstacle could be overcome using a dual SDA strategy where a large chiral SDA (>10Å length) could be combined with a smaller SDA. The large SDA would be able to span [001] fault planes thereby projecting “handedness” between adjacent layers. The smaller SDA is envisioned to occupy void volume in a similar manner to pore filling agents (PFAs)<sup>9, 10</sup>. A dual SDA approach was recently used to synthesize pure-silica LTA (ITQ-29) using tetramethylammonium hydroxide as the second SDA<sup>11</sup>. Competing nucleation selectivity between the large chiral SDA and smaller SDA is an obvious barrier to overcome. Recent advances in high-throughput (HT) methods could be applied to screen large combinations of SDAs and inorganic compositions<sup>12, 13</sup>.

The third study presented in Chapter Four investigated supramolecular SDAs created through adamantyl/ $\beta$ -cyclodextrin inclusion complexes. Experimental evidence for a 2:1 inclusion complex between  $\beta$ -CD and 1,3-bis(1-adamantyl)imidazolium chloride was

obtained from ITC. Initial inorganic reactions with the desired 2:1 inclusion complex showed no desirable perturbation to the product and significant cyclodextrin degradation was observed. Additional attempts using a 1:1  $\beta$ -CD/N,N,N-trimethyl-1-adamantanammonium complex gave similar degradation. Ultimately, carbohydrate-containing SDAs were not stable under molecular sieve synthesis conditions.

### 5.1: References

1. S. I. Zones, C. Y. Chen, A. Corma, M. T. Cheng, C. L. Kibby, I. Y. Chan and A. W. Burton, *Journal of Catalysis* **250** (1), 41–54 (2007).
2. L. B. McCusker and C. Baerlocher, *Chemical Communications* (12), 1439–1451 (2009).
3. D. H. Brouwer, R. J. Darton, R. E. Morris and M. H. Levitt, *Journal of the American Chemical Society* **127** (29), 10365–10370 (2005).
4. S. Cadars, D. H. Brouwer and B. F. Chmelka, *Physical Chemistry Chemical Physics* **11** (11), 1825–1837 (2009).
5. P. Kang and C. S. Foote, *Journal of the American Chemical Society* **124** (32), 9629–9638 (2002).
6. A. Corma, V. Fornes, S. B. Pergher, T. L. M. Maesen and J. G. Buglass, *Nature* **396** (6709), 353–356 (1998).
7. W. J. Roth, C. T. Kresge, J. C. Vartuli, M. E. Leonowicz, A. S. Fung and S. B. McCullen, *Catalysis by Microporous Materials* **94**, 301–308 (1995).

8. S. Maheshwari, E. Jordan, S. Kumar, F. S. Bates, R. L. Penn, D. F. Shantz and M. Tsapatsis, *Journal of the American Chemical Society* **130** (4), 1507–1516 (2008).
9. H. Lee, S. I. Zones and M. E. Davis, *Journal of Physical Chemistry B* **109** (6), 2187–2191 (2005).
10. S. I. Zones and S. J. Hwang, *Chemistry of Materials* **14** (1), 313–320 (2002).
11. A. Corma, F. Rey, J. Rius, M. J. Sabater and S. Valencia, *Nature* **431** (7006), 287–290 (2004).
12. M. Moliner, J. M. Serra, A. Corma, E. Argente, S. Valero and V. Botti, *Microporous and Mesoporous Materials* **78** (1), 73–81 (2005).
13. A. Corma, M. J. Diaz-Cabanas, J. L. Jorda, C. Martinez and M. Moliner, *Nature* **443** (7113), 842–845 (2006).