

Chapter 9

Summary and Future Work for Part II

9.1. Overall Summary and Conclusion

In 2016, the Davis group reported an extra-large-pore germanosilicate CIT-13 which has a novel framework closely related to two other extra-large-pore frameworks UTL and CIT-5. From the library of methylbenzylimidazolium-derivative OSDAs, it was experimentally confirmed that several organic cations are able to crystallize CIT-13 in fluoride media. The use of hydrogen fluoride could be avoided by replacing it with an equimolar quantity of ammonium fluoride. It was also possible to synthesize CIT-13 without fluoride. CIT-13 synthesized in hydroxide media showed a unique property in terms of structural transformation. The isomorphous substitution technique was also confirmed as experimentally feasible. The structure and possible disorders in the CIT-13 framework were investigated on the basis of the synchrotron powder X-ray diffraction. The presence of disorders in the *d4r* arrangement was suggested. CIT-13 was registered as the type material of the 236th framework type *CTH in the International Zeolite Association Structure Database. Its microporosity was studied based on argon adsorption isotherms and compared to that of UTL.

The transformation of Ge-CIT-13 into Ge-CIT-5 was discovered. This transformation proceeded spontaneously at room temperature with the presence of moisture from ambient air. The kinetics of the transformation were investigated on the basis of the nature of the parent Ge-CIT-13. High Ge content and use of hydroxide as the mineralizing agent significantly increased the rate of transformation. The role of moisture was also studied. Under environments where water cannot be easily sorbed within the pore system of

CIT-13, such as high temperature, dry inert gas, presence of hydrophobic molecules, the rate of transformation was significantly decreased. Exposure to water-saturated vapor phase greatly accelerated the transformation.

The microporosity of Ge-CIT-5 well matched that from the pure silica CIT-5 synthesized from the sparteine-derivative OSDA. The moisture-derived structural evolutions of other *d4r*-containing germanosilicates, UTL, IWW, and ITH were also studied. UTL lost its structure within one day. IWW and ITH retained their structures for 256 days with minor structural degradations. It was suggested that the two hierarchical arrangements—the arrangement of *d4r* units within the interlayer region and the arrangement of germanium T-atoms within the *d4r* units—were the key factors of transformability. Up to now, Ge-CIT-13 is the first and only germanosilicate which can undergo this type of transformation.

Possible topotactic transformation pathways of Ge-CIT-13 and Ge-CIT-5 were investigated. These two germanosilicates showed very different delamination behaviors. Ge-CIT-13 was effectively delaminated into layered silicate CIT-13P by weak acid solution and transformed into CIT-14 and CIT-15. The extent of delamination was important for the achievement of CIT-15. It was also discovered that Ge-CIT-13 synthesized in hydroxide media can be transformed directly into CIT-14 via the inverse sigma transformation pathway. The resultant CIT-14 from this pathway showed excellent microporosity without any sign of mesoporosity. On the other hand, Ge-CIT-5 was not easily delaminated possibly due to the structural difference between bridging *d4r* units and double-zigzag-chain units. No CIT-15 structure could be successfully obtained via the acid-delamination of Ge-CIT-5. Instead, Ge-CIT-5 was effectively delaminated using ammonium hydroxide. Lastly, the postsynthetic alumination of Ge-CIT-13 and Ge-CIT-5 were performed, and high-silica aluminosilicate versions of Al-CIT-13 and Al-CIT-5 were obtained with no octahedral aluminum species.

This work demonstrates the versatile transformability of CIT-13. Many important discoveries are involved in regards of topotactic transformation of germanosilicates such as

the transformation of CIT-13 to CIT-5. Here, the most extensive network of inter-zeolitic transformations and modifications to date was established in this work. I believe this work may not only exhibit a new possibility of germanosilicate modification, but also provide a sound guideline for researchers who seek further utilities for their germanosilicates.

9.2. Proposed Future Work

Initially, the fluoride-mediated hydrothermal synthesis was the only synthetic route to obtain germanosilicate CIT-13. Now that I discovered a new pathway for CIT-13 synthesis in hydroxide media, it is important to optimize the synthesis recipe and to correlate the synthetic parameters to the properties of resultant materials. I believe that CIT-13 from the hydroxide media has a germanium T-atom arrangement within *d4r* units fundamentally different to that of CIT-13 from the fluoride media, given that fluoride anions can intervene in the formation of *d4r* units.¹¹⁶ In terms of the transformation of CIT-13 to CIT-5, in this work it was experimentally shown that CIT-13/OH and CIT-13/F having the same EDS Si/Ge ratio have immensely different rates of transformation. Furthermore, CIT-13/OH was successfully transformed directly into CIT-14 via the inverse sigma transformation whereas CIT-13/F was not.

Based on these observations, I suggest a future study on the arrangement of germanium atoms within *d4r* units. There are several methodologies to investigate this. One is the use of fluoride anion as a probe for the *d4r* units. It is reported that fluoride anions can be postsynthetically inserted into empty *d4r* units by treating as-made germanosilicates with ammonium fluoride at elevated temperatures.²⁰³⁻²⁰⁴ The inserted fluoride anions can be characterized with ¹⁹F solid-state NMR spectroscopy.^{176, 203} Also, there are other germanosilicates which can be prepared in both fluoride and hydroxide media such as ITH-

type germanosilicate ITQ-13.^{149, 175, 205} I believe that making comparisons between these germanosilicates to CIT-13 would provide new insights.

Another important topic which should be considered is to solve the structure of CIT-14 using a Rietveld refinement. The ADOR-type transformation of CIT-13 into CIT-14 was already suggested by another research group,¹⁶⁵ but no refinement was reported. I believe that CIT-14 prepared from the inverse sigma transformation route can be a good candidate for the following synchrotron XRD study.