

Chapter 5

Introduction to Part II: Extra-large-pore Molecular Sieves and Germanosilicates

In this chapter, the topic of Part II of my thesis is introduced. First, a brief history of extra-large-pore zeolites is provided. Next, I describe why they are an important class of molecular sieves. The pros and cons of germanosilicates are discussed, and how the drawbacks related to the use of germanium may be overcome. I close with my motivations and objectives for this part of my thesis work.

5.1. Background

Zeolites and molecular sieves are one of the most frequently used heterogeneous catalysts in modern chemical industry.¹¹²⁻¹¹⁵ Their merits as catalysts encompass many advantageous properties such as well-defined pore structures, high thermal stability and environmental tolerance, excellent accessibility of catalytic sites and high catalytic activities, a wide array of elemental compositions, etc.¹¹⁶⁻¹²⁰ These beneficial properties of zeolites and molecular sieves have a very close relation with their structural architectures.^{112, 121} In this regard, discovery of new frameworks and modification of porosity are very important in the field of zeolite science.¹²²⁻¹²³ Thus, the scientific community has spared no effort in finding new structures of molecular sieves which can be used for many high-value-added industrial purposes. One of the hottest research topics is extra-large-pore frameworks.¹¹⁵

5.1.1. Extra-large-pore Molecular Sieves

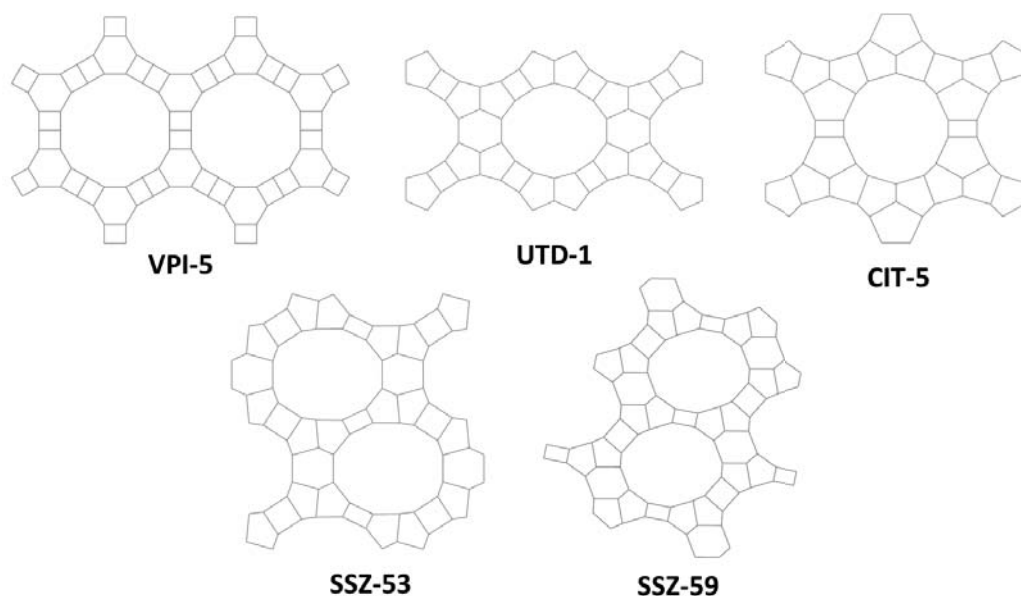


Figure 5.1. Examples of extra-large-pore frameworks.

Zeolitic frameworks having pore systems which are delimited by rings consisting of 8, 10, and 12 tetrahedral atoms (T-atoms) are called small-pore, medium-pore, and large-pore frameworks, as introduced in Chapter 1, Part I. While small-pore and medium-pore molecular sieves which have relatively narrow dimensions of cavities and/or channels (3–6 Å) are of interest due to their prominent shape selectivity (e.g., the topic of Part I of my thesis), larger-pore topologies are gathering attention thanks to their ability to process larger reactant molecules. *Extra-large-pore frameworks* are molecular-sieve structures having pore windows delimited by more than 12 T-atoms.¹¹⁴ These frameworks have ca. 1-nm-sized pore windows which are wider than most of commercial large-pore zeolites such as zeolite Y or Beta. Figure 5.1. shows several representative examples of extra-large-pore frameworks.

The first extra-large-pore molecular sieve is the aluminophosphates-based VPI-5 (VFI) and was discovered by Prof. Mark E. Davis and co-workers.¹²⁴⁻¹²⁵ VPI-5 has one-dimensional 18-ring channels with a 12.7 Å-wide pore dimension.¹²⁶ Interestingly, at elevated temperature ($T > 100^{\circ}\text{C}$) with the presence of sorbed moisture, VPI-5 could be transformed to $\text{AlPO}_4\text{-8}$ (AEI) which is another extra-large-pore molecular sieve having 14-ring channels.¹²⁷⁻¹²⁸ This captivating property of VPI-5 gathered tremendous scientific interest and ignited efforts in exploring new phosphate-based extra-large-pore molecular sieves. A 20-ring gallophosphate-based Cloverite (-CLO) is one example of accomplishments made in those days.¹²⁹

The late 1990's was the era of 14-ring aluminosilicates and borosilicates. 14-membered ring high silica zeolites UTD-1 (DON), CIT-5 (CFI), SSZ-53 (SFH), and SSZ-59 (SFN) were discovered one after the other.¹³⁰⁻¹³³ These aluminosilicate and borosilicate zeolites opened the field of catalysis of extra-large-pore molecular sieves in earnest.¹¹⁴ Many examples of catalytic reactions over extra-large-pore zeolites were developed such as cracking of 1,3-diisopropylbenzene, 1,3,5-triisopropylbenzene, gasoil, disproportionation of ethylbenzene, alkylation of biphenyl, etc.¹³⁴⁻¹³⁶

The number of extra-large-pore frameworks started to explosively increase as germanium was introduced within the frameworks by Corma et al.¹¹⁴ Examples include 2-dimensional 14/12-ring IM-12/ITQ-15 (UTL),^{116, 137} 3-dimensional 18/10/10-ring ITQ-33 (ITT, Figure 5.2.),¹³⁸⁻¹³⁹ 3-dimensional 30-ring mesoporous ITQ-37 (-ITV),¹⁴⁰ 3-dimensional 16/15-ring ITQ-40 (-IRY),¹⁴¹ and 2-dimensional 14/10-ring CIT-13 (*CTH)⁶³ which is the main topic of Part II of my thesis. Although germanosilicates only have a limited Lewis acidity as a heteroatom within the zeolite framework,¹⁴² their rich chemistry opened an entirely new field of zeolite science—*topotactic transformation*.

1.1.2. Germanosilicates

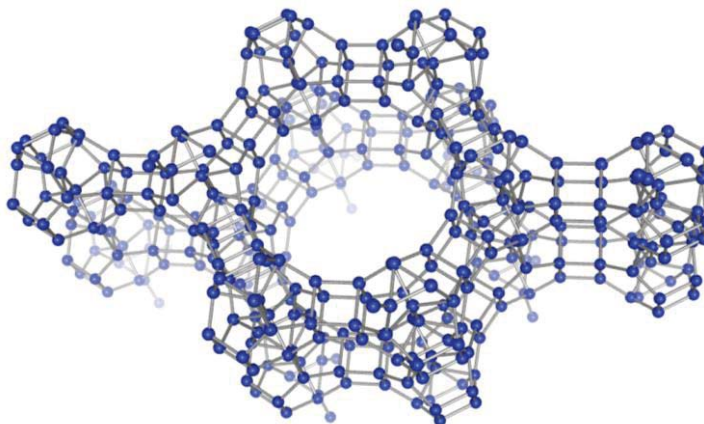


Figure 5.2. Extra-large-pore germanosilicate ITQ-33 (ITT) possessing a 3-dimensional 18/10/10-ring channel system.

It was computationally predicted that the presence of small-rings can decrease the framework density, thereby enabling frameworks to have higher probability to possess extra-large pores.¹⁴³ However, it is inevitable for small-ring building units such as 3-membered ring (3), double-3-ring (*d3r*) or double-4-ring (*d4r*) to have very small T-O-T angles ($< 145^\circ$) which are not energetically favored. Inclusion of germanium can solve this problem since Ge-O-T (T = Si, Ge) bonds can stabilize such units.^{116, 144} Indeed, many frameworks realized as germanosilicates possess *d4r* units.^{116, 137, 140, 145} All frameworks enumerated in the previous section as examples of extra-large-pore germanosilicates—UTL, ITT, -ITV, -IRY, *CTH—do have *d4r* units or even *d3r* units. The *d4r* units are also frequently found in other germanosilicates ITQ-22 (IWW), ITQ-13 (ITH), beta polymorph C (BEC), and ITQ-27 (IWW) which are not extra-large-pore frameworks.¹⁴⁶⁻¹⁴⁹

There are several drawbacks of inclusion of germanium within the frameworks. One is the cost of element. It is possible to collect leached germanium after postsynthetic stabilization,¹¹⁴ but the cost of the separation and purification processes must be also considered. Also, germanosilicates can be used as crystallization seeds for germanium-free zeolites. Cantin et al. reported that pure borosilicate ITQ-24 could be obtained on the basis of seeding strategy.¹⁵⁰

The other obstacle is the limited catalytic activity of the germanium sites.¹⁴² Isomorphous substitution can overcome this issue by incorporating second heteroatoms in the germanosilicate system. For example, IWR-type aluminogermanosilicate,¹⁵¹ B, Al, Ga-containing germanosilicates ITH,¹⁵² B, Al, Ga, Fe, In-incorporated germanosilicate UTL¹⁵³ were reported.

The most important drawback of germanosilicate is its weak hydrothermal stability.^{151, 154-157} This is simply because Ge-O-Ge bonds and Ge-O-Si bonds can be easily dissociated by hydrolysis.¹⁵⁷⁻¹⁵⁸ It is known that many germanosilicates having a very low Si/Ge ratio (< 2–3) can be immediately degraded into amorphous materials upon exposure to water.¹⁵⁴ Postsynthetic stabilization is one way to enhance the hydrothermal stability of germanosilicates by substituting germanium T-atoms within the frameworks with other stable T-atoms such as Al, Si, or Sn, etc. Many cases of postsynthetic modifications of germanosilicates have been reported in the literature.¹⁵⁸⁻¹⁶⁰ This postsynthetic modification of germanosilicate not only improves the stability of the frameworks, but also provides catalytic activity by introducing Brønsted or Lewis acid sites.¹⁵⁷

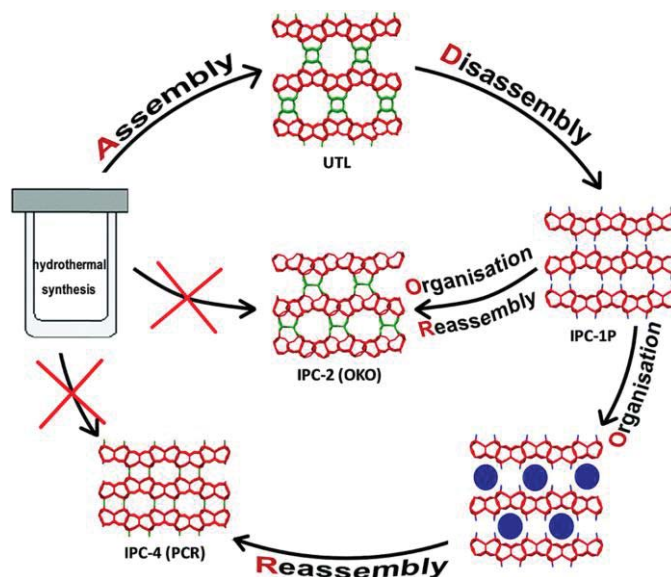


Figure 5.3. The ADOR process of UTL-type germanosilicate producing two structurally related frameworks OKO and PCR. Reproduced with Permission from Ref [50]. Copyright 2014 Royal Society of Chemistry.

It is also possible to make use of the chemical lability of framework germanium.¹⁴⁵ In the early 2010's, two milestone progresses were reported. One is the delamination of UTL-type germanosilicate IM-12,¹⁶¹ and the other is the inverse sigma transformation of the same molecular sieve.¹¹⁸ These two structural transformations of germanosilicates made use of the fact that germanium T-atoms regioselectively occupy the $d4r$ sites. The delaminated layered material IPC-1P was further transformed into many unseen frameworks such as IPC-2 and IPC-4,¹²² and later, IPC-9 and IPC-10¹⁶² by alkoxylation and/or condensation. This concept is called the ADOR (assembly-disassembly-organization-reassembly) strategy, and these types of transformations are called *topotactic transformations*. The topotactic transformation is structural transformation of crystalline materials where the crystal lattices of the parent phase and the product phase are closely related to one another on the basis of one or more crystallographically equivalent symmetry elements.¹⁶³ In the case of the

transformation of UTL into OKO and PCR, all three frameworks belong to the same space group $C2/m$. Thus the ADOR transition of UTL is a good example of topotactic transformation.

5.2. Motivation

In 2016, our group reported a new germanosilicate framework CIT-13.⁶³ CIT-13 was discovered in the course of studying the structure-directing ability of many imidazolium-based organic structure-directing agents (OSDAs). The structure of CIT-13 revealed on the basis of the rotational electron diffraction (RED) technique strikingly resembled that of UTL. UTL consists of *fer*-type layers connected with bridging *d4r* units while CIT-13 is composed of *cfi*-type layers similarly connected with *d4r* units. Therefore, it is easily expected that CIT-13 can undergo various transformations analogous to those of UTL.

Indeed, the discovery of CIT-13 immediately attracted interest of many research groups. Although CIT-13 was registered as the type material of framework *CTH, germanosilicates NUD-2¹⁶⁴ and SAZ-1¹⁶⁵ which are essentially isostructural to CIT-13 were reported one after the other. These germanosilicates were synthesized using similar imidazolium-based OSDAs. While we disclosed the transformation of CIT-13 into two novel frameworks CIT-14 and CIT-15,¹⁶⁶ IPC-16¹⁶⁵ (isostructural to CIT-14) and IPC-15¹⁶⁵ and ECNU-21¹⁶⁷ (isostructural to CIT-15) were reported. However, the full network of transformations in which CIT-13 is involved, and its rich chemistry has yet to be reported.

Furthermore, in December 2016, I discovered that calcined CIT-13 samples had been slowly transformed into another extra-large-pore CFI-type germanosilicates which I named Ge-CIT-5. This spontaneous transformation was completely reproducible. To the best of my knowledge, this is the first inter-germanosilicate transformation occurring at room

temperatures. The only pathway to obtaining the CFI-type molecular sieves had been the original protocol for CIT-5 using sparteine-derived OSDA which is hard to obtain and expensive. The introduction of Ge-CIT-5 will immensely widen the tunability of chemical and structural properties of CFI-type molecular sieves.

5.3. Objectives

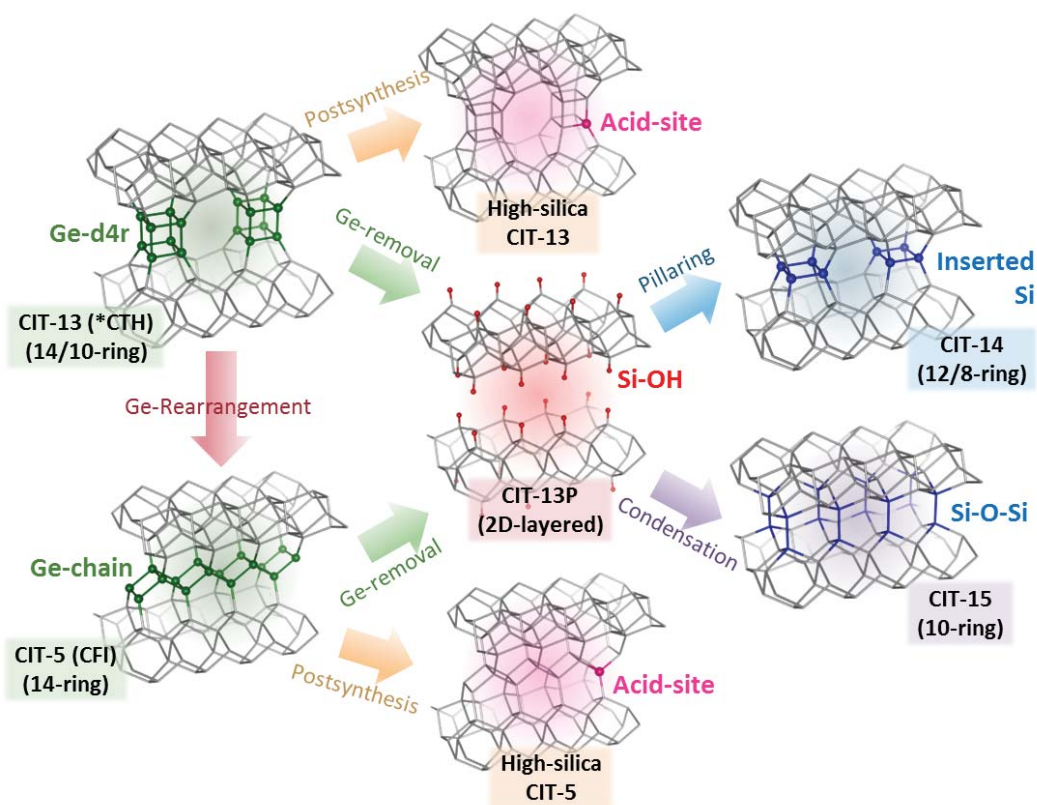


Figure 5.4. Schematic illustration of the full network of transformations of Ge-CIT-13 which will be discussed in Part II of my thesis.

The main purpose of Part II of my thesis is to elucidate the full transformation and postsynthesis network of germanosilicate CIT-13. For each of the structural and chemical modification steps shown in Figure 5.4, the most important synthetic parameters will be deduced and the preparation conditions will be optimized.

In Chapter 6, the synthesis, characterization and properties of Ge-CIT-13 will be presented. Many synthetic procedures to yield CIT-13-type molecular sieves will be illustrated, and the synthesis-property relationships will be discussed. In Chapter 7, the transformation of Ge-CIT-13 into Ge-CIT-5 will be presented, where the role of moisture is extensively investigated. In Chapter 8, various topotactic transformation and postsynthesis pathways are outlined and discussed. Lastly, in Chapter 9 the overall summary and future outlook will be provided.