Chapter 8

Topotactic Transformation and Postsynthetic Modification of CIT-13 and CIT-5

In this chapter, investigations involving the transformation of Ge-CIT-13 and Ge-CIT-5 into two novel structures CIT-14 and CIT-15 is presented. Also, the postsynthetic alumination of Ge-CIT-13 and Ge-CIT-5 yielding hydrothermally stable high-silica Al-CIT-13 and Al-CIT-5 is discussed.

8.1. Introduction

The topotactic transformations of UTL-type germanosilicate have attracted significant interest during the last decade.^{118, 122-123, 145, 162, 181, 195} Unlike other *d4r*-germanosilicates such as IWW or ITH, it was found that UTL has a unique arrangement of germanium T-atoms within its *d4r* units on the basis of the extended X-ray absorption fine structure (EXAFS) spectroscopy and solid-state NMR spectroscopy.^{118, 176} Starting with the 2D layered *fer*-type silicate IPC-1P which is the delamination product from IM-12,¹⁶¹ a number of novel frameworks were obtained such as IPC-2, IPC-4,¹²² IPC-6, IPC-7,¹²³ IPC-9, and IPC-10.¹⁶² Also, the inverse sigma transformation directly from IM-12 to COK-14 was demonstrated.¹¹⁸

It was already pointed out that Ge-CIT-13 can be transformed into two novel frameworks, large-pore CIT-14 and medium-pore CIT-15, via transformations analogous to the case of UTL. There are a couple of reports regarding the topotactic transformation of

CIT-13-type molecular sieves,^{165, 167} but the full picture of its rich chemistry has never been reported. In this chapter, the transformations from CIT-13 to CIT-14 and CIT-15 are discussed, focusing on the delamination time. Also, the inverse sigma transformation of Ge-CIT-13 is demonstrated for the first time. Furthermore, another set of transformations starting from Ge-CIT-5 are also discussed. Lastly, the postsynthetic alumination processes of Ge-CIT-13 and Ge-CIT-5 are demonstrated. Figure 8.1. graphically summarizes the scope of what is presented in this chapter.



Figure 8.1. Overview of the network of topotactic transformations and postsynthetic modification pathways discussed in this chapter.

8.2. Experimental

8.2.1. Preparation of Parent Materials

Parent Ge-CIT-13 samples were prepared according to the protocol described in Chapter 6. Parent Ge-CIT-5 samples were prepared from the transformation from Ge-CIT-13 as described in Chapter 7.

8.2.2. Hydrolytic Delamination of Weak Acid and Base

Delamination of Ge-CIT-13 and Ge-CIT-5 was conducted using 0.1 M HCl solution at 99 °C or 1–3% NH₄OH solution at room temperature.^{161, 167} Freshly calcined germanosilicate was dispersed in a desired concentration of weak acid or base solution in a solid : liquid ratio of 1 mg : 1 mL. The mixture was stirred continuously during the delamination. The resultant solid was collected using a centrifuge, and washed with distilled water and acetone. Drying was conducted at room temperature in a vacuum desiccator overnight.

8.2.3. Alkoxysilylational Pillaring

Alkoxysilylational pillaring of layered CIT-13P was performed as a procedure previously reported in the literature.¹²² Specifically, in a 23-mL PTFT-lined autoclave, layered CIT-13P was mixed with diethoxydimethylsilane (DEDMS) and 1 M nitric acid solution. The weight ratio CIT-13P : DEDMS : acid solution was 5 : 1 : 100. The mixture was sealed and heat-treated at 170 °C for 16 hours. The resultant solid was collected using a centrifuge, and washed with distilled water. The dried solid was calcined at 580°C for 6 hours.

8.2.4. Inverse Sigma Transformation

The inverse sigma transformation protocol for the transformation from Ge-CIT-13 to CIT-14 was performed on the basis of the original procedure reported by Verheyen et al.¹¹⁸ Freshly calcined Ge-CIT-13 was dispersed in 12 M HCl (37 wt. % in H₂O) in a PTFE-lined autoclave. The solid : acid weight ratio was 1 : 50. This suspension was tumbled in a rotating oven at 95 °C for 48 hours. The resultant solid was collected by centrifuge. This intermediate product (-CIT-14) was washed with distilled water and acetone, and dried at room temperature in vacuum for 24 hours. Finally, under an air flow, the dried -CIT-14 was calcined at 550 °C for 6 hours.

8.2.5. Direct Condensation of CIT-13P

The formation of CIT-15 was achieved by calcining CIT-13P samples prepared according to the procedure described in Section 8.2.2. The calcination was conducted at 580 °C for 6 hours under an air flow.

8.2.6. Degermanation and Alumination

Postsynthetic alumination was performed using 1 M aluminum nitrate solution.^{158, 160} Here, 1 N nitric acid was used together to control the acidity of treating solutions.¹⁵⁴ The compositions of acidic aluminum nitrate solutions were given in Table 8.1. Freshly calcined Ge-CIT-13 (or Ge-CIT-5) samples were dispersed in the desired amount of treating solutions. The solid-to-solution ratio was 100 mL of solution per a gram of solid. The mixture was charged in a 23-mL PTFE-lined Parr autoclave and placed in a rotating oven at 175 °C (CIT-13) or 185 °C (CIT-5). The treatment was performed for 24 hours. The resulting solid was separated by centrifuge, and repeatedly washed twice with 0.01 M HNO₃ and twice with distilled water. The final Al-CIT-13 (or Al-CIT-5) samples were dried at room temperature in a vacuum chamber.

8.2.7. Characterization

PXRD patterns were acquired using a Rigaku MiniFlex II benchtop diffractometer using Cu K α radiation ($\lambda = 1.54184$ Å) to assess the crystal structure and crystallinity of the products. Morphology and elemental composition were studied using a Zeiss 1550VP FE-SEM equipped with an Oxford X-Max SDD X-ray EDS. Pore volumes and pore-size information of microporous materials were studied based on Ar adsorption isotherms obtained using a Quantachrome Autosorb iQ at 87.45 K.

¹H, ²⁷Al and ²⁹Si MAS solid-state NMR spectra of samples were obtained using a Bruker Avance 500 MHz spectrometer with carrier frequencies of 499.843, 130.287 and 99.305 MHz, respectively. A 4-mm zirconia rotor with a Kel-F cap was charged with 50–100 mg of as-made or freshly calcined sample. The MAS rates were 8 kHz both for ¹H-²⁹Si CP and ¹H-decoupled ²⁹Si Bloch-decay experiments, and 12 kHz for ²⁷Al experiments.

8.3. Results and Discussion

8.3.1. Effects of Initial Germanosilicate Structure on Delamination

The first step of the topotactic transformations of Ge-CIT-13 and Ge-CIT-5 is the delamination that creates *cfi*-layers by removing Ge-rich *d*4*r* units connecting adjacent layers. In this chapter, the kinetics of the delamination process and physicochemical properties of layered CIT-13P/CIT-5P are discussed in terms of initial germanosilicate structures and delamination process parameters.



Figure 8.2. Schematic illustration of the acid- or ammonium-delamination of Ge-CIT-13 resulting in CIT-13P.



Figure 8.3. Typical ²⁹Si solid-state NMR spectra of CIT-13P.

Figure 8.2 briefly illustrates the delamination transformation of Ge-CIT-13 to CIT-13P. A layered 2D-silicate CIT-13P is produced by removing the bridging Ge-rich d4r units which is hydrothermally labile. The delamination can be accomplished using weak acid,^{122,} ^{161, 181} weak base,¹⁶⁷ or even distilled water.¹⁷⁶ The resultant CIT-13P possesses surface silanol groups (Si-OH) as a result of removal of d4r units. In a typical ²⁹Si NMR spectra (Figure 8.3), CIT-13P shows 2–3 peaks within the range from -90 ppm to -120 ppm. Unlike tectosilicates such as the parent CIT-13 or CIT-5, phyllosilicate CIT-13P shows a prominent peak at -105 ppm which is assigned to Q³-silanol (Si(OH)(OT)₃) silicon T-atoms having one disconnected –OH group. The majority of the Si T-atoms in CIT-13P are still completely connected Q⁴ Si-sites. The theoretically ideal CIT-13P in which no *d4r* remnants are present and with no defects within the remaining *cfi*-layers will show a Q³-site proportion of 33.3%. But, typically the actual CIT-13P samples show Q³-contributions much higher than 33% due to the presence of layer defects possibly generated by the degermanation directly from the *cfi*-layers. The example shown in Figure 8.3 shows a 45% of Q³-contribution. In the ¹H-²⁹Si CP-MAS spectrum of CIT-13P, Q²-silanediol (Si(OH)₂(OT)₂) T-sites could be also detected due to the Hartmann-Hahn amplification by proton nuclei. But those Q²-sites are typically few in number.

Ge-CIT-5 is produced from Ge-CIT-13 by the transformation of arrays of *d*4*r* units into double-zigzag chain (*dzc*) units. Thus, it can be easily deduced that the bridging *dzc* units in a Ge-CIT-5 framework are also consisting of Ge-rich T-sites which can be hydrolyzed by weak acid. The kinetics of delamination processes of Ge-CIT-13/F[4.33] and Ge-CIT-5 transformed from the former parent Ge-CIT-13 were studied. The design of this experiment is shown in Figure 8.4(a). The two parent germanosilicates were delaminated by 0.1 M HCl solution at 99 °C for controlled durations. In this work, the delamination product of Ge-CIT-5 is named as CIT-5P, following the same nomenclature. Figure 8.4(b–e) are the PXRD patterns of the parent materials (Ge-CIT-13 and Ge-CIT-5) and delaminated layered products (CIT-13P and CIT-5P). The calculated interlayer distances and Si/Ge ratios characterized on the basis of EDS are illustrated in Figure 8.5.

Clearly, the interlayer diffraction peaks of the CIT-13P products were shifted toward higher diffraction angles as the delamination time extended as shown in Figure 8.4(d). The interlayer distance which had been initially 13.7 Å (Ge-CIT-13) was decreased to 12.3 Å and

11.4 Å after 3 and 24 hours of delamination, respectively. However, the series of PXRD patterns of CIT-5P samples displayed in Figure 8.4(e) did not show any significant change in the interlayer distance in accordance with the extension of delamination time. All PXRD patterns of CIT-5P were overlapped at the same position. The calculated interlayer distance, which had been 12.6 Å (Ge-CIT-5) before delamination, was decreased to 12.2 Å after 3 hours of delamination and no further decrease was observed.



Figure 8.4. Kinetics of the acid-delamination of Ge-CIT-13 and Ge-CIT-5 (a) Design of experiment. PXRD patterns of (b) Parent Ge-CIT-13/F[4.33], (c) Ge-CIT-5, (d) a series of CIT-13P/H samples acid-delaminated for x hours. (e) a series of CIT-5P/H samples acid-delaminated for x hours. (x = 3, 6, 12, 24)



Figure 8.5. Time-dependent structural and compositional changes induced by aciddelamination. (a) Interlayer distances of CIT-13P/H/xHRs and CIT-5P/H/xHRs as functions of delamination time calculated from PXRD patterns shown in Figure 6.4(d–e). (b) Si/Ge molar ratios of CIT-13P/H/xHRs and CIT-5P/H/xHRs as functions of delamination time.

Curiously, germanium T-atoms were continuously being extracted in the course of delamination of both Ge-CIT-13 and Ge-CIT-5. In case of the CIT-13 delamination, the Si/Ge ratio was increased from 4.33 to 234 during 24 hours of delamination process. Although the interlayer distance was not changed after 3 hours of delamination, the Si/Ge ratio of CIT-5P kept increasing even after 3 hours of delamination with a rate slower than CIT-13 as illustrated in Figure 8.5(b). This observation suggests the presence of very refractory siliceous remnant moieties in CIT-5P. Since this trend was not observed in the series of CIT-13P, it can be concluded that the formation of these stable siliceous species are related to the CIT-13-to-5 transformation.



Figure 8.6. NMR spectra and morphologies of acid-delaminated germanosilicates. (a) ²⁹Si solid-state NMR spectra of CIT-13P and CIT-5 originated from the same parent Ge-CIT-13/F. SEM images of (b) CIT-13P and (c) CIT-5P.

A pair of CIT-13P and CIT-5P layered materials originating from the same parent Ge-CIT-13/F were subjected to the ²⁹Si solid-state NMR spectroscopy to acquire further information about the arrangements of Si and Ge T-sites. The NMR spectra and corresponding SEM and EDS results are provided in Figure 8.6. After the same delamination process, the resultant CIT-13P and CIT-5P had high Si/Ge ratios of 90 and 75 which correspond to 1.0 % and 1.3 % of T-site occupancies of germanium, respectively. So it can be assumed that the influence of remaining germanium would be negligible.

On the basis of ²⁹Si solid-state NMR spectra, proportions of Q³-silanol sites in CIT-13P and CIT-5P were of 38.0 % and 25.4 %, respectively. Considering the fact that the theoretically ideal CIT-13P will show a Q³-site contribution of 33.3%, CIT-5P is showing a too small of a Q³-contribution. The formation of new Si-O-Si bonds can be one explanation as a result of the formation of dzc units, but it is also hard to believe that silanol condensation forming Si-O-Si bonds can extensively occur at room temperature. Although it will be discussed later, a complete delamination of CIT-5 is actually possible if ammonium hydroxide is used as a delaminating base instead of dilute acid. This result suggests that the interlayer siliceous species within CIT-5P which could not be removed by acid can be removed by basic solution. Further experimental evidence must be collected to elucidate the nature of this interlayer remnant siliceous species in CIT-5P.

8.3.2. CIT-14 Formation by Ethoxysilylational Pillaring and Inverse Sigma Transformation

8.3.2.1. Ethoxysilylational Pillaring

In 2013, two topotactic transformations of UTL-type germanosilicate IM-12, which is a related germanosilicate of CIT-13, resulted in two zeolites IPC-2 (OKO) and IPC-4 (PCR) having novel topologies.¹²² The OKO-type IPC-2 was prepared by a protocol called ethoxysilylational pillaring.¹⁴⁵ IM-12 was firstly delaminated into IPC-1P layered silicate using weak acid, and pillared with a pillaring agent diethoxydimethylsilane (DEDMS). This pathway yielded the large-pore, high-silica IPC-2.

The structural similarity between IM-12 and CIT-13 enables an analogous pathway toward another novel framework. In this section, the topotactic transformation of Ge-CIT-13 to CIT-14 via the ethoxysilylational pillaring of layered CIT-13P will be discussed. The schematic description of this transformation is shown in Figure 8.7(a) The first step of the process is the substitution reaction between CIT-13P silanol and alkylsilane bonds of pillaring agents such as DEDMS or 1,3-diethoxy-1,1,3,3-tetramethyldisiloxane (DETMDS).¹⁸² This reaction forms diethoxysiloxane bridges between neighboring CIT-13P layers (Figure 8.7(c)). These diethoxysiloxane bridges are further condensed by calcination. The net overall change is the replacement of Ge-rich *d*4*r* units with pure-silica single-4-ring (*s*4*r*) units. The influences of the preceding delamination process will be also discussed.



Figure 8.7. Pathway from CIT-13 to CIT-14 via the pillaring process. (a) Schematic illustration of the topotactic transformation from Ge-CIT-13 to CIT-14 by the ethoxysilylational pillaring. (b) Examples of alkoxyalkylsilane species which can be used as pillaring agents. (c) Intermediate stage of CIT-13 layers linked with bridging diethoxysilane.



Figure 8.8. Structure, pore sizes, and expected topological information of CIT-14.

Most of the zeolite hydrothermal syntheses are still "black box" processes in which any reliable way to predict the structures of products *a priori* has yet to be established; however, in this case, the structure of desired framework can be exactly predicted. The predicted structure of CIT-14 was optimized using the GULP algorithm¹⁹⁸ with the Catlow parameters as a hypothetical pure-silica framework by Dr. Dan Xie at Chevron. The structure, pore sizes, and expected topological information calculated using a utility program for topological analysis of zeolite materials, TOTOPOL are provided in Figure 8.8.¹⁹⁹



Figure 8.9. Influence of degree of delamination on the formation of CIT-14 (a) Design of experiment. PXRD patterns of the resultant CIT-14 samples in the range of (b) $4-40^{\circ}$ and (d) $6-9^{\circ}$.

As the precursor material, Ge-CIT-13/F[4.33] was used. Calcined Ge-CIT-13 was delaminated in 0.1 M HCl solution at 99 °C for 3, 6, 12, and 24 hours, and four CIT-13P samples having different extents of delamination were obtained. These four CIT-13P samples are the same samples which were discussed in the previous section. Here, these samples are named as CIT-13P/H/xHRs (x = 3, 6, 12, 24). This series of CIT-13P samples was pillared with DEDMS at the same reaction condition. As a result, four pillared materials which are named as CIT-14/ESD/y (y = 1, 2, 3, 4), where ESD stands for ethoxysilylational pillaring, were produced. The design of this experiment and the resultant PXRD profiles are shown in Figure 8.9.



Figure 8.10. Material characterization of CIT-14/ESP. (a) Argon adsorption/desorption isotherm, (b) 8 kHz MAS ¹H-decoupled ²⁹Si solid-state NMR spectrum, and (c) SEM image of CIT-14/ESP/4.

All of the resultant materials showed their interlayer diffraction lines to be very close to the predicted position (8.06°) of the interlayer diffraction line of CIT-14. The peaks shown in the higher diffraction angle region $(20-30^{\circ})$ matched well with the theoretically predicted spectra. Interestingly, the interlayer distances of resultant CIT-14-type materials were barely influenced by the extent of delamination. Presumably, this observation is maybe because it is possible for the remnant T-atoms of Ge-rich d4r units which survived the degermanation

by acid-delamination to constitute a part of new s4r units during the following ethoxysilylation step.

The obtained CIT-14 via the ethoxysilylational pillaring was further investigated on the basis of the argon adsorption/desorption isotherm, ²⁹Si solid-state NMR spectroscopy, SEM, and EDS elemental analysis. The results are shown in Figure 8.10. The micropore volumes of CIT-14/ESP/4 estimated from its argon adsorption isotherm were 0.065 cc g⁻¹ and 0.102 cc g⁻¹ based on the t-plot method and the Saito-Foley model, respectively. These values were close to or somewhat lower than the predicted accessible volume (0.094 cc g^{-1}) calculated using TOTOPOL.¹⁹⁹ From the desorption isotherm, a hysteresis was observed which indicates the presence of mesoporosity. A similar hysteresis was reported for the UTLto-OKO ethoxysilylational transformation.¹²² This mesoporosity suggests the presence of defect sites and/or amorphous silica phase induced by the pillaring pathway.¹²² In the ²⁹Si NMR spectrum, CIT-14/ESP showed a broad signal across the range from -100 to -120 ppm. No deconvolution was attempted due to many T-sites (7) and possible presence of mesoporous impurities. No apparent change induced by the ethoxysilylational pillaring procedure was observed in the SEM image. The observed Si/Ge ratios of CIT-14/ESP/1, 2, 3, and 4 were 50.0, 92.6, 164, and 253. These values are very similar to the Si/Ge ratios of CIT-13P layered materials (45.1, 99.2, 195, and 234) used to prepare CIT-14 samples. Therefore, it can be concluded that no significant degermanation happened during the ethoxysilylational pillaring procedure.

8.3.2.2. Inverse Sigma Transformation

The inverse sigma transformation of IM-12 resulted in COK-14 which is the type material of the framework OKO that was reported by Verheyen et al. in 2012.¹¹⁸ The presence of pure-GeO₂ *s*4*r* parts occupying the one side of *d*4*r* units is essential for germanosilicates to undergo this type of transformation.¹⁷⁶ Such configuration of germanium T-atoms within *d*4*r* units was confirmed on the basis of the extended X-ray absorption fine

structure (EXAFS) spectroscopy in IM-12.¹¹⁸ However, up to this time, IM-12 was the only germanosilicate to have such transformability.

In this section, the inverse sigma transformation of Ge-CIT-13 will be discussed. Schematic illustration of the inverse sigma transformation of Ge-CIT-13 is shown in Figure 8.11. Calcined Ge-CIT-13 is treated with 37 wt. % HCl (12 M) at 95 °C for 48 hours. During this step, the pure-GeO₂ *s*4*r* parts are leached out of the *d*4*r* units by strong acid. After washing off leached germanium, an intermediate solid consisting of loosely connected *cfi*-layers remains. I named this intermediate -CIT-14 where (-) sign denotes the incompleteness of structure, following the notation of -COK-14.¹¹⁸ Calcining -CIT-14 results in a completely connected framework of CIT-14.



Figure 8.11. Schematic illustration of the inverse sigma transformation from CIT-13 to CIT-14.



Figure 8.12. Examples of the inverse sigma transformation from CIT-13/OH to CIT-14 examined on the basis of PXRD patterns in the range of (a) $4-30^{\circ}$ and (b) $5-10^{\circ}$.



Figure 8.13. Trials of the inverse sigma transformation using a high-Ge CIT-13/F and a low-Ge CIT-13/OH examined on the basis of PXRD patterns in the range of (a) $4-30^{\circ}$ and (b) $5-10^{\circ}$.

Interestingly, the inverse sigma transformation of Ge-CIT-13 was only possible for Ge-CIT-13/OH[y] (y < 3.71); i.e., only Ge-CIT-13 synthesized from *the hydroxide-media recipe having very high germanium content* underwent this type of transformation and yielded ordered CIT-14. Figure 8.12 shows the PXRD profiles of a couple of examples of inverse sigma transformation of parent Ge-CIT-13/OH samples yielding CIT-14 products. It is noteworthy that the intermediate -CIT-14 materials already showed PXRD patterns very similar to those of CIT-14 even before calcination. CIT-14 samples obtained by the inverse sigma transformation were referred to as CIT-14/IST where IST stands for inverse sigma transformation. Ge-CIT-13/F[3.87] synthesized in fluoride media and Ge-CIT-13/OH[4.33] having a high Si/Ge ratio resulted in disordered materials after acid-leaching of germanium followed by calcination (Figure 8.13).

It has been a long-standing question why only IM-12 could yield its inverse sigma transformation products. Kasian et al. investigated the germanium arrangement within the *d4r* units of UTL, ITH, and IWW frameworks in terms of ¹⁹F MAS NMR and ¹H-²⁹Si CP-MAS NMR spectroscopy.¹⁷⁶ Unlike ITH and IWW, as shown in Figure 8.14(a), UTL-type germanosilicate IM-12 showed no Q^2 signal in the ¹H-²⁹Si CP-MAS NMR spectrum after complete degermanated using distilled water.¹⁷⁶ The absence of Q^1 and Q^2 signals in completely degermanated *d4r*-containing frameworks in the ¹H-²⁹Si CP-MAS NMR spectra is possible only when one whole side of the *d4r* units consists only of germanium T-atoms.¹⁷⁶ Unlike UTL, ITH and IWW showed strong Q^2 signals.¹⁷⁶ They suggested this absence of Q^2 signal in the ¹H-²⁹Si CP-MAS NMR spectra that IM-12 has a unique arrangement of germanium T-atoms within the *d4r* units different to other germanosilicates.¹⁷⁶



Figure 8.14. Silanol characterization after water-degermanation of germanosilicates. (a) ¹H-²⁹Si CP-MAS NMR spectra of water-degermanated (WDG) ITQ-13, ITQ-22, and IM-12. Reproduced with Permission from Ref [176]. Copyright 2014 American Chemical Society. (b) ¹H-²⁹Si CP-MAS NMR spectra of water-degermanated Ge-CIT-13/F, Ge-CIT-13/OH, and IM-12 samples having various Si/Ge ratios. WDG stands for 'water-degermanated.'

Several CIT-13/OH, CIT-13/F, and IM-12/OH having various Si/Ge ratios were subjected to a similar degermanation experiment, and their ¹H-²⁹Si CP-MAS NMR spectra were acquired (Figure 8.14 (b)). Just like in Kasian's experiment, degermanated IM-12 samples showed very weak Q² signals. However, CIT-13/OH and CIT-13/F samples showed Q² signals of moderate and strong intensities. Interestingly, Ge-CIT-13/OH[3.71] showed the weakest Q² signal after degermanation among all degermanated CIT-13 samples. This

sample is the only Ge-CIT-13 which successfully underwent the inverse sigma transformation among all four Ge-CIT-13 samples subjected to this test. I believe that the arrangement of germanium T-atoms within the d4r units has a close relationship with the use of fluoride as the mineralizing agent. It is also known that fluorides can structure-direct the d4r units in high-silica gels and form a penta-coordinated germanium within the d4r units. Further experimental evidence must be obtained to elucidate the role of fluoride in the CIT-13 synthesis.



Figure 8.15. 8 kHz MAS ²⁹Si NMR spectra and ¹H-²⁹Si CP-MAS NMR spectra of the parent CIT-13/OH and the resultant CIT-14 produced via the inverse sigma transformation.

Si/Ge ratios of CIT-14 samples obtained from Ge-CIT-13/OH[3.56] and Ge-CIT-13/OH[3.71] were 14.5 and 17.5, respectively, which are much lower than CIT-14/ESP samples discussed in the previous section. This suggests that the remaining parts of *d*4*r* units still have a significant amount of germanium T-atoms. ²⁹Si MAS and ¹H-²⁹Si CP-MAS NMR spectra of the parent Ge-CIT-13/OH and the resultant CIT-14/IST were acquired. (Figure 8.15) The parent Ge-CIT-13/OH showed a typical "three-peak" shape of ²⁹Si spectrum of CIT-13 which was discussed in the previous chapter. CIT-14/IST showed a broad signal across the region from -100 to -120 ppm, which must be consisting of many signals originated from the combination of 7 T-sites of CIT-14 and the presence of germanium.

Lastly, argon adsorption isotherms of the parent CIT-13, CIT-14/IST and CIT-14/ESP (which were shown in the previous section) were compared and displayed in Figure 8.16. CIT-14/IST showed no mesoporosity-induced hysteresis and a micropore volume value (t-plot: 0.105 cc g^{-1} ; Saito-Foley: 0.141 cc g^{-1}) higher than that of CIT-14/ESP (t-plot: 0.065 cc g^{-1} ; Saito-Foley: 0.102 cc g^{-1}). This suggests that the inverse sigma transformation yields purer CIT-14 having better microporosity and crystallinity than the ethoxysilylational pillaring of layered CIT-13P method. The parent Ge-CIT-13/OH[3.56] showed a micropore volume of 0.202 cc g^{-1} on the basis of the Saity-Foley model (based on t-plot method, 0.141 cc g^{-1}). The ratio of the micropore volume of CIT-14/IST to that of Ge-CIT-13 is 0.698. The specific micropore volumes of CIT-14 and CIT-13 having Si/Ge ratios of 14.5 and 3.56 calculated using the TOTOPOL utility¹⁹⁹ are 0.088 cc g⁻¹ and 0.126 cc g⁻¹, respectively. The ratio of these theoretical values is also 0.698 which is very close to the observed CIT-14/CIT-13 microporosity ratio.



Figure 8.16. Argon adsorption isotherms (87.45 K) of the parent CIT-13/OH, two CIT-14 products from the inverse sigma transformation and the ethoxysilylational pillaring in (a) linear scale and (b) log scale.

8.3.3. CIT-15 Formation by Direct Condensation



Figure 8.17. Schematic illustration of the topotactic transformation from Ge-CIT-13 to CIT-15 by the direct condensation of CIT-13P.



Figure 8.18. Experimentally demonstrated topotactic transformation from Ge-CIT-13 to CIT-15 investigated on the basis of PXRD patterns.

Another novel framework that can be derived from Ge-CIT-13 is CIT-15, a mediumpore framework having one-dimensional channel system. This transformation is an analogue of the topotactic transformation of UTL to PCR.¹²² In this transformation, layered CIT-13P is directly condensed by calcination. This process is schematically described in Figure 8.17. Figure 8.18 shows the involved steps of transformation in terms of PXRD patterns. The interlayer diffraction peaks are labelled with arrows (\downarrow). Initially, the parent Ge-CIT-13 had an interlayer distance of 13.6 Å which is a typical (200) interlayer distance of CIT-13. After acid-delamination, this interlayer distance was decreased down to 11.1 Å. As a result of condensation, the interlayer distance was decreased again to 8.6 Å, which is corresponding to the theoretically predicted position of interlayer diffraction of CIT-15 (8.7 Å) calculated on the basis of the GULP algorithm.¹⁹⁸



Figure 8.19. Structure, pore sizes, and expected topological information of CIT-15.

Just like the case of CIT-14, the structure and topological information of the product (CIT-15) of this topotactic transformation can be predicted on the basis of computational chemistry. Figure 8.19 shows the predicted structural and micropore information of CIT-15 calculated based on the TOTOPOL analysis.¹⁹⁹



Figure 8.20. Influence of degree of delamination of Ge-CIT-13 on the formation of CIT-15 (a) Design of experiment. PXRD patterns of the resultant CIT-15 samples in the range of (b) $4-40^{\circ}$ and (c) $6-12^{\circ}$.

To successfully achieve the transformation from CIT-13 to CIT-15, all T-atoms formerly constituting the d4r bridging units must be eliminated from the system during the delamination. This engenders a key difference between the transformations from CIT-13 to CIT-14 and CIT-15. In the transformation from CIT-13 to CIT-14, it was experimentally observed that the extent of acid-degermanation is not an important factor presumably because a small amount of remnant T-atoms which had been parts of d4r units still can constitute

newly formed silica *s*4*r* units together with foreign silicon sources. However, since the transformation from CIT-13 to CIT-15 requires direct connections between neighboring *cfi*-layers, ideally, no interlayer remnant T-atom is allowed. As shown in the PXRD patterns of Figure 8.20, unlike the case of CIT-14, the interlayer distance of condensed phases has a close relation with the extent of delamination of Ge-CIT-13. The successful formation of CIT-15 framework was determined on the basis of PXRD patterns and, particularly, the position of interlayer diffraction which is predicted to be at 10.12° in two-theta. As clearly seen from the diffraction patterns, 48 hours of acid-delamination was required to fully delaminate the parent Ge-CIT-13/F[4.33]. An issue with the resultant CIT-15 products is its poor crystallinity.

In case of the UTL-to-PCR transformation, octylamine was necessarily intercalated between neighboring IPC-1P layers as a layer-reassembling agent to obtain the resultant PCR-type IPC-4 with a high crystallinity.¹²² To enhance the crystallinity of CIT-15, several aliphatic amines (octylamine, heptylamine, and dipropylamine) were intercalated within the interlayer region of CIT-13P. However, none of these aliphatic amines successfully improved the poor crystallinity of CIT-15 formed. The PXRD patterns of the resultant CIT-15 from amine-intercalation were provided in Figure B19.

The direct condensation of CIT-5P layered materials from Ge-CIT-5 which is also the preceding transformation from Ge-CIT-13 was attempted. As expected, due to the presence of interlayer siliceous remnant of acid-delamination which was discussed in the previous section, none of CIT-5P samples successfully condensed into CIT-15-type materials (Figure B20). Their interlayer distance peaks were observed within the range between 9.0° and 9.3° which is far lower-angle than the predicted position of CIT-15 interlayer diffraction (10.12°). Even a CIT-5P obtained from one week of acid-delamination of Ge-CIT-5 did not produced a CIT-15-type product (not shown). Instead of the acid-delamination using 0.1 M HCl solution which could not remove the delamination remnant of Ge-CIT-5, the base-delamination using ammonium hydroxide solution was tried in order to effectively remove the interlayer siliceous remnants which inhibited the direct connection between neighboring two *cfi*-layers of CIT-5P. Very recently, Liu and co-workers reported the formation of ECNU-21 which is essentially an isostructural framework of CIT-15 by delaminating Ge-CIT-13 with diluted ammonium hydroxide (1 % in H₂O) at room temperature.¹⁶⁷ In this work, the concentration of ammonium hydroxide was controlled. Ge-CIT-5[4.22] was dispersed in 1 wt. % and 3 wt. % of ammonium hydroxide solution and stirred for 24 hours at room temperature. The resultant CIT-5P/*x*%Am (x = 1, 3) was recovered by filtration and condensed by calcination.

The PXRD profiles of resultant materials are shown in Figure 8.21. The basedelamination using 1 % ammonium hydroxide could not fully delaminate Ge-CIT-5[4.33]. Although an interlayer diffraction close to the predicted position of CIT-15 was observed in the PXRD pattern of the condensed phase, the majority was still a disordered CIT-5-like phase in the PXRD pattern of CIT-5P/1%Am. On the other hand, 3 % ammonium hydroxide successfully delaminated Ge-CIT-5 leaving no remaining disordered parent phase. This CIT-5P/3%Am was condensed into a phase which shows a PXRD profile very similar to that of the theoretical CIT-15. The interlayer distance of the condensed CIT-5P/3%Am calculated from the peak position was 8.49 Å which is shorter than the theoretical value of 8.73 Å. This result suggests that the concentration of ammonium hydroxide is the key variable for the complete delamination of Ge-CIT-5 although materials can be "overly delaminated" if the concentration is too high.



Figure 8.21. Pathway from CIT-13 to CIT-15 and characterizations. (a) Schematic illustration of transformation from Ge-CIT-5 to CIT-15 via ammonium delamination. (b) PXRD patterns of intermediate and resultant products.

8.3.4. Effects of Solution Acidity on Alumination

8.3.4.1. Postsynthetic Degermanation and Alumination of Ge-CIT-13



Figure 8.22. Schematic illustration of postsynthetic degermanation/alumination of Ge-CIT-

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Sample	Parent Ge-CIT-13	Solution		Elemental Composition of Product		
Sample		$\left[H^{+}\right] (M)$	[Al ³⁺] (M)	Si/Al ratio (Al/T %)	Si/Ge ratio (Ge/T %)	
Al-CIT-13(1)		1	1	80 (1.2)	59 (1.6)	
Al-CIT-13(2)		1	0.67	120 (0.81)	61 (1.6)	
Al-CIT-13(3)	Si/Ge = 5.1	1	0.33	150 (0.66)	70 (1.4)	
Al-CIT-13(4)	16% Ge/T	0.67	1	46 (2.1)	76 (1.3)	
Al-CIT-13(5)		0.33	1	18 (5.2)	79 (1.2)	
Al-CIT-13(6)		0	1	12 (7.7)	79 (1.2)	
Al-CIT-13(7)	Si/Ge = 4.1	1	1	77 (1.3)	44 (2.2)	
Al-CIT-13(8)	20% Ge/T	0	1	12 (7.8)	56 (1.6)	



Figure 8.23. Material characterization of Al-CIT-13 samples. (a) PXRD profiles of aluminated Al-CIT-13 samples and those of the parent Ge-CIT-13s. SEM images of (b) Al-CIT-13(1) and (c) Al-CIT-13(7) samples.

No structural degradation was observed across all trials. For the sample series of Al-CIT-13(1), (2), and (3), the concentration of nitric acid were a fixed constant at $[H^+] = 1$ M and the concentrations of Al³⁺ were changed. The degree of alumination was almost proportional to the Al³⁺ concentration of acidic aluminum solution. The Si/Al ratios of the resultant Al-CIT-13 samples were in the range of 80–150. When the concentration of Al³⁺ was fixed, the lower the acidity was, the more Al was incorporated. The maximum Alincorporation was achieved when pure 1 M Al(NO₃)₃ solution was used (Al-CIT-13(6)). It is known that the isoelectric point (pI) of silica surface is approximately 2.0 which is lower than the pH of pure 1 M Al(NO₃)₃ solution (2.45).²⁰⁰ The presence of aluminum in the solution phase can prevent the structure degradation by occupying the defect sites previously occupied by germanium.¹⁵⁸



Figure 8.24. Al-site and defect characterizations of Al-CIT-13 samples. (a) 12 kHz MAS solid-state ²⁷Al NMR spectra of Al-CIT-13 samples. (b) 8 kHz MAS ¹H-decoupled solid-state ²⁹Si NMR spectrum and 8 kHz ¹H-²⁹Si CP-MAS solid-state NMR spectrum of Al-CIT-13(3) sample.

However, a low acidity also resulted in the formation of extra-framework aluminum species as shown in the ²⁷Al NMR spectra in Figure 8.24(a). The resonances for tetrahedral and octahedral (extra-framework) aluminum species were observed at 50–55 ppm and 0 ppm, respectively. No penta-coordinated aluminum species was observed. In the two samples Al-CIT-13(5) and (6) which had the highest extents of Al-incorporation, significant amounts of octahedral aluminum species were detected. These two samples are ones treated with solutions of low acidity ([H⁺] < 0.33 M). Shamzhy et al. conducted a similar study using only 1 M Al(NO₃)₃ solution to aluminate germanosilicate ITH-type molecular sieves; octahedral aluminum species were observed in all of their samples regardless of the elemental composition of the parent germanosilicate and/or the treatment temperature.¹⁶⁰ However, no extra-framework aluminum was detected in the other Al-CIT-13 samples. Therefore, it can be concluded that low acidity results in octahedral aluminum species. It is desirable to control the pH of solution below 0.17 ([H⁺] = 0.67 M) to prevent the formation of extra-framework aluminum species within the channel systems.

Also, the ²⁹Si NMR spectrum and ¹H-²⁹Si CP-MAS spectrum displayed in Figure 8.24(b) revealed that a majority of silicon atoms in Al-CIT-13(3) are not associated with silanol defects, showing mostly Q^4 -Si resonances. No deconvolution was attempted in this work. A small amount of Q^3 -silanols did exist in the samples. The observed extents of degermanation were almost the same across all samples. It can also be concluded that most of germanium atoms had presented within Ge-CIT-13 frameworks were replaced with framework silicon and aluminum atoms.



Figure 8.25. Catalysis of Al-CIT-13. (a) Conversions and yields of the decane hydrocracking/hydroisomerization reaction over Pt-CIT-13 catalyst by reaction temperatures. (b) Product distribution chart of the decane hydroisomerization of Pt-CIT-13. (c) Product distribution chart of the methanol to hydrocarbon reaction over Al-CIT-13 samples.

The hydrocracking/hydroisomerization reaction of decane over Pt-loaded Al-CIT-13 was performed by Dr. C. Y. Chen and collaborators from Chevron. (Figure 8.25(a) and (b)) *n*-decane in hydrogen flow (170 mL min⁻¹) was fed with a flow rate of 1 mL-liquid h⁻¹. The reaction pressure was 1.2 kpsi. Extra-large-pore CIT-13 required a higher temperature (ca. 300 °C for maximum isomerization; ca. 330 °C for 100% decane conversion) to isomerize n-decane into monomethyl nonanes than medium-pore Pt-ZSM-5 (ca. 185 °C for maximum isomerization; ca. 195 °C for 100% decane conversion),²⁰¹ but much lower than mesoporous Pt-MCM-41 which required higher than 400 °C for 100% decane conversion.²⁰² The decane isomerization product selectivity order from Pt-CIT-13 shown in Figure 8.25(b) was 3 - 4 - 2 - 5-methylnonane which was apparently different to that of Pt-ZSM-5 2 - 3 - 4 - 5 - 5-methylnonane.²⁰¹

The methanol conversion was also conducted to confirm the porosity and solidacidity of Al-CIT-13, and the result was compared to that of Al/Ge-CIT-13 directly synthesized from one of ternary-composition gels shown in Chapter VI. The product selectivity distributions of two Al-containing CIT-13 are shown in Figure 8.25(c). Here, the resultant product distributions were not analyzed in detail since the 14-ring channel of CIT-13 is too wide to expect any shape selectivity. But this result sufficiently proves the surface acidity of Al-CIT-13 prepared on the basis of postsynthetic alumination.

8.3.4.2. Postsynthetic Degermanation and Alumination of Ge-CIT-5



Figure 8.26. Schematic illustration of the CIT-13-to-5 transformation followed by the postsynthetic degermanation/alumination of Ge-CIT-13.

Similarly to the case of postsynthetic alumination of Ge-CIT-13 shown in the previous section, Ge-CIT-5 samples derived from Ge-CIT-13 were also subjected to the analogous postsynthetic alumination procedure. Here, Ge-CIT-5 having a Si/Ge ratio of 4.31 was treated with a series of mixtures of aluminum nitrate and nitric acid having varied concentrations. The treatment was performed at 185 °C for 24 hours. The concentrations of H⁺ and Al³⁺ and the elemental compositions of the resultant materials were shown in Table 8.2. Here, the CFI-type molecular sieves prepared from this postsynthetic alumination of Ge-CIT-5 were denoted Al-CIT-5(#) where # is the sample number shown in Table 8.2. The postsynthesis resultant material treated without aluminum (acid only) was denoted Si-CIT-5.

Sample	Parent Ge-CIT-5	Solution			Elemental Composition of Product	
		$\left[H^{+}\right] (M)$	$[Al^{3+}](M)$	pН	Si/Al ratio (Al/T %)	Si/Ge ratio (Ge/T %)
Al-CIT-5(1)		0	1	2.45	13 (7.0)	56 (1.6)
Al-CIT-5(2)	Si/Ge = 4.31	0.1	0.5	0.30	39 (2.5)	47 (2.0)
Al-CIT-5(3)	16% Ge/T	0.5	0.1	0.05	170 (0.7)	38 (2.6)
Si-CIT-5		1	0	0	-	33 (3.0)

Table 8.2. Summary of postsynthetic alumination of Ge-CIT-5

The overall process from Ge-CIT-13 to Al-CIT-5 is illustrated in Figure 8.27(a) with PXRD patterns of stages involved in the transformation. Similarly to the case of the postsynthetic alumination of Ge-CIT-5, the higher the concentration of aluminum of treating solution was, the higher aluminum content the resultant Al-CIT-5 had. It is noteworthy that the Si/Al ratio of Al-CIT-5(2) is much lower than that of aluminosilicate CIT-5 from a direct hydrothermal synthesis.¹³²



Figure 8.27. Material characterization of Al-CIT-5 samples. (a) a series of PXRD patterns showing the entire transformation sequence: Ge-CIT-13 \rightarrow Ge-CIT-5 \rightarrow Al-CIT-5. (b) PXRD patterns of resultant Al-CIT-5 samples and Si-CIT-5. (c) 12 kHz MAS solid-state ²⁷Al NMR spectrum of an Al-CIT-13 sample.

A disordered material (Al-CIT-5(1)) was produced when only aluminum nitrate was used. In the PXRD profile of Al-CIT-5(1) (the profile highlighted with red color in Figure 8.27(b)), an extra peak appeared at a diffraction angle (6.62°) lower than the typical (002) diffraction angle ($6.9-7.0^{\circ}$) of CIT-5. Although it cannot be clearly explained at this point due to a lack of further experimental evidence, some type of intercalation of T-atom might have happened at a low acidity, which resulted in an expansion of unit cell in the *c*-direction. The other Al-CIT-5 and Si-CIT-5 samples showed almost no structural degradation on the basis of PXRD patterns. Figure 8.27(c) shows the ²⁷Al NMR spectra of Al-CIT-5(2) in which

no extra-framework aluminum signal (ca. 0 ppm) is present. This result further supports the conclusion that increasing acidity of the solution phase prevents the formation of extra-framework aluminum species in postsynthetic alumination processes.

8.4. Summary

In this chapter, various transformations and postsynthetic modifications of Ge-CIT-13 and Ge-CIT-5 were discussed. First, the acid-delamination of Ge-CIT-13 and Ge-CIT-5 was investigated in terms of delamination time. While the interlayer distances of delaminated CIT-13P kept decreasing as the acid-delamination proceeded, the delamination products from Ge-CIT-5 showed no further decrease in the interlayer distances after 3 hours of acidtreatment. The ²⁹Si solid-state NMR spectra suggested that the extent of acid-delamination of Ge-CIT-5 was poor.

Secondly, CIT-14 was prepared via two protocols. One was the ethoxysilylational pillaring and the other was the inverse sigma transformation. The ethoxysilylational pillaring was not seriously affected by the extent of delamination of CIT-13P. The inverse sigma transformation of CIT-13 into CIT-14 was only possible for low-Si/Ge (< 3.71) CIT-13 samples synthesized from hydroxide-mediated recipes. The microporosity of CIT-14 from the inverse sigma transformation was better than that of CIT-14 from the ethoxysilylational pillaring.

Thirdly, the condensation of CIT-13P/5P layered materials forming CIT-15 was investigated. Unlike the case of CIT-14, the extent of delamination was important in the preparation of CIT-15 because the condensation must be completely achieved directly between the neighboring CIT-13P/5P layers. It was impossible to obtain CIT-15 from the condensation of CIT-5P presumably due to the presence of delamination remnant species.

Instead, the base-delamination was performed for CIT-5P and a structure very close to CIT-15 was obtained.

Lastly, postsynthetic alumination of Ge-CIT-13 and Ge-CIT-5 yielding Al-CIT-13 and Al-CIT-5 was examined in terms of the acidity of the treating solutions. Increasing acidity resulted in lower degrees of aluminum incorporation and formation of octahedral aluminum species.