Altering Framework Topology and Heteroatom Distributions of Molecular Sieves by Designed Organic Structure-Directing Agents

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ABSTRACT

The growing demand for chemical production combined with the urgent need to mitigate the accelerated climate and environmental changes motivates efforts to create highly efficient and selective catalysts and adsorbents. Zeolites and molecular sieves are a key class of materials for addressing these needs because of their high activity and selectivity with catalytic reactions. Additionally, they can show superior adsorption properties because of their structure and surface polarity that can also give shape selectivity with molecules smaller than ca. 1 nanometer. Further advancements in molecular sieve properties will rely on advancements in preparation methods. To this end, the research results presented here explore synthetic approaches for controlling the framework topology and the heteroatom incorporation within silicate-based molecular sieves by means of the strategic design of their organic structure-directing agents (OSDAs).

Part I presents the synthesis of STW-type germanosilicate molecular sieves with high-silica framework compositions and the enrichment of chirality. A chiral OSDA is computationally designed based on the predicted stabilization energy toward the pure-silica STW framework. An improved synthesis route for both enantiomers of the OSDA is developed. The enantiopure OSDA is capable of crystallizing a high-silica STW-type germanosilicate molecular sieve that shows distinct framework compositions from previously reported germanium-rich STW. The enantiomeric enrichment of powdered samples without occluded enantiopure OSDAs is characterized by the dynamical refinement of microcrystal electron diffraction data. The high-silica, enantiomerically enriched STW exhibits the framework stability upon thermal treatment and the enantioselective adsorption of 2-butanol. The results in Part I demonstrate the design strategy of OSDAs for crystallizing stable, enantio-enriched molecular sieves for enantioselective chemical separations and catalysis.

In Part II, the distribution of heteroatoms incorporated within borosilicate molecular sieves is studied with regard to its control by cationic OSDAs. To aid in the characterization of the heteroatom sites within borosilicate molecular sieves, the relationship between the ¹¹B NMR chemical shift and the local geometry of boron within tetrahedrally coordinated silicate frameworks is first investigated. From crystalline borosilicate minerals with highly ordered, tetrahedrally coordinated boron atoms, it is revealed that the chemical shifts from ¹¹B NMR linearly correlate with the local geometric parameters. Further studies on the borosilicate molecular sieves that possess more open space and wider angles suggest that the correlation between the average bond angles and ¹¹B NMR chemical

shifts can be employed for the entire class of three-dimensional, crystalline borosilicates. Two structurally similar quaternary ammonium OSDAs with different locations of positive charge are designed and synthesized. MWW-type borosilicate molecular sieves are crystallized by both OSDAs, and the quaternary ammonium moieties in the two OSDAs are found to interact with boron species with significantly different ¹¹B NMR chemical shifts. Using the correlation developed here, the characterization results demonstrate that the heteroatom siting within the molecular sieve framework can be selectively altered by tailoring the OSDA structure in terms of the position of positive charge.

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Chapter 1

INTRODUCTION TO PART I

This chapter introduces the concepts of molecular sieves and their synthesis. Then, a brief background of chiral molecular sieves and the previous efforts to prepare enantiopure molecular sieves are presented with the motivation for research. The overview of Part I is then discussed.

1.1. Introduction to Molecular Sieves

Global production in the chemical industry is projected to continue growing with an approximate rate of 3% per year, outpacing the rate of global population growth.¹ In the meantime, environmental and climate change caused by anthropogenic activities are gradually accelerating.² To meet the growing demand of chemical production while mitigating the impact of climate changes, the development of catalysts and adsorbents that can enable the efficient processes is essential. Molecular sieves are the class of materials to address these needs as they are finding a wide range of applications for chemical production and purification processes as heterogeneous catalysts and adsorbents with crystalline microporous structures.^{3–8} Zeolites, the aluminosilicate analogues of molecular sieves, are particularly serving as one of the essential catalysts for commercial processes including fluid catalytic cracking (FCC), biomass conversion, NO_x reduction, and methanol-to-hydrocarbons (MTH).⁹

The term molecular sieve, coined by J. W. McBain¹⁰ to describe a class of materials exhibiting selective adsorption properties, represents the crystalline tetrahedral frameworks

with various types of atoms coordinated to oxygen atoms. In typical molecular sieves with a tetrahedral oxide network of $TO_{4/2}$, T-atoms can be Si⁴⁺, Al³⁺, P⁵⁺, Ti⁴⁺, Ge⁴⁺, Co²⁺, etc. For example, zeolites have three-dimensional networks of tetrahedrally coordinated Si, Al atoms linked to each other by bridging oxygen atoms.¹¹ Pure-silica and aluminophosphate (AlPO)-based polymorphs of zeolites are also classified as molecular sieves.¹² The first natural zeolite was discovered in 1756, and the effort to produce synthetic zeolites was first reported in 1862.¹³ Since then, there have been over 250 different types of frameworks classified by the International Zeolite Association based on the pore size and the number of network dimensions.^{14,15} These various microporous structures are the key features of the molecular sieves, and each framework is assigned a three-letter code assigned by the Structure Commission of the international zeolite association (IZA-SC) based on the pore opening sizes and the connectivity of the pores. Some codes start with "-" or "*," which indicate an interrupted framework or a structure possessing intergrowth or disorders, respectively. For example, zeolite beta (*BEA) is an intergrowth of polymorphs A and B.¹⁶ The pore openings are described by the term 'Ring,' which contains information of the number of T atoms included: if a ring contains n T and n O atoms, it is called an nMR (nmembered ring). When a pore builds up a polyhedral shape with multiple faces, it is classified as a cage or a cavity, depending on the ring size. A cage is a multi-face pore with no ring larger than 6MR, while a cavity has at least one so that molecules larger than water can penetrate through it. The term cage is often used to cover the cavity as well. The pore with openings larger than 6MR and extended in one dimension is called a channel, which can form various networks from one-dimensional to three-dimensional intersections. Examples of the porous structures and corresponding assignments are shown in **Figure 1.1**. While CHA

and EEI both contain 8MR pores, the difference in their locations and connectivity to other types of pores result in distinct cages and overall topologies.



Figure 1.1. Pores, cages, and their three-dimensional connectivity of CHA and EEI frameworks (reproduced from ref. (17) with permission from American Chemical Society).

The framework structures of molecular sieves possess porous channels and cavities with the sizes of typical molecules of interest (5–12 Å), and the confined space within the porous structure alters the thermodynamics and transport of the substrate molecules including reactants, products, and the transition states, resulting in the shape-selective behavior on the catalytic reactions.^{18–21} The shape selectivity to reactants and products originates from the mass transport limitation by the pore size comparable to the molecules.²² Transition state selectivity occurs when the pores, cages, or cavities of a zeolite preferably stabilizes one of the possible transition states by interacting with each other. Therefore, it is important for industrial applications to produce a molecular sieve with specific structural properties that can result in desired catalytic behaviors.

The synthesis of targeted frameworks of molecular sieves is controlled by a combination of various conditions such as types of atoms and their sources, temperature, pH, and agitation. One of the most important factors for synthesizing desired frameworks is organic structure-

directing agents (OSDAs).²³ After Barrera and Denny²⁴ first reported using organic cations to increase the Si/Al ratio in the aluminosilicates, OSDAs have been widely used to facilitate the synthesis of new zeolite structures of high-silica molecular sieves or aluminophosphate (ALPO) materials with various framework topologies.²⁵ Not only adjusting the framework compositions, it has been reported that OSDAs can alter the heteroatom site distributions and the preferred framework topologies. Although OSDAs are not completely framework-specific and the same OSDA can lead to different zeolite structures depending on the experimental conditions²⁶, they still enable the targeted synthesis of molecular with particular framework topologies by filling the porous space and stabilizing the silicate framework during the synthesis (**Figure 1.2**). Based on their selectivity to specific frameworks, it has been reported that computationally predicted OSDAs could form the desired framework topologies, for example, SSZ-39 (AEI)²⁷, and SSZ-52 (SFW)²⁸, DAF-5 (CHA), and HPM-1(STW).

The research work presented here aims to design OSDAs to obtain molecular sieves with desired framework topology, framework compositions, and the altered distribution of the heteroatom-incorporated sites. The synthesis and characterization of designed OSDAs and corresponding molecular sieves are discussed.



Figure 1.2. (a) Schematic illustration of the synthesis of CHA-type zeolite with N,N,Ntrimethyladamanammonium hydroxide as OSDA (reproduced from ref. (29) with permission from Elsevier). (b) Simulated pore-filling conformation of OSDA within BEA-type frameowkr structure (reproduced from ref. (15) with permission from the Royal Society of Chemistry).

1.2. Background and motivation for Part I

Enantioselectivity is one of the characteristics of living systems as it is found in enzymatic reactions, messenger-receptor interactions, and metabolic processes.^{30,31} In pharmaceutics, one of the two enantiomers is often more active for a given action (eutomer) while the other (distomer) might contribute to side effects or show activity in different ways.³² Therefore, the development of enantiomerically pure compounds and revealing each enantiomer's functionality is critical. The agrochemical and crop protection industries have also set a high value on enantiomer separation in that the presence of a non-active or less active stereoisomer increases the amount of pollution rather than the benefit of the desired action.³³

In this regard, the synthesis of chiral zeolites and molecular sieves has intrigued researchers' interest due to their potential applications for asymmetric catalysis and chiral separations.^{3,16,34} A few zeolitic frameworks such as *BEA³⁵, CZP³⁶, GOO³⁷, and VNI³⁸ that have chiral features within the structure have been reported, and there have been efforts to synthesize enantiopure zeolites and molecular sieves with those frameworks. *BEA is a crystalline intergrowth of a racemic mixture of polymorphs A and achiral polymorph B. The synthesis of polymorph A (BEA) has been studied more than other chiral frameworks due to its wide industrial application such as benzene alkylation and separation of aromatic compounds from aqueous phases^{39,40}. Synthesis of polymorph A-enriched *BEA and observation of low ee's from chemical reactions have been reported.^{41–43} However, the intergrowing nature of *BEA makes it difficult to synthesize a pure BEA material. Moreover, the synthesis of enantiomerically enriched BEA materials is another demanding task.

Another chiral framework, STW, has also attracted research interest for its synthesis in an enantiomerically enriched form. STW contains a 10 MR helical channel. Unlike the normal definition of point chirality which employs the chiral centers in organic and coordination chemistry, the chirality of BEA and STW originates from the handedness of the spiral rotation of the helical channels (**Figure 1.3**). Thus, the handedness of the helical pore determines the space group between P6₁22 and P6₅22. While *BEA has a polymorph intergrowth nature, STW was first synthesized as a monomorphous, germanosilicate molecular sieve with a racemic mixture of two enantiomeric porous crystals.⁴⁴



Figure 1.3. The helical pore and its handedness in BEA: (a) and (b), reproduced from ref. (45) with permission from the Royal Society of Chemistry, and STW: (c) and (d), reproduced from ref. (46) with permission from Wiley.

After Camblor *et al.*⁴⁶ reported the pure-silica STW molecular sieve, Davis and Deem *et al.*⁴⁷ reported the computational results for stabilization energy of alkyl imidazolium compounds within a pure silica STW framework and showed that those with stabilization energy below -16 kJ/mol Si produced pure silica STW molecular sieves. The synthesis of aluminosilicate STW was also attempted using tetraethyl orthosilicate (TEOS) and aluminum isopropoxide as inorganic sources and 1,2,3,4,5-pentamethylimidazolium OSDA by Schmidt *et al.*²⁶, which in turn formed RTH in the presence of Al. The aluminosilicate STW (Si/Al = 110) was synthesized by Jo *et al.*⁴⁸ using TEOS and aluminum hydroxide as inorganic sources and 2-ethyl-1,3,4-trimethylimidazolium compound as an OSDA. The STW zeolite showed a superb activity and selectivity to the skeletal isomerization of 1-butene with resistance to deactivation. However, all these materials did not exhibit any enantio-enriched features due to the use of non-chiral OSDAs.



Figure 1.4. (a) OSDAs and their calculated stabilization energies (kJ/mol Si) in STW and (b) corresponding molecular sieve synthesis results (reproduced from ref. (47) with permission from Wiley).

Unlike the racemic forms with pure-silica composition, the molecular sieves with enantiomeric enrichment have been prepared in the presence of Ge in the synthesis gel. In 2017, Brand *et al.*⁴⁹ reported the synthesis of the first enantiomerically enriched STW molecular sieves by integrating computational prediction of stabilization energy of OSDAs and the employment of germanium as a substituent. The Deem group conducted the computational design of a rigid and chiral OSDA for STW. Since 1,2,3,4,5- pentamethylimidazolium (12345PMI) cation has an occupancy of two molecules per cage in STW, they simulated di-quaternary (diquat) OSDAs that have chiral alkyl linkers between two PMIs. The criteria for a proper OSDA were the stabilization energies lower than -15 kJ/mol Si for one enantiomer and larger than -2 kJ/mol for the other, and the di-quaternary alkyl imidazolium compound with the trans-1,2-dimethylclopropane moiety as a chiral linker was selected as an OSDA. They demonstrated that R- and S- aluminogermanosilicate STW imposed enantioselectivity to a ring-opening reaction of epoxy-alkanes when reagents are compatible with the OSDA in terms of the molecular shape and size. They also showed that

R- and S- STW germanosilicates adsorbed 2-butanol in an enantioselective manner. However, the enantiomerically enriched STW was formed only when the gel contained enough germanium (Si/Ge = 2). The product Si/Ge was less than 1.

More recently, the synthesis of another type of enantiomerically enriched molecular sieve, GTM-3 and GTM-4, was reported with the aid of Ge in the gel.^{50–52} By means of the extralarge pore structure of -ITV, GTM-3 and GTM-4 showed a promising enantioselectivity of these materials toward the epoxide ring opening reactions. Consistently, these materials contained a large amount of Ge in the product (e.g., Si/Ge = $2.6 \sim 2.8$).

As the same group element with a larger radius, germanium can substitute for the tetrahedral silicon sites within the framework structure. Sastre and Corma computationally showed that germanium substitution in a pure silica molecular sieve decreases the T-O-T angle (Si-O-Ge or Ge-O-Ge) smaller than 145°, while Si-O-Si angle tends to be stable between 155° and 160° (**Figure 1.5a**).⁵³ The small T-O-T angle facilitates the creation of small-ring secondary building units (SBUs) such as double-3-ring (d3r) and double-4-ring (*d4r*).^{54,55} Therefore, for the frameworks that contain small SBUs such as UOZ and ASV, the substitution of silicon by germanium relieves the structural strain by the preferable location of germanium atoms at smaller T-O-T angles. **Figure 1.5b** shows the simulation results indicating that the replacement of silicon by germanium can either increase or decrease the stability depending on the framework structure. STW consists of *d4r* as the only composite building unit (CBU), and Rigo *et al.*⁵⁶ reported that the addition of a proper amount of germanium substitution stabilizes the STW molecular sieve (**Figure 1.5c**).

In contrast to its advantage of stabilizing small-angle CBUs, germanium incorporation brings in the issues of (hydro)thermal stability. When OSDAs are removed and germanium is exposed to humidity, Ge-O bonds tend to hydrolyze by water vapor and form Ge-OH.⁵⁷ Gerich molecular sieves lose crystallinity even at ambient humidity. Similarly, the low thermal stability of germanium atoms makes them easily come out of the *d4r* positions by thermal treatments. Such structural instability of Ge is well found in Assembly-Disassembly-Organisation-Reassembly (ADOR) process, which often forms novel zeolites by chemically selective top-down disassembly from 3D to 2D structures *via* the collapse of *d4r* units.⁵⁸ However, the frameworks consisting of *d4r* with a three-dimensional arrangement such as STW tend to collapse as a result of Ge-O hydrolysis.⁵⁹ Post-synthesis treatments have been suggested to stabilize the germanosilicates by replacing germanium with silicon or aluminum, but they have been limited to a few frameworks such as BEC, and UTL.^{59,60} Therefore, the synthesis of STW molecular sieves and zeolite with high silicon and low or no germanium content is critical for a broad application of enantioselective catalysis and separation over molecular sieves.



Figure 1.5. (a) Plot of energetic stability of GeOGe, SiOSi, and GeOSi angles in zeotypes obtained from 4-ring cluster. (b) Ratio of unlikely TOT angles in SiO₂ and GeO₂ molecular sieves. (c) Yield and the free energy of product as a function of Ge molar fractions in STW.

(a) and (b) reproduced from ref. (53) with permission from American Chemical Society, (c) reproduced from ref. (56) with permission from the Royal Society of Chemistry.

The synthesis of germanosilicate STW has been more extensively studied with non-chiral diquaternary OSDAs where two imidazolium connected by alkyl chains. Lu *et al.*⁶¹ provided the computational result of stabilization energy of doubly charged cations consisting of two 1,2-dimethylimidazolium moieties connected by a linear methylene chain with n = 4, 5. Their experimental result showed that the OSDA with the lowest stabilization energy (n=4) formed both pure silica and germanosilicate STW while higher stabilization energy (n=5) was associated with the formation of germanosilicate STW only.

Collectively, we hypothesize that a chiral OSDA that has a similar structure with the previous OSDA for enantio-enriched STW but exhibits a better stabilization energy toward STW framework would enable the preparation of enantiomerically enriched STW-type molecular sieves with a higher Si content. The aim of part I is to examine this hypothesis by selecting a chiral OSDA based on computationally predicted stabilization energies, developing synthesis routes for the enantiopure forms of OSDAs, synthesizing STW-type molecular sieves, and characterizing their framework composition as well as the enantioselective functions.

1.3. Overview of Part I

Chapter 2 presents the synthesis and characterization of high-silica, enantiomerically enriched molecular sieves. New enantiopure OSDAs are computationally designed with the hypothesis that OSDAs with a better stabilization towards a pure-silica form of molecular

sieve framework would crystallize the product with a higher Si content. With the new chiral OSDA, the STW-type molecular sieves are synthesized with the highest Si content among the enantiomerically enriched molecular sieves reported to date. Further characterization results are discussed to demonstrate that rationally designed OSDA *via* a stabilization energy prediction approach can preferentially crystallize molecular sieves of single chirality with improved framework composition.

Chapter 3 summarizes the work of Part I and discusses the future directions regarding the studies on chiral molecular sieve.

Chapter 2

Synthesis and Characterization of High-Silica, Enantiomerically Enriched STW-Type Molecular Sieves

This chapter is reproduced from a manuscript to be submitted for publication:

Park, Y. et al., High-silica, enantiomerically enriched STW-type molecular sieves, *in preparation*.

Abstract

Enantiomerically enriched molecular sieves are of particular interest as they could open new opportunities in enantioselective catalysis and adsorption. The potential of utilizing these materials for practical applications relies on the preparation of a stable material that can survive the rigors of use and regeneration. To achieve high-silica framework composition within enantiomerically enriched molecular sieves, a chiral organic structure-directing agent (OSDA) is computationally designed based on the superior predicted stabilization energy toward STW framework. With the enantiopure forms of the designed OSDA, the synthesis of STW-type germanosilicate molecular sieves with the framework Si/Ge of 18 is achieved. The high-silica STW has a significantly higher Si framework composition from the previously reported germanium-rich STW and exhibits stability upon thermal treatment at 800 °C. The enantiomeric enrichment of the framework structure is characterized by the dynamical refinement of microcrystal electron diffraction data. The enantioselective adsorption of 2-butanol is demonstrated over the high-silica, enantioenriched STW. The enhanced stability of this high-silica molecular sieve enables a broader range of conditions that will be applicable for use.

2.1. Introduction

The production of enantiomerically pure compounds is industrially critical as the opposite enantiomers often show different biological activities.^{30–33} Materials that function as enantioselective catalyst and adsorbent are thus desired to obtain enantiomeric enrichment of target products. Since molecular sieves, the crystalline microporous materials based on tetrahedrally coordinated oxide (TO₄) units including aluminosilicate zeolites and silicoaluminophosphtes, are widely used in many applications of adsorption and catalysis, there have been continued efforts to achieve enantioselectivity over molecular sieves.^{3,16,34} The well-defined channel systems with sub-nanometer scale enable the molecular sieves to exhibit shape-selective adsorption and catalysis, and the chemistry of the substrate molecules strongly depends on the framework topology. Hence, the preparation of molecular sieves with chiral framework topology has been the primary goal to achieve enantioselective catalysis and adsorption.

The first synthesis of enantiomerically enriched molecular sieves was reported in 2017 by Brand et al. where the STW-type molecular sieves (the framework structures of molecular sieves are assigned distinct three-letter codes) were prepared using the enantiopure diquaternary OSDAs.⁴⁹ Among several inherently chiral framework topologies such as BEA, GOO, -ITV, and JRY (* and - indicates the intergrown and interrupted structures, respectively.⁶²), STW-type framework exhibits the structural chirality based on its 6-fold helical rotation of 10 membered-ring (10 MR, the pore composed of 10 connected TO₄ units) channel along the c-axis. Depending on the direction of the helical rotation of 10 MR channel, the two enantiomers crystallize in the space group of P6₁22 and P6₅22 (**Figure 2.1**). STW is not an intergrowth structure of different polymorphs, and each STW crystal grows as a single enantiomorph, making it a promising material for enantioselective applications. Since the two enantiomorphs of STW with the same chemical composition would have the same energy, it is essential to use enantiopure OSDAs that can energetically distinguish the two enantiomorphs of STW and favor the crystallization of specific enantiomorph over the opposite. Thus, Brand et al. designed a chiral OSDA with the aid of computational predictions of stabilization energy toward STW framework structure, and the STW molecular sieves prepared by these enantiopure OSDAs showed the chiral functionality in the adsorption of 2-butanol and the epoxide ring opening reactions.



Figure 2.1. Helical rotation of 10 MR channel within STW framework topology with the space group of P6₁22 and P6₅22.

Recently, de la Serna et al. reported the synthesis of other enantioenriched molecular sieves with -ITV framework topology, GTM-3 and GTM-4.^{50–52} The -ITV structure also exhibits the linear chirality based on the 4-fold helical rotation of the pore along the c-axis, generating two possible space groups of P4₁22 and P4₃22. The interrupted nature of -ITV framework topology that contains a significant amount of T-OH due to the unconnected T-O-T bond

provides an extra-large pore 30 MR channel. These materials were prepared using various derivatives of enantiopure (pseudo)ephedrine-based OSDAs and showed an improved enantioselectivity towards the ring-aperture reactions of bulky epoxides such as stilbene oxide.

While these successful syntheses proved the promise of chiral molecular sieves as enantioselective catalysts and adsorbents, improving the framework stability of these materials remains as the primary goal to achieve. The reported enantioenriched molecular sieves are mainly composed of d4r (double four-ring) units that are favorably built in the presence of fluoride (F) ion and germanium (Ge) in the synthesis gel. In particular, the high Ge content within the framework was unavoidable in both STW and -ITV-type molecular sieves with enantioenrichment. While the addition of Ge provides a better structural flexibility to form various framework topologies, it reduces the stability of the framework structure as Ge-O-Si(Ge) bond is easily hydrolyzed. Thus, Ge-rich germanosilicate molecular sieves are often susceptible to the loss of crystallinity upon removal of pore-filling structure directing agents. Therefore, it is desired to decrease the Ge content in the framework and improve the structural stability for better recyclability of the enantio-enriched molecular sieves.

Here, we present the synthesis of enantiomerically enriched high-silica STW-type molecular sieves using a new chiral OSDA. The OSDA is designed by the superior predicted stabilization energy toward STW framework and prepared *via* a new synthesis route. The high-silica enantioenriched STW exhibits the improved framework stability upon removal of OSDA by thermal treatment and the enantioselective adsorption of 2-butanol, demonstrating the potential for enantioselective gas separations over molecular sieves.
2.2. Methods

Computation of stabilization energy

Calculation of predicted stabilization energy of diquats was implemented by Dr. Michael Deem following the previously published method.^{47,63,64} A total of 84 chiral di-quaternary (CDQ) structures were generated by the combination of cyclopropane-based chiral linker and imidazole moiety with varied alkyl branches. The stabilization energy of enantiomers with (1S,2S) configuration (S-CDQ) was computed by the geometric placement of three S-CDQ molecules within a unit cell of the STW framework and energy minimizations, followed by molecular dynamics runs at 343 K. After six repeated computational runs, the stabilization energy of each S-CDQ was determined by the lowest predicted energy.

Materials Synthesis

Trans-1,2-bis(bromomethyl)cyclopropane and 2-ethyl-1,4-dimethylimidazole (2E14DMI) were synthesized separately, and CDQ2 bromide salt was prepared by the Menshutkin reaction of the two compounds. CDQ1 was similarly synthesized using 1,2,4,5-tetramethylimidazole (1245TMI) instead of 2E14DMI. For the synthesis of molecular sieves, the bromide (or iodide) salt of OSDAs were dissolved in distilled water and ion-exchanged to hydroxide form using Dowex ion-exchange resin. Then, germanosilicate STW was primarily synthesized with agitation in the fluoride media with a typical gel composition for CDQ2 as 1 SiO₂ : x (x = 0 – 0.1) GeO₂ : 0.5 ROH : 0.5 HF : 3 H₂O and the reaction temperature of 160 °C. The detailed synthesis procedures and characterization results are described in Appendix A.

Materials Characterization

The ¹H and ¹³C nuclear magnetic resonance (NMR) characterization on the OSDAs were implemented a Varian Inova 500 MHz and a Bruker 400 MHz spectrometer, respectively. For the identification of the framework topology and phase purity, powder X-ray diffraction (PXRD) profiles were obtained on an X-ray diffractometer (Rigaku Miniflex II) using Cu Kα radiation of 1.5410 Å. The PXRD measurement for the samples treated at various temperatures was implemented on Rigaku SmartLab. The morphology of particles and their elemental compositions were analyzed by Scanning electron microscopy and energy dispersive spectroscopy (SEM/EDS; ZEISS 1550VP; Oxford X-mas SDD detector). Allsolid-state, , ¹H-²⁹Si cross-polarized (CP) magic-angle spinning (MAS), ¹H-¹³C CP-MAS, and ¹⁹F MAS NMR spectroscopy experiments were conducted on a Bruker 500 MHz spectrometer using a 4 mm zirconia rotor. Thermogravimetric analysis (TGA) of the synthesized materials was implemented using STA6000 up to 800 °C at a ramping rate of 5 $^{\circ}$ C/min unless otherwise stated. The thermal treatment experiments at varied temperatures were conducted with a ramping rate of 2 °C/min and a 60-min hold under ultra-zero grade air. Calcination of the sample was implemented by a ramping rate of 2 °C/min and a hold at 120 °C for 2 h followed by a hold at 580 °C for 6h with a ramping rate of 2 °C/min. The circular dichroism spectra were acquired on Aviv 430 spectrometer. The microED diffraction data were collected at 80 K in a Thermo Fisher Scientific Talos Arctica transmission electromiscope. The detailed experimental and refinement procedures are described in Appendix A (microED measurement and structure refinement was conducted by collaborators of the Nelson group at Caltech: Dr. Lygia Silva de Moraes and Isabel

Hernandez Rodriguez). 2-butanol isotherm and N_2 physisorption experiments were implemented on Quantachrome Autosorb iQ.

2.3. Results and Discussion



Figure 2.2. (a) structures of the chiral di-quaternary OSDAs and their associated stabilization energies for STW framework, (b) STW framework occupied by di-quaternary OSDA.

The design of chiral OSDA structure for high-silica STW was conducted based on the calculated stabilization energy. The consideration of calculated stabilization energy for the crystallization of STW was initiated by Schmidt et al. where they showed that 1,2,3,4,5-pentamethylimidazolium (12345PMI) and 2-ethyl-1,3,4-trimethyl imidazolium (2E134TMI) with the predicted stabilization energy of $-16.5 \text{ kJ} \cdot (\text{mol Si})^{-1}$ successfully crystallize pure-silica STW while other alkyl imidazolium OSDAs with stabilization energy of $-15.7 \text{ kJ} \cdot (\text{mol Si})^{-1}$ or higher do not.⁴⁷ Since the stabilization energy is calculated on the pure-silica STW framework, we hypothesized that a better (lower) stabilization energy predicted in our

system would enable the higher Si content, and thus, the improved framework stability. Brand et al. reported the successful chiral OSDA that is composed of two 1,2,4,5tetramethylimidazole (1245TMI) moieties connected by a chiral linker (CDQ1, **Figure 2.2a**). In their computation result, the chiral linker with cyclopropyl group was selected over other candidate structures such as cyclobutane and pyrrolidine moieties based on the stabilization energy toward STW framework.⁴⁹ Thus, we generated the candidate di-quaternary OSDAs with different alkylimidazole moieties connected by the cyclopropane-based chiral linker and examined the stabilization within the STW frameworks (**Figure 2.2b**).

Among various candidate structures, a symmetric chiral OSDA with 2-ethyl-1,4dimethylimidazole (2E14DMI) moiety (CDQ2) was found to have a superior stabilization energy of -16.56 kJ · (mol Si)⁻¹ towards the pure-silica STW framework (**Figure 2.2a**). The structure of CDQ2 was considered reasonable since 2E134TMI has already proven to have a strong crystallization ability of pure-silica STW.⁴⁶ The consistent calculations on other diquaternary OSDAs provided higher stabilization energies than CDQ2, and 2-ethyl-1,4dimethyl (2E14DMI) imidazole moiety showed better predicted energy than 2-ethyl-1,5dimethyl imidazole (2E15DMI) when compared within the same structure of OSDA (**Figure 2.2a**). Collectively, we determined CDQ2 as the candidate OSDA to crystallize STW with a higher Si content.

Racemic and enantiopure forms of CDQ2 were prepared by reacting 2E14DMI with racemic and enantiopure trans-1,2-trans-1,2-bis(bromomethyl)cyclopropane (**Figure 2.3a**). Since the two chiral centers exhibit the same chirality, (1R,2R)- and (1S,2S)-enantiomers are denoted as R- and S-, respectively. The enantiopurity of CDQ2 was evaluated using (Λ ,R)-BINPHAT tetrabutylammonium salt as a chiral shift reagent that induces different ¹H NMR chemical shift near the ammonium groups in chiral compounds (**Figure 2.3b**).⁶⁵ The neat ¹H NMR spectrum of racemic and enantiopure OSDAs are identical (**Figure A.1.3**). Upon addition of BINPHAT to racemic CDQ2, two equally distributed, upfield-shifted resonances between 4.2 and 4.4 ppm appear. On the other hand, R- and S-CDQ2 exhibit only a single resonance amongst these shifted peaks. Since the ratio between the split resonances provides quantitative analysis of relative amount of two enantiomers, the absence of one of these resonances confirms the enantiopurity of R- and S-CDQ2.



Figure 2.3. (a) Compounds synthesized for CDQ2, (b) ¹H NMR of CDQ2 in the presence of BINPHAT.

The crystallization of STW using racemic, R-, and S-CDQ2 was confirmed by PXRD and SEM (**Figure A.1.4**). The tested synthesis conditions and the corresponding PXRD results are summarized in **Table A.1.1-3**. It is noted that the pure STW phase was obtained with the gel Si/Ge higher than 15, while the lower gel Si/Ge resulted in the formation of mixed phases with STW or even other phases. The observed undesired phases include *BEA and IWV as

well as the layered (organo)silicate materials and the phases that could not be identified. STW phase was more consistently obtained with higher Si/Ge of the gel. In the absence of Ge in the synthesis gel, no crystalline material was produced, showing that a small amount of Ge is needed to produce STW with CDQ2. The synthesis results with CDQ2 contrasts with the synthesis using CDQ1 where the pure STW phase was crystallized only with a Gerich synthesis gel such as the gel Si/Ge of 2.



Figure 2.4. (a) Range of framework Si/Ge within the STW product synthesized by CDQ1 and CDQ2. The EDS results for CDQ1-STW are adopted from reference.^{49,66} (b) ¹⁹F MAS NMR spectra of as-synthesized STW samples.

EDS analysis confirms the high-Si composition of the STW products synthesized using CDQ2 (**Figure 2.4a**). The elemental compositions of STW framework obtained from CDQ1 and CDQ2 show significant difference as CDQ1 forms STW with Si/Ge between 0.8 and 2.2 whereas CDQ2 leads to the framework Si/Ge of 8.1 to 18.6. Within the gel Si/Ge range that

can form pure STW phases, the product Si/Ge tends to increase as the gel Si/Ge increases. From the gel Si/Ge of 30, the obtained Si/Ge in the product does not further increase with the gel Si/Ge (**Figure A.1.5**). The framework Si/Ge of 18.6 obtained by CDQ2 is more than 8-fold increase of Si/Ge in the product STW compared to CDQ1, which agrees with our hypothesis that a better predicted stabilization energy toward pure silica STW framework would lead to a higher Si content within the product.

Solid-state NMR further confirmed the increased framework Si content within STW. STW framework is composed of five crystallographically distinct T-sites (T denotes a tetrahedrally coordinated atom), four of which form the d4r unit. STW does not contain any composite building units (CBUs) other than d4r. The small d4r units impose strain within the structure due to the small angles between the consisting T atom, and Ge is preferably located within d4r due to the higher flexibility of Ge-O-Ge and Ge-O-Si bonds compared to Si-O-Si.¹⁷ Thus, Ge has a strong structure-directing effect in the synthesis of molecular sieves containing d4r and the need of Ge in the synthesis of enantiomerically enriched STW can also be explained in this regard. Fluoride is also known as a structure-directing agent for molecular sieves with d4r based on its compactness and the covalent coordination with eight Si atoms in d4r.^{18,19} Pulido et al. demonstrated that ¹⁹F NMR reflects on the composition of Si and Ge by its changes in chemical shift.²⁰ The ¹⁹F MAS NMR spectra of 2E134TMI-STW (Si/Ge = ∞), CDQ1-STW (Si/Ge = 1.2), and CDQ2-STW (Si/Ge = 18) are shown in Figure 2.4b. 2E134TMI-STW shows a single resonance at -36 ppm, which corresponds to the d4r with 8Si (denoted as 8Si0Ge). In contrast, CDQ1-STW exhibits no resonance at -36 ppm. Instead, the resonance at -7 ppm that corresponds to 5Si3Ge and 4Si4Ge is dominant with a small portion of the peak around -18 ppm that corresponds to 6Si2Ge. A similar ¹⁹F NMR spectrum was obtained for CDQ1-STW with Si/Ge of 2.2.¹⁶ Interestingly, CDQ2-STW shows the dominant resonance at -36 ppm, revealing that the material is mostly composed of pure-silica d4r. A smaller fraction of 6Si2Ge unit is observed at -18 ppm, and the d4r unit with more Ge atoms is barely observed. The ²⁹Si CP-MAS NMR spectra also show a significant difference between CDQ1-STW and CDQ2-STW where CDQ2-STW exhibits a much smaller resonance between –90 ppm and –100 ppm (**Figure A.1.6**). Since the formation of Si-O-Ge bond induces a down-field shift of the ²⁹Si resonance, the relative intensity of these downfield resonances is proportional to the amount of framework-incorporated Ge.⁵⁶ Thus, the significantly lower intensity of the downfield resonance found in CDQ2-STW indicates the smaller composition of framework Ge.



Figure 2.5. PXRD pattern of CDQ2-STW (Si/Ge = 18) before and after thermal treatments. (i): as synthesized material. (ii)-(iv): (i) after thermal treatment at (ii) 300 °C, (iii) 600 °C, and (iv) 800 °C. (v): (iv) after a repeated thermal treatment at 800 °C.

The lability of Ge-O bond makes it vulnerable to hydrolysis, which breaks the Ge-O-Si bond and form Ge-OH and HO-Si moieties. Thus, germanosilicate molecular sieves with a high Ge content exhibit low framework stability upon removal of OSDA. As shown in **Figure A.1.7**, CDQ1-STW with framework Si/Ge of 1.2 maintains the crystal structure upon the thermal treatment at 400 °C. As the pore-filling SDAs are removed at 500 °C and above (**Table A.1.5**), the STW framework collapses and forms an amorphous phase.

In contrast, CDQ2-STW with the framework Si/Ge of 18 maintains the crystallinity after thermal treatments at higher temperatures (**Figure 2.5**). The change in the relative intensities of PXRD peaks upon removal of OSDA at 600 °C is consistent with the pure silica STW synthesized with 2E134TMI (**Figure A.1.8**). The STW framework structure is maintained upon repeated thermal treatment at 800 °C. The micropore volume of calcined R- and S-CDQ2-STW (0.109 ~ 0.162 cm³/g, **Table A.1.6**) further confirms the retained pore accessibility upon the removal of OSDA. These results demonstrate the potential for recyclable catalyst and adsorbent that can be regenerated by thermally removing the organic species occluded within the material (e.g., coke and adsorbate).

STW synthesis is facilitated by the addition of fluoride in the gel, which greatly hinders mass production for commercial use due to its toxicity. Shinno et al. demonstrated the fluoride-free synthesis of STW *via* a dry gel conversion (DGC) approach and the addition of Ge in the gel.⁶⁷ The synthesis was enabled by using 12345PMI that has a strong structure-directing ability to pure silica STW. Thus, DGC approach was tested for the fluoride-free synthesis of STW using S-CDQ2. STW was successfully synthesized using S-CDQ2 at various conditions (**Table A.1.7**, these products are denoted as DGC-CDQ2-STW). The framework

Si/Ge (2.1 ~ 3.3) of DGC-CDQ2-STW was lower than the products of fluoride-mediate synthesis, which is consistent with the results with 12345PMI where DGC resulted in Si/Ge of 4.3 while the fluoride-mediate synthesis can provide pure-silica STW. The crystallinity of DGC-CDQ2-STW was still partially retained after thermal treatment up to 750 °C (**Figure A.1.9**) and the TGA analysis shows that about 3 OSDAs are occluded within a unit cell (**Figure A.1.10**). The DGC synthesis results support the strong structure-directing ability of CDQ2 for STW framework based on the superior stabilization energy toward STW framework.

Since the improvement of the framework composition is associated with the use of new OSDA, it is critical to characterize CDQ2 within the crystalline product. Solid-state ¹H-¹³C CP-MAS NMR spectra of the as-synthesized CDQ2-STW showed that both racemic and enantiopure CDQ2 are intact within the material (Figure 2.6a). Also, the TGA analysis up to 800 °C showed that ~ 3.1 molecules of CDQ2 are occluded within a unit cell (Figure 2.6b). Since CDO2 is a diquaternary OSDA with two imidazolium moieties, this result is consistent with the ideal occupancy of achiral imidazolium OSDA, 6 molecules per unit cell.⁴⁷ CDQ2 contains imidazole moiety that absorbs UV light, and the chirality of CDQ2 was characterized by circular dichroism (CD) within the UV region (Figure 2.6c).⁶⁸ The CDQ2 bromide salt, when pelletized with KCl, exhibited the opposite polarities around 245 nm for R- and S-enantiomers. The as-synthesized R- and S-CDQ2-STW in the KCl pellet also showed the opposite polarities, and their directions were consistent with the CDQ2 bromide salt. The R- and S-CDQ2-STW were then dissolved in HF, and the CDQ2 extracted in the aqueous solution. While the wavelength of the absorbed light was shifted to 230 nm in the aqueous media, the CD spectra showed the consistent directions of CD signals for opposite



Figure 2.6. (a) ¹H-¹³C CP-MAS spectra of CDQ2-STW, (b) TGA plot of S-CDQ2-STW and (c) CD spectra of (i) CDQ2 bromide salt, (ii) as-synthesized CDQ2-STW, and (iii) CDQ2 within aqueous solution after the HF-mediated dissolution of CDQ2-STW.



Figure 2.7. Summary of residual factor wRall from dynamical refinement of R- and S-CDQ2-STW crystals with P6₁22 and P6₅22.

Previous synchrotron XPD studies have revealed the structure of R-CDQ1 occluded within the crystallized STW framework with P6₅22 space group, demonstrating the preferred fitting between the enantiopure OSDA and the corresponding STW framework.⁶⁶ Hence, the enantio-enrichment of STW is indirectly proven by the retained chirality of CDQ2.⁶⁶ However, the characterization of framework structure is still desired for the analysis of chirality of the polycrystalline material. Unlike CDQ2 of which the chirality can be characterized by spectroscopic analysis, determination of the structural chirality of the STW crystal without demonstrating the enantio-selectivity in the catalytic reactions and adsorption experiments is nontrivial. We have previously reported the chirality analysis of STW crystals by the 3D high-resolution transmission electron microscopy (HRTEM).⁴⁹ Since the two enantiomers of STW with space groups of P6₁22 and P6₅22 exhibit the opposite direction of six-fold helical rotation along the screw axis, the projection of the STW framework observed from the HRTEM shifts differently by the rotation of the crystal. Thus, by the comparison of the images aligned along $[2\overline{1}\overline{1}0]$ and $[1\overline{1}00]$ zone axes in the course of continuous tilting, the chirality of R- and S-STW crystals was determined.⁶⁹

While single-crystal XRD is a more frequently used technique to determine the absolute stereochemistry of crystalline materials, it is not amenable to CDQ2-STW due to the small crystal size (SEM images in **Figure A.1.4**). Three-dimensional, microcrystal electron diffraction (microED) has been a rapidly developing technique using TEM, and it has been proven to be an effective tool for the crystal structure analysis of submicrometric crystals.⁷⁰ Recently, Klar et al. demonstrated the absolute structure analysis of crystalline materials by the combination of dynamical and kinematical refinements of continuous-rotation microED data.⁷¹ The absolute structure of the as-synthesized form of a pure-silica STW-type molecular sieve, HPM-1, was solved by the dynamical refinement, and the space group of P6₁22 was determined. This approach could also provide comprehensive information of the crystal structure of HPM-1 other than the chirality. Thus, we employed the continuous-rotation microED to analyze the chirality of the high-silica STW crystals in this study.

To characterize the chirality of CDQ2-STW framework without the information of the occluded OSDA, the CDQ2-STW samples were calcined before the electron diffraction measurement. The diffraction datasets were first processed with kinematical reflection to refine the crystal structure of CDQ2-STW. For the analysis of absolute stereochemistry of the structure, 3 crystals of R- and S-CDQ2-STW were selected respectively, and the initial crystal structure was refined against the dynamical reflection file using 10 cycles of refinement, inverted, and refined against the same dynamical reflection file using 10 refinement cycles. After the refinement with both $P6_122$ and $P6_522$, the space with lower residual factors was assigned for each crystal (**Table A.1.10**). Figure 2.7 shows the wR_{all}

values of the STW crystals analyzed by the dynamical refinement. R- and S-CDQ2-STW crystals are determined with $P6_522$ and $P6_122$, respectively, which agrees with the predicted chirality consistent with the enantiopure OSDAs. Hence, the dynamical refinement of all the diffraction datasets demonstrates the stereochemistry of the STW crystals directed by the chirality of CDQ2.



Figure 2.8. 2-butanol adsorption isotherms of S-CDQ2-STW at 278 K.

Since STW framework shows linear chirality by the rotation of the helical pore, the key to the enantioselectivity of the STW molecular sieve is primarily on the geometric interaction between the pore surface and the molecule that passes through the pore. To examine whether enantioenriched CDQ2-STW exhibits enantioselective behaviors, the 2-butanol adsorption experiments were performed. S-CDQ2-STW was tested for the adsorption of racemic, (+)-, and (-)-2-butanol (**Figure 2.8**). (+)-2-butanol is more selectively adsorbed on the S-CDQ2-STW compared to (-)-2-butanol, while the amount of the racemic 2-butanol adsorption is

between the two enantiomers. The difference in the adsorption is observed from a low partial pressure of adsorbate. It has been computationally demonstrated that chiral alcohols are selectively adsorbed on enantiomeric STW.⁷² Combined with the superior thermal stability that enables the regeneration, the enantioselective adsorption property of CDQ2-STW demonstrates its potential as an adsorbent for the chiral gas separations.

2.4. Summary

We prepared the enantiopure forms of a new chiral di-quaternary OSDA, CDQ2, that was conceived by computational design based on the predicted stabilization energy of toward STW-type framework topology. Using a fluoride-mediated hydrothermal reaction condition with high Si content, CDQ2 crystallized the STW-type germanosilicate molecular sieves. EDS and solid-state NMR characterizations confirmed the high Si/Ge within the STW product. The high-silica STW prepared with enantiopure CDQ2 exhibits enhanced framework stability upon thermal treatment at 800 °C. The retained structure of enantiopure CDQ2 occluded in STW framework was characterized by solid-state NMR and CD measurements. Recently developed dynamical refinement, combined with the rotational microED technique, was applied to the calcined STW samples. Distinct space groups were assigned for STW samples prepared by opposite enantiopure CDQ2, demonstrating the characterization of enantio-enrichment of polycrystalline molecular sieves. The enantioenriched molecular sieve exhibits enantioselective adsorption of 2-butanol. Collectively, the results in this study confirmed the rational synthesis of enantiomerically enriched molecular sieve with the high-Si framework composition based on the stabilization energy of OSDA toward purely siliceous framework structure.

Chapter 3

OUTLOOK FOR PART I

The research work presented in Part I shows the first example of preparing enantio-enriched molecular sieves with improved thermal stability by designing chiral OSDA. Hence, there are several directions to explore and improve the systems investigated here. The possible opportunities could be found from OSDA design to the application of the enantiomerically enriched molecular sieves:

1) Development of characterization method for bulk analysis of crystal structure.

Continued studies on enantio-enriched STW system have shown that the retained chirality of the OSDA is reflected on the enantio-enrichment of the resulting STW framework when the OSDA is large enough to fit tightly within the helical channel and have preferential stabilization energy toward a single enantiomer crystal to the other. While this trend could be used as an indirect analysis method of the bulk enantiopurity of the polycrystalline molecular sieves by characterizing the bulk chirality of the OSDA occluded within the framework, the direct determination of bulk enantiopurity of molecular sieve framework is still desired. This is particularly essential for other enantio-enriched molecular sieves to be investigated in the field. One of the relevant ongoing research efforts is the development of high-throughput analysis of microED data.⁷³ Increasing the number of analyzed crystals is crucial for determining the bulk chirality of polycrystalline samples, and the high-throughput analysis methods have potential to efficiently characterize the chirality of enantio-enriched molecular sieves in a statistically reliable way.

2) Design of OSDAs that further reduces the complexity of synthesis.

The design of chiral OSDA is the key step in preparing enantiomerically enriched molecular sieves with desired properties. The synthesis of enantio-enriched molecular sieves without

Ge within framework is ultimately desired to achieve a durable molecular sieve for various applications. Also, eliminating the competing phase as the product and HF in the synthesis gel would be essential for the large-scale production. The computational design approaches could enable the search of these OSDAs by considering the stabilization energy. Also, designing a more synthetically viable OSDA would be crucial to reduce the time and cost for the synthesis process.

3) Toward various catalytic and adsorption applications with various elemental compositions within the framework structure.

The germanosilicate molecular sieves has shown enantioselective adsorption and Alcontaining enantio-enriched molecular sieves demonstrated the enantioselective catalysis on epoxide ring-opening reactions. Lewis-acidic metals such as Sn and Ti incorporated within molecular sieve framework are known to catalyze various reactions such as biomass conversion and epoxidation. Imposing chirality on the products of such reactions could provide an efficient way to produce enantiomers. Triose sugar conversion and Meerwein-Ponndorf-Verley (MPV) reduction are the examples of interesting reactions as they produce chiral alkyl lactates and chiral alcohols. Enantioselective epoxidation could also be a plausible reaction to investigate over enantio-enriched molecular sieves with helical channel structures.

Chapter 4

INTRODUCTION TO PART II

This chapter introduces the background on the borosilicate molecular sieves regarding the incorporation of heteroatoms and the characterization of the heteroatom sites. The motivation and the objective are discussed, and the overview of Part II is described.

4.1. Background and Motivation for Part II

Zeolites and molecular sieves are widely used as heterogeneous catalysts based on their advantages of environmentally benign nature, flexible chemical compositions, and a well-ordered microporous structure that has pores with selectivity to the dimension of molecular size.⁷⁴ Catalytic active sites of silicate (SiO₂)-based molecular sieves are typically generated by the isomorphous substitution of heteroatom into tetrahedral Si sites. For instance, zeolites are aluminosilicate molecular sieves where some of the Si atoms are replaced by Al. Due to the difference of their formal charge, the incorporation of Al associates with the negative charge on the Si-O⁻-Al bond and necessitates the charge-compensating cations. From proton (H⁺) that generates strong Brønsted acid site to transition metals such as Cu⁺/Cu²⁺ that are widely used for NH₃-selective catalytic reduction of NOx, these cations serve as key species of the catalytic active sites within zeolites.^{6,75} Therefore, the distribution of Al sites directly determines the positions of catalytic active sites within the zeolite framework structure.

The structure of molecular sieves consists of interconnected $TO_{4/2}$ tetrahedra, and these Tatoms are distinguished by their symmetrical position within the unit cell. Thus, the position of the active site among the crystallographically distinct T-sites further influences the catalytic behaviors of zeolites due to the difference of spatial constraints around the active sites.^{76,77} In this regard, there have been continued efforts to prepare zeolites with Al atoms with different ordering over distinct T-sites by varying synthesis conditions.⁷⁸ While the distribution of Al within the framework structure is in general kinetically determined and does not show T-site-specific incorporation,⁷⁹ it has been demonstrated that the positively charged organic structure-directing agents (OSDAs) with different structures can alter the thermodynamic stability of Al at distinct T-sites and thus result in the difference in Al distributions within the framework structure.⁸⁰

Zones and Hwang showed by magic-angle spinning nuclear magnetic resonance (MAS NMR) study that boron exists as borate anion in the solution phase while aluminum mostly maintains the solid phase during the crystal growth of molecular sieves.⁸¹ Thus, it is hypothesized that the borate anions would interact with the quaternary ammonium OSDAs more than solid aluminum, accelerating the inorganic synthesis and increasing the probability of boron sites near the positive charge of the OSDAs. When a bulky OSDA that does not freely rotate within the molecular sieve structure is used for the synthesis, it becomes more likely that B species are ordered at specific T-sites that are closely located to the positive charge of the OSDA. Such selective incorporation of B into specific tetrahedral sites can be a crucial step toward the selective distribution of Brønsted acid sites in aluminosilicate zeolites. For large-pore molecular sieves, B can be replaced by Al using an aqueous solution of Al(NO₃)₃.⁸² Al reinsertion into large-pore borosilicate provides opportunities to prepare strong acid catalysts (aluminosilicates) starting from weaker acid catalysts (borosilicates). Therefore, the synthesis of borosilicate molecular sieves with the selective distribution of

boron atoms could lead to the zeolites with selective active site distribution. Thus, the objective of Part II is the design of OSDAs with different positions of positive charges and the synthesis of borosilicate molecular sieves with altered boron sites.

To verify the altered heteroatom distribution of borosilicate molecular sieves, it is important to establish an analysis method for the location of substituted heteroatoms in the molecular sieves. In the case of aluminosilicates, various spectroscopy techniques, such as FT-IR, UV-Vis of Co²⁺-exchanged counterpart, extended X-ray absorption fine structure (EXAFS), and solid-state MAS NMR, have been employed to determine the aluminum locations⁸³. ²⁹Si and ²⁷Al MAS NMR spectroscopy have been extensively investigated to find a correlation between the chemical shift and zeolites' structural factors. While other structural indicators such as T-O bond distance did not show a clear relationship, it has been reported that the average T-O-T angle correlates with the chemical shift of ²⁹Si and ²⁷Al NMR resonances. Ramdas et al. classified the tetrahedral Si sites based on the number of connected Al and suggested a linear correlation between ²⁹Si NMR chemical shift and a sine function-based expression of mean T-O-T angle (Figure 4.1a).⁸⁴ Lippmaa and coworkers demonstrated an intuitive linear correlation between ²⁷Al NMR chemical shift and the average T-O-T angle based on the previously reported values (Figure 4.1b).⁸⁵ Liu et al. computationally explained that the chemical shielding becomes stronger as the Al-O-Si angle increases due to the change in the orbital hybridization, the location of oxygen lone pair, and the contribution from p-orbital electrons (Figure 4.1c).⁸⁶



Figure 4.1. Chemical shift (ppm) – mean T-O-T angle correlations in (a) ²⁹Si NMR and (b) ²⁷Al NMR NMR, (c) change in chemical environment of aluminum depending on Al-O-Si angle. (a) reproduced from ref. (84) with permission from Springer Nature, (b) reproduced from ref. (85) with permission from American Chemical Society, (c) reproduced from ref. (86) with permission from American Chemical Society.

Unlike aluminosilicates, the correlation between ¹¹B NMR chemical shift and the average T-O-T angles of tetrahedrally coordinated B atoms in borosilicate has not been reported. Boron substitution in silica-based molecular sieves creates much weaker acid sites than aluminum, and the tetrahedral B is associated with counterions that do not strongly interact with frameworks, such as Na⁺ and quaternary ammonium cations.⁸⁷ Tetrahedral boron sites tend to turn into trigonally coordinated B atoms as the material is changed to a H⁺ (proton) form,⁸⁸ which makes it more complicated to analyze by ¹¹B NMR in their functional H-form of molecular sieves. On the other hand, tetrahedral borosilicates can be found as natural minerals and glass, and there are several crystal structure refinements from which the average T-O-T angles of boron sites can be extracted. Researchers have also reported the ¹¹B NMR spectra and chemical shifts of tetrahedral boron sites in borosilicate materials.⁸⁹

Therefore, the correlation between ¹¹B NMR chemical shifts and the mean B-O-T angles will be initially studied in Part II. Since boron tends to have smaller bond angles,⁹⁰ B-O-Si angles would be different from Si-O-Si even at the same crystallographic tetrahedral site within a framework. In this regard, borosilicate minerals of which the structural refinement solutions are available by single-crystal XRD will be investigated first. Then, a similar approach is applied to the borosilicate molecular sieves with the aid of DFT calculations to examine the relationship between the local geometry (average B-O-T angles) and ¹¹B NMR chemical shift at each B site.

4.2. Overview of Part II

In Chapters 5 and 6, the local geometry of tetrahedrally coordinated boron sites within borosilicate minerals and molecular sieves is investigated by employing single-crystal XRD and the DFT calculation on the cluster models. The samples analyzed in these chapters were selected for having incorporated B with known T-site assignment and the measurable distinct ¹¹B NMR chemical shifts. It is then revealed that ¹¹B NMR chemical shifts from the borosilicate minerals and molecular sieves linearly correlates with the average B-O-T angles over a wide range of angles that can be found from borosilicate materials. The correlation found here is similar in its form to the well-known correlation for ²⁹Si and ²⁷Al chemical shifts within (alumino)silicates.

[Overview of Chapter 7 and 8 intentionally redacted: pp. 38-39]

Chapter 5

CORRELATION BETWEEN THE LOCAL GEOMETRY AND ¹¹B NMR CHEMICAL SHIFTS OF TETRAHEDRALLY COORDINATED BORON IN BOROSILICATE MINERALS

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Abstract

Chemical shifts from ¹¹B Nuclear Magnetic Resonance (NMR) spectra of crystalline borosilicate minerals with highly ordered, tetrahedrally coordinated boron atoms (B) linearly correlates with the local geometric parameters related to the B-O-T angles (T denotes a tetrahedrally-coordinated atom) obtained from single-crystal X-ray diffraction (XRD). The correlations between the ¹¹B NMR chemical shift and structural parameters are similar in functional form to the well-known correlations of ²⁹Si and ²⁷Al NMR chemical shifts with structural features of silicates and aluminosilicates, respectively. These correlations enable the use of ¹¹B NMR chemical shifts to elucidate the local geometry of tetrahedrally coordinated B and aid in establishing B ordering among the crystallographic T-sites within crystalline borosilicates.

5.1. Introduction

Borosilicate solids are useful materials in both their amorphous, e.g., borosilicate glass, and crystalline, e.g., molecular sieves, forms. Borosilicate glasses are used in a wide range of industries because of their thermal, chemical, and optical properties,^{91,92} and borosilicate molecular sieves are finding applications in catalysis as active catalysts themselves and as precursors to the preparation of other types of molecular sieve-based catalysts achieved *via* post-synthesis treatments.^{82,93} As the properties of these materials are the consequences of their atomic arrangements, efforts to define structural details continue to be important to their applications.

Solid-state ¹¹B (80.1 % natural abundance) NMR is a well-established technique to probe the structural chemistry of borosilicate materials. In borosilicates, the boron atoms can have trigonal (BO₃) and tetrahedral (BO₄) coordinations when connected to Si atoms *via* bridging O atoms. Trigonally and tetrahedrally coordinated boron atoms have distinct quadrupole coupling parameters (C_Q and η_Q), and different ranges of isotropic chemical shifts in boron-containing glasses, minerals, and molecular sieves. Tetrahedral BO₄ units typically exhibit quadrupolar coupling constants less than 0.8 MHz, which is smaller than those of 2 ~ 3 MHz in BO₃ trigons.^{89,94,95} Moreover, the isotropic chemical shift of tetrahedrally coordinated B varies within a range of -4 ~ 6 ppm, whereas the trigonal B shows isotropic chemical shifts of 12 ~ 25 ppm.⁹⁶

Beyond the use for distinguishing the coordination of B, there have been efforts to link ¹¹B NMR parameters to the local geometric features of borates and borosilicates that have focused on the trigonally coordinated B site. Kroeker and Stebbins reported that the ¹¹B NMR isotropic chemical shift of BO₃ units correlate with the sum of the cation-oxygen

bond strengths for binary borates.⁹⁷ Zhou et al. implemented a comprehensive experimental and computational study on the ¹¹B NMR parameters of trigonal and tetrahedral B sites in 18 different borate and borosilicate minerals.⁹⁸ In their report, the ¹¹B NMR chemical shift of trigonally coordinated B showed correlative behavior with respect to the number of bridging oxygen and the sum of oxygen bond valences. A linear correlation between ¹¹B NMR chemical shift and the average B-O-B angles of trigonally coordinated B has been demonstrated based on first-principle calculation on boroxol-based structures.⁹⁹ For BO₄ tetrahedra, a predictive rule has been suggested for the ¹¹B NMR chemical shift with regards to the relative content of SiO₄, BO₄, and BO₃ polyhedra.¹² This relationship uses the bulk composition of the homogeneous random mixture of glassy borosilicate rather than the local geometry around the tetrahedrally coordinated B within the solid.

Tetrahedrally coordinated BO₄ units are often found in crystalline, borosilicate molecular sieves that are topologically analogous to crystalline microporous aluminosilicates, i.e., zeolites. Despite having the same topology, borosilicate molecular sieves can possess different atomic arrangements compared to zeolites due to features of the B-O-Si bonding. Thus, examining the local geometry around the tetrahedrally coordinated B *via* NMR analysis can help understand the crystal chemistry and its effect on the catalytic activity of the borosilicate molecular sieves (and their Al-exchanged aluminosilicate analogues). Currently, the relationship between the ¹¹B NMR parameters and the local structure of BO₄ tetrahedra in crystalline borosilicates remains ill-defined.

The correlations between the local structures of tetrahedrally coordinated atoms and NMR chemical shifts can be found for silicates and aluminosilicates. Early investigations revealed a linear relationship between the ²⁹Si NMR chemical shift and the average of the

four Si-O-Si bond angles ($\langle \theta_{SiOSi} \rangle$) surrounding the SiO₄ tetrahedra.^{84,100} Using θ_{SiOSi} , Engelhardt and Radeglia proposed a linear correlation between the average s character of the bridging oxygen orbital $\langle \rho \rangle$, where $\rho = \cos(\theta_{SiOSi})/(\cos(\theta_{SiOSi}) - 1)$, and the ²⁹Si NMR chemical shift.¹⁰¹ Alternatively, a correlation of ²⁹Si NMR chemical shift to the average product of the Si-O bond length (r) and the s character of the oxygen orbitals in the Si-O-Si bonds (ρ), $\langle r\rho \rangle$, has been reported based on the single-crystal XRD data of highly siliceous MFI- and FER-type molecular sieves.¹⁰² More recently, Brouwer et al. used ²⁹Si NMR data from 39 different zeolite frameworks (from the International Zeolite Association Database of Zeolite Structures) to extensively correlate ²⁹Si NMR chemical shifts with the aforementioned local geometric parameters and the average Si-Si distance in pure-silica molecular sieves.¹⁰³ With zeolites, a linear dependence of ²⁷Al NMR chemical shifts on the mean Al-O-Si bond angles has been reported.^{85,104,105}

Here, we investigate the correlation between the ¹¹B NMR chemical shift and local geometric parameters of tetrahedrally coordinated B in crystalline mineral samples. Structural parameters were obtained based on B-O-T angle and B-O bond length from structure solutions of borosilicate minerals (see Figure 5.1 for schematic illustration of a representative atomic arrangement and definition of parameters). The minerals we selected for investigation have highly accurate structural parameters obtained from single-crystal XRD data. A primary objective of our work is to establish a correlation between ¹¹B NMR chemical shifts and local structural information so that ¹¹B NMR data can be used to aid in the structural characterization of less well-defined materials such as crystalline borosilicate molecular sieves that are not normally amenable to single crystal X-ray structure solution and typically do not have complete B ordering in tetrahedral site positioning.



Figure 5.1. Schematic illustration of the local geometry of tetrahedrally coordinated B site and the representative structural parameters. θ_{BOT} and r_{BO} denote the bond angle between B and neighboring tetrahedrally coordinated atoms and the bond length between B and O, respectively.

5.2. Methods

5.2.1. Mineral samples

To investigate the relationship between the ¹¹B NMR chemical shift and the local geometry of B, accurate structural data are essential. Hence, borosilicate minerals that meet the criteria listed below were collected and used for experimental measurements.

- (1) Single-crystal XRD structure solution.
- (2) Stoichiometric composition of B that is assigned at specific tetrahedrally coordinated sites, rather than being randomly distributed among different sites.
- (3) ¹¹B NMR spectra amenable to measure isotropic chemical shift.

Borosilicate minerals generally have well-ordered crystalline structures with relatively large crystals. Thus, most of the reported minerals have accompanying structure solutions obtained from single-crystal XRD that give data with high accuracy. Furthermore, B needs to be assigned at a specific tetrahedrally coordinated site for clear matching between the structural parameters and ¹¹B NMR chemical shift. A high occupancy of B can also reduce

the averaging effect of the structural parameters with other elements. Five borosilicate minerals that met all three criteria were used in this study: datolite (Massachusetts, USA), danburite (San Luis Potosi, Mexico), poudretteite (Mogok, Myanmar), reedmergnerite (Duchesne Co., Utah, USA), and leucosphenite (Quebec, Canada). Raman spectra were obtained with a Reinshaw inViaTM Qontor Raman microscope using 514 nm laser with 20x and 50x objective lenses to focus the laser on the surface of the sample.

5.2.2. Data Collection

5.2.2.1. Local geometric parameters of boron from crystal structures

The structural parameters around the tetrahedrally coordinated B were acquired from the atomic configuration of previously reported crystallographic structure data based on single-crystal XRD.^{106–109} The structure solutions were selected such that the localities of the analyzed minerals were the same as that for the minerals we collected for the ¹¹B NMR measurement. With poudretteite, the crystal structure was published for a sample from Quebec, Canada.¹¹⁰ Thus, for consistent analysis, the crystal structure of poudretteite sample from Mogok, Myanmar was analyzed here using single-crystal XRD.

5.2.2.2. Single-crystal XRD structure refinement of poudretteite

The single-crystal XRD structure analysis was performed using a Bruker D8Venture CCD diffractometer equipped with Mitegen MicroMount using Mo K α radiation (λ =0.71069 Å) at 100 K. The 2 θ range for data collection was 4.58 ° to 72.66 °. Based on the observed reflections, the structure solution was obtained from ShelXS software and refined using ShelXL refinement package with least-square method.

5.2.2.3. ¹¹B NMR chemical shift

Bruker AVANCE 500 MHz (11.7 T) and 200 MHz (4.7 T) spectrometers, 4 mm Bruker dual channel MAS probes, and a 4 mm ZrO₂ rotor set for reduced-volume measurements were employed for obtaining solid-state, magic-angle spinning (MAS) NMR spectra. Minerals were loaded in powder form. For the comparison of central-transition line positions at different magnetic field strengths, the spectra were recorded at room temperature at 160.4 MHz (11.7 T) and 64.2 MHz (4.7 T) with a $\pi/12$ pulse length of 0.5 us and the spinning rate of 8 ~ 10 kHz. The ¹H-decoupled ¹¹B MAS NMR spectra were also acquired at 160.4 MHz with a spinning rate of 4 kHz and a spectral width of 500 kHz. The chemical shifts were measured in ppm relative to neat boron trifluoride diethyl etherate (BF₃·O(C₂H₅)₂) as reference at 0 ppm. The line fittings of the measured spectra were accomplished using the DMFit software.¹¹¹

5.3. Results and Discussion

5.3.1. Identification of borosilicate minerals

The minerals obtained in this study were characterized by Raman spectroscopy (**Figure 5.2**). The Raman spectra were compared to the reported for each mineral and identified accordingly, and the obtained samples were identified as desired minerals without impurities.

5.3.1. Crystal structure of poudretteite

The single-crystal X-ray diffraction data of poudretteite, a member of osumilite group, gave a hexagonal unit cell with a = 10.250 (2) and c = 13.488 (5) in the space group of P6/mcc (**Table 5.1**). B and Si occupy each distinct T-site. The B site is connected to four

Si atoms that are crystallographically identical. Thus, all B-O-Si exhibit the same structural parameters. The refined structure is consistent with the previously reported crystal structure of poudretteite (Quebec, Canada)¹¹⁰, and the details of the obtained crystal structure can be found in **Table B.1.1- B.1.5 and Figure B.1.2**.

Structural formula	KNa ₂ B ₃ Si ₁₂ O ₃₀
Crystal system	Hexagonal
Space group	P6/mcc
Lattice parameters a	10.2495 (18) Å
b c	10.2495 (18) Å 13.488 (5) Å
V	1227.1 (6) Å ³
Z	2
Density (calculated)	2.529 g/cm ³
Absorption coefficient	0.977 mm ⁻¹
Final R indices $[I > 2\sigma (I)]$	R = 0.0152, wR = 0.0532
Final R indices	R = 0.0172, wR = 0.0541

Table 5.1. Crystallographic data for poudretteite (Mogok, Myanmar).

Based on the atomic configurations from the structure solution of single crystal X-ray diffraction, the structural parameters for the tetrahedrally coordinated B, average \angle B-O-T ($\langle \theta_{BOT} \rangle$), average bonding orbital hybridization function of bridging O ($\langle h(\theta_{BOT}) \rangle$), and the average product of B-O length (r_{BO}) and $h(\theta_{BOT})$ ($\langle r_{BO} \cdot h(\theta_{BOT}) \rangle$), are obtained. **Figure 5.1** illustrates a representative atomic arrangement and how θ_{BOT} and r_{BO} are defined, and **Table 5.2** lists the corresponding values of structural parameters. Here, the bonding orbital hybridization function, $h(\theta_{BOT}) = \cos \theta_{BOT}/(\cos \theta_{BOT} - 1)$, is calculated using the expression for the degree of s-hybridization of the oxygen bond orbitals ($\rho = \cos \theta/(\cos \theta - 1)$) in the Si-O-Si bond. Engelhardt et al. employed this methodology to describe the s character of

the bridging O in symmetric Si-O-Si bonds when studying the correlative trend of the ²⁹Si NMR chemical shift.¹⁰¹ Use of this parameter facilitates the interpretation of the correlation between the NMR chemical shift and the bond angle of the tetrahedrally coordinated nuclei based on the electronic configuration of the bond orbital with the neighboring O atoms. For asymmetric B-O-Si bonds in borosilicate minerals, $h(\theta_{BOT})$ is employed here as one of the structural parameters to explore its relationship to ¹¹B NMR chemical shifts. The consideration of the asymmetric bond has been reported for Si-O-Al bonds.¹¹² The linear relationship between the ²⁹Si NMR chemical shift and the s-hybridization term was established in addition to the constant term generated by the difference of the shybridization of the oxygen hybrid orbital in the Al-O and Si-O bonds due to the different electronegativities. The linearity of the correlation is preserved for asymmetric Si-O-Al bonds, and B-O-Si is expected to have more symmetric character as B (2.04) has a close electronegativity to Si (1.90) compared to Al (1.61). In addition, the product of B-O length (r_{BO}) and h(θ_{BOT}) (r_{BO}·h(θ_{BOT})) was calculated and used as another local geometric parameter of tetrahedrally-coordinated B site.

Mineral	Poudretteite	Datolite ¹⁰⁶	Danburite ¹⁰ 7	Reedmergnerite ¹⁰ ⁸	Leucosphenite ¹⁰⁹
Chemical Formula Number of	KNa ₂ B ₃ Si ₁₂ O ₃	CaB(SiO ₄)(OH)	CaB ₂ Si ₂ O ₈	NaBSi ₃ O ₈	BaNa4Ti2B2Si10O3 0
distinct B sites	1	1	1	1	1
Coordination of B site	Tetrahedral	Tetrahedral	Tetrahedral	Tetrahedral	Tetrahedral
Locality	Mogok, Myanmar	Massachusetts , USA	San Luis Potosi, Mexico	Utah, USA	Quebec, Canada
^a <θ _{BOT} > (°)	132.16	124.31	129.17	135.96	139.93
^b < h(θ _{BOT})> c	0.4016	0.3600	0.3867	0.4149	0.4157
<r<sub>BO·h(θ_{BOT})</r<sub>	0.5904	0.5308	0.5702	0.6082	0.6382

Table 5.2. Structure parameters of borosilicate minerals with tetrahedrally coordinated B.

^{a)} Average B-O-T bond angle, ^{b)} average bond orbital hybridization function of bridging O, ^{c)} average product of B-O distance (r_{BO}) and $h(\theta_{BOT})$

5.3.2. Local geometric parameters of borosilicate minerals

The structural parameters of the other four borosilicate minerals were obtained from the previously reported single-crystal structure refinements (**Table 5.2**). Datolite (CaBSiO₄(OH)) contains sheets of four- and eight-membered rings (the size of ring is defined by the number of connected T atoms *via* oxygen atoms) of alternating BO₃OH and SiO₄ tetrahedra. The well-defined tetrahedrally coordinated B site has three connections to tetrahedrally coordinated Si atoms *via* bridging oxygen atoms and one B-OH bond (**Figure B.1.3**, **Table B.1.6**). The tetrahedrally coordinated B atoms in all the other minerals are connected to other tetrahedrally coordinated atoms *via* bridging oxygen atoms. Danburite (CaB₂Si₂O₈) has distinct single tetrahedrally coordinated B and Si sites that are alternatively connected and form four- and eight-membered rings. The tetrahedral BO₄ unit

is connected to another B and three Si atoms (**Figure B.1.4, Table B.1.7**). Reedmergnerite (NaBSi₃O₈), the boron-analog of low-albite, has one tetrahedrally coordinated boron site that is connected to three distinct tetrahedrally coordinated Si sites forming four B-O-Si bonds (**Figure B.1.5, Table B.1.8**). Leucosphenite (BaNa₄Ti₂B₂Si₁₀O₃₀) has three T-sites, of which the first and second are occupied Si (Si1 and Si2) and the third is shared by B and Si3 with equal occupancy. The tetrahedrally coordinated B site has four B-O-T bonds with three distinct T-sites (**Figure B.1.6, Table B.1.9**).

From datolite to leucosphenite, there is a gradual increase in $\langle \theta_{BOT} \rangle$. A similar trend was found for $\langle h(\theta_{BOT}) \rangle$, which is consistent with the fact that $h(\theta_{BOT})$ is an increasing function of θ_{BOT} . In addition, $\langle r_{BO} \cdot h(\theta_{BOT}) \rangle$ also increases from datolite to leucosphenite, showing a comparable tendency with $\langle \theta_{BOT} \rangle ($ **Table 5.2**).

5.3.3. ¹¹B NMR chemical shift

¹¹B (I = $\frac{3}{2}$) exhibits the quadrupolar moment that couples with the electric field gradient to show quadrupolar interactions, which sensitively reflect bonding geometries of B atoms and often result in the NMR line broadening and different envelopes of spinning side band manifolds. In general, tetrahedrally coordinated BO₄ units exhibit smaller ¹¹B quadrupolar coupling interactions than trigonal BO₃ units.¹¹³ However, the quadrupolar coupling can still induce additional NMR chemical shift.¹¹⁴ Here, the isotropic chemical shifts of the ¹¹B NMR spectra are used for correlations to local structural information.

Comparing the ¹¹B NMR spectra obtained from different magnetic field strengths is one of the methods to estimate the isotropic chemical shift of the quadrupolar ¹¹B nucleus. The line broadening of the central transition resonance caused by the first-order quadrupole interaction diminishes by the fast magic-angle spinning. However, the second-order

quadrupole interaction can still cause the shift of central transition lines, which is in principle reduced by the higher Larmor frequency. In the presence of quadrupole-induced shift (δ_{QIS}), the observed chemical shift (δ_{obs}) is the sum of isotropic and quadrupole-induced chemical shifts.

$$\delta_{obs} = \delta_{iso} + \delta_{QIS} \quad (1)$$

 δ_{QIS} of the (m, m-1) transition can be calculated using an expression with integrating over all possible crystallite orientations¹¹⁵:

$$\delta_{QIS} = -\frac{3}{40} \frac{C_Q^2}{\omega_L^2} \frac{I(I+1) - 9m(m-1) - 3}{I^2(2I-1)^2} \left(1 + \frac{1}{3}\eta_Q^2\right) \qquad (2)$$

Thus, for a given material with specific C_Q and η_Q , the quadrupole-induced shift of central transition (m = $\frac{1}{2}$) of ¹¹B (I = $\frac{3}{2}$) NMR spectrum is inversely proportional to the square of Larmor frequency (ω_L^2). When the ¹¹B NMR central-transition line positions are acquired at two different strengths of magnetic field of 11.7 T (160.4 MHz) and 4.7 T (64.2 MHz), based on the equations (1) and (2), the observed ¹¹B NMR chemical shift and the isotropic chemical shift have the following relationship:

$$\delta_{64.2} - \delta_{iso} : \delta_{160.4} - \delta_{iso} = \frac{1}{64.2^2} : \frac{1}{160.4^2}$$
(3)

where $\delta_{64.2}$ and $\delta_{160.4}$ dictate the observed ¹¹B NMR chemical shift at 64.2 MHz and 160.4 MHz, respectively.

Figure 5.2 shows the central transition line positions of ¹¹B NMR spectra of collected borosilicate minerals at 64.2 MHz and 160.4 MHz. The minerals exhibit the resonances corresponding to a single tetrahedral ¹¹B site, which is consistent with the crystal structure data. There is a slight difference between the observed center-of-gravity line positions at two different magnetic fields. Using these values and equation (3), the isotropic chemical shift was calculated for each borosilicate mineral (**Table 5.3**).



Figure 5.2. ¹¹B NMR central transition line positions of borosilicate minerals. (a) Spectra at 64.2 MHz with MAS = 8 kHz, (b) spectra at 160.4 MHz with MAS = 10 kHz.

Table 5.3. Observed ¹¹B NMR chemical shift of central transition at Larmor frequencies of 64.2 MHz (4.7 T, with MAS = 8 kHz) and 160.4 MHz (7.4 T, with MAS = 10 kHz) and calculated isotropic chemical shifts.

Mineral	Locality	Chemical Shift at 64.2 MHz (ppm)	Chemical Shift at 160.4 MHz (ppm)	^a δ iso (ppm)	^b δ _{iso} (ppm)
Datolite	Massachusetts, USA	0.67 ± 0.12	0.96 ± 0.05	1.03 ± 0.03	0.99
Danburite	San Luis Potosi, Mexico	-1.50 ± 0.15	-0.70 ± 0.01	-0.55 ± 0.03	-0.52
Poudretteite	Mogok, Myanmar	-1.45 ± 0.03	-1.42 ± 0.01	-1.41 ± 0.02	-1.41
Reedmergnerite	Quebec, Canada	-2.23 ± 0.08	-1.82 ± 0.01	-1.75 ± 0.02	-1.76
Leucosphenite	Utah, USA	-2.67 ± 0.10	-2.65± 0.03	-2.64 ± 0.04	-2.69

^a obtained using equation (3), ^b obtained by line fitting of the ¹¹B MAS NMR spectra acquired at 160.4 MHz with MAS = 4 kHz (**Figure B.1.7**).

An alternative way to obtain the isotropic chemical shift is by line-fitting the ¹¹B MAS NMR spectra. The collected ¹H-decoupled spectra at 160.4 MHz with MAS = 4 kHz exhibit symmetric manifold of small spinning side bands (**Figure B.1.8**), and line-fitting of the ¹¹B MAS NMR spectra of datolite, danburite, reedmergnerite, poudretteite, and leucosphenite provided the isotropic chemical shifts of 0.99 ppm, -0.52 ppm, -1.41 ppm, -1.76 ppm, and -2.69 ppm, respectively (**Table 5.3**). The chemical shifts acquired in this manner are in good agreement with the results from two different magnetic fields, further verifying the calculated isotropic chemical shifts listed in **Table 5.3**.

In addition to the NMR chemical shifts measured in this study, the ¹¹B NMR parameters of several borosilicate minerals are found in literature. The previously reported ¹¹B NMR chemical shifts from datolite, danburite, and reedmergnerite are listed in **Table 5.4**. These values are also included for establishing the correlation.

 Table 5.4. Reported ¹¹B NMR chemical shifts of borosilicate minerals with single tetrahedrally coordinated B site.

Mineral	¹¹ B NMR chemical shift (ppm)
Datolite	1.0 89
	0.2 96
Danburite	~0.7 89
	-0.2 ⁹⁶
Reedmergnerite	-1.9 ⁸⁹

5.3.2. Correlations between ¹¹B NMR isotropic chemical shift and structural parameters The average B-O-T angles linearly correlate with the experimental ¹¹B NMR isotropic chemical shifts in borosilicate minerals investigated here (**Figure 5.3a**). The correlative relationship was examined using the data collected in this study (solid line) as well as the
data combined with the previously reported data (dotted line), and a similar trend was observed. This trend resembles the correlations that have been reported for tetrahedral Si and Al sites in crystalline (alumino)silicates. Based on the linearity of the correlation, the T-O-T bond angle-dependence on the ²⁹Si, ²⁷Al, and ¹¹B NMR chemical shifts can be compared using an equation of the following form:

$$\delta_{iso}(ppm) = \alpha \left(\frac{ppm}{deg}\right) < \theta_{TOT} > (deg) + \beta(ppm)$$

The correlation slope (α) has been reported as -0.47 ~ -0.58 for ²⁹Si^{100,103} and -0.5 ~ -0.54 for ²⁷Al.^{85,104,105} The slope from the correlation for ¹¹B in this study is -0.23, showing the similar behavior as ²⁹Si and ²⁷Al. A larger T-O-T angle leads to a higher s-hybridization of the bonding orbital of bridging O and more ionic character of the T-O bond, giving more atomic net charge on the T atoms. Wolff et al. calculated the ²⁹Si NMR chemical shifts and silicon atomic net charges in different compounds, and their parabolic relationship, showing that the Si-O-T tetrahedra are located in the region where the NMR chemical shift decreases as the atomic net charge of the nuclei increases.^{116,117} The similar relationship between the paramagnetic screening constant and the atomic net charge has also been theoretically derived for tetrahedrally coordinated ²⁷Al nucleus.¹¹⁸ Thus, the negative values of the slope found in the correlations for ²⁹Si, ²⁷Al, and ¹¹B nuclei imply similar properties of these nuclei in tetrahedral sites with regards to the atomic net charge.

A quantum calculation-based qualitative explanation of the linear correlation found in Al-O-Si bonds has been reported by Liu et. al., where ab initio computational results showed that the bonding orbital hybridization and the lone pair of the bridging O mainly contribute to the correlation. They also suggested that with the increasing T-O-T bond angle, the bond orbital has more s-character as the lone pair of O moves closer to the T-atoms.⁸⁶ The observed linear correlation from tetrahedrally coordinated B site intimidates that the changes in bridging O (bonding orbital hybridization and lone pair alignment) depending on the bond angle are similar with those in Al-O-Si bonds.

For aluminosilicate solids, the type of neighboring T atoms (Si and Al) has been reported to affect the NMR chemical shift of the tetrahedrally coordinated Si.¹¹⁷ The variation in the ¹¹B NMR chemical shift in borosilicate glass was also speculatively attributed to the different connectivity to the neighboring T atoms such as B-O-Si and B-O-B.¹¹⁹ In this regard, the correlation between ²⁹Si NMR chemical shift and the Si-O-T angles in crystalline aluminosilicate has been categorized by the number of Si-O-Al bonds.⁸⁴ In **Figure 3a**, the overall data exhibit the linear relationship including the three minerals with four B-O-Si bonds (poudretteite, reedmergnerite, and leucosphenite). The closer electronegativity of B and Si may result in less asymmetric properties of B-O-Si bonds compared to the heterogeneous bonds in aluminosilicates. The predominant dependence of ¹¹B NMR chemical shift on the B-O-T angles could also be viewed with respect to the molecular orbital (MO) simulation results reported by Nanda et al. that showed the comparable bond overlap population on the tetrahedrally coordinated B between B-O-Si and B-O-Si and B-O-Si bonds.¹²⁰

The least-squares regression line represents the linear correlation among the data from this study (solid) and all the data including the literature (dotted).

A local geometric barometer related to the B-O-T angle is the orbital hybridization function of the bridging O, h(θ_{BOT}). Within the range of bond angles in silicates (120 ° ~ 160 °), h(θ_{BOT}) is quite proportional to the B-O-T angle, θ_{BOT} (**Figure B.1.9**). The ¹¹B NMR chemical shifts obtained from the mineral samples exhibit a linear correlation with h(θ_{BOT}) except leucosphenite (**Figure 5.3b**). Unlike other minerals, leucosphenite has a large deviation in the four B-O-T angles ranging from 129.32 ° to 171.37 ° (**Table B.1.9**). In this case, the average of four $h(\theta_{BOT})$ values becomes smaller than the orbital hybridization function with the average angle, $h(<\theta_{BOT}>)$, and it shows a different trend from the B-O-T angles. On the other hand, $h(<\theta_{BOT}>)$ shows the similar linear correlation with ¹¹B NMR chemical shifts (**Figure B.1.9**) as expected from the observed trend in θ_{BOT} .

Another geometric parameter obtained from $h(\theta_{BOT})$ is $r_{BO'}h(\theta_{BOT})$, the product of B-O bond length (r_{BO}) and $h(\theta_{BOT})$. Using this parameter as a variable enables the simultaneous consideration of both closely structure-related values of bond length and angles. A linear correlation between the ²⁹Si NMR chemical shift and <d(T-O)· ρ_T >, where d(T-O) denotes the T-O distance and $\rho_T = \cos \theta_{TOT}/(\cos \theta_{TOT} - 1)$, has been reported for the T-sites in highsilica FER and MFI-type molecular sieves, cristobalite, and quartz.¹⁰² Although < $h(\theta_{BOT})$ > alone shows a weaker correlation due to the comparatively small $h(\theta_{BOT})$ of leucosephnite, the average of $r_{BO'}h(\theta_{BOT})$ exhibits a better linear correlation with ¹¹B NMR chemical shift (**Figure 5.3c**). When both the bond length and angle terms are considered, the deviation among the four B-O-T bonds becomes smaller and the linear trend again holds for the ¹¹B NMR chemical shift. This tendency also implies that the isotropic ¹¹B NMR chemical shift is closely related to the local geometry of BO₄ tetrahedra in borosilicates as seen for the ²⁹Si NMR chemical shift in silicates.



Figure 5.3. The correlation between ¹¹B NMR chemical shift and the local geometric parameters of (a) average B-O-T angle, θ_{BOT} , (b) bond orbital hybridization function of bridging O, h(θ_{BOT}), and (c) the product of B-O bond length (r_{BO}) and h(θ_{BOT}), r_{BO} ·h(θ_{BOT}).

The obtained correlations aid in use of ¹¹B NMR as a means of studying the local structure of tetrahedrally coordinated B within crystalline borosilicates. When the crystal structures of unknown borosilicates are determined, ¹¹B NMR correlation can be used in combination with X-ray refinement methods to understand the local geometry of B. (This methodology is already being utilized with ²⁷Al NMR correlations to understand the Al site distribution within zeolites.¹²¹) The correlations in this study enable the possible use of ¹¹B NMR chemical shift to analyze the ordering of B atoms among different T-sites. The approach should be useful for analyzing borosilicate molecular sieves that are not normally suitable for single crystal XRD and typically do not have T-sites with high B occupancy. It should be noted that the experimental data used for the correlations presented here cover a smaller range of angles (124 ° \sim 140 °) than what is typically found in zeolites (132 ° \sim 154 °).⁸⁵ Furthermore, the ¹¹B NMR chemical shift range obtained in this study (-2.7 \sim 1.0 ppm) is within a relatively lower-field range compared to the typically reported values of borosilicate molecular sieves $(-1.4 \sim -4.6 \text{ ppm})$.^{122–125} The higher-field ¹¹B NMR chemical shift of borosilicate molecular sieves implies that the local geometry of boron might have larger B-O-Si angles than the minerals reported in this study. There have been studies in aluminosilicate molecular sieves with the IFR and MFI framework topologies that suggested rather complicated relationships between the local environments around the tetrahedrally coordinated Al and ²⁷Al NMR based on the Density Functional Theory (DFT) calculations.^{126,127} The structural information used in those studies are not from single crystal X-ray diffraction data, and the accuracy of the experimental data with regards to site populations and local environments could contribute to the complexity. Further work to examine the correlations for higher-field 11B NMR chemical shifts and larger B-O-T

angles is ongoing and includes the borosilicate molecular sieves with multiple crystallographically distinct T-sites. For the analyses of these materials, attention towards assigning the ordered boron sites among distinct framework sites and obtaining reliable local geometric parameters of substituted sites with low occupancy of B is critical to obtain meaningful results. Such efforts will further help understand the crystal chemistry of borosilicates and analyze the B site ordering within borosilicate molecular sieves.

5.4. Summary

The B-O-T angles, orbital hybridization function of bridging O, and its product with the B-O bond length were obtained from the single-crystal XRD structure solutions of crystalline borosilicate minerals with tetrahedral B sites. Isotropic ¹¹B NMR chemical shifts from the borosilicate minerals correlated with the local geometric parameters of the tetrahedrally coordinated B sites. The linearity in the relationships of the isotropic ¹¹B NMR chemical shifts with θ_{BOT} and r_{BO} ·h(θ_{BOT}) was similar in form to the previously reported correlations found for ²⁹Si and ²⁷Al chemical shifts in crystalline silicates and aluminosilicates. The correlations reported here aid in the use of ¹¹B NMR to probe the local geometry of the tetrahedral B sites and can possibly be used to help assign the heteroatom ordering among the crystallographically distinct tetrahedral sites within crystalline borosilicates.

Chapter 6

CORRELATING LOCAL GEOMETRY TO ¹¹B NMR CHEMICAL SHIFTS OF TETRAHEDRALLY COORDINATED BORON IN MOLECULAR SIEVES

The content in this chapter is related to a research manuscript submitted to a scientific journal for publication:

Park, Y.; Koller, H.; Lew, C. M.; Zones, S. I.; Davis, M. E. Correlating Local Geometry to ¹¹B NMR Chemical Shifts of Tetrahedrally Coordinated Boron in Molecular Sieves. *submitted*

Abstract

The average B-O-T angles (B, O, and T denote boron, oxygen, and tetrahedrallycoordinated atoms, respectively) are used as local geometric parameters for frameworkincorporated B-sites within crystalline, borosilicate molecular sieves, and are obtained from density-functional theory (DFT) calculations. The linear relationship between the B-O-T angles and the ¹¹B NMR chemical shifts reported previously for smaller angles in minerals is shown here to extend to the larger angles more typical of crystalline molecular sieves. In total, the correlation can be employed to investigate tetrahedrally coordinated B for the entire class of three-dimensional, crystalline borosilicates.

6.1. Introduction

Borosilicate molecular sieves are gaining interest as components of catalysts and as precursors for synthesizing aluminum (Al)-containing molecular sieves via post-synthesis treatments.^{93,128} Unlike Al that has nonbonded radius comparable to silicon (Si), the smaller nonbonded radius of B enhances the potential for B to have ordered substitution within crystalline silicon oxide frameworks, i.e, specific T-site localization as opposed to a random distribution. Moreover, the water-soluble nature of borate as the BO_4^- unit and its interaction with cationic species in aqueous media during the synthesis of borosilicate molecular sieves can contribute to possible B ordering within the lattice that is formed.⁸⁸ A number of molecular sieve framework topologies have been synthesized as borosilicates, and it has been reported that when the framework contains large pores (a large pore is defined as 12 membered-ring, 12 MR, which consists of 12 T-atoms) or extra-large pores (greater than 12 MR), framework-incorporated B can be replaced by Al through postsynthetic treatments to impose stronger Brønsted acidity for a wider range of catalytic applications.⁸² The B-site ordering within the molecular sieve framework has been shown to be preserved during the Al reinsertion treatments.⁵ These features enable a strategy for creating molecular sieves with ordered heteroatom substitution that could potentially have enhanced properties such as better catalytic selectivity over randomly distributed T-site substituted materials. Thus, methods for elucidating B-site distributions for characterizing molecular sieves are desired to better understand how to exploit this strategy for preparing materials that have properties not obtainable by random substitutions.

There are continued efforts to identify the framework B-sites within the molecular sieves. X-ray diffraction (XRD) has been a major tool for locating B-sites within the borosilicate molecular sieve framework based on the difference in the X-ray scattering factors of B and Si.¹²⁹ The boron siting has also been analyzed by electron diffraction that is a relatively new technique to obtain the crystal structure of small particles.¹³⁰ Although the analysis using X-ray and electron diffraction requires data processing to solve the structures, these methods can provide detailed information on the location of T-sites occupied by heteroatoms such as B in borosilicate molecular sieves.

Solid-state NMR is a widely used technique to probe the chemical environment around ¹¹B nucleus. ¹¹B NMR has been used to detect the changes in the nature of framework B atoms within molecular sieves, particularly for distinguishing tetrahedral (BO₄) species fully incorporated within the framework and trigonal (BO₃) nuclei.⁹⁶ Recent NMR efforts have been able to reveal B ordering within molecular sieve frameworks by analyzing the ¹¹B-²⁹Si heteronuclear interactions. For example, Hsieh et al. employed 2D J-mediated heteronuclear multiple-quantum correlation (HMQC) ¹¹B{²⁹Si} NMR to assign B-sites among crystallographic distinct T-site within the framework structure of B-SSZ-70.¹³¹ This approach required the sample to be prepared using ²⁹Si-enriched silicon source to increase the signal intensity.

²⁹Si and ²⁷Al 1D NMR have been used to locate those atoms at specific T-sites using the linear relationships^{85,103} between the NMR chemical shift and the average bond angles. Computational studies suggest that the dependence of NMR chemical shift on the bond angle is the result of the change in the average s character of orbital in oxygen connected to the T atom, $\langle \rho \rangle$, where $\rho = \cos(\theta_{SiOSi})/(\cos(\theta_{SiOSi}) - 1)$.¹⁰¹ Note that θ_{SiOSi} denotes the bond angle between the two neighboring Si atoms. Recently, it was revealed that the ¹¹B NMR chemical shift also linearly correlates with the average of four B-O-T bond angles

(θ_{BOT} , depicted in **Figure 6.1**) in crystalline borosilicate minerals.¹³² This correlation does not rely on either 2D NMR or ²⁹Si enrichment. However, the correlation was developed using borosilicate minerals that had a somewhat narrow range of bond angles typically found in minerals. Thus, it remained unknown as to whether this correlation would be applicable to crystalline, borosilicate molecular sieves that have larger bond angles.

Here, we investigate the relationship between the ¹¹B NMR chemical shift and the average B-O-T angle of framework-incorporated B in crystalline molecular sieves. In our previous study on borosilicate minerals¹³², single-crystal XRD (SC-XRD) provided detailed information of local geometry of tetrahedrally coordinated boron species based on the large crystal sizes and the high B occupancies at specific tetrahedral sites of minerals. SC-XRD is not often applicable to borosilicate molecular sieves due to their small crystal sizes, e.g., single digit micrometer or sub-micrometer in length. Furthermore, they typically show low partial occupancies of B rather than the complete ordering of B at a specific T-site. Thus, DFT calculations with a finite cluster model were employed to examine the local environment of framework B atoms at its full occupancy. Large-pore and extra-large pore molecular sieves were selected for investigation as they possess larger porous spaces and wider bond angles compared to the borosilicate minerals where the structure is composed of smaller rings (equal to or less than 8 MR) and has narrower bond angles at the B sites. We show here that the correlation can in fact be extended to larger bond angles and is therefore appropriate for use with the entire class of three-dimensional, crystalline borosilicate materials with tetrahedrally coordinated B, demonstrating the potential for assigning B sites within borosilicates with unknown structure.

6.2. Methods

6.2.1. DFT Calculation of $\langle \theta_{BOT} \rangle$ and ¹¹B NMR chemical shift

The DFT calculations within this chapter were implemented by Dr. Hubert Koller at the University of Münster. The B-O-T angles at specific framework T-sites were obtained by DFT calculations based on finite cluster models. A finite cluster approach for framework Al atoms has been reported¹²⁴, and a similar procedure was taken by placing the B atom at the center instead of Al. The finite clusters were constructed based on the reported crystal structures by including all Si atoms within a radius of 9 Å that typically covers three shells of SiO₄ units surrounding the B atom at the center of the borosilicate molecular sieves. The SiO₃ groups at the cluster boundaries were then connected by additional SiO₃ to close small rings to expedite the energetic convergence by reducing the artificial flexibility of dangling entities at the boundaries. The Si-O bonds at the boundaries were then replaced by Si-H bonds.¹²⁴ A modified setup was applied for the minerals because they have a considerably higher charge density. The inner core of the clusters was filled with all the atoms of the structure, including additional boron besides the central B atom and their alkaline or alkaline earth counterions to achieve charge neutrality. For the outer shell of the cluster, boron atoms were replaced by Si and then unnecessary counterions were removed. This core-shell approach ensures that no artificial strain from incomplete cation coordination in the shell region would lead to strain in the structure that changes the bond angles at the central boron. The shell boundary was also completed by Si-H bonds. The hydrogen atoms at the boundaries of all clusters were frozen in the final geometry optimizations after an initial, selective optimization of their positions.



Figure 6.1. DFT cluster model for B at T5 in B-SSZ-82. The bond angle between the framework B and the neighboring T-atom is defined as the B-O-T angle (θ_{BOT}). $\langle \theta_{BOT} \rangle$ is the average of four θ_{BOT} values around the B atom. Blue: Si, green: B, red: O, and pink: H.

Once the cluster structure was initially established, all DFT calculations were performed using Turbomole 7.4. Finite cluster models were established for each T-site occupied by B and surrounded by SiO₄ tetrahedra. Geometry optimization was implemented with the Perdew-Burke-Ernzerhof $(PBE)^{133}$ functional and Grimme's D3 dispersion correction^{134,135} along with a triple- ζ basis set (def2-TZVP).¹³⁶ The resolution of identity approach with auxiliary basis sets (RI-DFT)¹³⁷ was also applied for the geometry optimization. Based on the optimized geometry, the calculation of chemical shielding constants was carried out using the B3-LYP functional. ¹¹B NMR chemical shifts were then obtained using the linear regression between the calculated chemical shielding constants and the experimental ¹¹B NMR chemical shifts that are assigned to specific Tsites (detailed method is provided in the Supporting Information, Figure B.2.1 and Table B.2.1-2).

6.2.2. Borosilicate molecular sieve samples

B-SSZ-53¹³⁸ (**SFH**), B-SSZ-55¹³⁹ (**ATS**), B-SSZ-59¹³⁸ (**SFN**), and B-SSZ-82¹⁴⁰ (**SEW**) were synthesized according to the reported procedures by Dr. Christopher M. Lew and Dr. Stacey I. Zones at Chevron. The detailed synthesis procedures are described elsewhere (**Supporting Information**). The synthesis procedures were chosen to be consistent with the previously reported studies for the synchrotron X-ray powder diffraction (XPD)-based structure refinement of the corresponding materials.¹⁴¹ The structure refinements of B-SSZ-53, B-SSZ-55, and B-SSZ-59 have been reported by Smeets et al.¹⁴¹ The structure refinement data related to the B sites in B-SSZ-82 were kindly provided by Dr. Lynne McCusker. The full structure refinement result will be reported separately.

6.2.3. Characterization

XPD patterns of the molecular sieves were collected on Rigaku MiniFlex II diffractometer using Cu K $\alpha_{1,2}$ radiation ($\lambda = 1.5418$ Å). Scanning Electron Microscope (SEM) images were obtained using a Zeiss 1550VP field emission scanning electron microscopy (FE-SEM). The Si and B contents were determined by inductively coupled plasma atomic emission spectroscopy performed by Galbraith Laboratories, Inc. Bruker AVANCE 500 MHz (11.7 T) and 200 MHz (4.7 T) spectrometers, together with a 4 mm zirconia rotor with a Kel-F cap, were used for obtaining solid-state, magic-angle spinning (MAS) NMR spectra. ¹¹B MAS NMR spectra were acquired at 160.4 MHz with a 90° pulse length of 0.5 us, spectral width of 500 kHz, and a spinning rate of 10 kHz, as well as at 64.2 MHz with a spinning rate of 8 kHz for the comparison of chemical shifts. The chemical shifts were obtained in ppm relative to neat boron trifluoride diethyl etherate $(BF_3O(C_2H_5)_2)$ as reference at 0 ppm. The line fitting of the measured spectra was implemented using the DMFit software.¹¹¹

6.3. Results and Discussion

6.3.1. Borosilicate Molecular Sieve Materials

Sample	$Si/B^{\text{This study}}$	Si/B ^{synthesis ref.}	Si/B ^{refinement}
B-SSZ-53	32.2	39 .2 ¹³⁸	25.7141
B-SSZ-55	26.7	15.5 ¹³⁹	20.4141
B-SSZ-59	47.4	46.2 ¹³⁸	41.1141
B-SSZ-82	37.5	35.7 ¹⁴²	36.9ª

Table 6.1. Chemical compositions of the borosilicate molecular sieves.

a) calculated from B occupancies in the refinement result.

The XPD patterns (**Figure B.2.2**) and the SEM images (**Figure B.2.3**) of the synthesized materials show representative data for each of products. B-SSZ-53, B-SSZ-55, B-SSZ-59, and B-SSZ-82 were selected for this study because their structures (including the location of framework boron sites) have been published. Smeets et al.¹⁴¹ solved the structure of several borosilicate molecular sieves with the OSDAs occluded within the framework by employing the synchrotron X-ray powder diffraction (XPD). They were also able to determine the T-sites where B substitution occurs and the occupancy of B at those sites. The structure of calcined B-SSZ-82 has been reported by Xie et al. using synchrotron XPD¹⁴² and it showed two B sites (T10 and T11). This result is not in agreement with the ¹¹B NMR spectrum that exhibits three major resonances. In a separate study currently

ongoing by McCusker et al. (unpublished), the structure of as-synthesized SSZ-82 was obtained from synchrotron XPD. Three T-sites (T5, T10, and T11) were determined to have B as a substituted heteroatom. The borosilicate materials used here were synthesized at conditions consistent with those used for the structure refinement studies to enable the use of the information on the B-siting. The hydrothermal synthesis of the samples was performed in hydroxide media using NaOH and an Organic Structure-Directing Agent (OSDA, Scheme B.2.1). As boron forms tetrahedrally coordinated anionic BO_{4/2}⁻ units when incorporated within the framework, the associated framework negative charge is compensated by the positive charges of Na⁺ and the OSDAs used in the synthesis. The chemical analyses of the synthesized borosilicate materials are provided in Table 6.1. The presence of B in the synthesized borosilicate materials is confirmed by the chemical analysis, and the compositional ratios between Si and B are comparable to the reported materials used in the structural analyses. Although SSZ-55 obtained here contains a smaller amount of B, the ¹¹B NMR is found to be consistent with that from a sample that was used for the structure refinement (see **Results and Discussion 6.3.3** below).



6.3.2. Local Geometry of Framework B-sites ($\langle \theta_{BOT} \rangle$)

Figure 6.2. (a) $\langle \theta_{BOT} \rangle$ of borosilicate minerals, (b) schematic illustration of framework structures of borosilicate molecular sieves and the T-site for B incorporation (subunits and composite building units are depicted to display where B sites are located), and (c) $\langle \theta_{BOT} \rangle$ of B-sites in borosilicate molecular sieves.

Previously, bond angles surrounding the T-sites within a molecular sieve framework have been obtained for structure models that are generated from purely siliceous frameworks (based on the distance least-squares optimization with the highest possible space group from structure refinements). The idealized structures are available on the International Zeolite Association (IZA) database of zeolite structures.⁶² This approach allows the assignment of ²⁹Si NMR chemical shifts to specific T-sites of pure-silica molecular sieves based on the well-known linear correlation with the θ_{TOT} of the Si-sites. Since the specific structure solutions are available for the borosilicate molecular sieves in this study, those XPD refinement results may also be used to obtain the bond angles of the T-sites where B is incorporated (θ_{BOT}). However, it should be noted that B atoms only partially occupy specific T-sites, sharing the same T-site with Si. For example, in the reported structure solution of SSZ-55, T1 contains B with the occupancy of 0.14 while T2 and T3 are refined to be purely siliceous.¹³⁹ If the entire crystal structure of B-SSZ-55 is viewed as the combination of the unit cells, 14% of the entire number of unit cells contain B at T1 whereas Si occupies T1 in the other 86% of unit cells. Thus, the bond angle around T1 in the XPD refinement is determined by the participation of both B and Si incorporated in T1, and the effect of the site-sharing Si should be considered.

Recently, Schroeder et al.¹²⁴ demonstrated the geometric optimization of the cluster models for Al sites within the molecular sieves and the calculation of corresponding ²⁷Al NMR chemical shifts. Using this method, they successfully showed that heteroatom siting was retained over the course of Al reinsertion into the framework B-sites. Since the cluster model is generated around the framework-incorporated heteroatom of interest, it enables the estimation of local geometry without the averaging effect of site-sharing Si atoms. Thus, in this study, a cluster model-based DFT computation approach was employed to estimate the bond angles surrounding the B-sites within the molecular sieve framework.

Mineral	Chemical formula	Number of distinct tetrahedral B-sites	$< \theta_{BOT} > (SC-XRD)$	$< \theta_{BOT} >$ (DFT)
Danburite	$CaB_2Si_2O_8$	1	129.17 ¹⁰⁷	129.86
Maleevite	$BaB_2Si_2O_8$	1	134.82 ¹⁴³	133.26
Pekovite	$SrB_2Si_2O_8$	1	132.60 ¹⁴³	131.41
Reedmergnerite	NaBSi ₃ O ₈	1	135.96144	134.95
Poudretteite	KNa ₂ B ₃ Si ₁₂ O ₃	01	132.15 ¹³²	130.75

Table 6.2. θ_{BOT} of borosilicate minerals obtained from single-crystal XRD and DFT calculation.

Table 6.3. Bond angles of B-sites in borosilicate molecular sieves.

Material	Number of distinct T-sites	B-site	<θ _{TOT} > (Idealized Structure)	<θ _{BOT} > (XPD)	$\langle \theta_{BOT} \rangle$ (DFT)
B-SSZ-53	8	T3	150.87	137.92	136.93
		T8	150.13	140.15	140.02
B-SSZ-55	3	T1	151.52	146.20	142.73
B-SSZ-59	8	T6	151.42	139.16	138.66
		T8	161.10	151.97	142.99
		T5	141.32	150.85	142.31
B-SSZ-82	11	T10	145.25	145.03	144.16
		T11	146.16	134.40	138.28

The DFT calculation of cluster models was first applied to the borosilicate minerals. Danburite, maleevite, pekovite, reedmergnerite, and poudretteite were investigated because they have a single tetrahedrally coordinated B-site that is fully occupied by B and is connected to four neighboring T-sites. Moreover, the SC-XRD structure solutions are available for these minerals, which enables the verification of the calculation results of our DFT cluster models. The obtained $\langle \theta_{BOT} \rangle$ from the borosilicate minerals are summarized in **Table 6.2**. Detailed information for the DFT calculation results can be found in **Table B.2.3-6**. As shown in **Figure 6.2(a)**, the DFT-calculated $\langle \theta_{BOT} \rangle$ of the borosilicate minerals are in good agreement with the $\langle \theta_{BOT} \rangle$ obtained from the SC-XRD structure

solutions. These results indicate that the geometric optimization using our DFT cluster model can provide estimates of the local geometry of tetrahedrally coordinated B-sites within the borosilicate framework structures.

DFT-calculated average B-O-T bond angles ($\langle \theta_{BOT} \rangle$) were also obtained for borosilicate molecular sieves (Table 6.3). Unlike the minerals that contain single B-site, the molecular sieves in this study have multiple T-sites occupied by B (Figure 6.2(b)). Thus, the cluster model was generated for each B- site. $\langle \theta_{BOT} \rangle$ values obtained from the DFT cluster model are summarized in **Table 6.3**, together with the $\langle \theta_{BOT} \rangle$ measured for the corresponding Tsites within the idealized structure models and the XPD structure solutions. As depicted in **Figure 6.2(c)**, $\langle \theta_{\text{TOT}} \rangle$ from idealized structures tends to be larger than $\langle \theta_{\text{BOT}} \rangle$. That is, the stabilized bond angle at a T-site becomes different depending on the type of incorporated atom between Si and B. This tendency is in agreement with the previous studies on molecular models where it was shown that the Si-O-B angle has narrow energy minimum at angles smaller than 140 ° while Si-O-Si and Si-O-Al angles have broad minimum with respect to the angle.^{90,145} Compared to the idealized structure models, the B-O-T angles from XPD structure solutions tend to be closer to the DFT-calculated angles (Figure 6.2(c)). This is consistent with the fact that XPD data are collected from molecular sieve samples that contain framework-incorporated B whereas the ideal structure models do not take any heteroatom into account. T5 in B-SSZ-82, located at the intersection between afs and *lau* composite building units (CBUs), is an exception to these trends as it has a small average bond angle from the idealized structure. $\langle \theta_{TOT} \rangle$ of 141.32 ° is below the smallest possible bond angles within pure-silica molecular sieves that have been assigned by ²⁹Si NMR.¹⁰³ Thus, this T-site appears to be an uncommon example that does not follow the trends between the bond angles.





Figure 6.3. ¹¹B NMR spectra of (a) B-SSZ-53, (b) B-SSZ-55, (c) B-SSZ-59, and (d) B-SSZ-82 measured at 160.4 MHz. The dotted line represents the fitted spectrum of deconvoluted resonances.

Material B s	B site	B site	B occupancy	${}^{11}\mathrm{B}~\boldsymbol{\delta}_\mathrm{DFT}$	¹¹ Β δ _{160.4}	Area	$^{11}\mathrm{B}~\boldsymbol{\delta}_{\mathrm{iso}}$
	D site	multiplicity		(ppm)	(ppm)	(%)	(ppm)
SSZ-53	Т3	8	0.15	-2.46	-2.41 ± 0.03	54.1	-2.39 ± 0.03
	T8	8	0.11	-2.68	-2.85 ± 0.03	40.3	-2.83 ± 0.04
SSZ-55	T1	8	0.14	-3.44	-3.22 ± 0.02	100	-3.19 ± 0.03
007.50	T6	4	0.13	-2.42	-2.68 ± 0.03	73.8	-2.66 ± 0.04
<u> 22-28</u>	T8	4	0.06	-3.16	-3.57 <u>+</u> 0.02	26.2	-3.56 ± 0.02
SSZ-82	T5	8	0.075	-2.83	-2.81 ± 0.01	45.2	-2.80 ± 0.02
	T10	8	0.075	-3.57	-3.47 ± 0.02	17.0	-3.46 ± 0.03
	T11	8	0.075	-2.21	-4.17 <u>+</u> 0.02	37.8	-4.16 ± 0.02

Table 6.4. Summary of B sites in borosilicate molecular sieves and their corresponding occupancy and ¹¹B NMR chemical shifts

The ¹¹B NMR spectra of the borosilicate molecular sieves are shown in **Figure 6.3**. The ¹¹B NMR resonances are between -2 to -4.2 ppm and correspond to tetrahedrally coordinated framework B species. No resonance was observed at lower-field chemical shifts of 10 - 20 ppm, which indicates the absence of trigonally coordinated B (**Figure B.2.4**). These results demonstrate that the B atoms in the molecular sieves are incorporated within the tetrahedral silica framework structures.

The NMR central transition line shapes are deconvoluted into separate peaks. ¹¹B (I = 3/2) is a quadrupolar nucleus that exhibits interactions between the quadrupolar moments and the electric field gradient, and these interactions are affected by the local environment around the B atoms. ¹¹B nucleus with tetrahedral coordination generally exhibits smaller quadrupolar interactions compared to the trigonal coordination. Thus, the chemical shift is often reported as sole ¹¹B NMR parameter of molecular sieves without quadrupolar coupling constant (C_Q) and the asymmetry parameter (η_Q). The ¹¹B NMR spectra of the borosilicate molecular sieves were collected at 160.4 MHz with MAS = 10 kHz (**Figure B.2.4**). They show low-intensity spinning side bands that give a symmetric envelope

focused on the central transition, which indicates the small quadrupolar interaction of the framework-incorporated ¹¹B nuclei. A more detailed analysis confirms this (**Table B.2.7**). Thus, the observed chemical shifts of central transition line positions are expected to be close to the isotropic ¹¹B chemical shifts.

To quantitatively estimate the isotropic ¹¹B chemical shift of each B-site, the ¹¹B NMR spectra were further obtained at a different magnetic field strength (64.2 MHz, **Figure B.2.5**). Since the magic-angle spinning can diminish the first-order quadrupole interaction that causes line broadening of the central transition resonances, the quadrupole-induced chemical shift (δ_{QIS}) can be evaluated by considering the second-order quadrupole interaction.

In the NMR spectrum, the chemical shift of observed resonance is the sum of isotropic chemical shift (δ_{iso}) and δ_{QIS} .

$$\delta_{obs} = \delta_{iso} + \delta_{QIS} - (1)$$

 δ_{QIS} of the central transition (m = $\frac{1}{2}$) of ¹¹B (I = $\frac{3}{2}$) NMR spectrum is calculated by considering the quadrupolar coupling constant (C_Q) and the asymmetry parameter of the electric field gradient (η_Q) at the boron position¹¹⁵:

$$\delta_{QIS} = -\frac{1}{40} \frac{c_Q^2}{\omega_L^2} \left(1 + \frac{1}{3} \eta_Q^2\right) - (2)$$

Considering that δ_{QIS} decreases in proportion to the square of Larmor frequency (ω_L^2), spectra acquired at stronger magnetic field (11.7 T or 160.4 MHz in this study) provides more accurate δ_{obs} in estimating δ_{iso} . δ_{iso} can be calculated by measuring chemical shifts at two different magnetic fields (160.4 MHz and 64.2 MHz in this study) and combining the equations (1) and (2):

$$\delta_{iso} = \frac{160.4^2 * \delta_{160.4} - 64.2^2 * \delta_{64.2}}{160.4^2 - 64.2^2} \quad \dots (3)$$

where $\delta_{64,2}$ and $\delta_{160,4}$ are ¹¹B NMR chemical shifts observed at 64.2 MHz and 160.4 MHz, respectively.

Figure B.2.5 shows the central transition line positions of borosilicate molecular sieves at 160.4 MHz and 64.2 MHz. The ¹¹B NMR chemical shift of each resonance was obtained by deconvoluting the spectrum. The isotropic chemical shift of each B-site was then calculated using these values and equation (3) (**Table 6.4**). The results confirm that the observed chemical shifts at 160.4 MHz are good estimates for the isotropic ¹¹B NMR chemical shifts of borosilicate molecular sieves. In this study, the isotropic chemical shifts are used for evaluating the correlation.

The difference in ¹¹B NMR chemical shift is the consequence of the distinct B environments among tetrahedrally coordinated B species within the framework. While B-SSZ-55 has been reported to have B incorporation at T1 and exhibits a single ¹¹B NMR resonance, other molecular sieves show multiple resonances in ¹¹B NMR spectra. Thus, each resonance can be assigned to a specific B-site. Note that the third B site in B-SSZ-53 corresponding to the ¹¹B resonance at -3.6 ppm was not found in the structure refinement, likely due to its small population.¹⁴¹ This resonance was left unassigned to a specific B-site.

A plausible approach to assigning B-sites is to compare the B-site occupancy with the relative area of the NMR peaks, which has been used for quantification of species of interest.^{87,88} Since the tetrahedrally coordinated B species exhibit small quadrupolar interactions, the relative peak area of center-of-gravity resonances are representative of relative quantities of framework-incorporated B-sites (see analyses in **Table B.2.7**). For

example, there are two peaks in the ¹¹B NMR spectrum of B-SSZ-59 (**Figure 6.3**(c)). The peak area for the resonance at -2.66 ppm is more than two times larger than that of resonance at -3.57 ppm, which is consistent with the structure refinement where the B occupancy of T6 is larger than T8. Considering their equal site multiplicity within the unit cell (**Table 6.4**), the two ¹¹B NMR resonances at -2.66 and -3.57 ppm of B-SSZ-59 are assigned to B6 and B8, respectively. This assignment is in agreement with the B/A1 exchange study of Schroeder et al. where they showed that the exchanged Al is mainly located at T6, and its amount is comparable to the B content of B-SSZ-59.¹²⁴ The preferred B incorporation T6 located within the double-zigzag (dzg) chains running along the 14 MR channel was further discussed in terms of the influence of dipole moment of pore-filling OSDA.¹⁴⁶

Regarding this approach, it should be noted that the B occupancy from the XPD data is refined based on the reduced diffraction at specific T-sites compared to the full occupancy of Si, and thus, it can be adjusted to some extent by adding vacancy based on the chemical analysis and other characterization techniques such as NMR.¹²⁹ Vacancies of T-site within synthetic molecular sieves can be observed by ¹H MAS NMR with the resonance at 10 ppm, which represents the SiO⁻ ··· HOSi hydrogen bond formed at the defect sites (**Figure B.2.6**).¹⁴⁷ In this case, the relative B occupancies from the refinement may be less reliable due to the increased degree of freedom as the vacancy can replace the B in the refinement. Thus, to further assign ¹¹B chemical shifts associated with B-sites within B-SSZ-53 and B-SSZ-82, the B3-LYP functional was employed to calculate the absolute chemical shielding constant of each B-site by DFT. Since chemical shift exhibits a linear relationship with shielding constant by its definition, ¹¹B chemical shift of each B site was estimated using

a linear regression between the calculated chemical shielding constant and the experimental ¹¹B chemical shifts of known B sites (**Table 6.4**, details described in **Supporting Information**). Here, the calculated ¹¹B NMR chemical shift is denoted as ¹¹B δ_{DFT} . By comparing the order of ¹¹B δ_{DFT} and ¹¹B δ_{iso} within the same material, ¹¹B NMR chemical shifts from B-SSZ-53 and B-SSZ-82 were assigned (**Table 6.4**). The DFT-based assignment for B-SSZ-59 was also consistent with the previous assignment result.

6.3.4. Correlation between ¹¹B NMR Chemical Shifts and the Local Geometry



Figure 6.4. Correlation between ¹¹B NMR chemical shift and $\langle \theta_{BOT} \rangle$ in borosilicates

Table 6.5. Correlation between ¹¹B NMR chemical shift and $\langle \theta_{BOT} \rangle$

Borosilicate Material	¹¹ B NMR chemical shift (ppm)
Minerals	$\delta_{^{11}B} = -0.225 < \theta_{BOT} > + 28.86 \ (R^2 = 0.89)^{^{132}}$
Minerals + Molecular Sieves	$\delta_{^{11}B} = -0.241 < \theta_{BOT} > + 30.93 \ (R^2 = 0.94)$

A linear correlation between ¹¹B NMR isotropic chemical shifts and the average B-O-T angles has been recently reported for minerals.¹³² The previously reported values are summarized in **Table B.2.8**. The correlative relationship was further examined for borosilicate molecular sieves (**Figure 6.4**). The ¹¹B NMR chemical shifts and the average B-O-T angles obtained in this study, combined with the data reported for minerals, exhibit a linear correlation. As shown in **Table 6.5**, the linear correlation obtained from a regression analyses, gives an equation that is comparable with the relationship found in minerals. This result indicates that the linear correlation found for B in tetrahedral coordination holds over a wide range of bond angles, providing a more general relationship that can be applied to various B-site environments.

Since the bond angles within the silicate materials are known to be related to the shybridization of the oxygen bond orbitals [$\rho = \cos(\theta)/(\cos(\theta) - 1)$],¹⁰¹ the correlation found in this study was further evaluated by employing the bonding orbital hybridization function, $h(\theta_{BOT}) = \cos(\theta_{BOT})/(\cos(\theta_{BOT}) - 1)$. $\langle h(\theta_{BOT}) \rangle$ can be obtained by averaging the $h(\theta_{BOT})$ of four B-O-T angles of each B site (**Table B.2.8-9**), and it is proportional to $\langle \theta_{BOT} \rangle$ (with the exception of leucosphenite that has a large deviation in the four angles¹³² (**Figure B.2.7**)). Accordingly, the ¹¹B NMR chemical shifts exhibit a linear correlation with $\langle h(\theta_{BOT}) \rangle$ (**Figure B.2.8**). This implies that the local geometry is closely related to the electronic structure surrounding the tetrahedrally coordinated B, thus correlating with the chemical shielding of ¹¹B nucleus.

There are differences in the correlations with B compared to Si and Al. First, the slope of the linear correlation found for ¹¹B is -0.24 whereas $-0.4 \sim -0.58^{100,103}$ and $-0.5 \sim -0.54^{85,104,105}$ have been reported for ²⁹Si and ²⁷Al, respectively. The atomic net charge on

the T-atom is directly related to its NMR chemical shift, and it increases when T-O-T becomes larger because it causes more s-hybridization of the bonding orbital of bridging O (resulting in more ionic character of the T-O bond). The relationship between the atomic net charge of the nuclei and the NMR chemical shifts or paramagnetic screening constants have been computationally shown for ²⁹Si^{116,117} and ²⁷Al¹¹⁸. While the negative values of the slope are indicative of similar relationship between the bond angles and the atomic net charge of ²⁹Si, ²⁷Al, and ¹¹B, the smaller absolute value for ¹¹B implies that its NMR chemical shift is less dependent on the change of bond angle compared to ²⁹Si and ²⁷Al. This may be attributed to the fact that B (2.04) has larger electronegativity than Si (1.90) and Al (1.61), which would lead to less ionic character of B-O bond. In addition, the bond angles collected for ¹¹B are narrower (124 ° \sim 145 °) than what is reported for ²⁹Si (138 ° \sim 160 °) and 27 Al (130 ° ~ 150 °) in crystalline silicates and aluminosilicates. These results are consistent with the previous computational studies that show that B-O-Si bonds tend to stabilize at narrower angles compared to Si-O-Si and Al-O-Si.^{90,145} Smaller T-O-T angle results in a shorter T-T distance, so substituting B for Si could cause a strain to the silicate frameworks that possess large space. Such property may limit the B occupancy at T-sites within molecular sieves, which could inhibit achieving low Si/B for molecular sieves with framework structures where low Si/Al can be achieved (i.e., FAU-type zeolites).

The ¹¹B NMR chemical shifts investigated for tetrahedral boron in this study cover the majority of reported values for borosilicate molecular sieves (-1.4 \sim -4.5 ppm).^{122–125} Considering that correlations of Si and Al are widely used to analyze the T-sites within molecular sieves and zeolites, the correlation obtained here will also contribute to the study of B-sites in molecular sieves using ¹¹B NMR spectra.

6.4. Summary

Local geometry of framework-incorporated B-sites within borosilicate molecular sieves was described by calculating the average B-O-T angles using DFT cluster models. The materials were synthesized and characterized by NMR spectroscopy. The ¹¹B NMR chemical shifts from the borosilicate molecular sieves correlated with the average B-O-T angles, showing the extension to larger bond angles of the correlation that was reported for the borosilicate minerals. The linear correlation covers a wide range of average B-O-T angles for tetrahedrally coordinated B within crystalline borosilicates, from small angles in natural minerals to larger angles present in porous molecular sieves. Based on the similarity with the correlations found for ²⁹Si and ²⁷Al chemical shifts that are often used to assign T-sites and analyze those sites by NMR spectroscopy, the correlation reported in this study can be employed to investigate the local geometry of framework-incorporated B sites by ¹¹B NMR and possibly assign and specific B-sites among distinct T-sites of borosilicate molecular sieves.

Chapter 7

SELECTIVE HETEROATOM INCORPORATION WITHIN MWW-Type Borosilicate Molecular Sieves

The content of this chapter is related to the manuscripts to be submitted for publication:

Park, Y. et al. Site-specific heteroatom incorporation within MWW-type borosilicate molecular sieves. *In preparation*.

Park, Y. et al. Selective acid site incorporation by Al reinsertion into MWW-type borosilicate molecular sieves. *In preparation*.

[Chapter 7 Intentionally Redacted: pp. 82-97]

Chapter 8

SUMMARY AND OUTLOOK FOR PART II

[Chapter 8 Intentionally Redacted: pp. 98-101]

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APPENDIX A: SUPPLEMENTARY INFORMATION FOR PART I

Appendix A.1. Supplementary Information for Chapter 2

Appendix A.2. References

Source of Chemicals

All chemicals were used as received without further purification. Trans-2phenylcyclopropane-1-carboxylic acid (Sigma Aldrich, 95%), water (house still, \geq 99.99%), trans-2-Phenylcyclopropane-1-carboxylic acid (Sigma-Aldrich, 95%), hexane (EMD Millipore, $\geq 95\%$), water (house still, $\geq 99.99\%$), sodium hydroxide (Alfa Aesar, 97%), diethyl ether (EMD Millipore, ≥99.0%), potassium carbonate (Sigma-Aldrich, anhydrous, 99.99% trace metals basis), methanol (EMD Millipore, ≥99.8%), sodium bicarbonate (Sigma-Aldrich, ≥99.7%), hydrochloric acid (AA blocks, 2 M), magnesium sulfate (Sigma-Aldrich, anhydrous, ≥99.5%), chloroform (EMD Millipore, ≥99.8%), ethyl acetate (EMD Millipore, ≥99.5%), hydrogen peroxide (EMD Millipore, 30% (w/w) in water), tetrahydrofuran (EMD Millipore, ≥99.5%), lithium aluminum hydride (Sigma-Aldrich, 95%), ammonium chloride (Sigma Aldrich, \geq 99.7%), tetrabromomethane (Sigma-Aldrich, \geq 99.5%), triphenylphosphine (Sigma-Aldrich, 99%), acetonitrile (Sigma-Aldrich, anhydrous, 99.8%), tetramethylimidazole (TCI Chemicals, \geq 98%), Dowex Marathon A, hydroxide from (Sigma-Alrich), [Tetrabutylammonium] $[(\Lambda,R)(1,1'-binaphthalene-$ 2,2'diolato) (bis (tetrachlor-1,2-benzenediolato) phosphat(V))] (SigmaAldrich, ≥95%), tetraethylorthosilicate (Sigma-Aldrich, 98%), hydrofluoric acid (Sigma-Aldrich, 48% (w/w) in water), germanium oxide (Strem, 99.99%).

Synthesis of Organic Structure-Directing Agents (OSDAs)

Preparation of CDQ2 requires the synthesis of two organic compounds, 2-ethyl-1,4dimethylimidazole and (1R,2R)- and (1S,2S)-trans-1,2-bis(bromomethyl)cyclopropane. While 2-ethyl-4(5)-methyl imidazole is commercially available, selective methylation to create an asymmetric alkyl imidazole with a methyl group located at C4 position is not trivial due to the very similar properties of 2E14DMI and 2E15DMI. Thus, a selective synthesis to 4-methyl imidazole was conducted *via* the catalytic hydroamination-cyclization that avoids the formation of 5-substituted imidazole ring.

In our previous report, the synthesis of enantiopure OSDA was achieved by the chiral resolution of 2-phenylcyclopropane-1-carboxylic acid.^{1,2} For a more viable route to preparing both enantiomers, in this study, we prepared the R- and S- trans-1,2-bis(bromomethyl)cyclopropane by the cyclopropanation of succinic menthyl diester. Synthesis of CDQ2 was then achieved the Menshutkin reaction between trans-1,2-bis(bromomethyl)cyclopropane and 2-ethyl-1,4-dimethylimidazole.

[1] Synthesis of 2-ethyl-1,4-dimethylimidazole



Scheme A.1.1. Synthesis route for 2-ethyl-1,4-dimethylimidazole.

N-2-propyn-1-yl-propanamide (1)

Following a procedure adopted from Wipf et al.³, 6.1 g (70 mmol) of propionyl chloride was slowly added to a mixture of 13.5 g (96 mmol) of triethylamine and 4.5 g (70 mmol) of propargylamine in 300 mL of DCM at 0 °C. The reaction mixture was stirred at room temperature (RT) for 4 h, poured into 1M HCl (100 mL) and extracted with chloroform three times. The combined organic layers were washed with brine, dried with NaSO₄, and concentrated under reduced pressure to obtain **1**. ¹H NMR (500 MHz, cdcl₃) δ 6.17 (s, 1H), 4.02 (dt, *J* = 5.3, 2.6 Hz, 2H),z 3.75 – 3.68 (m, 0H), 2.26 – 2.18 (m, 2H), 2.15 (d, *J* = 1.7 Hz, 0H), 1.14 (td, *J* = 7.6, 2.1 Hz, 2H). Isolated yield: 90%.

N-methyl-N-2-propyn-1-yl-propanamide (2)

2 was prepared by a procedure adapted from Yasui *et al*⁴. A solution of **1** (6.7g, 60 mmol) in THF (100 mL) was added to a solution of NaH (2.6g, 66 mmol) in THF (200 mL) at 0 °C under Ar and stirred for 1h. Then, iodomethane (5.6 mL, 90 mmol) was added to the solution dropwise. The reaction mixture was then stirred for 8h at RT. The reaction mixture was cooled to 0 °C again, quenched with sat. NH₄Cl (100 mL) and extracted with EtOAc three times. The combined organic layer was washed with brine, dried with NaSO₄, and concentrated under vacuum. The crude product was further purified by column chromatography on silica gel with 1:1 mixture of hexane and EtOAc as eluent. ¹H NMR (500 MHz, acetone) δ 4.18 (dd, *J* = 13.9, 2.5 Hz, 3H), 2.91 (s, 1H), 2.85 (q, *J* = 2.8 Hz, 0H), 2.68 (t, *J* = 2.5 Hz, 1H), 2.38 (dq, *J* = 34.2, 7.4 Hz, 2H), 1.04 (dt, *J* = 9.9, 7.4 Hz, 4H). Isolated yield: 51%

2-ethyl-1,4-dimethylimidazole (3)

3 was synthesized *via* catalytic hydroamination-cyclization reported by Safrygin *et al*⁵. In a typical reaction, **2** (7.13 g, 57 mmol) was dissolved in anhydrous anisole (225 mL). Zinc trifluoromethane sulfonate (1.4 g, 2.85 mmol) and NH₄Cl (6.10 g, 114 mmol) were added, and the mixture was stirred at 150 °C for 72 h. The solvent was evaporated, and the mixture was partitioned between EtOAc (250 mL) and sat. NaHCO₃ (aq) (250 mL). The aqueous solution was extracted with EtOAc (3 times), and the organic layer was combined, dried over MgSO₄, and concentrated *in vacuo*. **3** was obtained by vacuum distillation (85 °C, 900 mTorr). ¹H NMR (500 MHz, cdcl₃) δ 6.45 (q, *J* = 1.0 Hz, 1H), 3.47 (s, 3H), 2.62 (q, *J* = 7.6 Hz, 2H), 2.15 (d, *J* = 1.0 Hz, 3H), 1.28 (t, *J* = 7.6 Hz, 3H). Isolated yield: 20 %.

To verify the synthesis of 2-ethyl-1,4-dimethylimidazole other than the stereoisomer, 2ethyl-1,5-dimethylimidazole, ¹H-¹³C HSQC and HMBC spectra were obtained (**Figure A.1.1 and A.1.2**). Heteronuclear Single Quantum Coherence (HSQC) experiment (**Figure A.1.1**) confirms the connectivity between H and C atoms, and Heteronuclear Multiple Bond Correlation (HMBC) (**Figure A.1.2**) shows the correlations between H and C that are separated by two or three bonds. On HMBC spectra, H4 (H bonded to C4, assigned numbers are shown in **Figure A.1.1 and A.1.2**) shows correlation with C8, which would not be present if H4 is substituted with a methyl group.



Figure A.1.1. HSQC plot of 2-ethyl-1,4-dimethylimidazole.



Figure A.1.2. HMBC plot of 2-ethyl-1,4-dimethylimidazole.

[2] Synthesis of trans-1,2-bis(bromomethyl)cyclopropane

(1) Racemic mixture of trans-1,2-bis(bromomethyl)cyclopropane



Scheme A.1.2. Synthesis of racemic mixture of trans-1,2-bis(bromomethyl)cyclopropane

Trans-1,2-cyclopropanedicarboxylic acid (4)

Following the procedure reported by Inouye *et al.*⁶, a stream of ozone (62.5 mL/min of 6.7 % ozone in oxygen) was bubbled through a solution of trans-2-phenylcyclopropane-1-carboxylic acid (16.2 g, 99.9 mmol) in 220 mL of glacial acetic acid at 50 °C. The mixture was cooled down to room temperature after 72 h of stirring, followed by the addition of 70 mL of hydrogen peroxide (30 % aqueous solution). The mixture was stirred overnight and dried in *vacuo*. An additional 45 mL of 30 % aqueous hydrogen peroxide was added, stirred for 6 h, and the liquid was removed again *via* vacuum distillation. After repeating this 4 times, product (**2**) was recovered and dried under vacuum. ¹H NMR (500 MHz, D₂O) δ 2.18 – 2.10 (m, 2H), 1.49 – 1.42 (m, 2H). Isolated yield: 91%

Trans-1,2-dimethyl-1,2-cyclopropanedicarboxylate (5)

Sulfuric acid (1g, 10 mmol) was slowly added to a solution of **4** (9.1g, 70 mmol) in methanol (500 mL). The mixture was stirred under Ar with reflux for 16 h, and then

vacuum evaporated to remove methanol. The concentrated mixture was washed with brine, extracted with ether twice. The organic layer was combined, washed withed sat. NaHCO₃ solution, water, and brine, and then dried with MgSO₄. The solution was then dried under vacuum to obtain the product. ¹H NMR (500 MHz, cdcl₃) δ 3.70 (s, 6H), 2.21 – 2.15 (m, 2H), 1.48 – 1.41 (m, 2H). Isolated yield: 88 %

Trans-1,2-cyclropropanedimethanol (6)

6 was prepared by adapting the method reported by Kaithal *et al.*⁷ In a typical synthesis, a solution of **5** (13.2 g, 83.6 mmol) in THF (170 mL) was added dropwise to 150 mL of 2 M LiAlH₄ solution in THF at 0 °C under Ar. The mixture was warmed to room temperature, stirred for 2 h, and then refluxed for 16 h. The reaction mixture was cooled in an ice bath, added 200 mL of THF, and quenched by sequential dropwise addition of water (9.5 mL), aqueous NaOH (15 % w/v, 9.5 mL), and water (30 mL). After the mixture was filtered, the retentate was dispersed in ethyl acetate (200 mL), stirred for 1 h, and filtered (2 times). The organic solution was combined, dried over MgSO₄, and concentrated *in vacuo*. Product was obtained by silica gel chromatography with a mixture of EtOAc and iPrOH (6:1) as eluent. ¹H NMR (500 MHz, CDCl₃) δ 4.35 (s, 2H), 3.83 (dd, *J* = 11.5, 4.1 Hz, 2H), 2.98 (dd, *J* = 11.4, 8.8 Hz, 2H), 1.02 – 0.95 (m, 1H), 0.44 – 0.36 (m, 2H). Isolated yield: 65 %

Trans-1,2-bis(bromomethyl)cyclopropane (7)

By adjusting the procedure reported by Ishikawa et al.⁸, CBr₄ (11.4 g, 34 mmol) was slowly added to the stirring solution of PPh₃ (9 g, 34 mmol) in DCM (45 mL) at 0 $^{\circ}$ C and stirred for 10 min. **6** (1.5g, 15 mmol) in DCM (15 mL) was slowly added to the mixture, and the

reaction mixture was further stirred at RT for 16 h. Hexane was added dropwise until white precipitate is observed. Hexane was further added to form enough precipitate. The reaction mixture was filtered, and the filtrate was concentrated by rotary evaporation. The residue was dispersed in hexane and filtered, and the solution was concentrated again by rotary evaporation. The crude was purified by silica gel chromatography with hexane: EtOAc = 8: 1 as eluent. ¹H NMR (400 MHz, CDCl₃) δ 3.40 – 3.24 (m, 4H), 1.37 – 1.26 (m, 2H), 0.87 – 0.77 (m, 2H). Isolated yield: 71%

(2) Enantiomers of trans-1,2-bis(bromomethyl)cyclopropane

The synthesis of (1R,2R)- and (1S,2S)-trans-1,2-bis(bromomethyl)cyclopropane was conducted via the asymmetric cyclopropanation of dimenthyl succinate.⁹ The procedure has been reported for the (1S,2S)-enantiomer synthesis using (-)-menthol, and the same procedure leads to the synthesis of (1R,2R)-enantiomer when (+)-menthol is used. Here, the procedure is described for (1S,2S)-enantiomer. (1R,2R)-enantiomer was synthesized with the same procedure using (+)-menthol.



Scheme A.1.3. Synthesis of S-trans-1,2-bis(bromomethyl)cyclopropane.



Scheme A.1.4. Synthesis of R-trans-1,2-bis(bromomethyl)cyclopropane.

(-)-dimenthyl succinate (8)

(-)-menthol (50 g, 320 mmol) was added to a mixture of succinic anhydride (16 g, 160 mmol) and p-toluenesulfonic acid monohydrate (0.2 g, 1.1 mmol) in toluene (120 mL) and stirred for 30 min. The mixture was loaded with a Dean-Stark trap and heated under reflux for 24 h. During the reaction, water was collected in the Dean-Stark trap. The mixture was cooled to RT, diluted with hexane (160 mL), and added to a mixture of sat. NaHCO₃ solution (200 mL), methanol (80 mL), and water (160 mL). After rigorous stirring, the organic phase was separated, and the aqueous phase was extracted with hexane. The organic phases were combined, washed with brin, and dried over NaSO₄. The solvent was removed by vacuum evaporation. The obtained crude product was cooled to -78 °C and ether was added to the resulting solid. While the temperature was increased to RT, the solid product was continuously scratched so that small particles were formed. The resulting solid was dried under vacuum, 0.5 g of the solid was separated, and the remainder of crude product was cooled to RT, the separated solid was

added as seed, and the mixture was stored in 5 °C refrigerator for 24 h. The crystallized product was recovered by filtration and dried under vacuum overnight. ¹H NMR (500 MHz, cdcl₃) δ 4.70 (td, J = 10.9, 4.4 Hz, 1H), 2.67 – 2.53 (m, 2H), 1.98 (dddd, J = 12.0, 5.5, 3.5, 1.9 Hz, 1H), 1.86 (hd, J = 7.0, 2.7 Hz, 1H), 1.72 – 1.62 (m, 2H), 1.48 (tdt, J = 11.9, 6.7, 3.4 Hz, 1H), 1.37 (ddt, J = 12.5, 10.8, 3.1 Hz, 1H), 1.11 – 1.00 (m, 1H), 1.03 – 0.94 (m, 1H), 0.94 – 0.80 (m, 7H), 0.75 (d, J = 7.0 Hz, 3H). Isolated yield: 92 %

(-)-Dimenthyl-(1S,2S)-cyclopropane-1,2-dicarboxylate (S-9)

2.6 M n-butyllithium solution in hexane (65.5 mL, 164 mmol) was added to dry THF (230 mL) under Ar at 0 °C. To the stirring solution, 2,2,6,6-tetramethylpiperidine (28 mL, 164 mmol) was added dropwise. The resulting solution was cooled to $-78 \,^{\circ}$ C, and a solution of 8 (30.7 g, 78 mmol) in dry THF (80 mL) was added to the solution dropwise and then stirred for 1h. bromochloromethane (5 mL) was slowly added to the stirring solution over 30-min period. After the reaction mixture was stirred for 2h, isobutylraldehyde (2.9 mL) was added dropwise and the mixture was stirred for an additional 30 min. The temperature was increased to 0 °C, and the mixture was poured into 1N hydrochloric acid (300 mL) in an ice bath. After vigorous stirring, the mixture was extracted with ether three times. The organic phases were combined, washed with brine, dried over NaSO₄, and then concentrated by vacuum evaporation. The viscous crude product was purified by silica gel chromatography with a mixture of ether and hexane (1:18) as eluent. The obtained solid product was then recrystallized in methanol, recovered by filtration, and dried under vacuum overnight. ¹H NMR (500 MHz, cdcl₃) δ 4.68 (td, J = 10.9, 4.4 Hz, 1H), 2.16 – 2.10 (m, 1H), 2.00 (dtd, J =12.0, 4.0, 1.6 Hz, 1H), 1.88 (pd, J = 7.0, 2.7 Hz, 1H), 1.73 - 1.64 (m, 2H), 1.49 (dddd, J =

11.9, 8.5, 6.4, 3.4 Hz, 1H), 1.41 (dd, J = 7.6, 1.8 Hz, 1H), 1.42 – 1.35 (m, 1H), 1.03 (dtd, J = 30.0, 12.4, 10.5 Hz, 2H), 0.91 (d, J = 6.8 Hz, 7H), 0.77 (d, J = 7.0 Hz, 3H). [α]_D²² = 16.8 (CHCl₃ c 1.0). Isolated yield: 30 %

(1S,2S)-trans-1,2-cyclropropanedimethanol (S-10)

S-10 was prepared with a similar procedure with **6**. A solution of **S-9** (8.5 g, 21 mmol) in THF (52 mL) was added dropwise to 52 mL of 2 M LiAlH₄ solution in THF (52 mL, 105 mmol) at 0 °C under Ar. The mixture was warmed to room temperature, stirred for 2 h, and then refluxed for 16 h. The reaction mixture was cooled in an ice bath, added 160 mL of THF, and quenched by sequential dropwise addition of water (4 mL), aqueous NaOH (15 % w/v, 4 mL), and water (12 mL). After the mixture was filtered, the retentate was dispersed in ethyl acetate (200 mL), stirred for 1 h, and filtered (2 times). The organic solution was combined, dried over MgSO₄, and concentrated *in vacuo*. The crude was purified by vacuum distillation first and further purified by silica gel chromatography with EtOAc: iPrOH = 6: 1 as eluent. ¹H NMR (500 MHz, CDCl₃) δ 4.35 (s, 2H), 3.83 (dd, *J* = 11.5, 4.1 Hz, 2H), 2.98 (dd, *J* = 11.4, 8.8 Hz, 2H), 1.02 – 0.95 (m, 1H), 0.44 – 0.36 (m, 2H). Isolated yield: 60 %

(1S,2S)-trans-1,2-bis(bromomethyl)cyclopropane (S-11)

S-11 was produced with the same procedure as **7**. CBr₄ (11.4 g, 34 mmol) was slowly added to the stirring solution of PPh₃ (9 g, 34 mmol) in DCM (45 mL) at 0 °C and stirred for 10 min. **S-10** (1.5g, 15 mmol) in DCM (15 mL) was slowly added to the mixture, and the

reaction mixture was further stirred at RT for 16 h. Hexane was added dropwise until white precipitate is observed. Hexane was further added to form enough precipitate. The reaction mixture was filtered, and the filtrate was concentrated by rotary evaporation. The residue was dispersed in hexane and filtered, and the solution was concentrated again by rotary evaporation. The crude was purified by silica gel chromatography with hexane: EtOAc = 8: 1 as eluent. ¹H NMR (400 MHz, CDCl₃) δ 3.40 – 3.24 (m, 4H), 1.37 – 1.26 (m, 2H), 0.87 – 0.77 (m, 2H). Isolated yield: 65 %

[3] Synthesis of CDQ2



Scheme A.1.5. Synthesis of Racemic, R and S-CDQ2.

CDQ2 was prepared by the Menshutkin reaction between **3** and **7** (racemic), **R-11**, or **S-11**. For S-CDQ2, 3 (2 g, 16 mmol) and S-11 (1.6g, 7 mmol) were added to acetone (15 mL), and the reaction mixture was stirred under reflux for 3 d. The reaction mixture was filtered, and the retentate was recovered by filtration, dried under vacuum overnight. ¹H NMR (500 MHz, d₂o) δ 7.10 (d, *J* = 1.5 Hz, 1H), 4.16 (dd, *J* = 15.5, 5.1 Hz, 1H), 3.93 (dd, *J* = 15.4, 7.0 Hz, 1H), 3.75 (s, 3H), 2.96 (q, *J* = 7.6 Hz, 2H), 2.21 (d, *J* = 1.1 Hz, 3H), 1.35 (t, *J* = 6.4 Hz, 1H), 1.19 (t, *J* = 7.6 Hz, 3H), 0.91 (t, *J* = 7.1 Hz, 1H). Isolated yield: 72 %



Figure A.1.3. ¹H NMR spectra of CDQ2 bromide salt in D₂O. * denotes the solvent peak.

[4] Synthesis of other OSDAs

(1) 2-ethyl-1,3,4-trimethylimidazolium iodide



Scheme A.1.6. Synthesis of 2-ethyl-1.3.4-trimethylimidazolium iodide.

K₂CO₃ (6.9 g, 50 mmol) was added to the solution of 2-ethyl-4-methylimidazole (5.5 g, 50 mmol) in chloroform (100 mL). The mixture was cooled in an ice bath, and methyl iodide (6.3 mL, 100 mmol) was added. The reaction mixture was warmed to RT and further stirred for 16 h. The reaction mixture was filtered, and hexane was added to the filtrate dropwise with stirring until the precipitate is observed. Hexane was further poured into the mixture, and the mixture was filtered to recover solid product. The product was further dried under vacuum overnight. ¹H NMR (500 MHz, d₂o) δ 3.74 (s, 1H), 3.66 (s, 1H), 2.98 (q, *J* = 7.7 Hz, 1H), 2.25 (d, *J* = 1.1 Hz, 1H), 1.23 (t, *J* = 7.7 Hz, 1H). Isolated yield: 80 %

(2) S-CDQ1



Scheme A.1.7. Synthesis of S-CDQ1.

S-CDQ1 was prepared by the Menshutkin reaction between 1,2,4,5-pentamethylimidazole and S-11. 1,2,4,5-pentamethylimidazole (2 g, 16 mmol) and S-11 (1.6g, 7 mmol) were added to acetone (15 mL), and the reaction mixture was stirred under reflux for 3 d. The reaction

mixture was filtered, and the retentate was recovered by filtration, and dried under vacuum overnight. ¹H NMR (500 MHz, d₂o) δ 4.11 (dd, *J* = 15.4, 5.2 Hz, 1H), 3.83 (dd, *J* = 15.4, 7.4 Hz, 1H), 3.58 (s, 3H), 2.49 (s, 3H), 2.18 (d, *J* = 0.9 Hz, 3H), 2.10 (d, *J* = 0.9 Hz, 3H), 1.30 – 1.21 (m, 1H), 0.85 – 0.79 (m, 1H). Isolated yield: 85 %

Synthesis of STW-type molecular sieves

For the synthesis of germanosilicate molecular sieves, germanium oxide and the OSDA hydroxide solution (ROH) were loaded in a 23 mL PTFE liner, and then homogenized by stirring for 1 h (Note that ROH is based on the amount of hydroxide anion. For example, CDQ2 is a di-quaternary OSDA with two OH⁻ ions per molecule, so 1 ROH is equivalent to 0.5 CDQ2). TEOS was then added, and the mixture was stirred for 48 h to hydrolyze TEOS. The lid was then removed from the PTFE liner so that ethanol and water could evaporate under a stream of air until H₂O/SiO₂ reaches the desired ratio. Aqueous HF solution was added to the gel, followed by homogenization by hand. If needed, gels were additionally dried under air again to obtain the desired amount of water. The gel was aged for 24 h and then as-made pure-silica STW or enantio-enriched germanosilicate STW seed was added (5 wt% based on Si). The final mixture was loaded in a Teflon-lined stainless-steel autoclave and put in the oven with the rotation of 60 rpm. The synthesis temperature was 160 °C unless otherwise described. A typical gel composition for the germanosilicate STW was 1 SiO_2 : x (x = 0 - 0.1) GeO₂ : 0.5 ROH : 0.5 HF : 3 H₂O. The detailed synthesis conditions including gel compositions and crystallization time are summarized in Table A.1.1-4 with the PXRD results. After the synthesis, the reaction mixture was washed with distilled water and recovered by centrifugation (repeated four times), further washed with acetone, and then dried at 80 °C overnight.



Figure A.1.4. (a) XRD patterns of CDQ2-STW and SEM images of (b) Rac-CDQ2-STW, (c) S-CDQ2-STW, and (d) R-CDQ2-STW.



Figure A.1.5. Distribution of product Si/Ge of CDQ2-STW at various Si/Ge of synthesis gel. The gray bars depict the range of Si/Ge obtained from STW products and the black dots represent the average of measured Si/Ge values.

 Table A.1.1. Summary of molecular sieve synthesis using racemic CDQ2. 'A' denotes amorphous

 phase.

Si/Ge	ROH/SiO ₂	HF/SiO ₂	H ₂ O/SiO ₂	Seed (%)	Time (d)	Crystalline Product
2	0.5	0.5	5	5	45	STW+IWV
10	0.5	0.5	5	2	27	*BEA + STW
10	0.5	0.5	4	5	36	STW+IWV
20	0.5	0.5	3	2	32	STW
17	0.5	0.5	5	5	50	STW
20	0.5	0.5	4	5	13	А
25	0.5	0.5	4	5	50	STW
8	0.5	0.5	3	5	45	A
10	0.5	0.5	4	2	30	STW+*BEA
20	0.5	0.5	5	2	30	*BEA + STW
20	0.5	0.5	4	0	13	*BEA+STW
8	0.5	0.5	3	2	13	А
20	0.5	0.5	4	5	18	STW
20	0.5	0.5	4	5	39	STW
20	0.5	0.5	3	5	34	*BEA+STW
15	0.5	0.5	3	5	14	STW

20	0.5	0.5	3	5	11	IWV+*BEA+STW
20	0.6	0.6	3	5	28	*BEA+STW
35	0.5	0.5	3	5	16	STW + *BEA
35	0.5	0.5	3	5	16	STW+*BEA
35	0.5	0.5	3	5	16	STW
40	0.5	0.5	3	5	16	STW+*BEA
40	0.5	0.5	3	5	16	*BEA+STW
40	0.5	0.5	3	5	16	STW
40	0.5	0.5	3	5	16	STW

Table A.1.2. Summary of molecular sieve synthesis using S-CDQ2. 'A' denotes amorphous phase and 'U' denotes unidentified phase.

Si/Ge	ROH/SiO ₂	HF/SiO ₂	H ₂ O/SiO ₂	Seed (%)	Time (d)	Crystalline Product
20	0.5	0.5	5	5	30	STW
20	0.5	0.5	5	5	30	*BEA+STW+U
20	0.5	0.5	4	5	30	*BEA+STW
25	0.4	0.55	3	5	28	STW +*BEA
25	0.4	0.5	4	5	28	STW (+*BEA)
25	0.4	0.65	3	5	21	STW+*BEA
25	0.3	0.3	5	5	15	Layered+*BEA+STW
25	0.3	0.5	3	5	28	STW+*BEA+LTA
25	0.3	0.45	4	5	15	LTA+*BEA+STW
25	0.25	0.35	3	5	28	*BEA+STW
25	0.5	0.65	5	5	15	STW (+*BEA)
26	0.5	0.7	3	5	15	STW+*BEA
27	0.5	0.8	3	5	15	*BEA+STW
28	0.5	0.9	3	5	15	*BEA+STW
29	0.55	0.8	3	5	15	STW(+*BEA)
30	0.5	0.75	3	5	15	STW(+*BEA)
25	0.5	0.75	3	5	15	STW+*BEA
30	0.5	0.75	3	5	15	STW+*BEA
25	0.5	0.75	3	5	15	STW+*BEA
20	0.5	0.7	3	5	15	*BEA+STW
20	0.5	0.8	3	5	15	*BEA+STW
25	0.5	0.7	3	5	28	Layered
35	0.5	0.5	3	5	28	STW+*BEA
35	0.6	0.6	3	5	28	STW+*BEA
35	0.7	0.7	3	5	28	А
30	0.6	0.6	3	5	15	STW(+*BEA)
35	0.5	0.5	3	5	15	STW
35	0.6	0.6	3	5	15	STW
35	0.7	0.7	3	5	15	STW(+*BEA)
30	0.6	0.6	3	5	15	STW
35	0.5	0.5	3	5	15	STW(+*BEA)
35	0.6	0.6	3	5	15	STW
30	0.5	0.5	3	5	15	STW
30	0.5	0.6	3	5	15	STW
30	0.5	0.5	3	5	15	STW+*BEA
30	0.5	0.5	3	5	15	STW/+Δ)
10	0.5	0.5	3	5	15	STW(17)
20	0.5	0.5	3	5	15	STW

15	0.5	0.5	3	5	15	*BEA+STW
30	0.5	0.5	3	5	15	*BEA+STW
30	0.5	0.5	3	5	15	U
32	0.5	0.5	3	5	15	STW
35	0.5	0.5	3	5	15	STW + *BEA
35	0.55	0.55	3	5	15	STW
30	0.5	0.5	3	5	15	STW + *BEA
32	0.5	0.5	3	5	15	STW
35	0.5	0.5	3	5	15	STW
35	0.55	0.55	3	5	15	STW
30	0.5	0.5	3	5	15	STW+A
32	0.5	0.5	3	5	15	STW (+*BEA)
35	0.5	0.5	3	5	15	A+STW
35	0.55	0.55	3	5	15	STW+*BEA
35	0.5	0.5	3	5	15	STW
35	0.5	0.5	3	5	15	STW
35	0.5	0.5	3	5	15	STW
35	0.5	0.5	3	5	15	STW
35	0.5	0.5	3	5	15	STW
37	0.5	0.5	3	5	15	STW+*BEA
37	0.5	0.5	3	5	15	STW
40	0.5	0.5	3	5	15	STW
40	0.5	0.5	3	5	15	STW
00	0.5	0.5	3	5	15	А
00	0.5	0.5	3	5	15	А
~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	0.5	0.5	3	5	15	A

**Table A.1.3**. Summary of molecular sieve synthesis using R-CDQ2.

Si/Ge	ROH/SiO ₂	HF/SiO ₂	H ₂ O/SiO ₂	Seed (%)	Time (d)	Crystalline Product
20	0.5	0.5	3	5	35	STW
20	0.5	0.5	3	2	35	STW
20	0.5	0.5	3	5	28	*BEA + STW
20	0.5	0.5	3	2	28	*BEA + STW
20	0.5	0.5	3	5	21	*BEA + STW
20	0.5	0.5	3	5	21	*BEA + STW
20	0.5	0.5	3	5	21	*BEA + STW
20	0.5	0.5	3	5	21	*BEA + STW
20	0.5	0.5	3	2	21	*BEA + STW
20	0.5	0.5	3	2	21	*BEA + STW
20	0.5	0.5	3	0	21	*BEA + STW
20	0.5	0.5	3	2	16	STW
25	0.5	0.5	3	5	16	STW
30	0.5	0.5	3	5	16	STW
35	0.5	0.5	3	5	16	STW
40	0.5	0.5	3	5	16	STW

	OSDA	Si/Ge	ROH/SiO ₂	HF/SiO ₂	H ₂ O/SiO ₂	Seed (%)	Time (d)	Crystalline Product
	2E134TMI	20	0.5	0.5	3	5	16	STW
		2	1	0.5	4	2	10	STW+IWV
		2	1	0.5	4	5	10	STW+IWV
	CDQ1	2	0.5	0.5	4	10	10	STW
		2	0.75	0.5	4	10	10	STW
		2	0.75	0.6	4	10	10	STW+IWV
		2	1	0.75	4	10	10	STW+U
		2	1.1	0.55	4	10	10	STW
		2	1.2	0.6	4	10	10	STW
		2	0.5	0.25	4	10	10	IWV+STW
		2	0.5	0.5	4	2	10	STW+U

**Table A.1.4**. Summary of molecular sieve synthesis using 2-ethyl-1,3,4-trimethylimidazole(2E134TMI) and CDQ1.



Figure A.1.6. ²⁹Si CP-MAS NMR spectra of CDQ1-STW and CDQ2-STW.



**Figure A.1.7**. PXRD pattern of S-CDQ1-STW (Si/Ge = 1.2) before and after thermal treatments. (i): as-synthesized material. (ii)-(v): (i) was taken and thermally treated at (ii) 300  $^{\circ}$ C, (iii) 400  $^{\circ}$ C, (iv) 500  $^{\circ}$ C, and (v) 600  $^{\circ}$ C.

Table A.1.5. Weight loss of CDQ2-STW sample at different thermal treatment temperatures.

Treatment temperature (°C)	Weight loss (%)
200	0.5
300	0.9
400	1.8
500	16.8
600	23.3



Figure A.1.8. XRD patterns of as-synthesized and calcined pure-silica 2E134TMI-STW.

Table A.1.6. Framework compositions of CDQ2-STW and their micropore volume measured by  $N_2$  physisorption.

Material	Si/Ge product	Micropore volume (cc/g)
2E134TMI-STW	$\infty$	0.210
S-CDQ2-STW	18	0.162
R-CDQ2-STW	18	0.109

#### HF-free CDQ2-STW synthesis via dry-gel conversion (DGC)

The synthesis of CDQ2-STW without HF was implemented *via* a dry-gel conversion method. Germanium oxide, ammonium sulfate, and CDQ2 hydroxide solution was stirred in a PTFE liner for 1 h, and TEOS was added to the mixture followed by a rigorous stirring for 48 h. Then, the reaction mixture was heated at 80 °C while stirring until glassy solid is formed. The solid was crushed into powder and loaded in a small PTFE container (without lid) that fits in the 23 mL PTFE liner. Water was added in the space between the PTFE container and the 23 mL PTFE liner so that the synthesis mixture does not touch liquid water. Then, the 23 mL liner was sealed with a lid in a stainless-steal autoclave and loaded in the oven at 160 °C statically. After the synthesis, the reaction mixture was washed with distilled water and recovered by centrifugation (repeated four times), further washed with acetone, and then dried at 80 °C overnight.

**Table A.1.7.** Dry-gel conversion synthesis conditions and the corresponding results. The gel composition was (1-x) SiO2: x GeO2: 0.5 ROH: 0.1 (NH₄)₂SO₄: 1 H₂O: 0.1 SiO₂ (seed).

Si/Ge	ROH/SiO ₂	(NH4)2SO4/SiO2	H ₂ O/SiO ₂	Temperature (°C)	Time (d)	XRD Result	Si/Geproduct
2	0.5	0.1	1		28	IWV+STW	-
4	0.5	0.1	1	200	28	STW	2.6
9	0.5	0.1	1	200	28	STW	2.1
19	0.5	0.1	1		28	STW	3.3
4	0.5	0.1	1	160	28	STW	2.4
9	0.5	0.1	1	100	28	STW	2.2



**Figure A.1.9.** (a) XRD patterns of as-synthesized and calcined forms of DGC-CDQ2-STW (Si/Ge = 2.1), (b) SEM image of DGC-CDQ2-STW (Si/Ge = 2.1).



Figure A.1.10. TGA plot of DGC-CDQ2-STW with Si/Ge = 2.1.

#### Calculation of number of OSDAs per unit cell

The Si, Ge, and F content of the sample was determined by EDS. Then, the molecular weight of the unit cell was calculated based on the germanosilicate framework composition. The weight loss in TGA is attributed to fluoride and OSDA. Thus, the weight of OSDA occluded in the framework was calculated by substituting the weight of fluoride from the weight loss of TGA. The calculated weight of OSDA was divided by the molecular weight to obtain the number of OSDA molecules, which was then divided by the number of unit cells within the remaining weight of the sample.

## **Detailed Procedure of microED structure refinement**

The diffraction datasets were collected at 80 K in a Thermo Fisher Scientific Talos Arctica transmission electron microscope, with a Ceta-D CMOS 4k x 4k camera and accelerating voltage of 200 keV by continuous rotation of the stage at a rate of 0.3° s-1, integration of 3 seconds per frame, and binning by 2. Diffraction datasets were saved as .SER file movies and processed using the automated data workflow converting the .SER movies into individual SMV frames with the program ser2smv and indexing and integrating the frames using XDS software.¹⁰

The selected diffraction datasets were processed with Pets2.0 software,¹¹ with  $\lambda = 0.0251$  Å, aperpixel = 0.00123 Å⁻¹, bin = 2, in the continuous rotation mode with rotation semi-angle 0.45 °, steps of rotation ( $\alpha$  step) was fixed as 0.9 °, GY = 26 and  $\Psi$  = 780. Both kinematical and dynamical reflection files were obtained after processing the diffraction datasets with Pets2.0. The initial structural model was obtained using Jana2020 software,¹² where the kinematical reflection file was imported and the crystal structure was solved with Shelxt^{13–16} within Jana2020 suite. The crystal structure was modeled as the SiO₂ molecular sieve. When solution of the kinematical structure was not possible, the model was imported from another crystal for dynamical refinement. Refinement was performed with isotropic atoms and free atomic coordinates. All kinematical solutions were refined with 10 cycles of refinement, enabling atoms with too large isotropic ADPs and in  $F^2$ . The results of kinematical structure refinement are summarized in Table **A.1.8-9**.

From the processed diffraction movies, 3 datasets each of the R and S enantiomers were chosen for dynamical refinement. Images were converted from SMV to TIFF 16-bit format using an in-house script, and the TIFF images were further processed by rotating counterclockwise and vertically flipping the images.

For absolute stereochemistry determination, the dynamical reflection file was imported in the software and thickness was optimized with RSg(max) of 0.66. Dynamical refinement was carried out with 10 cycles of refinement in F. After refinement of the initial model, the enantiomorph was inverted and the same refinement procedure was performed. The correct enantiomer is assigned by the crystal structures with lower values of  $R_{obs}$ ,  $wR_{obs}$ ,  $R_{all}$ , and  $wR_{all}$ .



Figure A.1.11. CDQ2-STW crystal analyzed by 3D ED.

Identification code	Davis-S-GeO40Si19			
Empirical formula	GeO ₄₀ Si ₁₉			
Formula weight	1246.23			
Temperature/K	80.15			
Crystal system	hexagonal			
Space group	P6 ₁ 22			
a/Å	11.9600(15)			
b/Å	11.9600(15)			
c/Å	30.090(3)			
α/°	90			
β/°	90			
$\gamma/^{\circ}$	120			
Volume/Å ³	3727.5(10)			
Ζ	3			
$\rho_{calc}g/cm^3$	1.666			
µ/mm ⁻¹	0.014			
F(000)	592.0			
Crystal size/mm ³	0.001  imes 0.0007  imes 0.0005			
Radiation	electron ( $\lambda = 0.0251$ )			
$2\Theta$ range for data collection/°	0.146 to 1.598			
Index ranges	$-13 \le h \le 13, -11 \le k \le 11, -33 \le l \le 33$			
Reflections collected	10411			
Independent reflections	1750 [ $R_{int} = 0.2528$ , $R_{sigma} = 0.1707$ ]			
Data/restraints/parameters	1750/222/145			
Goodness-of-fit on F ²	1.115			
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.1375, wR_2 = 0.3148$			
Final R indexes [all data]	$R_1 = 0.2137, wR_2 = 0.3579$			
Largest diff. peak/hole / e Å ⁻³	0.19/-0.20			
Flack parameter	-10.0(10)			
<b>TADIC A.1.7.</b> Crystal uata and structure refinement for $K^{-}CDQ2^{-}ST$	Table A.1.9. Cr	vstal data and strue	cture refinement for	r R-CDO2-STW
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Identification code	Davis-R-GeO40Si19				
Empirical formula	GeO ₄₀ Si ₁₉				
Formula weight	1246.23				
Temperature/K	293(2)				
Crystal system	hexagonal				
Space group	P6 ₁ 22				
a/Å	12.0500(15)				
b/Å	12.0500(18)				
c/Å	29.830(3)				
α/°	90				
β/°	90				
$\gamma/^{\circ}$	120				
Volume/Å ³	3751.1(10)				
Ζ	3				
$\rho_{calc}g/cm^3$	1.655				
µ/mm ⁻¹	0.014				
F(000)	592.0				
Crystal size/mm ³	0.001  imes 0.0007  imes 0.0005				
Radiation	electron ( $\lambda = 0.0251$ )				
$2\Theta$ range for data collection/°	0.138 to 1.436				
Index ranges	$-12 \le h \le 12, -12 \le k \le 12, -29 \le l \le 29$				
Reflections collected	12912				
Independent reflections	1311 [ $R_{int} = 0.3568$ , $R_{sigma} = 0.1461$ ]				
Data/restraints/parameters	1311/281/145				
Goodness-of-fit on F ²	1.028				
Final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0905, wR_2 = 0.2174$				
Final R indexes [all data]	$R_1 = 0.1254, wR_2 = 0.2391$				
Largest diff. peak/hole / e Å ⁻³	0.11/-0.12				
Flack parameter	-10.0(10)				

Sample	Candidate Space Group	R _{obs} (%)	wR _{obs} (%)	R _{all} (%)	wR _{all} (%)	Assigned Space Group
R-CDQ2-STW	P6 ₁ 22	12.22	11.52	31.41	17.63	P6₅22
	P6 ₅ 22	11.37	11.13	30.3	17.34	
R-CDQ2-STW	P6122	15.02	13.61	30.32	18.06	P6₅22
	P6 ₅ 22	14.46	13.23	28.69	17.54	
R-CDQ2-STW	P6 ₁ 22	20.06	19.64	34.54	21.10	P6₅22
	P6 ₅ 22	18.93	18.18	33.55	19.77	
S-CDQ2-STW	P6 ₁ 22	11.12	10.49	33.72	14.76	DC 00
	P6₅22	11.61	11.07	34.45	15.42	FU1ZZ
S-CDQ2-STW	P6122	13.29	11.13	30.58	14.21	DC 00
	P6 ₅ 22	14.03	11.54	31.81	14.73	P0122
S-CDQ2-STW	P6122	17.55	15.03	27.89	16.88	DC 00
	P6₅22	19.1	16.83	29.07	18.43	P0122

 Table A.1.10.
 Summary of space group determination of STW crystals by dynamical refinement.

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## APPENDIX B: SUPPLEMENTARY INFORMATION FOR PART II.

[Appendix B Intentionally Redacted: pp. 148-202]