Chapter 1: Introduction and Organization of Thesis Presentation

1. Introduction to Zeolites and Molecular Sieves

Zeolites and molecular sieves comprise a class of microporous (0.2–2 nm pore size), crystalline oxide minerals whose structure arises from a three-dimensional network of atoms such as Si, Al, Ga, Ge, Zn, Be, etc. These tetrahedrally coordinated atoms, or T-atoms, are coordinated to four oxygen atoms and are linked to other T-atoms by sharing each oxygen with a neighboring T-atom tetrahedron.[1,2] This results in a framework ratio of oxygen to T-atoms of two. While pure silica materials have a neutral electronic structure due to the Si^{4+} ion, other oxide compositions, such as the aluminosilicates, have an overall charge resulting from the tetrahedral coordination of the Al^{3+} ions.[3] This requires the introduction of extra-framework cations to balance the net charge on the framework; the number of these cations depends on the amount of Al T-atoms in the material. Typically, these cations are protons, inorganic cations such as alkali and alkaline earth metals, ammonium ions, and / or organic cations. The general empirical formula for the composition of a zeolite is: $Al_2O_3 \bullet x\, SiO_2 \bullet y\, H_2O \bullet M_{2/n}O$, where M is a cation. The ratio of silica (SiO_2) to alumina (Al_2O_3) is variable, but because aluminum tetrahedra do not sit in adjacent positions due to the bond angle strain that would impose, it is always equal to or greater than two. The various combinations of tetrahedral SiO_4 and AlO_4^- units form a wide array of topologies with one-, two-, and / or three-dimensional pores. The pore architecture can be interconnected, with cages and channels fronted by rings of T-atoms of different sizes and shapes, and can contain water molecules and cations in the interior of the architecture. It is this crystalline pore structure that gives zeolites their unique and inherent ability to selectively adsorb molecules based on shape and size; for this reason, zeolites are referred to as “molecular sieves”.[4]

The traditional definition of a zeolite is a crystalline, microporous *aluminosilicate*. A distinction is then made between zeolites and molecular sieves: while all zeolites are molecular sieves, not all molecular sieves are zeolites. As mentioned above, molecular sieve materials can have a wide array of chemical compositions based on framework ion substitution (not necessarily isoelectronic substitution, however), while still maintaining the structural aspects of zeolites. For instance, purely siliceous molecular sieves can be made with framework topologies analogous to aluminosilicates, but these would not be technically zeolites (although they are often referred to as “pure-silica zeolites”). Other framework substitutions may be made, generating classes of materials with aluminophosphate, metalloaluminate, metallosilicate, germanosilicate, etc., compositions, each resulting in different chemical properties. For instance, neutral frameworks, such as the silicates, are more hydrophobic than charged frameworks, and exhibit low ion exchange capacity, since cations are not required to stabilize the framework. All, however, maintain the unique crystalline structure that gives rise to both the molecular sieving action and the improvement in mechanical strength over amorphous materials. More recent definitions of zeolites focus more on their pore structure and guest-host molecular interactions, rather than their chemical composition, resulting in a broader definition of zeolites with an empirical formula of $C_x[Si_{(1-y)}T_yO_{(2+x)}]A_v \bullet wM$, where C represents the nonframework cations, A the anions, M the neutral species, and T the atoms that structurally replace the silicon atoms in the framework.[5] In this thesis, we will refer to zeolites using this broader definition.

Zeolite nomenclature can be particularly complex, as each new zeolite composition and topology synthesized may be given use-names or trade-names based on the research group, the composition, the topology, etc. For instance, Linde type D describes a zeolite with the chabazite structure (a natural zeolite) made by Union Carbide. Additionally, there are many more zeolites that can be synthesized, in terms of composition and structure, in a laboratory than in nature. Natural zeolites are given typical mineral names, such as ferrierite, barrerite, mordenite, etc., which are not usually named based on structure or composition, but rather the place the mineral was found or the scientist who found it. When a zeolite is synthesized that is isostructural with a natural zeolite, it can be named based on that zeolite or modified to represent synthetic conditions, but when a zeolite with a new topology is created, how is it named? In response to this problem, the International Union of Pure and Applied Chemistry (IUPAC) Commission on Zeolite Nomenclature and the International Zeolite Association (IZA) have developed a series of rules governing the naming of zeolite structures using three letter structure codes. All zeolites, natural or synthetic, can be described in terms of their topology using these designations. To date, the IZA has recognized 191 zeolite topologies, many with a variety of framework compositions.[6] For instance, the structure code "LTA" is based on the original trade-name of "Linde type A," and comes in a variety of aluminosilicate, silicate, and germanosilicate compositions. In its aluminosilicate composition, it can also have various cation guests. Therefore, in literature reports, zeolites with the LTA structure can be denoted as zeolite A, NaA (for the sodium cation), 5A (for the pore size), pure-silica zeolite A, ITQ-29 (for the university that created the silicate and germanosilicate compositions), etc., each of which defines something different about the composition or synthetic conditions. The physicochemical properties of a given zeolite, with a defined composition and pore architecture, may be tailored by framework substitution, as mentioned earlier, dealumination / realumination, ion exchange of the charge-balancing cations, insertion of catalytically active guest molecules, such as transition metal ions, metal complexes, basic alkali metals, and metal oxide clusters, through guest-host interactions, and functionalization of the interior and / or exterior of the zeolite surface. For instance, Jones and Davis prepared pure-silica zeolite of the BEA* topology that contained sulfonic acid via silica functionalization techniques to study the synthesis of 2,2-pentamethylene-1,3-dioxolane via the acid catalyzed reaction of cyclohexane with ethylene glycol.[7] Functionalization and insertion of guest molecules can also be used to modify the accessible portions of the pore architecture, or to decrease the size of the pore channels and cages; this technique has been used extensively in the design of mesoporous, non-zeolite materials.[8] The ability to tailor zeolites in these ways makes them ideal candidates for the development of novel, porous materials.

2. Synthesis and Formation of Zeolites

Zeolites are generally synthesized hydrothermally from a precursor gel containing T-atom precursors, inorganics or organic cations, mineralizing agents, and water. T-atom precursors include, but are not limited to, (a) silica sources such as fumed silica, tetraethylorthosilicate (TEOS), colloidal silica, and dried silica gels, (b) alumina sources such as aluminum metal, aluminum hydroxide gels, and sodium aluminate, and (c) heteroatom (B, Zn, Ga, Ge, etc.) sources such as nitrates, acetates, and oxides. Inorganic cations can be introduced as strong bases, such as NaOH and KOH, or as fluoride-containing acids, such as HF or NH_4F, which also introduces sources for the mineralizing agent. The mineralizing agent, either OH^- or F^-, cleaves Si-O bonds. Organic cations, which are referred to as “structure-directing agents”, are typically quaternary ammonium compounds, such as tetrapropylammonium hydroxide. The selection of the gel composition plays an important role in determining the final structure of the zeolite.

For instance, the structure-directing agent, or SDA, can direct the formation of a specific crystalline structure, but it does not generally act as a true template (imposing its shape on the final pore structure of the zeolite). The effects of the SDA on the resulting zeolite depend more on the shape and size of the molecule than its inherent chemical properties, and for small SDAs in zeolites undergoing hydrothermal crystallization at high temperatures, the shape itself is not critical, as thermal motions of the SDA can mask the shape.[9] The potential for size and shape dependence can be seen through the synthesis of ZSM-48 (structure code *MRE) and ZSM-5 (structure code MFI). Both zeolites contain 10-membered rings (that is, pores structures enclosed by rings containing 10 T-atoms linked together), but ZSM-48 has a one-dimensional pore structure, where ZSM-5 has a three-dimensional structure. ZSM-48 is formed using either linear molecules, such as diethylamine or dipropylamine as the SDA, while ZSM-5 is formed using tripropylamine or triethylamine; thus, the presence of a branched SDA produces the three-dimensional pore architecture of ZSM-5.[9] The choice of heteroatom affects the bond lengths and angles (Si-O-X, where X is a heteroatom), resulting in different “building blocks”, or combinations of tetrahedral units, and therefore the overall pore structure. The presence or absence of alkali metal cations, such as Na and K, accelerates the nucleation and growth of crystals, probably through the polymerization reactions of the silicate species in solution.[10] The choice of mineralizing agent can affect the final crystal size, defect density (concentration of silanols sites, Si-O-H), and framework density attainable. For instance, using F^- as the mineralizing agent has been shown to stabilize the formation of open-framework (low density), pure-silica zeolites with very low framework density. It also tends to produce large (~ 10 μm) crystallites.[11,12,13] All of these precursor gel choices affect the final synthetic result.

In addition to the gel chemistry, the choice of reaction conditions plays a role in determining the final crystalline structure. These include reaction time, reaction temperature, presence of seeds, aging of the precursor gel, and static vs. rotating crystallization conditions. Zeolites are generally crystallized at temperatures ranging between 100 – 200 °C and for times of a few hours to several months. Because zeolites are not the thermodynamic product of synthesis (this is dense quartz for pure-silica zeolites), but are instead kinetically trapped phases, the selection of lower temperature conditions favors the selection of more open-framework, or less dense, structures. Additionally, the use of pre-formed zeolite seeds can both encourage the formation of a specific crystalline structure in a gel that might otherwise form a mixture of zeolite topologies, and it can decouple the nucleation and growth steps of zeolite formation, leading to larger crystallites.[11,14] Lastly, longer reaction times can result in different crystalline products from the same precursor gel; for instance, CIT-6 (structure code BEA*) and VPI-8 (structure code VET) crystallize in three and seven days, respectively, from the same zincosilicate gel.[15,16] By varying these conditions, novel zeolite structures may be obtained.

Despite the knowledge of how various gel and reaction conditions affect the final zeolite product, the mechanism for zeolite formation remains not fully understood. Studies of the synthesis of the pure-silica zeolite known as silicalite (structure code MFI), which is a simple model system whose precursor gel contains only tetraethylorthosilicate, tetrapropylammonium hydroxide (the SDA and mineralizing agent), and water, have provided some insight into zeolite formation.[17,18,19,20] These studies suggest that in the zeolite precursor gel, the hydrated SDA loses its hydration sphere and interacts with the inorganic silica species via van der Waals interactions. The increase in entropy in the gel is the driving force for the formation of aggregates from smaller building blocks (5 nm building blocks have been observed by small angle X-ray scattering experiments) or crystal nuclei. These aggregates grow into larger silicalite crystallites (50 – 100 nm), and continue to grow in size over the crystallization period, suggesting Ostwald ripening. The effects of nanoparticles and their formation has been shown to play a similar role in the production of aluminosilicates.[21] The implication of full understanding of the formation mechanism would be profound: with this knowledge, zeolites could be rationally designed even beyond our current modification capabilities by the proper selection of SDAs, heteroatoms, reaction conditions, etc., for their specific end use. This is the goal of a large selection of past and current zeolite research.

3. Zeolite Applications

Due to their compositional variety, uniform pore space, and structural symmetry, zeolites have high surface areas, the ability to sieve molecules based on size- and shape-selectivity, and internal physicochemical properties that can range from acidic to basic and hydrophobic to hydrophilic.[22] The unique, and tunable, physicochemical properties of zeolites have led to their use in a wide array of applications. For instance, due to (a) their high ion-exchange capacity if not created with a neutral framework, and (b) their ability to adsorb water and small molecules very easily, they have been used for gas purification, desiccation, and water softening. Because of (c) their shape and size selectivity, they are useful for separation processes; for example, ITQ-12 (structure code ITW) has been shown to selectively separate propane and propene from its mixtures.[23,24] Lastly, due to (d) the presence of Brønsted acid sites when a proton balances a negative charge of an alumina site is the basis for their use as a heterogeneous catalyst in applications such as catalytic cracking, hydrocracking, hydroisomerization, alkylation, methanol to gasoline conversion, NO_x reduction, etc. They may also be used as a shape- or size-selective catalyst, as total selectivity occurs when the gas molecules are similar in size to the pore apertures.[25] The combination of (c) and (d) makes them useful for combining reaction and separation operations, which could significantly reduce the operating and capital costs of industrial chemical syntheses by replacing thermal separation processes. This application makes use of the selectivity of the pore size, the chemical nature of the permeating molecules, and the adsorption properties of the zeolite to, for instance, selectively separate n-hexane from branched isomers in a hydroisomerization membrane reactor using silicalite, the pure-silica composition of the zeolite with structure code MFI (linear alkanes are preferentially adsorbed and supplied to the catalyst).[26] While many of these applications use zeolites in compressed powder form, such as pellets or granules, more recent applications frequently use zeolites in planar (thin film or membrane) form. For instance, zeolites have been suggested for use as separation membranes[27,28,29,30,31,32], membrane reactors[25,33,34], adsorption coatings[35], catalytic coatings[36,37], heat pumps[38,39], chemical sensors[40,41,42,43,44], and low dielectric constant (*k*) materials for semiconductors.[45,46,47,48,49,50,51,52,53,54,55,56,57,58,59] For these reasons, the study and development of zeolites and their uses is of great importance scientifically and industrially.

4. Thesis Organization

This thesis consists of two separate pieces of research into zeolite science. Both, however, are rooted in the development of new synthetic routes to zeolite films.

Part I presents the development of a new methodology of producing fluoride-mediated, pure-silica zeolite films, primarily for low-*k* applications. Chapter 2 provides a general introduction into zeolite films and membranes. This chapter contains information on how films and membranes are created, including support choice, synthetic strategies, characterization techniques, defect identification and elimination, the development of novel synthetic techniques, and a short discussion of selecting methods based on application intent. Chapter 3 discusses the need for the development of new methods to synthesize fluoride-mediated, zeolite thin films, and examines two novel methods for this purpose. The first method utilizes a seeding and dilution modification to typical *in situ* film syntheses, while the second applies the vapor phase transport method to the zeolite mineralizing agent, fluoride, to crystallize a precursor film deposited by dip-coating techniques. Both methods are evaluated via the synthesis of the silicate and germanosilicate compositions of the ITQ-29 zeolite (structure code LTA) thin films on a variety of substrates. The chapter also discusses film characterization to elucidate film quality, and suggests how the new methods could extend the current library of zeolite films available. Chapter 4 uses the methodology developed in Chapter 3 to demonstrate the film synthesis of the pure-silica zeolites with structure codes CHA, STT, ITW, and -SVR. Using these zeolites, as well as the pure-silica LTA from Chapter 3, we investigate their applicability for low-*k* materials using two different techniques for measuring the dielectric constant of the materials. Through this investigation, we demonstrate that these materials are appropriate for low-*k* applications, especially the LTA topology, which we found to have the lowest intrinsic dielectric constant of all the pure-silica zeolites. Additionally, we show that the Bruggeman effective medium correlation, which is a model for the behavior of a material's dielectric constant based on its porosity, is applicable to zeolites, but it does not take into account the effects of pore structure, which we show also plays a role in determining the dielectric constant of the material.

Part II is focused on the development of a new synthetic strategy for removing the structure-directing agent from the pores of zeolite films and membranes, a task usually accomplished via thermal calcination, which can structurally damage films and membranes. Here, we propose and test the use of a photo-cleavable structure-directing agents that can be disassembled through photolysis within the zeolite pore space and removed after zeolite formation. Chapter 5 introduces the subject, and discusses the need for this new route, its potential compatibility with various zeolite applications, and the requirements for developing new structure-directing agents. Chapter 5 also contains a brief review of organic photo-protecting groups, which could be used to develop a photolabile structure-directing agent, including their stabilities, cleavage mechanisms and compatibility with zeolite syntheses. It concludes with a discussion of the 2-nitrobenzyl family of photo-protecting groups, which has the potential to be an appropriate choice for zeolite syntheses. Chapters 7 and 8 discuss attempts to synthesize zeolites (silicates, aluminosilicates, and aluminophosphates) using two different photolabile structure-directing agents, and demonstrate the feasibility of the photolabile structure-directing agent route. Chapter 9 concludes the thesis, summarizes Parts I and II, and discusses future opportunities for using the techniques developed here for novel applications, such as zeolite film patterning.

5. References

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