Chapter One: Introduction

1.1: Molecular Sieve Synthesis

Molecular sieves comprise a family of porous inorganic materials. The crystalline nature of these materials offers defined pore diameters and high internal void volume. Pore dimensions are often on the order of small molecules and hence selective adsorption can be achieved. Materials are classified as microporous (pore diameter $\leq$2 nm) or mesoporous (2 <pore diameter $\leq$50 nm). Framework structures are assigned by the International Zeolite Association with an online database available[1]. Structure codes are three-letter designations of the material name; e.g., ZSM-5 has the MFI structure code. Various inorganic compositions have been reported with significant efforts devoted to high-silica molecular sieves. Pure-silica materials represent one molecular sieve subset where [SiO_4] tetrahedra are linked to form a three-dimensional SiO_2 framework. In the absence of lattice substitution the framework is neutral. Introducing tetrahedral aluminum into the framework results in negative framework charge and a cation is required for neutrality. This is shown schematically in Figure 1.1. If a proton is the cation a Brønsted acid is formed and the resulting material can be active in acid catalyzed reactions. In addition, the defined pore structure offers shape-selective catalysis. Aluminosilicate molecular sieves form the zeolite family, although all silica-based molecular sieves are often called zeolites. Research emphasis has been placed on zeolites due to applications in petrochemical and refining transformations, adsorption and as ion-exchange materials.

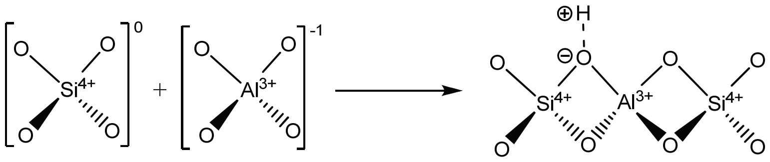

Figure 1.1: Schematic of Brønsted acid site

Figure 1.1 shows aluminum incorporation into a silicate lattice and this is just one example of possible substitution. Other examples of elements incorporated in silica-based molecular sieves include B, Ga, Ge, Be, Zn and Ti. Any lattice substitution must obey the bonding rules outlined by Pauling[2] and Loewenstein[3]. Molecular sieves of non-silica composition have been synthesized with the aluminophosphate (AlPO) family extensively studied. These materials have strictly alternating -Al^{3+}-O-P^{5+}-O- sequences and represent another family of neutral frameworks. Substitution of Si^{4+} for phosphorus creates negative framework charge as above and the resulting silicoaluminophosphate (SAPO) materials can show activity in acid catalyzed reactions. Similarly, substituting M^{2+} (e.g., Co^{2+}, Zn^{2+}) for Al^{3+} also produces negative framework charge. Most phosphate-based materials have significantly lower hydrothermal stability compared to high-silica materials and this has limited applications.

Early investigations into zeolite synthesis aimed to replicate geothermal conditions where natural zeolites are formed[4, 5]. Reaction gels containing alkali hydroxide, silica, alumina and water lead to materials such as Linde Type A (LTA) and zeolites X and Y (both isostructural with the mineral faujasite (FAU)). Further advances occurred with the introduction of quaternary ammonium molecules, starting with tetramethylammonium hydroxide[6]. Extension to tetraethylammonium lead to the discovery of zeolite Beta, with this being the first example of a high-silica zeolite ($Si/Al \geq 5$)[7]. Continued expansion of organic reaction components has lead to the discovery of numerous frameworks, with 179 structure codes assigned by the International Zeolite Association (as of May, 2009).

High-silica reactions involving organic molecules result in the organic species occluded within the product phase. Most organic molecules were capable of making more than one product depending on the reaction conditions (e.g., SiO_2/Al_2O_3 ratio, alkali cation addition, temperature). In addition, any given product could often be made using many different organic molecules. This lead to a proposed restriction of the term "template" to cases where one organic specified only one product[5]. One commonly cited example of a template is the tris-quaternary molecule used to make ZSM-18 (MEI)[8]. For all other cases the organic was deemed a structure directing agent (SDA). This latter designation covers the majority of organic molecules investigated to date and will be used in this thesis.

The organic-silicate distances observed in molecular sieves are of the order where van der Waals attractions can occur. This lead to experiments aimed at understanding organic-silicate interactions as the reaction gel transformed from X-ray amorphous to crystalline. Fundamental insights into the steps involved in high-silica material nucleation and crystal growth have been achieved using a model system. This system is the tetrapropylammonium hydroxide/sodium hydroxide/silica/water system that produces pure-silica MFI. The synthesis is reproducible and relatively fast making it ideal for temporal analysis. Solid-state magic angle spinning (MAS) NMR ^{1}H-^{29}Si experiments revealed polarization transfer from organic to silicate species before long-range order was observed by X-ray diffraction (XRD)[9]. Further experiments indicated overlap of silicate and SDA hydrophobic hydration spheres with ordered water release[10, 11]. These studies gave the first conclusive evidence of short-range association before crystallization occurred. Modification of the synthesis gel by using tetraethyl orthosilicate (TEOS) results in optically clear gels. These gels were examined under synthesis conditions by *in situ* dynamic light scattering (DLS) and were shown to contain particles ~3–10 nm in diameter[12]. Additional *in situ* experiments using synchrotron radiation confirmed the presence of these particles and a synthesis pathway was proposed[13, 14]. The proposed pathway is shown in Figure 1.2 and involves overlap of hydrophobic hydration spheres leading to ~3 nm diameter particles that can aggregate under appropriate conditions to form ~10 nm diameter particles. Nucleation was proposed to occur from these aggregates with subsequent crystal growth from the 3 nm “primary” units.

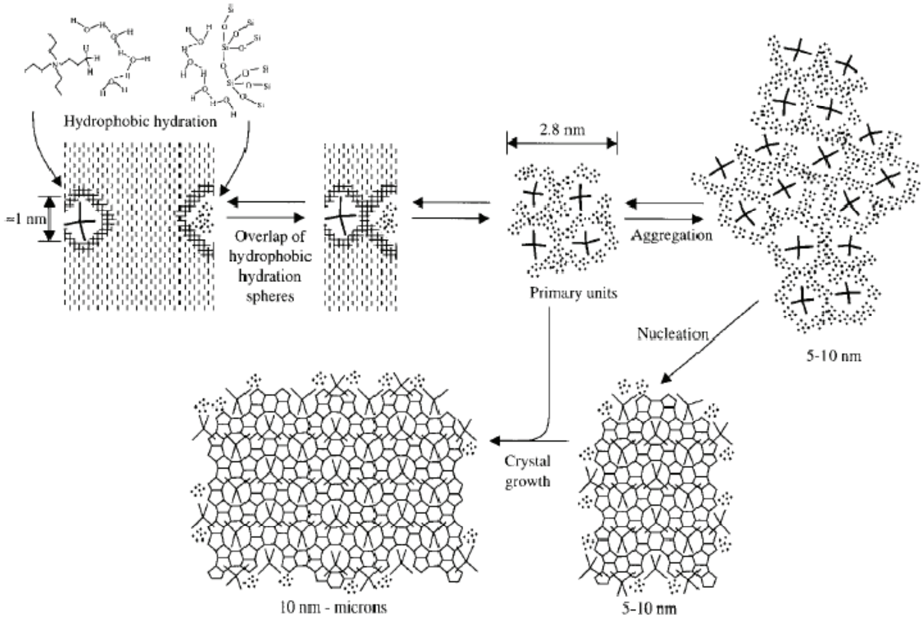

Figure 1.2: Scheme for Si-MFI-TPA crystallization (from Reference 13)

Another important aspect of high-silica molecular sieve synthesis was understanding synthesis thermodynamics. Calorimetry experiments for pure-silica molecular sieves showed enthalpies of transition between 6.8–14.4 kJ mol^{-1} relative to quartz[15]. The enthalpies span approximately twice the thermal energy (RT) at synthesis conditions indicating small energetic differences between porous frameworks and relatively small metastability compared to quartz. Accounting for the full synthesis cycle indicated enthalpy and entropy contributions were of comparable magnitude and were within several RT at synthesis temperature[16]. The study revealed a relatively flat energy landscape indicating product selectivity was largely determined by kinetic factors.

Recent developments in the use of fluoride and germanium have lead to many new framework discoveries. Reaction conditions for high-silica molecular sieves evolved from attempts to mimic geological conditions with hydroxide employed to mineralize silica. Early investigations into reactions containing fluoride showed no difference in product compared to hydroxide reactions[17, 18]. These studies were performed at relatively high water to silica ratios ($H_2O/SiO_2>20$) based on existing hydroxide preparations. Significantly reducing the water content ($2<H_2O/SiO_2<10$) resulted in the discovery of several new frameworks[19]. Many products under fluoride conditions show very few framework defects and trends have emerged where low framework density products become favored at low H_2O/SiO_2[20, 21]. In addition, pure-silica frameworks containing double-four membered rings (D4Rs, a cube) have emerged. This structural feature had not been observed in high-silica molecular sieves derived from hydroxide reactions. The addition of germanium also promotes the formation of D4Rs. Combining germanium, fluoride and low water content has lead to several very open structures being discovered, e.g., ITQ-21 (three-dimensional 12MR)[22] and ITQ-33 (18x10 MR)[23]. The longer Ge-O bond[24] results in preferential Ge substitution in D4R structures[25].

The advances in understanding high-silica molecular sieve synthesis are still not sufficient to predict what product will result from a given SDA. Molecular modeling has proven useful in certain cases to predict suitable SDAs for known products[26]. Without appropriate retrosynthetic methodologies the discovery of novel frameworks has relied on synthesizing various SDAs and observing what product is obtained. Some general guidelines for desirable SDA characteristics have been accumulated through these studies[27]. The inorganic conditions also play a significant role in determining the product with subtle changes in reagent selection offering different reaction outcomes[28]. Recent application of high-throughput (HT) techniques has resulted in several new discoveries through thorough reaction variable exploration[29]. Discovery of new frameworks will continue to rely on a combination of new SDAs coupled with appropriate inorganic conditions.

1.2: Previous Examples of Imidazolium Structure Directing Agents

Imidazolium SDAs have been used in molecular sieve synthesis with the first investigations in the 1980s[30, 31]. The phases obtained were ZSM-5 (MFI), ZSM-12 (MTW), ZSM-23 (MTT), Theta-1 (TON), KZ-2 (TON) and ZSM-48 (*MRE). All products are 10MR structures except MTW that is a puckered 12MR. In addition, all products are one-dimensional except MFI. SDAs with notable selectivity to the same product with decreasing SiO_2/Al_2O_3 ratios were 1,3-dimethylimidazolium (TON), 1,3-

diisopropylimidazolium (MTT) and 1,2,3-trimethylimidazolium (MTW). The SDAs were synthesized by imidazole alkylation, with cyclopentyl, neo-pentyl and benzyl groups the largest investigated. No products were reported using 1,3-dibenzylimidazolium or 1,3-dicyclopentylimidazolium, while MTT was reported for 1,3-bis(neo-pentyl)imidazolium. In addition, the early investigations used the SDAs as halide salts together with sodium silicate as silica source. This corresponded to $Na^+/SiO_2 \geq 0.59$ for all cases. Subsequent evolution in gel compositions now see SDAs used as hydroxide solutions with $Na^+/SiO_2 \sim 0.1\text{-}0.2$ and $SDA^+OH^-/SiO_2 \sim 0.15\text{-}0.25$ typical.

Further studies were performed under hydroxide conditions with a series of diquaternary imidazolium SDAs[32]. The SDAs studied were based on the selective SDAs outlined above with methylene spacers of varying length between imidazoliums. Starting imidazoles were 1-methylimidazole, 1-isopropylimidazole and 1,2-dimethylimidazole. Again, one-dimensional products TON and MTW were favored with three-dimensional MFI more common than above. In contrast, MTT was absent indicating sensitivity to periodicity along the pore. Several original imidazolium SDAs were revisited after the breakthroughs in fluoride mediated reactions at low water to silica ratios[19]. The results showed TON and MTT for 1,3-dimethylimidazolium and 1,3-diisopropylimidazolium respectively at all water to silica ratios[33]. In addition, a new phase named ITQ-12 (IWW) was discovered using 1,3,4-trimethylimidazolium[34]. IWW is a small pore material constructed from linked D4Rs forming slit-shaped cages. Obtaining a material rich in D4Rs is in contrast to the structures listed above that are rich in five membered rings (pentasil structures). Subsequent work showed 1,2,3-trimethylimidazolium also made IWW at all water to silica ratios[21]. Observing the same product at all H_2O/SiO_2 ratios was rarely observed across an entire SDA library. The implication was the imidazolium dominated nucleation selectivity to a greater extent than the fluoride anion. Single-crystal analysis of pure-silica MTT synthesized using 1,3-diisopropylimidazolium revealed the isopropyl lobes had similar periodicity to the undulating MTT framework. This guest/host pair appeared particularly favorable due to mutual periodicity.

Additional studies under boron-rich fluoride conditions with 1,3-diisopropylimidazolium lead to the discovery of a new material denoted SSZ-70[35]. Chapter Two of this thesis explores the synthesis of SSZ-70 as described below. Independent studies using 1-ethyl-3-methylimidazolium under germanosilicate fluoride conditions lead to the discovery of IM-16 (UOS)[36]. This material has a 10x8x8 MR pore topology and is rich in D4Rs owing to high Ge content (Si/Ge~1.4).

Finally, the unique properties of imidazolium ionic liquids were exploited to synthesize several new AlPO materials SIZ-1 to SIZ-11[37, 38]. This “ionothermal” method is unique in that the solvent also acts as the SDA. Reactions have been demonstrated at atmospheric pressure and solvent recycling has also been shown. Imidazolium ionic liquids 1-ethyl-3-methylimidazolium bromide, 1-isopropyl-3-methylimidazolium bromide, and 1-butyl-3-methylimidazolium bromide are examples used in this approach. No reports of high-silica molecular sieve synthesis have appeared although active research is expected in this area.

The examples listed above show imidazolium SDAs to be well suited in molecular sieve synthesis. Most studies have focused on small imidazoliums available through imidazole alkylation and therefore larger substituent groups have not been thoroughly investigated. Since the initial studies in the 1980s, alternative synthetic methods for 1,3-

disubstituted imidazoliums have emerged[39]. This allows expansion of previous studies with an emphasis on larger imidazolium SDAs.

1.2: Thesis Overview

The focus of this thesis was exploring larger imidazolium SDAs in molecular sieve synthesis. Chapter Two explores the synthesis of new material SSZ-70 using a library of 16 imidazolium SDAs. The majority of the SDAs studied had not been reported in molecular sieve synthesis before. Chapter Three evolved from the SSZ-70 work where Beta was a common product. This separate study explored chiral imidazolium SDAs with the aim of synthesizing Beta enriched in chiral polymorph A. The underlying theme of Chapters Two and Three was exploring guest/host relationships. The aim for these studies was to observe product (host) changes across different SDAs (guest) to find appropriate SDAs for the desired product. Both studies involved synthesis and characterization of imidazolium SDAs plus screening all SDAs in inorganic reactions. Of general interest in both studies was whether larger SDAs would show strong specificity to one product as in the case of 1,3-diisopropylimidazolium to MTT. Chapter Four sought to expand the results obtained with 1,3-bis(1-adamantyl)imidazolium in Chapter Two by creating supramolecular SDAs through adamantyl/β-cyclodextrin inclusion complexes. Finally, Chapter Five offers conclusions and considerations for future directions.

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