Chapter 5: Introduction to Part II of Thesis

1. Introduction

The unique chemical and structural properties of zeolites, such as their compositional variety, uniform pore spaces, structural symmetry, high surface areas, the ability to sieve molecules based on size- and shape-selectivity, etc., result in the use of zeolites in a wide array of applications.[1] Additionally, the potential to tailor many of these properties by modifying the zeolite synthesis conditions can yield materials that are exceptionally well-suited to their applications. These applications generally require full access to the internal surface area of the prepared materials, which necessitates the removal of any organics occluded during the synthetic process, such as structure-directing agents (SDAs) and pore filling agents, to open the pore space. There are four methods to clear the pore space of the organic materials: high-temperature calcination, ultra-violet (UV) irradiation / ozonolysis, extraction, and acid-cleavage / recombination.[2,3,4,5] The first three of these methods result in the destruction of the occluded organics, while the last method uses the chemical nature of the structure-directing agent to recover the original occluded organic after removal.

High-temperature calcination, which destroys the structure-directing agent via thermal decomposition at temperatures above 200 °C and more commonly between 500 – 700 °C, is the most frequently used method to remove occluded organics from inside the zeolite pore space. This is primarily due to the ease with which organic removal can be accomplished using a high temperature oven connected to gas sources such as air, nitrogen, or oxygen. However, it has several disadvantages. First, because this method removes the organic through combustion, it generates various CO_2, NO_x, etc., greenhouse gas species that must be removed from the effluent for environmental reasons. Second, for applications that require the use of zeolite nanoparticles of uniform size, calcination may cause aggregation of zeolite nanoparticle colloids due to Si-O-Si bridging, rendering the colloids unusable.[6] Third, calcination may result in the collapse of the zeolite framework due to thermal stresses or dehydration if the calcination temperature is too high. Fourth, in non-traditional applications that require zeolites in planar form, calcination can lead to crack formation, buckling, and/or delamination in zeolite thin films or membranes due to thermal stresses (typically caused by differences in the coefficients of thermal expansion between the planar zeolite and the substrate) within the film and at the film / substrate interface (Figure 5.1).[7] Fifth, calcination is a nondiscriminatory process through which all organic molecules are removed; this is a problem for new classes of zeolite-like materials, such as organic-inorganic hybrids with zeolite structures, which may contain organic molecules in the framework itself.[8,9] These disadvantages result in higher processing costs and unwieldy procedures to synthesize, for instance, zeolite films with minimal defects, and nanoparticles with minimal aggregation. For example, current methods for reducing aggregation during template removal include the use of organic or polymeric matrices to physically bar aggregation[10], the surface functionalization of colloidal particles to minimize interactions[11], and acid extraction of structure-directing agents from surface-modified zeolite nanoparticles.[12] To minimize crack formation in zeolite films, calcination studies are carried out for each film topology, thickness, substrate, etc.[13] Moreover, many films and membranes may be part of devices incompatible with high-temperature calcination procedures, thus disallowing "fixes" of this sort. For these types of applications, calcination may present a pyrrhic victory in terms of material costs and processing problems.

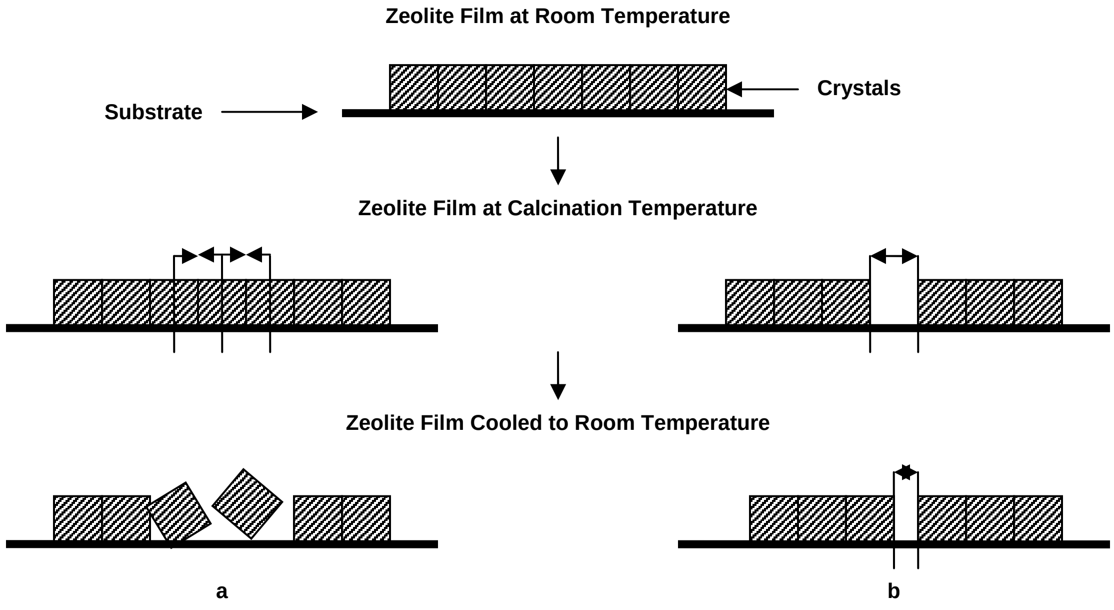

Figure 5.1 Schematic representation of the results of thermal stresses on zeolite films during calcination: (a) cracking at film / substrate interface if film is not well-adhered to substrate, (b) cracking within film if film is well-adhered to substrate

In an effort to address some of the problems with calcination, a solvent extraction approach was developed as a structure-directing agent removal technique wherein the occluded organic is washed out of the zeolite pore space with a solvent.[5] Although rarely used because it requires small structure-directing agents that can fit through the small pores and cages of the zeolite framework in order to exit the structure during extraction, it can be beneficial in applications where high temperatures would adversely affect the physicochemical properties of the final material. Because of this, it is frequently used to remove templating agents for mesoporous (non-zeolite) materials. In general, the ease with which an occluded organic molecule can be removed from the pore space correlates well with its decomposition temperature during Thermogravimetric Analysis (TGA).[5] For instance, the fraction of a structure-directing agent that can be removed, if the molecule is small in comparison to the zeolite's micropore size, via extraction has been shown to depend on the fraction of the molecule that is combusted below 400 °C. The fraction that combusts above this temperature may be strongly bound to the zeolite framework and solvent extraction of this portion of the molecule can damage the framework. Additionally, if the interaction between the organic molecule and the inorganic framework is too strong, the extraction technique does not work; for many zeolites, the interaction is quite large (-181 ± 21 kJ per mole SDA), rendering the technique unusable except in specific cases.[14]

UV irradiation / ozonolysis is a non-thermal, photochemical "calcination" approach that recently has been used as a replacement for calcination for applications that require planar zeolites. This approach was designed to eliminate the film defects caused by thermal stresses generated during calcination.[3,15] It has the additional benefit that it can be used in conjunction with masking techniques to generate spatial patterns over thin films, where some of the zeolite film has been photochemically treated to open the pore space, and other areas have not (Figure 2). However, this method also results in the destruction of the organic molecules through the proposed mechanism of photo-induced chemical reactions, in which short-wave UV radiation generates ozone and atomic oxygen that attack the organic species. Additionally, the method could potentially damage the inorganic framework, as the method generates activated species such as ions, free radicals, and excited organic molecules.[15]

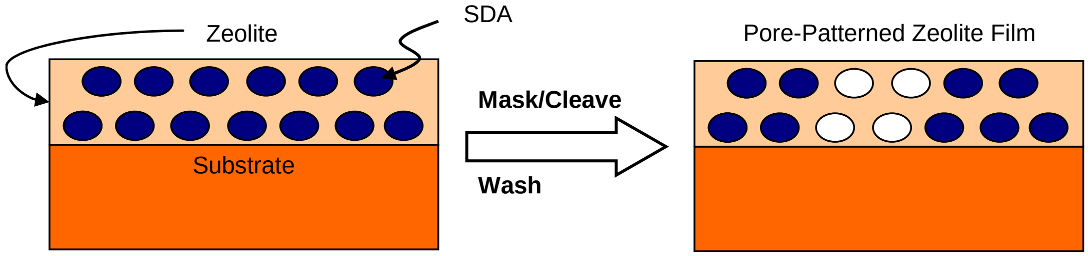

Figure 5.2 Schematic of zeolite film patterning using UV / ozonolysis photochemical "calcination" treatment to remove occluded organics

The three previously mentioned organic-removal techniques all result in the destruction of the structure-directing agent or other occluded organics. Recently, the use of larger, more complex and frequently more expensive structure-directing agents has increased due to industrial interest in creating new zeolite framework types with larger pores or nontraditional framework components.[16,2] Novel structure-directing agents often provide the best means to develop these new types of materials, as the structure-directing agents can act as direct templates around which the zeolite pores form, such as in the zeolite ZSM-18 (structure code MEI)[17], or as guides to the development of a given pore structure, without actually templating the zeolite.[18] Frequently, one structure-directing agent, like tetraethylammonium hydroxide, can synthesize several zeolite topologies through the use of differing synthesis conditions, such as reaction mixture composition, reaction / zeolite crystallization time, reaction temperature, etc. Additionally, slight changes in the size and shape of a structure-directing agent can greatly influence the resulting crystalline product.[19] For these reasons, investigations of various structure-directing agents are often of primary importance when attempting to crystallize a new zeolite structure. However, when novel structure-directing agents can account for up to 25% of the total cost of industrial zeolite syntheses, techniques that destroy the organics to open the pore space become cost-prohibitive.[1,20] For this reason, removal techniques that can result in a partially or wholly reusable structure-directing agent are desirable.

The fourth and final method to eliminate occluded organics addresses the issue of structure-directing agent expense by removing the organics via a combustion-free methodology: acid cleavage / recycling. In this case, the zeolite is formed using a structure-directing agent that is a member of a class of quaternary ammonium cation-containing acid-cleavable ketal compounds.[2,21] These compounds can be cleaved into much smaller ketone- and diol-containing fragments (Figure 5.3), which can then be removed from the pore space and recombined into the original molecule for further zeolite syntheses, as shown in Figure 5.4. Figure 5.5 shows the organic molecules that

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[1] For example, a typical SDA is tetrapropylammonium bromide (98%), which can be purchased in bulk for about 1/10 of the cost cited in the Fluka catalogue ($0.227 / g), or $0.028 / g. Generally, the SDA : SiO_2 molar ratio in synthesis is < 0.2, so for every pound of silica used, the SDA costs approximately $0.912. The SDA tends to be the most expensive chemical and its cost must be balanced against the average processing costs of $10-12 per pound of zeolite per day. Fairly inexpensive organic molecules like tetrapropylammonium bromide (98%), then, are approximately 7% of the overall cost of zeolite synthesis industrially.

have been used to date with this method, which has been shown to synthesize ZSM-5 (structure code MFI), ZSM-12 (structure code MTW), MOR, and VPI-8 (structure code VET).[21]

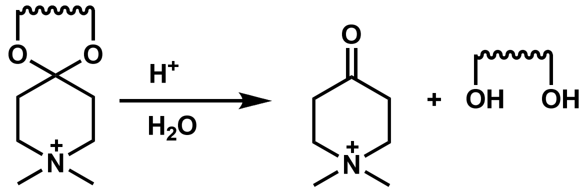

Figure 5.3 Cleavage reaction of ketal-containing structure-directing agent into smaller fragments[21]

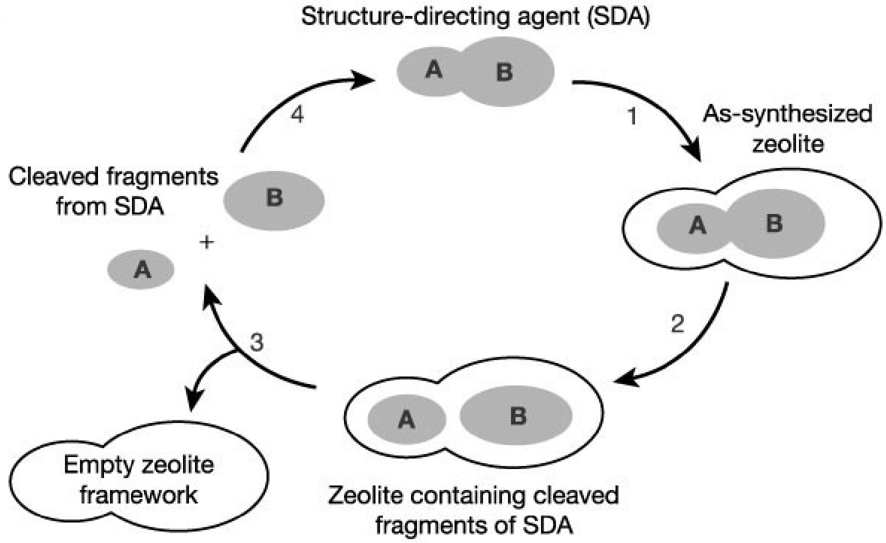

Figure 5.4 Recyclable structure-directing agent route – (1) zeolite synthesis; (2) cleavage of the organic molecules inside the zeolite pores; (3) removal of the cleaved fragments; (4) recombination of the fragments into the original SDA molecule[2]

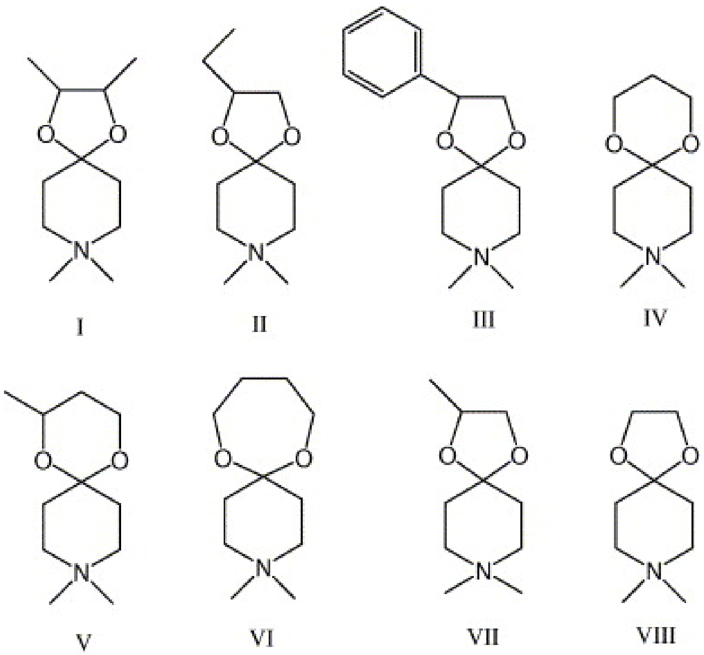

Figure 5.5 Various acid-cleavable ketal structure-directing agents [21]

Since this method allows for the removal and reuse of the structure-directing agent, it can be used as a low-cost zeolite preparation method. However, it may not be suitable for nanoparticle suspensions, thin films, or for many zeolite phases in general due to the nature of the extraction process – i.e., the presence of acid and water may change the suspension properties and can cause hydrolysis of unstable zeolite phases due to their siliceous nature. Hydrolysis is frequently a problem that occurs during high-temperature calcination of zeolites, because generation of water vapor during structure-directing agent destruction can lead to leaching of elements like Fe, Ga, and Zn (used in de-NO_x catalysts, chemical sensors, etc.) from the framework.[22] This places constraints upon the acid-cleavable, recyclable method of structure-directing agent removal.

While each of the aforementioned structure-directing agent removal techniques has advantages, each is limited by cost, effectiveness, or potential compatibility with end-use requirements. Although the recycling of structure-directing agents has addressed the reduction of zeolite cost, and the use of UV / ozonolysis photochemical “calcination” has reduced the problems associated with high-temperature calcination for thin films and nanoparticle suspensions, a method that can address both sets of problems simultaneously in a way that is compatible with more recent technologies that use zeolites in planar form would be beneficial. Given the recent attention to the development of these types of nontraditional zeolite applications, it is apparent that a structure-directing agent removal technique that is compatible with various planar zeolite fabrication processes, has a low cost, and is environmentally sustainable must be developed.

2. Photolabile Structure-Directing Agents

A pore-opening technique to remove occluded organics via a combination of recyclable structure-directing agents and a photochemical treatment wherein the original structure-directing agent is not completely destroyed could be developed using potentially recyclable, photolabile structure-directing agents. The proposed method is similar to the recyclable, acid-cleavable SDA method mentioned earlier and shown in Figure 5.3, in that the original structure-directing agent is cleaved post-zeolite synthesis; however, it differs in two major aspects. First, the organic molecule designed for zeolite synthesis is photoactive at a given wavelength of light; and second, the cleavage step inside the pores is carried out by photolysis. The cleaved molecule may then be washed out the pores using a simple extraction process. The cleavage products may then be recombined, or, if photocleavage results in one unstable cleavage product (as is common), the stable cleavage product may be photoprotected again for reuse as a structure-directing agent. UV cleavage neatly avoids the problems calcination presents in various systems, as well as the issues with the use of acid in the acid cleavage / recycling methodology.

The photolabile structure-directing agent method is particularly advantageous for the development of nanostructured, planar zeolite materials because, like UV / ozonolysis, it can be used in conjunction with micropatterning techniques. For instance, recyclable, photolabile structure-directing agents, in conjunction with physical masks to generate electronic features through filled and unfilled pore space, may provide an interesting method with which to synthesize pure-silica zeolitic thin films of various topologies by *in-situ* crystallization techniques that are suitable for extension into the semiconductor development process, and could avoid the problems associated with thin films and high temperature calcination. This could be useful for the development of pure-silica zeolite thin films for low-*k* materials. Micropatterning could also be used to selectively functionalize certain areas of a zeolite film for catalysis applications by eliminating organics in some regions whilst leaving the pore space filled in others. Lastly, micropatterning could also lead zeolites to be more readily used as media for the organization of semiconductor quantum dots, as nanoreactors, and as storage for nonlinear molecules, such as proteins.[23]

The development of a photolabile structure-directing agent (P-SDA) route to zeolite synthesis requires three items to demonstrate its feasibility. First, an organic molecule must be created that is capable of acting in a structure-directing role. Therefore, the molecule must be stable at common zeolite synthesis conditions (basic pH, 100 – 200 °C temperatures) and able to crystallize a zeolite. The molecule's ability to do this hinges on the ability of the P-SDA to interact with the hydrophobically hydrated silica whilst retaining enough hydrophilicity to remain in the reaction solution, a condition frequently satisfied by the presence of quaternary ammonium ions in the SDA.[24] Second, the molecule must be photolytically active, which requires the development of potential photolabile structure-directing agents using photochemical protecting groups common in organic chemistry research, in conjunction with small molecules that have shown potential as structure-directing agents for a variety of zeolites. Third and finally, these photolabile molecules must then be capable of cleavage inside the framework of the zeolites they have crystallized to yield organic-free zeolites, implying that the zeolite they become trapped within must have large enough pore structures with low enough inorganic-organic interactions to prevent steric hindrance of cleavage. These three conditions for proof of feasibility impose strict requirements on both the type of organic molecule that can be used, as well as the choice of zeolite synthetic chemistry, and guide the selection of potential photolabile structure-directing agents.

3. Photochemical Protecting Groups in Organic Synthesis

Protecting groups are widely used during the organic synthesis of polyfunctional molecules. In order to generate an array of functionalities on the same molecule, or substrate, individual functional groups must be blocked or protected in order to attach the next group without destroying the pre-existing groups. To do this, each functional group is directly converted into a derivative group, which is easily regenerated into the original group, and which is stable under the synthetic conditions of further steps. Typically, removal of the protecting group is affected via treatment or a combination of treatments with acids, bases, catalytic reduction, etc. In cases where the deprotection treatment is too harsh to guarantee survival of the substrate, blocking groups that respond to photochemical treatment can be used to avoid more rigorous regeneration conditions. These groups are light-sensitive chromophores, relatively stable to a variety of chemical reagents, responsive to wavelengths of light that will not damage the substrate, and able to regenerate the original functionality in good yield. Generally, protecting groups whose excited state lifetimes are short are preferred, as this can minimize the quenching processes that reduce overall cleavage yield. Based on these qualifications, several families of photoprotecting groups have been created. This section provides a brief overview of these families and the functional groups they protect.[25,26,27]

3.1 2-Nitrobenzyl Family

The 2-nitrobenzyl group (Figure 5.6), when a carbon-hydrogen bond is *ortho* to the nitro group, undergoes a light-induced intramolecular rearrangement where the nitro group (NO_2) is reduced to a nitroso group (NO) and an oxygen is inserted into the carbon-hydrogen bond at the 2-position. The nitroso-containing molecule that results from the hydrogen-abstraction mechanism (Figure 5.7) is relatively unstable, can decompose quickly under irradiation conditions, and cannot be used again to protect another molecule. However, this is a particularly useful group that can be used to generate a variety of photochemical protecting groups. For instance, the plain 2-nitrobenzyl group can protect (a) carboxylic acid functionalities in aromatic and aliphatic acids, (b) imidazole functionalities in histidine-type molecules, and (c) phenolic hydroxyl functionalities in tyrosine-like molecules. By adding an oxycarbonyl group to become the 2-nitrobenzyloxycarbonyl, it can protect amino functionalities by generating urethanes in molecules like tryptophan. If instead an ethylene glycol function is added to the group, the photoprotecting molecule becomes 2-nitrophenylethyleneglycol, which can protect the carbonyl functionalities of aldehydes and ketones. The 2-nitrobenzyl family is one of the most common photochemical protecting groups used in organic chemistry, due to the array of functionalities it can protect, and the relative stability of the groups to both acidic and basic conditions. A note should be made, however, that the 2-nitrophenylethyleneglycol group forms acetals and ketal bonds with aldehydes and ketones, respectively, which are acid-cleavable under strong acid conditions.

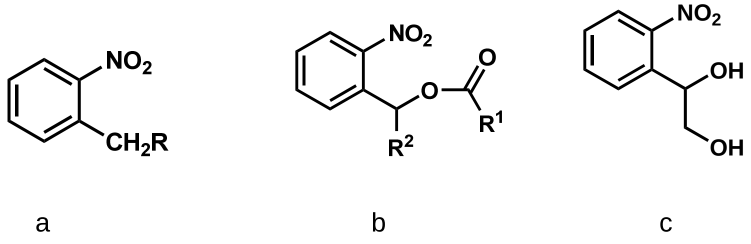

Figure 5.6 Examples of the 2-nitrobenzyl family of photochemical protecting groups: (a) 2-nitrobenzyl group, (b) 2-nitrobenzyloxycarbonyl, and (c) 2-nitrophenylethyleneglycol

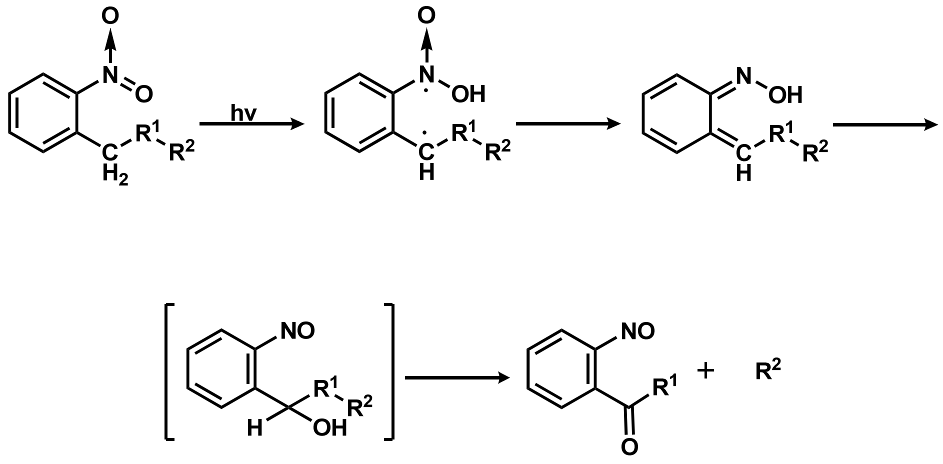

Figure 5.7 Schematic of the 2-nitrobenzyl group cleavage mechanism via hydrogen abstraction

3.2 Benzyloxycarbonyl Family

The benzyloxycarbonyl family of photochemical protecting groups (Figure 5.8) makes use of the different reactivity of its excited state with respect to its ground state to undergo light-induced cleavage that exactly regenerates the original functionality and partially regenerates the photochemical protecting group to the phenylmethanol molecule. Unlike the 2-nitrobenzyl family, which undergoes structural rearrangement to a new, unstable molecule, phenyl methanol can be regenerated into benzyloxycarbonyl using phosgene ($COCl_2$) chemistry. Generally, this molecule is used to protect amino functionalities via the formation of urethanes. The reactivity of this family may also be modified by the proper selection of moieties attached to the aromatic portion of the molecule. A typical example of this is the formation of the 3,5-dimethoxybenzyloxycarbonyl group, which has enhanced reactivity towards amino functionalities when compared with the benzyloxycarbonyl group itself, and is typically used during peptide synthesis. The primary disadvantage of this photochemical protecting family is the formation of side-products of the original photochemical protecting group during photolytic removal via *N*- and *C*-alkylation. Additionally, the use of substituents on the aromatic portion of the photochemical protecting group to enhance photolytic cleavage generates bulky molecules that may be unsuitable for use in zeolite applications.

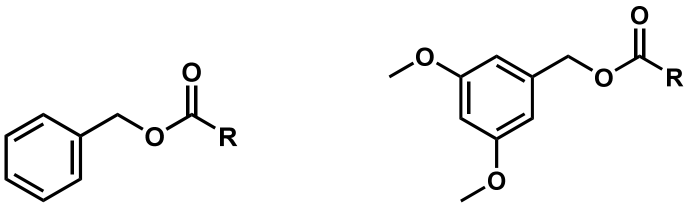

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Figure 5.8 Examples of the benzyloxycarbonyl family of photochemical protecting group: (a) benzyloxycarbonyl group, and (b) 3,5-dimethoxybenzyloxycarbonyl

3.3 3-Nitrophenyl Family

The 3-nitrophenyl family (Figure 5.9), like the benzyloxycarbonyl family, undergoes light-induced cleavage due to differences in ground state and excited state energies, again resulting in the regeneration of both the original photochemical protecting group and the functional group on the substrate. It is often used due to its stability in aqueous solutions over a wide pH range. Two typical examples of this family are the 3-nitrophenyloxy group, which protects pyrophosphate diester functionalities, and 3-nitrophenyloxycarbonyl, which protects amino functionalities.

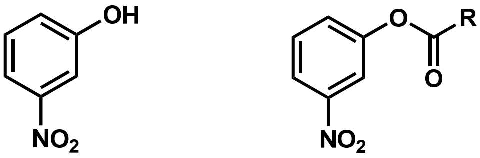

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Figure 5.9 Examples of the 3-nitrophenyl photochemical protecting group: (a) 3-nitrophenylhydroxide, and (b) 3-nitrophenyloxycarbonyl

3.4 Phenacyl Family

The phenacyl photochemical protecting group (Figure 5.10) is unusual in that it is the interaction between electrons in the carbonyl group and the phenyl ring that gives the phenacyl group low-lying excited states and makes light-induced cleavage possible. Like the benzyloxycarbonyl family, this photochemical protecting group's reactivity may be modified by placing substituents on the aromatic portion of the molecule. This family is primarily used to protect carboxylic functionalities.

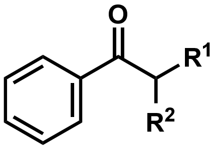

Figure 5.10 The phenacyl photochemical protecting group family

The selection of a particular family of photochemical protecting group depends on the type of functionality that must be protected, and conditions under which they must be stable. For common aluminosilicate zeolite syntheses, this requires stability in basic to extremely basic conditions (pH > 10), and thermal stability up to 200 °C. Other types of zeolite syntheses, such as fluoride-mediated syntheses and aluminophosphate syntheses, require stability at neutral (pH between 6 and 8) and acidic (pH < 4) conditions, respectively. The photochemical protecting groups discussed here can generally withstand these conditions, although the groups that form esters with the substrate, such as the phenacyl, 3-nitrophenyl, and benzyloxycarbonyl families, are unlikely to survive the zeolite synthesis. Thermal stability of the photochemical protecting group may be evaluated using Thermogravimetric Analysis; generally rigid molecules can withstand higher temperatures, and for these purposes all the photochemical protecting groups mentioned here could be applicable. Additionally, the synthesis of the photochemical protecting group must be reasonable; for instance, many of the reactions that generate the oxycarbonyl functionality to create the photochemical protecting group require the use of phosgene gas, which is inappropriate for laboratory-scale use. Lastly, the cleavage mechanism of the photochemical protecting group must be appropriate for the particular zeolite within which it becomes occluded. Cleavage that requires rotational freedom might not occur if the photoprotected molecule is tightly constrained inside the zeolite pore space.

4. Photofunctional Zeolites

The study of photochemistry inside zeolites is often aimed at discovering the effects of adsorption or constraint on the photochemical and photophysical properties of photoactive molecules, since the behavior of constrained molecules is very different from that of gas or liquid-phase molecules. Typical aluminosilicate, silicate, and aluminophosphate zeolites are inert to photochemistry (except for situations where photoactive elements are inserted into the inorganic framework), and therefore can be used as micro-reactors to investigate host-guest interactions and their role in photochemistry of the occluded molecules.[28]

The effects of zeolite constraint on the behavior of photoactive molecules are primarily the result of the chemical environment and pore architecture.[28] The silica to alumina ratio of aluminosilicate zeolites can affect the wavelength at which the molecule absorbs; for instance, a decrease in the ratio frequently causes shifts in the molecule's absorption spectra to longer wavelengths. This implies that when attempting to cleave a photoactive molecule inside a zeolite framework, the use of a UV lamp with a relatively broad band (for instance, UV-A or UV-B radiation) would be more likely to achieve cleavage than the use of a very specific wavelength lamp. The presence of charge-balancing cations can also affect the electrostatic fields and vacant space that is usable by the photoactive molecule. For instance, the polarity of the zeolite cavities can be increased by using lighter charge-balancing atoms, such as Li^+ and Na^+, causing interactions between the framework and any aromatic portions of the photoactive molecule, leading to some distortion in the symmetry of the molecule and potentially poor cleavage. Heavier charge-balancing cations, on the other hand, can enhance the generation of excited triplet states in some molecules, thus improving the cleavability of the occluded organic. The acidity of the surface hydroxyl groups and the basicity of the lattice oxygen can also affect the behavior of the photoactive molecule. Lastly, and perhaps most importantly, the cavity size or pore space can impose steric hindrance on the molecule, and potentially reduce cleavability. These factors imply that even if a photoactive molecule is capable of acting in a structure-directing role, it may be difficult to cleave if it is tightly constrained or bound within the zeolite it helps to form.

5. Development of a Photolabile Structure-Directing Agent

The ability of a molecule to act in a structure-directing role is determined in large part by its hydrophobicity. An intermediate hydrophobicity, represented by a C / N+ ratio of 12 – 13, gives the molecule the ability to transfer between an organic phase and the aqueous phase in the zeolite precursor gel; molecules within this range tend to direction the formation of zeolites. In general, the Liebau rules that describe conditions at which organic guest molecules best form clathrasils can be used as guidelines for the selection of molecules appropriate for use as structure-directing agents.[29] First, there must be sufficient room in a cage or pore for the organic guest. Second, the organic guest must be stable under synthetic conditions. Third, the organic guest should fit within the inner surface of the inorganic framework with as many van der Waals interactions as possible, but with the least deformation of the guest molecule. Fourth, the guest molecule should have only weak tendencies to form complexes with the solvent. Fifth, more rigid molecules will tend to form clathrasils more easily than flexible molecules. And sixth, a guest molecule’s tendency to form clathrasils will increase with the basicity or polarizability of a guest molecule.

In order to develop a photolabile structure-directing agent that reasonably fits within the criteria mentioned previously for photoactivity, cleavability, and structure-direction, the

2-nitrobenzyl family of photochemical protecting groups was chosen, to “protect” portions of two smaller molecules that have been shown to aid in the synthesis of zeolites: 1,1-dimethyl-4-oxopiperidinium- and imidazole / imidazolium-based molecules.[21,30,31] The first molecule was created using the 2-nitrophenylethylglycol group, to form the photolabile equivalent (Figure 5.11) of molecule III in Figure 5.5, 8,8-dimethyl-2-(2-nitrophenyl)-1,4-dioxa-8-azoniaspiro[4.5]decane hydroxide (P-SDA 1) by protection of the carbonyl functionality. The second molecule was created using the 2-nitrobenzyl group to form the photolabile compound 1-(2-nitrobenzyl)-1H-imidazole (Figure 5.12, P-SDA 2) by protection of the imidazole functionality. The benefits of the selection of both this family of photochemical protecting group and the small molecule substrates are (a) the chemistry of these molecules follows a well-understood pattern (although P-SDA 1 has not previously been synthesized), (b) examples exist in the literature of the use of the substrate molecules themselves or very similar molecules as structure-directing agents, (c) the molecules are stable within the thermal range of zeolite syntheses, and (d) each molecule has a different stability to pH (P-SDA 1 is very stable under basic conditions, while P-SDA 2 is stable under acidic to basic conditions). The primary disadvantage of these molecules is their inability to be completely regenerated upon cleavage, as the light-induced cleavage mechanism of the 2-nitrobenzyl family renders the photochemical protecting group unstable via the reduction of the nitro group to a nitroso group. However, the molecule is partially recyclable given that the original small molecule substrate is still intact and may be protected again. A choice of another family of photochemical protecting groups, like the benzyloxycarbonyl group, could avoid this disadvantage and render the structure-directing agent wholly recyclable following treatment with phosgene (a safety hazard), but the types of linkages the protecting group forms are unlikely to survive zeolite synthesis.

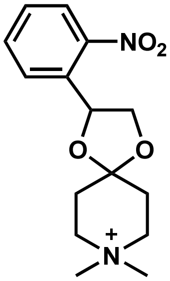

Figure 5.11 P-SDA 1, 8,8-dimethyl-2-(2-nitrophenyl)-1,4-dioxa-8-azoniaspiro[4.5]decane

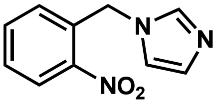

Figure 5.12 P-SDA 2**,** 1-(2-nitrobenzyl)-1H-imidazole

Part II of this thesis discusses the development of a new route to zeolite crystallization and occluded organic removal via the use of photolabile structure-directing agents. Chapters 6 and 7 detail the experimental work done to demonstrate the feasibility of this new method using P-SDA 1 and P-SDA 2, respectively. If this method is effective, it could make currently expensive zeolite syntheses commercially feasible, decrease the process’ detrimental environmental side effects, and lastly, increase the facility of further processing steps used in various industries.

6. References

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