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Multinuclear Solid State NMR and EPR Studies of Dibenzyl Ketones and
Benzocyclobutene Adsorbed on MFI Zeolites

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Abstract

Multinuclear Solid State NMR and EPR Studies of Dibenzyl Ketones and Benzocyclobutene Adsorbed on MFI Zeolites

Wei Li

High purity MFI zeolites with well-ordered structure and uniform size have been synthesized and characterized using solid state $^{29}$Si NMR and microscopic methods (SEM and AFM). Multinuclear solid state NMR ($^{29}$Si, $^{13}$C, $^2$H) was employed to study the adsorption and photochemical reaction products of dibenzyl ketones in synthetic MFI crystals. Electron Paramagnetic Resonance (EPR) spectroscopy was employed to study the photochemical reaction intermediate in MFI zeolites. Computer modeling was employed to facilitate the interpretation of the experimental findings.

DBK and p-Me-DBK were found to adsorb in the internal surfaces of MFI zeolites where the mobility of the molecules was greatly restricted. The transformation of the MFI structure indicated that the phenyl rings of the guest molecules tend to remain in the intersections. The adsorption of DBK in MFI zeolites was found to have at least two distinct environments; these two adsorption environments may be assigned to the two channel systems in MFI zeolites.
When o-Me-DBK adsorbs on an MFI zeolite, it first fills up all of the holes on the external surface before it fills the "flat" surface among the holes to form a monolayer. The mobility of o-Me-DBK in the monolayer was much more restricted when compared with o-Me-DBK molecules in the multilayers.

Photolysis of DBK generated persistent benzyl radicals in MFI zeolites due to supramolecular steric effects. The steady-state concentration of those reaction intermediates was much higher in NaZSM-5 than that in large synthetic silicalite crystals, possibly due to the strong π-cation interactions in NaZSM-5.

The reaction products from photolysis of DBKs@MFI were also studied by solid state NMR. For DBK@MFI, the photolysis product, DPE, induced stronger structural perturbation on the host zeolites. For o-Me-DBK@MFI, the sieving of the reaction product into the internal channels was clearly demonstrated by using solid state NMR.

The diffusion of benzocyclobutene is much faster than that of o-xylene in MFI zeolites. This was rationalized by the small critical size difference of the two molecules. Photolysis of benzocyclobutene in zeolites produced persistent benzocyclobutene radical cations due to electron transfer. Upon contact with air, the radical cation transformed to peroxy radicals.

Oxygen was confirmed to be the dominant factor determining the $^{29}$Si spin-lattice relaxation time. The effect of addition of organic molecules was found to be related to the guest structure as well as to loading.
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xx
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1 Introduction

1.1 Zeolites

1.1.1 Zeolite Composition

The term zeolite (from Greek zeo meaning "to boil" and lithos meaning "stone") was coined by the Swedish scientist Cronsted in 1756 to describe the property of the mineral, "stilbite", which, upon heating, behaved as if it were boiling. Zeolites have been the subject of intense study ever since.

Traditionally, zeolites are used in adsorptive gas separation, ion-exchange and most notably, shape-selective catalysts. The total annual zeolite consumption by industry is well over 550,000 metric tons, of which more than 100,000 tons are used as catalysts, 375,000 tons are used in detergent, and 40,000 tons are used as sorbents.

The basic building units of classical zeolites are tetrahedral units in which the silicon or aluminum sits in the center while the four oxygen atoms share the corners. Those basic tetrahedral units are interconnected by oxygen bridges and form the three dimensional zeolite framework as shown in Figure 1.1.

In the zeolite framework, if all of the tetrahedral sites are occupied by silicon atoms, the structure is electrically neutral. However, if some silicon atoms are replaced by aluminum, the trivalent aluminum bears a negative charge. Cations such as sodium ions are needed to neutralize the negative charges, as shown in Figure 1.1. The typical composition of the "classical" aluminosilicate zeolites may be represented by the empirical formula:

$$M_{2n}O\cdot(Al_2O_3)_n\cdot xSiO_2\cdot yH_2O$$

where M denotes an exchangeable cation, generally from the group I or II ions, although other metal, nonmetal, and organic cations may also be used to balance the framework charge. The number n represents the cation valence. The cations can be
incorporated into the zeolite either during synthesis or through post-synthesis ion exchange. The number \( y \) represents the physically adsorbed water inside the zeolite structure. These water molecules are readily removed in the activation process by heating the hydrated zeolites at high temperature (usually 550°C, depending on the zeolites, as some structures will decompose at this temperature) overnight. The value of \( x \) (Si/Al ratio) may be almost any number greater than one. Experimentally, no single zeolite has been found with a Si/Al ratio less than one.\textsuperscript{13} This is usually explained by Loewenstein's rule,\textsuperscript{14,15} which states that Al\textsuperscript{3+}-O-Al\textsuperscript{3+} linkages are energetically unfavorable in the zeolite framework due to electrostatic repulsion between the two neighboring negatively charged aluminum tetrahedral units. The lattice strain resulting from Al\textsuperscript{3+}-O-Al\textsuperscript{3+} linkages is also unfavorable in the zeolite structure.

![Figure 1.1 Basic structure of classical zeolites.](image)

Beginning in the 1950s, the classical zeolite family has expanded tremendously. Aluminum could be replaced by other trivalent elements such as B, Ga, Ti, Fe or Cr, and
silicon, by other tetravalent elements, such as Ge. In addition, beginning in the 1980s, a new class of molecular sieves, based on the structural model of the zeolites, was found. The association of a trivalent element, Al, with a pentavalent element, P, allowed the crystallization of numerous compounds with charge self-compensated frameworks. This type of framework, in which $T^{II}/T^{IV}=1$ ($T$ stands for the element in the center of the basic tetrahedral unit $TO_4$), could also be made with other elements such as Ga$^{III}$, Fe$^{III}$ and As$^V$.

1.1.2 Zeolite Structure

There are a number of ways to classify zeolites on the basis of different structural elements. The simplest level of classification is pore size. All zeolites that are significant for catalytic and adsorbent applications can be classified by the number of $T$ atoms which defines the pore opening of the zeolites. In the aluminosilicate zeolite system, there are only three pore openings to date that are of practical interest for catalytic application because of stability and activity time (coking issues). They are 8 (small pore, 4-5 Å), 10 (medium pore, 5-6 Å) and 12 (large pore, 7-8 Å) pore openings.

The zeolites that are discussed in this thesis are Silicalite and ZSM-5, which are members of a series of zeolites called pentasilts. They both belong to the family of medium pore zeolites with 10-member $T$ atom ring opening. According to the standard from the International Zeolite Association, a three-letter assignment is made for each known framework topology irrespective of composition.$^{13}$ Silicalite and ZSM-5 have the same framework topology and they belong to the MFI zeolite family. Silicalite is a special member of the MFI zeolite family$^{13}$ in which it is devoid of aluminum atoms.$^{16}$ Practically, a Silicalite does not exist, because all commercially available silica sources contain minor amounts of alumina as an impurity. Using commercially pure silica sources, a ZSM-5 zeolite with a Si/Al ratio between 300-600 is normally obtained. Taking considerable precautions to avoid any contamination it was possible to prepare a ZSM-5 zeolite with a Si/Al ratio equal to about 1500-2000.$^{17}$ Usually, ZSM-5 zeolites
synthesized without explicit addition of aluminum can be considered to be silicalite according to the literature.\textsuperscript{16,18-20} The magnified channel structure of an MFI zeolite relative to a single crystal is shown in Figure 1.2.

There are two types of channels in the MFI zeolite family as shown in Figure 1.2. The first type of channels are straight channels running along the [010] direction with elliptical pore opening of 5.1 Å x 5.7 Å (assuming ionic oxygen for all of the following size statements). The other channels are sinusoidal channels running along the [100] direction with circular pore opening of 5.3 Å x 5.5 Å. The angle between an intersecting straight channel and a zig-zag channel is 90 degrees. The angle between two intersecting zig-zag channel segments is about 112 degrees.

The [010] surface is also shown in the figure to indicate the external surface of an MFI zeolite. The surface can be roughly divided into two regions: one is the hole which is the entrance to the internal surface of the zeolite; the other is the "flat" framework separating the holes. Molecules can diffuse into the internal surface, remain in the hole or adsorb on the "flat" framework surface depending on their relative sizes and loading. In this thesis, we will show that molecules binding in these three sites have distinct characteristics and dynamics. This can yield detailed information about the interactions between the guest molecules and the host in the supramolecular system.

For comparison, we will also use another type of zeolite called FAU zeolites which belong to the large pore zeolite family (12-member ring pore opening). The structure of a FAU zeolite is shown in Figure 1.3. The external surface is also shown.

Instead of channels, FAU zeolites have relatively large and spherical cavities, termed supercages (left side in Figure 1.3), possessing a diameter of about 13 Å. The supercages are linked by four tetrahedral disposed, roughly cylindrical 12-member pores that serve as windows to the supercage. The free diameter of these windows is about 7.4 Å, as shown in the external surface of the FAU zeolites.
Figure 1.2  Zeolite channel structure of MFI zeolite
Figure 1.3  FAU zeolite supercage and its external surface. Cations are not shown in the figure.

FAU zeolites typically include Zeolite X and Y depending on the Si/Al ratio in the framework. In Zeolite X, the Si/Al ratio is around 1, while the ratio is around 2 in the Y zeolite.

1.1.3  Adsorption and Diffusion in Zeolites: the Basis of Sieving and Catalytic Action

In catalytic action the ability of a reactant to diffuse to an active site is a critical step in the reaction sequence. In zeolite structures, the geometry associated with the size and shape of the porous structure, in addition to the chemical and steric effects associated with the framework cations and adsorbed species, can control the diffusion and rotational motions of reactants within the zeolites. The interactions between the size and shape of the reactant species and the dimension, geometry and the chemical species occupying the channels and cages will play a dominant role in determining the catalytic effectiveness of
a zeolite. The very same features will determine the molecular sieving characteristics. There are three distinct diffusion situations that can be distinguished: (a) the diffusion of a guest molecule on the external surface of the crystal; (b) diffusion of a guest molecule from the external surface of the crystal through a hole that leads to the internal surface; and (c) the diffusion of a guest molecule within the internal surface. We will consider each individually.

A. Diffusion and mobility on the external surface

Diffusion and mobility of guest molecules on the external surface will be determined by the size and shape of the molecules relative to the holes (pore openings on the external surface) provided that there is no strong chemical binding involved. If the molecules are small compared to the pore opening, they will diffuse on the external surface until they react or enter the internal surface of the zeolites. The main driving force is the enormous internal surface area, since the external surface area only contributes several percent of the total area. If they are large compared with the pore opening, they will diffuse on the external surface, but they will not be able to enter the holes on the external surface totally. At equilibrium, molecules will reach a position on the external surface at the most favorable binding site.

B. Diffusion from the external to the internal surface

Entry into the internal pore of a zeolite strongly depends on the size and shape of the guest molecule relative to the size and shape of the windows in the zeolites. Those windows are the doors leading to the internal channels or cages of the zeolites. Although the windows at the external surface of the zeolite crystals are expected to be similar to the windows of the internal surface, they may not be identical. In addition, the molecules diffusing inside the channel systems may have some "memory" exerted by the channel shape and orientation, while molecules at the external surface do not have that "memory" of the channel or cage shape. The rate at which the molecule passes through the "external" surface's windows may be different from the rate at which the molecules pass
through analogous internal windows. As we will see later, this difference in diffusion rate results in very large dispersion of the measured diffusion coefficient when different methods or different crystal sizes are used.

C. Diffusion within the internal surface

Once a guest molecule has entered the internal surface, its rate of diffusion will be strongly dependent on its size and shape relative to that of the internal pores, as well as the adsorption forces (attractive). In addition, the number, location and size of the exchangeable cations presented inside the zeolite framework will strongly influence the diffusion and mobility of the guest molecules by both steric and electrostatic effects. If there are any coadsorbed molecules inside, or the loading of the molecules is so high that intermolecular interactions cannot be neglected, the diffusion and dynamics of the guest molecules will be further affected.

1.2 Photochemistry of DBK and Its Derivatives

1.2.1 Chemical Reactions in Constrained Reaction Media

The characterization of important factors determining the catalytic properties of zeolites has been greatly facilitated by the development of theories and methods which provide an understanding of the dynamics of reactions of species occluded in restricted media. Molecular probes that have smaller sizes than the entrance of the zeolite pores can diffuse into the zeolite and occupy one or more specific sites inside the zeolites. Depending on the relative sizes, these molecules can have different degrees of diffusion or rotational motion. Molecular probes which have larger sizes than the entrance to the zeolite pores can only stay on the zeolite external surface at room temperature. However, under strong adsorption conditions, such as adsorption in high temperature, slightly larger molecules can also diffuse into the channel system, but those molecules may experience a strong steric effect imposed by the relatively hard zeolite channel systems.
Experimentally, in order to obtain meaningful information related to the catalytic functions of zeolites, one must characterize the location of the molecule probe inside the zeolites, as well as their mobility and diffusion.

Photochemical probes have been developed to explore the structure of zeolites near the sites of adsorption and to examine the dynamics of reactions of molecules adsorbed on the zeolites. In this thesis, we will show how photochemical probes can yield information on the location and dynamics of guest molecules and on the zeolite's external surfaces.

1.2.2 The Mechanism of Photolysis of Dibenzyl Ketone and Its Derivatives

Photochemistry provides a powerful and versatile means of probing the dynamics of the species adsorbed on surfaces. The adsorption of light can produce reactive intermediates instantaneously on the time scale of diffusion and rotation. The chemistry of the intermediate is totally dependent on its mobility on the surface. By proper selection of the reactant species, information on the location and dynamics of the reactant precursor reactive intermediate can be locked into the products. Photolysis of asymmetric molecules produces two or more sterically different diffusing species. Analysis of their fate can provide information on their diffusion and other properties. Moreover, we will show that with proper selection of reactant precursors, the unique structure of the zeolite can preserve the reactive intermediate for a much longer time due to the supramolecular steric effect and/or the electrostatic interaction with cations in zeolites.

The mechanism of photolysis of dibenzyl ketone (DBK), its derivative ortho-methyl DBK (o-Me-DBK) and para-methyl DBK (p-Me-DBK) has been firmly established as shown in Figure 1.4. They have been successfully used as photochemical probes in supramolecular systems, such as porous silica, micelles, and zeolites.
Irradiation of asymmetric DBK and its derivatives (termed ACQB) in homogenous solution results in statistical formation of three radical coupling products (AA, AB, BB) in a ratio of 1:2:1. The cage effect, defined as

\[ \text{CageEffect} = \frac{AB - AA - BB}{AB + AA + BB} \]

is zero. In contrast, when the photolysis is carried out in confined environments, or the rate of diffusion of the radical segments is very slow, the geminate recombination product AB is favored, since the escape of the radical from the cage is impeded. In extreme cases, if the confinement is so strong that no radicals can escape after the photolysis, then only the recombination product can form in the reaction. The cage effect is 100%.

On the other hand, if the radical pair A and B is separated right after they are formed and kept apart by the environment so that there is no chance to form the recombination product AB, the cage effect will be -100%. This has been elegantly demonstrated by Turro and co-workers utilizing MFI zeolites.

Figure 1.5 shows the estimated size of p-Me-DBK and o-Me-DBK in relation to that of the pore opening of the MFI zeolite based on a conformational search using Macromodel software.

The cylinders represent the minimum and maximum sizes of both p-Me-DBK and o-Me-DBK. The size of DBK is expected to be close to that of p-Me-DBK. Based on calculations, the size of DBK and p-Me-DBK is slightly smaller than the channel opening of the MFI zeolite and so they adsorb into the internal surface. o-Me-DBK is slightly larger than the pore opening due to the methyl group in the ortho position and it adsorbs on the external surface. Photolysis of the ketones generates two radicals, A and B. In the
Figure 1.4  Schematic representation of the mechanism of photolysis of DBK and its derivatives.
Figure 1.5  Minimum and maximum sizes of p-Me-DBK and o-Me-DBK. Their size relative to the pore opening of MFI zeolites is also shown. The minimum cylinders needed to encompass the molecular conformation are shown together with their dimensions in Å.
Figure 1.6 Cage effect of p-Me-DBK and o-Me-DBK in MFI zeolites.
case of p-Me-DBK which initially adsorbs in the internal surface, the size of the radical is so close to the channel dimension that they cannot diffuse apart before they recombine to form the AB product, and the cage effect is close to 100%. However, upon photolysis of o-Me-DBK, the small benzyl radical can be readily sieved into the internal surface, while the larger ortho-benzyl radical can only stay on the external surface, inaccessible to the benzyl radical. As a result, only AA (A=benzyl radical) and BB (B=o-Me-benzyl radical) can form in the internal surface and external surface, respectively. The cage effect should be -100%. This process is demonstrated in Figure 1.6.

In this thesis, we will try to extend this photochemical approach and use those probe molecules as a powerful tool to characterize the zeolite and the supramolecular ketone@zeolite system by computational, solid state NMR and EPR techniques.

1.3 Application of High Resolution Solid State NMR in Supramolecular Studies

1.3.1 High Resolution Solid State NMR

High resolution NMR spectra of liquid samples usually yield sharp lines characterized by distinct chemical shifts and intensities. All interactions are averaged in liquids by the rapid thermal motions of the molecules. In solids, however, considerable line broadening often rises, because of the specific interactions of the nuclear spins tightly bound in the rigid lattice of the solid sample. There are mainly three interactions that result in line broadening in solid state NMR spectra: the dipolar-dipolar couplings between the observed nucleus and those of neighboring nuclei (\(^{1}\text{H}^{1}\text{H}, \text{H}^{13}\text{C}, \text{H}^{29}\text{Si}, \text{etc})\), the chemical shift anisotropy, and the quadrupole interaction in nuclei with spin \(I>1/2\).

Several methods have been developed to remove or, at least, substantially reduce those interactions in solid-state NMR.\(^{43,44}\) Line narrowing may be achieved by three different experimental procedures:
1. **Magic Angle Spinning** (MAS). Both dipolar coupling and chemical shift anisotropy contain angular dependence of the form \( (3\cos^2\theta-1) \), where \( \theta \) is the angle to the external magnetic field. When \( \theta \) is chosen to be 54.7° (the magic angle) so that the term \( (3\cos^2\theta-1) \) is zero, the dipolar interaction vanishes and the chemical shift anisotropy is averaged to its isotropic value. Experimentally, this is realized by fast rotation of the sample along the \( \theta=54.7° \) axis relative to the external magnetic field.

Ideally, the rotational speed should be larger than the linewidth of the static sample. If the spinning speed is slow, "spinning side bands" (SSB) will appear on both sides of the isotropic position.\(^{45}\) These SSB are separated by the spinning frequency, and can interfere with other isotropic peaks at slow spinning rates, making the assignment of the chemical shift more difficult. On the other hand, some useful interactions may be preserved by the SSB, and analysis of the SSB can yield dynamical information on the molecules in the solid.

2. **High power dipolar decoupling** (HPDEC). The dipolar broadening from the heteronuclear dipolar interaction can be removed by irradiating at the resonance frequency of the nucleus (e.g. \(^1\text{H}\)) while observing the nucleus under study (e.g. \(^{13}\text{C}\), \(^{29}\text{Si}\)).

3. **Multiple pulse sequences** (MPS). Homonuclear dipolar interactions can be removed by irradiation of precisely defined sequences of short, intense rf pulses that average the dipolar interaction by reorienting the nuclear spins. This is mainly used to improve the resolution of proton solid state NMR.

Another important technique in high resolution solid-state NMR for improving the sensitivity of the spectra of nuclei with low natural abundance is cross-polarization transfer (CP).\(^{46}\) In this technique, an indirect excitation of dilute spins \( S \) (which are the observed nuclei) by polarization transfer from abundant spins \( I \) (mostly \(^1\text{H}\)) is employed. The gain in sensitivity is given by the ratio \( \gamma_I/\gamma_S \), and amounts to a factor of four for \(^1\text{H}-^{13}\text{C}\), and about five for \(^1\text{H}-^{29}\text{Si}\). In addition, the repetition time for the CP pulse sequence
is much faster than that of direct excitation of S spin, since the former is determined by the shorter relaxation time rather than the much longer relaxation time of S spins such as $^{13}\text{C}$ and $^{29}\text{Si}$. This gives further enhancement of spectra sensitivity.

The CP efficiency depends on the strength of the I-S dipolar coupling. It is strongly distance-dependent as well as mobility-dependent. The dependence of cross-polarization on distance is governed by the $r^{-6}$ rule. At a distance larger than the sum of van der Waals radii, the cross-polarization virtually diminishes. In addition, if the protons have very fast dynamics, even it is close to the rare nuclei such as $^{13}\text{C}$ or $^{29}\text{Si}$, the efficiency of cross-polarization can also be reduced substantially.

Practically, those methods are usually combined in order to reduce the line width and achieve a sufficient signal-to-noise (S/N) ratio in solid state NMR. CP-MAS, HPDEC-MAS or CRAMPS (Combined Rotation And Multiple Pulse Spectroscopy) are commonly employed in high resolution solid state NMR. In this thesis, we mainly employed both HPDEC-MAS and CP-MAS.

1.3.2 Application of High Resolution Solid State NMR in Zeolites

Application of high resolution solid state NMR to zeolites began in the early 1980's.$^{47,48}$ Subsequently, interest in the application of multinuclear solid-state NMR to zeolites and other silicates and aluminosilicates has grown very rapidly. Progress in the field has been summarized in several excellent reviews and books.$^{49-53}$

All of the atoms making up the classical zeolite lattice (Si, Al, O) have NMR-active isotopes and thus can be investigated by solid state NMR. In aluminosilicate zeolite, the important nuclei, their natural abundance and their nuclei spins are $^{29}\text{Si}$ (4.7%, spin 1/2), $^{27}\text{Al}$ (100%, spin 5/2), and $^{17}\text{O}$ (0.04%, 5/2). However, the $^{17}\text{O}$ isotope has a very low natural abundance so that isotopic enrichment is often necessary and not always practical. In addition, the $^{17}\text{O}$ isotope has a spin larger than 1 which gives rise to line broadening. So far, $^{17}\text{O}$ NMR has limited use in zeolite chemistry. Although $^{27}\text{Al}$ is
an abundant nucleus, $^{27}$Al NMR also suffers from broad lines due to the quadrupole interaction.

The $^{29}$Si isotope has spin 1/2 and has relatively large natural abundance (4.7%), making it the favorite nucleus used in solid state NMR.\textsuperscript{54} HPDEC-MAS NMR is usually sufficient to remove the chemical shift anisotropy and the dipolar-dipolar coupling between the proton (either in the zeolite host or in the organic molecule guest) and the silicon.

![Figure 1.7: Characteristic chemical shift ranges of the five different local silicon environments.](image)

$^{29}$Si solid state NMR has been successfully used to study Si/Al ratio and the framework structure of zeolites. In general, the $^{29}$Si MAS NMR spectra of simple zeolites contain a maximum of five well-resolved peaks, corresponding to the five possible distributions of Si and Al around the a silicon nucleus at the center of an SiO$_4$ tetrahedron. Those distributions are described as Si[4Al], Si[3Al, 1Si], Si[2Al, 2Si],
Si[1Al, 3Si] and Si[4Si]. Each distribution has a characteristic chemical shift range, as shown in Figure 1.7.

In this thesis, we mostly use silicalite in high resolution solid state NMR studies. Essentially, only Si[0Al, 4Si] connections can exist in this structural framework. However, silicon nuclei in crystallographically non-equivalent sites of the unit cell will have slightly different chemical shifts. Although numerous studies on high resolution solid state NMR have been done in silicalite, poor resolution prevented detailed studies of the structure of silicalite by NMR. Since the late 1980s, extremely high resolution $^{29}$Si NMR spectra have been reported, mainly from Fyfe's group at the University of British Columbia, Canada.\textsuperscript{55,56} In order to improve the line width of the NMR spectra, extremely high crystalline samples are needed to achieve perfection of the local ordering, and careful selection and adjustment of the experimental parameters are also necessary. Under those conditions, nearly each crystallographically non-equivalent Si site in the framework can be clearly resolved. The effect of temperature and adsorbed simple organic molecules such as p-xylene has been shown to affect the symmetry of the $^{29}$Si NMR spectra.

High resolution $^{13}$C solid state NMR has been a powerful tool to study organic molecules occluded in zeolites. High resolution solid state $^{13}$C NMR using CPMAS has great potential in such investigations. The isotropic $^{13}$C chemical shift is highly sensitive to the environment of the carbon nucleus, and the $^{13}$C NMR usually displays narrow and well resolved lines for each kind of distinct carbon atom of the organic guest species.

Proton MAS NMR has also been successfully used to study the zeolite structure and the interactions of guest molecules with a zeolite host.\textsuperscript{57-60} In dehydrated zeolites, proton-proton dipolar interactions are relatively small due to large proton-proton distances, but the narrow range of proton chemical shifts complicates the proton NMR spectra. The spectra are further complicated when organic guest molecules are adsorbed in the zeolite, since the proton-proton dipolar interactions often dominate the spectra.
CRAMPS (Combined Rotation And Multiple Pulse Spectroscopy) has been successfully used to remove this interaction, but it is more instrument intensive.\textsuperscript{61} Nevertheless, fast MAS solid state NMR can be very useful in some cases.

1.4 Wideline Deuterium Solid State NMR

While the various interactions in solid state need to be removed in order to narrow the NMR linewidth, they themselves can also preserve valuable information. Static $^2$H solid state NMR spectroscopy has emerged as a powerful method for probing molecular motion in zeolites.\textsuperscript{62-67} Since the magnitude of the quadrupole coupling constant of the $^2$H nucleus is of the order of 10 to 250 kHz, this technique is useful for the study of relatively slow motions. Typically, interpretation of $^2$H NMR spectra for a powder sample proceeds by the proposal of a well-defined dynamic model followed by theoretical simulation of the $^2$H NMR lineshape for this motion and comparison, "by eye", of the experimental and simulated spectra.

The basic principles for analyzing $^2$H powder line shapes of systems involved in a dynamic process are well established in the literature.\textsuperscript{68,69} In the following section we briefly discuss the main conclusions from the theory and work out the "classical" simulations as references for our investigations.

The deuteron magnetic resonance frequency ($\omega$) in a magnetic field of intensity $B_0$ is given by

$$\omega = \gamma D B_0 \pm \frac{(3\cos^2 \theta - 1 - \eta \sin^2 \theta \cos 2\beta)}{2} \omega_Q$$

where $\gamma_D$ denotes the magnetogyric ratio of the deuteron and $\omega_Q = 0.75$ Qcc (Qcc stands for Quadrupole Coupling Constant, which is usually in the range of 100 kHz to 200 kHz for deuterium bonded to carbons), the quadruple frequency. Euler angles $\theta$ and $\beta$ describe the orientation of $B_0$ in the principal axis system. $\eta$ is the asymmetry parameter defined by
\[ 0 \leq \eta \leq 1 \]
\[ \eta = \frac{V_x - V_y}{V_z} \]

where \( V_{ii} (i=x, y, z) \) represents the three components of the electric field gradient tensor in the principle axis system.

For deuterium bonded to carbon, the asymmetry parameter has been found to be approximately zero, and with the \( z \) axis along the C-D bond. Hence the frequency expression reduces to
\[ \omega = \gamma_d B_0 \pm \frac{(3\cos^2 \theta - 1)\omega_Q}{2} \]

An isotropic distribution of C-D bonds over \( \theta \) yields a distribution of quadrupole splitting and a lineshape known as the "Pake Pattern" as shown in Figure 1.8. The spectrum is symmetric about the Larmor frequency \( \gamma_d B_0 \) and the dominant features of this lineshape are that two strong peaks are disposed symmetrically about the Larmor frequency and separated by \( \omega_Q \). The two extreme shoulders are separated by \( 2\omega_Q \). The former, corresponding to \( \theta = 90^\circ \) orientations, and the latter, to \( \theta = 0^\circ \) orientations.

![Diagram](image)

**Figure 1.8** Static \(^2\text{H}\) solid state NMR spectrum of powdered sample.

What makes deuterium NMR powerful is that the lineshape and relaxation time are sensitive to the molecular motion with a correlation time comparable to that of the
reciprocal of $\omega_Q$ ($\sim 10^{-5}$ second). Molecular motions in the range of $10^{-3}$ s or higher can average a certain type of the quadrupole interaction and change the lineshape and relaxation time to some extent. In addition, certain motional modes give a characteristic lineshape as the "fingerprint" of those motions. It will be useful to understand and simulate the "classical" cases in $^2$H NMR. We simulated those cases with the Turbopowder program provided by Professor Ann McDermott (Columbia University). Some of the simulation results are presented here for future reference. Spectra from two pulse sequences are simulated. One is Block decay and other is quadrupole echo as shown in Figure 1.9. In practically all of the experiments, quadrupole echo pulse sequence is used in order to overcome the technical problem called "probe ring down" time.

![Block decay](image)

![Quadrupole echo](image)

**Figure 1.9** Pulse sequences used in the simulations. Theoretically, Block decay should be used. Experimentally, quadrupole echo is usually used in order to overcome the "probe ring down" time.
1. \( \pi \)-flipping of phenyl ring, Block decay. The number beside the spectra indicates the jump rates in Hz.

**Block decay**

![Diagram of molecular structure and spectra]
2. π-flipping of phenyl ring, quadrupole echo. The number besides the spectra indicates the jump rates in Hz. Notice the intensity loss in spectra obtained from quadrupole echo compared with spectra obtained from Block decay.
3. **π-flipping** of phenyl ring, τ dependent quadrupole echo spectra. The number beside the spectra indicates the delay τ between the two 90 degree pulses. Notice the intensity loss when τ increases. The jumping rate is set to 3.5e5 Hz.

![Quadrupole echo diagram with τ=100 microsec.](image)
Two site jump from D$_2$O, a comparison between Block decay and quadrupole echo.
5. Two site jump from D$_2$O, $\tau$ dependence. The rate is set to 4e5 Hz.

\[ \text{FID} \]

$\tau = 100$ microsec.

- 40 kHz
- 20 kHz
- 15 kHz
- 10 kHz
- 5 kHz
- 0 kHz
6. Three site jump of methyl groups. The jump rate is labeled in the right side.
For MFI zeolites investigated in this thesis, the adsorbed molecules can have one or more combined motions depending on the nature of the guest molecules and the temperature:

1. Rigid molecule inside. This happens when the correlation time of motion of the molecules is longer than $10^{-3}$ s, such as a large aromatic group at very low temperatures adsorbed in the internal surface. The lineshape will be a static "Pake" pattern and will not change in this time range.

2. C-D bond reorientation (the change of direction of the C-D bond vector) along a certain axis. These motions include, for example, the two-site reorientation ($\pi$-flipping, as shown in simulated spectra 1 and 2 on preceding pages 27 and 28) or fast rotation of the phenyl ring in a molecule along its long axis and a CD$_3$ rotation along its C$_3$ axis as shown in simulated spectra 6, on the preceding page.

3. Diffusion from the straight channel to the zig-zag channel (90° jump) or the reverse way.

4. Diffusion from one segment of the zig-zag channel to the other segment of the zig-zag channel (112° jump)

5. Isotropic motion. In this motion, all three tensors are more or less averaged out, and the "Pake" pattern becomes a single line. Depending on the correlation time of the motion, the linewidth will change. When the correlation time of the motion is high enough (less than $10^{-8}$ s), all the anisotropic interactions are averaged out and the liquid-like sharp line is obtained. This happens, for example, when the molecules are adsorbed on the external surface or at very high temperature.

6. Diffusion along the straight channel. Strictly speaking, this motion will not be detected by deuterium NMR no matter how fast or slow it is, since there is no reorientation of the C-D bond vector involved in it.

By analyzing the lineshape and relaxation of the $^2$H NMR spectra and comparing them with the proposed dynamics model, it is possible to gain insight into the motion and
dynamics of guest molecules in the supramolecular complex. This information can be coupled with information obtained from solid state NMR of other nuclei (e.g. $^{29}$Si, $^{13}$C). The combination of multinuclear solid state NMR will be employed in this thesis.

1.5 **Electron Paramagnetic Resonance (EPR) Studies in Zeolite Chemistry**

EPR is another technique that has been extensively used in zeolite chemistry. The rigid framework of the channels or cages in zeolites can impose geometrical restrictions and isolate the otherwise very reactive free radicals generated from organic guest molecules, allowing the study of these reaction intermediates. In addition, zeolites can be used as electron donor or electron acceptor to produce radical anions and radical cations of the adsorbed guest molecules upon adsorption or with irradiation. Those radical cations or radical anions are usually well stabilized and protected by the high polarity of the zeolite's channels or cages. In this work, we used EPR spectroscopy to gather information on the photochemical reaction intermediates as well as studying the radical cation formation from guest molecules in MFI zeolites.

1.6 **Research Objectives**

Listed below are the objectives and methods used in the study of zeolites with photochemical probes.

1. Synthesis and characterization of high purity MFI large crystals with uniform size. MFI zeolites with uniform structure are crucial in producing high resolution solid state $^{29}$Si NMR spectra. The conditions for synthesizing MFI crystals will be studied based on the available synthetic reactants. The structure of the synthetic MFI zeolite crystals will be characterized by various spectroscopic methods in order to assure MFI structures suitable for high resolution solid state NMR studies.
2. We will then use p-xylene as a probe molecule and study the spin-lattice relaxation time of silicon nuclei in those MFI crystals. This also serves as a standard for subsequent studies of adsorption of photochemical probes adsorbed in MFI zeolites.

3. A major part of this work will concentrate on the location and dynamics of the photochemical probes (DBK, p-Me-DBK and o-Me-DBK) adsorbed in MFI zeolites. We will use combined information from solid state NMR and EPR spectroscopy, photochemistry and computer simulations to construct the picture. Solid state $^2$H and $^{13}$C NMR spectroscopy can yield information about the mobility and the interaction of the guest photochemical probes with the zeolite host. High resolution solid state $^{29}$Si NMR is sensitive to the structural change of the zeolite host due to its interaction with guest molecules and thus can provide direct information about the binding sites of guest molecules. Photochemistry and EPR spectroscopy can be used to characterize the reaction intermediates during photoreactions and study the diffusion of those intermediates which have similar properties as industrially important materials (e.g. toluene and xylenes). Computer simulations will facilitate the interpretation of the experimental results.

4. Finally, we will study the adsorption and diffusion of benzocyclobutene, an important C8 compound, in MFI zeolites. As in the previous part, we will use various spectroscopic methods and computer simulations to understand the interactions of benzocyclobutene with MFI zeolites and a commercial FAU zeolite.
References


2 Materials and Methods

2.1 Reagents

Dibenzyl ketone, para-methyl dibenzyl ketone, ortho-methyl dibenzyl ketone and their deuterium-labeled compounds were synthesized by Dr. Xue-Gong Lei according to literature procedures. The purity of those materials was at least 98% as determined by GC/MS and NMR spectroscopy. Isooctane (HPLC grade, Aldrich Chemical Company) was treated with 5 Å zeolite before it was used as solvent. Aerosil-200 (fumed silica dioxide, 99.8%-100.0%, Degussa Corporation), ammonium fluoride (Aldrich Chemical Company, 98%), tetrapropyl ammonium bromide (Aldrich Chemical Company, 98%), hydrated aluminum sulfate (Aldrich Chemical Company, 98%), p-Xylene-d\textsubscript{10} (Aldrich, 99+%), o-Xylene-d\textsubscript{10} (Aldrich, 99+%), benzocyclobutene (Aldrich, 99+%) were purchased from the indicated commercial source and were used without further purification. All other chemicals were the highest grade available from Aldrich Chemical Company and used without purification. Water was deionized (United States Filter Corporation, Pittsburgh, PA).

Commercial silicalite (Si/Al>100) and ZSM-5 (Si/Al=40) powders were given to us and characterized by Dr. David Corbin and Dr. Lloyd Abrams of the E. I. Du Pont Company's Central Research and Development Department. Characterization included measurement of the particle size using Scanning Electronic Microscopy (SEM) and measurement of the zeolite's external surface area by the Mercury Porosimetry Method. Commercial silicalite powder has an average size of 1 µm and an external surface of ca. 5 m\textsuperscript{2}. Commercial ZSM-5 powder has an average size of 0.3 µm and an external surface area of 16 m\textsuperscript{2}.
2.2 Standard Instrumentation

High-resolution $^{29}$Si, $^{13}$C and $^1$H solid state NMR measurements were taken in a Bruker DRX-300 wide-bore NMR system equipped with multinuclear solid accessories. The magic angle was precisely tuned with KBr. The sample spinning speed was 3.5-5 kHz for $^{29}$Si and $^{13}$C, and up to 10 kHz for $^1$H. The stability of temperature in variable temperature experiments was within 1 K.

Deuterium wide-line solid state NMR spectra were recorded on a Bruker AC-250 NMR system equipped with a CXP console. The quadrupole echo pulse sequence was employed to record the $^2$H spectra. $T_1$ measurements were made with an inversion-recovery pulse sequence. The 90-degree pulse width was 2.5 $\mu$s, and the recycle delay was 1 s unless otherwise indicated. Variable temperature experiments were performed with a Bruker VT-1000 temperature controller. The accuracy of the temperature was within +/-1K. Simulation of $^2$H NMR was performed using the program TURBOPOWDER, (Professor Ann McDermott, Columbia University). The program can simulate lineshape of quadrupole echo and inversion recovery experiments of I=1 nuclei undergoing reorientation in powder samples. The program needs an input file for the necessary parameters and data. The simulated spectra were interactively adjusted and compared with the experiment to determine a best fit.

EPR spectra were recorded in a Bruker EP380 and a Bruker EMX EPR spectrometer. g values of the radicals were calibrated with an internal DPPH standard. EPR spectra processing and simulation were performed with WinEPR (Bruker, Version 2.11, Shareware Version) and Simfonia (Bruker, Version 1.25, Shareware Version) programs.

Computer simulations of molecular conformation, diffusion and docking in zeolites were performed using MSI software (Molecular Simulations, Inc., San Diego,
CA), Macromodel (Shroedinger Inc.) and Spartan (Wavefunction, Inc., Irvine, CA) running on SGI workstations.

The morphology of both the synthetic zeolite crystals and commercial powders was checked with an optical microscope (Fisher scientific, Model Micromaster), Scanning Electron Microscope (SEM, Hitachi, Model S-510, taken by Mr. Rokan Ahmao in Professor Richard Osgood's lab at the School of Engineering and Applied Science, Columbia University).

Contact mode AFM imaging was done with a Nanoscope IIIa (Digital Instruments, Santa Barbara, CA, and taken in Professor Louis Brus's lab (Department of Chemistry, Columbia University) with the help of Dr. Todd Krauss and Mr. Guanglu Ge). The MFI crystals were fixed on a metal disk with glue. Triangular Si$_3$N$_4$ microcantilevers (Nanoprobe, NP-S, Digital Instruments) were used for tips. The scanning rate was between 2 and 10 Hz. The atomic-scale periodic distances were determined by two-dimensional fast Fourier transform (2D-FT).

2.3 Synthesis of MFI Zeolite Crystals

The silicalite and ZSM-5 crystals employed in this thesis investigation were synthesized as described in the literature with minor modification as described below. Instead of using a silicon source directly, we first made a "precursor" material from the silicon source. In a typical precursor preparation, 100 grams of Aerosil-200 and the desired amount of hydrated aluminum sulfate (in the case of ZSM-5) were dissolved in 400 grams of deionized water to form a thin gel. After thorough mixing, the gel was heated at 80°C to evaporate all the water. The resulting solid was then heated at 550°C in a furnace for 12 hours. The remaining solid was ground thoroughly to form a powder "precursor" material for the subsequent synthesis. Our experiments have shown that zeolites synthesized with this powder precursor maintain a very narrow size distribution (see Results section) and are nearly free of amorphous impurities.
In a typical zeolite synthesis, about 25 g of precursor was mixed with 25 g of NH$_4$F and 8 g of TPABr (Tetrapropyl Ammonium Bromide). The solid mixture was ground and mixed well in a mortar with a pestle. The mixture was then transferred into a 250 ml Teflon beaker containing 100 g of deionized water. The Teflon beaker was sealed in a stainless steel autoclave and heated at 170° C in an oven for 3-5 days. The product was separated from the solution and washed thoroughly with deionized water. After drying at 80°C, the zeolites were calcined at 550°C overnight to burn off the tetrapropyl ammonium ions inside the zeolite and convert the ammonium ions to protons. The calcined zeolites were washed with 1 M solution of sodium hydroxide to remove any impurities, and then were washed with deionized water thoroughly until pH=7 was achieved.

2.4 Loading and Photolysis of Organic Materials in MFI Zeolites

About 100mg to 300mg of freshly calcined zeolite was mixed with the desired amount of the guest materials in isoctane. After stirring overnight, the solvent was gently removed under Argon gas, and dried under high vacuum (10$^{-5}$ torr) overnight at room temperature before measurement.

For high loading of p-xylene and loading of o-xylene for high-resolution solid state NMR measurements, a pure liquid was mixed with freshly calcined silicalite in a quartz cell equipped with a side arm that was connected to a vacuum line. The sample tube was sealed under vacuum conditions and separated from the vacuum line. A picture of the cell is shown in Figure 7.1 in Chapter 7 of this thesis (Figure 7.1, cell 2). The mixture was then subjected to several cycles of freeze-pump-thaw to remove the air adsorbed in the zeolites. The sample was sealed in the vacuum and heated to 120°C overnight. After cooling down to room temperature, the excess liquid was removed. The mixture was washed with isoctane several times to remove any externally adsorbed
molecules. After drying with Ar gas, the sample was thoroughly dried in the vacuum line.

The photolysis was performed with a 400-Watt medium pressure Hanovia Hg lamp with an aqueous K$_2$CrO$_4$-Na$_2$CO$_3$ filter to isolate the 313 nm line. The sample was degassed to a pressure of 5x10$^{-5}$ torr, maintained under vacuum in a vacuum cell as shown in Figure 7.1 in Chapter 7 of this thesis and tumbled during photolysis at room temperature.
References


2) Kornatowski, J. Zeolites 1988, 8, 77-78.
3 Zeolite Synthesis and Characterization

3.1 Introduction

Synthesis of large MFI crystals has been explored extensively since the late 80's. However, a successful synthesis depends on many factors. For example, different silicon or aluminum sources can lead to very different products, since they have different surface area (particle size) resulting in different nucleation and crystallization rates. In addition, different silicon or aluminum sources contain different kinds of impurities, which may also affect zeolite crystallization. Consequently, the synthesis of MFI crystals still retains many of the characteristics of a trial and error process. Thus, it is worthwhile to study the effects of these various factors in order to improve the control of the products.

3.2 Results and Discussions

3.2.1 Factors Affecting MFI Zeolite Size and Morphology

3.2.1.1 Effect of Water/SiO₂ Mole Ratio

Figure 3.1 shows a plot of the effect of water/silicon mole ratio on the size of the synthetic MFI crystals. Synthesis with a very large amount of water (mole ratio of water/silicon > 200) did not yield MFI crystals which could be detected by optical microscopy. The typical range of water/SiO₂ mole ratio for our synthetic conditions was 10-70.

3.2.1.2 Effect of pH of the Gel Mixture

A higher pH value of the gel mixture generally leads to smaller crystal sizes. Crystals synthesized under low pH conditions are elongated, and prismatic in shape, because different crystal surfaces have different growing rates. This effect is shown in Figure 3.2.
Figure 3.1  Effect of water concentration on the size of synthesized NaZSM-5 (Si/Al=60) crystals. The synthesis was performed for 3 days at 160°C. Synthesis with a mole ratio of H₂O/SiO₂ larger than 200 did not yield detectable NaZSM-5 crystals.

(A) Average size ~ 30μm  
(B) Average size ~ 100μm

Figure 3.2  pH dependence of synthetic MFI zeolite crystals. (A). Crystals synthesized under high pH conditions (pH>14) using NaOH. (B). Crystals synthesized under low pH conditions (pH~9) using ammonium fluoride. The average size of the crystal is indicated under each SEM picture.
The high pH condition was obtained using NaOH as the mineralizing agent in the gel. The low pH condition was obtained using ammonium fluoride.

Similarly, lower Si/Al ratios gave smaller crystals due to the high pH values of the gel mixture. For example, large silicalite crystals (Si/Al>500) were the easiest to synthesize. Large ZSM-5 (Si/Al=60, mole ratio) crystals up to 150 μm could also be synthesized, but ZSM-5 crystals with a low Si/Al mole ratio (less than 40) could be synthesized with only smaller sizes (up to 10 μm).

We also varied the concentration of ammonium fluoride from NH₄F/SiO₂=1 (mole ratio) to 2 and we found that it had very little effect on the crystal size. The gel mixture was kept between 8 and 10 in all of the syntheses.

3.2.1.3 Reaction Time

In the literature, effects of reaction time on crystal size is a controversial topic. For our synthetic system, we found that three days was sufficient time to yield large crystals from the gel mixture. The longer reaction times (more than five days of reaction) led to slightly larger crystals under identical synthetic conditions. The products contained pure MFI crystals as examined by solid state ²⁹Si NMR (see characterization section).

3.2.1.4 Other Factors Influencing Crystal Size

There are many other factors during the synthesis that could affect the crystal size, e.g., the concentration of tetrapropyl ammonium bromide in the gel mixture, and the reaction temperature. Since these conditions have been reported in the literature, we used the same concentration of tetrapropyl ammonium bromide and temperature as reported throughout our synthesis.

The optimized synthetic condition for our system is as follows: at a temperature of 170°C, the reaction time is 3-5 days; mole ratio of water/SiO₂ is 10-70; mole ratio of
TPABr/Si is 0.067; mole ratio of fluorine/Si is 1 or 2. Table 3.1 lists the sizes of synthetic MFI zeolites with their corresponding synthetic conditions.

**Table 3.1** Some synthetic MFI zeolite crystals and their synthetic conditions

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>H₂O/Si mole ratio</th>
<th>Temperature (°C)</th>
<th>Si/Al mole ratio</th>
<th>F-/Si mole ratio</th>
<th>Crystal size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FL02</td>
<td>10</td>
<td>160</td>
<td>60</td>
<td>2</td>
<td>100 x 40</td>
</tr>
<tr>
<td>FL01</td>
<td>20</td>
<td>160</td>
<td>60</td>
<td>2</td>
<td>150 x 40</td>
</tr>
<tr>
<td>FL04</td>
<td>40</td>
<td>160</td>
<td>60</td>
<td>2</td>
<td>60 x 17</td>
</tr>
<tr>
<td>FL03</td>
<td>70</td>
<td>160</td>
<td>60</td>
<td>2</td>
<td>50 x 17</td>
</tr>
<tr>
<td>FL06*</td>
<td>40</td>
<td>160</td>
<td>60</td>
<td>OH=0.25</td>
<td>30 x 30 x 30</td>
</tr>
<tr>
<td>FL11</td>
<td>40</td>
<td>200</td>
<td>60</td>
<td>2</td>
<td>13 x 5</td>
</tr>
<tr>
<td>FL20**</td>
<td>40</td>
<td>160</td>
<td>60</td>
<td>2</td>
<td>80 X 23*</td>
</tr>
</tbody>
</table>

*NaOH, instead of ammonium fluoride, was used as a mineral agent. The mole ratio of NaOH/Si was 0.25 in the starting materials.

**Different silicon source, Aerosil-380 instead of Aerosil-200. All other syntheses were done using Aerosil-200.

3.2.2 Characterization of Synthetic MFI Crystals

3.2.2.1 Characterization of Morphology by Optical Microscope

Some of the synthesized MFI type crystals of variable sizes are shown in Figure 3.3. They are all monodispersed crystals, since the distribution of the crystal size is very narrow (no larger than 15% of the average crystal size by measuring a large number of crystals in the SEM picture). The morphology of these crystals is consistent with literature reports.²¹¹ The size distribution of each sample is very narrow (Figure 3.2 and Figure 3.3).
3.2.2.2 Characterization of MFI Crystals by Multinuclear Solid State NMR

The $^{13}$C and $^{29}$Si solid state NMR of the synthesized MFI zeolite are shown in Figure 3.4.

The carbon NMR originated from the occluded template TPABr (tetrapropyl ammonium bromide). The methyl group in TPABr becomes a doublet with equal intensities ($\delta=10.0$ ppm and $\delta=11.0$ ppm), indicating that the equivalent methyl groups are located in two different chemical environments. It has been reported that these two environments correspond to the straight channel and zig-zag channel of a MFI zeolite.$^{12,13}$ $^{29}$Si solid state NMR of the synthetic ZSM-5 crystal is consistent with spectra reported in the literature.$^{13-15}$
Figure 3.4  (A). Solid state CPMAS $^{13}$C NMR of the template TPABr inside a MFI zeolite framework. Recycle delay is 2 seconds, spin at 5 kHz, number of scans is 200. (B). One pulse $^{29}$Si solid state NMR of uncalcined zeolites. Spin at 5kHz, recycle delay is 15 seconds.

After calcination, the morphology (the channel structure and shape of the crystal) of the MFI zeolites remained unchanged. The internal channel systems previously occupied by the template (tetrapropyl ammonium) are now empty and become accessible to other molecules. But, the $^{29}$Si NMR indicated that the calcined structure changed to P2$_1$/n symmetry in which there are 24 independent silicon sites in the unit cell.$^{16}$ Figure 3.5 shows the one pulse $^{29}$Si NMR with its simulation based on reported literature reports.$^{17,18}$ Of the 24 theoretically proposed unequivalent silicon sites in the unit cell, 20
lines are clearly resolved. All the chemical shifts and relative intensity data are comparable with the best spectra reported in the literature.\textsuperscript{16}

Figure 3.5 One pulse silicon solid state NMR of calcined synthetic zeolite. a) Experimental spectra, NS=1400, recycle delay=5s; b) simulated spectra; c) peaks used for simulations
3.2.2.3 Characterization by Atomic Force Microscope (AFM)

Electron microscopy, electron diffraction and AFM are powerful tools for surface analysis. Electron microscopy and electron diffraction have been used to image zeolite frameworks and obtain structural information about complex zeolite structure types. However, those techniques require a high vacuum to work effectively. Moreover, the electron beam can damage the materials during data acquisition. The AFM allows the imaging of insulating surfaces under ambient conditions to obtain molecular resolution without destroying the surface. Hence, in the past decades, characterization of zeolite structure using AFM has attracted considerable attention and some excellent results have been reported for zeolite surfaces.

Thus, we employed AFM to image the external structure of our synthetic zeolite crystals. We obtained the best results of the [100] surface of a silicalite crystal (about 150 μm in length) by using the contact mode. Figure 3.6 shows the AFM image after noise filtering. On the right side of the figure, a computer model using MSI software of the MFI surface on the same scale as the experimentally scanned surfaces was generated for comparison.

The black dots in the AFM image may be assigned to the holes on the silicalite external surface. The white region around the holes indicated the external framework. The white lines in the computer model indicated the bonds between silicon atoms in the silicalite. The similarities between the AFM image and the computer model indicated that the synthetic crystals possess good external structure and topology of MFI zeolites.
Figure 3.6  AFM of synthetic silicalite crystals (left) and a computer generated model of [100] surface (right). Scan Size: 11.96 nm; scan rate: 5.31 Hz; number of samples: 256; image data: deflection; data scale: 3.531 mV.

3.3 Summary

Conditions for the synthesis of large MFI zeolite crystals were investigated and optimized. Variable sizes of MFI zeolite crystals can be obtained through slight variations of reagent compositions and synthetic conditions. The synthetic crystals have very good morphology, comparable to those reported in the literature. Multinuclear solid state NMR revealed that the crystals have good MFI structure. These crystals can be subsequently used to investigate the guest-host interactions.
References

11) Kornatowski, J. Zeolites 1988, 8, 77-78.
4. The p-xylene/MFI System: Oxygen and Structural Effects on $^{29}$Si Spin-Lattice Relaxation Times

4.1 Introduction

The ability to selectively adsorb p-xylene from mixtures of the three xylene isomers is an example of the exquisite size/shape selectivity and molecular sieve ability of the MFI family of zeolites.\textsuperscript{1-3} The p-xylene/MFI complex at room temperature can adopt three distinct known structures depending on the loading: a monoclinic one (termed P2$_1$/n) corresponding to the empty MFI zeolite, and two orthorhombic structures, one containing 2-4 p-xylene molecules per unit cell (termed Pnma), and a second orthorhombic one containing 8 p-xylene molecules in a unit cell (termed P2$_1$2$_1$2$_1$).\textsuperscript{4-6} Intermediate loading of p-xylene produces a mixture of two structures. The composition of the unit cell of silicalite is Si$_{96}$O$_{192}$. The monoclinic symmetry has 24 crystallographic non-equivalent silicon sites in the 96 silicon atoms in a unit cell. The first orthorhombic symmetry has 12 non-equivalent sites, and the p-xylene molecules occupy the intersections between the straight and zigzag channels, with their long axis parallel to the straight channels. The second orthorhombic symmetry again has 24 non-equivalent silicon sites in the unit cell, with 4 p-xylene molecules occupying the 4 intersections and the other 4 lying in the 4 segments of the zig-zag channels.

$^{29}$Si MAS NMR\textsuperscript{7} has been widely used to study zeolite structures.\textsuperscript{8} However, a detailed study of the p-xylene/MFI complex had been hampered by insufficient resolution of the NMR spectra. By the late 80's,\textsuperscript{9-11} it was reported that extremely high resolution in which essentially all of the 24 distinct Si atoms of the unit cell could be distinguished experimentally by examining high quality synthetic ZSM-5 single crystals which were dealuminated at 800°C for 9 days, coupled with optimal instrumental conditions.
Most of the high-resolution solid state NMR studies have concentrated on chemical shift analysis and silicon site connectivity using synthetic single crystals.\textsuperscript{7,9,12-16} To the best of our knowledge, spin-lattice relaxation, which is another very important parameter, has not been systematically studied and documented with high resolution $^{29}\text{Si}$ NMR spectroscopy. The studies reported in the mid 80's\textsuperscript{17,18} were hampered by relatively poor spectral resolution and only the relaxation times of aggregates of $^{29}\text{Si}$ atoms could be measured for MFI zeolites loaded with organic guest molecules.

The effect of oxygen, a ubiquitous paramagnetic molecule, on the relaxation of nuclei is particularly important for the slowly relaxing $^{29}\text{Si}$ nuclei that are embedded in the MFI framework. For example, it is generally agreed that collisions with oxygen are mainly responsible for the observed relatively short spin-lattice relaxation of $^{29}\text{Si}$ in an empty zeolite. However, the mechanism of $^{29}\text{Si}$ relaxation of a zeolite loaded with organic guest molecules is not clear, and contradictory results and, therefore, mechanistic interpretations have been reported.\textsuperscript{17,19,20}

To investigate the effect of adsorbed organic molecules on the $^{29}\text{Si}$ spin-lattice relaxation time, we loaded p-xylene on the synthetic samples, and measured the spin-lattice relaxation time of silicon nuclei in the silicalite.

\textbf{4.2 Research Purpose}

In this chapter, we will try to reproduce the high resolution solid state NMR spectra of silicalite loaded with p-xylene molecules reported in the literature using our synthetic silicalite crystals. These results will serve as standards for all of the solid state NMR work investigated in this thesis for various guest molecules and the bases for interpretation of $^{29}\text{Si}$ solid state NMR. We will then study the effect of oxygen and the adsorbed p-xylene molecules on $^{29}\text{Si}$ spin-lattice relaxation time.
4.3 **Results**

4.3.1 **Standardization of Samples**

The first task is to reproduce the high-resolution spectra from the literature. Figure 4.1 shows the one pulse \(^{29}\text{Si}\) NMR spectra of p-xylene/silicalite complex and their simulation based on the literature reported. Both spectra are well resolved and completely consistent with the literature.\(^{11,12,21}\)

Figure 4.2 shows the proton solid state NMR of the adsorbed guest p-xylene molecules inside the silicalite. At all loading ranges, proton NMR signals from p-xylene (\(\delta=2.3\) ppm for methyl group and \(\delta=7.0\) ppm for aromatic protons) are clearly resolved.\(^{6,22}\) At low loading (less than 1% wt%), there are an extra two proton signals appearing in the spectra. The broad proton signal at \(\delta=3.0\) ppm is due to the hydrogen-bonded silanols, and the sharp signal at \(\delta=1.7\) ppm is due to the isolated silanol groups.\(^{23}\) The relative intensities of those protons decrease constantly as the loading of p-xylene increases. Above loading of 5% wt%, those two signals are completely buried under the strong signal from p-xylene.

The proton spectrum of silicalite loaded with 5% p-xylene consists of two sharp lines corresponding to the methyl and aromatic protons, indicating the homogenous sorption environment of the p-xylene molecules. The presence of spinning sidebands in the proton spectra indicates the strong proton homonuclear dipole-dipole couplings.\(^{24-26}\) This is due to the fact that up to this loading, all the p-xylene molecules are in the intersections of the silicalite lattice with their long axis parallel with the straight channel.\(^{5,27}\) Thus, each kind of proton has the same chemical environment.

In the high loading form (10% wt%), four p-xylene molecules are in the intersections while the remaining p-xylene molecules are in the zig-zag channels. The slightly different environment of adsorption between the straight channel and the zig-zag
channel and the strong interactions between the two kinds of adsorption environment of p-xylene broaden the proton spectra substantially, as indicated in Figure 4.2.

All these results are completely consistent with the literature reported.

Figure 4.1  High-resolution $^{29}$Si NMR spectra of p-xylene/MFI complex and their simulations. Left: loading is four p-xylene molecules per unit cell; Right: loading is eight p-xylene molecules per unit cell.
Figure 4.2  Loading dependence of proton NMR spectra of silicalite loaded with p-xylene. The numbers on the left side indicate the weight percentage of loading. The numbers on the right side indicate the scaling of the spectra. The assignments of the proton signal are shown in the Figure. The spinning sidebands are indicated by stars (*).
4.3.2 Effect of Adsorbed p-xylene Molecules on $^{29}\text{Si}$ Spin-Lattice Relaxation Time

Having established that our silicalite crystals yield high-resolution spectra, we measured the $^{29}\text{Si}$ spin-lattice relaxation time for both empty silicalite and silicalite loaded with p-xylene molecules. We selected silicalite loaded with 5% wt% of p-xylene for this study. Figure 4.3 shows the spectra of spin-lattice relaxation measurements. Clearly, different peaks (corresponding to different silicon sites in the unit cell) have different recovering times. The $T_1$ values for each site is plotted in Figure 4.5.

In order to understand the effect of dipolar-dipolar coupling between guest protons and silicon atoms on the $^{29}\text{Si}$ spin-relaxation time, we also measured the $^{29}\text{Si}$ spin-lattice relaxation time for silicalite containing p-xylene-$d_{10}$ at the same loading. One would expect that the $^{29}\text{Si}$ spin-relaxation would be different between p-xylene/silicalite and p-xylene-$d_{10}$/silicalite if dipolar-dipolar coupling is the major relaxation mechanism. In fact, the $T_1$ spectra of p-xylene-$d_{10}$/silicalite are essentially the same as those for p-xylene/silicalite supramolecules (Figure 4.4).

Figure 4.5 plots the $T_1$ values for all of the above measurements. We concluded that: (a) In general, silicalite loaded with p-xylene has a shorter $T_1$ compared with that of empty silicalite; (b) isotope substitution of the guest molecule p-xylene does not affect the $T_1$ significantly, indicating that dipolar-dipolar coupling between protons in the guest molecule and lattice silicons does not contribute significantly to the $^{29}\text{Si}$ $T_1$ relaxation at that loading.
Figure 4.3 $^{29}\text{Si}$ $T_1$ spectra of empty silicalite (left) and the p-xylene/silicalite complex (right). Numbers in the spectra indicate the time delay between the two pulses during the $T_1$ measurement.
Figure 4.4 $^{29}\text{Si T}_1$ of silicalite loaded with 4 p-xylene-d$_{10}$ molecules per unit cell, scan 300. The numbers on the right side indicate the variable delays in the inversion-recovery measurements.
Figure 4.5  Effect of loaded organic molecules on the $^{29}$Si spin-lattice relaxation time

4.3.3  Effect of Oxygen in the Presence of p-xylene

We employed a novel and convenient method to investigate this effect. Endoperoxide 1 was used to generate and add molecular oxygen into the silicalite complex.

Endoperoxide is not stable at room temperature, and it releases singlet oxygen\textsuperscript{28} effectively by decomposition (Scheme 4.1).\textsuperscript{28,29} Singlet oxygen has a very short lifetime (microsecond to millisecond) and by the time it diffuses into the zeolite, it decays to normal ground state oxygen, a triplet paramagnetic molecule.\textsuperscript{30} This gives us the ability to generate molecular oxygen in the silicalite complex \textit{in situ}. From computational analysis of the molecular cross section of the endoperoxide 1 and comparison to the
size/shape characteristics of the pores (ca 5.4-5.6 Å diameter) on the external surface of a MFI crystal (Scheme 4.1), it is clear that neither the endoperoxide $1$ nor its decomposition product $2$ are able to access the internal surface. Therefore, neither $1$ nor $2$ is expected to affect the structure of silicalite or the resulting NMR spectra.

Scheme 4.1 Decomposition of $1$-(1'-hydroxylethyl)-4-methyl-1,4-epidioxy-1,4-dihydropnaphthalene $1$

Ideally, we should first remove all the oxygen from the silicalite sample, add a known amount of endoperoxide, seal the sample in vacuum and measure the $T_1$ of silicon nuclei upon decomposition of endoperoxide. This will give a definite concentration of oxygen in the sample and allow us to measure the spin-lattice relaxation time under different amounts of oxygen. We experienced some technical problems with this method. We did not have the specially designed rotor with o-ring cap to evacuate and seal the samples in high vacuum such as a "CAVERN" device described by Haw and coworkers.\textsuperscript{18,31,32} We also tried once to load the sample in a Pyrex glass insert
(purchased from Wilmad Glass, New Jersey, part number DWGSK2576-1) for the Bruker 4mm rotor in a glove box and sealed the sample with Epoxy resin, but failed to make the sample spin stable. We did not pursue this method further, although this seemed to be the most promising method for sealing samples in the rotor. Instead, we completed all of our experiments in the presence of air. The effect of oxygen was studied by the added oxygen from the decomposition of endoperoxide inside the rotor. We understand that this was not the best method, but with proper controlling experiments (see below) we could clearly observe and study the effect of added oxygen on the spin-lattice relaxation of silicon nuclei in silicalite.

We measured the spin-relaxation time of silicalite loaded with endoperoxide only and silicalite loaded with both p-xylene and endoperoxide in order to compare the oxygen effect on those two systems. As a control, we also measured the $T_1$ of silicalite loaded with 1,4-dimethyl naphthalene. Figure 4.6 shows the $T_1$ points of the silicalite loaded with endoperoxide, p-xylene/silicalite loaded with endoperoxide and the $T_1$ for their corresponding "empty" (e.g. air filled) samples.

From Figure 4.6, we can clearly see that loading with endoperoxide enhances the spin-lattice relaxation for the empty silicalite, but it doesn't change the spin-lattice relaxation time for the p-xylene/silicalite complex within experimental uncertainty. The $T_1$ values of the control experiment (silicalite loaded with 1,4-dimethyl naphthalene) show an identical spin-relaxation time with that of empty silicalite, indicating the large molecules adsorbed on the external surface did not change the structure and spin-lattice relaxation time of the silicalite.
Figure 4.6 Effect of oxygen on the $^{29}$Si spin-lattice relaxation time. Top, silicalite; Bottom: p-xylene/silicalite system.

4.4 Discussions

The results using high-resolution $^{29}$Si NMR measurements of synthetic silicalite loaded with p-xylene (5% wt%wt loading) show clearly that the $^{29}$Si spin-relaxation time is faster compared to empty silicalite. Different silicon sites apparently have different spin-lattice relaxation times in both of the two systems. Although this seems to have no correlation with the mean tetrahedral angle which determines the chemical shift of various silicon sites,\textsuperscript{15} it is interesting to note that for the silicon site with the largest mean tetrahedral angle (hence the largest absolute chemical shift value), the spin-lattice
relaxation time for empty silicalite is the smallest (-118 ppm, $T_1=5.15$ seconds), but the same silicon site in the p-xylene/silicalite complex has the longest spin-lattice relaxation time (-120 ppm, $T_1=7$ seconds). It seems that this site is more likely to be in the intersections of silicalite where it is more open to the channel system. In empty silicalite, this site has more time to be in contact with the paramagnetic molecular oxygen in the air so that it has a faster spin-lattice relaxation time. Since p-xylene tends to remain in the intersections, when p-xylene is adsorbed inside the silicalite channel system, the p-xylene has a more shielding effect to this silicon site. As a result, the oxygen has less contact with the silicon site, making the spin-lattice relaxation time longer for this site compared with other silicon sites. Using p-xylene as the guest molecule, we confirmed that adsorbed guest molecules indeed partially block or at least retard the diffusion of oxygen inside the silicalite crystal, making it less accessible to the silicon sites.

Experiments on silicalite loaded with endoperoxide 1 are also consistent with this result. Comparing the spin-lattice relaxation time of empty silicalite and silicalite loaded with endoperoxide, we found that the spin-lattice relaxation is enhanced when endoperoxide is added. As was previously stated, the endoperoxide 1 is not stable at room temperature and it slowly releases singlet oxygen. Since neither endoperoxide 1 nor its decomposition product can diffuse inside the silicalite framework, the net effect is that oxygen was added into the sealed rotors (the rotors were filled with air at the beginning of all the experiments). At this point, the oxygen was added continuously and its effect was an overall effect during the whole experiment. We realize that this is not a quantitative method of adding oxygen, but it is a simple way to study the effect of oxygen at this initial stage and the effect is obvious. For a similar experiment with p-xylene/silicalite, however, we found that the spin-lattice relaxation time is virtually unaffected within the experimental error. In the empty silicalite, the generated oxygen diffuses and is in contact with all the silicon sites freely, while the presence of p-xylene
blocks or retards the diffusion of the oxygen inside the silicalite framework. This result is consistent with the analysis of the silicon site with the largest chemical shift value.

Now we need to ask ourselves a question: why is the spin-lattice relaxation time of $^{29}\text{Si}$ nuclei in the p-xylene/silicalite complex smaller than that of empty silicalite? If the spin-lattice relaxation time is purely due to the interaction with oxygen wherever it comes from, one would expect a p-xylene/silicalite system to have a longer spin-lattice relaxation time, because the silicon sites have less accessibility to the oxygen. One possible explanation is the dipolar-dipolar couplings between the guest protons and the silicon atoms. Lebrev reported that $^{1}\text{H}-^{29}\text{Si}$ cross-polarization gave a strong signal at about 5% loading. Strong polarization transfer also means strong dipolar-dipolar couplings between the two nuclei. If this is true, then replacing hydrogen in the guest p-xylene molecule with deuterium will affect the silicon spin-lattice relaxation time. Since proton and deuterium have very different gyromagnetic constants, they will have different coupling strengths towards silicon nuclei. As we can see from Figure 4.5 ($T_1$ of p-xylene, p-xylene-$d_{10}$ and empty silicalite), all the silicon sites have almost identical spin-lattice relaxation times within the experimental error when we compare the p-xylene/silicalite and p-xylene-$d_{10}$/silicalite complex. We conclude that the dipolar-dipolar interaction does not contribute significantly to the $^{29}\text{Si}$ spin-lattice relaxation time.

It is interesting to note that in the literature report, adsorption of linear molecules inside the MFI channel system increases the spin-lattice relaxation time of $^{29}\text{Si}$ nuclei, while adsorption of aromatic molecules such as benzene decreases the spin-lattice relaxation time. Our result with silicalite loaded with 5% wt% of p-xylene also confirms this trend. However, when we measured the one pulse $^{29}\text{Si}$ NMR of silicalite loaded with eight p-xylene molecules per unit cell, the spectrum was saturated severely with a 10 second recycle delay, indicating a long spin-lattice relaxation time. On the other hand, the spectrum can be easily obtained by CPMAS (Cross-Polarization/Magic Angle Spinning) from protons in p-xylene molecules. Preliminary $^{29}\text{Si}$ spin-lattice
relaxation time measurement at this loading using inversion-recovery pulse sequence showed the cross point was around 15 seconds (recycle delay was 100 seconds), indicating that the spin-lattice relaxation time of $^{29}\text{Si}$ was longer than 10 seconds. This is probably due to the fact that oxygen was further blocked from accessing the silicon sites in the silicalite lattice at higher loading of p-xylene. Thus, while the effect of oxygen on the $^{29}\text{Si}$ spin-lattice relaxation is most likely due to its accessibility to the silicon nuclei, the effect of the adsorbed guest molecules can be rather complicated. The dipolar-dipolar interaction, the blocking of molecular oxygen and the structural change of zeolite can all contribute to the spin-lattice relaxation time. This is further complicated by the fact that different molecules have different mobility. The contact time of those molecules with silicon nuclei could vary drastically; hence the interactions with the zeolite lattice can be very different. For example, while adsorption of p-xylene gives the classical loading dependence of the MFI zeolite lattice, same loading of other molecules such as benzene does not give the same structural change. These are possibly due to the subtle change in the molecule's shape and size. Hence the effect of adsorbed molecules on the $^{29}\text{Si}$ spin-lattice relaxation cannot be fully explained until a sufficient amount of systems are studied. The p-xylene/MFI system is apparently one of the systems to begin with, and more information is needed for other systems.

4.5 Experimental Section

4.5.1 Silicalite Synthesis

Silicalite crystals were synthesized in a fluoride medium in the presence of the structure-directing TPABr template as described in Chapter 2 according to the literature method.\textsuperscript{36} They were activated in the furnace at 500\textdegree\text{C} for 12 hours before use.
4.5.2 Sample Loading

The loading of p-xylene into the silicalite was accomplished as follows. 300 mg of freshly calcinated silicalite was mixed with 15 mg of p-xylene in isoctane, producing a p-xylene/silicalite complex whose composition is ca. 3 p-xylene molecules per unit cell. After stirring overnight, the solvent was gently removed under Argon gas, and dried under high vacuum (10⁻⁵ torr) overnight. The sample was then fire sealed on a vacuum line and heated at 80°C for 12 hours to ensure homogenous distribution of guest molecules inside the silicalite crystals.

4.5.3 Preparation of 1-(1'-hydroxylehtyl)-4-methyl-1,4-epidioxy-1,4-dihydronaphthalene (1)

Synthesis of the racemic endoperoxide 1 was prepared as previously described.²⁹

4.5.4 Endoperoxide Loading on Silicalite

For the experiments producing oxygen through endoperoxide decomposition, about 15 wt% 1, was loaded onto silicalite and p-xylene/silicalite with CaH₂ dried methylene chloride as the solvent. After stirring thoroughly, the solvent was removed under Ar gas and the samples were dried under high vacuum for two hours to remove the solvent completely. The sample was quickly sealed in an NMR rotor and transferred to the NMR probe. Similarly loaded control samples of silicalite and silicalite loaded with p-xylene containing endoperoxide were analyzed for ¹⁸O₂ emission at 1268 nm, before and after NMR measurements. From those control samples, the intensity of emission of singlet oxygen was reduced by ~80% during the span of the NMR experiment.

4.5.5 Solid State NMR Measurements

²⁹Si MAS NMR spectra were obtained at 59.62MHz with a Bruker DRX-300 widebore spectrometer. The magic angle was set up using ⁷⁹Br resonance of KBr, and samples were spun at 5 kHz unless otherwise noted.
Spin-lattice relaxation times were measured using an inversion-recovery pulse sequence. The recycle delay was 20 seconds; typically 100 to 400 acquisitions were obtained.
References


36) Kornatowski, J. Zeolites 1988, 8, 77-78.
5 Locations and Dynamics of DBKs Adsorbed on Synthetic MFI Zeolites by Magnetic Resonance Methods

5.1 The Research Purpose

As mentioned in the Introduction, in addition to supramolecular structures, we studied the dynamics of DBK and related ketone molecules adsorbed on MFI zeolite crystals. We combined the results from the following methods to construct the picture: (a) $^2$H solid state NMR lineshape analysis of $^2$H labeled guest ketones; (b) high resolution solid state $^{29}$Si NMR of MFI zeolite hosts; (c) high resolution solid state $^{13}$C NMR of guest ketones and their reaction products; and (d) Electron Paramagnetic Resonance (EPR) of the intermediate radicals produced by photolysis. Attempts to employ $^1$H solid state NMR were also made. However, due to the poor resolution and interference from the zeolite host, the linewidth of $^1$H solid state MAS NMR was very large and did not give us much useful information. Therefore, $^1$H solid state NMR will not be discussed in this thesis. The application of the experimental methods is shown in Scheme 5.1.

Multinuclear solid state NMR was used to study the adsorption of guest ketones in the zeolite host (reactant, termed DBKs@MFI) and the photochemical reaction products (termed Products@MFI). EPR was used to study the reaction intermediates (termed Radicals@MFI). In this chapter we will mainly concentrate on DBK and p-Me-DBK adsorbed on synthetic MFI crystals. The systems were investigated as a function of loading of guest molecules in order to determine how supramolecular structure and dynamics vary as a function of composition. Analysis and application of o-Me-DBK adsorption will be discussed in the next chapter.
Scheme 5.1  Experimental methods for studying the adsorption and photochemical reaction of DBKs@MFI.

The probe molecules used were DBK, p-Me-DBK, o-Me-DBK and their selectively deuterium labeled compounds are shown in Figure 5.1. Based on the calculations in the Introduction, the minimum cross-sections of DBK and p-Me-DBK (~5 Å) are slightly smaller than the channel openings of MFI zeolites (~5.5 Å) while o-Me-DBK is slightly larger (~6 Å) due to the methyl group in the ortho position.

From these cross sections, we expected that at room temperature DBK and p-Me-DBK would diffuse into the channels, and o-Me-DBK would only remain outside. However, the benzene ring of o-Me-DBK could fit into the channel openings.
Figure 5.1 Labeled probe molecules under investigation. The molecules shown here are the deuterium labeled molecules.

5.2 $^2$H Solid State NMR Studies

As we know from Chapter 1, molecular motion, which can reorient the C-D bond vector with a correlation time in the range of $10^{-3}$ s to $10^{-8}$ s, can affect the lineshape and relaxation of $^2$H solid state NMR. A certain constrained motion mode can average the quadrupole interaction to some extent and usually gives a characteristic lineshape. A fast isotropic motion gives a narrow single line, and the linewidth depends on the correlation time of this motion. Thus, from analysis of the $^2$H NMR spectra lineshape, the mobility of the molecules can be studied and their adsorption sites can be inferred.

Figure 5.2 shows the $^2$H solid state NMR spectra of the four labeled ketones adsorbed in synthetic NaZSM-5 crystals (Si/Al=60 based on the initial synthetic gel mixture. No elementary analysis was performed). The crystals (see Chapter 3 for synthesis) are about 20 μm in length with uniform sizes as measured by using SEM (Figure 5.2).
Figure 5.2 $^2$H solid state NMR spectra of DBKs adsorbed on NaZSM-5 crystals. The loading is 10%, 10%, 0.1% and 6% wt% for DBK-d$_{10}$, p-Me-DBK-d$_5$, o-Me-DBK-d$_5$, and DBK-d$_4$ respectively.

Both DBK-d$_{10}$ and p-Me-DBK-d$_5$ gave a very broad $^2$H NMR spectrum with a half linewidth of 135 kHz. The DBK-d$_4$ produced a spectrum with a half width of 128 kHz. The broad spectra resulting from DBK-d$_{10}$ and p-Me-DBK-d$_5$ indicated that the mobilities of these molecules were strongly but not completely constrained. The quadrupole interaction could not be fully averaged out under this condition. In contrast, even a 0.1% loading of o-Me-DBK-d$_5$ gave a liquid-like narrow line with half linewidth of only 0.3 kHz, indicating that all the anisotropic interactions have been averaged out by rapid thermal motion.
These results on the dynamics of guest molecules confirmed the different binding sites of those probe molecules in MFI zeolites. DBK and p-Me-DBK bound to NaZSM-5 zeolite in its internal channels, while o-Me-DBK must bind wholly or partially on the external surface due to the steric constraint of the channel opening. Since the only difference between p-Me-DBK and o-Me-DBK is the position of the methyl group, it must be the larger molecule size of o-Me-DBK due to the ortho methyl group that inhibits diffusion into the internal framework.

A more precise description of the motion of DBK and p-Me-DBK can be revealed by a detailed lineshape analysis of the $^2\text{H}$ NMR spectra. Compared with the simulated $^2\text{H}$ NMR spectra of deuterons in a phenyl ring from the Introduction (Section 1.4, page 23), the motion of DBK-d$_5$ and p-Me-DBK-d$_5$ possesses the characteristics of the restricted motion of $180^\circ$ jumps of the phenyl ring.

\[
\text{ring flip}
\]

However, the $^2\text{H}$ NMR lineshape simulation is not unique, so that several motional modes could give the same lineshape, although the dynamics of different motional modes can be very different.$^{1-3}$ Thus, in addition to a lineshape analysis, at least one other set of experimental parameters is needed in order to make sure that the interpretation of the simulation is valid. One such experiment was the spin-spin relaxation time measurement, or $\tau$ dependent measurement in which the time delay between two $90^\circ$ pulses is varied in the measurement.
Different motions will result in different relaxation times of the deuterons in the molecule, and they usually have different \( \tau \) dependent behavior. If the proposed motional model fits both the lineshape and the intensity, it is very likely that it is a proper model to describe the dynamics in the system.

We measured the \( \tau \) dependence of the \( ^2\text{H} \) NMR spectra of the DBK-d\(_{10}\)/MFI zeolite sample for 8\% wt loading. The results are shown in Figure 5.3 with the simulations based on the 180\(^\circ\) jump motional mode. The simulation uses a quadrupole coupling constant \( Qcc=180 \) kHz,\(^4\)-\(^6\) asymmetric parameter \( \eta=0 \), and a jump rate of \( 5\times10^6 \) Hz.

There is a small sharp peak in the center of the experimental spectra. This peak could not be removed by washing with isoctane. This loading (8 wt\%) is below the saturation level of adsorption in the internal surface and all of the ketones are expected to be inside. Therefore, the sharp peak represents a different molecular dynamic and a possible different adsorption site for DBK inside the MFI channels. The simulated spectra based on the 180\(^\circ\) jump motional mode at \( \tau=30 \) \( \mu \)s and 100 \( \mu \)s are relatively close to the experimental spectra both in their lineshape and intensities except for the central regions. The jumping rate is very reasonable for phenyl ring flipping.\(^7\),\(^8\) The lineshape of the simulated spectrum at \( \tau=300 \) \( \mu \)s is also very close to the experimental spectrum, but the simulated intensity is much higher. In other words, the experimental relaxation time is faster than that of the theoretical prediction.
Figure 5.3 \( \tau \) dependence measurements of \(^2\)H of 8\% wt\% DBK-d\(_{10}\) on synthetic large MFI crystals. The \( \tau \) values (in \( \mu s \)) are labeled on the left side in the figure. The numbers on the right side show the relative integrals of the experimental and simulated spectra. The spectrum corresponding to 300 \( \mu s \) is magnified. Simulation conditions: \( Q_{cc}=180 \text{ kHz} \), \( \pi \)-flipping rate=5e6Hz and asymmetric parameter \( \eta=0 \).

It should be noted that in the theoretical treatment, we assume that the 180° flipping is the only relaxation mechanism. In heterogeneous systems, there could be a distribution of molecular dynamics due to the different adsorption sites or different constraints of molecule motion, as we will see later in this chapter. Thus, a single motional model with a uniform correlation time is often an oversimplified model in a supramolecular structure. Heterogeneity of motion has been observed by a two-dimensional \(^2\)H NMR study of labeled polymers and glycolipid bilayers.\(^{3,9}\) Nevertheless, the similarities between the experimental spectra and simulated spectra indicated that the
dominant motion for the DBK is the restricted π-flipping of the phenyl ring at this loading level (8 wt%).

![Diagram showing Hertz frequencies with 10%, 3%, and 1% loading levels.](image)

**Figure 5.4** Loading dependence of DBK-d₁₀ on silicalite crystals. The spectra were taken at room temperature with τ=30 μs, quadrupole echo pulse sequence.

Figure 5.4 shows the $^2$H spectra at different loading of DBK-d₁₀. At high loading (above 3%), the spectrum has the characteristic π-flipping of the phenyl ring. At low loading (1%), the spectrum changes to a more triangular shape with a sharp peak in the central region, and the spectral width is reduced to some extent. This can be understood when we consider the interactions between guest molecules inside the MFI zeolites. When the loading is low, there is a relatively larger space and freedom for each molecule to have additional motions besides the restricted π-flipping. Those motions may include
the small angle liberation of the phenyl ring, the gauche-trans isomerization around the -CO-CH₂- bond, or other types of motions. Similar results have been observed by Griffin and coworker in their study of tyrosyl motion in peptides.7 As the loading becomes higher, more molecules are adsorbed inside the silicalite channels and intersections. This leads to increased intermolecular interactions and reduces the freedom of molecular motion. As the loading approaches the saturation level (~15 wt% for DBK), most of the channels and intersections are occupied by the guest ketones, and the mobility of those ketones becomes more and more restricted to the π-flipping motion as we saw before. We will see a similar situation when we examine the EPR spectra later in this chapter.

On the ²H NMR time scales, there is no indication of a 90-degree or a 112-degree jump that corresponds to the diffusion between the straight channel and the zigzag channel or the diffusion between two zigzag channel segments, respectively. Those types of motions have been observed for p-xylene adsorbed in ZSM-5 zeolite at high temperature.¹⁰,¹¹ DBK has a size and length which is nearly double that of p-xylene, so that it is expected that such a large molecule would have a much slower diffusion rate than p-xylene at room temperature inside the MFI zeolite.

It should be noted that the ²H NMR lineshape is only sensitive to the reorientation of the C-D bond in the time scale 10⁻³ s to 10⁻⁸ s, and that very slow or strict translation diffusion will not be revealed from the NMR spectrum. It is highly probable that DBK can diffuse along the channels (otherwise DBK would not reach beyond 10% loading inside the internal channels) while it has the π-flipping motion, although this can not be seen directly from the deuterium NMR spectra.

The ²H NMR spectrum of α-Me-DBK-d₅ loaded on synthetic large crystals (crystal size ~100 μm in length) displays a sharp, liquid-like line even at the lowest loadings (0.1% wt) for which acceptable spectra could be obtained. Further reducing of the loading to 0.02% wt% (about 0.4 μmol of deuterons in the sample) only produced noise due to the detection limit of the NMR instrument even after hours of acquisition.
Figure 5.5 shows the spectra from a series of measurements. As the loading becomes higher, the linewidth decreases and approaches the linewidth of the liquid state o-Me-DBK-d₅ obtained under similar conditions (Figure 5.5, bottom).

The half linewidth of the spectrum is related to the mobility of the ketone. As we will see in the detailed analysis in the next chapter, when ketones are loaded on the zeolite surface, they first occupy the adsorption sites on the surface until a monolayer is formed. Additional ketones must adsorb above this monolayer to form multilayers. It is reasonable to assume that ketones in the monolayer will have less mobility due to their stronger interactions with the zeolite surface, resulting in a larger spectral width. Ketones in the multilayers will have less interaction with the zeolite surface and behave more or less as a liquid. This is shown schematically in Figure 5.6. Our interest was to study the ketones in the monolayer, since it is the supramolecular structure and dynamics of the guest/host that are of interest, not the guest-guest interactions in the multilayers.

We sought to estimate the loading of o-Me-DBK which corresponds to a monolayer and to compare this value to the limit of 0.02 wt% loading for which acceptable spectra could be obtained. Based on the size (100 μm x 50 μm x 50 μm) and density of the synthetic silicalite crystals (~1.8 g/ml), the external surface area could be estimated. One particle had a volume of 2.5 x 10⁻¹³ m³, and 1 g of this silicalite crystal contained 2.22 x 10⁶ particles. Each particle had an external surface area of 2.5 x 10⁻⁸ m². Therefore, 1 g of silicalite crystal had an external surface area of 5.5 x 10⁻² m². If we assume the size of o-Me-DBK to be 100 Å², then 9.1 x 10⁻⁸ mol or 2 x 10⁻⁵ g of o-Me-DBK is the estimate for a monolayer. This corresponds to a wt% loading is just 0.002%, an order of magnitude lower than the detection limit of our NMR instrument. Thus, zeolites with a much larger external surface area (i.e. much smaller size) were needed in order to study the behavior of o-Me-DBK in the monolayer. Such systems will be the subject of the next chapter, in
Figure 5.5 ²H NMR spectra of o-Me-DBK-d₅ loaded on large silicalite crystals (~100 μm in length, 50 μm in width) at different conditions at room temperature. The wt% loading of ketone and the spectral half linewidth are labeled in each spectra.
which we will discuss in more detail the use of very small commercial zeolite particles and the adsorption of o-Me-DBK in the monolayer. We will also show that we can use photochemical probe molecules to characterize zeolite surfaces.

![Diagram of Monolayer and Multilayers formed by o-Me-DBK on the external surface of MFI zeolites. Ketones will first adsorb on the external surface until a monolayer is formed. Additional ketones must adsorb in the multilayers above the monolayer.](image)

**Figure 5.6** Monolayer and multilayers formed by o-Me-DBK on the external surface of MFI zeolites. Ketones will first adsorb on the external surface until a monolayer is formed. Additional ketones must adsorb in the multilayers above the monolayer.

5.3 **MAS (Magic Angle Spinning) and CP/MAS (Cross Polarization/Magic Angle Spinning) Solid State NMR Studies**

5.3.1 $^{29}$Si MAS Solid State NMR Studies

Deuterium solid state NMR can yield rather direct information about the mobility of the labeled organic molecules adsorbed on zeolites. However, with this method the location of the molecules, whether it is inside or outside, can only be inferred indirectly based on the motion of the labeled molecules. $^{29}$Si solid state NMR is sensitive to the local chemical environment of the silicon nuclei. For large zeolite crystals discussed in this chapter (>20 μm), the amount of silicon atoms positioned on the external surface is
very small compared to the number of silicon atoms in the internal surface. The number of silicon atoms on the external surface is negligible for the total number of silicon atoms in the crystal. Thus, any information derived from $^{29}$Si solid state NMR concerns the silicon atoms inside the zeolite crystals.

As stated in the previous chapter, the $^{29}$Si NMR line pattern and chemical shift is directly related to the chemical environment of those nuclei. The adsorption of organic molecules inside the framework will interact with the silicon atoms and induce changes in the chemical shifts of silicon nuclei. On the other hand, if a molecule is adsorbed only on the external surface, it will not change the chemical environment of the silicon nuclei monitored by $^{29}$Si NMR. Thus, $^{29}$Si solid state NMR provides direct information on the location of the adsorbed organic molecules on the internal surface only.

In addition, since the nature of cross-polarization is dipole-dipole coupling between the abundant nuclei such as protons and the rare nuclei such as silicon, the efficiency of cross-polarization is strongly distance-dependent as well as mobility dependent. The efficiency of cross-polarization is proportional to $r^6$, where $r$ is the distance between a proton and a carbon (or silicon) nucleus. At a distance larger than the sum of van der Waals radii, the efficiency of cross-polarization virtually diminishes. In addition, for intermolecular cross-polarization transfer (i.e., polarization transfer from protons in guest ketones to $^{29}$Si in a host lattice), if the protons possess very fast dynamics, even they are close to the rare nuclei, the efficiency of cross-polarization can also be reduced substantially. Thus, by comparing the efficiency of cross polarization, we may obtain information about both the proximity between the guest ketones and the MFI zeolite framework and the motion of adsorbed molecules.

In the following section, we present $^{29}$Si solid state NMR measurements as a function of guest molecule structure, loading, and photolysis of guest ketones. This corresponds to monitoring DBKs@MFI and Products@MFI in Scheme 5.1.
5.3.1.1 Adsorption of DBK, p-Me-DBK and o-Me-DBK

Figure 5.7 shows the one pulse $^{29}$SiMAS NMR with proton decoupling of silicalite loaded with DBK, p-Me-DBK and o-Me-DBK molecules, respectively. For comparison, we also show the spectra of empty silicalite (Figure 5.7, bottom) and silicalite loaded with four p-xylene molecules per unit cell (Figure 5.7, top). The spectrum of silicalite loaded with 8 wt% p-Me-DBK is similar to that of silicalite loaded with 4 p-xylene molecules per unit cell, but it is broader. The spectrum of silicalite loaded with DBK also has some similarity to that of silicalite loaded with 4 p-xylene molecules per unit cell, but the spectrum is poorly resolved. The spectrum of silicalite loaded with 4 wt% o-Me-DBK gives an identical pattern with that of empty silicalite in the loading range of 1% to 10% wt%, although the resolution is somewhat poorer.

The most definable changes in the spectra occur for signals at -110 ppm and -119 ppm, respectively, the former decreasing with adsorption of molecules to the internal surface and the latter increasing with adsorption of molecules to the internal surface. Fyfe and coworkers have provided similar evidence in their study of p-xylene loading dependence. The peak intensity at -110 ppm, which is a peak characteristic of an empty silicalite, gradually decreased and a group of peaks around -118 ~ -119 ppm which are characteristic peaks of silicalite loaded with 4 p-xylene gradually appeared by increasing the loading of p-xylene. In addition, the spectral resolution becomes poor as the loading increases, indicating the complexity of the transition structures.
Figure 5.7 $^{29}$Si solid state MAS NMR of silicalite loaded with DBK, p-Me-DBK and o-Me-DBK. Spin rate is 5 kHz. The loading is expressed in both weight percentage and number of molecules per unit cell and indicated on the right of each spectrum. For comparison, spectra of empty silicalite and silicalite loaded with 4 p-xylene per unit cell are also shown at the bottom.
At a loading of 8% wt% p-Me-DBK (about 2 molecules per unit cell, roughly equivalent to four p-xylene molecules per unit cell), the pattern of the $^{29}$Si NMR spectrum appeared to be the same as that of the 4 p-xylene/silicalite complex. Loading of 8% wt% of DBK also changed the framework to that which is close to that of 4 p-xylene/silicalite complex but with a poor spectral resolution.

All of the spectra were taken after heating the sealed sample (in vacuum) at 80°C for one day to ensure homogenous distribution of the guest ketones. The heating was especially effective for the p-Me-DBK/silicalite sample. Before heating, the spectrum of p-Me-DBK showed poor resolution similar to that of DBK/silicalite. The poor resolution of the p-Me-DBK sample was drastically improved when the sample was heated. In contrast, heating the DBK sample for up to two days did not produce resolution equivalent to the p-xylene or p-Me-DBK samples.

It has been well established that the 12-line silicon NMR spectrum for p-xylene/silicalite complex results from the occupation of channel intersections by p-xylene molecules.\textsuperscript{15,16} The fact that the $^{29}$Si spectra of DBK/silicalite and p-Me-DBK/silicalite are identical to the 12-line spectrum of p-xylene suggests that the phenyl rings of DBK or p-Me-DBK prefer to stay in the intersections in the silicalite.

Under the experimental conditions of adsorption at ambient temperature, o-Me-DBK cannot diffuse into the internal system. Thus, the internal channel system of the silicalite is not perturbed, and the $^{29}$Si NMR is essentially identical to that of empty silicalite. The slight degrading in spectral resolution might be an indication that part of the o-Me-DBK molecules (the small benzyl part) could stick into the holes (channel openings on the external surface) and create a small distribution of $^{29}$Si chemical shift, but this speculation was not confirmed at this point.
5.3.1.2 Loading Dependence of DBK in Silicalite

The DBK loading dependence of the $^{29}$Si spectra is shown in Figure 5.8. In spite of the poor resolution, the characteristic disappearance of the signal at -110 ppm (empty zeolite) and the appearance of the signal at -118 $\sim$ -119 ppm (intersection occupied) are consistent with adsorption of DBK on the internal surface.

![DBK loading dependence of $^{29}$Si solid state MAS NMR spectra with proton decoupling for silicalite crystals. The spinning speed is 5 kHz. The loading is expressed in both wt% and number of molecules per unit cell.](image)

Figure 5.8 DBK loading dependence of $^{29}$Si solid state MAS NMR spectra with proton decoupling for silicalite crystals. The spinning speed is 5 kHz. The loading is expressed in both wt% and number of molecules per unit cell.
5.3.1.3 Isotope Substitution Dependence, CP/MAS Measurement

In an effort trying to obtain more detailed structural information on the location of DBK adsorbed in silicalite, $^1$H-$^{29}$Si cross polarization experiments employing DBK and its deuterium labeled compounds were performed. The ketones employed in this study were DBK and DBK-d$_{10}$ as shown in Figure 5.1.

The basic concept of these experiments was to study the proximity between protons in DBK and the silicon sites in the internal surface. Since the efficiency of cross-polarization is proportional to the r$^{-6}$, where r is the distance between the proton and silicon nucleus, from the relative intensity of the silicon NMR, we might be able to distinguish the proximity of protons and silicon sites. Figure 5.9 shows the $^1$H-$^{29}$Si cross polarization spectra for all the ketones studied. The CPMAS spectra are normalized as needed, since we are only interested in the relative intensity of peaks in each spectrum.

The one-pulse spectra of silicalite loaded with DBK and DBK-d$_{10}$ were expected and found to be identical, since one pulse excites and detects the silicon nuclei directly. Protons in the DBK molecules can efficiently transfer polarization to $^{29}$Si nuclei in the host lattice, indicating the tight fitting of DBK into the silicalite channel and that the motion of the molecule is very slow. In addition, the relative peak intensities of CPMAS spectra are modulated compared with their single pulse spectra. For example, the intensities of the middle region of the DBK-d$_{10}$/silicalite spectrum is weaker compared with that of silicalite loaded DBK. This seems to indicate that the aromatic groups are closer to the silicon sites in that region. Unfortunately, the current resolution is not high enough to make a detailed and unambiguous judgement regarding which silicon site is enhanced and which is not. The inherently poor resolution for DBK/silicalite prevented the analysis. Other molecules that can be readily labeled and yield well-resolved silicon NMR spectra are needed in order to make the assignments unambiguous.
5.3.1.4 Effect of Photolysis of DBK on the Solid State NMR Spectra

Since DBK is a photoactive ketone, it was of interest to determine if the photolysis of the ketone could have any effect on the $^{29}$Si spectrum. Figure 5.10 shows the $^{29}$Si MAS NMR of DBK/silicalite after one-hour photolysis at different loadings. The conversion of DBK ranged from ca. 60% (1% wt% loading) to ca. 30% (8% wt% loading). As a comparison, the corresponding spectra before photolysis and silicalite loaded with 7.5% wt% diphenyl ethane (DPE, major product from photolysis of DBK in zeolite) are also shown in Figure 5.10.
Figure 5.10 $^{29}$Si MAS NMR with proton decoupling of DBK/silicalite complex before and after one hour photolysis at different loading. Photolysis was carried out in a quartz cell in high vacuum using a 400-Watt medium pressure Hanovia Hg lamp. The samples were repacked into the NMR rotor for NMR measurements. Rotor spinning speed was 5 kHz. DPE was directly loaded into the silicalite and the spectrum was measured without photolysis.
The spectral pattern of silicalite loaded with 7.5 wt% DPE (Figure 5.10, top) is very similar to that of the 4 p-xylene/MFI complex, as is the 8 wt% photolyzed sample. Compared with the $^{29}$Si spectra before photolysis of DBK, two things are clear after photolysis: (1) The spectral pattern shifted more to that of the 4 p-xylene/MFI complex, as the peak around -119 ppm appeared in the spectrum of 1% loading. It is clear that in the sample of 3% loading the signal around -118 ppm before photolysis became two characteristic peaks for the transformed symmetry. For the high loading sample (8% wt%), the spectrum is identical to that of the 4 p-xylene/MFI complex, with the peak at -110 ppm completely disappearing. (2) The resolution at high DBK loading improved considerably as a result of the photolysis. The improvement in the spectral resolution for the DBK sample is most likely due to the production of diphenyl ethane (DPE) inside the MFI channel system. The initial adsorption of the ketone inside the zeolite may be highly heterogeneous, even with its being heated at 80°C for a day. The photoreaction product (DPE) is more mobile, and this could reduce the heterogeneous character of the supramolecular structure.

Photolysis of silicalite loaded with 10 wt% o-Me-DBK also changed the symmetry of the zeolite crystal. Figure 5.11 shows $^{29}$Si MAS NMR spectra of silicalite loaded with 10% o-Me-DBK before and after 1 hour photolysis. The conversion is expected to be higher than 50%, since all of the ketones are outside and the photolysis is efficient.
Figure 5.11 One pulse $^{29}$Si solid state NMR spectra of o-Me-DBK loaded on synthetic silicalite crystals at 10% wt% loading before and after photolysis for 1 hour. $^{29}$Si NMR of silicalite loaded with 1% DBK after photolysis is also shown on the right for comparison.

A change in the structure was detectable although it was not significant, and this change is assigned to the sieving of smaller product DPE into the MFI zeolite internal channels. As indicated from $^2$H NMR studies in the previous section, at 10 wt% loading, almost all of the o-Me-DBK was in the multi-layers due to the very small external surface of the large crystals (only about 0.002% of the loaded ketone is needed to form a monolayer). Photolysis of ketones in those multi-layers was similar to the photolysis of ketones in solution, and only B-B (diphenyl ethane) has access to the internal surface of MFI zeolites. A-A and A-B are both too large to enter the channel opening. We will reexamine this later using $^{13}$C solid state NMR (Figure 5.18).

We seek to compute the amount of DPE produced during the photolysis to determine the maximum amount of DPE being adsorbed on the internal surface. At 10
wt% loading of o-Me-DBK it is expected that about 1.2 wt% of DPE will be produced at 50% conversion \((10\%_{\text{loading}} \times 0.5_{\text{conversion}} \times 0.25_{\text{BB}} = 1.25\%)\). The spectrum after photolysis of o-Me-DBK in Figure 5.11 is indeed similar to that of silicalite loaded with 1 wt% DBK after photolysis, as expected if both of the samples possessed similar amounts of diphenyl ethane in the internal surface of the synthetic silicalite crystals. The \(^{29}\text{Si}\) NMR spectra are thus similar. Photolysis of very higher loading of o-Me-DBK (>30% wt%) would be expected to produce a spectrum that is similar to the 4 p-xylene/silicalite complex. We did not pursue this due to the large consumption of o-Me-DBK and such a high loading was not of interest to our investigations.

As we will see in the next chapter, for o-Me-DBK in the monolayer, the smaller benzyl portion tends to plug into the holes (channel openings on the external surface) while the larger o-Me-benzyl portion stays outside of the channels. Photolysis of o-Me-DBK in this monolayer is expected to have different product distributions from those in the multilayers. However, the amount of o-Me-DBK is so small that this difference is undetectable using \(^{29}\text{Si}\) solid state NMR. We will present a detailed study in the next chapter with smaller commercial powders.

5.3.2 \(^{13}\text{C}\) Solid State NMR of Ketones Inside MFI Zeolites

To complete the solid state NMR analysis, we have measured \(^{13}\text{C}\) NMR of the guest molecules. The chemical shifts of carbon nuclei could be affected by their chemical environment where the molecules were adsorbed. In addition, the CP-MAS can be readily employed to study the mobility and other properties such as conformation. In the following section, we present a study of \(^{13}\text{C}\) NMR as a function of loading, temperature and different ketone molecules.
5.3.2.1 Loading Dependence

Figure 5.12 shows the $^{13}$C CPMAS NMR of DBK inside the MFI channels at two different loadings.

The phenyl ring and carbonyl carbons showed strong spinning sidebands of the guest ketones as indicated by the stars in the Figure. The positions of those spinning sidebands changed as the spinning speed changed from 3.5 kHz to 4 kHz for the two samples, while the isotropic chemical shifts of the three groups of carbons did not change. This confirmed the assignment of the spinning sidebands in the spectra. The presence of the strong spinning sidebands is an indication that the motion of DBK is largely restricted.\textsuperscript{17} The relatively strong carbonyl carbon in the CP/MAS spectrum is due to its proximity to the four methylene protons. The intensity of the CPMAS spectra is much greater than that of direct excitation (one pulse) spectra. This is an indication that the $^1$H-$^{13}$C dipole-dipole interaction is very effective, as expected from the greatly restricted motion of DBK in a MFI zeolite. This result is consistent with the $^2$H NMR study in which the dominant motion of the phenyl ring is the restricted $\pi$-flipping at room temperature.

Surprisingly, the methylene groups in DBK show two distinct singlets with separation of about 7 ppm (δ=46 ppm and 53 ppm) in both loadings at room temperature suggesting that the two groups are not equivalent. The chemical shift of the methylene groups of DBK is equivalent in the solution state (CDCl$_3$ as solvent) and shows a singlet at 49 ppm. The two singlets still existed at lower loading (1 wt%).
Figure 5.12 $^{13}\text{C}$ solid state CP/MAS NMR of DBK in silicalite at different loadings. Stars (*) indicate the spinning sidebands (SSB) as their positions change with rotor spinning speed. Numbers above the spectra indicate the carbon signal assignment.

The DBK employed in this work had a purity of at least 99% as checked by GC/MS and NMR spectroscopy. Thus, the two singlets are not due to the impurities in the compound. Enolization of DBK in the adsorbed state can be ruled out since (1) the zeolites are synthetic silicalite crystals which have virtually no active sites as catalyst for this process. (2) The chemical shift of an enol carbon would be observed at $\sim 149$ ppm with the original methylene carbon at $\sim 93$ ppm as estimated from the DBK-enol structure using CS Chemdraw (Version 4.5, CambridgeSoft Corporation, MA), but none of them was observed in the carbon spectra.
In order to investigate the origin and the nature of the splitting, two kinds of experiments were carried out: an isotope label dependence and a temperature dependence, as reported in the following sections. For clarity of the spectra presented in the remainder of this chapter, we removed the spectral regions with spinning sidebands and only show the chemical shifts in the main positions (the isotropic position).

5.3.2.2 Isotope Substitution

Substitution of proton with deuterium could help with the investigation of the $^{13}$C spectra. Since the CPMAS depends on the dipolar-dipolar coupling between carbons and protons nearby, the carbon signals will be greatly reduced if its bonded $^1$H were substituted with $^2$H. The assignment of the peaks can be confirmed from the relative intensities of the carbon signals. Figure 5.13 shows the $^{13}$C CPMAS NMR spectra of DBK and DBK-d$_{10}$ in which the two phenyl rings are selectively labeled.

Compared with the unlabeled DBK, the relative intensities (peak area) of the methylene carbons were larger in the DBK-d$_{10}$ sample. The strong signal from the carbonyl carbon ($\delta=209$ ppm) was due to the polarization transfer from protons in the methylene groups in DBK. Such a strong dipolar-dipolar coupling in the relatively long range (two bond distance) is another indication that DBK is rigid inside the MFI channel system.

We also measured the one pulse $^{13}$C NMR spectrum of DBK-d$_{4}$, in which the two methylene groups were selectively deuterated. We measured the one pulse MAS NMR for a sample at 5 wt% loading. The result is shown in Figure 5.14.
Figure 5.13 $^{13}$C CPMAS solid state NMR of DBK and DBK-$d_{10}$ adsorbed in silicalite crystals. Top: 8% DBK in silicalite. Bottom: 8% DBK-$d_{10}$ in silicalite. The arrows correlate the carbons with their chemical shifts. For clarity, the regions of spinning sidebands were removed from the spectra.
Figure 5.14  One pulse $^{13}$C solid state NMR spectrum of DBK-d$_4$ loaded on synthetic silicalite crystals at 5% wt% loading. Stars (*) labeled the spinning sidebands from aromatic carbons.

The broad bump under the signals from the phenyl ring is probably due to the background signal from the probe. Methylene carbons in DBK-d$_4$ also produced two singlets with a separation of 7 ppm. The ratio of the two carbon signals is around 1:1. Thus, all of the ketones investigated have the two singlets with chemical shifts of 46 ppm and 53 ppm.

As a comparison, we also measured the $^{13}$C NMR spectra of diphenyl ethane (DPE) loaded in silicalite crystals. DPE is the major product from photolysis of DBK inside of MFI zeolites. The result is shown in Figure 5.15. As a comparison, $^{13}$C NMR of DPE in solution is also shown in the same range of chemical shift.

The two methylene groups in DPE also show a separation of ~7 ppm ($\delta = 36.6$ ppm and $\delta = 29.7$ ppm) when DPE is adsorbed in synthetic silicalite crystals. The ratio of the two peaks, however, was around 5:1 for DPE as determined by peak deconvolution. In addition, the positions of the two singlets are not equally separated with regard to the chemical shift of the methylene groups in solution. The smaller peak shifted more than that of the larger peak (Figure 5.15).
Figure 5.15  (A) Solid state $^{13}$C single pulse MAS NMR spectra of diphenyl ethane loaded in synthetic silicalite crystals (spinning at 5 kHz). The stars (*) indicate the spinning sidebands from the aromatic carbons.  (B) $^{13}$C NMR of DPE in solution phase (CDCl$_3$ as solvent).

5.3.2.3 Variable temperature dependence

Variable temperature experiments were carried out for the 8% DBK-d$_{10}$ sample in the range of 240K and 360K. The results are shown in Figure 5.16.

The two singlets gradually merged to the peak position in solution state (49 ppm) with increasing the temperature. This change is reversible upon decreasing the temperature. In addition, the spinning sidebands became weaker at higher temperature, an indication of the faster motion of DBK. The intensity of CPMAS signals changes from strong at T=240 K to weak at T=323 K and then becomes strong again at 360 K. (Note the scanning number in the spectra are different).
Figure 5.16  $^{13}$C solid state NMR of DBK-d$_{10}$ on silicalite at different temperatures. Temperature and spinning speed are shown on the figure. The asterisks indicate spinning sidebands.
<table>
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<th>295</th>
<th>323</th>
<th>360</th>
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<td>7.0</td>
<td>5.4</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 5.1 Chemical shift separation of the two methylene groups in DBK/silicalite as a function of temperature.

Table 5.1 shows the chemical shift separation of the two methylene groups at different temperatures. The separation of the two methylene groups did not change between 240K and 295K, indicating that DBK is already very rigid even at room temperature. As the temperature increases, the mobilities of DBK became faster. Eventually, the mobility of DBK was fast enough so that only the average chemical shift value shows up in the spectra at 360K.

5.3.2.4 Comparison of DBK and p-Me-DBK

It would be very helpful to compare DBK and p-Me-DBK, since both are adsorbed in the internal surface and the latter just has an extra methyl group. Figure 5.17 shows the $^{13}$C solid state NMR of 8% wt% DBK/silicalite and p-Me-DBK/silicalite samples.

The spectrum of p-Me-DBK also showed a separation of about 3.5 ppm for the two methylene groups. It should be noted that the two methylene groups are not strictly equivalent in p-Me-DBK, but the difference is much smaller in the solution state (less than 0.5 ppm). The intensity of the carbonyl carbon in p-Me-DBK is weaker than in DBK.
Figure 5.17 \(^{13}\text{C}\) CP/MAS NMR of guest ketones inside silicalite. Spinning speed was 3.5 KHz. The regions with spinning sidebands were removed for clarity.

5.3.2.5 Photolysis of o-Me-DBK@MFI

In previous studies of silicalite loaded with 10 wt\% of o-Me-DBK using \(^{29}\text{Si}\) solid state NMR (Figure 5.11), we showed that the structure of MFI zeolite changed slightly upon photolysis of the sample, and it was suggested that the DPE produced by photolysis had diffused into the internal surface. With \(^{13}\text{C}\) solid state NMR, we can detect the sieving of diphenyl ethane (DPE) into the internal framework directly. Figure 5.18 shows a series of measurements. Compared with the \(^{13}\text{C}\) NMR spectra in solution (CDCl\(_3\) as solvent), the two methylene carbons in o-Me-DBK (\(\delta=47.3\) ppm and 49.5 ppm in spectrum A) reduced substantially after photolysis (spectrum B). In the meantime, a
group of peaks around 35~37 ppm emerged after photolysis (spectrum B). The change in the spectra indicates that most of the reactant (o-Me-DBK@MFI) has been transformed to the photochemical products (products@MFI). In addition, when we measured the cross-polarization spectrum of products@MFI, we only detected DPE@MFI (spectrum C) as we determined by comparing the spectrum of pure DPE in solution (spectrum D).

The efficiency of cross-polarization is determined by the distance of the two nuclei and the mobility of the molecules. While the one pulse spectrum of products@MFI (spectrum B) shows all of the carbons in the sample, the CPMAS of products@MFI only shows the immobilized product (DPE@MFI). Only DPE has the size small enough to diffuse into the internal channel system and is immobilized. The other products, with sizes too large to enter into the channel, have much larger mobility on the external surface and the efficiency of cross-polarization is much weaker. However, the signal from DPE@MFI was very weak, indicating that the immobilized DPE is only a small portion of the total photoreaction products and it still possesses some mobility in the internal channels. The weak signal from DPE@MFI is consistent with the $^{29}$Si solid state NMR measurement in which only a slight change was detected.
Figure 5.18  $^{13}$C NMR of o-Me-DBK in CDCl$_3$ (spectrum A); one pulse $^{13}$C solid state NMR of photolysis of 10 wt% loading of o-Me-DBK on synthetic silicalite crystals (spectrum B); CPMAS $^{13}$C solid state NMR of spectrum B, and $^{13}$C NMR of pure diphenyl ethane (spectrum D). The asterisk indicates the spinning sideband. The arrow in spectrum B indicates the presence of the photoreaction products. See text for details.
5.3.3 Discussion

Solid state \(^2\text{H}\) NMR, \(^{29}\text{Si}\) NMR and \(^{13}\text{C}\) NMR all confirmed that at ambient temperatures, DBK and p-Me-DBK can readily diffuse into the MFI internal surface while o-Me-DBK can only stay on the external surface.

DBK and p-Me-DBK experienced significant restriction in their motion in the zeolite, as evidenced by the large spectral width in \(^2\text{H}\) NMR, the presence of strong spinning sidebands in their \(^{13}\text{C}\) solid state NMR and the effectiveness of cross-polarization of \(^1\text{H}-^{13}\text{C}\). The effectiveness of \(^1\text{H}-^{29}\text{Si}\) cross-polarization indicated that the protons and silicon are in close proximity in the supramolecular structure. As pointed out by Davis and coworkers, cross-polarization is most efficient when the distance between a proton and a carbon is less than 3.3 Å.\(^{19}\) An increase in interatomic distance to 3.7 Å or greater results in a drastic decrease in the cross-polarization efficiency as studied from a p-xylene/silicalite system.\(^{20}\) When selectively deuterated DBK molecules were used, the relative intensities of individual \(^{29}\text{Si}\) peak in the \(^1\text{H}-^{29}\text{Si}\) CP/MAS spectra were modulated (the intensity of different peaks was enhanced differently by cross-polarization) to a great extent, due to the different distance between \(^1\text{H}\) and \(^{29}\text{Si}\) nuclei. Although poor spectral resolution prevented a reliable analysis of the correlation between protons and silicon sites, the modulation clearly reflected the short distance between the two kinds of protons (methylene protons and aromatic protons) and the different silicon sites in the host structure.

As the loading of guest molecules increased, the crystal structure of the silicalite host gradually changed as expected from previous results for the adsorption of p-xylene. However, the heterogeneity of the adsorption of DBK degraded the spectral resolution. Upon photolysis, the reduction in adsorption heterogeneity of the product (diphenyl ethane) improved the spectral resolution.
The rather large chemical shift splitting of the two singlets of the two methylene carbons of DBK in MFI zeolites is interesting. The reversible temperature dependence of the separation clearly indicates that this separation is related to the mobility of the molecule. The two singlets were observed in all of the loading ranges (1% to 8%) and the separation does not depend on DBK loading (always ~7.0 ppm at room temperature). It could not be that some DBK adsorbed onto the external surface as in the case of very high loading of p-xylene shown by Olson and Satozawa,\textsuperscript{16,17} since the loading level (1 wt% to 3 wt%) is far below the saturation point of the internal surface. Enolization is also excluded from both the absence of the chemical shift of the expected carbon nuclei for the molecule and the nature of the host which does not have active sites to facilitate this process.

Turro et al. reported a result of $^{13}$C solid state NMR of DBK loaded inside FAU zeolites with a much larger cage (13 Å).\textsuperscript{21} No separation of the methylene peaks was observed in the spectra. The large pore zeolites seem to provide enough space for DBK to move nearly freely in the NMR time scales.

One possible explanation is that DBK may have two different adsorption sites in the MFI zeolite, and the methylene groups of those two adsorption sites are not equivalent, due to the different local supramolecular environments. The distribution of DBK in these two sites has a ratio of 1:1 indicated by the relative intensity of the two methylene peaks. These two environments may correspond to the straight channel and the zig-zag channel, as in the case of tetrapropyl ammonium inside the MFI zeolites,\textsuperscript{19,22} or the channel and intersections.

The intensity change of the CPMAS spectra at different temperatures supports this proposal. As we can see from Figure 5.16, the intensity of the CPMAS signal is very strong at low temperature, indicating the exchange rate is very slow on the NMR time scale. As the temperature increased, the separation of the two singlets became smaller and the intensity of the CPMAS became weaker (T=323 K). This may indicate that the
exchange rate is in the intermediate range and the relaxation is faster. As the temperature further increases (T=360 K), the exchange rate enters into the fast limit on the NMR time scale, and the intensity is partially recovered. Further evidence may come from $^{29}$Si NMR. The $^{29}$Si spectra resolution of silicalite loaded with DBK does not change upon heating at 80°C for a day, which may indicate a mixing of local structures due to the different adsorption sites of DBK. The extra methyl group in p-Me-DBK may have an anchoring effect inside the MFI zeolite, and the adsorption is more or less homogeneous, especially after being heated. Nevertheless, the difference still exists as the separation of the two methylene groups is larger in silicalite than in the solution phase.

The $^{13}$C measurement of silicalite loaded with diphenyl ethane (DPE) is consistent with the hypothesis of the heterogenous adsorption of DBK. The two singlets of the methylene groups in DPE also have about 7 ppm difference in their chemical shifts. This may indicate that the chemical shift difference is mainly determined by the environment provided by the zeolite structure. The ratio of those two adsorption sites, however, is different between DBK and DPE, and could be a reflection the different distribution of the two adsorption sites inside the MFI zeolite for DBK and DPE.

5.4 EPR Studies of Radicals from Photolysis of DBK on NaZSM-5 (~20 μm in length) with a Low Si/Al Ratio (Si/Al=10)

5.4.1 Generation of Benzyl Radicals in NaZSM-5 from DBK

As stated in the Introduction, the radical pairs from photolysis of DBK will be confined in the zeolite channel or cage (cage effect) before they diffuse apart. When the ketone decarbonylates, recombination requires the radical pairs to move toward each other and recombine. In zeolites, if the interaction between the guest molecules and the zeolite host is very strong, or the diffusion of the guest molecules is very slow, the radicals may have longer lifetimes before they can reach each other and recombine.
In order to study the reactivity of the reaction intermediates, we selected two synthetic zeolite crystals. One is silicalite (~20 \( \mu \text{m} \)) and the other is NaZSM-5 (~20 \( \mu \text{m} \)) with a Si/Al ratio of 10. Both were synthesized using identical methods except that no aluminum was used in the preparation of silicalite sample. We will show by Electron Paramagnetic Resonance (EPR) spectroscopy that the interaction of the phenyl ring in the ketone with the cations in ZSM-5 is strong enough to slow down the recombination of the radical pair compared to silicalite. We shall also show that the interaction of the phenyl groups in the ketones with silicalite, which has no cations, is relatively weak, and the radical pairs recombine faster to form the product.

The samples were prepared as described in the sample preparation section for the two synthetic zeolite crystals. Pumping at high vacuum (ca. \( 5 \times 10^{-5} \text{ torr} \)) was used to remove any residual solvent and oxygen. The sample was sealed in vacuum and was photolyzed for 10 min before the EPR spectra were measured. Figure 5.19 shows the EPR spectrum derived from the photolysis of 2% DBK in synthetic NaZSM-5 crystals and its simulation based on the hyperfine coupling constants (hfc) shown.\(^{23}\)
Figure 5.19  EPR spectrum from photolysis of 2% DBK in NaZSM-5 (Si/Al=10) and the spectral simulation. The simulation was completed using $g=2.00260$ and the hyperfine coupling constants shown in the spectra. The linewidth in the simulation is 1 G.

Clearly the simulated spectrum of the benzyl radical closely matches the experimental spectrum. The hyperfine-coupling constants (hfc) are consistent with that in the solution state reported in the literature.\textsuperscript{24}

The linewidth employed in the simulation of the EPR spectrum (ca. 1 gauss) is larger compared with radicals in the solution state (less than 0.2 gauss).\textsuperscript{25} The linewidth is related to the radical mobility and interaction between radicals. The large linewidth in Figure 5.19 is an indication that the motion of the benzyl radical in NaZSM-5 is restricted or that the radical-radical interaction is large in the supramolecular structures.

Following photolysis, the EPR intensity decayed, presumably due to the recombination of the radicals in the zeolite. Figure 5.20 shows the total intensity of the EPR signal vs. the time after 10 minute's photolysis of the sample at 2% wt% loading.
Figure 5.20  EPR intensity of the benzyl radical from photolysis of DBK in NaZSM-5 at 2% wt% loading. The EPR intensity did not change very much after 40 minutes. The photolysis time is 10 minutes. \( t=0 \) is the time when the first spectrum was taken. The curve was fitted as single exponential decay yielding a half lifetime of 10 minutes, while direct measurement on the graph gave a similar half lifetime of 7 minutes.
The intensity did not change much after 40 minutes, although it still has the characteristics of benzyl radicals, indicating that there is another type of benzyl radical in the supramolecular structure which has a much longer lifetime. The half lifetime of the benzyl radical in this sample is about 7 to 10 minutes for the fast decay.

5.4.2 Loading Dependence of the Benzyl Radical in NaZSM-5

The DBK loading dependence on the EPR spectra was measured in the range of 0.2% to 10% wt%. The resolution and linewidth of the EPR spectra from photolysis of DBK in NaZSM-5 did not depend on the loading up to about 2%, while the intensity of the EPR signals consistently increased with loading for the same length of time of photolysis. However, at loading above 5 wt%, both the EPR intensity and resolution dropped substantially. The EPR signal became much broader for the high loading sample, as shown in Figure 5.21.

In contrast, there is a very weak EPR signal from the photolysis of DBK in silicalite crystals compared with that in the NaZSM-5 sample for the loading range studied. Figure 5.22 shows the EPR spectrum of 2% loading of DBK in silicalite crystals (Si/Al>500, crystal size is about 100 μm in length) after 10 minute's photolysis. For comparison, the EPR spectrum on NaZSM-5 (Si/Al=10, crystal size is about 20 μm in length) is also shown in the same scale. The weak, broad EPR spectrum on silicalite was not present in the control EPR measurement before photolysis. The shape and intensity of the signal is comparable to the residual EPR signal (after about four hours) on NaZSM-5.
Figure 5.21 Loading dependence of the EPR signal from photolysis of DBK inside synthetic NaZSM-5 crystals. Photolysis time is 10 minutes for all the samples.
Figure 5.22  EPR spectrum of 2% loading of DBK in silicalite crystals after a 10 minute photolysis. For comparison, an EPR spectrum of the same loading on NaZSM-5 (Si/Al=10) is also shown in the same scale.

5.4.3 Discussion

It is well known that the lifetime of a benzyl radical in solution is very short (in the order of microseconds) and can only be detected by using a fast detection method such as laser flash photolysis or in flowing systems. From the results of photolysis of DBK in MFI zeolites, it is clear that the radical pairs can still diffuse rapidly and recombine in silicalite (Figure 5.22). The radical pairs in NaZSM-5 with low Si/Al ratio, however, can accumulate a relatively high steady-state concentration and have a much longer lifetime (Figure 5.22). This could be explained by the strong interaction of the benzyl radical with sodium cations in the supramolecular system.

In NaZSM-5 there are sodium cations present to compensate for the negative charges of the AlO₄⁻ tetrahedral units. The NaZSM-5 crystals used in this work have a Si/Al ratio of 10. The unit cell of the MFI zeolite contains 96 tetrahedral sites that can be
silicon or aluminum atoms. Therefore, theoretically, there are about 8–9 sodium cations to balance the aluminum in one unit cell. However, the Si/Al ratio we presented here is obtained based on the starting materials in the zeolite synthesis. It has been reported that the actual Si/Al ratio in the final zeolite crystal is usually much higher than that in the starting gel mixture and the distribution of aluminum in the zeolite crystals is not homogeneous, especially for large crystals.\textsuperscript{27,28} The aluminum content in the core of large crystals is usually much smaller (less than 1 Al per unit cell) than that on the rim of the crystals. We did not perform an elementary analysis for this NaZSM-5 sample, but the aluminum content is expected to be much less than 8 atoms per unit cell on average. Nevertheless, the presence of the cations in this NaZSM-5 sample clearly promotes the long lifetime of the benzyl radicals.

It is well established that positive charges such as the cations in NaZSM-5 interact strongly with the π clouds in electron rich molecules. Garcia and Weisz showed that the diffusion rate of o-xylene in silicalite (HZSM-5 with Si/Al=2604, essentially silicalite) is nearly one order higher than that in NaZSM-5 (Si/Al=40).\textsuperscript{29} This may indicate that the mobility of aromatic molecules inside NaZSM-5 is much slower compared with that in silicalite where there are no cations present. It is also possible that the cations serve as steric inhibitors to diffusional motion through the internal zeolite surface. This π-cation interaction is likely to hold the benzyl radical to some extent and to slow down the recombination process. As a result, the benzyl radicals can reach a higher steady-state concentration in NaZSM-5, and can be detected using EPR. It is important to note that there is a much faster decay of the radicals which precedes the slow decay we observed here, and the early fast decay cannot be observed by steady-state EPR.\textsuperscript{30} What we see may be a very small portion of all of the radicals that are associated with the cations in NaZSM-5.

As mentioned above, the presence of the sodium cations inside the NaZSM-5 zeolite channels can also interfere with the diffusion of the benzyl radicals. The NaZSM-
5 synthetic zeolite we used in this study has a relatively low Si/Al ratio so that a significant amount of sodium cations are expected to be present inside the channels, up to 8 per unit cell. However, this is not likely to be the reason for the strong EPR signal we saw in the NaZSM-5 sample, since it is well established from cage effect study that radical pairs from DBK molecules inside the MFI zeolite (both silicalite and ZSM-5) are mainly due to primary geminate radical pairs. Thus the observation of a strong EPR signal of benzyl radicals is due to the electrostatic interactions between the radical and the cations in NaZSM-5.

Turro and Lei have investigated the cation dependence of the loading and lifetime of DBK in LZ-105, a commercial ZSM-5 zeolite with Si/Al=20.\textsuperscript{31} When they loaded and photolyzed DBK-d\textsubscript{10} in Li\textsuperscript{+}, Na\textsuperscript{+}, K\textsuperscript{+}, Rb\textsuperscript{+} and Cs\textsuperscript{+} exchanged ZSM-5 (deuterated samples were used to simplify the spectra and enhance the signal/noise characteristics), they found some changes in intensity and linewidth of the EPR signal from the benzyl radical when the cations were different, as shown in Figure 5.23.

The EPR intensity of the benzyl radical consistently increased from Li-LZ105 to K-LZ105 and then dropped again as the size of the cation further increased. The half linewidth of the EPR signal also changed in a similar trend. K-LZ105 had the smallest linewidth of all of the M-LZ105. This trend may be due to a competition between steric effects which increases from Li to Cs and the polarization effect which decreases from Li to Cs. Although the exact mechanism of this cation dependence is still under investigation, the interaction between cation and the guest DBK contributes significantly to the stabilization of benzyl radicals in MFI zeolites.

The loading dependence of EPR linewidth and intensity is most likely due to the decreased mobility of the radicals as more molecules park inside the channels. The additional molecules serve as "plugs" to interfere with the diffusion of the radicals inside the NaZSM-5 zeolites. The recombination also became faster as the loading became
larger, consistent with the results obtained from $^2$H NMR studies (Section 5.2, Figure 5.4).

![Diagram of chemical reactions and EPR spectra]

Figure 5.23 Dependence of EPR intensity and linewidth of the benzyl radical on cation $M$ present in M-LZ105 zeolite. The EPR linewidth for each benzyl radical on each cation is indicated in the figure. The loading is 1 wt% (courtesy of Dr. Xue-Gong Lei)

5.5 Summary

The location and dynamics of DBK and its derivatives adsorbed in MFI zeolite crystals were studied by multinuclear solid state NMR. From deuterium NMR studies, it
was demonstrated that the very small size difference between p-Me-DBK (or DBK) and o-Me-DBK determines their adsorption locations. o-Me-DBK can only stay on the external surface of the MFI zeolite due to its large molecular size, while the latter two can readily be adsorbed inside. Studies from silicon and carbon NMR also support this result.

The mobility of p-Me-DBK and DBK inside the MFI zeolite is greatly restricted at room temperature. The dominant motion is the restricted ring flipping with a correlation time in the order of 0.1 μs derived from $^2$H solid state NMR lineshape simulations. Additional motion is present and this may include the trans-gauche isomerization around the -CO-CH$_2$- bond in the intersections of MFI zeolites. A single motional mode with a uniform correlation time is not sufficient to describe this heterogeneous set of motions. The motion of the ketone was found to depend on the loading. At low loadings, there is relatively more space and weak intermolecular interaction between ketones, rendering larger mobility of the ketones. Photolysis of DBK has a large effect on the transformation of MFI structure due to the more flexible photochemical product. The methyl group in p-Me-DBK may have some kind of "anchoring" effect in the MFI zeolite and the adsorption is more uniform than that of DBK. In addition, DBK may have different adsorption sites inside MFI zeolites at or below room temperature. At higher temperature, the two adsorption sites exchange very fast on the NMR time scale. These two adsorption sites may correspond to the straight channel and zig-zag channel or the channels and the intersections.

The motion of o-Me-DBK adsorbed on large MFI crystals also depends on its loading. At low loading, o-Me-DBK may form a monolayer around the MFI zeolite particle and have a relatively slow isotropic motion. Once the monolayer is formed, additional o-Me-DBK molecules will form multilayers above the monolayer and have a fast isotropic motion comparable with its liquid state. Diffusion of o-Me-DBK into the internal framework of the MFI zeolite is very difficult even at a relatively high temperature. Photolysis of o-Me-DBK produced a product molecule (diphenyl ethane)
which has a smaller size and can diffuse into the internal surface of MFI zeolites. Due to
the large particle size and small external surface area of the synthetic MFI zeolite
(necessary in order to obtain high resolution $^{29}$Si solid state NMR), the amount of o-Me-
DBK in the monolayer is too small to be studied by NMR and EPR. However, we will
present a detailed study using a very small commercial powder in the next chapter.

Benzyl radicals generated from photolysis of DBK inside NaZSM-5 with a low
Si/Al ratio have long lifetimes and can be studied by steady-state EPR. The half lifetime
of benzyl radical is much longer than that in solution. The intensity and mobility of the
benzyl radical depends on the loading of DBK and the type of cations present in zeolites.
In contrast, the benzyl radical has a much shorter lifetime in silicalite, possibly due to the
fast recombination in the absence of cations in the host.

5.6 Experimental Section

High-resolution $^{29}$Si and $^{13}$C solid state NMR measurements were taken in a
Bruker DRX-300 wide-bore NMR system equipped with multinuclear solid accessories.
The magic angle was precisely tuned with KBr.$^{32}$ The sample spinning speed was 3.5-5
kHz for $^{29}$Si and $^{13}$C, and up to 10kHz for $^1$H. The stability of the temperature in variable
temperature experiments was within 1 K.

Deuterium wide-line solid state NMR spectra were recorded on a Bruker AC-250
NMR system equipped with a CXP console. The quadrupole echo pulse sequence was
employed to record the $^2$H spectra. $T_1$ measurements were done with an inversion-
recovery pulse sequence. The 90-degree pulse width was 2.5μs, and the recycle delay
was 1 s unless otherwise indicated. Variable temperature experiments were performed
with a Bruker VT-1000 temperature controller. The accuracy of the temperature was
within +/-1K. Simulation of $^2$H NMR was performed using the program
TURBOPOWDER, originally written by Professor Robert Griffin's group at MIT and
kindly provided by Professor Ann McDermott here at Columbia University. The
program can simulate lineshape of quad echo and inversion recovery experiments of I=1 nuclei undergoing reorientation in powder samples. The program needs an input file for the necessary parameters and data. The simulated spectra were interactively adjusted and compared with the experiment to determine a best fit.

EPR spectra were recorded in a Bruker EP380 and a Bruker EMX EPR spectrometer. g values of the radicals were calibrated with a DPPH standard. EPR spectra processing and simulation were performed using WinEPR and Simfonia programs.

Computer simulations of molecular conformation, diffusion and docking in zeolites were performed using MSI software (Molecular Simulations, Inc., San Diego, CA), Macromodel (Shroedinger Inc.) and Spartan (Wavefunction, Inc., Irvine, CA) running on SGI workstations.

About 100mg to 300 mg of freshly calcined zeolite was mixed with the desired amount of the guest materials in isoctane. After stirring overnight, the solvent was gently removed under Argon gas, and dried under high vacuum (10^{-5} torr) overnight at room temperature before measurement.

The photolysis was performed with a 400-Watt medium pressure Hanovia Hg lamp with an aqueous K_{2}CrO_{4}-Na_{2}CO_{3} filter to isolate the 313 nm line. The sample was degassed to a pressure of 5x10^{-5} torr, maintained under vacuum and tumbled during photolysis at room temperature.
References


31) Turro, N. J.; Lei, X. G. unpublished results.
6. Adsorption of o-Me-DBK on the external surface of small MFI zeolite particles

6.1 Introduction

In the previous chapter, we presented a study of o-Me-DBK on large MFI crystals. Since the external surface area of the synthetic crystals is very small due to the large crystal sizes, the information we obtained from $^2$H (loading > 0.1 wt%) is mainly from ketones in the multilayers. Ketones in a multilayer structure are relatively insensitive to the zeolite structure.

In order to study o-Me-DBK molecules in the monolayer, which is in contact with the external zeolite surface, zeolites with a larger external surface area are needed. For this purpose, we shall compare our data on large crystals to those of two commercial zeolites. One is silicalite-1 and the other is NaZSM-5 with a Si/Al ratio of 40. We will show that using o-Me-DBK as a photochemical probe and combining the results from isotherm measurements and $^2$H NMR measurement, a detailed picture of ketone adsorption and the resulting supramolecular structure can be readily constructed. The probe molecules are o-Me-DBK-$d_4$ and o-Me-DBK-$d_5$ as shown below. Most of the experimental work on these systems was performed by Dr. Xue-Gong Lei in the Turro group.

![Chemical structures of o-Me-DBK-$d_4$ and o-Me-DBK-$d_5$](attachment:chemical_structures.png)
6.2 Characterization of the Commercial Zeolites

The two commercial zeolites (silicalite and ZSM-5) to be discussed in this chapter have an identical framework topology structure and they both belong to the MFI zeolite family. The chemical difference between the two zeolites is that in ZSM-5, a certain small quantity of aluminum is present in the framework as indicated by the Si/Al ratio (the lowest possible value for Si/Al ratio in a NaZSM-5 zeolite is expected to be around 3.1), and sodium ions are present as charge compensating cations for the Al atoms in the framework. A physical difference between these two zeolites is that the particle size of silicalite (ca. 1 um) is larger than that of NaZSM-5 (ca. 0.3 um), as measured by scanning electronic microscopy (SEM) provided by Dr. Lloyd Abrams of DuPont. Figure 6.1 shows the SEM of the two zeolites.

![Silicalite-1](image1.png) ![NaZSM-5](image2.png)

**Figure 6.1** SEM photographs of silicalite and NaZSM-5 samples. Left: silicalite powder, average size=1 um, external surface area=5 m²/g. Right: NaZSM-5 powder, average size=0.3 um, external surface area=16m²/g. The samples, their SEM and surface measurements were provided by Dr. Lloyd Abrams of DuPont CR&D Department.

The external surface area, which is mainly determined by the particle size, is thus different for the two zeolites. The silicalite has an external surface area of ca. 5m²/g
while the NaZSM-5 possesses an external surface area of ca. 16 m²/g as measured by the Mercury Porosimetry method by Dr. Abrams of DuPont CR&D department.

6.3 Computation of Ketone Loading and Ketone Coverage of the External and Internal Surface Characteristics from Unit Cell Dimensions

The unit cell of MFI zeolites (including silicalite and ZSM-5) has a dimension of 20Å x 20Å x 14 Å, with a 90° angle between each of the two axes.¹ The unit cell composition (using silicalite as the prototype) is Si₉₆O₁₉₂, giving a "molecular weight" of 5760 g/mol.² There are four intersections in a unit cell. The external surface of a MFI zeolite can be divided into two binding environments for o-Me-DBK. One is the "hole" or pore leading to the internal surface, and the other is the "flat" framework between the holes. Figure 6.2 shows a computer generated representation of the [010] surface of MFI zeolites.¹

Here are some simple calculations based on the parameters for these two zeolites.

1. Computation of the concentration of intersections in the internal surface

One unit cell has a volume of 5.6 x 10⁻²⁴ liters. Thus, one mole of unit cells would occupy a volume of 3.37 liter/mol. The concentration of a unit cell is thus 1/3.37=0.3 mol/liter. Since each unit cell contains four intersections, the concentration of the intersection is 1.2 mol/L. The density of the two zeolites is similar and the manufacturer reported it to be 1.8 g/ml. Therefore, 1 g of zeolite contains 6.7 x 10⁻⁴ mol of intersections.
Figure 6.2  Silicalite, viewed from the top of the straight channel. This is the [010] surface. The balls are the silicon atoms and are connected by oxygen atoms.
2. **Computation of the concentration of straight channel and zig-zag channel segments.**

As we can see from Figure 6.3, each intersection shares two straight channels and two zig-zag channel segments with its neighboring intersections. Each intersection is associated with $2 \times 1/2 = 1$ whole straight channels and one whole zig-zag channel segment. Therefore, the concentration of the straight channel or the zig-zag channel is the same as the intersections in MFI zeolites ($6.7 \times 10^{-4}$ mol per gram of zeolite). Together with the intersection, there are three binding sites in the internal surface (intersection, termed I; straight channel, termed S; and zig-zag channel, termed Z). Each binding site has the same concentration of $6.7 \times 10^{-4}$ mol per gram of zeolite.

![MFI zeolite channel structures. I, S, Z indicate the intersection, the straight channel segment, and the zig-zag channel segment, respectively.](image)

The above numbers do not have much relevance to o-Me-DBK for our studies, since under our experimental conditions the ketone does not diffuse into the internal surface. To host a molecule of p-Me-DBK, three consecutive binding sites (I-S-I, I-Z-I,
S-I-S, Z-I-Z, S-I-Z, etc.) are needed for the long molecule (13.3 Å, Figure 1.5, chapter 1). Therefore, when all of the internal binding sites are occupied by p-Me-DBK (MW=224.30 g/mol), the weight percentage loading will be 15 wt%. This loading may serve as the upper limit for adsorption of p-Me-DBK in the internal surface.

Experimentally, p-Me-DBK will first fill the internal surface, after which additional p-Me-DBK will adsorb on the external surface as calculated below. The actual maximum loading will also depend on the amount of cations in ZSM-5 zeolites, since those cations will also occupy space in the internal surface.

3. Computation of the concentration of holes on the external surface

The total surface area of a unit cell is 1920 Å². There are 12 holes on one unit cell surface; thus the average area of a hole is 1920/12 = 160 Å². For a zeolite with an external surface area of 10 m²/g, there are 6.25 x 10¹⁸ holes, or 1.04 x 10⁻⁵ moles of holes. For the commercial silicalite-1 (SA = 5 m²/g) and NaZSM-5 (SA = 16 m²/g) which was used in this section, 1 g contains 5 x 10⁻⁶ and 1.7 x 10⁻⁵ moles of holes, respectively.

Alternatively, if we use the [010] surface as a model, we can obtain a very similar result. The unit cell area on the [010] surface is 20Å x 14 Å = 280 Å². There are two holes on a unit cell surface, and the average area of a hole is 140 Å². For a zeolite with an external surface area of 10 m²/g, there are 7 x 10¹⁸ holes, or 1.16 x 10⁻⁵ moles of holes. From this calculation, 1 g of silicalite and NaZSM-5 samples we used here contain 6 x 10⁻⁶ and 1.8 x 10⁻⁵ moles of holes, respectively.

Since these two methods give nearly identical results, from now on we will use the [010] surface as a model of the external surface area. If each hole contains one o-Me-DBK (MW=224.30 g/mol), then when all of the holes are occupied, the weight percentage of loading is 0.13 wt% and 0.40 wt% for the silicalite and NaZSM-5 samples, respectively. Thus, given the approximations of the analysis, we expect that the holes
will be filled by o-Me-DBK at ca. 0.1 wt% and ca. 0.4% for the silicalite and ZSM-5 samples, respectively.

4. Computation of the area percentage of holes and framework

The percentage of the area of the external surface of a MFI zeolite can be estimated by using the [010] surface as a model and assuming that the hole has a circular shape with a diameter of 5.5 Å. Two holes on the [010] surface will have an area of 47.5 Å$^2$. Since the unit cell area on the [010] surface is 280 Å$^2$, the percentage of holes is 47.5/280=17%. Therefore, the binding sites on the external framework consist of ca. 20% "holes" and 80% "flat" framework for o-Me-DBK molecules.

5. Estimation of the monolayer coverage for o-Me-DBK on the external surface

It is important to have an estimate of the amount of ketone needed in order to fill a monolayer. The above computations and the computation of the "loading size" of o-Me-DBK allow such an estimate.

o-Me-DBK can be visualized as having two extreme possible orientations for binding on the external surface, as shown in Figure 6.4. These two orientations result in different surface coverage as determined by the area of molecular cross-sections. The orientation on the left in Figure 6.4 represents the maximum occupation of the MFI external surface by one ketone, and the orientation on the right represents the minimum occupation of the MFI external surface by one ketone molecule. If we arrange the ketones on the external surface in each orientation and allow them the van der Waals contact, we can estimate the range of ketones needed to cover all the external surface area as determined by the two extreme orientations. Table 6.1 shows this calculated weight percentage loading for the two commercial zeolites. All of the above computations are listed in Table 6.2.
<table>
<thead>
<tr>
<th></th>
<th>Min. loading</th>
<th>Max. loading</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wt%</td>
<td>Wt%</td>
</tr>
<tr>
<td>Silicalite powder</td>
<td>0.2</td>
<td>0.6</td>
</tr>
<tr>
<td>(SA=5 m²/g)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaZSM-5 powder</td>
<td>0.70</td>
<td>1.8</td>
</tr>
<tr>
<td>(SA=16 m²/g)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6.1  Estimation of wt% loading of o-Me-DBK in a monolayer coverage for the two extreme orientations.
Top: The two extreme orientations of o-Me-DBK on the external surface of MFI zeolites. Different orientations cover different surface areas as determined by their areas of cross-section. Bottom: Side view of the top presentation.
<table>
<thead>
<tr>
<th></th>
<th>Max. wt% Loading in Internal Surface (p-Me-DBK)</th>
<th>Max. wt% Loading In Holes (o-Me-DBK)</th>
<th>Max. wt% Loading For Monolayer (o-Me-DBK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicalite powder</td>
<td>15 wt%</td>
<td>0.13 wt%</td>
<td>0.2–0.6 wt%</td>
</tr>
<tr>
<td>(SA=5 m²/g)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaZSM-5 powder</td>
<td>15 wt%</td>
<td>0.40 wt%</td>
<td>0.7–1.8 wt%</td>
</tr>
<tr>
<td>(SA=16 m²/g)</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Table 6.2  Calculation results based on the particle size and measured external surface for the two MFI zeolite samples.

6.4  $^2$H NMR Studies of o-Me-DBK Adsorbed on MFI Zeolites

6.4.1  Adsorption of p-Me-DBK-d$_5$

We now seek to compare the computation of the binding of o-Me-DBK to the external surface to experimental data, specifically, the results of photochemical, $^2$H solid state NMR and isotherm measurements. We first compare the $^2$H solid state NMR spectra of p-Me-DBK-d$_5$ loaded in the two commercial zeolites, and then discuss the results for the commercial and synthetic zeolites. $^2$H solid state NMR spectra of the two commercial zeolites loaded with p-Me-DBK-d$_5$ are shown in Figure 6.5.

There is not much difference in the results (Figure 6.5) from these two commercial zeolite samples. As in the case of the large crystals we discussed in the previous chapter (Chapter 5, Figure 5.2 and Figure 5.4, see insert in Figure 6.5), the main motion of the $^2$H labelled phenyl ring is the restricted $\pi$-flipping unless the loading is very low (1 wt% loading).$^{3,4}$ The important conclusion from these comparisons is that the $^2$H NMR probe of commercial and synthetic zeolites yields equivalent data.
Figure 6.5 $^2$H solid state NMR spectra of commercial silicalite-1 (left) and NaZSM-5 (right) loaded with p-Me-DBK-d$_5$ at different loading. The simulation is based on the two site $\pi$-flipping model of the phenyl ring.
The motion of p-Me-DBK-d₅ in these two zeolites is similar at the same loadings. The difference in the external surface (particle size) of these two particles is not expected to influence the motion of p-Me-DBK adsorbed on the internal surface. Indeed, there is no substantial difference between the motion of p-Me-DBK in silicalite and NaZSM-5 based on our $^2$H NMR measurements for comparable loadings. It seems that the possible π-cation interactions⁵,⁶ presented in NaZSM-5 do not significantly modify the strong supramolecular steric effects imposed by the tight fit of the guest ketones in the zeolites.

The NaZSM-5 zeolite has a Si/Al ratio of 40. Thus, each unit cell contains 2.3 sodium cations on average (each unit cell contains 96 T sites which can be occupied by silicon or aluminum atoms). Table 6.3 lists the calculated numbers of cations or molecules of p-Me-DBK in one unit cell. Although the amount of cations is relatively large compared with the numbers of p-Me-DBK, the presence of cations in NaZSM-5 may only provide a small perturbation to the mobility of the adsorbed p-Me-DBK and this small perturbation cannot be revealed under current experimental conditions.

<table>
<thead>
<tr>
<th># of Cations/u.c</th>
<th># of p-Me-DBK/u.c at 1 wt% loading</th>
<th># of p-Me-DBK/u.c at 3 wt% loading</th>
<th># of p-Me-DBK/u.c at 5 wt% loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3</td>
<td>0.3</td>
<td>0.8</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Table 6.3 Calculations of cations and loading of p-Me-DBK in unit cells for NaZSM-5.

6.4.2 $^2$H NMR Studies of o-Me-DBK-d₅ and o-Me-DBK-d₄ Adsorbed on the Two Commercial Zeolites

Figure 6.6 shows the $^2$H NMR spectra of o-Me-DBK-d₅ loaded on the two zeolite samples. On both zeolites, narrow lines were observed at higher loadings, as in the case of large synthetic crystals. However, spectra with wider half linewidth were observed at low loadings and such broad signals were not observed with the large crystals. In addition, the half linewidth of the labeled ketone adsorbed on these two zeolites has very
different loading dependences. Table 6.4 shows the $^2$H NMR half linewidth at different loading for the two zeolites.

![Chemical structure and NMR spectra](image)

**Figure 6.6** Loading dependences of $^2$H NMR spectra of o-Me-DBK-$d_5$ on silicalite and NaZSM-5. The number on the right of each spectrum indicates the scaling factor of the spectral height in the plot (except for the sample with loading larger than 5 wt%; the spectra were measured by Dr. Xue-Gong Lei)
Table 6.4  **Half linewidth and its reciprocal of o-Me-DBK-d5 loaded on the two commercial zeolites.**

For a molecule executing fast isotropic motion or high symmetry motion (octahedral or tetrahedral), a Lorentzen single line is expected due to the average of the anisotropic interactions. The linewidth of this single peak depends on the rate of the motion. Qualitatively, the correlation time of the motion is proportional to the linewidth. The faster the molecular motion, the narrower the linewidth. The reciprocal of the linewidth is thus proportional to the rate of the molecular motion and carries information on the sites to which the ketones are located, since the motion of adsorbed molecules will depend on their supramolecular structure. The reciprocal of the linewidth is also listed in Table 6.4.

We now seek to determine if a correlation can be identified between the molecular motion deduced from $^2$H NMR and supramolecular structures. Careful examination of the data in Table 6.4 showed that there is a rather abrupt jump in the half linewidth of o-Me-DBK on the two zeolites at a certain loading. This jump happens at ca. 0.2wt% on silicalite and ca. 1 wt% on NaZSM-5. The $^2$H NMR study at lower loadings (down to 0.1 wt% for both of the zeolites) showed that the half linewidth of $^2$H NMR from o-Me-DBK-d$_5$ was roughly constant (10–14 kHz) below the loading of 0.2wt% and 1 wt% for silicalite and NaZSM-5, respectively. Above this loading, the half
linewidth is within the order of 1 kHz and slightly decreases as the loading further increases, approaching the linewidth of pure o-Me-DBK-d5 under similar experimental conditions. These two loadings in which the break in motion occurs are in the range of monolayer formation based on the calculations (Table 6.2). Therefore, it is very likely that these sudden jumps in the $^2$H linewidth correspond to the transition from a monolayer to multilayers, or from holes to the flat surface.

A plot of $1/\Delta H$ for the two zeolites is shown in Figure 6.7 A. From the figure it can be seen that for the same linewidth, the wt% loading of ketone on NaZSM-5 was about 6 times that on silicalite. Thus if we scale the loading of o-Me-DBK on silicalite by a factor of six, the two curves nearly overlap (Figure 6.7 B). This result supports the conclusion that the different loading dependences on the two zeolites comes from the different external surface areas (5 m$^2$/g for silicalite and 16 m$^2$/g for ZSM-5). Normalizing the loading based on the external surface will give the same "loading" dependence (Figure 6.7 B). This "loading" should be the coverage or fraction of a monolayer of ketones on the external surface rather than the wt% loading which does not involve surface area.
Figure 6.7  Plot of the reciprocal of $^2$H NMR half linewidth vs. loading (A) and layers (B).
Preliminary studies of $^2$H solid state NMR measurements of o-Me-DBK-d$_4$ adsorbed on the silicalite powder also support the interpretation of the loading dependence. Below the loading of 0.2 wt%, the linewidth is relatively broad, and above 0.4 wt%, the half linewidth reduced to about 1 kHz (Figure 6.8).

![Figure 6.8 $^2$H solid state NMR of o-Me-DBK-d$_4$ adsorbed on commercial silicalite powders. The wt% loading and spectral half linewidth are labeled in each spectrum (spectra taken by Dr. Xue-Gong Lei in the Turro group).](image)

Assuming that the external surface area measured by the Mercury Porosimetry method is relatively accurate, the difference between the ratio of the measured external surface area (ratio = 4) and the ratio obtained from the $^2$H NMR linewidth measurement (ratio = 6) may be an indication of a slight difference in the external surface for those two zeolites. Although at this point, we consider the ratios to be within the experimental uncertainties of the computational and data analysis, we should note that the aluminum amount on the external surface may be high for the NaZSM-5 sample (Si/Al=40), and the
external surface may be much richer in aluminum content than the internal core of the particle.\textsuperscript{7,8} The presence of the aluminum and the associated cations in the NaZSM-5 sample may slightly reduce the motion of the guest molecules through absorption or steric effects. As a result, the $^2\text{H}$ linewidth of o-Me-DBK-d$_5$ is slightly wider on NaZSM-5 compared with that on silicalite for the same surface coverage. Nevertheless, the correlation between the mobility and the external surface area is excellent.

Further information on the supramolecular structure of o-Me-DBK adsorbed on the external surface of MFI zeolites is available from the investigation of the cage effect of o-Me-DBK and the addition of o-Me-DBK on the EPR of electron spin probes as a function of the loading.\textsuperscript{9} Similar correlation factors between the measured property and the surface coverage were obtained.\textsuperscript{9} Therefore, results from $^2\text{H}$ solid state NMR, photochemistry, EPR and computer calculation all show break points for ketones in the monolayer and multilayers. These probes may thus provide a way to estimate the external surface area of similar zeolites.

Turro and Hirano studied another MFI zeolite, named Na-LZ-105 (Si/Al=20.5, external surface area = 15 m$^2$/g)\textsuperscript{10} using the Langmuir isotherm and persistent radicals (generated from photolysis of the parent ketones and persistent due to the supramolecular steric effects) method.\textsuperscript{11,12} Several derivatives of DBK were studied.

\begin{center}
\begin{tabular}{ccc}
\includegraphics[width=0.3\textwidth]{images/1.png} & \includegraphics[width=0.3\textwidth]{images/3.png} & \includegraphics[width=0.3\textwidth]{images/6.png} \\
1 & 3 & 6 \\
\end{tabular}
\end{center}

For the isotherm measurement of ketone loading less than a monolayer, they found that the Langmuir isotherm cannot be fitted with a uniform site adsorption model; however, it could be well fitted by a two-site adsorption model (Figure 6.9). The binding constants for the two adsorption sites are very different (Table 6.5).\textsuperscript{11}
Strong binding sites could be assigned to the holes, while the weak adsorption sites could be assigned to the flat framework on the external surface. When molecules are adsorbed on the external surface, it will first adsorb on the holes until all of the holes are filled. After that, ketones will then adsorb on the flat external surface among the holes until a monolayer is formed. Additional ketones will adsorb on top of the monolayer to form multilayers.

\[ A = M \cdot k \cdot C/(1+k \cdot C) \]  

\[ A = M_I \cdot k_I \cdot C/(1+k_I \cdot C) + M_{II} \cdot k_{II} \cdot C/(1+k_{II} \cdot C) \]

**Figure 6.9** Adsorption of TPA on the MFI external surface and its Langmuir isotherm analysis. (a) Langmuir analysis based on a one site adsorption model; (b) Langmuir analysis based on a two site analysis model. \( A \) is the amount (mg) of adsorbate adsorbed on 100 mg of LZ105 at equilibrium, \( M \) is the maximum amount adsorbed on 100 mg of LZ105 at equilibrium, \( k \) is the Langmuir constant which is related to an equilibrium constant, and \( C \) is the amount (mg) of adsorbate left in a 3 ml solution at equilibrium. (courtesy of Dr. Takashi Hirano)
<table>
<thead>
<tr>
<th>ketone</th>
<th>site I</th>
<th>site II</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_1$/mg</td>
<td>$k_I$</td>
</tr>
<tr>
<td>1</td>
<td>0.33 ± 0.03</td>
<td>300 ± 100</td>
</tr>
<tr>
<td>3</td>
<td>0.4 ± 0.2</td>
<td>200 ± 400</td>
</tr>
<tr>
<td>6</td>
<td>0.40 ± 0.02</td>
<td>350 ± 50</td>
</tr>
<tr>
<td>7</td>
<td>0.25 ± 0.03</td>
<td>120 ± 50</td>
</tr>
</tbody>
</table>

Table 6.5  Langmuir Isotherm Analysis of the Adsorption of 1, 3, 6, and 7 on LZ105 from Isooctane Solutions by Using the Two-Adsorption Site Model. The calculation was made by using the value of the adsorbed amount (mg) on 100 mg of LZ105. (courtesy of Dr. Takashi Hirano)
6.5 Summary

Photochemical methods, $^2$H solid state NMR, Langmuir isotherm analysis and computer simulations are all consistent with the following conclusions concerning the supramolecular structure: o-Me-DBK will first adsorb on the holes of the external surface where it has very strong binding. Before all of the holes are filled, the mobility of the ketones is relatively uniform and partially restricted due to similar adsorption environments. After all the holes are filled, additional ketones will adsorb on the "flat" external framework where the binding is weaker than in the holes. Upon formation of a monolayer, additional ketones will form a multilayer or a liquid film on top of the monolayer. Ketones adsorbed on these multilayers have similar molecular dynamics as those in solution. In order to describe the supramolecular structures, the weight percentage loading does not seem to be a good unit to use. The normalized unit, "coverage" of surface, is a better quantity in supramolecular structures. In addition, by proper selection of photochemical probes, the zeolite external surface could be characterized.
References


7. Solid State NMR and EPR Studies of Benzocyclobutene and ortho-xylene Adsorbed in MFI Zeolites

7.1 Introduction

Benzocyclobutene and related compounds possess structures that display both the thermodynamic stability provided by a benzoic aromatic system and the kinetic reactivity of a strained cyclobutene. It is a very important industrial material especially in the polymer industry.\textsuperscript{1-3} The first synthesis of a benzocyclobutene derivative was reported by Finkelstein in 1910,\textsuperscript{4} but it was not until 1956 that Cava and Napier succeeded in preparing the parent compound.\textsuperscript{5} Benzocyclobutene is a C\textsubscript{8} aromatic compound which has an inherent relationship with other important C\textsubscript{8} compounds such as xylenes.

\begin{center}
\begin{tabular}{ccc}
\& p-xylene & \& o-xylene & \& benzocyclobutene \\
\end{tabular}
\end{center}

Although diffusion and adsorption of p-xylene in MFI zeolites have been extensively studied,\textsuperscript{6,7} we are unaware of any reports on the adsorption, diffusion and mobility of benzocyclobutene in MFI zeolites. There have been many studies on diffusion coefficient measurements of o-xylene using traditional gas adsorption/desorption methods, but there is no direct evidence regarding the adsorption sites inside MFI zeolites and its mobility, perhaps due to the very slow diffusion rate of this molecule. In this work, we present a preliminary study of adsorption and diffusion of o-xylene and benzocyclobutene in synthetic silicalite crystals using solid state NMR. We used p-xylene, which has been extensively studied, as our reference. We will try to answer the following questions:

1. Where is the preferred binding site inside the zeolites?
2. How does the small difference in molecular sizes between o-xylene and benzocyclobutene affect their diffusion rates and mobility inside the MFI zeolites? How does this compare to the properties of p-xylene in MFI zeolites?

In addition, it has long been known that the mere exposure of some organic molecules such as diphenylethylene, triphenylamine, and quinoline, which have relatively low ionization potentials, to freshly calcined zeolite Y lead to the formation of cation radicals.\textsuperscript{8,9} In those cases, the zeolite serves as effective and practically useful electron acceptors, and stabilizes the cation radicals with its framework oxygen in the zeolite channels or cavities. In addition, many examples have been reported in which zeolites acted as electron donors to transform molecules such as trinitrobenzene into its radical anion and stabilize the radical anion by the cations presented in the zeolite framework.\textsuperscript{10,11} Avila et al. reported that photolysis of some benzocyclobutenes in solution at low temperature resulted in radical cations,\textsuperscript{12} which can be detected by conventional ESR. Bally et al. also reported detection of radical cations from benzocyclobutenone.\textsuperscript{13} On the other hand, Lorenz et al. reported xylyl radical anions in solution at low temperature upon photolysis of the precursors.\textsuperscript{14} Thus in this work, we also show that photolysis of benzocyclobutene and o-xylene in MFI zeolites (both commercial and synthetic silicalite and NaZSM-5) can produce stable benzocyclobutene radical cations from electron transfer and those radical cations can be readily detected by conventional EPR spectroscopy.

7.2 Experimental Section

All chemicals purchased from Aldrich Company were the highest grade and were used without further purification. Silicalite crystals were synthesized and characterized as described in Chapter 3. NaZSM-5 powder samples (pz-40, Si/Al=25) were obtained from Dr. Corbin at DuPont Central Research and Development Department. NaY zeolite
was purchased from the Zeolyst Company. All the zeolites were activated in a furnace at 500°C overnight before use.

To prepare the samples for solid state NMR measurement, a desired amount of benzocyclobutene or p-xylene in isoctane solution was mixed with 100mg to 300 mg of freshly calcined zeolite. After stirring overnight, the solvent was gently removed under Argon gas, and dried under high vacuum (10⁻⁵ torr) overnight at room temperature before taking NMR measurements.

To prepare the zeolite samples with high loading of o-xylene for solid state NMR measurements, about 1 ml of pure o-xylene liquid was mixed with 300 mg freshly calcined zeolite in a cell with a side arm that could be connected to a high vacuum line (Figure 7.1, cell 2). The mixture was degassed using freeze-pump-thaw for several cycles to make sure that air was removed from the zeolite sample. The sample was then sealed under vacuum and heated in an oven at 80°C to 140°C (the boiling point of xylene is around 145°C) for at least a day to achieve high loading of o-xylene. After the sample was cooled down, the excess liquid was removed and the sample was washed with isoctane several times to remove any materials adsorbed on the external surface. The washed sample was then transferred to a vacuum cell and was pumped at high vacuum to remove any residue solvent.

To prepare the zeolite samples loaded with benzocyclobutene or o-xylene for photolysis and EPR measurements, the loading cell, as shown in Figure 7.1, was used. The liquid in cell 1 was thoroughly degassed with 6-9 circles of freeze-pump-thaw to remove any gas inside the liquid reservoir. The zeolite sample in cell 2 was slowly heated to 500°C under vacuum using a heat gun or sand bath and the temperature was kept at 500°C for at least four hours to activate the zeolite. After the zeolite sample was slowly cooled down to room temperature, it was allowed contact with the saturated vapor generated by the liquid and the adsorption was kept for several minutes. Both of the cells were closed and cell 2 was separated from cell 1, ready for photolysis experiments.
Figure 7.1  Cell assembly for loading the guest molecule from the gas phase. Cell 1 contains pure liquid. Cell 2 contains an activated zeolite sample.
NMR and EPR spectra were measured according to the standard instrumentation as described in Chapter 2.

7.3 Computation Methodology:

7.3.1 General Approach

We used MSI 4.0.0 software (Molecular Simulations, Inc., San Diego, CA) to perform the adsorption, diffusion and molecular dynamics simulations. In all of the simulations, we used the following assumptions normally used by researchers using the software.¹⁵

a) Purely siliceous material (silicalite) was assumed in the simulation. The zeolite used in the experiments was synthetic silicalite crystals.

b) Changes of the framework structure due to the adsorption of guest molecules were neglected. The system we calculated had a loading of one guest molecule per unit cell. The change in the framework structure was very small.

We chose potential parameters from MSI's consistent valence force field (cvff.frc) which has been extensively tested.¹⁵ There were mainly two kinds of calculations.

7.3.2 Minimum Energy Adsorption and Conformation

The calculation uses MSI's Solids Docking module. A detailed description of the module can be found in the MSI Software manual. The main procedure and parameters are shown in Figure 7.2. This type of calculation gives information about the preferred adsorption sites of the guest molecules.
Figure 7.2  Procedure of Solid Docking calculations using MSI software.

It is generally accepted that aromatic molecules usually diffuse only along the straight channels, since the diffusion along the zig-zag channel requires sharp reorientation of 112° for the molecule's axis. Thus we define the straight channel as the diffusion pathway.
7.3.3 Diffusion of Guest Molecules in MFI Zeolites

The diffusion coefficient calculation was performed with Forced MD function in the Solids Diffusion module in the MSI software. The main calculation procedure is as follows: first, a starting point and a diffusion direction (the [010] direction which is the direction of the straight channel in MFI zeolites) of molecular diffusion was specified. Then a suitable external force was exerted on the molecule to push it along the specified direction while dynamical calculations were performed on the molecule. The relative diffusion rate can be obtained by analysis of the root mean square of the displacement of the molecule on the diffusion pathway vs. diffusion time calculated.

The diffusion of a molecule strongly depends on its orientation as well as its location.\textsuperscript{16,17} For example, p-xylene can only diffuse into the internal framework of the MFI zeolite when its long molecular axis is roughly parallel with the channel directions. Ideally, in order to obtain the diffusion rate for a molecule, infinite numbers of calculations need to be performed by putting the molecules in different starting positions and different initial orientations, and the diffusion rate is obtained by averaging all of the calculations. In the Force MD calculation we used here, an external force was added to encourage the otherwise slow diffusion of sluggish molecules (as the calculation time would be prohibitively long); extracting the self-diffusion rate is still a challenge to theorists (Newsam, J. M., Molecular Simulations, Inc., personal communication). However, with a sufficient number of calculations, the relative diffusion rates for different molecules can be obtained.
7.4 **Location and Diffusion of Benzocyclobutene and o-xylene in MFI Zeolites**

7.4.1 Binding Sites of o-xylene and Benzocyclobutene Inside MFI Zeolites

As stated in the previous chapters, the p-xylene/MFI system has been well characterized in the literature. Here we use the p-xylene/MFI system as a reference to study the adsorption sites of o-xylene in silicalite crystals using multinuclear solid state NMR.

Figure 7.3 shows $^{29}$Si solid state NMR spectra of o-xylene loaded into silicalite crystals under different conditions.

The two silicalite samples loaded with o-xylene at high temperature gave similar $^{29}$Si NMR spectra that were similar to those of silicalite loaded with 4 p-xylene/unit cell. The spectral resolution was relatively good, indicating homogeneous distribution of guest molecules inside the silicalite framework. For the experimental conditions studied here, the loading of o-xylene could not exceed 4 o-xylene/unit cell by comparing the spectra of silicalite loaded with p-xylene.

The spectrum of silicalite at a loading up to 4 p-xylene/unit cell has been described in the literature as well as in previous chapters. At this loading range, all the p-xylene molecules stay in the intersections of the silicalite framework with their long molecule axis parallel with the straight channels. The similarity in the NMR spectra between silicalite loaded with o-xylene and with p-xylene indicated that o-xylene mainly binds in the intersection of the silicalite framework where there is a larger space than in the channels. The fact that high loading of o-xylene cannot occur under current conditions is an indication that the binding for o-xylene in both the straight channel and zig-zag channel will be very unfavorable due to the strong steric effect of o-xylene in the smaller space in the channels.
Figure 7.3 $^{29}\text{Si}$ solid state NMR of synthetic silicalite crystals loaded with p-xylene and o-xylene under different conditions.
When 15 mg of benzocyclobutene in isoctane was brought into contact with 300 mg of silicalite crystals for 12 hours at room temperature, a $^{29}$Si MAS spectrum as shown in Figure 7.4 was obtained. For comparison, a $^{29}$Si MAS NMR spectrum of empty silicalite and silicalite loaded with 2–4 p-xylene per unit cell is also shown.

Clearly, the spectrum of silicalite loaded with benzocyclobutene is very different from that of empty silicalite, indicating that benzocyclobutene can indeed diffuse into the internal surface. However, the benzocyclobutene spectrum is also different from silicalite loaded with p-xylene molecules. Careful examination of the spectrum reveals that the pattern is similar to that of silicalite loaded with p-xylene, but the position of the peaks shifted to the left in the spectrum unequally. When we shift the benzocyclobutene spectrum to the right, not all peaks can overlap with those of silicalite loaded with p-xylene molecules. To the best of our knowledge, this pattern of spectrum has not been observed before, and it may be a reflection of the smaller size of benzocyclobutene. As we know, the $^{29}$Si chemical shift is determined by the average angle of the four O-Si-O angles for this particular silicon site.18,19 A larger average angle results in a larger value of the absolute chemical shift. Adsorption of guest molecules, especially molecules whose sizes are comparable with the channel dimensions (e.g. p-xylene), will induce enlarged average angles of the silicon sites and shift the $^{29}$Si chemical shift to a higher absolute value. The difference between silicalite loaded with benzocyclobutene and p-xylene may be a reflection of their different sizes and different perturbations to the framework structure of silicalite.
Figure 7.4 $^{29}$Si solid state NMR of synthetic silicalite crystals loaded with benzocyclobutene. For comparison, the spectrum of empty silicalite and silicalite loaded with p-xylene are also shown in the figure. Benzocyclobutene was loaded from an isoctane solution containing 15 mg benzocyclobutene and 300 mg silicalite.
When we measured $^{13}$C CPMAS solid state NMR, we found that the individual carbon linewidths were very different between p-xylene and o-xylene, and benzocyclobutene in silicalite, as shown in Figure 7.5.

Figure 7.5 Solid state $^{13}$C NMR of p-xylene, o-xylene and benzocyclobutene adsorbed in synthetic silicalite crystals. The asterisks indicate spinning sidebands from aromatic carbons in o-xylene.
The aromatic carbons in p-xylene displayed a broad peak, while those carbons in o-xylene displayed clearly resolved sharp peaks with spinning sidebands (indicated by asterisks in Figure 7.5). The spectrum of benzocyclobutene also consisted of individual sharp lines, but there were no spinning sidebands except a very small sideband at 190 ppm in the spectra. All the chemical shifts were very close to their values in solution.

The linewidth and spinning sidebands carry information about the mobility of the molecules inside the silicalite. The sharp line and spinning sidebands for the silicalite/o-xylene complex indicate that the motion of o-xylene was not fast enough to average out the chemical shift anisotropy at room temperature. This may indicate that the tumbling of o-xylene in the intersection is still hindered due to the larger size of the molecule. On the other hand, $^{13}$C NMR spectrum of benzocyclobutene gave a liquid-like NMR spectrum, indicating that the tumbling of the benzocyclobutene is fast enough on the NMR timescale to average out all of the anisotropic interactions. In view of the size of benzocyclobutene, this fast isotropic motion can only be rationalized by assuming that benzocyclobutene adsorbs exclusively in the intersections where there is a much larger space. The relatively small size of benzocyclobutene in the large intersection is not expected to have larger perturbations on the host structure compared with that of o-xylene. This is consistent with the study of $^{29}$Si MAS NMR.

The lineshape and intensity of $^{13}$C o-xylene loaded in silicalite is insensitive to the change in temperature or upon pumping for several days in high vacuum. Increasing the temperature from 295K to 335K did not give noticeable changes. After being pumped for three days at high vacuum ($5 \times 10^{-5}$ torr) at room temperature, neither the spectrum of $^{13}$C nor the spectrum of $^{29}$Si changed. These results confirmed that once o-xylene is absorbed into the intersection, it is very hard to diffuse out through the narrow channels, and the molecules are locked inside and have only restricted motion in the intersections.

Figure 7.6 shows the one pulse proton NMR spectra of synthetic silicalite crystals loaded with xylenes and benzocyclobutene. The empty silicalite has a very small peak
around 1.7 ppm and this peak can be assigned to the isolated silanol groups in silicalite. The proton NMR spectra of silicalite loaded with different amounts of o-xylene and 5% wt% loading of p-xylene show two well-separated peaks with strong spinning sidebands. Those two peaks correspond to the methyl protons and aromatic protons. High loading of p-xylene produced broad lines due to the strong dipole-dipole interactions between protons at this loading. The spectrum of silicalite loaded with benzocyclobutene produced a sharp line for the aromatic protons, but the methylene protons produced a much broader peak.

Similar to $^{13}$C solid state NMR, the presence of strong spinning sidebands and broadening of linewidths are indications that the mobility of guest molecules is still restricted in silicalite.
Figure 7.6 $^1$H one pulse MAS NMR spectra of silicalite loaded with xylenes and benzocyclobutene. Those peaks outside 0–10 ppm are spinning sidebands.
7.4.2 Competitive Adsorption and Diffusion of Benzocyclobutene on Silicalite

In an effort to compare the diffusion of o-xylene and benzocyclobutene in silicalite, we performed a competitive adsorption experiment. We first mixed benzocyclobutene and o-xylene to form a 50:50 (volume, 25 µl each, 1 ml of isoctane was added as solvent) mixture in an isoctane solution, and then we added silicalite crystals (300 mg) to it at room temperature. After stirring overnight, drying the zeolite complex and washing it with isoctane to remove any molecules on the external surface, we dried the zeolite complex again and measured $^1$H, $^{29}$Si and $^{13}$C solid state NMR. We found that only benzocyclobutene can diffuse into silicalite at room temperature, while there is no trace of o-xylene present in the internal framework. This is shown in Figure 7.7.

From $^{29}$Si NMR (spectrum A), we know that some molecules have diffused into the framework, and this spectra is identical to that of silicalite loaded with benzocyclobutene as in Figure 7.4. The $^{13}$C and $^1$H NMR spectra (spectra B and C) are exactly the same as those obtained when we only loaded benzocyclobutene at the beginning. The absence of spinning sidebands in the $^{13}$C NMR spectrum is an indication that benzocyclobutene enjoys fast, isotropic motion in the channel intersections.

Additional evidence comes from analysis of the supernatant. Before mixing with silicalite crystals, the 50:50 percent mixture of benzocyclobutene:o-xylene was checked by Gas Chromatography (GC). The supernatant was checked again after the silicalite crystals were added and the competitive loading was finished. The results are shown in Table 7.1.
Figure 7.7  Competitive adsorption of benzocyclobutene and o-xylene. An iso-octane solution with 50:50 percent benzocyclobutene:o-xylene was mixed with synthetic silicalite crystals. After thorough washing and drying, the NMR spectra showed only benzocyclobutene inside the silicalite crystals.
<table>
<thead>
<tr>
<th>Initial mixture</th>
<th>Final supernatant</th>
<th>Adsorbed amount (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzocyclobutene</td>
<td>48.5%</td>
<td>11%</td>
</tr>
<tr>
<td>o-xylene</td>
<td>51.5%</td>
<td>90%</td>
</tr>
</tbody>
</table>

Table 7.1  Competitive adsorption of benzocyclobutene and o-xylene on 300mg synthetic silicalite crystals.

Most of the benzocyclobutene disappeared from the solution phase while the amount of o-xylene remained almost the same. Together with the results from solid state NMR of the silicalite complex, it is clear that it is much easier for benzocyclobutenes to diffuse into the internal framework of silicalite.

Again, we see that when the molecular size is close to the size of the channel opening of MFI zeolites, zeolites have exceptional size selectivity. The very small difference between the size of benzocyclobutene and o-xylene completely determined their diffusion in MFI zeolites (Figure 7.8).

![Figure 7.8](image)

Figure 7.8  Sizes of p-xylene (5.3 Å), benzocyclobutene (5.8 Å) and o-xylene (6.2 Å).
7.4.3 Computer Simulations of Adsorption and Diffusion of Benzocyclobutene and Xylenes

Docking calculations of the three C8 molecules were completely consistent with the experimental results. The concentrations of guest molecules were set to 1 molecule per unit cell (corresponding to about 2 wt% loading). From our previous results, this level of loading does not change the structure of MFI zeolites substantially. Therefore, the change in the host structure was neglected in these docking calculations. The most favorite binding sites for benzocyclobutene, p-xylene and o-xylene are all at the intersections, as shown in Figure 7.9.

![Diagram of binding sites](image)

**Figure 7.9** Representation of calculated preferred binding sites of guest molecules in MFI zeolites.

The conformation of p-xylene in the intersection is relatively unique. The long axis of p-xylene is nearly parallel with the straight channel due to the oval shape of the molecule. The conformation of o-xylene and benzocyclobutene in the intersection, however, is somewhat flexible. As long as the phenyl ring is in the intersection, there is very little energy difference when the methyl groups and the four-membered ring face the straight channel or the zig-zag channel.

Relative diffusion rates were obtained by averaging several calculations performed using different starting points and initial conformation. The calculation results are shown in Figure 7.10.
Figure 7.10  Diffusion coefficient calculations of the p-xylene, benzocyclobutene and o-xylene in silicalite. The calculations were done with Force MD module in MSI software. Each calculation was repeated 6-9 times with different initial orientations and positions for 50 ps. All traces from a guest were averaged and the diffusion coefficients were calculated with Einstein’s equation.

The relative diffusion rate is p-xylene:benzocyclobutene:o-xylene=185:75:1, qualitatively consistent with the experimental ratio using various methods.21 The diffusion rate of o-xylene is nearly two orders slower than that of benzocyclobutene from
the calculation, indicating that when the molecule size is close to that of the pore opening, even a very small change in the molecule's dimensions can have a drastic effect on its sorptional and diffusional properties. This is what we see in the competitive diffusion experiment (Figure 7.8).

7.5 Radical Cation Formation From Photolysis of Benzocyclobutene

7.5.1 Photolysis of Benzocyclobutene Loaded on NaZSM-5 Zeolite

Coming into contact with freshly calcined zeolite pz-40 (a NaZSM-5 zeolite), benzocyclobutene showed a weak, broad EPR signal. In addition, the originally white pz-40 zeolite became yellowish upon loading with benzocyclobutene. This may be due to the formation of a very small amount of the radical cation of benzocyclobutene. A similar observation has been reported by Ramamurthy and coworkers when they produced radical cations from the adsorption of trans-stilbene and other diphenyl polyenes into activated NaZSM-5 (Si/Al=22). Subsequent heating of the sample in vacuum at 85°C for up to 2 days only increased the signal slightly. However, photolysis of the sample of benzocyclobutene with UV light gave a strong EPR signal as shown in Figure 7.11.

The EPR intensity consistently increased as the total time of photolysis increased. Figure 7.12 shows the time course of EPR intensity changes with continuous photolysis.
Figure 7.11  EPR signals from benzocyclobutene loaded in pz-40 (NaZSM-5) before and after photolysis. Benzocyclobutene was loaded from the gas phase.
Figure 7.12 Time course of EPR signals from photolysis of benzocyclobutene loaded in NaZSM-5 (pz-40).

The intensity of the EPR signal roughly increased linearly with the time of photolysis, an indication that the decay of the EPR signal is very slow in vacuum. To quantify the decay of the EPR signal, we fixed the magnetic field to 3460 Gauss which is roughly the position of the positive peak, and monitored the decay at the end of
photolysis. The EPR signal was very persistent with an intensity loss of less than 3% in 6 hours, as shown in Figure 7.13.

![Graph showing normalized intensity over time](image)

**Figure 7.13** Decay of the EPR signal from the photolysis of benzocyclobutene loaded in NaZSM-5 (pz-40). The magnetic field was fixed at 3460 gauss and the intensity of the EPR signal at that point was monitored as a function of time.

### 7.5.2 Effect of Addition of Oxygen and Methanol After Photolysis of Benzocyclobutene@NaZSM-5

Upon contact with air, the EPR signal changed to a shape that is characteristic of a peroxyl radical as shown in Figure 7.14. The decay of the peroxyl radical is faster than that of the original radical, but it is persistent for a long time. Pumping again to high vacuum did not recover the original EPR signal, indicating that the formation of peroxyl radicals was not reversible under current experimental conditions.
Figure 7.14  EPR signals from the photolysis of benzocyclobutene loaded in NaZSM-5 (pz-40) before and after opening the cell to air (A) and the decay of the peroxyl radical (B).

In a separate experiment, when methanol was added in the absence of oxygen after photolysis in vacuum, the EPR signal changed to broad, featureless signals with about half of the original intensity, as shown in Figure 7.15 (A). The decay of the radical after adding methanol was much faster than the decay of both the original signal and the
peroxyl radical (Figure 7.15 B). The half lifetime of the decay in the presence of saturated methanol vapors at room temperature is about half an hour.

![Graph](image)

**Figure 7.15** (A) EPR signal from the photolysis of benzocyclobutene loaded in NaZSM-5 (pz-40) before and after being in contact with methanol vapor in the absence of air. (B) Decay of the EPR signal after adding methanol vapor in the absence of air.

7.5.3 Loading Dependence of Photolysis of Benzocyclobutene@NaZSM-5 Loaded from Isooctane

The gas loading setup shown in Figure 7.1 did not allow us to control the exact amount of benzocyclobutene loaded on pz-40 zeolites. In an effort to study the loading
dependence of the EPR signal, we loaded benzocyclobutene in the solution phase using isooctane as a solvent. We mainly studied two loadings: 2 wt% and 10 wt%, as discussed in the following section.

Figure 7.16  Loading dependences of benzocyclobutene radical cation@NaZSM-5 and their reaction upon contact with oxygen in the air. Top: 2 wt% loading. Bottom: 10 wt% loading.

Photolysis of benzocyclobutene at 2 wt% and 10 wt% loading produced EPR signals with different linewidths (Figure 7.16). The sample with 2% loading was slightly more resolved than that with 10 wt% loading. When the sample was exposed to oxygen, the radical from photolysis of 2 wt% loading converted completely to a peroxyl radical. The sample of 10 wt% loading, however, only partially converted to peroxyl radicals.
The decay of the EPR signal for 10 wt% loading was much slower than that of 2 wt% loading after being open to air.

7.5.4 Photolysis of Benzocyclobutene in Silicalite Crystals and Its Characterization

Although the properties displayed by the radicals seemed to suggest that it is a radical cation, the rather broad spectra made it very difficult to do any assignment by spectral simulations. The zeolite used had a Si/Al of 25, and it is possible that the strong π-cation interaction immobilized the radical to such an extent that the radical had very small mobility. In addition, the adsorption environments of benzocyclobutene could be heterogeneous, resulting in a distribution in EPR signal. In fact, when the $^{13}$C solid state NMR of benzocyclobutene in pz-40 was measured and compared with that on silicalite crystals, a substantial line broadening was observed. In addition, strong spinning sidebands appeared in the spectrum, as shown in Figure 7.17, clearly demonstrating that the mobility of benzocyclobutene was significantly constrained in pz-40 due to its interactions with cations.

![Silicalite Crystal](image)

Figure 7.17  Solid state $^{13}$C NMR of benzocyclobutene loaded in synthetic silicalite crystals and in pz-40. Benzocyclobutene in pz-40 displayed a wider linewidth and indicated its much slower motion due to the interaction with cations in pz-40. The asterisks indicate the spinning sidebands.
In order to improve the resolution of the spectra, we studied the photolysis of benzocyclobutene in synthetic silicalite crystals. The absence of cation in silicalite may render better-resolved EPR spectra due to the increased mobility of benzocyclobutene.

Figure 7.18 showed the best EPR spectrum we obtained from photolysis of benzocyclobutene loaded in silicalite. The properties of the radical in silicalite were similar to those on pz-40 but with some differences.

1. As on pz-40, the generated radicals were very persistent, and the radicals partially became peroxyl radicals upon opening to the air. The decay of the peroxyl radical was much faster than that in pz-40. This may be due to the faster mobility of the radicals resulting in faster reactions killing the peroxyl radicals.

2. The intensity of the EPR signal is much weaker in silicalite than in pz-40. This may be due to the much less active sites (or defect sites) where the radicals were formed in silicalite crystals.

In either zeolite, the amount of the radicals was estimated to be much less than 5% of the total amount of benzocyclobutene by calibrating the radical intensity with an internal standard. In fact, $^{13}$C solid state NMR spectra were identical before and after thorough photolysis of benzocyclobutene in both silicalite and pz-40. No new chemical shifts or significant line broadening were observed.
Figure 7.18  Photolysis of benzocyclobutene loaded in synthetic silicalite crystals from the gas phase. The EPR spectrum obtained after a 10-minute photolysis.

Based on the fine structure of the EPR signal, we attempted to identify the radical by spectral simulations. It is well known that a zeolite host can serve as an electron donor to produce a radical anion or serve as an electron acceptor to produce a radical cation.\textsuperscript{9,23,24} The radical from photolysis of benzocyclobutene in the zeolite can be either a radical cation or a radical anion in four possible structures

\begin{align*}
\text{1} & : \text{Cyclobutene cation} \\
\text{2} & : \text{Cyclobutene anion} \\
\text{3} & : \text{Cyclohexadiene cation} \\
\text{4} & : \text{Cyclohexadiene anion}
\end{align*}

Radical anions from benzocyclobutene have been produced by metal or electrolytic reduction in the solution state, and the structure of the radical anion has proven to be 2 (the closed form) instead of 4 (the open form).\textsuperscript{14,25,26} The hyperfine coupling constants (hfcs) obtained from those experiments (A\textsubscript{methylen}=5.30G, 4H; A\textsubscript{ortho}=7.24G, 2H; A\textsubscript{meta}=1.40G, 2H), however, resulted in a much narrower spectrum
coverage when compared with the EPR spectra in Figure 7.18. The hfcs were too small for the EPR spectra in Figure 7.17. Thus the radical we observed must be a radical cation 1 or 3.

Davies and coworkers have reported the formation of radical cations from some benzocyclobutene derivatives (6, 7, and 8) in solution by UV irradiation in the presence of oxidizing reagents (Hg$^{2+}$ or Ti$^{3+}$) at low temperature (T=260 K). However, they failed to produce radical cations from 5 by all efforts.

Turro and Lei produced and identified radical cation 3 from photolysis of o-Me-DBK on a MFI zeolite, Lz105. The spectrum and its comparison with the EPR spectrum from photolysis of benzocyclobutene are shown in Figure 7.19. The large discrepancy between the two spectra indicates that our radical is not the open form radical cation 3. The only possibility left is the closed form radical cation 1.
Figure 7.19  Formation of the radical cation 3 from photolysis of o-Me-DBK loaded on Lz105 and its comparison with radicals formed from photolysis of benzocyclobutene. The simulated spectrum of 3 is also shown in the figure. Linewidth is taken as 3 Gauss. Spectrum of 3 is courtesy of Dr. Xue-Gong Lei.
Attempted simulation was performed and is shown in Figure 7.20. The large spectra coverage requires a hyperfine coupling constant of 13.5 G for the four methylene protons. This value is much larger than the radical anion 2 (5.30 G) and the open form radical cation 3 (9 G), but is very close to the hyperfine coupling constant of methylene groups obtained by Davies and Ng from radical cation 6 in solution (13.84G).\textsuperscript{27} This is an indication that the radical from photolysis of benzocyclobutene may be a closed form of radical cation 1.

![Graphical representation of EPR spectrum](image)

**Figure 7.20** Attempted simulation of an EPR spectrum produced from benzocyclobutene.

Additional support comes from theoretical calculations in Professor K. N. Houk's lab at UCLA. They calculated the hyperfine coupling constants (hfc) for the four possible radical structures using density function theory.\textsuperscript{28} The calculation results and the experimental results are listed in Table 7.2. The calculated hfc for the closed form radical anions and the open form radical cations are relatively close to the available experimental results, indicating those calculations are reasonable. Among all of the four possible structures, the closed form radical cation 1 has the most similar hfc to our experimental result.
Table 7.2 Calculated hyperfine coupling constants of the possible radicals and their comparison with that of experimental results. (a) experimental result from ref. 26 in solution; (b) experimental result from Turro and Lei, unpublished result; (c) experimental result from this work. See text for details.

7.5.5 Photolysis of Benzo[cyclobutene] in NaY Zeolite

Photolysis of benzo[cyclobutene] loaded on NaY zeolites also produced a strong EPR signal. The increase in the EPR signal was also roughly linear with irradiation time under the experimental conditions, as shown in Figure 7.21.
Figure 7.21 (A) Build-up spectra of EPR intensity from photolysis of benzocyclobutene loaded on NaY zeolites in the gas phase. (B) Intensity plot as a function of irradiation time. Power attenuation was 20 db, and 8 scans were accumulated for each spectrum.
The EPR spectrum was even wider than that from photolysis in silicalite, as shown in Figure 7.22. The EPR signal may still come from the radical cation 1. The larger hyperfine coupling constant may be an indication of the strong interaction between the radical and cations in NaY supercages. However, due to poor spectral resolution, any simulation will be uncertain and ambiguous.

![EPR spectra from photolysis of benzocyclobutene loaded in NaY and silicalite crystals from the gas phase. The sample was irradiated for 15 minutes. Note the different spectra coverage for those two signals.](image)

Figure 7.22  EPR spectra from photolysis of benzocyclobutene loaded in NaY and silicalite crystals from the gas phase. The sample was irradiated for 15 minutes. Note the different spectra coverage for those two signals.

Upon opening to air, the radical completely changed to the peroxyl radical, as shown in Figure 7.23.
Figure 7.23  EPR spectra from photolysis of benzocyclobutene loaded in NaY from the gas phase. The spectrum before opening to air (dashed line) was obtained after photolysis of the sample for 140 minutes using the lamp. The spectrum after opening to air (solid line) was obtained about 1 minute later after opening the sample to air. Attenuation of power was 20 db, and eight scans were accumulated for each spectrum.

7.6  Summary

Solid state NMR and computer simulations show that the preferred binding site of benzocyclobutene and o-xylene is the intersection in MFI zeolites. The diffusion rate of benzocyclobutene is much larger than that of o-xylene due to its slightly smaller molecular size. Similarly, the mobility of benzocyclobutene is much larger than that of o-xylene in MFI zeolites.

Photolysis of benzocyclobutene loaded in pz-40 (NaZSM-5), synthetic silicalite crystals and NaY produced the closed form of the benzocyclobutene radical cation. This radical cation persisted for a long time in vacuum possibly because of the isolation of ketones by the zeolite host structure. Upon contact with oxygen, the radical cation changed to a peroxyl radical. The lifetime of the peroxyl radical is loading dependent on NaZSM-5. At high loading, some of the peroxyl radicals seemed to be protected from reaction with oxygen molecules. Upon contact with methanol vapor, an unknown, broad
EPR signal appeared and the intensity of the original EPR signal dropped to ~50%. The decay of the new radical is much faster than both the radical cation and the peroxyl radicals.
References


