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I. CHARACTERIZATION OF ZEOLITE EXTERNAL SURFACE AREA USING
   ELECTRON PARAMAGNETIC RESONANCE

II. END LABELING EFFICIENCY IN THE ATOM TRANSFER RADICAL
    POLYMERIZATION OF STYRENE

ZHIQIANG LIU

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ABSTRACT

Part I. Characterization of Zeolite External Surface Area Using Electron Paramagnetic Resonance

Part II. End Labeling Efficiency in the Atom Transfer Radical Polymerization of Styrene

Zhiqiang Liu

EPR methods have been applied to a series of monodisperse silicalite crystals as sensitive and structurally specific methods for investigating silicalite external surface areas.

The absorption of ortho-methyldibenzyl ketone (oMeDBK) on the external surface of silicalite crystals was studied using a coadsorbed nitroxide probe. The displacement of the adsorbed nitroxide probe by coadsorbed oMeDBK leads to the conclusion that the adsorbate molecules first adsorb on stronger binding sites (pore openings) characterized by slow motion of the probe (broad EPR lines) and then the adsorbate molecules adsorb on weaker binding sites (external surface framework between pore openings) characterized by fast motion of the probe (narrow EPR lines). The transition point from slow to fast motion provides a quantitative measurement of silicalite external surface area.

Using nitroxide as the sole adsorbate with increasing surface coverage, the EPR line shape shows a progressive change as a result of increasing dipolar interaction and
electron spin exchange interaction at decreasing inter-spin distance. The minimum inter-spin distance as measured from the dipolar interaction corresponds to the complete coverage of the pore openings and the corresponding nitroxide loading is a measure of the external surface area of the silicalite crystals. The transition point from nearly zero to high spin-spin interaction is also surface coverage related and provides a highly sensitive means of characterization of the silicalite external surface area.

The adsorption strength on pore openings is molecular structure dependent and polar groups provide more significant contribution than the possible intercalation of phenyl/tolyl groups. Sequential adsorption of $^{14}$N and $^{15}$N spin labeled nitroxides shows the dynamic exchange between the adsorbates in the pore openings and those in solution or on weak binding sites.

The end labeling efficiency of polystyrenes prepared using Atom Transfer Radical Polymerization method was studied using spectroscopic and chromatographic methods. The labeling efficiency was found to be dependent on the monomer/initiator ratio of the starting material, with high ratios leading to low labeling efficiency.
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Part II End Labeling Efficiency in the Atom Radical Polymerization of Styrene

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Part I.

Characterization of Zeolite External Surface Area

Using Electron Paramagnetic Resonance
Chapter 1  Introduction

1.1 Zeolites

The word zeolite comes from the Greek: "zeo", which means "to boil" and "lithos" which means "stone". Literally, it means "boiling stone" because the naturally occurring zeolite samples tend to contain much water and therefore display a visual effect as if they are boiling when heated. The first zeolite type material (stilbite) was discovered by Alex F. Cronstedt, a Swedish mineralogist, in 1756.¹

Traditionally, zeolites have found wide applications in adsorptive gas separation, ion-exchange and shape-selective catalysis.²⁻⁵ 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.

1.1.1 Zeolite Compositions and Structures

By the latest definition proposed in 1998,⁶ a zeolite mineral is a crystalline substance with a structure characterized by a framework of linked tetrahedra, each consisting of four O atoms surrounding a cation (Si⁴⁺ or Al³⁺). This framework contains open cavities in the form of channels and cages. The channels and cages can be occupied by H₂O molecules and extra-framework cations. Water is generally reversibly adsorbed and the cations are generally exchangeable. The channels are large enough to allow the passage of guest species of appropriate size and shape, typically 2 to 8 Å. In the hydrated phase, dehydration occurs at temperatures mostly below about 400 °C and is largely reversible. The framework may be interrupted by (OH, F) groups; these occupy a tetrahedron apex that is not shared with adjacent tetrahedra.
While a SiO$_4$ tetrahedron is neutral, an AlO$_4$ tetrahedron carries a negative charge (AlO$_4^-$). The negative charges are balanced by cations that are present during synthesis or exchanged after synthesis. A representation of typical zeolite composition by the empirical formula is

$$\text{M}_{2n} \text{O} \cdot \text{Al}_2 \text{O}_3 \cdot x \text{SiO}_2 \cdot y \text{H}_2 \text{O}$$ (1.1)

where M stands for the charge balancing cation, $n$ is the valence of the cation, and $x$ is generally equal to or larger than 2. The structure of a zeolite showing connected and repeating SiO$_4$ and AlO$_4^-$ tetrahedra is described in Figure 1.1.

**Figure 1.1** Building zeolite crystals from SiO$_4$ and AlO$_4^-$ tetrahedra. M$^+$ is an extra-framework cation that balances the negative charge on the AlO$_4^-$ tetrahedron.

While most zeolites are aluminosilicates, Ga, Fe, P among other elements can replace Al and/or Si to a varying degree giving rise to gallosilicates, ferrisilicates, aluminophosphates, silicoaluminophosphates, etc.$^8,9$

M is typically alkaline, and alkaline earth metal cations, in particular, sodium, potassium, magnesium, calcium, strontium, and barium.$^{10}$ Extra-framework cations are usually mobile and can generally be replaced by a range of mono-, di-, or trivalent cations through ion exchange in an appropriate solution or molten salt.$^8$ The change in cations can lead to a dramatic change in the properties and applications of the zeolite due to the differences in ion size, ion siting, polarity and electrostatic effects.$^8$ The successful
incorporation of rare earth ions such as La\(^{3+}\) or Ce\(^{3+}\) improved the stability of faujasites in a steam atmosphere and enhanced catalytic activity by up to 10\(^4\) times.\(^8\)

Water mostly resides in the channels and interconnected voids and can be removed at high temperature. Zeolites possess an open framework structure that will reversibly sorb water, a variety of organic and inorganic molecules, or metal vapors and remain intact after many sorption/desorption cycles.\(^8\)

Zeolite structures are typically defined by using three letter words much like the three letter coding for amino acids in biochemistry.\(^11,12\) Examples are FAU (faujasites named after Barthelemy Faujas de Saint Fond (1971-1819), a French geologist) and MFI (for ZSM-5 zeolites).

There are more than 40 species of zeolite minerals\(^6\) and about 100 types of synthetic zeolites,\(^10\) among them, only a few having found practical significance. A major limitation is due to structural instability, e.g. collapse upon dehydration.\(^10\)

A comparison to other adsorbents also possessing micropores (less than 2.0 nm) can provide insight into the uniqueness of zeolitic materials. Activated carbons, activated clays, inorganic gels, such as silica gel and activated alumina, all possess micropores and can potentially be used in separation and adsorption applications.\(^10\) However, their pore sizes are not uniform, ranging from a fairly narrow distribution (20 to 50 Å) to a wide distribution (20 to a few thousand Å) as is the case for some activated carbons. As a result, all molecular species, with the possible exception of high molecular weight polymeric materials, may enter the pores. In contrast, zeolites are crystalline solids. They possess periodic pores of uniform size in the range of 3 Å to 10 Å uniquely determined by the unit structure of the crystal. The uniform pore size in a particular zeolite structure
determines the sites adsorbate molecule can access depending on its size and shape, and
the molecules that are larger than the pore openings are excluded from entering the
internal space. Pore openings are defined by the size of the ring defining the pore,
normally designated as an $n$-ring, where $n$ is the number of $T$-atoms ($T =$ tetrahedral
atoms such as Si, Al) in the ring. An 8-ring (as in erionite, ERI) is considered a small
pore opening, a 10-ring (as in ZSM-5, MFI) a medium one, and a 12-ring (as in Y zeolite,
FAU) a large one. They have free diameters of ca. 4.1 Å, 5.5 Å, 7.4 Å respectively.\textsuperscript{12,13}
Recent advances in the preparation field have provided materials with much larger pores
and channels. MCM-41 (MCM stands for Mobil Crystalline Material) is a silicate
material first developed in 1992, and provides mesopores in the range of 2 nm to 10
nm.\textsuperscript{14-16}

Widely used in the petrochemical industry for processing a variety of
hydrocarbons and aromatics, and on the central stage of this thesis investigation, are the
synthetic zeolites in the ZSM-5 family (crystal structures coded as MFI). ZSM stands for
Zeolite Socony Mobil as it was developed by Socony Mobil Corporation at late 1960s.\textsuperscript{17}

ZSM-5 zeolite has the unit cell composition of $[\text{Al}_n\text{Si}_{96-n}\text{O}_{192}]$ ($n < 27$) with
charge compensating cations and water molecules.\textsuperscript{18} The cation can be exchanged and the
water can be removed by thermal activation. Compared to the majority of other zeolites,
such as faujasites, ZSM-5 is considered siliceous, meaning it possesses low Al content.
When $n$ approaches essentially zero ($\text{Si}/\text{Al} > 1000$), the ZSM-5 zeolite is conventionally
called silicalite (or silicalite-1), which has the unit cell composition of $[\text{Si}_{96}\text{O}_{192}]$ and was
first reported by a joint research group at Union Carbide Corp. and the University of
Chicago.\textsuperscript{19} The siliceous nature of ZSM-5 zeolites, especially silicalite, makes them
hydrophobic and organophilic, and as a result, silicalite favors adsorption of organic molecules over water.\textsuperscript{20} In water isotherm tests, in which the amount of water adsorbed per unit area of adsorbent surface is plotted against the relative pressure of water vapor, it was shown that silicalite is more hydrophobic than is activated carbon.\textsuperscript{19} The high hydrophobicity adds extra qualifications to ZSM-5 zeolites for their application in the industry where organic molecules are to be processed in catalytic and separative applications.

A ZSM-5 crystal is typically hexagonal in shape (Figure 1.2), though it can take the shape of needles, spheres, etc. depending on the preparation method. The crystal possesses two sets of channel structures: one set of channels runs straight through the crystals with a pore size of about 5.4 x 5.6 Å, and the other set of channels runs sinusoidally and perpendicular to the first set, with a 10-ring pore with a size of about 5.1 x 5.4 Å. The intersection of the two sets of channels provides a cavity or "supercage" with a diameter about 9 Å, and therefore the cavity is capable of holding more or larger adsorbate moieties than do the channels.
macroscopic shape of a ZSM-5 crystal
microscopic porous structure and internal surface of a ZSM-5 crystal

Figure 1.2 Hexagonal shape of a ZSM-5 zeolite crystal and its channel systems. The crystal and the channels were not drawn to scale. (Courtesy of Wei Li)\textsuperscript{21}

1.1.2 Zeolite Applications

In view of their uniform pore size in the range of 3 Å to 10 Å and high acidity when $M = H^+$ (Formula 1.1 and Figure 1.1), it is no surprise that one of the major industrial applications of zeolitic material is as a shape/size selective catalyst for processing hydrocarbons and aromatics in the chemical industry.\textsuperscript{2} Other conventional uses include gas separation and purification, as well as for exchange, desiccation and sorbing processes.\textsuperscript{8} These main commercial applications of zeolites exploit different aspects of zeolite structural chemistry. As ion exchangers, zeolite structures provide substrates that support the mobilities of the extra-framework cations. As sorbents and molecular sieves, the zeolites offer hydrophilic or, in siliceous materials, organophilic micropores of controlled dimensions and accessibilities. Finally, in catalysis, zeolite materials provide highly active sites and the possibility of reactions being governed by shape-selective constraints.\textsuperscript{8}
ZSM-5 is particularly suitable for size/shape selective catalysis for several reasons.

1. ZSM-5 zeolites possess an exceptionally high degree of thermal stability thereby rendering them effective for use in industrial processes involving elevated temperatures.\textsuperscript{17} For example, silicalite is stable in air up to 1100 °C and only slowly degrades into amorphous glass at 1300 °C.\textsuperscript{19}

2. ZSM-5 zeolites possess exceptional chemical stability toward reactive and corrosive species. ZSM-5 zeolites contain essentially silicon dioxide, which is a very inert species. Silicalite has been found to be stable in most mineral acids, except hydrofluoric acid.

3. The uniform pore size of ZSM-5 zeolites at roughly 6 Å makes it particularly suitable for the size/shape selective catalytic processing of organic molecules of industrial importance, especially in the petroleum industry, i.e., linear and branched hydrocarbons, aromatics, etc.

When the size of an adsorbate molecule is evaluated for adsorption on the microporous solid, the term \textit{kinetic diameter} is typically used, which is defined as the intermolecular distance of closest approach for two molecules colliding with zero initial kinetic energy.\textsuperscript{10}

At room temperature, silicalite is known to adsorb molecules as large as \textit{n}-hexane (kinetic diameter 4.3 Å) and benzene (kinetic diameter 5.6 Å), but rejects molecules larger than 6 Å, such as neopentane (kinetic diameter 6.2 Å).\textsuperscript{19} Even though neopentane contains one less CH\textsubscript{2} unit than \textit{n}-hexane, the increased degree of branching makes a size/shape difference large enough to allow separation of \textit{n}-hexane from neopentane by silicalite.\textsuperscript{19}
Studies of diffusivity of aromatics in ZSM-5 show that a simple change of structure from \textit{p}-xylene (kinetic diameter 6.3 Å) to \textit{o}-xylene (kinetic diameter 6.9 Å) causes the diffusivity to diminish by 3 orders of magnitude.\textsuperscript{13} While \textit{p}-xylene can permeate and fill the channels upon contact, \textit{o}-xylene can only be loaded into ZSM-5 zeolites at elevated temperatures over a period of days.

Therefore, the adsorption of organic molecules, especially alkanes and aromatics, are very sensitive to the minute change in the structure, e.g. the carbon numbers, the branching of alkanes, and the substitution number and pattern on a benzene ring.

However, it is to be noted that, when the sizes of the adsorbate molecules are compared to the size of the zeolite pore openings to determine if the adsorbate molecules can enter the pores, care must be taken to examine the appropriateness of the pore size value chosen for comparison.\textsuperscript{22} With the framework \textit{T} (Si, Al) and O atoms in fixed positions determined by X-ray diffraction study, the size of the oxygen atom will determine the size of the pore opening. For a 10-ring pore opening (such as in ZSM-5), the pore opening diameter is 5.80 Å if oxygen is considered ionic (ionic oxygen diameter is 2.7 Å), or 7.05 Å if oxygen is considered covalent (covalent oxygen diameter is 1.5 Å). The framework oxygen in ZSM-5 zeolites is expected to possess more covalent than ionic character based on the hydrophobic nature of the zeolite. This would explain why ZSM-5 with pore sizes about 5.4 x 5.6 Å for the straight channels and 5.1 x 5.4 Å for the sinusoidal channels can readily adsorb \textit{p}-xylene, which has a kinetic diameter of 6.3 Å.

The result of this size/shape discriminative adsorption provides the size/shape selectivity in zeolite-catalyzed reactions. Industrially, ZSM-5 has been proven to be an
excellent catalyst for the conversion of methanol into hydrocarbons,\textsuperscript{23} alkylation of toluene with methanol,\textsuperscript{24} and comparative cracking of parafins.\textsuperscript{25}

Molecular shape-selective conversion of hydrocarbons on zeolites was first described by Weisz and Frilette,\textsuperscript{26} and has been rationalized and categorized by Csicsery depending on whether pore size limits the entrance of the reacting molecules, the departure of the product molecules, or the formation of certain transition states.\textsuperscript{2,27,28} The two categories are explained as follows,

1. Diffusion-controlled shape selectivity depending on the relative rates of diffusion of reagents and/or products.

When alcohols are dehydrated using non-shape-selective catalysts, secondary alcohols are more easily dehydrated than the corresponding primary alcohols, as expected from carbocation stability. However, when butanols are dehydrated on Ca-A zeolite, only \textit{n}-butanol is converted, because \textit{sec}-butanol, although expected to form a more stable carbocation with the loss of water, cannot enter the internal space of Ca-A (with a pore size ca. 5 Å), wherein the active sites are located.\textsuperscript{29} It is interesting to note that the use of a \textit{K}\textsuperscript{+} cation will reduce the pore size of an A type zeolite to 3 Å, which enables the zeolite to admit water but not hydrocarbons or alcohol, making it the material of choice for intensive drying of unsaturated hydrocarbon gas streams and polar liquids containing alcohols such as methanol and ethanol.\textsuperscript{8}

In the zeolite catalyzed xylene formation by alkylation of toluene with methanol, it has been found that \textit{p}-xylene was formed in higher than 80% selectivity if ZSM-5 type zeolites are used.\textsuperscript{24} In contrast, for larger pore zeolites, e.g. \textit{Y} zeolites (12-ring pore opening), both \textit{o}- and \textit{p}-xylene were primary products. This selectivity is attributed to
the fact that the pores of ZSM-5 zeolites permit rapid diffusion of toluene, methanol and $p$-xylene, but severely retard the diffusion of $o$- and $m$-xylenes. While formed $p$-xylene can escape from the interior of the zeolite, the $o$- and $m$-xylenes are trapped in the internal pores of ZSM-5 and they do not escape until isomerizing into $p$-xylene.\textsuperscript{27} In contrast, the large 12-ring pore openings in the Y zeolites provide no discrimination among the three xylenes and therefore offer essentially no shape selectivity in this reaction.

2. Transition state selectivity. Csicsery was the first to recognize the successful creation of the transition state complex in the confined environment of the zeolite micropore as a contributing factor for shape selective catalysis.\textsuperscript{1,27} When $m$-xylene is processed on zeolite catalysts, isomerization to $o$-xylene and $p$-xylene and transalkylation to trialkylbenzene are two competing reactions. When ZSM-5 zeolite is used, the transalkylation is essentially inhibited because there is not enough space for the large, bimolecular transition states for trialkylation.\textsuperscript{2}

Since the 1980s, there has been renewed interest in zeolitic materials for new applications.\textsuperscript{30} These potential applications include their use in the field of solar energy, zeolite electrodes and electron relays, zeolite batteries, zeolite fast ion conductors, intrazeolite semiconductors, zeolite chemical sensors, zeolite imaging and data storage materials, zeolite lasers and displays, as well as zeolite composites to form permselective membranes or thin films. All these applications depend on the impressive range of zeolite crystal structures and element substitution, structured uniform channel systems, rich cation modification, variety of encapsulated guests in the channels and/or cavities, tunable Bronsted acidity and lattice oxygen basicity, as well as the controllable
hydrophobic (e.g. aluminum-free silicalite)/hydrophilic (high aluminum content zeolite) character.\textsuperscript{30}

1.1.3 Adsorption on Zeolite

The adsorption phenomenon is critical in the application of zeolites and it is also used widely as a method to characterize the internal void space of zeolites.

The term adsorption was introduced by Kayser\textsuperscript{31} in 1881 to connote the condensation of gases on free surfaces. Adsorption (strictly speaking physical adsorption) has been internationally defined as the enrichment (i.e., positive adsorption or simply adsorption) or depletion (i.e., negative adsorption) of one or more components in an interfacial layer.\textsuperscript{32}

In principle, adsorption at an interface can either be chemical or physical in nature. Physical adsorption is the phenomenon most studied and is characterized by a series of features: 1) it is a general phenomenon on all interfaces, 2) there is minimum perturbation of the electronic state of the adsorbate and the adsorbent, 3) the adsorbed species are chemically identical with those in the liquid or gaseous phase, 4) the energy of interaction between the molecules of the adsorbate and the adsorbent is of the same order of magnitude as, but usually greater than, the energy of condensation of the adsorbed molecules, 5) an elementary step does not involve activation, 6) equilibrium is usually readily established between the adsorbate and the liquid or gaseous phase, and 7) under appropriate conditions, multilayer adsorption is possible.\textsuperscript{32}

When adsorption occurs, substances (adsorbate) from the gaseous or liquid phase preferentially partition onto the surface of a solid substrate (adsorbent). The relationship, at constant temperature, between the quantity of the adsorbate that is adsorbed on the
adsorbent, and the equilibrium partial pressure of the adsorbate species in the gaseous phase, or the equilibrium concentration of the adsorbate species in the liquid phase, is called an adsorption isotherm.\textsuperscript{33} The majority of the various adsorption isotherms may be conveniently grouped into five classes, as proposed by Brunauer, Deming, Deming and Teller,\textsuperscript{34} and Brunauer, Emmett and Teller (BET).\textsuperscript{35} The two celebrated isotherms, Langmuir isotherm for monolayer adsorption and BET isotherm for multilayer adsorption, will be discussed in detail in later sections.

The energetics of adsorption on a zeolite is a compilation of weak intermolecular forces including both van der Waals forces (dispersion-repulsion) and electrostatic interactions. The total interaction energy at the equilibrium distance is the summation of some or all of the following contributions: dispersion energy, close range repulsion, polarization energy, field-dipole interactions, field gradient-quadrupole interactions and adsorbate-adsorbate interactions.\textsuperscript{36} Except for close range repulsion, all other forces are attractive in nature. The dispersion, repulsion and polarization energy are nonspecific interaction energies. The dispersion energy and polarization energy are typically of the same order of magnitude and they are both proportional to the polarizability of the adsorbate molecules.\textsuperscript{3,37} When the adsorbates have permanent dipoles or quadrupoles, field-dipole and field gradient-quadrupole interactions may contribute to the total adsorption energy with a dominating share, and they are called specific interaction energies. Schirmer et al.,\textsuperscript{38} studied the contribution from specific and nonspecific interactions to the heats of adsorption of a series of adsorbates on 5A zeolite. Ethane, which has a zero permanent dipole, has a nonspecific contribution of 5.9 kcal/mole (compared to typical dispersion forces of just ca. 1 kcal/mole\textsuperscript{1} and strong ion-ion
electrostatic interaction of ca. 1-10 kcal·mole\(^{-1}\)),\(^{39}\) and zero specific contribution. In contrast, methanol with a 1.68 Debye permanent dipole has a similar nonspecific contribution at 4.3 kcal·mole\(^{-1}\), but a significant specific contribution at 15.2 kcal·mole\(^{-1}\). \(N\)-butane, while has no permanent dipole, has a nonspecific contribution of 10.4 kcal·mole\(^{-1}\) (compared to a typical hydrogen bonding of ca. 0.2-20 kcal·mole\(^{-1}\))\(^{39}\) due to relatively high polarizability (81.2 x 10\(^{-25}\) cm\(^3\)·molecule\(^{-1}\))\(^{37,40}\) and may be compared to ethane (44.7 x 10\(^{-25}\) cm\(^3\)·molecule\(^{-1}\)). Flanigen et al., showed that the adsorption of \(n\)-hexane on silicalite is highly energetic (16-18 kcal·mole\(^{-1}\)), illustrating the high dispersion energy when the adsorbate molecules can fit just into the zeolite channels.\(^{19}\)

Finally, upon adsorption of the adsorbate molecules on the adsorbent, the whole system should be treated as one supramolecular entity, whose structure and properties depend on the interaction details of the adsorbate and adsorbent. A convenient notation for this supramolecular system is guest@host, or adsorbate@adsorbent, wherein @ stands for non-covalent interactions, such as van der Waals, dipole-dipole forces, etc.

### 1.1.4 Zeolite External Surface

Zeolitic materials have two sets of surfaces, an internal surface comprising the walls of the channels and intersections (cavities), and an external surface comprising the pore openings and the framework space between the pore openings on the outside of the crystals (Figure 1.3).
External surface (pore openings and framework surface)

Internal surface (channel walls and intersections)

2-D representation

[010]

Figure 1.3 The external surface ([010] surface shown) vs. internal surface of a ZSM-5 zeolite crystal and a 2-D representation of the different surfaces (thin lines: internal, thick lines: external).

1.1.4.1 Significance of the Zeolite External Surface Area

Adsorbate molecules with a size smaller than the size of the pore openings will be able to access both the internal and external surface, while molecules considerably larger than the size of the holes can only access the external surface except for those at high temperature and/or pressure.

While catalytic sites on the internal surface and external surface are both effective (while the activity can be different\(^4\)), only the sites in the intracrystalline void can completely surround the adsorbed guest molecules and provide shape/size selectivity, whereas those on the external surface cannot. Therefore, larger crystals, which have a
smaller external surface area per unit mass (specific external surface area), should offer higher selectivity per unit mass of zeolite employed.\textsuperscript{42,43} Theoretical developments also confirmed that for zeolite crystals less than 1 μm in diameter, the effect of the external activity can become important, particularly for very rapid catalytic reactions or highly diffusion-limited reactions.\textsuperscript{43} However, the area of external surface determines the amount of openings to the inner surface, and larger crystals will have fewer passages into the selective sites within the crystals. As a result the catalysis proceeds at a lower rate for larger crystals due to limitations on diffusion of the guest molecules.\textsuperscript{44} As an excellent example, Pol et al., have studied the effect of particle size in the hydroxylation of phenol with hydrogen peroxide catalyzed by titanium silicalite samples.\textsuperscript{41,45} By increasing the mean crystal size from 0.2 to 10.0 μm, the initial reaction rate of desired product formation was reduced by ca. 94% due to pore diffusion limitations, and the yield of the desired products was reduced by ca. 80% due to the enhanced significance of side reactions when the desired reaction was retarded. In a word, the external surface area of the crystals plays an important role in the total selectivity and activity of zeolitic catalysts.\textsuperscript{46}

1.1.4.2 Measurement Methods of Zeolite External Surface Area

1. **Langmuir isotherm.** In a series of monumental papers published in the 1910s,\textsuperscript{47,48} Langmuir developed the monolayer adsorption model on surfaces. By equating the rates of condensation and evaporation, Langmuir obtained his isotherm equation in the form of equation 1.2

\[
\theta_1 = \frac{\alpha \mu}{\nu_1 + \alpha \mu}
\]  

(1.2)
wherein $\theta_1$ is the fraction of surface covered by the adsorbed molecules, $\mu$ is the number of molecules striking 1 cm$^2$ of surface per second, $\alpha$ is a condensation coefficient ($\alpha < 1$) and $v_1$ is the rate of evaporation from a completely covered surface.

A more familiar form of the Langmuir isotherm is given by equation 1.3

$$\theta = \frac{bP}{1 + bP}$$  \hspace{1cm} (1.3)

wherein $\theta$ is the surface coverage, and $P$ is the partial pressure of the adsorbate molecules in the gaseous phase and $b$ is the ratio of rate constant for adsorption to that for desorption.

Based on the surface coverage obtained from the Langmuir isotherm and the estimated cross-sectional area of the adsorbate molecules on the surface (16.2 Å$^2$ for N$_2$), one can easily find out the surface area of the adsorbent sample.

2. BET plot. Based on a generalization of the Langmuir monolayer treatment, the Brunauer-Emmett-Teller (BET) theory for multilayer adsorption on the surface was introduced in 1938. The assumptions are that under equilibrium conditions, the rates of condensation and evaporation are equal for each adsorbed layer and that the rate constants are the same for all layers after the first, and that the adsorption energy for the higher layers was equal to the energy of condensation. The form of the BET isotherm is given by equation 1.4.

$$\frac{v}{v_m} = \frac{cp / p_o}{(1 - p / p_o)[1 + (c - 1)p / p_o]}$$  \hspace{1cm} (1.4)

wherein $v$ is the multilayer surface coverage at a gas partial pressure of $p$, $v_m$ is the monolayer capacity, $c$ is a constant, and $p_0$ is the saturation pressure of the gas. If the
cross-sectional area of the adsorbate molecules are known, one can easily compute the surface area of the adsorbent sample.\textsuperscript{33}

Other isotherm models include the Gibbs Model, the Freundlich Model, and linear models, which suit different situations and are not discussed in this thesis.\textsuperscript{49}

Another interesting method, developed by Partyka et al.,\textsuperscript{50} and based on Harkins-Jura “absolute” method for surface area measurement,\textsuperscript{51} involves the calorimetric measurements wherein the adsorbent was first covered with a film of adsorbate thick enough to present an external surface identical in nature to the bulk adsorbate liquid. The external surface area is easily obtainable as the proportionality factor for the specific heat of immersion and surface enthalpy of the bulk liquid, when the treated adsorbent was immersed in the bulk liquid.\textsuperscript{33}

A history of studies on the experiment, theory and applications of physical adsorption can be found in a book edited by J. Fraissard.\textsuperscript{52}

In a typical BET analysis of the solid surface area, the experiment is conducted using nitrogen at low temperature (e.g. 77 K).\textsuperscript{35} Nitrogen, with a size ca. 3 Å along the long axis, is small enough to penetrate most of zeolite pores, and therefore, typical BET analysis offers a measurement of the total zeolite surface area, including both internal and external surfaces. Since the internal surface area typically overwhelms the external surface area, conventional BET measurements provide essentially no information on the external surface area.

BET-type measurements can be applied to the zeolite surface measurements if the adsorbate molecules are larger than the pore openings on the zeolite. One way to measure the zeolite external surface area using only BET-nitrogen adsorption is called filled-pore
BET measurements in which the pores are first plugged with molecules of appropriate size and then a simple BET measurement is carried out. 46

Non-Langmuir/BET type measurements for the zeolite external surface area determination have also been developed. These methods include a) an adsorption kinetics method in which the speed of adsorption on the external surface and internal surface is exploited when the size of the adsorbate is such that it can access both the internal and external surfaces;23 b) measurements in which the volume of adsorbed nitrogen is plotted against the statistical film thickness54 (t-plot); c) simple geometrical analysis using scanning electron microscopy (SEM); and d) mercury porosimetry.33,55

Mercury is a non-wetting fluid at room temperature for porous material, including zeolites. Washburn proposed that mercury injection into a porous material could be used to measure pore-size distribution.56,57 Washburn’s equation relates the radius of a circular cross-section capillary $r$ to the applied pressure $P$ via,

$$ r = \frac{-2\sigma \cos(\theta)}{P} \quad (1.5) $$

wherein $\sigma$ is the surface tension of the mercury, and $\theta$ is the contact angle. At low to medium pressure, mercury cannot penetrate the zeolite pores. With the data on pressure-intrusion volume, one can produce an estimate of the external surface area of a zeolite sample by measuring the incremental surface area contribution for each intrusion volume.55

These methods for the measurement of the zeolite external surface have been the subject of many publications including reviews53,58,59 and have been used in various combinations on zeolites including ZSM-5 zeolites46,60,61 and others.62
These methods for determining the external surface area have shown a varying degree of success depending on the specific systems. One of the major constraints is the necessity of mathematical disentangling of the external surface from the internal surface (for adsorption kinetics, t-plot). The second major disadvantage has to do with the fact that for most commonly used ZSM-5 zeolite crystals, the external surface area accounts for only a minute percentage of the total surface area. For ZSM-5 zeolites, the percentage of external surface tetrahedral sites, \( Ts(\%) \), either SiO\(_4\) or AlO\(_4\)\(^{-}\) can be estimated to be roughly determined by

\[
Ts(\%) = \frac{181}{D}
\]  

(1.6)

wherein \( D \) is the mean crystal size in nm.\(^{63}\) The strong dependence of external surface area on the size of the crystals is more readily appreciated by examining Figure 1.4. It is not surprising that for ZSM-5 crystals with \( D \) at about 1 \( \mu \)m or larger, the internal surface overwhelms the external surface. The external surface area measured, following a method involving disentangling internal and external areas, will provide results with limited accuracy. Simple geometrical analysis by SEM is very useful for large crystals, but the reliability can be adversely influenced by any irregularity of the crystal morphology, crystal defects, e.g. twinning, and the possible presence of mesoscale structure due to process like alkali treatment.\(^{64,65}\)
Figure 1.4 The percentage of external surface tetrahedral sites, $T_s$ (%) as a function of mean size crystal, $D$ (in nm).

In summary, even though various methods for external surface area determination are available, it is desirable to develop a method that measures exclusively the external surface with high sensitivity. The exclusive measurements of external surface area will simplify the data handling procedure and avoid distortions caused by the internal surface when the accuracy of the mathematical model is limited. The high sensitivity is desirable if large zeolite samples with small specific surface area are to be examined. Spectroscopic methods using probe molecules that adsorb exclusively on the external surface of zeolites are strong candidates.

1.1.4.3 Zeolite External Surface Parameters Other Than Surface Area

External surface area is not the only parameter of interest with respect to adsorption on the external surface. A series of important questions can be asked about the nature of the adsorption sites on the external surface. Is the external surface of zeolite homogeneous in nature when the interaction with adsorbate molecules is concerned? If
the external surface is heterogeneous, how many different sites are there? What is the relative amount of the different adsorption sites? What is the difference in binding strength between the adsorbate and the adsorbent at various adsorption sites? How do the structures of adsorbate molecules affect the binding strength and binding structure on the adsorption sites? How does binding strength vary as a function of the adsorbate loading?

In addition to the static or equilibrium picture obtained from the answer to the proceeding questions, it is also of both fundamental and industrial importance to understand the dynamic or kinetic nature of the adsorption on the external surface. Is there dynamic exchange between the adsorbate molecules on each particular site and adsorbate molecules on a different binding site, or in the liquid or gaseous phase?

Various methods, including calorimetry and spectroscopy, have been used in the study of the properties of the adsorption sites. The vast majority of the literature is focused on the characterization of acid sites (Bronsted: H\(^+\), Lewis: Al\(^{3+}\)) and basic sites (O\(^{2-}\), OH\(^-\))\(^6\) either directly using physical techniques or indirectly by the adsorption of a basic probe, such as ammonia, or an acidic probe, such as acetic acid.\(^6\) The major techniques are:\(^6\)

1. Infrared spectroscopy of hydroxyl groups, of adsorbed molecular probes, and of their further thermal desorption.\(^7\) This technique is most widely used and is capable of differentiating the Bronsted and Lewis sites.

2. Optical UV technique of adsorbed appropriate molecules.\(^6\)\(^8\)\(^9\) This technique is inherently very sensitive, but is plagued by limited quantitative determination and overlapping of broad peaks.
3. NMR techniques such as those applied to the analysis of proton jump frequency to examine the occupancy factor of the proton at the various oxygen atoms, solid state $^2$H-NMR study of dynamics of molecules adsorbed on zeolite$^{70}$, multinuclear ($^1$H, $^3$H, $^{27}$Al, $^{29}$Si) solid-state NMR study of the Bronsted acid sites.$^{71}$

4. Electron Paramagnetic Resonance (EPR) of radical ions.$^{72,73}$ More on EPR will be discussed in the next section.

5. Calorimetric determination of the differential heat of adsorption of a probe molecule at a given temperature.$^{74,75}$ One can obtain the strength and concentration of the various sites, but not their natures.

6. Temperature programmed desorption of the adsorbed probe molecules.$^{76,77}$ The nature of the site is not available.

7. Catalytic test reactions which are expected to occur only for a given site.$^{78,79}$

8. Chemical titration.

Zeolite external surface properties were also examined by studying the luminescence properties of 8-hydroxyquinoline upon complexation with surface coordination-unsaturated cations and Bronsted acid centers.$^{80}$

1.2 EPR and its Application in the Characterization of Solid Surface

Paramagnetic resonance is a form of spectroscopy in which an oscillating magnetic field induces magnetic dipole transitions between the energy levels of a system of paramagnets.$^{81}$ Electron paramagnetic resonance (EPR) is restricted to the study of magnetic dipoles of electronic origins. The simplest resonance condition is,$^{82}$
\[ hv = g_e \mu H_0 \]  

(1.7)

wherein \( h \) is Planck’s constant, \( \nu \) is the resonant frequency (Larmor frequency) typically in the microwave range, \( g_e \) is the electron g-factor and is equal to 2.0023 for a free electron, \( \mu \) is the electron spin magnetic moment and \( H_0 \) is the magnetic field strength.

### 1.2.1 EPR: Uses and Advantages

Since the first observation of an EPR peak in 1945 by Zavoisky,\(^{83,84}\) EPR has evolved into a powerful technique in the study of various systems. In principle, all atoms and molecules can be studied by EPR as long as the species possess a paramagnetic ground or excited state, having net electron angular momentum (usually spin angular momentum).\(^{85}\)

Typical systems that have been studied include the following:\(^{85}\) 1) Free radicals in the solid, liquid or gaseous phases,\(^{86}\) 2) Transition ions including actinide ions,\(^{87}\) 3) various point defects in solids,\(^{88}\) 4) Systems with more than one unpaired electron, such as triplet state systems, biradicals and so on,\(^{89-92}\) and 5) Systems with conducting electrons, such as in semiconductors and metals.\(^{93,94}\)

The advantages of EPR are multiple.

**A. EPR spectra provide rich structural and dynamic information about a system under investigation.**

By adding spin probes and labels, EPR has evolved into a very valuable analytical technique for the study of complex biological, polymeric, colloidal systems etc. EPR analysis has enabled scientists to obtain the following information about a biological system.\(^{95}\)
1. Calculation of the parameters of rotational diffusion of the spin labels, permitting the determination of microviscosity and study of the environmental microtopology. The slightest changes in these properties, such as those brought about by conformational or phase transitions, are immediately seen from the corresponding changes in the EPR spectra,

2. Determination of the distance between the spin-labeled portions from the magnitude of spin-spin interactions between the spin labels and between a spin label and paramagnetic atoms of a metal.

3. Evaluation of the environmental polarity in a solution, or a solid surface or liquid/solid interface.

4. Quantitative study of microdielectric and redox properties of the medium on the basis of the radical reduction rate.

5. Elucidation of the distribution of the spin-labeled, physiologically active compounds in biological structures.

In general, by measuring the spectral parameters of any paramagnetic species encountered, one can expect to identify it, deduce details of its structure, characterize its location, orientation and surroundings, as well as measure its concentration.  

**B. EPR is an inherently very sensitive method**, more sensitive than Nuclear Magnetic Resonance (NMR). The sensitivity of magnetic resonance is proportional to the excess of spins in the lower energy levels in a magnetic field. Due to the larger magnetic moment of an electron compared to the proton (a ratio of roughly 1000:1), the energy difference of the two spin levels in a typical magnetic resonance instrument is much larger for electrons in EPR than for nuclei in NMR. Consequently according to the
Boltzmann distribution, the lower spin energy level in EPR is more populated than in NMR and the signal/noise ratio is correspondingly higher for EPR. For example, a typical X-band EPR working at a magnetic field strength of 3390 Gauss provides a ΔE (separation between energy levels) of 3.8 J·mol⁻¹ and an excess of electrons in a lower energy state (300 K) of 1 in 700, while in comparison, a 60 MHz ¹H-NMR operating at 14,100 Gauss offers a ΔE of 2.4 × 10⁻² J·mol⁻¹ and an excess of ¹H nuclei in a lower energy state (300 K) of 1 in 100,000.⁹⁶

1.2.2 Nitroxide Radicals as EPR probes.

1.2.2.1 Nitroxide Structures

Suitable EPR probes require the presence of paramagnetism due to one or more unpaired electrons. An important family of organic compounds, which meets this requirement, are the nitroxides. An example is 2,2,6,6-tetramethyl-piperidin-1-oxyl (TEMPO) and its derivatives (Scheme 1.1) (TEMPO and its derivatives will be collectively called nitroxides, hereafter). Nitroxides can be easily prepared in large quantities and derivatized on the 4- position (R-). Even though it contains an unpaired electron, it is stable for months at room temperature provided it is not in contact with strong acids.

![Scheme 1.1](image)

**Scheme 1.1** Structure of TEMPO and its derivatives by functionalizing the 4-position. R can be =O, amino, hydroxy, carboxy, ester and etc.
1.2.2.2 Spin Hamiltonian for Nitroxides

The approximate spin Hamiltonians (omitting nuclear Zeeman term and other second-order effects) for nitroxide free radicals is made up of four terms:

\[
\hat{H} = \hat{\beta} S \cdot \mathbf{g} \cdot H_0 + \hbar S \cdot \mathbf{A} \cdot I + \sum_{i \neq i}^n r_{ik}^{-3} (3 \cos^2 \theta_{ik} - 1) \times (S_i S_k - 3 S_{z,i} S_{z,k}) - 2 \sum_{i<j} J_{ij} S_i \cdot S_j
\] (1.8)

The **first term** is called electron Zeeman interaction, and it represents the interaction of the electron spin angular momentum $S$ with the external magnetic field $H_0$. $\beta$ is the electron Bohr magneton, and $g$ is the electron $g$-factor tensor. This large interaction is mostly responsible for the correct wavelength of microwave frequency for EPR measurements. Currently most EPR spectrometers operate at 9.5 GHz (X-band), which leads to a magnetic field of ca. 3.4 kG for nitroxide radical EPR measurements.

The **second term** represents the electron-nuclear hyperfine coupling interaction between the unpaired electron and the nitrogen nucleus of the nitroxide N-O group. $\mathbf{A}$ is the nuclear hyperfine tensor, and $I$ is the nuclear spin angular momentum. This term is much weaker than the Zeeman interaction, but is responsible for the splitting of the EPR spectra into $2I + 1$ lines.

The **third term** is due to electron-electron dipole interaction of an electron spin $S_i$ with the other spin $S_k$ in close proximity. $r_{ik}$ is the distance between the two spins, $\theta_{ik}$ is the angle between the external magnetic filed vector $H_0$ and the vector $r_{ik}$ connecting the two spins $S_i$ and $S_k$. $S_z$ is the $z$ component of the electron spin angular momentum operator.
At close range, the magnetic moments of the radicals $k$ produce a local magnetic field $H_d$ at the site of radical $i$, and this local field is superimposed on the external field $H_0$.

In a system of immobilized and statistically distributed radicals, the local field $H_d$ fluctuates due to the fluctuations in the angle $\theta_{ik}$ and distance $r_{ik}$. Consequently, the resulting resonance field $H_0+H_d$ fluctuates from radical to radical and produces a broadening of the spectrum. The mean square value of the local magnetic field is expressed as in Equation 1.9, which provides a measure of the line width $\Delta H_d$ (in G) of a dipolar-broadened line.

\[
\langle H_d^2 \rangle = \frac{9}{16} \sum_k g^2 \beta^2 |r_{ik}|^{-6} (3\cos^2 \theta_{ik} - 1)^2
\]  

(1.9)

For the first derivative of a Gaussian line the following relation exists in the form of Equation 1.10:

\[
\Delta H_d = \sqrt{\langle H_d^2 \rangle}
\]  

(1.10)

Assuming a statistical distribution of the nitroxide probe molecules ($g = 2$) on the surface, one can relate the value of $\Delta H_d$ (in G) to the average distance between the radicals in the manner described by Equation 1.11, wherein $d$ (in Å) is the average distance between the nitroxide probe molecules.

\[
\Delta H_d = 3 \times 10^4 (1/d)^3
\]  

(1.11)

The dipolar broadening is reduced when the nitroxide molecules undergo tumbling motions, because the tumbling tends to average the local fields. The dipolar anisotropy is also averaged at the presence of strong spin exchange interaction (\textit{vide infra}) and Equation 1.11 cannot be used in such occasions.
The fourth term is called electron-electron exchange term and is significant only when two or more nitrooxide probes are close to one another, such as in a highly concentrated solution, or in a nitrooxide crystal, or closely positioned on a solid surface, in a membrane, along polymer chains, or di- and poly-nitroxides of suitable structures.\textsuperscript{97}

The exchange interaction is due to the fast exchange of electron spin states when there is efficient overlap of the N-O 2π orbitals between two or more nitrooxide probes.\textsuperscript{99,100} For two spins with spin quantum number $\frac{1}{2}$, such as the electrons, the interaction of two spins will yield a triplet state ($S = 1$) and a singlet state ($S = 0$). While two electrons with the parallel spins (triplet system) cannot be found at the same point of space at the same time due to Pauli principle, the two electrons with antiparallel spins (single system) can. Therefore, Coulomb repulsion is stronger for the singlet state than the triplet state and electron pairs in the singlet state have higher energy than those in the triplet state. The parameter $J_{ij}$ in Equation 1.8 is called exchange integral, which characterizes the value of the energy splitting between the triplet and single states.\textsuperscript{100}

$J_{ij}$, as the exchange integral for two interacting radicals $i$ and $j$, can be further expressed as the following:\textsuperscript{81,98}

\begin{equation}
J_{ij} = \int \int \Psi_i(i) \Psi_j(j) \left( \frac{e^2}{r_{ij}} \right) \Psi_i(i) \Psi_j(j) d\tau_i d\tau_j
\end{equation}

(1.12)

The value of $J_{ij}$ depends on the overlap between the two wave functions $\Psi_i$ and $\Psi_j$ and decreases rapidly with increasing distance $r_{ij}$ between the radicals. An exponential relationship between the exchange integral $J_{ij}$ and inter-spin distance $r_{ij}$ has been proposed as described by Equation 1.13, wherein $J_0$ and $\varepsilon$ are constants.\textsuperscript{101,102}

\begin{equation}
J_{ij}(r_{ij}) = J_0 \exp(-\varepsilon r_{ij})
\end{equation}

(1.13)
In a study of spin exchange in the semiconductor system,\textsuperscript{102} it was found that an increase of inter-spin distance from 6 to about 11 Å, leads to a decrease of $J_{ij}$ value by at least 5 orders of magnitude. At shorter distance, such as about 1 to 2 Å between atoms in molecules, the substantial orbital overlap leads to a spin exchange so large that the energy of exchange interaction is larger than the energy of thermal motion. The effect of this extremely strong electron exchange interaction is the formation of chemical bonds between atoms.\textsuperscript{100}

As a result of the strong distance dependence of the electron exchange, it is sufficient in most occasions to consider exchange interaction only between the nearest neighbors and to replace the exchange integral $J_{ij}$ by an average value $J$, assuming all nearest neighbor pairs are identically situated within the pair. The exchange frequency $\omega_{ex}$ is expressed in Equation 1.14 for immobilized radicals.

$$\omega_{ex} = J/\hbar$$

(1.14)

The electron-electron exchange between the unpaired electrons, if present in significant amounts, tends to dominate the EPR spectrum. The effect is discussed in more detail in Chapter 4.

1.2.2.3 Solution EPR Spectra of Nitroxides

A solution EPR spectrum of regular nitroxides at low concentration ($< 1 \times 10^{-3}$ mole-l\textsuperscript{-1}) in a non-viscous solvent exhibits three well-resolved lines, due to the nuclear-electron spin coupling from the $^{14}$N ($I = 1$) (Figure 1.5). The spectrum is conventionally acquired in the first derivative mode, because the use of magnetic field modulation during data acquisition to enhance the signal to noise ratio produces a derivatized spectrum. The
spectrum is also conventionally presented in the first derivative mode (as opposed to the absorptive mode in NMR), because fine details of the EPR spectrum can be better resolved in the first derivative mode, while in the absorptive mode there is frequently significant signal overlap.

![Diagram of EPR spectrum](image)

**Figure 1.5** EPR spectrum of a nitroxide (DPT) in a deoxygenated isoctane solution (0.5 x 10⁻³ mole·l⁻¹) at room temperature (A: first derivative mode, B: absorptive mode by integrating A). The spectrum displays a three-line pattern with narrow linewidth and each line is marked with the corresponding nitrogen nuclear spin number $M_I$. The isotropic hyperfine coupling from $^{14}$N nucleus is $A_{iso} = 15.2$ G. The rotational correlation time is calculated to be $3.05 \times 10^{-11}$ s.

The lines are sharp because the rapid rotational motion in the non-viscous (isoctane viscosity is 0.5 cP at 20 °C) isotropic medium leads to complete averaging of the spectral anisotropy ($g$-factor and hyperfine coupling from interaction with $^{14}$N nucleus) of the nitroxide spin labels, i.e., $g = (g_{xx} + g_{yy} + g_{zz}) / 3$ and nitrogen hyperfine
coupling $A_{iso} = (A_{zz} + A_{xx} + A_{yy}) / 3$. The designation of the principle axes are as follows: the $z$ axis is defined as being along the 2p-$\pi$ orbital of nitrogen, the $x$ axis is along the N-O bond, and the $y$ axis is perpendicular to these, as shown in Scheme 1.2.

Scheme 1.2  Definition of the principal axes system. $Z$ is along the 2p-$\pi$ orbital of nitrogen, $X$ is along the N-O bond, $Y$ is perpendicular to both $X$ and $Z$ and is omitted from the figure for simplicity.

The parameter that characterizes the rotational motion is called rotational correlation time, $\tau_R$, which is defined as the average time for which the molecule moves in any given direction before beginning rotation in some new direction. For the nitrooxide systems characterized by fast motion, which is defined by a small $\tau_R$ value between $10^{-11}$ s and $10^{-9}$ s, the $\tau_R$ value can be calculated from the lineheight and linewidth of the EPR first derivative spectrum using equation 1.15. The nitrooxide $\tau_R$ value for the system shown in Figure 1.5 was calculated to be $3.05 \times 10^{-11}$ s and is clearly in the range of fast motion.

$$\tau_R = 6.5 \times 10^{-10} \Delta H_0 \left( \frac{w_0}{w_{-1}} - 1 \right)$$ (1.15)
wherein $\Delta H_0$ (in G) is the linewidth of the central line ($M_1 = 0$ in Figure 1.5), and $w_0$ and $w_{-1}$ are the lineheights of central ($M_1 = 0$ in Figure 1.5) and high field ($M_1 = -1$ in Figure 1.5) lines, respectively.

When a viscous solvent (e.g. ethylene glycol, $\sim$14 cP at 25°C) is used, the linewidth increases and the lineheights differ for the three lines with increasing viscosity.\textsuperscript{97}

The term $A_{\text{iso}}$ is due to the Fermi contact and cannot be motion-averaged.\textsuperscript{85,108} The value of $A_{\text{iso}}$ is dependent on the spin density on the nitrogen nucleus (Figure 1.6), which in turn is affected by the solvent polarity (Figure 1.7).\textsuperscript{95,109} Of the two resonant structures, solvents with lower polarity favor the less ionic one on the left side (A) and lead to lower spin density on the nitrogen nucleus, while solvents with higher polarity favor the more ionic structure on the right side (B) and lead to higher spin density on the nitrogen nucleus. A correlation of $A_{\text{iso}}$ value with the spin density on nitrogen and oxygen atoms for nitroxides has been determined to be that shown in Equation 1.16,\textsuperscript{110-112}

\begin{equation}
A_{\text{iso}} = 23.9 \rho_N \pi + 3.6 \rho_O \pi
\end{equation}

wherein $\rho_N \pi$ is the spin density on nitrogen and $\rho_O \pi$ is the spin density on oxygen (for $^{17}$O, nuclear spin number $I = 5/2$, natural abundance 0.038%).
**Figure 1.6** Change in the electron density of the unpaired electron on the nitrogen nucleus as a function of solvent polarity. Polar solvent favors the more ionic structure (B) on the right side and leads to higher unpaired electron density on the nitrogen nucleus.

Based on the measurements conducted in various solvents with different polarities, $A_{iso}$ values of nitroxides have been linearly correlated to the various solvent polarity parameters, such as the Dimroth-Reichardt solvent polarity parameter (Figure 1.7).^{109}

**Figure 1.7** Relationship between the nitrogen hyperfine coupling constant $A_{iso}$ in 4-amino-TEMPO in various solvents and the Dimroth-Reichardt solvent polarity parameter, $E_T$ (30). Duplicated and reconstructed from published literature.^{109}
Another advantage of using nitroxides is that the small number of lines ensures a simple spectrum that is easily analyzed and provides stronger signal at the same concentration compared to species that give rise to a large number of lines. This is especially the case when $^{15}$N labeled nitroxides are used (Chapter 5).

1.2.3 Characterization of the Solid Surface using EPR/Stable Nitroxide Radicals

1.2.3.1 EPR Spectra of Nitroxides in Slow Motion

Upon adsorption of nitroxides on a solid surface, the lineshape of the spectrum may dramatically change from that of the non-viscous solution. The spectra of a nitrooxide adsorbed on a solid surface offer rich information on the local polarity, mobility and distance of the probes, which in turn can reveal the nature of the interaction of nitrooxide and adsorption sites. For example, Figure 1.8 is a spectrum of 4-oxo-TEMPO adsorbed on silicalite at low loading (less than 2% surface coverage). As a result of the interaction of the 4-oxo-TEMPO molecules with the surface structures of the solid, the rotational mobility (tumbling rate) of the 4-oxo-TEMPO molecules is reduced. The rotational correlation times ($\tau_R$) are typically in the range of $10^{-9}$ and $10^{-6}$ s and the EPR spectra are typically called slow-motion spectra. Due to the slow rotation of the nitrooxide molecules, the anisotropic nature of the g-factors ($g_{xx} \neq g_{yy} \neq g_{zz}$) and the nitrogen hyperfine coupling tensors ($A_{zz} \gg A_{xx} \approx A_{yy}$) are manifested in the magnetic field. As an example, from the measurements conducted with 4-oxo-TEMPO in single crystals of the reduced 4-oxo-TEMPO matrix, the g-factor tensors have been determined to be $g_{xx} = 2.0094$, $g_{yy} = 2.0061$, $g_{zz} = 2.0021$, and the hyperfine coupling tensors are $A_{xx} = 6.5$ G, $A_{yy} = 6.7$ G, $A_{zz} = 33.0$ G. The random distribution of molecular orientations with respect
to the magnetic field leads to the broad spectrum, as the superposition of all possible single-crystal spectra, which are sharp lines *per se* such as that in Figure 1.5 but with a different central position (g-factor) and splitting (nitrogen hyperfine coupling).\textsuperscript{97,103} In analyzing the line width, one can obtain the electron spin dipole-dipole interaction value, which in turn reveals the inter-probe distance (to be discussed in detail in Chapters 3 and 4).\textsuperscript{98}

The value of the nitrogen anisotropic hyperfine $A_{zz}'$, is measured to be one half of the distance between the extrema of the two outer EPR lines (Figure 1.8), and is composed of two terms,\textsuperscript{113}

\[ A_{zz}' = A_{iso} 1 + A_{dip} \quad (1.17) \]

The first term is the Fermi contact term $A_{iso}$, which is a function of electron spin density on the nitrogen nucleus (Equation 1.16) and an indicator of polarity in the vicinity of N-O moiety (Figure 1.6). The second term $A_{dip}$ corresponds to the classical dipolar coupling between magnetic dipoles and can be reduced to essentially zero due to averaging when the rotational motion of the probe is fast, as in the case of small nitroxide probe molecules dissolved in a non-viscous solvent (Figure 1.5).
Figure 1.8 EPR spectrum of 4-oxo-TEMPO on the external surface of silicalite at 2% surface coverage (Chapter 3). The double arrow shows the measurement for the $^{14}$N anisotropic hyperfine coupling tensor $A_{zz'}$.

Since the nitroxide probe molecules adsorbed on a solid surface at room temperature are in the range of slow rotational motion, the $A_{zz'}$ value is less than its maximum value due to partial averaging of the dipolar interaction term in Equation 1.16. By decreasing the rotational mobility (e.g., lowering the temperature of the sample), the averaging becomes less efficient and the value of $A_{zz'}$ increases. When the spectrum is measured at the rigid motion conditions typically by lowering the temperature to such an extent that $A_{zz'}$ no longer increases with the decrease in temperature, $A_{zz'}$ becomes equal to $A_{zz}$, which is related only to environmental polarity. Therefore, the examination of $A_{zz'}$ value can reveal valuable information on the surface polarity and rotational mobility of the probe molecules. The calculation of the $\tau_R$ value in the slow motion range can be carried out using an established formula (Equation 1.18)\textsuperscript{104} wherein the $a$, and $b$ are parameters evaluated from the line width and diffusion models (Brownian, jump, etc).\textsuperscript{114}
\[ \tau_R = a(1 - \frac{A_{zz}'}{A_{zz}})^b \] (1.18)

Computer-assisted simulations have proven extremely valuable in the determination of various EPR parameters. By means of a least square fitting method, the contribution of \( A_{zz} \) and \( \tau_R \) to a slow-motion spectrum can be independently assessed.\(^{115}\) A well-established simulation procedure is the nonlinear-least square analysis of slow-motion EPR spectra using a modified Levenberg-Marquardt algorithm, in which the dynamic parameters are obtained from a least square fitting of model calculations based on the stochastic Liouville equation to experimental spectra.\(^{116,117}\)

Another important parameter, the inter-spin distance can be calculated from the extent of the line broadening due to an electron-electron dipolar interaction (Equation 1.9 to 1.11).

At high nitroxide concentration in a solution or high loading of nitroxide on a solid, the EPR spectra will be dominated by a phenomenon called electron-electron spin exchange interaction, which will be discussed in more detail in Chapter 4.

There have been limited literature reports on the characterization of adsorption sites in terms of adsorption and mobility on the surface of alumina, silica gel and the external surface of selected zeolites using stable nitroxides and EPR. These surfaces are discussed here because they are most relevant to the external surface of ZSM-5 zeolites, in terms of composition and/or structures. These reports will be discussed in sub-sections according to composition and structure of the adsorbent (alumina, silica gel, and zeolite), in which a finer distinction, e.g., the identity of the probe molecules (nitroxide only or nitroxide and displacers) and the phase of the system (dry or slurry) will be further discussed.
1.2.3.2 Characterization of Alumina Surface Using EPR

The external surface of alumina contains two different acidic sites, which provide strong binding. The first and strongest is the Lewis $\text{Al}^{3+}$ site and the second is the Bronsted OH terminals, which include silanol and bridging hydroxyl groups as shown in Scheme 1.3.\textsuperscript{7}

![Scheme 1.3 Structures of two types of hydroxyl groups in a protonated zeolite: silanol and bridging hydroxyl groups.](image)

The use of nitroxide EPR for the detection of aprotic surface centers on alumina has been reported.\textsuperscript{118} In the alumina/benzene slurry system, if the alumina is not thermally activated before the probe molecules are adsorbed, a relatively weak EPR spectrum of the adsorbed molecules with somewhat hindered rotation is superimposed on the isotropic hyperfine structure of the free nitroxide in solution.\textsuperscript{118} The unavailability of $\text{Al}^{3+}$ for strong interaction on the surface was expected to be due to the hydration of $\text{Al}^{3+}$ without thermal activation. The thermal activation can efficiently remove water and creates strongly acidic sites for the binding of probe molecules.

For the samples prepared in the absence of thermal activation, when the solvent was removed and the solid sample was examined, it was found that the isotropic component was completely removed and only the spectrum of the strongly adsorbed (slow-motion) molecules remains.\textsuperscript{118} The lineshape is the regular three-line characteristic
of retarded motion, as seen on a silica sample without \( \text{Al}^{3+} \) and is similar to Figure 1.8, with a rotational correlation time at about \( 0.6 \times 10^{-8} \) s in the range of slow motion.

However, if thermally activated alumina is used, a finer structure is superimposed on the regular triplet lines as a result of the interaction of the unpaired electrons with the nuclei of both \( ^{14}\text{N} \) and \( ^{27}\text{Al} \) \( (I = 5/2) \). Interaction of the N-O unpaired electron with \( ^{27}\text{Al} \) has been demonstrated in \( \text{AlCl}_3 \) solution.\(^{119}\) The onset of the superhyperfine interaction of \( \text{Al}^{3+} \) with nitroxide on the thermally activated alumina is due to the removal of water from the \( \text{Al}^{3+} \) sites.

It was also found that the addition of water vapor turns the EPR spectrum of the adsorbed nitroxide on the activated dry alumina from the multiplex characteristic of the nitroxide-Al complex to the anisotropic three-line spectrum analogous to that obtained on silica gel or non-activated alumina.\(^{118}\) This change in EPR spectrum is due to the displacement of the nitroxide from the strong \( \text{Al}^{3+} \) binding sites by water molecules.

In another published study,\(^{120}\) the adsorption of nitroxide on thermally activated fluorinated alumina showed the presence of a second strong adsorption site in addition to the \( \text{Al}^{3+} \) sites even at low loading of nitroxide (superimposition of a three-line on the nitroxide-\( ^{27}\text{Al} \) multiplet). The second sites were considered to be OH sites based on the evidence of \( \text{Na}^+ \) poisoning (reduced three-line intensity upon partial replacement of \( \text{H}^+ \) by \( \text{Na}^+ \)), and the high hyperfine coupling constant (high polarity) was comparable to the value measured for nitroxide in a phosphoric acid solution. The presence of the two sites is also found on aluminosilicate. The decrease in the mobility of the radicals on aluminosilicate and fluorinated alumina is associated with the protonation of the radicals and strong attachment to the surface.
Amines were used as titrants for aprotic acidic centers and were coadsorbed with nitrooxide via gas phase onto a thermally activated alumina surface.\textsuperscript{121} With the increasing loading of amines, which displace the nitrooxides from the strong binding sites such as Al\textsuperscript{3+}, the EPR spectra were gradually changed from that characteristic of a nitrooxide-\textsuperscript{27}Al multiplet to the three-line pattern. When further addition of amines did not change the spectrum, the amine loading was regarded as an indication of complete coverage of strong acceptor centers. By using amines of different molecular size (ammonia and pyridine) and nitrooxides of different molecular size (TEMPO based nitrooxides and NO), the nature, accessibility and concentration of the acidic sites were examined.

In another published study,\textsuperscript{122} the EPR method used in the analysis of acidic acceptor centers of alumina was examined using a nitrooxide probe as well as a series of displacers, which were ranked by their efficiency in filling the acceptor centers: \textit{n}-butylamine \textless pyridine \textgreater alcohols \textless ammonia \textgreater water. Equilibrium was achieved in these systems, based on the observation that prolonged storage and heating did not change the form of the EPR spectrum, nor did the sequence of addition. One possible reason for the difference in the efficiency of displacement is the molecular size of the displacers, e.g., ammonia vs. \textit{n}-butylamine. Another reason for the different efficiencies for the molecules of similar sizes, is the added adsorption on centers other than the Al\textsuperscript{3+}, as in the case of water versus alcohol. The authors commented that the number of adsorption centers determined was dependent on the size of the displacers.

Regarding the distribution and mobility of nitrooxide on alumina,\textsuperscript{123} it was found that the nitrooxide distribution on a thermally activated alumina surface is very irregular, giving rise to strong dipole-dipole interactions even for systems in which the average
distances between radicals should be over 100 Å, indicating non-statistical distribution and the formation of local aggregates. At room temperature over a period of a few days, progression from triplet to multiplet could be achieved due to redistribution to stronger binding sites. Addition of water also moves the multiplet to a triplet by displacing nitroxide molecules from Al$^{3+}$ binding sites. If not enough water is added, then the EPR spectrum returns to a multiplet after a while when the nitroxides find other Al$^{3+}$ sites, the number of which correlates with the activation temperature.

1.2.3.3 Characterization of Silica Gel Surface Using EPR

The mobility of nitroxide molecules adsorbed on silica gel was reported in the literature.\textsuperscript{124} Rotational correlation times of nitroxides can be calculated from an empirical formula using line width and line height measured from the first-derivative EPR triplet spectrum (Equation 1.15). To test the role of surface OH groups in the adsorption of electron donating molecules, high surface area silica gel was activated at different temperatures. The rotational correlation time of the nitroxides adsorbed on the silica gel surface was found to be unrelated to the activation temperature. However, the rotational correlation time decreases upon addition of solvent e.g., toluene (thus forming a slurry). The activation energy of rotation on the surface in the range of 20 to 100 °C was found to be about 2 kcal·mole$^{-1}$ regardless of the method of adsorption and the treatment of the surface.

On the other hand, translational mobility of the adsorbed molecules depends strongly on the heat treatment of the surface. For the system loaded from the vapor phase (dry solid sample), a high local concentration can be found for relatively low statistical loadings (average probe distance > 100 Å), similar to the alumina system discussed
previously. Spontaneous decrease in the high local concentration can be observed at room temperature for hydroxylated silica gel that was either not thermally treated or treated at low temperature (e.g., 150 °C). The possibility of redistribution from the gas phase was ruled out. However, for silica gels thermally treated at 600 °C, no translational mobility was observed.

1.2.3.4 Characterization of Zeolite Surface Using EPR

Adsorption of nitroxides on thermally activated (550 °C) zeolite X and Y was also studied.\textsuperscript{124} It was found that the type of zeolites (X and Y), the nature of the exchangeable cation, and the degree of exchange do not affect rotational correlation time, probably due to the fact the adsorption is occurring in the vast internal surface by entering through the large pore openings (windows) and without specific binding between the nitroxide probe and the cations.

Stable nitroxide radicals in the TEMPO family are especially suitable for the selective characterization of the ZSM-5 zeolite external surface, because the pores of the ZSM-5 are uniform, unlike silica gel, alumina etc., and the pores providing access to the internal surface are smaller than the TEMPO probe molecules.

The external surface area of a superhigh-silica ZSM-5 zeolite was determined using TEMPO EPR.\textsuperscript{125} The basic concept was correlating the ratio of the heights of the two lines in the first-derivative EPR spectrum ($d_1/d$) to the average distance of the probe molecules (Figure 1.9).
Figure 1.9 Measurements of EPR line heights. $^{125}d_1/d$ ratio was correlated to inter-spin distances.

$^2$H-NMR was also employed in the study of ZSM-5 zeolite's external surface based on different line widths at different adsorbate loadings by Turro and his colleagues. $^{21,126}$ Deuterated ortho-methyl dibenzylketone molecules were loaded onto the external surface of the zeolite and the interaction with the zeolite surface was examined by studying the lineshape change as a result of change in the probe mobility at different surface coverage.

The spectroscopic methods, in addition to product analysis in the photolysis of ketones adsorbed on the zeolite’s external surface and Langmuir isotherm analysis, $^{126}$ lead to the conclusion that the supramolecular structure of the adsorbate@ (zeolite external surface) system is a function of adsorbate loading. The external surface of a ZSM-5 zeolite is well described using a two-site model. The first site, presumably the pore opening (hole) based on available evidence, is a strong binding site. The second one, presumably the framework (the rest of the external surface between the holes), is a weak binding site. Adsorbate molecules will initially bind preferentially on the surface by
interacting with the stong binding sites. After those sites are occupied, the adsorbate molecules will bind to the second weaker binding sites, after which a monolayer or even multi-layer can be formed at higher loading.

During these studies, the evidence suggested that the transition point at which the supramolecular structure of these guest@host systems changes is related to the total external surface area.\textsuperscript{126,127}

In light of the use of spectroscopic methods (especially EPR) in the study of adsorption on a solid surface, the focus of this thesis is the EPR study of static and kinetic details of the adsorption of organic molecules on the ZSM-5 zeolite's external surface and the correlation of adsorption parameters to the external surface area of the zeolite samples.

1.3 Research Objectives

The major objective of this research was to study the adsorption phenomena on the external surface of ZSM-5 zeolites, especially the study of specific external surface area as a function of crystal size using EPR.

The aluminum-free version of a ZSM-5 zeolite, silicalite, was chosen in this study because it is essentially SiO$_2$ with only trace amounts of aluminum in its structure (typically Si/Al > 1000). The near absence of aluminum makes the EPR spectrum of adsorbed nitroxide less complicated by removing the extensive superhyperfine splitting from nitroxide-$^{27}$Al interaction ($I = 5/2$). By removing the strong Al$^{3+}$ binding sites on the zeolite surface, it also ensures a more uniform surface property, because Al$^{3+}$ distribution in aluminum containing ZSM-5 zeolites has been known to be very sensitive to
preparation and purification procedures. An additional possible complication is that in some samples, Al$^{3+}$ ions preferentially reside on the outer surface.$^{128,129}$

The implementation of the research objectives includes the following steps,

1. Synthesis of a series of monodisperse silicalite samples with different crystal sizes. The use of monodisperse silicalite samples ensures the consistency of properties of the crystals within the same sample.

2. Determination of the external surface parameters of silicalite crystals including the external surface area using EPR by studying the spectrum of the nitroxides adsorbed on the silicalite surface and the spectral evolution as a function of ortho-methylidibenzyl ketone (oMeDBK) loading. It was hypothesized that the transition in the EPR spectrum of nitroxides due to the displacement by oMeDBK molecules would provide a means of surface area measurements. By varying the structures of the nitrooxide probes and the ketone displacers, the nature and strength of the interaction between the adsorbate molecules and the adsorbing sites on the adsorbent external surface could be studied.

3. Determination of the external surface parameters of silicalite crystals including their external surface areas by studying the spectral change of the nitroxides adsorbed on the silicalite surface as a function of loading without coadsorbate such as oMeDBK. The inter-probe distance parameter and spin-spin exchange frequency as a function of probe loading, as obtained from simulation of the experimental spectra, should provide a means of surface area measurements.

4. A study of the properties of the external surface binding sites by using regular nitroxides (natural abundance 99.6% N as $^{14}$N) and $^{15}$N spin labeled nitroxides,
with and without coadsorbate. The isotopical spin-labeling provides a means of studying the details of molecular interaction between the probe and the surface with a minimum structural change in the probe molecule, and thus provide more reliable results than conventional labeling, which disturbs the fundamental properties of the molecules by adding a probe moiety with un-negligible changes in the size, polarity and other properties of the molecules. The use of isotopes enables one to study the dynamics of the adsorbate on the zeolite surface if there is an active exchange between the adsorbate molecules on a particular site on the zeolite surface with those on another site or in the supernatant. The structural influence of the probe molecules on the strength of surface adsorption can also be studied conveniently using isotopically labeled nitrooxides.

1.4 References


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Chapter 2. Synthesis and characterization of silicalite and adsorbate samples

2.1 Material and Instrumentation

All reagents were obtained from Aldrich and used as received, unless otherwise noted. Amorphous silica in the form of fumed silica gel was obtained from Degussa (Aerosil 200, primary particle size 12 nm).

$^1$H-NMR and $^{13}$C-NMR measurements were conducted on Bruker NMR spectrometers at 400 (or 300) MHz and 100 (or 75) MHz, respectively. Gas chromatography (GC) was performed on an HP5890 gas chromatograph using an HP-5 capillary column. Gas chromatography/Mass Spectrometry (GC/MS) was performed on a Varian Star 3900 GC/MS instrument using electron ionization. Continuous wave EPR (CW-EPR) was carried out on an X-band Bruker EMX EPR spectrometer. X-ray Diffraction (XRD) measurements were carried out on a Scintag X2 X-ray Diffractometer operating at 45 KV and 35 mA. Scanning electron microscopy (SEM) images were taken on a JEOL JSM-5600 electron microscope.

2.2 Silicalite Synthesis and Characterization

2.2.1 Tunable Parameters in Silicalite Synthesis and Their Influence on Crystal Size

Silicalites of various crystal sizes can be synthesized via hydrothermal methods, in which water at elevated temperature and pressure lead to the formation of certain minerals. Reagents needed for the typical synthesis procedure of silicalites include silicon oxide, water, and organic template. By adjusting the silicon oxide source (amorphous SiO$_2$, homogenous alcohol solution of hydrolyzed tetraethoxysilane, etc), as well as the amount of template molecules, the pH value of the medium, the reaction
temperature, and additives (such as fluoride), silicalite crystals of various sizes can be prepared.\textsuperscript{1,2}

Silicon oxide (SiO$_2$) is the fundamental building block of silicalite crystals. SiO$_2$ supplied in a homogeneous manner, as hydrolyzed tetraethoxysilane (TEOS) (Scheme 2.1) in an alcoholic solution, is typically used for the synthesis of sub-micron crystals. Amorphous SiO$_2$ feed is typically used in the synthesis of crystals with a linear dimension of roughly 1 µm to tens of microns, and when additives such as fluoride are added, crystals up to about 100 µm can be prepared. Silicalite crystals with a size of ca. 0.7 x 0.2 x 0.2 mm have been made using unconventional high temperature (250 °C) and pressure (80 MPa).\textsuperscript{3} The world’s published record of largest silicalite crystals as of April 2001 was ca. 4 mm, and they were prepared by a bulk material dissolution technique using a piece of quartz tube as the silica source.\textsuperscript{4}

![Structures of tetraethoxysilane (TEOS), TPABr, and TPAOH.](image)

**Scheme 2.1** Structures of tetraethoxysilane (TEOS), TPABr, and TPAOH.

Template molecules are typically used in the synthesis of zeolites. In zeolite synthesis, templating refers to the filling of the void spaces of a zeolite structure by the organic/inorganic cations, which are frequently used as structure directing or structure-stabilizing agents.\textsuperscript{1} Templating contributes to the formation and stabilization of zeolite crystals and, more importantly, controls the zeolite topology through template geometry.\textsuperscript{1}
Template molecules used in the preparation of the MFI type zeolite is typically tetrapropylammonium salt, such as tetrapropylammonium bromide (TPABr) (Scheme 2.1).\textsuperscript{5,6} Tetrapropylammonium hydroxide (TPAOH) (Scheme 2.1) can also be used together with TPABr to modulate the pH value of the medium. The effect of TPABr concentration was studied systematically.\textsuperscript{2} The crystal size reduces as the TPABr concentration increases, due to fast nucleation at high template concentration.\textsuperscript{1}

The pH value of the medium also strongly influences the crystal size. Lower alkalinity typically favors the formation of larger crystals.\textsuperscript{7-9}

Typical reaction temperatures for ZSM-5/silicalite crystallization ranges from 80 to 170 °C. Higher temperatures generally favor faster nucleation and thus the formation of a large quantity of crystals of smaller sizes.\textsuperscript{1}

Various additives also influence the size of the crystals synthesized. The addition of an alkali-ion, especially Li\textsuperscript{+}, has been shown to produce large ZSM-5 crystals.\textsuperscript{9,10} In typical alkaline systems, the addition of fluoride results in the formation of smaller crystals.\textsuperscript{9} However, when the crystallization is carried out in neutral or acidic conditions, the addition of fluoride produces large ZSM-5/silicalite crystals.\textsuperscript{11}

Another interesting parameter in the synthesis of zeolite crystals is “aging”, a process in which the zeolite synthesis mixture (hydrogel) is kept below crystallization temperatures for a certain period of time before the hydrogel is heated to the desired crystallization temperature. Aging plays an important role in the crystallization kinetics. Typically, a longer aging period leads to faster crystallization with a shorter induction period, producing smaller crystals with a higher degree of crystallinity.\textsuperscript{1}
A long crystallization period leads to higher crystallinity of the sample by converting more amorphous silica into crystals. The formation of small crystals is kinetically favored, but the larger crystals are more thermodynamically stable due to the reduced number of atoms on their external surface, where the energy of the atoms is higher than the energy of the atoms in the internal structure. Therefore, a prolonged crystallization period leads to the formation of larger crystals at the expense of smaller crystals, a phenomenon called "Ostwald ripening".\textsuperscript{12}

2.2.2 Synthesis of Silicalite Crystals with Sizes Less Than 1 \( \mu \)m.

For samples with a size less than 1 \( \mu \)m and a monodisperse size distribution, synthesis was performed based on a published procedure, in which a clear homogeneous solution was used and the reaction was carried out by refluxing at 98 °C in polypropylene bottles.\textsuperscript{13}

The general molar composition of the synthesis mixture is as follows:

\[
a \text{TPABr : b TPAOH : 0.1 Na}_2\text{O : 25 SiO}_2 : c \text{H}_2\text{O} : 100 \text{EtOH}
\]  \hspace{1cm} (2.1)

<table>
<thead>
<tr>
<th>Run</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>Aging / heating time (hours)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZL5157</td>
<td>3.0</td>
<td>6.0</td>
<td>480</td>
<td>25/67</td>
<td>75</td>
</tr>
<tr>
<td>ZL5154</td>
<td>0</td>
<td>3.0</td>
<td>480</td>
<td>19/100</td>
<td>65</td>
</tr>
<tr>
<td>ZL613</td>
<td>0</td>
<td>3.0</td>
<td>1500</td>
<td>17/96</td>
<td>61</td>
</tr>
</tbody>
</table>

*Table 2.1* The composition of the reaction mixture, aging and heating time, and conversion for the synthesis of silicalite crystals with a size less than 1 \( \mu \)m. The notation "ZL" followed by the numbers is the code used in this thesis to uniquely identify each silicalite sample.
After aging the reaction mixture at room temperature for no less than 12 hours, the reaction was carried out by refluxing at 98 °C for the specified period of time and then the mixture was cooled to room temperature. The colloidal mixture was transferred to polypropylene test tubes and the solid was separated from the liquid using ultrahigh centrifugation (13,800 G for ZL613, and 27,000 G for ZL5154 and ZL5157). The solid was dispersed in deionized water, sonicated and re-separated from water using centrifugation. This dispersion, sonication and centrifugation cycle was repeated until the pH of the aqueous layer was lower than 8. This can be achieved typically in 3 cycles. The solid was dried at 130 °C, and then calcinated in an aerated furnace, with the following as a representative temperature program: 300 °C for 2 hours, 400 °C for 2 hours, and 500 °C until the solid was white.

The SEM images and XRD patterns are shown in Figure 2.1 (ZL5157), 2.2 (ZL5154) and 2.3 (ZL613).

![SEM image and XRD pattern](image)

**Figure 2.1** SEM image (left) and XRD pattern (right) of silicalite ZL5157.
Figure 2.2 SEM image (left) and XRD pattern (right) of silicalite ZL5154.

Figure 2.3 SEM image (left) and XRD pattern (right) of silicalite ZL613. The presence of interpenetrating twins is observed on all crystals.

The XRD results for all the silicalite crystals synthesized above are consistent with published XRD patterns.\(^{14,15}\) The high crystallinity of the synthesized crystals can be inferred from the absence of the broad hump centered at 20 to 22°, which is characteristic of amorphous material.\(^{16}\)

For the purpose of calculating the specific external surface area, the dimensions of ten crystals in each sample were taken and averaged. The crystals in sample ZL5157 can be approximated by spheres with a diameter of approximately 1.4 x 10\(^2\) nm. The crystals in sample ZL5154 can be approximated by spheres with a diameter of approximately 3.7 x
$10^2$ nm. The crystals in sample ZL613 can be approximated by a rectangular prism with dimensions of $0.5 \times 1.2 \times 1.4$ μm.

When the density of the template-free silicalite material is taken into account (1.76 g·cm$^{-3}$), the specific external surface area of each crystal, based on geometrical considerations, is,

$$S_{st}^{ex} = 24m^2g^{-1}$$  \hspace{1cm} (2.2)

$$S_{st}^{ex} = 9.2m^2g^{-1}$$  \hspace{1cm} (2.3)

$$S_{st}^{ex} = 4.0m^2g^{-1}$$  \hspace{1cm} (2.4)

### 2.2.3 Synthesis of Silicalite Crystals with Sizes in the Range of 1 to 10 μm.

Silicalite crystals with sizes in the range of 1 to 10 μm were synthesized following a published procedure with modifications, using amorphous fumed silica gel as the source of SiO$_2$ in a heterogeneous system.\(^2\)

The batch composition in molar ratio follows

a TPABr : 1.4 Na$_2$O : 100 SiO$_2$ : b H$_2$O  \hspace{1cm} (2.5)

<table>
<thead>
<tr>
<th>Run</th>
<th>a</th>
<th>b</th>
<th>Aging (hours)</th>
<th>Heating Program</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZL5148</td>
<td>16</td>
<td>1061</td>
<td>12</td>
<td>Start at 45°C, 0.3°C/min ramp to 170°C, hold for 47 hours</td>
<td>70</td>
</tr>
<tr>
<td>ZL5159</td>
<td>8</td>
<td>1000</td>
<td>6</td>
<td>Start at 45°C, 0.3°C/min ramp to 170°C, hold for 77 hours</td>
<td>60</td>
</tr>
</tbody>
</table>

**Table 2.2** The composition of the reaction mixture, aging and heating times, and conversion for the synthesis of silicalite crystals with sizes in the range of 1 to 10 μm.

TPABr, NaOH, SiO$_2$ in the form of fumed silica gel and deionized water were mixed in a polypropylene beaker. The slurry was then transferred to PTFE (Teflon)-lined steel autoclaves. After aging, the reaction was carried out in a static condition, under
autogeneous pressure, following the temperature program as detailed in Table 2.2. After the desired period of reaction time, the reaction was quenched by cooling under cold water. The product was then dispersed in deionized water, and sonicated. The crystalline solid was then separated from the supernatant containing unreacted gel by simple gravitational sedimentation or light centrifugation, followed by decantation. The sonication and separation cycle was repeated between 5 to 10 times, until the pH was less than 8 and the supernatant was clear, indicating the complete removal of unreacted gel. The crystalline solid was then calcinated according to the procedure detailed in the previous section.

The SEM images and XRD patterns are shown in Figure 2.4 (ZL5148) and Figure 2.5 (ZL5149).

![SEM image and XRD pattern](Figure 2.4 SEM image (left) and XRD pattern (right) of silicalite ZL5148. Twining is observed in some crystals.)
Figure 2.5 SEM image (left) and XRD pattern (right) of silicalite ZL5159. Twining is observed in most crystals.

The XRD results for all the silicalite crystals synthesized above are consistent with published XRD patterns.\textsuperscript{14,15} The high crystallinity of the synthesized crystals can be inferred from the absence of the broad hump centered at 20 to 22°, which is characteristic of amorphous material.\textsuperscript{16}

The crystals in ZL5148 can be approximated as a rectangular prism with dimensions of 1.5 x 3.2 x 4.4 µm. The crystals in ZL5159 can be approximated as a rectangular prism with dimensions of 2.8 x 6.0 x 11 µm.

Thus the specific external surface area can be calculated using geometry to be approximately,

\[ S_{5148}^{\text{ext}} = 1.4 \text{m}^2 \text{g}^{-1} \]  \hspace{1cm} (2.6)

\[ S_{5159}^{\text{ext}} = 0.70 \text{m}^2 \text{g}^{-1} \]  \hspace{1cm} (2.7)

2.2.4 Synthesis of Silicalite Crystals with Sizes in the Range of 10 to 100 µm

Silicalite-1 crystals with sizes in the range of 10 to 100 µm can be synthesized using a pH neutral or even slightly acidic composition containing fluoride in the form of a salt or hydrofluoric acid. The fluoride plays a mineralizing role, as OH\textsuperscript{-} does in conventional alkaline systems.\textsuperscript{11} The benefit includes the availability of large crystals around 100 µm,
with much less surface defects compared to the crystals prepared using an alkaline media.\textsuperscript{11}

The synthesis is based on published procedures,\textsuperscript{18,19} using the following molar ratio

\[ a \text{ HF} : b \text{ NaF} : c \text{ NaCl} : 1.25 \text{ TPABr} : 10 \text{ SiO}_2 : 330 \text{ H}_2\text{O} \]  \hspace{1cm} (2.8)

<table>
<thead>
<tr>
<th>Run</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>Aging (hours)</th>
<th>Heating Program</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZL5151</td>
<td>0</td>
<td>7</td>
<td>3</td>
<td>16</td>
<td>Start at 45°C, 0.3°C/min ramp to 170°C, hold for 91 hours</td>
<td>59</td>
</tr>
<tr>
<td>ZL619</td>
<td>0.25</td>
<td>0.75</td>
<td>0.25</td>
<td>0</td>
<td>Start at 45°C, 0.3°C/min ramp to 170°C, hold for 270 hours</td>
<td>88</td>
</tr>
</tbody>
</table>

\textbf{Table 2.3} The composition of the reaction mixture, aging and heating time, and conversion for the synthesis of silicalite crystals with sizes in the range of 10 to 100 µm.

The reagents were mixed together in a polypropylene beaker. The slurry was transferred to PTFE-lined steel autoclaves and (after the sample ZL5151 was aged) the reaction mixture was heated according to the temperature program described in Table 2.3. The reaction was quenched by cooling using tap water. The product was dispersed in deionized water and sonicated. The solid can be separated from the aqueous layer by simple decantation. The dispersion/sonication/decantation cycle was repeated roughly 10 times until the aqueous layer showed a pH less than 8 and became clear, indicating the absence of unreacted gel. The calcinations were carried out in a more controlled manner. After drying at 130 °C, the solid was heated to 300°C and then the temperature was increased at 20 °C/hour until 400 °C and held at 400 °C for more than 12 hours. The temperature was then raised at a 20 °C/hour ramp to 500 °C and was held at 500 °C until the crystals turned white.
The SEM images and XRD patterns are shown in Figure 2.6 (ZL5151) and 2.7 (ZL619).

![Figure 2.6 SEM image (left) and XRD pattern (right) of silicalite ZL5151.](image)

![Figure 2.7 SEM image (left) and XRD pattern (right) of silicalite ZL619.](image)

The crystals in sample ZL5151 can be approximated as a rectangular prism with dimensions of $4.9 \times 7.4 \times 35 \ \mu m$. The crystals in the sample ZL619 can be approximated as a rectangular prism with dimensions of $25 \times 32 \times 84 \ \mu m$.

Thus the specific external surface area calculated from geometry is,

$$S_{5151}^{ext} = 0.42 m^2 g^{-1}$$

$$S_{619}^{ext} = 0.094 m^2 g^{-1}$$

The XRD results for all the silicalite crystals synthesized above are consistent with published XRD patterns. The high crystallinity of the synthesized crystals can be
inferred from the absence of the broad hump centered at 20 to 22° characteristic of amorphous material.\textsuperscript{16}

2.3 Synthesis of Adsorbates and Their Precursors, Including EPR Probes.

The adsorbate molecules are categorized in several groups. The first group, as shown in Scheme 2.2, are the EPR probe molecules possessing an unpaired electron. The second group, as shown in Scheme 2.3, are the precursor molecules for the synthesis of EPR probe molecules in Scheme 2.2. The third group, as shown in Scheme 2.4, are the adsorbates that do not give an EPR signal.

\begin{align*}
\text{Scheme 2.2} & \quad \text{TEMPO derivatized EPR probes.} \\
\begin{array}{c}
\text{1} \\
\text{2} \\
\text{3} \\
\text{4} \\
\text{5} \\
\text{6}
\end{array}
\end{align*}

\begin{align*}
\text{Scheme 2.3} & \quad \text{Precursors for the synthesis of }^{15}\text{N-labeled EPR probe molecules.} \\
\begin{array}{c}
\text{7} \\
\text{8} \\
\text{9} \\
\text{10} \\
\text{11} \\
\text{12}
\end{array}
\end{align*}

\begin{align*}
\text{Scheme 2.4} & \quad \text{Adsorbate molecules that do not show an EPR signal.} \\
\end{align*}

4-Oxo-2,2,6,6-tetramethyl-1-piperidinyloxy-\textsuperscript{15}N (4-oxo-TEMPO-\textsuperscript{15}N, 2) was synthesized following a published secondary amine oxidation procedure using 7 as the starting material.\textsuperscript{20} The product mixture was purified using silica gel flash column
chromatography, eluting with a hexane/ethyl acetate mixture (from 4:1 to 3:1 v/v).
The product was collected as an orange-red solid in 38.8% yield. GC (> 98% pure).
GC/MS (EI) m/z (rel intensity): 171 (M⁺, 100), 172 (39), 157 (24), 141 (35), 115 (48), 83 (61).

4-Hydroxy-2,2,6,6-tetramethyl-1-piperidinylxoy-¹⁵N (4-hydroxy-TEMPO-¹⁵N, 4)
was synthesized by oxidation of the corresponding amine, 8.²⁰ GC (> 98% pure), GC/MS
(EI) m/z (rel intensity):

2,2,6,6-Tetramethyl-4-[(diphenylacetyl)oxy]-1-piperidinyl-oxy (DPT, 5) was
prepared following the method used for DPT-¹⁵N using TEMPOL with natural abundance
of N. MS (FAB+): 366.2 (M-H)⁺, 368.2 (M+H)⁺.

2,2,6,6-Tetramethyl-4-[(diphenylacetyl)oxy]-1-piperidinyl-oxy-¹⁵N (DPT-¹⁵N, 6)
was prepared following a published procedure for esterification at room temperature.²¹ 4-
Hydroxy-2,2,6,6-tetramethyl-1-piperidinylxoy-¹⁵N (1.04 g, 6.01 mmole), diphenylacetic
acid (1.40 g, 6.61 mmole), 4-pyrrolidinopyridine (98 mg, 0.66 mmole), and 1,3-
dicyclohexylcarbodiimide (1.86 g, 9.02 mmole) were dissolved in tetrahydrofuran (THF,
ca. 20 ml). After the TLC showed the completion of reaction, THF was removed under
vacuum. The sludge was partitioned in diethyl ether and water. After removing the urea
by filtering, the ether layer was collected and washed twice with a 50 ml 0.5 HCl aqueous
solution, a 50 ml saturated NaHCO₃ aqueous solution, and finally a 50 ml saturated NaCl
aqueous solution. The ether layer was collected and the solvent was removed under
vacuum. The product was further purified using silica gel flash column chromatography,
eluting with a mixture of hexane and ethyl acetate from 20:1 to 10:1 v/v. The product was
dried under vacuum. The yield was 66%. It was re-crystallized from ethyl acetate. It was characterized by EPR, MS (FAB+): 367.2 (M-H)^-, 369.2 (M+H)^-.

4-Oxo-2,2,6,6-tetramethyl-1-piperidine-^{15}N (7) was synthesized via a double Michael addition procedure.^{22} 2,6.-Dimethyl-2,5-heptadien-4-one (phorone, 9.70 g, 70.2 mmole), ammonium-^{15}N sulfate (98+ atom%) (3 g, 44.7 mmole ^{15}N), and benzene (23 ml) were added to a 100 ml glass pressure vessel (Chemglass). The mixture was frozen with acetone/dry ice and then Na_{2}HPO_{4}·7H_{2}O (5.51 g, 20.6 mmole) and NaOH (2.34 g, 58 mmole) in 7.5 g H_{2}O were added. The vessel was sealed immediately and heated to 90 °C in an oil bath with continuous stirring. After 10 days, the reaction was stopped by lowering the temperature to room temperature. The mixture was washed twice with 50ml diethyl ether. The ether extract was combined and dried over anhydrous MgSO_{4}. After filtration, the solution was dried under vacuum to yield an amber colored liquid. The product was purified using silica gel flash column chromatography, eluting first with methylene chloride/THF mixture (from 40:1 to 20:1 v/v), and then methylene chloride/methanol mixture (from 40:1 to 20:1 v/v). The fractions containing the product were combined and dried under vacuum. The product was obtained in the form of yellow needle-like crystals and a solid in 66% yield. GC (> 99% pure). GC/MS (EI) m/z (rel intensity): 156.1 (6.6), 141 (100), 99 (26.7), 83 (96), 59 (66). \(^{1}H\)-NMR (400MHz, CDCl_{3}) \(\delta\) 2.28 (d, 4H) and 1.24 (d, 12H). \(^{13}C\)-NMR (300MHz, CDCl_{3}) \(\delta\) 211.2, 55.5(d, 3.27Hz), 32.2.

4-Hydroxy-2,2,6,6-tetramethyl-1-piperidine-^{15}N (8) was synthesized by reducing 7 with sodium borohydride. Compound 7 (2 g, 12.8 mmole) was dissolved in 35 ml of ethanol/water mixture (50:50 v/v). The solution was dripped into a 10 ml solution of
NaBH₄ (0.242 g, 6.4 mmole) within a 6-minute period while keeping the temperature of the system at 0 °C using an ice/water mixture. The system was then allowed to warm up to room temperature. 19 hours later, salt (NaCl) was added to the reaction mixture and the product was extracted using 50 ml diethyl ether. The ether fraction was separated and dried over anhydrous potassium carbonate. After removal of the solvent under reduced pressure, a white solid was obtained at 94% yield.

1-Phenyl-3-o-tolyl-propan-2-one (oMeDBK, 9)²³, 1,3-di-o-tolyl-propan-2-one (α,α'-diMeDBK, 10)²⁴, 1,3-di-p-tolyl-propan-2-one (p,p'-diMeDBK, 11)²⁵, and 1,2-bis(2-methylphenyl)ethane (12)²⁴ were prepared by Dr. Xuegong Lei following published procedures.

2.4 Reference:


(20) Rauckman, E. J.; Rosen, G. M.; Abou-Donia, M. B. Synthetic Communications 1975, J, 409.


Chapter 3. Indirect Characterization of the Silicalite External Surface Area

Using EPR: Supramolecular Structure of oMeDBK@Silicalite Probed by Nitrooxides

3.1 Introduction

As discussed in Chapter 1, EPR is a very sensitive spectroscopic technique in the study of solid surface properties, and provides rich information about the details of adsorption in both their static and dynamic natures. This chapter focuses on the development of a particular EPR method in the study of silicalite external surface properties and the correlation of EPR parameters to the external surface area. In this particular method, the adsorption detail of a major adsorbate species, such as o-methyl dibenzylketone (oMeDBK) (Scheme 3.1), on the silicalite external surface was probed by the coadsorbed nitroxide probes.

\[
\text{Scheme 3.1} \quad \text{The structure of oMeDBK, the major adsorbate for the indirect EPR study.}
\]

3.1.1 Supramolecular Nature of the Adsorbate@Adsorbent System

It is convenient to visualize the adsorption phenomena if one regards the adsorbates (organic molecules, including oMeDBK and nitroxide derivatives) and adsorbents (zeolites, or particularly the zeolite's external surface as was studied in this research) as one supramolecular system denoted in the form adsorbate(s)@adsorbent, wherein the @ specifies a non-covalent interaction, such as van der Waals, hydrogen bonding, etc.\textsuperscript{1,2} The composition of the supramolecular system is made up by the
adsorbates and the adsorbents. The constitution of the system will be dependent on the specific manner and site of adsorption, the manner of interaction, and the mobility and dynamics of the adsorbate molecules.

On the scale of typical small organic molecules, which is about several angstroms, the zeolite's external surface is not of uniform structure. The external surface is comprised of pore openings and framework surface. The framework surface is the "solid" space between all the pore openings (Figure 3.1, Left). The pore openings and framework surface are two structurally distinct adsorption sites. While the framework surface is essentially a flat contact surface, the pore openings provide a concave structure, into which a part or all of the adsorbate molecules can intercalate if the size/shape of that site is suitable (Figure 3.1, Right). There is evidence suggesting that when this intercalation happens between adsorbate molecules and the zeolite pores that are complementary, i.e., very similar in size and shape, the non-specific dispersion interaction between the adsorbate molecule and the adsorbent can be enhanced due to maximized contact compared to the limited contact probability on the flat framework (Chapter 1). For example, nonpolar but highly polarizable n-alkane molecules (kinetic diameter = 4.3 Å) interact strongly with the ZSM-5/silicalite channel walls (diameter ≈ 5.5 Å).\textsuperscript{3-6} The nature of the interaction is almost entirely dispersion interactions, which are proportional to the polarizability of the adsorbates.\textsuperscript{7,8} Studies on the adsorption of p-xylene also suggest the role of specific interaction between the \(\pi\) electrons on the aromatic ring and the electric field gradients, such as those provided by Al\textsuperscript{3+} and/or lattice defects in the ZSM-5/silicalite network.\textsuperscript{9}
**Figure 3.1** Pore openings and framework surface on the external surface of silicalite crystals. Left: [010] surface of a crystal silicalite drawn in two dimensions. Right: (A) a one-dimensional representation of the pore openings and framework surface observed on the [010] surface. (B) adsorption of an adsorbate molecule on the pore opening with possible intercalation. (C) adsorption of an adsorbate molecule on the framework surface. The black filled circles represent the adsorbate molecules.

For adsorbate molecules that cannot enter the channels, intercalation leads to the fixing of the adsorbate molecules at the pore openings (Figure 3.1, Right B). Pore openings are the concave-shaped terminating sites of the crystals and are likely to possess more lattice defects (which provide electric field gradients) than does the framework surface. Moreover, it has been proposed, based on previous studies, that the pore openings have a higher concentration of silanol groups (Figure 3.2) than does the framework surface. The abundance of a polar silanol group not only contributes to dipole-dipole or dipole-induced dipole interaction, but has the potential of forming
hydrogen bonding with the appropriate adsorbate structures, such as ketones,\textsuperscript{12-14} and will therefore significantly increase the binding strength (Figure 3.2).

![Diagram](image)

**Figure 3.2** The silanol groups on the external surface of silicalite, preferentially residing on the pore opening. The possibility of forming hydrogen bonding between the silanol groups and the adsorbate molecules (e.g. ketone) is shown. The black filled circle represents an adsorbate molecule.

As a result of the external surface's structural heterogeneity on the angstrom scale, it would only be natural to expect that organic molecules adsorbed on these two different sites should lead to different supramolecular structures and properties. For example, if the two sites possess different affinity for the adsorbate molecules, there could be a preferential adsorption on the site that has a stronger affinity. If the affinity differences were large enough, one would be able to see stepwise adsorption phenomena by studying the loading dependence of certain EPR parameters. In addition to the affinity, the adsorbate might interact with two different sites via different forces, e.g., one could be through a specific interaction, like hydrogen bonding, while the other through a van der Waals interaction.

Aside from the nature of the binding sites and their respective strengths, one can expect certain probe molecules to interact with the surface in different orientations, so that the interaction with the adsorption site can be maximized. For example, if the probe molecule possesses a carbonyl or hydroxyl group, it might be the preferred moiety that
participates in the interaction with the surface through hydrogen bonding with surface silanol groups (Figure 3.2).

The mobility of the adsorbate molecules on different adsorption sites would be different too, depending on the binding strength and other factors, such as the number of sites occupied and the presence of co-adsorbates.

As expected from the analysis of the surface structures, and supported by various studies using a multitude of methods ($^2$H-NMR, Langmuir isotherm, EPR and photochemical product analysis),$^{15}$ the silicalite external surface can be adequately and conveniently described using a two-site model, with the pore openings having higher binding strength than does the framework surface. This two-site model will be used as the working paradigm in the analysis of the experimental results.

The difference in the two binding sites should be retrievable in the study of the adsorbed EPR probes by extracting various parameters from the spectra.

In order to study the external surface selectively, we need to find an EPR probe molecule that is too large to fit into the pores and enter the channels. TEMPO-based nitroxides (collectively called nitroxides, hereafter) meet this standard. Based on a bulky 2,2,6,6-tetramethylpiperidin-1-oxy structure (kinetic diameter = 11 Å), the nitroxides cannot enter the ZSM-5 channels, since they are larger than the pore openings (~ 5.5 Å).$^{16}$ When they are adsorbed onto the ZSM-5, nitroxides selectively populate only on the external surface and offer information about the local mobility, polarity and inter-probe distance and interactions at the particular binding sites in which nitroxide probes reside.
The loading, or concentration of the adsorbate molecules adsorbed on a solid adsorbent, can be described using the following two parameters: molality and coverage.

Molality, similar to the concept of molarity of a solute in solution, refers to the number of moles of adsorbate molecules per unit mass of adsorbent. One molal (abbreviated as 1 \( m \) following ACS guidelines\(^{17} \)) is the number of moles of adsorbate per kilogram of adsorbent. While molality is a very convenient parameter for carrying out the experiment, it is a bulk property and does not adequately provide the adsorption pattern on the molecular level.

Surface coverage is the parameter that describes the molecular detail of the loading concentration. Loadings of adsorbate with the same molality can produce completely different surface coverage depending on the surface area of the adsorbent per unit mass. If the surface area is large, the coverage could be significantly less than one monolayer (1 ML). If the surface area is small, the same molality can produce a monolayer or even multilayer.

The combination of the two parameters, molality and surface coverage, allow one to understand the concentration of adsorbates on a solid surface as both a bulk and molecular quantity.

3.1.2 Indirect versus Direct EPR Methods

There are two ways to acquire the structural information on the zeolite’s external surface using a nitroxide as an EPR probe: indirect and direct methods\(^{18} \). The indirect method is the topic of discussion in this chapter. The indirect method involves the adsorption of an organic species as the major adsorbate, which possesses all paired
electrons (EPR silent) and suitable molecular structure and size large enough to exclusively adsorb on the external surface. Nitroxide is added to the external surface as a co-adsorbate at very low loading (e.g. 2% ML) relative to the major adsorbate, and acts as essentially a spectator and reporter. The major adsorbate is chosen so that it interacts stronger than does the nitroxide with the zeolite external surface. When the amount of the major adsorbate species is varied, the interaction of the nitroxide probes with the zeolite’s external surface should be subject to competition for binding sites (Figure 3.3).

Accordingly, the EPR spectra of nitroxide should reflect the change in the supramolecular structure of adsorbate@zeolite’s external surface as a function of added major adsorbate.

![Diagram showing interaction of nitroxide and major adsorbate](image)

**Figure 3.3** Indirect EPR method for the analysis of silicalite’s external surface. The change in the supramolecular structure of the adsorbate@silicalite’s external surface system as a result of increasing loading of the major adsorbate (EPR silent), probed by a fixed low loading of TEMPO spin probes. At high loadings of the major adsorbate molecules, some TEMPO molecules can be displaced from the strong binding sites.

The other EPR method is a direct method. TEMPO is the sole adsorbate on the external surface of the zeolite. Different supramolecular structures on the ZSM-5 external
surface can be reached by varying the loading of a TEMPO derivative, and the structures and dynamics are readily deducible from the change in the EPR spectra (Figure 3.4). This direct method is the topic of discussion in Chapter 4.

![Diagram](image)

**Figure 3.4** Direct EPR method. The change in the supramolecular structure of the adsorbate@[silicalite external surface] as probed by increasing loading of the TEMPO spin probe.

In the indirect method, the major adsorbate needs to be of a particular structure so that it can interact specifically and differently with the two binding sites (the pore openings and the framework space), and provide a clear picture of change in the supramolecular structure at various loading stages. A proven candidate is \( \sigma \)-methyl dibenzylketone (oMeDBK) (Scheme 3.1),\(^{11}\) which possesses the following features: 1) size exclusion from the internal surface due to the presence of an \( \sigma \)-xylyl moiety on one side, which is bulky enough to keep oMeDBK exclusively on the external surface of ZSM-5 zeolites (Figure 3.5 A); 2) possible intercalation in the pore opening due to the presence of a tolyl moiety on the other side, which is just small enough to enter the pore openings and increase non-specific van der Waals interaction with the pore walls and the
interaction between the π-electrons and electric field gradient from the silanols at the pore openings (Figure 3.5 B); and 3) hydrogen bonding due to the presence of a carbonyl group in the middle, which is polar and has the potential of interacting through dipole-dipole or dipole/induced dipole, or even forming relatively strong hydrogen bonding to the silanol groups present, the latter generally having a high population at the pore openings (Figure 3.5 C). While the moieties that are actually operating at a certain instance depend on the orientation of the adsorbate on the external surface, all these structural properties potentially enable the oMeDBK molecules to act as a plug for the pore openings and have strong binding affinities for pore openings.

\[
\begin{align*}
\text{size exclusion} & \quad \text{intercalation} & \quad \text{hydrogen bonding} \\
\text{A} & \quad \text{B} & \quad \text{C}
\end{align*}
\]

**Figure 3.5** Possible binding mode of oMeDBK adsorbed on silicalite’s external surface. (A) exclusion of oMeDBK from the internal void due to the large o-xylyl moiety. (B) possible intercalation of tolyl moiety for enhanced interaction with the pore openings. (C) possible hydrogen bonding between the carbonyl group and the surface silanol groups that preferentially reside in, or in the vicinity of, the pore openings.

The framework surface is an essentially flat surface with a much lower silanol concentration as compared to the pore openings. Without the contribution from the intercalation and interactions with silanols, the framework surface will not appreciably adsorb oMeDBK until the pore openings are filled first.
3.1.3 Characterization of the External Surface Area From the EPR Parameters of the Supramolecular System

The ratio of the surface area (SA) of the pore openings to that of the framework surface on the [010] external surface is fixed by the crystal structure of ZSM-5 zeolites (SA = ca. 18 to 82) (Figure 3.1). The amount (molality) of adsorbate required to bring the adsorbate@ (zeolite external surface) into a particular supramolecular system should be a function of the absolute external surface area of the silicalite sample. Therefore, changes in the supramolecular structure adsorbate@silicalite as a function of the loading (molality) of the major adsorbate, as deduced from the change in the EPR spectra of the nitroxide reporter, should be translatable into the external surface area of a sample, provided that a suitable standard sample with known specific external surface area is available and characterized in the same manner.

To test the validity of the idea, i.e., the external surface area determination through the analysis of supramolecular structural change, it would be preferable to have access to a series of zeolite crystals, each of which has a monodisperse distribution of a distinct crystal size, but different specific external surface area (surface area per unit mass of silicalite sample). If the idea were valid, the loading (molality) for reaching a certain supramolecular structure should be linearly proportional to the specific external surface area of the sample as determined by other techniques, e.g., geometrical analysis using SEM.

However, certain requirements have to be met in order to achieve this linearity, if one wishes to compare the specific external surface area measured using EPR and a technique based on a totally different mechanism. For example, when Scanning Electron
Microscopy (SEM) is used for comparison with EPR, appropriate efforts need to be taken to maintain uniformity of the external surfaces across those samples. Silicalite crystals can possess grooves with sizes in the tens of nanometers on the external surface. SEM is either not adequate in resolving or quantifying these small structures. When these structures are present, the linear dimension of the bulk crystal measured from SEM images no longer provides adequate and accurate information for the determination of the specific external surface area. The population of these nanometer-scale structures is easily increased by post-synthesis alkaline treatment.\textsuperscript{20,21} a process typically employed in the MFI zeolite purification procedure for the complete removal of unreacted silica gel. To minimize the formation of these nanometer-scaled grooves, unreacted silica gel in all the silicalite samples synthesized for this study was removed using a combination of repeated sonication and centrifugation, rather than alkaline treatment. The silica gel was dissolved in water and subsequently removed as part of the aqueous/colloidal layer.

As discussed in Chapter 1, silicalite is chosen instead of aluminum containing ZSM-5 zeolites to avoid the complications of variable concentrations of Al\textsuperscript{3+} strong binding sites on the external surface.

3.2 Research Objective

The major research objective described in this chapter is the study of external surface properties of silicalites using the indirect EPR method. The adsorption detail, i.e. the supramolecular structure and dynamics of oMeDBK is monitored by observing the change in the EPR spectra of TEMPO as a function of oMeDBK loading. A set of suitable quantifiable supramolecular structures and parameters will be studied and
correlated to the external surface area and adsorption sites of the adsorbent silicalite sample.

3.3 Experimental Methods

3.3.1 Preparation Method of the Solid Samples

The loading of oMeDBK and TEMPO derivatives was carried out using the following steps.

1. The calcinated silicalite samples were activated at 500 °C for at least one hour in an aerated furnace, and then placed in a desiccator and allowed to cool to room temperature before use. It has been found by gravimetric analysis that the residual water in a ZSM-5/silicalite sample can be removed at 500 °C typically within an hour.

2. Stock solutions of each adsorbate in isooctane were prepared. Isooctane (2,2,4-trimethyl-pentane) (Scheme 3.2) was chosen as the preferred solvent for the sample preparation on silicalites due to the beneficial properties described as follows.\textsuperscript{22} Isooctane’s kinetic diameter is larger than the ZSM-5/silicalite pore openings and thus isooctane does not enter the zeolite’s internal void.\textsuperscript{23} The combination of exclusion from the internal void and isooctane’s low boiling point at 99.2 °C makes it easy to remove by moderate vacuum after the adsorbates are loaded. Isooctane is a saturated hydrocarbon with very low polarity (polarity index = 0.1 on the Snyder scale as compared to \textit{n}-hexane at 0.1, toluene at 2.4, \textit{o}-xylene at 2.5, and methyl ethyl ketone at 4.7),\textsuperscript{24} and consequently is not expected to significantly compete for binding sites with the desired adsorbates.
2,2,4-Trimethyl-pentane
(Isooctane)

Scheme 3.2  Structure of iso-octane.

3. Adsorbate molecules were loaded onto the silicalite's external surface by mixing stock solutions of an appropriate amount with dry silicalite samples. In an airtight container the slurry was stirred magnetically until the adsorption reached equilibrium, i.e., the ratio of adsorbed fraction versus the fraction in solution no longer changed over time. The equilibrium was typically achieved in less than 10 hours for the adsorbates studied in this thesis. The progress toward equilibrium was followed by checking the concentration of adsorbates in the supernatant using UV or GC after centrifugation.

4. The solvent was removed to prepare loaded dry (solvent-free) samples.

The solvent was removed under a gentle stream of an argon flow. The oMeDBK and TEMPO molecules were therefore forced to deposit onto the silicalite's external surface. The dry silicalite samples thus loaded with adsorbate molecules were further dried and degassed at moderate vacuum (ca. $5 \times 10^{-4}$ Torr) in a quartz tube, which can be sealed using a stopcock and has a side arm that can fit into a typical CW-EPR cavity.

3.3.2 Preparation Method of Liquid Samples

The presence of oxygen in the solvent will significantly broaden the EPR spectrum of nitroxide in a solution due to enhanced paramagnetic relaxation. Therefore, appropriate deoxygenation procedure needs to be performed prior to the EPR measurements. Such procedures can include the substitution of oxygen by a non-
paramagnetic gas, e.g. argon, through bubbling, or a more efficient freeze-pump-thaw procedure that was employed in this thesis.

Liquid samples were prepared by dissolving the appropriate amount of nitroxide probe in the desired amount of solvent, thoroughly deoxygenating the solution at least four times using a freeze-pump-thaw technique with liquid nitrogen.

3.3.3 Preparation Method of the Liquid Sample Using oMeDBK as Solvent

If a solution of nitroxide in oMeDBK is required for EPR measurements, a stock solution of nitroxide in isoctane was first prepared. The appropriate amount of stock solution was then added to the liquid oMeDBK with a volume ratio no more than 1 to 20.

3.3.4 EPR Spectrum Measurement

The EPR spectra were taken by default at room temperature (approximately 24 °C) using the lowest possible microwave power (≈ 2.01 mW at 20 dB) and with modulation frequency at 100 kHz and modulation amplitude smaller than the narrowest line width in the spectra except for the proton hyperfine lines.

Variable-temperature EPR spectra from 298 K to 100 K were measured using a liquid nitrogen variable temperature system. EPR spectra at 77 K were measured by placing the sample tube in a quartz liquid nitrogen dewar, the latter filled with liquid nitrogen and directly inserted into the EPR cavity.
3.3.5 Computer-assisted EPR Spectrum Simulation

Computer-assisted simulation for the slow motion EPR spectra was performed using a program named NLSL (Nonlinear Least-Squares for Slow Motion EPR Spectra) Version 1.6 by Budil (Northwestern University). The program is based on a well-established procedure by Freed and coworkers.25,26 The following parameters were used in the simulation of samples with nitroxide as the sole adsorbate based on literature values with modifications based on experimental measurements.11

1. $g_{ii}$ (components of the $g$ tensor for the magnetic field-electron spin coupling): $g_{xx} = 2.009$, $g_{yy} = 2.006$, $g_{zz} = 2.002$.

2. $A_{ii}$ (components of the $A$ tensor for the electron spin-nuclear spin coupling): $A_{xx} = 6$ G, $A_{yy} = 7$ G, $A_{zz}$, the rigid-motion $^{14}$N anisotropic hyperfine coupling constant along the $z$ axis, is an indication of polarity in the local environment and also is related to the structure of the nitroxide probe. Based on the estimation from low temperature ($\sim$100 K) EPR experiments, the $A_{zz}$ values for TEMPO, 4-oxo-TEMPO, 4-hydroxy-TEMPO, and DPT are approximately 38.0 G, 36.0 G, 37.5 G, and 37.5 G, respectively.

3. $\tau_c$ (rotational correlation time): $\tau_c$ is calculated typically assuming a non-Brownian jump motion especially in the case where Brownian motion assumption does not produce a satisfactory fit with the experimental results, and in the case where strong binding is expected between a nitroxide possessing very polar groups (such as carbonyl, hydroxyl etc) and surface strong specific binding sites, such as silanols.25

4. $\Delta H_D$ (dipolar broadening factor): The dipolar broadening value can be obtained from the result of the computer-assisted simulation. The $\Delta H_D$ value (in G)
allows the calculation of the mean distance between the nitroxide probe molecules in slow motion and in the absence of exchange interaction, $d$ (in Å) via the equation

$$\Delta H_D = 3 \times 10^4 \left( \frac{1}{d} \right)^3$$  \hspace{1cm} (3.1)

$\Delta H_D$ is only evaluated for the spectra taken at room temperature and its value is obtained by subtracting an intrinsic line width (typically 0.5 G) from the line width parameter $W1$, whose value is directly determined from the computer-assisted simulation.

3.4 Results and Discussions

3.4.1 EPR Parameters of Dilute Isooctane Solution of Nitroxides

The structure of the four TEMPO-based nitroxides studied in this chapter, TEMPO, 4-oxo-TEMPO, 4-hydro-TEMPO and 2,2,6,6-Tetramethyl-4-[(diphenylacetyl)oxy]-1-piperidinyl-oxy (abbreviated as DPT) are shown in Scheme 3.3.

![Scheme 3.3 Structures of TEMPO-based nitroxides for the analysis of silicalite’s external surface by indirect EPR methods.](image)

In a non-viscous solution at low concentration (less than 3 mM), regular nitroxides display a three-line pattern in the EPR spectra, such as 4-oxo-TEMPO (Figure 3.6).
4-oxo-TEMPO
in isooctane, 0.25 mM

\[ M_I = 1 \]

\[ A_{\text{iso}} = 14.2 \text{ G} \]

\[ A_{\text{iso}} = 14.2 \text{ G} \]

\[ M_I = 1 \]

\[ A_{\text{iso}} = 14.2 \text{ G} \]

Figure 3.6  EPR spectrum of 4-oxo-TEMPO in isooctane (0.25 mM). Modulation amplitude is 0.3 G. \(^{14}\)N isotropic hyperfine coupling constant is \(A_{\text{iso}} = 14.2 \text{ G}\). Satellite peaks from the hyperfine interaction with \(^{13}\)C (\(A = 5.03 \text{ G}\)) and \(^{15}\)N (\(A = 20.0 \text{ G}\)) are indicated by dashed arrows in the expanded view (bottom left). The low field line (\(M_I = 1\)) was also shown in an expanded view (top right).

As discussed in Chapter 1, the three-line pattern is due to the strong coupling of the \(^{14}\)N nucleus (nuclear spin quantum number \(I = 1\)) with the unpaired electron. The lines are sharp and of essentially equal height and width, because the rapid rotational motion (rotational correlation time is approximately \(5.0 \times 10^{-12} \text{ s}\) using Equation 1.15) in the isotropic medium leads to complete averaging of the spectral anisotropy (g-factor and hyperfine coupling from interaction with \(^{14}\)N nucleus) of the nitroxide spin labels. The hyperfine coupling with \(^{13}\)C (1.10% natural abundance, \(I = 1/2\)) (\(A_{\text{iso}} = 5.03 \text{ G}\)) and \(^{15}\)N (0.4% natural abundance, \(I = 1/2\)) (\(A_{\text{iso}} = 20.0 \text{ G}\)) were also resolved and shown in the expanded view (Figure 3.6).

As discussed in Chapter 1, the isotropic hyperfine coupling constant \(A_{\text{iso}}\) (as well as the g-factor) is an indicator of solvent polarity.\(^{27}\) The value 14.2 G for 4-oxo-TEMPO
measured in isooctane (polarity index = 0.1) is similar to that in CCl₄ (14.5 G, polarity index = 1.7), and significantly lower than that from water (16.1 G, polarity index = 10.2).²⁴,²⁸,²⁹

As a comparison, the EPR spectra of TEMPO, 4-hydroxy-TEMPO and DPT solution are shown in Figure 3.7 (TEMPO), Figure 3.8 (4-hydroxy-TEMPO) and Figure 3.9 (DPT).

TEMPO
in isooctane, 0.25 mM

\[ A_{\text{iso}} = 15.2 \text{ G} \]

\[ M_I = 1 \]

\[ 3450 \quad 3460 \quad 3470 \quad 3480 \quad 3490 \]

\[ \text{Magnetic Field (G)} \]

\[ 3452 \quad 3454 \quad 3456 \quad 3458 \quad 3460 \]

\[ \text{Magnetic Field (G)} \]

**Figure 3.7** EPR spectra of TEMPO in a dilute isooctane solution (0.25 mM). Modulation amplitude is 0.3 G. \(^{14}\text{N}\) isotropic hyperfine coupling constant is \(A_{\text{iso}} = 15.2 \text{ G}\). The low field line (\(M_I = 1\)) was shown in the expanded view (right).
Figure 3.8  EPR spectra of 4-hydroxy-TEMPO in a dilute isoctane solution (0.25 mM). Modulation amplitude is 0.3 G. $^{14}$N isotropic hyperfine coupling constant is $A_{iso} = 15.2$ G. The low field line ($M_I = 1$) was expanded to show the superhyperfine coupling from protons (right).

Figure 3.9  EPR spectrum of a TEMPO based nitrooxide (DPT) in an isoctane solution (0.25 mM). Modulation amplitude is 0.3 G. The spectrum displays a three-line pattern with narrow line width. The isotropic hyperfine coupling from $^{14}$N nucleus is $A_{iso} = 15.2$ G. The low field line ($M_I = 1$) was expanded to show the superhyperfine coupling from protons (right).
The larger $^{14}$N hyperfine coupling constants $A_{iso}$ (15.2 G) for TEMPO (Figure 3.7) 4-hydroxy-TEMPO (Figure 3.8) and DPT (Figure 3.9) than that (14.2 G) for 4-oxo-TEMPO (Figure 3.6) are inherent to the nitrooxide probes due to the different molecular conformations as a result of different substituents on the 4-position of the nitrooxide probes.$^{30}$ The different $A_{iso}$ values indicate the same polarity in the vicinity of the probe in the isoocetane solution.

The absence of resolvable peaks for $^{13}$C and $^{15}$N in the case of TEMPO, 4-hydroxy-TEMPO and DPT can be explained on the basis of the inhomogeneous line broadening as a result of the superhyperfine couplings interactions of the electron spin with the protons (Scheme 3.4).$^{30,21}$

![Scheme 3.4](image)

**Scheme 3.4** Proton hyperfine coupling constants for TEMPO-based nitroxides with different substituents on the 4-position.$^{30}$ Contributions from the $\alpha$, $\beta$, $\gamma$ protons are listed.

The magnitudes of the superhyperfine couplings from the 12 methyl protons and the 4 $\beta$ methylene protons are larger for TEMPO (Scheme 3.4, A), 4-hydroxy-TEMPO (Scheme 3.4, C) and its ester (Scheme 3.4, D) than for 4-oxo-TEMPO (Scheme 3.4, B). Compared to the other three nitroxides, 4-oxo-TEMPO does not possess any protons on the $\gamma$-position, and therefore is exempt from the further spectral splitting from coupling
with proton(s) on the γ-position. When the superhyperfine coupling lines are not fully resolved, the result is an inhomogeneously broadened spectrum, which might conceal the $^{13}$C and $^{15}$N hyperfine lines in the wings of the broad lines.$^{30,31}$

It is to be noted that if the lines due to proton hyperfine couplings are to be fully resolved, the spectra need to be measured under more stringent conditions, e.g., using lower modulation amplitude and using deuterated solvents. Since the proton hyperfine coupling phenomenon is not the focus of this thesis research, it is not further elaborated and interested readers are referred to the literature for more information.$^{28-30}$

### 3.4.2 External Surface Properties of a Crystalline Silicalite Sample:

#### Polarity, Mobility and Competitive Adsorption.

When nitroxides are adsorbed on a solid surface, important information on the polarity of the local environment at the adsorption sites, mobility of the nitroxides and other adsorption details can be revealed by examining their EPR spectra.

The nitroxides can be adsorbed on the surface alone, or with some co-adsorbates. When the latter is carried out, the competitive adsorption between nitroxides and the co-adsorbates for adsorption sites can be studied by examining the nitroxide EPR spectra.

When the molecular structures of the nitroxides and/or the co-adsorbates are varied, the influence of molecular structure (e.g., substituents) on the details of adsorption (e.g., adsorption strength) can be studied by the examination of nitroxide EPR spectra.

When silicalites are used as the solid adsorbents, all these EPR methods can potentially reveal the structure and properties of silicalite's external surface, and the supramolecular structure and dynamics of adsorbate@(silicalite external surface) systems.
3.4.2.1 Adsorption of Nitrooxides Without Co-Adsorbate

Upon adsorption on the silicalite's external surface, the sharp three-line EPR pattern (Figure 3.6 to 3.9) of the nitrooxide is turned into a different line shape depending on the surface coverage by the nitrooxides.

The seven silicalite samples with different crystal sizes and different specific external surface area were prepared and characterized as detailed in Chapter 2. The sample with batch number ZL5157 is selected as a representative, and its external surface area is 24 m$^2$·g$^{-1}$, the highest of all seven samples. The high surface area will lead to a high signal to noise ratio in the EPR measurements for the same surface coverage by the nitrooxide.

At low surface coverage, the nitrooxide molecules are separated from each other and the corresponding spectrum is a broad three-line pattern due to anisotropic broadening and dipolar interaction (Figure 3.10). In this Chapter, the focus is on the low nitrooxide surface coverage situation, and the situations at intermediate and high surface coverages by the nitrooxide will be discussed in Chapter 4.

The loading of 4-oxo-TEMPO in Figure 3.10 is 2 mm, i.e., 2 x 10$^{-3}$ mole of adsorbate molecules per kilogram of adsorbent.
Figure 3.10  EPR spectrum of 4-oxo-TEMPO on silicalite ZL5157 at low loading (2 mm). Solid line is the experimental spectrum and dashed line is from computer-assisted simulation. $A_{zz'} = 33.4$ G. The rotational correlation time ($\tau_\rho$) was determined to be $1.27 \times 10^{-9}$ s from computer-assisted simulations.

Treating a 4-oxo-TEMPO molecule as a sphere with a diameter at ca. 7 Å, the cross-sectional area is ca. 40 Å$^2$. Since the external surface area of silicalite ZL5157 has been determined to be ca. 24 m$^2$.g$^{-1}$ geometrically using SEM, the external surface coverage by 4-oxo-TEMPO at 2 mm loading is calculated to be approximately 0.02 ML. Because the strong binding site (pore openings) accounts for approximately 18% of the total external surface area, all the 4-oxo-TEMPO molecules in the spectrum shown in Figure 3.9, should be adsorbed at the pore openings at 2 mm loading (approximately 0.02 ML).

It can be readily seen that the EPR spectral pattern is qualitatively very similar to the reported spectra of nitroxides adsorbed on silica gel powders$^{32}$ or silicalite powders
and siliceous ZSM-5 zeolites. The asymmetric spectrum shown in Figure 3.10 can also be obtained by grinding up single crystals of nitroxides, or rapidly freezing a solution of paramagnetic species and therefore are referred to as the powder spectrum, the rigid glass spectrum or the polycrystalline spectrum. In our studies, since each solid sample used in the EPR measurement contains a large number of crystals rather than a single crystal, it should be referred to as the polycrystalline spectrum.

As discussed in Chapter 1, the \( A_{zz'} \) value measured from Figure 3.9 is affected by both environmental polarity and rotational mobility of the probe molecules. When one of the two variables is fixed, increasing environmental polarity or decreasing rotational mobility leads to a higher value for \( A_{zz'} \). The rotational motion can be reduced by lowering the temperature of the sample. When the temperature is low enough that the \( A_{zz'} \) value does not change with decreasing temperature, it equals \( A_{zz} \), the nitrogen hyperfine coupling tensor along the \( z \) axis. \( A_{zz} \) is affected by the nitroxide structure and when the same nitroxide is used, \( A_{zz} \) is a function of polarity only.

To test the possibility of using the temperature dependence of the \( A_{zz'} \) value to study the adsorption detail, each of the four nitroxides (Scheme 3.3) was adsorbed on the silicalite surface at low surface coverage and their variable temperature EPR spectra were measured (Figure 3.11).
The $A_{zz'}$ value measured at various temperatures for the nitroxide@silicalite system using nitroxides of different structures and silicalite ZL5157 at low surface coverage (~ 0.02 ML for TEMPO and 4-oxo-TEMPO, ~ 0.05 ML for 4-hydroxy-TEMPO and ~ 0.10 ML for DPT).

The polarity of the surface bindings at this coverage can be examined based on the $A_{zz'}$ value at the lowest temperature. Even though the $A_{zz'}$ value has not reached a plateau at 100 K, its value for TEMPO at 100 K (37.4 G) is significantly higher than the $A_{zz}$ value measured in a glassy matrix of toluene (34.6 G), and close to the $A_{zz}$ value measured in polar aqueous glycerol (37.8 G) and the $A_{zz}$ value measured on a silanol-abundant silica gel surface (38.0 G) using the same nitroxide.\(^{32,34}\) This high $A_{zz'}$ value at low temperature suggests that surface binding sites accessed by the probe molecules at this low surface coverage are very polar, and probably possess silanol groups that are capable of interacting with the probe molecules via hydrogen bonding. It is to be noted that $A_{zz}$ values were also measured at 77 K using a liquid nitrogen dewar. It was expected
that the lower temperature (77 K compared to 100 K) should yield a larger $A_{zz}$ value. However, comparable to even smaller values were observed at 77 K (37.1 G, 35.8 G, 36.6 G and 36.8 G at 77 K compared to 37.4 G, 35.7 G, 36.7 G and 37.0 G at 100 K for TEMPO, 4-oxo-TEMPO, 4-hydroxy-TEMPO and DPT, respectively). The discrepancy between the expected and measured value at 77 K is probably due to the use of different cooling method compared to the measurements conducted at 100 K and higher temperature. The use of a liquid nitrogen dewar leads to an unsteady magnetic field due to the constant evaporation of liquid nitrogen in the form of bubbles and the formation of ice in the sample holder, and therefore the measurements might be less reliable.

Just as $A_{iso}$ is a function of environmental polarity in a nonviscous solvent, $A_{zz}$ is a function of environmental polarity in the frozen state. Since the three nitroxides, TEMPO, 4-hydroxy-TEMPO, and DPT possess the same $A_{iso}$ value when the environmental polarity is the same (Figure 3.7, 3.8, and 3.9), it would be expected that they possess similar $A_{zz'}$ at very low temperature (when the motional averaging is eliminated and $A_{zz'}$ approaches $A_{zz}$) if they are adsorbing on the silicalite surface in the exact same manner. An examination of Figure 3.11 reveals that at the lowest temperature employed in the measurements ($101 \pm 1$ K), TEMPO possesses an $A_{zz'}$ value (37.36 G) that is significantly larger than that for 4-hydroxy-TEMPO (36.72 G) and DPT (37.00 G). Estimated from the trend of the $A_{zz'}$ as a function of temperature, this difference will become larger at an even lower temperature. 4-Hydroxy-TEMPO and DPT have essentially overlapping $A_{zz'}$-Temperature lines. 4-oxo-TEMPO, once shifted vertically for about 1 G, can also substantially overlap with the 4-hydroxy-TEMPO and DPT lines.
This vertical shift is attributed to the inherent difference in the $A_{iso}$ values of the three nitroxides (Figure 3.6, 3.8, and 3.9) regardless of their environmental polarity.

Therefore, the environmental polarity in the vicinity of the N-O moiety as detected using the four nitroxides with different molecular structures can be categorized into two groups, TEMPO and the other three nitroxides. When TEMPO is used, the environment in the vicinity of the N-O moiety is more polar as compared to the cases when the other three nitroxides are used.

The physical meaning of the different polarity detected by the four nitroxide probes with different molecules can be easily understood on the basis of the different mode of interaction with the surface silanol groups, as suggested in the literature, when silica gel and alumina were used as adsorbent.\textsuperscript{32,35} TEMPO has only one polar moiety, i.e., the N-O that can donate electrons and form hydrogen bonding with surface silanol groups. Therefore, when TEMPO molecules are adsorbed on the silicalite external surface’s strong binding sites, the molecules adsorb in such a manner that N-O interacts with the silanol groups (Figure 3.12, A). Consequently, a higher environmental polarity is reported. When the other three nitroxides (with carbonyl, hydroxyl or ester linkage) are used, the polar moieties on the 4-position have a stronger electron donating capability than does the N-O moiety, and they form stronger hydrogen bonding with the surface silanol groups. On the surfaces that possess a high concentration of strong binding sites, such as Al\textsuperscript{3+} on a alumina surface or silanols on silica gel, the nitroxide probes with polar groups on the 4-position can lie flat on the surface and take advantage of a strong interaction at both the N-O position and the 4-position with the surface’s strong binding sites. This two-ended strong interaction does not take place on the silicalite’s external
surface as suggested by the low polarity detected by nitroxides such as 4-oxo-TEMPO, and is probably due to the low concentration of strong binding sites or conformational constraints. On the silicalite surface, the nitroxide molecules adsorb in such a manner that the hydrogen bonding is formed between the silanol and the carbonyl, hydroxyl, or ester linkage on the 4-position of the nitroxide (Figure 3.12, B, C and D). Since the N-O is not directly interacting with the surface silanol group, a lower environmental polarity is reported.

![Figure 3.12](image) Adsorption mode of the nitroxide probes on the silicalite external surface’s strong binding sites. Adsorption takes place in the most energetically favored manner. Nitroxide EPR spectra reveal different environmental polarity depending on the specific adsorption mode.

The rotational mobility of the nitroxide probes is also dependent on the structure of the nitroxide, in addition to the temperature (lower mobility at lower temperature).

Assuming a constant surface polarity (a constant $A_{zz}$ value) for the nitroxide@silicalite system in the temperature range from 293 K to 100 K, the change in
A \tau_c^2 \text{ value can be attributed to the change in rotational mobility (Equation 1.16). The rotation correlation times calculated from the computer-assisted simulation are shown in Table 3.1.}

<table>
<thead>
<tr>
<th></th>
<th>\tau_c (293 K) (s)</th>
<th>\tau_c (100 K) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEMPO</td>
<td>4.79 x 10^{-9}</td>
<td>2.40 x 10^{-8}</td>
</tr>
<tr>
<td>4-Oxo-TEMPO</td>
<td>1.17 x 10^{-8}</td>
<td>1.12 x 10^{-8}</td>
</tr>
<tr>
<td>4-Hydroxy-TEMPO</td>
<td>8.91 x 10^{-9}</td>
<td>2.57 x 10^{-8} (a)</td>
</tr>
<tr>
<td>DPT</td>
<td>1.10 x 10^{-8}</td>
<td>4.26 x 10^{-8} (b)</td>
</tr>
</tbody>
</table>

**Table 3.1** The rotational correlation time, \( \tau_c \), of different nitroxides adsorbed on silicalite ZL5157, calculated for the two extreme temperature conditions, 293 K and 100 K. (a): measured at 102 K. (b): measured at 101 K.

At 100 K, all four nitroxides show similar rotational mobility on the silicalite’s surface. At 293 K, TEMPO shows the highest mobility, approaching the range of fast motion (< 10^{-9} s). The higher rotational mobility of TEMPO at high 293 K is probably due to the weaker binding between the N-O and the surface silanol group, compared to the stronger binding between the carbonyl, hydroxyl or ester linkage at 4-position of the nitroxides and the surface silanol groups.

3.4.2.2 Adsorption of Nitroxides with Co-Adsorbed oMeDBK

When oMeDBK is added to the samples of nitroxide@silicalite, the EPR spectrum of the nitroxide changes as a function of the oMeDBK. Nitroxide serves as a reporter of the adsorption details of oMeDBK on the external surface.

At low surface coverage of oMeDBK, the 4-oxo-TEMPO spectrum (Figure 3.13) resembles that of the oMeDBK-free samples (Figure 3.10), which is characterized by a
rotational correlation time in the slow motion range, indicating a strong binding to the adsorption site. With increased loading of oMeDBK, sharp lines corresponding to the isotropic nitrogen hyperfine coupling arise (Figure 3.13). At high loadings, oMeDBK competes with the 4-oxo-TEMPO molecules for strong binding sites (pore openings) and leads to the displacement of some of the 4-oxo-TEMPO to the weaker binding site (framework surface), where the nitroxide can have a fast tumbling rate with a rotational correlation time in the fast motion range. In the experiment shown in Figure 3.13, the critical loading range of oMeDBK for the onset of the nitroxide’s fast motion is between 119 and 149 millimolal.

In order to exclude the possibility of significant loss of adsorbate molecules under vacuum when the samples were dried and deoxygenated for EPR analysis, which could lead to a misinterpretation of the results, a series of spectra were taken at various vacuum levels, from no deoxygenation and no further degassing after drying with argon flow to a low pressure of $5 \times 10^{-5}$ Torr. The fast motion component always appears at the same range of loading, signifying that the vacuum level involved in the drying and deoxygenation procedure does not lead to distorted results from significant loss of adsorbate molecules. Deoxygenating the samples by vacuum to a certain level is desirable because it removes the line broadening effects by oxygen paramagnetism.
Figure 3.13  EPR spectra of 4-oxo-TEMPO of fixed loading with varying loading of added oMeDBK. The increase in oMeDBK loading (left side of the figure) leads to the onset and growth of isotropic sharp lines (indicated by arrows) in addition to the anisotropic broad lines. The isotropic hyperfine coupling constant of the emerging narrow lines remain constant with increasing oMeDBK loading (right).

To facilitate the quantitative understanding of the change in the adsorption detail on a molecular scale in the results presented in Figure 3.13, the amounts of oMeDBK required to fill the pore openings of the silicalite and form a monolayer on the silicalite's external surface need to be assessed.
From the unit cell structure of silicalites, it was determined that there is one pore opening per 140 Å² external surface.²⁸ For silicalite ZL5157 (external surface area 24 m²·g⁻¹), it will translate into 1.7 x 10¹⁹ pore openings, or 2.8 x 10⁻⁵ mole of pore openings per gram of crystals. Each pore opening has a cross-sectional area of 24 Å². Each oMeDBK molecule would cover a surface of approximately 100 Å², if oMeDBK were lying completely flat on the surface.²⁸ Assuming each pore opening contains one oMeDBK molecule, the loading of oMeDBK for a complete coverage of pore openings will be approximately 28 mm.

The orientation of oMeDBK molecules affects the loading required for monolayer coverage on the solid surface. Based on the two extreme possible orientations for the binding of oMeDBK on silicalite’s external surface examined by Li,²⁸ the loading of oMeDBK required to reach monolayer adsorption on silicalite ZL5157 is determined to be 40 to 120 mm.

A comparison of the loading dependent EPR results presented in Figure 3.13 and the calculated loading of oMeDBK for total coverage of the pore opening and monolayer on the external surface reveals the detail of the competitive adsorption on the molecular scale (Figure 3.14).
Figure 3.14  Molecular detail of adsorption on the external surface of silicalite and corresponding EPR spectra. A: low loading of nitroxide leads to the adsorption on the strong binding sites (pore openings) only and the EPR spectrum is characteristic of slow motion. B: coadsorbed oMeDBK favors the strong binding sites and up to a certain loading, does not disturb the nitroxide probe molecules on strong binding sites. C: At about monolayer coverage, oMeDBK competes with nitroxide for strong binding sites and some nitroxide probe molecules are displaced from strong binding sites. Correspondingly a fast motion component appears in the EPR spectrum (arrows).

The percentage of nitroxide molecules at fast motion at any oMeDBK loading can be calculated using the computer-assisted simulations (Figure 3.15). Separate EPR spectra, corresponding to the nitroxide molecules undergoing slow motion and fast motion respectively were generated in the simulation. The experimental EPR spectra with the two components were then reconstructed by adding the two kinds of EPR spectra at different ratios. When a good fit is found between the computer generated composite spectrum and the original experimental spectrum, the percentage of the nitroxide molecules undergoing fast motion can be calculated easily from the ratio of double integral values for the two computer generated spectra, which represent fast motion and slow motion, respectively.\textsuperscript{11}
Figure 3.15 Percentage of nitroxide molecules in fast motion as a function of oMeDBK loading. The lines showing the trend are not from data fitting and are for illustration only.

The existence of a critical oMeDBK loading range can be readily appreciated from the examination of Figure 3.15. Below the oMeDBK loading of 119 mm, essentially all nitroxide molecules are undergoing slow motion. Beyond the oMeDBK loading of 119 mm and within the range studied, the percentage of nitroxide molecules in fast motion is approximately proportional to the oMeDBK loading.

To further investigate the environment around 4-oxo-TEMPO@silicalite in the fast motion regime, an EPR spectrum of 4-oxo-TEMPO dissolved in liquid oMeDBK at room temperature was measured (Figure 3.16).
Figure 3.16  EPR spectra of 4-oxo-TEMPO in liquid oMeDBK (0.29 mM) at room temperature (deoxygenated). $A_{\text{iso}} = 14.6 \text{ G}$, $\tau_c = 1.1 \times 10^{-10}$ s.

The $A_{\text{iso}}$ value of 4-oxo-TEMPO in liquid oMeDBK is very close to that of the component undergoing fast motion on the silicalite samples co-loaded with oMeDBK (Figure 3.13, right). This suggests the possibility that TEMPO molecules in slow motion are solvated or surrounded by the oMeDBK molecules, as expected from the high surface coverage (roughly monolayer) when the fast motion component appears.

3.4.2.3  Adsorption of Nitroxides of Different Structures with Co-Adsorbed oMeDBK

To examine the influence of the nitroxide structure on the EPR spectra, DPT (Figure 3.17) and 4-hydroxy-TEMPO (Figure 3.18) are used instead of 4-oxo-TEMPO.
TEMPO was not used in the quantitative experiment on silicalite because of TEMPO's high volatility especially under moderate vacuum (\( \sim 10^{-5} \) Torr).

DPT was used to add the phenyl groups into the structure of the nitroxide molecule in order to explore the influence of possible intercalation of one of the phenyl groups into the pore opening on adsorption strength (Figure 3.5, B). For DPT, it can be seen that the spectra follow the same trend as was seen in the case using 4-oxo-TEMPO (Figure 3.13) and the same range of oMeDBK (119 to 149 mm) loading is required to reach the onset of the fast motion. The similarity in the required oMeDBK loading suggests that 4-oxo-TEMPO and DPT have a similar binding strength at the strong binding sites. The slightly larger isotropic \(^{14}\)N hyperfine coupling constants for DPT than those for 4-oxo-TEMPO are due to the structural difference as was seen in the isoctane solution (Figure 3.6 and 3.9).

Therefore, the phenyl groups on the DPT molecules do not provide enhanced interaction with the silicalite pore openings to any noticeable extent for the probe molecules studied.
Figure 3.17  EPR spectra of DPT of fixed loading with varying amounts of oMeDBK. The onset of the fast motion component is indicated by the arrows.
Figure 3.18  EPR spectra of 4-hydroxy-TEMPO of fixed loading with varying amounts of oMeDBK. The onset of the fast motion component is indicated by the arrows. The oMeDBK loading required for the onset of the fast motion (149 to 179 mm) is slightly larger than that obtained using 4-oxo-TEMPO.

4-Hydroxy-TEMPO is chosen due to the presence of a highly polar –HO group, which is capable of forming hydrogen bonding with appropriate structures in addition to binding possibilities through dipole-dipole and dipole-induced dipole interactions. When 4-hydroxy-TEMPO is used as the EPR spin probe, significant differences can be seen compared to 4-oxo-TEMPO (Figure 3.13) and DPT (Figure 3.17). The loading of oMeDBK required for the onset of the fast motion is between 149 to 178 mm, slightly higher than the loading obtained from experiments using 4-oxo-TEMPO and DPT (both
between 119 and 149 mm). More significantly, the percentage of the fast motion component is much smaller for the 4-hydroxy-TEMPO probed system compared to 4-oxo-TEMPO and DPT, at any high oMeDBK loading. These differences suggest that the –OH group provides significant enhancement in the binding strength of 4-hydroxy-TEMPO on the strong binding sites of the silicalite’s external surface (pore openings).

The nature of the enhanced interaction is probably due to the hydrogen bonding between the –OH group of the 4-hydroxy-TEMPO and silanol groups that are potentially present on the external surface, especially in the pore openings of silicalite.

3.4.2.4 Adsorption of Nitroxide with Co-Adsorbates of Different Structures.

To evaluate the influence of the co-adsorbate structure on the adsorption details on the silicalite’s external surface, a few organic molecules with structures similar to oMeDBK were used in place of oMeDBK; each was chosen based on a particular size shape selectivity on the silicalite crystals.

In Figure 3.19, oMeDBK was replaced with o,o’-diMeDBK, which does not possess a tolyl group that can potentially enhance the interaction with the pore openings through intercalation. Figure 3.19 (o,o’-diMeDBK) and Figure 3.13 (oMeDBK) are very similar in their spectral loading profiles; therefore, it is concluded that the potential intercalation of tolyl in the pore openings does not provide a noticeable increase in the binding energy in the system studied.
Figure 3.19  EPR spectra of 4-oxo-TEMPO of fixed low loading with varying amounts of \( o, o' \)-diMeDBK. The \( o, o' \)-diMeDBK loading required for the onset of the fast motion is between 119 to 149 mm. The onset of fast motion is indicated by the arrows.
Figure 3.20  EPR spectrum of 4-oxo-TEMPO of low loading with an excess of 1,2-bis(2-methylphenyl)ethane. The EPR spectrum shows only one component: slow motion.

When the carbonyl group was removed from the major adsorbate oMeDBK (Figure 3.20), it was obvious that even at high loading of major adsorbate species (larger than one monolayer coverage), the interaction of the major adsorbate molecules is not strong enough to displace a noticeable amount of TEMPO probe molecules. Therefore, the carbonyl group is an essential feature of the oMeDBK molecules that enables it to displace TEMPO molecules on the external surface's strong binding sites.

As a further control experiment, 1,3-di-p-tolyl-propan-2-one (p,p'-diMeDBK) was used instead of oMeDBK in Figure 3.21. Based on a p-xylene structure, p,p'-diMeDBK can diffuse into the internal surface of silicalite. Even though p,p'-diMeDBK possesses the essential structures for enhanced binding on the external surface as does oMeDBK, it certainly prefers the adsorption in the internal surface due to the large ratio
of internal versus external surface area and potentially high dispersion interactions in the channels due to molecular/channel size correlation.

![Diagram](image)

**Figure 3.21** EPR spectrum of 4-oxo-TEMPO of low loading with an excess of $p,p'$-diMeDBK. The EPR spectrum shows only one component: slow motion.

The adsorption pattern of $p,p'$-diMeDBK on silicalite is illustrated in Figure 3.22.
Figure 3.22  The adsorption of \( p,p' \)-diMeDBK in the internal surface of silicalite leaves the nitroxide adsorbed on the external surface pore openings.

3.4.3 External Surface Area Determined by the Competitive Adsorption

Method Using EPR

If the external surfaces of different silicalites were substantially the same in terms of interaction with the adsorbate molecules, one would expect the loading (molality) of oMeDBK to reach the onset of the fast motion of nitroxide molecules to be a parameter indicative of specific external surface area.

The seven silicalite crystals with different crystal sizes, whose preparation and characterization were detailed in Chapter 2, were used as adsorbents in the EPR analysis. Silicalite samples with low surface coverage of 4-oxo-TEMPO (approximately 2% of the required loading of oMeDBK to reach the onset of the fast motion, 0.02 ML) as the sole adsorbate were prepared. EPR analysis shows 4-oxo-TEMPO probe molecules possess
the same rotational correlation times (1.17 x 10^{-8} \text{s}) and spectral line width as represented by silicalite ZL5157 in Figure 3.10. Therefore, the strong binding sites on the external surfaces are essentially homogeneous and comparable across the seven crystals.

The lowest (critical) loading (molality) of oMeDBK required for the onset of nitroxide fast motion was examined using the co-adsorption of oMeDBK and 4-oxo-TEMPO. The loading of 4-oxo-TEMPO is always chosen to be approximately 2% of the critical oMeDBK loading (about 0.02 ML) so the nitroxide is only present in a negligible amount, while providing a decent signal to noise ratio. The critical oMeDBK loading results are plotted in Figure 3.23 against the calculated silicalite specific external surface area estimated from SEM geometrical analysis.

![Figure 3.23](image)

**Figure 3.23** The critical loading range of oMeDBK required to reach the onset of 4-oxo-TEMPO fast motion by EPR as a function of external surface area determined by geometrical analysis using SEM for all seven monodisperse silicalite crystals. Error bar for the oMeDBK loading at 12% of medium value is shown.

The relationship between the critical loading of oMeDBK and the external surface area by SEM is approximately linear. The slight aberration for ZL5157 (with the highest
specific external surface area) is probably due to the limited accuracy in the
determination of the specific external surface area using SEM geometrical analysis when
the crystals are very small (Figure 2.1). The significant aberration for ZL5159 (indicated
as ▲ in Figure 3.23) is probably due to the presence of mesopores. The mesopores could
form during the hydrothermal synthesis under alkaline condition,\textsuperscript{20,21} and they (with a
size of approximately 4 nm) are too small to be resolved at the SEM magnification level
employed (up to 30,000 times with a resolution at about a few hundred nanometers) and
therefore are not included in the estimation of the external surface area by SEM. These
mesopores, in contrast, are significantly larger than the molecular probe molecules
employed (less than 1 nm) and will contribute to the total external surface area measured
by EPR. Another possible reason for the observed errors are due to the presence of
twining and other surface structures, whose contribution to the total external surface area
are difficult to evaluate based on the SEM images.

It is therefore to be noted that SEM is a qualitative technique in the evaluation of
the total external surface area of silicalites. A more reliable external surface
determination method, such as mercury porosimetry, should be employed and cross-
checked with the EPR results.\textsuperscript{37}

Based on the approximately linear relationship between oMeDBK's critical
loading range and the specific surface area and further assuming the availability of a well
characterized standard adsorbent sample of the same structure, one can determine the
external surface area easily using EPR with high signal to noise ratio.
3.5 Conclusions

Adsorption of organic molecules on the silicalite’s external surface takes place with a molecular conformation and orientation that maximize the interaction energy.

The strong binding sites on the silicalite’s external surface are polar in nature probably due to the presence of silanol groups (as revealed by the high polarity probed by TEMPO at low temperature EPR measurements) and are capable of interacting strongly with suitable functional groups on the adsorbate molecules (probably through the formation of hydrogen bonding). Nitrooxide molecules adsorb on the strong binding sites through the interaction of N-O with the surface silanol groups. For molecules such as TEMPO-based nitroxides, the polar groups on the 4-position, e.g., hydroxyl, carbonyl, and COO ester linkage, have stronger interactions with surface strong binding sites than does the N-O moiety. The adsorbate molecules are tightly bound (as revealed by the lower rotational mobility compared to TEMPO adsorption at room temperature) to the surface’s strong binding sites with the 4-position polar groups interacting with the surface (as revealed by low polarity probed by N-O). When TEMPO is adsorbed on the silicalite surface at low coverage (0.02 ML), the N-O interacts with the surface silanol groups and the probe still enjoys relatively high rotational mobility due to weaker binding with the surface silanols, compare to carbonyl, hydroxyl groups etc.

Similarly the presence of the carbonyl group in the structure of the oMeDBK molecule is necessary for it to displace nitroxides from the surface’s strong binding sites.

The possible intercalation of phenyl/tolyl moieties (such as those in the structure of oMeDBK and the nitroxide DPT) in the pore openings does not provide a noticeable increase in binding strength for the adsorbate molecules studied. The contribution to the
binding strength from the possible intercalation into the pore openings is probably lower than the contribution from the interaction between the polar groups (carbonyl in oMeDBK and COO ester linkage in DPT nitroxide) and the surface silanols present at the pore openings. Therefore, when the conformation and orientation of the adsorbate molecules are such that the interaction between the polar moieties are maximized, the phenyl/tolyl groups are probably not capable of intercalating into the pore openings without incurring significant strains in the molecular structure.

When the pair of co-adsorbates are appropriately chosen, such as oMeDBK/4-oxo-TEMPO, the supramolecular structure of the adsorbates@ (silicalite's external surface) shows a continuous progression based on the loading of the major adsorbate. At low surface coverage of the major adsorbate molecules, the nitroxide binds on the strong binding sites, i.e., the pore openings and the rotational mobility of the nitroxides is in the range of slow motion. When the surface coverage of the major adsorbate molecules is increased to approximately one monolayer, the competition for strong binding sites leads to a partial displacement of the nitroxide molecules, which are characterized by fast motion.

Assuming the same surface coverage of oMeDBK when the nitroxide EPR shows the onset of fast motion, the total external surface area of a silicalite sample is proportional to the corresponding loading of the adsorbate. If a standard silicalite sample is available, whose external surface structure and area have been thoroughly characterized using independent methods, the absolute value of the total external surface of an unknown silicalite sample can be determined using the indirect EPR methods.
3.6 References:


(9) Richards, R. E.; Rees, L. V. C. *Zeolites* 1988, 8, 35.


(14) Bosacek, V.; Kubelkova, L. *Zeolites* 1990, 10, 64.


(18) The classification of indirect and direct methods in this thesis is different from that in conventional studies. In the well documented study of surface adsorption using IR, direct method implies the examination of solid surface structures like hydroxyls in the absence of probe molecules, while the indirect method means the study of probe molecules as perturbed by adsorption on the surface.


(22) Turro, N. J.; Lei, X.; Cheng, C. C.; Corbin, D. R.; Abrams, L. *Journal of the American Chemical Society* 1985, 107, 5824.


Chapter 4. Direct Characterization of Silicalite's External Surface Using EPR: Supramolecular Structure of Nitroxide@Silicalite from the Analysis of Electron-Electron Dipolar and Exchange Interactions

4.1 Introduction

In Chapter 3, the focus was placed on the indirect EPR method for the characterization of the silicalite's external surface, in which oMeDBK is the major adsorbate, and nitroxides are used in small and fixed quantities as probes for the oMeDBK@(silicalite’s external surface) supramolecular system.

In addition to the indirect EPR method, the structure and dynamics of adsorbate@(silicalite's external surface) supramolecular system can also be studied in a direct manner, using nitroxides as the sole adsorbate and studying the nitroxides@(silicalite’s external surface) system by examining the EPR spectra at different nitroxide coverages. This direct EPR method is the focus of this chapter.

4.1.1 Effects of Electron-Electron Dipolar Interaction and Exchange Interaction as a Function of Nitrooxide Coverage

In the studies using the indirect EPR methods, the coverage of the nitrooxide probe molecules is fixed and at a very low level (e.g., 0.02 ML). At this coverage level, assuming a Poisson distribution of the nitrooxide molecules on the silicalite surface, nitrooxide molecules are positioned far from each other (e.g., about 20 Å or larger in Figure 3.10 based on simulation), and therefore the electron-electron dipolar interactions are very weak, and electron-electron exchange interactions are absent (except for local
aggregates due to non-statistical distribution). The spin Hamiltonian can be approximated with three terms, i.e., the Zeeman interaction of the electron spin with the magnetic field, the hyperfine interaction of the spin with the nitrogen nucleus in a N-O bond, and a minor contribution from electron-electron dipolar interaction (Equation 4.1 is a simplified version of 1.8).

\[
\hat{H} = |\beta| \mathbf{S} \cdot \mathbf{g} \cdot H_0 + \hbar \mathbf{S} \cdot \mathbf{T} \cdot I + g \cdot \mathbf{S} \cdot \sum_{k \neq i} r_{ik}^{-3} (3 \cos^2 \theta_{ik} - 1) \times (S_i S_k - 3 S_{z,i} S_{z,k})
\] (4.1)

An analysis of EPR spectra can reveal the rotational mobility of the spin probes (\(\tau_c\) value) on the particular adsorption sites and the rotational mobility, in turn, is an indication of binding strength. The external surface area of a silicalite sample can be correlated to the lowest loading (molality) of EPR-silent adsorbate molecules that are required to transform the rotational mobility of some of the nitroxide probe molecules from slow to fast as an indication of saturation of the strong binding sites (reaching a specific external surface coverage).

Using direct EPR methods, the nitroxide coverage on silicalite is increased continuously, and correspondingly the average distance between the spin probes decreases. Electron-electron dipolar interaction is proportional to \(|r_{ij}|^3\) (Equation 4.1). When the distance between the nitroxide probes is reduced from 20 to 10 Å, the dipolar interaction increases to 8 times that of the original value. Electron-electron exchange interaction increases exponentially upon the decrease in inter-spin distance. A decrease of inter-spin distance from 11 to 6 Å will increase the exchange integral by 5 orders of magnitude as studied in the semiconductor system.\(^1\) Strong dipolar and exchange interactions could significantly change or even completely dominate the appearance of the EPR spectra.
The anisotropic dipolar broadening is reduced when the nitroxide molecules undergo fast rotational motions because the tumbling motion tends to average the local fields. As a result, the inter-spin distance measured from the dipolar broadening is the distance between the probe molecules at fixed positions under the conditions of low rotational mobility and low diffusional mobility, as diffusion leads to dynamic electron exchange interaction, which can also average the dipolar anisotropic effects.

At high surface coverage of the nitroxide probe molecules on the silicalite's external surface, the inter-spin distance is sufficiently short (typically below 10 Å) that efficient overlap of N-O 2pπ orbitals leads to strong spin exchange either statically (due to closeness in location and favorable orientation), or dynamically (due to diffusional encounter, i.e., probe molecules approaching a van der Waals distance). The exchange interactions lead to the exchange of spin states of the two interacting unpaired electrons. The Hamiltonian for electron exchange interaction between two spins in an isotropic system is in the form of Equation 4.2.4

$$\hat{H} = -2JS_1 \cdot S_2$$  \hspace{1cm} (4.2)

$J$ is the isotropic exchange integral, which reflects the degree of orbital overlap of the interacting spins, and characterizes the energy separation between the singlet and triplet states. A quantitative measure of the exchange efficiency is the term exchange frequency $\omega_{ex}$, which is defined as $\omega_{ex} = J/h$ for immobilized radicals such as those adsorbed and bound on the solid surface.

When electron exchange occurs, the line width of the EPR spectra depends on the relative magnitude of the exchange interaction, dipolar interaction, hyperfine interaction and on the Zeeman (Larmor) frequency ($\omega_B$) employed in the experiment.\textsuperscript{2,5}
For small nitroxides dissolved in a non-viscous solvent, where the fast rotational motion averages the dipolar anisotropic interactions, the EPR spectra show a dramatic change upon increasing exchange frequency as the concentration of the nitroxide is increased. Figure 4.1 shows the simulated first-derivative EPR spectra of nitroxide radicals as a function of exchange frequency reported by Sachse and Marsh. At essentially zero exchange frequency, the EPR spectrum is the three-line pattern with narrow lines (Figure 4.1, spectrum A). When the exchange frequency reaches $10^7 \text{ s}^{-1}$, significant line broadening can be seen for each of the three lines (Figure 4.1, spectrum B). At $10^8 \text{ s}^{-1}$, the exchange leads to the collapse of the three hyperfine lines into a broad single line (Figure 4.1, spectrum D). Further increase in the exchange frequency leads to exchange narrowing due to the Heisenberg uncertainty principle (Figure 4.1, spectra E and F). The nitroxide EPR line width has been shown to correlate linearly to the concentration of nitroxide in solution.
Figure 4.1  Simulated first-derivative EPR spectra of nitroxide radicals with various values of the spin-spin exchange frequency. Spectra are plotted with constant line height. Duplicated from Sachse and Marsh with added remarks.⁶

The line shape and line width of the nitroxide EPR spectrum are also dependent on the relative magnitude of the exchange frequency and $A_{iso}$, the value of isotropic hyperfine coupling constant due to Fermi contact between the electron spin and the nitrogen nucleus in the nitroxide molecule.⁷ As discussed in Chapters 1 and 3, the value of $A_{iso}$ is the separation of the adjacent lines in the nitroxide EPR spectrum (Figure 4.1, spectrum A, $A_{iso} = 14 G$). In the presence of a weak exchange interaction ($\omega_{ex} < A_{iso}$), the exchange interaction broadens the EPR lines and causes the convergence of the three-lines in a nitroxide EPR spectrum to the central position ($M_t = 0$) (Figure 4.1, spectrum C).⁷,⁸ The broadening of an individual line due to exchange interaction is $2 \omega_{ex}$, wherein the line width is defined as the frequency difference between the maximum and the minimum of a line of the first derivative EPR spectrum. When $\omega_{ex} \approx A_{iso}$, a very broad single line with breadth of the order of $A_{iso}$, centered at the central position ($M_t = 0$) is
observed (Figure 4.1, spectrum D, wherein $\omega_{\text{ex}}$ is equivalent to approximately 37 G on a X-band EPR, similar to the value of $A_{\text{iso}}$ at 14 G). When the exchange frequency is large compared to the value of the hyperfine coupling constant $A_{\text{iso}}$ ($\omega_{\text{ex}} \gg A_{\text{iso}}$), the width of the collapsed line decreases with increasing exchange frequency $\omega_{\text{ex}}$ (Figure 4.1, spectra E and F, wherein $\omega_{\text{ex}}$ is equivalent to approximately 180 and 370 G, respectively). The resulting single line is of the Lorentzian type and has a line width of $(A_{\text{iso}})^2/\omega_{\text{ex}}$.

When the rotational mobility of the nitroxide is limited and the dipolar interaction is not fully averaged by probe motion (e.g., nitroxides adsorbed on a solid surface), the EPR spectrum also depends on the relative magnitude of the dipolar interaction and exchange interaction. In cases in which $\omega_{\text{ex}}$ is larger than the magnitude of the dipolar interaction, the EPR spectrum consists of a sharp exchange narrowed line (similar to spectra E and F in Figure 4.1), because the rapid spin motions in the exchange process effectively average out the broadening interactions, including the dipolar interaction. If the exchange is of the same order of magnitude as the dipolar interaction, the dipolar interaction is not completely averaged and the result is a broadened EPR line (similar to spectrum D in Figure 4.1).

The width of the exchange-narrowed EPR line becomes dependent on the Zeeman frequency when the exchange and Zeeman frequencies are of the same order of magnitude. In general, when the Zeeman frequency is significantly smaller than the exchange frequency ($\omega_b \ll \omega_{\text{ex}}$), the line width measured is 10/3 wider than the width measured when the Zeeman frequency is significantly larger than the exchange frequency ($\omega_{\text{ex}} \ll \omega_b$) (hence the name "10/3 effect").
4.1.2 Correlation of EPR Parameters from Electron-Electron Dipolar Interaction and Exchange Interaction with Absorbent External Surface Areas.

The dipolar broadening contribution to the spectral line width can be easily obtained from the computer-assisted simulation of EPR spectra.\textsuperscript{13-15} Using equation 1.11, \( \Delta H_d = 3 \times 10^4 \left( \frac{1}{d} \right)^3 \), one can translate the dipolar broadening into inter-spin distance (d). Since silicalite crystals with different crystal sizes have the same external surface structures, i.e., pore openings and a framework surface with a fixed ratio of concentrations (approximately 18 to 82 based on [010] surface), the loading (molality) of the nitroxide probe molecules required to reach the same inter-spin distance, i.e., the same surface coverage, is expected to be a measurement related to the external surface area of the silicalite crystal.

At strong exchange interaction, the EPR spectrum exhibits a very unique single narrow line instead of multiple lines, the latter occurring in the absence of exchange interaction (Figure 4.1 spectrum F versus A). Because the electron-electron exchange interaction exponentially depends on the distance between the unpaired spins, the appearance of the single narrow line provides a means of determining a certain surface coverage density with very high signal to noise ratio. Therefore, the loading of the nitroxide probe molecules required to reach a certain exchange interaction level is expected to be a measurement of the external surface area.

The correlation of dipolar and exchange interaction parameters with the silicalite's external surface area at various nitroxide coverages is shown in Figure 4.2. At low surface coverage (\(<< 1\) ML) of the nitroxide probes, the probe molecules are positioned (e.g., strongly adsorbed on the pore openings) statistically far from each other.
except in the case of local aggregates’ formation. Dipolar interaction and especially exchange interaction contribute minimally to the EPR line shape. At higher surface coverage, e.g., at the adsorption saturation point of the pore openings (distance between the nearest pore opening centers is ~12 Å from crystallographic analysis),\textsuperscript{16} the strong dipolar anisotropy and weak, but non-negligible, exchange interaction are expected to affect the EPR spectra. At even higher surface coverage, e.g., 1 ML, the dipolar anisotropy is largely averaged due to increased probe mobility and exchange interaction. However, the exchange interaction becomes very strong at this short inter-spin distance and can dominate the EPR spectrum.

Since the dipolar and exchange interaction parameters in the EPR analysis are surface coverage dependent, and the loading (molality) of the nitroxide probes required to reach the same surface coverage is proportional to the silicalite’s total external surface area, it would be expected that the study of dipolar and exchange interaction parameters should reveal the silicalite’s external surface area.
4.2 Research Objective

The major research objective in this chapter is the study of the external surface properties of silicalites using the direct EPR method. The adsorption detail, i.e., the supramolecular structure and dynamics of the nitrooxide probe molecules is monitored by observing the change in the EPR spectra as a function of probe loading and other sample preparation parameters. The electron-electron dipolar interactions and exchange interactions at medium to high probe loading are analyzed and correlated to the external surface area and the properties of the adsorption sites on the silicalite external surface.

4.3 Experimental Methods

4.3.1 Methods for Sample Preparation

The following steps were followed to prepare the samples for EPR analysis.
1. Activation of the calcinated silicalite samples. The samples were heated at 500 °C for at least an hour in an aerated furnace and then placed in a desiccator, where the samples were cooled to room temperature.

2. Loading of the nitroxide probe molecules onto the silicalite's external surface from isoctane. For low loading samples, a stock solution of nitroxide was first prepared and the appropriate amount of the solution was mixed with the silicalite sample. For medium to high loading samples, nitroxide of the appropriate amount was directly mixed with the zeolite and isoctane. The silicalite/isoctane slurry was magnetically stirred for at least 10 hours in an airtight container.

3. Removal of solvent from the silicalite/isoctane slurry. The isoctane solvent was removed first by a gentle stream of dry argon flow, so that the nitroxide probe molecules previously dissolved in the supernatant were transferred to the external surface of the silicalite. The samples were further dried and deoxygenated at moderate vacuum (approximately 5 x 10⁻¹ Torr). The samples were then stored in a desiccator if aging effects were to be examined.

4. Removal of oxygen. The samples to be measured by EPR were deoxygenated in a quartz tube with a side arm that could fit into a typical CW-EPR cavity and a stopcock that could be used to seal the tube under vacuum.

4.3.2 Methods for EPR Measurements

The EPR spectra were taken at room temperature (24 °C) using lowest possible microwave power (e.g., 2.01 mW at 20dB), with a modulation frequency at 100 kHz and modulation amplitude smaller than the narrowest line width in the spectra (typically 1 G). The spectra were measured within a few hours after deoxygenation.
4.3.3 Computer-assisted EPR Spectrum Simulation

Computer-assisted simulation for the slow motion EPR spectra was performed in the same manner as detailed in Chapter 3 and one additional parameter, i.e., the electron-electron spin exchange frequency, was included. A Brownian motion (rather than a jump motion) was typically assumed due to the high loading of nitroxide and the fact that the Brownian motion assumption produces better fitting result for these samples.

4.4 Results and Discussions

4.4.1 Sample Preparation Methods: Equilibrium or Non-equilibrium?

When nitroxide probe molecules, isoctane and silicalite, are mixed in the loading step, the slurry is stirred until the relative amounts of nitroxide dissolved in the liquid phase and adsorbed on the solid surface did not change with time, i.e., the system reached an equilibrium. The samples prepared in this manner are assumed to be in a thermodynamically stable state.

Most preferably, the equilibrated slurry system should be studied directly using EPR. However, when the measurements are carried out, contribution of the nitroxide signal from the liquid phase of the slurry complicates the signal from those nitroxide molecules on the solid surface. Furthermore, small differences in the positioning of the sample in the EPR cavity can result in different degrees of contribution from the liquid phase.

In light of the difficulty in studying the slurry samples directly, efforts were made to study the dry samples, while attempting to preserve the adsorption equilibrium on the surface. The slurry samples were loaded onto a filter to remove the supernatant, and were
gently washed with a small amount of iso-octane, typically a few milliliters for a silicalite sample of approximately 200 mg (Figure 4.3). The silicalite sample (called an **equilibrated dry sample**) was then collected, dried, deoxygenated and analyzed using EPR.

![Diagram](image)

**Figure 4.3** Preparation methods for the equilibrated dry sample for EPR analysis. The rectangular prism stands for a closed container, such as a vial.

In Figure 4.4, the EPR spectra for the equilibrated samples prepared using the nitroxide DPT (structure shown in the Figure) and silicalite ZL5148 at various formal loadings of DPT assuming total deposition of the spin probes onto the surface can be seen. The loadings are formal because a significant amount of DPT remains in the supernatant from a visual inspection or EPR analysis and the fraction of probes in the supernatant are lost during the filtering and light washing procedures. An examination of Figure 4.4 immediately reveals that in spite of a nearly 30-fold increase in the DPT initially added to the slurry, the EPR spectra of the dried solid sample prepared in the manner of Figure 4.3
are essentially the same, which means the DPT molecules are probably at an equilibrium
distribution and occupy the same binding site(s), and possess the same rotational mobility.

![Graph showing EPR spectra]

**Figure 4.4** EPR spectra of DPT@silicalite ZL5148 *equilibrated* samples at
different formal loadings assuming all the DPT molecules were deposited onto the
silicalite surface. Black line: 2.2 mm. Blue line: 7.6 mm. Red line: 60 mm. The
spectra were measured within a few hours of preparation.

Following the same algorithm for the calculation of concentration of pore
openings for silicalite ZL5157 as detailed in Chapter 3, the concentration of pore
openings on the silicalite ZL5148 can be determined to be approximately 1.7 mm.

Considering the relative areas covered by the pore openings and framework surface on
the silicalite's external surface (approximately 18 to 82), the loadings of 2 mm, 7.6 mm,
and 60 mm would have resulted in the complete coverage of pore openings, monolayer
and multilayer, respectively, assuming complete adsorption of the nitroxide on the
surface in the slurry system.
To find out the adsorption detail of the DPT probes shown by the spectra in Figure 4.4, the sample with 2.2 mm (black line) was analyzed using computer-assisted simulations as detailed in Chapter 3 and the result is presented in Figure 4.5. The rotational correlation time is $5.65 \times 10^{-9}$ s in the slow motion range. The inter-spin distance is found to be approximately 15.6 Å from dipolar broadening, slightly larger than the distance between two nearest pore openings calculated from the unit cell dimension of silicalite (12 Å).\textsuperscript{16} Considering the low mobility of the adsorbed probes, the inter-spin distance, and the amount of DPT loading relative to the pore opening concentrations, it is concluded that the DPT probe molecules on the silicalite surfaces for all the three samples in Figure 4.4 essentially all reside only on the strong binding sites, i.e., the pore openings. The fact that the inter-spin distance determined from the dipolar broadening is relatively large at 15.6 Å suggests that the pore openings were not likely to be fully saturated.

The EPR results for the three different loadings, indicating adsorption on the pore openings only, clearly prove that the framework surface has a very weak binding strength with DPT. The probe molecules adsorbed on the framework surface are in fast dynamic equilibrium with the probe molecules dissolved in isooctane and the adsorbed probe molecules can be easily removed by washing with isooctane.
Figure 4.5 Experimental (black) and simulated (red) EPR spectra of DPT@silicalite ZL5148 equilibrated samples with a formal loading of 2.2 mm assuming a total adsorption on the surface (left). The adsorption pattern was assigned to an exclusive adsorption on the pore openings with most likely incomplete coverage (right).

In comparison, the dry samples were also prepared by evaporating the isoctane in the slurry using a gentle stream of dry argon flow (Figure 4.6). During the evaporation process, the nitrooxide probes previously dissolved in the liquid phase were transferred to the silicicate surface. Since the deposition of the extra amount of adsorbate molecules onto silicalite external surface are typically carried out within a short period, e.g. an hour, it is likely that the adsorption pattern on the surface is kinetically favored and not in its thermodynamically stable form and the adsorption pattern may change as the samples age at room temperature. These samples are called non-equilibrated dry sample and were also deoxygenated for EPR measurements.
**Figure 4.6** Preparation methods for the non-equilibrated dry sample for EPR analysis. The rectangular prism stands for a closed container, such as a vial.

In sharp contrast, the *non-equilibrated* samples, in which all the nitrooxide probe molecules are deposited onto the silicalite surface, show EPR spectra with distinct line features as a function of probe loading (Figure 4.7). Unlike the formal values assumed in the equilibrated samples shown in Figures 4.4 and 4.5, the loadings specified in Figure 4.7 are true loadings. At low loading (2 mm), the EPR spectrum in Figure 4.7 has three broadened lines similar to the case discussed in Figure 4.4. At intermediate loading (6 mm), the EPR spectrum is a broad one-line spectrum. At high loading (70 mm), the EPR spectrum in Figure 4.7 is a very narrow one-line spectrum. The patterns that are shown at intermediate and high loadings in Figure 4.7 are completely absent from the spectra taken with the samples prepared using the equilibrium loading method as displayed in Figure 4.4. The three different spectra in Figure 4.7 are analyzed using computer-assisted simulations and the results are presented in Figure 4.8 (2 mm), 4.9 (6 mm) and 4.10 (70 mm).
Figure 4.7  Experimental EPR spectra of DPT@*(silicalite ZL5148) non-equilibrated samples with loadings at 2 mm (top), 6 mm (middle) and 70 mm (bottom), respectively. Spectra are presented with normalized heights. The EPR spectra were recorded within a few hours of sample preparation.

Computer-assisted simulation for the low loading spectrum in Figure 4.8 reveals the rotational mobility and inter-spin distance. The fact that the values obtained on this sample are very similar to those obtained from the samples prepared using an equilibrium loading method (Figure 4.5) confirms that the two DPT@*(silicalite ZL5148) supramolecular systems are very similar. Both the two systems can be characterized by strong and exclusive adsorption on the pore openings of the zeolite surface, and strong electron-electron dipolar anisotropic interaction due to their close proximity.
Figure 4.8 Experimental (black) and simulated (red) EPR spectra of DPT@silicalite ZL5148 non-equilibrated sample with loading at 2 mm (left). The EPR spectrum was recorded 9 days after sample preparation. The adsorption pattern was assigned to an exclusive adsorption on the pore openings with approximately complete coverage (right).

The very broad single line spectrum at intermediate loading shown in Figure 4.9 is characteristic of the line broadening introduced by strong electron-electron dipolar anisotropic interactions due to relatively close proximity and weak but unnegligible electron-electron spin exchange interaction. Computer simulation results show that the average inter-spin distance calculated from dipolar broadening is 13.5 Å, a value comparable to the distance between the central points of the two closest pore openings, approximately 12 Å on the silicalite’s external surface, suggesting an approximately complete filling of the pore openings. Based on the relative concentrations of loading (6 mm) and pore openings (approximately 1.7 mm), some population of DPT on the framework surface is also expected (Figure 4.9). The electron-electron exchange frequency is $\omega_{ex} = 1.20 \times 10^8$ s$^{-1}$, a smaller value compared to that in the case of high loading sample (Figure 4.10). On the X-band EPR operating at approximately 9.5 GHz, the measured $\omega_{ex}$ value corresponds to approximately 40 G, which is close to the magnitude of the dipolar anisotropic interaction (approximately 12 G), and the isotropic ($A_{iso}$) and anisotropic ($A_{zz}$) $^{14}$N hyperfine coupling constants (approximately 15 G and 38 G, respectively). As a result of the comparable values for exchange interaction, dipolar interaction and hyperfine coupling constants, the EPR spectrum is the observed single broad line as expected from theoretical considerations detailed above.\textsuperscript{27,17}
Figure 4.9  Experimental (black) and simulated (red) EPR spectra of DPT@(silicalite ZL5148) non-equilibrated sample with loading at 6 mm. The EPR spectrum was recorded 9 days after sample preparation. The adsorption pattern was assigned to a complete coverage of the pore openings with probably some DPT adsorbed on the framework surface (right).

The EPR spectrum for the high loading sample (70 mm, Figure 4.10) prepared using the non-equilibrium method is a very narrow single line with a peak-to-peak line width of only 8.51 G, compared to 35.6 G in the case of intermediate loading shown in Figure 4.9. The narrow single line is evidence of the dominating effects of strong electron-electron spin exchange interaction. The exchange frequency is calculated to be \( \omega_{\text{ex}} = 2.57 \times 10^9 \text{ s}^{-1} \) from computer-assisted simulation. For an X-Band EPR spectrometer operating at 9.5 GHz, the \( \omega_{\text{ex}} \) value corresponds to approximately 940 G, which clearly demonstrates the overwhelming exchange interaction over dipolar broadening interaction (approximately 4.5 G) and hyperfine interaction (\( A_{\text{iso}} = 15 \text{ G} \) and \( A_{\text{zz}} = 38 \text{ G} \)). Since the \( \omega_{\text{ex}} \) is smaller than the Zeeman frequency, the dipolar broadening due to the so-called "10/3 effect" is not expected to be significant.\(^{2,9,10,12}\)

At very high nitroxide loading (e.g. 70 mm), the nitroxide molecules not only saturated the pore openings (approximately 1.7 mm for the silicalite ZL5148 employed),
but also occupy the framework surface (the area ratio of pore openings to framework surface being approximately 18 : 82), which is a weaker binding site. The probe molecules on the framework surface enjoy higher rotational mobility than those on the pore openings. Both the higher rotational mobility and strong spin exchange interaction efficiently average the dipolar interaction and reduce the dipolar anisotropy and therefore, a low dipolar broadening factor is obtained from the EPR line fitting (4.5 G in Figure 4.10 versus 12 G in Figure 4.9).

The inter-spin distance cannot be calculated from the dipolar broadening factor using the simple equation relating dipolar broadening and inter-spin distance (Equation 1.11, duplicated as Equation 4.3), because this simple equation is based on the assumption that there is no strong electron spin exchange in the system studied.

\[ \Delta H_d = 3 \times 10^4 \left( \frac{1}{d} \right)^3 \]  

(4.3)

Figure 4.10  Experimental (black) and simulated (red) EPR spectra of DPT@silicalite ZL5148 non-equilibrated sample with loading at 70 mm (left). The experimental and simulated spectra almost completely overlap when superimposed. The EPR spectrum was recorded 1 day after sample preparation. The adsorption pattern was assigned to a complete coverage of the external surface with possible multilayer formation (right).
From a comparison of the EPR spectra prepared using the two different methods, i.e., equilibrium versus non-equilibrium, several conclusions can be reached concerning the binding strengths of different sites on the silicalite’s external surface. When the samples are prepared using the equilibrium loading method, the adsorption of DPT probe molecules only takes place at the strong binding sites, i.e., the pore openings. The weak bindings site, i.e., the framework surface, has a low binding strength with the DPT probe molecules. The DPT molecules adsorbed on the framework surface are in fast equilibrium with the DPT probe molecules in the nonpolar isoctane supernatant and therefore can be easily removed by filtration and gentle washing. The DPT molecules adsorbed on the pore openings are tightly bound and cannot be removed to any significant extent by filtration and gentle washing in any significant amount.

It can be concluded that the non-equilibrium loading method provides a means of characterizing the complete silicalite external surface, as opposed to the equilibrium loading method, in which only the strong binding sites are probed. Therefore, the non-equilibrium loading method is used for sample preparation hereafter.

4.4.2 Aging Effects on the EPR Spectrum

In the non-equilibrium loading method, the fast deposition of a large amount of DPT probe molecules onto the external surface of silicalite within a short period of time, typically a few hours, raises an important question, i.e., are the probe molecules in a thermodynamically stable situation on the external surface?

One convenient way to check the thermodynamic stability of the DPT@silicalite external surface supramolecular system is by following the change in the EPR spectra as
a function of aging period. The samples were essentially left in a dry environment at a
certain temperature for an extended period of time and the EPR measurements were
conducted at various intervals. In general, a high temperature is preferred because the
system can reach the thermodynamically stable situation at a faster rate and it probably
reaches the adsorption pattern with global energy minimum at a high temperature.
However, temperature higher than room temperature is not recommended for the
DPT@ (silicalite external surface) system due to the reduced stability of the DPT
molecules at elevated temperatures. Therefore, the DPT@ (silicalite external surface)
samples with various loadings of DPT on different silicalites were stored in a dry aerated
environment (in a desiccator) for up to two months and the EPR spectra were measured
approximately every week for comparison.

The influence of sample aging on the appearance of EPR spectra can be
categorized into four groups, as exemplified by the EPR spectra of DPT@ (silicalite
ZL5148) with different loadings and measured within different aging periods.

The first group covers samples with DPT loadings up to approximately 3 mm. The
spectra show the typical three-line pattern for DPT at low concentration, and are
characteristic of slow motion on the surface (Figure 4.11). The line broadening is due to
not only the slow motion, but also significant electron-electron dipolar anisotropic
interactions. Computer-assisted simulation using one set of parameters generates a
spectrum that matches the experimental spectrum, indicating a single adsorption pattern
and very probably a single type of adsorption sites. The parameters obtained from the
simulation include an inter-spin distance at 15.1 Å, and a rotational correlation time at
1.05 x 10^-8 s. From the calculation provided previously in this chapter, the amount of
DPT molecules adsorbed is just sufficient to occupy the strong binding sites, i.e., the pore openings. The EPR spectrum did not change to any noticeable extent upon aging for approximately 2 months. The insensitivity toward aging at this loading is probably due to the fixed positions of the DPT molecules at the pore openings. It is also possible that the translational mobility is not insignificant, but the difference in the binding strengths for DPT molecules between the pore openings and the framework surface is large enough to fix the majority of the DPT molecules at the pore openings.

3 mm non-equilibrated on silicalite ZL5148

Aging time:

9 days
41 days
62 days
62 days (simulation)

Figure 4.11 Experimental and simulated EPR spectra of DPT@ (silicalite ZL5148) non-equilibrated sample with loading at 3 mm. The spectra were measured after different aging periods: 9 days (black), 41 days (red), 62 days (green) and the simulation was for the spectrum obtained after 62 days of aging (blue). The spectra were normalized by height. Values for various EPR parameters obtained from simulations are discussed in the text.

The second group of spectra covers loadings from approximately 4 to 7 mm. Within this loading range, the EPR spectra are in a transition from the well-resolved three-line pattern (Figure 4.11) to a single broad line (Figure 4.12). The extensive
broadening is due to the strong electron-electron dipolar interaction and to weak to
intermediate electron-electron exchange interaction (\( \sim 10^8 \text{ s}^{-1} \)). EPR spectra of the aging
effects are shown in Figure 4.12 using the sample with 6 mm loading of DPT. The shape
of the spectra measured during the aging period from 9 days to 62 days does not change
to any noticeable extent. The spectrum can be simulated using one set of parameters,
indicating the existence or dominance of a single type of adsorption sites. The extensive
broadening (peak-to-peak width at 32.9 G) is attributed to the strong dipolar anisotropic
interactions with probe molecules positioned at 13.6 Å apart (compared to the distance
between the centers of the two nearest pore openings at 12 Å), and the electron-electron
exchange interaction at an intermediate level (3.80 \( \times \) 10^8 \( \text{ s}^{-1} \). corresponding to 140 G on a
X-band EPR). At this series of DPT loadings, all the pore openings and a fraction of the
framework surface are occupied, leading to significant inter-spin dipolar and exchange
interactions due to their close proximity. The inter-spin interactions are expected to be
static in nature due to the strong binding strength at the pore openings.
Figure 4.12  Experimental and simulated EPR spectra DPT@(silicalite ZL5148) non-equilibrated sample with loading at 6 mm. The spectra were measured after different aging periods: 9 days (black), 41 days (red), 62 days (green) and the simulation was for the spectrum obtained after 62 days of aging (blue). The spectra were normalized by height. Values for various EPR parameters obtained from simulations are discussed in the text.

The third group of spectra is obtained from samples with DPT loadings in excess of 7 mm, but less than approximately 20 mm (Figure 4.13). In this loading range, the spectra taken within a day after sample preparation are characteristic of broad single line, similar to those in Figure 4.12, due to strong electron-electron dipolar interaction and intermediate electron-electron exchange interaction. However, upon aging, the samples typically show spectra with much narrower lines, indicating a more significant contribution from the electron-electron exchange interaction. Considering the fact that the exchange interaction strongly depends on the inter-spin distance in a static situation and on the diffusional encounter frequency of the spin probes in a dynamic situation, it is probable that local aggregates of DPT formed upon sample aging. At this range of
loading, the strong binding sites, i.e., the pore openings are expected to be fully occupied, and a significant number of the DPT probe molecules adsorb on the weak binding sites, i.e., the framework surface. Therefore, it would be reasonable to assume that the molecules adsorbed on the weak binding sites could migrate and form aggregates, and subsequently gain in thermodynamic stability via intermolecular interactions among the probe molecules, a process known in the literature by calorimetric studies on the adsorption of organic molecules on zeolites. Spectral simulation using one set of EPR parameters (and therefore assuming one type of surface adsorption sites) failed to yield a satisfactory match with the experimental spectrum. A careful perusal of the experimental spectra reveals the existence of two EPR-distinct surface adsorption patterns (indicated by the two arrows in Figure 4.13). One pattern is the narrow line indicative of local aggregates (right), the other is the bump on the wings of the spectrum (left), suggestive of probe molecules adsorbed on strong binding sites and interacting through dipolar anisotropic interaction and weak exchange interaction with nearby probes. Therefore, the simulation results based on one set of parameters, even for samples after a long aging period, should only be accepted with caution.
Figure 4.13  Experimental EPR spectra of DPT@silicalite ZL5148 non-equilibrated sample with loading at 20 mm. The spectra were measured after different aging periods: 1 day (black), 13 days (red), 29 days (green) and 44 days (blue). The spectra were normalized by height. Two different adsorption sites are indicated by the arrows.

The fourth and last group of spectra was obtained from samples with very high loadings of DPT molecules (> 20 mm) (Figure 4.14). The most obvious feature of this series of EPR spectra is the single narrow line (approximately 8.5 G). The strong electron-electron exchange interaction (approximately $2.57 \times 10^9$ s$^{-1}$, corresponding to approximately 940 G) totally dominates the spectrum and reduces it into a single narrow line as documented in the literature for various systems. In this loading range, the spectral change as a function of the aging period is negligible or completely absent (for loadings over approximately 70 mm). The insensitivity to aging is probably due to the fact that all the external surface adsorption sites are completely covered with essentially a monolayer or even a multilayer of DPT molecules. Translational motions by the probe
molecules do not produce a net change in the inter-spin distances and local nitroxide concentrations.

![Chemical structure](https://example.com/structure.png)

**70 mM** on silicalite ZL5148 **non-equilibrated**

Aging time:
- 1 day
- 29 days
- 44 days
- 1 day (simulated)

**Figure 4.14** Experimental and simulated EPR spectra of DPT@silicalite ZL5148 non-equilibrated sample with loading at 70 mM. The spectra were measured after different aging periods: 1 day (black), 13 days (red), 44 days (green) of aging and the simulation was for the spectrum measured at 1 day after preparation (blue). The spectra were normalized by height. Parameters obtained from simulation are presented and discussed in the text.

### 4.4.3 Conclusions on the Silicalite External Surface Parameters Studied

**Using the Direct EPR Method**

In summary of the analysis of the four groups of spectra discussed above, the EPR spectral patterns, translatable to the anisotropic dipolar interaction (as related to inter-spin distance between those having low rotational mobility and not in strong spin exchange interaction) and the electron-electron exchange frequency, undergo a drastic change with increased spin probe loading (more accurately, the surface coverage). At low coverage (e.g., ~ 0.2 ML for the saturation of the pores), the adsorption is characteristic of one-site adsorption at the pore openings with strong electron-electron anisotropic dipolar interaction.
interactions. The insensitivity of spectral patterns to aging suggests that that the probe molecules are very likely to be fixed at the pore openings due to strong binding. At intermediate coverage (more than 0.2 ML but less than 1 ML), the probe molecules adsorb on the framework surface after all the pore openings are saturated. The molecules on the framework surface have higher translational mobility and therefore could form aggregates at suitable sites if the aggregation is thermodynamically favored. The spectra tend to become narrower upon sample aging and may contain more than one EPR pattern. At very high coverage of probe molecules, the molecules essentially form a monolayer or multilayer on the surface. The EPR pattern is dominated by strong electron-electron exchange. The higher rotational mobility of the nitroxide molecules adsorbed on weak binding sites, in addition to exchange induced averaging of the dipolar anisotropic interactions, seems to account for the decrease in the anisotropic dipolar interaction strength.

4.4.4 Determination of the External Surface Area Using a Direct EPR Method

4.4.4.1 External Surface Area Determined from Dipolar Interaction

From the discussions on the change of EPR spectral patterns as a function of spin probe loading/coverage, it would be expected that the minimum inter-spin distance obtained from dipolar broadening should be a measure of titrating the concentration of pore openings on the silicalite’s external surface. This is because, when the amount of probe molecules is just sufficient to exclusively cover all the pore openings, the inter-spin distance between the immobile probe molecules are the shortest of all probe coverages. Since the concentration of pore openings is proportional to the silicalite’s specific
external surface area, the probe loading (molality) corresponding to the shortest inter-spin distance will be a measure of the total surface area per unit mass. Inter-spin distances (between the spins in fixed positions and not participating in strong electron-electron exchange) as a function of nitroxide loading for three representative silicalite samples (ZL5159, ZL613 and ZL5148) are shown in Figure 4.15, with the EPR spectra measured after a sample aging time of at least one month.

![Graph showing inter-spin distance vs. DPT loading](image)

**Figure 4.15** Inter-spin distance (in Å) calculated from dipolar broadening as a function of the DPT probe loading (in mm) for silicalite ZL5148, ZL613 and ZL5159. The lines are drawn to illustrate the trend in the experimental results and are not derived from data fitting or theoretical analysis. Solid lines are based on spectra with low exchange frequency. The dashed lines are based on spectra with high exchange frequency and are shown to illustrate the exchange averaging of dipolar anisotropy.

An examination of the lines presented in Figure 4.15 reveals that the inter-spin distance versus DPT loading is the expected “V” shape. While the right side of the “V” curve is only for the purpose of illustrating the exchange averaging of dipolar anisotropy, rather than representing the true inter-spin distance, the general trends especially in the
left part of the "V" curve reveal valuable information about the supramolecular system. Based on the silicalite's external surface structure and properties, the DPT loading values corresponding to the lowest inter-spin distance calculated from the anisotropic dipolar broadening analysis are expected to be the minimum loading required for a full coverage of pore openings because of the following two reasons. The first reason is the enhanced dipolar anisotropic interaction due to inefficient motional averaging by adsorption on the strong binding sites and a short inter-spin distance (about 12 Å). The second reason is that the inter-spin distance of 12 Å is sufficiently long to allow one to safely ignore the effect of strong spin exchange, which decreases with increasing inter-spin distance exponentially. Since the pore openings account for a fixed percentage of the external surface (about 18% by area), the DPT loadings corresponding to the full coverage of pore openings are proportional to the silicalite specific external surface area. As expected, the lowest values for inter-spin distance determined from dipolar broadening are between 12 to 14 Å as shown in Figure 4.15, which is similar to the distance between the centers of two nearest pore openings on the silicalite's external surface (12 Å). The minimum inter-spin distance measured for silicalite ZL5148 at approximately 14 Å seems to suggest the dominance of [001] surface in the total external surface of this particular silicalite sample. Further study with more silicalite samples is necessary to examine this possibility.

The correlation of DPT loadings for shortest inter-spin distances with the silicalite's external surface areas can be more easily appreciated by comparing the loadings for shortest inter-spin distance against the oMeDBK loadings for the onset of fast motion shown in Figure 3.23 using the indirect EPR method (Figure 4.16).
Figure 4.16  Loadings of DPT for shortest inter-spin distance in the direct EPR method versus loadings of oMeDBK for onset of fast motion in the indirect EPR method, for silicalite ZL5148, ZL613 and ZL5159. The 25% error bar is drawn based on the spread for trace ZL613 in Figure 4.15 at the shortest inter-spin distance.

In the results shown in Figure 3.23, where the oMeDBK loading for the onset of fast motion was plotted against the external surface area determined using SEM geometrical analysis, the external surface values determined for ZL5159 using the two different methods (SEM and indirect EPR) do not agree within the accepted error limit. The agreement between the indirect and direct EPR methods suggests that the indirect and direct EPR methods are probing the same surface sites on the silicalite’s external surface, and the SEM geometry method was not reliable in the external surface area determination for this particular sample, probably due to the presence of nanometer-scale structures on the external surface, which could not be resolved by SEM at the
magnification employed (up to 30,000 times with a resolution at about a few hundred nanometers).

4.4.4.2 External Surface Area Determined from Exchange Interaction

The electron-electron exchange frequency can also be correlated to the external surface area. After the pore openings are saturated, the excessive DPT molecules adsorb on the framework surface with low binding strength. Due to the reduced inter-spin distance and the formation of possible aggregates, the EPR spectrum displays a pattern for strong exchange effects. Beyond a certain loading/coverage, the exchange frequency reaches a plateau due to the fact that a monolayer or multilayer of DPT molecules form on the surface and close packing of the DPT molecules results in no change in the average inter-spin distance upon increased loading. Figure 4.17 shows the electron-electron exchange frequency as a function of DPT probe loading. The exact values are somewhat inaccurate partially due to the inaccuracy of the one-site simulation analysis for the range of intermediate loadings where the two adsorption sites are involved and resolved in the EPR spectra (Figure 4.13). At low coverage (< 0.2 ML), when adsorptions occur only at the pore openings (one-site pattern), and high coverage when adsorptions occur with monolayer or multilayer formation, the EPR spectra can be reliably simulated assuming one adsorption site. The DPT loadings required to reach the beginning point of the exchange rate plateau qualitatively agree with the results obtained by examining the inter-spin distance shown in Figure 4.15. More data points are desired before a thoroughly quantitative comparison can be conducted reliably.
Figure 4.17  Loadings of DPT for electron-electron exchange frequency versus DPT loadings in the direct EPR method, for silicalite ZL5148, ZL613 and ZL5159. The axes are shown in log format.

4.5 Conclusions

In a silicalite/isooctane slurry system, the adsorption of nitroxide probes on the silicalite’s external surface occurs primarily on the surface’s strong binding sites, i.e., the pore openings. The adsorption of nitroxide on the framework surface is of comparable strength compared to the interaction of nitroxide with isooctane molecules.

From the EPR spectra analysis, the nitroxides adsorbed on the pore openings seem to be fixed at the pore openings with a very low translational diffusivity. The nitroxides adsorbed on the framework surface, after the saturation of the pore openings, have a higher translational diffusivity and could form aggregates upon aging.

Results obtained from both the loading experiments using a slurry system and the aging effects on EPR spectra clearly and qualitatively demonstrate that the pore openings
on the silicalite's external surface have a higher binding affinity than the framework surface for the adsorbate molecules investigated.

Both the evolution of inter-spin distance obtained from the anisotropic dipolar broadening as a function of nitroxide loading, and the evolution of electron-electron exchange frequency as a function of nitroxide loading, have been shown to be a means of measuring the total external surface of the silicalite samples investigated, provided that a standard silicalite sample is available and fully characterized using the same EPR methods.

4.6 References


Chapter 5  Characterization of the Silicalite’s External Surface Using a Combination of $^{14}$N and $^{15}$N-labeled Nitroxides

5.1 Introduction

In the study of surface adsorption of organic molecules on the silicalite’s external surface, the desired information includes the site of adsorption, the strength of adsorption at each site, the dynamics (molecular exchange from one adsorption site to another and between solid surface and liquid phase), and the total external surface area.

From the indirect EPR method described in Chapter 3, and the direct EPR method described in Chapter 4, the pore openings were determined to be the stronger binding sites than the framework surface. While the two studies provided both a static (weak adsorption strength) and dynamic (reorganization and aggregate formation at high loadings) characterization for the framework surface and measurements of external surface area, they failed to offer an answer to the dynamics of adsorption on the strong binding sites.

In the iso-octane/silicalite slurry system, it has been concluded that the framework surface either does not provide enough interaction energy for the adsorption of nitrooxide spin probes or the adsorbed spin probes are in fast equilibrium with the probes in iso-octane. A similar question can be raised as to whether the spin probes adsorbed on the strong binding sites are in a dynamic equilibrium with the spin probes on the weak binding sites or in iso-octane.

This question of adsorption dynamics can be obtained using a second adsorbate species, which interacts with any particular adsorption sites in the same manner as those
with similar strength, but gives a distinct and resolvable signal when adsorbed together with the first probe. The first criterion essentially determines that the two probe molecules should have very similar or most desirably, the same molecular structures. These seemingly exacting criteria can be met easily for the EPR analysis by using nitroxide with a $^{15}\text{N}$ label.

Nitrogen has two stable isotopes $^{14}\text{N}$ and $^{15}\text{N}$, with a natural abundance of 99.6% and 0.4%, respectively. Therefore, the nitroxide spin probes synthesized using a natural source of nitrogen will provide essentially $^{14}\text{N}$-labeled species, which shows a three-line EPR spectrum due to a nuclear spin number of $I = 1$ for $^{14}\text{N}$ nucleus (Figure 5.1, spectrum A). If $^{15}\text{N}$ enriched nitroxide spin probes were prepared, a dramatically different EPR spectrum would appear. The new spectrum consists of only two lines ($^{15}\text{N}$ nuclear spin number $I = 1/2$) with larger separations between the lines (Figure 5.1, spectrum B) compared to its corresponding $^{14}\text{N}$ labeled species. In a deoxygenated dilute nonviscous solution ($< 10^{-3}$ mol·l$^{-1}$), the two nitroxides can be clearly resolved (Figure 5.1, spectra C and D).

A study of the EPR spectrum of $^{15}\text{N}$ labeled nitroxides has suggested a multitude of benefits of using a $^{15}\text{N}$ isotope.$^1$ Signal to noise ratio is higher for $^{15}\text{N}$ labeled nitroxides because the same EPR signal intensity is divided only into two lines, rather than three lines for $^{14}\text{N}$ labeled nitroxides. The overlap is less significant for $^{15}\text{N}$ EPR signals when the spectrum broadens at reduced rotational mobility, because of larger separations between the lines in $^{15}\text{N}$. The reduced overlap means that, if $^{15}\text{N}$ is used, the rotational correlation time can be studied at lower rotational mobility using simple lineshape analysis based on peak heights and widths.$^2$
Figure 5.1  EPR spectra of $^{14}$N and $^{15}$N labeled nitroxides DPT and their mixture in isooctane (deoxygenated). A: DPT-$^{14}$N, 0.5 M; B: DPT-$^{15}$N, 0.5 M; C: mixture of DPT-$^{14}$N at 0.25 M and DPT-$^{15}$N at 0.25 M; D: spectrum C displayed in adsorptive mode. The molar ratio of DPT-$^{14}$N to DPT-$^{15}$N was determined experimentally to be 49.8: 50.2 by integrating spectrum D.

5.2  Research Objective

A theoretical experiment on the study of dynamic exchange on the strong binding sites would involve adding a $^{14}$N enriched nitroxide species to the isooctane/silicalite slurry system and equilibrate, and subsequently add a $^{15}$N enriched nitroxide species
(with exactly the same molecular structure except the nitrogen isotope) and equilibrate. The possibility of dynamic exchange on the strong binding sites and its extent could be studied by examining the contribution of $^{14}\text{N}$ and $^{15}\text{N}$ nitroxide EPR lines to the experimental spectrum of the nitroxide adsorbed on the solid surface.

Using a mixture of two nitroxide spin probes, not only with different nitrogen isotopes, but also different molecular structures, the influence of molecular structures on the adsorption strength on the strong adsorption sites could be studied directly in one sample preparation and analysis, in addition to the indirect EPR method discussed in Chapter 3 using oMeDBK adsorption and separate sample preparation and analysis for two different spin probes.

5.3 **Experimental Methods**

Solution samples were prepared and deoxygenated using freeze-pump-thaw cycles as detailed in Chapter 3. Solid samples with co-adsorbed oMeDBK and nitroxides were prepared using the methods as detailed in Chapter 3. EPR measurements were conducted similarly as detailed in Chapter 3 and 4.

The stepwise loading experiment was conducted as follows: 300 mg of silicalite ZL5151 was loaded with 20 mM DPT-$^{14}\text{N}$ in isoctane slurry and was magnetically stirred for 6 hours. 20 mM equivalent of DPT-$^{15}\text{N}$ was added and the sample was stirred for another 6 hours. After centrifugation and filtration, the solid sample was collected and further stirred with fresh isoctane for 1 day. The solid sample was again separated from the isoctane layer and dried, deoxygenated and measured using CW-EPR.
5.4 Resolving $^{14}\text{N}$ and $^{15}\text{N}$-labeled Nitroxides in EPR Spectra Measured in Solution

The solution spectra of $^{14}\text{N}$, $^{15}\text{N}$-labeled DPT spin probes have been shown in Figure 5.1 and the EPR signals from the two isotopically different DPTs can be resolved. It is to be noted that the spectra presented in Figure 5.1 were obtained from the thoroughly deoxygenated samples using freeze-pump-thaw cycles.

![Diagram of nitroxides](image)

**Figure 5.2** EPR spectra of $^{14}\text{N}$ and $^{15}\text{N}$ labeled nitroxides DPT and their mixture in isoctane (air saturated). A: DPT-$^{14}\text{N}$, 0.5 M. B: DPT-$^{15}\text{N}$, 0.5 M. C: mixture of DPT-$^{14}\text{N}$ at 0.25 M and DPT-$^{15}\text{N}$ at 0.25 M. D: spectrum C displayed in adsorptive mode. The line broadening and overlapping are the result of enhanced paramagnetic relaxation from dissolved oxygen.
If the samples were not adequately deoxygenated, the resultant spectra would show broadened and overlapping lines due to paramagnetic relaxation caused by oxygen (Figure 5.2), which has been used to determine the oxygen concentration (oximetry) both in vitro\textsuperscript{3} and in vivo.\textsuperscript{4} This suggests that deoxygenation is a required procedure to ensure narrow and resolved lines in EPR spectra.

5.5 Resolving \textsuperscript{14}N and \textsuperscript{15}N-labeled Nitroxides in EPR Spectra Measured on the Silicalite Surface

Once the nitroxide is adsorbed on the external surface of silicalite and the dry (solvent-free) and deoxygenated samples were examined by EPR, the EPR lines become significantly broadened due to anisotropy upon interaction with the surface (Figure 5.3).
Figure 5.3  EPR spectra of DPT-$^{14}$N (left side), DPT-$^{15}$N (right side) adsorbed on the external surface of silicalite ZL5148 at different loadings, measured after aging for approximately 10 days (deoxygenated). A: 2 mm loading; B: 4 mm loading; C: 6 mm loading; D: 8 mm loading; E: 12 mm loading. From A to E, a progression from three-line slow motion to electron-electron dipolar interaction and finally to strong exchange interaction is observed.

When the $^{14}$N, and $^{15}$N nitrooxide probes are coadsorbed on the silicalite's external surface at various loadings, the anisotropy leads to spectra with broad and overlapping lines (Figure 5.4). Based on the results in Chapter 3, the strong binding site (pore openings) on the silicalite ZL5157 employed in this study is saturated with adsorbate loadings at approximately 100 mm. Consequently, spectrum A in Figure 5.4 with a total DPT loading of 10 mm is assigned to an exclusive adsorption of spin probes on the strong binding sites.
Figure 5.4  EPR spectra of equal amount of DPT-$^{14}$N and DPT-$^{15}$N, coadsorbed on the external surface of silicalite ZL5157 at different loadings, measured within a few hours of preparation (deoxygenated). A: low loading at 5 mm each; B: medium loading at 25 mm each; C: high loading at 100 mm each.

A qualitative inspection of EPR spectra in Figure 5.4 suggests that at the medium (Figure 5.4, spectrum B) and high loadings of DPT (Figure 5.4, spectrum C), the spectra from the mixed isotopes are not significantly different from the spectra of the individual isotopes, and possess single lines that are difficult to resolve. In contrast, it is more likely to resolve the signals from two isotopically labeled DPT probes at low loading where the dipolar interaction and exchange interaction are not dominating the lineshapes (Figure 5.4, spectrum A). Therefore, samples at low loadings with different ratios of DPT-$^{14}$N and DPT-$^{15}$N were prepared and analyzed using EPR (Figure 5.5). In these samples, the two
different DPTs are loaded concurrently, by mixing the stock solutions of each DPT before the addition of activated silicalite.

Figure 5.5  EPR spectra of DPT-\(^{14}\)N and DPT-\(^{15}\)N coadsorbed on the external surface of silicalite ZL5157 at a total loading of 10 mm, measured within a few hours of sample preparation (deoxygenated). From top to bottom, the \(^{14}\)N : \(^{15}\)N loading molal ratio is gradually increased.

From the series of spectra in Figure 5.5, it can be determined that even without computer-assisted simulations, the relative ratio of \(^{14}\)N, and \(^{15}\)N labeled nitroxides on the strong binding sites can be determined.

5.6 Dynamic Probe Exchange of Nitroxide Probes on Strong Bindings Sites with Those on Other Binding Sites or in Solution

To examine the possibility and efficiency of molecular exchange (not the spin exchange discussed in Chapter 4) between the adsorbate molecules on the strong binding
sites and the molecules in isooctane (or on the weak binding sites), a stepwise loading experiment was conducted. The adsorption equilibrium was first achieved with DPT-$^{14}$N probes in an amount that is more than the loading required for a complete coverage on the strong adsorption site assuming total adsorption; then DPT-$^{15}$N in the same amount was added and the system was again allowed to reach equilibrium. The loaded silicalite was separated and washed with fresh isooctane before it was dried, deoxygenated and measured in an EPR spectrometer. The EPR spectrum is shown in Figure 5.6. By comparing the EPR spectrum from the stepwise loading to the spectra from concurrent loading using different $^{14}$N/$^{15}$N ratios in Figure 5.5, it can be concluded that the stepwise loading produces a spectrum that resembles the equal loading spectrum from concurrent loading. Therefore, efficient probe exchange exists between the probes adsorbed on the strong binding sites and those in isooctane (or adsorbed on weak binding sites).
Figure 5.6 EPR spectrum of stepwise loaded sample (first DPT-\(^{14}\)N, then DPT-\(^{15}\)N, dashed line) using silicalite ZL5151. It is compared to the EPR spectra in Figure 5.5 for samples with concurrent loadings of DPT-\(^{14}\)N and DPT-\(^{15}\)N at various ratios (solid lines). The peak with a narrow linewidth indicated by the arrow is an artifact from unloaded zeolite and/or container tube as proven by control experiment.

5.7 Influence of Nitroxide Structures on the Binding Strength at the Strong Binding Sites

A mixture of 4-oxo-TEMPO and DPT-\(^{15}\)N with 1:1 molar ratio was used as probe molecules to examine the adsorption of oMeDBK on the silicalite external surface from
an isooctane solution. As discussed in Chapter 3, the amount of the nitroxides is fixed at a loading well below the amount required for a complete coverage of strong binding sites (the coverage is \(~10\%\) in Figure 5.7) and the amount of oMeDBK was varied to reach the onset of the fast motion, which indicates the complete coverage of strong binding sites by oMeDBK. The EPR spectra are shown in Figure 5.7.

![EPR spectra diagram](image)

**Figure 5.7** EPR spectra of 4-oxo-TEMPO and DPT-$^{15}$N coadsorbed on the external surface of silicalite ZL5157, each at 5 mm loading with varying amounts of oMeDBK (deoxygenated). The dashed arrow (left) indicates the fast motion from DPT-$^{15}$N. The solid arrow (right) indicates the fast motion from 4-oxo-TEMPO.

An inspection of Figure 5.7 suggests that while both nitroxides were displaced from strong binding sites at high oMeDBK loading, the quantitative and comparative detail (such as which nitroxide was displaced first and what is the percentage of probe in
fast motion for each nitroxide) is not obtainable from visual inspection. The computer-assisted simulation method accessible to the examiner is difficult to use in this case due to the presence and overlap of four EPR patterns ($^{14}$N slow motion, $^{14}$N fast motion, $^{15}$N slow motion and $^{15}$N fast motion). Qualitatively speaking, the fact that both nitroxides are displaced at similar, if not identical, ranges of oMeDBK loading, agrees with the results described in Chapter 3 and suggests that the adsorption strengths of the two nitroxides are similar on the strong binding sites of the silicalite's external surface.

In light of the difficulty encountered in Figure 5.7, a pair of nitroxides with a larger difference in adsorption strengths is desired for easier spectral analysis using qualitative methods. 4-Oxo-TEMPO and 4-hydroxy-TEMPO prove to be a good pair (Figure 5.8).
**Figure 5.8** EPR spectra of 4-oxo-TEMPO-$^{15}$N and 4-hydroxy-TEMPO coadsorbed on the external surface of silicalite ZL5157, each at 2.5 mm loading with varying amounts of oMeDBK (deoxygenated). The arrow indicates the fast motion from 4-oxo-TEMPO-$^{15}$N with $A_{iso} = 20.5$ G.

When 4-oxo-TEMPO-$^{15}$N and 4-hydroxy-TEMPO are coadsorbed on the strong binding sites of silicalite's external surface, the increased loading of oMeDBK clearly leads to the fast motion of 4-oxo-TEMPO-$^{15}$N first, judging from the characteristic $^{15}$N isotropic hyperfine coupling constant at approximately 20 G in isooctane (Figure 5.1). The stronger binding strength of 4-hydroxy-TEMPO agrees with the results discussed in Chapter 3, and suggests a strong interaction of the hydroxy groups on 4-hydroxy-TEMPO with the strong surface binding sites, probably through hydrogen bonding.
5.8 Conclusions

EPR spectra of $^{14}\text{N}$ and $^{15}\text{N}$-labeled nitroxides in a dilute solution of a non-viscous solvent can be readily resolved in deoxygenated conditions. When the mixture of isotopically labeled nitroxides is adsorbed on the silicalite surface, the low surface coverage samples (without strong electron-electron dipolar and exchange interactions) are more easily resolved than the samples with high surface coverage.

The stepwise adsorption of isotopically labeled nitroxides on the silicalite surface has been successfully used to examine the possibility of efficient dynamic exchange of nitroxides adsorbed on the strong binding sites with the nitroxides that are adsorbed on the weak binding sites or are in solution. The experimental results confirm the existence of the efficient dynamic exchange at room temperature on the time scale of several hours to a few days.

The coadsorption of isotopically labeled nitroxides with different molecular structures, in addition to a displacer (e.g., oMeDBK), has been used successfully to study the influence of molecular structure on the probe's binding strength on the silicalite surface’s strong binding sites. The experimental results qualitatively confirm that 4-oxo-TEMPO and DPT have similar binding strength on the strong binding sites, while the existence of a hydroxy group in 4-hydroxy-TEMPO makes its binding much stronger than 4-oxo-TEMPO.

5.9 References


Chapter 6. Conclusion and Outlook

6.1 Conclusion

The nitroxide@silicalite system has been studied using the indirect EPR method, direct EPR method and the isotopically labeling EPR method. The findings about this supramolecular system can be discussed in terms of static and dynamic properties. The determination of surface area through the analysis of static or dynamic properties is discussed separately, since it is the major objective of this thesis research.

6.1.1 Static Properties of the Nitroxide@Silicalite System

The presence of the two external surface adsorption sites (pore openings and framework surface, with the area ratio of approximately 18 to 82 on the [010] surface) for small organic molecules was confirmed. The adsorption strength on the pore openings is typically stronger than the adsorption on the framework surface. As a result of the site preference in the adsorption process, the supramolecular structure of the nitroxide@silicalite system is coverage dependent. Low coverage adsorption selectively occurs at the strong binding sites. After the strong binding sites are saturated, further adsorption occurs on the weak binding sites and eventually form a monolayer on the external surface of the silicalite.

Organic molecules adsorb on the silicalite’s external surface in a conformation that is most thermodynamically stable. Organic molecules containing a polar group in the structure, such as a carbonyl, hydroxyl or ester linkage, adsorb on the surface through the strong interaction of polar groups with the surface sites, possibly through hydrogen bonding with surface silanols. The possible intercalation of the phenyl/tolyl groups in the molecular structure does not contribute significantly to the binding strength compared to
that of the polar groups. If the molecular structure contains two groups that can interact strongly with the surface structures, such as the carbonyl group and the N-O moiety in 4-oxo-TEMPO, the adsorption occurs through the group that maximizes the interaction strength with the silicalite surface, which is the carbonyl group in the case of 4-oxo-TEMPO.

**6.1.2 Dynamic Properties of the Nitroxide@Silicalite System**

The adsorbate molecules possess a lower rotational mobility at the strong binding sites than at the weak binding sites. Investigation of EPR aging effects reveals that the translational mobility of the adsorbate molecules adsorbed at the strong binding sites are lower than those adsorbed at the weak binding sites, as aging leads to adsorbate migration in the latter case.

Using isotopically labeled nitroxides, it was concluded that the molecules adsorbed on the strong binding sites are in slow exchange with those in the isoctane solution. The exchange is slow enough on a time scale of minutes to allow the samples to be mildly washed without losing a significant amount of molecules from the adsorption sites, but is fast on a time scale of days.

The dynamic exchange between the adsorbate molecules adsorbed on the weak binding sites and those in the solution is fast on the time scale of minutes, and mild washing with isoctane leads to the complete removal of the adsorbates from the weak binding sites.

**6.1.3 Silicalite’s External Surface Area Determination Using EPR**

Using the indirect EPR method, the silicalite’s external surface area can be correlated to the amount of major adsorbate molecules (EPR-silent) required to reach a
certain surface coverage (approximately 1 ML) by following the change in the nitrooxide EPR spectral parameters (e.g., rotational correlation time) when some nitroxides are displaced from the strong binding sites by the major adsorbate molecules.

Using the direct EPR method, the silicalite's external surface area can be correlated to the amount of nitroxides required to fully occupy the surface's strong binding sites. At this surface coverage, the dipolar broadening caused by the nitroxides in slow motion and free from exchange averaging is at its maximum value. The Heisenberg exchange interaction increases with increasing surface coverage of the nitrooxide up to a plateau when the adsorbates reach a certain coverage on the weak binding sites and strongly interact with each other either statically due to closeness, or dynamically due to diffusional encounter.

Using the indirect EPR method and the direct EPR method, a comparison between the external surface areas confirms that the two methods essentially probe the same supramolecular structure on the external surface. Comparison of the EPR methods to the SEM geometrical analysis suggests that the SEM geometrical analysis is probably not reliable when there is the possible presence of surface structures in the nanometer scale.

6.2 Outlook

The external surface area of silicalite should be evaluated using a more reliable and accurate method, such as mercury porosimetry, than the SEM geometrical analysis employed in this work, and the more reliable and accurate results will provide a better examination of the accuracy and validity of the EPR methods developed in this work.
The possibility of studying the dominance of various external surfaces (e.g. [001] vs. [010]) in the total external surface of silicalite crystals, as suggested in Chapter 3, could be further examined using more silicalite samples prepared in the appropriate manners.

It has been concluded that the exchange of probe molecules between those adsorbed on the strong binding sites and those dissolved in the solution or adsorbed on the weak binding sites occurs on a time scale of days. A quantitative study on the exchange kinetics is desirable.

The strong binding between the adsorbate molecules possessing polar groups (such as carbonyl, hydroxyl and ester linkage) and surface adsorption sites suggests the possible involvement of hydrogen bonding in the interaction. This hypothesis can be examined using a multitude of experimental techniques. One is the infra-red spectroscopy, which measures the perturbation in the O-H vibration of the silanol groups or the C=O vibration of the adsorbate molecules caused by the adsorption.\(^1\) The binding of the N-O moiety with silanol groups as in the case of TEMPO adsorption can also be studied using ESEEM (Electron Spin Echo Envelope Modulation).\(^2-4\) ESEEM can be used to detect the presence of paramagnetic nuclei (such as H in the silanol) in the surroundings of the N-O moiety, through the study of periodic oscillation in the electron spin echo signal caused by the anisotropic coupling with neighboring nuclei.

The adsorption strengths of organic molecules on each of the two external surface binding sites can be studied quantitatively using variable temperature (VT) EPR experiments. In the VT-EPR experiments, the enthalpy and entropy of adsorption on each site can be revealed using the Gibbs free energy equation \(\Delta G = \Delta H - T \cdot \Delta S.\)\(^5\)
Measurements of solid external surface areas can be regarded as the measurements of inter-spin distance at a specific coverage. Therefore, other methods that can be used to measure inter-spin distance between the adsorbed nitroxides can be employed, too. The established methods for distance measurements in a noncrystalline system include fluorescence energy transfer (Forster dipolar coupling), NMR methods (Nuclear Overhauser Effects, and dipolar coupling of partially oriented molecules) and EPR methods. A multitude of EPR methods for distance measurements have been developed that can be carried out on Continuous Wave (CW) or pulsed Fourier Transform (FT) EPR spectrometers. Typical CW methods include progressive power saturation, CW line shape d, d, half-field transition intensity, deconvolution of the line shape, and the simulation of the full CW line shape. Typical FT (pulsed) methods include the measurement of $T_1$ (spin lattice relaxation time), $T_m$ (phase memory time), out-of-phase echo, 2+1 pulse, double quantum coherence, saturation recovery shape, ESE echo intensity, and DEER. These methods, which were developed and calibrated for different inter-spin distance ranges for the distance measurements have been critically reviewed.$^6,7$

The use of dipolar anisotropy from the simulation of CW-EPR spectra in the determination of inter-spin distance is not suitable for systems characteristic of strong spin exchange interaction, e.g., when the inter-spin distance is less than 10 to 15 Å. This limitation is manifested in the right side of the "V" curve as shown in Figure 4.15 when the surface coverage of nitroxide is beyond the saturation of pore openings and the nitroxide molecules are sufficiently close to undergo strong exchange interaction. One method for characterizing the distance of nitroxides at close proximity is the half-field transition intensity.$^6,8$
Anisotropic dipolar and exchange interactions between the two spins shift the triplet state \( m_s = \pm 1 \) energy levels relative to the \( m_s = 0 \) level and causes the transition probability of the normally forbidden transitions between the \( m_s = -1 \) \( m_s = -1 \) levels to become non-zero. The ratio of the integrated intensity of the half-field transition to the integrated intensity of the allowed transitions is a function of the inter-spin distance \( r \) and is independent of the exchange frequency (Equations 6.1 and 6.2).

\[
\text{Relative intensity} = \frac{\text{integrated intensity of half-field signal}}{\text{integrated intensity of allowed transitions}} \tag{6.1}
\]

\[
\text{Relative intensity} = \frac{(19.5 \pm 0.5)(9.1)^2}{r^2 v^2} \tag{6.2}
\]

In Equation 6.2, \( r \) is the inter-spin distance, and \( v \) is the microwave frequency. The half-field transition intensity method has been calibrated for an inter-spin distance of 4 to 12 Å and is suitable for the characterization of an inter-spin distance between the nitroxides at high surface coverage on silicalites as shown by the right side of the "V" curves in Figure 4.15. This method could potentially reveal the possible formation of a nitrooxide multilayer on the silicalite surface.

6.3 References


Part II.

End Labeling Efficiency in the Atom Transfer Radical Polymerization of Styrene
Chapter 7  End Labeling Efficiency in the Atom Transfer Radical Polymerization of Styrene

7.1  Introduction

Free radical polymerization (FRP) and anionic polymerizations are the two of the most frequently used processes for the preparation of polymeric materials.

Ignoring chain transfer and other possible complications, the sequence of steps involved in the FRP include initiation, propagation, and termination.\(^1\)

Initiation step consists of the dissociation of initiators \(I\) into radicals \(R^\cdot\) (Equation 7.1) and the addition of \(R^\cdot\) to a monomer \(M\) (Equation 7.2).

\[
I \xrightarrow{k_i} 2R^\cdot \tag{7.1}
\]

\[
R^\cdot + M \xrightarrow{k} M_1^\cdot \tag{7.2}
\]

Propagation consists of the growth of \(M^\cdot\) by the successive additions of large numbers of monomer molecules (Equation 7.3).

\[
M_n^\cdot + M \xrightarrow{k_2} M_{n+1}^\cdot \tag{7.3}
\]

Termination with annihilation of the radical centers occurs by bimolecular reactions between the radicals, either through combination (Equation 7.4) or disproportionation (Equation 7.5). The structures of the products from combination and disproportionation reactions are shown in Scheme 7.2.

\[
M_n^\cdot + M_m^\cdot \xrightarrow{k_t} M_{n+m} \tag{7.4}
\]
\[ M_a \rightarrow M_n \xrightarrow{\text{1,2}} M_n \rightarrow M_m \]  

(7.5)

7.1.1 Free Radical Polymerization versus Anionic Polymerization

The two polymerization methods both have their advantages and disadvantages.

1. Radicals are compatible with many functional groups such as carbonyl, ester and hydroxyl and therefore FRP can be used for the polymerization of a large variety of vinyl monomers, such as styrenes, acrylates, and methacrylates. Radical polymerization can be carried out in a large range of temperatures (typically -20 to 200 °C).

In contrast, anions react with a large variety of functional groups at the nucleophilic or acidic sites (Scheme 7.1). When the anionic method is used, the incompatible functional groups have to be protected during the polymerization process to prevent the undesired reactions that deactivate the propagating anions. or the polymerization should be conducted at a low temperature to minimize the undesired reactions. The protection and deprotection procedures are not only time-consuming and costly, but also lead to impure products. In addition to the possible side reactions in the protection and deprotection procedures, the protection and deprotection reactions usually cannot go to completion. Separating the polymer molecules with identical and long chains and only a minute difference in the end groups is practically impossible except in certain special cases. Temperatures lower than room temperature are typically more difficult and costly to reach and maintain than temperatures higher than room temperature and this is especially true in industrial settings.
Scheme 7.1 Anionic polymerization of methyl methacrylate and some representative undesired reactions. A: desired propagation reaction; B: undesired nucleophilic substitution reaction with the monomer; C: undesired intramolecular nucleophilic “backbiting”; D: undesired reactions with impurities, such as water. The reaction with acidic protons can also occur between the carbanions with hydroxyls in the polymer chains if such hydroxyls are present.

2. Radical polymerization also has the advantage of being tolerant to water and it can even be conducted in an aqueous solution of the monomers, as long as the reaction system is free from oxygen. In contrast, water and other protic impurities have to be completely removed before an anionic polymerization can be successfully conducted (Scheme 7.1, D) and this typically requires the use of high vacuum technique.
3. The major disadvantage of the conventional radical polymerization is the poor control of macromolecular structures including the degree of polymerization, polydispersities, end functionalities, chain architectures, and compositions. The limitations of the conventional radical polymerization is mainly due to the fact that the propagating chains have the capability of reacting with each other, either through combination or disproportionation reactions (Scheme 7.2). Combination gives rise to one polymer chain with a molecular weight of the sum of the two terminating chains and the polymer product cannot propagate any more. The disproportionation reaction gives rise to two polymeric chains, one of which has a saturated end without polymerization ability and the other has an unsaturated end and could potentially act as a macromonomer under certain conditions. Since combination and disproportionation reactions occur throughout the whole polymerization process, a mixture of polymer chains with different chain lengths is typically obtained in the final product. In contrast, the reactive centers in an anionic polymerization are the anions, which cannot react with each other. In the absence of impurities, such as water and oxygen, each polymer chain continues the propagation until the monomer is exhausted, resulting in a polymer chain product with a narrow distribution of the chain lengths.
A: termination by combination

\[ \text{H} \quad \text{C}^\cdot \quad \text{C} \quad \text{H} \quad \text{H} \quad \xrightarrow{k_{tc}} \quad \text{H} \quad \text{H} \]

\[ \text{X} \quad \text{X} \quad \text{C} \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{X} \quad \text{X} \]

B: termination by disproportionation

\[ \text{H} \quad \text{C}^\cdot \quad \text{C} \quad \text{H} \quad \text{H} \quad \xrightarrow{k_{td}} \quad \text{H} \quad \text{H} \]

\[ \text{X} \quad \text{X} \quad \text{C} \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH} = \text{CH} \quad \text{X} \quad \text{X} \]

**Scheme 7.2** The termination mechanisms in the conventional free radical polymerization. A: termination by combination resulting in one saturated polymer chain with a molecular weight of the sum of the two reacting radicals. B: termination by disproportionation resulting in one saturated polymer chain and another polymer chain with unsaturation at one end.

7.1.2 Average Molecular Weights and Molecular Weight Distribution

Polymers, in their purest form, are a mixture of chains with different chain lengths. The polydisperse or heterogeneous nature of the chains lies in the statistical variations present in the polymerization process, in addition to unwanted termination and transfer reactions, such as those in the FRP. Therefore, the characterization of the molecular weight of a polymer sample requires the use of at least two parameters: the average molecular weight and the exact distribution of the different molecular weights within a sample. The average molecular weight is typically presented in one of the following three manners:

1. The number-average molecular weight $M_n$, which is related to the colligative properties such as freezing-point depression, boiling point elevation, osmotic
pressure, and vapor pressure lowering.\(^1\) \(M_n\) is defined as the total weight of all the molecules in a polymer sample divided by the total number of polymer chains present (Equation 7.6).

\[
M_n = \frac{\sum N_i M_i}{\sum N_i}
\]  

(7.6)

where \(N_i\) is the number of moles of polymer chains whose molecular weight is \(M_i\).

2. The weight-average molecular weight \(M_w\), which is related to the light scattering properties of the polymer sample. \(M_w\) is defined by the Equation 7.7.

\[
M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}
\]  

(7.7)

3. The viscosity-average molecular weight \(M_v\), which is related to the viscosity measurements. \(M_v\) is defined by the Equation 7.8.

\[
M_v = \left[ \frac{\sum N_i M_i^{a-1}}{\sum N_i M_i} \right]^{\frac{1}{a}}
\]  

(7.8)

where \(a\) is a constant typically in the range of 0.5 to 0.9.

In an ideal polymer sample where all chains have exactly the same lengths, the three average molecular weights are of the same value, i.e., \(M_w = M_v = M_n\). For a polydisperse polymer, the relation between the three measurements of average molecular weight is \(M_w > M_v > M_n\), because of the increasing bias on the lower molecular weight fractions in the definition of \(M_w\), \(M_v\), and \(M_n\). The ratio of \(M_w\) to \(M_n\), called polydispersity index (PDI) (Equation 7.9), is a measurement of the distribution of the
chain lengths. PDI is always larger or equal to 1. The larger the PDI value is, the more polydisperse the polymer sample is.

\[
PDI = \frac{M_x}{M_n}
\]  

(7.9)

A polymer sample prepared using conventional free radical method would typically have a PDI value of 2 or higher mostly due to the uncontrolled termination reactions through combination and disproportionation. In contrast, a polymer sample prepared using anionic method would typically have a PDI less than 1.1. Polymer samples with a PDI less than 1.5 are called monodisperse samples.

7.1.3 Controlled/Living Free Radical Polymerization

The term *living* describes the mechanism of the polymerization and refers to a chain growth process without chain breaking reactions (transfer and termination). The term *controlled* describes the properties of the product and refers to the desired average molecular weight and a narrow molecular weight distribution. A living polymerization is also controlled, if the initiator is consumed at early stages of the polymerization and the exchange between species of various reactivities is fast in comparison with propagation. A typical anionic polymerization is a living and controlled process, while a conventional free radical polymerization is not either a living or a controlled process.

In light of the limitations of conventional free radical polymerization and anionic polymerization methods, it is desirable to combine the advantages of the two methods while avoiding the disadvantages. In the past few decades, a multitude of methods for controlled/living free radical polymerizations have been developed for the preparation of
well-defined polymers. Among these methods, Nitroxide Mediated Radical Polymerization (NMRP), Reversible Addition-Fragmentation Transfer polymerization (RAFT), and transition-metal catalyzed Atom Transfer Radical Polymerization (ATRP) (Scheme 7.3) have been widely used, especially for the polymerization of styrene and methacrylates. These methods combine the tolerance toward the trace amount of impurities (e.g., water and various functional groups), which is characteristic of radical polymerization, and the excellent control over the polydispersity of the polymer product, which was previously reserved for more tedious anionic synthetic methods. The mechanisms of these methods are free radical in nature, but the unwanted chain termination reactions (by combination and disproportionation) are suppressed. The excess of nitroxide in NMRP, and the excess of metal/ligand complex in ATRP, can reversibly react with the propagating chains and therefore maintain a low static concentration of propagating radicals (R·), e.g., 10⁻⁸ to 10⁻⁷ M in the bulk ATRP polymerization of styrene, methyl acrylate or methyl methacrylate at 130 °C. Since the rate of the termination reactions has a stronger dependence on the concentration of active chains than the rate of the propagation reactions (kₜ ≈ [R·]² versus kₚ ≈ [R·][Monomer]), the termination reactions are effectively suppressed and the polymerization process is close to being living. The fast exchange between the dormant chains R-X and the reactive radicals R· (Scheme 7.3) ensures that all polymer chains propagate at the same overall rate and thus a low polydispersity is obtained. The controlled/living free radical polymerization routinely provides polymer products with PDI less than 1.5 and in the optimized cases, the PDI value can approach the values previously reserved for anionic procedures, such as 1.1 or less.
Scheme 7.3 The mechanism of transition-metal catalyzed ATRP. M is the transition metal. X is a (pseudo)halogen atom. Y is another ligand or counterion. \( k_{\text{act}}, k_{\text{deact}}, k_p \) and \( k_t \) are the rate constants for activation of the dominant chain \( R-X \), deactivation of the active propagating chain \( R \cdot \), propagation reaction with monomers, and bimolecular termination reactions, respectively.

The structures of some frequently used ATRP initiators, transition metal compounds, and ligands are shown in Scheme 7.4.

Scheme 7.4 Structures of some frequently used ATRP initiators (A and B), transition metal compound (C), and ligands typically in the form of multidentate amines (D and E).\(^9\)

One of the major applications of the newer methods has been the preparation of monodisperse polymers with special end group, through the convenient use of initiators as the built-in end group,\(^{10,11}\) as exemplified in Scheme 7.5. The percentage of polymer chains in the product that have the desired end groups, i.e., degree of labeling is an important parameter for the applications of these polymers, including the study of polymer kinetics.\(^{12}\) If the assumption were valid that all the polymer chains were initiated by the designated initiators, the degree of labeling should be 100%. However, this assumption is not necessarily valid under all conditions.
Scheme 7.5 The synthesis of an end-labeled polystyrene using a labeled ATRP initiator. $R$ is the end label. $R$ is carried along the reaction and retained in the polymer product. Chain activation, deactivation and propagation steps are shown. The termination reactions are negligible due to the low static concentration of propagating radicals.

It is known that the molecular weight of polystyrene prepared by ATRP can reach values as high as $8 \times 10^4$ for a reaction temperatures of 110 $^\circ$C and $1.5 \times 10^5$ for a reaction temperature 100 $^\circ$C when initiated by 1-phenylethyl bromide (Scheme 7.4, A) and catalyzed by CuBr / 2 bipy (Scheme 7.4, C and D).\textsuperscript{13} Unlike methacrylate, styrene is known to autopolymerize at temperatures higher than 100 $^\circ$C, where the thermal self-initiation cannot be neglected in the bulk polymerization of styrene.\textsuperscript{14} When an end labeled polystyrene sample with a high molecular weight, e.g., larger than $1 \times 10^5$ is targeted in a reaction, the polymerization rate due to the thermal process can be even comparable to the overall polymerization rate due to the low concentration of initiator and catalyst.\textsuperscript{15} While each polymer chain initiated by the desired labeled initiator carries an end label, the polymer chain initiated by the thermal self-initiation does not possess such an end label, which was built into the initiator (Scheme 7.6). Even though the
polydispersity could remain low because of the excessive amount of the transitional metal/ligand complexes also regulate the growth of the thermally initiated chains and the efficient exchange reactions between the dormant and reactive chains, significant thermal self-initiation will reduce the percentage of polymer chains bearing the desired functionality.

A: ATRP reaction

\[ \text{A} \quad \text{ATRP reaction} \]

\[
\begin{align*}
\begin{array}{c}
\text{n} \\
\text{Ph}
\end{array}
\quad + \\
\begin{array}{c}
\text{R-O} \\
\text{CO} \\
\text{Br} \\
\text{CuBr/Ligand}
\end{array}
\quad \rightarrow \\
\begin{array}{c}
\text{R-O} \\
\text{CO} \\
\text{Br} \\
\text{Br}
\end{array}
\quad \left[ \text{Ph} \right]_n
\end{align*}
\]

labeled product

B: thermal autopolymerization

\[
\begin{align*}
\begin{array}{c}
\text{n} \\
\text{Ph}
\end{array}
\rightarrow \\
\begin{array}{c}
\text{X} \\
\text{Y}
\end{array}
\quad \left[ \text{Ph} \right]_n
\end{align*}
\]

unlabeled product

**Scheme 7.6** ATRP reaction using a labeled initiator produces an end-labeled polymer product and thermal autopolymerization results in a product without the desired end label. R- is the desired end label built in the ATRP initiator and is carried over to the final product. X- and Y- are moieties other than R-, e.g., Br-.

In the case of NMRP, several research groups have published studies on the degree of labeling as a function of chain length and monomer conversion.\(^{16,17}\) The results confirmed that for regular TEMPO nitroxide, high chain end labeling retention efficiency (> 90%) could only be achieved for short chains (\(M_n < 1 \times 10^4\)). In the case of ATRP, the published results have shown near 100% labeling, with the evidence again based on relatively short polymer chains using frequently Gel Permeation Chromatography, NMR, UV and mass spectrometry analyses. Long chain polystyrenes with high end labeling
efficiency are desirable for a variety of applications including their potential use in the
study of polymer kinetics in the entangled region. To the best of our knowledge, there
have not been any published results on the degree of labeling for long chain polymers
prepared by ATRP.

Another question could be raised about the similarities and differences in the
profiles (the number average molecular weights "M_n" and the polydispersity index "PDI")
of all the polymer chains in a sample and the labeled chains only. It is well known that
during prolonged polymerization reaction, the terminal reactivity of a significant number
of chains could be altered or even lost due to various mechanisms, e.g., formation of
peroxide, double bond formation from hydrogen abstraction and redox reactions. These factors tend to broaden the distribution of molecular weights, but do not affect the
degree of labeling. At high monomer conversion, thermal self-initiated polymerization of
styrene makes a larger contribution to the overall rate of polymerization due to the
decreased rate of the desired propagation reaction, and this effect not only increases the
PDI, but also reduces the degree of labeling. Therefore, for the polymer samples that have
high molecular weights, and are prepared from long reactions with low initiator
concentration, either or both of the factors could be prominent and the average molecular
weight and PDI of the overall sample might not provide an accurate characterization of
the labeled polymer chains.

7.2 Research Objective

The objective of this research is the understanding of the end labeling efficiency
of polystyrene prepared by ATRP at 100 °C as a function of chain length. The average
molecular weight and polydispersity of the labeled fraction are also compared those of the overall sample.

7.3 Experimental Methods

Materials and Instrumentation. The reagents were purchased from Aldrich and used as received unless otherwise noted. Styrene was distilled under reduced pressure over CaH₂ before it is used for polymerization. CuBr (Aldrich, 99.999%) was kept under argon atmosphere for storage. Tetrahydrofuran (THF, HPLC grade, inhibitor free) was used as solvent for Gel Permeation Chromatography (GPC), purification of polymer samples, and fluorescence lifetime measurements.

GPC measurements were conducted on a Polymer Laboratories (PL) GPC system, consisting of a guard column (5 Å), two PL mixed-D columns (5 Å, 30 cm, linear range of MW: 200 – 4.00 x 10⁵), and a 100 Å column connected in series. The polymers in the eluant was detected by a Groton Fluorescence (FL) detector and a Knauer Refractive Index (RI) detector connected in series, controlled by a PC running PL Cirrus 1.1 software. The GPC was calibrated with a PS-2 EasiCal polystyrene standard for optimal calibration for samples with MW less than 4.00 x 10⁵. For samples with MW fraction higher than 4.00 x 10⁵ but lower than 2.00 x 10⁶, two mixed-C columns (linear range of MW: 200 – 2.00 x 10⁶) were used instead of the mixed-D columns and the calibration was achieved using a PS-1 EasiCal polystyrene standard for calibration up to a MW of 2.00 x 10⁶. GPC analysis was carried out with a polymer concentration at 0.1%, i.e., 1 mg of polymer sample for 1 ml of THF.
For the analysis of pyrene labeled chains only, the fluorescence detector on the GPC was used with excitation wavelength of 344 nm (with a 345 nm cutoff long-pass filter) and emission wavelength of 396 nm.

Steady-state fluorescence excitation and emission spectra were recorded on a Fluoromax 2 spectrometer (SPEX). Fluorescence lifetime measurements were conducted using single photon counting on OB900 Fluorometer (Edinburgh Analytical Instrument) using a pulsed nitrogen lamp as excitation source (excitation wavelength: 337 nm).

$^1$H-NMR spectra were recorded on Bruker NMR spectrometer at either 300MHz or 400 MHz using C$_6$D$_6$ (for monomer conversion) or CDCl$_3$ as solvent as needed.

**Synthesis of 2-Bromo-propionic acid 4-pyren-1-yl-butyl ester, 1** (Scheme 7.7). 1-pyrenebutanol (1.73g, 6.30 mmole), 2-bromo-2-methylpropionic acid (1.16 g, 6.94 mmole), 1,3-dicyclohexylcarbodiimide (DCC, 1.69g, 8.20 mmole), and 4-pyrrolidinopyridine (0.187 g, 1.3 mmole) were mixed in a 25 ml THF for 24 hours in the dark, after which the THF was removed by rotary evaporation and a 50 ml dichloromethane was added. The solution was washed with 100 ml 0.5 N HCl for three times. After column chromatography (30:1 hexane: ethyl acetate, v/v), 1 was dried and recrystallized from hexane. $^1$H-NMR (CDCl$_3$, $\delta$, ppm): 1.70-2.13 (m, 10 H), 3.35, 3.38, 3.40 (t, 2 H, J$_{H-H}$ = 7.5 Hz), 4.23, 4.25, 4.27 (t, 2 H, J$_{H-H}$ = 6.6 Hz), 7.74-8.27 (m, 9 H). $^{13}$C-NMR (CDCl$_3$, $\delta$, ppm): 171.7, 136.2, 131.4, 130.9, 129.9, 128.6, 127.5, 127.3, 127.2, 126.6, 125.8, 125.1, 125.0, 124.9, 124.8, 124.7, 123.3, 123.3, 65.8, 55.9, 33.0, 30.8, 28.4, 28.0. MS (FAB): 423.35. Excitation and emission spectra were also recorded to attest to the absence of pyrene degradation.
Scheme 7.7  The synthesis of pyrene end-labeled ATRP initiator (1).

**General Procedure for Polymerization**

CuBr, \( N,N',N'',N''\)-pentamethyldiethylenetriamine (PMDETA, Scheme 7.4, E), initiator (1), distilled styrene and a stir bar were added into a test tube under argon. The test tube was connected to a vacuum line and degassed using three Freeze-Pump-Thaw cycles cooled with liquid nitrogen. The test tube was then partially filled with argon. The reaction mixture was heated at 100 °C in an oil bath with stirring. At appropriate time, the reaction was stopped by quenching the reaction mixture in a water/ice mixture.

**Purification and Characterization of Polymer Samples**

The polymer samples were diluted in THF and passed through first an alumina column to remove the copper complexes and then a syringe filter (Teflon, 1 μm) to remove particulate material. Then the solution was concentrated by rotary evaporation and three dissolve (in THF and/or \( \text{CH}_2\text{Cl}_2 \))-crash (methanol, HPLC)-filter (frit funnel, M) cycles were used to remove low molecular weight impurities. The solid sample was dried under strong vacuum (ca. 5 x 10⁻⁵ Torr) to remove solvent completely as evidenced by \(^1\text{H}-\text{NMR (CDCl}_3\)). Excitation and emission spectra were recorded to demonstrate the absence of pyrene photodegradation during reaction and purification.\(^{20-22}\)
7.4 Results and Discussion

7.4.1 The Choice of the Reagents and Reaction Conditions

Two of the most frequently used ATRP initiators are based on benzylic structure or 2-bromo-2-methylpropionic acid ester (Scheme 7.4, A and B). The latter was selected for this study due to the ease of functionalization by a simple esterification reaction (Scheme 7.7).\(^{23}\) Pyrene was chosen as a model fluorescent end label and was conveniently introduced to the initiator due to the following reasons.

1. The pyrene label in the ATRP initiator (1) can be selectively excited at 344 nm with a high extinction coefficient of \(\varepsilon_{\text{ex}} = 4.43 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}\), where phenyl rings in the polystyrene backbone do not absorb to any significant extent (\(\varepsilon_{\text{ex}} = 0.207 \text{ M}^{-1} \text{ cm}^{-1}\)) (Figure 7.1).
Figure 7.1  UV spectra of pyrene labeled polystyrene (solid spectrum) and unlabeled styrene (dashed spectrum). The concentration of repeat units (phenyl groups) is the same for the two spectra.

2. Pyrene label possesses a strong fluorescence emission at a relatively long wavelength (e.g., 396 nm) far from the polystyrene emission (Figure 7.2).
Figure 7.2  The fluorescence spectra of pyrene labeled ATRP initiator (1), pyrene end-labeled polystyrene with 169 phenyl groups per chain on average ($M_n = 1.80 \times 10^4$), and unlabeled polystyrene. The match of the fluorescence spectra for the initiator and the labeled polymer suggests that the contribution from the polystyrene backbone is negligible for this polymer sample.

3. Pyrene label has a demonstrated stability toward radicals in the reaction media.\textsuperscript{24}

Despite the fact that pyrene has the above-mentioned advantage for end labeling, care must be taken to avoid photodegradation due to extensive exposure to light, especially on solid support or in halogenated solvent.\textsuperscript{22} Excitation and emission spectra were also recorded to ensure the absence of the photodegradation products.

The ligand of choice was PMDETA (Scheme 7.4, E) due to its ability to maintain a low polydispersity while keeping a relatively fast reaction rate.\textsuperscript{25}
The reaction temperature employed was 100 °C. Temperature higher than 110 °C tends to result in low MW samples due to fast self-initiated polymerization and other side reactions, while temperature less than 100 °C will be unfavorable for styrene bulk polymerization due to vitrification and low copper complex solubility. Monomer conversion was varied from approximately 10% to 100%. The ratio of initial concentration of monomer to initiator was varied from 200:1 to 2,500:1 with theoretical $M_n = 2.00 \times 10^4$ to $2.50 \times 10^5$ assuming the absence of all side reactions, complete monomer conversion and unity initiation efficiency.

### 7.4.2 Determination of the Monomer Conversion

The monomer conversion was measured using $^1$H-NMR, by comparing the number of α (or β) protons in the monomeric styrene to that in the polymerized styrene using C₆D₆ as solvent (Figure 7.3). An inter-pulse delay time longer than $5 \times T_1$ was employed. Very viscous samples were first dissolved in benzene and then $^1$H-NMR spectra were measured in C₆D₆.
Figure 7.3  NMR spectrum of the reaction mixture in deuterated benzene. Peaks corresponding to the β protons in the unreacted styrene molecules and the polymer backbones are indicated. The relative signal intensities are used for the calculation of monomer conversion. In this sample, the conversion is determined to be 25%.

7.4.3 Determination of the Number-Average Molecular Weight $M_n$ and Polydispersity Index PDI

The $M_n$ and PDI of the overall polymer sample (labeled and unlabeled) can be easily determined using the refractive index detector on the GPC (abbreviated as GPC-RI). The response of RI detector is proportional to the product of chain length and number of chains with that length, i.e., the total number of repeat units in the light path at that instant. RI detector offers the ability to analyze the average molecular weight and its
distribution of all polystyrene chains, regardless of end label (Figure 7.4). RI signal
distortion resulting from "preferential solvation" of end label by water was deemed
unlikely since addition of up to 2% (by volume) water into the sample solution yielded no
difference in the calculated average molecular weight and distribution.\textsuperscript{16} The \( M_n \) value
obtained from GPC-RI analysis is designated as \( M_n \) (GPC-RI) and it is the true number-
average molecular weight of the overall polymer sample.

\[
\begin{align*}
\text{labeled} & \quad \text{refractive index detection} \\
& \quad \text{fluorescence detection} \\
\text{unlabeled} & \quad \text{refractive index detection only}
\end{align*}
\]

Figure 7.4 Detection of polymers with and without end labels. The pyrene end-labeled polymer (left) can be detected by both refractive index and
fluorescence detectors, and the unlabeled polymer (right) can only be detected by
the refractive index detector, but not the fluorescence detector optimized for
pyrene detection (excitation: 344 nm, emission: 396 nm).

The \( M_n \) of the overall polymer sample assuming each polymer chains carries
exactly one end label can be determined using \(^1\text{H}-\text{NMR}\) by comparing the integral of the
signals corresponding to the protons on the pyrene rings to the integral of the signals
对应的 protons on the polymer backbone. The \( M_n \) value obtained from \(^1\text{H}-\text{NMR}\) analysis is designated as \( M_n \) (\(^1\text{H}-\text{NMR}\)).

The \( M_n \) and PDI of the labeled fraction only can be determined using the
fluorescence detector on the GPC (abbreviated as GPC-FL). When the excitation (344
nm) and emission wavelength (396 nm) were set such that the pyrene moiety was
monitored, fluorescence detector offers a tool to selectively analyze the pyrene labeled polystyrene chains (Figure 7.4). The fluorescence detector also has a much higher signal to noise ratio compared to refractive index detector. Polymer chains that are produced through self-initiation of styrene do not bear a pyrene end group and therefore are not registered by the fluorescence detector. Commercial algorithms for the processing of detector response are typically written assuming a detector response linearly proportional to the total number of repeat units passing through the detector at any instant, such as the response of a refractive index detector. When the fluorescence detector is set to selectively monitor the pyrene end labels only, the detector response is linearly proportional to the total number of labeled polymer chains passing through the detector at any instant, regardless the number of repeat units in each chain. Therefore, the chromatograph obtained using a fluorescence detector was first processed using the default algorithm (designed for detectors such as RI) to generate a table of slice data displaying the retention time, the corresponding molecular weight determined from the calibration curve, and the corresponding detector response. The slice data were subsequently manually processed using spreadsheet software to yield the correct number and weight averaged molecular weight.

The $M_n$ value obtained from GPC-FL analysis is designated as $M_n$ (GPC-FL).

7.4.4 Determination of the Degree of Labeling

An intuitive manner of determining the degree of labeling would be using mass spectrometry, especially the MALDI-TOF (matrix-assisted laser desorption ionization-time of flight) method. However, acceptable resolution that is sufficient to distinguish the labeled and unlabeled polystyrene chains can only be achieved for polymer samples of
low molecular weights (e.g., MW < $1 \times 10^4$). Quantification of the degree of labeling using MALDI-TOF is further complicated by the bias of signal on the low molecular weight fractions.

The method chosen for the quantification of end labels is fluorescence. The integral of GPC-FL signal response corresponding to the pyrene labels was used in this study to quantify the amount of pyrene labels with high sensitivity. To ensure the validity of this method, various controls were checked and select experiments were conducted. Quenching of pyrene fluorescence by the polystyrene chain is negligible.\textsuperscript{28} Fluorescence measurements confirmed the absence of pyrene eximer formation at the highest polymer concentration employed in the analysis. Integration of fluorescence detector response on the GPC for the sample at various concentrations showed a linear detector response for the concentration range of interest (Figure 7.5).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure75.png}
\caption{The GPC-FL integrated response as a function of sample concentration for an end-labeled sample with Mn (GPC-RI) = $2.92 \times 10^4$, and PDI = 1.13. A linear relationship is observed.}
\end{figure}
Single photon counting measurements confirmed that for all the polymer samples with $M_n$ (GPC-RJ) from approximately $6.00 \times 10^3$ to $1.00 \times 10^5$, the fluorescence lifetimes are essentially the same at 21 ns in aerated THF solution (Figure 7.6). This ensures the same fluorescence quantum yield for all the samples when analyzed using the fluorescence detector in the GPC. It is to be noted that the fluorescence lifetime of the initiator at the same condition is 14 ns, making it unacceptable as a standard in generating a calibration curve for the quantification of pyrene end groups in the polymer samples.

![Fluorescence lifetime measurement](image)

**Figure 7.6** Single photon counting as a measurement of the fluorescence lifetime of the pyrene label on a polystyrene sample dissolved in THF. Blue line is the lamp profile, black line is the experimental spectrum and red line is the spectral fitting result. The experiment was conducted using an excitation wavelength of 337 nm, an emission wavelength of 396 nm, a time range of 200 ns, and 10,000 counts. The fluorescence lifetime of the pyrene label is determined to be 20.9 ns.
However, the initiator was added at a set concentration into the solution of polymers before the GPC analysis for two reasons. Firstly, the initiator can be used as a flow rate marker to offset the fluctuations in the solvent flow rate between separate runs, its suitability confirmed by comparison to the well-accepted flow rate marker toluene. Secondly, it was found that while during multiple runs of the same sample solution, the error of the measurement of fluorescence signal integral of the pyrene labels can be subject to an error as high as 10%, the ratio of the signal integral from the pyrene labels in the polymer sample to that of the pyrene moieties in the initiator is only subject to an error of no more than 2.5%, suggesting that the major error without initiator is due to the limited reproducibility of sample injection volume. Therefore, the ratio of signal integral from pyrene labels in the polymer to that from a constant concentration of pyrene labels in the initiator is used in the quantification of pyrene groups in a polymer sample. To obtain the absolute concentrations of pyrene labels in an unknown sample, a polymer sample with $M_n$ (GPC-RI) = 1.73 $\times$ 10$^5$ and $M_n$ ($^1$H-NMR) = 1.74 $\times$ 10$^5$ is assumed to have 100% labeling due to the excellent match in the $M_n$ values obtained from GPC-RI and $^1$H-NMR methods.

The concentration of the pyrene labels in a solution of the polymer sample is determined using the method as detailed above. The concentration of the polymer chains can be obtained from the calculation using $M_n$ (GPC-RI) of the polymer sample, the mass of the polymer sample and the volume of the solution. The ratio of the concentration of the pyrene labels to the concentration of polymer chains is regarded as the degree of labeling.
7.4.5 Degree of Labeling as a Function of Polymer Chain Length, $M_n$

The degree of labeling as a function of number-average molecular weight, $M_n$ (GPC-RI) for each sample prepared using a different initial monomer to initiator ratio, $[M]_0: [\text{Init}]_0 = 300, 600, 1000, 1500, 2500$ at $100\, ^\circ C$ is shown in Figure 7.7. It can be seen that for polymer products at the same molecular weight, the reaction that has the lower $[M]_0: [\text{Init}]$ gives higher degree of labeling. This is expected from the smaller contribution of autopolymerization to the product formation when the rate of the desired controlled propagation reaction is faster due to a higher concentration of propagating radicals. For the polymer products prepared with a $[M]_0: [\text{Init}] = 250,000$, the degree of labeling can be as low as approximately 50%. Another interesting observation is that for the reaction with $[M]_0: [\text{Init}]$ at 300 and 600, the degree of labeling was also low at low monomer conversion. A possible hypothesis is that at those conversions, the reaction time is so short that, the dissociation of initiator is not complete yet, therefore resulting in a growing but lower number of propagating chains. Therefore, at this early stage of reaction, the contribution from autopolymerization to the overall polymerization reaction is larger than that at the later stage.
Figure 7.7  Degree of labeling as a function of $M_n$ (GPC-RI) for polystyrene samples prepared at 100 °C with different $[M]_0$: [Init] ratio: 300, 600, 1000, 1500, 2500.

It is interesting to note that for some of the samples with low $[M]_0$: [Init]$_0$ ratio (e.g., $[M]_0$: [Init]$_0$ = 300) and intermediate monomer conversion, the average degree of labeling can be slightly higher than 100%. The number average molecular weight of the corresponding polymer samples assuming 100% labeling obtained from $^1$H-NMR, $M_n$ ($^1$H-NMR) analysis is smaller than that obtained by the RI detector on the GPC. $M_n$ (GPC-RI) (Figure 7.8). This confirms that some of the polymer chains at this condition could have more than one pyrene end groups, most possibly due to the combination reactions between the mono-labeled oligomeric/polymeric radicals since the concentration of propagating radicals are high due to high initial concentration of the
initiator. For polymer samples with degree of labeling significantly less than 100%, the $M_n$ by $^1$H-NMR is significantly higher than that by GPC-RI as expected.

![Graph showing the ratio of $M_n$ determined by $^1$H-NMR to that by GPC-RI as a function of degree of labeling for pyrene end-labeled polystyrenes.](image)

**Figure 7.8** Ratio of $M_n$ determined by $^1$H-NMR to that by GPC-RI, as a function of degree of labeling for pyrene end-labeled polystyrenes.

### 7.4.6 Number-Average Molecular Weight and Polydispersity Index of the Overall Sample versus Those of the Labeled Sample

The differences in the $M_n$ profiles of the labeled fractions versus the unlabeled fractions can be easily appreciated from Figure 7.9.

For polymer samples with degree of labeling close to 100%, $M_n$ (GPC-RI) is approximately the same as $M_n$ (GPC-FL). This result is expected, since at high degree of
labeling, both GPC-RI and GPC-FL methods are characterizing the same group of polymers. For those samples with degree of labeling significantly lower than 100%, especially the samples with long chains, it can be seen that $M_n$ (GPC-FL) is higher than $M_n$ (GPC-RI). This result suggests that while overall samples can have low average molecular weight, the labeled fraction has a slightly higher average molecular weight. The difference in PDI for the labeled and unlabeled chains is not as significant as the $M_n$.

![Graph showing the ratio of $M_n$ (GPC-FL) to $M_n$ (GPC-RI) as a function of degree of labeling for samples prepared at 100°C with different [M]_0: [Init] ratio: 300, 600, 1000, 1500, 2500.]

**Figure 7.9** Ratio of $M_n$ (GPC-FL) to $M_n$ (GPC-RI) as a function of degree of labeling for samples prepared at 100°C with different [M]_0: [Init] ratio: 300, 600, 1000, 1500, 2500.

7.5 Conclusion

The degree of end labeling in ATRP polymerization of styrene at 100 °C is dependent on the desired molecular weight of the polymer samples. When very low molecular weight samples are targeted in the synthesis, higher than 100% labeling could
be seen, possibly due to combination reactions. When high molecular weight samples are targeted in a synthesis, the degree of end labeling could be significantly lower than 100%.

For the polymer samples with less than 100% end labeling, the number average molecular weight of the labeled fraction is typically higher than that of the overall sample.

7.6 References

(6) Moad, G.; Rizzardo, E.; Thang, S. *Polymer Preprints (American Chemical Society: Division of Polymer Chemistry)* 2002, 43, 114.