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STUDIES OF PHOTOCHEMICAL ASSEMBLIES IN
ZEOLITE-Y AND MEMBRANE-LIKE LAYERED DOUBLE HYDROXIDES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By
Marlon Parchaso Borja, B.S.

*****

The Ohio State University
1997

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ABSTRACT

Two inorganic matrices, layered double hydroxides (LDH) and zeolite-Y were used to host photoreactive molecules. The structure and properties of these host materials were employed in orienting the photoactive species through steric, electrostatic and hydrophobic/hydrophilic interactions. The photoelectron transfer reactions between the photosensitive molecules and a variety of viologen molecules as electron acceptors were studied with the goal of retarding back electron transfer rate and increasing the production of charge separated species.

In order to host large photoactive molecules, the interlayer spacing of the LDH is expanded by incorporating long chain fatty acids (\(\text{CH}_3(\text{CH}_2)_n\text{COOH}, n = 10,12,14\)). The charge distribution of the metal hydroxide layer influences the packing characteristics where a monomolecular film is formed in \(\text{LiAl}_2(\text{OH})_6^+\), (25 \(\text{Å}^2/\text{unit charge}\)) while a bimolecular film is formed in \(\text{Mg}_3\text{Al}(\text{OH})_8^+\) (33 \(\text{Å}^2/\text{unit charge}\)).

Zinc tetraphenylporphyrinsulfonate, ZnTTPS is ion-exchanged in the LiAl\(_2\)-LDH-myristate as evidenced by the spectroscopic properties and the removal of a fraction of the
myristate ions. Upon photolysis in solution containing viologens, small quantities of viologen radicals are formed without any sacrificial electron donors. Ethanol remaining in the LDH can possibly act as an electron donor.

In zeolite-Y, the photosensitizer donor, trisbipyridine ruthenium (II), Ru(bpy)$_3^{2+}$ is trapped in the supercages. An electron mediating viologen, N,N'-tetramethylene-2,2'-bipyridinium (DQ$^{2+}$) is loaded in the zeolite by ion exchange while a zwitterionic viologen, propyl viologen sulfonate, PVS in solution acts as the ultimate electron acceptor. The occurrence of photoelectron transfer across a sensitized zeolite-solution interface is observed with an efficiency of $5 \times 10^{-4}$. This is possible because the mediating viologen, DQ$^{2+}$ has the appropriate redox potential. With benzyl viologen, BV$^{2+}$ as the relay agent, the redox potential is altered by the steric constraints imposed upon by the zeolite framework causing the non-planarity of the bipyridyl rings. The isolation of the donor molecules within the zeolite from the acceptor in solution makes the photochemically generated products easily accessible.
In memory of Papa

Dedicated to Mama, Kuya Totoy, Kuya Romy
Ate Nene, Cyrus, Cesar, Venus, Moises
Percival and Adonis
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**FIELDS OF STUDY**

**Major Field:** Chemistry  
**Minor Field:** Analytical Chemistry  
Inorganic Photochemistry
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Chapter 1

INTRODUCTION

There is considerable interest in photoinduced electron-transfer reactions and photochemical charge separation due to their importance in the light-to-chemical energy conversion and storage[1-4]. For at least three decades now researchers have been studying materials or systems that could capture solar energy, store this energy and then convert it to other forms like chemical energy or electrical energy. The impetus behind this search for ways to trap, store and convert the sun's energy stems from the limited reserves of fossil fuels and the continuous depletion of fossil resources on earth.

Estimates of the world's annual consumption of energy is placed at $\sim 10^{17}$ kcal[5,6]. This quantity is far less than the total amount of solar energy annually received by the earth estimated to be $\sim 1.34 \times 10^{21}$ kcal[5,6]. Only about 0.05% of this energy is converted to chemical energy by plant and bacterial photosynthesis. With the large fraction of solar energy still available for utilization, research is geared towards technology that would provide solar energy conversion and storage.
Thus particular attention is focused on photoinduced electron transfer and charge separation.

**Photoinduced electron transfer**

Photoinduced electron transfer reactions involve the excitation of a photosensitizer donor molecule, D and subsequent reaction between the sensitized molecule and a suitable electron acceptor generally denoted by A. This is illustrated by the following reactions:

\[
\text{hv} \quad D \rightarrow D^* \quad (1.1)
\]

\[
D^* + A \rightarrow D^* + A^- \quad (1.2)
\]

In order for the charged species D⁺ and A⁻ to be utilized, the separation has to be long-lived. At the same time these species must be accessible. Charge separation, however, is difficult to accomplish in systems where there is complete diffusional freedom, such as in homogeneous systems, because of the fast thermal back electron transfer as shown in the following reverse reactions:

\[
D^* + A^- \xrightarrow{k_b} D + A \quad (1.3)
\]

where \(k_b\) is the back electron-transfer rate constant. In such recombinations there is regeneration of the starting materials, hence the light energy consumed for excitation is wasted.
This is similar to the absorption of solar energy by a blackbody which is wasted by dissipation as heat energy.

In homogeneous systems, the thermal back electron transfer is prevented by using a sacrificial electron donor, $S$ which provides an electron to the oxidized species $D^*$, thus making $A^-$ available for further reactions\cite{7,8,9}. An example of a reaction of the photoreduced product is the photochemical cleavage of water under certain conditions of $\text{pH}$ and in the presence of catalytic colloidal platinum or palladium\cite{10-20}:

\[
2\text{H}_2\text{O} + 2A^- \rightarrow 2A + 2\text{OH}^- + \text{H}_2
\]  

(1.4)

The oxidized acceptor is regenerated with the fuel hydrogen gas as a reaction product. As one can see, fuel hydrogen could be produced photochemically from a cheap source, water. The above reaction also illustrates the need for the accessibility of the redox photoproducts from the electron transfer reaction in order to be of value for subsequent hydrogen generation process.

Inasmuch as the practical utility of reactions 1.1 and 1.2 in homogeneous systems are limited by the fast recombination of the redox products, photoinduced electron transfer studies in microheterogeneous systems have gained particular attention in recent years.
Photosynthetic Systems

The perfect example of an efficient photosynthetic system is that in chlorophyllous plants and photosynthetic bacteria. In photosynthetic bacteria, the sequence of charge separation involves electron donation from a bacteriopheophytin to a quinone and subsequent electron transfer to a second quinone[12]. In green plants, photosynthesis consists of two photosystems I and II as shown in Fig. 1.1. The chlorophyll-like molecules are denoted by P680 and P700 which are photoexcited and then a series of electron transfers occur from the excited states of P680 and P700 to different relay agents. The driving force of these transfers is the difference in redox potential from one relay agent to the next. It is obvious from Fig. 1.1 that the whole photosynthetic process is sufficiently complicated. So efficient in fact is the light capture and conversion of the energy in photosynthesis that it has become a model whereby researchers try to mimic the complex processes naturally occurring in such systems.

The overall reaction in plant photosynthesis is

\[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow (\text{CH}_2\text{O})_n + \text{O}_2 \]  \hspace{1cm} (1.5)

In photosynthesis involving anaerobic bacteria however, the reducing agent is H\(_2\)S and sulfur is formed.

In mimicking the functions of natural processes in plant photosynthesis, researchers are creating "artificial photosyn-
Figure 1.1 Schematic representation of the Z-scheme in the multi-step electron transfer reactions in plant photosynthesis [5].
thetic systems" using different approaches. These include covalently bonded donor-acceptor systems, organized interfacial systems and microheterogeneous systems. Although the design in these systems vary, they are unified by their elements, i.e., light capturing molecules which are capable of electron transfer reactions; and the possibility of separation of intermediate photoproducts which inhibit their recombination. Recombination of charge separated states is prevented in photosynthesis by the large distance between the final donor and acceptor molecules.

**Covalently bonded donor-acceptor systems**

One approach which is being employed in mimicking photosynthetic processes is the use of sensitizer donor molecules covalently bonded to an electron acceptor. The distance between the donor and acceptor molecules play a role in the efficiency of separating charged species.

There has been much progress in the synthesis of complex multicomponent molecules during the past few years. These are the covalently linked porphyrin-quinone systems (P-Q) from which has evolved dyads[22,23], triads[24-27], tetrads[28,29] and more recently the pentad[30]. The pentad (five-part molecule), $C-P_{zn}-P-Q_{A}-Q_{g}$, consists of covalently linked porphyrins $P_{zn}-P$ (metallated and free base), carotenoid C and diquinone species $Q_{A}-Q_{g}$.
The energy interconversion involves the excitation of the metallated porphyrin with subsequent energy transfer to the free base porphyrin and then followed by a series of fast electron transfer steps until the final charge separated state C\(^-\)-P\(_{a}\)-P-Q\(_{a}\)^- is reached. The large distance separating C\(^-\) and Q\(_{a}\)^- inhibits charge recombination. The effectiveness of charge separation in going from the dyad to the pentad molecules increases due to the increasing distances between the charged species.

The possible pathways leading to the charge separated states in the pentad resemble the Z-scheme in the photosynthetic process in that efficient and long-lived charge separation is achieved via a sequence of multistep electron transfers.

**Microheterogeneous systems**

The other approach to mimicking photosynthesis is the use of microheterogeneous systems as previously mentioned wherein organic and inorganic polymers are used as host materials for photosensitizer donor molecules[31]. Examples of these materials are micelles[32-35], vesicles[36-38], microemulsions[39], colloidal SiO\(_2\)[40-42], zeolites[43-50] and clays [51-54]. The properties of the host materials are employed in orienting the photoactive species through steric, electrostatic and hydrophobic/hydrophilic interactions.
In contrast with the multistep charge separation in the pentad, as discussed above, systems utilizing microheterogeneous systems are simpler in the sense that no complicated synthetic procedures are involved. Rather, the incorporation of donor and/or acceptor molecules into host species are through cavities, cages, pockets, pores and interlayers. It would follow then that charge separation in these systems can be illustrated by the more simplified scheme in Figure 1.2. In microheterogeneous environments, not only can the distance between the donor and acceptor molecules be influenced but also their molecular orientation due to constraints imposed by the structure of the host.

Scope of this work

The microheterogeneous systems used in this research work are layered double hydroxides (LDH) and zeolite-Y (Na-Y). These materials belong to a group of inorganic polymers and will be described later in this chapter. Suffice it to say at this point that the layered double hydroxides are two-dimensional while zeolites have a three-dimensional porous structure. The photoactive species that is incorporated into LDH is the zinc form of the anionic tetraphenylporphyrinsulfonate (ZnTPPS\textsuperscript{−}). On the other hand zeolite-Y encapsulates a ruthenium trisbipyridyl complex, Ru(bpy)\textsubscript{3}^2\textsuperscript{+} (RuBPY). The synthesis and characterization of the LDH used are described in Chapter 2 while the photochemistry in
Figure 1.2 Simplified scheme of electron transfer and charge separation in plant photosynthesis [5].
the LDH system is included in Chapter 3. The advances made in the efficiency of electron transfer and charge separation using $\text{Ru(bpy)}_3^{2+}$ in zeolite-Y systems are discussed in Chapter 4. The final chapter is devoted to the feasibility of generating small metal clusters in Na-Y. These metal clusters are of importance in photocatalytic reactions as potential catalytic centers.

**Hydrotalcite-type Anionic Clays**

The first of the two inorganic materials used in this research is layered double hydroxides more commonly known as anionic clays. These layered materials belong to the large class of hydrotalcite-like compounds. Hydrotalcite, which is one of the few naturally occurring minerals in this class, has the formula $\text{Mg}_6\text{Al}_2(\text{OH})_16\text{CO}_3\cdot4\text{H}_2\text{O}$[55]. The hydrotalcite-like compounds in this research are confined to $\text{Mg}_3\text{Al}(\text{OH})_6'\text{Cl}^-$ and $\text{LiAl}_2(\text{OH})_6'\text{Cl}^-$ which will be abbreviated here as $\text{Mg}_3\text{Al-LDH}$ and $\text{LiAl}_2$-LDH, respectively.

$\text{Mg}_3\text{Al}(\text{OH})_6'\text{Cl}^-$ belongs to the first type of hydrotalcite-like compounds given by the general formula

$$[\text{M(II)}_{1-x}\text{M(III)}_x(\text{OH})_2]^{x^-}(\text{A}^{n-/n})\cdot m\text{H}_2\text{O}$$

where A is the anion and M(II) and M(III) are divalent and trivalent metal cations respectively. The structure closely resembles that of brucite[56,57] (Fig. 1.3a) which consists of these divalent and trivalent metal cations octahedrally.
Figure 1.3 (a) Structure of brucite, Mg(OH)$_2$. (b) Structure of layered double hydroxides to which Mg$_2$Al(OH)$_6$Cl belongs [57].
coordinated to OH\(^-\) and sharing edges to form infinite sheets. Fig. 1.3b shows the structure of the layered double hydroxides. The positions of the cations are not in a well-ordered arrangement such that M(II) could be in place of M(III) in a given octahedron. These sheets which are held together by hydrogen bonding are stacked up on top of each other and are positively charged because of substitution of the trivalent metal cations in place of the divalent cations.

The other type of hydrotalcite-like compounds to which LiAl\(_2\)(OH)\(_6\)Cl\(^-\) belongs has the formula

\[ [M(\text{I})_{1-x}M(\text{III})_x(OH)_2]^{(2x-1)+}[A^{x-}(2x-1)/x] \cdot mH_2O \]

where univalent metal cations M(I) fill the octahedral vacancies of the gibbsite structure [57]. Unlike the brucite-like sheets, however, M(I) and M(III) are in a well-defined arrangement in a given sheet of edge-sharing octahedra as shown in Fig 1.4. In both types of hydrotalcite-like compounds the positively charged sheets are counter-balanced by the anions which lie in the interlayer of the sheets. This is in contrast with cationic clays which are more common in nature. Here the layered sheets are negatively charged and the interlayers are occupied by cations to compensate for the charge of the framework structure. The waters of hydration are also located in the interlayer in sites not occupied by the anions. The anions in the interlayers of a given hydrotalcite-like materials can be replaced by ion-exchanging
Figure 1.4 Structure of layered double hydroxides to which LiAl$_2$(OH)$_6$Cl$^-$ belongs [57].
with some other anions thus making it important in industrial applications. The ability to exchange other anions is important in changing the size of the interlayer which depends on the size of anions present within the interlayer.

These materials are useful in other applications the most important of which is in catalytic reaction such as hydrogenation and polymerization[57]. Aside from being a catalyst on its own, these materials serve as support for other catalysts.

**Zeolites**

Zeolites are crystalline aluminosilicates derived from the silicates by the isomorphous substitution of Si⁴⁺ by Al³⁺[58,59]. The primary building blocks are SiO₄ and AlO₄ tetrahedra. Twenty-four of the SiO₄ and/or AlO₄ tetrahedra when joined together forms the cubooctahedron (Fig. 1.5a) which consists of 6-four membered rings and 8-six membered rings. These cubooctahedra are the secondary building units of zeolites. When these cubooctahedra are joined together, they form a well-defined framework structure the type of which depends on the arrangement of the cubooctahedra. In zeolite A (Fig. 1.5b), the cubooctahedra are connected by bridging oxygen atoms between the four-membered rings. In faujasites, the X- and Y-type zeolites (Fig. 1.5c), the cubooctahedra are
Figure 1.5 (a) Structure of a cubooctahedron (b) sodalite framework structure and (c) Zeolite A structure [58].
connected by bridging oxygen atoms between the six-membered rings which results in the formation of large cavities called supercages[58].

The framework structure of X- and Y-type zeolites are similar and their difference lies in their silicon to aluminum ratio, Si/Al ratio. For zeolite-X, it is 1.0 - 1.5 while zeolite-Y has 1.5 - 3.0.

The zeolite used in this research is Na-Y zeolite. In Fig.1.6 is shown the framework structure of zeolite-X and -Y. The unit cell composition for the Na-Y aluminosilicate crystal is

\[ \text{Na}_3[(\text{AlO}_2)_{53}(\text{SiO}_2)_{139}] \cdot 250\text{H}_2\text{O} \]

It is cubic with a dimension of \(25\ \text{Å}[58]\). The framework structure is negatively charged because it has aluminum atoms substituted for silicon. This negative framework is counterbalanced by cations such as Na\(^+\) lying in both the sodalite cages and the supercages along with the water of hydration.

In a crystal of Na-Y with micrometer dimension, there are hundreds of supercages interconnected with each other. The size of these cavities vary depending on the type of the zeolites. The molecular sieving property of zeolites is based on this variation of the cavity size. There are three characteristic features of zeolites which are important to this research.
Figure 1.6 Framework structure of zeolite-X and -Y showing supercages [58].
(1) The presence of channels and cavities of molecular dimensions makes it possible for molecules of some shapes and sizes to pass through while larger-sized molecules are excluded. Thus, zeolites are also termed molecular sieves.

(2) The ion-exchange property of the zeolites makes it possible to vary the cations residing within the zeolite cages. The different cations change the reactivity and affect the chemistry that occurs in the zeolite.

(3) The negative framework structure of the zeolite electrostatically repels other negatively charged species that come in close proximity with the structure.

**Photosensitizer, Donor Molecules and Electron Acceptors**

Any molecular assembly for an electron transfer process will consist of an electron donor which gives up one or more electrons to an electron acceptor. The photosensitive molecule, which upon light absorption becomes excited, could act both as an electron donor or an electron acceptor as shown by the reactions below:

\[
S \rightarrow S^* \quad \text{(1.5)}
\]

\[
S^* + A \rightarrow S^* + A^- \quad \text{(1.6)}
\]

\[
S^* + D \rightarrow S^- + D^* \quad \text{(1.7)}
\]
In the photochemical systems that are the subject of this research, the photosensitizer is also the donor molecule and therefore the reaction is written as in Equation 1.2.

There are a number of different photosensitizer compounds which could be used in studies of this nature. The ones mostly commonly used, however, are the metal complexes of polypyridine and porphyrin. Even within the realm of these two types of inorganic complexes, there are a number of these which could be possibly synthesized depending upon which type of application the researcher needs.

For the LDH system, zinc tetraphenylporphyrin sulfonate, ZnTPPS⁻ (Fig. 1.7b) is used as the photosensitive donor complex. The parent ligand of ZnTPPS⁻ is porphine (Fig. 1.7a) which is metallated with zinc and has the substituents phenylsulfonate attached to each of the methine bridge of the pyrrole rings. The metallated porphyrins are generally called metalloporphyrins.

Metalloporphyrins are highly colored complexes which are mostly insoluble in water. However, the presence of ionic groups such as COO⁻, SO₃⁻ and NMe₃ as substituents makes the porphyrin derivatives very soluble in water. Because these ionic groups have to be introduced into the porphine moiety, these water soluble metalloporphyrins belong to the synthetic type of porphyrins as opposed to the naturally occurring ones like the chlorophyllous pigments from green plants and algae which are the photoactive molecules
Figure 1.7 (a) Porphine structure (b) structure of zinctetra-phenylporphyrinsulfonate, ZnTPPS$^{1-}$
in photosynthetic systems. The facility of synthesizing the water-soluble metalloporphyrins by introduction of the ionic groups makes them attractive for use in studies of this nature. Also, their solubility in water is important since the ultimate goal in photoinduced electron transfer studies is to use water as a cheap source for the production of hydrogen. Metalloporphyrin complexes are either neutral (without the ionic groups in the substituent) or charged when ionic groups are present. Of the charged complexes, they could be cationic as in zinc tetramethylpyridylporphyrin, ZnTMPyP⁺ where the substituent is methylpyridyl in each of the methine bridges or anionic like ZnTPPS⁻ and zinc tetracarboxyphenylporphyrin, ZnTPPC⁻ where the anionic substituents are -Phenyl-SO₃⁻ and -Phenyl-COO⁻, respectively. The choice of an anionic porphyrin complex as the photosensitizer in the LDH is obvious because the interlayer of the clay can only accommodate negative ions. ZnTPPS⁻ is more often used because of the limited tendency of this complex to self-aggregate compared to other porphyrins.

For zeolite-Y, the guest photosensitive complex is ruthenium trisbipyridyl, Ru(bpy)₃²⁺ which has three bipyridyl ligands chelated to the ruthenium center through the nitrogens of the pyridine rings (Fig 1.8). This complex is a widely studied photosensitizer for electron transfer studies and investigation of photochemical cleavage of water. With zeolite as host for Ru(bpy)₃²⁺, however, it was not until De Wilde, et al.[60] synthesized the complex in zeolite super-cages that
attention had been focused on the characterization and photochemical applications of these materials.

![Diagram of ruthenium trisbipyridyl complex, Ru(bpy)$_3$](image)

**Figure 1.8 Structure of ruthenium trisbipyridyl complex, Ru(bpy)$_3$**

The third component of a heterogeneous photochemical system is the electron acceptor. The most commonly used electron acceptors or electron relay mediators are quinones, their derivatives and alkyl viologens. In photosynthetic systems, the electron relay is through quinones and benzoquinones. In this research the electron acceptors are different alkyl viologens, the structures of which are shown in Fig. 1.9. These are methyl viologen, propyl viologen sulfonate, heptyl viologen and benzyl viologen and N,N'-tetramethylene-2,2'-bipyridinium. The property of the
Figure 1.9 Structures of alkyl viologens used in this research: (a) methyl viologen (b) benzyl viologen (c) propyl viologen sulfonate (d) heptyl viologen and (e) N,N'tetramethylene-2,2'-bipyridinium.
viologens associated with their structure and the different reduction potentials from one viologen to another are important parameters that are considered in selecting the electron acceptors used in this research.
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Chapter 2

INVESTIGATION OF MEMBRANE-LIKE STRUCTURE AND
DYNAMICS OF FATTY ACIDS IN LAYERED METAL HYDROXIDES

Introduction

The interest in layered materials such as layered double hydroxides lies in the possible use of these as hosts for aligning inorganic, organic and organometallic species as well as studying their interlayer reactivity[1-4]. These layered double hydroxides consist of sheets of positively charged edge-sharing $\text{M(OH)}_6$ octahedra which are exemplified by the hydrotalcite-like family of materials. The two types of hydrotalcite-like compounds are represented as

(a) $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x\text{(OH)}_2]A_{n/2}^{\text{n}^-}\cdot z\text{H}_2\text{O}$

and

(b) $[\text{M}^{\text{I}}_1\text{M}^{\text{II}}_x\text{(OH)}_2]A_{n/2}^{\text{n}^-}\cdot z\text{H}_2\text{O}$

where $\text{M}^i = \text{Li, Na, K}; \text{M}^{\text{II}} = \text{Mg, Zn, Fe, Co, Ni, Cu}$ and $\text{M}^{\text{III}} = \text{Al, Cr, Fe}$. The structure can be pictured as derived from brucite [Mg(OH)$_2$] in which sheets of Mg$^{2+}$ cations are octahedrally surrounded by edge-sharing OH groups. Upon replacement of a certain fraction of the Mg$^{2+}$ cations by Al$^{3+}$, the metal hydroxide layer becomes positively charged which make anions such as Cl$^-$ necessary to counterbalance the positively charged
layer. The anions are located in the interlayer of the sheets. The anion exchange properties of the hydrotalcite-like compounds make them interesting materials for the incorporation of anions [5-14] or guest species that have potential applications in solar energy storage and conversion.

The cationic layered compounds like montmorillonite and zirconium phosphates can intercalate long-chain polymethylene units with functionalities such as alcohols and amines [15,16]. The packing of these long chain polymethylene units and the dynamics of these chains resemble biological membranes[17]. Agglomerates of such long-chain hydrocarbon molecules exhibit characteristic and collective changes in structure, dictated primarily by the fluidity and flexibility of these chains[18-23]. The functional groups on these long chain hydrocarbons interact with the inorganic layer so as to orient the polymethylene chain in the interlayer space. The packing of these chains in the interlayer and the dynamics of these chains as effected by the temperature has previously been reported[24,25].

In order for large photosensitizer molecules or complexes like porphyrins to be introduced within the interlayer of the layered double hydroxides, the interlayer should be wide enough for the guest species to enter and be properly oriented. Expanding the interlayer space can be achieved by incorporating long-chain fatty acids \([\text{CH}_3(\text{CH}_2)_n\text{COOH}, n = 10, 12, 14]\) in between these layers.
The two layered double hydroxides used in this research are Mg$_3$Al(OH)$_6$Cl$^-$ (Mg$_3$Al-LDH) and LiAl$_2$(OH)$_6$Cl$^-$ (LiAl$_2$-LDH). The charge density of the two LDH's are different, Mg$_3$Al-LDH is 33 Å$^2$/unit charge and 25 Å$^2$/unit charge for LiAl$_2$-LDH[5,7,11]. There are other factors affecting the ion-exchanging ability of LDH besides the charge densities. As an example, V$_{10}$O$_{28}^{6-}$ will ion-exchange into the magnesium-aluminum and zinc-chromium LDH but not into lithium-aluminum LDH, although the charge densities of the latter two are similar[15,24]. In a similar manner, tartrate ion will not exchange in LiAl$_2$-LDH but exchanges in Zn-Cr LDH[11].

This chapter deals with the incorporation of the long-chain fatty acids within the interlayers of LiAl$_2$-LDH and Mg$_3$Al-LDH. The resulting materials are characterized to determine how the differences in charge densities and other properties between these materials influence the packing, inter- and intramolecular interactions and the dynamics of the polymethylene chains as affected by temperature.

**Experimental Section**

LiAl$_2$-LDH was synthesized by a variation of the method by Serna et al.[7]. Sodium hydroxide (0.2 mol) was dissolved in 80 mL of freshly boiled nanopure water. To this solution was slowly added 0.05 mol of aluminum powder until dissolved. Lithium chloride (0.25 mol) in 20 mL of solution was added to the mixture and heated for 48 h at 100° C. The mixture was
filtered after heating, and the residue was placed in 100 mL of 0.5 M sodium chloride and shaken for 24 h. The products were filtered and washed with water. The residue was stored wet in stoppered vials until further use.

Mg₃Al-LDH was prepared in a similar manner. Sodium hydroxide (0.725 mol) was dissolved in 240 mL of water to which aluminum (0.0725 mol) was added slowly until dissolved. Magnesium chloride hexahydrate (0.216 mol) dissolved in 60 mL water was added slowly while stirring and heated for 48 h at 100° C. The product was filtered and washed with 0.5 M sodium chloride solution and nanopure water.

The carboxylic acids used were lauric, myristic and palmitic acid, CH₃(CH₂)ₙCOOH, n = 10, 12, 14, respectively (Fig. 2.1). Prior to reaction with long-chain carboxylic acids, both lithium and magnesium aluminum LDH’s were washed with absolute ethanol. Incorporation of acids was carried out with separate 0.1 M ethanolic solutions of lauric, myristic and palmitic acids (Aldrich). The mixtures were shaken for 24 h, centrifuged and the residues were extensively washed with ethanol. The resulting products were air-dried and stored in stoppered vials. X-ray powder diffraction patterns, before and after ion-exchange, were obtained with a Rigaku Geigerflex D/Max 2B diffractometer using Cu K-α radiation. Temperature programmed X-ray powder diffraction patterns were obtained with Scintag XDS 2000. Infrared spectra were collected on a Mattson Cygnus FTIR spectrometer. Heating experiments were
Figure 2.1 Structural formula of (a) lauric acid, (b) myristic acid and (c) palmitic acid.
done with an IR heating cell equipped with a thermocouple, at a temperature control of ±1° C. Excitation for the Raman spectra was done with 15 mW of 406.7 nm radiation from a Coherent Innova 100 krypton ion laser.

The scattered light was collected and dispersed through a Spex 1403 double monochromator and detected with a GaAs PMT with photon counting. Differential scanning calorimetric experiments were performed using a Perkin-Elmer DSC 7 Series instrument. X-ray fluorescence was used for Cl⁻ analysis using a Kevex 0700/7000 energy dispersive instrument.

Results

Incorporation of the Acids

The X-ray powder diffraction patterns of the Cl⁻ form of Mg₃Al-LDH and LiAl₃-LDH are shown in Figure 2.2. The 2-θ values of the (001) reflections are similar although the charge densities are different. Here the only factor that determines the interlayer spacing is the anion, Cl⁻, present in both cases. However, the behavior of the two LDH's differ markedly for similar fatty acids. In Figure 2.3 are shown the X-ray powder diffraction patterns of Mg₃Al-LDH and LiAl₃-LDH after reaction with myristic acid in ethanol. The (001) reflections are marked on the figure. The reflection due to the Cl⁻ corresponds to the unexchanged sample and represents a fraction of the starting material. Even after repeated reaction of myristic acid with both LDH forms, an unreacted
Figure 2.2 X-ray diffraction patterns of the Cl\textsuperscript{-} form of (a) Mg\textsubscript{2}Al\textsubscript{2}-LDH and (b) LiAl\textsubscript{2}-LDH
Figure 2.3 X-ray powder diffraction patterns for myristic acid with (a) LiAl$_2$-LDH and (b) Mg$_2$Al-LDH. The (001) reflections are marked by x. Cl$^-$ corresponds to unreacted material.
fraction always remains. The interlayer spacing and film thickness (calculated as basal spacing less 4.8 Å) for myristic-LiAl₂-LDH and myristic-Mg₃Al-LDH are markedly different being 21.5 ± 0.2 and 39.3 ± 0.2 Å, respectively. The dimension of the myristic acid molecule, shown on Figure 2.1b, is 21.2 Å, based on an all-trans arrangement including the van der Waals radii of the terminal H and O atoms. Because the interlayer distance in myristic-LiAl₂-LDH is not significantly different than the dimension of the myristic acid, this suggests that a monolayer of myristic acid molecules is present in the lithium-aluminum system. On the other hand, the almost twice interlayer distance in myristic-Mg₃Al-LDH compared to molecular length of myristic acid indicates that a bilayer is forming in the magnesium-aluminum system. From the X-ray powder diffraction patterns of the two LDH's reacted with lauric and palmitic acids, the interlayer distances were calculated. A plot of the interlayer spacing against the number of carbon atoms in the fatty acid is shown in Figure 2.4. The slopes of the lines [(dY/dX), change in spacing over change in carbon number] are different for LiAl₂-LDH and Mg₃Al-LDH, being 1.22 and 2.35 Å/C, respectively. Since the C-C distance in paraffins is ~1.27 Å, an increase of 2.35 Å/C is a confirmation of a bilayer arrangement of myristic acid in the Mg₃Al-LDH. The slope for myristic-LiAl₂-LDH on the other hand is 1.22 Å/C which indicates that the CH₂ chains are arranged in monolayers almost perpendicular to the
Figure 2.4 Plots of interlayer spacing versus carbon number for lauric, myristic and palmitic acid in (a) Mg$_2$Al-LDH and (b) LiAl$_2$-LDH
horizontal metal hydroxide layer. Thus it is clear that pronounced differences exist between the arrangement of fatty acid molecules in LiAl$_2$-LDH and Mg$_2$Al-LDH.

Besides the fatty acids in the interlayers, there also appears to be a significant amount of ethanol in these materials which is not removed by air drying the sample. When both myristic-LiAl$_2$-LDH and myristic-Mg$_2$Al-LDH were heated at 90°C (boiling point of EtOH is 87°C) 30% weight loss was observed for the materials. It is also possible that some water is still trapped within the interlayers such that the weight loss could be attributed to both the ethanol and water both on the surface and in the interior of the material. It is, however, difficult to ascertain how much comes from the surface and how much comes from the interior. Also if the weight loss has a contribution from both water and ethanol, it is difficult to estimate how much of each there is. The quantity of Cl$^-$ in the LDH's was determined by X-ray fluorescence spectroscopy. From the ratios Cl/Al and Cl/Mg, it is apparent that the amount of Cl$^-$ in LiAl$_2$-LDH decreased by 90% whereas the Cl$^-$ in Mg$_2$Al-LDH remains unchanged as shown in Figure 2.5.
Figure 2.5  X-ray fluorescence analysis of (a) LiAl₂-LDH-Cl (b) LiAl₂-LDH-myristic acid (c) Mg₃Al-LDH-Cl and (d) Mg₃Al-LDH-myristic acid. (Analysis for Mg, Al was done with X-rays from a Rh source and for Cl, a secondary target of Ti was used.)
Figure 2.5

- Al
- Cl
- Mg

(a)
(b)
(c)
(d)
The C,H analysis for the dried (90 °C) LiAl₂-LDH and Mg₃Al-LDH with myristic acid were 39.57%, 8.62% and 35.66%, 7.70% respectively. Since the fraction of the unreacted starting material is unknown, the exact chemical composition of the reacted material could not be calculated. However, if an assumption is made that LiAl₂-LDH ion-exchanges into a monolayer while Mg₃Al-LDH intercalates a bilayer of the myristic acid as shown by the powder diffraction patterns and X-ray fluorescence analysis, then the C,H analysis indicates that 85.5% of LiAl₂-LDH and 55% of Mg₃Al-LDH have reacted.

From the discussion above it is evident that there is a fundamental difference in the incorporation of the myristic acid between the two materials. In the LiAl₂-LDH, the incorporation is via ion-exchange where the Cl⁻ is replaced by the carboxylate, thus having RCOO⁻ in the interlayer. On the other hand, in Mg₃Al-LDH, it is via intercalation of the RCOOH between the layers. The intercalation of intact organic acids into these layered compounds using non-aqueous solvents has also been previously reported[2].

State of the Carboxylic Group

The mechanism by which the fatty acids are incorporated into the two LDH's indicate ion-exchange in LiAl₂-LDH and intercalation in Mg₃Al-LDH and the state of the carboxylic group in the interlayer are evidence for the mechanism of introduction of the fatty acids into the interlayer. This
could be obtained from vibrational spectroscopy, both Raman and infrared, which complement each other. Aside from looking at the functional group in the interlayer, the packing of the chains within the interlayer could be obtained from spectroscopic data.

In Figure 2.6 is shown the infrared spectra of neat myristic acid, the myristic acid intercalated Mg\textsubscript{2}Al-LDH, myristic acid-LiAl\textsubscript{2}-LDH and Na-myristate. The focus of comparison is on the 1500-1700 cm\textsuperscript{-1} region which is characteristic of the carboxyl group vibrations\cite{26}. The band at 1701 cm\textsuperscript{-1} in myristic acid (Fig. 2.6a) is characteristic of the \( v(CO) \) of the associated carboxyl group. Upon ionization, \( v_{asym}(CO) \) is observed at 1558 cm\textsuperscript{-1} and the \( v_{sym}(CO) \) at 1424 cm\textsuperscript{-1} as seen in Na-myristate (Fig. 2.6d). In the myristic-Mg\textsubscript{2}Al-LDH (Fig. 2.6b) and myristic-LiAl\textsubscript{2}-LDH (Fig. 2.6c) samples, several bands are observed in the \( v_{sym}(CO) \) stretching region: 1542, 1557, 1589, 1637 cm\textsuperscript{-1} in myristic-Mg\textsubscript{2}Al-LDH and similar bands in myristic-LiAl\textsubscript{2}-LDH except that the 1546 cm\textsuperscript{-1} band is considerably enhanced. In addition, as shown in the inset, a weak shoulder is observed at 1720 cm\textsuperscript{-1} in the myristic-Mg\textsubscript{2}Al-LDH sample. This multiplicity of \( v_{sym}(CO) \) bands indicates that there is a diversity of COO\textsuperscript{-} groups present in the interlayers. Such a distribution can be structurally rationalized by proposing several COO\textsuperscript{-} groups having nonsymmetric interactions with positively charged centers. If the positive center interacts preferentially with one of the
Figure 2.6  Infrared spectra in the 1350-1800 cm$^{-1}$ region for (a) myristic acid (b) myristic acid-Mg$_2$Al-LDH (c) myristic acid-LiAl$_2$-LDH and (d) Na-myristate.
0 atoms of CO$_2$, it will introduce anisotropy between the two C-O bonds. This would result in the increase of the $v_{\text{asym}}$(CO) frequency. Unsymmetrical hydrogen bonding would also be expected to have a similar effect. Considering the high frequencies of the 1589-, 1637- and 1720-cm$^{-1}$ bands and the X-ray fluorescence data, it is likely that the myristic acid is actually intercalating in the carboxylic acid form RCOOH, the H$^+$ being subsequently ionized in the interlayers but remaining strongly associated with the carboxylate group as in C(O)OH. The 1542-cm$^{-1}$ band can be assigned to the unassociated carboxylate form of the myristic acid. In the case of myristic-LiAl$_2$-LDH, the major intensity is in the 1540-cm$^{-1}$ region due to myristate ions replacing Cl$^-$ ions in the interlayer. However, the presence of the bands at 1590 and 1640 cm$^{-1}$ indicates that a small amount of RCOOH molecules is also present in myristic-LiAl$_2$-LDH. The infrared spectra suggest that both ion-exchange and intercalation are indeed occurring in the mechanism for the uptake of the myristic acid, however, to different degrees in Mg$_2$Al-LDH and LiAl$_2$-LDH.

**Packing of the Hydrocarbon Chains**

The packing of the hydrocarbon chains was examined by vibrational spectroscopy. In all cases, the spectroscopic data will be presented for myristic acid in Mg$_2$Al-LDH and LiAl$_2$-LDH along with neat myristic acid and its sodium salt.
**Raman Spectroscopy:** The packing of the chains and both inter- and intramolecular interactions within these chains are of interest. Raman and infrared spectra have been extensively developed as probes for chain packing and dynamics, and were used to examine the long chain fatty acids in the Mg$_2$Al-LDH and LiAl$_3$-LDH. In the Raman spectra, the frequencies of interest lie in the 650-1600 cm$^{-1}$ and 2600-3200 cm$^{-1}$ region. These data for myristic acid are shown in Fig. 2.7 and 2.8. The skeletal C-C stretching modes at 1060, 1100, 1130 cm$^{-1}$ are characteristic of the all-trans conformer [27] and these bands are evident in myristic acid and its salt (Fig. 2.7a and 2.7d). These bands are preserved upon the introduction of myristic acid into the metal hydroxide layer, thus confirming a trans arrangement of the polymethylene chains in the interlayer space. The relative intensities of these bands differ in the myristic-LiAl$_3$-LDH and myristic-Mg$_2$Al-LDH, especially the increase in intensity of the 1130 cm$^{-1}$ band in myristic-Mg$_2$Al-LDH (Fig. 2.7b). The intensity of this band has been correlated with the all-trans feature of the polymethylene chain[27], and could indicate that there is more disorder in the myristic-LiAl$_3$-LDH system compared to the myristic-Mg$_2$Al-LDH system. However, since this band is also coupled with the methyl terminal rocking mode at 892 cm$^{-1}$ [28], packing differences could be the reason for the alteration in intensity of the 1130 cm$^{-1}$ band rather than any difference in the inherent disorder between the myristic-LiAl$_3$-LDH and
Figure 2.7 Raman spectra in the 650 - 1600 cm\(^{-1}\) region for (a) myristic and (b) myristic acid-Mg\(_2\)Al-LDH (c) myristic-LiAl\(_2\)-LDH and (d) Na-myristate. (Excitation - 406.7 nm)
Figure 2.8 Raman spectra in the 2600 - 3200 cm⁻¹ region for (a) myristic acid (b) myristic acid-Mg₂Al₂-LDH (c) myristic acid-LiAl₂-LDH and (d) Na-myristate. (Excitation - 406.7 nm)
myristic-Mg$_3$Al-LDH systems. Fig. 2.8 shows the Raman data in the C-H stretching region. The four significant bands at 2845, 2880, 2925 and 2968 cm$^{-1}$ are at frequencies appropriate for CH$_2$ symmetric, asymmetric, CH$_3$ symmetric and asymmetric stretches, respectively [29]. The myristic acid in Mg$_3$Al-LDH and LiAl$_2$-LDH exhibit similar frequencies for the CH$_2$ stretching modes (Fig. 2.8b and 2.8c). However, the spectra are quite distinct in the CH$_3$ stretching region. For example, the CH$_3$ symmetric and asymmetric stretch at 2925 and 2968 cm$^{-1}$ are broadened in the myristic-LiAl$_2$-LDH sample (Fig. 2.8c). The intensities of bands in this region are strongly influenced by Fermi resonance with overtones of the methyl deformation bands around 1400-1450 cm$^{-1}$ [29]. As seen in Fig. 2.7, two bands are observed in the 1400-1500 cm$^{-1}$ region, at 1430 and 1450 cm$^{-1}$, and can be assigned to CH$_3$ scissoring and a Fermi resonance band between the methylene rocking and asymmetric methyl deformation mode. The relative intensities between these bands are different in the myristic-Mg$_3$Al-LDH and myristic-LiAl$_2$-LDH samples, which would bring about changes in intensity in the C-H stretching region. Thus, the differences that are observed in the C-H stretching region for myristic acid in Mg$_3$Al-LDH and LiAl$_2$-LDH can result from differences in the intermolecular chain coupling which is reflected in the C-H stretching frequency region due to Fermi resonance effects. The infrared spectra discussed below confirm this assignment. The band at 2930 cm$^{-1}$ arises from
ordered packing in analogy with crystalline fatty acids [29]. Similar data were also obtained for the palmitic acid exchanged samples in LiAl$_2$-LDH and Mg$_3$Al-LDH. Therefore, the Raman spectra indicate that the polymethylene chains are ordered in an all-trans configuration in both LiAl$_2$-LDH and Mg$_3$Al-LDH, though the packing of the chains may be distinct in these two cases.

**Infrared Spectroscopy:** The infrared spectra of myristic acid in LiAl$_2$-LDH and Mg$_3$Al-LDH are compared in Fig. 2.9 through 2.11. (Along with Fig. 2.6 in the 1350 - 1800 cm$^{-1}$ region, these figures provide the complete mid-infrared spectra). In the CH$_2$ wagging region (Fig. 2.10) a progression of bands that is characteristic of an all-trans arrangement of the polymethylene chain is observed. This is consistent with the Raman data and interlayer spacing obtained from the diffraction profiles. The increased intensity of the bands in the wagging region as compared to long-chain alkanes is due to coupling with the $\nu$(CO) of the carboxylic group [30]. There is a subtle difference between the myristic-LiAl$_2$-LDH and myristic-Mg$_3$Al-LDH systems. The progression of bands is split into two in the latter case (Fig. 2.10b). There are two explanations for this effect. This progression could be due to CH$_3$ twisting modes, which occur in this region but typically have low intensities. The other possibility is that the CH$_3$ wag is splitting due to correlation effects. This will
Figure 2.9 Infrared spectra in the 600 - 1150 cm\(^{-1}\) region for (a) myristic acid (b) myristic acid-Mg\(_2\)Al-LDH (c) myristic acid-LiAl\(_2\)-LDH and (d) Na-myristate.
Figure 2.10 Infrared spectra in the 1150 - 1350 cm$^{-1}$ region for (a) myristic acid (b) myristic acid-Mg$_2$Al-LDH (c) myristic acid-LiAl$_2$-LDH and (d) Na-myristate.
Figure 2.11 Infrared spectra in the 2600 - 3100 cm\(^{-1}\) region for (a) myristic acid (b) myristic acid-Mg\(_2\)Al-LDH (c) myristic acid-LiAl\(_2\)-LDH and (d) Na-myristate.
be dependent on the number of polymethylene chains per unit cell. In an orthorhombic lattice, the unit cell contains two chains and the vibrations are expected to be split because of the in-phase and out-of-phase motions of the two chains in the unit cell. For triclinic or monoclinic symmetries there is only one chain per unit cell and such splittings are not expected. These splittings are usually quite marked for the CH₂ bending and rocking modes[31,32] Fig. 2.7b and Fig.2.9b show that in the myristic-Mg₃Al-LDH both the CH₂ bending (1465 and 1472 cm⁻¹) and CH₂ rocking (716 and 723 cm⁻¹) are split, whereas in myristic-LiAl₂-LDH, they appear as single bands at 1468 (Fig. 2.6c) and 721 (Fig. 2.9c) cm⁻¹, respectively. Similar observations were also made for the palmitic acid sample. Thus, the symmetry of packing of the polymethylene chains in the Mg₃Al-LDH is in an orthorhombic unit cell, whereas it is triclinic or monoclinic in the LiAl₂-LDH sample. The infrared spectra in the 2600-3200 cm⁻¹ region are shown in Fig. 2.11. As in the Raman spectra, the differences in the myristic acid C-H stretching region between the LiAl₂-LDH and Mg₃Al-LDH intercalated samples lie with the frequencies that involve the CH₃ group. Bands at 2961, 2938 and 2870 cm⁻¹ all decrease markedly in intensity in the myristic-LiAl₂-LDH (Fig. 2.11c) compared to myristic-Mg₃Al-LDH (Fig. 2.11b). These changes in intensities occur as a result of the changes in Fermi resonance between the CH₃ stretches and the deformation modes since correlation splittings for the deformation modes,
only appear in the myristic-Mg\textsubscript{2}Al-LDH material. Thus from the infrared spectra, it can be concluded that the packing of the polymethylene chains is in the all-trans configuration in both myristic-LiAl\textsubscript{2}-LDH and myristic-Mg\textsubscript{2}Al-LDH. However, the packing of the chains in myristic-Mg\textsubscript{2}Al-LDH leads to an orthorhombic unit cell, with two chains per unit cell, whereas in the myristic-LiAl\textsubscript{2}-LDH it is of lower symmetry with one molecule per unit cell.

Based on these results, an overall arrangement of the myristic acid molecules in LiAl\textsubscript{2}-LDH and Mg\textsubscript{2}Al-LDH can be proposed. These are shown schematically in Fig. 2.12 and Fig. 2.13. The monomolecular films in myristic-LiAl\textsubscript{2}-LDH can be arranged in two geometries (Fig. 2.12). In the case of myristic-Mg\textsubscript{2}Al-LDH, the Cl\textsuperscript{-} can H-bond with the -COOH group and thereby help in orienting the acid molecules. Again, there are two ways in which the Cl\textsuperscript{-} ions can be distributed, either neutralizing only one layer of metal hydroxide or alternate layers, as shown in Fig. 2.13. The present data do not distinguish between these two arrangements. In an earlier study on alignment of nitrohippuric acid intercalated into LiAl\textsubscript{2}-LDH, it was proposed that the Cl\textsuperscript{-} in one layer was interacting with the acid on the same side of the layers [2].

Temperature Dependent Dynamics Processes of Interlayer Species

The dynamics of the polymethylene chains as a function of temperature has been examined for membranes [33], polymers[34]
Figure 2.12 Schematic arrangement for myristic acid in LiAl$_2$-LDH.
Figure 2.13 Schematic arrangement for myristic acid in Mg₃Al-LDH.
and intercalated units in layered materials such as montmorillonite and zirconium phosphates [15,24]. In the latter system, which is of direct relevance to this study, the typical observation has been increased disorder in the polymethylene chain along with a shortening of the interlayer spacing. The influence of temperature on fatty acids in LiAl$_2$-LDH and Mg$_3$Al-LDH as determined by calorimetry, diffraction and infrared studies will be discussed below.

**Calorimetry**

Fig. 2.14a-d shows the differential scanning calorimetry curves between 50-100°C for the myristic acid-LiAl$_2$-LDH sample as synthesized, and samples heated to 100°, 150° and 200°C in air and then cooled to room temperature before the calorimetric measurement. For the as synthesized sample (Fig. 2.14a), two transitions are observed at 68° and 78°C. The second transition is not observed for the sample previously heated to 100°C (Fig. 2.14b). As mentioned earlier, there is considerable amount of ethanol in the as-synthesized sample and the endotherm at 80°C is assigned to the loss of ethanol. The sample previously heated to 150°C has the onset of transition shifted to 55°C (Fig. 2.14c), whereas no perceptible transition is observed for the samples previously heated to 200°C (Fig. 2.14d). The endotherms could be repeatedly observed for any of these samples heated to a particular temperature. However, none of the samples showed
Figure 2.14 Differential scanning calorimetry traces for the myristic acid-LiAl$_x$-LDH sample (a) as synthesized and heated to b) 100 °C (c) 150 °C (d) 200 °C. The samples were maintained for 15 minutes at the high temperature (in air) and cooled to room temperature before recording traces.
Figure 2.14

(a) 2.0 mW
(b) 2.4 mW
(c) 1.0 mW
(d) 0.5 mW

Temperature (°C)
any exothermic peak, though it is clear that order is being restored upon cooling, until heat treatments beyond 150°C. The transition at 68°C for the as-synthesized sample represents a phase transition involving the packing of alkyl chains. The onset of this transition does not change for the 100°C heated sample, though the ΔH shows a decrease from 53 to 49 J/g. Both the onset temperature and ΔH show a considerable decrease for the 150°C sample being 55°C and 15 J/g, respectively. No transition is observed for the 200°C heated sample, indicating that the chain packing is completely disordered and the system does not relax back to an ordered assembly upon cooling. Also, at these higher temperatures, decarboxylation as well as oxidation of the hydrocarbon chains will begin to occur. Therefore, it appears that heat treatment at progressively higher temperatures introduces disorder into the system which is only partially restored on cooling, the degree of restoration decreasing at higher temperatures. Similar results were obtained with the palmitic acid sample, except that the transition temperature of the alkyl chain disordering was higher by 5°C.

The data for as-synthesized myristic acid-Mg₃Al-LDH are shown in Fig. 2.15. There are two transitions at 95°C and 100°C. For a sample heated to temperatures above 120°C, no endothermic peak is observed (Fig. 2.15b). This implies that once the material goes through a transition, the ordered domains of the alkyl chains are completely destroyed and it
Figure 2.15 Differential scanning calorimetry traces for myristic acid-Mg$_2$Al-LDH (a) as synthesized sample and (b) heated to 120 °C. The sample was maintained at 120 °C for 15 minutes in air and cooled to room temperature before recording the data.
does not recover any order on cooling. This is clearly
distinct from the LiAl$_2$-LDH material. Palmitic-Mg$_3$Al-LDH
samples also show the same effect, with the onset of
transitions shifted upward by ~5°C. The first transition (~90
°C) is assigned to loss of ethanol and the second one (100°C)
to alkyl chain disordering. The higher temperature of
transition in the myristic-Mg$_3$Al-LDH compared to myristic-
LiAl$_2$-LDH could be due to the more symmetric packing of the
fatty acid molecules in Mg$_3$Al-LDH. Also, the ethanol molecules
are held more tightly in the myristic-Mg$_3$Al-LDH sample.

Diffraction

The powder diffraction data provide information about the
interlayer distance and thereby indirectly probe the specific
alignment of the chains in the interlayer. In order to explore
the chain dynamics as a function of temperature, diffraction
patterns were obtained using a hot stage diffractometer for
myristic acid-LiAl$_2$-LDH and myristic acid-Mg$_3$Al-LDH. Fig. 2.16
shows the data for the myristic-LiAl$_2$-LDH sample between 30-
100°C. The starting material has (001) reflections at 2$\theta$
= 3.3, 6.75 and 10.2 degrees, with a film thickness of 22 Å. At
60°C, a new set of reflections emerges at 2$\theta$ = 2.64, 5.33 and
8.14 degrees (marked by x in Fig. 2.16), indicating that the
film thickness has increased to 28.64 Å. With further heat
treatment, the spacing continues to increase and reaches a
steady state of ~43 Å around ~100°C (~15-20 minutes). Upon
Figure 2.16 Hot-stage X-ray powder diffraction patterns for myristic acid-LiAl$_2$-LDH.
Figure 2.16
Figure 2.16 (Continuation)
Figure 2.17 Room temperature X-ray powder diffraction patterns for (a) as-synthesized myristic acid-LiAl$_2$-LDH sample (b) heated to 100 °C for 10 minutes and (c) treated with ethanol for three hours.
cooling to room temperature, the expanded layer pattern is retained as shown in Fig. 2.17b. In the presence of ethanol the original as-synthesized XRD pattern is restored as shown in Fig. 2.17c. The dynamics representing the expansion of the layers as shown in Fig. 2.16 are novel and have not been observed in any other layered system. Considering that each C-C distance is \(1.27\text{Å}\), the increase in spacing between 50-60°C corresponds to a translation of \(\sim 4\text{ CH}_2\) groups. Similar increases are observed at the higher temperatures. The onset of appearance of the expanded layer at 60°C corresponds well with the transition observed in the calorimetry studies. However, since the sample heated to 100°C has the increased spacing frozen in upon cooling to room temperatures, the endotherm shown in Figure 2.15b must relate to transitions involving the alkyl chains in the expanded layer material.

The XRD patterns of a myristic acid-Mg\(_2\)Al-LDH sample obtained on a hot stage are shown in Fig. 2.18. Around 75°C, a \((001)\) pattern characteristic of a material with a decreased basal spacing is observed. From a film thickness of 39 Å at room temperature, a decrease to 32 Å is observed at 70 °C. The complete starting material is changed to the one with 32 Å spacing by 90°C. Around 100°C, a material with a basal spacing of 24 Å appears, and the 32 Å spacing material is completely converted to the 24 Å form at 140 °C. This stepwise decrease in basal spacing is similar to observations for long chain amines intercalated in montmorillonite, and is indicative of
Figure 2.18 Hot stage X-ray powder diffraction pattern for myristic acid-Mg\textsubscript{3}Al-LDH.
Figure 2.18 (Continuation)
the formation of kinks and gauche blocks [15]. In contrast to the myristic-LiAl\textsubscript{2}-LDH sample, the myristic-Mg\textsubscript{2}Al-LDH sample once heated to 140°C will not revert back to the starting material upon treatment with ethanol, indicating that the disorder is frozen. This is also in accordance with the calorimetry data (Fig. 2.14b) which show the lack of any transition, after the sample has been heated and thereby indicating a disordered system after the first heat treatment.

**Vibrational Spectroscopy**

Infrared spectra as a function of temperature provide molecular information that complements the diffraction and calorimetric studies. Raman studies, which would also have provided complementary information were not done because of the high background and poor S/N ratio. This observation is similar to a recent study of amine intercalated zirconium phosphate [24]. Infrared data were collected at various temperatures for the myristic-LiAl\textsubscript{2}-LDH and myristic-Mg\textsubscript{2}Al-LDH samples between 27°C and 130 °C, with a precision of ±1 °C. The $\text{CH}_2$ wagging progression region (1150 - 1350 cm$^{-1}$), which is very characteristic of the all-trans packing of chains, is compared in Fig. 2.19 and 2.20. The other changes are also discussed below. In both cases, the bands begin to broaden around 60 °C. However, the progression is apparent in the myristic-LiAl\textsubscript{2}-LDH sample until ~110°C, whereas it is hard to discern in the myristic-Mg\textsubscript{2}Al-LDH sample beyond 100°C. Bands
Figure 2.19 Infrared spectra of myristic acid-LiAl$_2$-LDH at temperatures of 27-130 °C with a control of ±1 °C.
Figure 2.20 Infrared spectra of myristic acid-Mg,Al-LDH at temperatures of 27-130 °C with a control of ±1 °C.
at ~1362, 1340 and 1310 cm\(^{-1}\) also appear in the LiAl\(_2\)-LDH sample upon heating. If these materials are heated to 150°C and then cooled to room temperature, the CH\(_2\) wagging progression representative of an all-trans structure is still observed for the myristic-LiAl\(_2\)-LDH material, but the order is destroyed in the myristic-Mg\(_3\)Al-LDH sample (Fig. 2.21). Only a prominent band around 1310 cm\(^{-1}\) remains. So, the trans structure of the chains that is lost upon heating beyond 150 °C is recovered in the myristic-LiAl\(_2\)-LDH case upon cooling but not in the myristic-Mg\(_3\)Al-LDH sample. This is in agreement with the calorimetric data which showed that the endothermic transition could be repeatedly observed in the myristic-LiAl\(_2\)-LDH sample but only during the first cycle in the myristic-Mg\(_3\)Al-LDH case. Also, the fact that the trans-like CH\(_2\) wagging progression can clearly be discerned in the myristic-LiAl\(_2\)-LDH sample between 60-100°C indicates that some degree of all-trans order is being maintained during the expansion of the film thickness and layer separation.

There are other significant changes in the infrared spectra of both myristic-LiAl\(_2\)-LDH and myristic-Mg\(_3\)Al-LDH. The correlation splitting in the 712 and 1460 cm\(^{-1}\) region is lost in the myristic-Mg\(_3\)Al-LDH sample between 45-60°C, indicating that the orthorhombic packing is being disrupted. In both myristic-LiAl\(_2\)-LDH and myristic-Mg\(_3\)Al-LDH, the \(v_s\)(C-O) stretching mode at 1540 cm\(^{-1}\) shifts to higher frequencies at ~60°C, (1575 cm\(^{-1}\) for myristic-LiAl\(_2\)-LDH and 1584 cm\(^{-1}\) for the
Figure 2.21 Infrared spectra taken at room temperature for (a) myristic acid-LiAl$_2$-LDH as-synthesized sample and (b) heated to 150 °C for 15 minutes. (c) myristic acid-Mg$_2$Al-LDH as-synthesized sample and (d) heated to 150 °C for 15 minutes.
myristic-Mg,Al-LDH sample). This could be due to replacement of the solvent ethanol molecules and direct interaction of the carboxylate with the metal hydroxide layer. In the C-H stretching region, the bands are increasingly broadened with temperature, for both myristic-LiAl₂-LDH and myristic-Mg,Al-LDH, and blue shifts of ~5 cm⁻¹ for the CH₂ symmetric and asymmetric modes are observed only in the case of myristic-Mg,Al-LDH. This is simply indicative of increased disorder and formation of gauche block structures [24].

DISCUSSION

It is clear from the data shown above that the packing and dynamics of the fatty acid chains in the LiAl₂-LDH and Mg,Al-LDH are quite distinct. The differences in packing and dynamics of fatty acid chains in the two forms of LDH are reviewed below based on published literature and a model will be provided which is consistent with the data.

Chain Packing

The film thicknesses (basal spacing less 4.8 Å) for CₙH₂ₙ₊₁COOH-LiAl₂-LDH complexes for n=11, 13 and 15 are 19.6, 21.4 and 23.7 Å, respectively. The calculated lengths for these fatty acid molecules in their completely extended all-trans form are 18.7, 21.2 and 23.7 Å, respectively. The change in spacing per -CH₂ unit corresponds to 1.22 Å, which would indicate that a monolayer of fatty acid molecules are
forming between the chains. This is consistent with the film thickness observed. Considering that addition of each CH₂ unit should contribute 1.27 Å, (chains held perpendicular to the layers), the result of 1.22 Å/C unit in LiAl₂-LDH leads to an almost perpendicular arrangement of the alkyl chain.

The film thickness in the Mg₃Al-LDH samples are considerably larger, being 35, 39 and 44 Å for n=11,13 and 15, respectively. The increase in spacing per -CH₂ unit corresponds to 2.35 Å. Both of these facts indicate that a bimolecular film of the fatty acid chains is forming. The orientation of these molecules is also near perpendicular to the metal hydroxide layer.

There is only one brief report of ion-exchange of fatty acids in double metal hydroxides, and it was done with carboxylate salts from an aqueous solution [11]. No exchange was reported for LiAl₂-LDH, but in the Mg₃Al-LDH and Zn₃Cr-LDH, a monomolecular film was formed. Clearly, the procedure herein for reaction of the carboxylic acid in ethanol results in a different intercalation mechanism. The exchange of long chain alkyl sulfates into Zn₃Cr-LDH has been examined more thoroughly [35]. A monomolecular film is formed from aqueous solution which expands in the presence of n-alkylalcohols and n-alkylamines. The monomolecular films can also incorporate small organic molecules such as ethylene glycol between the end of the chain and the metal hydroxide layers.
Vibrational spectra of the fatty acid molecules in the LiAl\textsubscript{2}-LDH and Mg\textsubscript{3}Al-LDH sample provide clues as to the state of the -COOH functionality. Bands at 1542, 1557, 1589, 1637 and \textasciitilde 1720 cm\textsuperscript{-1} are observed in the v(C-O) region whereas the presence of only -COOH or -COO\textsuperscript{-} would result in bands at 1700 and 1558 cm\textsuperscript{-1}. Clearly, the carboxylic group is present in different forms in the metal hydroxide layer. These could include -COOH (1720 cm\textsuperscript{-1}), -COO\textsuperscript{-} (H\textsuperscript{+}) (1637 cm\textsuperscript{-1}), -COO\textsuperscript{-}H\textsuperscript{+}(Cl\textsuperscript{-}), -COO\textsuperscript{-} M\textsuperscript{+}(OH) (1542-1589 cm\textsuperscript{-1}). XRF analysis indicates that all of the Cl\textsuperscript{-} signal is still retained in Mg\textsubscript{3}Al-LDH, whereas only about 15\% is retained in LiAl\textsubscript{2}-LDH. Thus, the RCOOH intercalating into Mg\textsubscript{3}Al-LDH is dissociating to a considerable degree. The intercalation into LiAl\textsubscript{2}-LDH is considerably less, the primary incorporation mechanism being through ion-exchange.

The progression observed in the CH\textsubscript{2} wagging region indicates that the chains are in an all-trans configuration for both the monomolecular and bimolecular films in LiAl\textsubscript{2}-LDH and Mg\textsubscript{3}Al-LDH. Such all-trans arrangement of alkylammonium ions in montmorillonites [15], phyllosilicates [36] and zirconium phosphates[24] has also been reported. An interesting result from the vibrational study is the presence of the correlation splitting observed for Mg\textsubscript{3}Al-LDH. This indicates that two alkyl chains are present per unit cell, suggesting a highly symmetric arrangement such as an orthorhombic unit cell. Whereas, in the LiAl\textsubscript{2}-LDH samples, a
lower symmetry such as triclinic or monoclinic arrangement is present. Previous studies of alkyl chain arrangements in layered systems has only noted the presence of unit cells having lower symmetry.

The origin of the different packing in LiAl₂-LDH and Mg₃Al-LDH must lie in the charge distribution of the metal hydroxide layer as well as in the arrangement of the cations, since these factors influence the packing of the fatty acid chains. Previous studies have hinted at the anomaly of the LiAl₂-LDH system as compared to the M²⁺ - M³⁺ type double hydroxide[11]. For example, secondary alkanesulfonates exhibited a higher spacing (1-2 Å) in LiAl₂-LDH compared to Zn-Cr, Zn-Al, Mg-Al and Ca-Al layered double hydroxides and showed an unusual effect of increased interlayer space upon drying by 1-2 Å. This was attributed to a different charge distribution in the Li⁺ - Al³⁺ case as compared to M²⁺ - M³⁺ hydroxides. The present study, however, shows a considerably greater difference in the packing of alkyl chains between LiAl₂-LDH and Mg₃Al-LDH systems. The major difference between this study and previous studies is that the reaction with the fatty acid was carried out in an ethanolic medium as compared to previous studies in aqueous solution. The lower polarity of the solvent medium markedly emphasizes the differences in the charge density and structure between the LiAl₂-LDH and Mg₃Al-LDH systems.
The arrangement of the cations in the octahedral layer has been examined in the literature [7,37] and is compared in Fig. 2.22. The distances between the closest Li ions are 5.32 Å in the LiAl₂-LDH, whereas in Mg₃Al-LDH, the positive charges are 6 Å apart. The area per cationic charge in LiAl₂-LDH is 24.5 Å², whereas in Mg₃Al-LDH it is 33 Å². In the closest possible packing of alkyl chains, as in polyethylene crystals [16], the unit area per chain is 19 Å². So, in LiAl₂-LDH the fatty acid chains can be expected to be more densely packed than in Mg₃Al-LDH. The crystal packings in the layers, as shown in Fig. 2.22 are idealized projections. This is evident from the low symmetry of packing (i.e. triclinic or monoclinic) of the alkyl chains in LiAl₂-LDH, which would indicate some disorder in the distribution of Li⁺ in the vacancies of the gibbsite structure. This was also noticed in an earlier spectroscopic study of LiAl₂(OH)₆·Cl[1]. In the case of Mg₃Al-LDH, the ordering as shown above for a hexagonal supercell or an orthorhombic supercell (Fig. 2.22b,c) is consistent with the higher symmetry of packing of the fatty acid chains.

The difference in charge density of the LiAl₂-LDH and Mg₃Al-LDH is not only reflected in the monomolecular versus bimolecular film but also the fact that in LiAl₂-LDH the process of incorporation of the fatty acid molecules is primarily by ion-exchange, whereas it occurs by intercalation in Mg₃Al-LDH. The charge density of the layers must determine
Figure 2.22  Idealized arrangement of metals in the metal hydroxide layer for (a) LiAl$_2$-LDH (b) hexagonal Mg$_3$Al-LDH and (c) orthorhombic Mg$_3$Al-LDH.
Figure 2.22
the balance in energetics between the increase in interlayer spacing and mutual attraction/repulsion between the layers. Since the mechanism of entry of these molecules is not yet understood, any detailed proposal of how the charge densities of LiAl2-LDH and Mg3Al-LDH influence the ion-exchange/intercalation process will have to be speculative.

Temperature - Dependent Dynamic Effects

The differences in the packing of chains in LiAl2-LDH and Mg3Al-LDH are also reflected in dynamics of these chains as a function of temperature. The transition temperature for myristic-LiAl2-LDH (65 °C) observed in DSC is about 35 °C lower than in myristic-Mg3Al-LDH (100 °C). This is probably a reflection of the bimolecular packing in Mg3Al-LDH. Typically, transition temperatures rise with increasing length of the alkyl chain.

The transitions observed in DSC for the as synthesized fatty acid-metal hydroxide samples lead to change in interlayer packing of the fatty acid chains. The most obvious effect is the shortening of the interlayer spacing in Mg3Al-LDH and an extension in the case of LiAl2-LDH. In myristic-Mg3Al-LDH, the film thickness decreases from 39 Å at room temperature to 24 Å at 140 °C. For a myristic-LiAl2-LDH sample, the film thickness increases from 22 Å at room temperature to 43 Å at 100 °C. Thus, it appears that in the myristic-Mg3Al-LDH, the bimolecular layer is becoming dis-ordered as a
function of temperature. No studies have been reported for the temperature dependent behavior of alkyl chains in layered metal hydroxides, but considerable work has been done for similar systems in montmorillonites, layered silicates and zirconium phosphates [5,24]. In all these cases, the interlayer spacing is found to decrease with temperature and proceed through the development of kink in the chain followed by gauche blocks. This is indeed what appears to be happening in the myristic-Mg$_2$Al-LDH sample. The first kink is manifested in the XRD pattern at 70 °C and involves a decrease in basal spacing of ~1.3 Å. This decrease is characteristic of a 2gl kink (...)tgttgt...). Between 70 and 75 °C, a marked decrease of 3.6 Å, corresponding to a 2g3 kink is observed. The next major transition occurs around 100 °C, coincident with the DSC transition and involves a decrease in interlayer spacing of ~7 Å. This corresponds to the formation of gauche blocks. The observation that various pretransitional phenomena are occurring well before the maximum in the DSC curve has also been made with alkylammonium ions in zirconium phosphate [24]. The gauche blocks are retained upon cooling, and the conformational changes are not reversible. Treatment with ethanol also does not have any effect on the heated samples. Vibrational spectra also provide information about the structural changes that occur. At temperatures as low as 60 °C, the correlation splitting of the 1460 and 720 cm$^{-1}$ due to packing of two chains in the unit cell is lost [41]. The 2-5
blue shifts of C-H stretches of CH₂ groups is observed with the formation of the gauche blocks around 100°C. The presence of kinks (gtg) upon heating is also confirmed by the increase in intensity of the band at ~1310 cm⁻¹ (Fig. 2.20). The tailing of the intensity towards the lower frequency (~1250 cm⁻¹) is indicative of distribution of kink sites and resembles the spectra observed in liquid alkanes [42]. The presence of end-gauche (~1340 cm⁻¹) or double-gauche (1353 cm⁻¹) structures could not be definitively deduced from the infrared spectra. That these kink defects are retained upon cooling the myristic-Mg₃Al-LDH sample is obvious from Fig. 2.21d which shows the prominent kink defect band at ~1310 cm⁻¹. The observations with the myristic-Mg₃Al-LDH are in reasonable agreement with previous studies on other layered supports. A schematic of the dynamics of the chains is shown in Fig. 2.23.

The behavior of the myristic-LiAl₂-LDH system is completely anomalous and has not been reported to date. The interlayer film thickness indicates an expansion from a monomolecular to a bimolecular film. Another explanation for the increased spacing could be rearrangement of the myristic acid molecules within the layer such that four metal hydroxide layers are required per unit cell. However, the observed change in interlayer spacing varies almost in a continuous fashion upon heating, whereas this model would have predicted a stepwise jump. The appearance of bands in the infrared spectra (Fig. 2.19) at 1315, 1340 and 1362 cm⁻¹ (not shown) in
Figure 2.23 Schematic description of temperature dependent changes in myristic acid-Mg,Al-LDH sample.
the myristic-LiAl\textsubscript{2}-LDH samples at 130°C indicates that both kinks (\textit{gtg}) and end-gauche (\textit{gt\textsubscript{a}}) defects are forming at these elevated temperatures [35,43]. Upon cooling the samples (Fig. 2.21b), the characteristic all-trans CH\textsubscript{2} wag progression is observed. The trans order of the chains as evident from the -CH\textsubscript{2} wagging progression appears to be maintained at higher temperatures and is also evident on cooling the samples. Thus the transitions can be repeatedly observed in DSC, since the conformational changes are reversed on cooling. The increased bimolecular type spacing observed at high temperature is also retained upon cooling.

The differences in binding fatty acids between the LiAl\textsubscript{2}-LDH and Mg\textsubscript{3}Al-LDH include:

a) formation of monolayer in LiAl\textsubscript{2}-LDH versus bilayer in Mg\textsubscript{3}Al-LDH with orthorhombic packing of chains;

b) expansion of the interlayer spacing in LiAl\textsubscript{2}-LDH upon heat treatment as compared to contraction in Mg\textsubscript{3}Al-LDH;

c) reversibility of the chain phase transformations upon heating and cooling in the LiAl\textsubscript{2}-LDH as compared to irreversible transformation in Mg\textsubscript{3}Al-LDH.

In the above analysis of the packing of fatty acid chains in LiAl\textsubscript{2}-LDH, it was mentioned that a monomolecular film results because of the balance of the interaction between the
positively charged layers with the increased spacing. Also, the high charge density of the metal hydroxide layer will promote dense packing of the fatty acid chains. Bilayers in lipids are known to undergo a large lateral expansion along with a longitudinal contraction on heating, due to the formation of nonplanar gauche structures [43]. A similar effect is occurring in the Mg₃Al-LDH sample, which is reflected in the decreased interlayer space and the appearance of the band at 1310 cm⁻¹ due to gtg defects. It is proposed here that ethanol molecules occupy space in between the chains. Loss of these solvent molecules upon heating leads to considerable space around the chains, thus promoting conformational disorder. Since the carboxylate ends of the molecules are anchored to the metal hydroxide layer, the disordering must begin and proceed from the CH₃ end of the molecule. In this respect, these systems resemble lipid bilayers rather than alkanes [42].

The expansion of the layers upon heating the myristic-LiAl₂-LDH is puzzling and more difficult to explain. The packing of the myristic acid molecules is more dense because of the higher charge density. The ethanol can therefore be expected to be between the layer and the carboxylate group rather than between the chains. Heating this material results in loss of ethanol, expansion of interlayer space and the appearance of end-gauche and kink defects indicative of conformational disorder. Cooling the sample results in
reordering of the carboxylic acid chains in an all-trans arrangement, but the expansion of interlayer remains frozen in. Treatment with ethanol brings about a decrease of the spacing and resembles the starting material. Therefore, it appears that the expansion of the layers is linked to the loss of ethanol. A possibility could be that the ethanol acts as a dielectric shielding the positively charged layers from each other, and its loss leads to repulsion between layers. The change in interlayer spacing during heating also supports this view since it changes in an almost continuous fashion and does not have the stepwise changes more characteristic of kink defect block formation. Based on the infrared data which show the formation of end-gauche and kink defects, a schematic of the chain disorder in myristic-LiAl₂-LDH as a function of temperature in Fig. 2.24. The denser packing in the myristic-LiAl₂-LDH leads to a system in which the chains do order upon cooling, whereas in the myristic-Mg₃Al-LDH, with the lower packing density the mutual interaction between chains is diminished and the system does not reorder upon cooling.
Figure 2.24 Schematic description of temperature dependent changes in myristic acid-LiAl$_2$-LDH sample.
CONCLUSIONS

This study has examined the packing and dynamics of long chain saturated fatty acid molecules in layered double metal hydroxides. The two hydroxides that form the focus are LiAl$_2$(OH)$_4$ and Mg$_3$Al(OH)$_6$ chosen because of their different charge densities, being 0.25 and 0.33 m$^{-2}$, respectively. The following conclusions can be drawn from this study:

1. A monomolecular film of fatty acid chains is packed with high density in an all-trans and in an almost perpendicular arrangement to the layer surface in LiAl$_2$-LDH. Ion-exchange is the primary means of incorporation of the acid molecules. The symmetry of the chain packing is triclinic or of lower symmetry. Ethanol, the solvent used for the reaction of fatty acid with LiAl$_2$-LDH, is also incorporated between the metal hydroxide layer.

2. A bimolecular and almost perpendicular film of myristic acid is formed in Mg$_3$Al-LDH. The chains are packed in orthorhombic or higher symmetry in an all-trans form. The primary method of incorporation of acid is via intercalation. The solvent ethanol is accommodated between the chains, for the packing is not as dense.

3. In both cases, an increase in temperature brings about major changes in the packing of chains. In LiAl$_2$-LDH, this results in expansion of the layers.
while the alkyl chains still maintain an all-trans conformation and exhibit repeatable phase transitions. The nonexpanded state can be reformed by treating the sample with ethanol. In Mg₂Al-LDH, the spacing between layers decreases through the intermediate formation of kink blocks and finally gauche blocks. Once the chains are in this state, the system cannot be reversed by cooling or ethanol, unlike the LiAl₂-LDH case.

(4) Layered double metal hydroxides provide an interesting and controllable environment for generating membrane like materials.
References


Chapter 3

PHOTOCHEMICAL STUDIES WITH ANIONIC ZINCTETRAPHENYL-PORPHYRINS IN FATTY ACID EXCHANGED LAYERED DOUBLE HYDROXIDES

Introduction

Photoinduced electron transfer reactions in microheterogeneous systems such as micelles[1,2], vesicles[3], microemulsions[4], porous vycor glass[5], etc. has gained wide attention in the past decade. The problem of fast back electron transfer in homogeneous systems has led researchers to find alternative means of controlling both the back electron transfer rate and the efficiency of charge separation.

Microheterogeneous systems are utilized as host materials for different photosensitizer molecules. There is a large number of photosensitizer molecules as guest species that can be supported on different host materials and the properties of these photosensitizer molecules are considered in determining which system to use.

Certain microheterogeneous systems are restricted in terms of their ability to host large photosensitizer molecules
because their openings and cavities are of specific sizes. In zeolites-X and Y for example, the supercage, its largest cavity is 13 Å. The window opening, however, is only 7 Å[6] which will not accommodate large sensitizer molecules like porphyrins and its derivatives and polypyridyl complexes of ruthenium. In layered materials, however, where the interlayer spacing can be expanded, the introduction of large sensitizers is more facile. For this reason, layered materials such as zirconium phosphonates, cationic clays and anionic clays have been used to introduce photosensitizer molecules both in the interlayer and to adsorb species[7-9].

Ungashe et al.[7] recently reported the assembly of a cationic porphyrin and viologen in zirconium phosphonate multilayers and indicated photoinduced vectorial electron transfer from the photosensitizer to the acceptor across a zirconium phosphonate bilayer interface. Zirconium phosphonates have also been used by Vermeulen and Thompson[10] to intercalate viologen electron acceptors in the interlayer and showed electron transfer from the zirconium phosphonate into the electron acceptor. As is apparent in these reports the guest species, i.e. the photosensitizer or the electron acceptor or both, are positively charged. Such is also the case for cationic clays where the interlayers are cations counterbalancing the negatively charged basal framework. An example is montmorillonite where the ruthenium trisbipyridyl, Ru(bpy)$_3^{2+}$, complex was used as photosensitizer[8]. Smectite
clays have also been utilized in studies with luminescent inorganic cations intercalated in the interlayers[11]. A limitation of these materials is their inability to host anionic complexes that are also of photoactive importance.

The layered double hydroxides (LDH) more commonly called anionic clays, circumvent this problem of introducing anionic sensitizers in cationic layered materials. These LDH's have a positively charged basal framework which results from the replacement of divalent cations by trivalent cations in the brucite-like Mg(OH)$_2$-type octahedral sheets, as in Mg$_3$Al(OH)$_6$Cl'MgaAl-LDH. In the case of LiAl$_2$(OH)$_6$Cl', LiAl$_2$-LDH, the monovalent cation occupies vacancies in a gibbsite-type structure. Both intercalation and ion-exchange of anions in these LDH's are possible. There are a few reports involving photoactive molecules in anionic clays. Giannelis et al.[9] synthesized Mg$_3$Al-LDH with the complex anion Ru(BPS)$_2^-$ intercalated in the interlayer. BPS is 4,7-diphenyl-1,10-phenanthroline disulfonate. It is important to note that Ru(BPS)$_3^-$ was introduced into the LDH during the synthesis of the LDH itself by coprecipitation of metal chloride salts and Ru(BPS)$_3^-$ with an aqueous solution of NaOH.

In Chapter 2, it was shown that the galleries of the LDH's can be expanded by the introduction of long-chain fatty acids in the interlayers. With such large interlayer distances, these materials can, in principle, accommodate photosensitizer molecules. Although both Mg$_3$Al-LDH and LiAl$_2$-
LDH with the long chain carboxylates can be utilized, LiAl₂-LDH was chosen due to the facility of synthesizing this LDH compared to Mg₃Al-LDH. The choice of which carboxylate-LDH system to use is not arbitrary either. Although lauric acid, myristic acid and palmitic acid-LDH's have interlayer distances larger than ZnTPPS 14.6 x 14.6 x 4.3 Å[12], the myristic acid system was chosen since the detailed characterization of the LDH's had been done primarily with the myristic acid.

It is of interest to use the long-chain fatty acid-LDH system because it has the novel membrane-like properties which have characteristics similar to membranes of importance in biological photoelectron transfer reactions. Moreover, the hydrophobic character of the material could be used to advantage reducing the back electron transfer rates, similar to the effects induced by micelles and vesicles.

Experimental

The myristic-LiAl₂-LDH was synthesized by the procedure described in Chapter 2. The material was left soaking in ethanol so as not to dry up. About 5 g of the material was added with 100 mL of a 0.1 M ethanolic solution of ZnTPPS⁻ (Porphyrin Products, Inc) and the mixture was shaken for 10 minutes. The resulting supernatant was discolored which indicates incorporation of the ZnTPPS⁻ into the LDH. The supernatant was discarded and fresh ZnTPPS⁻ solution was added
and the mixture shaken. The discolored supernatant was
discarded. This procedure was repeated until the saturation
limit of loading the LDH with the ZnTPPS\(^{4-}\) had been reached
where the color of the ZnTPPS\(^{4-}\) solution above the LDH remained
red. The myristic-LiAl\(_2\)-LDH with the ZnTPPS\(^{4-}\) will simply be
referred here as LDH-ZnTPPS. The LDH-ZTPPS was filtered, the
filtrate washed with ethanol and then air-dried.

X-ray powder diffraction patterns were obtained using a
Rigaku Geigerflex D/Max 2B diffractometer with Cu K\(\alpha\)
radiation. Infrared spectra were collected on a Mattson-
Cygnus FTIR spectrometer.

The diffuse reflectance spectra of the LDH-ZnTPPS was
taken with a Harrick Diffuse reflectance apparatus which was
attached to a Shimadzu UV-265 Spectrophotometer. The diffuse
reflectance spectrum was taken on the powdered sample. The
spectrum in % transmittance was converted to Kubelka-Munk with
BaSO\(_4\) as reference. The equation to convert to Kubelka-Munk
is:

\[
K.M. = \frac{(1 - \frac{S}{R})^2}{2\frac{R}{S}}
\]

where R is the reference BaSO\(_4\), spectrum and S is the sample
spectrum.
Quantitation of ZnTPPS$^{4-}$ in the LDH

The determination of the amount of ZnTPPS$^{4-}$ in the LDH was done by atomic absorption spectroscopy of zinc metal using a Perkin Elmer atomic absorption spectrometer Model 3100 equipped with a Perkin Elmer Zn hollow cathode lamp. The operating current was 15 mA, wavelength of absorption was at 213.9 nm and a slit width of 0.7 nm was used.

A 10.00 mg sample of the LDH-ZnTPPS was weighed into a 100-mL volumetric flask and 20 mL of 0.5 N HCl added. The mixture was sonicated to dissolve the LDH-ZnTPPS and then diluted to 100.0 mL. The color of the resulting solution was green which is indicative of the demetallated porphyrin, TPPS$^{4-}$, in solution. The reference standard solutions were prepared by dilution of a primary stock standard 1030 ppm Zn made by dissolution of metallic Zn in 0.5 N HCL. The absorbance of the reference standards was plotted against the concentration (Fig. 3.1) and the Zn concentration determined from the calibration curve. The equivalence of Zn is related to the molar quantity of ZnTPPS$^{4-}$ in a 1:1 ratio.

Preparation of Propyl Viologen Sulfonate

The electron acceptors methyl viologen, MV$^{2+}$ and heptyl viologen, HV$^{2+}$ (N,N'-diheptyl-4,4'-bipyridinium bromide) shown in Fig. 3.2 were used as received from Aldrich Chemicals. Propyl viologen sulfonate, PVS, on the other hand, was synthesized.
Figure 3.1 Calibration curve in the quantitation of ZnTPPS⁺ in the LDH by atomic absorption spectroscopy of Zn metal after dissolution of the LDH-ZnTPPS in HCl.
Figure 3.2. Structural formula of (a) methyl viologen, \( \text{MV}^{2+} \) and b) heptyl viologen, \( \text{HV}^{2+} \).

The synthesis of PVS was based on the procedure described by Willner and Ford[12]. In a 150 mL round bottom flask containing 60 mL reagent acetone 4,4'-dipyridyl dihydrate (5 mmoles) was dissolved. To this solution was added 10.5 mmoles of 1,3-propane sultone dissolved in 5 mL of acetone. The reaction mixture was stirred under nitrogen for 10 minutes and then refluxed for 30 min when a precipitate developed. The mixture was cooled to room temperature and the precipitate, which is the reaction product, was filtered off. The precipitate was washed with acetone, dried and stored in a screw-capped vial placed in a desiccator. The reaction is:
Photolysis Experiments

A 20 mg semi-circular pellet of LDH-ZnTPPS was degassed for ~12 hours in a vacuum line at a pressure of ~10^{-5} torr. After degassing, the vacuum tube containing the pellet was placed in a nitrogen environment within a glove box. All the viologen acceptors in aqueous solution were freeze-pump-thawed several cycles before placing in the dry box. Three mL of the solution was pipetted into an anaerobic UV-visible cell and the pellet was dropped into the solution.

The illumination was performed using a 150 W Xenon lamp from Photon Technology, Inc. The output radiation from the lamp covers the infrared, visible and ultraviolet regions of the spectrum. To remove the infrared, a water filter was attached to the lamp housing. The visible radiation from 420-680 nm was reflected onto the sample using a reflecting dichroic mirror which transmitted the ultraviolet radiation. The radical viologens formed were measured with a Shimadzu UV-265 spectrophotometer.

Results and Discussion

Incorporation of the ZnTPPS^- in the LDH

The introduction of ZnTPPS^- in the LDH was carried out in ethanol although ZnTPPS^- is very soluble in water. The choice of ethanol arises from the fact that the LDH is hydrophobic because of the presence of myristate anions in the interlayers of the clay. There are two possible mechanisms
by which ZnTPPS\(^{--}\) could be incorporated in the zeolite, either by ion-exchanging with the myristate and the remaining chloride ions or by intercalation. The X-ray powder diffraction pattern was followed after each 100 mL 0.1 M solution of ZnTPPS\(^{--}\) had been reacted. Fig. 3.3 shows the X-ray powder diffraction patterns of the LDH, the starting material before introduction of ZnTPPS\(^{--}\) (3.3a), at a low level of ZnTPPS\(^{--}\) (3.3b), at an intermediate level of ZnTPPS\(^{--}\) loading (3.3c) and at the saturation level (3.3d). The initial stages of ZnTPPS\(^{--}\) introduction seem to indicate some rearrangements within the interlayer because of changes in the intensities and positions of the peaks compared to the original LDH. Fig. 3.3b shows peak shifts to lower 2θ values. With such shifts in peaks, the 001 reflection may have been shifted to a 2θ value less than 2° which was the starting point of the scan. This infers that the interlayer distance has been initially expanded in order to accommodate the ZnTPPS\(^{--}\). At the intermediate loading level of ZnTPPS\(^{--}\), XRD peaks due to sodium myristate appear together with original peaks of the LDH before the incorporation of ZnTPPS\(^{--}\). White crystalline particles also begin to appear on the surface of the LDH-ZnTPPS sample. This observation and the XRD pattern at intermediate loading (Fig. 3.3c) clearly indicate removal of some of the myristate ions from the interlayer and concomitant deposition as the sodium myristate. Upon saturation with ZnTPPS\(^{--}\), the XRD pattern (Fig. 3.3d) shows the same peaks as
Figure 3.3 X-ray diffraction patterns of (a) LDH-myristate before introduction of ZnTPPS\(^{2-}\), (b) at low ZnTPPS\(^{2-}\) level, (c) at intermediate ZnTPPS\(^{2-}\) level and (d) at saturated level of ZnTPPS\(^{2-}\).
in the original LDH. Tying this observation with that of Fig. 3.3c and the appearance of white crystals of sodium myristate infer that a certain fraction of myristate ions are exchanged out of the interlayer. This is similar to the incorporation of carboxylates in LDH-Cl where not all of the chloride ions are ion-exchanged as described in Chapter 2. The sodium myristate evolved from the incorporation of ZnTPPS\(^{+}\) in LDH is removed by washing the sample with ethanol. The resulting powder of LDH-ZnTPPS after drying has an orange brown color. Since the long chain carboxylates are oriented almost perpendicular to the layer, it is reasonable to assume that the ZnTPPS\(^{+}\) has a similar orientation where the molecular plane is also perpendicular to the layer. This is illustrated in Fig. 3.4. An arrangement where the ZnTPPS\(^{+}\) molecular plane is parallel to the layer would involve perturbation of the long-chain carboxylate orientation that would result to a different XRD pattern. Also, the perturbation on the carboxylates when the ZnTPPS\(^{+}\) molecular plane is parallel to the layer may result in removal of a large fraction of the myristate. This will decrease the interlayer separation as illustrated in Fig. 3.5.

The incorporation of neutral (meso-TPP), cationic (ZnTMPyP\(^{+}\)) and other anionic (meso-TPPS\(^{-}\), ZnTPPC\(^{-}\)) porphyrins (whose structures are shown in Fig. 3.6) into the LDH was examined. The results of these experiments show that both meso-TPP and ZnTMPyP\(^{+}\) are not accommodated in the interlayer.
Figure 3.4 Possible orientation of ZnTPPS⁻ in the LDH where the molecular plane is perpendicular to the layer.
Figure 3.5 ZnTPPS\(^-\) orientation in the interlayer where the molecular plane is parallel to the layer.
Figure 3.6 Structures of (a) neutral meso-porphyrin (meso-TPP) and anionic carboxylate meso-porphyrin (meso-TPPC\(^{\text{a}}\)) and (b) cationic zinctetramethylpyridylporphyrin (ZnTMPyP\(^{\text{a}}\))
while the anionic porphyrins, meso-TPPS\(^{-}\) and ZnTPPC\(^{-}\) were easily incorporated. It is not surprising that only the anionic porphyrins are accommodated while the neutral or cationic ones are not. This is the reverse of cationic clays like smectite that will not intercalate anionic molecules. Thus, based on these results, there are reasons to believe that the incorporation of ZnTPPS\(^{-}\) proceeds via ion-exchange. First, only the anionic porphyrins were incorporated in the myristate-LDH. Although the ZnTMPyP\(^{+}\), being positively charged, was not expected to be intercalated or ion-exchanged, the meso-TPP could have been accommodated because the size of meso-TPP is smaller than the gallery height. Secondly, the presence of pure sodium myristate (white crystals) on the surface of the LDH after reaction with ZnTPPS, (also shown in the XRD patterns (Figs. 3.3c and Fig.3.7) strongly suggests ion-exchange of ZnTPPS\(^{-}\).

Although it is reasonable to state that the bulk of the ZnTPPS\(^{-}\) lies in the LDH-myristate interlayer, there is a possibility that ZnTPPS\(^{-}\) is also adsorbed on the surface of the particles. LiAl\(_2\)(OH)\(_6\)Cl\(^{-}\) was also shaken with ethanolic ZnTPPS\(^{-}\) solution and the powder appeared greenish in color upon drying. The XRD powder pattern after the reaction has the same reflections as in the Cl\(^{-}\) form of the LDH (Fig. 3.8). It is not possible for the ZnTPPS\(^{-}\) to lie in the interlayer of the LDH-Cl with a gallery height of \(~3\ \text{Å}\) in parallel orientation to the layer as in Fig. 3.5 without
Figure 3.7 X-ray powder diffraction patterns of (a) pure sodium myristate and (b) ZnTPPS" loaded LDH-myristate at intermediate loading. The peak denoted by x in (b) is the 001 reflection of the pure sodium myristate.
Figure 3.8 X-ray powder diffraction patterns of LDH in the Cl⁻ form (a) before and (b) after loading with ZnTPPS⁻.
changing the gallery height and therefore the XRD pattern of the sample. Since there was no change in the XRD pattern before and after the introduction of ZnTPPS\(^{\text{-}}\) into LDH-Cl, the ZnTPPS\(^{\text{-}}\) in LDH-Cl must be surface-adsorbed rather than intercalated or ion-exchanged ZnTPPS\(^{\text{-}}\).

The analysis of zinc in the LDH-Cl-ZnTPPS was done by atomic absorption spectroscopy of the solution prepared by dissolving the sample in HCl. The measurement yielded 4.7% ZnTPPS\(^{\text{-}}\) in the LiAl\(_2\)(OH)\(_6\)Cl\(^{-}\). On the other hand the ZnTPPS\(^{\text{-}}\) in the LDH-myristate was determined to be 23.9% of the total weight of the sample. It is reasonable to assume that the difference, 19.2% (23.9 - 4.7) would be in the interlayer because the surface area of the two clay samples are the same although the spacing between layers of LDH-myristate had been expanded. The surface adsorbed ZnTPPS\(^{\text{-}}\) did not come off even when washed with ethanol. Although ZnTPPS\(^{\text{-}}\) is very soluble in water, the hydrophobicity of the material makes it difficult to wash off the surface ZnTPPS\(^{\text{-}}\) with water. It is probable that an electrostatic interaction between the surface of the cationic layer and the anionic porphyrins exists. This may explain why even the surface species of ZnTPPS\(^{\text{-}}\) remain on the LDH after washing with ethanol. Treatment of the LDH-ZnTPPS with ethanolic NaCl resulted in the green coloration of the suspension indicative of the ZnTPPS\(^{\text{-}}\) exchanging out of the LDH and being adsorbed onto the LDH that has now reverted back to the Cl\(^{-}\) form. The removal of the long chain carboxylate in
the interlayer resulted in the loss of hydrophobicity of the material. Upon centrifugation the supernatant remained colorless and the green coloration of the ZnTPPS\(^-\) mixes with the white LDH-Cl. The diffraction pattern of the resulting solid was expected to have the characteristic peaks of the Cl\(^-\) form of the LDH. Although the reflections from the Cl\(^-\) are seen in the XRD pattern they are not as strong as in the original LDH-Cl\(^-\). This maybe due to the limited solubility of NaCl in ethanol and the masking by the ZnTPPS onto the clay surface.

**Spectroscopy of the ZnTPPS\(^-\) in LDH**

To obtain more information about the structure and possible orientation of the ZnTPPS\(^-\), spectroscopic characterization was performed. In the characterization of the carboxylic acids in the LDH, the optical transitions due to the framework LDH do not interfere with those of the carboxylic acids. In the same manner, the framework transitions are not expected to interfere with the transitions characteristic of the ZnTPPS\(^-\).

**Diffuse Reflectance Spectroscopy**

The diffuse reflectance of the LDH-ZnTPPS is shown in Fig. 3.9c while the corresponding electronic spectra of a 10\(^{-5}\) M aqueous solution of ZnTPPS\(^-\) is in Fig. 3.9a. The planar ZnTPP (without the sulfonato groups) has a D\(_{4h}\) symmetry where
Figure 3.9 Visible spectra of (a) $10^{-5}$ M aqueous solution of ZnTPPS$^{4-}$ (b) ZnTPPS$^{4-}$ on LDH-Cl and (c) ZnTPPS$^{4-}$ in LDH-myristate. Spectra (a) and (b) are diffuse reflectance spectra converted by Kubelka-Munk.
the relatively weak bands in the 500-600 nm and the more intense bands at 400 - 420 nm are labeled Q and B bands respectively[14]. The ZnTPPS^- in solution also exhibits both of these band groups. The Q bands at 598 nm and 555 nm in the solution spectra are labelled α and β bands respectively. The B band which is also called the "Soret" band appears at 420 nm. Both the Q and B bands arise from the II-I* transitions in the delocalized II system of the tetrapyrrole. α corresponds to the lowest energy excited state of the metalloporphyrin while β to its vibronic envelope. The B band corresponds to the second excited singlet state of the metalloporphyrin[14].

The closed d-shell configuration of Zn does not allow for an MLCT (d-II'), LMCT (II-d) or d-d transitions. With LDH-ZnTPPS, all the bands are blue-shifted. The α band appears as a very weak band at 595 nm while the β band is blue-shifted to 549 nm. The Soret band is also blue shifted about 8 nm to 411 nm with a shoulder at 427 nm. This blue shift has also been reported in literature for TPPS^- (demetallated ZnTPPS^-) in Zn-Al-LDH[12] and for ZnTPPC [Zinc meso-tetrakis(4-carboxyphenyl-porphyrin] in LiAl-LDH-myristate [15]. Cationic porphyrins such as CoTMPyP^4+ have also been shown to exhibit shifts in the Soret band when incorporated into clays[16]. In the case of ZnTPPS^- on the LDH-Cl^-, the diffuse reflectance spectra (Fig. 3.9b) shows red shifting of the Q and B bands. The α and β bands appear at 602 and 560 nm, respectively whereas the Soret peak is at 427 nm. The red shift could be
attributed to the adsorption of ZnTPPS$^{-}$ on LDH-Cl. It is possible that there are interactions between ZnTPPS$^{+}$ and the hydroxy groups of the host layered double hydroxide. This could possibly be the reason for the band shifts to higher wavelengths. This red shift has also been noted in metalloporphyrins where the metals interact with other ligands in addition to chelation with the nitrogens in the porphyrin ring\cite{14}. It should be noted that there is also a shoulder for the Soret band in the LDH-Cl$^{-}$ system at 412 nm. These Soret bands and their shoulders could be interpreted in terms of where the ZnTPPS$^{+}$ ions are located in the clays. The 412 nm band could be assigned to the interlayer ZnTPPS$^{+}$ while the 427 nm band is to the surface ZnTPPS$^{+}$. Aside from the peak shifts, band broadening is observed in the clay systems which could be attributed to the intermolecular attractions between the porphyrin molecules as they are packed in the LDH.

**Vibrational Spectroscopy**

The vibrational spectroscopy of the myristic acid in LDH has been detailed in Chapter 2 using both Raman and infrared spectroscopy. The vibrational spectroscopy of ZnTPPS$^{+}$ in myristate-LDH in this research has been limited to infrared spectroscopy due to the strong fluorescence that interferes with the Raman scattering technique.

The infrared spectra of the ZnTPPS in the myristate-LDH not only establish the incorporation of the photosensitizer
into the inorganic host but also serves as a probe to examine the interactions between the ZnTPPS$^{2-}$ and the myristate that are present in the interlayers of the LDH. The infrared spectra of neat ZnTPPS$^{2-}$ in KBr (a), myristate-LDH with ZnTPPS$^{2-}$ (b) and myristate-LDH without ZnTPPS$^{2-}$ (c) are shown in Figs. 3.10 - 3.12 for different wavenumber regions. The carbonyl stretching region of the myristate-LDH is not expected to be affected by the presence of ZnTPPS$^{2-}$ because the carboxylate group of the myristate lies closer to the basal plane (See Fig. 2.12). Such is the case as shown in Fig. 3.11 where the peaks at 1416 and 1466 cm$^{-1}$ due to the myristate are not affected by the ZnTPPS$^{2-}$. The 1547 cm$^{-1}$ is blue-shifted by 3 cm$^{-1}$ which may be explained by the proximity of the carboxylate group to the sulfonate group of the ZnTPPS$^{2-}$. The spectral region that could be affected is the C-H stretching region (2800 - 3000 cm$^{-1}$) because of possible intermolecular interactions between the myristate originally in the LDH and the ZnTPPS$^{2-}$.

The C-H stretching bands in the pure ZnTPPS$^{2-}$ (Fig. 3.10a) are much weaker compared to the C-H stretching bands of the myristate-LDH either with or without the ZnTPPS$^{2-}$. The presence of ZnTPPS$^{2-}$ in the myristate-LDH does not have any effect on the C-H stretching bands of the myristate-LDH as observed in Figs. 3.10b and 3.10c. This indicates that possibly there is no change in the intermolecular interaction between the myristate ion upon ZnTPPS$^{2-}$ incorporation.
Figure 3.10 Infrared spectra in the 2600 - 3100 cm$^{-1}$ region for (a) neat ZnTPPS$^{+}$ in KBr (b) ZnTPPS$^{+}$ in myristate-LDH and (c) myristate-LDH without ZnTPPS$^{+}$. 

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Figure 3.11 Infrared spectra in the 1350 - 1800 cm\(^{-1}\) region for (a) neat ZnTPPS\(^{+}\) in KBr (b) ZnTPPS\(^{+}\) in myristate-LDH and (c) myristate-LDH without ZnTPPS\(^{+}\).
Figure 3.12 Infrared spectra in the 1150 - 1350 cm\(^{-1}\) for (a) neat ZnTPPS\(^{++}\) in KBr (b) ZnTPPS\(^{++}\) in myristate-LDH and (c) myristate-LDH without ZnTPPS\(^{++}\).
into the interlayers of the myristate-LDH. This is more apparent in the CH₂ wagging region (1150 - 1350 cm⁻¹) as shown in Fig. 3.12. Pure ZnTPPS⁻ (Fig. 3.12a) has two convoluted bands between 1150 and 1250 cm⁻¹ while myristate-LDH has the progression of bands from 1150 - 1350 cm⁻¹ (Fig. 4.12c) which is typical of the all-trans structure of molecules with long methylene chains. With the incorporation of the ZnTPPS⁻, the progression of the bands is still evident and there are no peak shifts observed with the 1271, 1294 and 1317 cm⁻¹ bands. Because of the broad convoluted band of the pure ZnTPPS⁻ between 1182 and 1250 cm⁻¹, the LDH-ZnTPPS shows overlap of the convoluted bands of pure ZnTPPS⁻ and the 1194, 1221 and 1246 cm⁻¹ of myristate-LDH resulting to the 1182, 1217 and a shoulder at 1246 cm⁻¹, respectively. Since there are no major changes in the infrared spectra of the myristate-LDH upon introduction of the ZnTPPS⁻ except for overlap of the bands, it is reasonable to assume that there are only weak intermolecular interactions between ZnTPPS⁻ and the myristate in the LDH. Should strong intermolecular interactions have been occurring, then the vibrational bands of the LDH-ZnTPPS would show additional bands due to these interactions. Although weak interactions would not show major effects on the vibrational spectra of LDH-ZnTPPS, there should be some effect because of the proximity of the two molecules to each other.
Viologen Adsorption on LDH-ZnTPPS

With the photosensitizer ZnTPPS\(^{-}\) in the interlayer of the layered double hydroxides, studying the electron transfer from photoexcited ZnTPPS\(^{-}\) to viologens of different length of alkyl groups is the next step. The goal here is to see the effect of having the long-chain carboxylates together with the ZnTPPS\(^{-}\) on the formation of viologen radicals.

In order to evaluate the results of photochemical studies in the LDH system, it is necessary to find out how the three different viologens would partition between the organophilic clay and water in which these viologens are dissolved. Since the clay is organophilic, the chain length of the alkyl group of the viologen may play a role in their sorption properties in the clay. The sorption properties in the clay are important in proposing a possible mechanism for charge separation that could be observed in the myristate-LDH system. Because of the long chain myristate in the interlayer of the organoclay, the relatively longer chain heptyl viologen may be adsorbed more than methyl viologen.

The experiments were done by taking 150 mg of the organoclay (LDH-myristate) and shaking for 24 h with 10.00 mL of 2,4,6,8 and 10 \(\mu\)mol/L aqueous solutions of HV\(^{2+}\), MV\(^{2+}\) and PVS. The viologens in solution before shaking and in the supernatant separating from the organoclay after shaking were both determined by uv-visible spectroscopy. There was no significant change in the amounts of viologens before and
ZnTPPS, it should be existent because of the proximity of the two molecules to each other.

It has been mentioned in the preceding chapter that after the exchange of the long chain fatty acids in the LDH interlayer, a considerable amount of ethanol which was used as the solvent is present in the interlayers as solvent pools. The solvent used to incorporate the ZnTPPS into the interlayers of the LDH is also ethanol. Thus the ZnTPPS should be dispersed in the ethanol pools within the interlayer. The ethanol-ZnTPPS as solute-solvent interactions and the ethanol-myristate solute-solvent interactions may be stronger than the possible myristate-ZnTPPS interactions which may explain why the vibrational spectra of the LDH-myristate-ZnTPPS does not show appreciable change from LDH-myristate after ZnTPPS is introduced.

Viologen Adsorption on LDH-ZnTPPS

With the photosensitizer ZnTPPS in the interlayer of the layered double hydroxides, studying the electron transfer from photoexcited ZnTPPS to viologens of different length of alkyl groups is the next step. The goal here is to see the effect of having the long-chain carboxylates together with the ZnTPPS on the formation of viologen radicals.

In order to evaluate the results of photochemical studies in the LDH system, it is necessary to find out how the three different viologens would partition between the organophilic
after shaking indicating no partitioning of the viologens from water to the organoclay. That the viologens do not sorb into the organoclay can be explained by the high solubility of the viologens in water. Even with the long chain heptyl group inHV$^{2+}$, the possible association of the heptyl group with the long chain methylene group of the myristate in the clay is not strong enough to overcome the solute-solvent interactions between HV$^{2+}$ and water.

The sorption studies were repeated on the organoclay, LDH-ZnTPPS. The "sorption" plots are shown in Fig. 3.13. It can be seen that the viologens are readily incorporated into the LDH and the amounts of viologen that go with the LDH-ZnTPPS follow the order: HV$^{2+}$ > PVS > MV$^{2+}$. Because the viologens do not sorb into the organoclay without the ZnTPPS$^{4-}$, it must be the ZnTPPS$^{4-}$ in the organoclay that interacts with the viologens and draws them into the clay. It has been reported in the literature that a complex is formed between anionic sensitizers and cationic viologens in aqueous solution[17-19]. When MV$^{2+}$ or HV$^{2+}$ is added to a solution containing ZnTPPS$^{4-}$, there is a decrease in the intensity of the Soret band which is indicative of the formation of the complex. This is in agreement with the literature[17]. This complex formation is attributed to the strong electrostatic interactions between the negatively charged ZnTPPS$^{4-}$ and the cationic alkyl viologens. In light of the fact that complex formation results even in solution, it is not surprising that
Figure 3.13 "Sorption" plots, $\mu$moles of (a) heptyl (b) propyl sulfonate and (c) methyl viologen adsorbed per g of LDH-ZnTPPS against $\mu$moles viologen left in solution.
complex formation could also occur in the organoclay as long as the ZnTPPS$^{4-}$ is accessible to the viologens. This is certainly the case herein. In the case of the PVS, the neutral molecule is not expected to associate well with the negatively charged ZnTPPS$^{4-}$. The complexation of PVS and ZnTPPS$^{4-}$, however, has also been reported in the literature[20,21]. A comparison of curves (b) and (c) for PVS and MV$^{2+}$, respectively in Fig. 3.13 shows better association of PVS with ZnTPPS$^{4-}$ compared to MV$^{2+}$. This is surprising because electrostatic interactions between negatively charged ZnTPPS$^{4-}$ and the positively charged MV$^{2+}$ should be stronger than the electrostatic attraction between PVS and ZnTPPS$^{4-}$. Such is the case in aqueous solution as reported in literature[20,21]. However, in this system ZnTPPS$^{4-}$ is in the LDH-fatty acid environment where other electrostatic effects between myristate-LDH and PVS enhance the association of ZnTPPS$^{4-}$ with PVS compared to ZnTPPS$^{4-}$ with MV$^{2+}$.

Photochemical Studies

The LDH-ZnTPPS was used in photoinduced electron transfer experiments that utilized heptyl viologen (HV$^{2+}$), methyl viologen (MV$^{2+}$) and propyl viologen sulfonate (PVS) as electron acceptors. The choice of these three electron acceptors stem from the possible comparison between two cationic viologens (HV$^{2+}$) and (MV$^{2+}$) which differ in the chain length of the alkyl group bonded to the nitrogen atoms of the bipyridinium and a
comparison between the cationic viologens and the zwitterionic PVS. The LDH-ZnTPPS is in pellet form which is submerged in an aqueous solution of the electron acceptor. The concentration of the electron acceptors used was held constant at 0.001 moles/L. In Fig. 3.14 are shown the electronic spectra of the radical HV\textsuperscript{•}, PVS\textsuperscript{•} and MV\textsuperscript{•} taken every thirty minutes of irradiation of the pellet with 420-680 nm visible light. The scale on the absorbance axis is the same for the viologen radicals that were formed. Since the electron acceptors all contain the bipyridinium unit, the electronic spectra of their corresponding radicals have similar bands at 395 and 602 nm. It is obvious from the uv-visible spectra that the yield of HV\textsuperscript{•} is greater than PVS\textsuperscript{•}, and the PVS radical yield greater than the MV\textsuperscript{•} at the same time interval of irradiation. Plots of the radical yield versus the time of irradiation in Fig. 3.15 also show the comparison among HV\textsuperscript{•}, PVS\textsuperscript{•} and MV\textsuperscript{•}. Although the yields are only in nanomolar quantities, it is interesting to note that charge separation is taking place between the ZnTPPS\textsuperscript{3−} in the LDH and the electron acceptors in solution without any externally added sacrificial electron donor.

It would have been better if the efficiency of the photochemical system could have been expressed in terms of quantum yields in order to determine the differences in each system. However, the scattering effects of the myristate-LDH particles present a difficulty for such measurements. To have
Figure 3.14  Electronic spectra of the radical viologens (a) HV' (b) PVS' and (c) MV' taken every thirty minutes of photolysis.
an appropriate measure of the relative photochemical efficiency of the system, all the conditions of photolysis, i.e. sample size, light intensity, concentration of the three viologens were kept similar.

It should be recognized here that a similar trend exists in both the photolysis and in the sorption of the viologens in the LDH-ZnTPPS. The yield of the radical viologen, and therefore the charge separation, is greater in HV$^{2+}$ than in PVS and least with MV$^{2+}$. In the same manner, the amount of HV$^{2+}$ that is sorbed in LDH-ZnTPPS is greater than that of PVS and again, MV$^{2+}$ with the least. Because the mechanism by which the viologens are sorbed in the LDH-ZnTPPS is through complexation of the ZnTPPS$^{4-}$ with the viologens, the association of HV$^{2+}$ with ZnTPPS$^{4-}$ in the clay is greater than that of PVS, followed by MV$^{2+}$. Such association and formation of a complex in homogeneous aqueous systems do not result in charge separated radical species because the back electron transfer occurs rapidly when the donor and acceptor molecules are close to each other.

There are two possibilities why such an electron transfer and subsequent charge separation occurs in the clay. The first is that the myristate in the interlayer acts as a membrane-like boundary between the ZnTPPS$^{4-}$ and the viologens in solution which are adjacent to the ZnTPPS$^{4-}$. In the photolysis, a pellet of LDH-ZnTPPS was used which is at the bottom of the cell surrounded by the aqueous solution of the viologens.
Figure 3.15 Plot of radical yield vs irradiation time for (a) HV\(^-\), (b) PVS\(^-\) and (c) MV\(^-\).
Without agitation (shaking or stirring), it is unlikely that the viologens would be able to associate well with the ZnTPPS\(^{4-}\) because of the hydrophobicity of the LDH-ZnTPPS.

The effect of hydrophobicity or lipophilicity of the viologen on the charge separation of viologen radical and oxidized ZnTPPS has been reported in sodium dodecyl sulfate (SDS) micelles\([22]\). The enhancement of the attraction of the positively charged viologens with the micelles in the SDS results in increased photoproduct ions because the ZnTPPS-viologen association is minimized. Similarly, in the binding of long chain alkyl viologens to anionic dihexadecylphosphate (DHP) vesicles, electrostatic repulsive forces are strong enough to prevent the association of ZnTPPS\(^{4-}\) with the alkyl viologen \([23]\). Thus, charge separated species are also produced.

The results which show the yield of PVS\(^{2-}\) radical formation is better than MV\(^{2+}\) in the myristate-LDH system indicate that the myristate chains do not act in a similar manner as the anionic micelles and vesicles. The effect of the anionic micelles and vesicles is to bind preferentially the cationic viologens and prevent association with the ZnTPPS\(^{4-}\) in aqueous medium. In myristate-LDH, the hydrophobic nature of the myristate chains helps to draw the viologens towards the ZnTPPS\(^{4-}\) depending on the lipophilic character of the viologen. This would explain the order of sorption of the viologen to the LDH-ZnTPPS and the degree of charge separation
for each of the viologens relative to each other. The surprisingly better association of PVS with ZnTPPS\(^{-}\) compared to MV\(^{2+}\) with ZnTPPS\(^{-}\) in myristate-LDH can also be explained by this hydrophobic character of the myristate-LDH. Moreover the neutrality of PVS in contrast to the positively charged MV\(^{2+}\) helps in positioning the molecules closer to the interlayer of the myristate-LDH containing the ZnTPPS\(^{-}\).

The other possibility why charge separation is observed in the myristate-LDH system is the presence of an electron donor in the system. It has been mentioned that ethanol is still present in the LDH-ZnTPPS as solvent pools. Ethanol acting as a sacrificial electron donor has been observed\cite{24}. The sulfur containing mercaptoethanol has also been used as a sacrificial electron donor in other reports\cite{17,18}. It is highly probable that the ethanol pools in the LDH-ZnTPPS system are acting as a sacrificial electron donor. This supports the observation that only a limited amount of the viologens are formed because it is limited by the quantity of the sacrificial electron donor. In order to verify the effect of ethanol, photolysis was done on a LDH-ZnTPPS pellet in ethanolic solution of 0.001 M methyl viologen and separately, an ethanolic solution consisting of 1 \(\times\) \(10^{-6}\) M ZnTPPS\(^{-}\) and 0.001 M methyl viologen, whose spectra are shown in Figs. 3.16 and 3.17, respectively. The spectra were taken after every 30 seconds of irradiation. In Fig. 3.16, no Soret band due to ZnTPPS\(^{-}\) was observed because ZnTPPS\(^{-}\) does not go into
Figure 3.16  Electronic spectra of the MV$^+$ radical formed when LDH-ZnTPPS is photolyzed with 0.001 M ethanolic solution of methyl viologen.
solution. In Fig. 3.17 however, the band at \( \sim 420 \text{ nm} \) is not the strong Soret band seen for ZnTPPS\(^{-}\) in aqueous solution but a broad and weaker band which could be attributed to the complexation of ZnTPPS\(^{-}\) with MV\(^{2+}\) in the presence of ethanol. The band at 420 does not change in intensity as photolysis goes on because there is a turnover of ZnTPPS\(^{-}\) due to the presence of ethanol. It can be seen that the yield of the radical MV\(^+\) in the LDH-ZnTPPS was significantly increased even with a reduction in the irradiation time. Such an increase in the charge separation was effected by the presence of ethanol. It should be mentioned here that no leaching of ZnTPPS\(^{-}\) into the solution occurs which indicate that it is the ZnTPPS\(^{-}\) in myristate-LDH that is the photosensitizer rather than ZnTPPS\(^{-}\) as species in solution. In the case of the homogeneous aqueous solution, a blank experiment without alcohol did not result in charge separation because of the fast back electron transfer from the viologen radical to the oxidized ZnTPPS\(^{-}\). However, as seen in Fig. 3.17, using ethanol as solvent and a sacrificial electron donor at the same time resulted in formation of MV\(^+\).

It is difficult to determine what the mechanism is for the electron transfer and charge separation in the LDH-ZnTPPS system based on the preceding observations. The following equations, however, may explain such results (using MV\(^{2+}\) as the viologen):

\begin{align*}
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\end{align*}
Figure 3.17 Electronic spectra of the MV$^-$ radical formed when $10^{-6}$ M ZnTPPS$^-$ is photolyzed with 0.001 M methyl viologen in ethanol as solvent.
\[ \text{ZnTPPS}^{4-} + \text{MV}^{2+} \rightarrow [\text{ZnTPPS}^{4-}\ldots \text{MV}^{2+}] \]

\[ [\text{ZnTPPS}^{4-}\ldots \text{MV}^{2+}] \rightarrow [\text{ZnTPPS}^{3-}\ldots \text{MV}^{+}] \]

\[ [\text{ZnTPPS}^{4-}\ldots \text{MV}^{2+}] \rightarrow [\text{ZnTPPS}^{4-}\ldots \text{MV}^{2+}] \]

\[ [\text{ZnTPPS}^{3-}\ldots \text{MV}^{+}] + \text{EtOH} \rightarrow \text{ZnTPPS}^{3-} + \text{MV}^{+} + \text{other products} \]

**Conclusions**

The layered double hydroxides containing long chain fatty acids are new materials used here to incorporate the photosensitizer ion ZnTPPS\(^{4-}\). Based on the results, some conclusions may be drawn:

1. The ZnTPPS\(^{4-}\) is ion-exchanged into the interlayer of the myristate-LDH which results in the removal of a fraction of the long chain carboxylate as evidenced by the spectroscopic properties. Being in the interlayer suggests that it is within a hydrophobic environment.

2. Alkyl viologens dissolved in water do not show appreciable sorption into the LDH due to its hydrophobicity but associate well in the presence of ZnTPPS\(^{4-}\) in the myristate-LDH. Complexation of viologens and ZnTPPS\(^{4-}\) occur in aqueous solutions. Although it is not certain that the complexation in water is similar in the myristate-LDH,
association of the viologens with ZnTPPS\(^{-}\) in myristate-LDH is aided by the interlayer carboxylates.

3. Small quantities of radical viologens are formed in the absence of externally added sacrificial electron donors. It is difficult to ascertain the role of the long chain carboxylate and its hydrophobic character in the yield of the radical viologen that is formed. The small amount of ethanol present in the interlayer is possibly acting as sacrificial electron donor.
References


Chapter 4

INVESTIGATION OF ZEOLITE-SOLUTION INTERFACIAL ELECTRON TRANSFER: TRIAD SYSTEMS IN ZEOLITE-Y

Introduction

Zeolites are another class of inorganic materials which continues to gain a lot of interest as host materials for photosensitive molecules. These are crystalline alumino-silicates whose applications range from catalysis and catalyst supports to ion-exchangers and sorbents. The three dimensional structure of zeolites is able to incorporate the photosensitive molecules because of the presence of channels, cavities or pores of varying dimensions which are filled with cations and water. Also the inherent property of the zeolites to exchange cations in and out of the cavities make them versatile for inclusion of different cations that could affect the chemistry within the zeolites.

The photosensitizer complex most extensively studied in zeolites is the ruthenium trisbipyridyl complex, Ru(bpy)$_3^{2+}$. For example, Mallouk and co-workers[1] have organized a molecular triad which consists of Ru(bpy)$_3^{2+}$ covalently bonded to an electron acceptor DQ$^{2+}$ and ion-exchanged into zeolite-L
which had been previously doped with benzyl viologen (BV$^{2+}$). Because the window size of zeolite-L (7.1 Å) is smaller than the size of Ru(bpy)$_3^{2+}$ complex, 12 Å, only the DQ$^{2+}$ end of the sensitizer-acceptor assembly is introduced into the channel of zeolite L. DQ$^{2+}$ is in close proximity to BV$^{2+}$ which acts as secondary electron acceptor. In this configuration the photosensitizer is held "dangling" in the solution.

The Ru(bpy)$_3^{2+}$ complex could also be held immobile within the supercages of zeolites, more specifically Na-Y. Although the complex would not pass through the 7.4 Å window of Na-Y[2], it could fit snugly into the 13 Å diameter of the supercage. Thus, simple ion-exchange of the complex is not possible and it would need to be synthesized in the supercages. Since the initial report on the synthesis and characterization of the photosensitizer Ru(bpy)$_3^{2+}$ in Na-Y by De Wilde et al.[3,4], there has been a number of studies that involve the use of this microheterogeneous system to investigate photoinduced electron transfer reactions[5,6,7].

The absorption and emission spectra together with the lifetimes of the excited state of Ru(bpy)$_3^{2+}$ in zeolite-Y have been well characterized by Lunsford and co-workers[4]. Dutta and Incavo on the other hand were the first to report the photoelectron transfer between the excited Ru(bpy)$_3^{2+}$ and the electron acceptor, methyl viologen, MV$^{2+}$ which are spatially separated in different supercages of Na-Y[5]. Both the Ru(bpy)$_3^{2+}$ and MV$^{2+}$ are held immobile in the dehydrated zeolite
supercages. The formation of the blue radical $\text{MV}^+$ was observed upon illumination of the degassed dehydrated $\text{Ru(bpy)}_3^{2+}$-$\text{MV}^{2+}$-$\text{Na-Y}$ with visible light from Kr or Ar ion lasers.

The dynamic quenching of the excited $\text{Ru(bpy)}_3^{2+}$ at different concentrations in $\text{Na-Y}$ by $\text{MV}^{2+}$ at different loading levels was investigated by Turbeville and Dutta[7]. They have shown that the maximum yield of the radical viologen, $\text{MV}^-$, results when the $\text{MV}^{2+}$ concentration in the zeolite is $\sim 2$ $\text{MV}^{2+}$ molecules per supercage. Although $\text{MV}^{2+}$ in supercages adjacent to a supercage containing $\text{Ru(bpy)}_3^{2+}$ quenches the excited $\text{Ru(bpy)}_3^{2+}$ via electron transfer with subsequent formation of the radical $\text{MV}^-$, the inaccessibility of the reduced photoproduct makes it difficult to utilize the radical viologen for further reactions. Initial investigations of using $\text{MV}^{2+}$ in aqueous solution also showed radical formation and charge separation, albeit in very low yields[8]. It is the objective of this research to increase the efficiency of electron transfer and charge separation in order to increase the yield of radical viologens in aqueous solution.

**Experimental**

**Preparation of Ru(bpy)$_3^{2+}$ in Zeolite-Y**

As mentioned in the introduction, $\text{Ru(bpy)}_3^{2+}$ cannot be ion-exchanged into the supercage of $\text{Na-Y}$ because of the size restriction on the window of the zeolite. For this
reason, it has to be synthesized in situ. The synthesis was based on the procedure described by De Wilde et al.\[3\]. The quantities of the starting materials were all scaled up in order to make a large amount of sample necessary for all the experiments.

Three grams of zeolite powder from Union Carbide were shaken overnight with 500 mL of 1 M NaCl in order to ensure the zeolite was in the Na\(^+\) form. The powder was filtered and washed with plenty of water in order to remove any adsorbed NaCl from the zeolite. It was then calcined at 500°C in flowing O\(_2\) for 24 hours. After the calcination, the sample was rehydrated by flowing nitrogen saturated with water over it. The desired concentration of Ru(bpy)\(_2\) was 50 μmole for every gram of zeolite such that 150 μmoles of Ru(NH\(_3\))\(_6\)Cl\(_3\) were weighed for ion-exchange in zeolite. It is assumed that with this low concentration, all of the Ru(NH\(_3\))\(_6\) would be ion-exchanged and later completely react with bipyridine. The Ru(NH\(_3\))\(_6\)Cl\(_3\) was dissolved in 100 mL of deionized water and the zeolite was placed into the solution. The pH of the mixture was adjusted to ~5.2 so that the amine in the ruthenium complex will not be replaced by OH\(^-\). The mixture was stirred overnight for about 12 hours to allow for ion-exchange to take place. While stirring, the suspension was bubbled with N\(_2\) in order to prevent atmospheric O\(_2\) from reacting with Ru(NH\(_3\))\(_6\)\(^3+\) which can be irreversibly converted to ruthenium red. This has the structure: [((NH\(_3\))\(_2\)Ru\(^{3+}\)-O-Ru\(^{4+}\)(NH\(_3\))\(_4\)-O-Ru\(^{3+}\)(NH\(_3\))\(_5\)]\(^6+\)[8].
After the exchange process, the zeolite was filtered via suction filtration and washed with ~500 mL of distilled water. The residue was placed in a vacuum oven at room temperature to dry. The dried zeolite sample was placed in an agate mortar along with 0.60 moles [which is four times the amount of Ru(NH₃)₆³⁺] of 2,2'-bipyridine and mixed thoroughly and as quickly as possible still avoiding O₂. The powdered mixture was then pressed into 13 mm (diameter) pellets whose thickness was about one mm. Each pellet was about 200 mg. The pellets were then placed in a glass tube that was attached to the vacuum line. The sample was degassed for 6 hours after which the tube was closed off from the line and the Ru(NH₃)₆³⁺ and bipyridine allowed to react by heating at 200°C for 24 hours. After the reaction, the tube was opened to the vacuum line again for 6 hours in order to remove any vapors like NH₃ and some unreacted 2,2'-bipyridine. The distinct orange color of the pellet was due to the Ru(bpy)₂⁺ in the zeolite. The pellets were ground into powder and placed into a porous Soxhlet thimble. Soxhlet extraction with ethanol as solvent was done on the sample to remove the excess bipyridine. UV-Visible spectra of the washings were taken every week in order to check whether all the unreacted bipyridine had been completely extracted. After complete removal of the excess bipyridine, which took about a month, the zeolite sample was shaken with 500 mL of 0.50 M NaCl so as to remove any surface species of Ru(bpy)₂⁺ and the little amount of unreacted
Ru(NH$_3$)$_6^{3+}$. The sample was filtered and washed with a copious amount of deionized water. The sample was air-dried and stored in a screw-capped vial. The reaction is that of a reduction of the Ru$^{3+}$ by bipyridine to form the Ru(bpy)$_3^{2+}$:

$$2 \text{Ru}^{3+} + 8 \text{bpy} \rightarrow 2 \text{Ru(bpy)}_3^{2+} + C_{20}H_{14}N_4 + 2 H^+ \quad (4.1)$$

**Diffuse Reflectance Spectroscopy**

The diffuse reflectance spectra of the Ru(bpy)$_3^{2+}$ in zeolite were taken using a Harrick Diffuse Reflectance Apparatus which was attached to a Shimadzu UV-265 Spectrophotometer. The spectra in % transmittance were converted to Kubelka-Munk where BaSO$_4$ is the reference. The equation to convert to Kubelka-Munk is:

$$K.M. = \frac{(1 - \frac{S}{R})^2}{2 \frac{R}{S}}$$

where $R$ is the reference BaSO$_4$ spectrum and $S$ is the sample spectrum.

**Quantitation of Ru(bpy)$_3^{2+}$ in zeolite**

The amount of Ru(bpy)$_3^{2+}$ in the zeolite was determined by X-ray fluorescence. The quantitative procedure was first published by Dutta and Incavo using energy dispersive X-ray fluorescence[5]. The X-ray fluorescence of the sample was compared with that of the standards which were prepared by ion-exchanging Ru(NH$_3$)$_6^{3+}$ into clean zeolite samples as in the
initial steps in the procedure for the synthesis of Ru(bpy)$_2$ in zeolite. The reference and sample size were the same and the pellets were pressed at the same pressure.

The spectrometer used was an energy dispersive Kevex 0700/7000 with the Rh anode in the X-ray tube equipped with seven different secondary targets. The detector is a Si(Li) drift detector with a multichannel analyzer. The acquisition conditions for the measurement of the intensities of fluorescence (in counts/second) of the Ru K$\alpha$ peak from the entrapped ruthenium are: voltage = 35 kV, current = 0.8 mA with a preset value of 500 seconds in a 40 eV/channel range. The measured intensities have errors of approximately 2%.

The intensities of the reference standards were plotted against the concentration and the sample concentration was determined from this calibration curve.

**Preparation of Propyl Viologen Sulfonate**

The electron acceptors methyl viologen, MV$^{2+}$, N,N'-tetramethylene-2,2'-bipyridine, DQ$^{2+}$ (Fig. 4.1a) and benzyl viologen, BV$^{2+}$ (Fig. 4.1b) are commercially available from Aldrich and Sigma Chemicals and were used as received.

Propyl viologen sulfonate, PVS, however was synthesized. The synthesis of PVS was based on the procedure described by Willner, et al.[9] and was outlined in the experimental section of Chapter 3.
Two procedures were developed for sample preparation for photolysis experiments. The first method used Ru(bpy)$_3$-$\text{zeolite-Y}$ pellets using an anaerobic UV-visible cell, while the second used the Ru(bpy)$_3$-$\text{zeolite-Y}$ in its powdered form in an NMR tube. In all the photolysis experiments, care was taken to exclude oxygen from the system as it reacts with the radical viologens that are formed. This necessitated that experiments using the anaerobic UV-visible cell be restricted to four hours during which oxygen leakage was minimal. In the case of experiments using the NMR tube, oxygen did not present a problem once the NMR tube was sealed with an acetylene flame while on the vacuum line.
(a) **Pellet/A anaerobic UV-visible cell**

A 20 mg semi-circular pellet of Ru(bpy)$_2$$^+$ in zeolite was degassed for ~12 hours in a vacuum line at a pressure of ~$10^{-5}$ torr. After degassing, it was placed in a nitrogen glove box. Aqueous viologen solutions were freeze-pump-thawed several cycles before placing them in the glove box. Three mL of the solution was transferred into the anaerobic UV-visible cell and the pellet dropped into the solution. Silicon grease was used to make the ground glass seal air-tight.

(b) **Powder/NMR tube**

Five milligrams of the powder were placed into a 5 mm diameter NMR tube having a microstirring bar. A quantity of the viologen which would result in one mL of 0.1 M solution was weighed and placed in the tube. The NMR tube was attached to a vacuum line by using a 10 mm to 5 mm O.D. universal adapter. The sample and tube were degassed for ~12 hours in the vacuum line at a pressure of ~$10^{-5}$ torr. This was done by very carefully opening the valve opening leading to the tube so that the powder will not be suctioned out of the NMR tube at the initial stages of degassing. Water, which had been previously freeze-pump-thawed several cycles, was distilled into the NMR tube to about 1 mL.

The photolysis was done using a 150 W Xenon lamp with a universal power supply from Photon Technology, Inc. The output from the lamp consists of infrared, visible and UV-visible radiation. A water filter was attached to the lamp.
housing which absorbs infrared radiation from the output. Only the visible light at 420 - 680 nm was reflected onto the sample using a reflecting mirror which transmits the ultraviolet. The reduced radical viologen formed in the solution above the zeolite was monitored using a Shimadzu UV-Vis 265 spectrophotometer. In the NMR tube, the samples were centrifuged before measurement of the UV-visible spectra.

**Quantum Yield Determination**

To determine the quantum yield, the light absorbed by Ru(bpy)$_3^{2+}$ was calculated by comparing the light transmitted by the zeolite with Ru(bpy)$_3^{2+}$ and the same amount of zeolite without Ru(bpy)$_3^{2+}$ over a period of 30 minutes. The excitation was at 457.9 nm using Ar ion laser. The difference between the two samples was used to estimate the number of photons absorbed by the Ru(bpy)$_3^{2+}$ in zeolite. This was done using an NMR tube and the Ru(bpy)$_3^{2+}$-zeolite-Y in powder form. After irradiation, the sample was centrifuged and the radical viologen formed was measured with the uv-visible spectrophotometer equipped with an adapted sample holder for the NMR tube.
Raman Spectroscopy

The Raman spectra of the zeolites with different loading levels of MV$^{2+}$ and BV$^{2+}$ were taken with the Spectra-Physics Argon ion laser using excitation at 406.7 nm radiation. The spectra were collected using a SPEX 1403 double monochromator and detected with a GaAs photomultiplier with photon counting.

Results

The Ru(bpy)$_3^{2+}$ had to be synthesized in the supercages of Na-Y because the 7 Å window is too small for the 12 Å complex to penetrate into the zeolite via a simple ion-exchange process. Once the complex is synthesized, it is held firmly in the 13 Å supercage of Na-Y. Thus, each molecule is held immobile within a supercage. The X-ray diffraction pattern of the zeolite is not changed after the synthesis which indicates that the crystal structure remains unmodified.

The diffuse reflectance spectra of Ru(bpy)$_3^{2+}$ in Na-Y is shown in Fig. 4.2b. The metal to ligand charge transfer (MLCT) band at 456 nm corresponds to the metal to the ligand $\pi^*$ transition and is similar to the electronic spectra of Ru(bpy)$_3^{2+}$ in solution (Fig. 4.2a). This is indicative of Ru(bpy)$_3^{2+}$ present in the zeolite and is consistent with previously reported data[5,7]. The 5 nm shift in the MLCT band is usually observed in inorganic matrices. Turbeville and Dutta[7] have investigated the electronic spectra of Ru(bpy)$_3^{2+}$ in Na-Y and found that there is no major shift in the MLCT
Figure 4.2 Visible spectra in the 360 - 600 nm region of 
(a) Ru(bpy)$_2^{2+}$ solution and (b) Ru(bpy)$_3^{2+}$ in Na-Y. 
The diffuse reflectance spectra of Ru(bpy) in Na-Y was converted to Kubelka-Munk to obtain (b).
band or the $\pi - \pi^*$ band of the complex as the concentration changes from 33 $\mu$moles Ru(bpy)$_3^{2+}$/g Na-Y to 270 $\mu$mole Ru(bpy)$_3^{2+}$/g Na-Y. In the case of even higher loading, like 470 $\mu$mole Ru(bpy)$_3^{2+}$/g Na-Y, the strong red shift that is observed in the MLCT band may be due to the ruthenium bisbipyridyl complex that is formed instead of the tris-complex.

The amount of Ru(bpy)$_3^{2+}$ in Na-Y was determined by X-ray fluorescence spectroscopy. The calibration curve based on a set of reference standards is shown in Fig. 4.3. From the equation of the straight line through the points in the calibration curve, the sample was found to contain 44 $\mu$moles Ru(bpy)$_3^{2+}$/g Na-Y. This quantity corresponds to 1 molecule of the complex per 10 supercages.

The characterization of Ru(bpy)$_3^{2+}$ in Na-Y using vibrational (Raman) spectroscopy has been reported in the literature[4,5]. The absorption and emission characteristics have also been investigated. Recent literature has focused on the photoinduced electron transfer where both the donor and acceptor molecules are held within neighboring supercages. Oxidative quenching of the Ru(bpy)$_3^{2+}$ by MV$^{2+}$ occurs readily in the zeolite and is proposed to proceed via electron hopping from the MV$^{2+}$ to other viologens in neighboring supercages which results in charge separation[5,6]. The latter experiments were done in the solid state either in the dehydrated or hydrated form.
Figure 4.3 Calibration curve of Ru²⁺ standards in X-ray fluorescence measurements.
The observation of photoelectron transfer with both donor and acceptor molecules in the solid state in the zeolite is a significant contribution to the field of electron transfer using zeolitic systems. However, the practical utility of such a solid state system in terms of hydrogen production is very limited. Increasing the efficiency of electron transfer and charge separation with an electron acceptor in the solution phase and the donor photosensitizer in the zeolite is the major point of consideration here. The photogeneration of redox products through ion-exchange serves as a base point for electron transfer across the zeolite-solution interface.

Photogenerated Redox Species via Ion-Exchange in Zeolites

In the photolysis of Ru(bpy)$_3^{2+}$-MV$^{2+}$-zeolite in the solid state[6,7], the photolytic reaction is:

$$\text{Ru(bpy)}_3^{2+}(z) + \text{MV}^{2+}(z) \rightarrow \text{Ru(bpy)}_3^{3+}(z) + \text{MV}^{+*}(z)$$  \hspace{1cm} (4.2)

where the intrazeolitic species are denoted by $z$. For the optimum generation of MV$^{+}$ radical, the loading of MV$^{2+}$ had to be ~2 molecules per supercage[7]. The ion exchange property of the zeolite may then be used in order to exchange out MV$^{+}$(z) from the zeolite into the solution. The ion-exchange process may be written as:

$$2 \text{MV}^{+*}(z) + \text{MV}^{2+}(s) \rightarrow 2 \text{MV}^{+*}(s) + \text{MV}^{2+}(z)$$  \hspace{1cm} (4.3)
where s denotes the solution around the zeolite. From Eqn. 4.3, it is evident that MV^{2+} must be present in the solution. In order to decide on the concentration of the solution species that needs to be used, the loading level of the MV^{2+} in the zeolite and the MV^{2+} in the solution surrounding the zeolite must be considered. To do so, the isotherm for MV^{2+} exchange with the Na-Y was examined. The curve for the isotherm data is plotted on Fig. 4.4. The loading level of MV^{2+} at maximum exchange is about 1.3 molecules/supercage. In the solid state studies, the intrazeolitic loading level was kept high at ~2 molecules/supercage[6,7,8]. The concentration of MV^{2+} in solution that leads to a saturated loading of MV^{2+} in the zeolite via ion-exchange is 0.1 M (shown by the arrow in Fig. 4.4). This was found to be optimum for photolysis studies through the ion-exchange mechanism.

The kinetics of reaction 4.3 are important for the removal of the MV^{•} from the zeolite into solution. This process is dependent on intrazeolitic diffusion of MV^{2+} into the zeolite and MV^{•} out of the zeolite. With the large size of an ion of MV^{2+} having dimensions of 13.6 x 6.4 x 3.8 Å[10], the overall process would be limited by diffusion. There is only limited information about the kinetics of the ion-exchange of cations in zeolites[11-13], and large ions in particular. To investigate the ion-exchange of MV^{•} out of the zeolite into solution, a significant amount of the radical inside the zeolite must be present which is very difficult to
Figure 4.4 Plot of $\mu$moles of MV$^{2+}$ in zeolite against $\mu$moles MV$^{2+}$ remaining in solution. (The curve is just a guide to the eye.)
accomplish. Also, from the limited information available on the kinetics of ion-exchange of cations in zeolites, it is difficult to determine the feasibility of reaction 4.3. Since chemical preparation of MV\(^-\) exchanged zeolite-Y necessitates the presence of other interfering ions in solution, direct information about its rate of ion-exchange cannot be obtained. A measure of the kinetic efficiency could be obtained by examining zeolites containing ions similar in size to MV\(^-\). The dimensions of Co(C\(_5\)H\(_5\))\(_2\)\(^+\) are 6.8 x 5.6 Å\([14]\) and it serves as a good model molecule to simulate ion-exchange process of MV\(^-\) since its diffusion coefficient has been reported as similar to that of MV\(^2+\)[15]. A mass of cobalticinium-exchanged zeolite-Y was dropped into 3.0 mL solution of 0.10 M MV\(^2+\) and the cobalticinium coming out of zeolite into solution was monitored as a function of time by the electronic band at 405 nm (\(ε = 220\))[16]. Figure 4.5 shows the concentration of cobalticinium that exchanges into solution with MV\(^2+\) as the counterions. It is clear that the ion-exchange process reaches equilibrium within the time period of photolysis (tens of minutes) and supports the use of reaction 4.3 for separating the photoproducts.
Figure 4.5 Concentration of cobalticinium in zeolite-Y that exchanges out into solution using $\text{MV}^{2+}$ as counterions.
Neutral Zwitterionic Viologen as an Electron Acceptor

As has been previously mentioned, interfacial electron transfer from the excited Ru(bpy)$_3^{2+}$ in supercages near the solution to the electron acceptor species in the solution, is feasible. This is particularly true when the electron acceptor can not be exchanged into the zeolite due to the neutrality of the acceptor. Such is the case with propyl viologen sulfonate. The electronic spectra of the aqueous solution of PVS before and after the photolysis with a pellet of Ru(bpy)$_3^{2+}$ in Na-Y showed no change in the absorbance of the 260 nm band that is characteristic of PVS. This is not surprising because there is no driving force for PVS to go into the zeolite.

The yield of the radical PVS$^-$ is twice that of the MV$^-$ at the same concentration of 0.01 M viologen in solution. Fig 4.6a shows the electronic spectra of the MV$^-$ radical while Fig. 4.6b shows the PVS$^-$ radical formed upon irradiation every hour for 4 hours. Fig. 4.7 compares the curves for radical MV$^-$ and PVS$^-$ formation against irradiation time. For both radicals, the absorbance at 395 nm ($\epsilon = 37,000$) was used to quantify the yields. The significant difference in the radical yield with the zwitterion as the electron acceptor can be attributed to the electrostatic repulsion between the negatively charged photoreduced product and the anionic framework of the zeolite. This causes PVS$^-$ to be repelled from the framework causing charge separation and reduced back
Figure 4.6 Electronic spectra of (a) MV\textsuperscript{+} and (b) PVS\textsuperscript{−} taken each hour after photolysis reaction for four hours.
Figure 4.7 Plots of μmol of viologen (a) MV and (b) PVS radical formed against irradiation time.
electron transfer rate. In previous work on colloidal silica gel and PVS[18], the back electron transfer was slowed down whereas here, actual charge separation is observed. This is presumably due to the complete encapsulation of Ru(bpy)$_2^{2+}$ which precludes contact between Ru(bpy)$_3^{3+}$ and radical and also the higher charge density of the zeolite framework. The charge density expressed as OH$^-$ ions nm$^{-2}$ for colloidal SiO$_2$ in the pH range of 7-8 is 0.1-0.25[19]. In contrast, the aluminosilicates have a charge density which readily exceeds 2 negative charges per nm$^2$[19].

It should be noted here that charge separation takes place in the absence of an ion-exchange process with the use of PVS in solution as electron acceptor. This indicates that the electron transfer proceeds from the zeolite interface into the solution. This explains why the yield of photoinduced redox species is low because only the entrapped Ru(bpy)$_2^{2+}$ in the zeolite with direct access to the viologen in solution takes part in the photochemical process.

**Photoinduced electron transfer in a triad system: Ru(bpy)$_3^{2+}$-DQ$^{2+}$-Y/PVS**

The solid state dynamic quenching of excited Ru(bpy)$_3^{2+}$ by MV$^{2+}$ in adjacent supercages and the result of using PVS as an electron acceptor in solution whereby the radical PVS$^-$ is repelled by the zeolite framework was coupled together in
order to attain a triad molecular assembly. This is organized in such a manner that both Ru(bpy)$_2^{2+}$ and a cationic viologen are held immobile in the zeolite supercages. Inasmuch as only 1 in 10 supercages is occupied by Ru(bpy)$_2^{2+}$, a large fraction of the supercages could be occupied by the cationic viologen which would serve as a primary electron acceptor. PVS is still in solution surrounding the zeolite.

The sodium ions in Ru(bpy)$_2^{2+}$-NaY were exchanged by stirring the zeolite in 0.1 M aqueous solution of N,N'-tetramethylen-2,2'-bipyridinium cation, DQ$^{2+}$. It must be remembered that Ru(bpy)$_2^{2+}$ would not exchange because the molecule is too big to pass through the 7 Å window. So, only Na$^+$ could be replaced by DQ$^{2+}$. The loading of DQ$^{2+}$ was determined to be 1.1 molecule per supercage but excludes the supercages which were occupied by Ru(bpy)$_2^{2+}$. Thus, all of the Ru(bpy)$_2^{2+}$ are surrounded by DQ$^{2+}$ in surrounding supercages. The resulting zeolite after the exchange is denoted as Ru(bpy)$_2^{2+}$-DQ$^{2+}$-Y. DQ$^{2+}$ was chosen as the primary electron acceptor by virtue of its reduction potential of -0.65 V (relative to the normal hydrogen electrode, NHE)[9,17] being lower than that of the PVS in water which is -0.41 V (relative to NHE)[9,17]. Thus, Ru(bpy)$_2^{2+}$-DQ$^{2+}$-Y along with 0.01 M PVS in solution surrounding the zeolite, comprise the first of the molecular triad assemblies investigated. A structural representation of this architecture is shown in Fig. 4.8.
Figure 4.8 Structural representation of the triad assembly Ru(bpy)$_3^{2+}$-DO$_2^-$-Y with PVS in solution surrounding the zeolite.
The electronic spectra in Fig. 4.9 show the growth of the PVS radical in solution upon visible light illumination for at 60-minute intervals for 4 hours. Fig. 4.10 is a comparison of the rate of radical formation with DQ^2+ in the zeolite and without DQ^2+ (Ru(bpy))_3^{2+-Na-Y, solid line, b). It can be seen that the rate of radical PVS formation is an order of magnitude higher in Ru(bpy)_3^{2+-Na-Y} than in Ru(bpy)_3^{2+-Na-Y}. This increase in radical formation rate is explained in terms of vectorial electron transfer which occurs in the system containing DQ^2+. The photoexcited Ru(bpy)_3^{2+} transfers an electron to DQ^2+ in the zeolite forming the radical DQ^+ which subsequently transfers the charge across the zeolite-solution interface to the PVS. In Fig. 4.11 is shown the schematic representation of the vectorial electron transfer across the zeolite-solution interface. The occurrence of intrazeolitic oxidative electron transfer between Ru(bpy)_3^{2+} and MV^2+ has been reported in the literature[5,7,8]. Thus, a similar oxidative electron transfer is expected with DQ^2+ that results in the formation of Ru(bpy)_3^{3+}. The vectorial electron transfer is assured by the difference in the reduction potentials between the primary electron acceptor couple, DQ^2+/DQ^+ (E° = -0.65 V vs NHE), also called the electron relay mediator, and the secondary electron acceptor, PVS/PVS^- (E° = -0.41 V vs NHE).
Figure 4.9 Electronic spectra of the PVS$^{-}$ radical taken every hour of irradiation for 4 hours in the Ru(bpy)$_2$$^{3+}$-DQ$^{2+}$-Y/PVS system.
Figure 4.10 Comparative plots of the PVS⁻ radical growth in (a) Ru(bpy)₂²⁺-DQ²⁻-Y and (b) Ru(bpy)₂²⁺-Na-Y (solid line) and Ru(bpy)₂²⁺-MV²⁺-Y (broken line) with PVS in solution.
Figure 4.11 Schematic representation of the vectorial electron transfer across the zeolite-solution interface in the Ru(bpy)$_3^{2+}$-DQ$^{2+}$-Y/PVS system.
The reactions are illustrated by the chemical equations written below:

\[
Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{2+*} \quad (4.4)
\]

\[
Ru(bpy)_3^{2+*} + DQ^{2+} \rightarrow Ru(bpy)_3^{3+} + DQ^* . \quad (4.5)
\]

\[
DQ^* + PVS \rightarrow DQ^{2+} + PVS^- . \quad (4.6)
\]

Slama-Schwork et al. [20] have reported similar charge separation by using a mobile electron relay to transfer an electron from the photoexcited pyrene to viologen. Both the pyrene and the viologen are held immobile in a sol-gel glass. The difference in reduction potential between the electron relay and the tightly held (in sol-gel glass) viologen was also exploited to achieve the charge separation.

**Confirmation of the vectorial electron transfer with Ru(bpy)_3^{2+}-MV^{2+}-Y/PVS**

The vectorial electron transfer discussed above is based upon the differences in reduction potential between Ru(bpy)_3^{3+}/Ru(bpy)_3^{2+} (E° = -0.87 V vs NHE) [21] and DQ^{2+}/DQ^+ (E° = -0.65 V vs NHE), and that between the DQ^{2+} redox couple and PVS/PVS^- (E° = -0.41 V vs NHE). In order to confirm this transfer mechanism, DQ^{2+} was replaced by MV^{2+} whose reduction
potential is \(-0.44\) V vs NHE. This potential is comparable to the potential of PVS (\(\Delta E^o = 0.03\)) such that the driving force for interfacial electron transfer from MV\(^+\) to PVS is absent. The broken line in Fig. 4.11b for the PVS\(^-\) radical formed with the Ru(bpy)\(_3\)\(^{2+}\)-MV\(_2\)\(^{2+}\)-Y system shows that with the Ru(bpy)\(_3\)\(^{2+}\)-MV\(_2\)\(^{2+}\)-Y, the rate of PVS radical formation is comparable to the Ru(bpy)\(_3\)\(^{2+}\)-Na\(^+\)-Y. This confirms that the directional interfacial electron transfer between DQ\(^+\) and PVS is necessary for higher yields in photochemical charge separated states.

In the Ru(bpy)\(_3\)\(^{2+}\)-MV\(_2\)\(^{2+}\)-Y system, two separate electron transfer reactions may occur. The first is from \(\text{Ru(bpy)}^*\) to MV\(_2\)\(^+\) adjacent to the excited Ru(bpy)\(_3\)\(^{2+}\). The other reaction is that of electron transfer from Ru(bpy)\(_3\)\(^{2+}\) which has direct access to the PVS in solution. These two reactions may be regarded as competitive reactions:

\[
\text{Ru(bpy)}_3^{2+} + \text{MV}^2_\text{(z)} \rightarrow \text{Ru(bpy)}_3^{3+} + \text{MV}^+ \text{(z)} \tag{4.7}
\]

\[
\text{Ru(bpy)}_3^{2+} + \text{PVS}_\text{(s)} \rightarrow \text{Ru(bpy)}_3^{3+} + \text{PVS}^- \text{(s)} \tag{4.8}
\]

The subscripts \((z)\) and \((s)\) mean the viologens are in the zeolite and solution, respectively. The slightly higher reduction potential of PVS makes it more energetically favorable to accept the electron compared to MV\(_2\)\(^+\). In Fig. 4.12 is shown the schematic representation of the electron transfer reactions in the Ru(bpy)\(_3\)\(^{2+}\)-MV\(_2\)\(^{2+}\)-Y system. Because the redox
Figure 4.12 Schematic representation of electron transfer in the Ru(bpy)$_3^{2+}$-MV$_2^{2+}$-Y system.
potential of the $\text{MV}^{2+}/\text{MV}^+$ and the $\text{PVS}/\text{PVS}^-$ are not significantly different, there is no driving force for the electron to transfer from $\text{MV}^-$ to PVS (indicated by a cross mark in Fig.4.12). Instead, the electron transfer is across the zeolite-solution interface from $\text{Ru(bpy)}_2^{2+}$ to PVS. A controlled experiment using $\text{DQ}^{2+}$-Na-Y and PVS in solution in the absence of the photosensitizer did not result in the formation of the radical viologen.

**Vectorial Electron Transfer with $\text{Ru(bpy)}_3^{2+}$-$\text{BV}^{2+}$-Y/\text{PVS}**

In the $\text{Ru(bpy)}_3^{2+}$-$\text{MV}^{2+}$-Y, the low production rate of radical PVS$^-$ is expected because of the comparable reduction potential of the $\text{MV}^{2+}$ and PVS redox couples. Another cationic electron relay mediator which was investigated was benzyl viologen, $\text{BV}^{2+}$. Benzyl viologen was ion-exchanged into the zeolite in lieu of either $\text{DQ}^{2+}$ or $\text{MV}^{2+}$. The reduction potential of the $\text{BV}^{2+}/\text{BV}^+$ couple in water is $-0.34$ V vs NHE, which is higher than that of PVS ($E^\circ = -0.41$ V vs NHE). Based on these values, the photolysis of the $\text{Ru(bpy)}_3^{2+}$-$\text{BV}^{2+}$-Y with PVS surrounding the pellet would be expected to yield comparable rates of production of the PVS$^-$ radical with that of the $\text{Ru(bpy)}_3^{2+}$-Na-Y and $\text{Ru(bpy)}_3^{2+}$-$\text{MV}^{2+}$-Y. The directional electron transfer is not thermodynamically favorable from $\text{BV}^+$ ($E^\circ = -0.34$ V vs NHE) to PVS ($E^\circ = -0.41$ V vs NHE). Surprisingly however, the rate of radical formation is similar to the $\text{Ru(bpy)}_3^{2+}$-$\text{DQ}^{2+}$-Y which indicates vectorial electron transfer.
occurring from BV⁻ to PVS. The electronic spectra of the PVS⁻ using this system are shown in Fig. 4.13 while Fig. 4.14 shows the comparative plots of radical PVS produced with (a) Ru(bpy)₃²⁺-BV²⁺-Y and (b) Ru(bpy)₃²⁺-DQ²⁺-Y. It is obvious that the rate of viologen radical production in the system containing BV²⁺ is the same as that for the system containing DQ²⁺, although their reduction potentials in water are different. Fig. 4.15 shows the schematic representation for the Ru(bpy)₃²⁺-BV²⁺-Y system.

From the above results, it may be inferred that the benzyl viologen reduction potential in a highly loaded zeolite sample is not the same as its potential in water. The broken vertical arrow in Fig. 4.15 indicates a possible shift in the reduction potential of BV²⁺ in zeolitic systems. Thus, directional electron transfer could occur. This could be due to the steric effects when there is a high loading of benzyl viologen in the zeolites. With the length of the BV²⁺ cation being 24 Å, the whole cation will not be accommodated in a supercage and the benzyl groups would need to be accommodated in a neighboring supercage. Such an arrangement would induce steric effects which make it difficult for the two bipyridyl rings to assume the planar structure required in the radical state[9]. When the two bipyridyl rings do not assume a planar structure, the dihedral angle between the pyridinium rings is affected which in turn affects the redox potential of the viologen. There is a strong correlation between the dihedral
Figure 4.13  Electronic spectra of the PVS⁻ radical taken every hour of irradiation for 4 hours in the Ru(bpy)₃²⁺-BVT⁺-Y/PVS system.
Figure 4.14 Comparative plots of the radical $\text{PVS}^-$ formed in (a) $\text{Ru(bpy)}_3^{2+}\text{-DQ}^2-\text{Y}$ and (b) $\text{Ru(bpy)}_3^{2+}\text{-BV}^2-\text{Y}$ with PVS in solution.
Figure 4.15 Schematic representation of the vectorial electron transfer across the zeolite-solution interface in the Ru(bpy)$_3^{2+}$-BV$^{2-}$-Y/PVS system.
angle of the two pyridinium rings and the reduction potential as reported in the literature[22]. Fig. 4.16 shows homologues of 2,2'-bipyridinium salts, their dihedral angles and their corresponding redox potentials. The change in the substituent groups in the pyridinium rings affects the dihedral angle and therefore the redox potentials[22]. Changing the methylene length bridging the nitrogen atoms of pyridinium rings changes the dihedral angle between the pyridinium rings. As the dihedral angle increases, the distortion from planarity of the two pyridine rings increases and the redox potential decreases. This is also true for benzyl viologen, BV$^{2+}$ and the corresponding substituted benzyl viologen, BMV$^{2+}$. The reduction potential of BMV$^{2+}$ is -0.67 V (vs NHE) which is negatively shifted by 330 mV compared to BV$^{2+}$ which is -0.34 V (vs NHE). Thus the bulky methyl groups in the 3,3'-position of BMV$^{2+}$, (N,N'-dibenzyl-3,3'-dimethyl-4,4'-bipyridinium) induce steric effects in the bipyridinium rings to affect the dihedral angle.

When photolysis of Ru(bpy)$_3$$^{2+}$-BV$^{2+}$-Y was done in 0.01 M PVS solution, which also contains 0.02 M NaCl, there was a marked decrease in the yield and rate of PVS$^-$ production. Upon using 0.20 M NaCl, the production rate was further decreased to the level comparable to the Ru(bpy)$_3$$^{2+}$-MV$^{2+}$-Y and Ru(bpy)$_3$$^{2+}$-Na-Y systems. In Fig. 4.17 is shown the comparative plots of radical PVS$^-$ production in the absence of NaCl and with NaCl at the two different concentrations. These results have
Figure 4.16 Homologues of 2,2-bipyridinium salts, their dihedral angles and their corresponding redox potential [22].
<table>
<thead>
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<th>Compound</th>
<th>Dihedral angle (°)</th>
<th>$E^0$ (Volt vs NHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Compound 1" /></td>
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<td>-0.37</td>
</tr>
<tr>
<td><img src="image2" alt="Compound 2" /></td>
<td>38.7</td>
<td>-0.55</td>
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</tr>
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<td>77.1</td>
<td>-0.78</td>
</tr>
<tr>
<td><img src="image5" alt="Compound 5" /></td>
<td>91.3</td>
<td>-0.98</td>
</tr>
</tbody>
</table>

**Figure 4.16**
Figure 4.17 Comparative plots of the radical PVS\(^-\) yield in the Ru(bpy\(_3\))\(^{2+}\) – BV\(^2\) – Y system (a) in the absence of NaCl (b) with 0.02 M NaCl and (c) with 0.20 M NaCl in solution with the 0.01 M PVS.
some bearing on the strain factor. The Na⁺ ions exchanges with the BV²⁺ in the zeolite. As the concentration of NaCl is increased, the amount of BV²⁺ that remains in the zeolites is decreased. At lower loading of BV²⁺ in the zeolite, the PVS⁻ yield decreases. With the 0.20 M NaCl with the PVS in solution, ion-exchange of BV²⁺ must be complete. The zeolite form is again Ru(bpy)₃²⁺-Na-Y.

The Raman spectrum of BV²⁺ in a 0.1 M aqueous solution is compared to that of BV³⁺ exchanged hydrated zeolite-Y shown in Fig. 4.18. By comparison to the spectrum of the BV²⁺ aqueous solution (Fig. 4.18a) with the published Raman spectra on methyl viologen in solution[23,24], the observed bands can be classified into three groups: those localized on the bipyridyl moiety, on the benzyl group and on the N⁻CH₃ connector. In the group involving the bipyridyl moiety are bands at 658, 846, 1236, 1302, 1538 and 1652 cm⁻¹. Of these, the bands at 1302 and 1652 cm⁻¹ assigned to the bipyridyl inter-ring C-C stretch and the pyridine ring stretch[23] shift by 4-6 cm⁻¹ to lower frequencies upon ion-exchange into the zeolite. Vibrational bands due to the benzyl part of the molecule are observed at 550, 620, 684, 772, 1007, 1032, 1236 and 1608 cm⁻¹. Upon incorporation of BV²⁺ into the zeolite, changes are observed in the C₆H₅-CH₃ stretching bands in the 1200 cm⁻¹ region, with the appearance of a band at 1192 cm⁻¹ and a shoulder at 1240 cm⁻¹. The band due to stretching motion of the N⁻CH₃ bond connecting the pyridinium and benzyl moieties
Figure 4.10. Raman spectra of (a) 0.1 M BV⁺ in solution and (b) BV⁺-zeolite-X.
at 1160 cm\(^{-1}\) remains unchanged upon introducing the BV\(^{2+}\) in the zeolite.

The electronic spectrum of an aqueous solution of BV\(^{2+}\) (Fig 4.19a) is compared with the diffuse reflectance spectrum of the hydrated BV\(^{2+}\) zeolite (Fig. 4.19b). Upon ion-exchange into the zeolite, a red shift of 44 nm is observed for the \(\Pi^-\Pi^+\) transition.

Quantum Yield Determination

The experiments discussed above were all done with a pellet of zeolite sample and therefore, only the surface particles participated in the photochemical process. In order to estimate the photochemical efficiency of the process, all the zeolite particles should have access to the radiation. This was done by photolyzing a stirred, suspension of powder of Ru(bpy)\(^2+\)-DQ\(^2-\)-Y in a sealed NMR tube. The NMR tube was centrifuged and the PVS\(^-\) in the solution was measured. The growth of the viologen radical as a function of time is plotted in Fig. 4.20. The rate of the formation corresponds to 0.12 mole viologen radical hr\(^{-1}\) per mole of Ru(bpy)\(^2+\) with a visible light illumination of 200 mW (420-680 nm). Thus, the rate of growth of the viologen per hour corresponds to ~12% of the sensitizer present. The system approaches a steady state as the radical reaches ~60% of the total sensitizer concentration. As the concentration of the viologen radical in the solution increases, the absorption of photons by the
Figure 4.19  (a) Electronic spectrum of 0.01 M BV$^{2+}$ solution  
(b) Diffuse reflectance spectrum of BV$^{2+}$-zeolite Y (Kubelka-Munk corrected).

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Figure 4.20 Growth of the viologen PVS⁻ radical as a function of time in Ru(bpy)₃²⁺-DQ²⁺-Y system sealed in an NMR tube. (The curve is just a guide to the eye.)
sensitizer in the sample decreases because of an inner filter effect. This is the likely cause of the gradual decrease in the rate of radical formation.

A more quantitative measure of the efficiency of this process is via the quantum yield. This is difficult to determine because the scattering from the zeolite particles interferes with the measurement of the light absorbed by the \( \text{Ru(bpy)}^2^+ \) in the zeolite. The addition of refractive-index-matching solutes such as sucrose to alleviate this problem can interfere with the photoredox process\[25,26\]. Therefore, to calculate the light absorbed by the \( \text{Ru(bpy)}^2^+ \) in zeolite-Y, the light transmitted by this sample is compared to the light transmitted by a sample of Na-Y. The difference is used to estimate the number of photons absorbed. The quantum yield using laser excitation at 457.9 nm over a period of 30 minutes was estimated to be \( 5 \times 10^{-4} \). This should be considered an approximate measure. A major factor in this low quantum yield could be the zeolite size. It should be noted here that this quantum yield is for both of the systems containing DQ^2+ and BV^2+.

Discussion

It is clear from the above results that the charge separation is increased by having an electron relay agent, DQ^2+ and BV^2+ available to mediate electron transfer from a photosensitized donor, \( \text{Ru(bpy)}^2^+ \) to the ultimate electron
acceptor, PVS. The competition to having long-lived charge separated species \( \text{Ru(bpy)}_3^{3+} \) and \( \text{PVS}^- \) is the geminate recombination between \( \text{Ru(bpy)}_3^{3+} \) and \( \text{DQ}^+ \text{ or BV}^- \). This would result in wastage of the photon used to excite the photosensitizer molecule. However, the presence of PVS in solution gives an alternate pathway for the electron to transfer from the radical \( \text{DQ}^- \text{ or BV}^- \) to the PVS.

The shift from a diad system consisting only of the photosensitive donor molecule and an electron acceptor to the triad system where another electron acceptor serves as an intermediate step for electron transfer is fairly obvious. The goal is to look at model systems with efficient separation of charges and reduced back electron transfer rate.

In the zeolitic systems, the triads \( \text{Ru(bpy)}_3^{2+} \text{DQ}^2^- \text{Y} \) and \( \text{Ru(bpy)}_3^{2+} \text{BV}^2^- \text{Y} \) with PVS surrounding the zeolites are the first systems where very long-lived charge separated species have been achieved. The radical PVS\(^-\) remained in solution for several months. This is true particularly for the experiments that were done in sealed NMR tubes where the quenching of the radical viologen by atmospheric oxygen does not present a problem. Thus the blue solution due to the negatively charged PVS radical remains. The only other triad in zeolite cages reported to date is that of \( \text{Ru[(CH}_3)_2\text{bpy)}_3^{2+} \) and \( \text{DQ}^2^- \) covalently bonded to each other by the replacement of one of the methyl groups of one \( \text{(CH}_3)_2\text{bpy ligand} \) with an ethylene unit. One end of the ethylene unit is connected to the bipyridyl ligand. The
other end is connected to the 2-position of the DQ$^{2+}$. BV$^{2+}$ has been previously exchanged[1]. It should be noted here that their DQ$^{2+}$ is a dimethylene connected to the pyridinium nitrogens whereas the DQ$^{2+}$ in this research is a tetramethylene bridging the two nitrogens of the pyridinium rings. It is also important to realize that the systems presented in the present work have the secondary electron acceptor present in solution in contrast to the other triad which has both DQ$^{2+}$ and BV$^{2+}$ in the zeolite supercages. This has some bearing on the accessibility of the reduced species for further reaction.

The other triad which has a direct semblance to this work is the pyrene-MV$^{2+}$ in a sol-gel with N,N'-tetramethylene-2,2'-bipyridinium cation (which they denoted as TV$^{2+}$)[20]. The directional electron transfer was also observed where again TV$^{2+}$ acts as an electron relay mediator. In this case, however, the secondary electron acceptor, MV$^{2+}$ is held immobile in the sol-gel as is the photosensitive pyrene. Again, the accessibility of the reduced species is the important consideration here. In the present work, not only are there long-lived charge separated states, but the other big advantage is the easily accessible PVS$^{-}$ in solution available for further reaction towards the photochemical cleavage of water.

In both the sol-gel(pyrene/MV$^{2+}$/TV$^{2+}$)[20] and the zeolite {Ru[$\text{CH}_3$]$_2$ bpy}$_3$-DQ$^{2+}$-BV$^{2+}$[1], the electron acceptors, are both cationic. The configuration in the present work has a cationic
relay agent and a neutral zwitterionic secondary acceptor, PVS in solution. When reduced PVS becomes negatively charged thus being repelled by the negatively charged framework of the zeolite. An assembly of both cations as electron acceptors in the present work is difficult due to the possibility of exchange between the zeolitic electron acceptor and the secondary electron acceptor that is in solution. Such directional electron transfer as between DQ$^{2+}$ and BV$^{2+}$ is possible, however, due to their difference in redox potential.

The vectorial electron transfer occurs when the reduction potentials of the photosensitizer, the electron relay and the electron acceptor have successively higher values. Such is the case for the excited Ru(bpy)$_3^{2+}$, DQ$^{2+}$ and PVS. However, in the case of BV$^{2+}$, the behavior seemed to be anomalous since the redox potential of BV$^{2+}$ is higher than that of PVS. This comparison of the redox potentials is true for aqueous solutions of these electron acceptors. In the zeolite supercages, however, different factors such as solvation within the supercages, geometrical arrangement and packing of the viologens in the supercage could possibly change the redox potential in the zeolite matrix.

It has been reported in the literature that the distortion of two pyridinium rings to an antiperiplanar configuration causes a change in the reduction potential of bipyridinium compounds. When bulky substituents are present in the 3,3' position of the benzyl viologen, for example, the
reduction potential is negatively shifted by 330 mV relative to an unsubstituted BV$^{2+}$ such that the potential becomes $E^\circ = -0.67$ V vs NHE. From the photolysis results in the Ru(bpy)$_3$$^{2+}$-BV$^{2+}$-Y/PVS system, it can be postulated here that the reduction potential of BV$^{2+}$ in zeolite is lower than $-0.34$ V vs NHE. The loading of $\sim 0.8$ molecules of BV$^{2+}$ per supercage could present steric hindrance to the pyridinium rings and prevent ring coplanarity. The deviation from ring coplanarity of the bipyridinium tends to reduce the stability of the free radical viologen relative to the unreduced viologen upon electron transfer. If the free radical is of lesser stability, the reduction is more difficult and the reduction potential is lower.

The dimensions of a methyl viologen cation are 12.6 x 6.4 x 3.8 Å$^{10}$. Because the size of the supercage of Na-Y is $\sim 13$ Å, MV$^2^+$ could easily fit the supercage of the zeolite with portions of the methyl group probably positioned in the channels of the zeolite. In the case of BV$^2^+$, which is a homologue of MV$^2^+$ having benzyl group instead of the methyl group attached to the nitrogen atom of the pyridinium, the methylene groups at each end may be in the channels while the phenyl ring could reside in the adjacent supercage. At higher loadings this would lead to at least one molecule per supercage.

Referring to the structure of BV$^2^+$, the length of the molecule encompassing the bipyridine part of the molecule
(CH$_2$-NC$_6$H$_4$-NC$_6$H$_4$-CH$_2$) is about 13 Å[10,27] and is about the linear dimension of a supercage. This immediately implies that the molecule cannot fit into a single supercage. If the bipyridinium part of the molecule is in a supercage, the benzene groups must be located in neighboring supercages and the molecule thereby spans several supercages. This is also reflected in the lower saturation loading in the zeolite for the BV$^{2+}$ (0.8 per supercage) as compared to MV$^{2+}$ (2 per supercage)[28].

The Raman spectra do exhibit changes for vibrations centered around the C-C stretching of the bond connecting the bipyridyl rings (1302 cm$^{-1}$) and the C-C stretch of the bond connecting the phenyl group to the methylene unit (1200 cm$^{-1}$) upon incorporation of the BV$^{2+}$ into the zeolite. Focusing first on the C-C inter-ring mode, it has been shown that this band exhibits considerable increase (30-55 cm$^{-1}$) in frequency upon one-electron reduction for methylviologen, biphenyl and benzidine[23,29]. This is explained by the planar nature of the reduced state, which increases the bond order of the C-C bond. Upon incorporation of the BV$^{2+}$ into the zeolite, there is a decrease of this frequency by 4 cm$^{-1}$ as compared to free BV$^{2+}$ in solution. For MV$^{2+}$ in solution, the angle between the bipyridinium units is in the order of 40°[30,31] and it is expected that a similar deviation from planarity exists for BV$^{2+}$ in solution. This would suggest that upon incorporation into the zeolite, the pyridinium units are being further
removed from planarity, due to the steric constraints of the zeolite. The changes in the C-H stretching region are harder to explain but they clearly indicate that steric constraint in the zeolite is influencing the benzyl group.

The electronic spectrum of BV\textsuperscript{2+} undergoes a major perturbation upon incorporation into the zeolite, with a red shift of the \( \pi-\pi^* \) transition from 256 to 300 nm. Studies of biphenyl have shown that the first excited state (S\textsubscript{1}) assumes a planar geometry\[32\]. Though explicit studies have not been done for viologens, it is reasonable to assume that a similar planar geometrical arrangement is also present in the excited state. Comparison of the \( \pi-\pi^* \) transition of MV\textsuperscript{2+} with DQ\textsuperscript{2+} shows a red shift from 260 to 280 nm. As mentioned before, DQ\textsuperscript{2+} will have greater difficulty achieving a planar state than MV\textsuperscript{2+} due to the 2,2' substitution. Thus, it appears that the energy of the transition shifts to a lower value with increasing difficulty for the two pyridine rings to assume a planar state. This would suggest that in the case of BV\textsuperscript{2+} entrapped in zeolite, there is considerably more resistance for the excited state to assume a planar geometry as compared to solution. Considering that the benzyl groups in the BV\textsuperscript{2+} will have to occupy different supercages than the bipyridine moiety, it is not surprising that rotation around the inter-ring C-C bond necessary to achieve planarity is going to be more difficult in zeolite.
As shown here the Ru center is oxidatively quenched by the neighboring viologens fairly efficiently. In that case, the competition to charge separation arises from the geminate recombination between Ru(bpy)$_3^{3+}$ and DQ$^+$ or BV$^+$. Providing an alternate pathway for the electron transfer from DQ$^+$ or BV$^+$ to PVS at the zeolite-solution interface increases the charge separation. For the DQ$^+$ or BV$^+$ molecules that are generated in the internal cages of the zeolite, the charge must propagate to the surface of the particle by means of an electron hopping on intrazeolitic viologen molecules[7,8], in direct competition with the back electron transfer reaction. This can be the bottleneck to efficient charge separation.

Conclusions

The investigations in this chapter deal with electron transfer reactions that occur in a ternary system in zeolites, more specifically, the directional electron transfer from the excited photosensitizer donor molecule Ru(bpy)$_3^{2+}$ in a zeolite to the neutral zwitterionic electron acceptor PVS in solution through a mediator, DQ$^{2-}$ or BV$^{2+}$. Several conclusions could be drawn in this study.

1. Photoinduced electron transfer through a zeolite-solution interface occurs between Ru(bpy)$_3^{2+}$ entrapped in zeolite-$Y$ and an electron acceptor present in solution surrounding the zeolite.
(2) Electrostatic repulsions between the negatively charged PVS\(^{-}\) radical and the zeolite framework results in increased charge separation and a slowing down of the back electron transfer rate.

(3) There are further increase in the efficiency of charge separation and further reduction of the back electron transfer when electron relay mediators such as BV\(^{2+}\) and DQ\(^{2+}\) are present in the neighboring supercages of the entrapped photosensitizer Ru(bpy)\(_3^{2+}\), while the PVS is in solution.

(4) The approximate quantum yield has been determined for the systems mediated by DQ\(^{2+}\) and BV\(^{2+}\) to be 5 \(\times\) 10\(^{-4}\).
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Chapter 5

ULTRAVIOLET PULSED LASER PHOTOLYSIS OF Fe(CO)₅
IN Na-Y ZEOLITES: GENERATION OF NANOMETER-SIZED
METAL CATALYSTS

Introduction

The utilization of the photoproducts in electron transfer reactions seen in chapters 3 and 4 are of considerable interest. The photoreduced viologen radical could be used in the photocleavage of water in the presence of colloidal platinum or palladium at the right pH to form hydrogen and hydroxy anions and subsequent regeneration of the oxidized form of the viologen (as illustrated in reaction 1.4). The other half of the splitting process is the oxidation of water to form oxygen which is photoassisted by metal catalysts such as Pt or Rh and metal oxides like TiO₂ and RuO₂. The size of these metal or metal oxides catalyst is an important consideration in photocatalytic reactions. In general, the smaller the size of the catalyst, the better is the reaction. This is the reason why colloidal systems of platinum and palladium are preferred over suspensions of larger metal particles.
The interest in nanometer-sized metal and semi-conductor metal clusters is due to their better photocatalytic activity than larger sized particles. There is a wide range of research on the formation of these nanometer-sized metals and metal oxides where volatile transition metal compounds are precursors for metal deposition because of the facility of decomposing these compounds while leaving the metal intact.

The generation of radical viologens by using zeolites is in itself promising for the photocatalytic transformation of water. It should be interesting too if the photocatalysts (nanometer-sized particles or clusters) could be generated and encapsulated within the cages and cavities of zeolites. This would make the molecular assembly in the zeolite comprised of the photosensitizer donor molecule, electron relay acceptor and the small metal clusters. Before such an assembly could be realized, however, the encapsulation of the metal clusters in the zeolite has to be treated separately first. The model system for such a study is the iron pentacarbonyl (Fig. 5.1). The volatility of this compound for ease in incorporation in zeolite supercages and the decomposition to remove the carbonyls leaving the iron makes this a good model compound.

There have been many studies on the thermal decomposition of iron pentacarbonyl adsorbed in zeolite matrices [1,2,3,4]. The generation of iron clusters as well as their oxidation to iron oxide have been examined in these studies. The other route for generating such materials is through photochemical
decomposition. Two reports, both based on continuous photolysis of Fe(CO)$_5$ in NaY and HY came to different conclusions about the final product [6,7]. Complete decarbonylation could not be achieved in NaY, whereas Fe clusters were reported in HY. Photolytic decomposition of Fe(CO)$_5$ on other substrates has been examined with pulsed, UV laser sources [8,9]. Direct excitation into the d-d or charge transfer bands of Fe(CO)$_5$ becomes possible. In this preliminary study, the photodecomposition of Fe(CO)$_5$ in NaY using 355 nm radiation from a Nd-YAG laser is examined. The pulse width of the laser is ~20 ns with a repetition rate of 30 Hz. Because of the low duty cycle of the laser, steady-
state heating of the sample is not expected to be a problem as with continuous sources. The results are contrasted with thermal studies. The iron particles formed by laser decomposition can be oxidized with oxygen to form encapsulated iron oxide particles that exhibit quantum size effects.

Experimental

Materials Zeolite-Y (Union Carbide) was washed with a 0.1 M aqueous solution of NaCl, rinsed with distilled water until chloride-free and dried at room temperature. Pentacarbonyl iron (Alfa) was degassed by freeze-pump-thaw cycles prior to use while carbon monoxide was used as received.

Preparation of NaY-Fe(CO)5 A 10-20 mg self-supporting wafer of NaY (diameter = 13 mm) was placed in a glass vacuum tube which was connected to a vacuum line. The zeolite was heated slowly to 450°C and activated at this temperature for two hours under 10^-4 torr. Oxygen was introduced for 30 minutes to remove any carbonaceous impurities in the zeolite. The wafer was allowed to cool and further evacuated for three hours.

Iron pentacarbonyl was loaded in the zeolite by allowing the wafer to contact with 10^-2 torr of Fe(CO)5 vapor for 10 seconds (approximate loading of 1 Fe(CO)5 molecule per unit cell). The sample was then transferred into an IR cell equipped with KBr windows. This cell was held air-tight with
0-rings and was equipped with a valve which allowed evacuation or addition of gas. Infrared measurements were obtained using Mattson-Cygnus FTIR with DTGS detector.

**Treatment on NaY-Fe(CO)$_5$** Photolysis was done using a Quantel Nd-YAG 580 pulsed laser at 355 nm. For thermolysis the wafer was heated to 250°C for 1 hour. After these treatments on different NaY- samples, CO at 760 torr was equilibrated in the cell through the vacuum line for 1 hour. After evacuation of the CO from the cell, FTIR spectra were again obtained.

**Results and Discussion**

Figure 5.2 shows the infrared spectra of Fe(CO)$_5$-NaY in the CO stretching region as a function of photolysis time at 355 nm (150 mW). The loading of Fe(CO)$_5$ was 1 molecule per unit cell. In general, all the bands are decreasing in intensity, but at unequal rates. This is in contrast with thermal decomposition studies reported in the literature and reproduced in our laboratory, in which all the infrared bands decrease in intensity at the same rate. Also, no new bands are observed in Figure 5.2. Beyond 50 minutes of illumination, the laser power had to be increased from 150 to 450 mW to bring about complete photodecomposition. In an earlier study of Fe(CO)$_5$ on NaY [10], it was found that the vibrational spectrum (Figure 5.2a) has contributions from three Fe(CO)$_5$ species. The major contribution to the CO intensity arises from Fe(CO)$_5$ molecules in the supercages and
Figure 5.2 Photolysis of Fe(CO)$_5$-NaY at 355 nm as a function of time. Infrared spectra taken at (a) 0 min, (b) 10 min, (c) 20 min, (d) 30 min, (e) 50 min, (f) 70 min and (g) 100 min.
Figure 5.2
gives rise to the broad band centered at 2000 cm\(^{-1}\). The contribution of this species to the infrared band can be clearly observed in the difference spectrum between two subsequent loadings. The sharp bands at 2122, 2058, 2011, 1985 and 1961 cm\(^{-1}\) were assigned to Fe(CO)\(_5\) at a site (site IA) in the zeolite that constrains the molecule into a trigonal bipyramid geometry. Another set of bands at 2122, 2044 and 1946 cm\(^{-1}\) were assigned to Fe(CO)\(_5\) on a different site (site IB), in which the molecule assumed a square pyramidal geometry. The Fe(CO)\(_5\) at site IA was found to be more accessible to reactants such as PMe\(_3\) to form L-Fe(CO)\(_4\) adducts, whereas molecules at site IB only reacted with smaller molecules, such as NH\(_3\).

In the first 30 minutes of photolysis, the intensity in the ~2000 cm\(^{-1}\) region decreases preferentially, indicating that the Fe(CO)\(_5\) molecules in the supercages are being photolyzed. The percent decrease in integrated intensity during the first 30 minutes of illumination was 98%. The Fe(CO)\(_5\) molecules at site IB are characterized by the sharp bands at 2044 and 1946 cm\(^{-1}\) and are most resistant to photolysis. This is in agreement with its inaccessibility towards large reactants. A possibility is that the confinement of the Fe(CO)\(_5\) molecules at these sites results in a cage effect which prevents the escape of photolyzed CO and favors recombination. This is supported by the observation in Figure 5.3, in which a completely photolyzed sample was exposed to CO. Though the
Figure 5.3 Infrared spectra (a) after complete photolytic decarbonylation and (b) reexposure to CO followed by evacuation.
intensity that is recovered is only a few percent of the original intensity, the bands characteristic of Fe(CO)$_5$ at the constrained sites are only observed. This is interpreted as evidence that isolated Fe(0) clusters are being trapped at these sites which can reform Fe(CO)$_5$ upon exposure to CO. The Fe(0) formed in the supercages, on the other hand, can migrate to form clusters which are not redispersed by reaction with CO. The laser light pulses are about 20 ns in width and repeat every 33 msec. The wavelength of the light 355 nm represents about 85 kcal/mole and is capable of dissociating 3 CO molecules from Fe(CO)$_5$. The d-d transition of Fe(CO)$_5$ occurs in the 350 nm wavelength range and provides a mechanism for absorption of the photons [11]. The possibility that the decomposition of Fe(CO)$_5$ is taking place thermally can not be excluded. However, the infrared spectra during photochemical decomposition and the reappearance of the Fe(CO)$_5$ signal after complete photodecomposition and exposure to CO is different from the observation in the thermal decomposition studies, in which all the bands of Fe(CO)$_5$ decreased at the same rate and no Fe(CO)$_5$ could be regenerated from a completely thermally decomposed sample.

Photolysis of Fe(CO)$_5$-NaY using a low power (40 Wm$^{-2}$) continuous light source (Hg lamp, $\lambda_{max}=254$ nm) and a thermostatted sample at 290K only produced Fe$_x$(CO)$_y$ species and no Fe(0) clusters were reported [6]. High power densities as available from a pulsed laser source (the typical experiments
used 10' W/cm²) is necessary to photolyze a sample completely, although loss of light intensity from the highly scattering zeolite sample also decreases the yield. Another study of complete photochemical decomposition of Fe(CO)₅ in HY has been published using wavelengths greater than 300 nm [7]. However, it has been pointed out that since the temperature of the surface was not measured [6], it is possible that a considerable part of the metal carbonyl may have decomposed thermally. In this study, no temperature control was used, but since the laser pulse only lasts for ~20 nsec, steady state temperature increase can be expected to be minimal.

Exposure of the photolyzed samples to oxygen results in formation of iron oxide type species. The XPS of this material is shown in Figure 5.4, with peaks at 723 and 711 eV characteristic of the 2P₃/₂ and 2P₅/₂ transition of Fe₂O₃ [12]. Scanning electron micrographs as well as the X-ray diffraction showed no evidence of Fe₂O₃ particles, indicating that these particles are smaller than ~200 Å. The uv-visible diffuse reflectance spectra of Fe₂O₃ particles is compared with the photolyzed samples in Figure 5.5. From the absorption spectrum it is clear that the band gap transition of the Fe₂O₃ inside the zeolite shows a blue shift of ~175 nm. This shift can be attributed to the quantum size effect [13] and strongly suggests that the pulsed laser procedure followed by oxidation is making small particles of Fe₂O₃, which are trapped within the zeolite cavities.
Figure 5.4 XPS of oxygen-exposed photolyzed samples of Fe(CO)$_5$-NaY.
Figure 5.5 UV-visible diffuse reflectance spectra of encapsulated Fe\textsubscript{3}O\textsubscript{3} in zeolite NaY cages. Inset - bulk Fe\textsubscript{3}O\textsubscript{3} (Kubelka-Munk corrected)
In conclusion, this study shows that UV pulsed laser photolysis of Fe(CO)$_3$ in NaY cages is different from that of thermal decomposition. This method also allows for the generation of small intracrystalline Fe$_3$O$_4$ particles. It lies in the future to examine the photocatalytic properties of the encapsulated iron oxide particles as well as examining lower wavelength UV lasers for photodecomposition.
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