Technical Progress for Period 1/15/90 - 8/31/90.

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Title of Project: Photoinduced Electron Transfer Reaction in Zeolite Cages.

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Our accomplishment during the current budget period can be divided into three categories:

A. Instrumentation: In order to determine the kinetics of the forward and back reactions of photoexcited species in zeolites with quencher molecules, it is necessary to obtain transient emission and absorption spectra of the molecules involved in the reaction. Typically, a gated device such as the boxcar or a transient digitizer are used to obtain time discriminated information. We had proposed to examine the new generation of fast oscilloscopes (relatively low cost) that can provide information about low-repetitive signals. From the monies, we have purchased a Tektronix DSA 601 signal analyzer with a 1 GHz bandwidth (time resolution ~ 1ns). With the schematic of the apparatus shown below, we can obtain rapid measurement of lifetimes (typically 5 seconds as compared to 5 minutes with our previous boxcar system), as exemplified for $\text{Ru}(\text{bpy})_3^{2+}$ in zeolite Y.

Time-resolved diffuse reflectance absorption spectral measurements with this system is presently being pursued.

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B. Photochemical Electron Transfer Reaction in Zeolites:

There is considerable interest in using zeolites as hosts for encapsulating a diverse group of photochemically relevant systems such as colloids, polymers, photoactive molecules, etc. In this sense the zeolite medium acts as a solvent. However, compared to our understanding of solvents in general, very little is known of the fundamental nature of zeolite as a solvent. In order to address this problem, we have, based on the solvatochromic properties of the molecule salicylideneaniline, defined a scale for zeolites that measures the 'solvent-like' ability of the zeolite to stabilize polar structures in its cavities. A plot of this scale (α scale based on the definition by Taft and coworkers) for a series of zeolites and hydroxylic solvents is shown in the figure below.

This figure indicates that as the Si/Al ratio of the framework increases from 1, the ability of the framework to stabilize polar structure through H-bonding interactions (α parameter) also increases until a maximum is reached around Si/Al of 7. This is followed by a decline in α as the structure becomes more hydrophobic as in ZSM-5 and the completely dealuminated zeolite Y. The relevance of this scale in explaining intrazeolitic behavior by molecules is being explored.

In another area, we have perfected the synthesis of $\text{Ru}(\text{bpy})_3^{2+}$ in zeolite Y at yields approaching 90-95%. Various loadings of the metal complex have been generated. These systems will form the basis for exploring intrazeolitic photochemical reactions. A reaction that has been examined under steady state conditions is

In order to slow down the back-electron transfer reaction, the process was carried out in the H^+ form of zeolite Y (which contains very strong Bronsted acids). The strategy was to examine if protonation of the MV^+ radical ($\text{H}_3\text{C}-\overset{\text{H}}{\underset{+}{\text{N}}}\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\overset{+}{\text{N}}\text{CH}_3$) would slow down the back reaction. The steady state data, as shown below, shows no evidence for the stabilization of the radical. Transient data is being acquired to determine the effects of the protonation on the rate of the back reaction.

C. Photoelectron Transfer in a Clay-Membrane System:

Our group has been investigating the intercalation properties of the material $\text{LiAl}_2(\text{OH})_6^+ \cdot \text{X}^-$. This material can be pictured as layers of lithium and aluminum coordinated by OH groups and separated from each other by interlayer space in which X^- ions are present. A schematic is shown below

We have been able to introduce long chain carboxylic acids (palmitic, C_{16} and myristic C_{14}) into these layers resulting in an inorganic framework encapsulating a membrane like layer. From the X-ray powder pattern shown below, we calculate that the interlayer spacing increases from $\sim 3\text{\AA}$ to $23\text{\AA}$ in the case of myristic acid intercalation. This indicates the formation of a bilayer, reminiscent of a membrane, in between the inorganic lithium aluminate layers.

We have been able to intercalate Zn-tetraphenylporphyrin-sulfonate (sensitizer) into these layers, and a diffuse reflectance spectrum of this material is shown below.

We have also synthesized the zwitterionic propyl viologen sulfonate and plan to incorporate it into the layer along with Zn TPPS. These stable, artificial membranes will form the focus for investigation of photoelectron transfer reactions in the next budget period.

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