Final Technical Report

Title: Photochemical Charge Separation in Zeolites:Electron Transfer Dynamics, Nanocrystals and Zeolitic Membranes

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Summary of Accomplishments

Zeolites and microporous materials continue to attract attention as novel hosts for photochemical reactions, as evident from recent publications. Our research has primarily focused on how the process of encapsulation within the zeolite alters the photophysical and photochemical properties of molecules. In particular, we have made use of transient measurements to measure the photoelectron transfer dynamics in the zeolite and exploited other morphological forms of zeolites, such as nanocrystals and zeolitic membranes. The photochemical system that we focused on consists of polypyridyl complexes of ruthenium and bipyridinium ions. We have evaluated which features within the zeolite, including reduction potentials, solvent reorganization and orbital overlap control electron transfer dynamics. We have investigated synthesis of 10 - 100 nm crystallites of zeolites. The advantage of nanocrystallites as photochemical hosts arises from better charge separation efficiency. A particularly exciting application is the development of optically clear dispersions of zeolites, which made it possible to use solution-based physical measurements. We have also studied RuO_2 as both water oxidation and reduction catalysts. Correlation between the microstructure of the RuO_2 and the catalytic activity has been established. Finally, we have made the first attempts at separating oxidation and reduction chemistry using the two opposite sides of a zeolitic membrane. Our overall effort is to integrate all aspects of zeolite based photochemical charge separation and catalysis into an architecture suitable for photochemical splitting of water.

Major Discoveries

Zeolite encapsulation alters the photochemical electron transfer dynamics

Analysis of the photoinitiated electron transfer dynamics of intrazeolitic $Ru(bpy)_3^{2+}$-bipyridinium system has shown that the back electron transfer from the bipyridinium radical ion to $Ru(bpy)_3^{3+}$ is significantly slowed down (several orders of magnitude) in the zeolite as compared to the forward electron transfer reaction. Results indicate that the organic ions around $Ru(bpy)_3^{2+}$ in the zeolite can promote increase in quantum yield of emission as well as extend the lifetime of the MLCT state. This should promote the forward electron transfer quenching of $Ru(bpy)_3^{2+*}$ by bipyridinium ions.

The close fit of the $Ru(bpy)_3^{2+}$ into a zeolite Y supercage restricts its translational and rotational motion. We have proposed that this steric constrainment is the most important reason for slowing of the back electron transfer reaction. The reasoning is as follows. The forward electron transfer occurs from the ligand of the MLCT state to a viologen in a neighboring cage

that can be as close as in van der Waals contact. This facilitates the forward electron transfer reaction. The back electron transfer occurs from the diquat radical to the Ru(III) center in the center of the neighboring supercage. Since the metal t_{2g} orbital has very little mixing with the bpy orbital, the back electron transfer would be facilitated if the $Ru(bpy)_3^{2+}$ molecule could rotate so that the t_{2g} orbital faces across the 7Δ window separating the Ru center from the diquat radical. This is difficult in zeolite Y. For every orientation of $Ru(bpy)_3^{2+}$ in the zeolite that we have examined, there are multiple 'bad' contacts (of the order of 15 or so) between the $Ru(bpy)_3^{2+}$ and the supercage atoms, i.e. the atoms are at distances closer to each other than 0.9 times their van der Waals radii. This implies that rotation of the $Ru(bpy)_3^{2+}$ inside the zeolite Y is going to be highly restricted. In order to prove that immobilization of $Ru(bpy)_3^{2+}$ is responsible for slowing the back electron transfer, we needed to have the $Ru(bpy)_3^{2+}$ in a zeolite supercage in which it has some rotational freedom, with minimal perturbation on the rest of the system. We have done this with the hexagonal variant of faujasite called EMT. It contains a hypercage of 13 x 14 Δ dimensions, providing more mobility for the $Ru(bpy)_3^{2+}$ molecule. The models were constructed using crystallographic data. The number of bad contacts between $Ru(bpy)_3^{2+}$ and zeolite Y is 15, whereas it is two for EMT. This was typical of all the orientations we examined. Thus, rotational mobility of $Ru(bpy)_3^{2+}$ in EMT is considerably more favorable than in zeolite Y. We have found that the dynamics of the electron transfer reaction within the EMT framework is faster than zeolite Y, suggesting that the orbital hypothesis is reasonable.

Nanocrystalline zeolites provide better kinetic data and promote efficient charge separation.

We have demonstrated that slowing of the back electron transfer reaction provides an opportunity for long-lived charge separation. Use of nanocrystalline zeolites that provide a high surface to volume area is a promising material for study. However, better control over size distribution and agglomeration are required. The possibility of colloidal zeolites suspended uniformly in a medium also provides opportunities for better physical measurements and charge separation and was exploited. Nanocrystalline zeolites with sizes below ~100 nm was examined. We have made clear solutions of the nanocrystallites in organic solvents by making the surface hydrophobic. We have done this by silylating the surface OH groups on the nanocrystalline zeolite with n-octadecyltrichlorosilane. The availability of optically clear solutions of zeolite encapsulated complexes has made possible many exciting opportunities for both spectroscopy and photochemistry, including Stern Volmer plots for both intensity and lifetimes of $Ru(bpy)_3^{2+*}$ as a function of diquat concentration and electron transfer dynamics between intrazeolitic

$Ru(bpy)_3^{2+}$ and diquat ions by conventional flash photolysis methods.

Utilization of photochemically charge-separated species in chemical reactions by zeolite-based catalysts

The species that need to be utilized are $Ru(bpy)_3^{3+}$ and bipyridinium radical cation in an oxidation and reduction reaction. We have demonstrated that synthesis of RuO_2 fibers on a zeolite via thermal decomposition of $Ru_3(CO)_{12}$ leads to the most active water decomposition catalyst reported to date.

We have also optimized the preparation of the RuO_2/zeolite Y catalyst system for H_2 evolution and determined the nature of photodecomposition of the viologen radicals. Areas of study included the role of the RuO_2 morphology on H_2 evolution, the fate of bipyridinium ion as a function of photolysis conditions, including pH and defining turnover numbers.

Integration of the reduction and oxidation parts of the photochemical system into a single zeolite membrane architecture

The water oxidation and reduction reactions need to be spatially separated to minimize recombination reactions. We have used zeolite membranes to keep the sites for reduction and oxidation chemistry at opposite sides of an impermeable membrane. What was needed was a channel zeolite in which all the crystallites are oriented with the channels all approximately aligned along the membrane axis. Gmelinite is an excellent choice for a framework since it has channels of the 7 Δ that can readily fit viologen (diquat) molecules and has a Si/Al ratio of 3, which indicates that it has reasonably large ion-exchange capacity, necessary for packing of viologen (diquat) ion. We have synthesized membranes of approximately 0.7 cm by 0.7 cm. The integrity of self-supporting membranes of this thickness was poor, especially considering all the steps that will be necessary to assemble the photochemical architecture onto the zeolitic membrane. Thus, our strategy was to grow the gmelinite membrane onto porous supports. Supports that were investigated include porous metal grids, alumina, porous vycor glass and porous polymer films. Because the integrity of these structures were found to be fragile, we have developed a new procedure for making zeolite membranes by spin coating of nanocrystalline zeolites and blocking of the pinholes by a positive photoresist. Charge transport through such a membrane has been demonstrated and incorporation of catalysts into this form of the membrane is being examined.

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SUBJECT: PATENT CLEARANCE OF CONTRACT NO: DE-FG02-90ER14105

This office has the responsibility for conducting a patent review of the subject contract and arranging patent clearance for final payment.

The patent certification submitted to this office lists an invention disclosure entitled: "Nanocrystalline Zeolite Y Containing Films for the Optical Sensing of Oxygen" has not been reported to this office. Our letter dated February 5, 1990 states:

A written disclosure of each invention must be forwarded to us within two months after the inventor discloses the invention to you. Additionally, you are required to promptly notify us of the acceptance of any manuscript describing the invention for publication or of any on sale or public use planned for the invention.

Therefore, it is requested that a copy of the disclosure, application or any issued patent be submitted to this office. Upon receipt, we will continue with our closeout procedure.

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cc: To Palmer