PHOTOCHEMISTRY IN CONSTRAINED SPACES: ZEOLITES AND LAYERED DOUBLE METAL HYDROXIDES

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Progress Report

We have continued our research in the field of assembly and reactions of photochemical systems in zeolites and layered lithium aluminates. For the sake of convenience, we have separated the discussions on these systems.

(a) Zeolites: Zeolites are crystalline aluminosilicates with cages and channels of molecular dimensions. Our focus has been on faujasitic zeolites, which contain supercages of ~13 Å dimensions surrounded by four ~7 Å ring openings. The experimental strategy in this project has been to build Ru(bpy)$_2^+$ (dimension ~12 Å) inside the supercage, and examine the photoelectron transfer from this entrapped complex to acceptor molecules (viologens) through the 7 Å ring openings. In earlier studies, we have shown that a pathway for stabilization of the photogenerated radical MV$^{**}$ (methylviologen) via stacking of the viologens in neighboring zeolite cages is possible. However, the yields of the photoproducts were small.

Thus, our recent efforts have focused on improving the photochemical yields. Towards that end, we have designed a ternary system, as shown below schematically in which an intermediate viologen in the zeolite acts as the shuttle to transfer the photogenerated electron to a neutral viologen in solution. The separated charges (Ru$^{3+}$ and PVS$^-$) are indefinitely stable since they do not have access to each other.
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The unique feature of this system is that the photogenerated electron is resident on the PVS in solution and is readily accessible. However, in making the system truly catalytic, it is also necessary to access the hole, which is in the form of the entrapped Ru(bpy)$_3^{3+}$.

We have spent considerable effort in understanding the chemistry of Ru(bpy)$_3^{3+}$ in zeolite Y. The reactions of Ru(bpy)$_3^{3+}$ in aqueous solutions has been examined previously, and is determined to a great degree by bimolecular degradative reactions. The zeolite cages, by definition, isolates Ru(bpy)$_3^{3+}$ from each other and the degree of contact between molecules in neighboring can be readily controlled by the loading of Ru during the synthesis process. Thus, the chemistry of Ru(bpy)$_3^{3+}$ in zeolite cages is expected to be quite distinct from aqueous solutions and is indeed found to be so.

When samples of Ru(bpy)$_3^{3+}$ in zeolite Y are exposed to water, the regeneration of Ru(bpy)$_2^{2+}$ is found to be very slow, of the order of days, as compared to minutes in an aqueous solution. Diffuse reflectance spectra during this time show clear isobestic point at 334, 566 and 780 nm, indicative of a simple equilibrium between the Ru$^{3+}$ and Ru$^{2+}$ species. EPR spectra during
the reaction with water show the presence of four radical species, in addition to Ru(bpy)$_3^{3+}$. These occur at $g$- 2.31 2.23, 2.01 and 2.00, and are assigned to Ru$^{3+}$ coordinated to bpy ligands subjected to attack by H$_2$O, OH$^-$ as well as $\cdot$OH and O$_2$ radicals. The presence of H$_2$O$_2$ was also detected by reaction with o-toluidine and O$_2$ was evolved as well, as measured by GC. A mechanism consistent with these observations is shown in Scheme 1.

The reduction of Ru(bpy)$_3^{3+}$ in zeolite Y is markedly accelerated by the presence of Co(II) ions exchanged into the zeolite. The regeneration of Ru(bpy)$_2^{3+}$ is 10 times faster than in the absence of Co(II), through similar isobestic behavior is observed. The EPR spectra were quite distinct, indicating absence of the metal centered radicals and $\cdot$OH, but showed the presence of O$_2$. H$_2$O$_2$ was also detected by the o-toluidine test, though no evolution of O$_2$ was observed. A mechanism consistent with these observations is shown in Scheme 2.

These studies show that Ru(bpy)$_3^{3+}$ can be stabilized within zeolite Y cages by virtue of encapsulation and Ru(bpy)$_2^{3+}$ regenerated with formation of H$_2$O$_2$ by intrazeolitic Co$^{2+}$ ions.

(b) Layered Lithium Aluminum Double Hydroxides: Our effort has primarily been with a layered double hydroxide (LDH) of composition LiAl$_2$(OH)$_x$$X^-$. Lithium and aluminum make up the metal hydroxide layer, while charge neutralizing ($X^-$) are present in the interlayers. We have previously reported on creation of organized hydrophobic domains in the interlayers by replacing $X^-$ with long chain carboxylic acids. The packing of the hydrocarbon chains and phase transitions have been explored. Our current focus has been on incorporation of photoactive molecules in these interlayers, with particular emphasis on pyrene and Zn porphyrins.
Sorption isotherms of pyrene by organo-LiAl-LDH (organo-myristic, hexanoic and succinic acids) were carried out in methanol/water mixtures, because of the limited solubility of pyrene in water. Using co-solvent theory partition coefficients (log $K_{oc}$) for pyrene into myristic-LDH and hexanoic-LDH were found to be 4.06 and 3.44, respectively. Succinic-LDH showed no sorption of pyrene, suggesting that partitioning into the interlayer space was controlled by the width of interlayer spacings. Infrared studies show that the acid chain packing is altered upon incorporation of pyrene into hexanoic-LDH.

The spectroscopic properties of pyrene also provide information about the nature of the interlayer space. These studies were carried out with myristic-LiAl-LDH, which as mentioned before readily incorporates pyrene. In an earlier study, we had observed that the interlayer packing of the myristic acid chains can be altered by removing ethanol (which is incorporated during synthesis) from the Li-Al LDH. This leads to an expansion of interlayer space (from about 20 to 40 Å) and can be reversed by addition of ethanol. The pyrene fluorescence from the as prepared myristic-LDH sample showed the environment to be considerably non-polar (I/III vibronic ratio) and indicated the presence of dimers (~500 nm band). Upon removing the ethanol, the dimer band disappeared and the polarity surrounding the pyrene increased. This was accompanied by a significant increase in lifetime of the monomer pyrene. Infrared studies indicate that removal of ethanol leads to -COOH groups H-bonding with the framework. In addition, the long chain alkyl groups appear to be considerably disordered upon removal of ethanol. It appears that ethanol exists as solvent pools, in the interlayer which forces the pyrene to form dimers. Upon removal of ethanol, the pyrene solubilizes in the more
hydrophobic myristic acid like environment.

(b) **Zinc porphyrins** ZnTPPS (zinc tetraphenyl porphyrin sulfonate) can also be readily incorporated into the interlayer of myristic-LDH. Unlike pyrene, this occurs by ion-exchange with the myristate ion. Neutral ZnTPPS or cationic ZnTMPyP are not incorporated. The loading of Zn as ZnTPPS is significant, being 23.9 % by weight of the sample. The diffuse reflectance spectra show that both the Soret and \(a, \beta\) bands are blue-shifted upon incorporation. The peak shifts and band broadening are indicative of intermolecular interactions.

Viologens including HV\(^{2+}\) (heptyl), MV\(^{2+}\) and PVS were not incorporated into the myristic-LDH, but showed significant uptake into the ZnTPPS-myristic-LDH, in the order HV\(^{2+}\) > PVS > MV\(^{2+}\). This shows that the viologens are being incorporated via interaction with the zinc porphyrins. Photolysis of these samples showed the generation of the viologen radical, the yields being HV\(^{+}\) > PVS\(^{-}\) > MV\(^{+}\). We believe that the radical is being formed due to the presence of the ethanol pools in the interlayers, with ethanol acting as a sacrificial electron donor (presence of ethanol pools also supported by the pyrene experiments). These studies are showing that the LDH's are interesting substrates for photochemical processes, including charge separation. Work is continuing on evaluating the porphyrin viologen interactions, and the mechanism of charge separation.

Publications during this period:

- Dutta and Turbeville, J. Phys. Chem. 96, 9410, 1992
- Dutta and Borja, Nature, 362, 43, 1993
- Dutta and Borja, JCS Chem Comm, in print, 1993
Schemes for reaction of $\text{Ru(bpy)}_3^{3+}$ in zeolite Y with water.

Scheme 1

**Neighboring $\text{Ru(bpy)}_3^{3+}$**

\[
\text{Ru(bpy)}_3^{3+} + \text{H}_2\text{O} \rightarrow \text{Ru(bpy)}_2(\text{bpy-OH}_2)^{3+} + \text{H}^+ \rightarrow \text{Ru(bpy)}_2(\text{bpy-OH})^{2+} \quad \text{(EPR)}
\]

- neighboring molecules react rapidly

Scheme 2

\[
\begin{align*}
\text{Ru(bpy)}_3^{3+} + \text{Co(II)-O}_2 & \rightarrow \text{Ru(bpy)}_3^{2+} + \text{Co(III)-O}_2 \\
\text{Ru(bpy)}_3^{3+} + \text{Co(III)-O}_2 & \rightarrow \text{Ru(bpy)}_3^{2+} + \text{Co(IV)-O}_2 \\
\text{Co(IV)-O}_2 + \text{H}_2\text{O} & \rightarrow \text{Co(II)-O}_2 + \text{H}_2\text{O}_2
\end{align*}
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