Spectroscopic investigations of the photochemical properties of I. Spiropyran on y zeolite for photochromic applications II. Rhenium(I) bipyridyl tricarbonyl on mesoporous ZSM-5 zeolite and silica for photocatalytic reduction of carbon dioxide

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Spectroscopic investigations of the photochemical properties of I. Spiropyran on Y zeolite for photochromic applications II. Rhenium(I) bipyridyl tricarbonyl on mesoporous ZSM-5 zeolite and silica for photocatalytic reduction of carbon dioxide

Abstract
Immobilization of photoactive molecules on porous and nano-sized solid supports provides unique interactions which affect photophysical properties. In situ diffuse reflectance FTIR and UV-vis spectroscopies were primarily used to investigate the properties of surface functionalized materials. Spectroscopic characterization of photochromic spiropyran molecules physically adsorbed on Y zeolite revealed the importance of surface water in controlling kinetics and reversibility of photoswitching by stabilizing the merocyanine isomer. Re(bpy)(CO)3Cl was both physically adsorbed on a mesoporous ZSM-5 zeolite and covalently bound via the bipyridyl ligand on fumed silica to generate photocatalytic CO2 reduction materials. Upon light irradiation of the solids in the presence of CO2, in situ FTIR spectroscopy shows the formation of Re(bpy)(CO)3(COOH) and Re(bpy)(CO)3(CH0), respectively. FTIR photoexperiments using isotopic 13CO2 and EPR characterization of one electron reduced Re(bpy)(CO)3Cl•- after photoirradiation support findings that successful CO2 photoreduction was achieved at the gas-surface interface.

Keywords
Chemistry, General, Chemistry, Inorganic, Engineering, Materials Science, Chemistry
SPECTROSCOPIC INVESTIGATIONS OF THE PHOTOCHEMICAL PROPERTIES OF
I. SPIROPYRAN ON Y ZEOLITE FOR PHOTOCHROMIC APPLICATIONS
II. RHENIUM(I) BIPYRIDYL TRICARBONYL ON MESOPOROUS ZSM-5 ZEOLITE
AND SILICA FOR PHOTOCATALYTIC REDUCTION OF CARBON DIOXIDE

BY

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THESIS

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ABSTRACT

SPECTROSCOPIC INVESTIGATIONS OF THE PHOTOCHEMICAL PROPERTIES OF

I. SPIROPYRAN ON Y ZEOLITE FOR PHOTOCHROMIC APPLICATIONS
II. Rhenium(I) Bipyridyl Tricarbonyl on Mesoporous ZSM-5 Zeolite
    and Silica for Photocatalytic Reduction of Carbon Dioxide

BY

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University of New Hampshire, May 2013

Immobilization of photoactive molecules on porous and nano-sized solid supports provides unique interactions which affect photophysical properties. In situ diffuse reflectance FTIR and UV-vis spectroscopies were primarily used to investigate the properties of surface functionalized materials. Spectroscopic characterization of photochromic spiropyran molecules physically adsorbed on Y zeolite revealed the importance of surface water in controlling kinetics and reversibility of photoswitching by stabilizing the merocyanine isomer. Re(bpy)(CO)₃Cl was both physically adsorbed on a mesoporous ZSM-5 zeolite and covalently bound via the bipyridyl ligand on fumed silica to
generate photocatalytic CO₂ reduction materials. Upon light irradiation of the solids in the presence of CO₂, in situ FTIR spectroscopy shows the formation of Re(bpy)(CO)₃(COOH) and Re(bpy)(CO)₃(CHO), respectively. FTIR photoexperiments using isotopic ¹³CO₂ and EPR characterization of one electron reduced Re(bpy)(CO)₃Cl⁻ after photoirradiation support findings that successful CO₂ photoreduction was achieved at the gas-surface interface.
1.1 Spiropyrans and Photochromism

Photochromism is the reversible isomerization of a molecule between species which possess different optical and often other physiochemical properties, for examples, dielectric constant and geometric structure. Organic photochromic molecules, such as spiropyrans, diarylethenes, bithienylethenes, and fulgides, are finding many exciting applications, and specifically, spiropyrans are extensively studied and well suited for inclusion in new systems for optical applications. As shown in Figure 1.01, upon UV irradiation, the nitro-substituted spiropyran undergoes cleavage of the C-O bond resulting in the reversible isomerization of the colorless spiropyran form to the intensely colored merocyanine (MC) form.

![Figure 1.01: Photochromic equilibrium between spiropyran and merocyanine](image)
As a result of the different hydrogen bonding of each isomer, the molecular environment is crucial in determining which isomer is present, and to what degree the system is reversible.\textsuperscript{8} Previously, it has been shown that incorporating spiropyrans in zeolites and other porous aluminosilicates has increased the lifetimes of zwitterionic species as compared to common organic solvents.\textsuperscript{7-9} Using porous solids such as zeolites, silica, and polymers as host materials to support photochromic molecules eliminates the need for organic solvents, and thus, facilitates incorporation of these materials in devices. These solid-state nanocomposite materials have potential applications as optical switches, memory media, and chemical sensors.\textsuperscript{10}

1.2 Research Goals

Zeolite crystals in the nanometer size range (100 nm or less) have advantages over the commercially available micrometer sized crystals due to increased pore accessibility and external surface area.\textsuperscript{11} The aim of our research was to study the interactions between NaY and spiropyran, and to explore how different molecular environments affect the equilibrium and kinetics of photoisomerization. Detailed in Chapter 2, we controlled both the size of the NaY particles and the amount of spiropyran adsorbed. Diffuse reflectance UV-vis and FTIR spectroscopies were used to characterize the properties of these synthesized materials.
2.1 Materials

1',3'-dihydro-1',3',3'-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-(2H)-indole] (98%) (SP), aluminum isopropoxide (>98%) (Al(OiPr)_3), tetraethyl orthosilicate (>99.0%) (TEOS), tetramethylammonium hydroxide (25 wt% in water) (TMAOH), sodium hydroxide (>98%) (NaOH), and sodium Y zeolite (NaY) were all purchased from Sigma Aldrich and used without further purification.

2.2 Experimental Synthesis

The method used for synthesizing nanocrystalline NaY (nano-NaY) is a combination of two methods reported in the literature. 11,12 17.2 g Al(OiPr)_3 and 0.3 mL 1M NaOH were added to 200 mL 1M TMAOH aqueous solution and stirred until fully dissolved. To the clear solution, 37 mL TEOS was added and this mixture was stirred overnight to form a homogeneous sol-gel solution. The final composition of the gel was 0.07 Na : 2.4 TMAOH : 1.0 Al : 2.0 Si : 132 H_2O : 3.0 iPrOH : 8.0 EtOH. This
was refluxed at 95 °C for 10 days. After collection of NaY from the colloidal suspension via centrifugation, 2.5 mL 1M NaOH was added and the solution returned to reflux for another 48 hrs with subsequent extraction of NaY thereafter. This cycle was repeated 5 more times in order to increase the yield of nano-NaY. After samples were collected, they were washed several times with deionized water and calcined in a Lindberg/Blue Mini-mite tube furnace with flowing O\textsubscript{2} (industrial grade, Airgas) at 500°C for 16 hours.

For spiropyran adsorption on NaY, 1 mg (MC-NaY-0.005), 15 mg (MC-NaY-0.075), or 120 mg (MC-NaY-0.6) of spiropyran was mixed with 200 mg of either synthesized nanocrystalline NaY or commercial NaY in 30 mL dichloromethane and refluxed for 7 days. The number in the sample names corresponds to the weight ratio of spiropyran to NaY before they were collected by centrifugation and washed with ethanol until supernatant after centrifugation was colorless. The materials were collected and air dried in dark at room temperature.

2.3 Experimental Methods

Powder X-ray diffraction (XRD) of the zeolites was performed using Cu K\textsubscript{α} radiation in a q-q Rigaku D-MAX/B diffractometer. Scanning electron microscopy (SEM) images were obtained on a 3300FE field emission scanning electron microscope. Visible light irradiation was achieved using an optic fiber from a Fiber-Lite series 180 illuminator.
UV/vis spectra were obtained with a Cary 50 Bio spectrophotometer fitted with a Barrelino diffuse reflectance probe using BaSO₄ as a standard and powder samples pressed on BaSO₄ pellets. In UV-vis photoswitching experiments, spectra were obtained after the sample was irradiated with visible light (\( \lambda > 425 \text{ nm} \), measured to be 100 mW/cm²) for 1 hr, and after allowed to sit in complete dark for 1 hr. This was repeated for 5 cycles. In UV-vis dark recovery experiments, spectra were collected after 1 hr visible light irradiation and after each hour of sitting in complete dark, up to 6 hrs. Infrared spectra were collected on a Nicolet 6700 FTIR spectrometer with a DTGS detector, equipped with a Harrick Praying Mantis diffuse reflectance accessory and three-window high-temperature photoreaction chamber. In infrared photoexperiments, approximately 10 mg powder sample was placed on a KBr pellet in the photoreaction chamber and initial spectrum was recorded. Spectra were recorded after samples were irradiated (\( \lambda > 425 \text{ nm} \), measured to be 300 mW/cm²) through a KBr window of the photoreaction chamber for 1 hr and after the sample was allowed to sit in complete dark for a subsequent 1 hr.

2.4 Results and Discussion

Nanocrystalline NaY (nano-NaY) with approximately 120 nm crystal size was successfully synthesized. Scanning electron microscope (SEM) images for both the commercial NaY and the synthesized
nano-NaY can be seen in Figure 2.01. Several failed attempts to synthesize this material provide insight into some important aspects of generating such small NaY crystals. One key component is the use of the Na\(^+\) cation as a limiting reactant. The zeolite Y framework is inherently anionic due to the relatively high Al content, and as such requires cations to counterbalance the charge. If concentrations of cation are maintained very low, nucleation is favored over crystal growth because large crystals would not be stable with inadequate amounts of counter cations. In addition, the amount of Na\(^+\) in the sol-gel was crucial for selection of crystal structure. Zeolite NaA is synthesized using the same template molecule (TMAOH) and similar Si and Al concentrations. A lower Na\(^+\) concentration favors the NaY structure over the NaA structure because the zeolite Y framework is more stable when the [Na\(^+\)] is limited. As a result, the successful syntheses of nanocrystalline NaY incorporated multiple additions of small amounts of NaOH to the sol-gel over an extended duration.
Conversely, in the synthesis of NaA, the entirety of Na\(^+\) required is added at the onset of hydrothermal treatment. Nanocrystals were collected by centrifugation a total of 7 times, which was required for sufficient yields as crystal growth was suppressed by limiting [Na\(^+\)] and using low temperature. The first 2 crystal extractions contained a mix of NaA and NaY, as evidenced by the presence of peaks corresponding to both structures that were seen in powder X-ray diffraction (XRD) patterns. The XRD pattern of the third extraction contained only very small magnitude peaks representative of NaA, and extractions 4-7 were all determined to be pure NaY material based on XRD peak patterns. A comparison of powder XRD peak patterns of commercial 1000 nm NaY and synthesized 120 nm nano-NaY is displayed in Figure 2.02. As expected, the diffraction peaks of nano-NaY are shortened and broadened.
relative to NaY with larger crystal size. This result is expected due to
the fact that nano-NaY would have a higher ratio of external to internal
(inner pore wall) surface area, the former being more heterogeneous.

In our investigations, spiropyran molecules were physically
adsorbed on to the surfaces of NaY and diffuse reflectance UV-vis
spectroscopy was used to determine relative abundances of spiropyran
and merocyanine isomers. In organic solvents, the relative population of
merocyanine to spiropyran form increases as the solvent polarity
increases. During physical adsorption of spiropyran to NaY, it was
observed that the DCM dispersion slowly changed from colorless to
yellow to deep orange/red over the week long reflux, corresponding to
the increase of merocyanine over time. This agrees with previous reports
that hydrogen bonding between the zwitterionic merocyanine and
surface silanol groups lowers the energy of this isomer (Figure 2.03). Both spiropyran and merocyanine isomers are adsorbed to the surface
of NaY, and the strong color of these materials indicate that
merocyanine is in larger proportion than in DCM or pure solid form.

![Figure 2.03: Schematic diagram of hydrogen bonding between NaY surface and merocyanine](image)
As the final step of NaY synthesis, the material is calcined under flowing O\textsubscript{2} at high temperature to remove the template molecules from the pores. Calcination also improves crystallinity and availability of surface hydroxyl groups to engage in hydrogen bonding. Spiropyran was adsorbed to the surface of both calcined and uncalcined nano-NaY in DCM. After washing, the calcined MC-nano-NaY possessed significantly more spiropyran and merocyanine on the surface than the uncalcined MC-nano-NaY material, as judged by the UV-vis spectra (Figure 2.04). Broad absorption peaks at 413 and 520 nm correspond to merocyanine and the peak around 350 nm to spiropyran.\textsuperscript{15} NaY possesses a micropore diameter of 1.4 nm, which is large enough to accommodate spiropyran molecules, however, pore openings with 0.74 nm diameter will not allow diffusion of the molecules into the pores.\textsuperscript{7} Thus, the

![Figure 2.04: Diffuse reflectance UV-vis spectra of spiropyran adsorption on calcined and uncalcined nano-NaY](image-url)
conclusion is that the materials synthesized have spiropyran adsorbed on the external surface but do not have any adsorbed into the internal pore space. The 120 nm nano-NaY was originally synthesized in order to determine if crystal size would affect the photochromism of the spiropyran molecules. The increased external surface area of nano-NaY relative to commercial NaY did appear to enable more spiropyran to adsorb to the surface based on absorbance values in diffuse reflectance UV-vis spectra, however, this characterization method is not quantitative. Even though similar amounts of materials were used for recording the spectra, many factors can affect reflection and scattering of light which limits quantification using this method. The photochromic properties of MC-nano-NaY and MC-NaY were quite similar, but since it was presumed that the internal pore space of the materials was not utilized, this result is not unexpected. Note that all UV-vis characterization of materials was performed in a dark room, as UV and visible light will favor the merocyanine and spiropyran isomers, respectively.

Diffuse reflectance UV-vis spectroscopy was also used to probe the properties of materials with different amounts of spiropyran adsorbed onto the NaY surface. To synthesize these materials, weight ratios of 0.005, 0.075, and 0.6 (spiropyran to commercial NaY) were mixed in DCM at 40°C for 7 days to ensure complete adsorption. After washing and drying the synthesized materials, UV-vis spectra were obtained for the materials before irradiation, after 1 hr visible light
irradiation, and up to 6 hrs in dark after light irradiation (Figure 2.05). As mentioned, diffuse reflectance UV-vis methods are not quantitative, however, a trend in absorbance can be seen. The material with the highest spiropyran loading (MC-NaY-0.6) has the strongest absorbance in the UV and visible region, and conversely, the material with the lowest spiropyran loading (MC-NaY-0.005) has the weakest UV-visible absorption (using approximately the same mass of material for analysis). After 1 hr visible light irradiation, absorption bands at 413 and 520 nm are drastically decreased for all materials, consistent with a large amount of merocyanine photoisomerizing to spiropyran. Over a period of 6 hrs in complete dark, the bands at 413 and 520 nm steadily return, but they do so with varying rates and extent of recovery. Figure 2.05 shows very little photorecovery of merocyanine absorption bands for MC-NaY-0.005, however, MC-NaY-0.6 shows extensive photorecovery. The approximate 100-fold increase in surface loading of spiropyran for MC-NaY-0.6 over MC-NaY-0.005 resulted in at least faster spiropyran to merocyanine photoisomerization rates. It would appear that the higher surface loading also increased the final extent to which merocyanine is reformed in dark, however, UV-vis spectra were not recorded beyond 6 hrs. Regardless, it can be concluded that spiropyran surface density on NaY is an important factor which controls photochromic behavior. MC-NaY-0.6 was chosen for study of its photoisomerization reversibility because it exhibited the fastest isomerization in the dark recovery period. UV-vis spectra were recorded after alternating periods of visible
Figure 2.05: UV-vis spectra of 6 hrs dark recovery of (a) MC-NaY-0.005, (b) MC-NaY-0.075, and (c) MC-NaY-0.6
light irradiation and confinement in dark. The consistent photoswitching shown by this material can be seen in Figure 2.06. Absorbance values were normalized to initial absorbance before light irradiation. Over several cycles of light irradiation and dark recovery, forwards and backwards photoisomerization occurs with extreme uniformity. At both wavelengths monitored, initial absorbance is not fully recovered after the first cycle, however, complete recovery occurs for the 4 cycles thereafter. This result shows that spiropyran adsorbed on NaY is a promising material for photoswitching applications.

Diffuse reflectance FTIR spectroscopy was employed to gain further insight into the interaction between NaY and surface immobilized spiropyran. Similar to UV-vis characterization of NaY with different amounts of spiropyran, Figure 2.07 shows FTIR spectra with

![Graph showing normalized absorbance over time for MC-NaY-0.6](image)

Figure 2.06: Photoswitching of MC-NaY-0.6 over 10 hrs measured at (a) 413 nm and (b) 520 nm
different amounts of spiropyran, Figure 2.07 shows FTIR spectra with increasing intensity for characteristic peaks of spiropyran as surface amount increases (spiropyran spectrum collected with a Nicolet iS10 FTIR spectrometer with attenuated-total-reflectance (ATR) accessory). MC-NaY materials were exposed to visible light for 1 hr and then dark for 1 hr, and FTIR spectra were recorded. Difference spectra were FTIR

![FTIR spectra](image)

Figure 2.07: FTIR spectra (a) bare NaY, (b) MC-NaY-0.005, (c) MC-NaY-0.075, and (d) MC-NaY-0.6 (top); ATR-FTIR spectrum of pure spiropyran (bottom)
spectrometer with attenuated-total-reflectance (ATR) accessory). MC-NaY materials were exposed to visible light for 1 hr and then dark for 1 hr, and FTIR spectra were recorded. Difference spectra were calculated by subtracting the baseline spectrum of each material from the spectrum recorded after 1 hr of either light exposure or dark

Figure 2.08: FTIR difference spectra of (a) MC-NaY-0.005, (b) MC-NaY-0.075, and (c) MC-NaY-0.6 after 1 hr light (spectra after 1 hr dark in grey)
confinement (Figure 2.08). Inspection of these difference spectra reveals that all 3 MC-NaY materials with varying surface loadings of spiropyran undergo the same spectral changes upon light irradiation and the following seclusion in dark. In the difference spectra, there are broad negative features ~1600-1700 cm⁻¹ and ~3100-3600 cm⁻¹ after exposure to visible light. Both are due to the loss of water from NaY, presumably due to moderate heating of the material as a result of photoirradiation. The disappearance of these negative peaks in the difference spectra after 1 hr in dark indicates that surface water was readsoberbed to the material. Positive absorption features appear at 1640 cm⁻¹ and 3695 cm⁻¹ after 1 hr visible light irradiation and also give insight into the hydrated surface environment. The peaks are characteristic of water adsorbed on NaY, with the latter specifically due to stretching of free OH groups of water bound to a Na⁺ cation.¹⁶,¹⁷ Inspection of the 1640 cm⁻¹ absorption band of bare NaY in Figure 2.07 shows that it is a broad band which extends between 1600-1700 cm⁻¹, indicating that water on the NaY zeolite exists in several hydrogen bonding environments. For these materials, this includes the hydrogen bonding interaction between water and merocyanine. Visible light irradiation will drive photoisomerization of merocyanine to spiropyran, resulting in net reduction of hydrogen bonding interactions between water and these coadsorbed compounds. Simultaneous reduction of both water and merocyanine concentrations on the surface yield increased absorbance at 3965 and 1640 cm⁻¹ because the water molecules
responsible for these signals in the FTIR spectra are less engaged in hydrogen bonding interactions. After 1 hr dark confinement, these peaks have decreased absorbance and appear broader as a result of the increased hydrogen bonding environment provided by readsorbed water and reformed merocyanine. These results strongly imply that surface water assists in stabilizing the merocyanine isomer.

It was previously observed that photorecovery of merocyanine on NaY actually improved with increasing wait time between photoirradiation experiments and material synthesis. Specifically, after over a month of storage in a light-blocked vial under ambient temperature and moisture, the reemergence of the bands at 413 and 520 nm was drastically enhanced over the 6 hr period in dark for MC-NaY-0.005 and MC-NaY-0.075 (Figure 2.09). Photorecovery in dark of MC-NaY-0.6 did not show significant improvement because its original recovery was already quite extensive. For the two materials which showed enhanced photorecovery, the month duration was ample time to adsorb water from the atmosphere, effectively changing the material's properties. Precedence exists for increased physisorbed water improving the reversibility of dye color changes on solid surfaces.\(^\text{18}\) Inspired by these findings, a new diffuse reflectance FTIR experiment was designed to probe further the role of water in determining photochromic behavior in these materials. MC-NaY-0.075 was once again subjected to 1 hr visible photoirradiation and 1 hr dark recovery periods, this time while dry argon gas was constantly flowing.
Figure 2.09: UV-vis spectra of 6 hrs dark recovery of (a) MC-NaY-0.005 and (b) MC-NaY-0.075 after over a month in dark, ambient conditions through the photoreaction chamber. Figure 2.10 shows the difference spectra after periods of light and dark. After dark confinement, the negative peaks at ~1600-1700 cm\(^{-1}\) and ~3100-3600 cm\(^{-1}\) are exaggerated, not reversed to baseline values as seen before. Upon light irradiation, the water which desorbs from the NaY surface is lost
Figure 2.10: FTIR difference spectra of MC-NaY-0.075 after 1 hr visible light and 1 hr dark under constant dry argon purge from the system by flowing argon gas and cannot be readorsed once the visible light source is removed. In previous experiments, the photoreaction chamber was initially purged with argon, but closed off before exposure to light. This allowed the water vapor which evacuated from the NaY as a result of photoirradiation to be retained, and
ultimately readsobered. The crucial role of water in regulating photoswitchability of spiropyran on the surface of NaY is supported by these findings.

2.5 Conclusions

In summary, aluminosilicate materials such as NaY zeolite are promising supports for adsorption of photochromic spiropyran molecules for use as solid-state materials in optical switching applications. Hydrogen bonding on the surface stabilizes the merocyanine isomer and increases its relative population on the surface. Hydrogen bonding interactions with the zeolite framework and with surface adsorbed water occur. Based on diffuse reflectance UV-vis and FTIR characterization during photoexperiments, it would appear that water content on the surface is a greater factor in determining photoswitching activity than zeolite crystal size or surface density of spiropyran. Congruent with the results of these photoexperiments, it may be possible that reduced water content after many cycles of light irradiation ultimately limits the lifetimes of these photoswitching materials. Future experiments which could be performed in our lab would be to repeat similar trials, but this time for many cycles of visible light and dark periods. Flowing argon gas which is humidified to varying degrees and determining effect on lifetimes of the photochromic materials could provide further insight.
PART II
CHAPTER 3

INTRODUCTION TO PHOTOCATALYTIC CO₂ REDUCTION MATERIALS

3.1 CO₂ Reduction

Over the last few decades, carbon dioxide (CO₂) has gathered increasing attention as a greenhouse gas. Reducing the amount of CO₂ released into the atmosphere as a product of combustion is an ongoing world-wide effort. Arguably a larger challenge is to recycle the abundant amount of CO₂ in the atmosphere, using it as a carbon source for the production of useful chemicals and materials.¹⁹,²⁰ Recently, research efforts aimed at developing new ways of using CO₂ in a sustainable manner have greatly increased, as evidenced by several recent review articles.²¹,²²,²³ Methods by which CO₂ can be converted to other useful carbon compounds include hydrogenation,²⁴,²⁵ electrochemical reduction,²⁶,²⁷ and photochemical reduction.²⁸,²⁹ All methods require energy in the form of heat, light, or electricity, but photochemical CO₂ conversion has the potential to use sunlight as the renewable energy source. Incorporation of light-driven CO₂ conversion catalysts into materials and devices is an attractive strategy for future generation of fuels and other industrially useful chemicals.
Carbon dioxide is a very thermodynamically stable and nonpolar, owed to its high symmetry. In the CO$_2$ molecule, the carbon atom is in a fully oxidized (4+) state, surrounded on either side by more electronegative oxygen atoms. Obligating CO$_2$ to react exploits targeting of this relatively electropositive carbon atom as the site of reduction. Single-electron CO$_2$ reduction is energetically costly due to the structural differences between linear CO$_2$ and bent CO$_2^-$, and can only be achieved at high potentials (Figure 3.01, Reaction 1). Coupling proton (H$^+$) and electron (e$^-$) transfers (Figure 3.01, Reactions 2-6) to CO$_2$ requires much lower energies, and thus, is a more likely means of reduction. Formic acid (HCOOH) and carbon monoxide (CO), which are generated from CO$_2$ by addition of 2e$^-$ and 2H$^+$ (Figure 3.01, Reactions 2-3), are common end products of reduction by electrochemical and photochemical catalysts. The ability to accumulate multiple redox equivalents is a key feature of efficient CO$_2$ reduction catalysts. Though CO$_2$ conversion to methanol (CH$_3$OH) and

\[
\begin{align*}
    \text{CO}_2 + \text{e}^- & \rightarrow \text{CO}_2^{2-} \quad E^\circ = -1.90 \text{ V} \\
    \text{CO}_2 + 2\text{H}^+ + 2\text{e}^- & \rightarrow \text{HCOOH} \quad E^\circ = -0.61 \text{ V} \\
    \text{CO}_2 + 2\text{H}^+ + 2\text{e}^- & \rightarrow \text{CO} + \text{H}_2\text{O} \quad E^\circ = -0.53 \text{ V} \\
    \text{CO}_2 + 4\text{H}^+ + 4\text{e}^- & \rightarrow \text{HCHO} + \text{H}_2\text{O} \quad E^\circ = -0.48 \text{ V} \\
    \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- & \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad E^\circ = -0.38 \text{ V} \\
    \text{CO}_2 + 8\text{H}^+ + 8\text{e}^- & \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad E^\circ = -0.24 \text{ V}
\end{align*}
\]

Figure 3.01: Thermodynamics of proton-assisted multi-electron CO$_2$ reduction (vs. NHE, pH 7 aqueous solution)
methane (CH₄) are quite favorable thermodynamically, few catalysts are able to accumulate the high number of e⁻ (and H⁺) required to produce these products (Figure 3.01, Reactions 5-6). To compound the issue, when CH₄ and CH₃OH do occur, it is typically with low efficiencies.³¹

3.2 Properties of Re(I) Diimine Tricarbonyl Complexes and Mechanism of Photocatalytic CO₂ Reduction

Homogeneous photocatalysts which exhibit the highest activity in are transition metal containing complexes possessing multiple redox states with appropriate potentials for CO₂ reduction. Such molecular compounds include Re and Ru diimine carbonyl complexes, Ni and Co tetraazamacrocycles, and Fe and Co porphyrins.³²,³³ In 1983, Lehn and co-workers first reported CO₂ reduction by Re(I) diimine tricarbonyl compounds,³⁴ and since then they have been extensively studied as CO₂ reduction photocatalysts and electrocatalysts. These Re(I) organometallic complexes possess metal-to-ligand charge transfer (MLCT) bands in the visible region of the spectrum, which allow them to efficiently harvest solar irradiation and reduce CO₂ without the need for other light-absorbing molecules. However, addition of photosensitizers such as Ru(bpy)₃²⁺ increase quantum yields of CO₂ photoreduction and are often used to enhance these systems. In addition, Re(I) photocatalysts are extremely selective for CO generation over other
possible products.

The basic progression of homogeneous photoreduction of CO$_2$ by Re(bpy)(CO)$_3$X compounds (Figure 3.02)\textsuperscript{35} starts with light absorption by the catalyst, promoting it to a photoexcited state. This excited state is quenched by e\textsuperscript{-} transfer from high reduction potential compounds, commonly tertiary amines such as triethylamine (TEA) or triethanolamine (TEOA). In the case that a light harvesting photosensitizer is used, the photosensitizer is photoexcited, reductively quenched, and subsequently transfers e\textsuperscript{-} to the catalyst. The most labile ligand (X) will dissociate to form a one electron reduced (OER) intermediate, opening a coordination site to which it is believed CO$_2$ binds. The final step is dissociation of the reduced carbon product (CO, HCOOH) and reformation of the catalyst. CO$_2$ insertion is a critical step in the catalytic cycle. Density functional theory computations have predicted Re(bpy)(CO)$_3$(H) and CO$_2$-bridging catalyst dimer structures as likely intermediates.\textsuperscript{36,37} In electrochemical reduction of CO$_2$, carbonate (CO$_3$$^{2-}$) is often seen in addition to CO as a product of catalysis due to an abundance of available e\textsuperscript{-} and absence of H\textsuperscript{+} donating molecules. Alternatively, in CO$_2$ photoreduction which employs sacrificial e\textsuperscript{-} donors, H\textsuperscript{+} sources can be these same tertiary amines or residual water.

Substitution in 4,4\textsuperscript{-} position of the 2,2\textsuperscript{-}bipyridyl ligand of Re-bpy complexes has been performed previously to affect the physical properties of the molecules, and ultimately, their activity in CO$_2$ photocatalysis. It has been shown that electron withdrawing groups
such as carboxylic acid (-COOH)\textsuperscript{38} and trifluoromethyl (-CF\textsubscript{3})\textsuperscript{39} lower MLCT energies and reduction potentials, but generally also reduce catalytic activity. Stronger electron donating groups such as amino (-NH\textsubscript{2}) and methoxy (-OMe) have the opposite effect of raising MLCT energies and reduction potentials which also reduce catalytic activities.\textsuperscript{40} Substitution of bipyridine by weak electron donating alkyl groups such as methyl (-CH\textsubscript{3}) or tertiary-butyl (-tBu) have little effect on physical properties but serve to enhance catalytic activities.\textsuperscript{38}
3.3 Surface Immobilization of Re(I) Diimine Tricarbonyl Complexes

Some drawbacks inherent to solvent-based homogeneous photocatalysis include low solubility of CO₂ and instability of catalysts under photochemical conditions. In attempts to remedy these shortcomings and to generally improve catalyst activities and stabilities, Re-bpy complexes have been immobilized on solid-state supports. For example, Re-bpy adsorbed materials have been prepared by encapsulating the catalyst in NaY and Al-MCM-41. It was shown that upon light irradiation, the zeolite frameworks acted as electron donors for reduction of CO₂ into CO and CO₃²⁻. Re(COOH-bpy)(CO)₃Cl has been grafted on a rutile TiO₂ surface through a carboxylate linkage, which demonstrated that the carbonyl ligands of the catalyst were outward facing and in proper position for CO₂ photocatalysis. Using click chemistry, fac-Re(I,10-phenanthroline)(CO)₃Cl was immobilized on a silica surface and was probed with ultrafast two-dimensional infrared vibrational echo spectroscopy. Synthesis of a charge transfer molecular chromophore by grafting tricarbonyl Re(I) onto a polyoxometalate (POM) produced a material which strongly absorbs light in the entire UV and visible regions due to the formation of a Re(I)-to-POM charge transfer band. Incorporation of a modified Re-bpy complex in a highly stable and light-absorbing metal-organic framework (MOF) displayed significantly higher photocatalytic activity than the corresponding homogeneous complex. Similarly, Re-bpy
has been covalently anchored in a biphenyl bridged periodic mesoporous organosilica (PMO) which showed a four-fold enhancement of CO₂-to-CO conversion over the homogeneous analog upon UV light irradiation.\textsuperscript{47}

3.4 Research Goals

As mentioned, materials which are capable of photocatalytic CO₂ reduction have several advantages over homogeneous catalysts. The aim of our research was to synthesize materials in which Re-bpy was either physically or chemically adsorbed onto mesoporous zeolite and silica surfaces. Physical adsorption was achieved by simple liquid phase mixing of catalyst and support, whereas covalent bonding of catalyst to the surface of silica involved synthesis which took advantage of trialkoxysilane coupling agents. Diffuse reflectance FTIR spectroscopy was used to characterize these materials during different stages of photocatalysis in the hope of determining important catalyst intermediate structures and determining how catalyst structure and interactions with the solid-state support affect catalytic performance. Infrared is particularly useful in characterizing Re-carbonyl structures due to the sharp bands produced by C=O stretching of metal-bound carbonyl groups which occur in a region of the spectrum where few other chemical moieties absorb.
CHAPTER 4

ADSORPTION AND PHOTOCHEMICAL PROPERTIES OF Re(bpy)(CO)₃Cl
IN MESOPOROUS ZSM-5

NOTE: Results presented in this chapter were published in

4.1 Materials

Triethylamine (>99%) (TEA), triethanolamine (>99.0%) (TEOA), and
tris(2,2’-bipyridyl)dichlororuthenium(II) hexahydrate (99.95% trace metal
basis) (denoted as “Ru(bpy)₃²⁺”) were all purchased from Sigma-Aldrich
and used without further purification. ZSM-5 was purchased from Zeolyst
and used as received. A hierarchical mesoporous ZSM-5 (meso-ZSM-5)
was synthesized by Anton Petushkov at the University of Iowa, and its
synthesis was described in detail in their published article. Mesopore
volumes of Zeolyst ZSM-5 and meso-ZSM-5 were measured to be 0.359
and 0.040 cm³/g, respectively, on a Quantachrome Nova 1200 surface
area and pore size analyzer. fac-Re(bpy)(CO)₃Cl (denoted as
“Re-bpy”) was synthesized by Elizabeth Garcia Cardona in our research
group, following a method previously reported in the literature.¹⁸
¹H NMR (THF-d₈) δH: 7.65 (t), 8.15 (t), 8.50 (d), 9.05 ppm (d). FTIR (CH₂Cl₂)
u(CO): 2023, 1919, and 1898 cm⁻¹.
4.2 Experimental Synthesis

For adsorption studies, 10 mg Re-bpy was mixed with 100 mg of either meso-ZSM-5 or ZSM-5 in ethanol and stirred at room temperature for 24 hrs. The materials were collected by centrifugation and washed with excess ethanol, and this was repeated until supernatant after centrifugation was colorless. The materials were collected and air dried at room temperature.

For photochemical studies, 10 mg Re-bpy, 16 mg Ru(bpy)$_2^{2+}$, both (molar ratio 1:1), or neither, were mixed with 100 mg of either meso-ZSM-5 or ZSM-5 in 5 mL TEA. While stirring, 20 µL TEOA (in 0.1 mL TEA) was added, and this suspension was stirred in dark at room temperature for 24 hrs. After stirring the suspension was allowed to settle, the excess TEA was decanted, and the solid air dried in dark at room temperature.

4.3 Experimental Methods

UV-visible spectra were obtained on a Cary 50 Bio spectrophotometer fitted with a Barrelino diffuse reflectance probe using BaSO$_4$ as a standard and powder samples pressed on BaSO$_4$ pellets. Infrared spectra were collected on a Nicolet 6700 FTIR spectrometer with a DTGS detector, equipped with a Harrick Praying Mantis diffuse reflectance accessory and three-window high-temperature photoreaction chamber. In adsorption studies,
approximately 10 mg powder sample was placed on a KBr pellet in the photoreaction chamber and purged with argon at room temperature for 1 hr before recording spectrum. In photochemical experiments, two additional aliquots of 20 μL TEOA (in 0.1 mL TEA) were added to the recovered solid material and grinded with 400 mg KBr (spectrograde, Harrick Scientific) before loading a 10 mg sample into the photoreaction chamber. The sample was purged with argon at 60 °C for 1 hr and then cooled to room temperature before recording spectrum. Spectra were recorded upon closing photoreaction chamber after flowing CO₂ (99.999%, Airgas) for 5 min, and upon 0.5, 1, 2, and 4 hrs of visible light irradiation (λ > 425 nm, measured to be 300 mW/cm²). Samples were irradiated through a KBr window of the photoreaction chamber using an optic fiber from a Fiber-Lite series 180 illuminator. After 4 hrs of light irradiation, sample temperature was measured to be between 30 and 35 °C. Note that once the photoreaction chamber was closed after CO₂ flow, it remained closed throughout the entire duration of the photoexperiment. In isotopic studies, ¹³CO₂ (>99% ¹³C, <1% ¹⁸O, Cambridge Isotope Laboratories) was used as the reactant gas.

4.4 Results and Discussion

Re{bpy}(CO)₃Cl (denoted as "Re-bpy") was adsorbed on to mesoporous (meso-ZSM-5) and non-mesoporous (ZSM-5) zeolite
materials by simple mixing in ethanol at room temperature. Diffuse reflectance FTIR spectra of each material before and after Re-bpy adsorption can be seen in Figure 4.01. The only differences in the spectra of the two zeolites before Re-bpy adsorption that exist are due to the presence of the ammonium (NH$_4^+$) counter cation in the non-mesoporous ZSM-5. Specifically between 1300 and 2100 cm$^{-1}$, this
accounts for the absorption band which occurs at ~1400-1500 cm\(^{-1}\). After Re-bpy adsorption in ethanol and significant ethanol washing, the infrared spectra show only that the meso-ZSM-5 retained sufficient amounts of Re-bpy to express its characteristic carbonyl stretching bands [\(\nu(\text{CO})\)] between 1800 and 2100 cm\(^{-1}\). In the meso-ZSM-5 spectrum after adsorption, two sharp bands are visible between 1450 and 1500 cm\(^{-1}\) which are characteristic of 2,2'-bipyridine. Though ZSM-5 is a microporous zeolite, the pore openings (0.55 nm) are too small for diffusion of Re-bpy. Due to aggregation, ZSM-5 does have a non-zero amount of mesopore volume which may be able to accommodate Re-bpy, however, meso-ZSM-5 possesses 10 times the mesopore volume as measured by nitrogen adsorption. For this reason, it is concluded that Re-bpy persists after washing because it resides inside these mesopores.

Diffuse reflectance UV-vis spectra were also recorded for the zeolite materials before and after adsorption (Figure 4.02). Like the FTIR characterization, UV-vis spectra show a significant difference in amounts of Re-bpy retained on the two zeolite materials. The metal-to-ligand charge transfer (MLCT) band of Re-bpy occurs at approximately 365 nm, and the visible absorbance seen for Re-bpy adsorbed on to meso-ZSM-5 shows good loading. Facial tricarbonyl Re-bpy features three well-resolved \(\nu(\text{CO})\) bands at 2025, 1918, and 1902 cm\(^{-1}\) in acetonitrile. The infrared spectrum of Re-bpy adsorbed in meso-ZSM-5 shown in Figure 4.03 contains multiple overlapping absorbance peaks, suggesting that the catalyst is possibly hydrogen
bonding with several different moieties on the surface. The FTIR spectrum of meso-ZSM-5 before adsorption of Re-bpy contains peaks at 3750 and 1630 cm\(^{-1}\), corresponding to silanol and surface adsorbed water, respectively, of which either could engage in hydrogen bonding with one or more carbonyl ligands of Re-bpy. To probe these interactions, Re-bpy adsorbed meso-ZSM-5 was exposed to flowing triethylamine (TEA) in argon. This resulted in a decrease of the aggregate absorption band widths between 1800 and 2100 cm\(^{-1}\). Specifically, bands at 2039 and 1941 cm\(^{-1}\) seem to disappear, indicating that adsorption of TEA to the surface results in a less heterogeneous environment for the Re catalyst. TEA may be preferably hydrogen bonding with the surface or Re-bpy. Photoexperiments were attempted in which the meso-ZSM-5 with Re-bpy after TEA adsorption
was irradiated with visible light, however, no noticeable changes appeared in the infrared spectrum. It was suspected that TEA was not a sufficient e– donating molecule, or that it was not sufficiently adsorbed into the meso-ZSM-5.

In an attempt to solve this limitation, triethanolamine (TEOA) was co-adsorbed with Re-bpy into meso-ZSM-5, with and without Ru(bpy)$_3^{2+}$ as a photosensitizer. Control materials, in which only TEOA and TEOA and Ru(bpy)$_3^{2+}$ were adsorbed into meso-ZSM-5, respectively, were also synthesized. Diffuse reflectance FTIR and UV-vis characterization for these materials are displayed in Figure 4.04. The 1300-2100 cm$^{-1}$ region of the infrared spectra for the Re-bpy containing meso-ZSM-5 materials display similar peaks as seen previously. For meso-ZSM-5 control materials with no Re-bpy adsorbed, there are no absorption features
between 1800 and 2100 cm\(^{-1}\). Since Ru(bpy)\(^{3+}\) and TEOA have no absorbance in this region, their presence does not obstruct the stretching bands of the carbonyl ligands of Re-bpy in the meso-ZSM-5 materials. In contrast, the UV-vis spectra of the Re-bpy materials with and without Ru(bpy)\(^{3+}\) are drastically different. Ru(bpy)\(^{3+}\) strongly

![Infrared and UV-vis spectra](image)

**Figure 4.04:** Infrared (top) and UV-vis (bottom) spectra of meso-ZSM-5 materials with (a) TEOA only, (b) Re-bpy with TEOA, (c) Ru(bpy)\(^{3+}\) with TEOA, and (d) Re-bpy and Ru(bpy)\(^{3+}\) with TEOA
adsorbs visible light between 400 and 600 nm which enhances absorptivity in these materials. Again, TEOA adsorbed into meso-ZSM-5 has virtually no affect on the characteristic visible light adsorption of the Re catalyst.

In situ diffuse reflectance FTIR spectroscopy experiments were conducted to study the interactions of the surface adsorbed photocatalyst with CO$_2$ at the solid-gas interface. Materials were mixed with KBr and placed in a photoreaction chamber capable of flowing gases and allowing light irradiation of the sample. After initial purging of the chamber with argon, CO$_2$ was flowed for several minutes in dark and the gas inlet and outlet were closed. Infrared spectra (Figure 4.05) show a new peak at 1650 cm$^{-1}$ after exposure of the materials to CO$_2$, which corresponds to the stretching mode of bidentate bicarbonate (HCO$_3^-$).\textsuperscript{50,51} After the gas lines were reopened and argon gas was again purged through the chamber, the intensity of the peak at 1650 cm$^{-1}$ reduced significantly. The peak at 1630 cm$^{-1}$ shows that there is residual water adsorbed on the surface of these materials, and in the presence of water, an equilibrium exists between gaseous CO$_2$ and HCO$_3^-$ adsorbed on amines (Figure 4.05).\textsuperscript{52} Lower intensity absorbance peaks at 1650 cm$^{-1}$ are visible in the spectra before CO$_2$ exposure due to previously adsorbed HCO$_3^-$ from the synthesis of these materials in the presence of atmospheric CO$_2$. After the photoreaction chamber was filled with CO$_2$, samples were irradiated with visible light (λ > 425 nm) for up to 4 hrs. Difference spectra were generated by
(HOC₂H₄)₃N + CO₂ + H₂O ⇌ (HOC₂H₄)₃NH⁺ + HCO₃⁻

Figure 4.05: CO₂ and adsorbed HCO₃⁻ equilibrium [top]; and FTIR spectra of TEOA in meso-ZSM-5 (a) before and (b) after CO₂ adsorption, and of TEOA and Re-bpy in meso-ZSM-5 (c) before and (d) after adsorption of CO₂ [bottom]

subtracted spectra recorded after exposure to CO₂ from the corresponding spectra recorded after subsequent periods of photoirradiation. Figure 4.06 shows FTIR difference spectra after visible light irradiation for 30 min, as well as control studies in the absence of either CO₂ or light. If meso-ZSM-5 with Re-bpy, Ru(bpy)₃²⁺, and TEOA adsorbed is irradiated under argon and deprived of CO₂, there are no changes in the region between 1300 and 2100 cm⁻¹. Similarly, if this material is exposed to CO₂ and deprived of light (heated to 45°C as this was the measured sample temperature after 30 min visible light irradiation), again, no changes in the FTIR spectra are evident. It is only
with both CO₂ and light that changes in the infrared spectra are seen which suggest changes in the Re-bpy structure, which increase with increasing photoirradiation time (Figure 4.06). A negative peak at ~2030 cm⁻¹ and positive peaks at 2017, 1911, and 1867 cm⁻¹ in the difference spectrum are consistent with loss of fac-Re(bpy)(CO)₃Cl and formation of a new Re-carbonyl compound, respectively. Fac-Re(bpy)(CO)₃(COOH), which has ν(CO) at 2014, 1914, and 1864 cm⁻¹, has been observed after homogeneous CO₂ reduction to CO by Re-bpy in organic solvents. The new peaks in the FTIR difference spectra after light irradiation in the presence of CO₂ are very similar in position, thus, it is determined that formation of fac-Re(bpy)(CO)₃(COOH) did occur in these materials. Notice that after 4 hrs of light, a peak at 1923 cm⁻¹ is prominent in the difference spectra. This is in agreement with the observed ν(CO) of a fac-Re(bpy)(CO)₃(OCO) species with a formato ligand coordinated to the Re center. Re-bpy and TEOA adsorbed meso-ZSM-5 with no Ru(bpy)₃²⁺ shows the same changes after 30 min light, only to a lesser extent. Thus, Ru(bpy)₃²⁺ is successfully enhancing the photoactivity of this material. The broad decrease at 1650 cm⁻¹ in the infrared spectra after irradiation in the presence of CO₂ is caused by the desorption of bicarbonate.

In order to confirm the assignments of the changes seen in the FTIR spectra, photoexperiments were repeated using isotopic ¹³CO₂ as the reactant gas. In Figure 4.07, the FTIR spectrum after initial exposure
Figure 4.06: FTIR difference spectra of Re-bpy and Ru(bpy)$_3$$^{2+}$ with TEOA in meso-ZSM-5 after 30 min of (a) CO$_2$ in dark at 45°C, (b) visible light under argon (no CO$_2$), (c) CO$_2$ with visible light, and (d) Re-bpy with TEOA in meso-ZSM-5 in CO$_2$ after 30 min visible light [top]; FTIR difference spectra of Re-bpy and Ru(bpy)$_3$$^{2+}$ with TEOA in meso-ZSM-5 in CO$_2$ after up to 4 hrs visible light [bottom].

of $^{13}$CO$_2$ to meso-ZSM-5 with TEOA only shows a new peak at 1600 cm$^{-1}$, which is assigned to $^{13}$C-substituted bicarbonate ($\text{H}^{13}\text{CO}_3^-$) adsorbed to TEOA. When Re-bpy, Ru(bpy)$_3$$^{2+}$, and TEOA containing meso-ZSM-5 was...
irradiated with visible light in the presence of $^{13}\text{CO}_2$, new absorption features at 2004 and 1855 cm$^{-1}$ appeared in the difference spectra in addition to the previously seen absorption bands at 2017, 1923, 1911, and 1867 cm$^{-1}$ (Figure 4.08). The appearance of both previously seen and new peaks in the difference spectra can be explained by the previous observation that bicarbonate is adsorbed during synthesis of the materials, as evidenced by a small peak at 1650 cm$^{-1}$ before exposure to CO$_2$. Previous experiments showed the decrease of the 1650 cm$^{-1}$ band as a result of photoirradiation, which corresponded to bicarbonate desorption and regeneration of CO$_2$. These findings suggest that during photoirradiation of the materials in isotopic $^{13}\text{CO}_2$ studies, the composition of the gas phase likely contains at least some
non-isotopic $^{12}$CO$_2$ from the H$^{12}$CO$_3^-$ which was instilled in the material during synthesis. To solve this confusion, a new material was synthesized in which Re-bpy, Ru(bpy)$_3^{2+}$, and TEOA were adsorbed into meso-ZSM-5. In this synthesis, before TEOA was added to the zeolite dispersion, it was stirred for 2 days in TEA in a light-blocked vial which was purged with $^{13}$CO$_2$. This minimized the amount of H$^{12}$CO$_3^-$ adsorbed in the material, and thus, no significant amount of $^{12}$CO$_2$ was desorbed into the chamber headspace during the isotope experiment. As seen in Figure 4.08, this change in synthesis procedure resulted in only absorption peaks at 2004 and 1855 cm$^{-1}$ in the difference spectra after 2 hrs visible light irradiation. As mentioned previously, these new peaks are ascribed
to the $\nu$($\text{CO}$) of fac-Re{bpy}$_3$(CO)$_3$(COOH). In order for this isotopic shift to occur, $^{13}$C must be incorporated into at least one of the carbonyl ligands on the Re catalyst. This implies that at least one $^{13}$CO$_2$ molecule has been converted to a $^{13}$CO molecule, even if it has not dissociated from the Re center, as seen in the structures shown in Figure 4.08. An isotopic shift of 13 cm$^{-1}$ for $\nu$(CO) is reasonable for Re{bpy}$_3$(CO)$_3$(COOH), which contains multiple carbonyl ligands on the same metal center. For example, the $\nu$(CO) isotopic shift seen for Rh($^{12}$CO)($^{13}$CO) relative to Rh($^{12}$CO)$_2$ is 17 cm$^{-1}$. Therefore, it has been shown that co-adsorption of Re-bpy and Ru{bpy}$_2^{2+}$ with TEOA as a sacrificial e$^-$ donor in meso-ZSM-5 is an active CO$_2$ reduction material. One major drawback of these in situ FTIR experiments is that products of CO$_2$ photoreduction such as carbon monoxide (CO) were not detected. If any CO was evolved as a result of photocatalysis, its concentration was below the detection limit of the infrared spectrometer.

4.5 Conclusions

In summary, in situ diffuse reflectance FTIR spectroscopy was used to study Re-bpy adsorbed into mesoporous ZSM-5 zeolite for CO$_2$ photoreduction. It was shown that in the presence of e$^-$ donating TEOA, CO$_2$ was adsorbed to the material as HCO$_3^-$; Upon visible light irradiation, structural changes in the Re catalyst were seen via changes
in the 1800-2100 cm⁻¹ region of the infrared spectrum where the ν(CO) of the tricarbonyl compound occur. Isotopic ¹³CO₂ was used to confirm the formation of Re(bpy)(CO)₃(COOH), an important intermediate in the photocatalytic cycle which converts CO₂ to CO. The co-adsorption of Ru(bpy)₃²⁺ amplified the changes seen in the FTIR spectra, showing that the mesopores of ZSM-5 are capable of functioning as “reaction vessels” for photochemical CO₂ reduction at the gas-solid interface, eliminating the need for organic solvents (Figure 4.09). Such materials have the potential of addressing the diffusional limitation of CO₂ in traditional homogeneous photocatalysis. Further spectroscopic investigations which look at the specific manner of adsorption of the Re-bpy could provide useful information in order to optimize the photoactivity of these materials.

Figure 4.09: Schematic of ZSM-5 mesopore “reaction vessel” with adsorbed Re-bpy, Ru(bpy)₃²⁺, and TEOA
CHAPTER 5

COVALENT ATTACHMENT AND PHOTOCATALYTIC CO₂ REDUCTION
OF Re(4-R-4'-R'-bpy)(CO)₃CI ON SILICA

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5.1 Materials

Triethylamine (>99%) (TEA), triethanolamine (>99.0%) (TEOA),
thionyl chloride (99.5%, <5ppm iron) (SOCl₂), N,N-dimethylformamide
(99.9%) (DMF), 3-aminopropyltrimethoxysilane (97%) (APTMS),
triethoxymethylsilane (99%) (TEMS), 2,2'-bipyridyl-4,4'-dicarboxylic acid
(98%) (4,4'-COOH-2,2'-bpy), tris-(2,2'-bipyridyl)dichlororuthenium(II)
hexahydrate (99.95% trace metal basis) (denoted as "Ru(bpy)₃²⁺").
pentacarbonylchlororhenium(I) (98%) (Re(CO)₅Cl) were all purchased
from Sigma-Aldrich and used without further purification.
4,4'-diamino-2,2'-bipyridine (>95%) (4,4'-NH₂-2,2'-bpy) was purchased
from BOC Sciences. 2-(carbomethoxy)-trimethoxysilane (95%) (CMTES),
p-aminophenyl-trimethoxysilane (90%) (PAPTMS), ethyl-4-(triethoxysilyl)-
benzoate (90%) (ETESB), and 11-aminoundecyltriethoxysilane (95%)
(AUTES) were all obtained from Gelest and used as received. Aerosil 200 nonporous fumed silica (SiO$_2$) was obtained from Evonik and is reported to have a surface area of ~200 m$^2$/g. fac-Re(bpy)(CO)$_3$Cl (denoted as "Re-bpy"). Re-L1, and Re-L2 were synthesized by Alexander Vorushilov in our research group, and characterization for these compounds recorded by Chao Liu in our research group can be found in our recent publications.$^{56,57}$ Re-L1-SBA-15 and Re+SBA-15 were synthesized by He in our research group and properties of these materials are discussed in our report.$^{56}$ 4-methyl-4'-carboxylic acid-2,2'-bipyridine (4-Me-4'-COOH-bpy) was synthesized by Justin Massing here in the chemistry department at the University of New Hampshire following a previously reported procedure.$^{58}$

5.2 Experimental Synthesis

The synthesis of Re-L1-SiO$_2$ and Re-L3-SiO$_2$ is a modification of a synthesis procedure previously reported.$^{59}$ First, 150 mg of fumed SiO$_2$ was heated in the oven for 1 hr at 120°C and dispersed in 30 mL dry toluene using ultrasonication. While stirring, either 90 µL of APTMS (L1) or 89 mg PAPTMS (L3) was added, and the resulting dispersion was refluxed for 12 hrs. After reflux, each was collected with centrifugation and washed with excess toluene, diethyl ether, and DCM. Each was then air dried at room temperature to give APTMS-SiO$_2$ and PAPTMS-SiO$_2$. In a separate flask, 75 mg of 4,4'-COOH-2,2'-bpy was refluxed under
nitrogen in 10 mL of SOCl\textsubscript{2} for 6 hrs and dried under vacuum to remove excess SOCl\textsubscript{2} and any generated amounts of HCl or SO\textsubscript{2}. Under nitrogen, the resulting 4,4'-bis(chlorocarbonyl)-2,2'-bipyridine product was dissolved in 30 mL of dry DCM, added drop wise to either APTMS-SiO\textsubscript{2} or PAPTMS-SiO\textsubscript{2} dispersed in 30 mL of dry DCM and 1 mL TEA, and subsequently refluxed for 12 hrs. After reflux, each was centrifuged and washed with excess DCM and diethyl ether, and redispersed into toluene. To this, 30 mg of Re(CO)\textsubscript{5}Cl was added and heated at 70°С overnight. The final products (Re-L1-SiO\textsubscript{2} and Re-L3-SiO\textsubscript{2}) were centrifuged and washed with toluene, diethyl ether, and DCM, and air dried at room temperature.

Similar to the above procedure, the synthesis of Re-L2-SiO\textsubscript{2} and Re-L4-SiO\textsubscript{2} began with heating 150 mg of fumed SiO\textsubscript{2} in the oven for 1 hr at 120°С, and dispersing in 30 mL dry toluene using ultrasonication. While stirring, 90 μL of either CMTES (L\textsubscript{2}) or ETESB (L\textsubscript{4}) was added and the resulting dispersion was refluxed for 12 hrs, and collected and washed as above to give CMTES-SiO\textsubscript{2} and ETESB-SiO\textsubscript{2}. Each was redispersed into 40 mL dry DMF, to which 60 mg of 4,4'-NH\textsubscript{2}-2,2'-bpy was added and subsequently heated at 85°С for 24 hrs. After heating, each was centrifuged and washed with excess DCM and diethyl ether, and redispersed into toluene. To this, 30 mg of Re(CO)\textsubscript{5}Cl was added and heated at 70°С overnight. The final products (Re-L2-SiO\textsubscript{2} and Re-L4-SiO\textsubscript{2}) were centrifuged and washed with toluene, diethyl ether, and DCM, and air dried at room temperature.
For synthesis of Re-L$_5$-SiO$_2$ and Re-L$_6$-SiO$_2$, 500 mg fumed SiO$_2$ was dried in the oven at 120°C for 1 hr and dispersed in 50 mL dry toluene using ultrasonication. While stirring, 180 µL of TEMS and 20 µL of APTMS (L'1) were added in quick succession and the resulting dispersion was refluxed for 12 hrs. After reflux, this product (TEMS-APTMS-SiO$_2$) was collected with centrifugation, washed with excess toluene and DCM, and then air dried at room temperature. In separate flasks, 10 mg of 4,4'-COOH-2,2'-bpy and 4-Me-4'-COOH-2,2'-bpy were refluxed under nitrogen in 10 mL of SOCl$_2$ for 6 hrs and dried under vacuum to remove excess SOCl$_2$ and any generated amounts of HCl or SO$_2$. These 4,4'-bis(chlorocarbonyl)-2,2'-bpy and 4-Me-4'-chlorocarbonyl-2,2'-bpy products were dissolved in 20 mL dry DCM, added drop wise to 100 mg of Me-NH$_2$-SiO$_2$ dispersed in 30 mL of dry DCM and 1 mL TEA, and subsequently refluxed for 12 hrs. After reflux, each was centrifuged and washed with consecutively with DCM, acetonitrile, and acetonitrile containing ~5% water and ~5% TEA until solid changes color from pink to white. This was washed several times again with acetonitrile and DCM, and then each was redispersed into toluene. To each, 25 mg of Re(CO)$_5$Cl was added and heated at 70°C overnight. The final products (Re-L$_5$-SiO$_2$ and Re-L$_6$-SiO$_2$) were centrifuged and washed with toluene, diethyl ether, and DCM, and air dried at room temperature.
5.3 Experimental Methods

UV-visible spectra were obtained on a Cary 50 Bio spectrophotometer fitted with a Barrelino diffuse reflectance probe using BaSO₄ as a standard and powder samples pressed on BaSO₄ pellets. Rhenium content of materials was quantified using a Varian Vista AX induced coupled plasma atomic emission spectrometer after acid digestion of the material in concentrated nitric acid at 180°C using a CEM Discovery SP microwave system in a pressurized vessel. Infrared spectra of materials before and after solution phase photocatalysis experiments were collected on a Nicolet 6700 FTIR spectrometer with a DTGS detector, equipped with a Harrick Praying Mantis diffuse reflectance accessory and three-window high-temperature photoreaction chamber.

For photocatalytic testing, 10 mg of material was dispersed in 3 mL DMF and 1 mL TEOA in a 13x100 mm Pyrex test tube and sealed with a rubber septum (approximately 4 mL solution and 4.4 mL headspace). While stirring in dark, CO₂ (99.999%, Airgas) was bubbled through the solution and test tube head space for 40 min before testing. An ozone-free Xe arc lamp with liquid water filter (10 cm path length), with Air Mass 1.5 Global optical filter (λ > 350 nm) was used to irradiate samples at room temperature. The test tube head space was sampled with a 50 μL gastight syringe at different time intervals and injected into an Aigilent 7820 gas chromatograph with a TCD detector, equipped
with and a 60/80 Carboxen-1000 packed column (Superlco) for carbon monoxide (CO) separation and detection. Re-bpy, Re-L1, Re-L2, Re-L1-SiO₂, Re-L2-SiO₂, Re-L3-SiO₂, Re-L4-SiO₂ were all tested by Chao Liu in our research group and light intensity was measured to be 25 mW/cm². Light intensity for testing of Re-L5-SiO₂ and Re-L6-SiO₂ was measured to be 50 mW/cm².

For solid-state studies, infrared spectra were collected on a Nicolet 6700 FTIR spectrometer with a DTGS detector, equipped with a Janis Research Company VPF-100-FTIR transmission accessory with four window photoreaction chamber. Approximately 10 mg powder sample was pressed on to a tungsten mesh and secured to the sample holder in the photoreaction chamber, and degassed under vacuum to total pressure of ~30 mTorr for 30 min (in dark) before recording spectrum. Another spectrum was recorded after 1 hr of light irradiation (λ > 475 nm, measured to be 75 mW/cm²). Samples were irradiated through a CaF₂ window of the photoreaction chamber using an ozone-free Xe arc lamp with liquid water filter (10 cm path length), and Air Mass 1.5 Global and 475 nm long-pass optical filters. EPR spectra were collected at room temperature on an X-band (9.5GHz) Bruker EleXsys E-500 cw-EPR/ENDOR spectrometer before and after 5 min visible light irradiation (λ > 425 nm, measured to be 200 mW/cm²) using an optic fiber from a Fiber-Lite series 180 illuminator.
5.4 Results and Discussion

As demonstrated in Chapter 4 of this thesis, adsorbing Re(bpy)(CO)₃Cl (denoted as "Re-bpy") into mesoporous ZSM-5 can be an effective strategy for the generation of solid-state catalysts which operate at the solid-gas interface. However, catalytic activity was assumed to be quite low based on the fact that no carbon monoxide (CO) was detected by infrared spectroscopy. In addition, it is possible that Re-bpy which is physically adsorbed might not be in an optimal orientation for photocatalysis. For example, a likely mode of adsorption is hydrogen bonding of the carbonyl ligands of the catalyst, which may obstruct access to the metal center or restrict ligand coordination geometries needed for CO₂ reduction.

In order to compare physical adsorption and covalent immobilization of catalysts on to the surface of mesoporous materials, He He in the research groups synthesized Re-bpy on mesoporous SBA-15 (Re-L1-SiO₂) (Figure 5.01). In this material, the 2,2'-bipyridyl ligand contains C-bound amide group substitution at the 4,4'-positions which bond it to the surface. For comparison, Re-bpy was immobilized on SBA-15 via liquid-phase adsorption (Re+SBA-15). Diffuse reflectance FTIR characterization for these two materials is shown in Figure 5.01. An important observation to note is the presence and absence of a silanol O-H stretching band (3745 cm⁻¹) in the spectra of Re+SBA-15 and Re-L1-SBA-15, respectively. Reaction of the surface hydroxyl groups with
3-aminopropyltrimethoxysilane coupling agent during synthesis of Re-L1-SBA-15 eliminates this moiety from the surface. Also present exclusively in the infrared spectrum of Re-L1-SBA-15 are absorption bands between 1300 and 1700 cm\(^{-1}\) which are characteristic of amide stretching frequencies. Both materials display bands between 1800 and 2100 cm\(^{-1}\) which correspond to the \(\nu(\text{CO})\) of the tricarbonyl Re catalyst.

Both Re+SBA-15 and Re-L1-SBA-15 were tested for CO\(_2\) photocatalytic activity in 3:1 acetonitrile/TEA solutions contained in sealed vessels which were purged with CO\(_2\). After 4 hrs UV and visible light irradiation, Re-L1-SBA-15 produced almost 10 times the amount of CO as Re+SBA-15 per GC analysis (Figure 5.02). Elemental analysis of
Re-L1-SBA-15 and Re+SBA-15 calculates 5.1 and 1.5 μmol of Re catalyst per 10 mg of material, respectively. This shows that in addition to a higher catalyst loading per mass of material, the Re-L1-SBA-15 material exhibited higher CO₂ reduction activity per Re catalyst molecule. In addition, the FTIR spectra after photoreaction (Figure 5.02) show that only a fraction of the physically adsorbed Re-bpy in Re+SBA-15 was

Figure 5.02: CO production [top] and diffuse reflectance FTIR spectra [bottom] of (a) Re+SBA-15 and (b) Re-L1-SBA-15 after 4 hrs light irradiation in DMF/TEOA under CO₂ atmosphere
Figure 5.03: Structures of Re-L1 and Re-L2

retained in the material. Another observation was that the amide substitution on the 2,2'-bipyridyl ligand induced a red shift in the position of the MLCT band of the covalently bound catalyst on Re-L1-SBA-15. In order to determine the possible effect of bipyridine substitution on catalytic activity, Alexander Vorushilov in the research group synthesized Re-L1 and Re-L2 homogeneous catalysts (Figure 5.03). As shown in Figure 5.04, the MLCT absorbance band of the different structured compounds is affected by the electron donating or withdrawing nature of the substituents, as measured by UV-vis spectroscopy in DMF solutions. Specifically, the electron withdrawing amide group which is C-bound to bipyridine induces a red-shift of 24 nm of the MLCT of Re-L1 relative to Re-bpy. Oppositely, the electron donating amide group which is N-bound to bipyridine induces a blue-shift of 6 nm of the MLCT of Re-L2 relative to Re-bpy. Re-bpy, Re-L1, and Re-L2 were tested for CO₂ photocatalytic activity in 3:1 DMF/TEOA.
solutions contained in sealed vessels which were purged with CO\textsubscript{2}. After 4 hrs UV and visible light irradiation, Re-bpy produced almost 5 times as much CO as both Re-L1 and Re-L2, which displayed similar photocatalytic activities (Figure 5.04). An interesting result was that addition of Ru(bpy)\textsubscript{3}\textsuperscript{2+} as a photosensitizer enhanced CO production of
Re-L1 more so than Re-bpy and Re-L2 under only visible light irradiation.

In an effort to exhaustively probe the effects of synthetic strategy and catalyst structure on the \( \text{CO}_2 \) photoreduction activity of the resulting material, Re catalysts with derivatized bipyridyl ligands were synthesized on the surface of fumed \( \text{SiO}_2 \) nanoparticles. The schematic structures of these covalently-bound surface catalysts are shown in Figure 5.05. These materials were originally designed to further explore
the effect of reversing the orientation of the amide substitution (Re-L1-SiO2 and Re-L3-SiO2 vs. Re-L2-SiO2 and Re-L4-SiO2) and also explore the effect of extended electronic delocalization (Re-L1-SiO2 and Re-L2-SiO2 vs. Re-L3-SiO2 and Re-L4-SiO2). As it would happen, more insight was gained into the relative success of synthetic strategies than into effect of structure of catalytic performance. The first step in the synthesis of these materials was to functionalize the surface of SiO2 with different silane coupling agents. 3-aminopropyltrimethoxysilane (APTMS), 2-(carbomethoxy)-trimethoxysilane (CMTES), p-aminophenyl-trimethoxysilane (PAPTMS), and ethyl-4-(triethoxysilyl)-benzoate (ETESB) were all refluxed in toluene dispersions of SiO2, and diffuse reflectance FTIR spectra of these materials can be seen in Figure 5.06. In all spectra, characteristic absorption peaks of either amino (-NH<sub>2</sub>) (APTMS-SiO2 and PAPTMS-SiO2) or ester (-O(C=O)-) (CMTES-SiO2 and ETESB-SiO2) moieties

![Figure 5.06](image)

Figure 5.06: Diffuse reflectance FTIR spectra of (a) APTMS-SiO2, (b) PAPTMS-SiO2, (c) CMTES-SiO2, and (d) ETESB-SiO2
of the organosilanes are evident, suggesting at least partial surface functionalization. However, the presence of a silanol peak at 3750 cm\(^{-1}\) for all materials excluding APTMS-Si\(_2\)O\(_2\) suggests that full coverage of surface ligand was not achieved in those materials. It was suspected in the cases of CMTES and ETESB, that the ester moiety of the silane coupling agents may have possessed fairly strong hydrogen bonding with the surface, thus competitively inhibiting the reaction between the trialkoxysilyl portion of the molecules and the SiO\(_2\) surface. It may also be possible that the bulky phenyl groups of PAPTMS and ETESB may have sterically hindered adjacent surface sites which resulted in less than full coverage. Though not a quantitative measure, it does appear that the relative intensity of the silanol peak of the ETESB-SiO\(_2\) material may be higher than the in the spectra of the other materials, which would support either hypothesis.

Regardless of the suspected extent of surface coverage, these materials were reacted with 4,4'-NH\(_2\)-2,2'-bpy (L2 and L4) or 4,4'-chlorocarbonyl-2,2'-bpy (L1 and L3), and after washing, subsequently reacted with Re(CO)\(_5\)Cl to provide the respective surface immobilized Re catalyst materials. Figure 5.07 shows diffuse reflectance FTIR and UV-vis spectra of the synthesized materials after exhaustive washing. Though not every absorption peak in the spectra can be assigned, some features seen can provide useful insights. For example, the FTIR spectra of Re-L1-SiO\(_2\) and Re-L3-SiO\(_2\) show smooth and fairly symmetrical \(\nu(CO)\) bands between 1800 and 2100 cm\(^{-1}\), whereas in this
Figure 5.07: Diffuse reflectance FTIR spectra [top] and UV-vis spectra [bottom] of (a) Re-L1-SiO2, (b) Re-L3-SiO2, (c) Re-L2-SiO2, and (d) Re-L4-SiO2. In the region for Re-L2-SiO2 and Re-L4-SiO2, there are several sharp peaks within each aggregate absorption band. It was found based on comparison of band positions that the sharp bands in these spectra corresponded to the homogeneous NH2-bpy-Re catalyst structure. It is believed that a significant amount of this complex is retained on the surface after
washing due to strong hydrogen bonding. This may also be true to a lesser extent in Re-L1-SiO₂ and Re-L3-SiO₂ which may contain small amounts of homogeneous COOH-bpy-Re catalyst adsorbed on the surface. Despite the relative amounts, it is the case that the MLCT band position is shifted in the same direction by both surface immobilized catalyst and undesired homogeneous catalysts physically adsorbed on the surface, as seen in the UV-vis spectra for each (Figure 5.07).

Induced coupled plasma atomic emission spectroscopy (ICP-AES) was used to quantify rhenium content per mass of synthesized material after acid digestion. Amounts of rhenium detected for Re-L1-SiO₂, Re-L2-SiO₂, Re-L3-SiO₂, and Re-L4-SiO₂ were 2.9, 1.5, 2.8, and 0.8 µmol per 10 mg of material, respectively. These measured amounts seem to correlate well with the interpreted success of each synthetic strategy as judged by their infrared spectra.

All 4 materials were tested for CO₂ photocatalytic activity in 3:1 DMF to TEOA solutions contained in sealed vessels which were purged with CO₂. After 4 hrs UV and visible light irradiation, only Re-L1-SiO₂ showed significant CO₂-to-CO photoconversion (Figure 5.08). Based on the ICP-AES results, turnover number of CO (mol of CO produced per mol of catalyst) by Re-L1-SiO₂ was very close to that observed for the homogeneous Re-L1. In the case of the other three materials, incomplete synthesis seemed to dramatically limit their photocatalytic activity towards CO₂ reduction. Homogenous Re catalysts which were possibly formed and adsorbed on to the SiO₂ surface (NH₂-bpy-Re and
COOH-bpy-Re) would be expected to show little CO\textsubscript{2} photoreduction activity.[ref] Inspection of FTIR spectra of collected materials after photoreaction (Figure 5.08) supports this theory, as \nu(CO) bands for all but Re-L1-SiO\textsubscript{2} have significantly reduced similar to what was seen for Re+SBA-15 after photoreaction. For Re-L1-SiO\textsubscript{2}, attempts to run a

Figure 5.08: Turnover numbers of CO production [top] and diffuse reflectance FTIR spectra [bottom] after 4 hrs light irradiation in DMF/TEOA under CO\textsubscript{2} atmosphere of (a) Re-L1-SiO\textsubscript{2}, (b) Re-L3-SiO\textsubscript{2}, (c) Re-L2-SiO\textsubscript{2}, and (d) Re-L4-SiO\textsubscript{2}
second 4 hr duration of photocatalysis on recollected material yielded almost no CO production. But inspection of the FTIR spectrum after the first photoreaction cycle shows retention of $\nu$(CO) which would suggest that the original catalyst structure should still be present on the material, and thus, the material should still be photocatalytically active. It is possible, however, that a Re(bpy)_{3}(CO)_{3}(OCHO) compound has formed, as the $\nu$(CO) of this complex are very similar in energy to those

![Diffuse reflectance FTIR spectrum and revised structure of Re-L1-SiO2](image-url)

**Figure 5.09:** Diffuse reflectance FTIR spectrum [top] and revised structure [bottom] of Re-L1-SiO2
of Re-bpy.54

Looking closely at the FTIR spectrum for Re-L1-SiO2 (Figure 5.09), a small shoulder on the highest energy v(CO) band was noticed. Likely possibilities for this observation are the presence of either homogeneous COOH-bpy-Re adsorbed on surface or free –COOH groups on bipyridine which has only one tether to the SiO2 surface (depicted in Figure 5.09). The matter of whether Re-L1-SiO2 surface catalyst molecules have one or two tethers to the surface is important because –COOH substitution on bipyridine should impart reduced CO2 reduction activity versus the amide counterpart.

A quick proof-of-concept experiment was conducted in which Re-L5-SiO2 and Re-L6-SiO2 (Figure 5.10) were synthesized. As expected, Re-L5-SiO2 exhibited higher frequency v(CO) bands and a lower energy MLCT band relative to Re-L6-SiO2, as seen in FTIR and UV-vis spectra, respectively (Figure 5.11). Also a predicted result was the higher CO2

![Figure 5.10: Structures of Re-L5-SiO2 and Re-L6-SiO2](image-url)
Figure 5.11: Diffuse reflectance FTIR spectra [top] and UV-vis spectra [bottom] of (a) Re-L5-SiO2 and (b) Re-L6-SiO2

Though the amount of Re catalyst on the surface of each material was never quantified, the methodology chosen for synthesis of these two materials would predict very comparable surface loadings. Specifically, SiO2 was functionalized with APTMS in a 1:10 volume ratio with triethoxymethylsilane (TEMS) which provides for an –NH2 functionality in
dilute concentrations on the surface. This material was used for subsequent coupling of either 4,4'-COOH-2,2'-bpy or 4-Me-4'-COOH-2,2'-bpy, which should have the same yields of reaction under the same conditions. Likewise, Re coordination to surface-bound bipyridine should occur with the same efficiency in both cases. Washing procedures were identical for both materials, thus, it is a safe assumption that surface loadings are approximately equal. Given these assumptions, these results suggest that perhaps a "one-arm" covalently bound catalyst could be a useful strategy to optimize catalyst structures on the surface.

Coming back full circle to the solid-state photoreduction of CO₂ discussed in Chapter 4 of this thesis, Re-L₁-SiO₂ was grinded with TEOA and KBr and pressed on to a tungsten mesh for in situ transmission FTIR
Figure 5.13: Transmission FTIR spectra [top] and EPR spectra [bottom] of solid-state Re-L1-SiO2 mixed with TEOA and KBr (a) before and (b) after visible light irradiation study. Under 30 mTorr constant vacuum, the material within the photoreaction chamber was irradiated with visible light for 1 hr. As seen in Figure 5.13, a shift of the $\nu$(CO) of the material occurs. The shifting of $\nu$(CO) bands to lower energy as a result of 1 e$^-$ reduction of Re-bpy has been seen previously, though in solution the shift is $\sim$20 cm$^{-1}$ for the
The smaller magnitude of the shifts in this experiment could be a result of the electron withdrawing nature of the amide substitution, the fact that not every Re catalyst molecule will be reduced by TEOA, or a combination of both. EPR spectroscopy was used to confirm the formation of a reduced species on Re-L1-SiO2 (Figure 5.13). Before visible light irradiation, the EPR spectrum is unremarkable, however, after photoirradiation shows characteristic signal of the paramagnetic 1 e⁻ reduced bipyridine containing resonance from interaction with the Re(I) metal center. These solid-state FTIR and EPR results in the absence of CO₂ show that e⁻ transfer from TEOA to Re-L1-SiO₂ occurs upon light irradiation. FTIR photoexperiments in the presence of CO₂ show new peaks at 2005, 1905, and 1897 cm⁻¹ in the difference spectra (Figure 5.14) corresponding to formation of Re(bpy)(CO)₃(CHO), which again

Figure 5.14: FTIR difference spectrum of Re-L1-SiO₂ with TEOA after 30 min visible light irradiation in presence of CO₂
confirms successful CO\textsubscript{2} reduction in a solid-gas phase system.

5.5 Conclusions

In summary, Re-bpy derivatized with amide groups was covalently bound to the surface of silica. The orientation of the amide substitution on bipyridine affects the physical properties and activity of the catalyst molecules. Each was synthesized using different silane coupling agents and synthetic conditions and insights into the interactions of these organic moieties and the surface were gained using FTIR spectroscopy. Photocatalyst materials were tested in solution phase CO\textsubscript{2} photocatalysis, with one material (Re-L1-SiO\textsubscript{2}) standing out as the best combination of synthetic strategy and catalyst structure. This resulted in far greater turnover numbers for CO production than any of the other tested materials. FTIR and EPR studies showed that this Re-L1-SiO\textsubscript{2} material is capable of being reduced by TEOA upon visible light irradiation in the solid-state, making it a promising heterogeneous catalyst material which could operate at the solid-gas interface.
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