Solar CO_2 Reduction using a Molecular Re(I) Catalyst Grafted on SiO_2 via Amide and Alkyl Amine Linkages

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Heterogenized molecular catalysts have shown interesting activities in different chemical transformations. In our previous studies, a molecular catalyst, $Re(bpy)(CO)_3Cl$ where bpy is 2,2'-bipyridine, was covalently attached to silica surfaces via an amide linkage for use in photocatalytic CO_2 reduction. Derivatizing the bpy ligand with electron-withdrawing amide groups led to detrimental effects on the catalytic activity of $Re(bpy)(CO)_3Cl$. In this study, an alkyl amine linkage is utilized to attach $Re(bpy)(CO)_3Cl$ onto SiO_2 in order to eliminate the detrimental effects of the amide linkage by breaking the conjugation between the bpy ligand and the amide group. However, the heterogenized Re(I) catalyst containing the alkyl amine linkage demonstrates even lower activity than the one containing the amide linkage in photocatalytic CO_2 reduction. Infrared studies suggest that the presence of the basic amine group led to the formation of a photocatalytically inactive Re(I)-OH species on SiO_2. Furthermore, the amine group likely contributes to the stabilization of a surface Re(I)-carboxylato species formed upon light irradiation, resulting in the low activity of the heterogenized Re(I) catalyst containing the alkyl amine linkage.

Introduction

Photocatalytic CO_2 reduction has been extensively investigated in recent years as a sustainable way to utilize CO_2 as a renewable C1 feedstock [1-3] Different systems, including homogeneous and heterogeneous photocatalysts, have been developed to convert the thermodynamically stable CO_2 molecule to less stable molecules such as CO and HCOOH.[4-8] In homogeneous systems, some molecular catalysts can function as photocatalysts by themselves since they can harvest light and activate CO_2, while others require the use of additional photosensitizers for light harvesting.[9-12] Diimine-tricarbonyl Re(I) complexes, in particular $Re(bpy)(CO)_3Cl$ where bpy is 2,2'-bipyridine, have demonstrated excellent reactivity and selectivity towards CO formation in both photocatalytic and electrocatalytic CO_2 reduction.[13, 14]

While molecular catalysts are often highly efficient in mediating CO_2 reduction, many of them suffer from poor stability under photochemical conditions. Different strategies have been designed to enhance the robustness and recyclability of molecular catalysts. For instance, heterogenized molecular catalysts can be obtained by attaching molecular catalysts onto solid-state surfaces.[15-19] Such photocatalysts generally show enhanced activity and improved photostability. Many studies utilized $Re(bpy)(CO)_3Cl$ as a model complex to obtain heterogenized molecular catalysts on photoactive surfaces[20-23] for enhanced CO_2 reduction under solar irradiation.

We have employed SiO_2 as a model support for $Re(bpy)(CO)_3Cl$ to carry out spectroscopic investigations since SiO_2 is almost "transparent" in studies using many spectroscopic techniques,[24] including diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). In our previous studies, covalent attachment of $Re(bpy)(CO)_3Cl$ on SiO_2 involved derivatization of the bpy ligand with amide groups.[25-27] However, such ligand derivatization resulted in significantly changes in the photophysical, electrochemical, and photocatalytic properties of $Re(bpy)(CO)_3Cl$.[26, 27] For instance, the metal-to-ligand charge transfer (MLCT) transition of $Re(bpy)(CO)_3Cl$ was shifted from ~370 nm to ~400 nm upon covalent attachment on SiO_2 via the amide linkage. Derivatizing the bpy ligand with the electron-withdrawing amide groups also shifted the redox potentials of $Re(bpy)(CO)_3Cl$ to more positive values. Consequently, the activity of $Re(bpy)(CO)_3Cl$ was found to be much lower than Re-bpy in photocatalytic CO_2 reduction.[26] Derivatizing $Re(bpy)(CO)_3Cl$ with amide groups also showed detrimental effects in electrocatalytic CO_2 reduction. In particular, covalent linkages containing the amide groups were shown to be unstable under highly reducing conditions, while alkyl linkages were more stable.[28]

In addition to ligand derivatization, some surface features could also affect the structure, complexation, and behavior of molecular catalysts grafted on surfaces. For example, it was shown that the binding structure of surface attached $Re(bpy)(CO)_3Cl$ can be significantly influenced not only by the nature and length of the covalent linkages, but also by the crystallographic facet of the surface.[29] Our studies using DRIFTS spectroscopy showed that the presence of surface water had profound effects on the complexation of $Re(bpy)(CO)_3Cl$ attached onto SiO_2 surfaces. In particular, three infrared absorptions associated with the formation of a photochemically inactive Re(I)-OH species were observed in the

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Electronic Supplementary Information (ESI) available: Structures, UV-vis spectra, DRIFTS spectra and photocatalytic activities of two isomeric Re(I) catalysts. See DOI: 10.1039/x0xx00000x

DRIFTS spectrum of a heterogenized $Re(bpy)(CO)_3Cl$ in the presence of triethanolamine (TEOA) and water.[30] This Re(I)-OH species was formed upon replacing the Cl^- ligand of $Re(bpy)(CO)_3Cl$ with –OH, which could be produced in the reaction between the basic TEOA and water on the surface.

In this current study, an alkyl amine linkage is utilized to covalently attach $Re(bpy)(CO)_3Cl$ onto SiO_2 to break the conjugation between the bpy ligand and the amide group. Surprisingly, the resulting heterogenized Re(I) catalyst demonstrates lower activity than the one containing the amide linkage in photocatalytic CO_2 reduction. We utilize DRIFTS spectroscopy to explore possible reasons for this observation, including the formation of the Re(I)-OH species and the stabilization of a surface Re(I)-carboxylato species generated upon light irradiation.

Experimental

Materials. Aerosil 200 silica, hydrochloric acid, triethylamine (TEA), triethanolamine (TEOA), toluene, diethyl ether, dichloromethane (DCM), dimethylformamide (DMF), thionyl chloride, 2,2'-bipyridine-4,4'-dicarboxylic acid, pentacarbonyl chlororhenium (I) (98%), N-bromosuccinimide, azobisisobutyronitrile, and tris(2,2'-bipyridine) dichlororuthenium(II) hexahydrate (99%) were obtained from Sigma-Aldrich. Two silane coupling agents, *p*-aminophenyl trimethoxysilane and *m*-aminophenyl trimethoxysilane, were obtained from Gelest. All chemicals were used as received without any further purification.

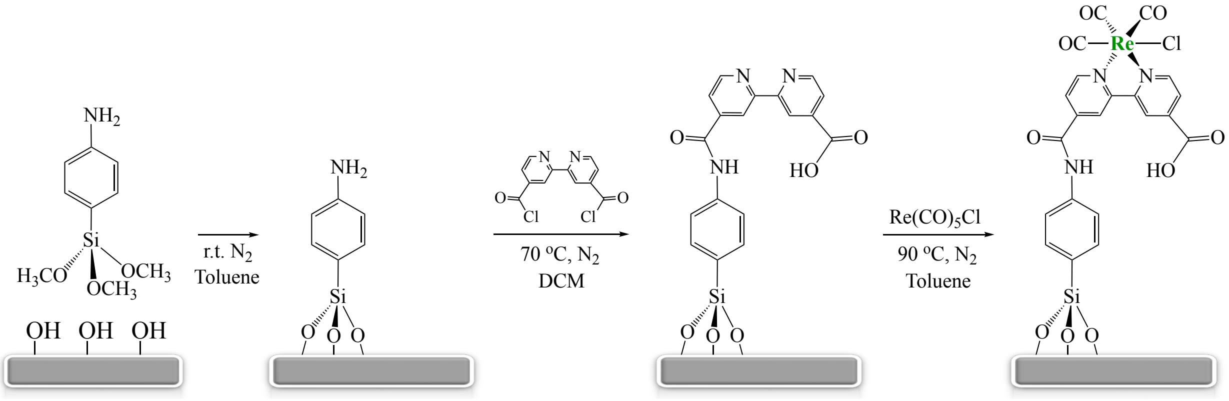
Synthesis of Aminophenyl Functionalized SiO_2. 100 mg of Aerosil 200 silica (SiO_2) was dried at 100 °C for 2 hours before being dispersed in 50 mL dry toluene under an inert atmosphere, to which 0.189 g of *p*-aminophenyl trimethoxysilane was added. The resulting mixture was refluxed for 24 hours under a nitrogen atmosphere. The product was recovered via centrifugation and washed three times with toluene, diethyl ether, and DCM, respectively. The resulting brown powder was then dried under vacuum.

Covalent Attachment of $Re(bpy)(CO)_3Cl$ on SiO_2 via an Amide Linkage. The molecular Re(I) complex was attached to SiO_2 surface via an amide linkage following our previous studies (Scheme 1).[26, 27] In a typical synthesis, 100 mg of 4,4'-dicarboxylic-2,2'-bipyridine was dispersed in 15 mL of thionyl chloride. This solution was heated to 85 °C under an inert atmosphere and refluxed overnight. Rotary evaporation was used to isolate the acylated yellow powder. The freshly synthesized 4,4'-bis(chlorocarbonyl)-2,2'-bipyridine was then dispersed in 15 mL DCM and added dropwise to 100 mg of *p*-aminophenyl functionalized SiO_2 in 40 mL DCM under N_2 flow. The solution was then heated to 70 °C and stirred overnight. The product was retrieved via centrifugation and washed three times with DCM, diethyl ether, and DCM again, respectively. A light yellow powder was isolated via drying under vacuum. Next, 150 mg of the resulting material was dispersed in 50 mL dry toluene, to which 50 mg of pentacarbonyl chlororhenium(I) was added under stirring. The mixture was then heated to 95 °C under an inert atmosphere and was stirred overnight while covered with foil to reduce light exposure. The product was then retrieved via centrifugation and washed three times with toluene, diethyl ether, and then repeatedly with DCM, respectively. A brown powder was isolated and dried under vacuum. The final product bearing an amide linkage is denoted "Re-1-SiO_2" (Scheme 1).

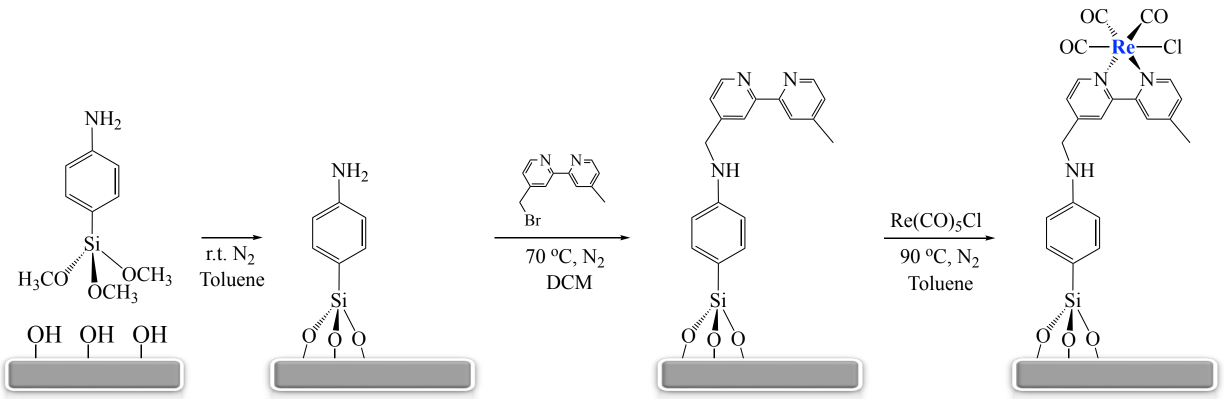
Synthesis of 4-(bromomethyl)-4'-methyl-2,2'-bipyridine. In our study, 4-(bromomethyl)-4'-methyl-2,2'-bipyridine was synthesized following a method reported by Joseph and co-workers.[31] In this synthesis, 1 g of 4,4'-dimethyl-2,2'-bipyridine and 1 g of N-bromosuccinimide were dissolved in 50 mL of carbon tetrachloride at which point a catalytic amount of azobisisobutyronitrile (5 mg) was added. The reaction mixture was refluxed at 77 °C for 16 hours under nitrogen. The hot reaction mixture was then filtered and the filtrate was concentrated using rotary evaporation. The resulting residue was purified using column chromatography (~30% yield).

Covalent Attachment of $Re(bpy)(CO)_3Cl$ on SiO_2 via an Alkyl Amine Linkage. Following a method similar to Scheme 1, a surface Re(I) catalyst containing an alkyl amine linkage, denoted "Re-2-SiO_2", was synthesized using 4-(bromomethyl)-4'-methyl-2,2'-bipyridine instead of 4,4'-bis(chlorocarbonyl)-2,2'-bipyridine (Scheme 2).

Following the approaches shown in Schemes 1 and 2, two isomeric Re(I) catalysts, Re-3-SiO_2 and Re-4-SiO_2, were also synthesized starting with SiO_2 functionalized with *m*-aminophenyl trimethoxysilane (see Figure S1 for their structures).



Scheme 1. Synthesis of Re-1-SiO_2 featuring an amide linkage.



Scheme 2. Synthesis of Re-2-SiO$_2$ featuring an alkyl amine linkage.

Characterization. Elemental analysis of the metal content in the synthesized materials was performed using a Varian Vista AX inductively coupled plasma atomic emission spectrometer. The loadings of Re were determined to be 1.8 and 3.4 μmol per 10 mg of Re-1-SiO$_2$ and Re-2-SiO$_2$, respectively. Optical spectra of the samples were obtained using a Cary 50 Bio spectrophotometer outfitted with a Barrelino diffuse reflectance probe. DRIFTS spectra were collected on a Nicolet 6700 FTIR spectrometer equipped with a Harrick Praying Mantis diffuse reflectance accessory.

Photocatalytic Testing. In a typical photocatalytic test, 10 mg of a heterogenized catalyst sample was dispersed in 4 mL of a DMF : TEOA (3:1 v/v) solution in a quartz test tube. A molecular photosensitizer, tris(2,2'-bipyridine) dichlororuthenium(II) hexahydrate, was added to the reaction solution (3 mg for each test). The test tube was sealed with a septum and parafilm, then bubbled with CO$_2$ (99.999% Airgas) for 30 minutes in the dark before being exposed to light irradiation provided by a Fiber-Light series 180 lamp fitted with a 420-nm long-pass optical filter (see Figure S2 for the output spectrum). The light intensity was fixed at 100 mW/cm^2. While the reaction solution was stirred under light, the head space was sampled using a gas tight syringe for analysis using an Agilent 7820 GC equipped with a thermal conductivity detector and a 60/80 Carboxen 1000 column. Possible products in the solution phase were monitored using nuclear magnetic resonance spectroscopy.

Results and Discussion

The heterogenized Re(I) catalysts synthesized following Schemes 1 and 2 display different colors. Their optical spectra were collected using a UV-visible spectrophotometer fitted with a diffuse reflectance accessory. Figure 1 shows the spectra of Re-1-SiO$_2$ and Re-2-SiO$_2$, which feature MLCT bands around 400 nm and 370 nm, respectively. In our previous study,[26] the MLCT band of the homogeneous Re(bpy)(CO)$_3$Cl complex was recorded to be at 369 nm, and was shifted to 396 nm upon derivatizing the bpy ligand with amide groups. Therefore, the 30 nm shift in the MLCT band of Re-1-SiO$_2$ compared to Re-2-SiO$_2$ originates from the amide derivatization on the bpy ligand. More specifically, this shift most likely occurs due to stabilization of the bpy π* based lowest unoccupied molecular orbital of the complex upon derivatization with the electron withdrawing amide group. The MLCT transition of Re-2-SiO$_2$ is similar to that of the homogeneous Re(bpy)(CO)$_3$Cl complex, indicating that ligand derivatization with the alkyl amine group has minimal effect on the MLCT band.

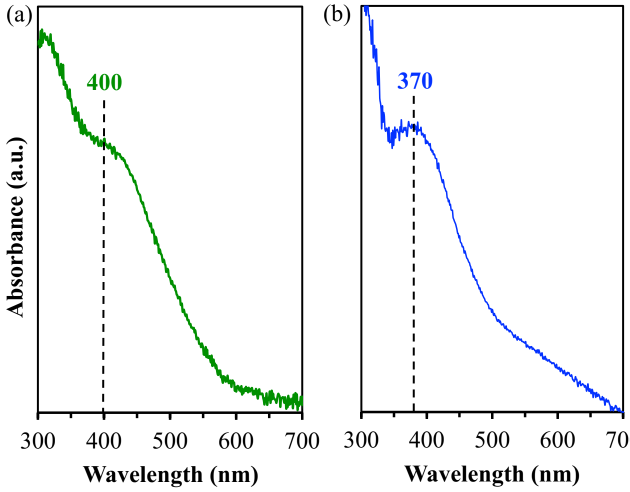


Figure 1. Diffuse reflectance UV-vis spectra of (a) Re-1-SiO$_2$ and (b) Re-2-SiO$_2$. Barium sulfate was used as the background.

In our study, two isomeric heterogenized Re(I) catalysts, Re-3-SiO$_2$ and Re-4-SiO$_2$, were synthesized starting with SiO$_2$ functionalized with *m*-aminophenyl trimethoxysilane (Figure S1). The same difference was observed in the MLCT bands of Re-3-SiO$_2$ and Re-4-SiO$_2$, which contain amide and alkyl amine linkages, respectively (Figure S3).

The carbonyl groups of the heterogenized Re(I) catalysts can be used as a sensitive molecular probe to investigate the complexation and structures of the Re(I) centers. The infrared spectrum of Re(bpy)(CO)$_3$Cl in the molecular state contains three carbonyl stretches in the 1900–2100 cm^{-1} range, corresponding to one high-energy, fully symmetric mode and two nearly degenerate lower-energy modes.[20, 32] In the DRIFTS spectra of Re-1-SiO$_2$ and Re-2-SiO$_2$, the high-energy stretch is seen at 2025 cm^{-1} while the two lower-energy modes coalesce to one broad feature at 1905 cm^{-1} (Figure 2), similar to our previous observations of heterogenized Re(I) catalysts.[25, 26, 30] This coalescence is attributed to peak broadening due to surface heterogeneity rather than any change in symmetry at the Re center. Additional features in the DRIFTS spectrum of Re-1-SiO_2 include absorptions associated with amide groups at 1664, 1524, and 1400 cm^{-1} (Figure 2a), similar to those observed in our prior studies.[25] Furthermore, an absorption at 1726 cm^{-1} is present in the spectrum of Re-1-SiO_2 shown in Figure 2a, corresponding to the -COOH group[26] on the bpy ligand (see the structure of Re-1-SiO_2 in Scheme 1). Both spectra shown in Figure 2 also contain an absorption around 1600 cm^{-1}, which is attributed to the phenyl group in both Re-1-SiO_2 and Re-2-SiO_2.

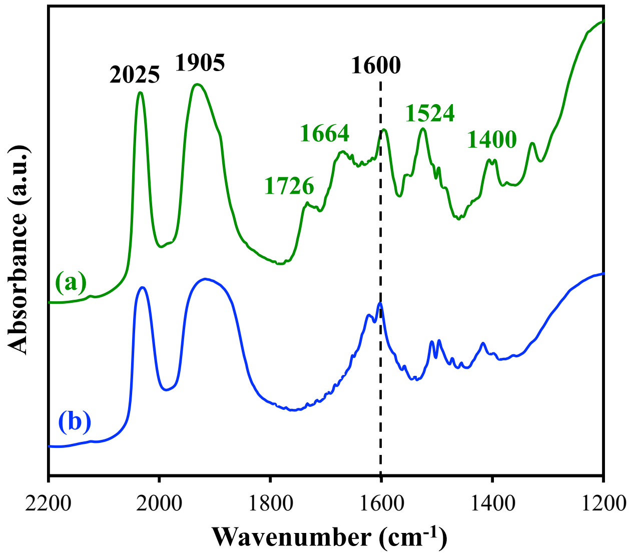


Figure 2. DRIFTS spectra of (a) Re-1-SiO_2 and (b) Re-2-SiO_2. Potassium bromide was used as the background.

The two lower-energy modes of the Re(I)-carbonyl stretches can be resolved by exposing the surface Re(I) complexes to TEOA and CO_2.[24, 26, 33] In this study, the heterogenized Re(I) catalysts in the powder form were diluted with KBr and then mixed with a few drops of TEOA. The resulting mixture was then placed in the DRIFTS cell. Prior to spectrum collection, the mixture was purged with CO_2 in the dark. Figure 3 shows the DRIFTS spectra of Re-1-SiO_2 and Re-2-SiO_2 collected under CO_2. In the spectrum of Re-1-SiO_2 (Figure 3a), three peaks at 2021, 1917, and 1895 cm^{-1} are present, indicating the formation of a CO_2-bound Re(I) adduct, Re(I)-OOC-$OCH_2CH_2NR_2$ where R is CH_2CH_2OH, in the presence of TEOA and CO_2.[34] The Re(I)-OOC-$OCH_2CH_2NR_2$ species was suggested to be the real catalyst in photocatalytic CO_2 reduction using diimine-tricarbonyl Re(I) catalysts and TEOA.[34]

Under the same experimental conditions, three additional Re(I)-carbonyl stretches at 1995, 1875, and 1850 cm^{-1} are seen in the DRIFTS spectrum of Re-2-SiO_2 (Figure 3b). These three peaks are associated with a photochemically inactive Re(I)-OH species according to our previous study[30] and studies by Gibson and co-workers.[35] Since these three peaks are not present in the spectrum of Re-1-SiO_2, it can be deduced that the formation of the Re(I)-OH species in Re-2-SiO_2 is due to the presence of the basic amine group, which likely produced -OH to replace the Cl^- ligand on Re-2-SiO_2. The same difference was observed in the DRIFTS spectra of Re-3-SiO_2 and Re-4-SiO_2 (Figures S4 and S5), further confirming the observed effect of the basic amine group.

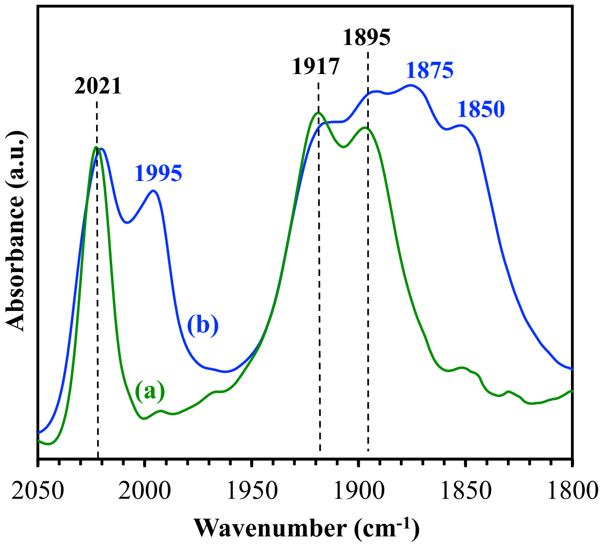


Figure 3. DRIFTS spectra of (a) Re-1-SiO_2 and (b) Re-2-SiO_2 in the presence of TEOA and CO_2.

The synthesized samples demonstrated poor activity in photocatalytic CO_2 reduction under simulated solar irradiation (Figure S6). In this study, the heterogenized Re(I) catalysts were coupled with a molecular Ru(II) photosensitizer in visible-light CO_2 reduction in the presence of TEOA as a sacrificial electron donor. Diimine-tricarbonyl Re(I) complexes are known for their activity in selective reduction of CO_2 to CO, though formation of CH_4 was recently reported in photocatalytic CO_2 reduction using a molecular Re(I) complex.[36] Under the experimental conditions employed in this study, CO and a small amount of H_2 were detected as the only products; no appreciable production of HCOOH, HCHO, CH_3OH, or CH_4 was detected. Turnover numbers (TONs) for CO production of 13.6 and 4.5 were obtained using Re-1-SiO_2 and Re-2-SiO_2, respectively, after photocatalysis for 120 minutes (Figure 4). Similar comparison was observed in photocatalysis using Re-3-SiO_2 and Re-4-SiO_2 (Figure S7).

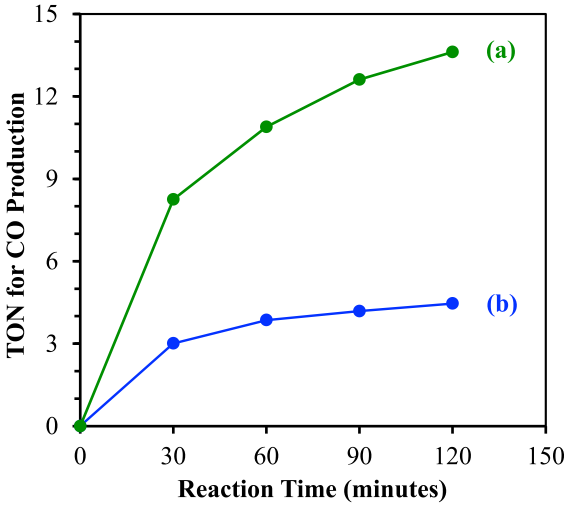


Figure 4. CO production in photocatalytic CO_2 reduction using (a) Re-1-SiO_2 and (b) Re-2-SiO_2 under visible light using a molecular Ru(II) photosensitizer. Light intensity was 100 mW/cm^2.

The photocatalysis results shown in Figure 4 are surprising since the alkyl amine linkage in Re-2-SiO_2 was expected to alleviate the detrimental effect of the electron-withdrawing amide group in Re-1-SiO_2. One of the reasons for the relatively lower activity of Re-2-SiO_2 is the formation of photocatalytically inactive Re(I)-OH species in the presence of TEOA, as indicated by its DRIFTS spectrum shown in Figure 3b. As discussed earlier, the formation of Re(I)-OH species in Re-2-SiO_2 is due to the presence of the basic amine group.

Additional effects of the amine group were discovered using *in situ* DRIFTS experiments. In such experiments, the heterogenized Re(I) catalysts were mixed with a few drops of TEOA and purged with CO_2. For each sample, DRIFTS spectra were collected prior to and after exposing the samples to light irradiation. Difference spectra shown in Figure 5 were obtained by subtracting the spectra after light irradiation for 2, 10, 30 and 60 min from the spectrum collected prior to irradiation. In the difference spectra, positive peaks are associated with the formation of new species, while negative peaks are associated with the consumption of species formed prior to light irradiation. In the difference DRIFTS spectra of both Re-1-SiO_2 and Re-2-SiO_2 (Figure 6), negative peaks at 2025 and 1925 cm^{-1} are present and the peaks became more intense over time, indicating the consumption of the CO_2-bound Re(I) adduct, Re(I)-OOC-$OCH_2CH_2NR_2$, upon light irradiation. Positive peaks around 2003 and 1873 cm^{-1} are seen in the spectra shown in Figure 6. These positive peaks are associated with the formation of a reduced species similar to $[Re(bpy)(CO)_3Cl]^{\bullet-}$.[27] Such negative and positive peaks, representing changes in the spectra upon light irradiation, are also seen in the difference DRIFTS spectra of Re-3-SiO_2 and Re-4-SiO_2 (Figure S8).

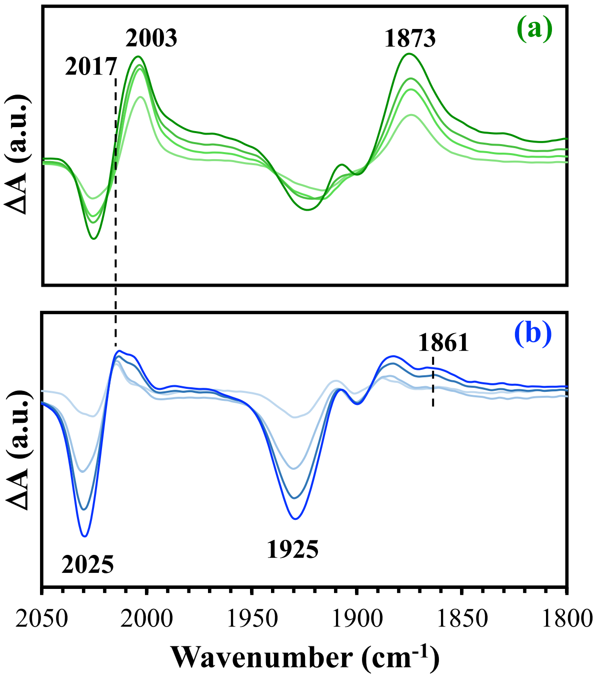


Figure 5. Difference DRIFTS spectra of (a) Re-1-SiO_2 and (b) Re-2-SiO_2 upon light irradiation in the presence of TEOA and CO_2. The spectra were obtained by subtracting spectra collected before light irradiation (t = 0) from corresponding spectra collected after light irradiation for different times (2, 10, 30, and 60 min).

A unique feature in the difference spectra of Re-2-SiO_2 is the presence of a peak around 2017 cm^{-1}, which is absent from the spectra of Re-1-SiO_2 (Figure 5). This peak, together with a less obvious absorption around 1861 cm^{-1}, suggests the formation of a Re(I)-carboxylato complex on Re-2-SiO_2 upon light irradiation.[37] These two peaks are also seen in the difference DRIFTS spectra of Re-4-SiO_2 but not in the difference spectra of Re-3-SiO_2 (Figure S8). A viable intermediate in CO_2 reduction using diimine-tricarbonyl Re(I) catalysts, the Re(I)-carboxylato species requires additional protons to be converted into CO.[35, 38] The comparison shown in Figures 5 and S7 implies that the photochemically produced Re(I)-carboxylato species is stabilized in Re-2-SiO_2 and Re-4-SiO_2 that contain the alkyl amine linkage. In the presence of the alkyl amine group, electrostatic interactions may be hindering the Re(I)-carboxylato intermediate from participating in C-OH bond cleavage and releasing CO as the product.

Discussions on the spectra shown in Figures 3 and 5 suggest that the alkyl amine linkage contributed to (i) formation of the Re(I)-OH species and (ii) stabilization of the Re(I)-carboxylato species generated upon light irradiation. Our previous studies[30] demonstrated that the Re(I)-OH species is photochemically inactive. Stabilization of the Re(I)-carboxylato species prevented its further conversion to CO, the final product of CO_2 reduction. These two consequences of using the alkyl amine linkage in catalyst heterogenization likely contributed to the observed relatively low activity of Re-2-SiO_2 (Figure 4) and Re-4-SiO_2 (Figure S7).

Due to the presence of the phenyl group, the alkyl amine in Re-2-SiO_2 and Re-4-SiO_2 should be less basic than TEOA, although it is more basic than the amide group in Re-1-SiO_2 and Re-3-SiO_2. Since the spectra shown in Figures 3 and 5 are collected in the presence of TEOA, our results suggest that local basicity of the alkyl amine group could have some impact on the fate of the heterogenized Re(I) catalysts. In Re-2-SiO_2 and Re-4-SiO_2, the basic amine group is in close proximity with the Re(I) center, and led to the formation of Re(I)-OH and stabilization of Re(I)-carboxylato. In our study, these Re(I) species were not detected by DRIFTS in Re-1-SiO_2 or Re-3-SiO_2, even in the presence of the more basic TEOA. There are other possible reasons that could account for the observed difference in photocatalytic activities. For instance, the aniline unit in Re-2-SiO_2 and Re-4-SiO_2 could potentially alter the photophysical properties of the reaction system under the experimental conditions employed in this study. Further studies using time-resolved spectroscopic techniques are needed to reveal possible differences in photophysical properties.

Conclusions

We have utilized an amide linkage and an alkyl amine linkage to obtain heterogenized molecular catalysts by covalently attaching Re(bpy)$(CO)_3$Cl onto silica surface. Since derivatizing the bpy ligand with the amide group was previously shown to have detrimental effects on the photocatalytic activity of the Re(I) catalyst, using the alkyl amine linkage was expected to achieve improved photocatalysis. However, the opposite trend was observed in photocatalytic CO_2 reduction using these heterogenized Re(I) catalysts. Infrared studies suggest that the basic amine group led to the formation of a photocatalytically inactive Re(I)-OH species and contributed to the stabilization of a surface Re(I)-carboxylato species formed upon light irradiation. These spectroscopic observations were used to explain the low activity of the heterogenized Re(I) catalyst containing the alkyl amine linkage relative to the one containing the amide linkage. Our studies provide useful insights on the design of covalent linkages for the heterogenization of molecular catalysts for photocatalytic applications.

Conflicts of Interest

There are no conflicts to declare.

Acknowledgements

This research was supported by the U.S. National Science Foundation through grants 1352437 (materials synthesis, characterization, and photocatalysis) and 2247575 (analysis of infrared spectra).

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