

Cite this: *Dalton Trans.*, 2024, **53**, 2645

Solar CO₂ reduction using a molecular Re(I) catalyst grafted on SiO₂ via amide and alkyl amine linkages†

Thomas Fenton, Esraa Ahmad and Gonghu Li *

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 CO₂ 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 SiO₂ 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 CO₂ 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 SiO₂. 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.

Received 30th October 2023,
Accepted 3rd January 2024

DOI: 10.1039/d3dt03623e

rsc.li/dalton

Introduction

Photocatalytic CO₂ reduction has been extensively investigated in recent years as a sustainable way to utilize CO₂ as a renewable C1 feedstock.^{1–3} Different systems, including homogeneous and heterogeneous photocatalysts, have been developed to convert the thermodynamically stable CO₂ 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 CO₂, 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 CO₂ reduction.^{13,14}

While molecular catalysts are often highly efficient in mediating CO₂ 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 CO₂ reduction under solar irradiation.

We have employed SiO₂ as a model support for Re(bpy)(CO)₃Cl to carry out spectroscopic investigations since SiO₂ 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 SiO₂ involved derivatization of the bpy ligand with amide groups.^{25–27} However, such ligand derivatization resulted in significant 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 SiO₂ 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, activity of the amide-derivatized Re(I) complex was found to be much lower than Re(bpy)(CO)₃Cl in photocatalytic CO₂ reduction.²⁶ Derivatizing Re(bpy)(CO)₃Cl with amide groups also showed detrimental effects in electrocatalytic CO₂ 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

Department of Chemistry, University of New Hampshire, Durham, New Hampshire, 03824, USA. E-mail: gonghu.li@unh.edu

† Electronic supplementary information (ESI) available: Structures, UV-vis spectra, DRIFTS spectra and photocatalytic activities of two isomeric Re(I) catalysts. See DOI: <https://doi.org/10.1039/d3dt03623e>



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 $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ 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 $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ attached onto SiO_2 surfaces. In particular, three infrared absorptions associated with the formation of a photochemically inactive $\text{Re}(\text{I})\text{-OH}$ species were observed in the DRIFTS spectrum of a heterogenized $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ in the presence of triethanolamine (TEOA) and water.³⁰ This $\text{Re}(\text{I})\text{-OH}$ species was formed upon replacing the Cl^- ligand of $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ with $-\text{OH}$, 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 $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ onto SiO_2 to break the conjugation between the bpy ligand and the amide group. Surprisingly, the resulting heterogenized $\text{Re}(\text{I})$ 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 $\text{Re}(\text{I})\text{-OH}$ species and the stabilization of a surface $\text{Re}(\text{I})\text{-carboxylato}$ 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 tri-

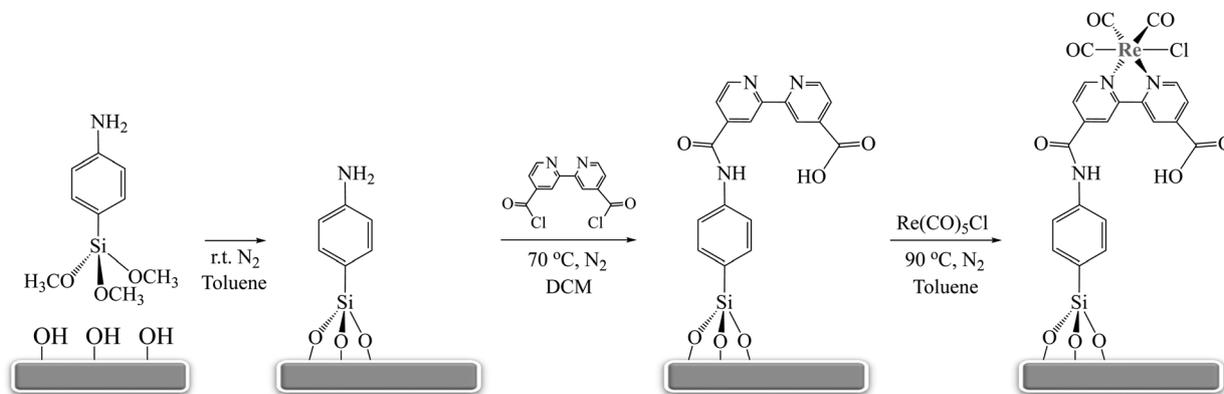
methoxysilane, were obtained from Gelest. All chemicals were used as received without any further purification.

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 $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ on SiO_2 *via* an amide linkage

The molecular $\text{Re}(\text{I})$ 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 yellow powder was isolated and dried under vacuum. The final product bearing an amide linkage is denoted "Re-1- SiO_2 " (Scheme 1).



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



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 SiO₂ 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-SiO₂", 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-SiO₂ and Re-4-SiO₂, were also synthesized starting with SiO₂ functionalized with *m*-aminophenyl trimethoxysilane (see Fig. S1† for their structures).

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-SiO₂ and Re-2-SiO₂, respectively. Optical spectra of the samples were obtained using a Cary 50 Bio spectrophotometer outfitted with a Barreliano diffuse reflectance probe. DRIFTS spectra were collected on a Nicolet 6700 FTIR spectrometer equipped with a Harrick Praying Mantis diffuse reflectance accessory.

Photocatalytic testing

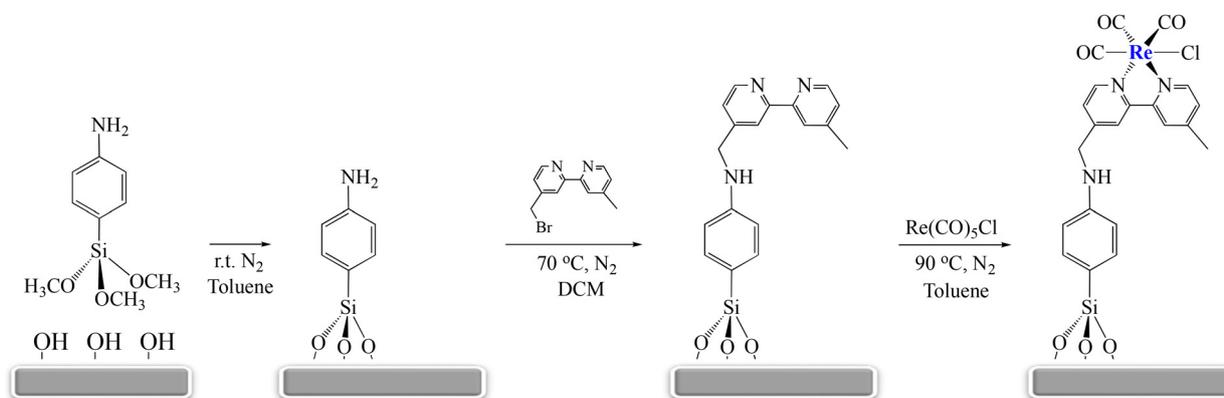
In a typical photocatalytic test, 10 mg of a heterogenized catalyst sample was dispersed in 4 mL of a DMF : TEOA (3 : 1 v/v) solution in a quartz test tube. A molecular photosensitizer, tris

(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 CO₂ (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 Fig. 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 slightly different colors. Their optical spectra were collected using a UV-visible spectrophotometer fitted with a diffuse reflectance accessory. Fig. 1 shows the spectra of Re-1-SiO₂ and Re-2-SiO₂, 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)₃Cl 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-SiO₂ compared to Re-2-SiO₂ 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-SiO₂ is similar to that of the homogeneous Re(bpy)(CO)₃Cl complex, indicating that ligand derivatization with the alkyl amine group has minimal effect on the MLCT band.

In our study, two isomeric heterogenized Re(I) catalysts, Re-3-SiO₂ and Re-4-SiO₂, were synthesized starting with SiO₂ functionalized with *m*-aminophenyl trimethoxysilane (Fig. S1†). The same difference was observed in the MLCT bands of Re-3-



Scheme 2 Synthesis of Re-2-SiO₂ featuring an alkyl amine linkage.



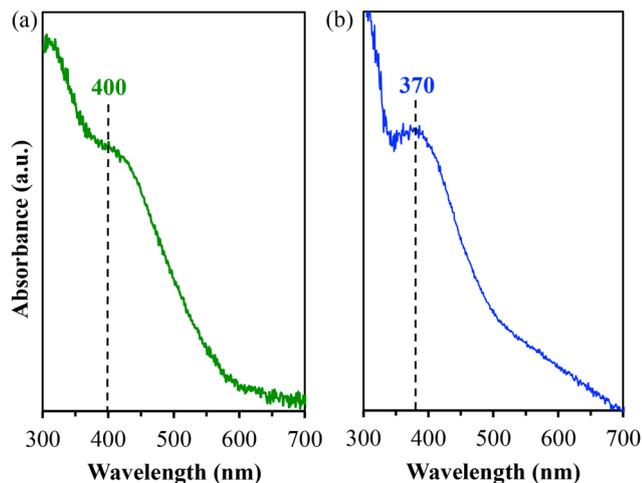


Fig. 1 Diffuse reflectance UV-vis spectra of (a) Re-1-SiO₂ and (b) Re-2-SiO₂. Barium sulfate was used as the background.

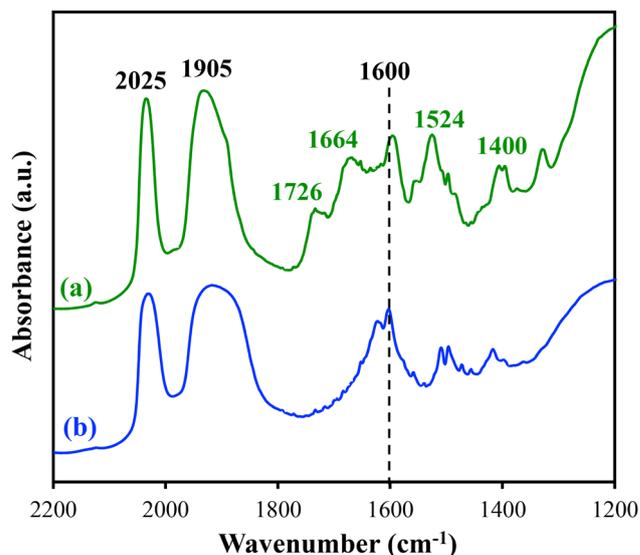


Fig. 2 DRIFTS spectra of (a) Re-1-SiO₂ and (b) Re-2-SiO₂. Potassium bromide was used as the background.

SiO₂ and Re-4-SiO₂, which contain amide and alkyl amine linkages, respectively (Fig. 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)₃Cl 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-SiO₂ and Re-2-SiO₂, 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 (Fig. 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-SiO₂ include absorptions associated with amide groups at 1664, 1524, and 1400 cm⁻¹ (Fig. 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-SiO₂ shown in Fig. 2a, corresponding to the -COOH group²⁶ on the bpy ligand (see the structure of Re-1-SiO₂ in Scheme 1). Both spectra shown in Fig. 2 also contain an absorption around 1600 cm⁻¹, which is attributed to the phenyl group in both Re-1-SiO₂ and Re-2-SiO₂.

The two lower-energy modes of the Re(i)-carbonyl stretches can be resolved by exposing the surface Re(i) complexes to TEOA and CO₂.^{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 CO₂ in the dark. Fig. 3 shows the DRIFTS spectra of Re-1-SiO₂ and Re-2-SiO₂ collected under CO₂. In the spectrum of Re-1-SiO₂ (Fig. 3a), three peaks at 2021, 1917, and 1895 cm⁻¹ are present, indicating the formation of a CO₂-bound Re(i) adduct, Re(i)-OOC-OCH₂CH₂NR₂,

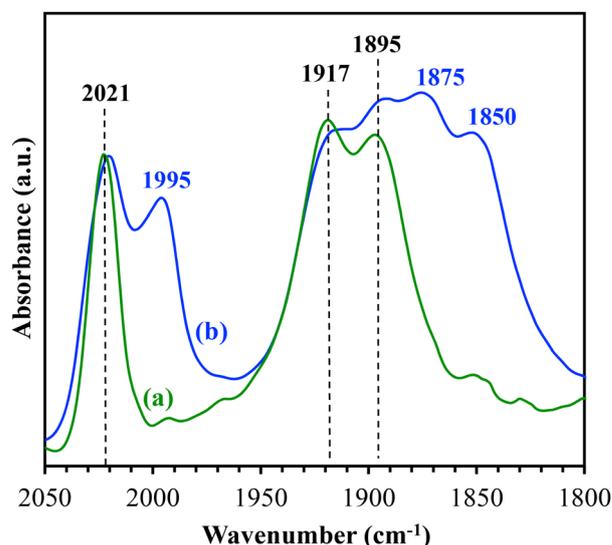


Fig. 3 DRIFTS spectra of (a) Re-1-SiO₂ and (b) Re-2-SiO₂ in the presence of TEOA and CO₂.

where R is CH₂CH₂OH, in the presence of TEOA and CO₂.³⁴ The Re(i)-OOC-OCH₂CH₂NR₂ species was suggested to be the real catalyst in photocatalytic CO₂ reduction using diimine-tri-carbonyl 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-SiO₂ (Fig. 3b). These three peaks are associated with a photochemically inactive Re(i)-OH species according to our previous study³⁰ and studies by Gibson and co-workers.³⁵ Since these three peaks are not present in the spectrum of Re-1-SiO₂, it can be deduced that the formation of the Re(i)-OH species in Re-2-SiO₂ is due to the



presence of the basic amine group, which likely produced $-OH$ to replace the Cl^- ligand on Re-2-SiO₂. The same difference was observed in the DRIFTS spectra of Re-3-SiO₂ and Re-4-SiO₂ (Fig. S4 and S5[†]), further confirming the observed effect of the basic amine group.

The synthesized samples demonstrated poor activity in photocatalytic CO₂ reduction under simulated solar irradiation (Fig. S6[†]). In this study, the heterogenized Re(I) catalysts were coupled with a molecular Ru(II) photosensitizer in visible-light CO₂ 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 CO₂ to CO, though formation of CH₄ was recently reported in photocatalytic CO₂ reduction using a molecular Re(I) complex.³⁶ Under the experimental conditions employed in this study, CO and a small amount of H₂ were detected as the only products; no appreciable production of HCOOH, HCHO, CH₃OH, or CH₄ was detected. Turnover numbers (TONs) for CO production of 13.6 and 4.5 were obtained using Re-1-SiO₂ and Re-2-SiO₂, respectively, after photocatalysis for 120 minutes (Fig. 4). Similar comparison was observed in photocatalysis using Re-3-SiO₂ and Re-4-SiO₂ (Fig. S7[†]).

The photocatalysis results shown in Fig. 4 are surprising since the alkyl amine linkage in Re-2-SiO₂ was expected to alleviate the detrimental effect of the electron-withdrawing amide group in Re-1-SiO₂. One of the reasons for the relatively lower activity of Re-2-SiO₂ is the formation of photocatalytically inactive Re(I)-OH species in the presence of TEOA, as indicated by its DRIFTS spectrum shown in Fig. 3b. As discussed earlier, the formation of Re(I)-OH species in Re-2-SiO₂ 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

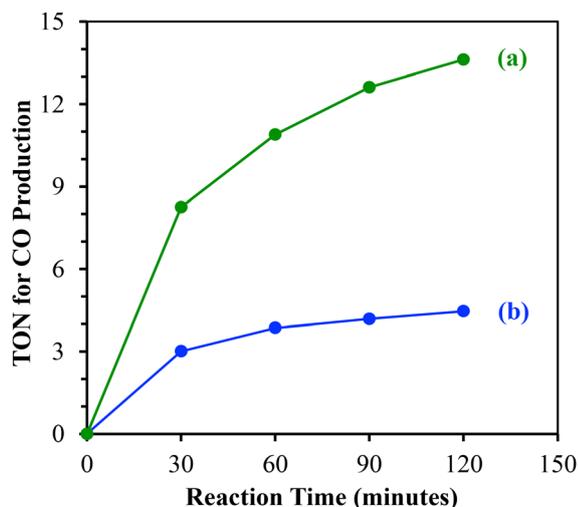


Fig. 4 CO production in photocatalytic CO₂ reduction using (a) Re-1-SiO₂ and (b) Re-2-SiO₂ under visible light using a molecular Ru(II) photosensitizer. Light intensity was 100 mW cm⁻².

purged with CO₂. For each sample, DRIFTS spectra were collected prior to and after exposing the samples to light irradiation. Difference spectra shown in Fig. 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-SiO₂ and Re-2-SiO₂ (Fig. 5), negative peaks at 2025 and 1925 cm⁻¹ are present and the peaks became more intense over time, indicating the consumption of the CO₂-bound Re(I) adduct, Re(I)-OOC-OCH₂CH₂NR₂, upon light irradiation. Positive peaks around 2003 and 1873 cm⁻¹ are seen in the spectra shown in Fig. 5. These positive peaks are associated with the formation of a reduced species similar to [Re(bpy)(CO)₃Cl]⁻.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-SiO₂ and Re-4-SiO₂ (Fig. S8[†]).

A unique feature in the difference spectra of Re-2-SiO₂ is the presence of a peak around 2017 cm⁻¹, which is absent from the spectra of Re-1-SiO₂ (Fig. 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-SiO₂ upon light irradiation.³⁷ These two peaks are also seen in the difference DRIFTS spectra of Re-4-SiO₂ but not in the difference spectra of Re-3-SiO₂ (Fig. S8[†]). A viable intermediate in CO₂ reduction

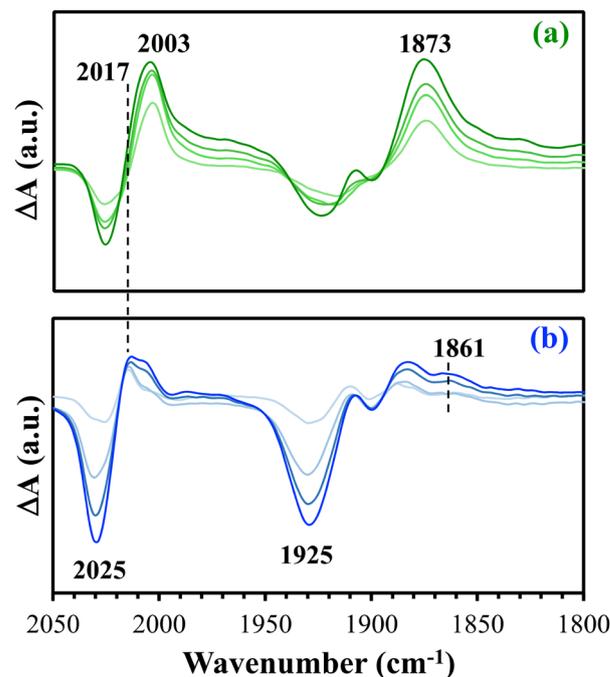


Fig. 5 Difference DRIFTS spectra of (a) Re-1-SiO₂ and (b) Re-2-SiO₂ upon light irradiation in the presence of TEOA and CO₂. The spectra were obtained by subtracting spectra collected before light irradiation ($t = 0$) from corresponding spectra collected after light irradiation for different times (2, 10, 30, and 60 min).



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 Fig. 5 and S7† implies that the photochemically produced Re(I)-carboxylato species is stabilized in Re-2-SiO₂ and Re-4-SiO₂ 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 Fig. 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 studies³⁰ 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 CO₂ reduction. These two consequences of using the alkyl amine linkage in catalyst heterogenization likely contributed to the observed relatively low activity of Re-2-SiO₂ (Fig. 4) and Re-4-SiO₂ (Fig. S7†).

Due to the presence of the phenyl group, the alkyl amine in Re-2-SiO₂ and Re-4-SiO₂ should be less basic than TEOA, although it is more basic than the amide group in Re-1-SiO₂ and Re-3-SiO₂. Since the spectra shown in Fig. 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-SiO₂ and Re-4-SiO₂, 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-SiO₂ or Re-3-SiO₂, 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-SiO₂ and Re-4-SiO₂ 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)₃Cl 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 CO₂ 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).

References

- 1 M. Mikkelsen, M. Jorgensen and F. C. Krebs, The Teraton Challenge. A Review of Fixation and Transformation of Carbon Dioxide, *Energy Environ. Sci.*, 2010, **3**, 43–81.
- 2 P. D. Tran, L. H. Wong, J. Barber and J. S. C. Loo, Recent advances in hybrid photocatalysts for solar fuel production, *Energy Environ. Sci.*, 2012, **5**, 5902–5918.
- 3 A. M. Appel, J. E. Bercaw, A. B. Bocarsly, H. Dobbek, D. L. DuBois, M. Dupuis, J. G. Ferry, E. Fujita, R. Hille, P. J. A. Kenis, C. A. Kerfeld, R. H. Morris, C. H. F. Peden, A. R. Portis, S. W. Ragsdale, T. B. Rauchfuss, J. N. H. Reek, L. C. Seefeldt, R. K. Thauer and G. L. Waldrop, Opportunities, and Challenges in Biochemical and Chemical Catalysis of CO₂ Fixation, *Chem. Rev.*, 2013, **113**, 6621–6658.
- 4 B. Kumar, M. Llorente, J. Froehlich, T. Dang, A. Sathrum and C. P. Kubiak, Photochemical and photoelectrochemical reduction of CO₂, *Annu. Rev. Phys. Chem.*, 2012, **63**, 541–569.
- 5 J. L. White, M. F. Baruch, J. E. Pander, Y. Hu, I. C. Fortmeyer, J. E. Park, T. Zhang, K. Liao, J. Gu, Y. Yan, T. W. Shaw, E. Abelev and A. B. Bocarsly, Light-Driven Heterogeneous Reduction of Carbon Dioxide: Photocatalysts and Photoelectrodes, *Chem. Rev.*, 2015, **115**, 12888–12935.
- 6 Y. Tamaki and O. Ishitani, Supramolecular Photocatalysts for the Reduction of CO₂, *ACS Catal.*, 2017, **7**, 3394–3409.
- 7 Y. Wang, D. He, H. Chen and D. Wang, Catalysts in electro-, photo- and photoelectrocatalytic CO₂ reduction reactions, *J. Photochem. Photobiol., C*, 2019, **40**, 117–149.
- 8 K. E. Dalle, J. Warnan, J. J. Leung, B. Reuillard, I. S. Karmel and E. Reisner, Electro- and Solar-Driven Fuel Synthesis with First Row Transition Metal Complexes, *Chem. Rev.*, 2019, **119**, 2752–2875.



- 9 E. Fujita, Photochemical carbon dioxide reduction with metal complexes, *Coord. Chem. Rev.*, 1999, **185–186**, 373–384.
- 10 A. J. Morris, G. J. Meyer and E. Fujita, Molecular Approaches to the Photocatalytic Reduction of Carbon Dioxide for Solar Fuels, *Acc. Chem. Res.*, 2009, **42**, 1983–1994.
- 11 C. D. Windle and R. N. Perutz, Advances in molecular photocatalytic and electrocatalytic CO₂ reduction, *Coord. Chem. Rev.*, 2012, **256**, 2562–2570.
- 12 E. Boutin, L. Merakeb, B. Ma, B. Boudy, M. Wang, J. Bonin, E. Anxolabéhère-Mallart and M. Robert, Molecular catalysis of CO₂ reduction: recent advances and perspectives in electrochemical and light-driven processes with selected Fe, Ni and Co aza macrocyclic and polypyridine complexes, *Chem. Soc. Rev.*, 2020, **49**, 5772–5809.
- 13 J. Hawecker, J.-M. Lehn and R. Ziessel, Efficient Photochemical Reduction of CO₂ to CO by Visible Light Irradiation of Systems Containing Re(bipy)(CO)₃X or Ru(bipy)₃²⁺-Co²⁺ Combinations as Homogeneous Catalysts, *J. Chem. Soc., Chem. Commun.*, 1983, 536–538.
- 14 G. Sahara and O. Ishitani, Efficient Photocatalysts for CO₂ Reduction, *Inorg. Chem.*, 2015, **54**, 5096–5104.
- 15 C. D. Windle and E. Reisner, Heterogenised Molecular Catalysts for the Reduction of CO₂ to Fuels, *Chimia*, 2015, **69**, 435–441.
- 16 M. E. Louis, T. G. Fenton, J. Rondeau, T. Jin and G. Li, Solar CO₂ Reduction Using Surface-Immobilized Molecular Catalysts, *Comments Inorg. Chem.*, 2016, **36**, 38–60.
- 17 K. Maeda, Metal-Complex/Semiconductor Hybrid Photocatalysts and Photoelectrodes for CO₂ Reduction Driven by Visible Light, *Adv. Mater.*, 2019, **31**, 1808205.
- 18 A. Perazio, G. Lowe, R. Gobetto, J. Bonin and M. Robert, Light-driven catalytic conversion of CO₂ with heterogenized molecular catalysts based on fourth period transition metals, *Coord. Chem. Rev.*, 2021, **443**, 214018.
- 19 P. Huang, E. Shaaban, E. Ahmad, A. St. John, T. Jin and G. Li, Well-defined surface catalytic sites for solar CO₂ reduction: heterogenized molecular catalysts and single atom catalysts, *Chem. Commun.*, 2023, **59**, 9301–9319.
- 20 N. M. Orchanian, L. E. Hong, J. A. Skrainka, J. A. Esterhuizen, D. A. Popov and S. C. Marinescu, Surface-Immobilized Conjugated Polymers Incorporating Rhenium Bipyridine Motifs for Electrocatalytic and Photocatalytic CO₂ Reduction, *ACS Appl. Energy Mater.*, 2019, **2**, 110–123.
- 21 M. Abdellah, A. M. El-Zohry, L. J. Antila, C. D. Windle, E. Reisner and L. Hammarström, Time-Resolved IR Spectroscopy Reveals a Mechanism with TiO₂ as a Reversible Electron Acceptor in a TiO₂-Re Catalyst System for CO₂ Photoreduction, *J. Am. Chem. Soc.*, 2017, **139**, 1226–1232.
- 22 C. D. Windle, E. Pastor, A. Reynal, A. C. Whitwood, Y. Vaynzof, J. R. Durrant, R. N. Perutz and E. Reisner, Improving the Photocatalytic Reduction of CO₂ to CO through Immobilization of a Molecular Re Catalyst on TiO₂, *Chem. – Eur. J.*, 2015, **21**, 3746–3754.
- 23 C. L. Anfuso, R. C. Snoeberger III, A. M. Ricks, W. Liu, D. Xiao, V. S. Batista and T. Lian, Covalent Attachment of a Rhenium Bipyridyl CO₂ Reduction Catalyst to Rutile TiO₂, *J. Am. Chem. Soc.*, 2011, **133**, 6922–6925.
- 24 K. D. Dubois, A. Petushkov, E. G. Cardona, S. C. Larsen and G. Li, Adsorption and Photochemical Properties of a Molecular CO₂ Reduction Catalyst in Hierarchical Mesoporous ZSM-5: An In Situ FTIR Study, *J. Phys. Chem. Lett.*, 2012, **3**, 486–492.
- 25 K. D. Dubois, H. He, C. Liu, A. S. Vorushilov and G. Li, Covalent attachment of a molecular CO₂-reduction photocatalyst to mesoporous silica, *J. Mol. Catal. A: Chem.*, 2012, **363–364**, 208–213.
- 26 C. Liu, K. D. Dubois, M. E. Louis, A. S. Vorushilov and G. Li, Photocatalytic CO₂ Reduction and Surface Immobilization of a Tricarbonyl Re(i) Compound Modified with Amide Groups, *ACS Catal.*, 2013, **3**, 655–662.
- 27 T. G. Fenton, M. E. Louis and G. Li, Effect of ligand derivatization at different positions on photochemical properties of hybrid Re(i) photocatalysts, *J. Mol. Catal. A: Chem.*, 2016, **411**, 272–278.
- 28 X. Jia, H. S. Nedzbal, S. R. Bottum, J. F. Cahoon, J. J. Concepcion, C. L. Donley, A. Gang, Q. Han, N. Hazari, M. C. Kessinger, M. R. Lockett, J. M. Mayer, B. Q. Mercado, G. J. Meyer, A. J. Pearce, C. L. Rooney, R. N. Sampaio, B. Shang and H. Wang, Synthesis and Surface Attachment of Molecular Re(i) Complexes Supported by Functionalized Bipyridyl Ligands, *Inorg. Chem.*, 2023, **62**, 2359–2375.
- 29 A. Ge, B. Rudshiteyn, P. E. Videla, C. J. Miller, C. P. Kubiak, V. S. Batista and T. Lian, Heterogenized Molecular Catalysts: Vibrational Sum-Frequency Spectroscopic, Electrochemical, and Theoretical Investigations, *Acc. Chem. Res.*, 2019, **52**, 1289–1300.
- 30 H. He, C. Liu, M. E. Louis and G. Li, Infrared studies of a hybrid CO₂-reduction photocatalyst consisting of a molecular Re(i) complex grafted on Kaolin, *J. Mol. Catal. A: Chem.*, 2014, **395**, 145–150.
- 31 K. L. V. Joseph, J. Lim, A. Anthonysamy, H.-i. Kim, W. Choi and J. K. Kim, Squaraine-sensitized composite of a reduced graphene oxide/TiO₂ photocatalyst: π - π stacking as a new method of dye anchoring, *J. Mater. Chem. A*, 2015, **3**, 232–239.
- 32 J. M. Smieja and C. P. Kubiak, Re(bipy-tBu)(CO)₃Cl-improved Catalytic Activity for Reduction of Carbon Dioxide: IR-Spectroelectrochemical and Mechanistic Studies, *Inorg. Chem.*, 2010, **49**, 9283–9289.
- 33 M. E. Louis and G. Li, Infrared studies of surface carbonate binding to diimine-tricarbonyl Re(i) and Mn(i) complexes in mesoporous silica, *J. Coord. Chem.*, 2019, **72**, 1336–1345.
- 34 T. Morimoto, T. Nakajima, S. Sawa, R. Nakanishi, D. Imori and O. Ishitani, CO₂ Capture by a Rhenium(i) Complex with the Aid of Triethanolamine, *J. Am. Chem. Soc.*, 2013, **135**, 16825–16828.
- 35 D. H. Gibson, X. Yin, H. He and M. S. Mashuta, Synthesis and reactions of fac-[Re(dmbpy)(CO)₃X] (dmbpy = 4,4'-dimethyl-2,2'-bipyridine; X = COOH, CHO) and their derivatives, *Organometallics*, 2003, **22**, 337–346.



- 36 J. K. Nganga, L. M. Wolf, K. Mullick, E. Reinheimer, C. Saucedo, M. E. Wilson, K. A. Grice, M. Z. Ertem and A. M. Angeles-Boza, Methane Generation from CO₂ with a Molecular Rhenium Catalyst, *Inorg. Chem.*, 2021, **60**, 3572–3584.
- 37 D. H. Gibson and H. He, Synthesis and properties of fac-Re(dmbpy)(CO)₃CHO (dmbpy = 4,4'-dimethyl-2,2'-bipyridine), a possible intermediate in reductions of CO₂ catalyzed by fac-Re(dmbpy)(CO)₃Cl, *Chem. Commun.*, 2001, 2082–2083.
- 38 C. Riplinger, M. D. Sampson, A. M. Ritzmann, C. P. Kubiak and E. A. Carter, Mechanistic Contrasts between Manganese and Rhenium Bipyridine Electrocatalysts for the Reduction of Carbon Dioxide, *J. Am. Chem. Soc.*, 2014, **136**, 16285–16298.

