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Photoinduced activation of CO_2 by rhenium complexes encapsulated in molecular sieves[†]

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The photochemical activation and reduction of CO_2 over a molecular-sieve-encapsulated rhenium complex was investigated under photoirradiation ($\lambda > 350$ *nm*) at room temperature. $Re(CO)_3(bpy)Cl$ and $[Re(CO)_3(bpy)(py)]^+$ were respectively encapsulated in the microporous NaY and the mesoporous AlMCM-41 molecular sieve acting as supramolecular heterogeneous host. The molecular-sieve-encapsulated rhenium complexes were characterized by diffuse reflectance (DR) ultraviolet–visible (UV–vis), photoluminescence, and Fourier transform infrared (FTIR) spectroscopy. The interaction between the excited state of encapsulated rhenium complexes and the adsorbed CO_2 was observed in photoluminescence spectra. The radicals of rhenium complexes encapsulated in NaY and AlMCM-41 were produced with photoirradiation and confirmed by DR UV–vis spectra. By monitoring the photoreaction of CO_2 over the molecular-sieve-encapsulated rhenium complexes using FTIR spectroscopy and gas chromatography, the conversion of CO_2 into CO and carbonate species was observed. The molecular-sieve-encapsulated rhenium complexes showed photocatalytic activity for the activation and reduction of CO_2. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: $Re(CO)_3(bpy)Cl$; $[Re(CO)_3(bpy)(py)]^+$; molecular sieve; NaY; AlMCM-41; photochemical activation and reduction of CO_2; FTIR; photoluminescence

INTRODUCTION

The activation and reduction of carbon dioxide into fuels and organic compounds has been an active and important area of research due to the increase of CO_2 emission and global environmental problems.[1] The CO_2 activation has been accomplished by chemical,[2] electrochemical,[3] and photochemical reactions.[4] Photochemical reduction of CO_2 has been extensively studied as a major goal of artificial photosynthesis using various photocatalyst systems.[4–7] The photocatalyst systems for CO_2 reduction are classified into heterogeneous semiconductor suspensions,[4] homogeneous aqueous solutions of organic dye,[5] and transition metal complexes.[6,7] Recently, the interest in photophysics and photochemistry of rhenium(I) complexes has increased owing to their potential utility for the activation and reduction of CO_2 in artificial photosynthetic systems.[4–7] Rhenium complexes such as $ReX(CO)_3(bpy)$ ($X = Cl$, Br) and $Re(CO)_2(bpy)[P(OEt)_3]_2$ have been used as photocatalysts for CO_2 reduction to CO in a solvent mixture of triethanolamine–dimethylformamide.[6,7] Most of the research on photochemical activation and reduction of CO_2 using rhenium(I) complexes has focused on the homogeneous solution systems. There are few reports concerned with encapsulation of rhenium complexes into zeolite and their photochemical application to CO_2 reduction.

Based on host–guest interaction, molecular sieves have been used as heterogeneous hosts for the encapsulation of guest molecules, such as organic molecules, metal complexes and organometallic fragments.[8,9] Such inorganic solid-state supramolecular systems generate the microheterogenization of the encapsulated molecular assemblies that show the photocatalytic activity. For zeolite-entrapped complexes, the steric and electrostatic constraints imposed on the complexes within the channels or cages of zeolites can alter the photochemical and photophysical properties of the guest complexes and diminish the photodegradation and undesirable electron transfer reactions.[9]

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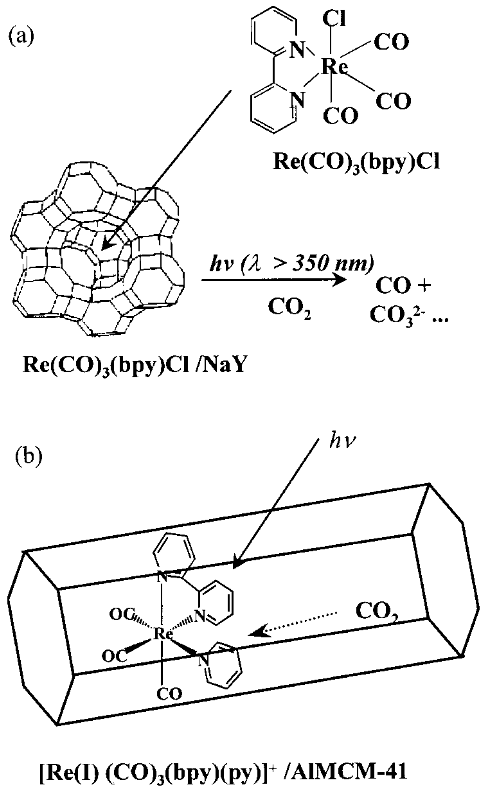

Figure 1 Process of photoinduced activation and reduction of CO_2 over encapsulated rhenium complexes: (a) $Re(CO)_3(bpy)Cl/NaY$; (b) $[Re(CO)_3(bpy)(py)]^+/AlMCM-41$.

In this study, $Re(CO)_3(bpy)Cl$ and bulky $[Re(CO)_3(bpy)(py)]^+$ encapsulated in NaY and AlMCM-41 molecular sieves have been applied to photochemical activation and reduction of CO_2. Encapsulated rhenium complexes were characterized by Fourier transform infrared spectroscopy (FTIR), diffuse reflectance (DR) ultraviolet–visible (UV–vis) spectroscopy, and photoluminescence spectroscopy with photoirradiation. The photoactivation and reduction of CO_2 over rhenium-complex-encapsulated molecular sieves were studied by *in situ* FTIR and gas chromatography (GC) with photoirradiation at room temperature.

EXPERIMENTAL

Two rhenium complexes, $Re(CO)_3(bpy)Cl$ (bpy = 2,2′-bipyridine) and $[Re(CO)_3(bpy)(py)]^+$, were used as photosensitizers. $Re(CO)_3(bpy)Cl$ (bpy = 2,2′-bipyridine) was encapsulated into the microporous NaY zeolite by liquid adsorption. The bulky $[Re(CO)_3(bpy)(py)]^+$ complex was encapsulated into the mesoporous AlMCM-41 (Si/Al = 30) molecular sieve by the ion-exchange method using an aqueous solution of $[Re(CO)_3(bpy)(py)]^+PF_6^-$. The encapsulated rhenium complexes were evacuated ($<10^{-4}$ Torr) at 100 °C for 16 h and characterized by FTIR, DR UV–vis, and photoluminescence spectroscopy. To study the photoreaction of CO_2 over these encapsulated rhenium complexes using *in situ* FTIR, the pellet of $Re(CO)_3(bpy)Cl/NaY$ or $[Re(CO)_3(bpy)(py)]^+/AlMCM-41$ was placed into an *in situ* quartz cell with a CaF_2 window for FTIR measurement and evacuated to about 10^{-4} Torr at 200 °C for 12 h. Then, CO_2 was adsorbed onto the evacuated pellet followed by photoirradiation ($\lambda > 350$ nm) from a 300 W high-pressure xenon arc lamp (Oriel Instruments). FTIR spectra were recorded according to photoirradiation time. Bulk photoreaction of CO_2 over encapsulated rhenium complexes was done in a quartz tube connected to a vacuum line and the product analyzed by GC.

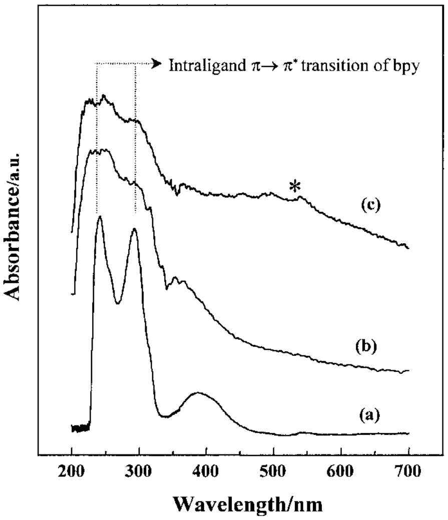

Figure 2 UV–vis absorption spectra of (a) solution of $Re(CO)_3(bpy)Cl$ in CH_2Cl_2, (b) $Re(CO)_3(bpy)Cl/NaY$, and (c) $Re(CO)_3(bpy)Cl/NaY$ after photoirradiation.

RESULTS AND DISCUSSION

The molecular-sieve-encapsulated rhenium com-

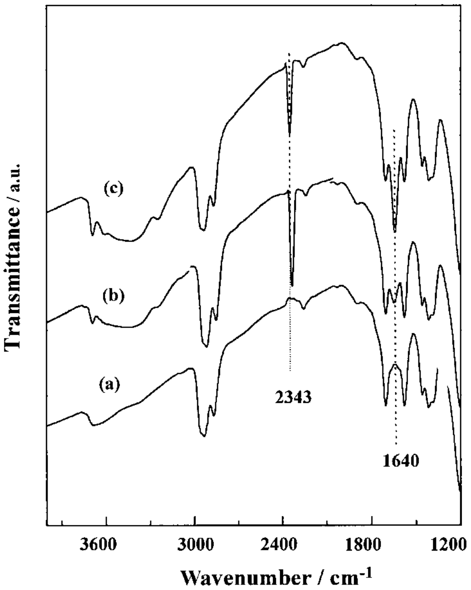

Figure 3 FTIR spectra of Re(CO)$_3$(bpy)Cl/NaY (a) after evacuation, (b) with CO$_2$ adsorption, and (c) with photoirradiation.

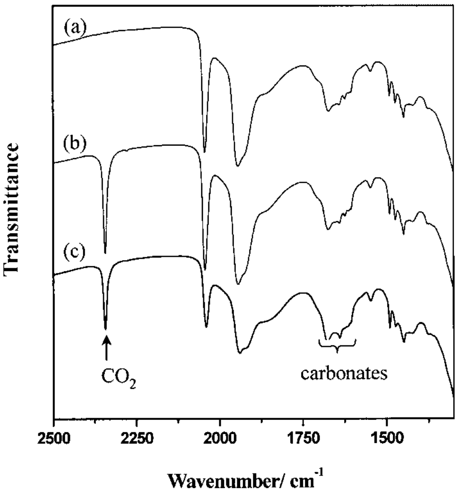

Figure 4 FTIR spectra of [Re(CO)$_3$(bpy)(py)]$^+$/AlMCM-41 (a) after evacuation, (b) with CO$_2$ adsorption, and (c) with photoirradiation at room temperature.

plexes of Re(CO)$_3$(bpy)Cl/NaY and [Re(CO)$_3$(bpy)(py)]$^+$/AlMCM-41 are shown in Fig. 1. Both encapsulated complexes showed the photocatalytic activities for CO$_2$ activation and reduction into CO and carbonate. The results are discussed as follows.

Re(CO)$_3$(bpy)Cl/NaY system

As shown in Fig. 2(a), the DR UV–vis spectrum of Re(CO)$_3$(bpy)Cl complex in CH$_2$Cl$_2$ solution shows two absorption bands at 250 and 280 nm due to an intraligand $\pi \rightarrow \pi^*$ transition of bpy ligand and an absorption band at 390 nm due to metal-to-charge transfer (MLCT) transition from the rhenium ($d\pi$) to the bpy ($p\pi^*$) orbital.[10] The DR UV–vis spectrum of Re(CO)$_3$(bpy)Cl/NaY in Fig. 2(b) also shows three absorption bands at 250, 280, and 380 nm. Upon photoirradiation ($\lambda > 350$ nm) of Re(CO)$_3$(bpy)Cl/NaY in the presence of CO$_2$, a new absorption band appeared at 520 nm which is assigned to [Re(CO)$_3$(bpy$^{\cdot -}$)Cl]$^-$.[11] The radical of [Re(CO)$_3$(bpy$^{\cdot -}$)Cl]$^-$/NaY produced by photoirradiation seems to be an active species for the activation and reduction of CO$_2$.

Photoirradiation over Re(CO)$_3$(bpy)Cl/NaY under 100 Torr CO$_2$ for 2 h led to the formation of CO in the gas-phase analysis by GC. In addition to CO, carbonate (CO$_3^{2-}$) species adsorbed on the NaY surface were obtained after photoirradiation of Re(CO)$_3$(bpy)Cl/NaY in the presence of CO$_2$. Figure 3 shows the FTIR spectra of CO$_2$ and CO$_3^{2-}$ species adsorbed on Re(CO)$_3$(bpy)Cl/NaY proceeding from the photoreaction using the *in situ* FTIR cell. The FTIR spectra in Fig. 3 can be assigned as follows:[12] (1) the main bands at 1473 and 1413 cm^{-1} correspond to the symmetric and asymmetric stretching vibration modes of unidentate carbonate (species I) Na—O—CO$_2^{2-}$ coordinated to the sodium ions of NaY zeolite; (2) the bands at 1704 and 1576 cm^{-1} are due to bidentate carbonate (species II) Na—(O)$_2$—C=O coordinated to the sodium ions of NaY zeolite; (3) the band at 1640 cm^{-1} corresponds to the bicarbonate (species III) Na—O—C(=O)OH formed from the interaction between CO$_2$ and the OH group on the zeolite surface. In addition, the band at 2343 cm^{-1} comes from CO$_2$ adsorbed on the zeolite surface. With photoirradiation, the C=O stretching band at 1640 cm^{-1} for bicarbonate species III gradually increased along with a reduction of the CO$_2$ peak intensity at 2343 cm^{-1}, while the amounts of other carbonate species such as unidentate and bidentate carbonates did not change significantly. These results indicate that the carbonate species are formed along with CO via a photoinduced reduction of CO$_2$ over Re(CO)$_3$(bpy)Cl/NaY as evidenced by FTIR and GC analyses.

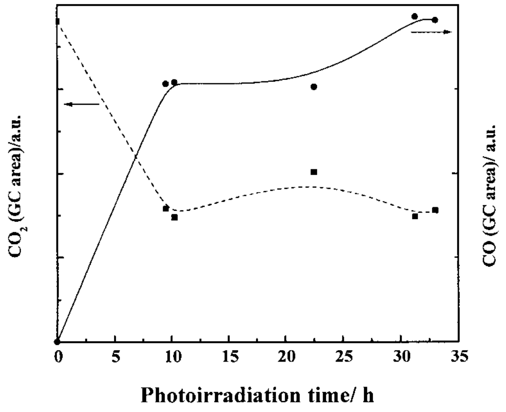

Figure 5 Plots of GC area changes of CO and CO_2 according to CO_2 photoreaction over $[Re(CO)_3(bpy)(py)]^+$/AlMCM-41.

It has been known that the surface of the framework of the aluminosilicate zeolites shows an electron-donating property to proper electron acceptors encapsulated in their pores with or without photoirradiation.[9] In the $Re(CO)_3(bpy)Cl$/NaY system, the NaY framework may act as an electron donor to generate a $[Re(CO)_3(bpy^{\cdot -})Cl]^-$ radical with photoirradation and mediate the electron transfer from the $[Re(CO)_3(bpy^{\cdot -})Cl]^-$ radical to CO_2, resulting in the conversion of CO_2 into CO and carbonate species.

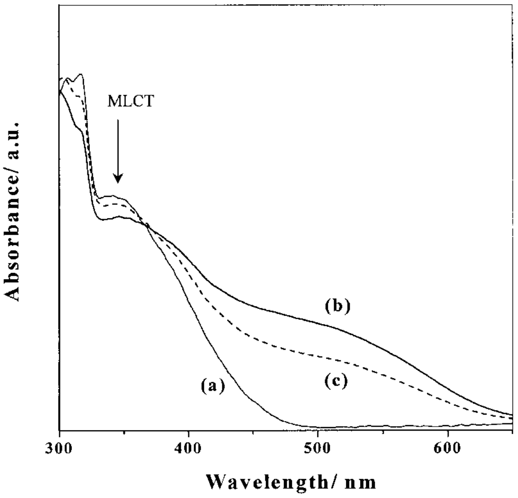

Figure 6 DR UV–vis spectra of $[Re(CO)_3(bpy)(py)]^+$/AlMCM-41 (a) after evacuation, (b) with photoirradiation, and (c) with CO_2 adsorption.

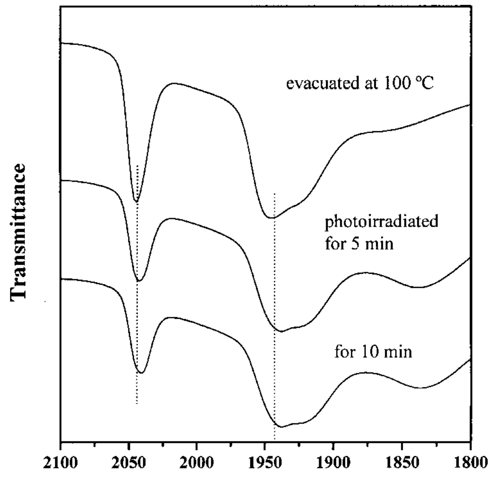

Figure 7 FTIR spectra of $[Re(CO)_3(bpy)(py)]^+$/AlMCM-41 with photoirradiation.

$[Re(CO)_3(bpy)(py)]^+$/AlMCM-41 system

Since the cationic $[Re(CO)_3(bpy)(py)]^+$ is too bulky to fit the cage of microporous NaY, the mesoporous AlMCM-41 molecular sieve with a pore size of about 21 Å was used as a heterogene-

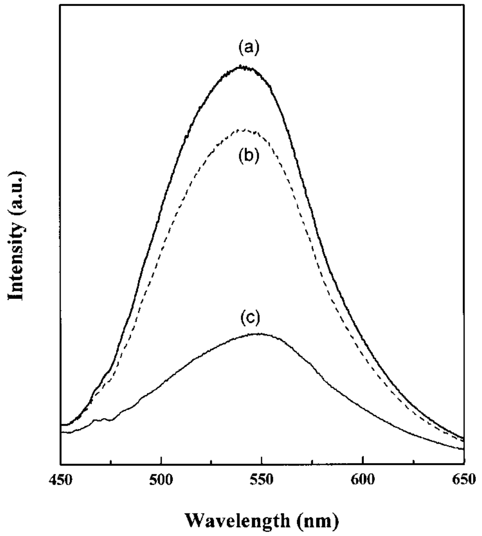

Figure 8 Photoluminescnce spectra of $[Re(CO)_3(bpy)(py)]^+$/AlMCM-41 at 77 K (a) after evacuation, (b) CO_2 adsorption, and (c) with photoirradiation.

ous host for the encapsulation of this rhenium complex by the ion-exchange method using an aqueous solution of $[Re(CO)_3(bpy)(py)]^+PF_6$.

With photoirradiation onto CO_2-adsorbed $[Re(CO)_3(bpy)(py)]^+$/AlMCM-41, the formation of carbonates and CO was confirmed by FTIR and GC analyses. In Fig. 4, the intensity of the CO_2 band at 2343 cm^{-1} decreased and the carbonate bands at 1400–1700 cm^{-1} increased.[12] From the GC analysis in Fig. 5, CO was also produced along with carbonated species over $[Re(CO)_3(bpy)(py)]^+$/AlMCM-41. This result indicates that $[Re(CO)_3$-$(bpy)(py)]^+$/AlMCM-41 shows photocatalytic activity for photoinduced activation and reduction of CO_2 into CO and $CO_3{}^{2-}$ like $Re(CO)_3(bpy)Cl$/NaY.

The DR UV–vis absorption spectra of $[Re(CO)_3(bpy)(py)]^+$/AlMCM-41 are shown in Fig. 6. After photoirradiation new absorption bands appeared at 380–530 nm, as shown in Fig. 7(b), which are assigned to $[Re(CO)_3(bpy^{\cdot-})(py)]$.[13] With CO_2 adsorption, the absorbance at 380–530 nm decreased as shown in Fig. 6(c), which means that CO_2 reacts with $[Re(CO)_3(bpy^{\cdot-})(py)]$ in AlMCM-41. The FTIR spectra in Fig. 7 also support the formation of the $[Re(CO)_3(bpy^{\cdot-})(py)]$ radical in AlMCM-41 with photoirradiation. The v(CO) values of $[Re(CO)_3(bpy)(py)]^+$/AlMCM-41 shift to lower frequency as shown in Fig. 7, which indicates the formation of $[Re(CO)_3(bpy^{\cdot-})(py)]$.[14] It has been known that the reduction of the metal–carbonyl complexes is accompanied by a lowering of v(CO) in the reduced complexes due to back-donation.[14] These results indicate that $[Re(CO)_3(bpy)(py)]^+$ in AlMCM-41 is reduced into $[Re(CO)_3(bpy^{\cdot-})(py)]$ with photoirradiation. Like the NaY framework, the framework of aluminosilicate AlMCM-41 is assumed to act as an electron donor to provide an electron to $[Re(CO)_3(bpy)(py)]^+$ to form the radical of $[Re(CO)_3(bpy^{\cdot-})(py)]$ in AlMCM-41, which is an active species for photoactivation and reduction of CO_2.

$[Re(CO)_3(bpy)(py)]^+$/AlMCM-41 showed photoluminescence at 77 K due to the MLCT band, as shown in Fig. 8(a). With CO_2 adsorption and photoirradition, the photoluminescence intensity decreased greatly, as shown Fig. 8(c); this indicates that CO_2 interacts with $[Re(CO)_3(bpy^{\cdot-})(py)]$.[15] The results suggest that $[Re(CO)_3(bpy)(py)]^+$ in AlMCM-41 is reduced into the radical of $[Re(CO)_3(bpy^{\cdot-})(py)]$ by photoirradiation in the presence of CO_2 followed by activation and reduction of CO_2.

CONCLUSIONS

The encapsulated rhenium complexes of $Re(CO)_3(bpy)Cl$/NaY and $[Re(CO_3(bpy)(py)]^+$/AlMCM-41 showed activity for photoinduced activation and reduction of CO_2 in CO and carbonate species. It is assumed that the aluminosilicate frameworks of microporous NaY and mesoporous AlMCM-41 molecular sieves act as electron donors to form $[Re(CO)_3(bpy^{\cdot-})Cl]^-$ and $[Re(CO)_3(bpy^{\cdot-})(py)]$ radicals, which are active species for the activation and reduction of CO_2 into CO and carbonate species.

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