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Photocatalytic Activation of CO_2 under Visible Light by Rhenium Complex Encapsulated in Molecular Sieves

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Abstract−The photocatalytic activation of CO_2 over molecular sieve-encapsulated cationic rhenium complex has been investigated under visible light (λ>350 nm). The cationic rhenium complex, $[Re(I)(CO)_3(bpy)(py)]^+$ (bpy=2,2'-bipyridine, py=pyridine), has been encapsulated by ion-exchange method using the aqueous solution of $[Re(I)(CO)_3(bpy)(py)]^+PF_6^-$ into the microporous NaY and the mesoporous AlMCM-41 molecular sieve acting as supramolecular heterogeneous host. To confirm the encapsulation of $[Re(I)(CO)_3(bpy)(py)]^+$ into the pores of molecular sieve, Xe-NMR and FT-IR spectroscopies have been applied before and after the $[Re(I)(CO)_3(bpy)(py)]^+$ encapsulation. To investigate the photophysical and photochemical properties, molecular sieve-encapsulated cationic rhenium complex has been studied by UV-Visible diffuse reflectance spectroscopy (UV-DRS) with photoirradiation (λ>350 nm) at room temperature. By monitoring the photoreaction of CO_2 over the photocatalysts, the conversion of CO_2 into CO and carbonate species has been observed by using *in-situ* FT-IR and time-resolved mass spectroscopy. From the experimental results, the photocatalytic activation mechanism of CO_2 on the catalyst under visible light (λ>350 nm) could be proposed via the photo-induced reaction of two electrons and two protons, resulting from water decomposition.

Key words: Cationic Rhenium Complex, FT-IR, Mass Spectroscopy, Molecular Sieve, Photocatalytic Activation of CO_2, UV-DRS, Visible Light

INTRODUCTION

Since photosensitized decomposition of water on TiO_2 electrodes was discovered, semiconductor photocatalysis has received much attention due to its potential to convert solar energy into electrical or chemical energy [Chevaleeski et al., 2001; Anpo et al., 2000]. The continued increase of the atmospheric CO_2 concentration due to human and anthropogenic activities is predicted to lead to significant changes in climate [Cox et al., 2000]. On-going efforts of recycling CO_2 into useful fuels and organic compounds have received much attention of many research groups because of the concern for solving global warming problems [Meyer, 1989]. The CO_2 activation was accomplished by chemical, electrochemical, and photochemical reactions [Reinking et al., 1989; Amatore et al., 1981; Halmann, 1978]. Photocatalytic activation of CO_2 has been extensively studied as a major goal of artificial photosynthesis using various photocatalyst systems [Halmann, 1978; Hawecker et al., 1986; Sullivan et al., 1984]. The photocatalyst systems for CO_2 activation are classified into heterogeneous semiconductor suspensions, homogeneous aqueous solutions of organic dye, and transition metal complexes. Recently, the interest in photochemistry of Re (I) complexes has increased due to their potential utility for the CO_2 activation in artificial photosynthetic systems. Rhenium complexes such as $ReX(CO)_3(bpy)$ (X=Cl, Br) and $Re(CO)_3(bpy)[P(OEt)_3]_2$ have been used as photocatalysts for CO_2 reduction to CO in solvent mixture of triethanolamine/dimethylformamide. Most of the research on photochemical activation of CO_2 using Re (I) complexes has focused on the homogeneous solution systems. Some efforts have been reported in connection with encapsulation of rhenium complexes into zeolite and their photochemical application to CO_2 activation [Sung-Suh et al., 2000; Park et al., 2000].

Based on host-guest interaction, molecular sieves have been used as heterogeneous host for the encapsulation of guest molecules such as organic molecules, metal complexes and organometallic fragments [Bein et al., 1996; Kim et al., 2001]. Such inorganic solid-state supramolecular systems generate the microheterogenization of the encapsulated molecular assemblies which show the photocatalytic activity. For zeolite-entrapped complexes, the steric and electrostatic constraint 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 [Kim et al., 2001].

In this study, $[Re(CO)_3(bpy)(py)]^+$ encapsulated in NaY and Al-MCM-41 molecular sieves was applied to photocatalytic activation of CO_2. The encapsulated cationic rhenium complex was characterized by using FT-IR and Xe-NMR spectroscopies. The photoactivation of CO_2 on the catalyst was studied by UV-DRS, *in-situ* FT-IR and time-resolved mass spectroscopy with photoirradiation under visible light. The photocatalytic activation mechanism of CO_2 on the catalyst under visible light could be proposed via the photo-induced reaction of two electrons and two protons, resulting from water decomposition.

EXPERIMENTAL

The experimental method is described elsewhere [Sung-Suh et al., 2000; Park et al., 2000]. The cationic rhenium complex, [Re(CO)$_3$

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(bpy)(py)]$^+$ (bpy=2,2'-bipyridine, py=pyridine) was used as a photosensitizer. The complex was encapsulated into the microporous NaY and mesoporous AlMCM-41 (Si/Al=30) molecular sieves by ion exchange method using the aqueous solution of [Re[CO]$_3$(bpy)(py)]$^+$PF$_6^-$. The encapsulated samples were evacuated (<10^{-4} torr) at 100 °C for 16 hours and characterized by FT-IR, Xe-NMR and UV-DRS spectroscopies. To study the photoreaction of CO$_2$ over these encapsulated rhenium complexes using *in-situ* FT-IR, the pellet of [Re(CO)$_3$(bpy)(py)]$^+$/AlMCM-41 was placed into a *in-situ* quartz cell with CaF$_2$ windows for FT-IR measurement and evacuated to about 10^{-4} torr at 200 °C for 12 hours. Then, CO$_2$ was adsorbed onto the evacuated pellet followed by photoirradiation (λ> 350 nm) from a 300 W-high pressure xenon-arc lamp (Oriel Instruments). *In-situ* FT-IR spectra were recorded with photoirradiation time. The photocatalytic reduction of CO$_2$ over encapsulated rhenium complexes was done in a quartz tube connected to a vacuum line analyzing the product by time-resolved IGA (Intelligent Gravimetric Analyzer) mass spectroscopy.

RESULTS AND DISCUSSION

The experimental processes with molecular sieve-encapsulated rhenium complexes of [Re(CO)$_3$(bpy)(py)]$^+$/NaY and [Re(CO)$_3$(bpy)(py)]$^+$/AlMCM-41 are schematically shown in Fig. 1. Both encapsulated complexes show the photocatalytic activities for CO$_2$ activation into CO and carbonate.

1. Encapsulation of Rhenium Complex into Molecular Sieves

Fig. 2 shows Xe-NMR spectra of NaY and AlMCM-41 and their encapsulated rhenium complexes. The difference of chemical shifts of these Xe-NMR spectra supports that the rhenium complex is encapsulated inside the pores of NaY and AlMCM-41 [Park et al., 2000]. Really if the Re-complex is encapsulated inside molecular sieves, then the electron cloud of Xe atom is deformed by the interaction between Xe and Re-complex. FT-IR spectra in Fig. 3 also support the encapsulation of [Re(CO)$_3$(bpy)(py)]$^+$ into the pores of NaY and AlMCM-41. The frequencies of three CO ligands of [Re(CO)$_3$(bpy)(py)]$^+$ are changed after encapsulation into the NaY micropores and AlMCM-41 mesopores. This frequency change due to the encapsulation seems to be ascribed to the steric hindrance and electronic interaction exerted on [Re(CO)$_3$(bpy)(py)]$^+$ restricted inside the NaY micropores and AlMCM-41 mesopores. Both Xe-NMR and FT-IR spectra evidence the encapsulation of [Re(CO)$_3$(bpy)(py)]$^+$ into the NaY micropores and AlMCM-41 mesopores.

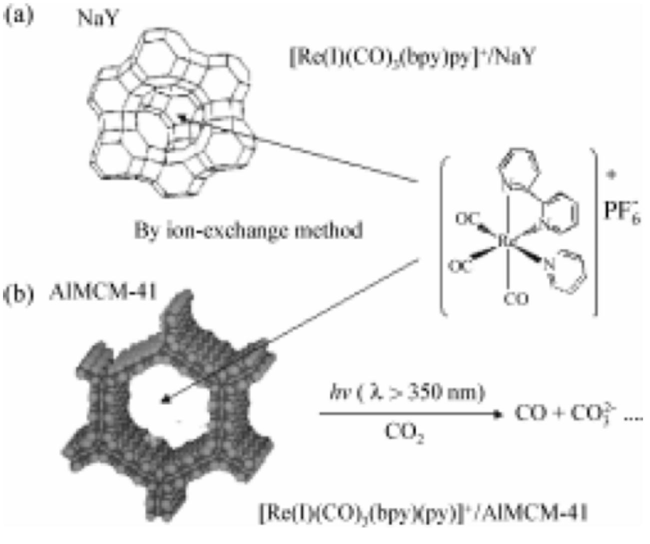

Fig. 1. Process of photocatalytic CO$_2$ activation over cationic rhenium complex encapsulated in molecular sieves: (a) [Re(CO)$_3$(bpy)(py)]$^+$/NaY, (b) [Re(CO)$_3$(bpy)(py)]$^+$/AlMCM-41.

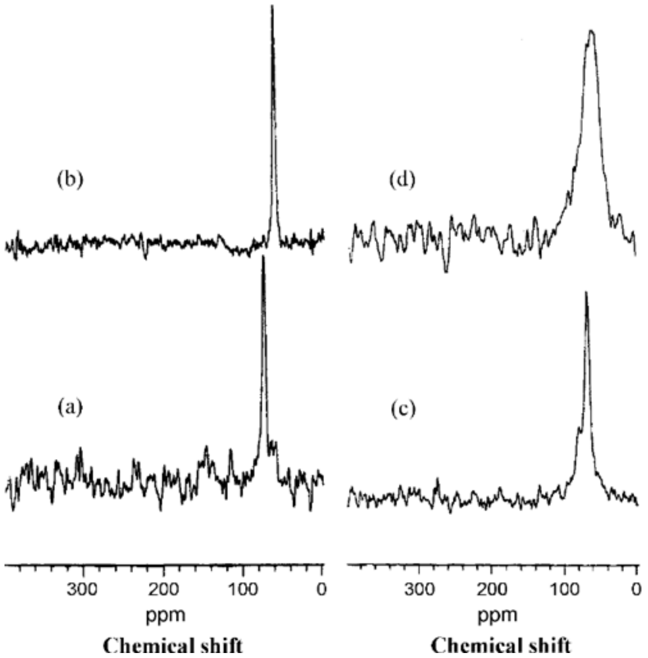

Fig. 2. Xe-NMR spectra of (a) NaY, (b) [Re(I)(CO)$_3$(bpy)(py)]$^+$/NaY, (c) AlMCM-41 and (d) [Re(I)(CO)(bpy)(py)]$^+$/AlMCM-41.

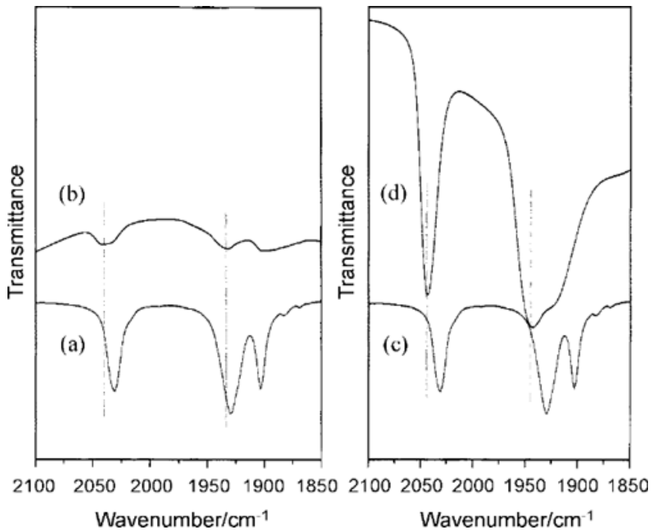

Fig. 3. FTIR spectra of (a) [Re(I)(CO)$_3$(bpy)(py)]$^+$, (b) [Re(I)(CO)$_3$(bpy)(py)]$^+$/NaY, (c) [Re(I)(CO)$_3$(bpy)(py)]$^+$ and (d) [Re(I)(CO)$_3$(bpy)(py)]$^+$/AlMCM-41.

2. Photocatalytic Activation Study of CO$_2$

To study the photocatalytic CO$_2$ activation on the surface of molecular sieve-encapsulated rhenium complexes, UV-DRS spectra are measured with photoirradiation under visible light and CO$_2$ adsorp-

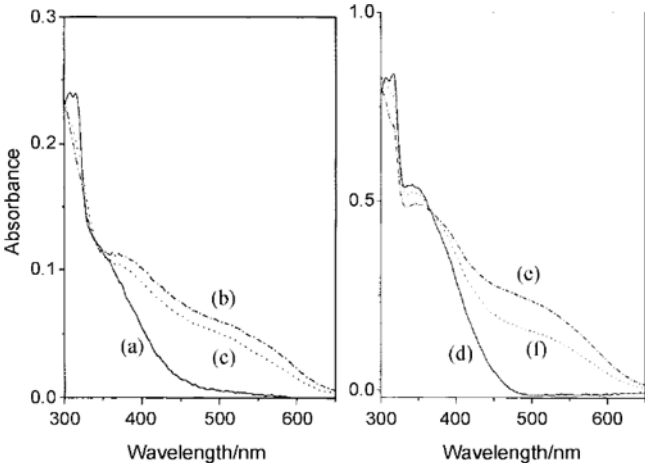

Fig. 4. UV-Vis absorption spectra of [Re(I)(CO)$_3$(bpy)(py)]$^+$/NaY (a) after evacuation, (b) with photoirradiation, and (c) with CO$_2$ adsorption and [Re(CO)$_3$(bpy)(py)]$^+$/AlMCM-41 (d) after evacuation, (e) with photoirradiation, and (f) with CO$_2$ adsorption.

tion, as shown in Fig. 4. The band at 390 nm can be assigned as metal-to-ligand charge transfer (MLCT) transition from the rhenium (dπ orbital) to the bpy (pπ* orbital) [Kalyanasundaram, 1986]. This MLCT transition indicates that metal complex could play as a photocatalyst. With photoirradiation, the new absorption bands appeared at 380-530 nm as shown in Fig. 4(b, e). These new bands are assigned to the [Re(I)(CO)$_3$(bpy$^-$)(py)] radical [Kalyanasundaram, 1986]. The spectra in Fig. 4(b, e) are similar to UV-visible absorption spectrum of [Re(I)(CO)$_3$(bpy$^-$)(py)] radical photoinduced in the solution of [Re(CO)$_3$(bpy)(py)]$^+$ and TEOA (triethanolamine) in DMF. It has been known that TEOA acts as an electron donor [Park et al., 2000]. In [Re(I)(CO)$_3$(bpy)(py)]$^+$/zeolites, the [Re(I)(CO)$_3$(bpy$^-$)(py)] radical was produced with photoirradiation in the absence of electron donor such as TEOA. It has been known that the frameworks of the zeolites show the electron-donating property to proper electron acceptors encapsulated in their pores and that the steric hindrance stabilizes the generated radical species restricted in the pores [Park et al., 2000]. Upon CO$_2$ adsorption as shown in Fig. 4(c, f), the new broad absorption bands are slightly quenched. It means that adsorbed CO$_2$ on zeolites reacts with electrons of surface-trapped conduction band. From the results of UV-DRS, it can be supposed that the frameworks of the zeolites may act as an electron donor in the photoinduced formation of [Re(I)(CO)$_3$(bpy$^-$)(py)] radical in zeolites. And the AlMCM-41 encapsulated Re-complex shows better photocatalytic reactivity than NaY sample.

3. Photocatalytic Reduction of CO$_2$ on [Re(CO)$_3$(bpy)(py)]$^+$/AlMCM-41

With photoirradiation onto CO$_2$-adsorbed [Re(CO)$_3$(bpy)(py)]$^+$/AlMCM-41, the formation of carbonates and CO can be confirmed by using *in-situ* FT-IR and time-resolved mass spectroscopy. In Fig. 5, the intensity of CO$_2$ band at 2,343 cm^{-1} decreased and the carbonate bands at 1,400-1,700 cm^{-1} increased [Nakamoto, 1978]. Time-resolved IGA (Intelligent Gravimetric Analyzer) mass spectroscopy was also used for detection of the gas phase products of CO$_2$ photoreaction. Since molecular weight of CO (m/e=28) is equal to that of N$_2$ (m/e=28), the isotope labeling experiment was carried out by using ^{13}CO$_2$ instead of regular ^{12}CO$_2$ to observe the photoreduced product ^{13}CO (m/e=29) distinguished from N$_2$. As shown in Fig. 6, slow growth of peak at m/e=29 with decrease of peak at m/e=45 represented ^{13}CO$_2$ explains that carbon dioxide is reduced to carbon monoxide by photolysis over the [Re(CO)$_3$(bpy)(py)]$^+$/AlMCM-41. The formation of photolysis products could not be detected without water. Fig. 7 shows the photocatalytic decomposi-

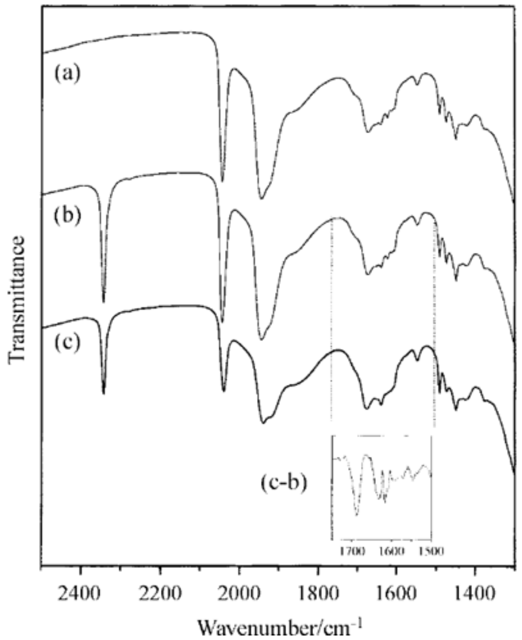

Fig. 5. FTIR spectra of [Re(CO)$_3$(bpy)(py)]$^+$/AlMCM-41 (a) after evacuation, (b) with CO$_2$ adsorption, and (c) with photoirradiation.

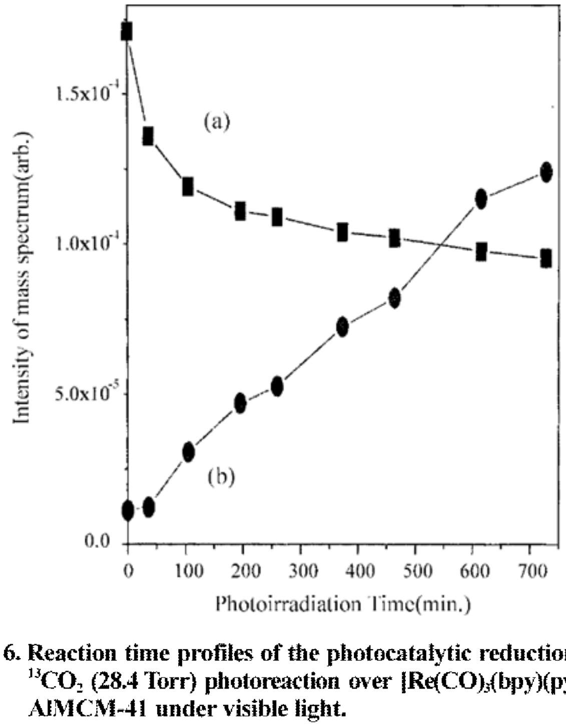

Fig. 6. Reaction time profiles of the photocatalytic reduction of ^{13}CO$_2$ (28.4 Torr) photoreaction over [Re(CO)$_3$(bpy)(py)]$^+$/AlMCM-41 under visible light.
(a) ^{13}CO$_2$ (m/e=45) and (b) ^{13}CO (m/e=29)

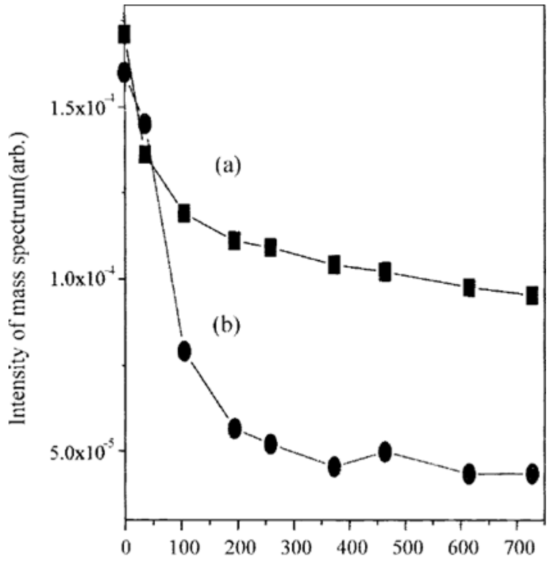

Fig. 7. Reaction time profiles of the photocatalytic reduction of $^{13}CO_2$ (28.4 Torr) photoreaction over [Re(CO)$_3$(bpy)(py)]$^+$/AlMCM-41 under visible light.
(a)$^{13}CO_2$ (m/e=45) and (b) H_2O (m/e=18)

tion of water with photoreduction of CO_2, suggesting that the photocatalytic reduction of CO_2 is initiated by the photocatalytic decomposition of water on the catalyst surface. From the results of *in-situ* FT-IR and time-resolved mass spectroscopy, CO was also produced along with carbonated species over [Re(CO)$_3$(bpy)(py)]$^+$/AlMCM-41. It indicates that [Re(CO)$_3$(bpy)(py)]$^+$/AlMCM-41 shows the photocatalytic activity for photoinduced reduction of CO_2 into CO and HCOOH. From the whole experimental results, we would propose the reaction scheme for the photoreduction of CO_2 using [[Re(CO)$_3$(bpy)(py)]$^+$/AlMCM-41 under visible light as shown in Scheme 1.

CONCLUSIONS

The cationic rhenium complex encapsulated in molecular sieves of [Re(CO)$_3$(bpy)(py)]$^+$/NaY and [Re(CO)$_3$(bpy)(py)]$^+$/AlMCM-41 showed the activity for photoinduced activation of CO_2 into CO and carbonate species under visible light (λ>350 nm). It is assumed that the frameworks of microporous NaY and mesoporous AlMCM-41 molecular sieves act as an electron donor to form [Re(CO)$_3$(bpy$^-$)(py)] radicals which are active species for the activation and reduction of CO_2 into CO and carbonate species.

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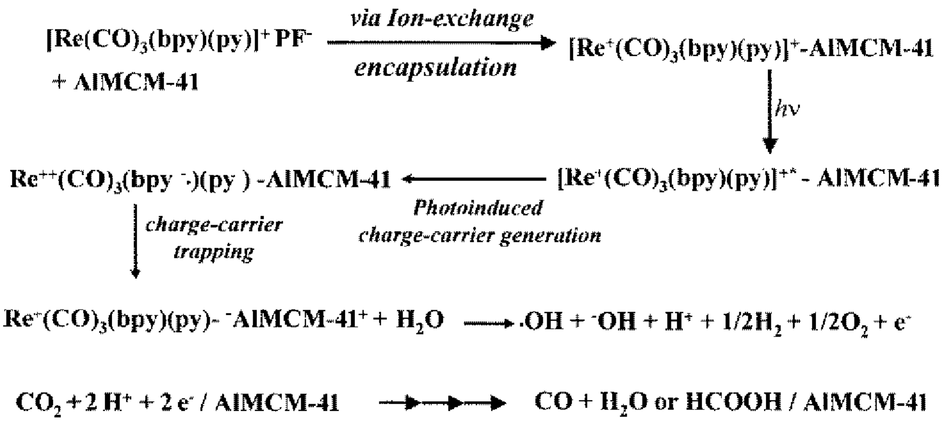

Scheme 1. Photocatalytic activation mechanism of CO_2 under visible light over [Re(CO)$_3$(bpy)(py)]$^+$/AlMCM-41.

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