

Photocatalytic Activation of CO₂ under Visible Light by Rhenium Complex Encapsulated in Molecular Sieves

Jin-Soo Hwang, Dae Sung Kim, Chul Wee Lee and Sang-Eon Park[†]

Catalysis Center for Molecular Engineering (CCME),
Korea Research Institute of Chemical Technology (KRICT), Daejeon 305-606, Korea
(Received 7 September 2001 • accepted 15 October 2001)

Abstract—The photocatalytic activation of CO₂ over molecular sieve-encapsulated cationic rhenium complex has been investigated under visible light ($\lambda > 350$ nm). The cationic rhenium complex, $[\text{Re}(\text{I})(\text{CO})_3(\text{bpy})(\text{py})]^+$ (bpy = 2,2'-bipyridine, py = pyridine), has been encapsulated by ion-exchange method using the aqueous solution of $[\text{Re}(\text{I})(\text{CO})_3(\text{bpy})(\text{py})]^+\text{PF}_6^-$ into the microporous NaY and the mesoporous AlMCM-41 molecular sieve acting as supramolecular heterogeneous host. To confirm the encapsulation of $[\text{Re}(\text{I})(\text{CO})_3(\text{bpy})(\text{py})]^+$ into the pores of molecular sieve, Xe-NMR and FT-IR spectroscopies have been applied before and after the $[\text{Re}(\text{I})(\text{CO})_3(\text{bpy})(\text{py})]^+$ 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 ($\lambda > 350$ nm) at room temperature. By monitoring the photoreaction of CO₂ over the photocatalysts, the conversion of CO₂ 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 CO₂ on the catalyst under visible light ($\lambda > 350$ 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 CO₂, UV-DRS, Visible Light

INTRODUCTION

Since photosensitized decomposition of water on TiO₂ electrodes was discovered, semiconductor photocatalysis has received much attention due to its potential to convert solar energy into electrical or chemical energy [Chevaleski et al., 2001; Anpo et al., 2000]. The continued increase of the atmospheric CO₂ 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 CO₂ 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 CO₂ activation was accomplished by chemical, electrochemical, and photochemical reactions [Reinking et al., 1989; Amatore et al., 1981; Halmann, 1978]. Photocatalytic activation of CO₂ 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 CO₂ 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 CO₂ activation in artificial photosynthetic systems. Rhenium complexes such as $\text{ReX}(\text{CO})_3(\text{bpy})$ (X = Cl, Br) and $\text{Re}(\text{CO})_3(\text{bpy})[\text{P}(\text{OEt})_3]_2$ have been used as photocatalysts for CO₂ reduction to CO in solvent mixture of triethanolamine/dimethylformamide. Most of the research on photochemical activation of CO₂ 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 CO₂ 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, $[\text{Re}(\text{CO})_3(\text{bpy})(\text{py})]^+$ encapsulated in NaY and AlMCM-41 molecular sieves was applied to photocatalytic activation of CO₂. The encapsulated cationic rhenium complex was characterized by using FT-IR and Xe-NMR spectroscopies. The photoactivation of CO₂ 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 CO₂ 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, $[\text{Re}(\text{CO})_3$

[†]To whom correspondence should be addressed.
E-mail: separk@pado.kRICT.re.kr

$(\text{bpy})(\text{py})]^+$ (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 $[\text{Re}(\text{CO})_3(\text{bpy})(\text{py})]^+\text{PF}_6^-$. 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 $[\text{Re}(\text{CO})_3(\text{bpy})(\text{py})]^+/\text{AlMCM-41}$ 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 ($\lambda > 350$ 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 $[\text{Re}(\text{CO})_3(\text{bpy})(\text{py})]^+/\text{NaY}$ and $[\text{Re}(\text{CO})_3(\text{bpy})(\text{py})]^+/\text{AlMCM-41}$ 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 $[\text{Re}(\text{CO})_3(\text{bpy})(\text{py})]^+$ into the pores of NaY and AlMCM-41. The frequencies of three CO ligands of $[\text{Re}$

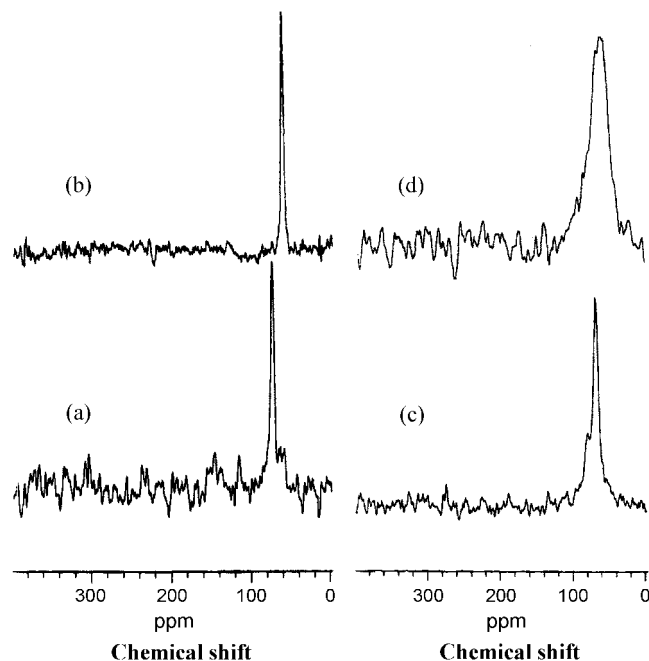


Fig. 2. Xe-NMR spectra of (a) NaY, (b) $[\text{Re}(\text{I})(\text{CO})_3(\text{bpy})(\text{py})]^+/\text{NaY}$, (c) AlMCM-41 and (d) $[\text{Re}(\text{I})(\text{CO})_3(\text{bpy})(\text{py})]^+/\text{AlMCM-41}$.

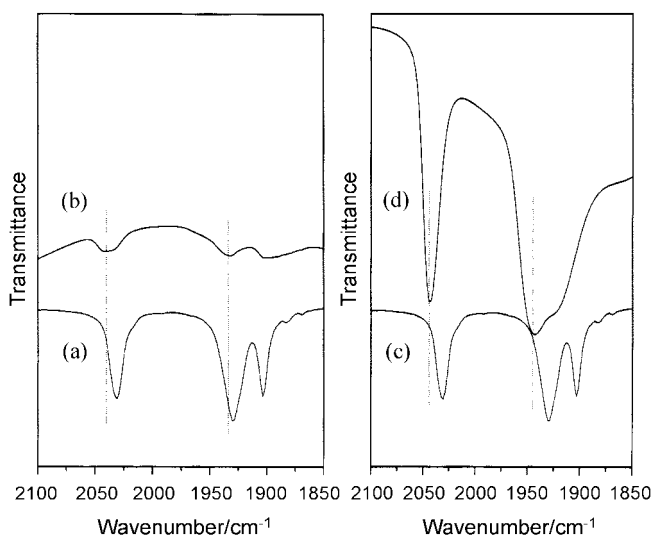


Fig. 3. FTIR spectra of (a) $[\text{Re}(\text{I})(\text{CO})_3(\text{bpy})(\text{py})]^+$, (b) $[\text{Re}(\text{I})(\text{CO})_3(\text{bpy})(\text{py})]^+/\text{NaY}$, (c) $[\text{Re}(\text{I})(\text{CO})_3(\text{bpy})(\text{py})]^+$ and (d) $[\text{Re}(\text{I})(\text{CO})_3(\text{bpy})(\text{py})]^+/\text{AlMCM-41}$.

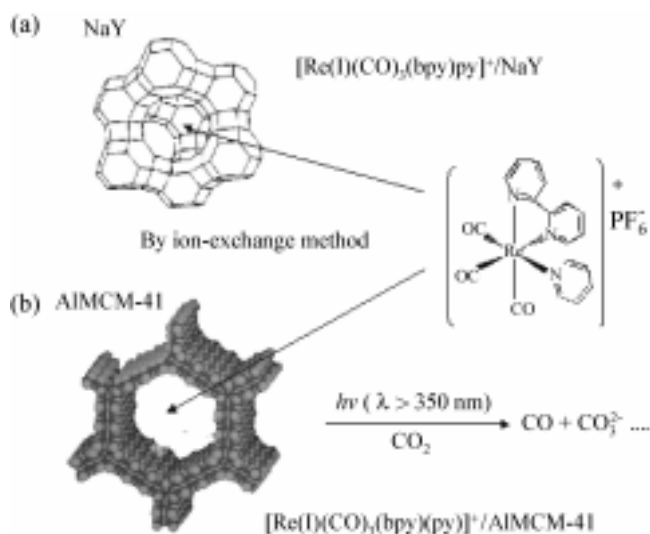


Fig. 1. Process of photocatalytic CO_2 activation over cationic rhenium complex encapsulated in molecular sieves: (a) $[\text{Re}(\text{CO})_3(\text{bpy})(\text{py})]^+/\text{NaY}$, (b) $[\text{Re}(\text{CO})_3(\text{bpy})(\text{py})]^+/\text{AlMCM-41}$.

$(\text{CO})_3(\text{bpy})(\text{py})]^+$ 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 $[\text{Re}(\text{CO})_3(\text{bpy})(\text{py})]^+$ restricted inside the NaY micropores and AlMCM-41 mesopores. Both Xe-NMR and FT-IR spectra evidence the encapsulation of $[\text{Re}(\text{CO})_3(\text{bpy})(\text{py})]^+$ into the NaY micropores and AlMCM-41 mesopores.

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-

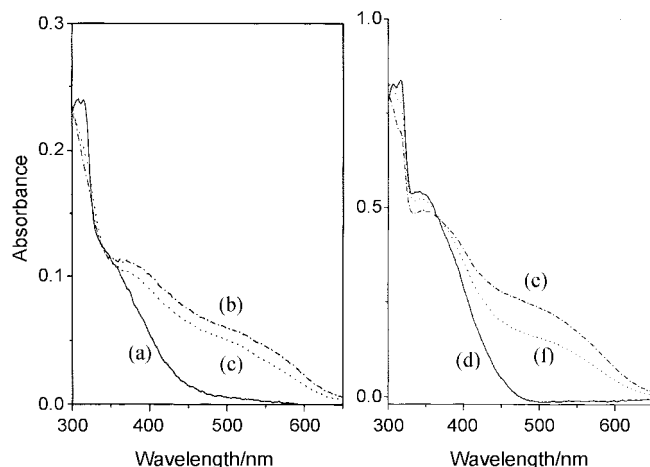


Fig. 4. UV-Vis absorption spectra of [Re(I)(CO)₃(bpy)(py)]⁺/NaY (a) after evacuation, (b) with photoirradiation, and (c) with CO₂ adsorption and [Re(CO)₃(bpy)(py)]⁺/AIMCM-41 (d) after evacuation, (e) with photoirradiation, and (f) with CO₂ adsorption.

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 ($d\pi$ orbital) to the bpy ($p\pi^*$ 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 CO₂ adsorption as shown in Fig. 4(c, f), the new broad absorption bands are slightly quenched. It means that adsorbed CO₂ 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 AIMCM-41 encapsulated Re-complex shows better photocatalytic reactivity than NaY sample.

3. Photocatalytic Reduction of CO₂ on [Re(CO)₃(bpy)(py)]⁺/AIMCM-41

With photoirradiation onto CO₂-adsorbed [Re(CO)₃(bpy)(py)]⁺/AIMCM-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 CO₂ 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 CO₂ photoreaction. Since molecular weight of CO ($m/e=28$) is equal to that of N₂ ($m/e=28$), the isotope labeling experiment was carried

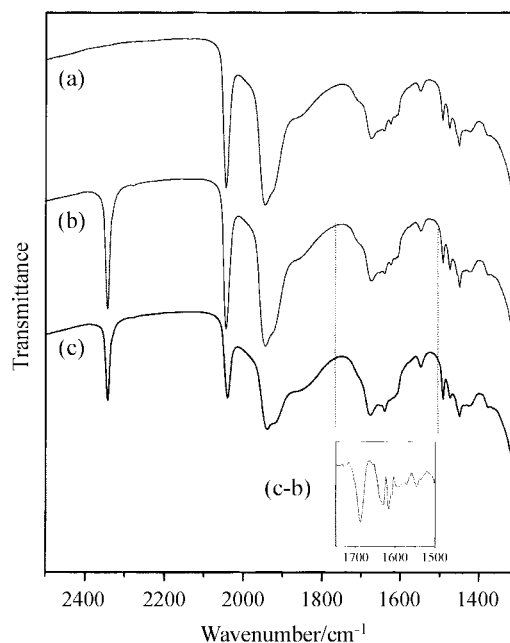


Fig. 5. FTIR spectra of [Re(CO)₃(bpy)(py)]⁺/AIMCM-41 (a) after evacuation, (b) with CO₂ adsorption, and (c) with photoirradiation.

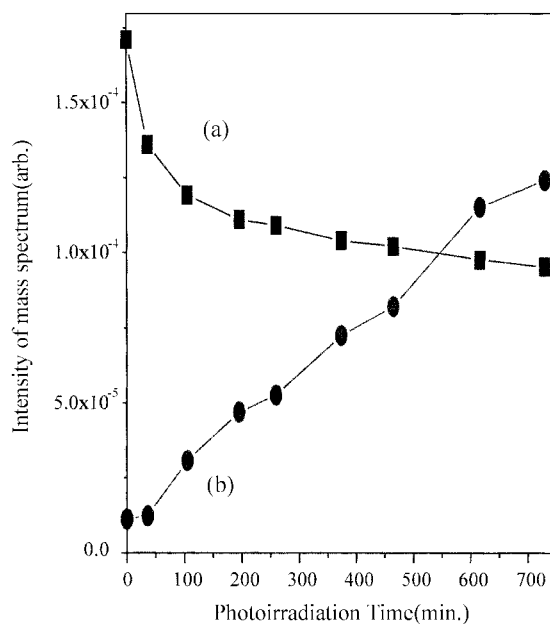


Fig. 6. Reaction time profiles of the photocatalytic reduction of ¹³CO₂ (28.4 Torr) photoreaction over [Re(CO)₃(bpy)(py)]⁺/AIMCM-41 under visible light.

(a) ¹³CO₂ ($m/e=45$) and (b) ¹³CO ($m/e=29$)

out by using ¹³CO₂ instead of regular ¹²CO₂ to observe the photoreduced product ¹³CO ($m/e=29$) distinguished from N₂. As shown in Fig. 6, slow growth of peak at $m/e=29$ with decrease of peak at $m/e=45$ represented ¹³CO₂ explains that carbon dioxide is reduced to carbon monoxide by photolysis over the [Re(CO)₃(bpy)(py)]⁺/AIMCM-41. The formation of photolysis products could not be detected without water. Fig. 7 shows the photocatalytic decomposi-

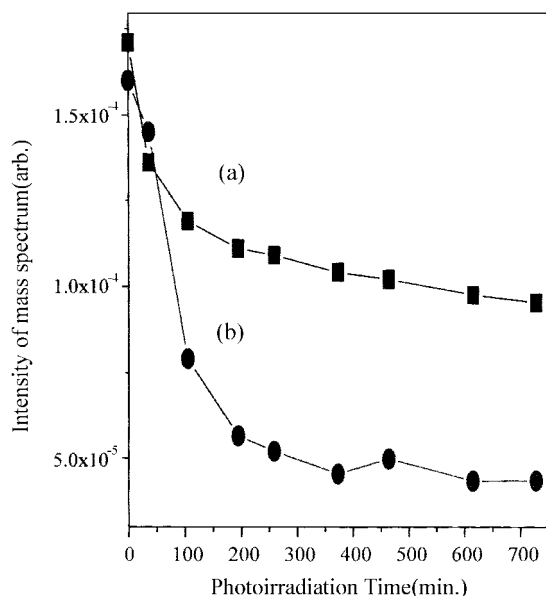


Fig. 7. Reaction time profiles of the photocatalytic reduction of $^{13}\text{CO}_2$ (28.4 Torr) photoreaction over $[\text{Re}(\text{CO})_3(\text{bpy})(\text{py})]^+/\text{AlMCM-41}$ under visible light.

(a) $^{13}\text{CO}_2$ ($m/e=45$) 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 $[\text{Re}(\text{CO})_3(\text{bpy})(\text{py})]^+/\text{AlMCM-41}$. It indicates that $[\text{Re}(\text{CO})_3(\text{bpy})(\text{py})]^+/\text{AlMCM-41}$ 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 $[\text{Re}(\text{CO})_3(\text{bpy})(\text{py})]^+/\text{AlMCM-41}$ under visible light as shown in Scheme 1.

CONCLUSIONS

The cationic rhenium complex encapsulated in molecular sieves of $[\text{Re}(\text{CO})_3(\text{bpy})(\text{py})]^+/\text{NaY}$ and $[\text{Re}(\text{CO})_3(\text{bpy})(\text{py})]^+/\text{AlMCM-41}$ showed the activity for photoinduced activation of CO_2 into CO

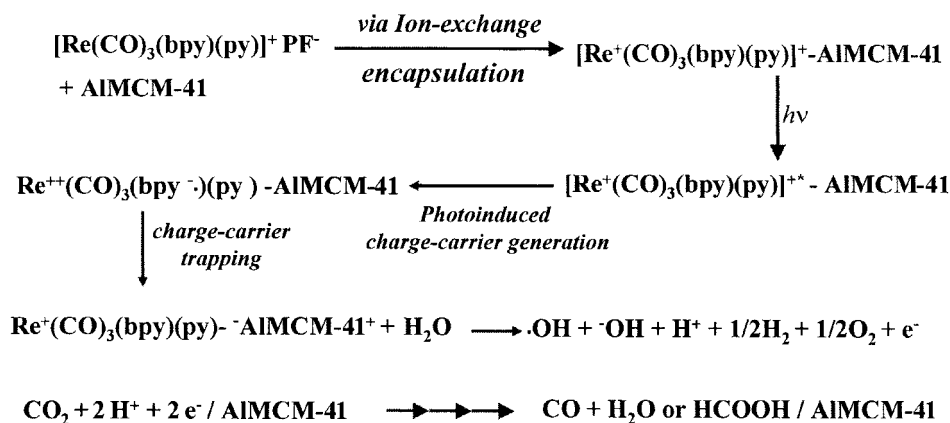
and carbonate species under visible light ($\lambda > 350 \text{ nm}$). It is assumed that the frameworks of microporous NaY and mesoporous AlMCM-41 molecular sieves act as an electron donor to form $[\text{Re}(\text{CO})_3(\text{bpy})(\text{py})]$ radicals which are active species for the activation and reduction of CO_2 into CO and carbonate species.

ACKNOWLEDGEMENT

This work was financially supported by the Ministry of Science and Technology in Korea and partly by the Korea Science and Engineering Foundation (KOSEF).

REFERENCES

- Amatore, C. and Saveant, J.-M., "Mechanism and Kinetic Characteristics of the Electrochemical Reduction of Carbon Dioxide in Media of Low Proton Availability," *J. Am. Chem. Soc.*, **103**, 5021 (1981).
- Anpo, M., Matsuoka, M., Yamashita, H., Ju, W. S., Park, S. E. and Shul, Y. G., "Photocatalytic Decomposition of NO on Transition Metal Ion-exchanged Zeolite Catalysts," *J. Ind. Eng. Chem.*, **6**, 133 (2000).
- Anpo, M., Yamashita, H., Matsuoka, M., Park, D. R., Shul, Y. G. and Park, S. E., "Design and Development of Titanium and Vanadium Oxide Photocatalysts Incorporated within Zeolite Cavities and their Photocatalytic Reactivities," *J. Ind. Eng. Chem.*, **6**, 59 (2000).
- Bein, T., "Inclusion Chemistry of Organometallics in Zeolites," In *Comprehensive Supramolecular Chemistry*, Bein Y. and Alberti G., eds., Pergamon Press, Rugby, UK, 579 (1996).
- Chevaleeski, O. and Larina, L., "New Trends in Solar Photovoltaics: from Physics to Chemistry," *Korean J. Chem. Eng.*, **18**, 403 (2001).
- Cox, P. M., Betts, R. A., Jones, C. D., Spall, S. A. and Totterdell, I. J., "Acceleration of Global Warming due to Carbon-Cycle Feedbacks in a Coupled Climate Model," *Nature*, **408**, 184 (2000).
- Halmann, M., "Photoelectrochemical Reduction of Aqueous Carbon Dioxide on p-type Gallium Phosphide in Liquid Junction Solar Cells," *Nature*, **275**, 115 (1978).
- Hawecker, J., Lehn, J.-M. and Ziessel, R., "Photochemical and Electrochemical Reduction of Carbon Dioxide to Carbon Monoxide Mediated by (2,2-Bipyridine)tricarboxylchlororhenium (I) and Related Complexes as Homogeneous Catalysts," *Helv. Chim. Acta*, **69**, 1990 (1986).
- Kalyanasundaram, K., "Luminescence and Redox Reactions of the



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

- Metal-to-ligand Charge-transfer Excited State of Tricarbonylchloro(polypyridyl)rhenium (I) Complexes," *J. Chem. Soc. Faraday Trans.*, **2**, 2401 (1986).
- Kim, Y., Hwang, J.-S. and Park, S.-E., "Characteristics and Application of Zeolite Photocatalysts through Supramolecular Chemical Approaches," *J. Kor. Ind. Eng. Chem.*, **4**, 1 (2001).
- Meyer, T. J., "Chemical Approaches to Artificial Photosynthesis," *Acc. Chem. Res.*, **22**, 163 (1989).
- Nakamoto, K., "Infrared and Raman Spectroscopy of Inorganic and Coordination Compounds," Wiley, New York, 243 (1978).
- Park, S.-E., Sung-Suh, H. M., Kim, D. S. and Ko, J., "Photoactive Characteristics of Rhenium Complexes Encapsulated in AlMCM-41 by Ion-exchange Method," *Stud. Surf. Sci. Cat.*, **129**, 807 (2000).
- Reinking, M. K., Ni, J., Fanwick, P. E. and Kubiak, C. P., "Carbon Dioxide Chemistry of a Binuclear Iridium (0) Complex. Rapid and Reversible Oxygen Atom Transfer from Carbonate," *J. Am. Chem. Soc.*, **111**, 6459 (1989).
- Sullivan, B. P. and Meyer, T. J., "Photoinduced Irreversible Insertion of CO₂ into a Metal-Hydride Bond," *J. Chem. Soc. Chem. Commun.*, 1244 (1984).
- Sung-Suh, H. M., Kim, D. S., Lee, C. W. and Park, S.-E., "Photoinduced Activation of CO₂ by Rhenium Complexes Encapsulated in Molecular Sieves," *Appl. Organomet. Chem.*, **14**, 826 (2000).
- Tazuke, S. and Kitamura, N., "Photofixation of Carbon Dioxide to Formic Acid in Vitro using Water as Hydrogen Source," *Nature*, **275**, 301 (1978).