**[Regular Paper]**

Reactivity Kinetics of Carbon Dioxide with Phenyl Glycidyl Ether by TEA-CP-MS41 Catalyst

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CP-MS41 was synthesized by hydrolysis of tetraethoxysilicate, as a silicon source, with 3-chloropropyltriethoxysilane as an organosilane using cetyltrimethylammonium bromide as a template. TEA-CP-MS41 was synthesized by immobilization of triethylamine on the mesoporous MCM-41 and was dispersed in organic liquid as a mesoporous catalyst for the reaction between carbon dioxide and phenyl glycidyl ether (PGE). Carbon dioxide was adsorbed into the PGE solution in a stirred batch tank with a planar gas-liquid interface within a range of 0-2.0 kmol/m³ of PGE and 333-363 K at 101.3 kPa. The measured values of absorption rate were analyzed to obtain the reaction kinetics using the mass transfer mechanism associated with the chemical reactions based on the film theory. The overall reaction of CO2 with phenyl glycidyl ether (PGE), which is assumed to consist of two steps: (i) A reversible reaction between PGE (B) and catalyst of TEA-CP-MS41 (QX) to form an intermediate complex (C1), and (ii) irreversible reaction between C1 and CO2 to form QX and five-membered cyclic carbonate (C), was used to obtain the reaction kinetics through the pseudo-first-order reaction model. Polar solvents such as N,N-dimethylacetamide, N-methyl-2-pyrrolidinone, and dimethyl sulfoxide affected the reaction rate constants.

Keywords
Carbon dioxide absorption, Phenyl glycidyl ether, Triethylamine, MCM-41 catalyst

1. Introduction

The chemical fixation of carbon dioxide has become an important research topic because of the danger posed by global warming, and conversion of carbon dioxide into valuable substances is an extremely attractive solution. The reaction of CO2 with oxiranes leading to 5-membered cyclic carbonates is well known1), and these product carbonates can be used as polar aprotic solvents, electrolytes for batteries, and sources of reactive polymers2).

Research on oxirane-CO2 reactions has focused on the reaction mechanism, the overall reaction kinetics, and the effect of the catalyst on the conversion3)–5). Diffusion may affect the reaction kinetics6) in the mass transfer associated with the chemical reactions, so this effect on the reaction kinetics of the gas-liquid heterogeneous reaction between CO2 and oxirane is important to investigate.

Various functionalized catalysts such as polymers, amorphous, and fumed silica have mild activity due to the low accessibility caused by the low/non porosity. However, the discovery of the M41S family7) generated a great deal of interest in the synthesis of organically functionalized, mesoporous materials for application in the fields of catalysis, sensing, and adsorption, based on their high chemical and thermal stabilities are also promising for the reactions of bulky substrate molecules. In general, hybrid organic-inorganic materials have been prepared via post-grafting or co-condensation techniques. In 2000, a grafting technique was developed through a co-condensation method for hybrid MCM-41 using halogenated organosilanes8). Recently, a new synthetic approach has been developed for the preparation of hybrid inorganic-organic mesoporous materials based on the co-condensation of siloxane and organosiloxane precursors in the presence of different templating surfactant solutions9). Also, a new grafting technique was described for the synthesis of hybrid MCM-41 and trialkylamine-immobilized ionic liquids containing high catalytic activity for the synthesis of cyclic carbonates10).

The kinetics of the reaction between CO2 and oxiranes, such as phenyl glycidyl ether (PGE) and glycidyl methacrylate, have been studied using catalysts such as
Alquat 336(2,13), 18-crown-6(14), tetrabutylammonium bromide(15), tetrabutylammonium chloride(16), and tetraethylammonium chloride(17). The reaction rate constants were obtained using the measured absorption rate of CO$_2$, analyzed with the mass transfer mechanism associated with the chemical reactions.

In this study, PGE and the mesoporous particle, TEA-CP-MS41(11), of triethylamine-immobilized ionic liquid on hybrid MCM-41 were used as the reactant and catalyst in a heterogeneous system, respectively, to investigate the absorption kinetics of CO$_2$.

2. Theory

To determine the reaction kinetics between PGE and carbon dioxide using a quaternary onium salt catalyst such as TEA-CP-MS41, it is necessary to understand the absorption mechanism in a heterogeneous system. Although the reaction mechanism shown in Eq. (i) is assumed for homogeneous(8) and heterogeneous(11) oxirane-CO$_2$ reactions, no reliable evidence has yet been reported. The rate-determining step is the attack of the anionic portion of the catalyst on the oxirane. The importance of this portion of the catalyst can be explained by this mechanism, whereby the overall reaction between CO$_2$ and PGE to form the 5-membered cyclic carbonate is as follows:

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{R} & \quad \text{R} \\
\text{CO}_2 \text{(A)} & \quad \text{cat (QX)} \\
\text{B} & \quad \text{QX} & \quad \text{C} & \quad \text{C}_1 \\
\text{A} & \quad \text{C}_1 & \quad \text{C} & \quad \text{QX}
\end{align*}
\]

where R is a functional group of $-\text{CH}_2\text{-O-C}_6\text{H}_5$. The overall reaction of Eq. (i) in this study is assumed to consist of two steps: (1) A reversible reaction between PGE (B) and TEA-CP-MS41 (QX) to form an intermediate complex (C$_1$), and (2) irreversible reaction between C$_1$ and CO$_2$ (A) to form QX and the five-membered cyclic carbonate (C):

\[
\begin{align*}
\text{B} + \text{QX} & \quad \overset{k_1}{\underset{k_2}{\rightleftharpoons}} \quad \text{C}_1 \\
\text{A} + \text{C}_1 & \quad \overset{k_3}{\rightarrow} \quad \text{C} + \text{QX}
\end{align*}
\]

The reaction rate of CO$_2$ under the condition of a steady-state approximation to form C$_1$ is presented as follows:

\[
r_A = \frac{C_{\text{B}}S_i}{k_1} + \frac{1}{K_1k_3} + \frac{C_{\text{B}}}{k_3C_A}
\]

If the value of $k_1$ is very large, such that $1/k_1$ approaches 0, Eq. (1) is arranged to

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\[
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\]

Under the assumptions that B is a nonvolatile solute, the gas phase resistance to absorption is negligible by using pure CO$_2$, and thus Raoults’ law applied. The mass balances of CO$_2$ and PGE, using film theory accompanied by chemical reactions, and boundary conditions are given as follows:

\[
D_A \frac{d^2C_A}{dz^2} = r_A
\]

\[
D_B \frac{d^2C_B}{dz^2} = r_A
\]

\[
z = 0; \quad C_A = C_{\text{AI}}; \quad \frac{dC_B}{dz} = 0
\]

\[
z = z_L; \quad C_A = C_{\text{AL}}; \quad C_B = C_{\text{Bo}}
\]

If the diffusion rate of CO$_2$ is not smaller than the reaction rate, and the amount of dissolved CO$_2$ that reacts in the diffusion film adjacent to the phase boundary is negligible, compared to the CO$_2$ which reaches the bulk liquid phase in the unreacted state, the CO$_2$ concentration in the bulk liquid phase is a finite quantity ($C_{\text{AL}}$) and can be obtained from the following Eq. (11):

\[
k_{\text{loc}}aC_{\text{A}}S_i = \frac{C_{\text{AL}}C_{\text{Bo}}S_i}{K_1k_3} + \frac{C_{\text{Bo}}}{k_3}
\]

The enhancement factor of CO$_2$, defined as the ratio of the flux of CO$_2$ with chemical reaction to that without chemical reaction, is shown as follows:

\[
\beta = \frac{\frac{dC_A}{dx}}{\frac{dC_A}{dx}}_{x=0}
\]

where $a = C_{\text{B}}/C_{\text{AI}}$ and $x = z/z_L$.

At the initial absorption of CO$_2$, C$_B$ in the liquid film is constant as C$_{\text{Bo}}$ and Eq. (2) for the reaction between CO$_2$ and PGE is arranged as

\[
r_A = k_oC_A
\]

where $k_o$ is the pseudo-first-order reaction rate constant and $k_o = C_{\text{Bo}}S_i / [1/(K_1k_3) + C_{\text{Bo}}/k_3]$ is rearranged accordingly:

\[
\frac{C_{\text{Bo}}S_i}{k_o} = \frac{1}{K_1k_3} + \frac{C_{\text{Bo}}}{k_3}
\]

The mass balance of CO$_2$ with the film theory accompanied by a pseudo-first-order reaction is given as follows:

\[
D_A \frac{d^2C_A}{dz^2} = k_oC_A
\]
From the exact solution of Eq. (11), the enhancement factor of CO$_2$ ($\beta$) can be derived as follows:

$$\beta = \frac{Ha}{\tanh Ha}$$

(12)

where $Ha$ is the Hatta number, $\sqrt{k_c D_A / k_{loc}}$.

3. Experimental

3.1. Chemicals

All chemicals were of reagent grade and were used without further purification. Purity of both CO$_2$ and N$_2$ was greater than 99.9%. PGE, tetramethylammonium chloride, triethylamine, 3-chloropropyltriethoxysilane, bromoethane, cetyltrimethylammonium bromide, tetraorthosilicate, and solvents such as $N$-$N$-dimethylacetamide (DMA), $N$-methyl-2-pyrrolidinone (NMP), and dimethyl sulfoxide (DMSO) were supplied by the Aldrich chemical company, USA.

3.2. Absorption Rate of CO$_2$

Absorption experiments were carried out in an agitated vessel and the experimental procedure was duplicated in detail as previously reported$^{18}$. The absorption vessel was constructed of glass with an inside diameter of 0.073 m and a height of 0.151 m. Four equally spaced vertical baffles, each one-tenth of the vessel diameter in width, were attached to the internal wall of the vessel. The gas and liquid phase were agitated with an agitator driven by a 1/4 hp variable speed motor. A straight impeller 0.034 m in length and 0.05 m in width was used as the liquid phase agitator and located at the middle position of the liquid phase. The surface area of the liquid was calculated as the ratio of the volume (300 cm$^3$) of added water to the measured height (7.3 cm) of water in the absorber, and was found to be 41.096 cm$^2$. The gas and liquid in the vessel were agitated at 50 rpm, which was adequate to maintain a planar gas-liquid interface. The value of the cumulaton volume of the bubbles was measured by a soap bubbler with change in absorption time to obtain the absorption rate (dv/dt) of CO$_2$. Each experiment was duplicated at least once under identical conditions. The volumetric rising rate of the bubbles in the soap bubbler attached to the absorption vessel was assumed to be equal to the absorption rate of CO$_2$. The absorption experiments were carried out in a range of 0-2.0 kmol/m$^3$ of PGE and 333-363 K at atmospheric pressure using pure CO$_2$. 2 g of catalyst, and solvents such as DMA, NMP, and DMSO.

3.3. Synthesis of TEA-CP-MS41

CP-MS41 was synthesized by hydrolysis of tetraorthosilicate, as the silicon source, with 3-chloroppropyltriethoxysilane as an organosilane using cetyltrimethylammonium bromide as a template. TEA-CP-MS41 was synthesized by immobilization of triethylamine on mesoporous MCM-41. The synthesis of MCM41 and TEA-CP-MS41 followed previous reports$^{11}$. The surface area and size of MCM41 were measured by BET isotherm and SEM, and were measured as 884.6 m$^2$/g and 5.0 μm, respectively.

3.4. Physical Properties

The solubility ($C_A$) of CO$_2$, diffusivity ($D_A$) of CO$_2$ and PGE, and mass transfer coefficient ($k_{loc}$) of CO$_2$ in the solvent, required to solve Eqs. (3) and (4), were obtained as follows:

$C_A$ was measured by the pressure measuring method, which involved measuring the pressure difference of CO$_2$ before and after equilibrium in the gas and liquid phases, similarly to a previously reported procedure$^{19}$, and the experimental procedure was duplicated in detail as previously reported$^{17}$.

The viscosities ($\mu$) of the solvent and the PGE solution were measured using a Brookfield viscometer (Brookfield Eng. Lab. Inc., USA).

$D_A$ of species $i$ in the solvent was estimated by the method modified with viscosity in the Stoke-Einstein equation$^{20}$ as follows:

$$D_A = 7.4 \times 10^{-12} \frac{T \mu S^{1/2}}{\mu ^{2/3} V_{\nu}}$$

(13)

The experimental data$^{21}$ were better correlated through the use of two-thirds power of the viscosity in Eq. (13) rather than a power of 1, as shown in the Stoke-Einstein equation.

From measurements of the volume change of CO$_2$ according to the change of time in the soap bubbler, the instantaneous mass balance$^{22}$ for the mass flux of CO$_2$ in solvent at a constant pressure and temperature gives:

$$N_{Ao} = \frac{P}{RT A} \frac{dV}{dt} = k_{loc} (C_A - C_L)$$

(14)

From Eq. (14) and Henry’s law, $k_{loc}$ at the initial time is obtained:

$$k_{loc} = \frac{P}{C_A RT A} \left( \frac{dV}{dt} \right)_{t=0}$$

(15)

The values of the mass transfer coefficients ($k_{loc}$) of CO$_2$ in various solvents were obtained from Eq. (16). The mass transfer coefficient ($k_{loc}$) in reactant PGE solution can not be measured given the reaction of CO$_2$ with PGE. In this study, $k_{loc}$ was estimated using the relationship between the mass transfer coefficient ($k_{loc}$) with a solvent and diffusivity ratio of $D_A$ to $D_{AS}$ as following$^{22}$:

$$k_{loc} = k_{loc} \frac{(D_A / D_{AS})^{3/2}}{D_A}$$

(16)

where $D_A$ is the diffusivity of CO$_2$ in PGE solution, estimated by Eq. (13) using the $\mu$ of PGE solution. The values of $\mu$, $C_A$, $D_{AS}$, DBS, and $k_{loc}$ are listed in Table 1 and the measured absorption rates (dv/dt) of CO$_2$ are listed in Table 2.
4. Results and Discussion

The experimental enhancement factor ($\beta_{\text{exp}}$), due to the chemical reaction in gas absorption, was obtained as the ratio of $dv/dt$ with reaction to that without reaction. Figure 1 shows typical plots of $\beta_{\text{exp}}$ against $C_{\text{Bo}}$ in DMA for the experimental parameter of temperature, and demonstrates that $\beta_{\text{exp}}$ increases with increasing $C_{\text{Bo}}$ and temperature. These results are similar for other solvents. The solid line presents the calculated value ($\beta_{\text{cal}}$) of $\beta$, to be discussed later. The measured $\beta_{\text{exp}}$ and Eq. (12) give $k_0$, and then, $K_1$ and $k_3$ are evaluated from the slope and intercept of the plots of $C_{\text{Bo}}S/k_o$ against $C_{\text{Bo}}$ according to Eq. (10). Typical plots of $S_tC_{\text{Bo}}/k_o$ against $C_{\text{Bo}}$ are presented in Fig. 2 for the same conditions as shown in Fig. 1. The linear plots allow $k_3$ and $K_1$ to be obtained from the slope and intercept of the straight line according to Eq. (10), respectively. These results are similar for other solvents.

Figure 3 shows the Arrhenius plots of $k_3$ with parameters of solvents. The Arrhenius plots are linear and the linear regression analysis of the Arrhenius plots with $r^2 > 0.992$ gives the activation energy for the forward reaction rate constant in the irreversible reaction of (iii) with 25.3, 22.6, 17.9 kJ/mol for DMA, NMP,
Various empirical measurements of the solvent effects have been proposed and correlated with the reaction rate constant \( k_3 \) and \( K_1 \). Some measurements have a linear relationship to the solubility parameter (\( \delta \)) of the solvent with logarithms of \( k_3 \) and \( K_1 \) plotted against \( \delta \) of DMA, NMP, and DMSO (22.1, 23.1, 24.6 (J/m\(^3\))\(^{0.5} \)), respectively, in Fig. 4. The plots are linear, and \( k_3 \) and \( K_1 \) increase and decrease with higher \( \delta \), respectively. The solvent polarity increased with higher \( \delta \). Presumably the increased instability and solvation of complex (C1), arising from increased solvent polarity, enhance the dissociation reaction of C1 and the reaction between C1 and CO\(_2\), as in an SN\(_1\) (nucleophilic substitution) reaction\(^{25}\). The results in Fig. 4 suggest that the magnitude of the rate constants may be a function of the stabilization of the zwitterionic intermediates by the solvent\(^{3}\).

Using the obtained values of \( k_3 \) and \( K_1 \) at given \( C_{Bo} \), \( C_{Ai} \), \( D_A \), \( D_B \), and \( k_{Loc} \), Eqs. (3) and (4) were numerically solved by a finite element method to give the profiles of \( C_A \) and \( C_B \), and then, the theoretical value (\( \beta_{cal} \)) of \( \beta \) was calculated from Eq. (8) for various PGE concentrations, solvents, and temperatures. Typical values are shown as symbols of the solid line in Fig. 1. As shown in Fig. 1, \( \beta_{exp} \) approaches to \( \beta_{cal} \). All values of \( \beta_{exp} \) and \( \beta_{cal} \) for various PGE concentrations and temperatures in various solvents were compared in Fig. 5. As shown in Fig. 5, \( \beta_{exp} \) approached \( \beta_{cal} \) within a mean deviation of 1.23% with \( r^2 \) of 0.996.

5. Conclusions

Carbon dioxide was absorbed to react with a PGE solution of DMA, NMP, and DMSO in a flat-stirred vessel at 101.3 kPa. A mathematical model for the CO\(_2\) absorption associated with reaction with PGE was developed on the basis of the film theory with a non-linear reaction rate equation according to the zwitterion mechanism. Absorption data of CO\(_2\) were used to obtain pseudo-first-order reaction rate constants, from which the elementary reaction rate constants were evaluated. The logarithmic reaction constants showed a close to linear dependence on the solubility parameter of the solvent.

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References

テトラオルトサリケート、3-クロロプロピルトリエトキシシラン、セチルトリメチルアンモニウムブロマイドから得た CP-MS41 にトリエチルアミンを固定化することで TEA-CP-MS41 触媒を調製した。バッチ式反応器を用い、様々な溶媒中での TEA-CP-MS41 触媒による二酸化炭素とフェニルグリシジルエーテル（PGE）との反応について調べた。二酸化炭素と PGE との反応は、(1) PGE が TEA-CP-MS41（QX）に吸着し、中間体種（C1）を形成する可逆ステップ、(2) C1 と二酸化炭素 が QX 上で反応して 5 員環カーボネートを形成する非可逆ステップよより進行するものと推定した。333 ～ 363 K で 2 kmol/m³ の PGE 溶液へ 101.3 kPa の二酸化炭素の吸収速度を測定し、凝似的な一次反応式により反応速度論解析を行った。N,N-ジメチルアセトアミド、N-メチル-2-ピロリジノン、ジメチルスルホキシド溶媒を用い、溶媒の極性と反応速度定数との相関について調べた。

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