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

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CP-MS41 was synthesized by hydrolysis of tetraorthosilicate, as a silicon source, with 3-chloropropyl-triethoxysilane 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 absorbed 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 conversion^{3)–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 surface areas and large ordered pores ranging from 20 to 100 Å⁸⁾ with narrow size distributions. 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 organosilanes⁹⁾. 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 solutions¹⁰⁾. 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 carbonates¹¹⁾.

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

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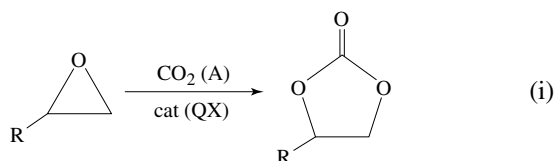
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Alquat 336^(12),13), 18-crown-6⁽¹⁴⁾, tetrabutylammonium bromide⁽¹⁵⁾, tetrabutylammonium chloride⁽¹⁶⁾, and tetraethylammonium chloride⁽¹⁷⁾. The reaction rate constants were obtained using the measured absorption rate of CO₂, analyzed with the mass transfer 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 CO₂.

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⁽³⁾ and heterogeneous⁽¹¹⁾ oxirane-CO₂ 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 CO₂ and PGE to form the 5-membered cyclic carbonate is as follows:



where R is a functional group of -CH₂-O-C₆H₅. 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 (C₁), and (2) irreversible reaction between C₁ and CO₂ (A) to form QX and the five-membered cyclic carbonate (C):



The reaction rate of CO₂ under the condition of a steady-state approximation to form C₁ is presented as follows:

$$r_A = \frac{C_B S_t}{\frac{1}{k_1} + \frac{1}{K_1 k_3 C_A} + \frac{C_B}{k_3 C_A}} \quad (1)$$

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

$$r_A = \frac{C_A C_B S_t}{\frac{1}{K_1 k_3} + \frac{C_B}{k_3}} \quad (2)$$

Under the assumptions that B is a nonvolatile solute, the gas phase resistance to absorption is negligible by using pure CO₂, and thus Raoult's law applied. The mass balances of CO₂ and PGE, using film theory accompanied by chemical reactions, and boundary conditions are given as follows:

$$D_A \frac{d^2 C_A}{dz^2} = r_A \quad (3)$$

$$D_B \frac{d^2 C_B}{dz^2} = r_A \quad (4)$$

$$z = 0; \quad C_A = C_{Ai}; \quad \frac{dC_B}{dz} = 0 \quad (5)$$

$$z = z_L; \quad C_A = C_{AL}; \quad C_B = C_{Bo} \quad (6)$$

If the diffusion rate of CO₂ is not smaller than the reaction rate, and the amount of dissolved CO₂ that reacts in the diffusion film adjacent to the phase boundary is negligible, compared to the CO₂ which reaches the bulk liquid phase in the unreacted state, the CO₂ concentration in the bulk liquid phase is a finite quantity (C_{AL}) and can be obtained from the following Eq. (11):

$$k_{Loc} a_v (C_{Ai} - C_{AL}) = \frac{C_{AL} C_{Bo} S_t}{\frac{1}{K_1 k_3} + \frac{C_{Bo}}{k_3}} \quad (7)$$

The enhancement factor of CO₂, defined as the ratio of the flux of CO₂ with chemical reaction to that without chemical reaction, is shown as follows:

$$\beta = - \left. \frac{da}{dx} \right|_{x=0} \quad (8)$$

where $a = C_A/C_{Ai}$ and $x = z/z_L$.

At the initial absorption of CO₂, C_B in the liquid film is constant as C_{Bo} and Eq. (2) for the reaction between CO₂ and PGE is arranged as

$$r_A = k_o C_A \quad (9)$$

where k_o is the pseudo-first-order reaction rate constant and $k_o = C_{Bo} S_t / [1/(K_1 k_3) + C_{Bo}/k_3]$ is rearranged accordingly:

$$\frac{C_{Bo} S_t}{k_o} = \frac{1}{K_1 k_3} + \frac{C_{Bo}}{k_3} \quad (10)$$

The mass balance of CO₂ with the film theory accompanied by a pseudo-first-order reaction is given as follows:

$$D_A \frac{d^2 C_A}{dz^2} = k_o C_A \quad (11)$$

From the exact solution of Eq. (11), the enhancement factor of CO₂ (β) can be derived as follows:

$$\beta = \frac{Ha}{\tanh Ha} \quad (12)$$

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

3. Experimental

3.1. Chemicals

All chemicals were of reagent grade and were used without further purification. Purity of both CO₂ and N₂ 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 CO₂

Absorption experiments were carried out in an agitated vessel and the experimental procedure was duplicated in detail as previously reported¹⁸. 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 cm³) of added water to the measured height (7.3 cm) of water in the absorber, and was found to be 41.096 cm². 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 cumulative volume of the bubbles was measured by a soap bubbler with change in absorption time to obtain the absorption rate (dv/dt) of CO₂. 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 CO₂. The absorption experiments were carried out in a range of 0-2.0 kmol/m³ of PGE and 333-363 K at atmospheric pressure using pure CO₂, 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-chloropropyltriethoxysilane 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 reports¹¹. The surface area and size of MCM41 were measured by BET isotherm and SEM, and were measured as 884.6 m²/g and 5.0 μ m, respectively.

3.4. Physical Properties

The solubility (C_{Ai}) of CO₂, diffusivity (D_{iS}) of CO₂ and PGE, and mass transfer coefficient (k_{Lo} , k_{Loc}) of CO₂ in the solvent, required to solve Eqs. (3) and (4), were obtained as follows:

C_{Ai} was measured by the pressure measuring method, which involved measuring the pressure difference of CO₂ before and after equilibrium in the gas and liquid phases, similarly to a previously reported procedure¹⁹, and the experimental procedure was duplicated in detail as previously reported¹⁷.

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

D_{iS} of species i in the solvent was estimated by the method modified with viscosity in the Stoke-Einstein equation²⁰ as follows:

$$D_{iS} = 7.4 \times 10^{-12} \frac{T M_S^{1/2}}{\mu^{2/3} V_i} \quad (13)$$

The experimental data²¹ 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 CO₂ according to the change of time in the soap bubbler, the instantaneous mass balance¹⁸ for the mass flux of CO₂ in solvent at a constant pressure and temperature gives:

$$N_{Ao} = \frac{P}{RTA} \frac{dV}{dt} = k_{Lo}(C_{Ai} - C_A) \quad (14)$$

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

$$k_{Lo} = \frac{P}{C_{Ai}RTA} \left(\frac{dV}{dt} \right)_{t=0} \quad (15)$$

The values of the mass transfer coefficients (k_{Lo}) of CO₂ 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 CO₂ with PGE. In this study, k_{Loc} was estimated using the relationship between the mass transfer coefficient (k_{Lo}) with a solvent and diffusivity ratio of D_A to D_{AS} as following²²:

$$k_{Loc} = k_{Lo}(D_A / D_{AS})^{2/3} \quad (16)$$

where D_A is the diffusivity of CO₂ in PGE solution, estimated by Eq. (13) using the μ of PGE solution. The values of μ , C_{Ai} , D_{AS} , DBS, and k_{Lo} are listed in **Table 1** and the measured absorption rates (dv/dt) of CO₂ are listed in **Table 2**.

Table 1 Physical Properties of the CO₂/PGE System

T [K]	Solvent	C _{Ai} [kmol/m ³]	μ [cP]	D _{Ao} × 10 ⁹ [m ² /s]	D _{Bo} × 10 ⁹ [m ² /s]	k _{Lo} × 10 ⁵ [m/s]
333	DMA	0.0562	0.594	3.921	1.403	3.994
	NMP	0.0593	0.854	3.283	1.175	2.697
	DMSO	0.0528	1.082	2.489	0.890	2.633
343	DMA	0.0494	0.521	4.407	1.577	4.597
	NMP	0.0587	0.691	3.895	1.393	3.026
	DMSO	0.0524	0.761	3.242	1.160	3.136
353	DMA	0.0387	0.468	4.872	1.743	5.122
	NMP	0.0582	0.603	4.389	1.570	3.269
	DMSO	0.0520	0.498	4.426	1.583	3.860
363	DMA	0.0315	0.445	5.181	1.854	5.344
	NMP	0.0578	0.508	5.060	1.810	3.601
	DMSO	0.0517	0.345	5.813	2.080	4.625

Table 2 Experimental Data in the CO₂/PGE System

Solvent	C _{Bo} [kmol/m ³]	T [K]	μ [cP]	dv/dt [cm ³ /s]	T [K]	μ [cP]	dv/dt [cm ³ /s]	T [K]	μ [cP]	dv/dt [cm ³ /s]	T [K]	μ [cP]	dv/dt [cm ³ /s]
DMA	0	333	0.594	0.4587	343	0.521	0.4717	353	0.468	0.4184	363	0.445	0.3610
	0.1		0.598	0.4717		0.523	0.4926		0.470	0.4505		0.447	0.4032
	0.5		0.615	0.5051		0.527	0.5405		0.476	0.5076		0.453	0.4673
	1.0		0.628	0.5291		0.531	0.5714		0.484	0.5348		0.460	0.5025
	2.0		0.656	0.5587		0.543	0.5988		0.496	0.5650		0.473	0.5155
NMP	0	333	0.854	0.3268	343	0.691	0.3690	353	0.603	0.4016	363	0.508	0.4464
	0.1		0.861	0.3425		0.696	0.4049		0.609	0.4525		0.539	0.5556
	0.5		0.894	0.3906		0.719	0.4854		0.637	0.5848		0.602	0.7519
	1.0		0.923	0.4348		0.743	0.5495		0.663	0.6623		0.663	0.8621
	2.0		0.992	0.4739		0.795	0.6250		0.722	0.7194		0.722	0.9346
DMSO	0	343	1.082	0.2841	343	0.761	0.3413	353	0.498	0.4237	363	0.345	0.5128
	0.1		1.084	0.2950		0.763	0.3623		0.499	0.4630		0.348	0.5882
	0.5		1.098	0.3311		0.770	0.4274		0.500	0.5780		0.354	0.7752
	1.0		1.108	0.3690		0.777	0.4902		0.502	0.6667		0.361	0.8929
	2.0		1.134	0.4149		0.793	0.5556		0.505	0.7519		0.370	1.0101

4. Results and Discussion

The experimental enhancement factor (β_{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 β_{exp} against C_{Bo} in DMA for the experimental parameter of temperature, and demonstrates that β_{exp} increases with increasing C_{Bo} and temperature. These results are similar for other solvents. The solid line presents the calculated value (β_{cal}) of β , to be discussed later. The measured β_{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 $C_{\text{Bo}}S_1/k_0$ against C_{Bo} according to Eq. (10). Typical plots of S_1C_{Bo}/k_0 against C_{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 for-

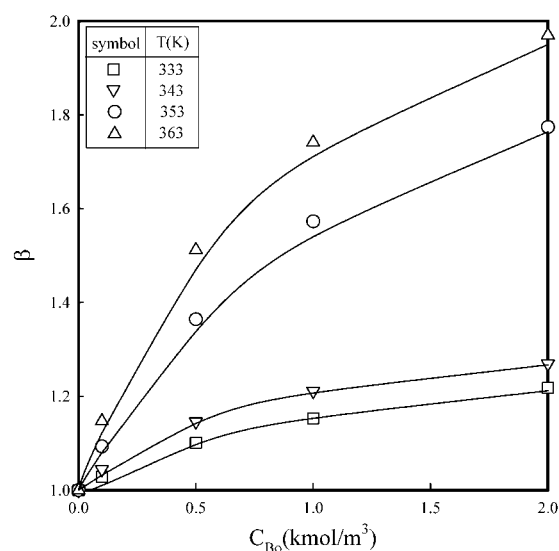


Fig. 1 Enhancement Factor vs. C_{Bo} in DMA at Various Temperatures

ward reaction rate constant in the irreversible reaction of (iii) with 25.3, 22.6, 17.9 kJ/mol for DMA, NMP,

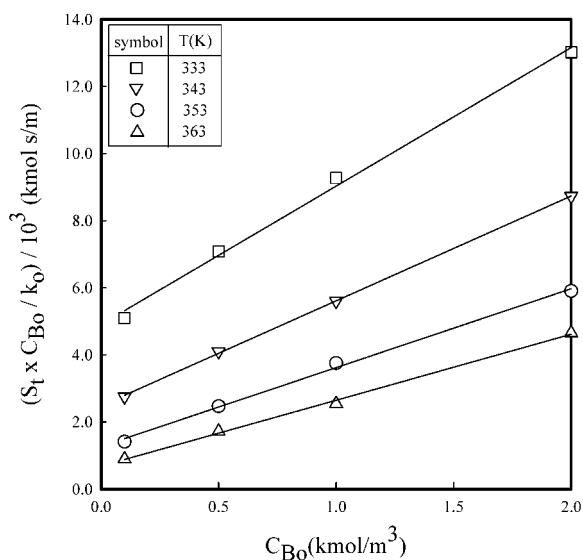


Fig. 2 $S_t C_{Bo}/k_0$ vs. C_{Bo} with the Same Conditions Shown in Fig. 1

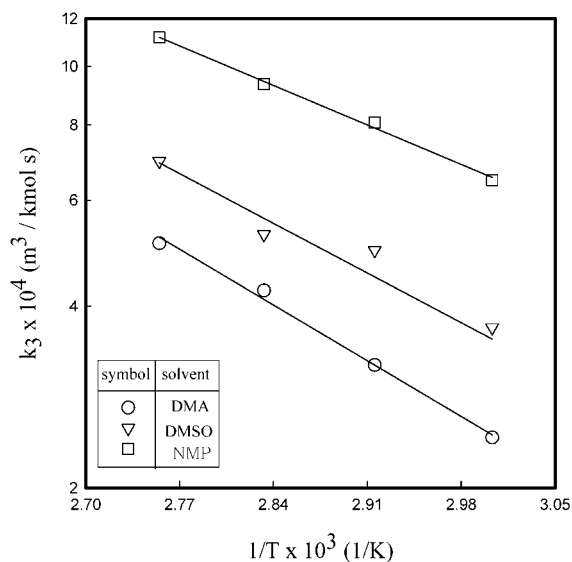


Fig. 3 Arrhenius Plot of the CO₂-PGE System

and DMSO, respectively.

Various empirical measurements of the solvent effects have been proposed and correlated with the reaction rate constant²³. Some measurements have a linear relationship to the solubility parameter (δ) of the solvent with logarithms of k_3 and K_1 plotted against δ^{24} of DMA, NMP, and DMSO (22.1, 23.1, 24.6 (J/m³)^{0.5}), respectively, in Fig. 4. The plots are linear, and k_3 and K_1 increase and decrease with higher δ , respectively. The solvent polarity increased with higher δ . Presumably the increased instability and solvation of complex (C_1), arising from increased solvent polarity, enhance the dissociation reaction of C_1 and the reaction between C_1 and CO₂, as in an SN_1 (nucleophilic substi-

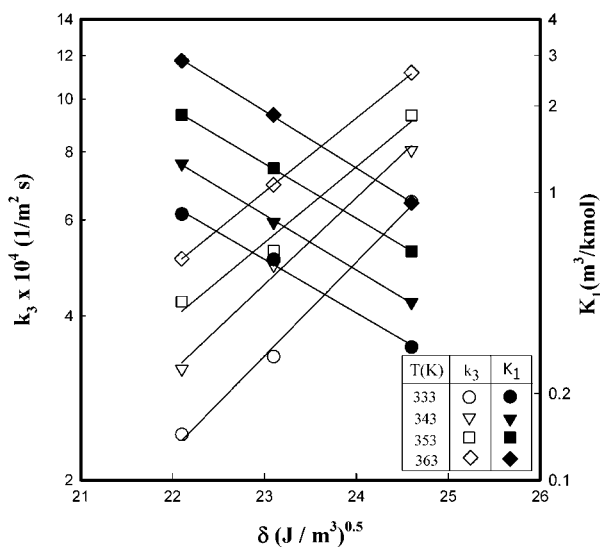


Fig. 4 Relationship between Reaction Rate Constant and Solvent Solubility Parameter

tion) reaction²⁵). 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 solvent³.

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 (β_{cal}) of β 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, β_{exp} approaches to β_{cal} . All values of β_{exp} and β_{cal} for various PGE concentrations and temperatures in various solvents were compared in Fig. 5. As shown in Fig. 5, β_{exp} approached β_{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 CO₂ 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 CO₂ 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.

Acknowledgments

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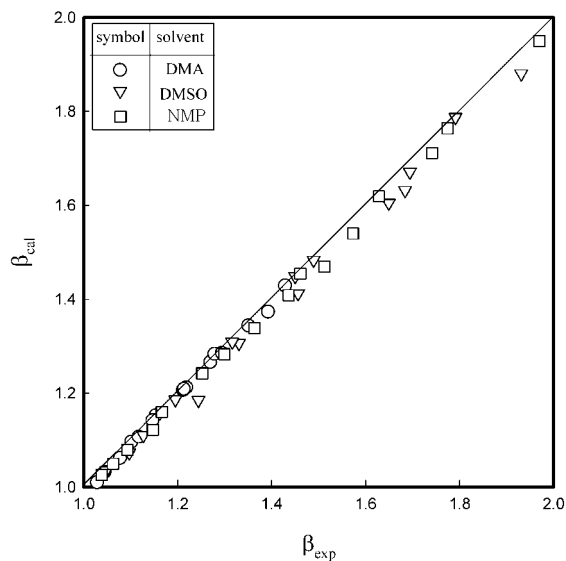


Fig. 5 Comparison of the Calculated and Measured Values of the Enhancement Factor of CO₂

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要 旨

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との反応速度論

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テトラオルトシリケート，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，種々の溶媒中での 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，疑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。