1. Introduction

Increasing carbon dioxide (CO₂) emissions have become one of the most crucial environmental issues worldwide, and endanger the continuation of human society[1]. Reduction in CO₂ emissions and methods of CO₂ fixation and transformation are the main approaches to controlling emissions of CO₂. Chemical production via CO₂ transformation is expected to become an important method of recycling CO₂, and can be classified into two types of CO₂ transformation, reduction and acid-base reaction. For example, hydrogenation of CO₂[2], synthesis of methanol[3] and artificial photosynthesis[4] are categorized as reduction reactions. The products are lower carbon number molecules such as methane, methanol, formic acid and formamide. These products have uses as fuel, C₁ feedstock and H₂ carrier. Reduction reactions involve the decrease of the oxidation number of carbon in CO₂, and require energy input from reductant, electrolysis or solar energy. On the other hand, CO₂ addition is categorized as an acid-base reaction. The products are higher carbon number molecules and are high value-added chemical compounds, such as urea, carbonate, carbonic acids and lactones[5]. Cyclic carbonate synthesis was reported for the first time in the 1930s[6]. The reaction proceeded by depolymerization of linear polycarbonates at high temperature. Now, five and greater member cyclic carbonates are obtained via cycloaddition of CO₂ to cyclic ethers and β,γ-unsaturated alcohols[7] and is categorized as an acid-base reaction without decrease of the oxidation number. Cyclic carbonate is widely used as an electrolyte component in lithium batteries[10] and polar solvents[11]. Furthermore, production of cyclic carbonate as the precursor of polycarbonates[12] and polyurethane[13] has replaced the conventional toxic phosgene and isocyanate process[13],[14]. Unsaturated cyclic carbonates are useful intermediates for various chemicals such as oxazolidinones[15] and β-oxopropyl carbones[19]. Enantioselective hydrogenation of α-methylene cyclic carbonates can form optically active bicyclic carbonates and 1,2-diols with very high enantioselectivities in the presence of ruthenium catalyst[20]. Therefore, unsaturated cyclic carbonate has great potential as a new intermediate leading to high-value chemical products. Typical

Methylated nitrogen-substituted SBA-15 (MeNSBA-15) was demonstrated to catalyze cyclic carbonate synthesis using β,γ-unsaturated alcohol and CO₂. The methylated nitrogen in the framework acts as the catalytic active site. The turnover frequency (TOF) as function of CO₂ partial pressure and β,γ-unsaturated alcohol concentration reflected the major active surface species. The CO₂ dependence could be explained by the adsorption equilibrium of CO₂ over the active site. The formation of carbamate species is the key to this reaction. Less β,γ-unsaturated alcohol is adsorbed on the catalytic site than CO₂. The reaction could involve the following five steps: carbamate formation, interaction of β,γ-unsaturated alcohol with the carbamate species, deprotonation and associated C-O bond formation, intramolecular cyclization, and desorption of the unsaturated cyclic carbonate. Compared with cyclic carbonate synthesis from cyclic ether, the difference in pressure dependence of the cyclic carbonate syntheses could be explained by the competing adsorption (or activation) of the counter reactants with CO₂. The adsorption of β,γ-unsaturated alcohol on the methylated nitrogen is much less than that of cyclic ether.

Keywords
Solid catalyst, Carbon dioxide fixation, Porous material, Alkylidene cyclic carbonate, Silica nitridation

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cyclic carbonate synthesis using $\beta,\gamma$-unsaturated alcohols is catalyzed by phosphine\textsuperscript{21)}, tri-$n$-butylphosphine\textsuperscript{22)}, tBuOF\textsuperscript{23) and metal complexes containing ruthenium\textsuperscript{16)}, cobalt\textsuperscript{24)}, palladium\textsuperscript{25)}, copper\textsuperscript{18)}, silver\textsuperscript{26)} and gold\textsuperscript{27)}. Such conventional syntheses use highly toxic reagents such as phosphine and organic solvent. Therefore, a novel synthetic route is required to reduce the environmental impact\textsuperscript{22)}. An environmental benign reaction system including a catalyst is very desirable to capture $\text{CO}_2$ efficiently under mild conditions as the $\text{C}_1$ source into a wide range of substrates, especially fine chemicals. A new method of unsaturated cyclic carbonate synthesis uses an ionic liquid activated by microwaves\textsuperscript{28)} and a silica-supported ionic-liquid\textsuperscript{15,32)} as catalysts, and offers various advantages such as high reactivity and easy purification.

Our previous study\textsuperscript{33)} found that methylated nitrogen-substituted SBA-15 (MeNSBA-15), a mesoporous material\textsuperscript{34,35)}, catalyzed cyclic carbonate synthesis from cyclic ether. Kinetic analysis revealed that the reaction on MeNSBA-15 occurs through the Langmuir-Hinshelwood mechanism\textsuperscript{33)}. Both cyclic ether and $\text{CO}_2$ are adsorbed on neighboring sites of methylated nitrogen and ring-opened alkoxide intermediate to form the carbamate intermediate. Subsequently, cyclic carbonate was produced as the kinetic limiting bimolecular reaction.

The present study found that MeNSBA-15 also catalyzed cyclic carbonate synthesis from $\beta,\gamma$-unsaturated alcohol. Only the methylated type of a series of SBA-15 catalysts (MeNSBA-15, NSBA-15, and SBA-15) catalyzed the reaction. These results clearly indicate that formation of methylated nitrogen is essential for the reaction. Kinetic analysis was carried out to investigate the reaction mechanism on MeNSBA-15.

2. Experimental

2.1. Chemicals

Carbon dioxide (liquefied gas) with 99.5 % purity was obtained from Jyotou Gas Co., Ltd. (Japan). Tetrabutylammonium bromide (TBABr, Wako Pure Chemical Industries, Ltd., >98.0 %), trimethylamine (NMe\textsubscript{3}, Tokyo Chemical Industry Co., Ltd., 25 % in isopropyl alcohol), 2-methyl-3-butyn-2-ol (Tokyo Chemical Industry Co., Ltd., >98.0 %), 3-methyl-1-pentyne-3-ol (Tokyo Chemical Industry Co., Ltd., >98.0 %), $N,N$-dimethylformamide (DMF, Wako Pure Chemical Industries, Ltd., >99.5 %), and diethyl ether (Wako Pure Chemical Industries, Ltd., >99.5 %) were used without further purification.

2.2. Preparation of MeNSBA-15

MeNSBA-15 was prepared as described previously\textsuperscript{16)}. SBA-15 was synthesized by the hydrothermal method\textsuperscript{37)}. Specifically, triblock copolymer surfactant, Pluronic P-123 (Aldrich, PEG 30 wt%, average $M_n$ of 5800), was dissolved in 2 M aqueous hydrochloric acid solution (Wako Pure Chemical Industries, Ltd., volumetric analysis grade) with stirring at 313 K for 3 h. Tetraethyl orthosilicate (Wako Pure Chemical Industries, Ltd., >95.0 %) was then added to the solution, and hydrolyzed at 313 K for 24 h under stirring. The resultant solution was placed in an electric oven for hydrothermal treatment at 373 K for 24 h. The chemical composition of the synthetic solution was $\text{SiO}_2/0.017\text{P123}/6\text{HCl}/190\text{H}_2\text{O}$. The precipitated sample was collected by filtration and washed with distilled water. The sample was calcined at 823 K for 6 h to remove the template surfactants. Nitrogen substitution of the synthesized SBA-15 was performed by passing 99.999 % ammonia gas (Jyotou Gas Co., Ltd., Japan) at 1173 K for 10 h with a flow rate of 2 L min\textsuperscript{−1}. The obtained NSBA-15 and potassium carbonate (K$_2$CO$_3$, Wako Pure Chemical Industries, Ltd., >99.5 %) were placed in a two-neck flask equipped with a reflux condenser\textsuperscript{36,38)}. The flask was flushed and filled with inert gas (house nitrogen). Anhydrous ethanol (Wako Pure Chemical Industries, Ltd., >99.5 %, water <0.001 %) was added as a solvent, and then methyl iodide (CH$_3$I, Wako Pure Chemical Industries, Ltd., >99.5 %) was added. Molar ratios of CH$_3$I to N-atom in NSBA-15 (N-atom) and CH$_3$I to K$_2$CO$_3$ were 15 and 3, respectively. The reaction was conducted at 350 K for 24 h under reflux conditions. The product was filtered, washed with 50 vol% ethanol aqueous solution to remove potential potassium salts, and dried at 373 K for 12 h. Potassium atoms were hardly detected by analysis with an Inductively Coupled Plasma-Atomic Emission Spectrometer (SPS4000, Seiko Instruments Inc.) in the washed products.

2.3. Catalyst Characterization

Powder X-ray diffraction (XRD) patterns were obtained with a Rigaku RINT2100 using Cu Kα radiation ($\lambda = 0.1542$ nm, 40 kV, 40 mA) between 0.75° and 3° (2θ) with scanning step of 0.02° and scanning speed of 1° min\textsuperscript{−1}. Nitrogen adsorption isotherms were collected on a Quantachrome Quadrasorb Evo. Samples were pretreated at 573 K for 3 h under evacuation. The chemical composition of the synthesized series of SBA-15 samples was analyzed with an Elementar Analysensysteme GmbH Vario Micro Cube. Fourier transform infrared (FT-IR) spectra were obtained with a JASCO FT/IR 4100 with a MCT detector. Samples were pretreated at 423 K for 10 min under vacuum, and the spectra were measured at 323 K.

2.4. Catalytic Activity Tests

Reaction procedures were similar to those in the previous study\textsuperscript{33)}. Cyclic carbonate synthesis from $\text{CO}_2$ and $\beta,\gamma$-unsaturated alcohol was carried out using a 5-mL stainless-steel reactor. Typically, 10-20 mg of catalyst (MeNSBA-15, NSBA-15, TBABr or tri-$n$-butylphosphine) and 1.5-25 mmol of $\beta,\gamma$-unsaturated alcohol were put into the reactor, and the reactor was
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sealed. CO₂ was then charged into the reactor up to 0.5-5.0 MPa. The reactor was heated in an oil bath at 353-423 K for 24 h. The reactor was cooled and degassed, then rinsed with diethyl ether to collect all the reactants and products. After adding mesitylene as an internal standard, the diluted sample was analyzed with a SHIMADZU GC-14B gas chromatograph equipped with a capillary column (ZB-1, 30 m × 0.25 mm diameter × 0.50 μm).

The TOF of each catalyst was measured as the number of product molecules per number of ideal catalytic sites in one hour. The number of ideal catalytic sites was assumed as the numbers of C- and N-atoms in MeNSBA-15 and NSBA-15, respectively. The number of active species was assumed as the molar numbers of TBABr and tri-n-butylphosphine. All reactions were conducted under reaction conditions below the CO₂ supercritical point (7.38 MPa, 304 K).

3. Results and Discussion

3.1. Catalyst Preparation

XRD patterns exhibited three main peaks in all SBA-15 samples (Fig. S1), suggesting that these catalysts possessed 2D hexagonal periodic mesostructures. The peaks were shifted to higher angles after nitridation, probably due to the structural shrinkage caused by the high temperature of nitridation treatment at 1173 K. The methylation process did not cause any significant changes in the periodic mesoporous structure. The N₂ sorption isotherms are shown in Fig. S2. All SBA-15 samples showed the type-IV isotherm, clearly suggesting the formation of uniform mesoporous structures. Based on these results, preparation of mesoporous SBA-15 series samples was successful, without modifying the mesostructures by nitridation or methylation.

Figure 1 shows the FT-IR spectra of the series of SBA-15 samples. All catalysts showed a peak assigned to the surface silanol group at around 3740 cm⁻¹. NSBA-15 and MeNSBA-15 showed a new peak at 3365 cm⁻¹ assigned to the N-H vibration in secondary amine, and only MeNSBA-15 showed another peak at 2970 cm⁻¹ assigned to the C-H vibration. The amounts of carbon and nitrogen atoms were measured by elemental analysis and summarized in Table S1. Comparison of N- and C-atom amounts revealed that about one tenth of N-atoms were methylated. Therefore, we assumed that methylation occurred only on nitrogen in the SBA-15 silica framework.

3.2. Catalytic Performance in Cyclic Carbonate Synthesis

Table 1 summarizes the results of catalytic cyclic carbonate synthesis from CO₂ and β,γ-unsaturated alcohol (2-methyl-3-butyn-2-ol) over heterogeneous SBA-15-type catalysts and the well-known homogeneous catalysts, TBABr and tri-n-butylphosphine. TOF and selectivity were 1.82 h⁻¹ and >99% on MeNSBA-15 catalyst. In contrast, NSBA-15 showed little catalytic activity (TOF less than 1.0 × 10⁻³ h⁻¹). The reaction did not proceed without catalyst under the present conditions. The remarkable increase in catalytic activity caused by methylation could be primarily explained by enhanced nucleophilicity of the nitrogen site, similar to

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Table 1  Summary of the Catalytic Performances for Cyclic Carbonate Synthesis Using Carbon Dioxide and Unsaturated Alcohol

| Catalyst          | TOF [h⁻¹] | Conversion/Selectivity [%] |
|-------------------|-----------|---------------------------|
| MeNSBA-15         | 2.24      | 4.4 (>99)                 |
| NSBA-15           | <10⁻³     | (-)⁰                     |
| TBABr             | 0.68      | 2.0                       |
| Tri-n-butylphosphine | 2.58     | 6.1 (>99)                 |

Reaction conditions: 3 MPa CO₂, 5 mmol unsaturated alcohol and reaction temperature 423 K.

Amounts of catalysts used were 20, 20, 10 and 10 mg for MeNSBA-15, NSBA-15, TBABr and tri-n-butylphosphine, respectively.

a) TOF was calculated at the reaction time of 24 h.
b) Conversion and selectivity were calculated at the reaction time of 24 h.
c) Unsaturated cyclic carbonate was not detected.

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the previous finding for cyclic carbonate synthesis from cyclic ether\textsuperscript{33}). The observed TOF value over MeNSBA-15 was comparable to those over conventional homogeneous catalysts (Table 1). Few byproducts were observed under the present conditions. Reuse tests were conducted over MeNSBA-15, and little catalyst deactivation was observed in the second and third uses (Fig. 2). Therefore, leaching of the catalytic site into the solvent phase (probably due to the N-site decomposition) was insignificant.

Figure 3 shows the TOF values over MeNSBA-15 as a function of CO\textsubscript{2} partial pressure (Fig. 3(a)) and 2-methyl-3-butyln-2-ol concentration (Fig. 3(b)) as calculated from the measured solubility of 2-methyl-3-butyln-2-ol into DMF, and those with CO\textsubscript{2} and cyclic ether are also shown for comparison in Figs. S1 and S2, respectively\textsuperscript{33}). Figure 3(a) shows TOF increased linearly with higher CO\textsubscript{2} partial pressure, and became constant at around 3.5 MPa. On the other hand, TOF maintained the linear increase as a function of 2-methyl-3-butyln-2-ol concentration in Fig. 3(b). These observed dependences were different from that of cyclic carbonate formation from CO\textsubscript{2} and cyclic ether\textsuperscript{33)}, as shown in Fig. S3. The observed TOF dependences showed increase and subsequent decrease with the reactant partial pressure of both CO\textsubscript{2} and cyclic ether. Both reactions, especially for CO\textsubscript{2}, were conducted in the same pressure range from 1 to 6 MPa, so adsorption behavior on the catalytic sites would be similar. Therefore, these differences in dependences would reflect the difference in reactants and the reaction mechanism. In other words, the TOF tendency suggests changes in the major active surface species formed by adsorption of reactants. The CO\textsubscript{2} pressure dependence observed in this study (Fig. 3(a)) could be explained by the adsorption equilibrium of CO\textsubscript{2} over the active site. This proposal also suggests less interaction of $\beta,\gamma$-unsaturated alcohol with the catalytic active site. As suggested for the reaction between CO\textsubscript{2} and cyclic ether\textsuperscript{33)}, the CO\textsubscript{2} pressure dependence (Fig. S3(a)) could be explained by the competitive adsorption of both CO\textsubscript{2} and cyclic ether on the active sites.

Activation of CO\textsubscript{2} is the key step in these cyclic carbonate syntheses. These two reactions showed different CO\textsubscript{2} pressure dependences although both were tested in the same CO\textsubscript{2} pressure range (Figs. 3(a) and S3(a)).
The most plausible state of CO₂ on the methylated-nitrogen site is a carbamate-like species (Scheme 1), as observed by the previous spectroscopic study[39]. The carbamate species may only form on the methylated-nitrogen site in MeNSBA-15, whereas end-on adsorption of CO₂ proceeds over non-methylated nitrogen site of NSBA-15[39]. The catalytic reactions (Table 1) clearly showed that methylated nitrogen was essential for the reaction, which strongly suggested that the formation of carbamate species is the key for the reaction, as found for the reaction with cyclic ether[33]. Therefore, based on the formation of the carbamate species, the differences in pressure dependence could be explained by the competing adsorption (or activation) of the other reactants, cyclic ether and β,γ-unsaturated alcohol. Higher CO₂ partial pressure hampered the competing adsorption of cyclic ether[33], resulting in lower reaction rate. On the other hand, CO₂ adsorption simply saturated at around 3.5 MPa and the most abundant surface intermediate was the carbamate species for β,γ-unsaturated alcohol, under the reaction conditions applied here. Interaction of the methylated nitrogen site with β,γ-unsaturated alcohol would be much less compared with cyclic ether because of the ring opening reaction to release the distortion energy of the structure.

The hydroxyl groups in the β,γ-unsaturated alcohols could be deprotonated by the basic sites of both nitrogen and methylated nitrogen. Figure 4 shows the TOF of the reaction using different types of β,γ-unsaturated alcohols as a function of their pKa values at 298 K calculated using Advanced Chemistry Development software. The tested β,γ-unsaturated alcohols and resulting cyclic carbonates are summarized in Table 2. The measured TOF increased with lower pKa values, suggesting that deprotonation of these alcohols or intermediates derived from the alcohols with similar structural properties forms the rate limiting step. Few byproducts were observed under the conditions applied for this study. The pKa values of these reactants ranged from 12.5 to 14.5. The most likely active site was considered to be the more strongly basic methylated nitrogen, so deprotonation of the hydroxyl group of β,γ-unsaturated alcohols is very plausible. However, the reaction did not proceed over NSBA-15 catalyst (Table 1), indicating that methylation is critical for catalyzing the reaction. Therefore, deprotonation of the β,γ-unsaturated alcohol or the intermediate derived from the alcohol by another nucleophile is probably involved in the rate limiting step, although the surface nitrogen sites can be excluded. Consequently, the deprotonation rate limiting step probably involves another nucleophile, most probably the oxygen atom in the carbamate (i.e., activated CO₂ formed on methylated nitrogen). Based on this assumption, a metathesis-like reaction between non-adsorbed β,γ-unsaturated alcohol and carbamate on the site may proceed, i.e., deprotonation of the hydroxyl group by oxygen in the N⁺(C = O) O⁻ anionic moiety and simultaneous C-O bond formation between oxygen in the hydroxyl group and carbon in CO₂ (Scheme 2).

Based on the present experimental data, discussion, and previous studies[23,26,27], a reaction scheme can be proposed as shown in Scheme 3. The reaction involves the following steps: 1) carbamate formation via CO₂ adsorption (CO₂*) on the methylated nitrogen similar to the previous study[33], 2) interaction of β,γ-unsaturated alcohol with the carbamate species (UAC*), 3) deprotonation and simultaneous C-O bond formation between the carbamate and β,γ-unsaturated alcohol species to form an alkyl hydrogen carbonate-like intermediate (AC*), 4) intramolecular cyclization of the intermediate between the hydroxyl and alkyne groups to form an adsorbed cyclic carbonate (UCC*), and 5) desorption of the unsaturated cyclic carbonate (UCC). Adsorption/desorption of CO₂ as the carbamate (Step 1) is assumed to be quasi-equilibrated. Subsequently, β,γ-unsaturated alcohol interacts with the carbamate,
Table 2  Cyclic Carbonate Synthesis Using CO\textsubscript{2} and Unsaturated Alcohol (The numbers in Fig. 4 correspond to those shown here.)

| Entry | Reactions\(^a\) | \(pK_a\)\(^b\) |
|-------|-----------------|-----------------|
| 1     | \(\equiv\)OH + CO\textsubscript{2} \(\rightarrow\) | 14.56 ± 0.29 |
| 2     | \(\equiv\)OH + CO\textsubscript{2} \(\rightarrow\) | 13.34 ± 0.29 |
| 3     | \(\equiv\)OH + CO\textsubscript{2} \(\rightarrow\) | 13.34 ± 0.29 |
| 4     | \(\equiv\)OH + CO\textsubscript{2} \(\rightarrow\) | 13.34 ± 0.29 |
| 5     | \(\equiv\)OH + CO\textsubscript{2} \(\rightarrow\) | 13.34 ± 0.2 |
| 6     | \(\equiv\)OH + CO\textsubscript{2} \(\rightarrow\) | 13.14 ± 0.1 |
| 7     | \(\equiv\)OH + CO\textsubscript{2} \(\rightarrow\) | 13.07 ± 0.29 |
| 8     | \(\equiv\)OH + CO\textsubscript{2} \(\rightarrow\) | 12.53 ± 0.29 |
| 9     | \(\equiv\)OH + CO\textsubscript{2} \(\rightarrow\) | 12.53 ± 0.29 |

\(^a\) Byproducts were hardly observed under the conditions applied in this study.

\(^b\) \(pK_a\) values were calculated at 298 K using Advanced Chemistry Development software.

Scheme 2  C-O Bond Formation between Oxygen in the Hydroxyl Group of \(\beta,\gamma\)-Unsaturated Alcohol and Carbon of the Carbamate Formed on MeNSBA-15 Catalyst
and the hydrogen atom of hydroxyl group in the \( \beta,\gamma \)-unsaturated alcohol undergoes nucleophilic attack from the oxygen atom in the carbamate, and simultaneous C-O bond formation proceeds (Steps 2 and 3). The other pathway may be important at Step 3, in which deprotonation and simultaneous C-O bond formation are accompanied by the desorption of the molecule (UAC* and subsequent Step 3' in Scheme 3). This step forms a released alkyl hydrogen carbonate molecule (AC), which is unstable and the equilibrium is largely on the reactant side (i.e., CO\(_2\)ʴ \( \beta,\gamma \)-unsaturated alcohol, as shown in Scheme 3)\(^{40} \). Then, the intermediate (AC*) undergoes intramolecular cyclization between the hydroxyl group and unsaturated bond (Step 4). Finally, the formed cyclic carbonate desorbs (Step 5). Intramolecular cyclization (Step 4) is the rate-determining step based on previous studies, in which activation of the unsaturated bond by a metal site\(^{26,27} \) or formation of active hypoiodite (i.e., R\(_{\text{O}}\)\( \text{I} \))\(^{23} \) enhanced the reaction step. However, the correlation between TOF and pKa value of \( \beta,\gamma \)-unsaturated alcohol in Fig. 4 is important. The step involving the \( \beta,\gamma \)-unsaturated alcohol (Steps 2 and 3) is probably not the rate limiting step, as the observed correlation reflects the correlation between TOF and an intermediate derived from \( \beta,\gamma \)-unsaturated alcohol, i.e., alkyl hydrogen carbonate-like intermediate (AC*). The discussion assumes a somewhat linear correlation between the pKa values of \( \beta,\gamma \)-unsaturated alcohols and the corresponding alkyl hydrogen carbonate, so experimental comparison is necessary to confirm the assumption in the future.

According to Scheme 3, the formation rate of the unsaturated cyclic carbonate \( (r_{UCC}) \) is proportional to the concentration of alkyl hydrogen carbonate-like intermediate (AC*) on the methylated N-atom sites:

\[
r_{UCC} = k_4[AC*]
\]

(1)

where, \( k_4 \) is the rate constant for the formation of the intermediate. Equation (1) takes a new form after accounting for the quasi-equilibrated CO\(_2\) adsorption (Step 1) and a pseudo steady-state for the intermediates:

\[
\frac{r_{UCC}}{L} = \frac{K_1k_2k_3}{k_3} \left[ UAC \right] \frac{[CO_2]}{k_3 + K_1[CO_2]}
\]

(2)

where \( [L] \) is the total number of methylated N-atoms:

\[
[L] = \left[ * \right] + \left[ CO_2 \right]
\]

(3)

\( K_1 \) is the equilibrium constant for the adsorption of CO\(_2\) and \( k_2, k_3 \) and \( k_3 \) are the rate constants for the interaction of \( \beta,\gamma \)-unsaturated alcohol, deprotonation to form an alkyl hydrogen carbonate-like intermediate, and deprotonation accompanying the desorption of alkyl hydrogen carbonate, respectively. The obtained rate expression in Eq. (2) could explain the experimen-
tal results in Fig. 3 and does not contradict the previous studies (23,26,27). Compared with the previously proposed reaction mechanisms over other catalysts (23,26,27), the present study proposes the formation of adsorbed alkyl hydrogen carbonate as an intermediate (AC*). As described above, the intermediate desorbs and forms alkyl hydrogen carbonate molecule, then easily self-decomposes into CO₂ and β,γ-unsaturated alcohol. Over MeNSBA-15 catalyst, the key is the formation of the adsorbed state of alkyl hydrogen carbonate, which is optimum for the subsequent intramolecular cyclization reaction. The formation of the carbamate species is critical to the formation of the intermediate in its adsorbed state via the reaction with β,γ-unsaturated alcohol.

4. Conclusions

MeNSBA-15 catalyzes cyclic carbonate synthesis from CO₂ and β,γ-unsaturated alcohol. The TOF as a function of CO₂ partial pressure and 2-methyl-3-buten-2-ol concentration reflects the major active surface species. The difference in pressure dependence of the cyclic carbonate syntheses can be explained by the competing activation of the reactants. The affinity of the methylated nitrogen site with β,γ-unsaturated alcohol would be much lower than that of cyclic ether. Cyclic carbonate synthesis from β,γ-unsaturated alcohol over MeNSBA-15 involves two steps in the proposed reaction mechanism. First, MeNSBA-15 chemisorbs CO₂ and forms carbamate intermediate. Then, MeNSBA-15 also promotes intramolecular cyclization of the intermediate between the hydroxy and alkynyl or alkenyl groups. MeNSBA-15 traps alkyl hydrogen carbonate, which is easily decomposed to CO₂ and β,γ-unsaturated alcohol in the gas phase on the catalytic site, and suppresses the reverse reaction to form alkyl hydrogen carbonate.

Supporting Information

Supplementary data associated with this article can be found, in the online version, at https://jstage.jst.go.jp/browse/jpi/-char/en (DOI: doi.org/10.1627/jpi.63.149).

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要 旨

メチル基修飾した窒素置換 SBA-15 を触媒とする β,γ-不飽和アルコールと CO₂から環状カーボネートへの変換反応における反応経路に関する考察

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メチル基修飾した窒素置換 SBA-15（MeNSBA-15）は、骨格中のメチル基修飾された窒素原子が触媒活性点として働き、不飽和アルコールと CO₂からの環状カーボネート合成に対して触媒作用を有する。合成された不飽和環状カーボネートは様々な化成品の合成中間体になり得る有用な化合物である。MeNSBA-15 のこの反応に対する触媒作用を解明するために、反応基質であるアルコール体と CO₂のそれぞれの濃度に対する훨은オーバー頻度 (TOF) の変化を測定した。その変化の傾向から、CO₂の触媒表面に対する親和性が不飽和アルコールよりも高く、反応中において活性点上でカルバメート種と呼ばれる CO₂が活性化した種が存在する考えた。このことにより、MeNSBA-15 によってこの反応は、カルバメート種の生成、カルバメート上への不飽和アルコールの吸着、アルコールの脱プロトン化とそれに伴う C-O 結合生成、分子内環化、生成物の脱離という5段階の反応過程を経て進行していると推定した。