

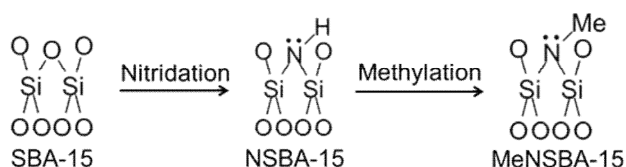
## 論文の内容の要旨

論文題目 **Clarifying catalysis of nitrogen-substituted mesoporous SBA-15 in CO<sub>2</sub> transformation**  
(CO<sub>2</sub>変換反応における窒素置換SBA-15の触媒作用解明)

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Carbon dioxide Capture and Utilization (CCU) is a main topic for chemical industry to contribute to reduction of CO<sub>2</sub> emission. CO<sub>2</sub> can be considered as one of the sustainable C1 resources and useful to form complex organic products.<sup>1, 2</sup> If a high-valued chemical is able to be produced by CO<sub>2</sub> transformation, utilization of CO<sub>2</sub> is attractive.

CO<sub>2</sub> transformation is divided into two types of reactions, reduction and acid-base reaction. Various alkanes and alcohols have been mainly produced by the reduction and



**Figure 1.** Nitridation and subsequent methylation over SBA-15.

used as energy carriers. On the other hand, high value-added chemical compounds, such as carbonate, carboxylic acid, and lactone, have been produced by the acid-base reactions.

Nitrogen-substituted mesoporous silicas, such as NMCM-41 and NSBA-15, have been proposed as a solid base catalyst.<sup>3, 4</sup> NSBA-15 possesses 2D hexagonal mesoporous structure, uniform pore size, and high surface area. It is synthesized by substitution of nitrogen atom with oxygen in the silica framework via nitridation.<sup>5</sup> We found that subsequent methylation on the nitrogen atom (shown in Figure 1) enhanced the basicity, and methyl group prevented the nitrogen atom site from deactivation by water.<sup>3</sup> Methylated nitrogen-substituted SBA-15 (MeNSBA-15) was shown to catalyze cyclic carbonate synthesis, which is one of CO<sub>2</sub> transformation. In this dissertation, methylated nitrogen-substituted SBA-15 (MeNSBA-15) was applied as a catalyst in some cyclic carbonate syntheses. The catalysis of MeNSBA-15 in the CO<sub>2</sub> transformation is clarified in order to elucidate mechanisms of CO<sub>2</sub> and lay out theoretical plans for development of catalyst for CO<sub>2</sub> transformation. The best-laid plan let us select an optimal catalyst for each CO<sub>2</sub> transformation catalyzed by an acid or base function.

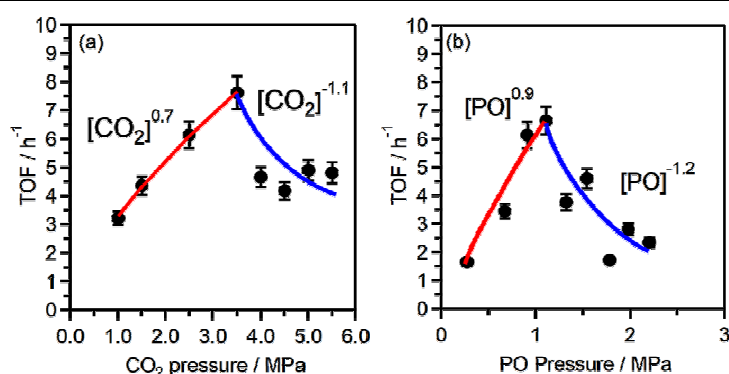
Table 1 summarizes the results of the cyclic carbonate synthesis from PO and CO<sub>2</sub> over SBA-15-type and other well-studied homogeneous base catalysts. The reaction did not proceed without catalyst under the conditions applied in this study. The activation energy was 203 kJ mol<sup>-1</sup>, determined by DFT calculations.<sup>6</sup> Among the catalysts tested, MeNSBA-15 was found to show high TOF (6.4 h<sup>-1</sup>) and selectivity (>99%). In contrast, NSBA-15 showed little catalytic activity (TOF less than 1.0 × 10<sup>-3</sup> h<sup>-1</sup>).

Figure 2 shows the changes in the TOF of cyclic carbonate synthesis over MeNSBA-15 as a function of CO<sub>2</sub> (Fig. 2a) and PO (Fig. 2b) partial pressure. Both plots had a maximum TOF under a certain reactant partial pressures. These results suggest that both adsorbed CO<sub>2</sub> and PO work as reaction inhibitors under high partial pressure conditions (CO<sub>2</sub> partial pressure over 3.0 MPa and PO partial pressure over 1.0 MPa), and most plausibly, block the catalytic sites. CO<sub>2</sub> is a well-known probe molecule for basic sites and should adsorb on the methylated N-atoms of the catalyst. PO also interacts with the basic N-atom through the β-carbon of the molecule to form an alkoxide.<sup>7-9</sup> Thus, it is suggested that the both reactants, CO<sub>2</sub> and PO, compete to adsorb on the methylated N-atoms and occupy the sites under excess conditions.

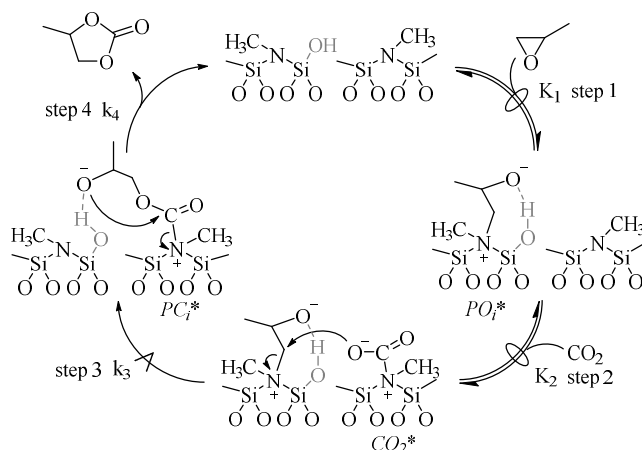
The observed pressure dependences could be explained by the Langmuir-Hinshelwood type mechanism rather than the Eley-Rideal type mechanism. The most plausible reaction site on MeNSBA-15 is a

**Table 1.** The catalytic performances of cyclic carbonate synthesis from PO and CO<sub>2</sub> (3 MPa CO<sub>2</sub>, 1 MPa PO, 373 K reaction temperature).

Catalyst	TOF [h <sup>-1</sup> ]	Conversion (Selectivity) [%]	E <sub>a</sub> [kJ mol <sup>-1</sup> ]
None	-	- (-)	203
MeNSBA-15	6.4	13.3 (>99)	43.2
NSBA-15	<10 <sup>-3</sup>	- (-)	-
TBABr	7.5	22.3 (>99)	45.2
NMe <sub>3</sub>	0.64	40.8 (83)	68.9



**Figure 2.** Changes in the TOF of propylene carbonate synthesis on MeNSBA-15 (50 mg catalyst, 373 K, 6 h) as a function of (a) CO<sub>2</sub> pressure (1.0 MPa PO) and (b) PO amount (3 MPa CO<sub>2</sub>).



**Figure 3.** Proposed sequence of reaction steps for propylene carbonate synthesis on MeNSBA-15.

neighboring methylated N atom pair (Figure 3). Ring-opening reaction of PO proceeds on the basic site followed by a bimolecular reaction with CO<sub>2</sub> adsorbed on the neighboring basic sites, forming propylene carbonate. The rate expression for propylene carbonate synthesis was given as follows

$$\frac{r_{PC}}{[L]} = K_1 K_2 k_3 \frac{[PO][CO_2]}{(1 + K_1[PO] + K_2[CO_2])^2}$$

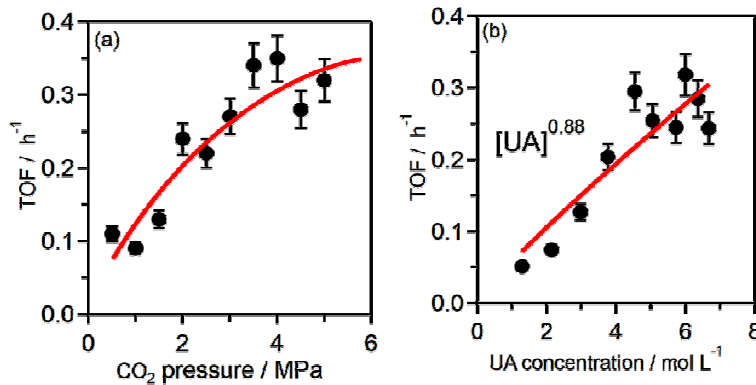
where  $[L]$  is the total number of available methylated N-atoms forming the pair sites. This expression could mathematically explain the experimental results in Fig 2.

Table 2 summarizes the results of cyclic carbonate synthesis from unsaturated alcohol (2-methyl-3-butyn-2-ol, UA) and CO<sub>2</sub> over SBA-15-type, TBABr, and tri-*n*-butylphosphine (3 MPa CO<sub>2</sub>, 5 mmol UA, 423 K reaction temperature). The reaction did not proceed without catalyst under the

**Table 2.** The catalytic performances of cyclic carbonate synthesis from CO<sub>2</sub> and UA (3 MPa CO<sub>2</sub>, 5 mmol UA, 423 K reaction temperature).

Catalyst	TOF [h <sup>-1</sup> ]	Conversion (Selectivity) [%]	<i>E<sub>a</sub></i> [kJ mol <sup>-1</sup> ]
MeNSBA-15	2.24	4.4 (>99)	66.1
NSBA-15	<10 <sup>-3</sup>	(-)	-
TBABr	0.68	2.0	41.6
Tri- <i>n</i> -butylphosphine	2.58	6.1 (>99)	24.4

conditions applied in this study. TOF and selectivity were 1.82 h<sup>-1</sup> and >99% on MeNSBA-15. In contrast, NSBA-15 showed little catalytic activity (TOF less than 1.0 × 10<sup>-3</sup> h<sup>-1</sup>).



**Figure 4.** Changes in the TOF of cyclic carbonate synthesis from UA on MeNSBA-15 (20 mg catalyst, 373 K, 24 h) as a function of (a) CO<sub>2</sub> pressure (5 mmol UA) and (b) UA concentration (3 MPa CO<sub>2</sub>)

function of UA concentration (CO<sub>2</sub> partial pressure was 3 MPa). The TOF dependences lead that this reaction proceeds on MeNSBA-15 according to the Eley-Rideal mechanism.

Plausible reaction steps are shown in Figure 5. The rate expression is given as follows

$$\frac{r_{VCC}}{[L]} = K_1 k_2 \frac{[UA][CO_2]}{(1 + K_1[CO_2])}$$

where,  $[L]$  is the total number of methylated N-atoms. This expression could mathematically explain the experimental results in Fig 4. Formation of carbamate intermediate and interaction of MeNSBA-15 with

unsaturated alcohol were discussed by ab initio molecular orbital calculation. (MP2/6-31g(d) or MP2/6-31+g(d,p) over Gaussian16) Figure 6 shows a diagram of potential energy of critical state in cyclic carbonate synthesis from unsaturated alcohol. Almost all protons seem to be abstracted from UA because CO<sub>2</sub> adsorption on MeNSBA-15 is an endothermic process; on the other hand proton abstraction on MeNSBA-15 is an exothermic process. However, it is difficult to form cyclic carbonate via proton abstraction, because formation of monoalkylcarbonate anion requires several times larger energy than formation of carbamate intermediate. Therefore, it seems that this reaction proceeds via formation of carbamate intermediate.

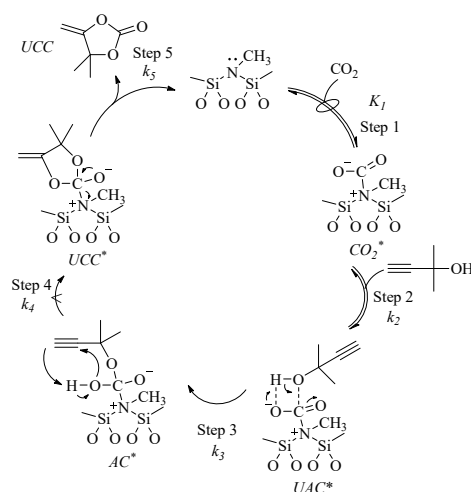
Through the studies in the dissertation, it was found that the reaction mechanism of cyclic carbonate synthesis from CO<sub>2</sub> and propylene oxide was the Langmuir-Hinshelwood mechanism and the reaction mechanism of cyclic carbonate synthesis from CO<sub>2</sub> and unsaturated alcohol was the Eley-Rideal mechanism.

MeNSBA-15 catalyzes both two cyclic carbonate syntheses by forming a bent CO<sub>2</sub>. The bent CO<sub>2</sub> seems unstable and more active than a linear-shaped CO<sub>2</sub>.

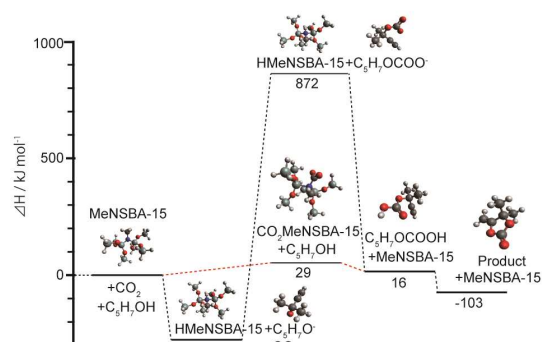
For development of a solid base catalyst for CO<sub>2</sub> transformation, this dissertation indicates that solid material is required to adsorb CO<sub>2</sub> with endothermic process for CO<sub>2</sub> activation.

## References

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**Figure 5.** Proposed sequence of reaction steps for cyclic carbonate synthesis from UA on MeNSBA-15.



**Figure 6.** Potential energy diagram of cyclic carbonate synthesis from UA on MeNSBA-15.