Kinetic analysis of cyclic carbonate synthesis over methylated nitrogen-substituted SBA-15

Kiyoyuki Yamazaki, Takahiko Moteki, Masaru Ogura*

Institute of Industrial Science, The University of Tokyo, Tokyo, 153-8505, Japan

**Corresponding author: oguram@iis.u-tokyo.ac.jp*

Abstract:

Methylated nitrogen-substituted mesoporous silica, MeNSBA-15, was found to catalyze cyclic carbonate synthesis via cycloaddition of CO_2 with cyclic ethers. The kinetic analysis of propylene carbonate synthesis over MeNSBA-15 was performed, and the interpretation of the turn-over frequency (TOF) of the products clarified the reaction mechanism. The most plausible mechanism was proposed to be a Langmuir–Hinshelwood type mechanism involving a kinetically relevant bimolecular reaction step over the methylated-nitrogen pair sites.

Keywords: Functionalized mesoporous silica, CO_2 transformation, Kinetic analysis

1. Introduction

Nitrogen-substituted mesoporous silicas, such as NMCM-41 and NSBA-15, have been recently proposed for a solid base catalyst[1,2]. NSBA-15 has mesoporous 2D hexagonal structure (Fig.1), uniform pore size, and high surface area. Nitrogen atom could be substituted for oxygen atom in the mesoporous silica framework by nitridation[3], and the N atom works as a basic site. In previous works, our group found that subsequent methylation on the N atom (Fig.2) strengthened the basicity, and that methyl group prevented them to be deactivated by H_2O[1]. In this work, we report that methylated nitrogen-substituted SBA-15 can catalyze cyclic carbonate synthesis. Kinetics for this reaction and properties of catalysts are elucidated.

Figure 1. NSBA-15 having mesoporous 2D hexagonal structure

Figure 2. Nitridation and subsequent methylation over SBA-15

2. Experimental

Calcined SBA-15 was heated at 1173 K in ammonia gas flow of 1L/min for 10 h to form NSBA-15. MeNSBA-15 was prepared by methylating NSBA-15 with methyl iodide in anhydrous ethanol solution at 350 K for 24 h.

Synthesis of propylene carbonate was carried out in a 5 mL stainless steel reactor. First, 25−50 mg of catalyst and 7.1−41.7 mmol of cyclic ether were placed in the reactor. Then, CO_2 was charged into the reactor to 1−6 MPa, and the reactor was heated at 353−423 K for 1−48 h. After the reactor was cooled and degassed, the product was abstracted by acetone. The filtrate was analyzed by a gas chromatograph. Tested catalysts were MeNSBA-15, NSBA-15, and tetrabutylammonium bromide (TBABr).

3. Results and Discussion

Table 1 summarizes the results of the propylene carbonate synthesis from CO_2 and propylene oxide (PO) over SBA-15-type and TBABr catalysts (3 MPa CO_2, 1 MPa PO, 373 K, 1−6 h). The reaction did not proceed without catalyst under the conditions applied in this study. Among the tested catalysts, MeNSBA-15 showed the highest TOF (6.4 h^{-1}) and selectivity (>99%). Pretreatment for catalyst activation was not necessary for the MeNSBA-15 catalyst. Compared with MeNSBA-15, NSBA-15 showed little catalytic

activity (TOF less than 1.0×10^{-3} h^{-1}). The remarkable increase in the catalytic activity caused by methylation could be explained by the enhanced basicity or nucleophilicity, similar to the previous published examples in Knoevenagel condensation[1] and Morita-Baylis-Hilman reaction[2].

Figure 3 shows the changes in the TOF of cyclic carbonate synthesis over MeNSBA-15 as a function of CO_2 and PO initial pressures. Both plots had maximum along with the reactant initial pressures. These results suggest that both adsorbed CO_2 and PO would work as reaction inhibitors, and most plausibly, block catalytic active sites under high partial pressure conditions (CO_2 and PO reactant initial pressure over 3 and 1 MPa, respectively). Carbon dioxide, a well-known probe molecule for basic sites, would easily adsorb on the methylated N atoms to form a carbamate. PO would also interact with the N atom through the β-carbon of the molecule to form an alkoxide[5,6].

Table 1. Summary of the catalytic performances for propylene carbonate synthesis (3 MPa CO_2, 1 MPa PO, 373 K)

Catalyst	TOF [h^{-1}]	Selectivity[b] [%]	E_a [kJ mol^{-1}]
None	-[a]	-	203[c]
MeNSBA-15	6.4	>99	45.0
NSBA-15	$<1.0\times10^{-3}$	-	-
TBABr	1.7	>99	46.1

a: Propylene carbonate is not detected by a gas chromatograph

b: Selectivity at reaction time of 6 h

c: The value referred to the Reference 4.

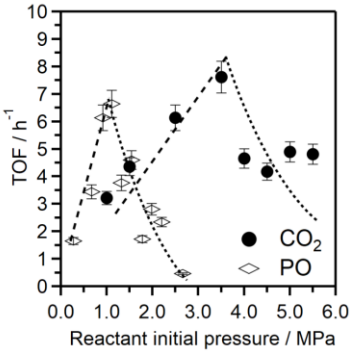

Figure 3. Change in the TOF as a function of CO_2 (1.0 MPa PO) and PO (3.0 MPa CO_2) initial pressure

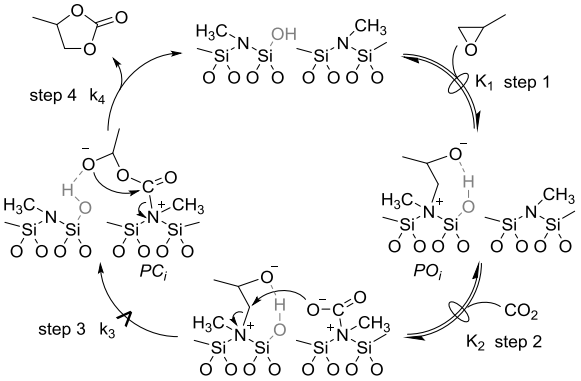

Figure 4. Proposed sequence of reaction steps

The pressure dependences shown in Figure 3 could be explained by the Langmuir-Hinshelwood type mechanism rather than the Eley-Rideal type mechanism proposed in other catalysts. The most plausible reaction site on MeNSBA-15 is a neighboring methylated N atom pair (Fig.4). It can be also assumed that CO_2 or PO on a non-functionalized N atom reacts with a PO or CO_2 intermediate on a neighboring methylated N atom. However, these assumptions could not provide the rate expression that explains the experimental results. The negative dependence of TOF at high reactant partial pressures could be explained only when methylated N atom pair is assumed as an active site. This suggests that the formation of more reactive carbamate and alkoxide species are necessary. Figure 4 shows the proposed reaction steps, in which ring-opening reaction of PO proceeds on the basic site followed by a bimolecular reaction with CO_2 adsorbed on a neighboring basic site, forming propylene carbonate.

4. Conclusions

MeNSBA-15 was shown to catalyze cyclic carbonate synthesis. The observation of a drastic increase in the TOF value clearly indicated that the activity of the catalyst was enhanced by methylation. The kinetic analysis revealed the Langmuir–Hinshelwood mechanism with a kinetically relevant bimolecular reaction step between a ring-opened alkoxide intermediate and a carbamate over neighboring methylated nitrogen pair sites.

References

1. K. Sugino, N. Oya, N. Yoshie, M. Ogura, J. Am.Chem. Soc., 133 (2011) 20030.
2. Y. Furukawa, M. Ogura, J. Am. Chem. Soc., 136 (2014) 119.
3. T. Hasegawa, C. K. Krishnan, M. Ogura, Micropor. Mesopor. Mater., 132 (2010) 290.
4. F. Castro-Gomez, G. Salassa, A.W. Kleij, C. Bo, Chem. - Eur. J., 19 (2013) 6289.
5. M. North, R. Pasquale, Angew. Chem., Int. Ed., 48 (2009) 2946.
6. V. Butera, N. Russo, U. Cosentino, C. Greco, G. Moro, D. Pitea, E. Sicilia, ChemCatChem, 8 (2016) 1167.