Evaluation of catalytic performance of methylated nitrogen-substituted mesoporous silica for synthesis of cyclic carbonate

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A lot of research has been carried out for applying mesoporous silica materials as catalyst, adsorbent, separation membrane, molecule sensor, and drug delivery case[1]. These characters come from their uniform mesoporosity compared with microporous zeolite[2].

Nitrogen-substituted mesoporous silicas such as MCM-41 and SBA-15 have recently been proposed for a solid base catalyst. These mesoporous silicas have a 2D hexagonal structure, large pore size and high surface area. Nitrogen atom is substituted for O atom in mesoporous silica by nitridation[3]. The N atom in mesoporous silica framework becomes basic sites. In previous works, our group found that methylation (**Fig.1**) reinforced the basicity of nitrogen-substituted solid materials, and that methyl group prevented them to be deactivated by H_2O [4] In this work, we will report that methylated nitrogen-substituted SBA-15(MeNSBA-15) can promote a reaction of carbon dioxide and epoxide. This reaction forms cyclic carbonate which is a precursor of polycarbonate. (**Fig.2**) Then, scheme of this reaction and properties of catalysts are elucidated by trying synthesis of cyclic carbonates using various substrates.

Calcined SBA-15 was heated at 1173 K under ammonia gas flow at 1L/min for 10 h. Then, alomost a half of O atom on SBA-15 was replaced by N atom [3] to be NSBA-15. MeNSBA-15 was prepared by methylating NSBA-15 with methyl iodide in EtOH solution at 350 K for 24 h.

Synthesis of propylene carbonate was carried out in a 5 mL stainless steel reactor. Catalyst and propylene oxides were placed into the reactor. Then, CO_2 was charged into the reactor to 3MPa, and the reactor was heated to a 100 °C. After a while the reactor was degassed. Acetone for the abstraction of the catalyst was added to the solution. The filtrate was analyzed by gas chromatograph. The catalytic performances of MeNSBA-15 and NSBA-15 were compared with those of tetrabutyl ammonium bromide (TBABr), trimethylamine (NMe_3), cesium ion-exchanged SBA-15(CsSBA-15) and CeO_2.

Table 1 shows TOF and activation energy for synthesis of propylene carbonate, which is one of cyclic carbonates. MeNSBA-15 showed the better TOF than other catalysts tested so far. On the other hand, NSBA-15 could not catalyze this reaction under the conditions used in this study. Therefore, methylation was found drastically influenced on the activity of NSBA-15.

Table 1 Results of synthesis of propylene carbonate

Catalyst	TOF(h^{-1})	E_a(kJ mol^{-1})
None[5]	-	203[5]
NSBA-15	$<10^{-3}$	-
MeNSBA-15	4.2	45.0
TBABr	1.7	46.1
NMe_3	0.52	68.9
CsSBA-15	$<10^{-3}$	-
CeO_2	$<10^{-3}$	-

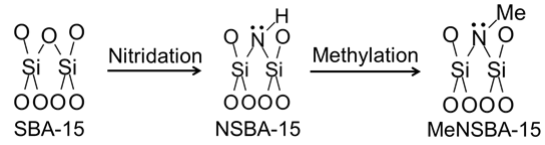

Fig. 1 Formation of nitrogen-substituted and N-methylated silica (SBA-15)

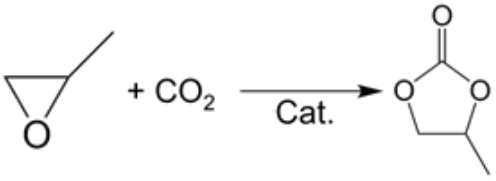

Fig. 2 Synthesis of cyclic carbonate

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