

Homogeneous and heterogeneous 4-(*N,N*-dialkylamino)pyridines as effective single component catalysts in the synthesis of propylene carbonate

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Abstract

4-(*N,N*-Dimethylamino)pyridine (DMAP) is shown to catalyze the reaction of propylene oxide with carbon dioxide in high yields without added co-catalyst. Moreover, propylene carbonate is the only product obtained when the reaction is conducted under rigorously dry conditions. This result contrasts previous findings indicating minimal or no conversion of the epoxide using DMAP alone. Additionally, a new immobilized DMAP analog has been synthesized that shows productivity comparable to the homogeneous catalyst. The supported catalyst is characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA), N₂ physisorption, solid state ¹³C and ²⁹Si CP-MAS NMR, and FT-Raman spectroscopy. This supported catalyst can be readily recovered without utilization of high temperature distillation.

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Keywords: Cyclic carbonate; 4-(*N,N*-Dimethylamino)pyridine; DMAP; SBA-15; Supported catalyst

1. Introduction

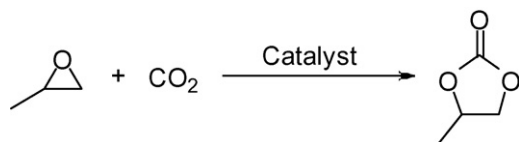
The synthesis of cyclic carbonates is of continuing interest for two principal reasons [1–5]. First, cyclic carbonates are useful molecules as precursors in fine chemical and pharmaceutical syntheses due to their cyclic and chiral nature [6]. Second, these compounds have applications as specialty polar solvents, as precursors to 1,2-diols, as curing agents, and in electrolytic formulations for high-energy density batteries [7]. Cyclic carbonates are also interesting from an environmental standpoint due to the utilization of carbon dioxide (CO₂) as a reactant in the synthesis (Scheme 1).

Many bifunctional catalysts possessing both acidic and basic sites have been reported for the synthesis of cyclic carbonates, including alkali-loaded zeolites [8–10], mixed oxides [11], and amine-functionalized oxide materials [5,12–14]. In many of these cases, it is suggested that the basic sites activate the CO₂ molecule and the acidic sites activate the epoxide. Homogeneous systems combining Lewis acids and Lewis bases also

have been reported for this reaction [15]. Another common class of catalytic system for cyclic carbonate production combines a transition metal compound, often a salen complex, with a Lewis basic co-catalyst. Both heterogeneous [16–20] and homogeneous versions of this system have been studied [21–31]. In these cases, the most frequently suggested mechanism shows the metal species activating the epoxide and the base opening the epoxide ring. A final class of catalysts that has been commonly employed is quaternary onium salts. Catalysts of this type can be used as single component catalysts in either homogeneous [32] or supported form [33–37], although it was recently reported that reaction rates can be substantially increased by combining the onium salt with a weak Bronsted acid such as silanols on silica surfaces [36].

One aspect of the catalysis of cyclic carbonate reactions where there are many conflicting reports is the activity of the Lewis basic co-catalyst in the reaction. One recent report suggests that a single Lewis basic component may be able to promote the coupling of epoxides and CO₂. In this work, Du and coworkers studied polymer resins with primary, secondary, and tertiary amine groups as single component catalysts in the synthesis of propylene carbonate, and they found all of these materials to be active at 80 bar CO₂ pressure and 100 °C

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Scheme 1.

[34]. In contrast, Zhang and coworkers found that a silica supported strong tertiary amine base, 1,5,7-triazabicyclo[4,4,0]dec-5-ene (TBD), was completely inactive at 20 bar CO₂ pressure and 150 °C when the surface silanols, hypothesized to be co-catalysts, were rendered unreactive via a capping reaction [14]. Another example of conflicting data concerns the use of 4-(*N,N*-dimethylamino)pyridine (DMAP) as a single component catalyst. Shen and coworkers report that DMAP is inactive as a single component catalyst at 36 bar CO₂ pressure and 120 °C [15]. In contrast to Shen, Sankar found DMAP to be an active catalyst under the relatively mild conditions of 4 bar CO₂ pressure and 120–140 °C [16]. In bifunctional metal complex/DMAP systems, it is often assumed that both components are needed to effect catalysis. The above examples showing the activity of the Lewis base alone suggest that this may not be the case. In agreement with that suggestion and in concert with the work of Sankar, we report here the use of DMAP as a single component catalyst in the non-enantioselective synthesis of propylene carbonate.

One drawback to the use of DMAP as a homogeneous catalyst in the synthesis of cyclic carbonates is that it can be expensive to separate the pure carbonate from the catalyst. Since cyclic carbonates have high boiling points, purification by distillation can engender significant energy costs as well as thermally degrade the catalyst. Therefore, an equally productive and selective heterogeneous catalyst that could be recovered from the product without the need for high temperature separation is an attractive goal. Supporting analogs of selective and active homogeneous catalysts on solid supports has been an active area of research for quite some time, and there are reports of numerous silica-supported organic base hybrid catalysts used for cyclic carbonate synthesis [5,12–14,34,37]. Similarly, there are reports of DMAP type functionalities immobilized on organic and inorganic supports including polymers and sol–gels [17,38–43], although to our knowledge these have not been evaluated for cyclic carbonate synthesis. Building on these precedents, we have synthesized a new DMAP analog tethered to an SBA-15 support. We show that this supported catalyst gives comparable productivity to the homogeneous catalyst under the conditions used and can be easily separated from the product by filtration.

2. Experimental

2.1. Materials

4-(Dimethylamino)pyridine (Acros), 4-methylaminopyridine (Aldrich), and 2,2'-azo-bis(isobutyronitrile) (AIBN) (Aldrich) were dried under vacuum and stored in a nitrogen dry box. 3-Mercaptopropyltrimethoxysilane (Alfa-Aesar), *n*-butyllithium 1.6 M in hexanes (Aldrich), tetraethyl orthosilicate

(TEOS) (Aldrich), poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Aldrich), and 99.999% pure research grade carbon dioxide (<3 ppm water) (Airgas) were used as received. Phenol (Acros) was used as received except where otherwise indicated. Propylene oxide (Aldrich) and dichloromethane (Fisher) were dried with calcium hydride; chloroform (Aldrich) was dried with 4 Å molecular sieves; and allyl bromide (Acros) was dried with magnesium sulfate. Tetrahydrofuran (THF) and toluene were used after purification and drying via a packed bed solvent system made of copper oxide and alumina columns in the case of THF and dual alumina columns in the case of toluene [44].

2.2. Synthesis of 4-(*N*-allyl-*N*-methylamino)pyridine (**1**)

A solution of 4-(methylamino)pyridine (MAP) (2.0 g, 18.5 mmol) in THF was prepared in a nitrogen dry box and then stirred under argon at 0 °C for 2 h. *n*-Butyllithium (13 ml of 1.6 M in hexanes, 21 mmol) was added via syringe to the MAP/THF mixture while under an argon purge and stirred for an additional 1 h at 0 °C. Dry allyl bromide (3.4 g, 28.1 mmol) in THF was added via syringe, and the mixture was allowed to warm to room temperature overnight while being stirred. Excess *n*-butyllithium was quenched with DI water, and volatile components were removed under vacuum. Compound **1** was recovered as a dark yellow oil by extraction from dichloromethane/DI water and dried.

1: yield 72%. ¹H NMR (400 MHz, CDCl₃): δ 8.2 (d, 2H), δ 6.5 (d, 2H), δ 5.8 (m, 1H), δ 5.1–5.2 (dd, 2H), δ 3.9 (d, 2H), δ 3.0 (s, 3H). ¹³C NMR (400 MHz, CDCl₃): δ 153.7, 150.1, 132.1, 116.8, 106.8, 53.9, 37.4.

2.3. Synthesis of 4-[*N*-methyl-*N*-(3'-(3'-(trimethoxysilyl)propylthio)propyl)amino]pyridine (**2**)

A solution of **1** (2.0 g, 13.5 mmol) in chloroform was prepared in a nitrogen dry box. 3-Mercaptopropyltrimethoxysilane (12 g, 61 mmol) was added to the solution along with AIBN (150 mg, 0.9 mmol). The reaction mixture was then stirred under reflux conditions under an argon blanket overnight. Solvent was removed under vacuum, and excess 3-mercaptopropyltrimethoxysilane was distilled off at 110 °C under vacuum to isolate compound **2** as a brown oil.

2: yield 95%. ¹H NMR (400 MHz, CDCl₃): δ 8.2 (d, 2H), δ 6.5 (d, 2H), δ 3.5 (s, 9H), δ 3.4 (t, 2H), δ 2.9 (s, 3H), δ 2.5 (m, 4H), δ 1.8 (m, 2H), δ 1.7 (m, 2H), δ 0.7 (t, 2H). ¹³C NMR (400 MHz, CDCl₃): δ 153.3, 149.8, 106.4, 50.5, 50.0, 37.5, 35.2, 29.1, 26.4, 22.9, 8.6. MS (ESI): *m/z* 345.2 [*M*+*H*]⁺. Accurate mass: anal. calcd. for C₁₅H₂₉N₂O₃SSi, 345.16627; found, 345.1647.

2.4. Synthesis of SBA-15

SBA-15 was synthesized according to literature procedures [45]. In a typical batch, the copolymer template (18 g) was dissolved in HCl (103.5 g) and DI water (477 g). TEOS (38.4 g) was added to the solution which was stirred for 20 h at 35 °C. Then, the solution was heated to 80 °C and maintained at that

temperature for 24 h. The reaction mixture was quenched with DI water, filtered, and washed with several portions of DI water to remove the copolymer and obtain SBA-15 as a white powder. The SBA-15 was dried for 3 h at 50 °C and then calcined according to the following temperature program: (1) ramp to 200 °C at 1.2 °C/min, (2) hold at 200 °C for 1 h, (3) ramp to 550 °C at 1.2 °C/min, and (4) hold at 550 °C for 6 h. Finally, the calcined SBA-15 was heated under vacuum at 200 °C for 3 h and stored in a nitrogen dry box. The procedure yielded approximately 12 g of SBA-15.

2.5. Synthesis of 4-[N-methyl-N-(3'-(3'-(trimethoxysilyl)propylthio)propyl)amino]pyridine supported on SBA-15 (DMAP-SBA, 3)

Compound **2** (1.0 g, 2.9 mmol) was added drop-wise to a solution of calcined SBA-15 (1.5 g) in dry toluene in a nitrogen dry box. The solution was stirred under reflux conditions under an argon blanket overnight. The functionalized DMAP-SBA was then filtered in the dry box and washed with toluene and hexanes. Finally, compound **3** was dried overnight under vacuum to give a pale brown powder. The procedure yielded approximately 2 g of compound **3**.

2.6. Catalytic reactions

In a representative reaction, DMAP or an immobilized analog (0.36 mmol), propylene oxide (5.20 g, 89.5 mmol), and dichloromethane (1.33 g, 15.7 mmol) were charged into a 50 ml Parr stainless steel reactor and sealed inside a nitrogen dry box. The reactor was then removed from the glove box and connected to a supply of 3.4 bar of CO₂ for 10 min with no heating. Next, the reactor was heated to 120 °C, and the CO₂ supply pressure was increased to 17.2 bar. The contents were maintained at these conditions for the length of the reaction, and then the reaction was quenched by placing the reactor in an ice bath. The excess pressure was released, and the reactor contents were transferred into a round-bottom flask. Unreacted propylene oxide and dichloromethane were removed under vacuum, and the yield of propylene carbonate was determined from the residual weight after subtracting the weight of the charged catalyst [22]. Production of propylene carbonate was verified by GC comparison with a known standard of propylene carbonate (99.5% pure, Acros) and by ¹H and ¹³C NMR.

2.7. Supported catalyst characterization

Solid state cross-polarization magic angle spinning (CP-MAS) NMR analyses were conducted on a Bruker DSX 300-MHz spectrometer with samples packed in 7-mm zirconia rotors. For ¹³C CP-MAS samples, the following parameters were used: 5 kHz spin rate, 16,000 scans, 90° pulse length of 5 μs, and repetition time between scans of 4 s. For ²⁹Si CP-MAS samples, the following parameters were used: 5 kHz spin rate, 18,000 scans, 90° pulse length of 5 μs, and repetition time between scans of 5 s. Solution NMR was conducted on a Varian Mercury Vx 400 spectrometer. FT-Raman spectra were collected on a Bruker

FRA-106. Three thousand scans were collected with a resolution of 2–4 cm⁻¹. Thermogravimetric analyses (TGA) were performed on a Netzsch STA409. Samples, under an air blanket, were heated from 30 to 900 °C at a rate of 10 °C/min. The organic loading was determined from the weight loss between 200 and 700 °C and calculated by assuming two methoxy groups having reacted with the surface and one equivalent of methane evolved in the TGA from the silane end of the ligand. Nitrogen physisorption measurements were taken on a Micromeritics ASAP 2010 at 77 K. Prior to analysis, SBA-15 samples were degassed by heating at 150 °C under vacuum overnight, and DMAP-SBA samples were degassed by heating at 50 °C under vacuum overnight. X-ray diffraction (XRD) samples were analyzed using Cu Kα radiation on a PAN analytical X'Pert Pro powder X-ray diffractometer equipped with a PW3011 proportional detector with a parallel plate collimator. Gas chromatography was conducted on a Shimadzu GC 14-A equipped with a flame-ionization detector and an HP-5 column (length = 30 m, inner diameter = 0.32 mm, and film thickness = 0.25 μm). The temperature profile was as follows: heat to 50 °C, wait 2 min, ramp to 140 °C at a rate of 30 °C/min, ramp to 300 °C at 40 °C/min, and hold for 2 min.

3. Results and discussion

3.1. Carbonate reactions with homogeneous catalysts

We began our exploration into the catalytic role of DMAP by investigating the co-catalyst system of phenol and DMAP reported by Shen and coworkers to produce cyclic carbonates [15]. It should be noted that the majority of our experiments were conducted at greatly reduced CO₂ pressure compared to their original work (35.7 bar in their work versus 17.2 bar in this work). Reaction results from the catalytic systems that we examined are shown in Table 1. In the phenol and DMAP co-catalyst system, each catalyst was added at a loading of 4 mmol cat/mol propylene oxide (PO), and we achieved 86% conversion of the epoxide. In this case, propylene carbonate was the only product seen by GC and ¹H NMR. As a control experiment, we reacted

Table 1
Cyclic carbonate reactions^a

Catalyst	Conversion ^b (%)	# products ^c
Phenol, DMAP	86	1
None (ambient conditions)	48	2
None (anhydrous conditions)	0	0
DMAP	85	1
DMAP ^d	92	1
DMAP-SBA 3	81	1
Aminopropyl functionalized SBA	0	0
Mercaptopropyl functionalized SBA	0	0
Capped DMAP-SBA 3	81	1

^a Reaction conditions: propylene oxide (89.5 mmol), methylene chloride (15.7 mmol), and catalyst (0.36 mmol) were heated at 120 °C and 17.2 bar CO₂ pressure for 4 h.

^b Conversion determined by residual weight after removing volatile components and subtracting catalyst weight.

^c Determined by GC-FID and NMR.

^d CO₂ pressure was 34 bar in this case.

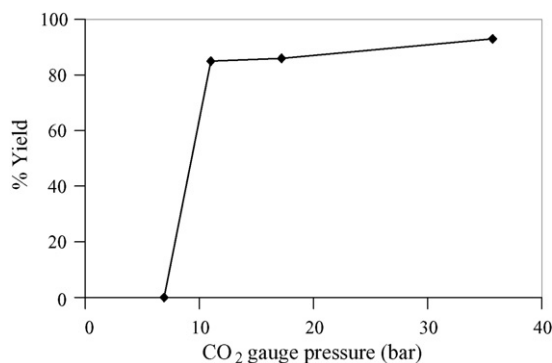


Fig. 1. Yield of propylene carbonate vs. pressure with DMAP as the only added catalyst. Reaction conditions: propylene oxide (89.5 mmol), methylene chloride (15.7 mmol), and DMAP (0.36 mmol), 120 °C, 4 h.

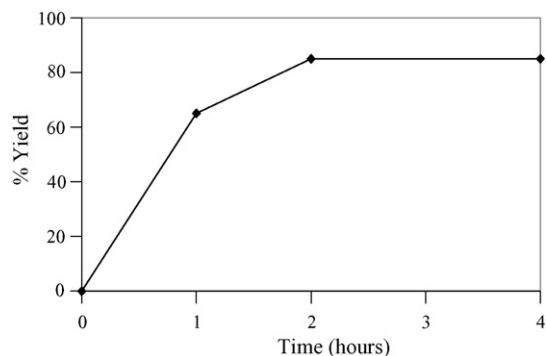
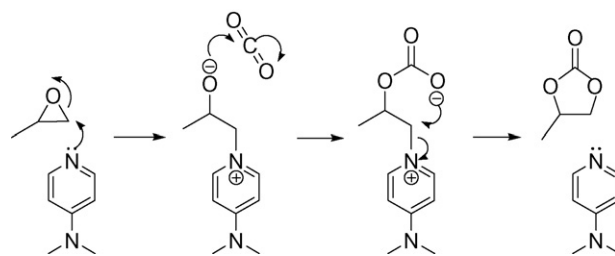


Fig. 2. Yield of propylene carbonate vs. time with DMAP as the only added catalyst. Reaction conditions: propylene oxide (89.5 mmol), CH₂Cl₂ (15.7 mmol), and DMAP (0.36 mmol), 120 °C, 17.2 bar CO₂ pressure.

PO and CO₂ under the same conditions with no catalyst, and we saw a conversion of PO around 50%. However, in this case, there were two product peaks in the GC trace. One peak was the desired cyclic carbonate, and the other peak was identified as propylene glycol by comparison with a known standard. Postulating that the presence of water could cause the formation of the glycol, we rigorously dried all reagents and charged and sealed the reactor in a nitrogen dry box. After this careful exclusion of water, we saw no conversion in the reaction of PO and CO₂ without any catalyst at these conditions. This suggests that water can act as a catalyst and reagent under these conditions if the system is not rigorously dry.

The next system we examined was DMAP alone without the presence of phenol. The loading was again 4 mmol DMAP/mol PO. Using the reaction conditions of Shen (120 °C and 35.7 bar), we unexpectedly observed yields of 92% with propylene carbonate as the only product by GC and ¹H NMR. At the same temperature and only 17.2 bar CO₂ pressure, we obtained yields of 85%. To further explore the effect of pressure, we ran additional experiments at 120 °C and various pressures. These results, shown in Fig. 1, suggest that once a sufficiently high pressure is employed, a further increase in CO₂ pressure does not significantly increase the yield.¹ We also explored the effect of the reaction time on the yield. The data in Fig. 2 indicate that the homogeneous reaction has reached the maximum conversion after approximately 2 h. This conversion was not observed to increase even after 24 h. It also should be noted that when the temperature was decreased to 100 °C for reactions run for 2 h at 17.2 bar, only 30% yield was produced versus the 85% yield observed at 120 °C. In the case of DMAP alone, we also observed that if the reactor was charged in ambient atmosphere, propylene glycol was occasionally obtained as a side product, but the glycol was not seen if the reaction conditions were kept dry.

¹ With our experimental set-up, it is difficult to determine the minimum pressure required for reaction due to the phase behavior of the system. If the initial pressure is set at 3.4 bar, the reactor will pressurize beyond the desired amount as it is heated. If the initial pressure is set lower than 3.4 bar, the epoxide and solvent will vaporize as the reactor is heated, and the catalyst will char onto the bottom of the reactor.

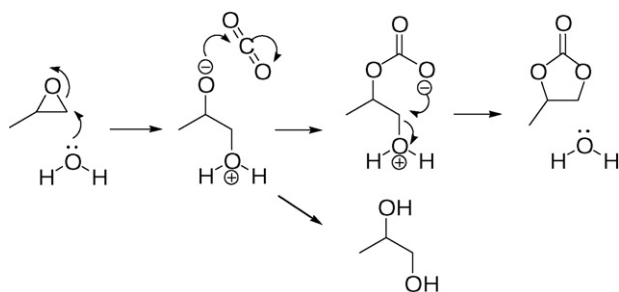


Scheme 2.

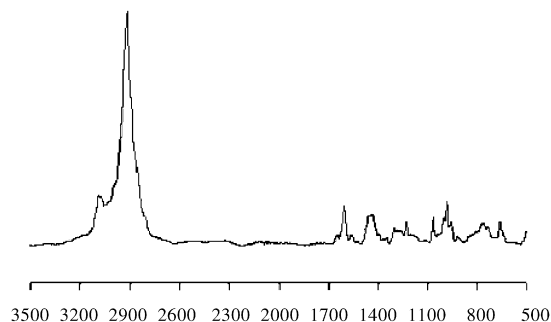
Previously reported mechanisms for this reaction involve both a Lewis acid and Lewis base site for the catalytic cycle as discussed in the introduction. For most of these cases, a lone pair of electrons from the Lewis base attacks the least hindered carbon of the epoxide ring. Since DMAP is known to be a strong base, and in light of our data suggesting DMAP promotes the reaction without the addition of another catalyst, we propose a mechanism like that shown in Scheme 2 may be operating for our system when the reaction is conducted under anhydrous conditions. This mechanism involves the lone pair on the pyridyl nitrogen from a single DMAP molecule attacking the epoxide ring with subsequent insertion of the carbon dioxide. It should be noted that a related mechanism involving two DMAP molecules working in concert might also be reasonable [16]. To ensure that we were not adding trace acid, that would be able to act as the Lewis acid site, from the dichloromethane that was used as the solvent, we tested both dichloromethane treated with base and dichloromethane distilled from CaH₂. In both cases, the reaction results were the same as reported above. Additionally, the use of rigorously dry solvents, gases and techniques suggests that traces of water likely do not play a co-catalytic role.²

We additionally offer an alternate mechanism for those reactions not conducted under anhydrous conditions in Scheme 3. This mechanism is based on our observation of two products in the non-catalyzed reaction of PO and CO₂ conducted in ambient atmosphere and seeing no products in the non-catalyzed reac-

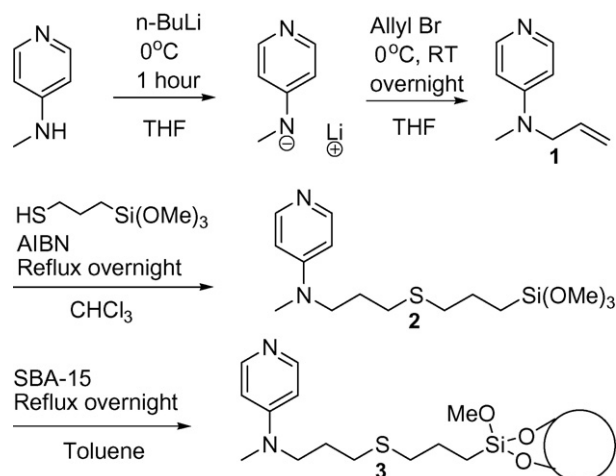
² As nearly all cyclic carbonate syntheses are carried out at high temperatures in autoclaves, one cannot conclusively rule out the presence and possible importance of traces of dissolved transition metal species in solution that may leach from the reactor walls.



Scheme 3.



Assignment	cm ⁻¹
aromatic C-H (ν _{C-H})	3075
aromatic C=C (ν _{C=C})	1600
aromatic N-R ₂ (ν _{C-N})	1380
4-monosubstituted pyridine (ν _{skeletal})	985
aliphatic tether (ν _{CH₂as})	2915
CH ₂ -S in tether (δ _{CH₂-S} and ω _{CH₂-S})	1440, 1260

Fig. 4. FT-Raman spectrum of DMAP-SBA **3** with peak assignments.

Scheme 4.

tion of PO and CO₂ conducted under anhydrous conditions. In this mechanism, the water molecule attacks the least hindered carbon of the epoxide ring and opens it. Once the epoxide is in the ring opened form, it may undergo proton transfer to give propylene glycol, or it may undergo carbon dioxide insertion to produce propylene carbonate.

3.2. Characterization of DMAP-SBA (**3**)

We ultimately set out to obtain an effective catalyst that could be easily separated from the product without the use of distillation. Therefore, after attaining good yields with homogeneous DMAP as the catalyst, we wanted to test the effectiveness of an immobilized DMAP analog supported on mesoporous SBA-15 by the method shown in Scheme 4. In order to better understand the properties of the immobilized catalyst **3**, it was extensively

characterized to confirm the covalent nature of the immobilization as well as the nature of the organic functionality on the surface.

The solid state ¹³C CP-MAS NMR spectrum of **3** exhibited peaks corresponding to those present in the solution ¹³C NMR spectrum of the ligand **2** prior to tethering (Fig. 3). Also, the solid state ²⁹Si CP-MAS NMR spectrum showed Q², Q³, and Q⁴ silicon resonances between -90 and -110 ppm associated with the silica framework and T¹, T², and T³ resonances between -40 and -60 ppm corresponding to one, two, and three methoxy groups from the silane reacting with the surface [46]. This suggests the organic moiety is covalently bound to the silica surface.

FT-Raman spectroscopy was also conducted on **3** to further confirm the nature of the organic species on the surface. The spectrum is shown in Fig. 4 along with a table listing the res-

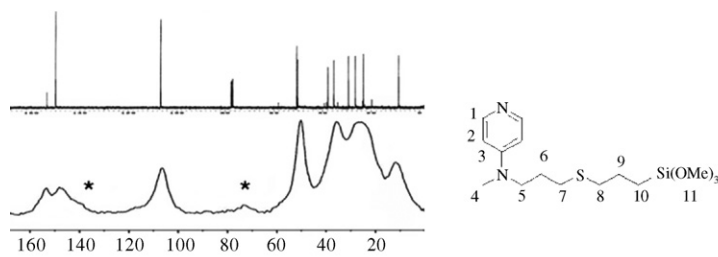


Fig. 3. Top spectrum—solution ¹³C NMR of compound **2** prior to immobilization; bottom spectrum—solid state CP-MAS ¹³C NMR of DMAP-SBA **3** with peak assignments.

Carbon	δ	Carbon	δ
1	149.8	6	26.4
2	106.4	7	29.1
3	153.3	8	35.2
4	37.5	9	22.9
5,11	50.0, 50.5	10	8.6

onances of interest [47]. This analysis further suggests that the DMAP analog has in fact been immobilized onto the SBA-15 support.

Thermogravimetric analysis (TGA) was performed to determine the amount of catalyst loaded onto the silica surface. This measurement indicated a loading of 1.77 mmol catalyst/g SiO₂. This result was used to determine the catalyst loading in the propylene carbonate reactions conducted with the immobilized catalyst.

Nitrogen physisorption provided further evidence that the catalyst was in fact immobilized onto the silica support material. Both bare SBA-15 and DMAP–SBA demonstrate a type IV isotherm with hysteresis. Bare SBA-15 exhibited a BJH average adsorption pore diameter of 67 Å, whereas DMAP–SBA exhibited a BJH average adsorption pore diameter of 41 Å. This suggests that the catalyst is in fact inside the mesopores of the SBA-15. Also, the BET surface area for the silica material decreased from 964 m²/g before functionalization to 201 m²/g after functionalization. This can be explained by the fact that organic loading inside the pores blocks access to the micropores that are known to exist in SBA-15, and thus much or all of the microporous surface area is no longer included in the total surface area calculation [48].

Finally, to ensure that the immobilization procedure did not alter the ordered structure of the SBA-15 support material, X-ray diffraction patterns were analyzed for bare SBA-15 and DMAP–SBA and are shown in Fig. 5. In the diffraction pattern for the bare SBA-15, three peaks corresponding to the (100), (110), and (200) reflections are seen. These peaks are ascribed to an ordered mesoporous structure with 2-d hexagonal (*p6mm*) symmetry [45]. In the diffraction pattern for the DMAP–SBA prior to use, the same three peaks are still present. These results indicate that the ordered nature of the SBA-15 support material is maintained after functionalization with ligand **2**. Additionally, we collected the XRD pattern for the supported catalyst after

reaction, and it indicates that the ordered nature of the support material is maintained.

3.3. Carbonate reactions with immobilized catalyst

Under the same reaction conditions used with the homogeneous catalyst, the immobilized catalyst **3** produced propylene carbonate yields of 81%, which is remarkably close to the homogeneous result. Also, catalyst **3** could be efficiently separated from the product by simple filtration, leaving behind pure propylene carbonate as the filtrate since excess PO and CO₂ were removed under vacuum prior to filtration as described in Section 2. When the catalyst was recycled, the propylene carbonate product was again produced, although the yield was less than with the fresh supported catalyst. The decreased yield on recycle could be associated with several things, including pore clogging, degradation of the DMAP moiety, leaching, etc. It should be noted that we did not conclusively determine if traces of the DMAP functionality leached from the surface, although NMR and GC analyses of the propylene carbonate produced did not detect any catalyst species. In addition, the DMAP was confirmed to be still present on the surface after use by both FT-Raman and FTIR spectroscopy.

We conducted control experiments to confirm that it was the DMAP functionality on the SBA-15 that was performing the catalysis. We conducted experiments with 3-aminopropyl functionalized SBA-15 [49,50] and 3-mercaptopropyl functionalized SBA-15 [49,51], neither with DMAP, and we saw no conversion of the epoxide. Additionally, catalyst **3** was treated with 1,1,1,3,3,3-hexamethyldisilazane (HMDS) to cap the accessible surface silanols and then tested, and it produced the same yield of propylene carbonate as the untreated material. These results plus the observed productivity of soluble DMAP without the addition of another catalyst suggest that DMAP can behave as a single component catalyst (see Footnote 2). Thus, although DMAP is not the most productive catalyst available, it is noteworthy that it can behave as a single component catalyst under the conditions reported here, and therefore investigators using DMAP as a co-catalyst should rigorously show that DMAP does not act as a single component catalyst under the conditions they are employing.

4. Conclusions

We have shown that homogeneous 4-(*N,N*-dimethylamino)pyridine, DMAP, can catalyze the reaction of propylene oxide and carbon dioxide giving propylene carbonate yields of 85% without the addition of a co-catalyst. The reaction forms only propylene carbonate when conducted under anhydrous conditions. Also, a new immobilized DMAP analog was synthesized which produced propylene carbonate yields of 81% and could be easily separated from the product by filtration. Although most of the literature concerning CO₂ fixation to epoxides to form cyclic carbonates suggests the need for bifunctional catalytic systems, our results indicate that multiple reaction mechanisms, including those utilizing only one catalytic component, may be possible under the reaction conditions studied here.

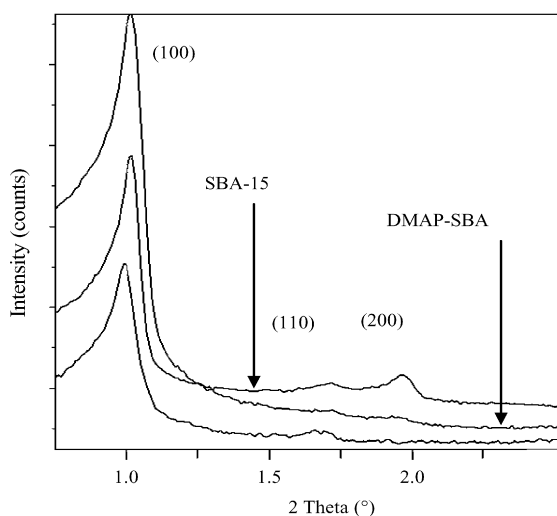


Fig. 5. XRD patterns for bare SBA-15 (top pattern on right portion of graph) and DMAP–SBA **3** (middle pattern is prior to reaction and bottom pattern is after reaction).

Acknowledgements

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References

- [1] D. Darensbourg, M.W. Holtcamp, *Coord. Chem. Rev.* 153 (1996) 155.
- [2] K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida, K. Kaneda, *J. Am. Chem. Soc.* 121 (1999) 4526.
- [3] R. Nomura, A. Ninagawa, H. Matsuda, *J. Org. Chem.* 45 (1980) 3735.
- [4] M. Yoshida, M. Ihara, *Chem. Eur. J.* 10 (2004) 2886.
- [5] R. Srivastava, D. Srinivas, P. Ratnasamy, *J. Catal.* 233 (2005) 1.
- [6] K. Biggadike, R.M. Angell, C.M. Burgess, R.M. Farrell, A.P. Hancock, A.J. Harker, W.R. Irving, C. Ioannou, P.A. Procopiou, R.E. Shaw, Y.E. Solanke, O.M.P. Singh, M.A. Snowden, R.J. Stubbs, S. Walton, H.E. Weston, *J. Med. Chem.* 43 (2000) 19.
- [7] A.G. Shaikh, S. Sivaram, *Chem. Rev.* 96 (1996) 951.
- [8] R.J. Davis, *J. Catal.* 216 (2003) 396.
- [9] M. Tu, R.J. Davis, *J. Catal.* 199 (2001) 85.
- [10] E.J. Doscocil, S.B. Bordawekar, B.G. Kaye, R.J. Davis, *J. Phys. Chem. B* 103 (1999) 6277.
- [11] H. Yasuda, L.-N. He, T. Takahashi, T. Sakakura, *Appl. Catal. A* 298 (2006) 177.
- [12] A. Barbarini, R. Maggi, A. Mazzacani, G. Mori, G. Sartori, R. Sartorio, *Tetrahedron Lett.* 44 (2003) 2931.
- [13] R. Srivastava, D. Srinivas, P. Ratnasamy, *Micropor. Mesopor. Mater.* 90 (2006) 314.
- [14] X. Zhang, N. Zhao, W. Wei, Y. Sun, *Catal. Today* 115 (2006) 102.
- [15] Y.-M. Shen, W.-L. Duan, M. Shi, *Eur. J. Org. Chem.* (2004) 3080.
- [16] M. Sankar, N.H. Tarte, P. Manikandan, *Appl. Catal. A* 276 (2004) 217.
- [17] M. Alvaro, C. Baleizao, E. Carbonell, M.E. Ghouil, H. Garcia, B. Gigante, *Tetrahedron* 61 (2005) 12131.
- [18] K. Mori, Y. Mitani, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, *Chem. Commun.* 26 (2005) 3331.
- [19] M. Alvaro, C. Baleizao, D. Das, E. Carbonell, H. Garcia, *J. Catal.* 228 (2004) 254.
- [20] M. Ramin, F. Jutz, J.-D. Grunwaldt, A. Baiker, *J. Mol. Catal. A: Chem.* 242 (2005) 32.
- [21] R. Paddock, S.-B.T. Nguyen, *J. Am. Chem. Soc.* 123 (2001) 11498.
- [22] H. Jing, S.K. Edulji, J.M. Gibbs, C.L. Stern, H. Zhou, S.-B.T. Nguyen, *Inorg. Chem.* 43 (2004) 4315.
- [23] R. Eberhardt, M. Allmendinger, B. Riger, *Macromol. Rapid Commun.* 24 (2003) 194.
- [24] Y.-M. Shen, W.-L. Duan, M. Shi, *J. Org. Chem.* 68 (2003) 1559.
- [25] R. Paddock, S.-B.T. Nguyen, *Chem. Commun.* (2004) 1622.
- [26] D.J. Darensbourg, C.C. Fang, J.L. Rogers, *Organometallics* 23 (2004) 924.
- [27] H. Tanaka, Y. Kitaichi, M. Sato, T. Ikeno, T. Yamada, *Chem. Lett.* 33 (2004) 676.
- [28] X.-B. Lu, Y.-J. Zhang, K. Jin, L.-M. Luo, H. Wang, *J. Catal.* 227 (2004) 537.
- [29] X.-B. Lu, X.-J. Feng, R. He, *Appl. Catal. A* 234 (2002) 25.
- [30] X.-B. Lu, R. He, C.-X. Bai, *J. Mol. Catal. A: Chem.* 186 (2002) 1.
- [31] R. Srivastava, T.H. Bennur, D. Srinivas, *J. Mol. Catal. A: Chem.* 226 (2005) 199.
- [32] W.N. Sit, S.M. Ng, K.Y. Kwong, C.P. Lau, *J. Org. Chem.* 70 (2005) 8583.
- [33] T. Nishikubo, A. Kameyama, J. Yamashita, M. Tomoi, W. Fukuda, *J. Polym. Sci. Part A* 31 (1993) 939.
- [34] Y. Du, F. Cai, D.-L. Kong, L.-N. He, *Green Chem.* 7 (2005) 518.
- [35] Y. Du, J.-Q. Wang, J.-Y. Chen, F. Cai, J.-S. Tian, D.-L. Kong, L.-N. He, *Tetrahedron Lett.* 47 (2006) 1271.
- [36] T. Takahashi, T. Watahiki, S. Kitazume, H. Yasuda, T. Sakakura, *Chem. Commun.* (2006) 1664.
- [37] H. Xie, H. Duan, S. Li, S. Zhang, *New J. Chem.* 29 (2005) 1199.
- [38] A. Corma, H. Garcia, *Chem. Rev.* 102 (2002) 3837.
- [39] A. Corma, H. Garcia, A. Moussaif, M.J. Sabater, R. Zniber, A. Redouane, *Chem. Commun.* 10 (2002) 1058.
- [40] P. McMorn, G.J. Hutchings, *Chem. Soc. Rev.* 33 (2004) 108.
- [41] M. Benaglia, A. Puglisi, F. Cozzi, *Chem. Rev.* 103 (2003) 3401.
- [42] S. Rubinsztajn, M. Zeldin, W. Fife, *Macromolecules* 23 (1990) 4026.
- [43] H.-T. Chen, S. Huh, J.W. Wiench, M. Pruski, V.S.-Y. Lin, *J. Am. Chem. Soc.* 127 (2005) 13305.
- [44] A.B. Pangborn, M.A. Giardello, R.H. Grubbs, R.K. Rosen, F.J. Timmers, *Organometallics* 15 (1996) 1518.
- [45] D. Zhao, Q. Huo, J. Feng, B. Chmelka, G. Stucky, *J. Am. Chem. Soc.* 120 (1998) 6024.
- [46] D.W. Sindorf, G.E. Maciel, *J. Am. Chem. Soc.* 105 (1983) 3767.
- [47] Baranska, Labudzinska, Terpinski, *Laser Raman Spectroscopy: Analytical Applications*, John Wiley & Sons, New York, 1987, p. 93.
- [48] K. Miyazawa, S. Inagaki, *Chem. Commun.* 21 (2000) 2121.
- [49] A. Stein, B. Melde, R. Schrodin, *Adv. Mater.* 12 (2000) 1403.
- [50] K.M.R. Kallury, P.M. Macdonald, M. Thompson, *Langmuir* 10 (1994) 492.
- [51] T. Kang, Y. Park, J. Yi, *Ind. Eng. Chem. Res.* 43 (2004) 1478.