# Silica-supported aminopyridinium halides for catalytic transformations of epoxides to cyclic carbonates under atmospheric pressure of carbon dioxide

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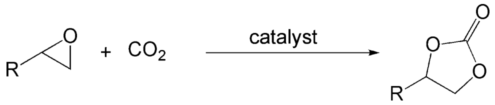
***Received 12th May 2009, Accepted 10th August 2009***
***First published as an Advance Article on the web 8th September 2009***
**DOI: 10.1039/b916764c**

Silica-supported 4-pyrrolidinopyridinium iodide was prepared by quaternization of 4-pyrrolidinopyridine with silica-supported alkyl iodide. The pyrrolidinopyridinium structure on the silica surface was confirmed by solid-state $^{13}$C CP MAS NMR. The silica-supported 4-pyrrolidinopyridinium iodide showed excellent catalytic performances for transformations of various epoxides to cyclic carbonates under atmospheric pressure of carbon dioxide ($CO_2$). The reactions took place without any solvents or additives other than the catalyst. The catalyst was reusable with retention of activity and selectivity. 1-*n*-Hexyl-4-pyrrolidinopyridinium as a homogeneous catalyst showed a lower catalytic performance than the supported catalyst. Bifunctional catalysis involving acidic surface silanol and the basic 4-pyrrolidinopyridinium iodide was proposed.

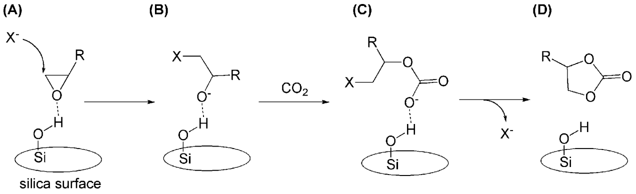
## Introduction

The transformation of epoxide to cyclic carbonate in the presence of carbon dioxide ($CO_2$) (eqn (1)) has been the subject of much attention because of the usefulness of the cyclic carbonate products as aprotic polar solvents, parts of fine chemicals, and raw materials of polycarbonates.[1] Various catalysts have been reported for the cycloaddition reaction,[1] however there have been few reports of reactions under 1 atm of $CO_2$.[2,3,4] In addition, solvents, homogeneous additives, and/or reactive epoxides are required in these catalyst systems. The development of a new catalyst is necessary for efficient production of cyclic carbonates under $CO_2$ at atmospheric pressure.



(1)

We,[5] and other groups[6] have reported several procedures for the synthesis of acid–base bifunctional catalytic surfaces. Acid–base cooperative mechanisms for the catalytic reactions of epoxides with $CO_2$ has also been proposed.[1b,c,e,7–9] Sakakura and co-workers demonstrated the use of silica-supported phosphonium halides as acid–base bifunctional catalysts for the reaction of epoxides with $CO_2$.[1c,e,7] Si–OH groups on the silica surface act as a weak acid to activate the epoxide, then, the activated epoxide undergoes nucleophile attack by the halide anion ($X^-$)(eqn (2A)), which results in ring-opening (eqn (2B)). A cyclic carbonate is formed by insertion of $CO_2$ into the ring-opened epoxide (eqn (2C–D). Because $CO_2$ insertion into the intermediate is the rate-determining step under low $CO_2$ pressure (< 50 atm),[7] stabilization of the ring-opening structure (B) is a key issue to reduce the pressure of $CO_2$.



(2)

It has been reported that the stability of counter anions increases in the presence of large, delocalized counter cations with resonance forms.[10] This fact encouraged us to choose 4-aminopyridinium halides as catalysts for the reaction of epoxide with $CO_2$. Compared with other ammonium halides with resonance forms, the use of 4-aminopyridinium halides is advantageous for the following reasons: (i) ease of synthesis of various structures from 4-aminopyridines and alkylhalides, and (ii) ease of handling and stability under air. In this work, silica-supported 4-pyridinium halides were examined as acid–base bifunctional catalysts for the transformations of epoxides to cyclic carbonates under atmospheric pressure of $CO_2$.

## Results and discussion

Ammonium halides and silica-supported ammonium halides are denoted as *n*(X) and $SiO_2$-*n*(X), where *n* = **1–7** and X = I, Br, or Cl, as shown in Chart 1. Silica-supported 4-pyrrolidinopyridinium iodide ($SiO_2$-**1**(I)) was prepared by a silane-coupling reaction of 3-iodopropyltrimethoxysilane with silica (Aerosil 300), followed by quaternization of 4-pyrrolidinopyridine with the $SiO_2$-supported propyl iodide (denoted as $SiO_2$-$C_3H_6$-I), as shown in eqn (3). Elemental analysis of $SiO_2$-**1**(I) showed amine loading of 0.85 mmol $g^{-1}$. The structures of $SiO_2$-$C_3H_6$-I and $SiO_2$-**1**(I) were confirmed by

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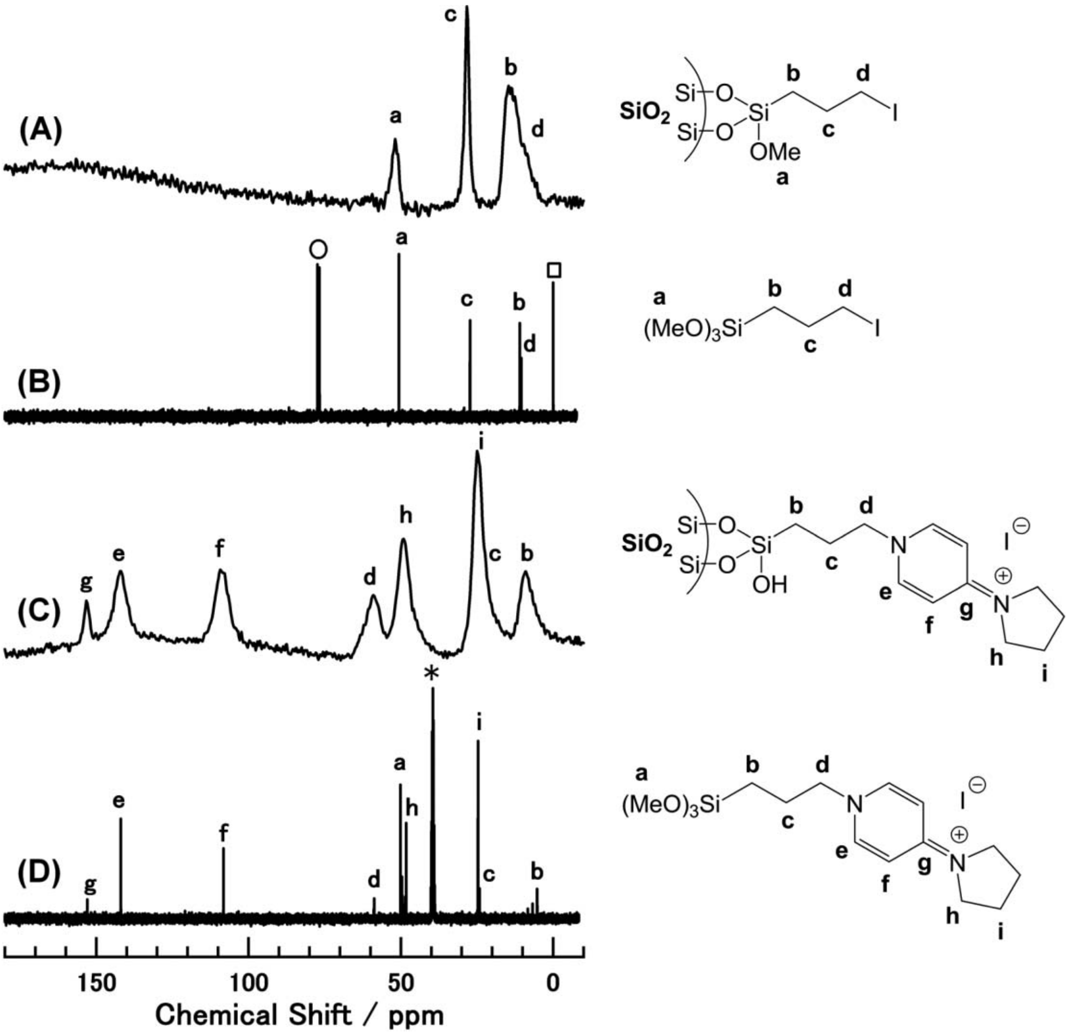
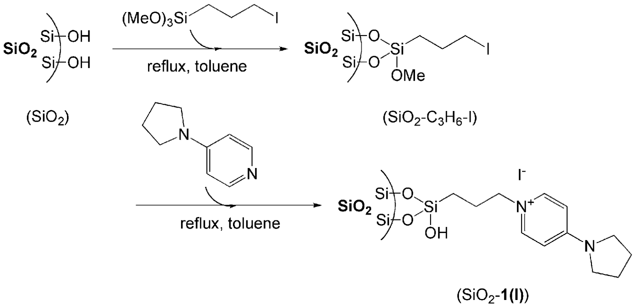


**Fig. 1** (A) Solid-state $^{13}$C CP MAS NMR spectrum of $SiO_2$-$C_3H_6$-I, (B) $^{13}$C NMR of 3-iodopropyltrimethoxysilane in $CDCl_3$, (C) Solid-state $^{13}$C CP MAS NMR of $SiO_2$-**1**(I), and (D) $^{13}$C NMR of the homogeneous analog **1**(I) in DMSO-$d_6$. $CDCl_3$ (○), TMS (□), and DMSO (*).

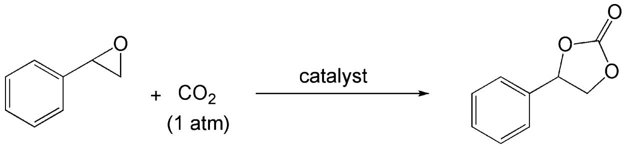
solid-state $^{13}$C CP MAS NMR analysis, as shown in Fig. 1. The $^{13}$C NMR spectrum of $SiO_2$-$C_3H_6$-I (Fig. 1A) shows retention of the iodopropyl structure of 3-iodopropyltrimethoxysilane (Fig. 1B). Fig. 1C shows the $^{13}$C NMR spectrum of $SiO_2$-**1**(I), synthesized from $SiO_2$-$C_3H_6$-I and 4-pyrrolidinopyridine, with the signals at $\delta$ (b) 9.2, (c, i) 20–29, (h) 49.5, (d) 59.0, (f) 109.3, (e) 142.2, and (g) 153.2 assigned as (b) the carbon next to Si, (c) the center carbon of the C3 chain and the pyrrolidine ring, (h) the carbon next to N in the pyrrolidine ring, and (f), (e) and (g) the carbons of the *ortho*, *metha*, and *para*-positions, respectively, of the pyridine ring. The homogeneous analog of $SiO_2$-**1**(I) was synthesized from 3-iodopropyltrimethoxysilane and 4-pyrrolidinopyridine, and its $^{13}$C NMR spectrum is shown in Fig. 1D. The signal positions are similar to those of $SiO_2$-**1**(I). The reaction of the homogeneous analog with $SiO_2$ afforded similar $SiO_2$-supported ammonium halides. Other silica-supported ammonium halides were prepared and characterized by similar procedures, and their structures are shown in Chart 1. Silica-supported methylaminopyridine ($SiO_2$-$C_3H_6$-MAP) was also prepared according to a previous literature method.[11]



(3)

The reaction of styrene oxide was carried out using various $SiO_2$-supported ammonium halides under 1 atm of $CO_2$ without any solvents or additives other than the catalyst, as shown in Table 1. $SiO_2$-**1**(I) showed excellent catalytic performance, affording styrene carbonate in 89% yield (entry 1). Catalytic activity decreased when $SiO_2$-supported 4-pyrrolidinopyridinium bromide ($SiO_2$-**1**(Br)) or chloride ($SiO_2$-**1**(Cl)) was used, with yields of 74% (Br, entry 2) and 19% (Cl, entry 3). In the case of supported alkylaminopyridinium iodides, the product yields

**Table 1** Reaction of styrene oxide with $CO_2$ using various catalysts



| Entry | Catalyst | Conversion (%) | Yield (%) |
|---|---|---|---|
| 1 | $SiO_2$-**1**(I) | 91 | 89 |
| 2 | $SiO_2$-**1**(Br) | 79 | 74 |
| 3 | $SiO_2$-**1**(Cl) | 37 | 19 |
| 4 | $SiO_2$-**2**(I) | 72 | 60 |
| 5 | $SiO_2$-**3**(I) | 85 | 78 |
| 6 | $SiO_2$-**4**(I) | 83 | 72 |
| 7 | $SiO_2$-**5**(I) | 87 | 68 |
| 8 | $SiO_2$-**6**(I) | 67 | 51 |
| 9 | $SiO_2$-**7**(I) | 94 | 89 |
| 10 | $SiO_2$-$C_3H_6$-MAP | 42 | Trace |
| 11 | $SiO_2$-$C_3H_6$-I | 36 | Trace |

Reaction conditions: styrene oxide (4.4 mmol), $CO_2$ (1 atm), catalyst ($3.8 \times 10^{-2}$ mmol), 100 °C, 20.5 h.

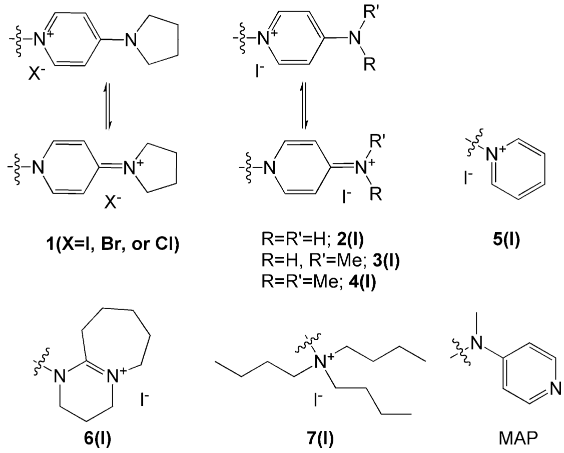
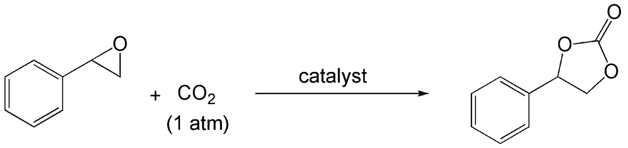


**Chart 1**

were greater than 70% (entries 5 and 6, $SiO_2$-**3**(I) and -**4**(I)). The yield and selectivity of styrene carbonate in the pyridinium iodide-catalyzed reaction (entry 7, $SiO_2$-**5**(I)) were lower than when the alkylaminopyridinium iodides were used. A supported ammonium iodide prepared from 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) with strong basicity [12] ($SiO_2$-**6**(I)) did not show good performance (entry 8). The reaction proceeded smoothly when supported tetraalkyl ammonioum iodide ($SiO_2$-**7**(I)) was used, giving an 89% yield of styrene carbonate in 20.5 h (entry 9). The carbonate product did not form at all with $SiO_2$-$C_3H_6$-MAP or $SiO_2$-$C_3H_6$-I (entries 10 and 11).

The reusability of $SiO_2$-**1**(I) and $SiO_2$-**7**(I) was examined, and the results are shown in Table 2. $SiO_2$-**1**(I) was recovered easily from the reaction mixture by simple filtration. The recovered catalyst could be reused at least three times without any appreciable loss of activity and selectivity (entries 2–4). In contrast, the activity decreased in the recovered $SiO_2$-**7**(I) (entry 6). Amine loading decreased significantly in the recovered $SiO_2$-**7**(I) (0.35 mmol $g^{-1}$) compared with the value obtained before use (0.98 mmol $g^{-1}$).

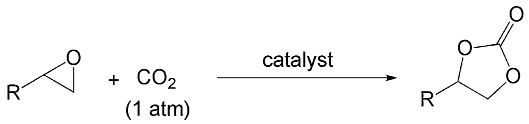
**Table 2** Reuse of $SiO_2$-**1a**(I) and $SiO_2$-**1g**(I)

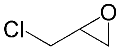
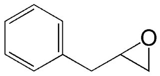
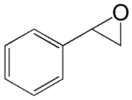
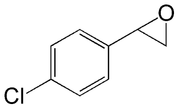
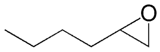


| Entry | Catalyst | Conversion (%) | Yield (%) |
|---|---|---|---|
| 1 | $SiO_2$-**1**(I) (fresh) | 91 | 89 |
| 2 | $SiO_2$-**1**(I) (reuse 1) | 89 | 87 |
| 3 | $SiO_2$-**1**(I) (reuse 2) | 90 | 88 |
| 4 | $SiO_2$-**1**(I) (reuse 3) | 89 | 85 |
| 5 | $SiO_2$-**7**(I) (fresh) | 94 | 89 |
| 6 | $SiO_2$-**7**(I) (reuse 1) | 71 | 69 |

Reaction conditions: styrene oxide (4.4 mmol), $CO_2$ (1 atm), catalyst ($3.8 \times 10^{-2}$ mmol), 100 °C, 20.5 h.

**Table 3** Reactions of various epoxides with $CO_2$ using $SiO_2$-**1**(I) catalyst

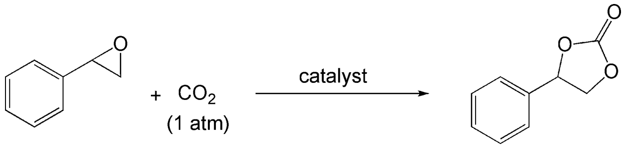


| Entry | Epoxide | *t*/h | Conversion (%) | Yield (%) |
|---|---|---|---|---|
| 1 |  | 8.0 | 97 | 86 |
| 2 |  | 17.0 | 88 | 88 |
| 3 |  | 20.5 | 91 | 89 |
| 4 |  | 20.5 | 83 | 80 |
| 5 |  | 24.0 | 88 | 84 |

Reaction conditions: styrene oxide (4.4 mmol), $CO_2$ (1 atm), $SiO_2$-**1**(I) ($3.8 \times 10^{-2}$ mmol), 100 °C.

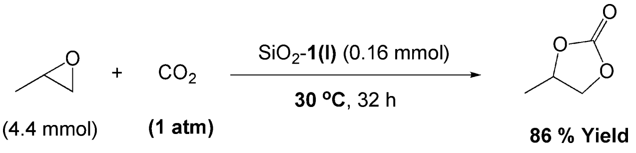
The reaction of propylene oxide occurred at 30 °C under 1 atm of $CO_2$ to afford an 86% yield of propylene carbonate, as shown in eqn (4). Table 3 shows the results of transformations of various epoxides to cyclic carbonates at 100 °C using $SiO_2$-**1**(I) as a catalyst. All the reactions in Table 3 were carried out under atmospheric pressure of $CO_2$ without any solvents. Epichlorohydrin reacted with $CO_2$ to form the corresponding carbonate in 86% yield in 8 h (entry 1). The reaction of 2-benzyloxirane also proceeded to afford the corresponding carbonate product with excellent yield and selectivity (entry 2). $SiO_2$-**1**(I) also showed high catalytic activity in the reaction of 1,2-hexene oxide, giving a yield of 84% for the hexane carbonate (entry 5). In the case of cyclohexene oxide, the reaction rate decreased: the corresponding carbonate product was obtained in 5% yield at 12 h under 5 atm of $CO_2$.

**Table 4** Effect of $SiO_2$



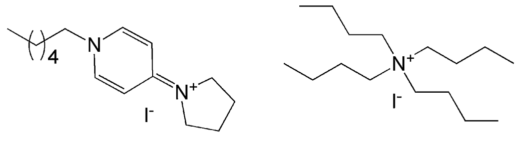
| Entry | Catalyst | Conversion (%) | Yield (%) |
|---|---|---|---|
| 1 | $SiO_2$-**1**(I) | 91 | 89 |
| 2 | $SiO_2$ + HPPN(I) | 87 | 83 |
| 3 | HPPN(I) | 74 | 62 |
| 4 | $SiO_2$-**7**(I) | 94 | 89 |
| 5 | $SiO_2$ + TBA(I) | 80 | 77 |
| 6 | TBA(I) | 58 | 41 |
| 7 | $SiO_2$ | 33 | Trace |

Reaction conditions: styrene oxide (4.4 mmol), $CO_2$ (1 atm), catalyst ($3.8 \times 10^{-2}$ mmol), 100 °C, 20.5 h, $SiO_2$ ($5.0 \times 10^{-2}$ g).



(4)

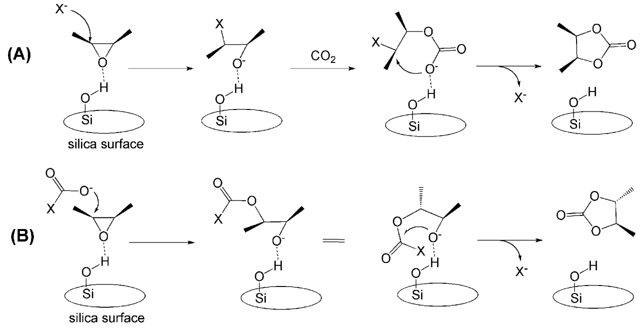
The effect of $SiO_2$ on the transformation of styrene oxide to carbonate is summarized in Table 4. 1-*n*-Hexyl-4-pyrrolidinopyridinium iodide (HPPN(I)) and tetra-*n*-butyl ammonium iodide (TBA(I)) were used as homogeneous analogs of $SiO_2$-**1**(I) and $SiO_2$-**7**(I), respectively. The structures of these ammonium iodides are shown in Chart 2. In both cases, the addition of $SiO_2$ to styrene oxide solutions with the ammonium iodides enhanced the reaction rate (entry 2 *vs.* 3, and entry 5 *vs.* 6). Interestingly, $SiO_2$-supported catalysts showed higher performances (entries 1 and 4) than the mixtures containing $SiO_2$ (entries 2 and 5). The presence of $SiO_2$ alone did not promote the formation of cyclic carbonates (entry 7).



**HPPN(I)** **TBA(I)**

**Chart 2**

Carbonate formation catalyzed by $SiO_2$-**1**(I) stopped completely after simple filtration of the catalyst at *ca.* 40% conversion of styrene oxide. In addition, $SiO_2$-**1**(I) catalyst was highly reusable (Table 2). These facts rule out any contribution to the observed catalysis from amine leaching into the reaction solution. The reaction occurs at the surface of the catalyst. The catalytic activity of $SiO_2$-**1**(X) increased with increasing anion nucleophilicity in liquid phase ($I^- > Br^- > Cl^-$) (Table 1, entries 1–3). The reaction did not proceed in the presence of $SiO_2$-supported aminopyridine (Table 1, entry 10). These results suggest that the halide anions act as catalytic basic sites. In addition, mixtures of $SiO_2$ and ammonium iodide showed higher activity than the ammonium iodides alone (Table 4). It can be proposed that the Si–OH species and the halide anions act as acid and base sites, respectively, in the $SiO_2$-supported aminopyridinium catalyst system; this is a similar acid–base reaction mechanism to the Sakakura's phosphonium catalyst system.[7] We examined the reaction of styrene oxide using $SiO_2$-**1**(I) with higher loadings of the iodopropyl group. A 25% increase of the iodopropyl group at the $SiO_2$ surface induced a decrease of catalytic activity (70% yield of styrene carbonate at 20.5 h). This result also supports that the Si–OH species acts as active sites. Paddock and co-workers reported retention of configuration of both *cis*- and *trans*-2,3-eopxybutane in the cycloaddition through the acid–base cooperative mechanism.[13] We also examined the reaction of both *cis*- and *trans*-2,3-epoxybutane using $SiO_2$-**1**(I) catalyst. The carbonate product showed retentions of configuration: *cis–trans* ratio of carbonate product were 91 : 9 for *cis*-2,3-epoxybutane and 3 : 97 for *trans*-2,3-epoxybutane, respectively. These results support the proposed acid–base reaction mechanism, including double inversion of carbon center, which is attacked by base site on $SiO_2$-**1**(I) (Scheme 1, path (A)). Ring-opening by activated $CO_2$ (path (B)) seems to be a minor pathway. The delocalized aminopyridinium counter cation and the acidic surface of the silica may act to strongly stabilize the ring-opened intermediate, which enables the reaction to take place even under atmospheric pressure of $CO_2$.[14] Because the $SiO_2$-supported catalysts ($SiO_2$-**1**(I) and -**7**(I)) showed higher activities than the mixtures of $SiO_2$ and ammonium iodides (Table 4, entries 1 and 4 *vs.* 2 and 5), it is suggested that the concentration of halide anions on the $SiO_2$ surface may affect the catalytic performance.



**Scheme 1**

## Conclusion

Silica-supported pyrrolidinopyridinium iodide was found to be an excellent catalyst for the transformation of epoxides to cyclic carbonates under atmospheric pressure of $CO_2$. The reaction proceeded successfully in the absence of solvent and without any additive other than the catalyst. The catalyst was reusable at least three times, retaining of high activity and selectivity. The presence of a silica support enhanced the catalytic performance, suggesting an acid–base bifunctional reaction mechanism.

## Experimental

### Characterization

$^1H$ and $^{13}C$ NMR spectra were measured on a JNM-AL400 spectrometer at 400 MHz using $CDCl_3$, DMSO-$d_6$, or acetone-$d_6$ as a solvent. Solid-state $^{13}C$ MAS NMR spectra were recorded on a Chemagnetics CMX-300 spectrometer operating at 75.5 MHz. $^{13}C$ MAS NMR spectra with cross polarization (CP) were acquired at a contact time of 0.5 ms. The rotor spin rate was 6 kHz, with delay time of 10 s. Hexamethylbenzene ($^{13}C$: 17.17 and 176.46 ppm) was used as an external standard for the calibration of chemical shifts. The accumulation number was fixed at about 20 000. Analytical GLC was measured using a Shimadzu GC-7A equipped with a FFAP column and a flame ionization detector. The products were confirmed by comparison with reported mass and NMR data.

### Materials

Unless otherwise noted, materials were purchased from Wako Pure Chemicals, Tokyo Kasei Co. Kanto Kagaku, and Aldrich Inc., and were used without further purification. The silica used was Aerosil 300.

**Preparation of silica-supported pyrrolidinopyridinium iodide ($SiO_2$-1(I)).** $SiO_2$ was pre-treated at 393 K for 3 h under vacuum. The treated $SiO_2$ (1.0 g) was added to 16 mL of a toluene solution of 3-iodopropyltrimethoxysilane (4.0 mmol) and refluxed for 2 h. The solvent was then removed by filtration and the resulting functionalized $SiO_2$ ($SiO_2$-$C_3H_6$-I) was washed with toluene, followed by drying under vacuum. The dried $SiO_2$-$C_3H_6$-I (1.0 g) was added to 10 mL of a toluene solution of 4-pyrrolidinopyridine (4.2 mmol) and refluxed for 16 h, after which the solvent was removed by filtration. The resulting solid was washed with toluene, water, and dichloromethane, followed by drying under vacuum to afford silica-supported pyrrolidinopyridinium iodide ($SiO_2$-**1**(I)). $SiO_2$-**1**(I) was also prepared by a silane-coupling reaction of $SiO_2$ with 4-pyrrolidino-(3-(trimethoxysilyl)propyl)pyridinium iodide in acetonitrile solution under reflux for 16 h.

**Preparation of 1-*n*-hexyl-4-pyrorridinopyridinium iodide (HPPN(I)) and 4-pyrrolidino-(3-(trimethoxysilyl)propyl)-pyridinium iodide (1(I)).** 1-Iodohexane (2.5 mmol) and 4-pyrrorilinopyridine (2.5 mmol) were placed in a 20 mL Pyrex glass reactor, and the mixture was heated at 120 °C for 16 h. HPPN(I) was obtained in quantitative yield. Compound **1**(I) was also synthesized using 3-iodopropyltrimethoxysilane by a similar procedure. Decomposition of some of the methoxy group was observed by $^1H$ NMR, but this would not affect the $^{13}C$ NMR shifts of the 4-pyrrolidinopyridinium skeleton for comparison in Fig. 1.

1-*n*-Hexyl-4-pyrrolidinopyridinium iodide (HPPN(I)): $^1H$ NMR (400 MHz, acetone-$d_6$): $\delta$ 0.87 (t, $J = 6.8$ Hz, 3 H), 1.34 (m, 6 H), 1.92 (quint, $J = 7.3$ Hz, 2 H), 2.14 (quint, $J = 3.2$ Hz, 4 H), 3.65 (t, $J = 6.7$ Hz, 4 H), 4.42 (t, $J = 7.4$ Hz, 2 H), 7.00 (d, $J = 7.3$ Hz, 1 H), 8.54 (d, $J = 7.3$ Hz, 2 H). $^{13}C\{^1H\}$ NMR (100.4 MHz, acetone-$d_6$): 14.2, 23.0, 25.7, 26.2, 31.7, 31.9, 49.4, 58.2, 109.3, 143.0, 154.5.

4-Pyrrolidino-(3-(trimethoxysilyl)propyl)pyridinium iodide (**1**(I)): $^1H$ NMR (400 MHz, DMSO-$d_6$): 0.51 (quint, $J = 4.3$ Hz, 2 H), 1.74–1.84 (m, 2 H), 2.01 (t, $J = 6.7$ Hz, 4 H), 3.47 (s, 9 H), 3.50 (t, $J = 6.7$ Hz, 4 H), 4.14 (t, $J = 6.9$ Hz, 2 H), 6.90 (d, $J = 6.8$ Hz, 2 H), 8.30 (m, 2 H). $^{13}C\{^1H\}$ NMR (100.4 MHz, DMSO-$d_6$): 5.4, 24.3, 24.9, 48.5, 50.3, 58.9, 108.4, 142.1, 153.1.

**Typical procedure for transformation of epoxide to cyclic carbonate using $SiO_2$-1(I).** $SiO_2$-**1**(I) ($3.43 \times 10^{-2}$ g, $3.8 \times 10^{-2}$ mmol) and styrene oxide (4.4 mmol) were placed into a 10 mL Pyrex glass reactor. The air in the reactor was replaced with 1 atm of carbon dioxide using a balloon, and the mixture was vigorously stirred at 100 °C. After 20.5 h, the catalyst was separated by filtration, and GC analysis of the filtrate showed 91% conversion of styrene oxide and an 89% yield of styrene carbonate. The product was identified by comparison with reported $^1H$ and $^{13}C$ NMR and mass spectral data. Naphthalene and *p*-xylene were used as internal standards for GC and $^1H$ NMR quantitative analysis, respectively. The recovered $SiO_2$-**1**(I) was washed with toluene, and then calcined at 120 °C for 3 h under vacuum. Then the catalyst was reused under identical conditions.

## Acknowledgements

This work was supported by JSPS (19760541, 21760626).

## References

1 Reviews: (*a*) I. Omae, *Catal. Today*, 2006, **115**, 33; (*b*) M. Yoshida and M. Ihara, *Chem.–Eur. J.*, 2004, **10**, 2886; (*c*) T. Sakakura, J.-C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365; (*d*) D. J. Darensbourg, *Chem. Rev.*, 2007, **107**, 2388; (*e*) T. Sakakura and K. Kohno, *Chem. Commun.*, 2009, 1312.

2 Various epoxides: (*a*) T. Iwasaki, N. Kihara and T. Endo, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 713; (*b*) V. Caló, A. Nacci, A. Monopoli and A. Fanizzi, *Org. Lett.*, 2002, **4**, 2561; (*c*) J. Meléndez, M. North and R. Pasquale, *Eur. J. Inorg. Chem.*, 2007, 3323; (*d*) Reactive epoxides: K. Mori, Y. Mitani, T. Hara, T. Mizugaki, K. Ebitani and K. Kaneda, *Chem. Commun.*, 2005, 3331.

3 Pd-catalyzed reaction of allylic and propargylic oxiranes:(*a*) T. Fujinami, T. Suzuki, M. Kamiya, S. Fukuzawa and S. Sakai, *Chem. Lett.*, 1985, 199; (*b*) B. M. Trost and S. R. Angle, *J. Am. Chem. Soc.*, 1985, **107**, 6123; (*c*) M. Yoshida, T. Murao, K. Sugimoto and M. Ihara, *Synlett*, 2007, 575.

4 Very recently, one-component catalyst for cyclic carbonate synthesis without any additives under 1 atm of $CO_2$ was reported:J. Meléndex, M. North and P. Villuendas, *Chem. Commun.*, 2009, 2577.

5 (*a*) K. Motokura, M. Tada and Y. Iwasawa, *J. Am. Chem. Soc.*, 2007, **129**, 9540; (*b*) K. Motokura, M. Tomita, M. Tada and Y. Iwasawa, *Chem.–Eur. J.*, 2008, **14**, 4017; (*c*) K. Motokura, M. Tada and Y. Iwasawa, *Chem.–Asian J.*, 2008, **3**, 1230; (*d*) K. Motokura, M. Tada and Y. Iwasawa, *Angew. Chem., Int. Ed.*, 2008, **47**, 9230.

6 (*a*) E. L. Margelefsky, R. K. Zeidan and M. E. Davis, *Chem. Soc. Rev.*, 2008, **37**, 1118; (*b*) S. Huh, H.-T. Chen, J. W. Wiench, M. Pruski and V. S.-Y. Lin, *Angew. Chem., Int. Ed.*, 2005, **44**, 1826; (*c*) J. D. Bass, A. Solovyov, A. J. Pascall and A. Katz, *J. Am. Chem. Soc.*, 2006, **128**, 3737; (*d*) R. K. Zeidan, S.-J. Hwang and M. E. Davis, *Angew. Chem., Int. Ed.*, 2006, **45**, 6332; (*e*) R. K. Zeidan and M. E. Davis, *J. Catal.*, 2007, **247**, 379.

7 T. Takahashi, T. Watahiki, S. Kitazume, H. Yasuda and T. Sakakura, *Chem. Commun.*, 2006, 1664.

8 K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida and K. Kaneda, *J. Am. Chem. Soc.*, 1999, **121**, 4526.

9 For closely related reports to the acid–base cooperative catalysts for cyclic carbonate synthesis, see: (*a*) X. Zhang, Y.-B. Jia, X.-B. Lu, B. Li, H. Wang and L.-C. Sun, *Tetrahedron Lett.*, 2008, **49**, 6589; (*b*) C.-X. Miao, J.-Q. Wang, Y. Wu, Y. Du and L.-N. He, *Chem. Sus. Chem.*, 2008, **1**, 236.

10 K. Suzawa, M. Ueno, A. E. H. Wheatley and Y. Kondo, *Chem. Commun.*, 2006, 4850.

11 H.-T. Chen, S. Huh, J. W. Wiench, M. Pruski and V. S.-Y. Lin, *J. Am. Chem. Soc.*, 2005, **127**, 13305.

12 Y. Wei, G. N. Sastry and H. Zipse, *J. Am. Chem. Soc.*, 2008, **130**, 3473.

13 R. L. Paddock, Y. Hiyama, J. M. McKay and S. B. T. Nguyen, *Tetrahedron Lett.*, 2004, **45**, 2023.

14 The reaction of styrene oxide using $SiO_2$-**1**(I) was examined under 5 atm of $CO_2$. The product yield increased compared with the reaction under 1 atm of $CO_2$ (5 atm: 43% at 2 h, 1 atm: 26% at 2 h). These results suggest that the rate determining step is still $CO_2$ insertion.