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Organic sulphonate salts tethered mesoporous silicas as catalysts for CO_2 fixation into cyclic carbonates

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A series of mesoporous silica materials tethered with sulphonate salt of organic bases were synthesized and their catalytic activity for CO_2-epoxide cycloaddition was investigated. The sulphonate group has been supported on silica through the functionalization and subsequent oxidation of 3-mercaptopropyltrimethoxysilane (3-MPS) by post-grafting method. All the synthesized materials have been characterized using various physicochemical techniques such as SAXS, BET, SEM, TEM, FTIR and XPS. The so formed SBA-15(SO_3H) was neutralized with different organic bases such as 4-dimethylaminopyridine, triethanolamine and triethylamine, such that the SO_3H group ionizes to stay as SO_3^- ion. These materials along with KI displayed promising CO_2 conversion yields with excellent selectivity towards the desired product, cyclic carbonates with turnover frequency (TOF) as high as 1900 h^{-1}. The catalysts were thermally stable and their reusability studies were also performed. The synergistic play between SO_3^- and KI is supposed to be the reason behind the good catalytic rates exhibited by this catalytic system and all the parameter studies have also been carried out.

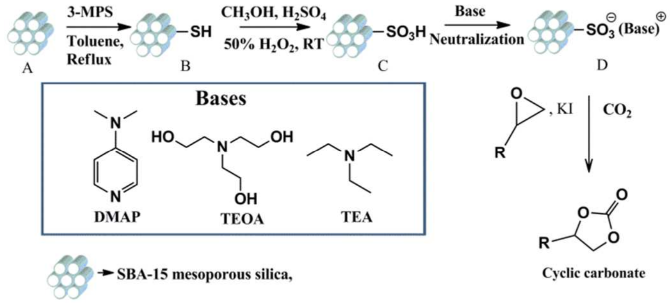
Introduction

The alarming levels of atmospheric CO_2 consequences increased global warming which should be dealt at the earliest with utmost attention [1]. An efficient capture from the major CO_2 outlets followed with its proper sequestration could be stated as the only viable technique available so far as a mitigation measure. However, towards a brighter side of utilizing this seemingly non-depletable C1 feedstock, CO_2 could be employed as a possible replacement for the toxic CO and $COCl_2$ for the synthesis of fine chemicals [2]. Hence on grounds of environmental preservation and resource utilization, the chemical fixation of CO_2 into industrially relevant chemical products is receiving ever increased attention. The conversion of CO_2 to cyclic carbonates via epoxide substrates is a 100% atom economic reaction, and the products are of wide applicability as electrolytes of Li ion batteries, aprotic solvents, degreasing agents, monomers for polymer synthesis etc [3]. However, a non-catalytic route is highly unfavourable for this reaction to proceed, out of the thermodynamic stability of CO_2. To materialize this transformation at viable reaction conditions, rigorous research has been conducted since few decades and the results were suggestive of that, a binary catalytic system in which a strongly nucleophilic while easy leaving anion such as halide ion along with a Lewis acid metal center promotes the reaction most efficiently via a synergistic pathway; for example, Cr-salen complexes with tertiary ammonium halides [4]. Likewise metal oxides [5a-b], transition metal complexes [5c-f], Schiff base [5g-h], ion exchange resins [5i], functional polymers [5j-k], quaternized amine [5l] and ionic liquids [5m-p] were also used to synthesize cyclic carbonates. As an abundant and economic catalyst, alkali metal halides are among the most promising co-catalysts for this coupling reaction. However they are inefficient when used alone for cyclic carbonate synthesis [6]. Hence, plentiful research has been done with alkali metal as co-catalyst with, crown ether [6b], cellulose [6c], lecithin [6d], phenol [6e], amino acid [6f], formic acid

[6g] etc. In the meantime, the approaches to achieve heterogeneity which aids in better catalyst recycling also gained momentum and was best exemplified through the use of silica supported active catalysts such as ionic liquids.

Mesoporous silica materials possess high surface area, large pore volumes and tunable pore sizes for potential applications in adsorption, catalysis, drug-delivery, and various electrochemical devices [7]. By proper tuning of the synthetic strategy, such as reaction conditions, organic templates and other chemical ratios, mesoporous materials with high-surface area in dimension, composition and morphology can be achieved. Ample amount of research on ionic liquid tethered silica catalyst for cyclic carbonate synthesis have been conducted. It was found that, the above mentioned synergism was applicable to the hydrogen bonding groups and halide ions on silica grafted catalysts also, such that, the silica supported ionic liquids with hydroxyl [6m] or carboxyl [6m, n] or amine groups [6o] were found efficient catalysts for this cyclo addition, which sustained green credentials. It was generally observed that, TOF of the catalysts increased with the presence of hydrogen bonding moieties such as –OH, –COOH and $–NH_2$ [6m-o]. However, attempts to investigate the effect of $–SO_3H$ and $-SO_3^-$ moieties on silica to engage in synergism with the halide ions for epoxide-CO_2 cycloaddition has never been done. Hence, herein we are reporting a series of SBA-15 based sulphonate materials (SBA-15-pr-SO_3H) synthesized through simple oxidation of the thiol group supported on silica which was then neutralized with organic bases (Scheme 1). The catalytic activity of these materials with KI co-catalyst towards the synthesis of cyclic carbonates from CO_2-epoxide cycloaddition and the characterization details are discussed in the following sections.

We believe that, it will be of academic interest to investigate this study since it shall contribute to a better understanding of the synergy between iodide ions and sulphonate moieties in cyclic carbonate synthesis.



Scheme 1 Schematic representation of cyclic carbonate synthesis using sulphonate salt tethered mesoporous silica.

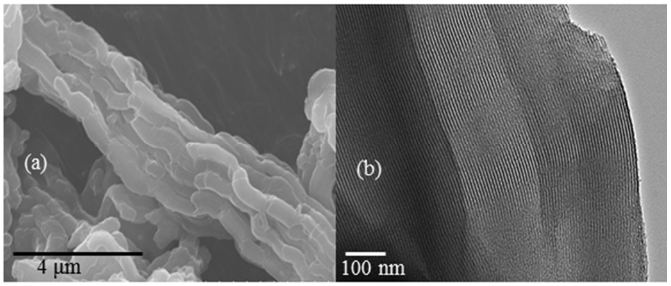


Fig. 1 SEM (a) and TEM (b) of thiol functionalized SBA-15

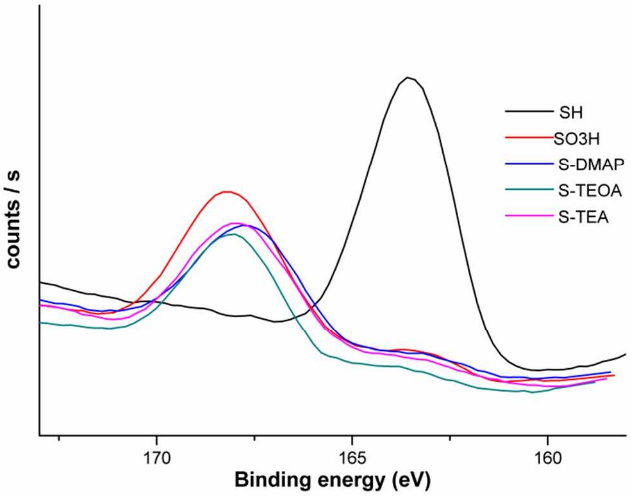


Fig. 2 XPS spectra for the S2p region of SBA-15-SH, SBA-15-SO_3H and S-base catalysts

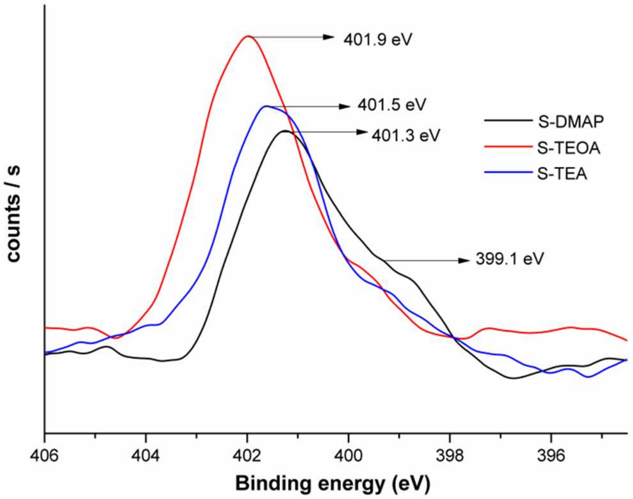


Fig. 3 XPS spectra for the N1s region of S-base catalysts

Results and discussion

Characterization

The 2D hexagonal framework of SBA-15 and SBA-15-SH were confirmed from their corresponding SAXS patterns exhibiting the (100), (110) and (200) planes which corroborates that they belongs to p6mm symmetry as shown in supporting information (Fig. S1a and S2a) [8]. And a long established N_2-physisorption isothermal plot with H_1 type hysteresis loop study also suggests the cylindrical pore arrangement of the aforementioned materials (Fig. S1b and S2b). Moreover, SEM and TEM images in Fig.1 displayed the 2D framework of SBA-15-SH with long channeled rod-like arrangement. The subsequent oxidation of –SH group (B) towards $–SO_3H$ moiety (C) was confirmed (Scheme 1) using XPS analysis (Fig. 2), wherein, the former one (B) exhibits a S2p peak at 163.5 eV and latter one (C) at 168.3 eV [9]. Since the peak at 163.5 eV was almost invisible in 'C', it could be surmised that the oxidation of–SH groups to $–SO_3H$ group was almost complete. Since, in general the cyclic carbonate synthesis is better accomplished with ionizable solid catalyst systems, the $–SO_3H$ was neutralized with common

Table 1 Catalytic activity of S-base/KI in propylene carbonate (PC) synthesis

Entry	Catalyst	Co-catalyst	PC yield [Sel]%[a]	TOF[b]
1	-	KI	3[98]	-
2	SO_3H	-	6[88]	-
3	SO_3H	KI	84[95]	854
4	S-DMAP	-	8[82]	-
5	DMAP	-	9[96]	-
6	DMAP	KI	75 [97]	779
7	S-DMAP	KI	98[99]	1048
8	S-TEOA	-	8[89]	-
9	TEOA	-	4[96]	-
10	TEOA	KI	70[98]	746
11	S-TEOA	KI	98[99]	1040
12	S-TEA	-	5[75]	-
13	TEA	-	4[96]	-
14	TEA	KI	41[99]	443
15	S-TEA	KI	97[99]	1039

Reaction conditions: Propylene Oxide (PO)-20 mmol, sulphonic/base/S-base-0.02 mol%, KI-0.4 mol% , 110 °C, 1.1 MPa, 4 h. [a]From GC analysis with Toluene as an internal standard, Sel-Selectivity. [b]TOF-Turnover frequency calculated based on sulphur mole value, as obtained from Elemental analysis (Table S1).

Table 2 Effect of KI amount on PC synthesis

Entry	S-base	S-base:KI	Catalyst ratio	Conv[a] (%)	Sel[a] (%)	TOF[b]
1	S-DMAP	0.02 : 0.1	1:5	91	98	954
		0.02 : 0.2	1:10	96	99	1017
		0.02 : 0.4	1:20	99	99	1048
2	S-TEOA	0.02 : 0.1	1:5	88	99	932
		0.02 : 0.2	1:10	95	99	1006
		0.02 : 0.4	1:20	99	99	1040
3	S-TEA	0.02 : 0.1	1:5	88	99	932
		0.02 : 0.2	1:10	95	99	1007
		0.02 : 0.4	1:20	98	99	1039

Reaction conditions: PO-20 mmol, 110 °C, 1.1 MPa, 4 h. [a] Determined by GC, Conv-Conversion, Sel-Selectivity. [b] TOF-Turnover frequency.

organic (strong) bases such as 4-dimethylaminopyridine (DMAP), triethanolamine (TEOA) and triethylamine (TEA) in Scheme 1, and the so formed materials were named as S-DMAP, S-TEOA and S-TEA, respectively. The aforementioned base neutralized sulphonate silica materials also displayed S2p peaks around 168.3 eV similar to the $–SO_3H$ based silica (Fig. 2). Further confirmation of post neutralization using the bases was provided by the N1s peak of S-DMAP, S-TEOA and S-TEA, at 401.3, 401.9 and 401.5 eV (Fig. 3), respectively, characteristic of ionic nitrogen [5l].

CO_2 fixation

The catalytic activity exhibited by SBA-15-SO_3H and organic sulphonate salt tethered SBA-15 (S-base) with KI co-catalyst towards PO-CO_2 cycloaddition is shown in Table 1. KI has previously been proven to be an efficient and economical co-catalyst for many catalytic species in cyclic carbonate synthesis [6]. However, as can be seen from entries (1, 2) of Table 1, neither KI nor SBA-15-SO_3H yielded any significant PC yield under the employed reaction conditions. The scenario with S-base catalyst alone was also not different, which produced a maximum of only 8% PC yield with 82% PC selectivity (entry 4). But, the combined use of $–SO_3H$/KI binary system manifested an appreciable PC yield of 84% with better selectivity of 95% (entry 3) under the same conditions; while, the more ionized S-DMAP/KI (entry 7) motif yielded an even higher PC yield of 98% with a maximum selectivity of 99% PC. Similar catalytic patterns were exemplified by other S-base /KI systems such as S-TEOA/KI (entry 11) and S-TEA/KI (entry 15) in Table 1, which resulted 98 and 97% PC yield, respectively, without compromising the PC selectivity (99%). The TOF achieved by entries 7, 11 and 15 of Table 1 lies in the range of 1048 h^{-1}, 1040 h^{-1} and 1039 h^{-1}, respectively, which to date is the highest value achieved by any reported silica based catalyst in PO-CO_2 cycloaddition under the employed reaction conditions. The reason behind this high catalytic rate of SBA-15-SO_3H/KI and SBA-15-SO_3^-/KI system shall be surmised to the synergism of SO_3H or SO_3^- with I^- ions. The promoting role of synergism by halide and H-bonding groups has been well explained by ample number of authors [6]. From their extensive works which include both experimental and theoretical results, the hydrogen bonding groups such as –COOH, $–NH_2$ or –OH activate the epoxide substrate, while the halide ions helps in stabilizing a crucial ring opened intermediate (discussed in detail in the mechanism section). The Table 1 entries 6, 10 and 14 for DMAP/KI, TEOA/KI and TEA/KI respectively show that, the base/KI system (which has no sulphonic ion /sulphonate ion moiety) procured less PC yields of 75%, 70% and 41% respectively, which were indicative of the inevitable role played by sulphonic/sulphonate groups. Also, we noticed that, among the sulphonic acid and sulphonate based silica materials, the latter one procured higher PC yield (entries 7, 11 and 15 of table 1), which shall be accounted in such a way that, the SO_3^- entered into better synergism with I^- compared to SO_3H.

A transparent comparison of the catalytic activities exhibited by this sulphonate loaded silica to other related catalysts is provided by the TOF as given in Table S2. Imidazolium based ionic liquid tethered silicas represented a series of perfectly reusable heterogeneous catalysts in cyclic carbonate synthesis; however, the TOF's obtained were not quite high [10e-f]. But the introduction of ionic liquids with hydrogen bonding functional groups such as –OH and –COOH equipped the silica catalysts with better TOF values of the order of 53 and 104 [5m]. From the above reports it was noticed that, –COOH group have better promoting role than –OH group in CO_2 epoxide cyclo addition. However, the results of the present study, indicates that $–SO_3H$ group and SO_3^- anion can engage in better synergism with halide ions than –COOH and –OH groups as indicated by their comparatively very high TOF value of 1947 h^{-1} [Table S2, entry 9]. To the best of our knowledge, this is the highest TOF displayed by any silica based catalyst in cyclic carbonate synthesis.

Influence of reaction parameters

PC synthesis primarily depends on number of active sites on the catalyst, time, temperature and pressure of the reaction system. Since all S-base/KI procured similar catalytic activity, the parameter studies to optimize the reaction conditions were done for all of them. The effect of S-base to KI ratio in the cyclic carbonate yield was investigated. Since the sulphonate acts as CO_2 activator [11], it has been tested with different KI mole ratios as shown in Table 2. As is evident from Table 2, about 1/10 of S-base amount to the KI was adequate enough to forward the cycloaddition to more than 90%, irrespective of the base used (entries 1, 2 and 3) and with lesser KI amounts, lower catalytic activities were observed as expected. The catalyst-cocatalyst ratio was optimized to be 1:20. It was observed that, the cyclic carbonate synthesis proceeded with very less mesoporous silica (25 mg) than the usually employed (500 mg) [5m-n]; the 25 mg silica in this study contains 4.67×10^{-3}mmol sulphur as calculated from the elemental analysis (Table S1)

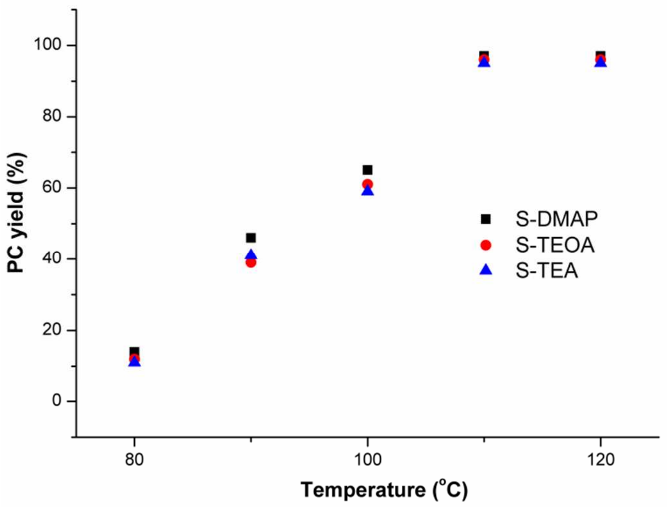


Fig. 4 Effect of temperature in the S-base/KI catalyzed cycloaddition. Reaction conditions: PO-20 mmol, S-base-0.02 mol%, KI-0.4 mol%, 1.1 MPa, 4 h. Selectivity of PC >99%.

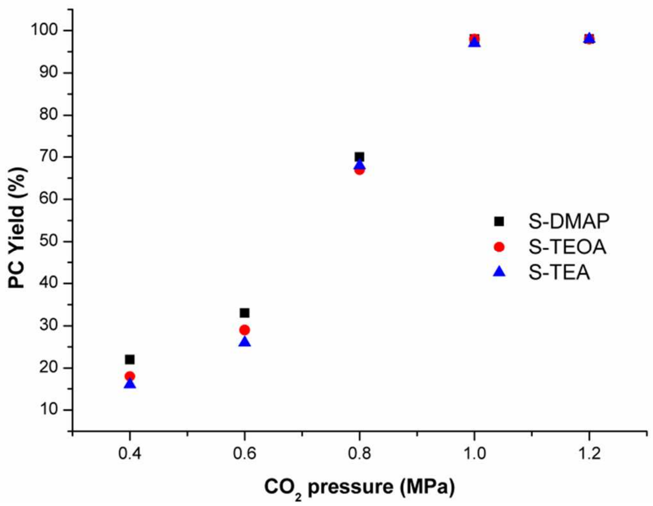


Fig. 5 PC Yield – CO_2 pressure dependence with S-base/KI catalyst system. Reaction conditions: PO-20 mmol, S-base-0.02 mol%, KI-0.4 mol%, 110 °C, 4 h. Selectivity of PC >99%.

We also investigated the crucial role of temperature and pressure in the fixation of CO_2 with propylene oxide mediated by the sulphonate/KI catalysts with mole ratio of 1:20. The influence of temperature on the yield and selectivity of propylene carbonate (Fig. 4) clearly indicated that the catalytic activity is sensitive to reaction temperature. At a lower temperature of 80°C, the PC yield was very less (<20%); there was a slight increase in percentage conversion and reached 67% for S-DMAP upon raising the temperature from 90 °C to 100 °C and with a further increase in temperature to 110 °C, all the catalysts yielded conversion rates as high as 99% PO conversion and 99% PC selectivity. The effect of CO_2 pressure on the cycloaddition of PO and CO_2 in the presence of sulphonate catalyst at 110 °C for 4 h is shown in Fig. 5. The catalyst mixture reaches an average of >98% of conversion and 99% selectivity even at 1 MPa pressure. Obviously at lower CO_2 pressure (<0.8 MPa), PO conversion was less but the selectivity remained high. Similarly, the time study of S-base mediated PC synthesis was also carried out keeping the other reaction parameters constant (Fig. 6). All the catalysts have been tested at different time interval of reactions. The initial rate of catalysis was higher which then found to gets slower, probably because the active sites were less accessible. A maximum conversion of 99% was achieved at 4 h with a PC selectivity of 99%.

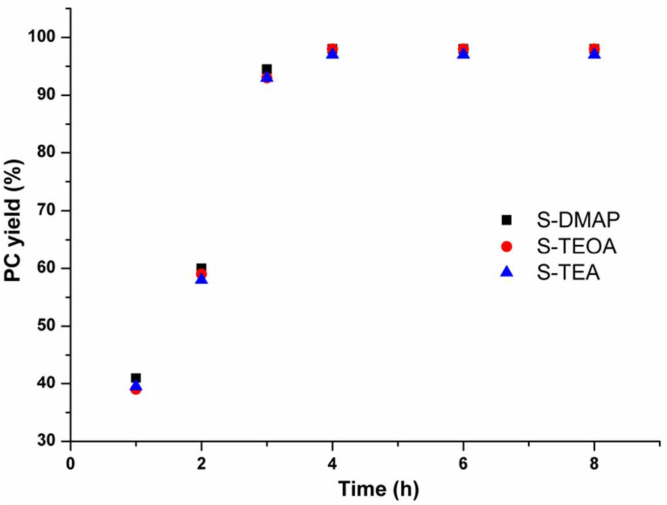


Fig. 6 Time variant study of PC synthesis using S-base/KI catalyst systems. Reaction conditions: PO-20 mmol, S-base-0.02 mol%, KI-0.4 mol%, 110 °C, 1.1 MPa. Selectivity of PC >99%.

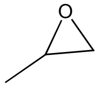
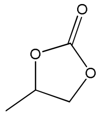
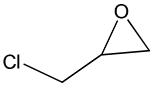
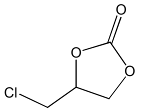
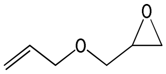
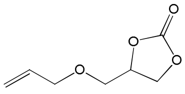
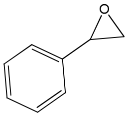
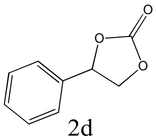
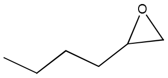
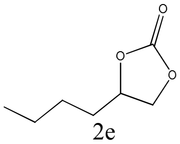
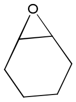
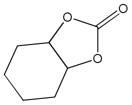
Scope of other epoxides

A series of commercially available epoxides such as propylene oxide (1a), epichlorohydrin (1b), allyl glycidyl ether (1c), styrene oxide (1d), 1,2-epoxyhexane (e) and cyclohexene oxide (1f) has been surveyed for understanding the versatility of S-base/KI catalytic system. All the reactions have been performed with 0.02 mol% of sulphonate catalyst under identical condition (1.1 MPa CO_2 pressure, 110 °C, 4 h). Most of the terminal epoxide provided their corresponding cyclic carbonates with high yield and excellent selectivities indicating the high versatility of this catalyst system as noted in Table 3. However in agreement with the previous reports, the internal epoxide cyclohexene oxide (CHO) gave a low conversion of 13% only with 98% selectivity (cyclohexene carbonate) which is generally attributed to the high steric hindrance.

Mechanism of cycloaddition

By rationalizing our experimental results and relating it to the numerous reports on hydrogen bonding groups and halide moiety enabled synergistic catalysis of PO-CO_2 cycloaddition [5m], we arrived at a plausible mechanism for the SO_3H/KI and SO_3^-/KI catalyzed PC synthesis (Scheme 2). In case of SO_3H/KI, a hydrogen bond is generated between the $–SO_3H$ moiety and the epoxide 'O' atom, which weakens the beta carbon oxygen bond of the epoxide (βC−O). Eventually the ring opens and the I^- ion makes a nucleophilic attack on the beta carbon(βC) atom of the epoxide forming a halide intermediate. As is evident from Table 1 (entry 2 and 4) in the absence of KI, the catalytic activity was negligible which emphasizes the significance of this halide intermediate formation in the completion of the catalytic loop [6f]. At the same time, the oxy anion of the epoxide binds the CO_2 molecule through a nucleophilic attack. The halide ion leaves the ring opened epoxide and finally ring closure occurs forming the product PC.

Table 3: Synthesis of other cyclic carbonates over S-DMAP and KI catalysts

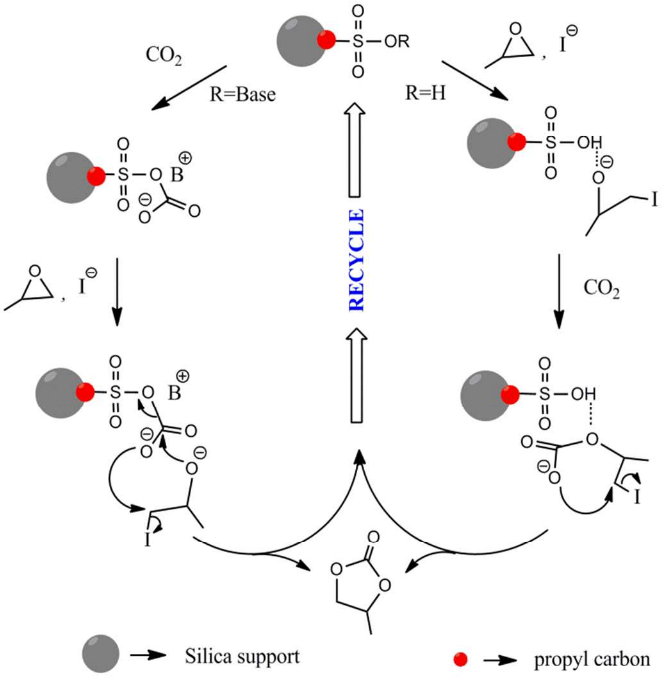
Entry	Epoxide	Product	Yield %	Sel %
1	 1a	 2a	98	99
2	 1b	 2b	80	99
3	 1c	 2c	97	99
4	 1d	 2d	95	98
5	 1e	 2e	96	98
5^g	 1f	 2f	13	98

Reaction condition: epoxide-20 mmol, S-DMAP-0.02 mol%, KI-0.4 mol%, 110 °C, 1.1 MPa, 4 h, ^{g} 12 h. Sel-Selectivity.

In case of SO_3^-/KI system, the catalytic cycle propagates in a different way, such that, the I^- ions attacks the βC of the epoxide while the negatively charged O atom of the SO_3^- groups makes a nucleophilic attack to CO_2 [11]. As the halide ion leaves the ring opened epoxide, the newly formed O^- atom of carbonate entity ($–SO_3–CO–O^-$) attacks the beta carbon and subsequently, the SO_3^- group regenerates, which leaves the 'C' atom of CO_2 with a net positive charge. Finally, the terminal oxy anion of ring opened epoxide attacks this delta plus carbon, completing the PC formation.

Catalyst reusability

The reusability studies of both the catalysts viz., SBA-15-SO_3H and S-bases with KI co-catalyst have been tested (Fig. 7). The SBA-15-SO_3H catalyst maintained its catalytic activity without any significant loss even after 5 consecutive cycles; the PC in yield in the 5th cycle remained similar to that of the fresh catalyst. But, in case of S-base/KI reusability study, the PC yield was found to decrease gradually, probably because of the leaching occurred to the protonated base moieties upon washing (Fig. S3).



Scheme 2 The probable mechanism of S-base or sulphonic acid with KI catalyzed cycloaddition of CO_2 with propylene oxide to yield the propylene carbonate (where B-base (DMAP or TEOA or TEA)).

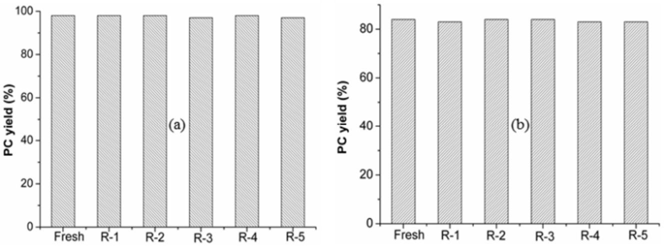


Fig. 7 Recycles of (a) S-base (after regenerating with bases for 5 minutes) b) SBA-15-SO_3H in the synthesis of PC at 1.1 MPa CO_2 pressure, 110 °C, 4 h. Amount of KI = 0.4 mol% in all cases.

This was visualized through the peak splitting occurred at 2930 cm^{-1} for R2 in FT-IR spectra (Fig. S4) suggesting the leaching of the organic bases. However the activity was totally regainable by treating the spent catalyst with bases for a very short period of time (Fig. 7a). Further characterizations done with BET revealed that even after the 4th cycle, the catalyst maintained its well-ordered textural property which proposed the morphological stability of the catalyst used in this work [Table S3].

Thermogravimetric analysis

Even though the surface neutralization of mesoporous silica sulphonate (S-base) materials is easy, economical and catalytically active, their thermal stabilities are slightly lesser than the SBA-15 (SO_3H) materials (Fig. 8), as evidenced by thermo gravimetric analysis (TGA). SBA-15(SO_3H) showed moderate thermal stability up to 460 °C at which point, the degradation occurred via pyrolytic fragmentation of organic groups. S-DMAP showed its first thermal degradation at temperatures around 270 °C, which is lesser than the starting material sulphonic acid. However this material showed its third degradation at 460 °C similar to the starting material, suggesting that the sulphonate groups are stable even at high temperature. Their earlier degradation at 270 °C must be a direct consequence of organic bases. However, cycloaddition reactions are performed under 115 °C, which is much lower than the first thermal degradation temperature (~270 °C) of S-DMAP and SBA-15-SO_3H (~470 °C), the catalyst maintained its stable nature all along the catalysis.

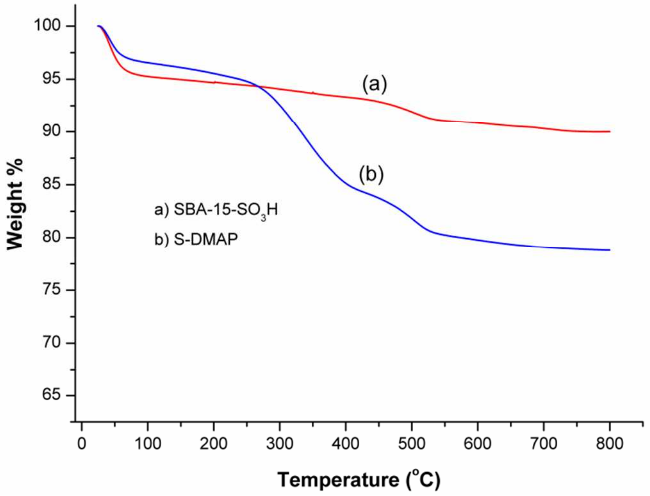


Fig. 8: Thermo gravimetric analysis curves of Sulphonic and sulphonate catalysts

Conclusion

A series of heterogeneous sulphonic/sulphonate supported mesoporous silica materials were easily synthesized and were found to act as environmentally benign and efficient catalysts with KI for CO_2-epoxide cycloaddition. The multi-functional S-base/KI catalyst system was found to yield the corresponding cyclic carbonates in excellent selectivity under solvent free conditions of 1.1 MPa CO_2 and 110 °C in a short time of 4 h with a very low catalytic amount of 0.02 mol% of sulphonate. Among the different sulphonate(S-base) employed, we found that the catalyst activity was irrespective to the base moiety used. The mechanism of this cycloaddition is thought to have involved a synergistic play between the iodide ions and sulphonate/sulphonic acid moieties. The results pointed out that, the sulphonate anions enters into better synergism with iodide ions than the sulphonic acid. Though, the sulphonic acid moieties were less active than sulphonate moieties, it has higher recyclability prominently by about 5 times. The TOF achieved by this catalyst significantly surpasses those obtained using ionic liquid and metal impregnated silica catalysts in cyclic carbonate synthesis from CO_2-epoxide cycloaddition.

Experimental

Material synthesis

The synthesis of 2D SBA-15 mesoporous materials by the solvothermal method employed Pluronic P123/TEOS/HCl/H_2O and 3–MPS [9]. Typically, Pluronic P123 was dissolved in aqueous HCl solution with magnetic stirring until a clear solution was obtained. This is followed by the addition of TEOS to the solution; and the pH (~1.2) was maintained. The resulting mixture was stirred for further 24 h at 30 °C, and then transferred to Teflon–lined stainless steel autoclave and heated to 100 °C for 24–36 h. The obtained materials were filtered and washed using distilled water followed by ethanol, and dried in vacuum at 60 °C for 6 h and then calcination was done at 550 °C for 6 h to remove the surfactant from the as–synthesized materials. The pristine SBA-15 materials was functionalized with 3-MPS by dispersing in toluene at refluxed condition for 6 h and then filtered, washed and dried at oven at 55 °C for 3 h. Then, the obtained SBA-15-SH were dispersed in methanol / 50% H_2O_2 solution and stirred for 6 h under acidic condition (H_2SO_4). The oxidized material was filtered and dried in vacuum oven at 55 °C for 8 hours. Henceforth, the obtained materials were successfully characterized.

Neutralization

The SBA-15(SO_3H) were dispersed in 30% base solution in methanol and stirred for 10 minutes at room temperature. Then, the materials were filtered and washed with excess methanol repeatedly to remove the excess base from the silica materials and the obtained material was named as S-base.

Characterization

Small angle X–ray scattering (SAXS) was performed at Pohang Accelerator Laboratory (PAL) with Co–Kα radiation ($\lambda = 1.608$ Å) in the energy range 4–16 keV (energy resolution: $\Delta E/E = 5 \times 10^{-4}$; photon flux: 10^{10}–10^{11} ph./s, Beam size: <1 mm^2) over the scan range 0.4 $nm^{-1} < q < 5.0$ nm^{-1}. Nitrogen adsorption and desorption isotherms were measured using an ASAP 2020 surface–area and pore–size analyzer. Prior to the measurement, the samples were dehydrated at 90 °C for 5 h. The BET (Brunauer–Emmett–Teller) method was used to calculate the specific surface area. The pore size distribution was calculated from the analysis of the isotherm desorption branch by the BJH (Barret–Joyner–Halenda) method coupled with the apparatus software. Field emission Scanning electron microscope (Fe-SEM) images measurement were recorded on a JEOL JSM–6700F instrument. Transmission electron microscope (TEM) image measurements were recorded on a JEOL 2010 electron microscope operating at 200 kV. The powder samples were dispersed in ethanol, then deposited and dried on a perforated Cu grid. Images were recorded at magnifications 150,000× and

200,000×. XPS analysis was performed using an X–ray photoelectron spectrometer (VG, ESCALAB 250) with monochromatic Al Kα radiation (hν = 1486.6 eV). Elemental analyses were measured on vario MICRO CHNS analysis technic. The infrared spectra were recorded on a Nicolet 6700 FT–IR spectrometer.

Cycloaddition

The synthesis of the cyclic carbonate from propylene oxide (PO) and CO_2 (Scheme 1) using the S-base catalyst was performed in a 50 mL stainless steel autoclave equipped with a magnetic stirrer. For each typical batch operation, S-base catalyst (25 mg) and PO (20 mmol) were charged into the reactor without solvent. The reactor was then pressurized with CO_2 to a preset pressure, 0.4–1.1 MPa, at room temperature. The reactor was heated to the desired temperature, and then the reaction was started by stirring the reaction mixture at 450 rpm. The reactor pressure increased to about 1.2–2.4 MPa, depending on the reaction temperature, because of the vapor pressure of the reactants. After the completion of the reaction time, the cycloaddition was stopped by cooling the reaction mixture to less than 10 °C and vent the remaining CO_2. The product (4-methyl-1,3-dioxolan-2-one) was dissolved in toluene and filtered to remove the catalyst. Product analysis was carried out via gas chromatography/mass spectrometry (GC-MS, Micromass, UK) analysis. The conversion of PC was obtained from gas chromatography (GC, HP 6890, Agilent Technologies, Santa Clara, CA, USA) data.

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Notes and references

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