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State-of-the-Art Catechol Porphyrin COF Catalyst for Chemical Fixation of Carbon Dioxide *via* Cyclic Carbonates and Oxazolidinones

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The highly porous, crystalline catechol porphyrin COF synthesized and applied as an organocatalyst for the chemical fixation of carbon dioxide to synthesis value added chemicals such as cyclic carbonates and oxazolidinones under solvent free and transition-metal free condition. The high surface area as well as functionalities of COF catalyst shows synergistic effect to activates the starting material. The 2,3-DhaTph shows excellent activity towards cyclic carbonates at the atmospheric pressure of carbon dioxide. Additionally, this catalytic system is recyclable in nature and provides high turnover number than the previously reported organocatalysts.

Introduction

Annually about 35 gigatonnes carbon dioxide (CO_2) produced and it covers up to 82 % of the total amount compared to other greenhouse gases. Further increase of concentration of CO_2 will produce large and disorderly impact on environment.[1] Although CO_2 is considered as an alternative view as a sustainable C1 source, its synthetic applications are limited due to the low reactivity of CO_2.[2] Given their large applications in the pharmaceutical and fine chemical industries the cyclic carbonates synthesized form CO_2 and epoxides has been received intense attention.[2b] The synthesis of cyclic carbonates and oxazolidinones from CO_2 gives the 100% atom economical reactions. Although various catalysts reported to synthesize the cyclic carbonates, most of the processes demands harsh reaction conditions like, use of transition metals, high pressure, high temperature and separation problems.[3] The catalytic fixation of carbon dioxide at mild conditions remains challenging, very few reports are available in the literature for the synthesis of cyclic carbonates at mild conditions such as low pressure as well as low temperature.[3j-m]

Covalent Organic Frameworks (COF) are represents a special emerging class of porous materials with pure organic group and highly crystalline materials, with high surface area, formed by using strongly covalent bonding between light weight elements like C, N, B, Si and O with reticular network of molecular building block.[4] This material exhibits an exceptional high surface area and uniform distribution of pore size and high stability hence considered as promising material in the field of catalysis,[5] gas storage,[6] opto-electronics[7] and Sensing.[8] Recently, published crystalline, porous, chemically stable porphyrin based COFs (2,3-DhaTph and 2,3-DmaTph) have very active catalytic sites such as acidic (catechol), basic (porphyrin). These functionalities make them highly active organocatalyst for the organic transformations such as tandem/cascade/one pot synthesis.[5d] Additionally, these COFs are highly stable and crystalline in nature. We thought, the integration of permanent porosity with separate antagonist site with high surface area and high stability, of the 2,3-DhaTph COF could be provide an excellent catalytic platform for the fixation of carbon dioxide at the milder reaction conditions.

It is widely accepted that the catalyst bearing hydrogen bond donor (HBD) has ability to accelerate the cycloaddition reaction of CO_2 with epoxides.[9-18] In this illustration the cooperative effect of HBD catalyst promote the ring opening of epoxide by nucleophillic attack by an anion and stabilize the oxyanion intermediate, the stabilized intermediate then undergoes the attack of CO_2 and yield the cyclic carbonates.[18c] Recently, Sun *et al*. also demonstrated the computational evidences for the synergistic effect of hydroxyl functional group with epoxide for accelerating the rate of reaction towards the synthesis of cyclic carbonates.[22] The accelerating effect of the HBD catalyst for this reaction using the spectroscopic evidences also well known in literature.[3k,9c,23] Herein we applied 2,3-DhaTph and 2,3-DmaTph COFs as an organocatalyst for the chemical fixation of CO_2 to synthesis the cyclic carbonates and oxazolidinones. The 2,3-DhaTph bearing HBD was found to be highly active, selective and recyclable catalyst HBD for the chemical fixation of CO_2 to cyclic carbonates at the atmospheric pressure. Additionally, it is worth mentioning that the developed COF catalyst provides high turnover number and proceeds under solvent free as well as transition-metal free condition.

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Results and discussion

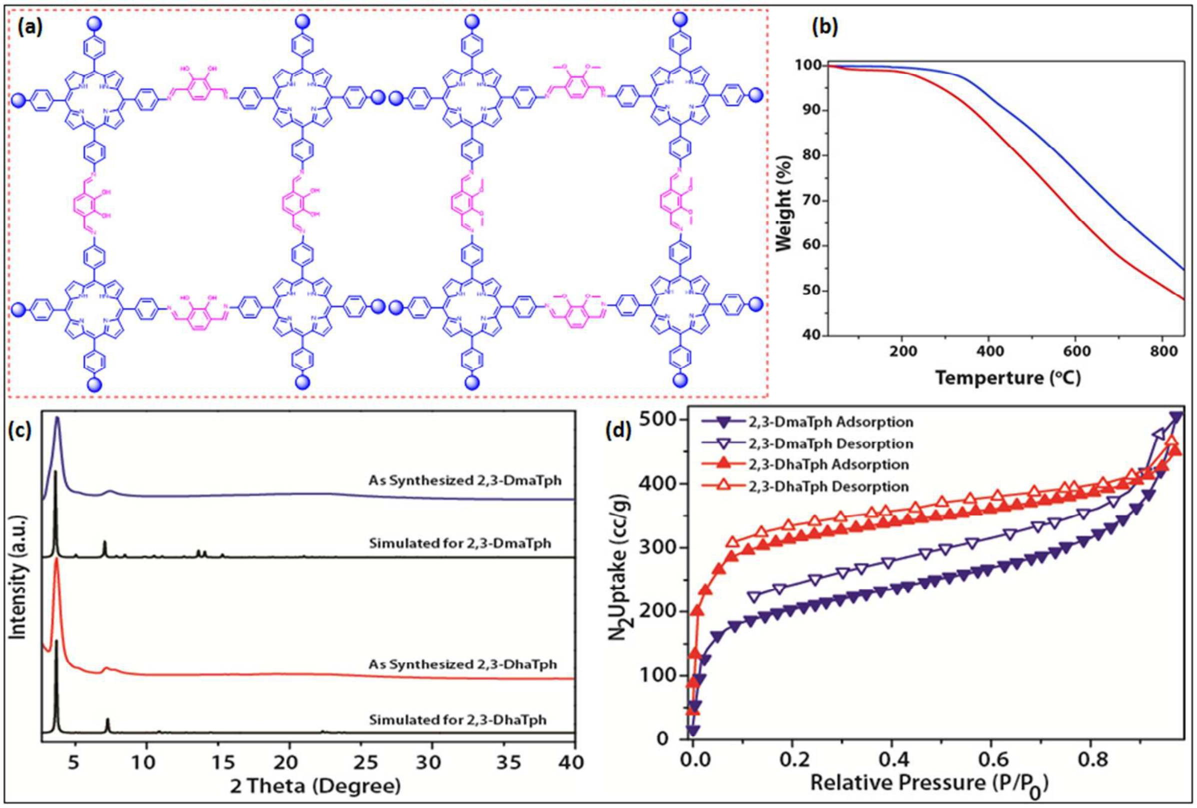
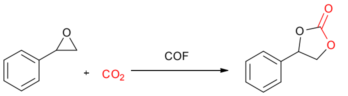


Fig. 1 (a) Chemical structures of 2,3-DhaTph and 2,3-DmaTph COF (b) Thermogravimetric analysis 2,3-DhaTph (blue) 2,3-DmaTph (red), (c) PXRD analysis 2,3-DhaTph and 2,3-DmaTph (d) N_2 adsorption isotherm of 2,3-DhaTph (red) and 2,3-DmaTph (Blue).

Table 1 Catalysts screening for the synthesis of cyclic carbonate.

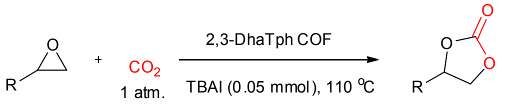


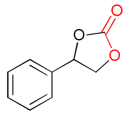
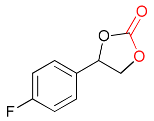
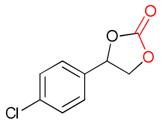
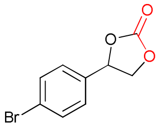
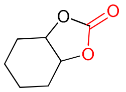
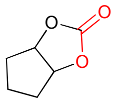
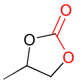
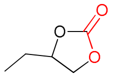
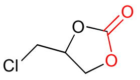
Entry	COF (mmol)	Co-cat	Solvent	Yield (%)[b]	Sel.(%)[b]	TON
1	-	-	-	-	-	-
2	-	TBAB	-	16	99	-
3	2,3-DhaTph	TBAB	PhMe	42	99	210
4	2,3-DhaTph	TBAB	THF	50	99	250
5	2,3-DhaTph	TBAB	-	77	99	385
6	2,3-DmaTph	TBAB	-	63	99	315
7	2,3-DhaTph	TBAI	-	94	99	470
8	2,3-DmaTph	TBAI	-	76	99	380
9	2,3-DhaTph	KI	-	90	99	450
10	2,3-DmaTph	KI	-	72	99	360
11	2,3-DhaTph	NaI	-	82	99	410
12	2,3-DmaTph	NaI	-	75	99	375
13[c]	2,3-DhaTph	TBAI	-	98	99	490
14[d]	2,3-DhaTph	TBAI	-	98	99	980
15	2,3-DhaTph	-	-	Traces	-	-
16[e]	Catechol	TBAI	-	48	99	120

[a] Reaction conditions: SO (10 mmol), COF (0.02 mmol), CO_2 (1 atm.), Co-catalyst (0.05 mmol), 110 °C for 12 h. [b] Determined by GC and GCMS. [c] CO_2 (1 Mpa), 100 °C 4 h. [d] SO (20 mmol) 100 °C and 1 Mpa 4 h. [e] Catechol (0.04 mmol).

The 2,3-DhaTph and 2,3-DmaTph were synthesized using previously reported method by Schiff base reaction using 2,3-dihydroxyterephthalaldehyde (2,3-Dha)/2,3-dimethoxyterephthalaldehyde (2,3-Dma) and a 5,10,15,20-tetrakis(4-aminophenyl)-21*H*,23*H*-porphine (Tph) unit.[5-d] These synthesized material characterized by using FT-IR, TGA, SEM, BET and XRD techniques (Fig 1). Ensuring the high surface area (~1000 m^2 g^{-1} ESI-fig. 3), high thermal stability (fig. 1b) and the presence of acid base nature of synthesized 2,3-DhaTph COF, we applied this catalytic system for the cycloaddition reaction of epoxide with carbon dioxide to synthesis the cyclic carbonates. At the atmospheric pressure of CO_2 the cycloaddition reaction with styrene oxide (SO) to synthesis the styrene carbonate (SC) was chosen as a model reaction using COF catalysts and results are listed in Table 1. Without using the catalyst and co-catalyst no any conversion of SO to SC was observed (Table 1, entry 1), negligible yield of SC was observed when the reaction carried out using only co-catalyst (Table 1, entry 2). Next, we studied effect of solvent on reaction condition, and we observed that the polar as well non-polar solvents also accelerate the reaction effectively and gives moderate yield (Table 1, entries 3-4). Next, we carried out the reaction at the neat condition and it provides good yield of SC using the TBAB as a co-catalyst (Table 1, entry 5).

Table 2 Various cyclic carbonates syntheses using the 2,3-DhaTph COF catalysts



 Yield: 94 % TON: 470 Sel: >99	 Yield: 90 % TON: 460 Sel: >99	 Yield: 95 % TON: 475 Sel: >99
 Yield 94 % TON: 470 Sel: >99	 Yield 93 % TON: 460 Sel: >99	 Yield 90 % TON: 450 Sel: >99
 Yield: 78 % TON 390 Sel: >99	 Yield: 84 % TON 420 Sel: >99	 Yield: 88 % TON: 440 Sel: >99

[a] Reaction Conditions: Epoxide (10 mmol), CO_2 (1 atm.) 2,3-DhaTph (0.02 mmol), TBAI (0.05 mmol), 110 °C, 12 h. Yield and selectivity calculated by GC.

Thus, we concluded that the solvents are not necessary for this reaction. Encouraged by these results, the comparative study of hydrogen bond donor COF (2,3-DhaTph) and without hydrogen bond donor COF (2,3-DmaTph) were studied. Next, we examined the effect of various co-catalysts such as TBAB, TBAI, KI and NaI for the nucleophillic ring opening of epoxide, using the both 2,3-DhaTph and 2,3-DmaTph catalyst system. Among the various co-catalysts studied TBAI gives excellent yield up to 94 % (Table 1, entry 7). Next, the comparative study of 2,3-DhaTph and 2,3-DmaTph COFs as a catalyst have been studied and we observed that the catalyst which bearing hydrogen bond donor capability 2,3-DhaTph was more active than the 2,3-DmaTph at the atmospheric pressure (Table 1, entries 6-12). High selectivity towards the synthesis of cyclic carbonates were observed (up to 99 %). In the next set of experiments, reaction were carried out at the 1 MPa pressure of carbon dioxide, increased yield of SC was observed (Table 1, entry 13). The high TON of SC was observed when the reaction was carried out at 1 MPa pressure by increasing the concentration of SO (Table 1, entry 14). Next, we observes that the without using the co-catalyst (TBAI) negligible yield was noted, TBAI needed for the nucleophillic ring opening of the epoxide (Table 1, entry 15). Next, we the cycloaddition reaction performed by using only catechol (1,2-benzenediol) as catalysts and moderate yield of SC were observed (Table 1, entry 16), thus we concluded that the presence of high surface area of 2,3-DhaTph COF also plays crucial role for the cycloaddition reaction. The high catalytic activity of 2,3-DhaTph COF as compared to 2,3-DmaTph COF for chemical fixation of CO_2 should be mainly due to the presence of high density of active sites with well oriented hydroxyl functional group and porphyrin group together which could promote the interactions between incoming substrates and active sites of the COF to convert the product very effectively. Next, we observed that the catalyst

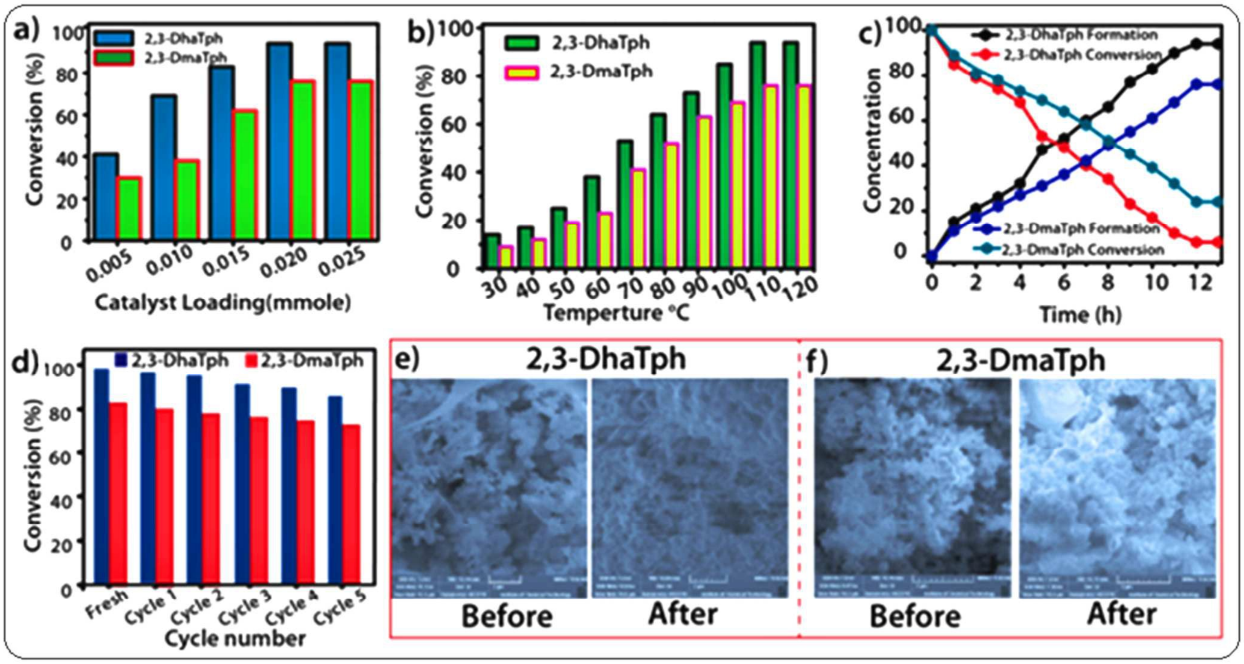


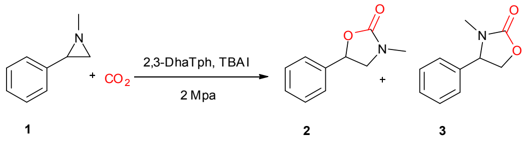
Fig. 2 (a) effect of amount of loading of COF catalyst, (b) effect of temperature, (c) effect of reaction time, (d) recycle study of COFs, (e) SEM image of 2,3-DhaTph and (f) SEM images of 2,3-DmaTph COF before and after the cycloaddition reactions.

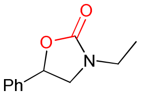
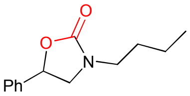
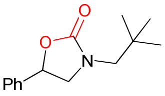
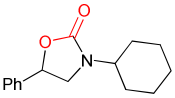
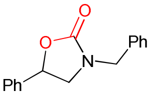
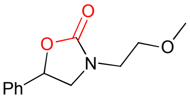
loading for the cycloaddition reaction at the atmospheric pressure of carbon dioxide plays the key role to provide the high yield and TON, as the loading of catalyst decreases yield also decreases, 0.02 mmol of catalyst loading is optimum loading to achieve the highest conversion (Fig. 2a). Next, we studied the effect of temperature; 110 °C is the effective temperatures to achieve highest conversion of SC, as the temperature of reaction system decreased the decreased amount of SC were observed (Fig. 2b). After this we studied the effect of time on reaction condition and it was observed that the 12 h was optimum time to achieve the highest conversion of SC, further increase of time was not effective (Fig. 2c).

After the optimization conditions in hand, a variety of substrates were tested under the optimized reaction condition to synthesize the cyclic carbonates (Table 2). In substrate study, it was observed that the developed catalytic system is applicable for the synthesis of various cyclic carbonates including aliphatic as well as aromatic carbonates. The cyclic aliphatic carbonates are also well tolerated. It is worth mentioning that, the epoxides with aromatic substituent like styrene oxide and functional styrene oxide like Cl, F and Br gives the high yield and turnover number as compared to the aliphatic epoxides.

To prove the HBD catalysis by using the 2,3-DhaTph we carried out the FT-IR spectroscopy and NMR (ESI-Fig. S-8) by using the 1,2-benzendiol. The comparative IR spectra of epoxide

Table 3 Synthesis of oxazolidinones using 2,3-DhaTph COF as a catalyst system



Entry	Oxazolidinones	Time	Yield (%)[b]	Regio-sel.[c]	TON
1[d]	2	3	39	98:2	195
2	2	1	71	98:2	355
3	2	3	96	97:3	480
4		3	97	97:3	485
5		3	93	98:2	465
6[e]		12	59	99:1	295
7		15	86	98:2	430
8		8	96	99:1	480
9		8	92	99:1	460

[a] Reaction conditions: Aziridines (5 mmol), 2,3-DhaTph (0.01 mmol), TBAI (0.05 mmol), CO_2, 2 Mpa, 50 °C . [b] Determined by GC and GC MS. [c] Molar ratio **2** to **3** by GC. [d] 1 Atm. pressure $CO_{2.}$ [e] 80 °C.

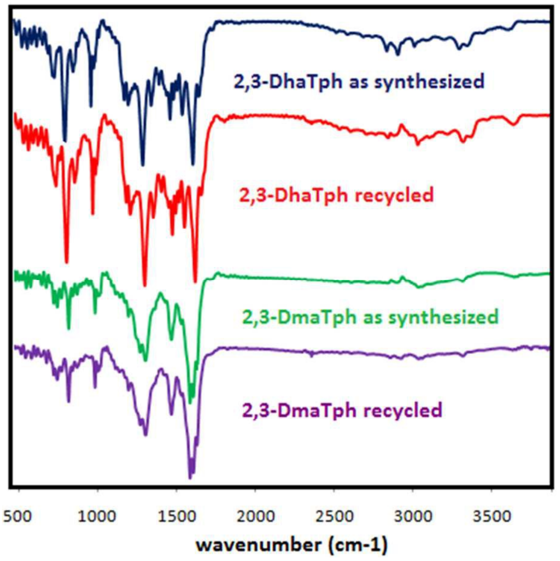


Fig.3 Comparatives IR data 2,3-DhaTph and 2,3-DmaTph COF catalyst.

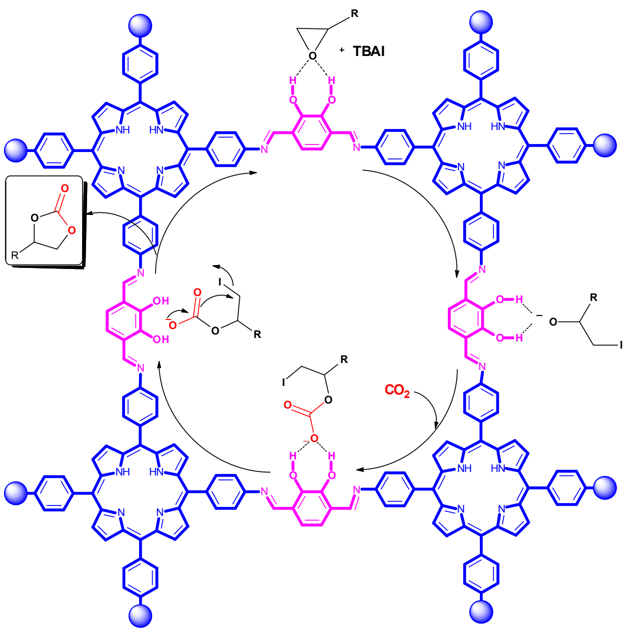


Fig.4 Proposed reaction mechanism for the synthesis of cyclic carbonates from carbon dioxide and epoxide catalysed by 2,3-DhaTph COF as a catalyst system.

(epichlorohydrin) and reference HBD catalyst as 1,2-benzenediol were taken (Fig. 5). Initially, the 1,2-benzenediol showing two sharp peak (~3300-3400 cm^{-1}), the mixture of epichlorohydrin and 1,2-benzenediol gives the broad peak (3389.85 cm^{-1}). This broad peak clearly indicates the presence of hydrogen bonding between 1,2-benzenediol and epoxide.

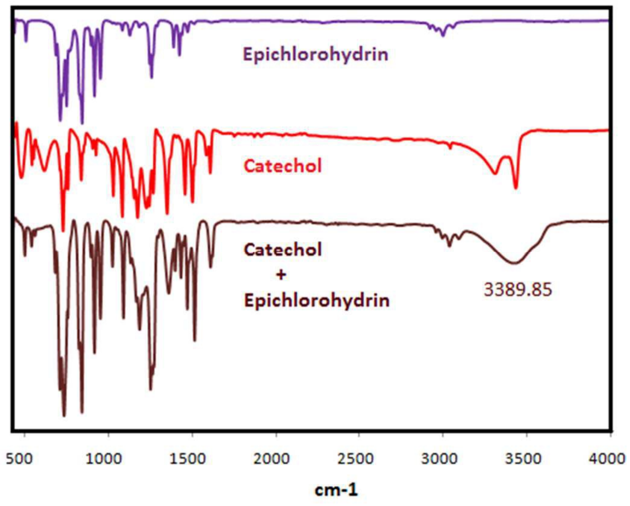


Fig. 5 IR spectroscopic evidences for HBD promoted reactions

After such encouraging results for the synthesis of cyclic carbonates we further extended this protocol for the synthesis of oxazolidinones by coupling of CO_2 with aziridines (Table 3) using the 2,3-DhaTph as a catalyst system. Oxazolidinones are the most important class in the field of chiral auxiliaries, synthetic and medicinal chemistry.[19] Various 1-alkyl-2-arylaziridines were synthesized and applied for the synthesis of 5-aryl-2-oxazolidinones at low temperature and moderate pressure using the 2,3-DhaTph COF as a catalyst system under solvent free condition. The carboxylation reaction of carbon dioxide with 1-methyl-2-phenylaziridine (1) to 3-methyl-5-phenyloxazolidin-2-one (3) was investigated as model reaction. At the atmospheric pressure of carbon dioxide the low yield of 3 was noted (Table 3, entry 1), thus we performed reaction at the high pressure, good yield of the 3 observed for the 1h of time (Table 1, entry 2). Excellent yield and selectivity was observed when reaction performed for 3h. Aziridines substituted with aliphatic amine group provides excellent yield as well as the regioselectivity (Table 3, entries 3-5), while the bulky aziridines provide poor yield, by increasing the time and temperature of the reaction system gives moderate yield (Table 3, entry 6). Cyclic aziridines including aliphatic as well as aromatic also found to reactive and provide high TON (Table 3, entries 7-8). The yield and turnover number for the synthesis of oxazolidinones using 2,3-DhaTph was also high at the milder temperature and moderate pressure of carbon dioxide. Additionally, the 2,3-DhaTph COF provides the excellent regioselectivity towards the synthesis of 5-aryl-2-oxazolidinones under mild and solvent free reaction conditions.

Based on the reported method for the cycloaddition reaction of CO_2 with epoxide promoted by HBD catalysis[9-18,22] we have developed a tentative mechanism using the 2,3-DhaTph COF as a catalyst system (Fig. 4). The presence of vicinal catecholic group of 2,3-DhaTph COF helps to polarize the C-O bond of epoxide[16b,22] using the hydrogen bonding which subsequently attacked by the anion generated from the co-catalyst to open the epoxide ring. The opening of epoxide ring generates the oxyanion intermediates which also stabilized by hydrogen bonding of the catecholic group of 2,3-DhaTph COF. Next, the oxyanion intermediate adds the carbon dioxide molecule and fallow the subsequently cyclization to from cyclic carbonate. Hence, we concluded that the presence of 2,3-DhaTph catalyst with high surface area showing the accelerating effect for the cycloaddition reaction of epoxides with carbon dioxide.

As the 2,3-DmaTph COF showing the high activity towards the synthesis the cyclic carbonates we checked the co-operative effect of 2,3-DhaTph (hydrogen bond donor) catalyst and co-catalyst by using the hot filtration method.[20] To check the leaching study of 2,3-DhaTph COF catalyst we followed the method reported by He.[20b] The cycloaddition reaction of SO to SC was investigated at the optimized reaction condition, after 6 h the reaction mixture was hot filtered and resultant reaction mixture kept for the further reaction. The reaction mixture analysed after every two hour by GC negligible amount increased conversion were noted this may be due to the dissolved TBAI in reaction mixture. (ESI-Fig-S6). The hot filtered mixture then evaporated on SEM holder[5e] and analysed by using the EDS, I and N elements were detected (ESI, S-13). Next, to study the leaching of COF same experiment was performed without using co-catalyst (TBAI) and reaction mixture evaporated on SEM holder for elemental analysis, the N element was not detected hence, we concluded that there is no leaching of 2,3-DhaTph in to the reaction mixture while, the co-catalyst (TBAI) leached (leached co-catalyst also detected by using the GC-MS). and no leached amount of 2,3-DhaTph were noted.

A significant advantage of any porous heterogeneous catalyst is that they could be conveniently recycled and reused[21] To investigate the recyclability of the developed COF catalyst the cycloaddition reaction of SO to SC were performed at the optimized reaction conditions and we observed that the 2,3-DhaTph COF catalyst could be recycled up to five consecutive recycle without loss of its catalytic activity(Fig. 2d), for each recycle fresh amount of TBAI were added along with 2,3-DhaTph COF. The slightly decreased yields of carbonates for each cycle were noted this may be due to handling loss of catalyst. After the fifth recycle the catalyst were characterized using the SEM (Fig. 2e and f) and FT-IR analysis (fig. 3) no any significant structural changes were observed. The higher catalytic activity of 2,3-DhaTph over 2,3-DmaTph for the synthesis of cyclic carbonates were may be due to the unique structural features of the 2,3-DhaTph such as presence of high surface area with abundant HBD ability. The high surface area with abundant HBD of 2,3-DhaTph helps activate the epoxide as well as the porphyrin group helps to adsorb the carbon dioxide molecule effectively.

Conclusions

In conclusion, we have developed a highly efficient catalytic method for the synthesis of cyclic carbonates as well as oxazolidinones by cycloaddition reaction using the 2,3-DhaTph and 2,3-DmaTph COF as a catalyst for the first. The developed COF represents high surface area with abundant hydrogen bond donor ability, which helpful for the activation of epoxide and carbon dioxide. This catalyst system demonstrates the high TON for the synthesis of cyclic carbonate as well as synthesis of oxazolidinones with high regioselectivity. The catalyst could be recycled for five consecutive recycle runs as well as proceeds under solvent free and metal free conditions. Efforts are underway to develop more environmentally benign catalyst for fixation of carbon dioxide at ambient conditions.

Acknowledgements

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State-of-the-Art Catechol Porphyrin COF Catalyst for Chemical Fixation of Carbon Dioxide *via* Cyclic Carbonates and Oxazolidinones

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