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Green and efficient cycloaddition of CO_2 toward epoxides over thiamine derivatives/GO aerogels under mild and solvent-free conditions

Ziqi Yi[1†], Donghui Lan[1,2†], Ying Wang[1], Lang Chen[1], Chaktong Au[1,2] & Shuangfeng Yin[1*]

[1]State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China
[2]Department of Chemistry, College of Chemistry and Chemical Engineering, Hunan Institute of Engineering, Xiangtan 411104, China

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Thiamine derivatives that are cheap, readily available, non-toxic and green are used as heterogeneous catalyst for the generation of cyclic carbonates through cycloaddition of CO_2 to epoxides without the need of co-catalyst and solvent. The interaction between thiamine hydrochloride (VB_1-Cl) and substrates (CO_2 and propylene oxide) was proven by ultraviolet-visible spectroscopy and ^1H nuclear magnetic resonance analysis, and it is deduced that the synergistic action among multi-functional groups (hydroxyl, halide anion and amine) is a favorable factor for cycloaddition reaction. A series of VB_1/GO aerogels were facilely prepared through the addition of aqueous VB_1 derivatives to a suspension of GO in ethanol at room temperature. It was found that the aerogel generated through the interaction of VB_1-Cl with GO shows catalytic activity and stability higher than those of VB_1-Cl. It is because the electrostatic interaction between GO and VB_1-Cl enhances the nucleophilicity and leaving ability of anion. The effects of reaction temperature, catalyst loading, CO_2 pressure and reaction time on CO_2 cycloaddition to propylene oxide were thoroughly studied.

thiamine B_1, graphene oxide, aerogels, synergetic effect, carbon dioxide, cycloaddition reaction

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1 Introduction

Carbon dioxide (CO_2) is a greenhouse gas blamed for global warming [1]. Nonetheless, being abundant, inexpensive, safe and renewable, it has the potential of replacing harmful reactants such as CO and phosgene for the production of valuable chemical materials [2,3]. From the viewpoints of "green chemistry" and "atom economy", it is attractive to utilize CO_2 for the generation of cyclic carbonates that are used as polar solvents, high-permittivity electrolyte components and fuel additives [4,5].

A large number of homogeneous and heterogeneous catalysts were developed for the generation of cyclic carbonates, such as metal salts [6], organic bases [7], ionic liquids (ILs) [8,9], metal complexes [10,11], metal oxides [12], supported catalysts [13], metal-organic frameworks [14], and carbon materials [15]. With the metal-based ones holding a prominent position [16], there is a compilation of elements that are considered "endangered" [17]. For the sake of sustainability, it is desirable to design efficient catalysts for the cycloaddition reactions based on metal-free resources that are cheap, non-toxic and readily available. Furthermore, the method has to be tunable, easy-to-handle, and solvent-free.

It is well known that thiamine (VB_1) is an essential nutrient

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[†]These authors contributed equally to this work.
*Corresponding author (email: sf_yin@hnu.edu.cn)

for animals. It contains a pyrimidine ring (with a primary amine) and a thiazolium salt (with a hydroxyl and quaternary ammonium salt) that are linked together by a methylene bridge. The VB_1 derivatives are cheap, readily available, and non-toxic. They were used as green catalysts for a number of reactions but not for cycloaddition [18–20]. In previous studies, it was found that the synergetic effects of acid sites and halide anions for ring opening of epoxide and the role of basic sites for CO_2 adsorption and activation are essential for the cycloaddition reactions [21–24]. It is hence envisaged that in a case such as thiamine hydrochloride (VB_1-Cl) with multifunctional groups (hydroxyl, quaternary ammonium salt, pyrimidine ring and primary amine), there should be efficient catalytic activity for cycloaddition of CO_2 toward epoxides. However, VB_1-Cl is stable only up to 100 °C at a pH of 3.5 [25]. It is hence meaningful to find a method to improve the thermal stability and activity of VB_1-Cl. As reported by Song *et al.* [26], the thermal stability and mechanical properties of polycaprolactone could be enhanced through composition with graphene oxide (GO). As reported, GO has plenty donors for hydrogen bonding (e.g., hydroxyl and carboxyl) and becomes negatively charged upon hydration [27,28]. In this regard, a VB_1/GO composite material could be stabilized by effects such as electrostatic interaction, hydrogen bonding and esterification reaction. The consequence is improvement of thermal stability and mechanical properties as well as promoted catalytic activity as a result of enhancement in nucleophilicity of anion.

In the present work, VB_1 derivative/GO aerogels were prepared by adding aqueous VB_1 derivatives to a GO suspension in ethanol at room temperature. The process is simple and efficient. For the first time, VB_1 derivatives and VB_1 derivative/GO aerogels are tested as heterogeneous catalyst for the synthesis of cyclic carbonates through CO_2 cycloaddition to epoxides under mild conditions without the use of co-catalyst and solvent. In addition, VB_1-Cl interaction with propylene oxide (PO) and CO_2 was investigated by ultraviolet-visible (UV-Vis) and ^{1}H nuclear magnetic resonance (^{1}H NMR) methods. A possible mechanism is proposed for the cycloaddition reaction over VB_1-Cl.

2 Experimental

2.1 Materials

All chemicals for the synthesis of materials and testing of catalytic activity were purchased from Sinopharm Chemical Reagent Co., Ltd. (China), and directly used without purification.

2.2 Catalysts preparation

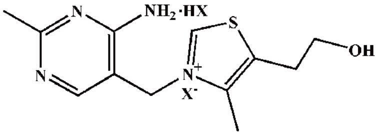

Figure 1 Structure of VB_1 derivative VB_1-X (X=Cl, Br, I).

The synthesis of VB_1-I (Figure 1) was by means of ion exchange. First, 5 mmol of VB_1-Cl was added to a flask with 30 mL ethanol, and the mixture was stirred for 10 min. Then 12 mmol of NaI was added and the mixture was stirred for 24 h. The as-obtained white powder was collected by centrifugation and washed 7 times with ethanol/glycerin (9:1, *v*/*v*), followed by washing with ethanol to remove residual glycerin. Finally, the purified powder named herein as VB_1-I was obtained after drying at 60 °C in a vacuum oven. The VB_1-Br was prepared likewise, employing LiBr instead of NaI.

GO was prepared by following the procedure published elsewhere [22]. The typical procedure for the preparation of VB_1-Cl/GO aerogel is as follows. First, the purified GO (0.2 g) was dispersed in 60 mL of ethanol/H_2O (2:1, *v*/*v*) and subject to ultrasonication for 2 h. After the addition of 4 mL of aqueous VB_1-Cl (1.6 mmol), the mixture was stirred for 24 h. With drying under vacuum using a rotary evaporator at 50 °C, the VB_1-Cl/GO was ready for use. The VB_1-Br/GO and VB_1-I/GO was prepared similarly, using VB_1-Br and VB_1-I instead of VB_1-Cl, respectively.

2.3 Catalyst characterization

The catalysts were characterized by UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS), ^{1}H NMR, scanning electron microscopy (SEM) and thermogravimetry (TG). The UV-Vis DRS spectra of samples were obtained over a UV-Vis spectrophotometer (Cary 100, Agilent, USA) using $BaSO_4$ as reference. The ^{1}H NMR spectra were recorded over a Bruker AV 400/500 M NMR spectrometer (Germany) using DSS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) as internal reference and (methyl sulfoxide)-d_6 (DMSO-d_6) as solvent. The morphology of the samples was observed by SEM (HITACHI S-4800 microscope, Japan). The TG curve was obtained by heating the sample from 50 to 550 °C at a constant rate of 10 °C/min under a N_2 flow on a NETZSCH-STA-449C equipment (Germany).

2.4 Procedure for cycloaddition reactions

The cycloaddition reaction was conducted in a stainless steel autoclave of 30 mL equipped with a magnetic bar. In a typical run, catalyst, biphenyl, and epoxide were added into the flask. Then, the reactor was pressurized with an appropriate amount of CO_2 and heated to a desired temperature in an oil bath. After a designated period, the reactor was cooled to 0 °C, followed by venting of the remaining CO_2. The cyclic carbonate yield and selectivity were qualified by gas chromatography (GC) analysis (7820A GC, Agilent, USA).

The used catalysts can be easily recovered by centrifugation. After being washed with PO for five times and dried at 60 °C for 12 h, the recovered catalyst was used again for the next run.

3 Results and discussion

3.1 Catalyst characterization

Enriched with oxygen-containing functional groups such as hydroxyl, carboxyl and epoxy, GO is a carbon material that can be dispersed uniformly in hydrophilic solvent [29]. Shown in Figure 2(a) are the photographic images of a GO dispersion (2 mg/mL) after ultrasonication for 1 h in ethanol and followed by static settling for 1 h. One can see well dispersion of GO in ethanol. When 1 mL of aqueous VB_1-Cl solution (5 mg/mL) was added to 1 mL of the GO (2 mg/mL) dispersion, a hydrogel as illustrated by having the tube inverted was quickly formed (Figure 2(b, c)). A gray precipitate was immediately observed upon the mixing of aqueous VB_1-Cl solution and aqueous GO dispersion. The formation of the gray precipitate is attributed to the electrostatic interaction between GO (negatively charged) and VB_1-Cl (with thiazole ring that is positively charged). The generation of the VB_1-Cl/GO aerogel could be a combined result of electrostatic interaction, hydrogen bonding and esterification reaction (Figure 3).

Displayed in Figure 4 are the SEM images of GO and VB_1-Cl/GO. The SEM images of GO show a sheet structure with wrinkles plausibly induced upon drying as a result of volume contraction. The cross section of VB_1-Cl/GO shows a close-packed layered structure. The amplified SEM image of VB_1-Cl/GO aerogel also shows a sheet structure with wrinkles.

The TG curves of GO, VB_1-Cl and VB_1-Cl/GO are displayed in Figure 5. One can see that VB_1-Cl is stable up to 158 °C, and pyrolysis starts above 158 °C and major pyrolysis occurs between 219 and 226 °C. However, the pyrolysis of VB_1-Cl/GO begins above 221 °C. The slight weight loss of VB_1-Cl/GO below 221 °C is ascribed to the loss of adsorbed species such as H_2O and CO_2. It is apparent that the thermal stability of VB_1-Cl is improved by forming the aerogel. It is an indication that there is interaction between GO and VB_1-Cl.

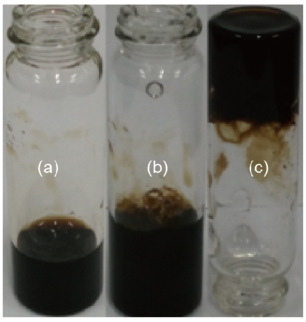

Figure 2 Photographs of (a) GO dispersion in EtOH (2 mg/mL GO); (b) VB_1-Cl/GO aerogel; (c) VB_1-Cl/GO aerogel inverted (color online).

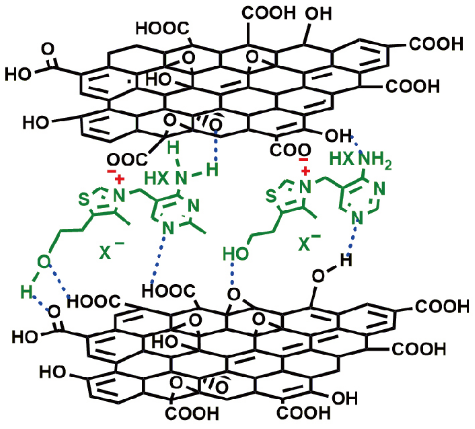

Figure 3 Generation of VB_1-X/GO (X=Cl, Br, I) (color online).

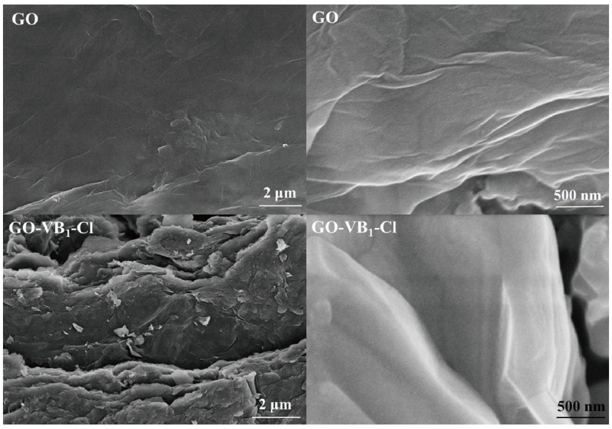

Figure 4 SEM images of GO and VB_1-Cl/GO.

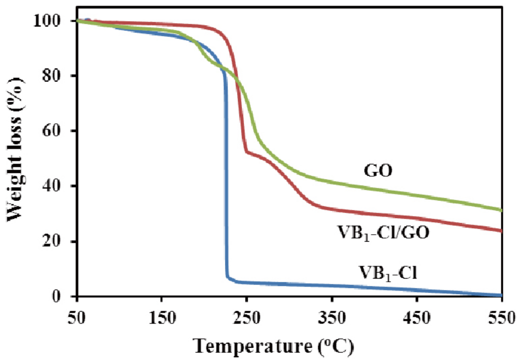

Figure 5 TG curve of GO, VB_1-Cl and VB_1-Cl/GO (color online).

3.2 Catalytic performance

3.2.1 Catalytic performance of catalysts

The cycloaddition of CO_2 towards PO was chosen as the model reaction to test the activity of VB_1-Cl, and the results are summarized in Table 1. One can see that over VB_1-Cl, the propylene carbonate (PC) yield is 24.7% at 100 °C for 6 h, and PC yield is up to 83.3% when the reaction is prolonged to 14 h (Table 1, entries 1 and 2). A higher temperature means more effective collision between the reactant molecules. The catalytic activity of VB_1-Cl is sensitive to reaction temperature: the PC yield increases rapidly with the rise of temperature and is up to 99.4% at 120 °C (Table 1, entries 2–4). However, the increase of reaction temperature results in the decomposition of VB_1-Cl. The VB_1-Cl changed from a white powder to a red and sticky substance when the reaction temperature was increased from 100 to 120 °C. It was observed that VB_1-Cl changed from white to yellow, and then to red when the experiment was conducted at 100 °C in the absence of CO_2. The above results are ascribed to the fact that PO is a weak base and there is partial decomposition of VB_1-Cl under basic conditions [25]. Also, the stability of VB_1-Cl is enhanced in the presence of CO_2, and there is interaction between PO and CO_2 under high pressure [30].

In order to eliminate the possibility of VB_1-Cl being a pre-catalyst, the experiment was conducted with VB_1-Cl and PO pretreated at 120 °C for 2 h without CO_2, and then in 2 MPa of CO_2 for 4 h; and 51.9% yield of PC was obtained over the 4-h period (Table 1, entry 7). Since following the normal procedure the yield of PC at 120 °C for 4 h was 77.6%, there is obvious decline of PC yield (55.4%) as a consequence of the pretreatment. The results indicate that VB_1-Cl does not act as a pre-catalyst, and the decline of activity of VB_1-Cl after pretreatment is due to the decomposition of VB_1-Cl as a result of PO presence.

Previously, we reported the synergetic effect of GO and Bu_4NBr on cycloaddition [15]. In this regard, the presence of GO should enhance the catalytic activity of VB_1-Cl (Table 1, entries 5, 8 and 9). In the case of VB_1-Cl/GO, the yield of PC is up to 85.3%, higher than that of VB_1-Cl and GO (Table 1, entries 5, 8 and 10). It may be ascribed to the electrostatic interaction between GO and VB_1-Cl that enhances the nucleophilicity and the leaving ability of anion. As shown in Figure 5, the thermal stability of VB_1-Cl was improved by forming aerogel with GO, similar to that reported by Song *et al.* [26] and He *et al.* [31]. As shown in Figure S1 (Supporting Information online), there is obvious decline of catalytic performance for VB_1-Cl while only slight decline for VB_1-Cl/GO in a test of five runs. The above results clearly demonstrate that VB_1-Cl/GO is superior to VB_1-Cl not only in catalytic performance but also in stability.

As reported, the nucleophilicity and leaving ability of anions have a remarkable influence on the activity of a catalyst in the cycloaddition reaction [32]. The catalytic efficiency of VB_1 derivatives with different anions can be arranged in the order of VB_1-I>VB_1-Br>VB_1-Cl (Table 2, entries 1–3). The

Table 1 The catalytic activity of VB_1-Cl for cycloaddition of CO_2 toward PO a)

Entry	*T* (°C)	*t* (h)	Yield (%)	Selectivity (%)
1	100	6	24.7	99.9
2	100	14	83.3	99.9
3	110	6	38.1	99.9
4	120	6	99.4	99.9
5	120	4	77.6	99.9
6 b)	120	4	55.4	99.3
7 c)	120	4	51.9	99.8
8 d)	120	4	1.3	99.9
9 e)	120	4	84.6	99.8
10 f)	120	4	85.3	99.8

a) Reaction conditions: 28.6 mmol PO with 2.2 mol% VB_1-Cl, initial CO_2 pressure 2 MPa; b) recovered VB_1-Cl after the second cycle; c) 28.6 mmol PO with 2.2 mol% VB_1-Cl was stirred at 120 °C for 2 h, then pressurized with CO_2 and stirred at 120 °C for 4 h; d) using 80 mg of GO as catalyst; e) using 80 mg of GO and 2.2 mol% VB_1-Cl as catalyst; f) using VB_1-Cl/GO (containing 80 mg of GO and 2.2 mol% VB_1-Cl) as catalyst.

Table 2 The catalytic activity of VB_1 derivatives for cycloaddition of CO_2 toward PO a)

Entry	Catalysts	VB_1 derivatives (mol%)	GO (mg)	Yield (%)	Selectivity (%)
1	VB_1-Cl	2.2	–	24.7	99.9
2	VB_1-Br	2.2	–	50.6	99.5
3	VB_1-I	2.2	–	86.8	99.3
4 b)	VB_1-I	1.1	–	41.5	99.4
5 b)	VB_1-I/GO	1.1	80	69.3	99.5
6 b)	VB_1-I/GO	1.1	160	93.2	99.5
7 b)	VB_1-I/GO	2.2	80	92.3	99.5

a) Reaction conditions: 28.6 mmol PO, 100 °C, initial CO_2 pressure 2 MPa, 6 h; b) reaction temperature 90 °C.

excellent performance of VB_1-I is attributed to the strong nucleophilicity and leaving ability of I^- [32]. To further improve the activity of VB_1-I, VB_1-I/GO aerogel was prepared and tested. The PC yield over VB_1-I/GO is significantly higher than that of VB_1-I. In addition, the catalytic activity of VB_1-I/GO increases with the increased amount of GO or VB_1-I, suggesting that both GO and VB_1-I are essential ingredients for excellent performance of VB_1-I/GO. In addition, VB_1-I/GO is efficient for the cycloaddition reaction even under mild conditions (Figure S2).

3.2.2 Comparison of different heterogeneous catalysts

The performance of various heterogeneous catalysts for cycloaddition of PO and CO_2 is depicted in Table 3. One can see that the immobilized ILs catalysts (F-PIL-Br, [BisAm-OH-i-PS]I_2, CS-[$BuPh_3P$]Br, GO-DMEDA-I) show excellent catalytic activity at 120 °C, and GO-DMEDA-I performs the best. However, there is obvious decline of catalytic activity with these immobilized ILs catalysts when the cycloaddition reactions were conducted at 90 °C. Compared to the VB_1-I/GO catalyst (TOF: 14.1 h^{-1}), the immobilized catalysts are inferior in catalytic activity at 90 °C. Furthermore, the preparation of VB_1-I/GO is environment-benign and not as complicated and time-consuming. Taking into account the cost and performance, it can be concluded that VB_1-I/GO is superior among the listed heterogeneous catalysts.

3.2.3 Catalytic activity towards different epoxides

To demonstrate the applicability of the process, we conducted the cycloaddition of CO_2 toward other epoxides, and the results are displayed in Table 4. Obviously, the VB_1-I/GO catalyst is applicable to a variety of terminal epoxides, showing high yield and selectivity. In the case of cyclohexene oxide, the catalytic activity is relatively low plausibly due to steric hindrance and electronic effect [36,37].

3.3 Mechanism investigation

It was reported that the synergetic effect of hydroxyl groups and halide anions is important for ring opening of epoxides [37–42]. The hydrogen bonding between PO and VB_1-Cl was studied by ^{1}H NMR. Figure 6 shows the ^{1}H NMR spectra of PO, VB_1-Cl and PO mixed with VB_1-Cl. One can see a clear upfield shift of the VB_1-Cl H signal, and a new signal at 5.3 ppm assignable to the OH proton of VB_1-Cl. In addition, there is an upfield shift of the PO H (CH_3) signal (from 1.2 to 1.1 ppm). The above results suggest hydrogen bonding between PO and VB_1-Cl as previously reported [37–42].

On the other hand, the basic sites is effective for CO_2 adsorption and activation [43,44]. The process of CO_2 activation and fixation was studied using a homogeneous system of VB_1-Cl in H_2O monitored by UV-Vis technique. Shown in Figure 7 are the UV-Vis DRS spectra of aqueous VB_1-Cl solution before and after bubbling with CO_2. Before CO_2 bubbling, the aqueous VB_1-Cl solution shows two typical signals: the strong one at 232 nm from pyrimidine ring and the weak one at 263 nm from thiazole ring. After CO_2 bubbling, there is a clear shift of the pyrimidine ring peak (from 232 to 237 nm). The red shift may be attributed to the adsorption and activation of CO_2 at the pyrimidine ring. Prasetyanto *et al.* [45]

Table 3 Catalytic performance of various heterogeneous catalysts for cycloaddition of CO_2 to PO

Catalyst	*T* (°C)	*t* (h)	Cat. (mol%)	Yield (%)	TOF [a] (h^{-1})
F-PIL-Br	120	9	1	94.0	10.4 [33]
[BisAm-OH-i-PS]I_2	130	2.5	0.75	99.3	53 [34]
[BisAm-OH-i-PS]I_2	90	2.5	0.75	21.0	11.2 [34]
CS-[$BuPh_3P$]Br	120	4	1.5	96.3	16.0 [35]
CS-[$BuPh_3P$]Br	90	4	1.5	63.0	10.5 [35]
GO-DMEDA-I	120	3	0.65	89.4	45.8 [22]
GO-DMEDA-I	90	6	0.65	51.6	13.2 [22]
SiO_2-$(CH_2)_3(EtOH)_3N^+I^-$	90	6	2	86.0	7.2 [9]
VB_1-I/GO	90	6	1.1	93.2	14.1 [b]

a) TOF=mole of synthesized propylene carbonate over per mole ILs in per hour; b) this work.

Table 4 Catalytic activity of VB_1-I/GO for CO_2 cycloaddition toward various epoxides [a]

Entry	Substrate	Yield (%)	Selectivity (%)
1	Ethylene oxide	95.4	99.2
2	Propylene oxide	93.2	99.5
3	Epichlorohydrin	96.5	97.9
4	1,2-Epoxybutane	76.1	98.6
5	Styrene oxide	59.2	98.9
6	Cyclohexene oxide	6.3	93.8

a) Reaction conditions: 0.3 g VB_1-I/GO, 28.6 mmol epoxide, temperature 90 °C, initial CO_2 pressure 2 MPa, time 6 h.

proposed that the combination of secondary and tertiary amine at a certain position resulted in a CO_2 activation rate higher than that of the single type amine species. It is suggested that with a primary amine in pyrimidine ring, VB_1-Cl activates CO_2 through synergetic interaction between the primary amine and the tertiary amine.

Based on the above results and those of previous reports [21,22], a possible mechanism is suggested for the catalytic reaction as depicted in Figure 8. First, there is hydrogen bonding of PO with the hydroxyl group of VB_1-Cl, while CO_2 is adsorbed and activated under the synergetic influence of primary amine and tertiary amine. Second, the nucleophilic Cl^- attacks the less hindered carbon atom of the activated ring to generate the oxygen anion that is stabilized through hydrogen bonding with the hydroxyl group of VB_1-Cl. Then, the oxygen anion reacts with an activated CO_2 molecule to give an alkylcarbonate anion. Finally, PC is formed through an intramolecular cyclic step, together with the release of catalyst.

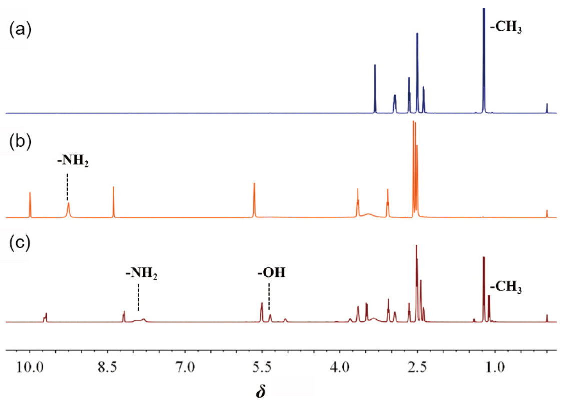

Figure 6 ^1H NMR spectra of (a) PO, (b) VB_1-Cl, (c) PO and VB_1-Cl.

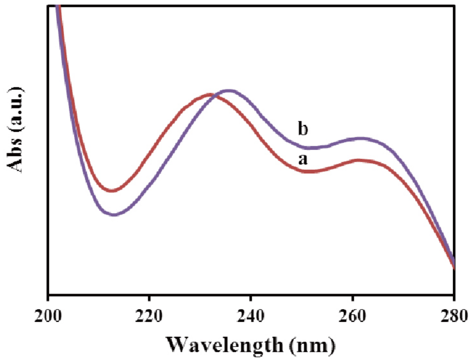

Figure 7 UV-Vis DRS spectra of aqueous VB_1-Cl solution (8 mg/L) (a) before and (b) after bubbling CO_2 for 0.5 h.

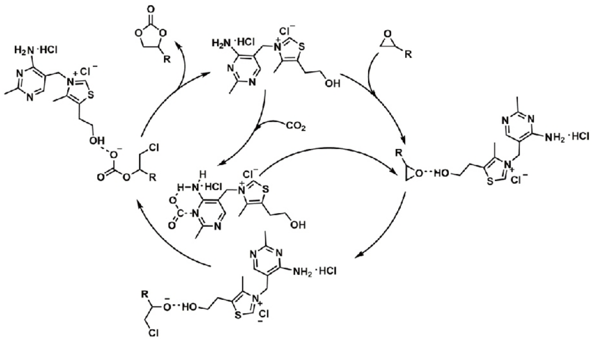

Figure 8 Possible reaction mechanism over VB_1-Cl.

4 Conclusions

Cheap, readily available, and non-toxic thiamine derivatives are used as heterogeneous catalyst for the synthesis of cyclic carbonates through CO_2 cycloaddition toward epoxides. As confirmed by UV-Vis and ^1H NMR studies, there is interaction between VB_1-Cl and substrates (CO_2 and PO). A possible mechanism for the cycloaddition reaction referring to the synergistic action of multi-functional groups (hydroxyl, halide anion and amines) is suggested. To achieve better catalytic activity and stability of thiamine derivatives, GO was employed for the generation of VB_1/GO aerogels by adding aqueous VB_1 derivatives to a GO ethanol suspension at room temperature. Among the prepared catalysts, VB_1-I/GO performs the best under mild conditions without the need of using any solvent or co-catalyst.

Conflict of interest The authors declare that they have no conflict of interest.

Supporting information The supporting information is available online at http://chem.scichina.com and http://link.springer.com/journal/11426. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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