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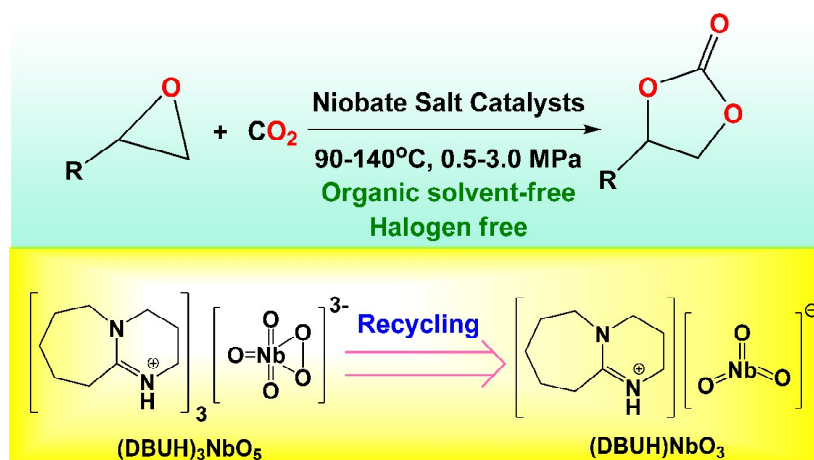
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## Graphic abstract



Peroxonibate salts of amidine and guanidine have been utilized as halogen-free catalyst for the synthesis of cyclic carbonates from epoxides and CO<sub>2</sub> under solvent-free and halide-free conditions.

## Niobate Salts of Organic Base Catalyzed Chemical Fixation of Carbon Dioxide with Epoxides to Form Cyclic Carbonates

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A series of peroxoniobate salts of amidine and guanidine were prepared successfully and utilized as halogen-free catalyst for the synthesis of cyclic carbonates from epoxides and CO<sub>2</sub> under solvent-free and halide-free conditions. The reaction could be performed with high activity and selectivity with assistance of the environmentally benign catalysts. CO<sub>2</sub> could be chemically activated through organic base dissociated from the parent catalyst during the reaction, while niobate anions played a crucial role in immobilizing catalytically active organic cations and thus improving the recyclability of the catalyst. The structural characterization of the catalysts indicated that peroxoniobate anions had undergone structural changes and were transformed into more stable niobate anions in the consecutive cycles. It was exhibited that the catalyst could be reused with high conversion and selectivity by a really straightforward process. Furthermore, this protocol was found to be applicable to a variety of epoxides producing the corresponding cyclic carbonates in high conversion and selectivity. The process herein represents a simple, ecologically friendly and efficient route for CO<sub>2</sub> chemical fixation into high value chemicals.

**Keywords:** Carbon Dioxide, Epoxides, Cyclic Carbonates, Peroxoniobates, Amidine, Guanidine

## Introduction

The potential problems of climate change caused by anthropogenic carbon dioxide emissions constitute major issues faced by scientists today.<sup>1</sup> Atmospheric CO<sub>2</sub> levels are at their highest recorded level since records began. Further increases are predicted to produce large and uncontrollable impacts on the world climate.<sup>2</sup> Meanwhile, in respect that carbon dioxide is an abundant, inexpensive, recyclable and nontoxic biorenewable resource, the use of carbon dioxide as a renewable and environmentally friendly source of carbon has attracted increasing attention.<sup>3</sup> Current research and technological strategies directed toward reducing the consequences of CO<sub>2</sub> emission can be separated into two categories, namely, capture and storage of CO<sub>2</sub> and applications of captured CO<sub>2</sub>.<sup>4</sup> A promising methodology in this area is the cycloaddition of epoxide and carbon dioxide to afford cyclic carbonates.<sup>5</sup> Owing to their high solubility, high boiling and flash points, low odor levels and evaporation rates, low toxicities and biodegradability, Cyclic carbonates have found extensive use as excellent aprotic polar solvents, electrolytes in secondary batteries, precursors for polycarbonates and other polymeric materials, and intermediates in the production of pharmaceuticals and fine chemicals like dialkyl carbonates, glycols, carbamates, pyrimidines, purines, etc.<sup>6</sup>

Numerous catalysts have been reported previously for the cycloaddition reaction. Metal complexes,<sup>7</sup> alkali metal halide,<sup>8</sup> bromine,<sup>9</sup> quaternary ammonium and phosphonium salts<sup>10</sup>, ionic liquids<sup>11</sup> and their supported catalysts<sup>12</sup> proved to be very efficient catalyst. However, most of these catalyst systems suffer from the use of halide, which normally causes lots of environmental pollution problems. Metal oxides,<sup>13</sup> smectites,<sup>14</sup> titanosilicates,<sup>15</sup> zeolites<sup>16</sup> and polyoxometalates<sup>17</sup> have been employed to achieve a greener approach for this transformation, nevertheless, these catalysts normally need high pressure of carbon dioxide, high reaction temperature or longer duration for the completion of reaction. Organic bases have also been reported to be efficient for the CO<sub>2</sub> cycloaddition reactions.<sup>18</sup> Although good conversion and selectivity have been achieved, there still remained huge challenges in separating the

catalyst after the reaction for reuse. Besides, some heterogeneous Lewis basic catalysts have been prepared for chemical fixation of carbon dioxide into cyclic carbonates,<sup>19</sup> whereas these catalytic systems carry the following disadvantages: 1) Organic solvent was normally added for the reaction; 2) The preparation of catalyst was complicate. Furthermore, the activity of supported catalyst is lower than that with the homogeneous counterpart in this reaction due to some diffusion resistance. From these points, it is highly promising to exploit a halogen-free reusable catalyst with excellent catalytic performance.

In the previous work, although some kinds of Lewis basic ionic liquids derived from tetramethylguanidine (TMG), 1,4-diazabicyclo[2.2.2]octane (DABCO), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5,7-triazabicyclo[4.4.0]-dec-5-ene (TBD) and hexamethylenetetramine (HMTA) have been reported to afford high catalytic activity for the cycloaddition reaction,<sup>20</sup> these ionic liquid catalysts consisted of halogen and suffered from the complicated separation procedure of ionic liquid from cyclic carbonates due to the miscibility between them.

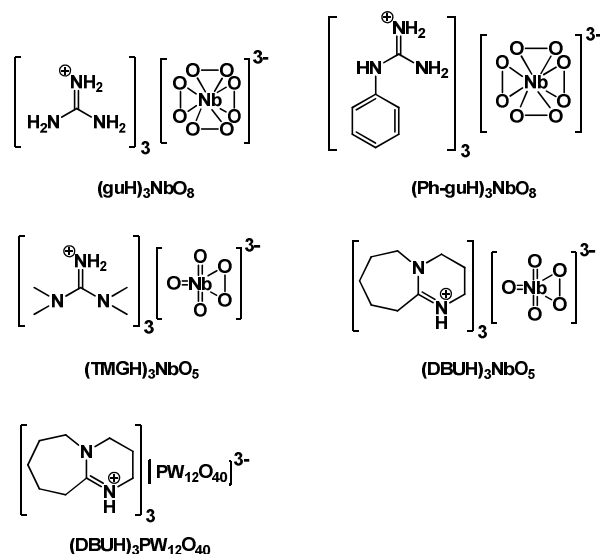
It has been known that niobium-containing materials are presently of great interest in heterogeneous catalysis where they are used as catalyst components or are added in small amounts to catalysts.<sup>21</sup> Notwithstanding several niobium-based catalysts have been used in the catalytic conversion of carbon dioxide and epoxides into carbonates under mild conditions,<sup>22</sup> these niobium compounds regarded as Lewis acid were involved in the recycling of catalysts. The addition of suitable nucleophiles, moreover, as co-catalysts is required in order to maintain high activity. Nevertheless, in the present work a series of peroxoniobate salts of organic base has been functioned as a halogen-free catalyst for the cycloaddition reaction of epoxides and CO<sub>2</sub>. Otherwise, this catalyst has the advantage of air stability and facile preparation from commercially available and relatively inexpensive starting materials. These Lewis basic niobium-based materials are firstly developed as halogen-free, single-component, easily preparing and recyclable catalysts for the cycloaddition reaction of CO<sub>2</sub> with epoxides under solvent-free condition. It is also worth noting that the present catalyst still demonstrated high conversion and selectivity even under

the low CO<sub>2</sub> pressure condition (0.5 MPa).

## Results and discussion

### Catalyst preparation and characterization

A series of peroxoniobate salts of amidine and guanidine has been prepared by ionic exchange method (Scheme 1). Firstly, peroxy niobic acid was prepared because it owned much better solubility in water than niobic acid. Freshly prepared niobic acid could be suspended in water and treated with H<sub>2</sub>O<sub>2</sub> to get a transparent pale yellow peroxy niobic acid solution. Then the neutralization of peroxy niobic acid with organic bases such as amidine and guanidine resulted in forming conveniently peroxoniobate salts in water. Because these peroxoniobates have the different solubilities in water, (Ph-guH)<sub>3</sub>NbO<sub>8</sub> and (guH)<sub>3</sub>NbO<sub>8</sub> were easily separated from water by adding anti-solvent, whereas (DBUH)<sub>3</sub>NbO<sub>5</sub> and (TMGH)<sub>3</sub>NbO<sub>5</sub> were gained by removing water under vacuum. All peroxoniobate salts have been characterized by FT-IR, TGA, NMR, HRMS, elemental analysis and ICP-AES analysis. Numbers of peroxide bonds were determined by potential difference titration of Ce<sup>3+</sup>/Ce<sup>4+</sup>.<sup>23</sup> For the sake of comparison, (DBUH)<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> was also prepared according to the convenient procedure (Figure S5). It was worth noting that the results of HRMS showed that peroxoniobate anions could be decomposed through loss of labile peroxy bonds during HRMS experiments (Figure S1-S4).



**Scheme 1.** Chemical structures of different catalysts used in this work and their designations.

### Catalytic performance

The synthesis of cyclic carbonate from CO<sub>2</sub> and epoxide was carried out in the presence of a series of peroxoniobate salts or phosphotungstate (Scheme 1) under the identical reaction conditions. Propylene oxide (PO) was chosen as a substrate in the model reaction. As a result, the organic cations paired with peroxoniobate anions have strong impacts on the catalytic activities, and the corresponding catalytic activities were summarized in Table 1. The results revealed that catalytic efficiency decreased in the order of (DBUH)<sub>3</sub>NbO<sub>5</sub> > (TMGH)<sub>3</sub>NbO<sub>5</sub> > (Ph-guH)<sub>3</sub>NbO<sub>8</sub> > (guH)<sub>3</sub>NbO<sub>8</sub> (Table 1, entries 1-4). It demonstrated that the conjugate basicity of the present cations played a crucial role in affecting the catalytic performance. For instance, the strength of the conjugate base DBU and TMG was much stronger than that of Ph-gu and gu, and thus their cationic salts afforded much better activity than that of Ph-gu and gu, which was in accordance with the previous research about the role of base catalyst in the cyclic addition reaction.<sup>18b,d,24</sup> Moreover, (Ph-guH)<sub>3</sub>NbO<sub>8</sub> showed higher catalytic activity than that of (guH)<sub>3</sub>NbO<sub>8</sub> possibly because the former was more hydrophobic, which resulted in more easy accessibility of hydrophobic substrate molecules.<sup>11c,d</sup> It should be noting that phosphotungstate such as (DBUH)<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> afforded poor activity, showing the influence of anion on the reaction (Table 1, entry 5). This can be explained that the superacid H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> neutralized the basicity of DBU even under reaction conditions, resulting in the decrease of activity. In contrast, the protonation of DBU by weak peroxy niobic acid was not strong, which can remain the free conjugate base DBU molecules during the reaction.<sup>25</sup> In addition, (DBUH)<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> catalyst exhibited poor selectivity to cyclic carbonate, yielding main side-product 1,2-propylene glycol due to acid hydrolysis of PO by the acid catalyst. Interestingly, single DBU exhibits a comparable conversion and selectivity to (DBUH)<sub>3</sub>NbO<sub>5</sub> (Table 1, entry 6 and 4), which might imply the similar approach to activate carbon dioxide. However, considering both the activity and the recyclability

of the catalyst,  $(\text{DBUH})_3\text{NbO}_5$  has been chosen as the catalyst for further investigations.

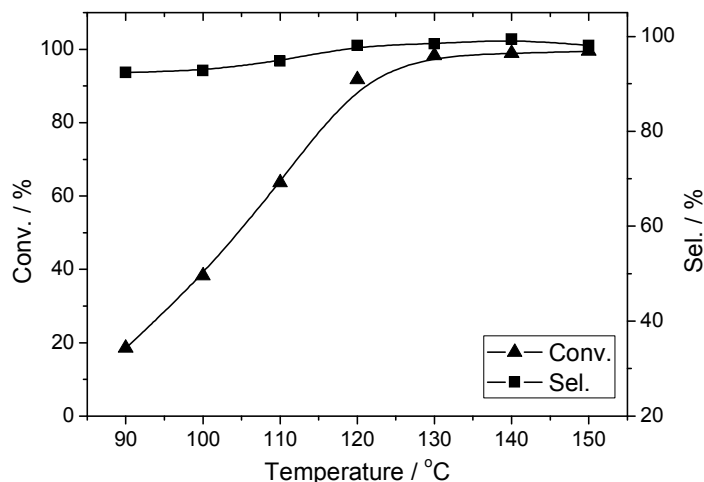
**Table 1.** Conversions and selectivities of cycloaddition reactions over different catalysts<sup>a</sup>

Entry	Catalyst	pK <sub>a</sub> of cations <sup>c</sup>	Conv. (%)	Sel. (%)
1	$(\text{guH})_3\text{NbO}_8$	(13.5)	50.6	86.5
2	$(\text{Ph-guH})_3\text{NbO}_8$	-	77.7	90.0
3	$(\text{TMGH})_3\text{NbO}_5$	23.3	91.7	94.0
4	$(\text{DBUH})_3\text{NbO}_5$	24.3	98.3	98.4
5	$(\text{DBUH})_3\text{PW}_{12}\text{O}_{40}$	24.3	40.0	82.6
6 <sup>b</sup>	DBU		94.2	97.5

<sup>a</sup> Reaction condition: PO 0.7 ml (10 mmol), catalyst 0.3 mmol, temperature 130°C, reaction pressure 3.0 MPa, time 5 h. <sup>b</sup> 0.9 mmol DBU was added as a catalyst. <sup>c</sup> The pK<sub>a</sub> value of the cations in acetonitrile or water (brackets).<sup>18d,26</sup>

Subsequently, the effects of several parameters on the catalytic activity of  $(\text{DBUH})_3\text{NbO}_5$  were investigated under identical reaction conditions. As depicted in Figure 1, the temperature had a prominently positive effect on the reaction when it varied from 90 to 130°C. Both conversion and selectivity of reaction were increased with temperature and leveled off around 130°C. When the temperature was at higher range, the catalytic activity and selectivity can be still maintained at high level. Nevertheless, higher temperature might bring about the decomposition of catalyst. Consequently, 130°C was the appropriate temperature for propylene carbonate (PC) synthesis.

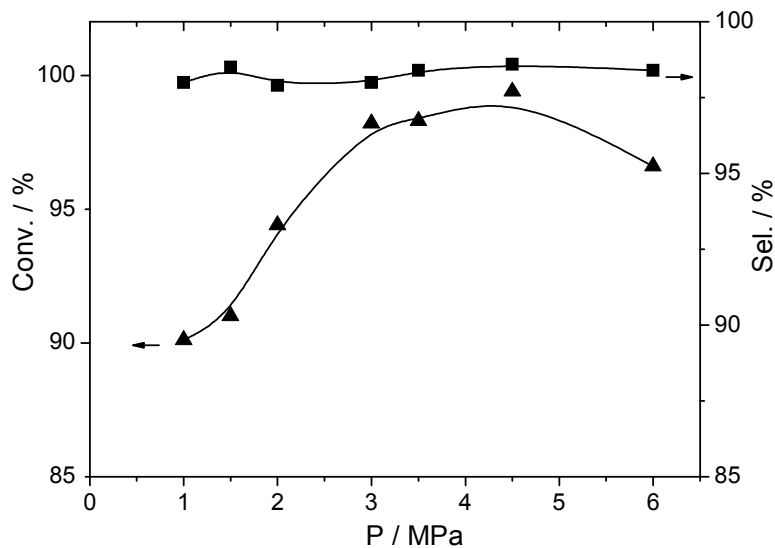




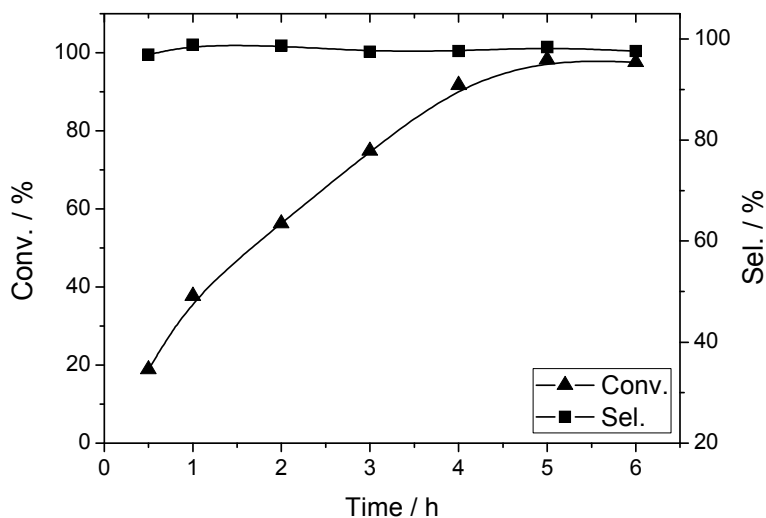
**Figure 1.** Effect of the reaction temperature on the cycloaddition reaction of PO and carbon dioxide. Reaction conditions: PO 0.7 ml (10 mmol),  $(\text{DBUH})_3\text{NbO}_5$  0.3 mmol, 3.0 MPa, 5 h.

The effect of reaction pressure on the cycloaddition reaction was investigated afterwards. As illustrated in Figure 2, the conversion increased slowly with the carbon dioxide pressure under the pressure range from 1.0 to 3.0 MPa, and then reached up to about 99% over 3.0 MPa. At higher pressure range, the reaction pressure had no obvious effect on selectivity, but lowered slightly conversion. Within a certain reaction time, the decrease in the conversion of propylene epoxide might be caused by the lowered PO concentration in the vicinity of the catalyst with the increasing pressure of  $\text{CO}_2$ , which has also been observed in our or other group's previous reports.<sup>12d,e,18a,d</sup>

The influence of reaction time on the PC synthesis was given in Figure 3. The time dependence of the cycloaddition reaction was performed under 130°C, 3.0 MPa. The reaction time had a remarkable influence on the reaction; the conversion of PO increased sharply within the first 4 h and then remained almost invariant with high selectivity, which showed a reaction time of 5 h is needed for complete PO conversion with the assistance of  $(\text{DBUH})_3\text{NbO}_5$ .



**Figure 2.** Dependence of PO conversion and PC selectivity on CO<sub>2</sub> pressure. Reaction conditions: PO 0.7 ml (10 mmol), (DBUH)<sub>3</sub>NbO<sub>5</sub> 0.3 mmol, 130°C, 5 h.



**Figure 3.** Influence of reaction time on PO conversion and PC selectivity. Reaction conditions: PO 0.7 ml (10 mmol), (DBUH)<sub>3</sub>NbO<sub>5</sub> 0.3 mmol, 130°C, 3 MPa.

Sequentially, the kinetic studies of the cyclic addition of CO<sub>2</sub> and PO were investigated. The dependence of the reaction rate on temperature was depicted in Figure S8, where the reaction rate constants under different reaction temperature were determined from the experimental data assuming pseudo-first order reaction kinetics. Thus the activation energy for the process was determined using the Arrhenius

equation based on the calculated rate constants at different temperatures (Figure S9). The linearity of the Arrhenius plots was examined to determine the activation energy, which was  $E_a = 64.0$  kJ/mol. The activation energy under the present conditions was similar to that reported for the cycloaddition reaction using the different catalysts, in which  $E_a$  was in the range of about 35-70 kJ/mol.<sup>27</sup>





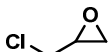
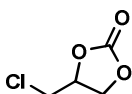
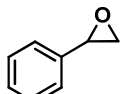
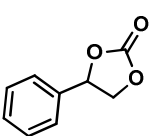
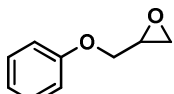
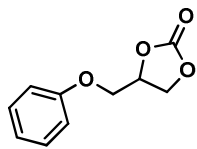
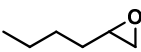
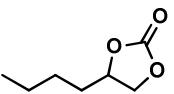

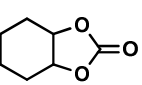
### Substrate scope and recyclability of the catalyst

Firstly, a series of epoxides was tested to synthesize the corresponding cyclic carbonates under optimized condition in order to examine the scope of the substrates over the present catalyst and the results were summarized in Table 2. Both terminal and internal epoxides could be transformed to the corresponding cyclic carbonates in high conversion and selectivity. It could also be found that PO and epichlorohydrin were the most active among the epoxides surveyed, and good results were achieved in a reaction time of five hours (Table 2, entry 1 and 3). Because of the higher steric hindrance of 1,2-epoxyhexane and 1,2-epoxycyclohexane compared to the other epoxides, longer reaction times had to be needed to obtain higher epoxide conversion (Table 2, entries 6 and 7). It should be worth noting that even if CO<sub>2</sub> pressure was lowered to 0.5 MPa, the present catalyst still offered good conversion and selectivity after 5 h reaction time (Table 2, entry 2).

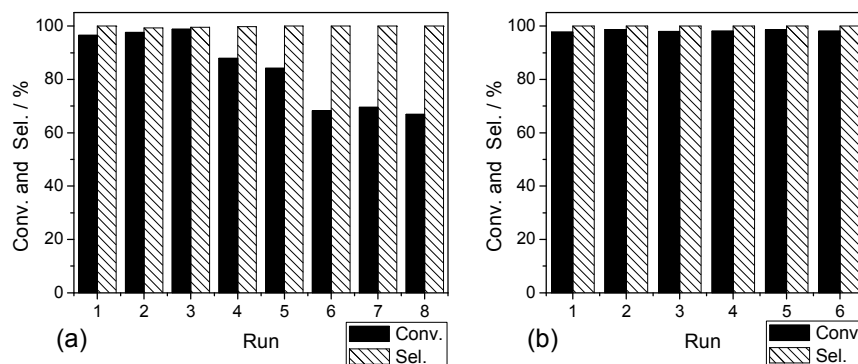
In the next step, the recyclability of catalysts was examined under the optimal conditions (Figure 4). After reaction, ethyl ether was added to the reaction mixture. The catalyst was recovered by simple centrifugation, followed by rinsing with ethyl ether and vacuum drying. Then the recovered catalyst can be reused for the next recycle. The (DBUH)<sub>3</sub>NbO<sub>5</sub> catalyst was recycled and the results were shown in Figure 4a. It indicated that the conversion and selectivity were almost constant in the initial three recycles. However, during the fourth and fifth run, the conversion of PO decreased slightly, which might be caused by the structural changes of catalyst. What should be noticed is that there was not any obvious more loss of activity from the sixth to the eight catalytic recycles (Figure 4a). These results strongly suggested that the present catalyst peroxoniobate salts could act actually as a catalyst precursor and

might transform into a more stable structure in the consecutive recycles. To confirm the assumption above, the reused catalyst has been characterized detailedly and the discussion was given in following section.

**Table 2.** Different epoxides as substrates for the cycloaddition reaction with carbon dioxide catalyzed by  $(\text{DBUH})_3\text{NbO}_5$ <sup>a</sup>

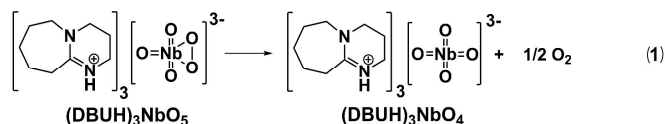
Entry	Substrate	Product	t (h)	Conv. (%)	Sel. (%) <sup>b</sup>	Yield (%) <sup>c</sup>
1			5	98.1	98.4	91.8
2 <sup>d</sup>			5	90.0	98.7	-
3			5	99.7	98.6	90.2
4			5	94.6	98.4	86.7
5			5	94.9	97.0	87.4
6			10	97.0	96.3	89.2
7			50	98.9	74.0	63.2

<sup>a</sup> Reaction condition: epoxide 10 mmol, catalyst 0.3 mmol, temperature 130°C, reaction pressure 3.0 MPa, time 5 h. <sup>b</sup> Corresponding diols were produced as major byproducts. <sup>c</sup> Isolated yield. <sup>d</sup> The reaction was performed under the constant CO<sub>2</sub> pressure (0.5 MPa).



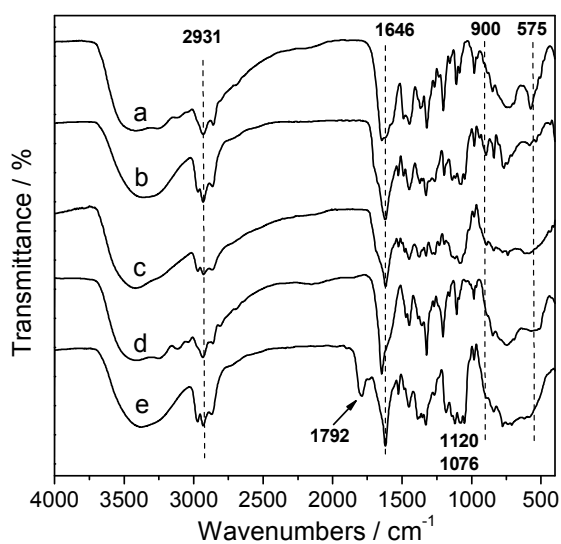
**Figure 4.** Recyclability of the catalyst (a)  $(\text{DBUH})_3\text{NbO}_5$ ; (b)  $(\text{DBUH})\text{NbO}_3$ . Reaction conditions:  $(\text{DBUH})_3\text{NbO}_5$  0.3 mmol or  $(\text{DBUH})\text{NbO}_3$  0.9 mmol, PO 0.7 ml (10 mmol), 130°C, 3 MPa, 5h.

After the reused catalyst had been washed thoroughly with ethyl ether and dried under vacuum, it was subjected to element analysis (C, H, N), ICP-AES analysis (Nb), FT-IR spectra and TGA. As shown in Table 3, it could be observed that the mass percentage of carbon, hydrogen and nitrogen of the fresh catalyst and the catalyst after the first run were almost the same, and ICP-AES analysis proved that the mass percentage of Nb remained virtually unchanged after the first run (Table 3, entry 2), which was also proved by the results of TGA analysis (Figure S10, a and b). The only difference was that the peroxy group was absent after the first run, as observed by FT-IR (Figure 5a and 5b). The IR bands of the peroxide could be assigned to the typical vibrational modes of the antisymmetric Nb-O stretching and the coordinated side-bonded peroxo ligands, the O-O stretching. The band at 575  $\text{cm}^{-1}$  in the IR spectra (Figure 5a) was attributed to the  $\nu_{\text{as}}(\text{Nb-O-O})$  band.<sup>28</sup> This typical absorption peak of catalyst hardly observed after the first run (Figure 5b), which indicated that peroxy bonds were decomposed. The absence of peroxide bond for the catalyst after the first run was also confirmed by a standard titration of  $\text{Ce}^{3+}/\text{Ce}^{4+}$ . Consequently, regarding elemental analysis, TGA, FT-IR and titration,  $(\text{DBUH})_3\text{NbO}_5$  has been transformed into  $(\text{DBUH})_3\text{NbO}_4$  after the first run (eq 1), which was also proved by HRMS characterization (Experimental section). Actually, the decomposition of  $\text{Nb}(\text{O}_2)$  into  $\text{Nb}=\text{O}$  species has also been reported previously.<sup>29</sup>



**Table 3.** Elemental analysis (C, H and N) and ICP-AES measurement (Nb) for the fresh  $(\text{DBUH})_3\text{NbO}_5$  and that reused one and eight times

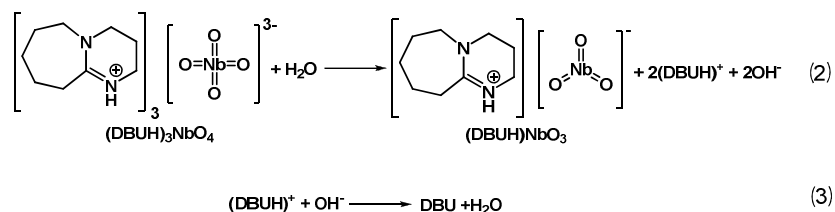
Entry	Catalysts	Element content (%)				Formula from elemental analysis
		C	H	N	Nb	
1	fresh	51.00	8.05	13.08	14.97	$(\text{DBUH})_3\text{NbO}_5$
2	after the first run	51.26	8.17	12.55	15.66	$(\text{DBUH})_3\text{NbO}_4$
3	after the eight run	37.19	5.46	7.05	32.57	$(\text{DBUH})\text{NbO}_3$



**Figure 5.** The FT-IR spectra of (a) fresh catalyst  $(\text{DBUH})_3\text{NbO}_5$ ; (b) the catalyst after the first run; (c) the catalyst after the eighth run; (d) fresh catalyst  $(\text{DBUH})\text{NbO}_3$ ; (e) the catalyst after the six run.

It should be remarkable that the mass percentage of elements between the fresh catalyst and the catalyst after the eighth run showed a great difference. The content of carbon, hydrogen and nitrogen decreased, whereas the content of niobium increased

after the reaction. The deficient amount of nitrogen of the reused catalyst could be attributed to the partial loss of organic cations of the catalyst (Table 3, entry 3). The FT-IR characterization revealed that peroxy bonds in the reused catalyst was decomposed but the major structures did not obviously change, as compared with the fresh catalyst, because the peak at  $2931\text{ cm}^{-1}$  which could be attributed to  $\text{N}^+\text{-H}$  vibration and the peak at  $1646\text{ cm}^{-1}$  which could be attributed to  $\text{C}=\text{N}^+$  vibration remained unchanged on the spectrum of the reused catalyst (Figure 5c). The peak at about  $900\text{ cm}^{-1}$  corresponding to  $\text{Nb}=\text{O}$  vibration<sup>28d</sup> also remained unchanged on the FT-IR spectrum. TGA curves of the fresh and the reused catalyst revealed that the fresh catalyst lost about 80% of its weight, while the catalyst after the eighth run lost about 56.4% of its weight (Figure S10, a and c), all of which matched perfectly with the results of elemental analysis (Table 2, entry 1 and 3). The above analysis clearly demonstrated that the  $(\text{DBUH})_3\text{NbO}_4$  was transformed into more stable  $(\text{DBUH})\text{NbO}_3$  after the sixth run (eqs 2 and 3).<sup>28d,30</sup>



PO conversion decreased in the initial five recycles, but it was not obviously changed again after the sixth run (Figure 4a), implying that a more catalyst might be formed as well. To identify the stable catalytic species, the fresh  $(\text{DBUH})\text{NbO}_3$  catalyst has been prepared by reacting ammonium tetraperoxoniobate  $[(\text{NH}_4)_3\text{NbO}_8]$  with the bicarbonate salt of DBU  $[(\text{DBUH})\text{HCO}_3]$ , which has been characterized by FT-IR, TGA, NMR, HRMS, elemental analysis and ICP-AES analysis (Figure S7), and then it was employed for the consecutive catalytic recycles (Figure 4b). It can be seen that the  $(\text{DBUH})\text{NbO}_3$  catalyst indeed showed exceptional recyclability. Moreover, because  $(\text{DBUH})_3\text{NbO}_4$  lost two DBU molecules and then was converted into  $(\text{DBUH})\text{NbO}_3$ , more  $(\text{DBUH})\text{NbO}_3$  was needed to attain the same activity as that of  $(\text{DBUH})_3\text{NbO}_4$  (Figure 4b). It was observed that the recovery rate of the catalyst

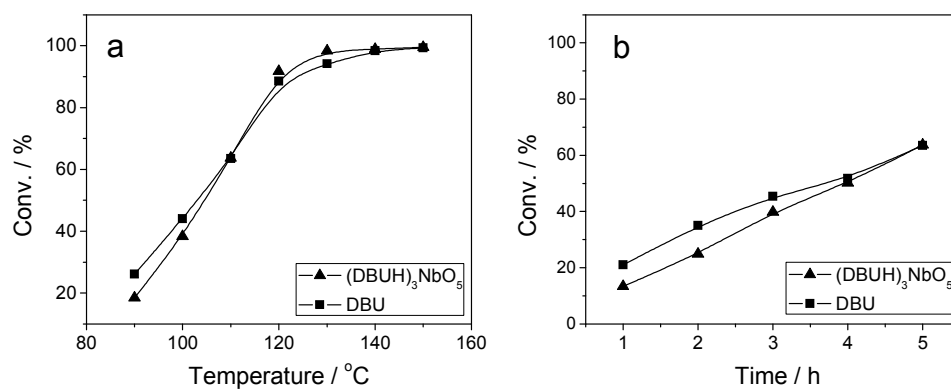
(DBUH)NbO<sub>3</sub> was over 95% in each recycle. Additionally, the fresh catalyst (DBUH)NbO<sub>3</sub> and the catalyst after the sixth run were also studied by using FT-IR spectroscopy (Figure 5d and 5e). The unchanged N<sup>+</sup>-H band near at 2931 cm<sup>-1</sup>, C=N<sup>+</sup> band at 1646 cm<sup>-1</sup> and Nb=O band near 900 cm<sup>-1</sup> indicated the major structure of (DBUH)NbO<sub>3</sub> did not change obviously in the catalytic recycles. The new bands at 1792 cm<sup>-1</sup> were assigned to the C=O stretching and the band at 1120 cm<sup>-1</sup> and 1076 cm<sup>-1</sup> were assigned to the C-O stretching of the residual propylene carbonate.<sup>31</sup> The TGA curves of the fresh (DBUH)NbO<sub>3</sub> and the reused catalyst were shown as Figure S11. The similar weight loss indicated the structural stability of the (DBUH)NbO<sub>3</sub> catalyst. Regarding the characterization of ICP-AES analysis and FT-IR spectra, it was suggested strongly that (DBUH)<sub>3</sub>NbO<sub>5</sub> has underwent a structural transformation and was transformed finally into a more robust catalyst in the consecutive recycles.

### Reaction mechanism

The discussion above, especially through elemental analysis for the fresh and the reused catalyst, indicated that the cation of catalyst might be the active site, considering that conjugate base could be formed in-situ from the dissociation of organic cation under reaction condition. Lewis basicity and nucleophilicity of organic base like DBU have also been reported to be efficient for the CO<sub>2</sub> cycloaddition reactions.<sup>18</sup> To prove that, both (DBUH)<sub>3</sub>NbO<sub>5</sub> and single DBU have been employed as catalysts for the comparison of the conversion of PO under the same reaction conditions. As shown in Figure 6, the loading amount of DBU for two catalysts was kept same. Figure 6a showed typical conversion/temperature profiles obtained for (DBUH)<sub>3</sub>NbO<sub>5</sub> vs DBU, and the two curve were really analogous, although (DBUH)<sub>3</sub>NbO<sub>5</sub> afforded a little lower catalytic activity than DBU at low temperature, which was attributed to homogeneous DBU and essentially heterogeneous (DBUH)<sub>3</sub>NbO<sub>5</sub> at low temperature. Nevertheless, (DBUH)<sub>3</sub>NbO<sub>5</sub> afforded almost the same catalytic activity as that of DBU at temperature range of 120-140°C. On the other hand, dependence of PO conversion obtained for (DBUH)<sub>3</sub>NbO<sub>5</sub> vs DBU on reaction time was illustrated in Figure 6b. This comparison revealed that



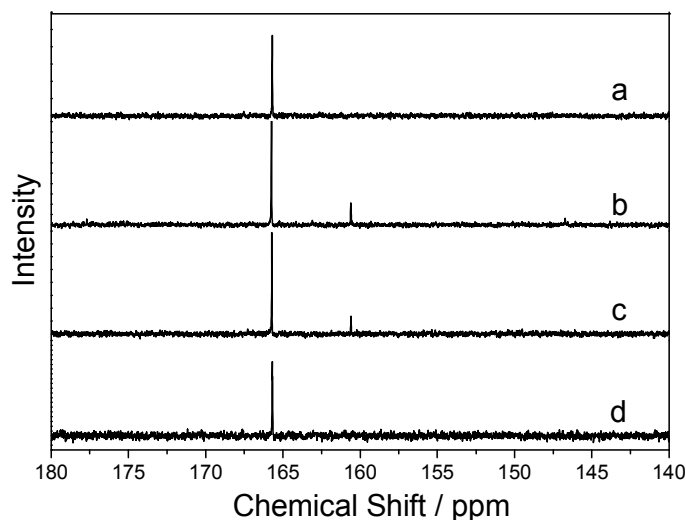
(DBUH)<sub>3</sub>NbO<sub>5</sub> exhibited a little lower reaction rate than DBU at the beginning of reaction as a result of heterogeneity of (DBUH)<sub>3</sub>NbO<sub>5</sub>, whereas, (DBUH)<sub>3</sub>NbO<sub>5</sub> and DBU showed very similar activities after the reaction for 5 h. Based on the above discussions, the catalytic performance of (DBUH)<sub>3</sub>NbO<sub>5</sub> might be chiefly attributed to DBU dissociated from the parent catalyst.



**Figure 6.** Comparison of the conversion of PO over DBU and (DBUH)<sub>3</sub>NbO<sub>5</sub> catalysts. (a) Dependence of PO conversion on temperature. Reaction conditions: PO 0.7 ml (10 mmol), (DBUH)<sub>3</sub>NbO<sub>5</sub> 0.3 mmol or DBU 0.9 mmol, 3 MPa, 5h; (b) Dependence of PO conversion on reaction time. Reaction conditions: PO 0.7 ml (10 mmol), (DBUH)<sub>3</sub>NbO<sub>5</sub> 0.3 mmol or DBU 0.9 mmol, 110°C, 3 MPa.

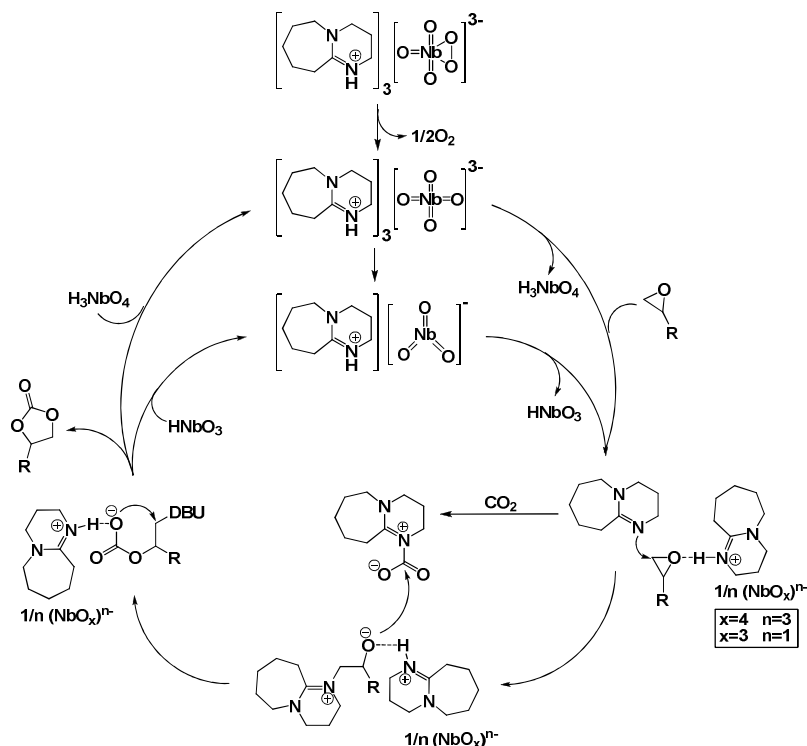
In the past decades, metal oxides were reported to be efficient for the cycloaddition reactions at relatively higher temperature because they possessed both acid and base surface sites.<sup>13</sup> Recently, monomeric tungstate which possessed basic property due to the high charge density of oxygen were found to have great ability to CO<sub>2</sub> chemical activation.<sup>32</sup> Similarly, there could also be Lewis acid site and Lewis basic sites in the niobate owing to different electronegativity of niobium and oxygen. To further elucidate the possible role of niobate anions in the cyclic addition reaction, the specific interaction of (DBUH)<sub>3</sub>NbO<sub>5</sub> with CO<sub>2</sub> was investigated by <sup>13</sup>C NMR technique. As shown in Figure 7, the signal at  $\delta = 165.7$  ppm in the <sup>13</sup>C NMR spectrum of (DBUH)<sub>3</sub>NbO<sub>5</sub> could be attributed to the carbon of C=N<sup>+</sup> (Figure 7a). When the CDCl<sub>3</sub> solution of (DBUH)<sub>3</sub>NbO<sub>5</sub> was exposed to CO<sub>2</sub> (0.1 MPa), a new

$^{13}\text{C}$  signal appeared at  $\delta = 160.8$  ppm (Figure 8b), thus suggesting the presence of a new carbonyl. DBU and other organic bases have been reported to react with  $\text{CO}_2$  to form a new zwitterionic adduct.<sup>33</sup> However, the DBU- $\text{CO}_2$  zwitterionic adduct would be transformed into the bicarbonate  $[\text{DBUH}][\text{HCO}_3]$  in the presence of water, then the  $^{13}\text{C}$  NMR data for the compound would show two signals at 160.7 and 166.4 ppm corresponding to a bicarbonate and an amidinium carbon, respectively.<sup>33a,b</sup> Therefore, the new  $^{13}\text{C}$  signal at  $\delta = 160.8$  ppm (Figure 7b) could arise from  $[\text{DBUH}][\text{HCO}_3]$  bicarbonate. It was indicated that DBU dissociated from  $(\text{DBUH})_3\text{NbO}_5$  might be transformed into DBU- $\text{CO}_2$  adduct with exposition to carbon dioxide, then bicarbonate would generate because of the little water from the  $(\text{DBUH})_3\text{NbO}_5$ . The same product could be produced by feeding  $\text{CO}_2$  to the  $\text{CDCl}_3$  solution of  $(\text{DBUH})_3\text{NbO}_4$  which can be prepared by vacuum drying  $(\text{DBUH})_3\text{NbO}_5$  at  $80^\circ\text{C}$  for long time (Figure 7c). Notably, the catalyst after reaction washed with ethyl ether and dried in vacuum did not have signal at about  $\delta = 160$  ppm in the  $^{13}\text{C}$  NMR spectrum, which demonstrated that the catalyst might easily be changed back to  $(\text{DBUH})_3\text{NbO}_4$  after post-treatment (Figure 7d). In addition, not being similar to tungstate- $\text{CO}_2$  adduct,<sup>32</sup> niobate- $\text{CO}_2$  adduct was not detected by  $^{13}\text{C}$  NMR spectrum, which suggested that niobate- $\text{CO}_2$  adduct might be not stable or more difficult to generate.



**Figure 7.**  $^{13}\text{C}$  NMR spectra of (a)  $(\text{DBUH})_3\text{NbO}_5$  in  $\text{CDCl}_3$ ; (b)  $(\text{DBUH})_3\text{NbO}_5$  with  $\text{CO}_2$  at atmospheric pressure (0.1 MPa) in  $\text{CDCl}_3$ ; (c)  $(\text{DBUH})_3\text{NbO}_4$  with  $\text{CO}_2$  at

atmospheric pressure (0.1 MPa) in  $\text{CDCl}_3$ ; (d) the reused  $(\text{DBUH})_3\text{NbO}_5$ , washed by ethyl ether and dried under vacuum.



**Scheme 2.** The proposed mechanism for  $(\text{DBUH})_n(\text{NbO}_x)^{n-}$ -catalyzed cycloaddition reaction.

Based on the results above and the previous reports, a probable catalytic cycle was proposed for the cycloaddition of  $\text{CO}_2$  to epoxides using  $(\text{DBUH})_3\text{NbO}_5$  as a catalyst as described in Scheme 2. Firstly, the proton was coordinated with the oxygen of the epoxide through a hydrogen bond, resulting in activation of an epoxide,<sup>10,12,18-20</sup> and simultaneously, the nucleophilic attack of DBU dissociated from  $(\text{DBUH})_3\text{NbO}_4$  on the less sterically hindered  $\beta$ -carbon atom of the epoxide furnished the ring-opened intermediate.<sup>18b-d,19b</sup> In the meantime,  $\text{CO}_2$  was activated by DBU due to  $\text{DBU-CO}_2$  adduct as what had been well described before.<sup>33</sup> Thereafter, the ring-opened structure of epoxide made a nucleophilic attack on the  $\text{DBU-CO}_2$  adduct to produce a new alkyl carbonate compound. Finally, the cyclic carbonate was formed by subsequent

intramolecular ring-closure and the catalyst was regenerated by DBU and niobate species. It should be noticed that only the fresh catalyst could own peroxyoniobates according to the present results. However, after the first run, the peroxyoniobates was actually transformed into  $\text{NbO}_4^{3-}$  due to the decomposition of labile peroxy bonds, but the activity can retain because both of two salts consisted of three  $\text{DBUH}^+$  cations (Table 3, entry 1 and 2). Moreover, after the fifth run (Figure 4a), the  $(\text{DBUH})_3\text{NbO}_4$  could lose two  $\text{DBUH}^+$  cation and be transformed into more stable  $(\text{DBUH})\text{NbO}_3$ , which can be recycled sequentially at least for six times (Figure 4a and 4b). Although the peroxyoniobate anions has changed into the different niobate anions in the consecutive recycles, all of them played a very important role in immobilizing/stabilizing  $\text{DBUH}^+$  cation most likely through electrostatic interaction, resulting in the excellent recyclability of the niobate catalyst.

## Conclusions

In summary, a series of Lewis basic peroxyoniobate was easily synthesized and developed for the synthesis of cyclic carbonates from epoxides and  $\text{CO}_2$  under solvent-free and halide-free conditions. High epoxide conversion and excellent cyclocarbonate selectivity could be achieved under the optimal reaction conditions. Furthermore, the catalyst could be easily reused with high activity and selectivity. Characterization indicated that although peroxyoniobate underwent the structural transformation in the catalytic recycles, they played a very crucial role in immobilizing catalytically active organic cation. Furthermore,  $\text{CO}_2$  could be chemically activated under mild condition and the catalytic performance might be chiefly attributed to DBU dissociated from the parent catalyst. The results of this work provided a new kind of catalyst with the advantages of homogeneous catalyst and heterogeneous catalyst, which provides a new approach for the design of efficient catalyst used for transformation of carbon dioxide.

## Experimental

### Materials

All chemicals were obtained from SCRC (Sinopharm Chemical Reagent Co., Ltd, Shanghai). All solvents (analytical grade) were dried by using the standard methods.

### Characterizations

The FT-IR spectra were recorded at RT on a Nicolet Magna 550 FT-IR spectrometer. All NMR spectra were recorded on a Bruker AVANCE 400 MHz instrument (400 MHz  $^1\text{H}$  NMR, 100 MHz  $^{13}\text{C}$  NMR) using  $\text{D}_2\text{O}$ ,  $\text{CDCl}_3$  and  $d^6$ -DMSO as solvent and TMS as reference, respectively. Electrospray ionization high resolution mass spectra (ESI-HRMS) were acquired on a microTOF II spectrometer by using  $\text{H}_2\text{O}$  and DMSO as solvent. The elemental analysis of C, H and N was performed on an Elementar vario EI III CHNOS elemental analyzer and the ICP-AES analysis of niobium on a Vanan 710 instrument, respectively. The reaction products were analyzed by using GC [Shimadzu GC-2014 gas chromatograph equipped with the KB-50 capillary column (30 m  $\times$  0.32 mm  $\times$  0.50 mm)] and GC-MS [Agilent 6890/5973 GC-MS equipped with the HP-5MS column (30 m  $\times$  0.25 mm  $\times$  0.25 mm)]. A Perkin Elmer Pyris Diamond was used for the TGA measurements. A constant heating rate of  $10^\circ\text{C}/\text{min}$  was used in air. All samples were vacuumed at  $60^\circ\text{C}$  for 4 h to remove the solvent molecules before TGA. The samples were heated from RT to  $800^\circ\text{C}$  (heating rate:  $10^\circ\text{C}/\text{min}$ ) under the flow of anhydrous air (flow rate: 20 ml/min). Numbers of peroxide bonds were estimated by potential difference titration of  $\text{Ce}^{3+}/\text{Ce}^{4+}$ .

### Catalyst preparation

*Preparation of Niobic acid.* Niobic acid ( $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ ) was synthesized by using the previously reported method.<sup>34</sup> In brief, solid KOH (3.92 g, 70 mmol) and commercial  $\text{Nb}_2\text{O}_5$  (1.86 g, 7 mmol) were fused in a nickel crucible at  $550^\circ\text{C}$ . After cooling it, the unreacted  $\text{Nb}_2\text{O}_5$  was filtered and the pH value of the clear filtrate was adjusted to 5 by slowly adding acetic acid (1 mol/L). A white precipitate was obtained, which was

washed with distilled water until neutral pH was attained, followed by drying at 60°C for 1 h. The water content in the wet  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  was about 70%.

*Preparation of (guH)<sub>3</sub>NbO<sub>8</sub>.* The guanidine tetraperoxoniobate ((guH)<sub>3</sub>NbO<sub>8</sub>) was prepared according to a previously reported method.<sup>28c</sup> In brief, the freshly prepared niobic acid (2 g, 2.25 mmol) was suspended in water (10 ml) at 0°C and treated with 30% aq H<sub>2</sub>O<sub>2</sub> (7 ml, 60 mmol) under stirring to prepare a transparent pale yellow niobium peroxide solution. Then, guanidine carbonate (1.22 g, 6.75 mmol) was added. The cloudy solution was agitated for a few hours. When the solid was totally dissolved, addition of acetone (100 ml) yielded a white precipitate, which was filtered off, washed with acetone and air-dried (Figure S1). Elemental analysis calcd (%) for (guH)<sub>3</sub>NbO<sub>8</sub>: C 8.98, H 4.52, N 31.42, Nb 23.16; found: C 9.05, H 4.48, N 31.36, Nb 22.93. <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O): δ 157.9. HRMS (ESI): m/z 68.98 [NbO<sub>2</sub>(O<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)]<sup>3-</sup>, 78.96 [HNbO<sub>4</sub>]<sup>2-</sup>, 96.96 [HNbO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2-</sup>, 112.98 [HNbO<sub>2</sub>(O<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2-</sup>, 140.89 [NbO<sub>3</sub>]<sup>-</sup>, 156.89 [NbO<sub>2</sub>(O<sub>2</sub>)]<sup>-</sup>. Number of peroxide bonds: 4.12.

*Preparation of (Ph-guH)<sub>3</sub>NbO<sub>8</sub>.* The phenyl guanidine tetraperoxoniobate ((Ph-guH)<sub>3</sub>NbO<sub>8</sub>) was prepared in a similar way. In brief, the freshly prepared niobic acid (2 g, 2.25 mmol) was suspended in water (10 ml) at 0°C and treated with 30% aq H<sub>2</sub>O<sub>2</sub> (7 ml, 60 mmol) under stirring to prepare a transparent pale yellow niobium peroxide solution. Meanwhile, phenyl guanidine bicarbonate (2.66 g, 13.50 mmol) was dissolved in distilled water (30 ml) at 70°C while stirring to prepare a transparent solution. Then, niobium peroxide solution was added to the phenyl guanidine bicarbonate solution after cooling down at room temperature. The cloudy solution was agitated for a few hours. When the solid was totally dissolved, addition of acetone (250 ml) yielded a white precipitate, which was filtered off, washed with acetone and air-dried (Figure S2). Elemental analysis calcd (%) for (Ph-guH)<sub>3</sub>NbO<sub>8</sub>: C 40.07, H 4.80, N 20.03, Nb 14.76; found: C 40.14, H 4.77, N 20.35, Nb 14.35. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): δ 7.22-7.24 (m, 2H), 7.30-7.34 (m, 1H), 7.39-7.43 (m, 2H); <sup>13</sup>C NMR (100 MHz, d<sup>6</sup>-DMSO): δ 124.5, 126.4, 129.7, 135.4, 155.6. HRMS (ESI): m/z 96.96

$[\text{HNbO}_4(\text{H}_2\text{O})_2]^{2-}$ , 112.98  $[\text{HNbO}_2(\text{O}_2)_2(\text{H}_2\text{O})_2]^{2-}$ , 194.94  $[\text{H}_2\text{NbO}_4(\text{H}_2\text{O})_2]^-$ . Number of peroxide bonds: 3.75.

*Preparation of (TMGH)<sub>3</sub>NbO<sub>5</sub>.* The tetramethyl guanidine peroxoniobate ((TMGH)<sub>3</sub>NbO<sub>5</sub>) was prepared in a similar way. In brief, the freshly prepared niobic acid (2 g, 2.25 mmol) was suspended in water (10 ml) at 0°C and treated with 30% aq H<sub>2</sub>O<sub>2</sub> (7 ml, 60 mmol) under stirring to prepare a transparent pale yellow niobium peroxide solution. The solution turned rapidly to colorless by adding tetramethyl guanidine (TMG, 1.55 g, 13.50 mmol). The solution was agitated for several minutes. The unreacted niobium peroxide was precipitated by addition of ethanol (50 ml), which was filtered off. The solvent in filtrate was removed on a rotary evaporator under vacuum at 40°C to obtain a moist pale yellow solid. This material was thoroughly dried in a vacuum at 60°C for 4 h to get the pale yellow solid (Figure S3). Elemental analysis calcd (%) for (TMGH)<sub>3</sub>NbO<sub>5</sub>: C 34.55, H 8.12, N 24.17, Nb 17.82; found: C 34.85, H 8.25, N 24.58, Nb 17.53. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): δ 2.82 (s, 12H); <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O): δ 38.8, 170.9. HRMS (ESI): m/z 78.96  $[\text{HNbO}_4]^{2-}$ , 96.96  $[\text{HNbO}_4(\text{H}_2\text{O})_2]^{2-}$ . Number of peroxide bonds: 0.88.

*Preparation of (DBUH)<sub>3</sub>NbO<sub>5</sub>.* The DBU-based (1,8-diazabicyclo[5.4.0]undec-7-ene) peroxoniobate ((DBUH)<sub>3</sub>NbO<sub>5</sub>) was prepared following the same way but replacing TMG with DBU (2.06 g, 13.50 mmol) to get the pale yellow solid (Figure S4). Elemental analysis calcd (%) for (DBUH)<sub>3</sub>NbO<sub>5</sub>: C 51.26, H 8.12, N 13.28, Nb 14.69; found: C 51.00, H 8.05, N 13.08, Nb 14.97. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): δ 1.70-1.75 (m, 6H), 2.03 (quintet, J = 6.0 Hz, 2H), 2.64-2.67 (m, 2H), 3.35 (t, J = 6.0 Hz, 2H), 3.52-3.59 (m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 21.0, 25.0, 27.7, 29.4, 34.7, 41.1, 48.5, 53.5, 165.7. HRMS (ESI): m/z 78.96  $[\text{HNbO}_4]^{2-}$ , 96.96  $[\text{HNbO}_4(\text{H}_2\text{O})_2]^{2-}$ , 140.89  $[\text{NbO}_3]^-$ , 155.08  $[(\text{DBUH})\text{NbO}_4]^{2-}$ , 163.08  $[(\text{DBUH})\text{NbO}_5]^{2-}$ . Number of peroxide bonds: 1.08.

*Preparation of (DBUH)<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>.* The DBU-based phosphotungstate ((DBUH)<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) was prepared in a straightforward method. In brief, DBU (1.00 g,

6.57 mmol) and  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (2.19 mmol) were respectively dissolved in ethanol (10 ml). Precipitate generated by adding solution of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  to solution of DBU, which was filtered off, washed with ethanol. This material was thoroughly dried in a vacuum at  $80^\circ\text{C}$  for 4 h to get the white solid (Figure S5). Elemental analysis calcd (%) for  $(\text{DBUH})_3\text{PW}_{12}\text{O}_{40}$ : C 9.72, H 1.54, N 2.52, P 0.93, W 66.11; found: C 10.00, H 1.52, N 2.55, P 0.87, W 68.4.  $^1\text{H}$  NMR (400 MHz,  $\text{d}^6$ -DMSO):  $\delta$  1.64-1.70 (m, 6H), 1.96 (t,  $J = 6.0$  Hz, 2H), 2.66-2.68 (m, 2H), 3.28 (s, 2H), 3.52 (s, 2H), 3.60 (s, 2H), 9.48 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{d}^6$ -DMSO):  $\delta$  18.9, 23.3, 25.9, 28.3, 31.8, 37.6, 47.9, 53.5, 165.4. HRMS (ESI):  $m/z$  958.73  $[\text{PW}_{12}\text{O}_{40}]^{3-}$ , 1438.60  $[\text{HPW}_{12}\text{O}_{40}]^{2-}$ .

*Preparation of  $(\text{DBUH})_3\text{NbO}_4$ .* The DBU-based ortho-niobate  $((\text{DBUH})_3\text{NbO}_4)$  was prepared by vacuum drying  $(\text{DBUH})_3\text{NbO}_5$  at  $80^\circ\text{C}$  for 5 h (Figure S6). Elemental analysis calcd (%) for  $(\text{DBUH})_3\text{NbO}_4$ : C 52.59, H 8.34, N 13.63, Nb 15.07; found: C 52.29, H 8.28, N 13.76, Nb 15.82.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.60-1.64 (m, 6H), 1.83 (t,  $J = 5.6$  Hz, 2H), 2.58-2.61 (m, 2H), 3.27-3.29 (m, 4H), 3.34 (t,  $J = 5.6$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.0, 24.9, 27.7, 29.4, 34.4, 40.9, 48.5, 53.5, 164.1. HRMS (ESI):  $m/z$  78.96  $[\text{HNbO}_4]^{2-}$ , 96.96  $[\text{HNbO}_4(\text{H}_2\text{O})_2]^{2-}$ . Number of peroxide bonds: 0.

*Preparation of  $(\text{DBUH})\text{NbO}_3$ .* The DBU-based niobate  $((\text{DBUH})\text{NbO}_3)$  was prepared in a two-step approach. In brief, the freshly prepared niobic acid (2 g, 2.25 mmol) was suspended in water (10 ml) at  $0^\circ\text{C}$  and treated with 30% aq  $\text{H}_2\text{O}_2$  (7 ml, 60 mmol) under stirring to prepare a transparent pale yellow niobium peroxide solution. Then 25% aq ammonia was added dropwise until  $\text{pH} = 11$  to form ammonium tetraperoxoniobate  $((\text{NH}_4)_3\text{NbO}_8)$ .<sup>28c,30b</sup> Meanwhile, the bicarbonate salt of DBU  $((\text{DBUH})\text{HCO}_3)$  was prepared by bubbling  $\text{CO}_2$  for 10 min through the liquid DBU (0.69g, 4.5mmol).<sup>33a,b</sup> Thereafter,  $(\text{DBUH})\text{HCO}_3$  was added into the solution of  $((\text{NH}_4)_3\text{NbO}_8)$  and the solution was agitated for several hours. The solvent was removed on a rotary evaporator under vacuum at  $40^\circ\text{C}$  to obtain a moist pale yellow solid. This material was thoroughly dried in a vacuum at  $80^\circ\text{C}$  for 6 h to get the pale yellow viscous solid (Figure S7). Elemental analysis calcd (%) for  $(\text{DBUH})\text{NbO}_3$ : C



36.75, H 5.83, N 9.52, Nb 31.58; found: C 36.91, H 5.87, N 9.76, Nb 31.47.  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  1.53-1.57 (m, 6H), 1.87 (quintet,  $J = 6.0$  Hz, 2H), 2.49-2.51 (m, 2H), 3.19 (t,  $J = 6.0$  Hz, 2H), 3.38 (t,  $J = 5.6$  Hz, 2H), 3.41-3.44 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  18.9, 23.3, 25.8, 28.4, 32.7, 37.9, 48.2, 54.0, 165.9. HRMS (ESI):  $m/z$  140.89  $[\text{NbO}_3]^-$ . Number of peroxide bonds: 0.

### Typical reaction procedure for the catalytic synthesis of cyclic carbonates

In a typical procedure, cycloaddition reactions between carbon dioxide and epoxides were carried out in 50 ml stainless autoclave equipped with a magnetic stirrer and automatic temperature control system. The catalyst (0.3 mmol) and epoxides (10 mmol) were added into the autoclave. The reactor was purged with  $\text{CO}_2$  for 3 times and then charged with  $\text{CO}_2$  to the desired pressure. Then the autoclave was heated to the reaction temperature. After the reaction, the reactor was cooled in ice water bath, and the excess carbon dioxide was slowly vented. When the ethyl ether was added to the reactor, the insoluble residue would be obviously precipitated. The mixture was separated by centrifugation. The catalyst was washed with ethyl ether and dried in a vacuum at  $60^\circ\text{C}$  for recycling tests. Meanwhile, the liquid phase was subjected to GC-MS analysis. The products can be isolated by silica gel column chromatography with petrol ether:ethyl acetate (2:1, v/v) as an effluent.

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