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Novel hydrazine-bridged covalent triazine polymer for CO₂ capture and catalytic conversion

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1. Introduction

ABSTRACT

Carbon dioxide (CO₂) capture and catalytic conversion has become an attractive and challenging strategy for CO₂ utilization since it is an abundant, inexpensive, and renewable C1 resource and a main greenhouse gas. Herein, a novel hydrazine-bridged covalent triazine polymer (HB-CTP) was first designed and synthesized through simple polymerization of cyanuric chloride with 2,4,6-trihydrazinyl-1,3,5-triazine. The resultant HB-CTP exhibited good CO₂ capture capacity (8.2 wt%, 0 °C, and 0.1 MPa) as well as satisfactory recyclability after five consecutive adsorption-desorption cycles. Such a polymer was subsequently employed as a metal-free heterogeneous catalyst for the cyclo-addition of CO₂ with various epoxides under mild and solvent-free conditions, affording cyclic carbonates with good to excellent yields (67%–99%) and high functional-group tolerance. The incorporation of hydrazine linkages into HB-CTP's architecture was suggested to play the key role in activating epoxides through hydrogen bonding. Moreover, HB-CTP can be reused at least five times without significant loss of its catalytic activity.

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Nowadays, carbon dioxide (CO_2) capture and sequential catalytic conversion has been rationally proposed and deployed to address the issue of excessive CO_2 emission, as it is a nontoxic, easily available, and sustainable C1 building block in organic synthesis and a greenhouse gas that causes global warming and environmental crises [1–3]. In this context, a diversity of bifunctional materials with ordered porosity and efficient catalytic sites has been developed, such as metal-organic frameworks (MOFs), zeolites, and porous carbons [4–6]. Among these, MOFs and zeolites have shown excellent CO_2 capture performance due to the presence of metal cations,

from insufficient long-term stability and/or deactivation by moisture [9–12]. Notably, porous polymers, with the advantages of high stability toward heat and humidity, as well as low density and metal-free features, have been shown to be feasible and powerful as solid adsorbents for CO_2 capture and heterogeneous catalysts for CO_2 conversion [13,14]. Therefore, the development of reliable technologies for CO_2 capture and conversion by such organic materials is certainly attractive and promising.

The 1,3,5-triazine moiety possesses a nitrogen-rich feature, as well as planar, rigid, and high-symmetry structural characteristics, rendering it desirable for the construction of extended CO₂-specific networks with permanent porosity [15,16]. Meanwhile, as one commercial available industrial chemical, cyanuric chloride (CC) is the chlorinated derivative of triazine.

as well as donor ligands and polar functional sites, within the

structure [7,8]. However, their practical applications suffer

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Owing to the electron-deficient nature of carbons residing in the triazine ring, CC has been widely applied in the construction of porous triazine polymers by electrophilic substitution of its chlorine atoms with different nucleophiles [17-19]. For instance, porous covalent organic polymers from reaction of CC with piperazine have been devised, with CO2 adsorption capacities up to 5616 mg/g at 65 °C and 20.0 MPa, which have been proved to be stable in boiling water for at least 1 week [20]. Porous sulfur-bridged covalent organic polymers derived from CC and 1,3,5-benzenetrithiol could also provide up to 3294 mg/g of CO₂ at 45 °C and 20.0 MPa, while being highly stable against heating up to 400 °C [21]. In addition, ferrocene-functionalized microporous aromatic polymers were synthesized by a one-step Friedel-Crafts reaction of ferrocene and CC and have been shown to have a good CO2 adsorption capability of 16.9 wt% at 0 °C and 0.1 MPa [22].

However, although chemical fixation of CO2 into value-added chemicals has been a long-sought goal in both academia and industry, the inherent thermodynamic stability and kinetic inertness of CO₂ pose a challenge for its chemical conversion under industrially viable conditions [23,24]. In order to overcome this obstacle, employment of high-energy starting materials seems to be the wisest choice for utilization of inactive CO₂ as a reactant. Therefore, the atom-economical reaction involving the cyclo-addition of CO2 with epoxides to render five-membered cyclic carbonates has been intensively studied [25-30]. Among the variety of catalysts developed, it is worth mentioning that porous organic polymers have been demonstrated as recyclable organocatalysts for this transformation [31–35]. However, the reaction protocols involving such polymers as heterogeneous catalysts often need high temperature [31], solvents [32,33], and/or transition-metal components [34,35] to enhance their reactivity. Hence, polymer-type metal-free catalysts that can operate under mild and solvent-free conditions are still in demand.

Herein, a novel hydrazine-bridged covalent triazine polymer (HB-CTP) was designed and synthesized through a simple nucleophilic substitution reaction of 2,4,6-trihydrazinyl-1,3,5-triazine with CC promoted by sodium carbonate at 110 °C, as shown in Scheme 1. This new material was devised to acquire two outstanding advantages for CO_2 capture and conversion: (1) numerous triazine units to facilitate the reversible adsorption of CO_2 through their basic nitrogen sites that decorate the inside of the material's pores and (2) massive hydrazine moieties activated by electron-deficient triazines to coordinate with the substrates by formation of hydrogen bonds [33,36,37]. Indeed, HB-CTP was discovered to be not only a viable and stable

 $\rm CO_2$ adsorbent but also an active and recyclable catalyst for cyclo-addition of $\rm CO_2$ with various epoxides to afford cyclic carbonates at high efficiency. Hence, this work provides a facile method for the first synthesis of a hydrazine-bridged covalent triazine polymer, which shows promising applications in $\rm CO_2$ capture and catalytic conversion.

2. Experimental

2.1. Chemicals

CO₂ (99.999%) was used as received without further purification. The 1,4-dioxane was distilled from sodium/ benzophenone under N₂. CC was purchased from J&K Scientific (USA). Hydrazine hydrate was acquired from Alfa Aesar of ThermoFisher Scientific (USA). Tetra-*n*-butylammonium bromide (TBAB) was obtained commercially from Tianjin Guangfu Fine Chemical Research Institute (China). 2,4,6trihydrazinyl-1,3,5-triazine was synthesized according to the established method [38]. Glycidyl propargyl ether and 4-(2,3-epoxypropyl)-morpholine were prepared by coupling a reaction of corresponding terminal propargylic alcohol or morpholine with epichlorohydrin according to the literature methods with modifications [39,40]. Other epoxides and the remaining reagents were obtained commercially and used without further purification.

2.2. Characterization

Nuclear-magnetic-resonance (NMR) spectra were recorded on a Bruker AdvanceII 400M-type spectrometer. Fouriertransform infrared (FTIR) spectroscopy was measured using a Nicolet NEXUS FTIR spectrophotometer. Thermal gravimetric analysis (TGA) was carried out by a Mettler Toledo TGA2 STAR* SYSTEM under a N2 atmosphere with a ramp rate of 10 °C/min. Elemental analysis was determined with an Elementar Vario EL III elemental analyzer. Solid-state ¹³C CP/MAS NMR spectra were recorded on a Varian Infinity-Plus 400 spectrometer. X-ray powder diffraction (XRD) measurements were performed on a Rigaku D/MAX 2400 X-ray diffractometer. Adsorption-desorption measurements for N₂ and CO₂ were conducted on a Quantachrome Autosorb iQ² apparatus. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area. Scanning electron microscopy (SEM) investigations were performed on a Hitachi UHR FE-SEM SU8200 instrument. Transmission electron microscopy (TEM) images were obtained on a FEI TF30



Scheme 1. Synthesis of HB-CTP.

apparatus.

2.3. Catalyst preparation

In a Schlenk apparatus under dry nitrogen atmosphere, sodium carbonate (18 mmol, 1.91 g), CC (3 mmol, 0.55 g), and 2,4,6-trihydrazinyl-1,3,5-triazine (3 mmol, 0.51 g) was added to 1,4-dioxane (20 mL) at room temperature. The above mixture was stirred at room temperature for 6 h and then at 110 °C for 48 h. Afterwards, the light yellow precipitate was collected by filtration and washed consecutively with dimethylformamide, water, and methanol. Finally, the quantitatively yielded product, designated HB-CTP, was dried at 120 °C under vacuum for 24 h. Elemental analysis results were as follows: calculated value (%) N 63.78, C 33.42, H 2.80; found value (%) N 60.75, C 27.89, H 2.65.

2.4. General procedure for the cyclo-addition reaction

A 15-mL oven-dried autoclave containing a magnetic stir bar was charged with a corresponding epoxide (10 mmol), HB-CTP (50 mg), and TBAB (0.5 mmol, 0.16 g). The autoclave was then purged with CO_2 three times. The sealed autoclave was pressurized to 2 MPa CO_2 and continuously stirred at 80 °C for 12 h. Afterwards, the autoclave was cooled to room temperature, and the remaining CO_2 was vented slowly. Yields of the target products were determined by ¹H NMR with 1,5-dichloro-2,4-dinitrobenzene as an internal standard.

2.5. Characterization data for cyclic carbonates

4-Ethyl-1,3-dioxolan-2-one (**2a**). ¹H NMR (400 MHz, CDCl₃): δ = 4.68–4.63 (m, 1H), 4.52 (t, *J* = 6.4 Hz, ¹H), 4.07 (t, *J* = 6.0 Hz, 1H), 1.84–1.71 (m, 2H), 1.02 (t, *J* = 5.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 155.2, 78.1, 69.1, 27.0, and 8.5.

4-(chloromethyl)-1,3-dioxolan-2-one (**2b**). ¹H NMR (400 MHz, CDCl₃): δ = 4.97–4.94 (m, 1H), 4.59 (t, *J* = 8.7 Hz, 1H), 4.42 (dd, *J* = 8.8 and 6.3 Hz, 1H), 3.80–3.71 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 154.2, 74.3, 67.1, and 43.7.

4-(bromomethyl)-1,3-dioxolan-2-one (**2c**). ¹H NMR (400 MHz, CDCl₃): δ = 4.98–4.92 (m, 1H), 4.59 (t, *J* = 8.8 Hz, 1H), 4.35 (dd, *J* = 8.9 and 5.9 Hz, 1H), 3.58–3.57 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 154.2, 74.1, 68.2, and 31.5.

4-(hydroxymethyl)-1,3-dioxolan-2-one (**2d**). ¹H NMR (400 MHz, DMSO-d₆): δ = 5.25 (t, *J* = 4.4 Hz, 1H), 4.81–4.77 (m, 1H), 4.52–4.45 (m, 1H), 4.29–4.27 (m, 1H), 3.68–3.64 (m, 1H), 3.53–3.48 (m, 1H). ¹³C NMR (100 MHz, DMSO-d₆): δ = 155.2, 70.0, 65.9, and 60.6.

4-methyl-1,3-dioxolan-2-one (**2e**). ¹H NMR (400 MHz, CDCl₃): δ = 4.88–4.79 (m, 1H), 4.53 (t, *J* = 8.1 Hz, 1H), 4.00 (t, *J* = 8.3 Hz, 1H), 1.45 (d, *J* = 6.3 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 155.1, 73.6, 70.7, and 19.4.

4-butyl-1,3-dioxolan-2-one (**2f**). ¹H NMR (400 MHz, CDCl₃): δ = 4.73–4.66 (m, 1H), 4.52 (t, *J* = 8.1 Hz, 1H), 4.06 (t, *J* = 7.8 Hz, 1H), 1.81–1.67 (m, 2H), 1.40–1.37 (m, 4H), 0.91 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 155.2, 69.5, 33.7, 26.5, 22.3, and 13.9. 4-hexyl-1,3-dioxolan-2-one (**2g**). ¹H NMR (400 MHz, CDCl₃): δ = 4.83–4.66 (m, 1H), 4.51 (t, *J* = 8.0 Hz, 1H), 4.06 (t, *J* = 8.0 Hz, 1H), 1.81–1.63 (m, 2H), 1.46–1.29 (m, 8H), 0.88 (t, *J* = 6.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 155.1, 77.1, 69.4, 33.9, 31.5, 28.8, 24.3, 22.5, and 14.0.

4-(methoxymethyl)-1,3-dioxolan-2-one (**2h**). ¹H NMR (400 MHz, CDCl₃): δ = 4.81–4.77 (m, 1H), 4.48 (t, *J* = 8.4 Hz, 1H), 4.43–4.37 (m, 1H), 3.65–3.52 (m, 2H), 3.40 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 155.1, 75.2, 71.5, 66.3, and 59.7.

4-(isopropoxymethyl)-1,3-dioxolan-2-one (**2i**). ¹H NMR (400 MHz, CDCl₃): δ = 4.80–4.77 (m, 1H), 4.48 (t, *J* = 8.4 Hz, 1H), 4.40–4.37 (m, 1H), 3.67–3.59 (m, 3H), 1.16 (d, *J* = 6.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ = 155.2, 75.4, 72.8, 67.1, 66.4, 59.7, 21.9, and 21.8.

4-(butoxymethyl)-1,3-dioxolan-2-one (**2j**). ¹H NMR (400 MHz, CDCl₃): δ = 4.82–4.76 (m, 1H), 4.47 (t, *J* = 8.4 Hz, 1H), 4.38–4.35 (m, 1H), 3.67–3.56 (m, 2H), 3.49 (d, *J* = 6.4 Hz, 2H), 1.57–1.50 (m, 2H), 1.38–1.29 (m, 2H), 0.89 (d, *J* = 7.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 155.1, 75.2, 71.9, 69.7, 66.4, 31.6, 19.2, and 13.9.

4-((dodecyloxy)methyl)-1,3-dioxolan-2-one (**2k**). ¹H NMR (400 MHz, CDCl₃): δ = 4.82–4.76 (m, 1H), 4.48 (t, *J* = 8.0 Hz, 1H), 4.40–4.36 (m, 1H), 3.67–3.58 (m, 2H), 3.49 (d, *J* = 6.8 Hz, 2H), 1.59–1.52 (m, 2H), 1.25 (m, 18H), 0.87 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 155.1, 75.2, 72.4, 69.8, 66.5, 32.0, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 29.5, 26.1, 22.8, and 14.2.

4-(phenoxymethyl)-1,3-dioxolan-2-one (**2l**). ¹H NMR (400 MHz, CDCl₃): δ = 7.33–7.29 (m, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 2H), 5.06–5.00 (m, 1H), 4.62 (t, *J* = 8.4 Hz, 1H), 4.54 (dd, *J* = 8.5 and 5.9 Hz, 1H), 4.24 (dd, *J* = 10.5 and 4.4 Hz, 1H), 4.16 (dd, *J* = 10.5 and 3.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ = 157.9, 129.9, 122.2, 114.8, 74.2, 67.1, and 66.4.

4-((benzyloxy)methyl)-1,3-dioxolan-2-one (**2m**). ¹H NMR (400 MHz, CDCl₃): δ = 7.38–7.26 (m, 5H), 4.60–4.54 (m, 1H), 4.57 (q, *J* = 12.0 Hz, 2H), 4.47 (t, *J* = 8.4 Hz, 1H), 4.37 (dd, *J* = 8.3 and 6.0 Hz, 1H), 3.73–3.59 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 155.0, 137.2, 128.4, 127.9, 127.6, 75.1, 73.5, 68.9, and 66.2.

4-((allyloxy)methyl)-1,3-dioxolan-2-one (**2n**). ¹H NMR (400 MHz, CDCl₃): δ = 5.90–5.83 (m, 1H), 5.30–5.21 (m, 2H), 4.82–4.81 (m, 1H), 4.52–4.48 (m, 1H), 4.06–4.04 (m, 1H), 3.70–3.67 (m, 2H), 3.63–3.59 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 155.0, 133.8, 118.1, 75.1, 72.7, 69.0, and 66.4.

4-((prop-2-yn-1-yloxy)methyl)-1,3-dioxolan-2-one (**20**). ¹H NMR (400 MHz, CDCl₃): δ = 4.86–4.83 (m, 1H), 4.50 (t, *J* = 8.4 Hz, 1H), 4.40–4.36 (m, 1H), 4.27–4.16 (m, 2H), 3.79–3.69 (m, 2H), 2.48 (t, *J* = 2.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ = 155.0, 78.6, 75.7, 74.8, 68.5, 66.3, and 58.9.

4-phenyl-1,3-dioxolan-2-one (**2p**). ¹H NMR (400 MHz, CDCl₃): δ = 7.46–7.42 (m, 3H), 7.38–7.35 (m, 3H), 5.68 (t, *J* = 8.0 Hz, 1H), 4.80 (t, *J* = 8.4 Hz, 1H), 4.37–4.35 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ = 154.9, 135.9, 129.9, 129.4, 126.0, 78.1, and 71.3.

4-(morpholinomethyl)-1,3-dioxolan-2-one (**2q**). ¹H NMR (400 MHz, CDCl₃): δ = 4.82–4.75 (m, 1H), 4.48 (t, *J* = 8.3 Hz, 1H), 4.18 (t, *J* = 7.7 Hz, 1H), 3.61 (t, *J* = 4.3 Hz, 4H), 2.62 (d, *J* = 5.3 Hz, 2H), 2.48 (m, 4H). ¹³C NMR (100 MHz, CDCl₃): δ = 154.7, 74.8, 67.6, 66.4, 69.8, and 54.0. 4,4-dimethyl-1,3-dioxolan-2-one (**2r**). ¹H NMR (400 MHz, CDCl₃): δ = 4.13 (s, 2H), 1.50 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ = 154.7, 81.8, 75.5, and 26.1.

Hexahydrobenzo[d][1,3]dioxol-2-one (**2s**). ¹H NMR (400 MHz, CDCl₃): δ = 4.69–4.64 (m, 2H), 1.87–1.85 (m, 4H), 1.63–1.54 (m, 2H), 1.43–1.35 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 155.4, 75.8, 26.8, and 19.2.

3. Results and discussion

3.1. Characterization

The functional connectivity and structure of HB-CTP were investigated with FTIR spectroscopy by comparison of the spectra of CC, 2,4,6-trihydrazinyl-1,3,5-triazine, and the resultant HB-CTP (Fig. 1). The disappearance of the characteristic stretching vibration of C-Cl of CC at 850 cm⁻¹, together with the immense enhancement of N-H absorption around 3367 cm⁻¹, would reveal the total substitution of all three Cl atoms of CC, as well as the massive formation of hydrazine linkages. In addition, the strong bands in the 1200–1600 cm⁻¹ region correspond to the stretching modes of triazine units, while their breathing mode could be assigned near 805 cm⁻¹.

In the solid state ¹³C CP/MAS NMR spectroscopy (Fig. 2(a)), the only theoretical signal for aromatic triazine carbons of HB-CTP was observed at 168.1 ppm. Such a clean chart without any impurity peaks indicates the integrity of the corresponding triazine framework. Meanwhile, the XRD pattern was found to be featureless (Fig. 2(b)), illustrating an amorphous structure. The morphology of HB-CTP was further investigated by SEM and TEM as depicted in Fig. 2(c) and (d), which show that the



Fig. 1. FTIR spectra of CC (1), 2,4,6-trihydrazinyl-1,3,5-triazine (2), and HB-CTP (3).

HB-CTP material mainly exists in aggregate form. Finally, as shown in Fig. 2(e), the thermal stability of such hydrazine-rich polymer was disclosed, and the initial degradation could be observed at above 250 °C.

3.2. N₂ and CO₂ adsorption

The porosity of the HB-CTP material was measured by nitrogen-adsorption analysis carried out at -196 °C. As shown in Fig. 3, the adsorption-desorption process displays a reversible



Fig. 2. 13C CP/MAS NMR spectrum (a), XRD pattern (b), SEM (c) and TEM (d) images, and TGA curve (e) of HB-CTP.



Fig. 3. N2 adsorption-desorption isotherm of HB-CTP.

type-II isotherm, representing a nearly non-porous or macroporous adsorbent that tends to proceed through unrestricted monolayer-multilayer adsorption [41]. Indeed, the BET surface area was found to be 51.2 m²/g, and the total pore volume was 0.28 cm³/g at $P/P_0 = 0.99$. Such a low level of porosity should be attributed to the strong interaction between triazine framework layers through massive hydrogen bonds donated by the hydrazine linkages. Furthermore, the average pore size calculated from the Barrett-Joyner-Halenda method also lies largely in the macroporous region.

Despite poor surface area and porosity, the HB-CTP material has shown good CO₂ capture capacity (1.86 mmol/g, 8.2 wt%) at 0 °C and 0.1 MPa conditions (Fig. 4(a)). This abnormal achievement could be reasonable if one considers the fact that polymers based on triazine units and hydrazine linkages would hold an extremely high N content (60.75%, determined by elemental analysis) to intrinsically favor CO2 adsorption through dipole-quadrupole interactions between the polarizable CO2 molecule and the vast number of basic N sites [42-45]. Moreover, the HB-CTP still exhibited satisfactory capture performance after at least five consecutive adsorption-desorption cycles, rendering good recyclability (Fig. 4(b)).

3.3. Catalytic performance

The successful capture of CO₂ with 8.2 wt% capacity by HB-CTP gave us an opportunity to test its catalytic performance for conversion of CO₂ into cyclic carbonates by cyclo-addition reaction. Primary catalytic studies were performed with 2-ethyloxirane **1a** and CO₂ (2 MPa) at 60 °C for 4 h (Table 1). Without the catalyst HB-CTP, only 15% yield of the corresponding cyclic carbonate **2a** was observed by the co-catalyst TBAB (5 mol%) (entry 1). It was found that the introduction of HB-CTP would have an obviously positive effect on reaction outcome, indicating the feasibility of our catalyst design (entry 2). Raising reaction temperature from 60 to 80 °C resulted in further enhancement of catalytic activity (entry 3). Positively, a 97% yield of **2a** could be obtained when the reaction time was extended to 12 h (entry 4). Furthermore,



Fig. 4. CO_2 adsorption-desorption isotherm (a) and recyclability (b) of HB-CTP.

lowering either HB-CTP loading or CO₂ pressure would lead to a notable decrease in reaction efficiency (entries 5 and 6).

Subsequently, various functionalized terminal and internal epoxides were subjected to the optimized conditions in order to test the generality of the present reaction. As shown in Scheme 2, a number of cyclic carbonates were selectively synthesized with broad substrate scope owing to the remarkable catalytic activity of HB-CTP. Epoxides bearing alkyl,

Table 1

Cyclo-addition of CO2 with 2-ethyloxirane 1a catalyzed by HB-CTP.

	Et +	CO ₂ -	HB-CTP	- 0	0
Entry	HB-CTP (mg)	(O ₂ (MP ₂)	T (°C)	<i>t</i> (h)	Et
1		202 (Mi a)	60	<u>t (II)</u> 4	15
2	50	2	60	4	34
3	50	2	80	4	56
4	50	2	80	12	97
5	25	2	80	12	75
6	50	1	80	12	69

Reaction conditions: **1a** (10 mmol), TBAB (5 mol%). ^a Determined by ¹H NMR.



Scheme 2. Substrate scope of the cyclo-addition. Reaction conditions: epoxides (10 mmol), HB-CTP (50 mg), TBAB (5 mol%), 2 MPa, 80 °C, 12 h.

allyl, phenyl, benzyl, propargyl, ether, hydroxyl, halide, and morpholinyl groups reacted smoothly to give the corresponding products in good to excellent yields under metal- and solvent-free conditions (2a-2q). Notably, the less reactive substrate 1k with lauryl substituent as well as gem-substituted 2,2-dimethyloxirane 1r both furnished the target cyclic carbonates (2k and 2r) in acceptable yields. Furthermore, the internal cyclohexene oxide 1s could also be successfully converted with high efficiency. It is worth mentioning that HB-CTP alone could act as sufficient catalyst for cyclo-addition of CO₂ with epichlorohydrin 1a, epibromohydrin 1b, or glycidol 1c affording comparable yields, although a higher reaction temperature should be provided (Scheme 3).

3.4. Catalyst recycling

One advantage of the HB-CTP catalyst is its heterogeneous nature, which can operate under solvent-free conditions. Hence, recycling experiments were conducted to test its recyclability and stability. The results depicted in Fig. 5(a) demonstrate that, by simple centrifugation and vacuum drying, HB-CTP could be reused for at least five runs without significant loss of catalytic activity, rendering the present reaction potentially viable for practical applications. In addition, by the comparison of the FTIR spectra of HB-CTP before and after recycling (Fig. 5(b)), the structure of such catalyst was shown to be largely intact (the rare difference at



X = CI, 99%; Br, 96%; OH, 83%

Scheme 3. Cyclo-addition of CO_2 with epoxides catalyzed by HB-CTP alone. Reaction conditions: epoxides (10 mmol), HB-CTP (50 mg), 2 MPa, 120 °C, 8 h.

2960 cm⁻¹ was due to the residue of TBAB co-catalyst), which indicates its remarkable stability toward reaction conditions.

3.5. Plausible reaction mechanism

It has already been reported that hydroxyl groups attached to the catalyst could play a key role for the high efficiency in cyclo-addition of CO_2 with epoxides [46]. In addition, hydroxyl-functionalized porous polymers could also activate the epoxides by forming hydrogen bonds along the solid/liquid interface [33,36,37]. Therefore, on the basis of these results, a plausible reaction mechanism was proposed in which the catalytic cycle within this process tends to proceed via the



Fig. 5. (a) Recyclability of HB-CTP in cyclo-addition of CO_2 with 1a, (b) FTIR spectra of HB-CTP before (1) and after (2) recycle. Reaction conditions: 1a (10 mmol), HB-CTP (50 mg), TBAB (5 mol%), 2 MPa, 80 °C, 12 h.



Scheme 4. Plausible mechanism for cyclo-addition of CO₂ with epoxide catalyzed by HB-CTP.

synergistic operation of hydrogen-bond activation and bromide anion nucleophilic attack toward the epoxide substrate, as shown in Scheme 4. First, the hydrazine group within the structure of HB-CTP acts as donor to polarize the C–O bond of an epoxide through hydrogen bonding, illustrated as **A**. Then, a nucleophilic attack on the less sterically hindered carbon of epoxide made by the bromide anion would result in the ring-opening intermediate **B**. Subsequently, the alkoxide within **B** could be rapidly transferred into carbonate anion species **C** in the CO₂-rich environment. Finally, the intramolecular nucleophilic ring closure initiated by the carbonate anion of **C** renders cyclic carbonate and simultaneously releases the HB-CTP and bromide anion for the next catalytic cycle.

4. Conclusions

A hydrazine-bridged covalent triazine polymer was devised and applied for the first time in CO₂ capture and catalytic conversion. This novel polymer was prepared by a facile reaction based on CC and 2,4,6-trihydrazinyl-1,3,5-triazine, which have good CO₂ capture capacity as well as satisfactory recyclability. Moreover, provided with a hydrogen-bond donor property by the massive hydrazine linkages within its molecular structure, the heterogeneous HB-CTP exhibited high catalytic activity and reusability for cyclo-addition of CO₂ with epoxides under mild and solvent-free conditions with excellent tolerance to a wide range of functional groups. This HB-CTP may have various utilizations in base and/or hydrogen-bond-promoted reactions, and the exploration of its further applications is ongoing in our laboratory.

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Graphical Abstract

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Novel hydrazine-bridged covalent triazine polymer for $\ensuremath{\text{CO}}_z$ capture and catalytic conversion

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A novel hydrazine-bridged covalent triazine polymer was synthesized by simple polymerization of cyanuric chloride with 2,4,6-trihydrazinyl-1,3,5-triazine, which can be employed as both a CO₂ adsorbent and heterogeneous organocatalyst for cyclo-addition of CO₂ with epoxides under solvent-free conditions.

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新型肼桥联共价三嗪聚合物在二氧化碳捕集和催化转化方面的应用

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摘要: 二氧化碳的捕集和催化转化是近年来二氧化碳利用方面的研究热点. 其原因, 一方面二氧化碳是储量丰富、廉价易 得的可再生碳资源, 另一方面它又是带来环境问题的温室气体. 以金属有机框架、沸石和多孔聚合物材料为代表的同时具 有规则孔道和活性催化位点的双功能材料为实践这一新概念创造了条件. 但是, 金属有机框架和沸石的应用面临由其自 身结构所带来的热稳定性和/或水稳定性较低等问题. 多孔聚合物材料则由于其高稳定性、低密度以及非金属等优点, 逐渐 成为该领域的研究重点. 然而, 当前关于利用多孔聚合物类材料作为有机催化剂以实现二氧化碳固定的报道, 其反应过程 一般需要较高温度、有机溶剂和/或过渡金属催化组分, 仍有较大改进余地. 本文设计合成了新型肼桥联共价三嗪聚合物 (HB-CTP), 意图在利用其富氮三嗪结构单元促进二氧化碳捕集的同时, 以大量肼官能团通过氢键作用活化环氧化物, 进而 将二氧化碳在无溶剂和非金属的温和条件下催化固定为环状碳酸酯.

HB-CTP 材料的合成方法简便易行,由 2,4,6-三肼基-1,3,5-三嗪与三聚氯氰发生的亲核取代反应制得.采用多种表征 手段分析了该类新材料的结构和形态:红外光谱表明三聚氯氰的 C-Cl 键在聚合过程中反应完全,其位于 850 cm⁻¹ 处的吸 收信号彻底消失;固体核磁谱图仅在 168.1 ppm 处显示三嗪环的单峰信号,表明了该材料结构的完整性;X 射线粉末衍射 测试并未发现特征峰,表明 HB-CTP 呈无定形态;透射电镜和扫描电镜的观测结果则进一步证实了该材料的团聚形态;最 后,热重分析显示 HB-CTP 具有良好的热稳定性,250 ℃ 以上才开始分解.然后,通过氮气吸附测定了 HB-CTP 比表面积 (51.2 m²/g)和总孔容 (0.28 cm³/g),其吸附等温线呈 II 型,表明材料结构以大孔为主,通过层间吸附.随后的二氧化碳吸附 测试发现,HB-CTP 在 0 ℃、0.1 MPa 条件下显示出较高的二氧化碳捕集容量 (8.2 wt%),并且经过连续吸附脱附循环五次, 仍能保持较好的二氧化碳捕集能力.在 HB-CTP 材料良好的二氧化碳捕集容量基础上,本文考察了其催化活性,发现带有 多种取代基的环氧化物均能在无溶剂、非金属的温和条件下,以较高的收率被转化为环状碳酸酯类产物;并且底物结构中

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CO₂ Capture & Conversion

的卤素、羟基、炔基、烯丙基和苄基等官能团均未发生副反应,显示出良好的底物适用范围.此外,HB-CTP 材料可通过简单的离心操作实现分离回收,且经连续使用五次,其催化活性也没有明显降低.

综上所述,该类新型肼桥联共价三嗪聚合物不仅能够高效捕集二氧化碳,而且还可以将其在温和条件下催化转化为环 状碳酸酯类产物,具有一定理论研究意义和实际应用价值.

关键词: 共价三嗪聚合物; 捕集; 催化; 二氧化碳; 环状碳酸酯

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