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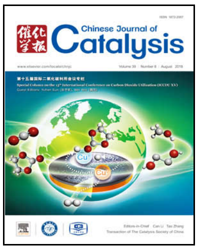

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Novel hydrazine-bridged covalent triazine polymer for CO_2 capture and catalytic conversion

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ABSTRACT

Carbon dioxide (CO_2) capture and catalytic conversion has become an attractive and challenging strategy for CO_2 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 CO_2 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 CO_2 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.

1. Introduction

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, as well as donor ligands and polar functional sites, within the structure [7,8]. However, their practical applications suffer 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 CO_2-specific networks with permanent porosity [15,16]. Meanwhile, as one commercial available industrial chemical, cyanuric chloride (CC) is the chlorinated derivative of triazine.

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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 CO_2 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 CO_2 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 CO_2 adsorption capability of 16.9 wt% at 0 °C and 0.1 MPa [22].

However, although chemical fixation of CO_2 into value-added chemicals has been a long-sought goal in both academia and industry, the inherent thermodynamic stability and kinetic inertness of CO_2 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 CO_2 as a reactant. Therefore, the atom-economical reaction involving the cyclo-addition of CO_2 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 CO_2 adsorbent but also an active and recyclable catalyst for cyclo-addition of 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 CO_2 capture and catalytic conversion.

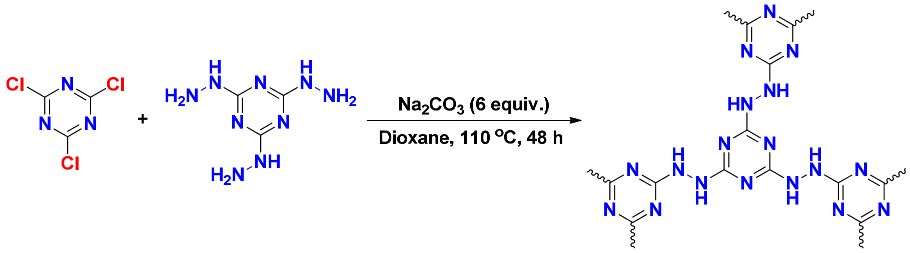
2. Experimental

2.1. Chemicals

CO_2 (99.999%) was used as received without further purification. The 1,4-dioxane was distilled from sodium/benzophenone under N_2. 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). 2,4,6-trihydrazinyl-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. Fourier-transform 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 N_2 atmosphere with a ramp rate of 10 °C/min. Elemental analysis was determined with an Elementar Vario EL III elemental analyzer. Solid-state ^{13}C 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 N_2 and CO_2 were conducted on a Quantachrome Autosorb iQ^2 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.