

Contents lists available at ScienceDirect

Journal of CO₂ Utilization



journal homepage: www.elsevier.com/locate/jcou

Highly efficient cycloaddition of diluted and waste CO₂ into cyclic carbonates catalyzed by porous ionic copolymers



Wei Hui^{a,1}, Xue-Mei He^{b,1}, Xin-Yi Xu^a, Yue-Miao Chen^a, Yan Zhou^a, Zhang-Min Li^a, Liqi Zhang^c, Duan-Jian Tao^a,*

^a College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang, 330022, China

^b Department of Chemistry, School of Science, Jiangxi Agricultural University, Nanchang, 330045, China

^c State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan, 430074, Hubei Province, China

ARTICLE INFO

Keywords: Porous ionic copolymer Cycloaddition Diluted CO₂ Cyclic carbonate

ABSTRACT

It is believed that porous heterogeneous materials with excellent properties are promising candidates for efficient fixation of diluted and waste CO₂. Herein, a family of mesoporous porous ionic copolymers (PIPs) was designed and prepared from the copolymerization of divinylbenzene (DVB) with vinyl-functionalized ionic liquids monomers through free radical copolymerization process. It was demonstrated that the heterogeneous PIP poly(divinylbenzene-1-allyl-tetramethylguanidinium bromide) PDVB-[AlTMG]Br-0.2 showed excellent activities in facile cycloaddition of CO₂ into cyclic carbonates without using any external co-catalysts or metal additives. The results of characterizations and quantum mechanical calculations further showed that the specic hierarchical meso-macroporous structure of PDVB-[AlTMG]Br-0.2 offered the strongest binding interaction with SO and besides had a relatively good CO₂ affinity, which results to the best cataltic activity for cycloaddition of CO₂. Moreover, PDVB-[AlTMG]Br-0.2 exhibited high activities and good reusability in cycloaddition of 15 % diluted CO₂ with various epoxides. It is believed that our work would have a great potential in energy-effective fixation of industrial combustion CO₂ into high-value organic carbonates.

1. Introduction

In the past decades, the excessive emission of carbon dioxide (CO₂) into the atmosphere may cause "greenhouse effect" and pose destructive impacts on the environment and eco-system [1–6]. Then, the development of carbon capture and utilization (CCU) technologies with obtainable valuable chemical products has been considered as a feasible approach to deal with the excessive CO₂ in the atmosphere. Take for example, coupling CO₂ with epoxides as an atom economic route can produce high value-added cyclic carbonates [7–10]. The key of this methodology is that developing highly efficient catalysts to activating inert CO₂ to react with epoxides effectively.

In the past decades, various homogenous and heterogeneous materials such as ionic liquids (ILs) [11,12], SBA-15 [13,14], metal organic frameworks (MOFs) [15,16], porous organic polymers (POPs) [9,17], and porous hypercrosslinked ionic polymers (HIPs) [18,19] have been reported and employed for the cycloaddition of epoxides with CO_2 . For example, Zhang et al. [12] reported their pioneer work that hydroxyl-functionalized ILs could form hydrogen bonds with epoxides, which showed high reactivity toward the coupling of epoxide and CO_2 without any additional co-catalyst. In order to suit the convenience of catalyst recycling and product separation, He et al. [20] prepared PEG-supported quaternary ammonium salt as heterogeneous catalysts for efficient fixation of CO_2 to cyclic carbonates at a very high pressure (8 MPa). After that, some other materials ILs-UiO-67 [16], Co/ POP [21], and HIPs-Br [18] had been examined as high active catalysts for efficient cycloaddition of CO_2 with epoxides. However, since the concentration of CO_2 is about 15 % and large amounts of N_2 are present in flue gas, the direct fixation of diluted and waste CO_2 from the industrial tail gas is an important issue and remains to be explored.

Recently, Meng and co-workers used the porphyrin based porous organic polymer Co/POP-TPP as catalysts for fixation of low-concentration CO_2 (1.0 bar, 15 % CO_2 and 85 % N_2) [21]. However, the yield of cyclic carbonates was found to be only 44 % at 0.15 bar CO_2 pressure, even adding the co-catalyst tetrabutyl ammonium bromide (TBAB). Subsequently, Zhou et al. [18] used both porous cross-linked polymer HIPs-Br and co-catalyst ZnBr₂ for cycloaddition of diluted CO_2 , in which a very long reaction time (e. g. 120 h) resulted to 90 % yield of

* Corresponding author.

¹ These authors contributed equally to this work.

https://doi.org/10.1016/j.jcou.2019.11.003

Received 4 July 2019; Received in revised form 23 October 2019; Accepted 1 November 2019 2212-9820/ © 2019 Elsevier Ltd. All rights reserved.

E-mail address: djtao@jxnu.edu.cn (D.-J. Tao).



Scheme 1. Synthetic procedure of PIPs through copolymerization of vinyl-functionalized IL monomers with DVB.

cyclic carbonates. Despite the progress of the reaction with diluted CO_2 , there are significant improvements still to be made. The absence of any co-catalysts or additives (e.g. $ZnBr_2$, KBr, TBAB) to achieve high-efficiency fixation of diluted and waste CO_2 (preferably 15 % CO_2) is highly conceived and remains challenging.

It has been reported that the protic IL can be used as an efficient media for CO₂ capture and conversion [22,23]. Also, the exploration of highly active heterogeneous catalysts always depends on the porous materials with tunable porosity [24]. Inspired by these, it is very promising and rational conceived to combine the advantages of porous polymers and protic ionic liquids to synthesize novel porous materials termed as protic ionic polymers. With the regulation of catalytic active sites and mesoporosity, such exciting porous polymers would show a great potential for efficient cycloaddition of diluted and waste CO₂ into cyclic carbonates at ambient conditions [25–27].

Herein, we report a family of mesoporous protic ionic copolymers (PIPs) as the sole heterogeneous catalyst for highly efficient cycloaddition of diluted and waste CO_2 from simulated flue gas (1.0 bar, 15 % CO_2 and 85 % N_2) without using an external base additive or co-catalyst. Scheme 1 shows the synthetic procedure of PIPs through free radical copolymerization of vinyl-functionalized IL monomers and divinylbenzene (DVB) at different molar ratios. Systematic characterizations manifested the obtained PIPs show moderate surface area, tunable mesoporosity, and rich ionic sites. The tests for cycloaddition of diluted CO_2 with epoxides featured excellent activity, good reusability, and broad substrate scope under mild conditions. Moreover, the catalytic reusability and hot filtration test of mesoporous PIP were also investigated.

2. Experimental

2.1. Materials

Tetramethylguanidine (TMG, 99 %), diazabicycloundecene (DBU, 98 %), divinylbenzene (DVB, 80 %), 3-bromopropene (98 %), 3-chloropropene (98 %), 4-vinylbenzyl chloride (90 %), 2,2'-azobis(2-methylpropionitrile) (AIBN, 98 %), tetrabutylammonium bromide (TBAB), and styrene oxide (SO, 98 %) were purchased from Shanghai Adamas Reagent Co. Ltd. CO_2 (99.999 %) and N_2 (99.999 %) were obtained from Nanchang Huasheng Gas Co. Ltd. The other chemicals were purchased from commercial suppliers and used as received without further purification.

2.2. Synthesis of vinyl-functionalized ILs monomers

shows the structures of four vinyl-functionalized IL Scheme 1 including monomers 1-(4-vinylbenzyl)-tetramethylguanidinium chloride ([VBTMG]Cl). 1-allyl-tetramethylguanidinium chloride ([AlTMG]Cl), 1-allyl-diazabicycloundecene bromide ([AlDBU]Br), and 1-allyl-tetramethylguanidinium bromide ([AlTMG]Br). In a typical synthesis of [AlTMG]Br, 3-bromopropene (1.20 g, 10 mmol) and TMG (1.15 g, 10 mmol) were dissolved in acetonitrile (10 mL) while stirring at 60 °C for 24 h under nitrogen atmosphere. After cooling to room temperature, the obtained crude salt was washed with acetone (5 \times 10 mL) and dried under vacuum condition, giving to the white solid [AlTMG]Br. The synthetic procedure of the other three vinyl-functionalized ILs were similar to that of [AlTMG]Br. These structures were confirmed by ¹H and ¹³C nuclear magnetic resonance spectra (Supplementary material, Figures S1-8).

2.3. Preparation of PIPs

As shown in Scheme 1, mesoporous PIPs were prepared by copolymerization of vinyl-functionalized ILs monomers with DVB at different molar ratios. In a typical run, [AlTMG]Br (5 mmol), DVB (25 mmol), THF (20 mL), H₂O (2.5 mL), and AIBN (0.08 g) were added to a stainless-steel autoclave. Then the reaction mixture was stirred at room temperature for 3 h followed by heating at 100 °C for 24 h. After cooling to room temperature, the filtrated precipitate was washed with tetrahydrofuran and deionized water for 5 times (5 × 10 mL), and then purified by Soxhlet extraction in methanol for 24 h to further remove possible impregnated IL monomer. Thus, the white solid powder PDVB-[AlTMG]Br-0.2 (0.2 represents the initial molar ratio value of IL monomer to DVB) was obtained and dried at 80 °C under a vacuum oven prior to use. For comparison, nonionic PDVB were synthesized by selfpolymerization of DVB in the absence of vinyl-functionalized ILs under identical conditions.

2.4. Characterizations

¹H and ¹³C NMR spectra were collected on a Bruker Ascend 400. Powder X-ray diffraction (XRD) were recorded on a Rigaku RINT-2200 X-ray diffractometer using Cu Ka radiation (40 kV, 20 mA). Fourier transform infrared (FT-IR) spectra were carried out on a NEXUS870 FT-IR spectrometer. Thermogravimetric analysis (TGA) was performed on a PerkinElmer Diamond instrument with a heating rate of 10 °C/min under nitrogen atmosphere. The nitrogen adsorption-desorption isotherms were measured on a Micromeritics TriStar II 3020 Instrument at 77 K. The BET surface area, pore size distribution, and average pore diameter were then calculated by Brunauer-Emmett-Teller (BET) and Barrett-Jovner-Halenda (BJH) method. Scanning electron microscopy (SEM) images were recorded on a HITACHI SU8020 cold field-emission instrument. Transmission electron microscopy (TEM) experiments were conducted on a JEOL JEM-2100 instrument. The X-ray photoelectron spectroscopy (XPS) spectra were performed on a Thermo ESCALAB 250 with Al Ka radiation, and the binding energies were calibrated using the C1 s peak at 284.8 eV.

2.5. Cycloaddition of CO_2 with epoxide into cyclic carbonate

A typical procedure of cycloaddition reaction is as follows: styrene oxide (SO, 10 mmol), CO2 (1 bar, balloon), and the catalyst PDVB-[AlTMG]Br-0.2 (0.05 g) were charged into a 25 ml glass flask equipped with a magnetic stirrer. The reaction mixture was stirred at 100 °C for 6 h. After the completion of reaction, the solid catalyst was removed by centrifugation and filtration. Then the reactants and products were qualitatively determined using a gas chromatography-mass spectrometer (GC-MS, Thermo Trace 1300-ISQ) and quantitatively analyzed by a gas chromatography (GC, Agilent HP7890B), where ethylbenzene was used as an internal standard. For chemical fixation of diluted CO₂, a balloon containing 15 % CO_2 mixed with 85 % N_2 in volume was used and other conditions were the same except that the reaction time was extended to 48 h. In addition, the reusability of PDVB-[AlTMG]Br-0.2 catalyst was examined in a five-run cycling experiment. The solid catalyst was successfully recovered by centrifugation, filtration, washed with ethanol for five times, and dried at 70 °C for 10 h under vacuum. Then, the recycled PDVB-[AlTMG]Br-0.2 was reused with a fresh amount of reactants for the next run under identical conditions.

2.6. Definition of styrene carbonate selectivity and yield

Qualitative analysis of GC–MS confirmed that SO reacted to give styrene carbonate (SC) and 1-phenyl-1,2-ethanediol (PE) as the unique products and no other products were detected in the reaction. Thus the yield of SC is defined as the ratio of the number of moles of SC production in the reaction to the total number of moles of SO initially added. The selectivity for SC is defined as the ratio of the number of moles of SC to the number of moles of SC and PE.

$$SC yield = \frac{moles of(SC)produced}{moles of SO initially added}$$
$$SC selectivity = \frac{mol(SC)}{mol(SC) + mol(PE)}$$

3. Results and discussion

3.1. Characterization of PIPs

Four kinds of PIPs-0.2 with the anions of Cl– and Br– were successfully prepared and they are insoluble in several common organic solvents such as ethyl acetate, ethanol, tetrahydrofuran, dimethyl sulfoxide, and N,*N*-dimethylformamide. Fig. 1 shows the XRD patterns of these four PIPs-0.2 and PDVB, indicating that all these PIPs materials



Fig. 1. XRD patterns of (a) PDVB, (b) PDVB-[4-VBTMG]Cl-0.2, (c) PDVB-[AlTMG]Cl-0.2, (d) PDVB-[AlDBU]Br-0.2, and (e) PDVB-[AlTMG]Br-0.2.

have the amorphous nature of polymer networks. As listed in Table 1, the CHN analysis indicated that the N contents of PIPs-0.2 were in the range of $3.08 \sim 4.93$ wt.%, which are equivalent in $1.08 \sim 1.17$ mmol/g IL units in the polymer frameworks. Moreover, the porosities of the obtained PIPs-0.2 were quantitatively measured by N2 adsorption analysis (Fig. 2). It is found that these four PIPs-0.2 samples exhibited hysteresis loops at the relative pressures above 0.45, displaying characteristic type IV isotherms in this range, which indicates the presence of typical mesoporous structure. PDVB-[AlTMG]Cl-0.2 sample had the largest surface area of 187 m²/g, while the surface area of PDVB-[AlTMG]Br-0.2 sample decreased to $152 \text{ m}^2/\text{g}$ because of the larger size of bromide ion. For comparison, the other four PIPs-1 samples possessing high IL contents in the polymer frameworks were further prepared by copolymerization of DVB with IL monomers at the initial molar ratio of 1:1. The results demonstrated that all the PIPs-1 displayed nonporous structures with a very small surface area (Supplementary material, Figure S9 and Table S1), indicating that more IL moieties in the polymers leads to agglomeration and results to the nonporosity of the PIPs-1 samples [24,28].

Fig. 3 shows the SEM and TEM images of PDVB-[4-VBTMG]Cl-0.2 and PDVB-[AlTMG]Br-0.2, respectively. It is indicated that these primary particles interconnect with each other to form a cross-linked framework with pore sizes ranging from several nanometers to tens of nanometers, which is confirmed by the TEM images. Moreover, compared with PDVB-[4-VBTMG]Cl-0.2, PDVB-[AlTMG]Br-0.2 has rich hierarchical meso-macroporous structure owing to its larger BET surface area. Fig. 4 shows the FT-IR spectra of ILs monomers, PIPs, and PDVB samples. It is showed that PDVB exhibited typical stretching vibrations peaks of the skeletal benzene ring at 1452, 1491, and 1515 cm⁻¹ [26,28]. These three absorption bands were also observed in PDVB-[AlDBU]Br-0.2 and PDVB-[AlTMG]Br-0.2, indicating the successful copolymerization of IL monomer with DVB. In addition, the IL [AlTMG]Br monomer and PDVB-[AlTMG]Br-0.2 showed the N-H bending vibration at 1561 cm^{-1} [29], whereas the IL [AlDBU]Br monomer and PDVB-[AlDBU]Br-0.2 did not have.

The chemical states of the C, N, and Br species in PIP-0.2 materials were characterized in detail by XPS. The full-range XPS survey confirmed the existence of C, N, and Br species in PDVB-[AlTMG]Br-0.2 and PDVB-[AlDBU]Br-0.2 (Supplementary material, Figure S10). Moreover, as shown in Fig. 5A, the N 1s spectra of PDVB-[AlTMG]Br-0.2 and PDVB-[AlDBU]Br-0.2 materials were deconvoluted into two peaks. The peaks at the binding energies of 400.0 and 401.1 eV can be attributed to pyrrolic N and quaternary N, respectively [30,31]. In the bromide region (Fig. 5B), the binding energies at 66.8 eV and 67.8 eV

Table 1

The physical properties of PIPs-0.2 samples.

Samples	N content ^a (wt.%)	IL/DVB units molar ratio	$S_{BET}^{b}\left(m^2/g\right)$	V_{P}^{c} (cm ³ /g)	D _P ^d (nm)
PDVB-[AITMG]Br-0.2	4.69	0.196:1	152	0.98	18.7
PDVB-[AITMG]Cl-0.2	4.93	0.198:1	187	0.65	10.1
PDVB-[AIDBU]Br-0.2	3.08	0.204:1	91	0.46	10.6
PDVB-[4-VBTMG]Cl-0.2	4.52	0.197:1	73	0.79	7.5

^a Measured by elemental analysis.

^b BET surface area.

^c Total pore volume.

^d Average pore size.



Fig. 2. N₂ adsorption-desorption isotherms of PIPs-0.2 materials.

were assigned to Br $3d_{5/2}$ and Br $3d_{3/2}$ of PDVB-[AlDBU]Br, respectively [18,28,32]. Noteworthy, PDVB-[AlTMG]Br-0.2 showed the higher binding energy of Br 3d at 67.1 eV and 68.2 eV. The enhanced binding energy was largely ascribed to the decreased electron density of Br– as well as the simultaneous presence of H-bonding interaction of NH-Br in PDVB-[AlTMG]Br-0.2. In addition, the thermogravimetric analysis test further showed that these four PIP-0.2 materials as well as the ILs monomer and PDVB raw material exhibited high thermal stability (Supplementary material, Figures S11 and S12). Moreover, the DTG curves in Figure S12 further showed that the degradation process of these four as-prepared PIPs materials could be divided in two steps. The first step is degrading of ionic liquids segments at the temperature ranging from $30 \sim 400$ °C, and the second step is the decomposition of



Fig. 4. FT-IR spectra of PDVB, ILs monomers, and PIPs-0.2 samples.

PDVB during the temperature from $400 \sim 800$ °C.

3.2. Catalytic evaluation for cycloaddition of pure CO_2

The fixation of pure CO_2 into styrene carbonate (SC) through the cycloaddition of CO_2 with SO was chosen as model reaction to evaluate the catalytic activity of the as-prepared PIPs-0.2 materials. The reaction conditions were initially optimized by screening the reaction parameters such as temperature, catalyst loading and reaction time (Supplementary material, Table S2). It was indicated that PDVB-[AlTMG]Br-0.2 resulted to a 99 % yield of SC (Table 2, entry 1). Also, the characterization results of ¹H NMR and ¹³C NMR confirmed the



Fig. 3. (a, b) SEM and (c) TEM images of PDVB-[4-VBTMG]Cl-0.2. (d, e) SEM and (f) TEM images of PDVB-[AlTMG]Br-0.2.



Fig. 5. N 1s and Br 3d spectra of PIP-0.2 materials.

Table 2Cycloaddition of pure CO_2 with SO using various catalysts.^a.

$\bigcup_{so}^{0} + co_{2} \longrightarrow \bigcup_{sc}^{0}$					
Entry	Catalysts	Yield (%)	Selectivity (%)	TOF (h^{-1})	
1	PDVB-[AlTMG]Br-0.2	99	99	29.6	
2^{b}	PDVB-[AlTMG]Br-0.2	91	99	1.7	
3	PDVB-[AlTMG]Cl-0.2	65	99	15.8	
4	PDVB-[AlDBU]Br-0.2	43	99	9.8	
5	PDVB-[4-VBTMG]Cl-0.2	54	95	11.2	
6 ^c	PDVB-[AlTMG]Tf2N-0.2	11	78	3.3	
7 ^d	PDVB + TBAB	38	96	4.1	
8	PDVB	-	-	-	
9	-	-	-	-	

^a Reaction conditions: SO (1.2 g, 10 mmol), CO₂ (balloon, 1 bar), catalyst (50 mg, 1 mmol/g halogen sites), 100 °C, 6 h. Turnover frequency (TOF) = [mol (product)]/[mol (halogen sites) × (reaction time)]. ^bRoom temperature, 96 h. ^cTf₂N is bis[(trifluoromethyl)sulfonyl] imide anion. ^dThe same molar number of halogen sites in PDVB-[AlTMG]Br-0.2.

structure of SC (Figures S13 and S14), and the isolated yield of SC was 91 %. Then the optimum conditions were set as reaction temperature of 100 °C, reaction time of 6 h, and catalyst amount of 4.2 wt.% (based on the mass of SO). Notably, PDVB-[AlTMG]Br-0.2 also catalyzed the cycloaddition reaction of pure CO₂ with SO smoothly even at room temperature with a 91 % yield of SC (Table 2, entry 2). However, the other three PIPs-0.2 were found to have relatively low catalytic activities for cycloaddition of pure CO₂ under optimum conditions (Table 2, entries 3–5). Further, PDVB-[AlTMG]Tf₂N-0.2 induced only 11 % SC yield (Table 2, entry 6), again indicating the key role of halogenated anion Br⁻. A SC yield of 38 % was obtained in the presence of PDVB catalyst and TBAB co-catalyst (Table 2, entry 7). Also, the cycloaddition reaction of CO₂ with SO could not take place using PDVB or without the catalyst (Table 2, entries 7,8).

3.3. Probing into the catalytic active sites

In order to clarify the excellent catalytic performance of PDVB-[AlTMG]Br-0.2, CO_2 uptake capacity of these four PIPs-0.2 was measured to study their CO_2 affinities. It is seen from Figure S17 that PDVB-[AlTMG]Br-0.2 and PDVB-[AlTMG]Cl-0.2 had relatively good CO_2 affinity in compared to the other two PIP-0.2. Also, as listed in Table S3, the CO_2 uptake performance of PDVB-[AlTMG]Br-0.2 had reached a comparable level respect to the reported results in the previous literatures [18,24,28]. Furthermore, we had employed density functional calculations at the M06/6-311+G (2d, 2p) level to investigate the binding strengths of corresponding ILs monomers with CO₂ and SO, respectively. It is seen from Fig. 6 that the binding strength of [AlTMG]Cl-0.2 with CO₂ is slightly larger than the binding strength of [AlTMG]Br with CO₂, verifying the experiment results shown in Figure S17 that PDVB-[AlTMG]Cl-0.2 has better CO2 affinity than PDVB-[AlTMG]Br-0.2. However, as shown in Figure S18, [AlTMG]Br-0.2 showed much larger binding interaction with SO than [AlTMG]Cl-0.2. The binding interaction of allyltrimethylammonium bromide ([AlTMA] Br) with CO₂ and SO was also found to be much lower than that of [AlTMG]Br, showing the important role of guanidinium moieties of [AlTMG]Br. As well known, many previous works [18,23,33] demonstrated that the nucleophilic ring-opening step of epoxides is the ratedetermining step of cycloaddition reaction of CO₂. Thereby, owing to the strongest binding strength of the IL monomer [AlTMG]Br-0.2 with SO, PDVB-[AlTMG]Br-0.2 exhibited the best catalytic activity for cycloaddition reaction of CO₂ among these four PIPs-0.2, although the CO₂ affinity of Br anion is slightly weaker than that of Cl anion.

In addition, the effect of surface area of PDVB-[AlTMG]Br samples on the cycloaddition of CO2 was also explored. The results are listed in Table S4. It is found that PDVB-[AlTMG]Br-0.1 and PDVB-[AlTMG]Br-0.2 had larger surface areas, but the catalytic activity of PDVB-[AlTMG] Br-0.2 was much higher than PDVB-[AlTMG]Br-0.1, which is due to the low concentration active sites (Br-) in PDVB-[AlTMG]Br-0.1. When the copolymerization of the IL monomer [AlTMG]Br with DVB was set as the initial molar ratio of 0.3, 0.5, and 1, the corresponding samples PDVB-[AlTMG]Br-0.3, PDVB-[AlTMG]Br-0.5, and PDVB-[AlTMG]Br-1 displayed nonporous structures with a very small surface area and exhibited very low CO2 adsorption capacties because of unfavorable exposure of Br⁻ sites (Supplementary material, Figure S17). As a result, these PIP samples with a small surface area had an an obvious decrease in catalytic activities. Therefore, the specic hierarchical meso-macroporous structure of PDVB-[AlTMG]Br-0.2 offers high SO- and CO2philicity and good dispersion of Br- sites, and thus shows the highest catalytic activity for cycloaddition of CO₂.

3.4. Cycloaddition of dilute CO_2 from simulated flue gas

For the viewpoints of industrial application and pollution reduction, it is very important and attractive to directly convert diluted and waste CO_2 in flue gas into valuable chemicals. Then the PIPs-0.2 materials were studied to test their catalytic activities in cycloaddition of diluted and waste CO_2 from a simulated flue gas (1 bar, 15 % $CO_2/85$ % N₂). The results are shown in Fig. 7. It is obvious that PDVB-[AlTMG]Br-0.2 maintained high catalytic activity for cycloaddition of SO with 15 % diluted CO_2 . By contrast, the other three PIPs-0.2 induced very low SC



Fig. 6. (a) $[AITMG]Br-CO_2$, (b) $[AITMG]CI-CO_2$, (c) $[AIDBU]Br-CO_2$, (d) $[4-VBTMG]CI-CO_2$, and (e) $[AITMA]Br-CO_2$. ΔH of interaction are also shown. C gray, O red, N blue, Br vermilion, Cl green.



Fig. 7. The catalytic performance of PIP-0.2 materials for cycloaddition of 15 % diluted CO_2 with SO. Reaction conditions: SO (1.2 g, 10 mmol), simulated flue gas balloon (1.0 bar, 15 % CO_2 and 85 % N_2), catalyst (50 mg, 1 mmol/g halogen sites), 100 °C, 48 h.

yields, when the concentration of CO_2 was reduced to 15 % in volume. Moreover, we further screened the optimized reaction parameters for fixation of 15 % CO₂, and the optimized conditions were set as the temperature of 100 °C and reaction time of 48 h to obtain a 99 % yield of SC (Supplementary material, Table S5, entries 1–7). In addition, the impact of O₂ and H₂O on the cycloaddition of diluted CO₂ was studied (Supplementary material, Table S5, entries 8,9). The results indicated that the yield for cycloaddition of SO with the simulated flue gas (1 bar, 15 % CO₂, 79 % N₂, and 6 % O₂) had a slight drop, and SC was obtained with a yield of 92 % at 100 °C and 48 h. However, the amount of water has a negative effect on the cycloaddition reaction. When 1 % of water vapor was added to the reaction mixture, the conversion of SO was 96 % but the selectivity of SC obviously reduced to 79 %. This is because that SO is favorably hydrolyzed to 1-phenyl-1,2-ethanediol in the presence of water.

Subsequently, we further explored the cycloaddition of various epoxides with pure and diluted CO_2 (100 % CO_2 or 15 % CO_2/85 % N_2) using PDVB-[AlTMG]Br-0.2 as the solo catalyst. The results are summarized in Table 3. It is obvious that all kinds of epoxides examined could be converted to the corresponding cyclic carbonates with high yields of $85 \sim 99$ % (Table 3, entries 1–7). The ¹H NMR and ¹³C NMR spectra results of some typical cyclic carbonates were also shown in Figures S13-S16). Compared with styrene oxide, the yield for cycloaddition of alkene oxides had a slight drop. This is because that the electron donation effect of alkene group may enhance the electronegativity of the carbon center and would deactivate the ring-opening process. Moreover, to the best of our knowledge, it is still extremely difficult for a heterogeneous catalyst to achieve good yield for cycloaddition of cyclohexene oxide with 15 % CO2 [34]. Clearly, PDVB-[AlTMG]Br-0.2 catalyzed the cycloaddition of cyclohexene oxide to obtain more than 85 % yield of corresponding cyclic carbonates (Table 3, entry 8). These results demonstrate the superiority of PDVB-[AlTMG]Br-0.2 in chemical fixation of 15 % diluted CO2 in the simulated flue gas containing 15 % CO_2 and 85 % N_2 .

Table 3				
Cycloaddition of dilu	ted CO2 with vario	us epoxides using PDV	/B-[AlTMG]Br-0.2 as	catalyst.ª.

Entry	Substrate	Product	CO ₂ (bar)	Time (h)	Yield (%)	Selectivity (%)	TOF (h^{-1})
1	<u> </u>		1 0.15	6 48	99 99	99 99	29.6 3.7
2	C4H9	CHL O	1 0.15	6 48	98 95	99 99	29.3 3.5
3	O C ₁₂ H ₂₅	O-O Curller O	1 0.15	6 72	96 90	99 99	28.7 2.2
4	a		1 0.15	6 48	96 92	99 99	28.7 3.4
5			1 0.15	6 48	99 96	99 99	29.6 3.6
6			1 0.15	6 48	97 99	99 99	28.9 3.7
7	γ^{o}	\rightarrow^{0}	1 0.15	6 48	96 93	99 99	28.7 3.5
8	ο		1 0.15	17 96	85 90	99 99	8.9 1.7
9	Br		1 0.15	6 72	89 86	99 99	26.6 2.4

^a Reaction conditions: epoxide (1.2 g, 10 mmol), catalyst (50 mg, 1 mmol/g halogen sites), 100 °C. Turnover frequency (TOF) = [mol (product)]/[mol (halogen sites) × (reaction time)].

3.5. Comparison of the performance of PIPs with the previous results

For comparison, the cycloaddition of pure or diluted CO2 into cyclic carbonates under different reaction conditions according to previous works were also summarized in Table S6 in the Supplementary material. It is demonstrated that for those reactions in absence of any cocatalyst, organic solvent or other metallic additives, either the yields of SC are relatively low or a harsh condition (e.g. 30 bar, 150 °C) is needed. By contrast, while by using PDVB-[AlTMG]Br-0.2 as catalyst, the reaction can be conducted to obtain a 99 % yield of SC under mild conditions (1.0 bar, 100 °C) without the addition of any co-catalysts and metal additives. Moreover, it is also showed that previous results relative to the heterogeneous cycloaddition of 15 % CO2 relied on an extremely long reaction time and adding either a halogenated additive TBAB or a co-catalyst ZnBr₂. In addition, the TOF value of PDVB-[AlTMG]Br-0.2 in cycloaddition of CO2 was further superior to most of catalysts in the previous literatures, showing its outstanding catalytic activity. Therefore, PDVB-[AlTMG]Br-0.2 is considered to be the outstanding metal-solvent-additive free heterogeneous catalyst for highly efficient cycloaddition of pure or diluted CO₂ under mild conditions.

3.6. Catalyst recycling test

Recycling tests were carried out to evaluate the reusability of PDVB-[AlTMG]Br-0.2 in the cycloaddition of CO₂ with epoxide under atmospheric pressure. After five runs, the catalyst performance still keeps initial activity (Fig. 8). Further, compared with fresh PDVB-[AlTMG]Br-0.2, the FT-IR spectrum of the reused one after 5th run reveal the wellpreserved characteristic peaks of the skeletal benzene ring from PDVB at 1452 and 1491 cm⁻¹, and the NH– bending vibration from TMG at 1561 cm⁻¹ (Supplementary material, Figure S19), reflecting good reusability of PIPs materials in the cycloaddition reaction. Hot filtration test was also employed to investigate the heterogeneous nature of PDVB-[AlTMG]Br-0.2 and check whether there existed the homogeneous active species after leaching the PIPs catalysts. The cycloaddition reaction of CO₂ with SO under atmospheric pressure was



Fig. 8. Reusability test of PDVB-[AlTMG]Br-0.2 in five runs. Reaction conditions: SO (1.2 g, 10 mmol), CO₂ (balloon, 1 bar), catalyst (50 mg, 1 mmol/g halogen sites), 100 °C, 6 h.

prematurely stopped after 3 h at 100 $^{\circ}$ C. Solid catalyst was separated by filtration, and the filtrate was rejected into the reactor for further reaction (Supplementary material, Figure S20). Subsequent detection showed that cycloaddition reaction was no longer proceeded after the removal of catalyst, which confirms the absence of leaching active site of PIPs in the recycle test.

4. Conclusion

In summary, we designed and prepared a family of mesoporous PIPs-0.2 materials through the copolymerization process of DVB with four vinyl-functionalized ILs monomers. It was found that the specic hierarchical meso-macroporous structure of PDVB-[AlTMG]Br-0.2

exhibited the strongest binding interaction with SO and also had a relatively good CO₂ affinity. Then PDVB-[AlTMG]Br-0.2 showed high catalytic activities in cycloaddition of various epoxides with 15 % diluted CO₂ in 15 % CO₂/ 85 % N₂ without using any external co-catalysts or metal additives. All kinds of epoxides could be converted into the corresponding cyclic carbonates with high yields of 85~99 %. Furthermore, PDVB-[AlTMG]Br-0.2 could be reused at least five times without an obvious decrease in catalytic performance. This work provides a promising heterogeneous candidate for fixation of diluted CO₂ and shows a great potential in making use of flue gas as CO₂ source.

Declaration of Competing Interest

The authors declare no competing financial interest.

Acknowledgments

We thank the National Natural Science Foundations of China (Nos. 21566011, 31570560), the Natural Science Foundation of Jiangxi Province (No.20192ACBL20025), the Jiangxi Province Sponsored Programs for Distinguished Young Scholars (No. 20162BCB23026), and the Science & Technology Programs of Jiangxi Province Department of Education (No. GJJ160272) for financial support. It is also supported by the Foundation of State Key Laboratory of Coal Combustion (FSKLCCA1809).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcou.2019.11.003.

References

- C. Wang, X. Luo, H. Luo, D.E. Jiang, H. Li, S. Dai, Tuning the basicity of ionic liquids for equimolar CO2 capture, Angew. Chem. Int. Ed. 50 (21) (2011) 4918–4922.
- [2] F.F. Chen, K. Huang, J.P. Fan, D.J. Tao, Chemical solvent in chemical solvent: a class of hybrid materials for effective capture of CO2, AIChE J. 64 (2) (2018) 632–639.
- [3] E.M. Maya, E. Rangel-Rangel, U. Díaz, Marta Iglesias. Efficient cycloaddition of CO2 to epoxides using novel heterogeneous organocatalysts based on tetramethylguanidine-functionalized porous polyphenylenes, J. CO₂ Util. 25 (2018) 170–179.
- [4] C. Calabrese, L.F. Liotta, E. Carbonell, F. Giacalone, M. Gruttadauria, C. Aprile, Imidazolium-functionalized carbon nanohorns for the conversion of carbon dioxide: unprecedented increase of catalytic activity after recycling, ChemSusChem 10 (6) (2017) 1202–1209.
- [5] O. Coulembier, S.B. Moins, V. Lemaur, R. Lazzaroni, P. Dubois, Efficiency of DBU/ iodine cooperative dual catalysis for the solvent-free synthesis of five-membered cyclicc arbonates unde ratmospheric CO2 pressure, J. CO₂ Util, 10 (2015) 7–11.
- [6] C. Calabrese, F. Giacalone, C. Aprile, Hybrid catalysts for CO2 conversion into cyclic carbonates, Catalysts 9 (4) (2019) 325.
- [7] V. Laserna, G. Fiorani, C.J. Whiteoak, E. Martin, E. Escudero-Adán, A.W. Kleij, Carbon dioxide as a protecting group: highly efficient and selective catalytic access to cyclic cis-diol scaffolds, Angew. Chem. Int. Ed. 53 (39) (2014) 10416–10419.
- [8] G.W. Coates, D.R. Moore, Discrete Metal-based catalysts for the copolymerization of CO2 and epoxides: discovery, reactivity, optimization, and mechanism, Angew. Chem. Int. Ed. 43 (48) (2004) 6618–6639.
- [9] A. Jawad, F. Rezaei, A.A. Rownaghi, Porous polymeric hollow fibers as bifunctional catalysts for CO2 conversion to cyclic carbonates, J. CO₂ Util. 21 (2017) 589–596.
- [10] X.H. Song, Y. Wu, D. Pan, J. Zhang, S. Xu, Li. Gao, R. Wei, G. Xiao, Functionalized DVB-based polymer catalysts for glycerol and CO2 catalytic conversion, J. CO₂ Util. 28 (2018) 326–334.
- [11] V.B. Saptal, B.M. Bhanage, Bifunctional ionic liquids derived from biorenewable sources as sustainable catalysts for fixation of carbon dioxide, ChemSusChem 10 (6) (2017) 1145–1151.
- [12] J. Sun, S. Zhang, W. Cheng, J. Ren, Hydroxyl-functionalized ionic liquid: a novel

efficient catalyst for chemical fixation of CO2 to cyclic carbonate, Tetrahedron Lett. 49 (22) (2008) 3588–3591.

- [13] C. Calabrese, L.F. Liotta, F. Giacalone, M. Gruttadauria, C. Aprile, Supported POSS based materials as highly active organocatalysts for the conversion of CO2, ChemCatChem 11 (1) (2019) 560–567.
- [14] W. Zhang, Q. Wang, H. Wu, P. Wu, M. He, A highly ordered mesoporous polymer supported imidazolium-based ionic liquid: an efficient catalyst for cycloaddition of CO2 with epoxides to produce cyclic carbonates, Green Chem. 16 (11) (2014) 4767–4774.
- [15] X. Zhou, Y. Zhang, X. Yang, L. Zhao, G. Wang, Functionalized Irmof-3 as efficient heterogeneous catalyst for the synthesis of cyclic carbonates, J. Mol. Catal. A Chem. 361–362 (2012) 12–16.
- [16] L.G. Ding, B.J. Yao, W.L. Jiang, J.T. Li, Q.J. Fu, Y.A. Li, Z.H. Liu, J.P. Ma, Y.B. Dong, Bifunctional imidazolium-based ionic liquid decorated Uio-67 type MOF for selective CO2 adsorption and catalytic property for CO2 cycloaddition with epoxides, Inorg. Chem. 56 (4) (2017) 2337–2344.
- [17] T. Ying, X. Tan, Q. Su, W. Cheng, L. Dong, S. Zhang, Polymeric ionic liquids tailored by different chain groups for the efficient conversion of CO2 into cyclic carbonates, Green Chem. 21 (9) (2019) 2352–2361.
- [18] J. Li, D. Jia, Z. Guo, Y. Liu, Y. Lyu, Y. Zhou, J. Wang, Imidazolinium based porous hypercrosslinked ionic polymers for efficient CO2 capture and fixation with epoxides, Green Chem. 19 (11) (2017) 2675–2686.
- [19] J. Wang, W. Sng, G. Yi, Y. Zhang, Imidazolium salt-modified porous hypercrosslinked polymers for synergistic CO2 capture and conversion, Chem. Commun. 51 (60) (2015) 12076–12079.
- [20] Y. Du, J. Wang, J. Chen, F. Cai, J. Tian, D. Kong, L. He, A poly(ethylene glycol)supported quaternary ammonium salt for highly efficient and environmentally friendly chemical fixation of CO2 with epoxides under supercritical conditions, Tetrahedron Lett. 47 (2006) 1271–1275.
- [21] Z. Dai, Q. Sun, X. Liu, C. Bian, Q. Wu, S. Pan, L. Wang, X. Meng, F. Deng, F.S. Xiao, Metalated porous porphyrin polymers as efficient heterogeneous catalysts for cycloaddition of epoxides with CO2 under ambient conditions, J. Catal. 338 (2016) 202–209.
- [22] Z. Zhang, F. Fan, H. Xing, Q. Yang, Z. Bao, Q. Ren, Efficient synthesis of cyclic carbonates from atmospheric CO2 using a positive charge delocalized ionic liquid catalyst, ACS Sustainable Chem. Eng. 5 (4) (2017) 2841–2846.
- [23] T. Wang, D. Zheng, J. Zhang, B. Fan, Y. Ma, T. Ren, L. Wang, J. Zhang, Protic pyrazolium ionic liquids: an efficient catalyst for conversion of CO2 in the absence of metal and solvent, ACS Sustainable Chem. Eng. 6 (2) (2018) 2574–2582.
- [24] X. Wang, Y. Zhou, Z. Guo, G. Chen, J. Li, Y. Shi, Y. Liu, J. Wang, Heterogeneous conversion of CO2 into cyclic carbonates at ambient pressure catalyzed by ionothermal-derived meso-macroporous hierarchical poly(ionic liquid)s, Chem. Sci. 6 (12) (2015) 6916–6924.
- [25] J. Yuan, D. Mecerreyes, M. Antonietti, Poly(ionic liquid)s: an update, Prog. Polym. Sci. 38 (7) (2013) 1009–1036.
- [26] R.Q. Fu, J.J. Woo, S.J. Seo, J.S. Lee, S.H. Moon, Sulfonated polystyrene/polyvinyl chloride composite membranes for pemfc applications, J. Membr. Sci. 309 (1) (2008) 156–164.
- [27] M. Carafa, E. Mesto, E. Quaranta, DBU-promoted nucleophilic activation of carbonic acid diesters, Eur. J. Org. Chem. 2011 (13) (2011) 2458–2465.
- [28] Z. Guo, Q. Jiang, Y. Shi, J. Li, X. Yang, W. Hou, Y. Zhou, J. Wang, Tethering dual hydroxyls into mesoporous poly(ionic liquid)s for chemical fixation of CO2 at ambient conditions: a combined experimental and theoretical study, ACS Catal. 7 (10) (2017) 6770–6780.
- [29] I. Cota, R. Chimentao, J. Sueiras, F. Medina, The DBU-H2O complex as a new catalyst for aldol condensation reactions, Catal. Commun. 9 (11) (2008) 2090–2094.
- [30] R. Fang, R. Luque, Y. Li, Selective aerobic oxidation of biomass-derived HMF to 2,5diformylfuran using a MOF-derived magnetic hollow Fe–Co nanocatalyst, Green Chem. 18 (10) (2016) 3152–3157.
- [31] F. Liu, L. Wang, Q. Sun, L. Zhu, X. Meng, F.S. Xiao, Transesterification catalyzed by ionic liquids on superhydrophobic mesoporous polymers: heterogeneous catalysts that are faster than homogeneous catalysts, J. Am. Chem. Soc. 134 (41) (2012) 16948–16950.
- [32] P. Bhunia, E. Hwang, M. Min, J. Lee, S. Seo, S. Some, H. Lee, A non-volatile memory device consisting of graphene oxide covalently functionalized with ionic liquid, Chem. Commun. 48 (6) (2012) 913–915.
- [33] Z. Xue, J. Jiang, M.G. Ma, M.F. Li, T. Mu, Gadolinium-based metal-organic framework as an efficient and heterogeneous catalyst to activate epoxides for cycloaddition of CO2 and alcoholysis, ACS Sustainable Chem. Eng. 5 (3) (2017) 2623–2631.
- [34] W. Wang, C. Li, L. Yan, Y. Wang, M. Jiang, Y. Ding, Ionic liquid/Zn-PPh3 integrated porous organic polymers featuring multifunctional sites: highly active heterogeneous catalyst for cooperative conversion of CO2 to cyclic carbonates, ACS Catal. 6 (9) (2016) 6091–6100.