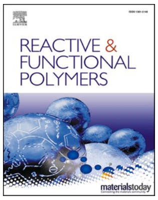
Reactive and Functional Polymers 165 (2021) 104976

Contents lists available at ScienceDirect

Reactive and Functional Polymers

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



Perspective Article

Rosin-based porous heterogeneous catalyst functionalized with hydroxyl groups and triazole groups for CO_2 chemical conversion under atmospheric pressure condition

Shilin Lai, Jinbin Gao, Xingquan Xiong *

College of Materials Science and Engineering, University of Huaqiao, Xiamen 361021, China

ARTICLE INFO

Keywords:
Rosin-based porous polymers
CO_2
Cyclic carbonates
Atmospheric pressure

ABSTRACT

Development of efficient, green and recyclable heterogeneous catalysts for the chemical conversion of CO_2 into cyclic carbonates with excellent yields under atmospheric pressure condition is still a very challenging task. Herein, a class of biomass-derived hyper-cross-linked porous heterogeneous catalysts MPAc-Br and MPAc-OH-Br, based on easily available and sustainable rosin, was synthesized by Friedel–Crafts polymerization and the further *N*-alkylation of triazole groups. Compared with MPAc-Br, the bifunctional catalyst MPAc-OH-Br (bearing triazole IL groups and -OH groups) exhibited higher catalytic activity for direct chemical conversion of CO_2 into cyclic carbonates (up to 99% yields) under metal-, solvent-free and atmospheric pressure conditions. The rosin-based porous molecular structure and bifunctional groups on the surface of MPAc-OH-Br played a very important role in the promoting the cycloaddition of CO_2 with epoxides under the optimal conditions. Furthermore, MPAc-OH-Br exhibited good stability and reusability (96% yield after 10 recycles).

1. Introduction

Since the industrial revolution, the mass consumption of fossil fuels and a large number of carbon dioxide (CO_2) emissions have led to the increasing concentration of CO_2 in the air year by year, seriously destroying the natural carbon cycle, resulting in a series of serious environmental and social problems [1,2]. Thus, the chemical fixation and conversion of CO_2 into commercially relevant fine chemicals has attracted much public attention since CO_2 is a cheap, easily available, and environmentally friendly renewable C1 resource [3–7]. The chemical conversion of CO_2 can not only reduce CO_2 emissions, but also provide a green technological route, which is of great significance for green and sustainable social development [8–10]. Among them, the chemical conversion of CO_2 with terminal epoxides into cyclic carbonates through a cycloaddition reaction is the most promising strategy due to 100% atom economy [11–16]. The cyclic carbonate products are green solvents in the field of catalysis, and used extensively as precursors in organic synthesis as important intermediates in the synthesis of fine chemicals.

However, the kinetic inertness and thermodynamic stability of CO_2 make it a great challenge to activate this greenhouse gas [17–19]. Thus, the development of highly efficient catalysts for the production of value-added cyclic carbonates from CO_2 is currently a hot point from the viewpoint of green synthesis chemistry. Up to now, a series of catalysts have been developed for the production of cyclic carbonates through CO_2 cycloaddition, such as ionic liquids (ILs) [20–22], metal complex catalysts [23–25], porous materials [26–31], bifunctional dendrimer [32], organocatalysts [33–35]. Although most of the catalytic systems show good to excellent yields of cyclic carbonates, high CO_2 pressure are always needed in these studies. To further enhance the efficiency of chemical fixation of CO_2 with epoxides into cyclic carbonates relatively mild reaction conditions, great efforts have been focused on the preparation of highly efficient and sustainable catalytic systems [36,37].

Task-specific ionic liquids (ILs), regarded as efficient and green homogeneous catalysts, have been extensively used in the field of chemical fixation of CO_2 into cyclic carbonates. The functional ILs, especially the —NH_2, —OH, or —COOH functionalized ones, could exhibit obviously enhanced catalytic activities for the chemical fixation of CO_2 with epoxides. Unfortunately, these homogenous ILs catalysts are often expensive, difficult biodegradable, sometimes toxic, which limit their industrial applications. Furthermore, the homogenous ILs catalysts are minimally recyclable and, therefore, are not desirable for industrial

---

* Corresponding author.
E-mail address: xxqluli@hqu.edu.cn (X. Xiong).

https://doi.org/10.1016/j.reactfunctpolym.2021.104976
Received 5 May 2021; Received in revised form 4 July 2021; Accepted 7 July 2021
Available online 10 July 2021
1381-5148/© 2021 Elsevier B.V. All rights reserved.

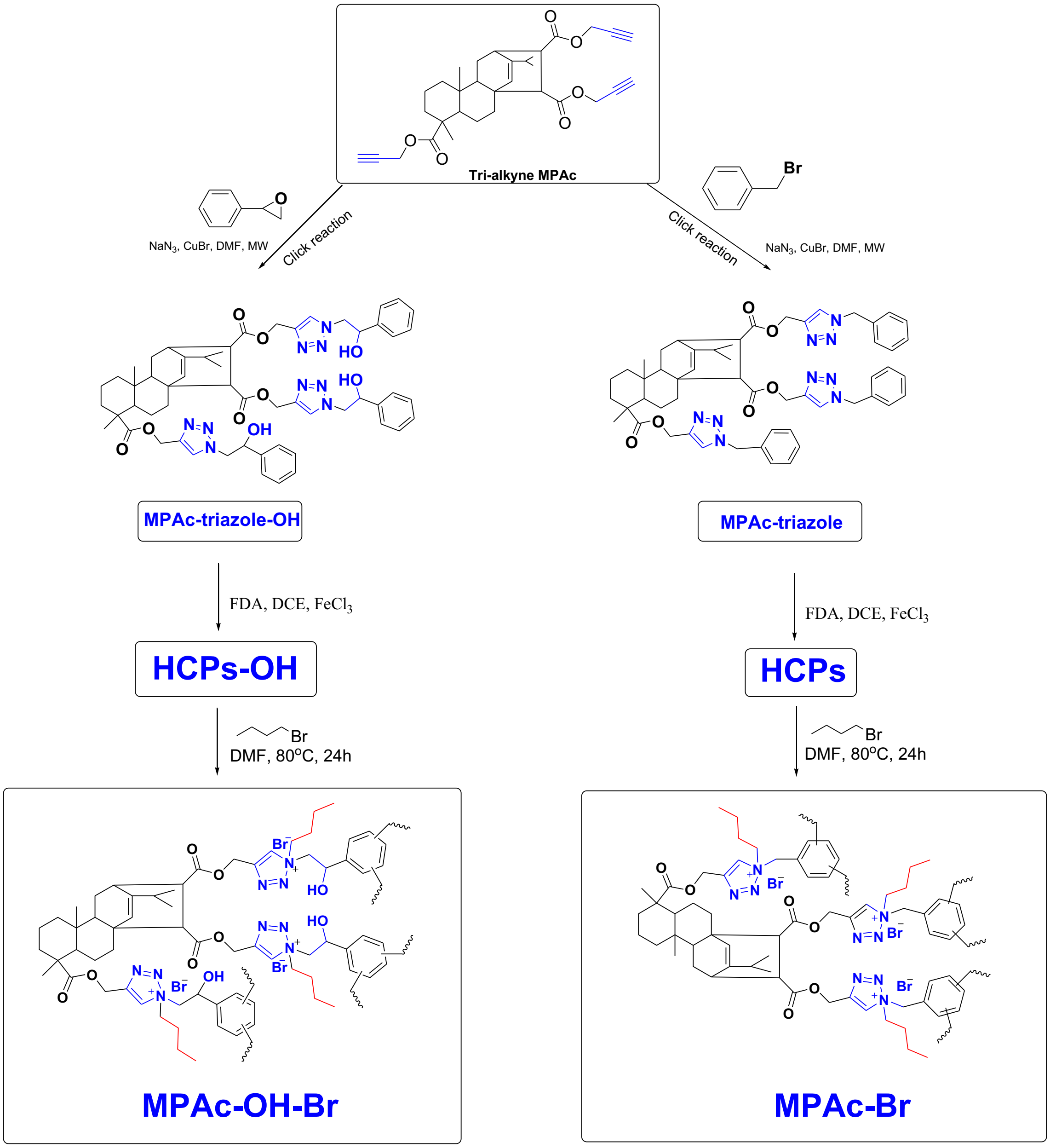
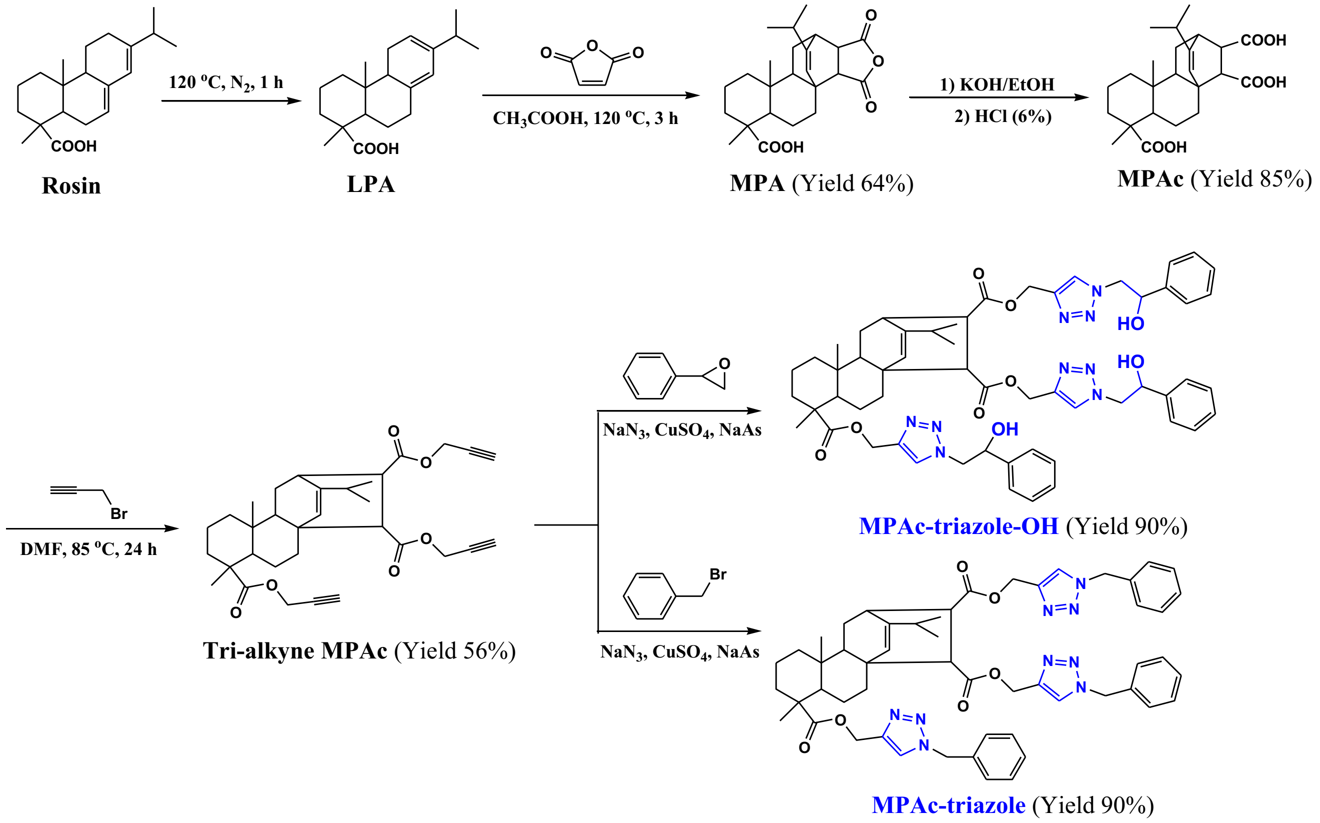


Fig. 1. Schematic illustration of the fabrication of rosin-based hyper-cross-linked porous heterogeneous catalysts MPAc-OH-Br and MPAc-Br *via* the Friedel–Crafts reaction, followed by post-modification with n-butyl bromide using the triazole groups on the surface.

purposes. To solve the above problems, an alternative to homogenous ILs catalysts in cyclic carbonates synthesis requires further research. Nowadays, porous ionic networks (PINs) have been widely used in the field of functional materials [38–41]. PINs present some of the unique properties of ILs (thermal/chemical stability, and ionic conductivity) together with excellent catalytic performance. So far, several PINs catalysts have been reported as efficient catalysts for cyclic carbonate production [42–47]. However, all the PINs catalysts are made from non-renewable sources, which will result in environmental problem and cost issue. Therefore, it is still highly desirable to develop low-cost, highly efficient, environmentally friendly but easily prepared heterogeneous catalysts for chemical fixation of CO_2 with epoxides.

With the declining petroleum resources and associated the environmental problems caused by the rapid industrial development, the design and synthesis of sustainable bio-based materials has received widespread attention both in academia and industry [48]. In recent years, due to the rising environmental awareness and depletion of fossil resources, as one of the most abundant natural resources, rosin has been extensively used as raw material in the organic chemistry because of their renewable and low-cost properties. Compared with the obvious achievements made with traditional polymeric materials derived from fossil oil, the development of polymers prepared from renewable natural resources has been limited. As a kind of important renewable natural resource, rosin and its derivatives have been used widely in the field of modern chemical production industry as chemical raw materials, which not only enhances the value of natural resource but also reduces the dependence on fossil oil resources [49,50]. The potential for chemical modification of rosin and its derivatives also makes them valuable bio-based monomers in the synthesis of polymeric materials. Therefore, rosin-based monomers are potential substitutes for the petroleum-based monomers used in polymers.

In continuation of our efforts to develop efficient and cost-effective approaches for the synthesis of cyclic carbonates [51,52], we report here a new kind of bifunctional hyper-cross-linked porous



Scheme 1. Synthesis of bio-based monomer MPAc-triazole-OH and MPAc-triazole from rosin.

heterogeneous catalyst MPAc-OH-Br (bearing triazole IL groups and —OH groups) from rosin for green and low-cost preparation of cyclic carbonates from CO_2 and epoxides under metal-, solvent-free and atmospheric pressure conditions (Fig. 1). In addition, the porous polymer MPAC-Br without hydroxyl functionalization was used as a contrast. Obviously, the rosin-based porous molecular structure and bifunctional groups on the surface of MPAc-OH-Br played a key role in the promoting the cycloaddition of CO_2 with epoxides under the optimal conditions. The inherent rigid structure of rosin-based porous heterogeneous catalyst can not only promote gas adsorption process in an entropic manner, but only enhance the thermal and chemical stabilization of material. Furthermore, the porous structure increases the specific surface area of MPAc-OH-Br, and the hydroxyl groups are able to coordinate to the epoxide through hydrogen bonding and enhance the activity for this reaction.

2. Experimental section

2.1. Chemicals and reagents

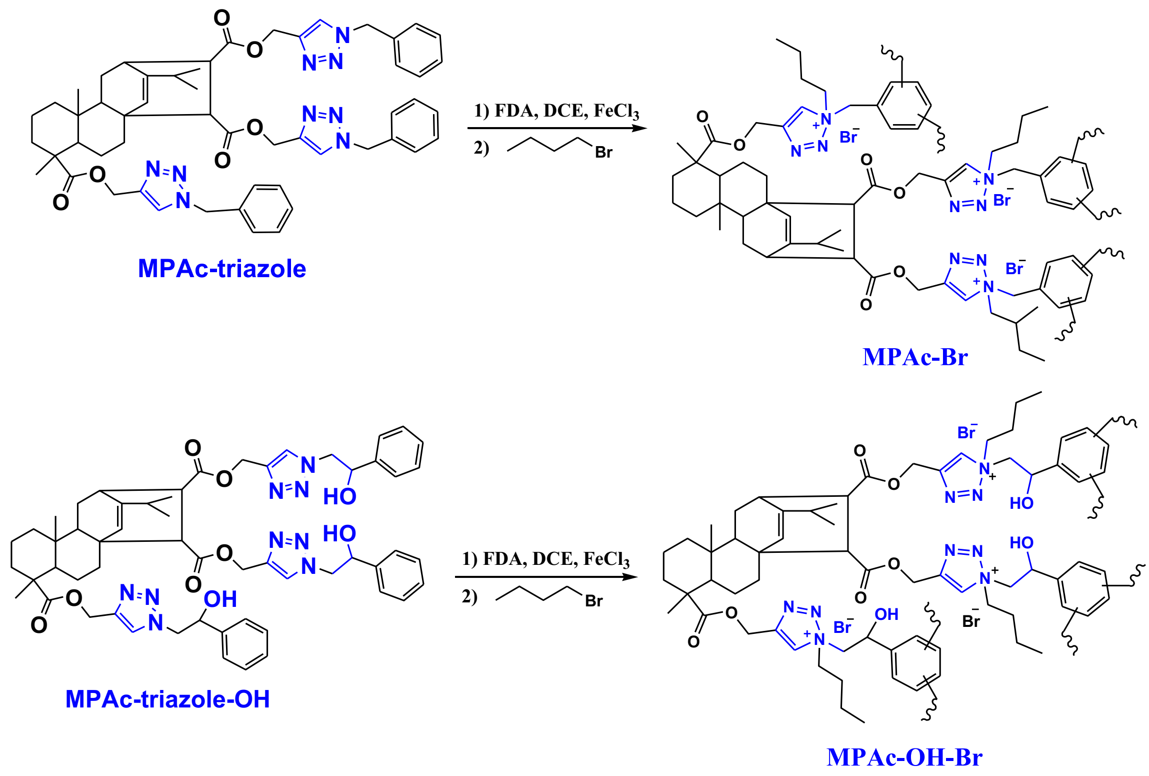
Rosin acid (75%) with an acid number of 166 mg KOH g^{-1} was purchased from Guangxi Wuzhou Pine Chemicals Ltd., China. It was a mixture of abietic acid and other rosin acids. Maleic anhydride (powder, 99%), propargyl bromide (98%, stabilized with MgO), bisphenol A diglycidyl ether (≥85%), and 4,4′-bis(chloromethyl)biphenyl (96%) were obtained from Aladdin Chemicals Ltd. DMF and CH_3COOH were obtained from Xiamen Lvyin Reagent Company. CO_2 (99.99%) was purchased from Xiamen Kongfente Gas Co., Ltd. All chemicals were obtained commercially and used as received, without further purification.

2.2. Instruments

FT-IR spectra were recorded on a Nicolet Nexus FT-IR instrument at 4 cm^{-1} resolution and 32 scans and samples for FT-IR analysis were prepared using the KBr press disc method. ^1H NMR spectra were recorded on a Bruker AVANCE III-500 spectrometer. TGA was carried out run in Ar atmosphere with a heating rate of 20 °C/min on TG instruments DTG-60H. The scanning electron microscopy (SEM) observation was performed on a HitachiSU8020 microscope operated at a 3 kV/10 μA accelerating voltage. The organic element analyzer was performed on a 230 V/EURO E device manufactured by Leeman China. The polymer surface areas, N_2 adsorption isotherms (77.3 K) and pore-size distributions were measured using a Micromeritics 3Flex surface area and porosity analyzer. Before analysis, the samples were degassed at 150 °C for 8 h under vacuum (10^{-5} bar). The yields of the obtained products are isolated yields.

2.3. Preparation of malaypimaric anhydride

The preparation of malaypimaric anhydride (MPA) were carried out according to the similar procedure described in other literatures [53,54]. In a three-necked round-bottomed flask (250 mL) equipped with a magnetic stirrer and a reflux condenser, rosin acid (75% purity, 20 g) and CH_3COOH (50 mL) was heated to 120 °C. Then, the mixture is refluxed for two hours under N_2 atmosphere to complete the isomerization of abietic acid. To this mixture were added 8.0 g of maleic anhydride (81.6 mmol) and the reaction mixture was refluxed for three hours. Then, 20 mL of CH_3COOH were added into the reaction mixture. After the reaction mixture was cooled to room temperature for 24 h, a white solid MPA was obtained (12.9 g, yield: 64%).



Scheme 2. Synthesis of the rosin-based hyper-cross-linked porous heterogeneous catalysts MPAc-Br and MPAc-OH-Br.

2.4. Preparation of malaypimaric acid

MPA (50.0 g) was dissolved in hot ethanol (150 mL) in a round bottom flask (500 mL). The mixture was stirred and the pH value reached 8–9 by adding an appropriate potassium hydroxide-ethanol solution. The resulting mixture was stirred continuously until the solid appeared completely. After that, the rosin-based potassium salt was collected *via* filtration and dried in a vacuum oven. Next, the rosin-based potassium salt (10.0 g) was dissolved in 75% ethanol solution and the mixture was acidified by 6% dilute hydrochloric acid (mass fraction) at room temperature. Then, the crude product was completely precipitated by slowly adding deionized water and obtained *via* filtration. The crude product was purified using recrystallization with 75% ethanol to gain white solid of pure malaypimaric acid (MPAc, 85%).

2.5. Preparation of tri-alkyne MPAc

10.0 g of MPAc (23.9 mmol), 11.8 g of K_2CO_3 and 30 mL of DMF were added into a 250 mL one-necked flask to get a white mixture under magnetic stirring. Then a solution of propargyl bromide (10.2 g, 85.0 mmol) dissolved in DMF (5.0 mL) was added drop by drop. After the reaction mixture was refluxed at 80 °C for 24 h, the reaction was stopped and cooled slowly to room temperature. And then, the reaction solvent was removed under reduced pressure on a rotary evaporator. The product was extracted with EtOAc (3 × 50 mL) and the organic phase was washed with distilled water (3 × 10 mL). The organic layer was washed with saturated NaCl solution, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to give the crude tri-alkyne MPAc product. Further purification was performed by silica gel flash column chromatography with a mixture of PE/EtOAc (4/1) as eluent to afford the pure tri-alkyne MPAc (yield: 7.13 g, 56%).

2.6. Synthesis of 1,2,3-triazole-modified monomer MPAc-triazole-OH from rosin

1,2,3-Triazole-modified rosin-based monomer MPAc-triazole-OH was prepared by cycloaddition reaction of alkynyl groups of tri-alkyne MPAc and organic azide using copper sulfate/sodium ascorbate as catalyst in THF. To a homogeneous solution of tri-alkyne MPAc (0.50 g) and 2-azido-1-phenylethanol (0.55 g, 3.36 mmol) in 15 mL of THF, $CuSO_4$/water mixture (0.28 mmol/1.0 mL) and NaOAc/water (0.56 mmol/1.0 mL) were added, and the resulting mixture was vigorously stirred at room temperature overnight. After removal of the solvent, the residue was dissolved in ethyl acetate (25 mL) and transferred to a separatory funnel. Then, the organic layer was washed with brine, dried, filtered and concentrated. The crude product was purified by column chromatography on silica gel to obtain MPAc-triazole-OH. The yield of MPAc-triazole-OH was 90%. The monomer MPAc-triazole was also synthesized by the similar procedure (Scheme 1).

2.7. Synthesis of rosin-based porous heterogeneous catalyst MPAc-OH-Br

In an oven dried 50 mL round-bottom flask, MPAc-triazole-OH (2.05 g, 2 mmol), formaldehyde dimethyl acetal (FDA, 1.52 g, 20 mmol) were dissolved in 15 mL of 1,2-dichloroethane (DCE). Then, anhydrous ferric chloride (3.24 g, 20 mmol) was added to the above mixture and was stirred at 45 °C for 5 h. After that, the resulting mixture was heated to 85 °C and maintained for 48 h to complete the formation of the HCP network. Upon cooling, the resulting precipitate was collected by vacuum filtration and washed twice with ethanol, then further Soxhlet-extracted by ethanol for 24 h in a Soxhlet extraction unit. Finally, the obtained polymer HCPs-OH was dried at 80 °C under vacuum for 12 h.

HCPs-OH (1.0 g) and 1-bromobutane (1.37 g) was dissolved in DMF (10 mL) in a round bottom flask (50 mL) and heated at 85 °C for 24 h. Upon cooling, the catalyst was separated by filtration, and the solid was washed three times with ethanol, and dried under vacuum at 50 °C for

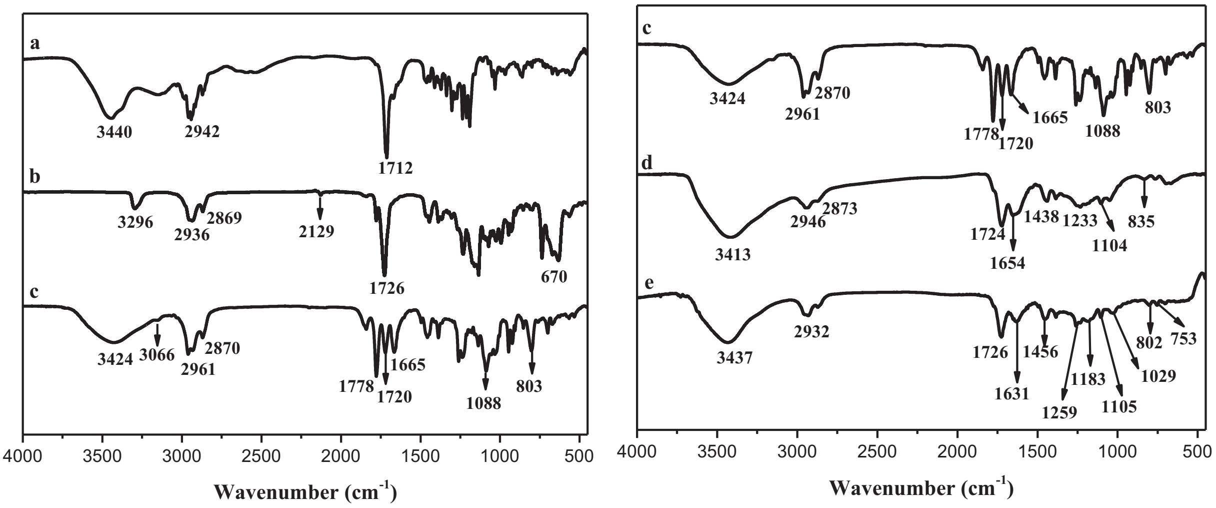


Fig. 2. FT-IR spectra of MPAc (a), tri-alkyne MPAc (b), MPAc-triazole-OH (c), HCPs-OH (d), and MPAc-OH-Br (e).

12 h. The product was named as MPAc-OH-Br. MPAc-Br was also synthesized by the similar procedure (Scheme 2).

2.8. General procedure for chemical fixation of CO_2 with epoxides

The chemical fixation of CO_2 with epoxides were carried out in a Teflon-lined stainless-steel reactor (20.0 mL) equipped with a magnetic stirrer. In the general procedure, epoxide (10.0 mmol), MPAc-OH-Br (30.0 mg), and TBABr (0.1 mmol, 2.0 mol%) were placed into the reactor. The reactor was then purged with CO_2 three times. Subsequently, the reactor was heated to the desired reaction temperature under the desired pressure condition. After completion of the reaction, the reactor was removed from the oil bath and then immediately placed in the iced water bath to quench the reaction. The excess CO_2 was released slowly. EtOAc (15 mL) was added into the reaction mixture, and then MPAc-OH-Br was recovered by precipitation. Subsequently, the obtained catalyst was washed two times with EtOAc and dried under vacuum at 50 °C for 5 h for further use.

3. Results and discussion

3.1. Synthesis of bio-based monomers from rosin

The synthesis route of MPAc-alkyne is shown in Scheme 1. Firstly, the synthesis of MPAc were carried out according to the similar method used in previous literatures [53,54]. In the next step, MPAc, K_2CO_3, and propargyl bromide were used as raw materials to synthesize tri-alkyne MPAc. The obtained results showed that esterification of the carboxyl groups using K_2CO_3/DMF reaction system resulted in a moderate yield (24 h, 80 °C, 56%). 1,2,3-Triazole-modified rosin-based monomers MPAc-triazole-OH and MPAc-triazole were prepared by cycloaddition reaction of alkynyl groups of tri-alkyne MPAc and styrene oxide/NaN_3 (or benzyl bromide/NaN_3) using copper sulfate/sodium ascorbate as catalyst in THF.

3.2. Synthesis of rosin-based porous heterogeneous catalyst

The synthesis route of MPAc-OH-Br is shown in Scheme 2. In this study, rosin-based MPAc-OH-Br was synthesized by Friedel–Crafts coupling polymerization and quaternization reaction from rosin-based monomer MPAc-triazole-OH. Firstly, the obtained bio-based monomer MPAc-triazole-OH or MPAc-triazole was hyper-crosslinked *via* Friedel–Crafts alkylation coupling reaction with formaldehyde diethyl acetal (FDA) upon the activation of anhydrous $FeCl_3$ in dichloroethane. After polymerization at 85 °C for 48 h, the brown porous polymer was filtered and washed three times with methanol. The obtained solid was further purified by Soxhlet extraction methanol for 48 h, and then dried in a vacuum oven at 50 °C for 12 h to obtain HCPs-OH or HCPs. HCPs-OH or HCPs HCPs-OH (1.0 g) and 1-bromobutane (2.0 mL) was dissolved in DMF (10 mL) in a three-necked flask and heated at 80 °C for 36 h. After simple filtration and washing with EtOAc, MPAc-OH-Br or MPAc-Br was obtained and then dried at 50 °C for further use.

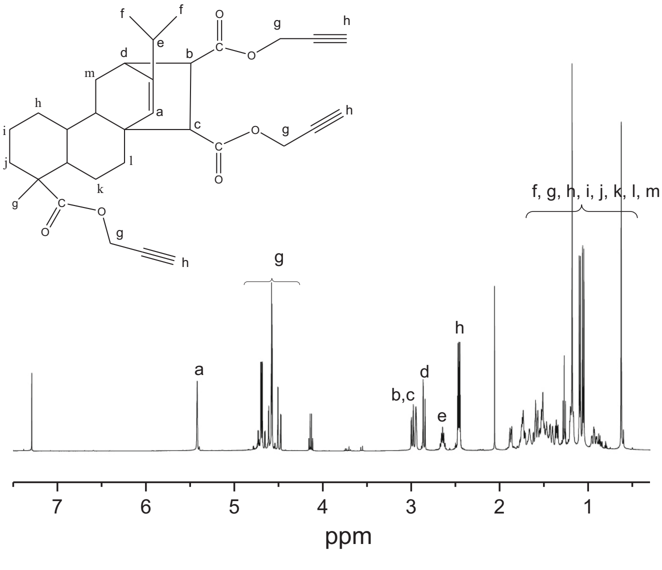


Fig. 3. ^1H NMR spectrum of tri-alkyne MPAc in $CDCl_3$ with assignment.

3.3. Characterization of rosin-based monomer and porous heterogeneous catalyst

The chemical structures of the intermediates and tri-alkyne MPAc were identified by FT-IR, ^1H NMR and ^{13}C NMR, respectively. As shown in Fig. 2a, the peak at 1712 cm^{-1} was the stretching coupling vibration of the C═O bond of carboxylic groups in MPAc. Fig. 2b is the FT-IR spectrum of tri-alkyne MPAc. It can be seen that the broad absorption peak of carboxylic groups from 3000 to 3500 cm^{-1} for MPAc almost disappeared after esterification of MPAc with propargyl bromide. At the same time, several new peaks appeared at 3296 cm^{-1}, 2129 cm^{-1}, 1726 cm^{-1} and 670 cm^{-1}, which are due to the adsorption of the unsaturated terminal C≡C bonds, ester functional groups, and the ≡C—H groups of

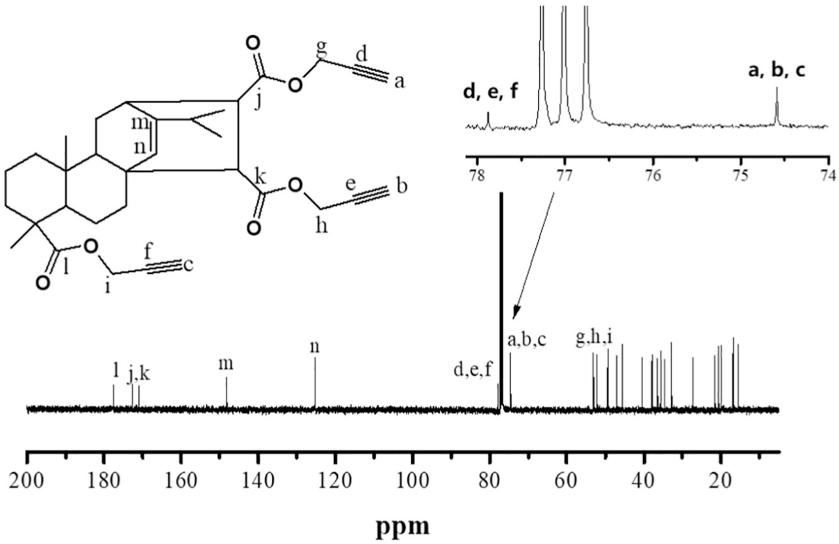


Fig. 4. ^{13}C NMR spectrum of tri-alkyne MPAc in $CDCl_3$ with assignment.

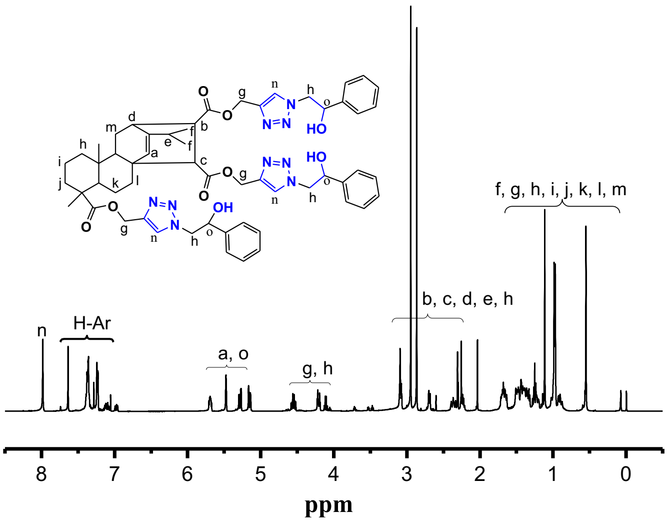


Fig. 5. ^{1}H NMR spectrum of MPAc-triazole-OH in $CDCl_3$ with assignment.

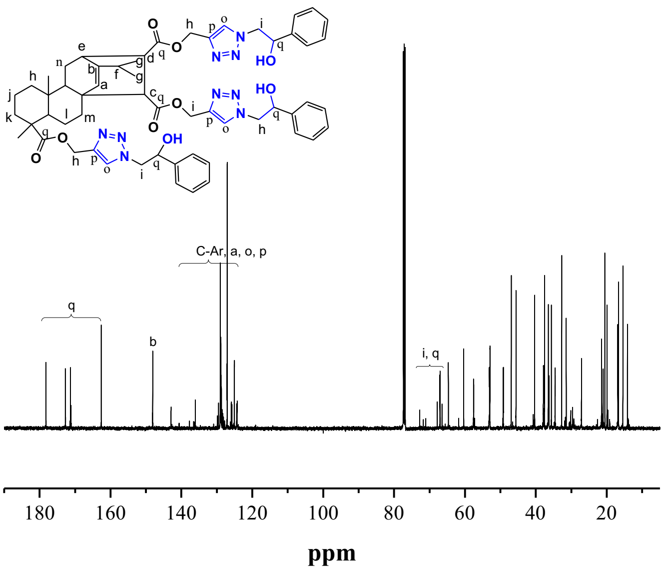


Fig. 6. ^{13}C NMR spectrum of MPAc-triazole-OH in $CDCl_3$ with assignment.

tri-alkyne MPAc.

After the click reaction of tri-alkyne MPAc and 2-azido-1-phenylethanol, the peak at 2129 cm^{-1} for alkyne groups in the spectrum of MPAc-triazole-OH have disappeared, and these new emergence peaks centered at 3066 cm^{-1} and 1665 cm^{-1} are related to the stretching vibration of aromatic C═C bonds of benzene rings and triazole rings (Fig. 2c). As shown in Fig. 2d and e, the following characteristic FT-IR stretching peaks were found in HCPs-OH and MPAc-OH-Br an aliphatic C—H vibration peak emanating from —CH_2— linkers at 2932 cm^{-1} and 2946 cm^{-1}, respectively. Additionally, the characteristic FT-IR stretching peaks of hydroxyl groups in HCPs-OH and MPAc-Br-OH were found as a broad peak centered at about 3400 cm^{-1}. The bands at 1724 and 1726 cm^{-1} could be attributed to C═O stretching of ester groups in MPAc-OH and MPAc-OH-Br, respectively. Furthermore, the N content of HCPs-OH and MPAc-Br-OH were determined to be 5.59% and 5.56% by using elemental analysis (EA), respectively. Obviously, the results of FT-IR and EA suggested that most of MPAc-triazole-OH was involved in the formation of the network.

In the ^{1}H NMR spectrum of tri-alkyne MPAc (Fig. 3), the peaks between 0.55 and 1.90 ppm were assigned to the protons of rosin-based ternary phenanthrene ring structure. The single peak at 2.42 ppm corresponded to the protons of —C≡CH. The peaks between 4.45 and 4.70 ppm were assigned to the protons of —OCH_2C≡CH. The chemical structure of —$COOCH_2C$≡CH was further verified using ^{13}C NMR (Fig. 4). After esterification of MPAc with propargyl bromide, the peaks of the carbons in the propargyl groups (a, b, c, d, e and f) in C≡C bonds were at 74.6, 77.8 ppm. The obtained results showed that terminal alkynes have been successfully grafted into MPAc.

MPAc-triazole-OH was synthesized by treating tri-alkyne MPAc with an excess of 2-azido-1-phenylethanol (1.2 eq). The successful click reaction between tri-alkyne MPAc and 2-azido-1-phenylethanol can also be confirmed by ^{1}H NMR spectroscopy (Fig. 5). The peaks at about 8.0 ppm are assigned to the proton of 1,2,3-triazole ring, and the signals between 7.0 and 8.0 ppm are assigned to the protons of benzene rings. In addition, the peaks between 0.50 and 2.00 ppm were assigned to the protons of ternary phenanthrene ring structure of rosin.

The molecular structure of MPAc-triazole-OH was further verified by using ^{13}C NMR spectroscopy (Fig. 6). The peaks between δ = 160–180 ppm represented the carbonyl carbons of ester groups. Eighteen aromatic carbons are resonated between δ = 115–140 ppm. The

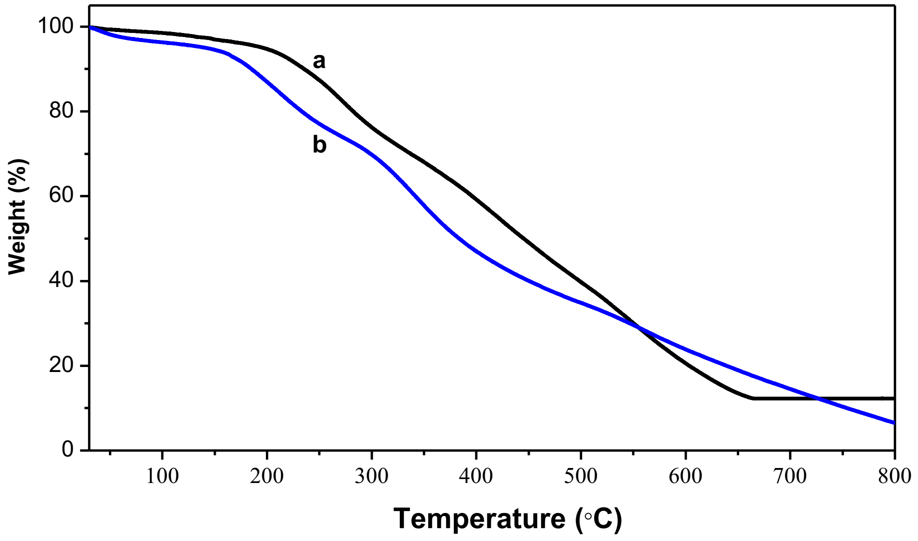


Fig. 7. TGA of MPAc-OH (a) and MPAc-OH-Br (b).

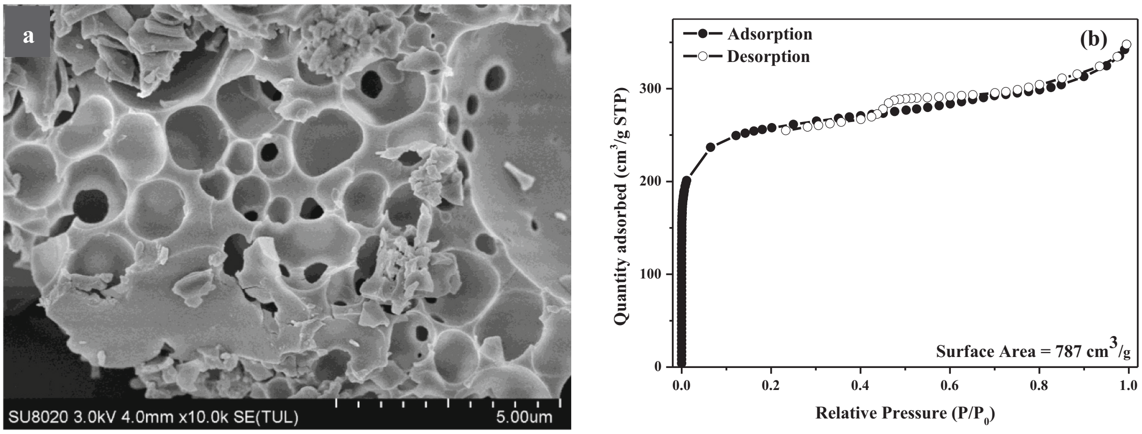
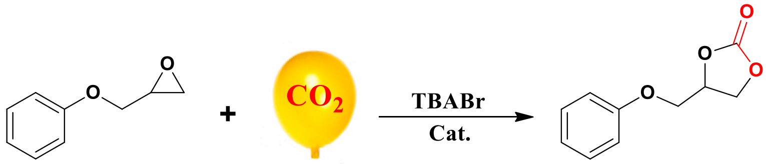


Fig. 8. SEM image (a) and N_2 adsorption-desorption isotherm of MPAc-OH-Br (b).

peaks at $\delta = 140–150$ ppm confirmed the presence of the C$=$C groups in the 1,2,3-triazole ring. In addition, the FT-IR spectrum in Fig. 2c gives the further evidence. The disappearance of the alkynyl absorption at 2129 cm^{-1} suggests the complete transition from tri-alkyne MPAc to MPAc-triazole-OH. In addition, the nitrogen content of MPAc-OH-Br were found to be 5.56 wt% by elemental analysis. Clearly, the

Table 1
Effect of different rosin-based polymeric catalysts catalyzed cyclization reaction between CO_2 and 2-(prop-2-enoxymethyl)oxirane.[a]



Entry	Catalyst	Catalyst (mg)	TBABr (mmol)	Isolated yield (%)
1	None	0	0.1	26
2	HCPs	30	0	31
3	HCPs	30	0.1	69
4	HCPs-OH	30	0	46
5	HCPs-OH	30	0.1	76
6	MPAc-Br	30	0	48
7	MPAc-Br	30	0.1	90
8	MPAc-OH-Br	30	0	61
9	**MPAc-OH-Br**	**30**	**0.1**	**99**

Bold indicates the best catalytic result of rosin-based porous catalyst reported in this paper.

[a] Reaction condition: 2-(phenoxymethyl)oxirane (10.0 mmol), CO_2 (atmospheric pressure), 130 °C, 300 min.

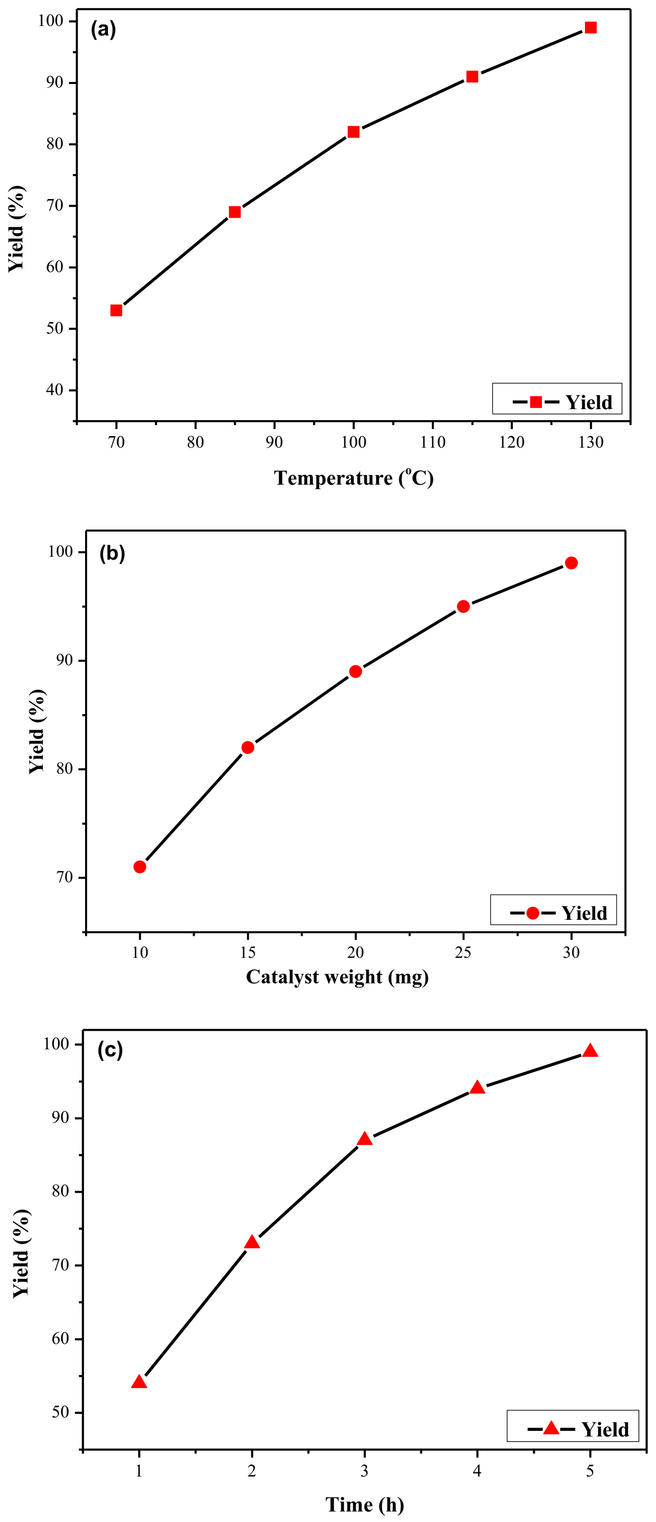


Fig. 9. Effect of reaction parameters on cyclic carbonate yield over MPAc-OH-Br: reaction temperature (a), catalyst amount (b), and reaction time (c).

obtained results showed that the benzene rings have been successfully grafted into MPAc *via* CuAAC reaction.

The thermal stability of MPAc-OH and the catalyst MPAc-OH-Br was analyzed by means of thermogravimetric analysis (TGA). As demonstrated by TGA in a nitrogen atmosphere (Fig. 7), only slight weight loss was observed below 150 °C, due to the removal of residual solvents and/or adsorbed H_2O. In the TGA plot of MPAc-OH-Br (Fig. 7b), about 15% weight loss is observed between 150 °C to 300 °C, which could be due to the decomposition of the grafted n-butyl bromide. The obvious decrease in the weight of MPAc-Br and MPAc-OH-Br in the temperature range of 300 °C to 800 °C is ascribed to the destruction of rosin skeleton in the hyper-cross-linked porous polymer networks. The obtained results indicated that MPAc-Br and MPAc-OH-Br could have potential applications in CO_2 chemical transformation.

The morphology and surface characteristics of MPAc-OH-Br were investigated by scanning electron microscope (SEM) and Brunauer–Emmett–Teller (BET) N_2 gas adsorption–desorption isotherms. As shown in Fig. 8a, there were open and closed cells in the sample of MPAc-OH-Br, which exhibited highly porous morphology. Furthermore, the result of N_2 gas sorption analysis further proved this fact and the BET surface area of MPAc-OH-Br was 787 m^3/g. According to Fig. 8b, the N_2 adsorption isotherms told a sharply gas uptake at low relative pressure ($P/P_0 < 0.01$) and continuous increase at a high relative pressure ($0.2 < P/P0 < 1.0$) with a hysteresis loop, which indicated that the rosin-base MPAc-OH-Br was a multi-stage porous material with abundant micropores and macropores structure.

3.4. Effect of rosin-based porous catalysts on cyclic carbonate yields

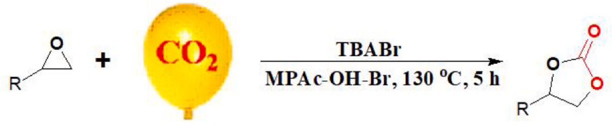
The catalytic activity of the rosin-based porous catalysts was examined using CO_2 and 2-(phenoxymethyl)oxirane as model reactants (Table 1). The model reaction was carried out over two rosin-based porous catalysts under 130 °C and atmospheric pressure conditions. As expected, MPAc-OH-Br was found to exhibit excellent catalytic activity for highly efficient synthesis of cyclic carbonates *via* chemical fixation of CO_2 with 2-(phenoxymethyl)oxirane under metal-, solvent-free and atmospheric pressure conditions, as illustrated in Table 1. When the reaction was carried out using TBABr alone, the desired cyclic carbonate yield was only 26% (entry 1, Table 1). When rosin-based catalyst was used alone, the desired cyclic carbonate yield was very low or only medium (31%–61%, entries 2, 4, 6, 8, Table 1). The combination of HCPs and TBABr under the same reaction condition provided 69% yield. The combination of MPAc-Br and TBABr provided 90% yield. To our delight, the bifunctional catalyst MPAc-OH-Br (bearing triazole IL groups and —OH groups) showed excellent catalytic performance with a yield of 99% owing to the molecularly cooperative effect among triazole cations and —OH groups. Since MPAc-OH-Br contains triazole IL groups and —OH groups, hydrogen bonds may play an important role in the synergetic catalysis of the reaction. Based on these obtained results, MPAc-OH-Br/TBABr was selected as the best catalytic system for further investigations.

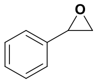
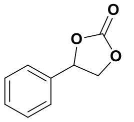
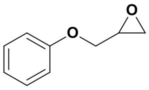
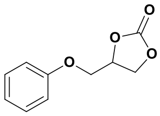
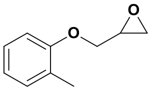
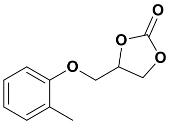
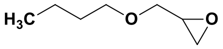
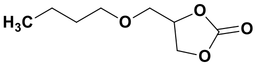
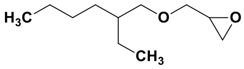
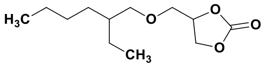
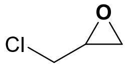
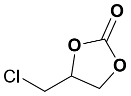
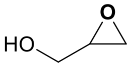
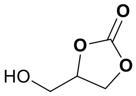
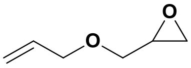
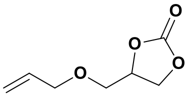
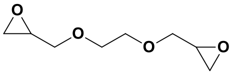
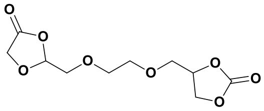
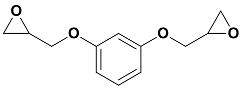
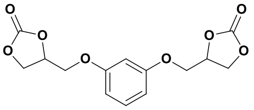
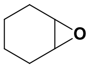
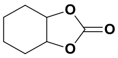
3.5. Optimization of cyclization reaction parameter

CO_2 chemical conversion depends on the primary factors, such as reaction temperature, catalyst amount, and reaction time of the reaction system. Therefore, the influence of these reaction factors on the cycloaddition reaction was then examined, and the obtained results are shown in Fig. 9. Fig. 9a shows the effect of reaction temperature on the chemical fixation of CO_2. The reaction temperature played an important role in deciding the yield of cycloaddition reaction. The yields of cycloaddition reaction increased rapidly from 53% to 99% when the reaction temperature increased from 70 °C to 130 °C.

Fig. 9b shows the influence of catalytic amounts in the MPAc-OH-Br mediated catalysis of CO_2 and 2-(phenoxymethyl)oxirane cycloaddition. It was found that cyclic carbonate yield was obviously increased when increasing the amounts of MPAc-OH-Br from 10 mg to 30 mg. As illustrated in Fig. 9b, the yield of the desired cyclic carbonate reached the maximum within 30 mg, up to 99%. At last, the effect of the reaction time was examined while keeping other parameters (such as catalyst 30 mg, atmospheric pressure, and 130 °C) constant in Fig. 9c. The yield increased with reaction time and reached a maximum of 99% within 300 min. Up to now, the optimal reaction conditions for the chemical

Table 2
Cyclization reaction between CO_2 and various epoxides under the optimized reaction condition.



Entry[a]	Substrate	Product	Isolated Yield (%)
1			88
2			99
3			92
4			95
5			96
6			99
7			93
8			91
9			88
10			96
11			68

[a] Reaction conditions: epoxide (10.0 mmol), CO_2 (atmospheric pressure), MPAc-OH-Br (30 mg), TBABr (0.1 mmol), 5 h.

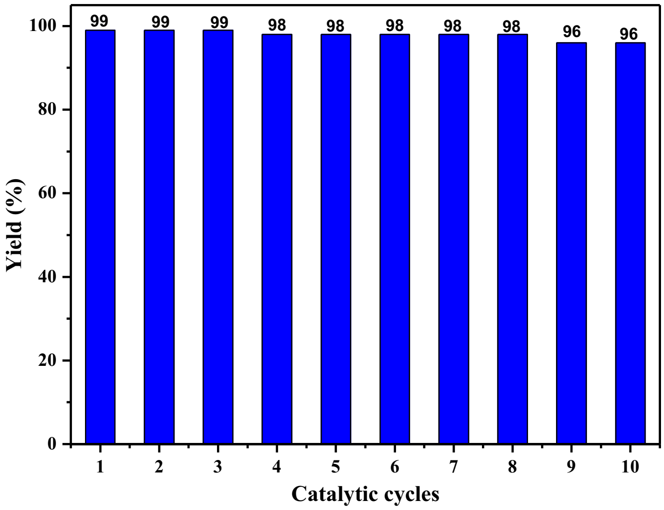


Fig. 10. Recyclability of MPAc-OH-Br under the optimal conditions.

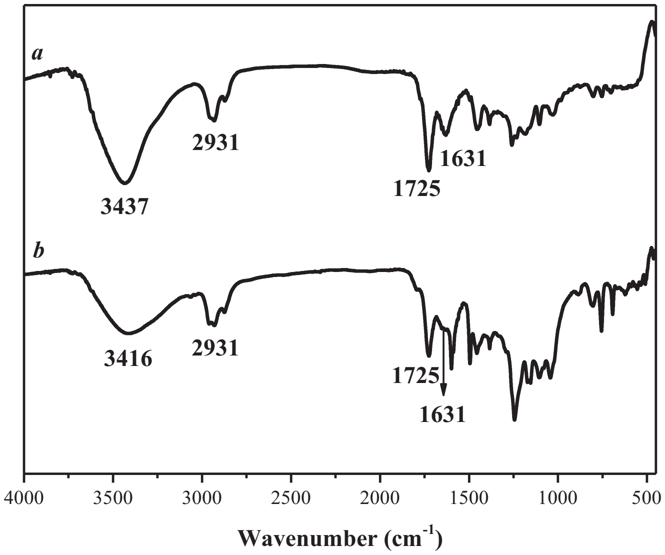


Fig. 11. FT-IR spectra of the fresh MPAc-OH-Br and the recovered MPAc-OH-Br after ten consecutive cycles.

fixation of CO_2 (atmospheric pressure) with epoxide (10.0 mmol) were established as MPAc-OH-Br (30 mg) at 130 °C and 300 min reaction.

3.6. MPAc-OH-Br for chemical fixation of CO_2 with other epoxides

To determine the potential applicability of the MPAc-OH-Br catalyst, the substrate scope of cycloaddition reaction that involved epoxides with different substituents was examined under the optimal reaction conditions (130 °C, atmospheric pressure, 5 h). The detailed results are summarized in Table 2. As shown in Table 2, high yields were achieved for the mono-substituted terminal epoxides (Entries 1–11). All the epoxides tested could be converted into the corresponding cyclic carbonates with good to excellent yields. The steric effect may affect the yield. For example, the reactive activity of the terminal epoxides decreased with increasing their alkyl length (entries 4 and 5). Compared with glycidol, epichlorohydrin showed a better result, probably due to the electron-withdrawing property of the Cl atom (entries 6 and 7). In addition, the epoxides with an oxymethylene moiety were also converted to the corresponding products in excellent yields, indicating the facilitated nucleophilic attack at the epoxide ring carbon atoms. However, owing to the higher barrier height of ring opening, the yield of corresponding product was only 68% (entry 11) when cyclohexene oxide was used as the substrate in the same reaction conditions.

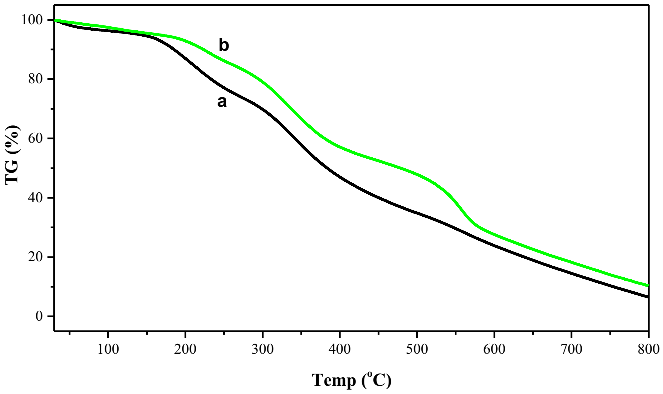


Fig. 12. TGA of the fresh MPAc-OH-Br (a) and the recovered MPAc-OH-Br after ten consecutive cycles (b).

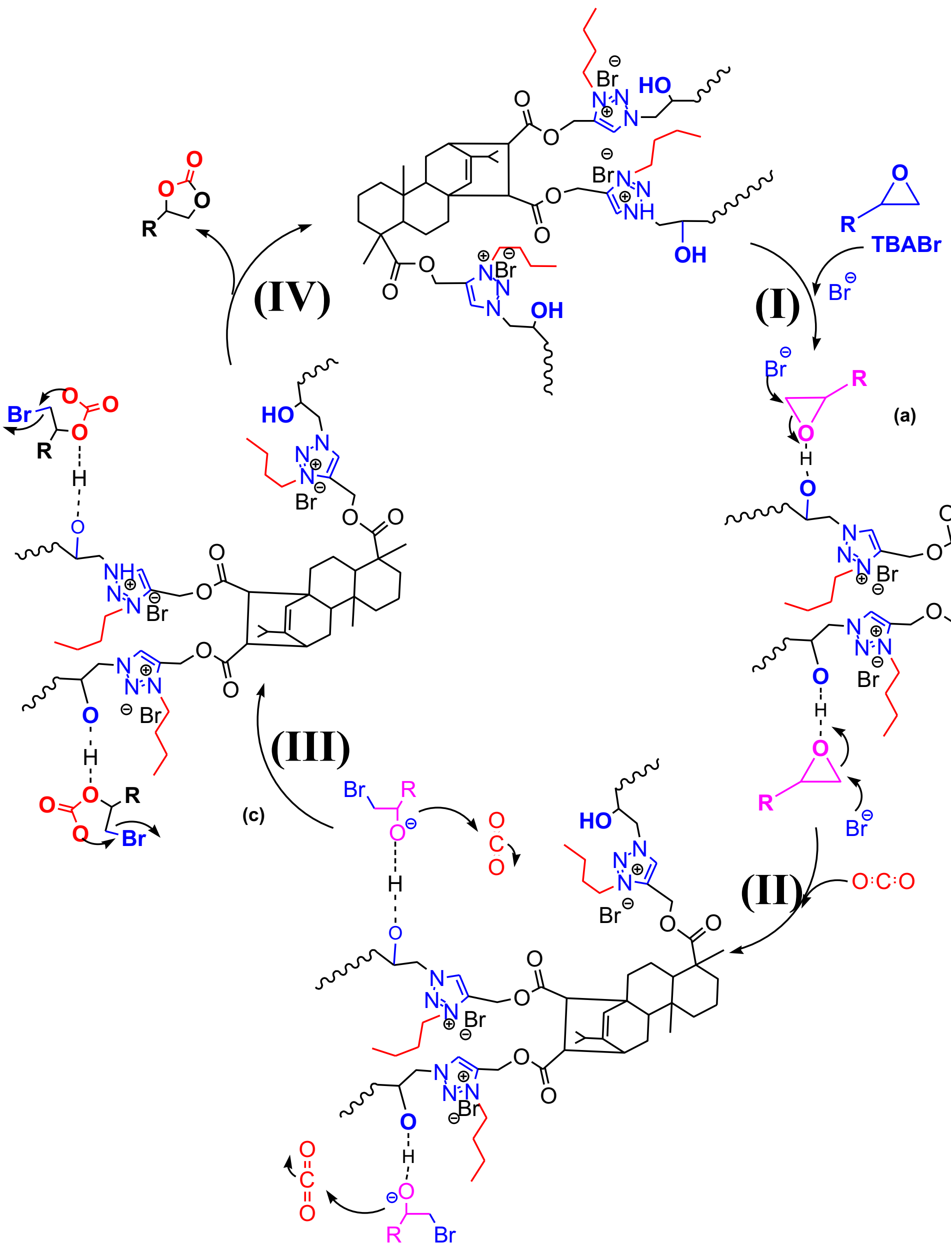
3.7. Stability of MPAc-OH-Br

In order to develop a greener and more economical process for cyclic carbonates synthesis, the reusability of MPAc-OH-Br was examined under the optimal conditions in the following step. It was observed that the MPAc-OH-Br catalyst exhibited good to excellent catalytic activity for ten consecutive cycles, reflecting good stability of MPAc-OH-Br (Fig. 10).

In the next step, the chemical and thermal stability of the recycled MPAc-OH-Br after ten cycles were studied by FT-IR, EA and TGA analysis. The FT-IR of the reused MPAc-OH-Br catalyst was displayed in Fig. 11. Compared with the fresh catalyst, after ten consecutive cycles, the obtained catalyst still remains the characteristic peaks of MPAc (1725 cm^{-1}, ester functional groups) and hydroxyl groups (3400–3500 cm^{-1}), which indicated that the skeleton structure of MPAc-OH-Br was stable during catalytic reactions and after 10 times recycle. EA showed that the N contents still well-preserved in the recovered MPAc-OH-Br, still up to 4.91% (the fresh catalyst, 5.56%), which further testified the outstanding chemical stability of MPAc-OH-Br. In addition, the catalyst reused in ten consecutive runs was analyzed by TGA (Fig. 12b) and showed a very similar TGA curves between 25 °C to 170 °C compared to the fresh catalyst (Fig. 12a). These results indicate that the catalyst MPAc-OH-Br has good stability. Thus, all of these results indicate that the MPAc-OH-Br was a well-reusable and robust catalyst for the chemical fixation CO_2 with epoxides.

3.8. Possible reaction mechanism of the cycloaddition of CO_2 with epoxides

Based on the present results and previous published results [55,56], a plausible mechanism was proposed for the chemical fixation epoxides with CO_2 over the MPAc-OH-Br catalyst (Scheme 3). MPAc-OH-Br with —OH functional groups demonstrated better catalytic activity, as the —OH functional groups might play a very important role in the activation of epoxides. Initially, the cycloaddition reaction is initiated by activation of epoxy ring through hydrogen bonding of —OH functional groups on the surface of MPAc-OH-Br (I). Secondly, the nucleophilic Br anion attacks the less-hindered carbon atom of the activated epoxide, followed by the ring opening of the epoxy ring and formed the ring-opened intermediate (II). Next, CO_2 inserted into the intermediate and an acyclic ester was obtained (III). In the final step (IV), the acyclic ester was further converted to the corresponding cyclic carbonate through the intramolecular ring-closure. At the same time, the catalyst MPAc-OH-Br was regenerated. The excellent catalytic performance of MPAc-OH-Br



Scheme 3. A plausible mechanism for the chemical fixation of CO_2 with epoxides over MPAc-OH-Br.

can be attributed to the obvious cooperative effect of between –OH functional groups and nucleophilic Br anions.

3.9. Comparison of MPAc-OH-Br with the reported heterogeneous catalysts in the chemical fixation of CO_2 with epoxides

To identify the potential of the rosin-based heterogeneous catalyst MPAc-OH-Br for the preparation of cyclic carbonates, we have compared the obtained result with previously reported catalytic systems for cycloaddition of CO_2 with epoxide. The result from our catalytic system and the data from previously reported catalyst systems are summarized in Table 3. As shown in Table 3, PIM2, I_{C2}HCP-5, IHCP-OH (1), BPyBr-$ZnCl_2/SiO_2$, PNPs-Im_2ZnBr_4, and PS-$MimFeCl_4$ are examples of catalysts which have been used for cycloaddition of CO_2 with epoxide. By comparing the previously reported results, it can be found that our catalyst has higher catalytic activity. Obviously, the rosin-based porous structure and the -OH groups on the surface of MPAc-OH-Br played an important role to enhance catalytic activity. Compared with the existing heterogeneous catalysts, MPAc-OH-Br exhibited obvious advantages, short reaction time (5 h), mild reaction condition (atmospheric pressure), and excellent yield (99%) for the synthesis of cyclic carbonates.

Table 3
Comparison of catalytic performance of reported porous polymers.

Entry	Catalyst	Temp. (°C)	Time (h)	Pressure (MPa)	Yield (%)	Ref.
1	PIM2	130	8	1.0	96	[57]
2	I_{C2}HCP-5	120	28	3.0	92	[58]
3	IHCP-OH (1)	135	7	3.0	90	[59]
4	BPyBr-$ZnCl_2/SiO_2$	120	4	1.7	88	[60]
5	PNPs-Im_2ZnBr_4	120	3.5	2.0	88	[61]
6	PS-$MimFeCl_4$	100	6	8	96	[62]
7	MPAc-OH-Br	**130**	**5**	**Balloon**	**>99**	**This work**

Bold indicates the best catalytic result of rosin-based porous catalyst reported in this paper.

4. Conclusions

In summary, a class of biomass-derived bifunctional porous heterogeneous catalyst MPAc-OH-Br (bearing triazole IL groups and —OH groups), based on easily available and sustainable rosin, was synthesized by Friedel–Crafts polymerization and the further *N*-alkylation of triazole groups. The synthesized rosin-based polymeric monomers and the MPAc-OH-Br catalyst was thoroughly characterized by different techniques, such as FT-IR, ^{1}H NMR, ^{13}C NMR, TGA, SEM, and BET. Compared with MPAc-Br, bifunctional MPAc-OH-Br displayed a remarkable catalytic activity for chemical fixation of CO_2 with epoxides into cyclic carbonates (up to 99% yields) under metal-, solvent-free and atmospheric pressure conditions (130 °C, 5 h). In addition, MPAc-OH-Br exhibited good stability and reusability (96% yield after 10 recycles). The present study demonstrated that the rosin-based porous molecular structure and bifunctional groups on the surface of MPAc-OH-Br played a very important role to enhance its catalytic activity.

Declaration of Competing Interest

None.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (21004024), the Natural Science Foundation of Fujian Province (2016J01063), the Program for New Century Excellent Talents in University of Fujian Province (2012FJ-NCET-ZR03) and the Subsidized Project for Postgraduates' Innovative Fund in Scientific Research of Huaqiao University.

References

[1] J.L. Schnoor, Ocean acidification: the other problem with CO_2, Environ. Sci. Technol. 48 (2014) 10529–10530, https://doi.org/10.1021/es503107u.

[2] D.A. Lashof, D.-R. Ahuja, Relative contributions of greenhouse gas emissions to global warming, Nature 344 (1990) 529–531, https://doi.org/10.1038/344529a0.

[3] J. Artz, T.E. Müller, K. Thenert, Sustainable conversion of carbon dioxide: an integrated review of catalysis and life cycle assessment, Chem. Rev. 118 (2018) 434–504, https://doi.org/10.1021/acs.chemrev.7b00435.

[4] Y. Zhou, W.L. Zhang, L. Ma, Y. Zhou, J. Wang, Amino acid anion paired mesoporous poly(ionic liquid)s as metal/halogen-free heterogeneous catalysts for carbon dioxide fixation, ACS Sustain. Chem. Eng. 7 (2019) 9387–9398, https://doi.org/10.1021/acssuschemeng.9b00591.

[5] Z.J. Guo, Q.W. Jiang, Y.M. Shi, J. Li, X.N. Yang, W. Hou, Y. Zhou, J. Wang, Tethering dual hydroxyls into mesoporous poly(ionic liquid)s for chemical fixation of CO_2 at ambient conditions: a combined experimental and theoretical study, ACS Catal. 7 (2017) 6770–6780, https://doi.org/10.1021/acscatal.7b02399.

[6] J. Li, D.G. Jia, Z.J. Guo, Y.Q. Liu, Y.N. Lyu, Y. Zhou, J. Wang, Imidazolinium-based porous hypercrosslinked ionic polymers for efficient CO_2 capture and fixation with epoxides, Green Chem. 19 (2017) 2675–2686, https://doi.org/10.1039/C7GC00105C.

[7] M. Aresta, A. Dibenedetto, A. Angelini, Catalysis for the valorization of exhaust carbon: from CO_2 to chemicals, materials, and fuels. Technological use of CO_2, Chem. Rev. 114 (2014) 1709–1742, https://doi.org/10.1021/cr4002758.

[8] R. Babu, A.C. Kathalikkattil, R. Roshan, J. Tharun, D. Kimb, D. Park, Dual-porous metal organic framework for room temperature CO_2 fixation *via* cyclic carbonate synthesis, Green Chem. 18 (2016) 232–242, https://doi.org/10.1039/C5GC01763G.

[9] J. Liang, Y. Xie, Q. Wu, X. Wang, T. Liu, H. Li, Y. Huang, R. Cao, Zinc porphyrin/imidazolium integrated multivariate zirconium metal–organic frameworks for transformation of CO_2 into cyclic carbonates, Inorg. Chem. 57 (2018) 2584–2593, https://doi.org/10.1021/acs.inorgchem.7b02983.

[10] J. Chen, M. Zhong, L. Tao, L. Liu, S. Jayakumar, C. Li, H. Li, Q. Yang, The cooperation of porphyrin-based porous polymer and thermal-responsive ionic liquid for efficient CO_2 cycloaddition reaction, Green Chem. 20 (2018) 903–911, https://doi.org/10.1039/C7GC03801A.

[11] A. Tortajada, F. Juliá-Hernández, M. Bçrjesson, T. Moragas, R. Martin, Transition-metal-catalyzed carboxylation reactions with carbon dioxide, Angew. Chem. Int. Ed. 57 (2018) 15948–15982, https://doi.org/10.1002/anie.201803186.

[12] H. Seo, L.V. Nguyen, T.F. Jamison, Using carbon dioxide as a building block in continuous flow synthesis, Adv. Synth. Catal. 361 (2019) 247–264, https://doi.org/10.1002/adsc.201801228.

[13] S. Dabral, T. Schaub, The use of carbon dioxide (CO_2) as a building block in organic synthesis from an industrial perspective, Adv. Synth. Catal. 361 (2019) 223–246, https://doi.org/10.1002/adsc.201801215.

[14] Y.R. Wang, L.Y. Guo, L.Z. Yin, Progress in the heterogeneous catalytic cyclization of CO_2 with epoxides using immobilized ionic liquids, Catal. Lett. 149 (2019) 985–997, https://doi.org/10.1007/s10562-019-02669-y.

[15] A.J. Kamphuis, F. Picchioni, P.P. Pescarmona, CO_2-fixation into cyclic and polymeric carbonates: principles and applications, Green Chem. 21 (2019) 406–448, https://doi.org/10.1039/C8GC03086C.

[16] P. Bhanja, A. Modak, A. Bhaumik, Porous organic polymers for CO_2 storage and conversion reactions, ChemCatChem 11 (2019) 244–257, https://doi.org/10.1002/cctc.201801046.

[17] S. Wang, C.J. Xi, Recent advances in nucleophile-triggered CO_2-incorporated cyclization leading to heterocycles, Chem. Soc. Rev. 48 (2019) 382–404, https://doi.org/10.1039/C8CS00281A.

[18] G. Zhao, X. Huang, X. Wang, X. Wang, Progress in catalyst exploration for heterogeneous CO_2 reduction and utilization: a critical review, J. Mater. Chem. A 5 (2017) 21625–21649, https://doi.org/10.1039/C7TA07290B.

[19] S.N. Habisreutinger, L. Schmidt-Mende, J.K. Stolarczyk, Photocatalytic reduction of CO_2 on TiO_2 and other semiconductors, Angew. Chem. Int. Ed. 52 (2013) 7372–7408, https://doi.org/10.1002/anie.201207199.

[20] S. Zeng, X. Zhang, L. Bai, X. Zhang, H. Wang, J. Wang, D. Bao, M. Li, X. Liu, S. Zhang, Ionic-liquid-based CO_2 capture systems: structure, interaction and process, Chem. Rev. 117 (2017) 9625–9673, https://doi.org/10.1021/acs.chemrev.7b00072.

[21] M. Liu, L. Liang, X. Li, X. Gao, J. Sun, Novel urea derivative based ionic liquids with dual-functions: CO_2 capture and conversion under metal- and solvent-free conditions, Green Chem. 18 (2016) 2851–2863, https://doi.org/10.1039/C5GC02605A.

[22] L.W. Sun, J.Y. Luo, M. Gao, S.K. Tang, Bi-functionalized ionic liquid porous copolymers for CO_2 adsorption and conversion under ambient pressure, React. Funct. Polym. 154 (2020) 104636, https://doi.org/10.1016/j.reactfunctpolym.2020.104636.

[23] Y. Liu, Y. Song, J.H. Zhou, X.P. Zhang, Modified polyether glycols supported ionic liquids for CO_2 adsorption and chemical fixation, Mol. Catal. 492 (2020) 111008, https://doi.org/10.1016/j.mcat.2020.111008.

[24] S. Suleman, H.A. Younus, N. Ahmad, Z.A.K. Khattak, H. Ullah, J. Park, T. Han, B. J. Yu, F. Verpoort, Triazole based cobalt catalyst for CO_2 insertion into epoxide at ambient pressure, Appl. Catal. A 591 (2020) 117384, https://doi.org/10.1016/j.apcata.2019.117384.

[25] Q. Zhang, P. Yu, B. Lei, H.J. Yang, J.C. Hu, L.H. Wang, T.F. Zhou, Q.Q. Jiang, J. J. Zhu, B.X. Han, Efficient solvent-free synthesis of cyclic carbonates from the cycloaddition of carbon dioxide and epoxides catalyzed by new imidazolinium functionalized metal complexes under 0.1 MPa, Catal. Lett. 150 (2020) 2537–2548, https://doi.org/10.1007/s10562-020-03163-6.

[26] G.J. Chen, Y.D. Zhang, J.Y. Xu, X.Q. Liu, K. Liu, M.M. Tong, Z.Y. Long, Imidazolium-based ionic porous hybrid polymers with POSS-derived silanols for efficient heterogeneous catalytic CO_2 conversion under mild conditions, Chem. Eng. J. 381 (2020) 122765, https://doi.org/10.1016/j.cej.2019.122765.

[27] S.S. Dhankhar, C.M. Nagaraja, Porous nitrogen-rich covalent organic framework for capture and conversion of CO_2 at atmospheric pressure conditions, Micropor. Mesopor. Mat. 308 (2020) 110314, https://doi.org/10.1016/j.micromeso.2020.110314.

[28] Z.L. Shi, J.C. Jiao, Q.X. Han, Y. Xiao, L.K. Huang, M.X. Li, Synthesis Cu(I)-CN-based MOF with in-situ generated cyano group by cleavage of acetonitrile: highly efficient for catalytic cyclization of propargylic alcohols with CO2, Mol. Catal. 496 (2020) 111190, https://doi.org/10.1016/j.mcat.2020.111190.

[29] Y.P. Wang, J.Q. Nie, C.F. Lu, F.Y. Wang, C. Ma, Z.X. Chen, G.C. Yang, Imidazolium-based polymeric ionic liquids for heterogeneous catalytic conversion of CO_2 into cyclic carbonates, Micropor. Mesopor. Mat. 292 (2020) 109751, https://doi.org/10.1016/j.micromeso.2019.109751.

[30] B.B. Gu, T. Xu, G.R. Xu, J. Bai, C.P. Li, Synthesis of styrene carbonate from styrene and CO_2 catalyzed by walnut-like zeolite LZ-276, Micropor. Mesopor. Mat. 293 (2020) 109779, https://doi.org/10.1016/j.micromeso.2019.109779.

[31] M. Cipriana, K.H. Ruiza, M. Kassymova, T.T. Wang, S. Zhuiykov, S. Chaemchuen, R. Tu, F. Verpoort, 3D derived *N*-doped carbon matrix from 2D ZIF-L as an enhanced stable catalyst for chemical fixation, Micropor. Mesopor. Mat. 285 (2019) 80, https://doi.org/10.1016/j.micromeso.2019.04.053.

[32] L.C. St'astná, A. Krupkova, R. Petrickovic, M. Mullerova, J. Matousek, K. Kostejn, P. Curinova, V. Jandova, S. Sabata, T. Strasak, Multivalent bifunctional carbosilane dendrimer-supported ammonium and phosphonium organocatalysts for the coupling of CO_2 and epoxides, ACS Sustain. Chem. Eng. 8 (2020) 11692–11703, https://doi.org/10.1021/acssuschemeng.0c03367.

[33] M.K. Alavijeh, M.M. Amini, B. Notash, G. Mohammadnezhad, Formation of a potassium coordination polymer based on a novel 2-sulfono-benzene-1,3,5-tricarboxylic acid: synthesis, characterization, and application of the organocatalyst in CO_2 cycloaddition reaction, J. Mol. Struct. 1232 (2021) 130045, https://doi.org/10.1016/j.molstruc.2021.130045.

[34] A.-I. Adeleyea, S. Kellici, T. Heil, D. Morgan, M. Vickers, B. Saha, Greener synthesis of propylene carbonate using graphene-inorganic nanocomposite catalysts, Catal. Today 256 (2015) 347–357, https://doi.org/10.1016/j.cattod.2014.12.032.

[35] L.L. Hu, Q.J. Xie, J.T. Tang, C.Y. Pan, G.P. Yu, K.C. Tam, Co(III)-Salen immobilized cellulose nanocrystals for efficient catalytic CO_2 fixation into cyclic carbonates under mild conditions, Carbohydr. Polym. 256 (2021) 117558, https://doi.org/10.1016/j.carbpol.2020.117558.

[36] C. Claver, M.B. Yeamin, M. Regueroa, A.M. Masdeu-Bultó, Recent advances in the use of catalysts based on natural products for the conversion of CO_2 into cyclic carbonates, Green Chem. 22 (2020) 7665–7706, https://doi.org/10.1039/D0GC01870H.

[37] L.P. Guo, K.J. Lamb, M. North, Recent developments in organocatalyzed transformations of epoxides and carbon dioxide into cyclic carbonates, Green Chem. 23 (2021) 77–118, https://doi.org/10.1039/D0GC03465G.

[38] A. Chinnappan, A.H. Tamboli, W.J. Chung, H. Kim, Green synthesis, characterization and catalytic efficiency of hypercross-linked porous polymeric ionic liquid networks towards 4-nitrophenol reduction, Chem. Eng. J. 285 (2016) 554–561, https://doi.org/10.1016/j.cej.2015.10.032.

[39] Z.H. Hei, G.L. Song, C.Y. Zhao, W.H. Fan, M.H. Huang, Supramolecular porous ionic network based on triazinonide and imidazolium: a template-free synthesis of meso-/macroporous organic materials via a one-pot reaction-assembly procedure, RSC Adv. 6 (2016) 92443–92448, https://doi.org/10.1039/C6RA20590A.

[40] K. Täuber, A. Dani, J. Yuan, Covalent cross-linking of porous poly(ionic liquid) membrane *via* a triazine network, ACS Macro Lett. 6 (2017) 1–5, https://doi.org/10.1021/acsmacrolett.6b00782.

[41] S. Li, Z. Chen, X.C. Ling, J.J. Cao, Q. Wang, Y. Zhou, J. Wang, Engineering polyoxometalate anions on porous ionic network towards highly catalytic active noble metal clusters, Appl. Surf. Sci. 496 (2019) 143650, https://doi.org/10.1016/j.apsusc.2019.143650.

[42] Y. Zhi, P. Shao, X. Feng, H. Xia, Y. Zhang, Z. Shi, Y. Mu, X. Liu, Covalent organic frameworks: efficient, metal-free, heterogeneous organocatalysts for chemical fixation of CO_2 under mild conditions, J. Mater. Chem. A 6 (2018) 374–382, https://doi.org/10.1039/C7TA07691F.

[43] Z.W. Liu, B.H. Han, Ionic porous organic polymers for CO_2 capture and conversion, Curr. Opin. Green Sustain. Chem. 16 (2019) 20–25, https://doi.org/10.1016/j.cogsc.2018.11.008.

[44] Y.Q. Wang, J. Nie, C. Lu, F. Wang, C. Ma, Z. Chen, G. Yang, Imidazolium-based polymeric ionic liquids for heterogeneous catalytic conversion of CO_2 into cyclic carbonates, Micropor. Mesopor. Mat. 292 (2020) 109751, https://doi.org/10.1016/j.micromeso.2019.109751.

[45] Y. Zhang, K. Liu, L. Wu, H. Zhong, N. Luo, Y. Zhu, M. Tong, Z. Long, G. Chen, Silanol-enriched viologen-based ionic porous hybrid polymers for efficient catalytic CO_2 fixation into cyclic carbonates under mild conditions, ACS Sustain. Chem. Eng. 7 (2019) 16907–16916, https://doi.org/10.1021/acssuschemeng.9b04627.

[46] Y. Xie, J. Liang, Y. Fu, J. Lin, H. Wang, S. Tu, J. Li, Poly(ionic liquid)s with high density of nucleophile/electrophile for CO_2 fixation to cyclic carbonates at mild conditions, J. CO_2 Util. 32 (2019) 281–289, https://doi.org/10.1016/j.jcou.2019.04.023.

[47] E.M. Maya, E. Verde-Sesto, D. Mantione, M. Iglesias, D. Mecerreyes, New poly (ionic liquid)s based on poly(azomethine-pyridinium) salts and its use as heterogeneous catalysts for CO_2 conversion, Eur. Polym. J. 110 (2019) 107–113, https://doi.org/10.1016/j.eurpolymj.2018.07.030.

[48] Y.Q. Zhu, C. Romain, C.K. Williams, Sustainable polymers from renewable resources, Nature 540 (2016) 354–362, https://doi.org/10.1038/nature21001.

[49] P.A. Wilbon, F. Chu, C. Tang, Progress in renewable polymers from natural terpenes, terpenoids, and rosin, Macromol. Rapid Comm. 34 (2013) 8–37, https://doi.org/10.1002/marc.201200513.

[50] Z. Wang, M.S. Ganewatta, C. Tang, Sustainable polymers from biomass: bridging chemistry with materials and processing, Prog. Polym. Sci. 101 (2020) 101197, https://doi.org/10.1016/j.progpolymsci.2019.101197.

[51] X.Q. Xiong, H. Zhang, S.L. Lai, J.B. Gao, L.Z. Gao, Lignin modified by deep eutectic solvents as green, reusable, and bio-based catalysts for efficient chemical fixation of CO_2, React. Funct. Polym. 149 (2020) 104502, https://doi.org/10.1016/j.reactfunctpolym.2020.104502.

[52] S.L. Lai, J.B. Gao, H. Zhang, L. Cheng, X.Q. Xiong, Luffa sponge supported dendritic imidazolium ILs with high-density active sites as highly efficient and environmentally friendly catalysts for CO_2 chemical fixation, J. CO2 Util. 38 (2020) 148–157, https://doi.org/10.1016/j.jcou.2020.01.004.

[53] J.S. Lee, S.I. Hong, Synthesis of acrylic rosin derivatives and application as negative photoresist, Eur. Polym. J. 28 (2002) 387–392, https://doi.org/10.1016/S0014-3057(00)00204-4.

[54] X. Liu, W. Xin, J. Zhang, Rosin-based acid anhydrides as alternatives to petrochemical curing agents, Green Chem. 11 (2009) 1018–1025, https://doi.org/10.1039/B903955D.

[55] J.A. Castro-Osma, J. Martínez, F. Cruz-Martínez, M.P. Caballero, J. Fernández-Baeza, J. Rodríguez-López, A. Otero, A. Lara-Sánchez, J. Tejeda, Development of hydroxy-containing imidazole organocatalysts for CO_2 fixation into cyclic carbonates, Catal. Sci. Technol. 8 (2018) 1981–1987, https://doi.org/10.1039/C8CY00381E.

[56] Y. Wang, S. Li, Y. Yang, X. Shen, H. Liu, B. Han, A fully heterogeneous catalyst Br-LDH for the cycloaddition reactions of CO_2 with epoxides, Chem. Commun. 55 (2019) 6942–6945, https://doi.org/10.1039/C9CC03052B.

[57] Y.P. Wang, N.Q. Nie, C.F. Lu, F.Y. Wang, C. Ma, Z.X. Chen, G.C. Yang, Imidazolium-based polymeric ionic liquids for heterogeneous catalytic conversion of CO_2 into cyclic carbonates, Micropor. Mesopor. Mat. 292 (2020) 109751, https://doi.org/10.1016/j.micromeso.2019.109751.

[58] W.L. Zhang, F.P. Ma, L. Ma, Y. Zhou, J. Wang, Imidazolium-functionalized ionic hypercrosslinked porous polymers for efficient synthesis of cyclic carbonates from simulated flue gas, ChemSusChem 13 (2020) 341–350, https://doi.org/10.1002/cssc.201902952.

[59] D.G. Jia, L. Ma, Y. Wang, W.L. Zhang, J. Li, Y. Zhou, J. Wang, Efficient CO_2 enrichment and fixation by engineering micropores of multifunctional hypercrosslinked ionic polymers, Chem. Eng. J. 390 (2020) 124652, https://doi.org/10.1016/j.cej.2020.124652.

[60] M.I. Kim, S.J. Choi, D.W. Kim, D.W. Park, Catalytic performance of zinc containing ionic liquids immobilized on silica for the synthesis of cyclic carbonates, J. Ind. Eng. Chem. 20 (2014) 3102–3107, https://doi.org/10.1016/j.jiec.2013.11.051.

[61] P. Mao, W.L. Dai, W.Y. Yang, S.L. Luo, Y. Zhang, J. Mao, X.B. Luo, J.P. Zou, Polymer nanoparticles grafted zinc-containing ionic liquids: a highly efficient and recyclable catalyst for cooperative cycloaddition of CO_2 with epoxides, J. CO2 Util. 28 (2018) 96–106, https://doi.org/10.1016/j.jcou.2018.09.017.

[62] J. Gao, Q.W. Song, L.N. He, C. Liu, Z.Z. Yang, X. Han, X.D. Li, Q.C. Song, Preparation of polystyrene-supported Lewis acidic Fe(III) ionic liquid and its application in catalytic conversion of carbon dioxide, Tetrahedron 68 (2012) 3835–3842, https://doi.org/10.1016/j.tet.2012.03.048.