

# Imidazolium ionic liquid functionalized UiO-66-NH<sub>2</sub> as highly efficient catalysts for chemical fixation of CO<sub>2</sub> into cyclic carbonates

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## ABSTRACT

Imidazolium ionic liquids functionalized UiO-66-NH<sub>2</sub> MOFs were synthesized by two different approach, further applied as efficient catalysts for the catalytic conversion of CO<sub>2</sub> into cyclic carbonates. The functionalized UiO-66-NH<sub>2</sub> were investigated using various characterization technologies including XRD, NMR, FT-IR, XPS, TG-DTG, TEM, N<sub>2</sub>-adsorption, and NH<sub>3</sub>-TPD. The octahedron structure of UiO-66-NH<sub>2</sub> becomes rough after UiO-66-NH<sub>2</sub> interacted with 1-(4-carboxybutyl)-3-methylimidazolium bromide via amidation, while some small grains were formed around UiO-66-NH<sub>2</sub> species when UiO-66-NH<sub>2</sub> was functionalized by 1-(3-sulfopropyl)-3-methylimidazolium bromide ([SPMIM]Br) via the H<sub>2</sub>N- and HSO<sub>3</sub>- interaction. Moreover, when [SPMIM]Br was grafted onto the surface of UiO-66-NH<sub>2</sub>, a higher catalytic activity was found to exhibit 98.12% conversion of epichlorohydrin (ECH) and 98.23% selectivity to chloropropene carbonate (CPC) under optimized conditions (Initial pressure 2.5 MPa, 1.2 wt% catalyst of ECH, 95 °C, reaction time 8 h). No significant deactivation of the catalyst was observed after the [SPMIM]Br functionalized UiO-66-NH<sub>2</sub> was reused three times. Furthermore, several additional coupling reactions were investigated with other epoxides as substrates.

## 1. Introduction

The increasing exhaustion of fossil energy, as well as the excessive emission of carbon dioxide, have made the environment to confront a greater challenge in the world [1,2]. Therefore, it is expedient to develop a sustainable strategy for carbon dioxide utilization, and in particular, for the synthesis of organic products under mild conditions. Carbon dioxide as the nontoxic, hugely abundant and sustainable C<sub>1</sub> source has been extensively studied as a substrate for the synthesis of fine chemicals such as methanol [3], dimethyl carbonate [4–6], diethyl carbonate [7], methyl *N*-phenylcarbamate [8], formic acid [9,10], diphenyl carbonate [11], oxazolidinone [12], cyclic carbamates [13], and cyclic carbonates [14–16]. Importantly, the efficient production of cyclic carbonates via cycloaddition is one of the significant routes for carbon dioxide utilization due to the broad applications of the cyclic carbonates in the industry [17–19].

Carbon dioxide typically does not react with the epoxide to form carbonates under the mild conditions due to the low activity of the CO<sub>2</sub> molecule, although, the atomic utilization can be reached to 100%. The

deployment of a catalyst during the coupling process is usually a necessary strategy to lessen activation energy to enhancing the reaction rate, hence achieve relatively high yield. Until now, several homogeneous and heterogeneous catalysts, including functionalized resins [20], functionalized polymers [21–23], metal oxides [24], metal complexes [25–27], metal-organic framework materials [28–32], and organic bases [33,34] have been employed to promote cycloaddition reactions. In most cases, however, the catalytic systems can only be improved in the presence of additional promoters and/or organic solvents under high operating temperature and pressure.

Ionic liquids (ILs) such as anion-cation ions, have been widely used to accelerate various reactions, especially CO<sub>2</sub> cycloaddition with epoxides [35]. Because anion-cation ions within ILs can efficiently promote the reaction processes including ring-opening of epoxide, CO<sub>2</sub> can be inserted into activated epoxide as well as the ring-closing of the final product. Besides, when the ILs are applied in a catalytic system, other additives may not be required. The reaction rate can be efficiently promoted as well under benign conditions [36]. The excellent catalytic performance of ILs is primarily associated with its various unique

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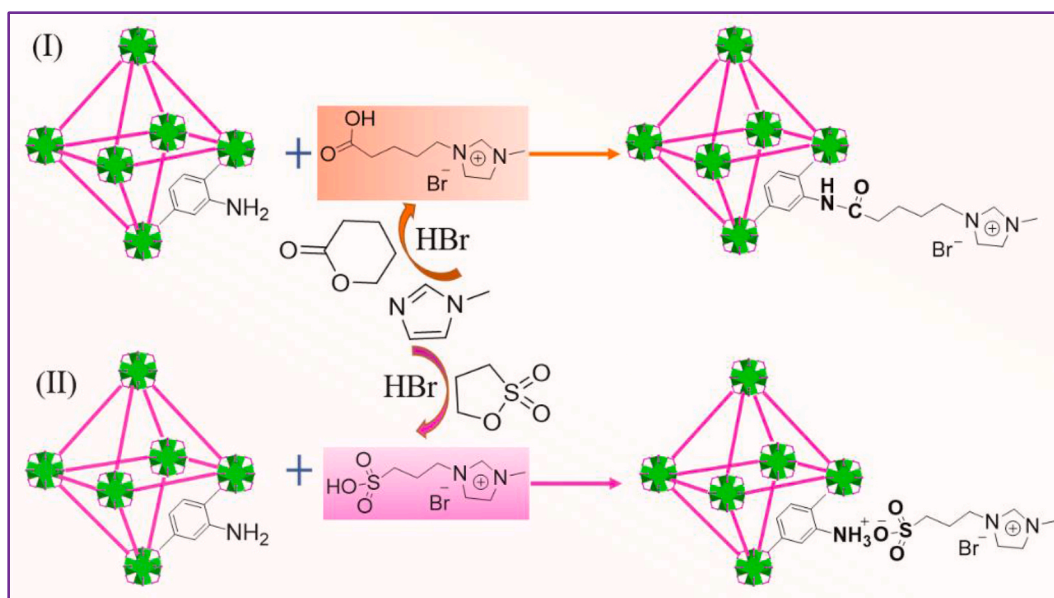
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**Scheme 1.** Synthesis of imidazolyl ionic liquids functionalized UiO-66-NH<sub>2</sub>.

properties, including high adsorption capacity, high activity, good thermal stability, and high solubility [37,38]. For example, organic salts were used as the catalysts for CO<sub>2</sub> *N*-Formylation with the amines as substrates [39]. Furthermore, acid ILs were found with the high catalytic activity in the efficient transformation of duckweed into methyl levulinate with 88% conversion and 73.7% yield under 170 °C for 5 h [40]. Carboxyl and hydroxyl functionalized imidazolium ILs were investigated in CO<sub>2</sub> cycloaddition, with a higher conversion reported in the presence of hydroxyl-containing ILs [41]. Besides, it was also found that carboxymethyl cellulose supported imidazolium ionic liquid can be used as heterogeneous catalyst for CO<sub>2</sub> chemical fixation [42]. In most cases, however, the homogeneous ILs were difficult to be separated from the reaction system and the subsequent purification process was also relatively complicated. Therefore, grafting ILs onto functionalized supports could efficiently overcome the separation difficulty, in addition to simultaneously achieving the highly catalytic activity for CO<sub>2</sub> conversion.

Metal–organic frameworks (MOFs) consisting of metallic ions and organic ligands endow them with organic and inorganic hybrid properties, of which large surface areas and adjustable pore sizes afford these materials with potential applications in various fields, especially as catalyst supports. Besides, it has been widely reported that the metal nodes of MOFs can serve as the Lewis acid sites, while the organic linkers containing-nitrogen usually have the ability to enhance base-catalyzed reactions [43,44]. Therefore, the incorporation of ILs in MOFs combines multiple advantages together, synchronously showing the required bifunctionality [45,46]. However, most researchers only introduced the ILs into MOFs cages [47–49]. As a result, the ILs were easily leached when ILs supported MOFs were adopted in the liquid reactions, hence, the graft of ILs onto the surface of MOFs via chemical bonds will be beneficial for both structural stability and convenient recovery.

In the present work, a series of protic imidazolium ionic liquids with different alkyl chains were employed for CO<sub>2</sub> conversion, of which the IL consisting of 1-methylimidazole and 1-bromopropane was observed with the highest catalytic activity, after which two synthetic pathways were adopted to graft the ILs containing 1-methylimidazole onto the UiO-66-NH<sub>2</sub> surface via the formation of chemical bonds. The ILs functionalized UiO-66-NH<sub>2</sub> samples were further applied in the catalytic conversion of CO<sub>2</sub> into cyclic carbonates. Besides, reaction conditions including operating temperature, initial pressure, reaction time, catalyst dose and

recyclability were systemically investigated, while the coupling of epoxide with CO<sub>2</sub> was also extensively studied under the optimal conditions. Finally, a coupling mechanism was also proposed.

## 2. Experimental section

### 2.1. Synthesis of UiO-66-NH<sub>2</sub>

In a typical process, 2-aminoterephthalic acid (0.181 g, 1.0 mmol) and ZrCl<sub>4</sub> (0.466 g, 2 mmol) were first dissolved in DMF (60 mL), after which 3.5 mL acetic acid was added into the mixed system. After being stirred for another 30 min, the mixed system was sealed and heated at 120 °C for another 72 h in a stainless-steel autoclave. Thereafter, the stainless-steel autoclave was cooled down to room temperature, and the obtained milky white suspension was centrifuged and washed with the organic solution (DMF/methanol) three times, followed by drying at 60 °C for 24 h.

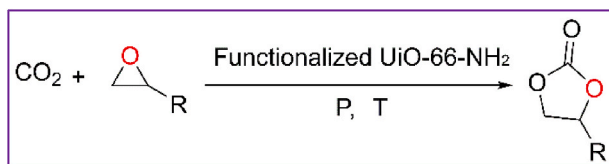
### 2.2. Synthesis of imidazolyl ionic liquid functionalized UiO-66-NH<sub>2</sub>

#### 2.2.1. 1-(4-carboxybutyl)-3-methylimidazolium bromide, CB@UiO-66-NH<sub>2</sub>

The process (Scheme 1I) for the synthesis of 1-(4-carboxybutyl)-3-methylimidazolium bromide ([CBMIM]Br) is similar with Reinhardt's report [50], with the only different that 5-bromovaleric acid was replaced by delta-valerolactone and hydrogen bromide, and the result was characterized by <sup>1</sup>H NMR (Fig. S3). The obtained [CBMIM]Br (10 mmol), thionyl chloride (60 mmol) and toluene (10 mL) were mixed and stirred at 90 °C. After the reaction was maintained for another 4 h, UiO-66-NH<sub>2</sub> (0.2 g) was added in the evaporated mixture. Subsequently, 15 mmol trichloromethane and moderate methylbenzene were charged into above system until the UiO-66-NH<sub>2</sub> was fully dissolved (room temperature). After stirring for another 3 h, [CBMIM]Br functionalized UiO-66-NH<sub>2</sub> (CB@UiO-66-NH<sub>2</sub>) was obtained after being washed and dried (60 °C, 12 h).

#### 2.2.2. 1-(3-sulfofpropyl)-3-methylimidazolium bromide, SP@UiO-66-NH<sub>2</sub>

1-(3-sulfofpropyl)-3-methylimidazolium bromide ([SPMIM]Br) was synthesized according to a modified method reported by Shi [51]. As shown in Scheme 1II, the mixture including 1-methylimidazolium (1.642 g, 20 mmol), 1,3-propyl sultone (2.442 g, 20 mmol) and



**Scheme 2.** Catalytic conversion of CO<sub>2</sub> into cyclic carbonates.

diethyl ether (20 mL) were reflux for 6 h. Thereafter, the reacted mixture was washed with diethyl ether thrice, and then acidified by hydrogen bromide (Fig. S4, <sup>1</sup>H NMR). The obtained [SPMIM]Br (0.5 g) and UiO-66-NH<sub>2</sub> (0.5 g) were thereafter dispersed in 25 mL deionized H<sub>2</sub>O, and subsequently heated at 120 °C for 12 h under magnetic stirring. After being washed and dried overnight (60 °C), the [SPMIM]Br functionalized UiO-66-NH<sub>2</sub> was obtained and labeled as SP@UiO-66-NH<sub>2</sub>.

To unveil the characteristic of the ILs functionalized UiO-66-NH<sub>2</sub>, various tests including XRD, FT-IR, TEM, XPS, TGA, N<sub>2</sub>-adsorption, CO<sub>2</sub>-adsorption, and NH<sub>3</sub>-TPD were employed and the detailed parameters were described in Supplementary Materials.

### 2.3. Catalyst performance test

The catalytic activities of all the as-synthesized catalysts were detected via the enhancement of CO<sub>2</sub> into cyclic carbonates as performed in a 100 mL stainless autoclave equipped with a thermocouple and an electromagnetic stirrer (Scheme 2).

Generally, the catalyst and epoxide were charged into the reactor sequentially, and the mixture was quickly sealed and pressurized with carbon dioxide at an explored pressure. Subsequently, the autoclave was heated to a target temperature and maintained there for 6 h. At the end

of the reaction, the mixture was cooled down in an ice bath. When the temperature was detected as ~5 °C, the reacted mixture was immediately separated via centrifugation, followed by a gas chromatograph (GC-6890) analysis. The conversion of epoxide and selectivity to cyclic carbonate were calibrated using ethylene glycol butyl ether as internal standard.

$$\text{Epoxide conversion} = \frac{\text{mol of epoxide}_{\text{initial}} - \text{mol of epoxide}_{\text{residual}}}{\text{mol of epoxide}_{\text{initial}}} \times 100\% \quad (1)$$

$$\text{CLC selectivity} = \frac{\text{mol of CLC}_{\text{formed}}}{\text{mol of CLC}_{\text{formed}} + \text{mol of by-products}} \times 100\% \quad (2)$$

## 3. Results and discussion

### 3.1. Characterization of the functionalized UiO-66-NH<sub>2</sub>

It can be seen that the crystal structure of all the synthesized samples was very similar to each other according to the XRD patterns (Fig. 1a), and also in consistent with the literatures [52,53], suggesting that the crystal structure of UiO-66-NH<sub>2</sub> remained unchanged during the preparation.

The chemical groups of the synthesized samples were detected by FT-IR spectra, and the results was shown in Fig. 1b. The bands associated with carboxylate groups were only detected at 1570-1490 cm<sup>-1</sup> and 1427-1376 cm<sup>-1</sup> instead of the characteristic region (1800-1680 cm<sup>-1</sup>), suggesting that the saturated coordination between organic ligands and zirconium ions have resulted into complete deprotonation of -COOH (2-aminoterephthalic acid) [54-56]. Besides, the residual DMF was also confirmed by the C=O stretching vibration of amide compounds (1646

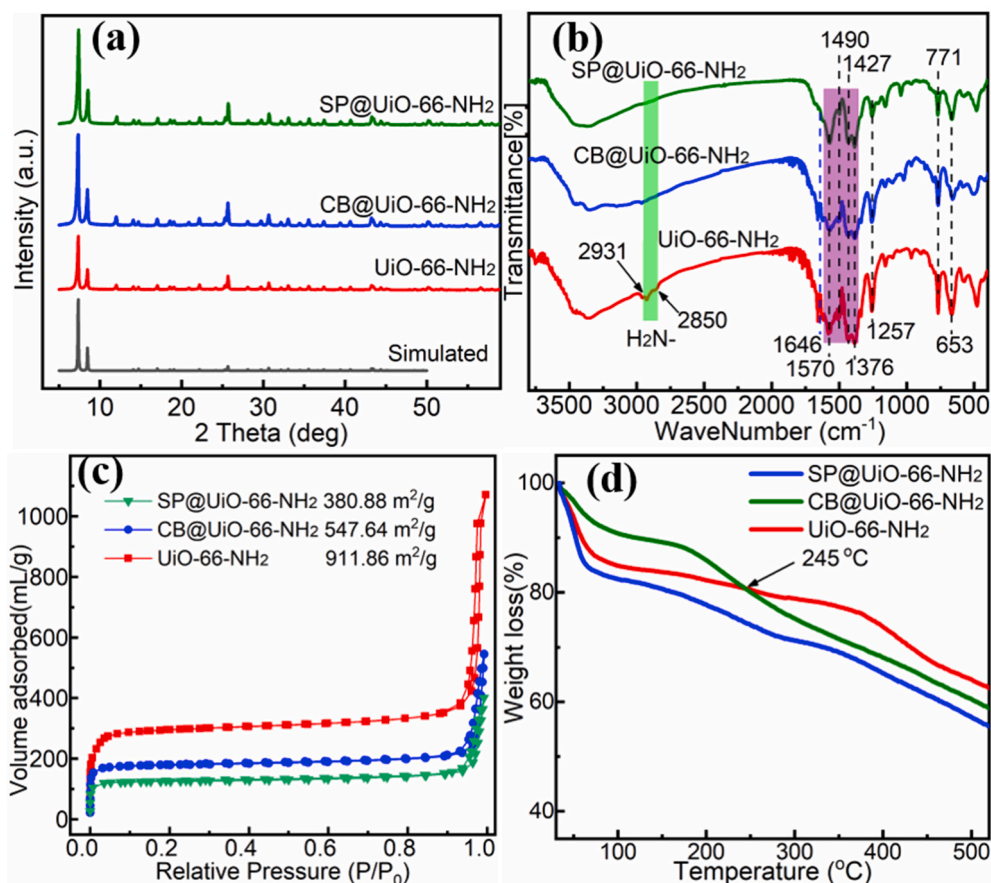


**Fig. 1.** (a) XRD patterns, (b) FT-IR spectra, (c) N<sub>2</sub>-adsorption-desorption isotherms, TGA profiles of UiO-66-NH<sub>2</sub>, CB@UiO-66-NH<sub>2</sub>, SP@UiO-66-NH<sub>2</sub>.

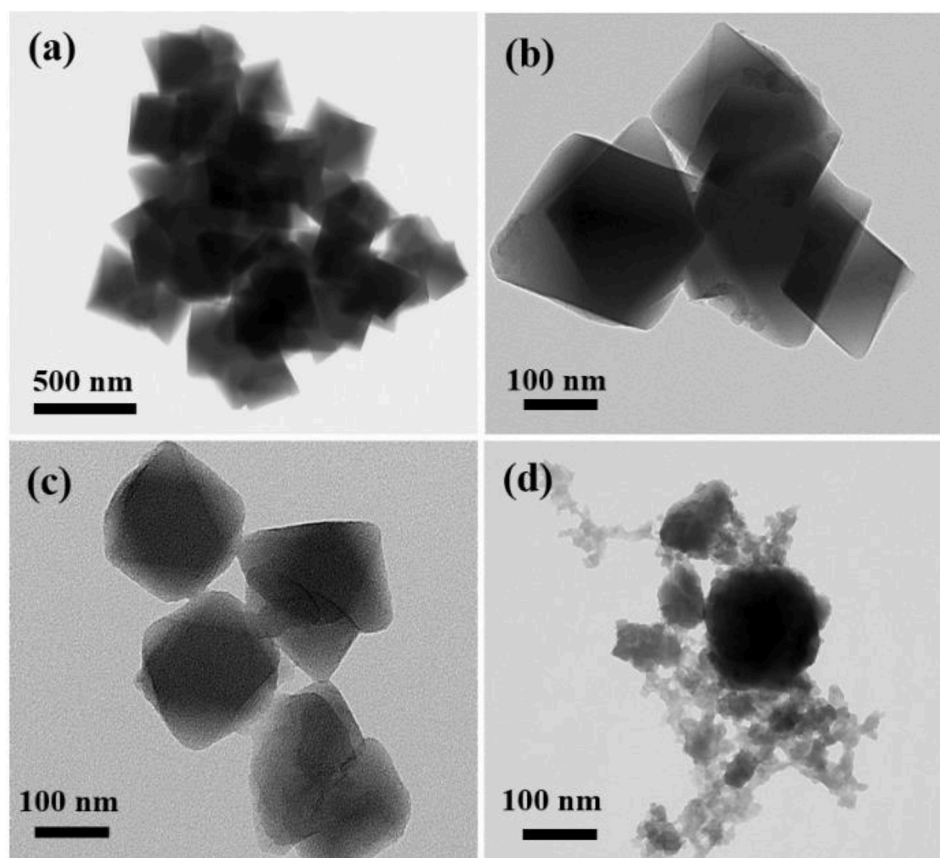


Fig. 2. TEM images of (a–b) UiO-66-NH<sub>2</sub>, (c) CB@UiO-66-NH<sub>2</sub>, (d) SP@UiO-66-NH<sub>2</sub>.

cm<sup>-1</sup>) [57]. The adsorption bands appearing in the range of 2931–2850 cm<sup>-1</sup> were assigned to the H<sub>2</sub>N– groups of 2-aminoterephthalic acid [58]. However, the signals of H<sub>2</sub>N– groups were hardly observed both for CB@UiO-66-NH<sub>2</sub> and SP@UiO-66-NH<sub>2</sub>, implying that H<sub>2</sub>N– groups of UiO-66-NH<sub>2</sub> have sufficiently reacted with HSO<sub>3</sub><sup>-</sup>/HOOC<sup>-</sup>.

N<sub>2</sub> adsorption-desorption data of the three samples were recorded at liquid nitrogen conditions (Fig. 1c, Table S1). All the studied samples were found to possess type I isotherms, indicating that both microporous and mesoporous structures coexisted within the materials [47]. Moreover, the BET surface area and pore volume were in the order as follows, UiO-66-NH<sub>2</sub> (911.86 m<sup>2</sup>/g, 1.656 mL/g) > CB@UiO-66-NH<sub>2</sub> (547.64 m<sup>2</sup>/g, 0.844 mL/g) > SP@UiO-66-NH<sub>2</sub> (380.88 m<sup>2</sup>/g, 0.621 mL/g), of which SP@UiO-66-NH<sub>2</sub> has a larger decrease than CB@UiO-66-NH<sub>2</sub>. This indicated that the pores of UiO-66-NH<sub>2</sub> partially made to occur by ILs via the formation of chemical bonds, while [SPMIM]Br ILs were more easily grafted onto the surface of the framework via H<sub>2</sub>N– and HSO<sub>3</sub><sup>-</sup>.

The thermal analysis profiles presented in Fig. 1d were mainly consisted of two weight loss in the range of 30–500 °C. A less weight loss (30–245 °C) for CB@UiO-66-NH<sub>2</sub> was observed compared with UiO-66-NH<sub>2</sub>, which was associated with dissociation of the residual DMF and methanol solvents during the preparation. Moreover, SP@UiO-66-NH<sub>2</sub> was observed to possess a larger weight loss than CB@UiO-66-NH<sub>2</sub>, suggesting that more ionic liquids were grafted onto the surface of the SP@UiO-66-NH<sub>2</sub> via NH<sub>2</sub><sup>-</sup> and HSO<sub>3</sub><sup>-</sup> interaction.

TEM images of UiO-66-NH<sub>2</sub>, CB@UiO-66-NH<sub>2</sub>, and SP@UiO-66-NH<sub>2</sub> were shown in Fig. 2. The microstructure of UiO-66-NH<sub>2</sub> was octahedron in shape (Fig. 2a and b) [59]. After the interaction of UiO-66-NH<sub>2</sub> with [CBMIM]Br via amidation, the surface of UiO-66-NH<sub>2</sub> becomes rough (Fig. 2c), suggesting that [CBMIM]Br was grafted to the crystal structure of UiO-66-NH<sub>2</sub> via covalent bond. However, the small grains were formed around UiO-66-NH<sub>2</sub> species (Fig. 2d) when [CBMIM]Br was replaced by [SPMIM]Br, which was attributed to the presence of

more interaction between [SPMIM]Br and UiO-66-NH<sub>2</sub>. Besides, the similar microstructures of the functionalized samples were also observed by SEM characterization (Fig. S3).

The newly-formed chemical bonds within the synthesized materials can be characterized by XPS technology. Apart from O1s, N1s, Zr3p, Zr3d, C1s, S2p signals, the appearance of Br3d signal for the two samples further confirmed the presence of bromide ion inside the functionalized catalysts (Fig. 3a). To analyze the chemical state clearly, three symmetrical components were used to fit the C1s spectrum (Fig. 3b), which correspond to C–C, C–N/C=N, and –COO– functional groups respectively [60,61]. The binding energies (B.E.) of C–N/C=N and –COO– both for the CB@UiO-66-NH<sub>2</sub> and SP@UiO-66-NH<sub>2</sub> shifted downwards compared to that of UiO-66-NH<sub>2</sub>, suggesting that the newly-formed chemical bonds were more stable compared with the UiO-66-NH<sub>2</sub>. Besides, the area corresponding to –COO– for SP@UiO-66-NH<sub>2</sub> decreases obviously, which was due to the volatilization of carboxyl-containing groups during the preparation. N 1s spectra of functionalized samples were divided into several symmetrical peaks, and the results were shown in Fig. 3c. The B.E. centered at 399.4 eV, 400.7 eV and 401.4 eV were related to N–C [62], N–H [63], and imidazole [64,65], respectively, while the area representing imidazole nitrogen of SP@UiO-66-NH<sub>2</sub> was higher than that of CB@UiO-66-NH<sub>2</sub>. This result confirmed the successful grafting of ILs onto the surface of UiO-66-NH<sub>2</sub>, and [SPMIM]Br was more easily linked to amino of UiO-66-NH<sub>2</sub> via H<sub>2</sub>N– and HSO<sub>3</sub><sup>-</sup>.

The catalytic activity in the promotion of CO<sub>2</sub> conversion was associated with Lewis basic-acid sites within the internal structure or/and exposed onto the surface of the synthesized material. The catalytic activity of acid site is generally categorized into three grades based on the NH<sub>3</sub>-TPD profile (Fig. 4a). The areas appearing into the temperature range of 50–200 °C, 200–400 °C and >400 °C represented as weak, moderate, and strong acid sites, respectively [66]. The area appearing in 50–200 °C for both CB@UiO-66-NH<sub>2</sub> and SP@UiO-66-NH<sub>2</sub> showed a

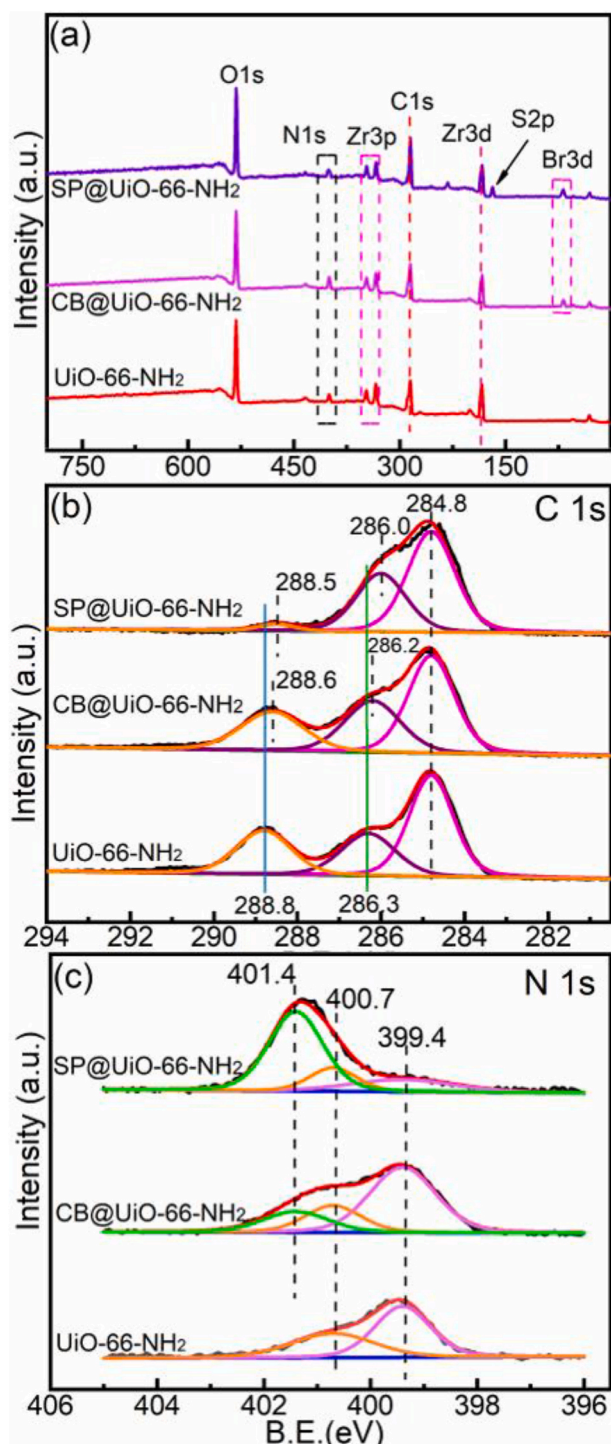


Fig. 3. XPS spectra of UiO-66-NH<sub>2</sub>, CB@UiO-66-NH<sub>2</sub>, SP@UiO-66-NH<sub>2</sub>. (a) Full spectrum, (b) C1s, (c) N1s.

slight decrease compared to that of UiO-66-NH<sub>2</sub>. However, when the desorption temperature increased from 200 to 350 °C, the area associated with SP@UiO-66-NH<sub>2</sub> becomes larger than that of CB@UiO-66-NH<sub>2</sub>, suggesting that the amount of the moderate acid sites rises following with the decrease in weak basic sites, while more moderate acid sites were formed when UiO-66-NH<sub>2</sub> was grafted by [SPMIM] Br via NH<sub>2</sub><sup>-</sup> and HSO<sub>3</sub><sup>-</sup> interactions. To confirm the presence of Lewis basic sites within the synthesized materials, CO<sub>2</sub> desorption was carried out under ambient conditions, with the results displayed in Fig. 4b. The capacity of SP@UiO-66-NH<sub>2</sub> for CO<sub>2</sub> adsorption (34.78 mL/g) was

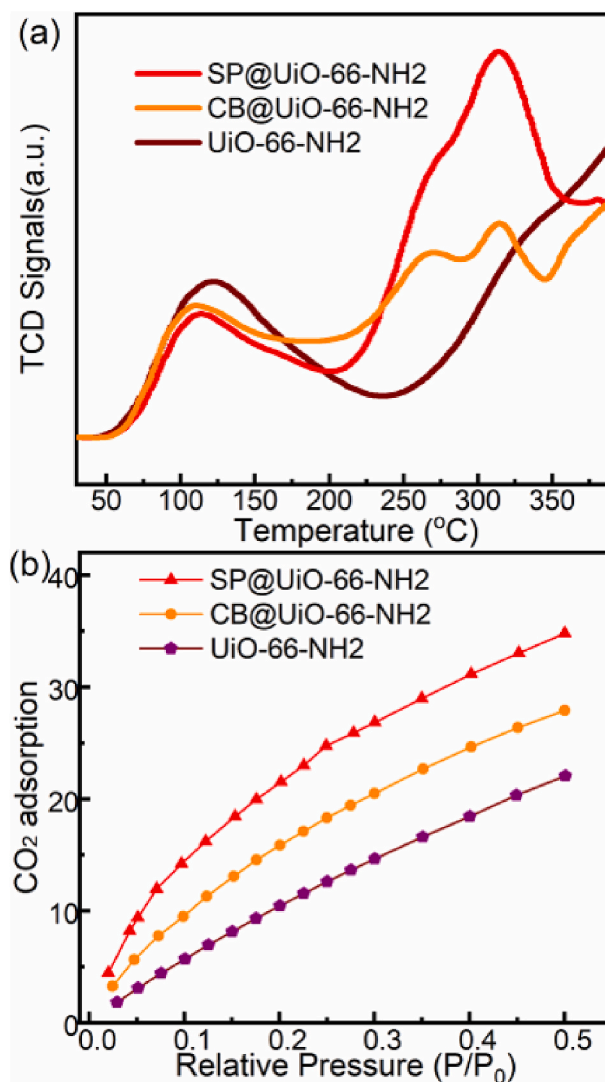


Fig. 4. (a) NH<sub>3</sub>-TPD and (b) CO<sub>2</sub>-adsorption profiles of UiO-66-NH<sub>2</sub>, CB@UiO-66-NH<sub>2</sub>, SP@UiO-66-NH<sub>2</sub>.

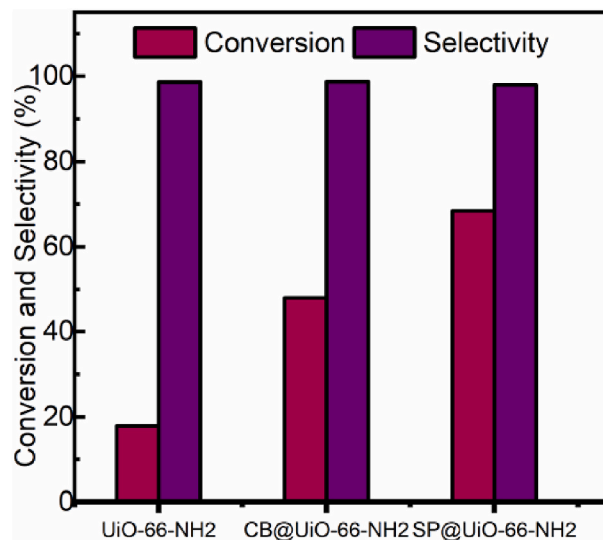
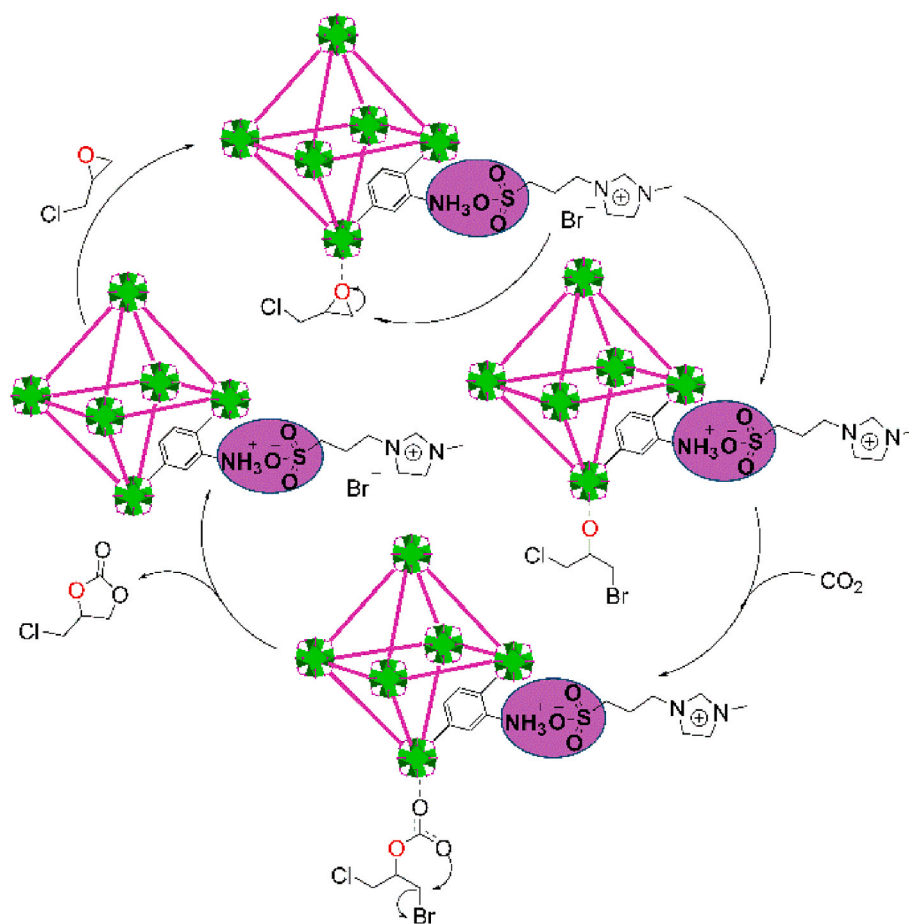


Fig. 5. Catalytic activity of CB@UiO-66-NH<sub>2</sub> and SP@UiO-66-NH<sub>2</sub> in promotion of CO<sub>2</sub> conversion. Reaction conditions: 90 °C, 1.0 wt% catalyst of ECH, initial pressure 2.5 MPa, 8 h.



**Scheme 3.** A proposed reaction path of CO<sub>2</sub> coupling with epoxide in the presence of SP@UiO-66-NH<sub>2</sub>.

larger compared with that of CB@UiO-66-NH<sub>2</sub> (27.91 mL/g), while the  $S_{\text{BET}}$  of SP@UiO-66-NH<sub>2</sub> (380.88 m<sup>2</sup>/g) was less than CB@UiO-66-NH<sub>2</sub> (547.64 m<sup>2</sup>/g), suggesting that the increasing adsorption capacity of SP@UiO-66-NH<sub>2</sub> was mainly related to the nitrogen-containing groups [67–69], and a larger number of [SPMIM]Br were grafted onto the surface of UiO-66-NH<sub>2</sub>.

### 3.2. CO<sub>2</sub> coupling with ECH and optimized operating conditions

Because of 1-butyl-3-methylimidazolium bromide processing the highest catalytic activity for CO<sub>2</sub> fixation (Table S1), therefore, two kinds of ILs containing 1-methylimidazole and bromide ion were employed for the synthesis of functionalized UiO-66-NH<sub>2</sub>.

Catalytic performance of CB@UiO-66-NH<sub>2</sub> and SP@UiO-66-NH<sub>2</sub> for CO<sub>2</sub> conversion was studied with ECH as the probe (Fig. 5). It can be seen that the higher catalytic performance of 68.43% ECH conversion and 97.98% selectivity of CPC was achieved when the SP@UiO-66-NH<sub>2</sub> was employed in the fixed system, while 47.96% conversion and 98.73% selectivity was observed in the presence of CB@UiO-66-NH<sub>2</sub>. This can be accounted by the following reasons: A larger number of moderate acid sites were formed within SP@UiO-66-NH<sub>2</sub> (Fig. 4a), which can efficiently promote the ring-opening process (Scheme 3). Simultaneously, the capacity of CO<sub>2</sub> adsorption was also enhanced when UiO-66-NH<sub>2</sub> was functionalized by [SPMIM]Br (Fig. 4b), suggesting that a larger number of [SPMIM]Br ionic liquids within UiO-66-NH<sub>2</sub> (Fig. 3b) can make carbon dioxide become more active during the fixed system. Hence, it can be confirmed that the higher catalytic activity is in good agreement with increasing basic-acid sites.

Since SP@UiO-66-NH<sub>2</sub> was observed with the highest catalytic activity, it was thereafter chosen to optimize operating reaction

conditions. Operating temperature as one of the reaction conditions affecting the ECH conversion was explored at a series of fixed conditions (2.5 MPa, 1.0 wt% catalyst of ECH, 8 h), and results were shown in Fig. 6a. When the reaction temperature was gradually changed from 80 °C to 110 °C, the conversion of ECH increased from 41.09% (80 °C) to 92.94% (95 °C), and thereafter exhibited a slight increase to 97.18% (110 °C), which was mainly associated with the decrease in ECH and increase in CPC. In other words, the continuous conversion was observed to be trace at the end of the fixed reaction system. Considering the conversion of ECH as well as the energy consumption, 95 °C was adopted for later sections.

Carbon dioxide concentration including the gas and liquid phase within the autoclave, as one of the factors in determining ECH conversion, was investigated via initial pressurization from 2.0 MPa to 3.0 MPa (Fig. 6b). The conversion of ECH was obviously promoted from 79.48% (2.0 MPa) to 92.94% (2.5 MPa), after which it showed a slight fluctuation. In general, the effects on the conversion can be clarified with the following interpretation: low carbon dioxide concentration cannot provide rich molecules to participate in the CPC synthesis. Therefore, considering an industrial production (to obtain more product with minimum reaction pressure), 2.5 MPa was regarded as the optimal CO<sub>2</sub> concentration.

For a chemical reaction, catalyst concentration is the key factor affecting the reaction procedure, and this was studied via altering the initial pressure (Fig. 6c). With an increasing SP@UiO-66-NH<sub>2</sub> concentration (from 0.6%wt. To 1.4%wt. of ECH), ECH conversion was obviously accelerated from 67.38% (0.6%wt. of ECH) to 98.12% (1.2%wt. of ECH), followed by a slight increase to 98.56% (1.4%wt. of ECH), implying that low concentration of catalyst within the reaction liquid cannot provide ample active sites for enhancing CO<sub>2</sub> insertion into ECH.

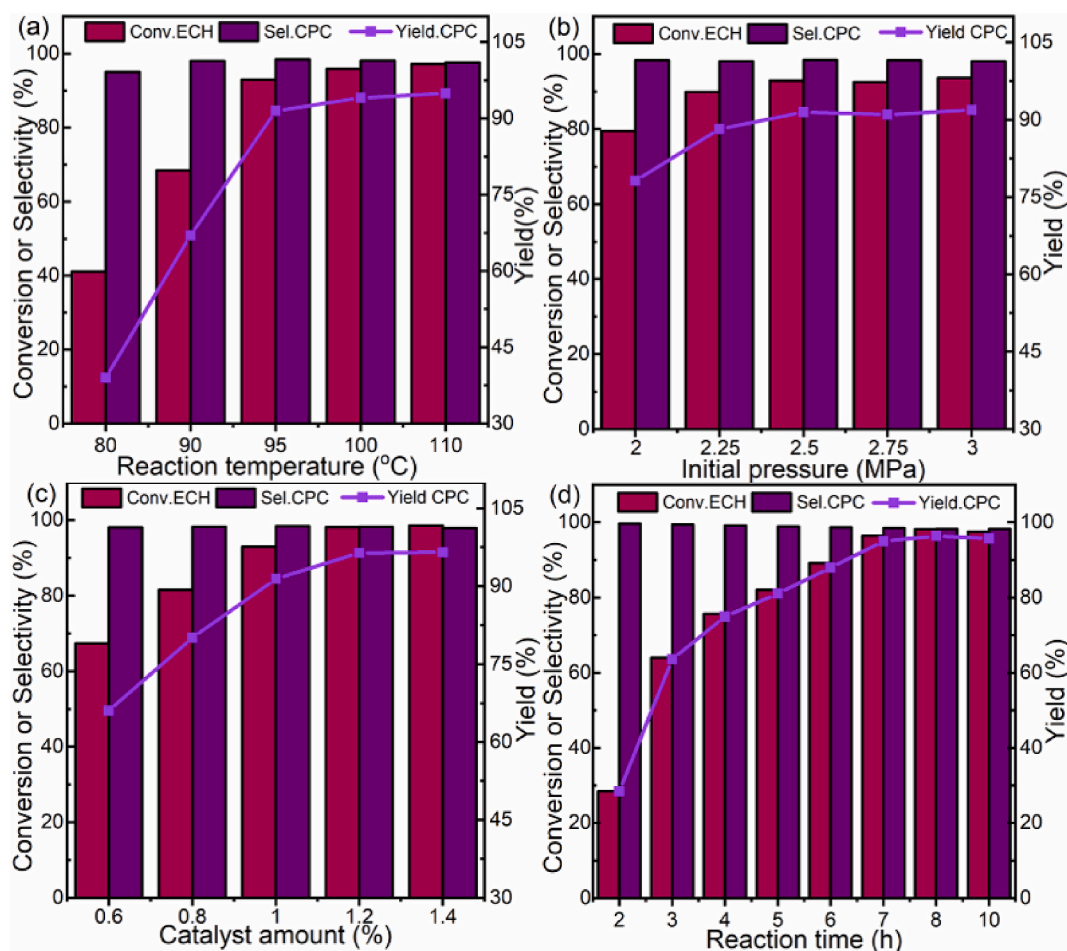


**Fig. 6.** (a) Effects of reaction temperature, (b) Effects of initial pressure, (c) Effects of catalyst amount, (d) Effects of reaction time. The optimized conditions: 95 °C, 1.2 wt% catalyst of ECH, initial pressure 2.5 MPa, 8 h.

In addition, the slow increase in ECH conversion is attributed to the abundant catalyst molecules. Hence, to achieve the higher CPC yield with less catalyst amount, 1.2wt. catalyst of ECH was more suitable for this fixed system.

Reaction time is also an important factor in valuing product synthesis, especially for industrial production. Generally, the process was investigated via the prolongation of the reaction time (Fig. 6d). When the reaction was carried out at 95 °C, the conversion of ECH was instantly enhanced from 28.46% (2 h) to 96.43% (7 h), thereafter exhibited a near constant increase (98.12%, 8 h) with time, which suggested that ECH has been completely converted after the reaction was achieved above 8 h.

According to the above analysis, when the coupling reaction was performed at 2.5 MPa initial pressure, 95 °C (8 h) and 1.2 wt% catalyst of ECH, the best result with 98.12% conversion of ECH and 98.23% selectivity to CPC can be achieved in the presence of SP@UiO-66-NH<sub>2</sub>.

### 3.3. Recyclability of SP@UiO-66-NH<sub>2</sub>

The reusability of SP@UiO-66-NH<sub>2</sub> onto promoting carbon dioxide into ECH was investigated under the optimized reaction conditions. During the process of reobtaining the SP@UiO-66-NH<sub>2</sub>, the liquid mixture including the synthesized CPC and trace ECH was separated via centrifugation, and the residual precipitate was directly charged into the autoclave for the next coupling reaction (Fig. 7a). It could be seen that only a slow deactivation of SP@UiO-66-NH<sub>2</sub> in ECH conversion was observed after being reused thrice. The decreasing conversion of ECH may be associated with the slow leaching of the grafted imidazolium

ionic liquid instead of the collapse in UiO-66-NH<sub>2</sub> crystal structure. To confirm this viewpoint, the residual precipitate was washed with ethanol, and then dried at 60 °C for 12 h, for XRD, FT-IR, N<sub>2</sub>-adsorption characterization (Fig. 7b–d). Intriguingly, XRD patterns (Fig. 7b) and FT-IR spectra (Fig. 7d) of the recovered sample were very similar with the fresh sample, suggesting that the crystal structure of UiO-66-NH<sub>2</sub> was stable during the liquid reaction, and the catalytic activity of SP@UiO-66-NH<sub>2</sub> was easily regenerated via the grafting of the ionic liquid. While only the S<sub>BET</sub> showed an obvious decrease for the recovered sample (Fig. 7c), implying that the adsorbed organics have covered the active sites.

### 3.4. CO<sub>2</sub> coupling reaction with other epoxides

To further study the coupling ability of SP@UiO-66-NH<sub>2</sub> used as a catalyst to convert carbon dioxide insertion into cyclic carbonates, additional epoxides including propane oxide (PO), allyl-glycidyl ether (AGE), styrene oxide (SO), and butyl-glycidyl ether (BGE) were adopted as the substrates to react with CO<sub>2</sub> (Table 1). It can be observed that various carbonates derived from all the studied substrates were efficiently promoted at 95 °C for 8 h, and the synthesized carbonates were also confirmed by <sup>1</sup>H NMR (Fig. S6). However, the relatively low conversion was obtained for BGE when employed as the coupling reagent. This was mainly associated with the large steric hindrance of BGE molecule, making BGE difficulty enter into the pore structure. In other words, the end oxygen atom of BGE molecule was not easily adsorbed by the metal node, which leads to a low conversion. Besides, the solubility of CO<sub>2</sub> within the studied epoxides may be another factor for

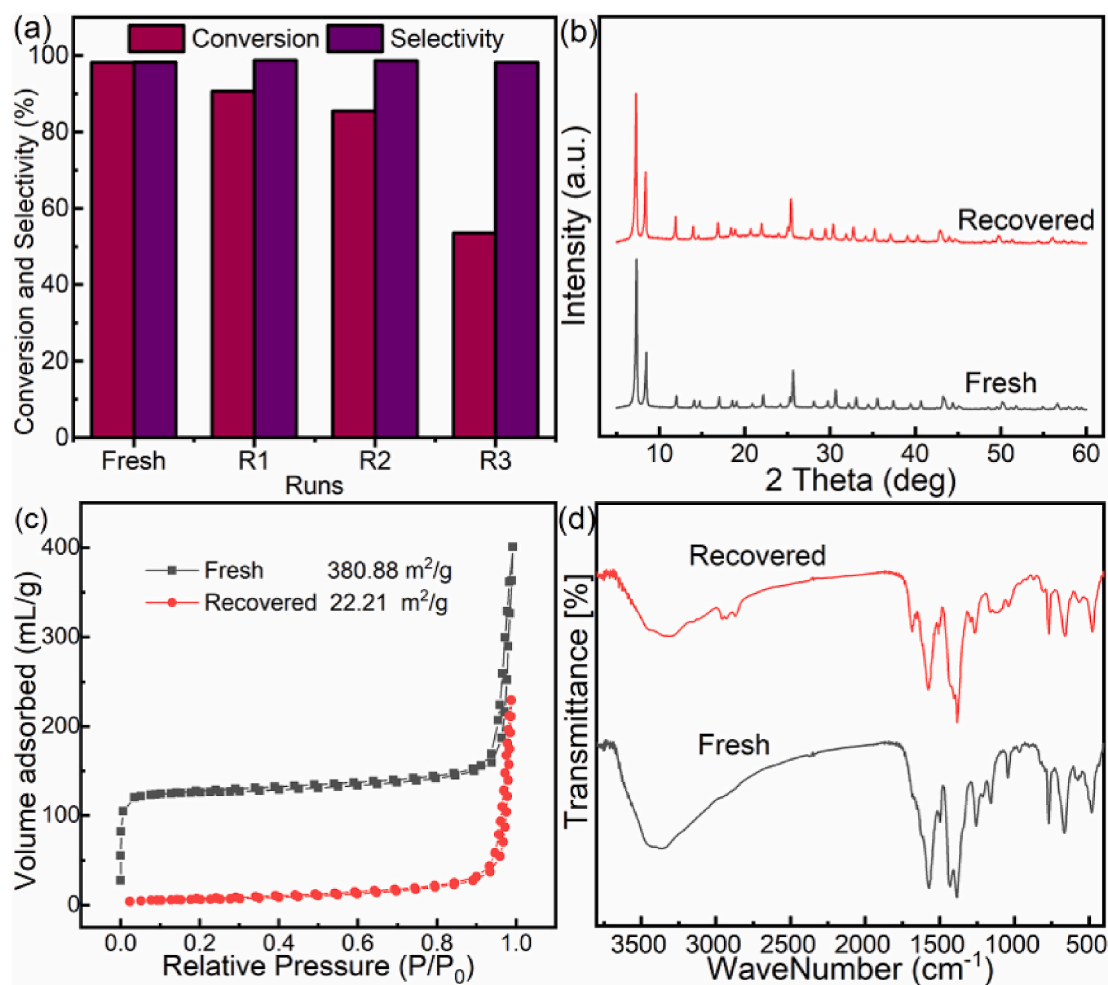


**Fig. 7.** (a) The reused results of SP@UiO-66-NH<sub>2</sub>. This reaction was conducted using the optimal conditions. (b) XRD patterns, (c) N<sub>2</sub>-adsorption profiles, (d) FT-IR spectra of recovered SP@UiO-66-NH<sub>2</sub>.

**Table 1**

CO<sub>2</sub> cycloaddition with other epoxides catalyzed by SP@UiO-66-NH<sub>2</sub>\*

| Entry          | Epoxides                                                                            | Co-catalyst | Conc. (%) | Sel. (%) | Yield (%) | Temp. (°C) | Time(h) |
|----------------|-------------------------------------------------------------------------------------|-------------|-----------|----------|-----------|------------|---------|
| 1 <sup>a</sup> |  | —           | 98.12     | 98.23    | 96.38     | 95         | 8       |
| 2 <sup>a</sup> |  | —           | 66.54     | 99.58    | 66.26     | 95         | 8       |
| 3 <sup>a</sup> |  | —           | 60.47     | 98.71    | 59.68     | 95         | 8       |
| 4 <sup>a</sup> |  | —           | 40.36     | 96.84    | 39.08     | 95         | 8       |
| 5 <sup>a</sup> |  | —           | 58.84     | 96.21    | 56.61     | 95         | 8       |
| 6 <sup>b</sup> |  | —           | —         | —        | 99        | 100        | 24      |
| 7 <sup>c</sup> |  | TBAB        | —         | —        | 95        | 100        | 18      |
| 8 <sup>d</sup> |  | TBAB        | —         | —        | 92        | 90         | 9       |

<sup>a</sup> Reaction conditions: epoxide 16.66 g, 95 °C, 1.2 wt% catalyst of epoxide, initial pressure 2.5 MPa.

<sup>b</sup> ECH 0.508 g, catalyst 50 mg, 1 bar [70].

<sup>c</sup> ECH, catalyst 0.2 mol %, TBAB 0.4 mol %, 1 bar [71].

<sup>d</sup> ECH 0.796 g, TABA 2.5 mol%, catalyst 0.025 mmol, 2.5 bar [72].

interpreting the difference in yield of cyclic carbonates. In addition, compared with other catalysts (Table 1), the functionalized UiO-66-NH<sub>2</sub> was found to process excellent catalytic activity for CO<sub>2</sub> conversion when employed alone under mild conditions. Besides, the SP@UiO-66-

NH<sub>2</sub> showed an almost equal catalytic activity when less sample was added in the cocatalyst-free system (Table S2).

### 3.5. A proposed reaction pathway for CO<sub>2</sub> conversion

It has been reported that the coupling process includes ring opening of epoxide, CO<sub>2</sub> insertion, and ring closure of the intermediate, of which the ring-opening state of epoxide is a key step for CO<sub>2</sub> cycloaddition: the step is significantly affected by the activity of the electrophilic reagent (Lewis acid sites) and nucleophilic reagent (Br<sup>−</sup>) [73]. Since the synthesized SP@UiO-66-NH<sub>2</sub> possesses structure with anion ions (Br<sup>−</sup>), the metal ions within the crystal structure can be functionalized as Lewis acid sites. Hence, a possible reaction path was proposed for CO<sub>2</sub> conversion in the presence of SP@UiO-66-NH<sub>2</sub> (Scheme 3). The O atom of epoxide firstly coordinated with metal node (Zr ions) within UiO-66-NH<sub>2</sub>, and then a ring-opening intermediate was formed via Br ion attacking the less sterically hindered carbon of the coordinated epoxide. Subsequently, the C atom of the activated CO<sub>2</sub> molecules was attacked by the O atom in O–Zr bond of the ring-opening intermediate, forming another intermediate which finally underwent the ring closure to produce carbonate and the SP@UiO-66-NH<sub>2</sub> was also regenerated.

### 4. Conclusions

A series of imidazolium ionic liquids were prepared, of which 1-butyl-3-methylimidazolium bromide IL was found to exhibit the highest catalytic activity for CO<sub>2</sub> cycloaddition. Two kinds of ILs containing 1-methylimidazole and Br<sup>−</sup> ions (1-(3-sulfoxypropyl)-3-methylimidazolium bromide, [SPMIM]Br; 1-(4-carboxybutyl)-3-methylimidazolium bromide, [CBMIM]Br) were employed for the synthesis of functionalized UiO-66-NH<sub>2</sub> via amidation as well as H<sub>2</sub>N– and HSO<sub>3</sub>– interaction, respectively. It was found that UiO-66-NH<sub>2</sub> became more active while functionalized by [SPMIM]Br, which was ascribed to the more graft of [SPMIM]Br ILs onto the surface of UiO-66-NH<sub>2</sub> via H<sub>2</sub>N– and HSO<sub>3</sub>– interaction. The structure and physiochemical properties of functionalized UiO-66-NH<sub>2</sub> were determined by various techniques. The best results of 98.12% conversion of epichlorohydrin and 96.38% yield of chloropropene carbonate were observed at 95 °C for 8 h, CO<sub>2</sub> pressure of 2.5 MPa, and 1.2 wt% catalyst of ECH. Moreover, no significant catalyst deactivation was observed after functionalized UiO-66-NH<sub>2</sub> was reused for three times. Furthermore, the coupling reactions were also expansively studied with other epoxides as substrates.

### CRediT authorship contribution statement

**Yuanfeng Wu:** Experimental, Writing - original draft, DFT calculations. **Yang Xiao:** Writing - review & editing, Language revision. **Hui Yuan:** XRD Testing. **Zhongqi Zhang:** FT-IR Testing. **Shengbin Shi:** Synthesis of ionic liquids and NMR Testing. **Ruiping Wei:** Supervision. **Lijing Gao:** Supervision. **Guomin Xiao:** Writing - review & editing.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.micromeso.2020.110578>.

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