MCM-41 supported quaternary ammonium ionic liquids as an effective heterogeneous catalyst for CO$_2$ cycloaddition reaction

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Abstract

Ionic liquid immobilization is an effective means for preparing metal-free heterogeneous catalysts for the CO$_2$ conversion. Herein, a series of quaternary ammonium ionic liquids functionalized MCM-41 heterogeneous catalysts, integrating hydrogen bond donors and nucleophilic ion sites, were prepared by a post-synthetic modification method for the CO$_2$ cycloaddition reaction. The physicochemical properties of the catalysts were analyzed by XRD, EA, SEM, TEM, BET, FT-IR, TGA, NMR and XPS. The results show that the quaternary ammonium ionic liquids are successfully immobilized onto the MCM-41 molecular sieves. The obtained catalysts maintain an excellent pore structure and have the good thermal stability. The effects of catalytic conditions on the catalytic performance, the recyclability of the catalysts and their generalizability to epoxide substrates were systematically investigated. In addition, the catalytic performance was evaluated for low concentrations of CO$_2$ (20% CO$_2$, 80% N$_2$). The synergy of multifunctional active sites makes the obtained materials exhibit the high catalytic activity without metals, co-catalysts and solvents. Furthermore, a possible mechanism for the conversion of CO$_2$ to cyclic carbonate catalyzed by the MCM-41-N/CH$_3$(1:3) was proposed.

Keywords CO$_2$ · Ionic liquids · Cycloaddition reaction · MCM-41 · Immobilization

1 Introduction

The greenhouse effect caused by the massive emission of greenhouse gases (GHGs) has attracted extensive concerns, and carbon dioxide (CO$_2$) accounts for approximately 60% of the total GHGs [1–3]. However, as a renewable, poison-free and cheap C1 resource, CO$_2$ is abundant in nature and can be used to produce various chemicals. Thus, the utilization of carbon dioxide resources can not only bring significant economic benefits, but also solve environmental problems [4, 5]. The reaction route of chemically transforming CO$_2$ with epoxides to prepare high-value-added chemical products cyclic carbonate has a low substrate raw material price and a 100% reaction atom utilization rate, following the concept of the circular economy and green chemistry [6,

7]. Since carbon dioxide is a stable molecule with the chemical inertness, it is important to develop rational and efficient catalysts for the carbon dioxide cycloaddition reaction.

At present, various homogeneous and heterogeneous catalytic systems, including metal oxides [8], organic bases [9], metal complexes [10], ionic liquids [11], porous organic polymers (POPs) [12] and metal–organic frameworks (MOFs) [13], have been developed for the CO$_2$ cycloaddition to prepare cyclic carbonates. Among them, metal functionalized catalysts exhibit the good catalytic activity for the CO$_2$ cycloaddition reactions. However, metal based catalysts have the disadvantages of the high cost, poor durability, susceptibility to gas poisoning, and are prone to the environmental pollution. Therefore, it is of great significance to create a series of metal-free environmentally friendly catalysts for CO$_2$ cycloaddition reactions. Ionic liquids have the advantages of the excellent solubility, adjustable acidity, simple preparation, low flammability, low toxicity, outstanding electrochemical and thermal stability, making them more advantageous in the field of catalysis [14–17]. Ionic liquids exhibit the excellent catalytic activity resulting from their nucleophilic halogen sites, and are considered promising catalysts to replace conventional metal-based catalysts for

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CO_2 cycloaddition reactions [18–21]. Among them, quaternary ammonium ionic liquids have the advantages of simple structure, easy preparation, adjustable acid–base active sites, and have been industrialized to catalyze the cycloaddition of CO_2 with epoxides to prepare cyclic carbonates. However, homogeneous ionic liquid catalysts have the high viscosity and are difficult to separate from the products, requiring the high energy consumption for the cumbersome catalyst recovery process [22–25]. Therefore, ionic liquid immobilization is an effective means to address these issues.

MCM-41 molecular sieve is widely used in the adsorption and catalysis due to its uniform mesoporous structure, structural stability, large specific surface area, easy preparation, and abundant silica hydroxyl groups [26–28]. The silica hydroxyl groups on the MCM-41 molecular sieves can graft ionic liquids through the chemical bonding, and the resulting ionic liquid immobilized catalysts have excellent pore structure, which can increase the effective contact area between ionic liquids and substrates, improving the mass transfer and enhancing the recoverability of the catalyst [29]. Moreover, hydrogen bond donors have been proven to effectively activate the ring opening of epoxides, promoting cycloaddition reactions [30, 31]. Dai et al. [19] prepared a series of HBDs functionalized phosphine-based ionic liquids (FPBILs), and the hydrogen bond donors –COOH, $-NH_2$, and –OH groups in FPBILs could activate the ring-opening of epoxides, and the halogen anions could nucleophilically attack epoxides, enabling the prepared FPBILs catalyst to catalyze CO_2 conversion at the conditions of solvent-free and co-catalyst-free. Peng et al. [23] synthesized six polyhydroxylated quaternary ammonium ionic liquids as multifunctional catalysts for catalyzing CO_2 cycloaddition reactions. The synergistic interaction of hydroxyl groups and halogen anions can effectively activate the epoxides, which enables this catalyst system to catalyze the cycloaddition reaction even under the atmospheric pressure. Jentys et al. [32] confirmed that there are abundant silicon hydroxyl groups on the MCM-41 molecular sieve through the infrared spectroscopy, which can serve as hydrogen bond donors to assist halogen ions in ionic liquids in promoting the epoxide ring opening. Inspired by the pioneering works, the incorporation of task-specific ionic liquids into MCM-41 is a prospective strategy to construct metal-free heterogeneous catalyst for the CO_2 conversion to cyclic carbonates.

Herein, a series of MCM-41 immobilized quaternary ammonium ionic liquid catalysts were constructed by a post-synthesis modification method for efficiently catalyzing the CO_2 cycloaddition reaction. The obtained catalysts maintain a good pore structure, and the synergy of multifunctional active sites enable the resulting metal-free materials to exhibit a high catalytic activity under cocatalyst-free and solvent-free reaction conditions. In addition, the catalysts are recyclable with the outstanding versatility for various

epoxides. The catalytic performance in cycloaddition reaction still achieves high yields at low carbon dioxide concentrations. Furthermore, a feasible reaction mechanism for the MCM-41-N/CH_3(1:3) was also proposed.

2 Experimental

2.1 Materials

N_2 (99.999%) and CO_2 (99.999%) were purchased by Dehai Gas Co., Ltd. The MCM-41 (H-type, All-silica) was provided by Tianjin Nankai Catalyst Plant. Styrene oxide (SO), propylene oxide (PO), cyclohexene oxide (CO), epichlorohydrin (ECH), allyl glycidyl ether (AGE), 1,2-butylene oxide (BO), 1,4-butanediol diglycidyl ether (BDE), 1,6-hexanediol diglycidyl ether (HDK), diethylenglykol-diglycidylether (DEDG), biphenyl, toluene, methylene chloride, anhydrous ethanol, n-butyl bromide, 1-bromobutyric acid, 3-aminopropyltrimethoxysilane (APTS), ethyl acetate and 1,2-dibromobutane were purchased from Aladdin Chemical Co., Ltd.

2.2 Catalyst synthesis

In a typical run, 5.44 mmol of APTS and 2.00 g of dried MCM-41 molecular sieves (120 °C for 4 h) were added into 50 ml of dry toluene. After the reaction at 110 °C with the continuous stirring for 24 h under N_2 atmosphere, the solids were collected and washed with methylene chloride and anhydrous ethanol, and then dried at 70 °C for 12 h. The obtained sample was named as MCM-41-NH_2. Subsequently, MCM-41-NH_2 samples were placed into the round-bottomed flask with varying amounts of n-butyl bromide, and 50 ml of dry toluene was added. The mixture was refluxed at 110 °C for 24 h under the N_2 atmosphere. After that, a series of quaternary ammonium ionic liquids functionalized MCM-41 samples were obtained, and denoted as MCM-41-N/CH_3(x:y), where x is the amount of APTS and y is the amount of n-butyl bromide. To investigate the catalytic performance of quaternary ionic liquids functionalized MCM-41 catalysts with different end groups of alkyl compounds, a series of MCM-41-N/Br(x:y) and MCM-41-N/COOH(x:y) catalysts were synthesized by substituting n-butyl bromide with 1-bromobutyric acid and 1,2-dibromobutane, respectively according to the aforementioned steps, and the synthetic routes are shown in Scheme 1.

2.3 Sample characterization

The structural properties for MCM-41 molecular sieves and MCM-41 functionalized with ionic liquids were analyzed using a D-MAX 2500/PC X-ray diffractometer. The low-angle scanning range is $2\theta = 1°–10°$ and the wide-angle

Scheme 1 Schematic synthesis of MCM-41-N/X(x:y) (X=CH$_3$, Br or COOH)
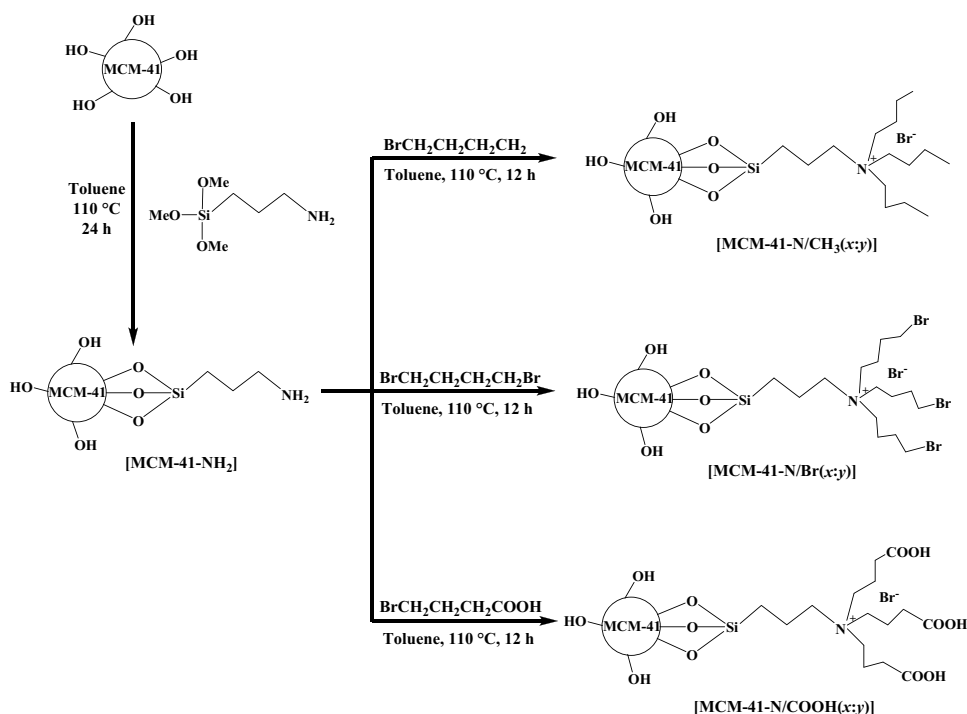
scanning range is $2\theta = 5°$–$80°$. The changes in functional groups of MCM-41 before and after the ionic liquids immobilization were detected using a Nicolet iS10 FTIR spectrometer, and the FT-IR curves of the samples were determined in the range of 400–4000 cm^{-1}. The mass percentages of the elements N, H and C in the samples were determined using a Vario EL III model elemental analyzer (EA). An TGA/DSC 1 thermogravimetric analyzer (TGA) was used to determine the variation of sample mass with the temperature in N$_2$ atmosphere. The textural properties were measured by using the ASAP 2460 automatic physical adsorption instrument to measuring the N$_2$ adsorption/desorption isotherms at 77 K. The microstructures of the samples were observed using the Sigma 500 scanning electron microscope (SEM) and HT7800 transmission electron microscope (TEM). An ESCALAB 250Xi X-ray photoelectron spectrometer (XPS, Thermo Fisher Scientific) and a Varian Infinity Plus 400 NMR spectrometer were used to examine chemical compositions of the samples.

2.4 Cycloaddition reactions and analytical methods

The cycloaddition reactions of CO$_2$ with epoxides were conducted in an autoclave (25 ml). Typically, a given amount of PO and catalyst was added into the autoclave, and CO$_2$ was pressed to a specified pressure. Subsequently, the reactor was sealed and heated to the given temperature using the oil bath. After reacting under stirring for a period of time, the reactor was cooled and depressurized slowly. The solid phase was gathered by the centrifugation, and the collected

liquid phase was analyzed by GC and GC–MS using ethyl acetate as the solvent and biphenyl as the internal standard. In the cyclic stability test, the recovered catalyst was washed repeatedly with ethyl acetate then dried for 6 h at 70 °C for the next reaction.

3 Results and discussion

3.1 Catalyst characterizations

Figure 1 shows the low and wide angle X-ray diffraction patterns of MCM-41 before and after the functionalization. It can be observed that MCM-41 molecular sieve has two weak peaks at $2\theta = 4.4°$ and $3.8°$ and an obvious diffraction peak at $2\theta = 2.2°$, belonging to typical (200), (110) and (100) planes for the MCM-41 molecular sieve, respectively, showing the existence orthocrystalline arrangement of hexagonal mesopores [33]. In addition, the MCM-41 molecular sieves retain the obvious characteristic peaks after immobilizing the three quaternary ammonium ionic liquids, showing that the crystal structure of the immobilized samples does not change and still retains the mesoporous structure. Additionally, it can be seen that the intensity of the (100), (110) and (200) peaks on the planes of the immobilized samples is weakened or even disappeared, suggesting that the quaternary ionic liquids do not simply attach onto the external surface of the MCM-41 molecular sieves but enter the pores, which has some effect on the ordering of the MCM-41 pores
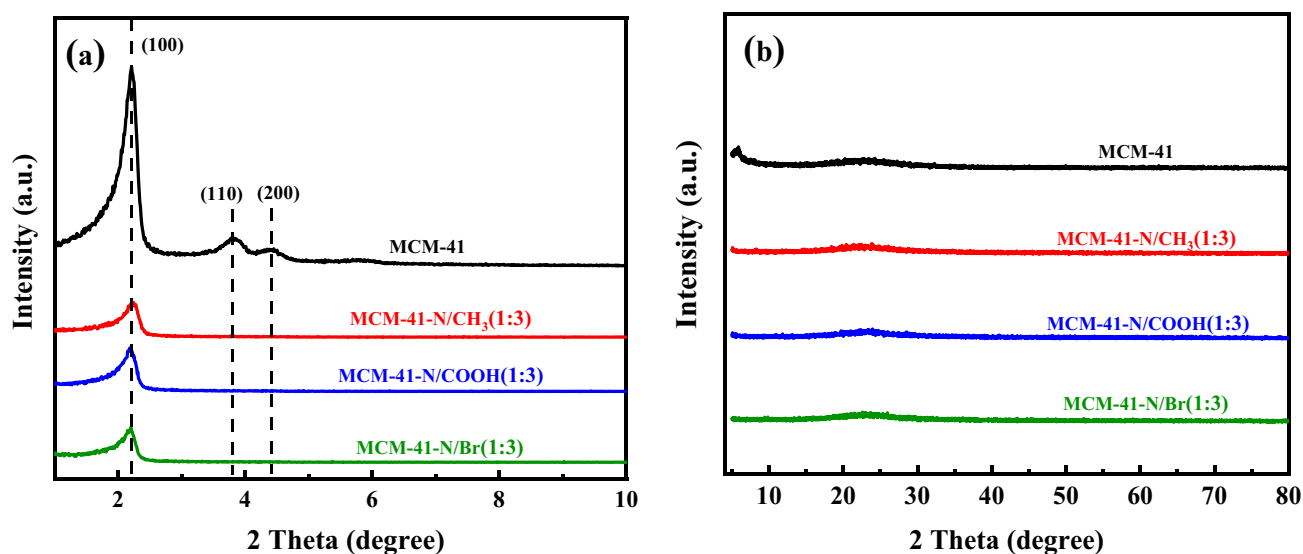
Fig. 1 XRD patterns of MCM-41 before and after the functionalization: **a** low angle and **b** wide angle

Table 1 Elemental analysis of MCM-41-NH$_2$ and MCM-41 immobilized ionic liquids samples

Samples	C (wt%)	H (wt%)	N (wt%)
MCM-41-NH$_2$	7.98	2.39	2.76
MCM-41-N/COOH(1:3)	10.52	2.58	2.41
MCM-41-N/Br(1:3)	10.02	2.18	2.30
MCM-41-N/CH$_3$(1:1)	10.10	2.47	2.45
MCM-41-N/CH$_3$(1:2)	10.85	2.30	2.53
MCM-41-N/CH$_3$(1:3)	11.24	2.67	2.42
MCM-41-N/CH$_3$(1:4)	11.39	2.43	2.43

[34]. The results indicate that the quaternary ionic liquids are successfully introduced into the MCM-41 pores.

The contents of elements N, H and C in the intermediate (MCM-41-NH$_2$) and the immobilized catalysts were determined by the elemental analysis, and the data are listed in Table 1. The N elements were detected in the MCM-41-NH$_2$ intermediates and the quaternary ammonium ionic liquids immobilized catalysts, which indicates that the APTS is successfully immobilized onto the surfaces of MCM-41 molecular sieve. Furthermore, compared to the MCM-41-NH$_2$ intermediate, the contents of H and C elements in the samples MCM-41-N/Br(1:3), MCM-41-N/COOH(1:3) and MCM-41-N/CH$_3$(1:3) are higher, indicating a successful connection of alkyl compounds to APTS, suggesting the successful functionalization of ionic liquids onto molecular sieves surfaces.

Figure 2 demonstrates the FT-IR spectra of MCM-41, intermediate (MCM-41-NH$_2$), immobilized catalysts and pure quaternary ammonium salt ionic liquid tetrabutylammonium bromide (Bu$_4$NBr). In the FT-IR spectra
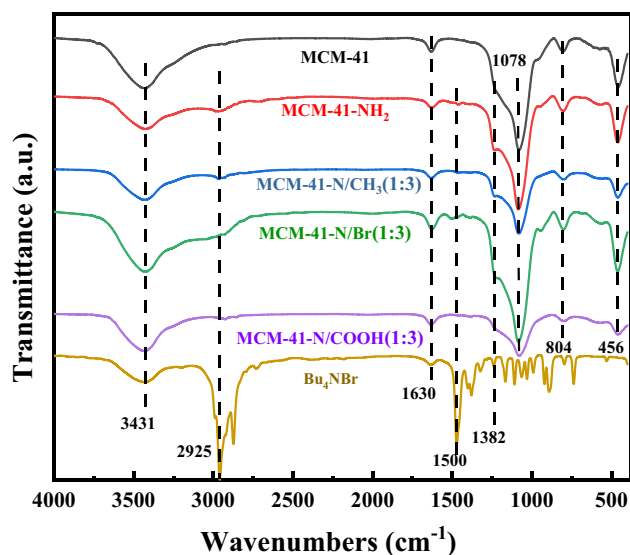

Fig. 2 FT-IR spectra of Bu$_4$NBr, MCM-41 with and without the functionalization

of MCM-41 molecular sieve, the peaks at 3431 cm^{-1} and 1630 cm^{-1} correspond to the stretching vibration of –OH groups on the surface of MCM-41 molecular sieve and physically adsorbed water, respectively [35]. The vibrational peak at 456 cm^{-1} belongs to the silicon–oxygen bonds, the peak at 1078 cm^{-1} is symmetric stretching vibration peak of silicon–oxygen–silicon bonds, and the peak at 804 cm^{-1} is asymmetric stretching vibration peak of silicon–oxygen–silicon bonds [36]. After the immobilization with the silane coupling agent APTS and quaternary ammonium ionic liquid, all adsorption peaks of MCM-41 were also detected, which indicates that the fundamental structure of MCM-41

molecular sieves are retained in all the composites. The characteristic absorption peak near 2925 cm^{-1} in the FT-IR spectrum of MCM-41-NH$_2$ is the stretching vibration peak of the C–H group, which slightly shifts after grafting the alkyl compounds, which may be due to the increase in the C-H groups, enhancing the interaction with other molecules, affecting its vibrational frequency [37]. In addition, in the samples MCM-41-NH$_2$ and functionalized ionic liquid catalysts, the absorption peaks around 1382–1502 cm^{-1} are the C–N bond stretching vibration peaks, suggesting that APTS is successfully immobilized onto MCM-41. Moreover, the functionalized ionic liquid catalysts show the similar position of C–N absorption peaks with Bu$_4$NBr, indicating that the quaternary ammonium ionic liquids are successfully immobilized onto MCM-41 molecular sieves.

The N$_2$ adsorption/desorption isotherms and pore size distribution curves of MCM-41 before and after the immobilization are shown in Fig. 3, and Table 2 presents the total pore volume, average pore size and specific surface area. From Fig. 3a, all samples exhibit typical IV representative adsorption isotherms, which illustrates that MCM-41 molecular sieves maintain mesoporous properties after immobilizing APTS and quaternary ammonium ionic liquids. As shown in Table 2, MCM-41 molecular sieves have excellent pore diameter, pore volume and large specific surface area, which facilitates the immobilization of ionic liquids. The pore parameters of MCM-41 molecular sieves are decreased after the amine functionalization and quaternary ammonium ionic liquid immobilization, which is attributed to the fact that APTS and quaternary ammonium ionic liquid occupy the partial surface area and pore volume of MCM-41 molecular sieves, suggesting that ionic liquids are successfully integrated onto the surface of MCM-41. In addition, the pore size distribution curves (Fig. 3b) further confirm

Table 2 Textural properties of MCM-41 before and after the functionalization

Samples	BET surface area (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})	Average pore diameter (nm)
MCM-41	1025	0.921	3.169
MCM-41-NH$_2$	906.3	0.726	3.100
MCM-41-N/CH$_3$(1:3)	610	0.343	2.510
MCM-41-N/Br(1:3)	697	0.380	2.473
MCM-41-N/COOH(1:3)	865	0.436	2.443

the presence of mesopores and the partial blockage of pores after the ionic liquid functionalization. The mesoporous structure in catalysts is conducive to the sufficient contact between active sites and substrates.

The morphologies of MCM-41 molecular sieves and the immobilized quaternary ammonium ionic liquid catalysts were analyzed by SEM and TEM. From Fig. 4a, it can be observed that MCM-41 molecular sieve consists of fragments with different sizes. The SEM images of the immobilized quaternary ammonium ionic liquid catalysts samples (Fig. 4b–d) show that the overall morphology of MCM-41 molecular sieve has no obvious change after the modification, while the surface of the particles becomes flatter. From the TEM images of MCM-41 before and after the ionic liquid immobilization (Fig. 4e–h), all the samples show the uniform and ordered pores pore channels, suggesting that the MCM-41 support is intact and maintains a uniform pore structure after grafting ionic liquids. In addition, it can be observed that the pores of immobilized ionic liquid catalysts become darker compared with the parent MCM-41, indicating a successful confinement of ionic liquids into
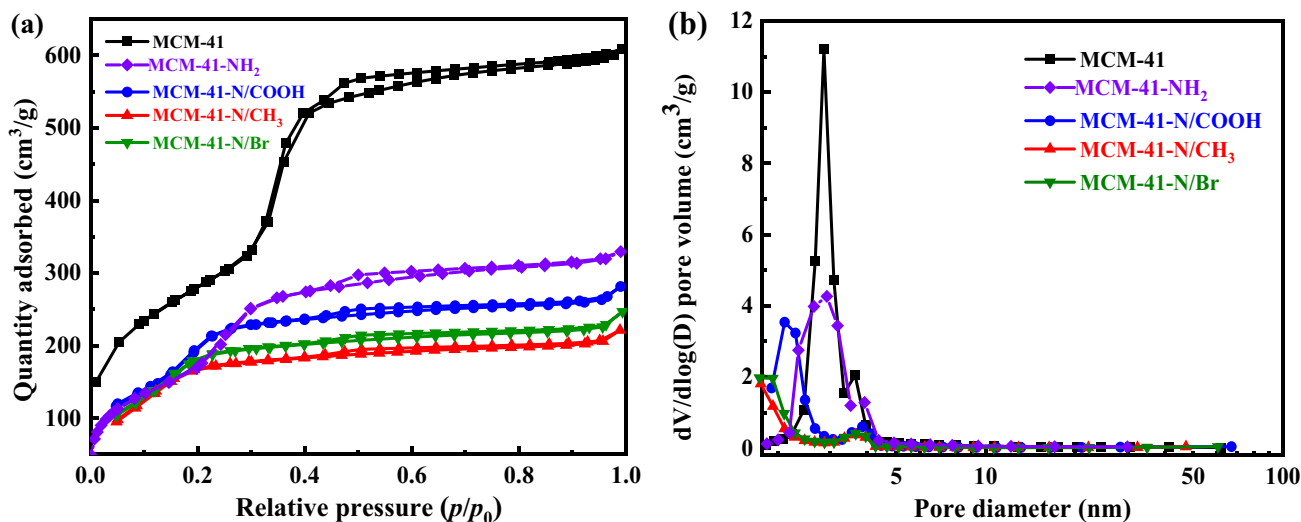
Fig. 3 **a** N$_2$ adsorption and desorption isotherms at 77 K and **b** pore size distribution curves of MCM-41 before and after the functionalization
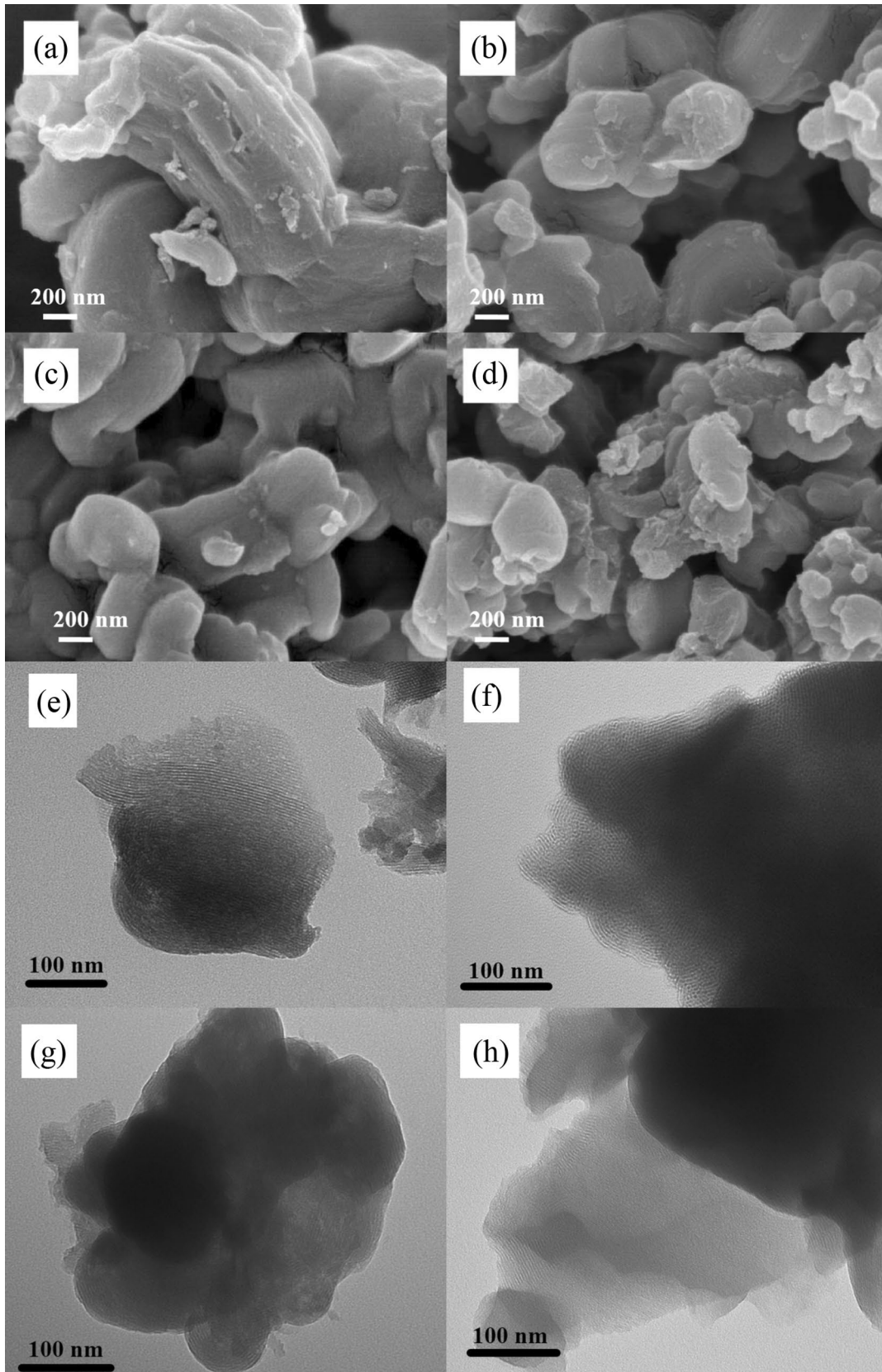
Fig. 4 SEM images of **a** MCM-41, **b** MCM-41-N/CH$_3$(1:3), **c** MCM-41-N/Br(1:3) and **d** MCM-41-N/COOH(1:3); TEM images of **e** MCM-41, **f** MCM-41-N/CH$_3$(1:3), **g** MCM-41-N/Br(1:3) and **h** MCM-41-N/COOH(1:3)

the mesopores of MCM-41. Combined with FT-IR, EA and XRD analysis results, it can be confirmed that APTS and quaternary ammonium ionic liquids are successfully introduced MCM-41 molecular sieves without destroying the MCM-41 molecular sieves, and the presence of silane coupling agents make the inter-particles more compact.

Figure 5 shows the thermogravimetric analysis of the MCM-41 and three quaternary ammonium ionic liquid immobilized catalysts. It can be seen that the weight of all the samples is lost by about 2% from 30 to 110 °C, which is due to the removal of other gas components and water in the samples. When further increasing the temperature to 600 °C, the weight of MCM-41 molecular sieve is almost constant, and the quaternary ammonium ionic liquid immobilized
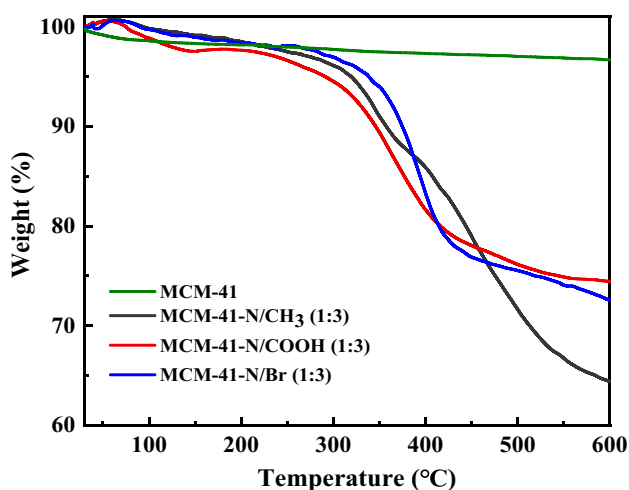
Fig. 5 TGA curves of MCM-41 and quaternary ionic liquid functionalized catalysts

catalysts show a good stability in the range of 110–300 °C. Generally, the reaction temperature of the CO_2 cycloaddition is within 150 °C, which indicates that the prepared quaternary ammonium ionic liquid catalysts exhibit the excellent structural stability.

Figure 6a shows the ^{13}C-MAS-NMR of MCM-41-N/CH$_3$(1:3), MCM-41-N/Br(1:3), and MCM-41-N/COOH(1:3). For the samples MCM-41-N/CH$_3$(1:3) and MCM-41-N/Br(1:3), the signals of all the methylene and terminal carbon atoms on the branched chain connected to the quaternary ammonium nitrogen are detected at around 13–60 ppm [38, 39]. For the sample MCM-41-N/COOH(1:3), in addition to the methylene signals, the signal at 169 ppm is ascribed to the C=O carbon atoms in the carboxyl groups [11]. Figure 6b shows the ^{29}Si-MAS-NMR spectrogram of MCM-41-N/CH$_3$(1:3). The signals at − 110 ppm and − 105 ppm belong to siloxane Q^4 [Si(OSi)$_4$] and Q^3 [Si(OSi)$_3$(OH)] in MCM-41, respectively, and the signals at − 71 ppm and − 62 ppm belong to the organic siloxane T^3 [RSi(OSi)$_3$] and T^2 [RSi(OSi)$_2$(OH)], respectively [40]. The NMR results confirm the successful connection of quaternary ammonium ionic liquids with MCM-41.

The chemical composition and elemental valence states of the prepared MCM-41-N/CH$_3$(1:3) were further analyzed by XPS. As shown in Fig. 7a, C, N, O, Br and Si elements were detected in the survey scan spectrum of MCM-41-N/CH$_3$(1:3), indicating the successful modification of MCM-41. As shown in Fig. 7b, the N 1s signal of MCM-41-N/CH$_3$(1:3) was deconvoluted into two peaks at 400.5 eV and 398.0 eV, representing the C–N$^+$ bond (quaternary ammonium) and C–N bond (tertiary amine), respectively [41]. Based on the peak intensity of N 1s signal, most of the nitrogen atoms are in the form of quaternary ammonium
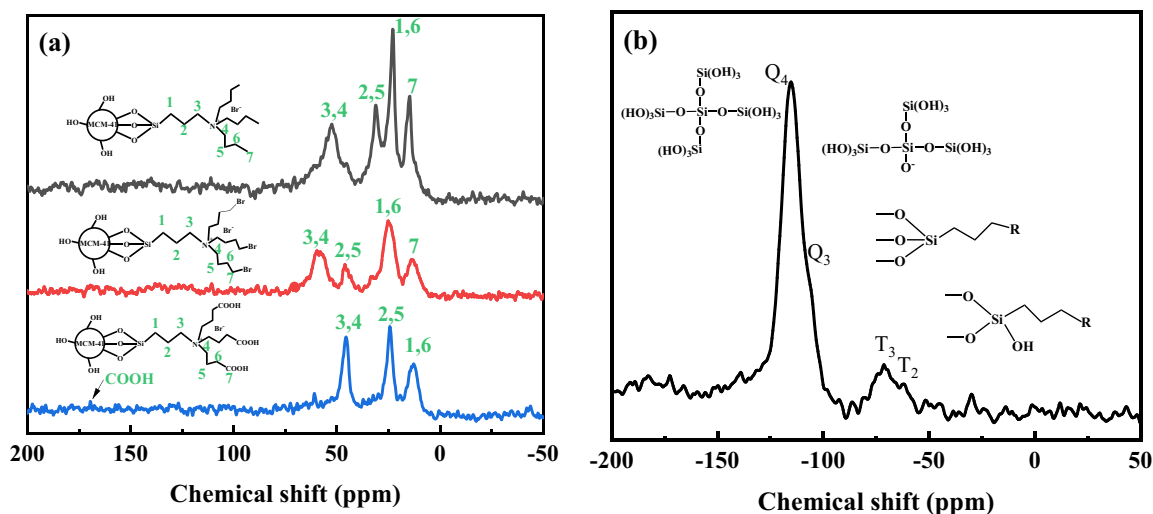
Fig. 6 **a** ^{13}C MAS-NMR of MCM-41-N/CH$_3$(1:3), MCM-41-N/Br(1:3) and MCM-41-N/COOH(1:3) and **b** ^{29}Si-MAS-NMR of MCM-41-N/CH$_3$(1:3)
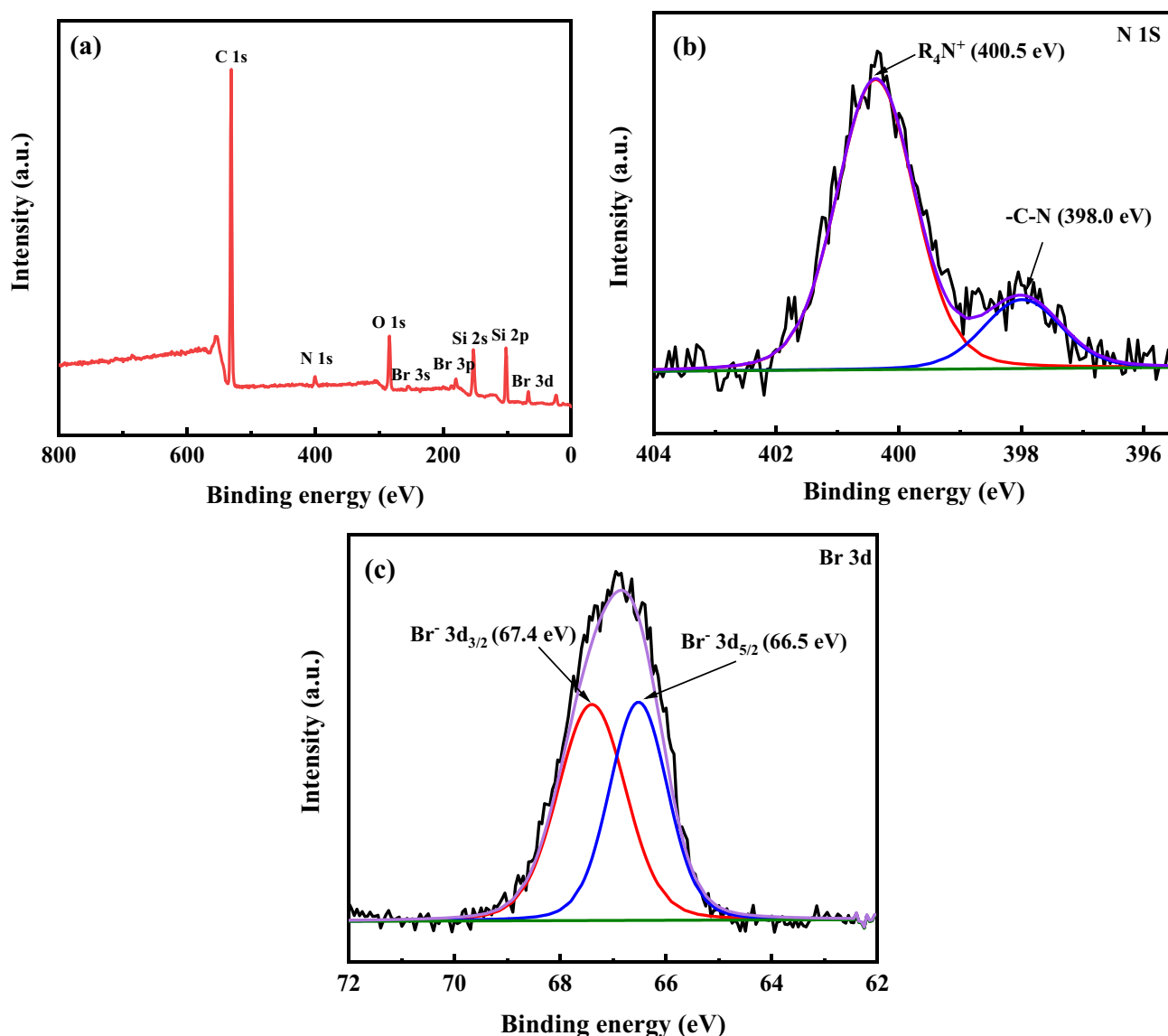
Fig. 7 **a** Survey scan, **b** N 1s, and **c** Br 3d XPS spectra of MCM-41-N/CH$_3$(1:3)

salts. As shown in Fig. 7c, the Br 3d signal was deconvoluted into two peaks at 67.4 eV and 66.5 eV, corresponding to Br$^-$ 3d$_{3/2}$ and Br$^-$ 3d$_{5/2}$, respectively [25], indicating the existence of nucleophilic active sites free Br$^-$ anions in the catalyst. The XPS analysis further confirms that the quaternary ammonium salt ionic liquid is successfully integrated onto the surfaces of MCM-41 molecular sieves.

3.2 Catalyst performance for cycloaddition reactions

3.2.1 Catalyst screening

The catalytic properties of MCM-41 molecular sieves before and after the modification were tested for the CO$_2$ cycloaddition using PO as the model substrate, and the results are summarized in Table 3. From Table 3, MCM-41 molecular sieves have no activity for the CO$_2$ cycloaddition reaction. With the introduction of APTS, the MCM-41-NH$_2$ intermediate have the low activity, and the yield of PC is only 47.6% with a selectivity of 92.5%. After immobilizing quaternary ammonium ionic liquids, the catalytic performance is greatly improved, and the yield of PC increases with the increase in the proportion of alkyl compounds in MCM-41-N/COOH(x:y) and MCM-41-N/Br(x:y) catalysts. This is due to the increase in ionic liquid active sites, which facilitates the activation of the epoxide, promoting the cycloaddition reaction. For MCM-41-N/CH$_3$(x:y) catalysts, the PC yield gradually increases to 92.5% when the ratio of APTS to alkyl compounds is increased from 1:1 to 1:3,

Table 3 Catalytic activities of MCM-41 before and after the modification for the cycloaddition reaction

Catalyst	Yield (%)[a]	Selectivity (%)[a]
MCM-41	–	–
MCM-41-NH$_2$	47.6	92.5
Bu$_4$NBr	53.43	96.6
MCM-41-N/COOH(1:1)	79.3	96.7
MCM-41-N/COOH(1:2)	84.5	96.8
MCM-41-N/COOH(1:3)	85.0	96.9
MCM-41-N/COOH(1:4)	90.2	97.0
MCM-41-N/Br(1:1)	82.7	97.4
MCM-41-N/Br(1:2)	85.7	97.7
MCM-41-N/Br(1:3)	90.2	95.8
MCM-41-N/Br(1:4)	90.5	97.9
MCM-41-N/CH$_3$(1:1)	85.2	95.6
MCM-41-N/CH$_3$(1:2)	88.8	95.8
MCM-41-N/CH$_3$(1:3)	92.5	96.6
MCM-41-N/CH$_3$(1:4)	90.6	95.5

Reaction conditions: PO 1.0 g (17 mmol), catalyst addition amount 150 mg, initial pressure 2.0 MPa, reaction temperature 140 °C, reaction time 3 h

[a]Determined by GC analysis

and when further increasing this ratio to 1:4, the PC yield decreases. According to the results of elemental analysis, the ionic liquid content in MCM-41-N/CH$_3$(1:4) is higher than that in MCM-41-N/CH$_3$(1:3), so the decrease in the yield of MCM-41-N/CH$_3$(1:4) might be due to the introduction of excessive n-butyl bromide, leading to the blockage of part of the pores. In addition, it can be found that at the same ratio of APTS to alkyl compounds, the PC yield of MCM-41-N/CH$_3$ is better than those of MCM-41-N/Br and MCM-41-N/COOH, and the PC selectivities are all above 95.0%. The above results indicate that the catalytic activity of MCM-41-N/CH$_3$(1:3) is superior to other catalysts, which may be due to the abundant hydroxyl hydrogen bond donors in MCM-41 molecular sieves, and the introduction of more hydrogen-bonding donors have little effect on the CO$_2$ cycloaddition catalytic activity. In addition, the pure quaternary ammonium salt ionic liquid Bu$_4$NBr shows a catalytic activity of 64% PC yield, which is significantly lower than that of ionic liquid functionalized MCM-41 catalysts, highlighting the roles of abundant pore structures for the CO$_2$ enrichment and the substrate diffusion in the catalytic process.

3.2.2 Effect of reaction parameter

The influence of reaction conditions on the catalytic performance was further investigated for the catalyst MCM-41-N/CH$_3$(1:3). Figure 8a illustrates the changes in the catalytic activity with the reaction temperature. The yield of PC increases from 66.9 to 92.5% when the temperature is increased from 100 to 140 °C, and decreases slightly when the reaction temperature continues to increase to 150 °C. This is due to the fact that within a certain temperature range, molecules gain energy by increasing the temperature, which increases the probability of collision, thereby improving the yield. Excessive temperature will promote the occurrence of side reactions, resulting in a slight decrease in the PC yield [42]. The catalyst MCM-41-N/CH$_3$(1:3) shows a high PC selectivity of above 95.0% at different reaction temperatures.

The effect of the reaction pressure on the yield and selectivity of PC is shown in Fig. 8b. The selectivity of PC is about 95.0% at different pressures. The yield of PC increases from 71.4 to 92.5% with increasing the pressure from 1.0 to 2.0 MPa. This is attributable to the increase in the CO$_2$ concentration as the reaction pressure increases, which accelerates the rate of the cyclization reaction. When further increasing the pressure to 3.0 MPa, the PC yield remains almost unchanged owing to the given amount of PO in the reactor, and increasing CO$_2$ concentration has little effect on the reaction while the reaction rate is maximized [43].

The influence of the reaction time on the catalytic cycloaddition performance of the catalyst is shown in Fig. 8c. From Fig. 8c, the yield of PC gradually increases from 74.9 to 92.5% when the reaction time is increased from 1 to 3 h. When the reaction time is further increased to 4 h, the PC yield has no obvious change. The catalyst MCM-41-N/CH$_3$(1:3) shows a high PC selectivity in this temperature range, which is higher than 95.0%. However, as the time prolongs, the yield and selectivity of PC begin to decrease, mainly attributed to a decrease in the concentration of PO and CO$_2$, and the inability to separate PC in a timely manner when the reaction substrate is completely converted. At a certain temperature and pressure, PC may undergo side reactions such as the polymerization or isomerization, resulting in a large number of by-products and a slight decrease for the target product yield.

Figure 8d shows the effect of the catalyst dosage on the catalytic performance of MCM-41-N/CH$_3$(1:3). It can be seen that when the dosage is increased from 50 to 150 mg, the catalyst active site increases, resulting in a changes in yield of PC from 71.6 to 92.5%. When further increasing the catalyst dosage, both the yield and selectivity show a decreasing trend. This may be attributed to that the excessive catalyst dosage will hinder the surface quality and heat transfer of some catalysts and block the active sites, reducing the catalytic efficiency, thereby resulting in a corresponding decrease in PC yield [44]. In addition, the selectivity of PC is basically the same at different catalyst dosages, which is maintained at about 96.0%.
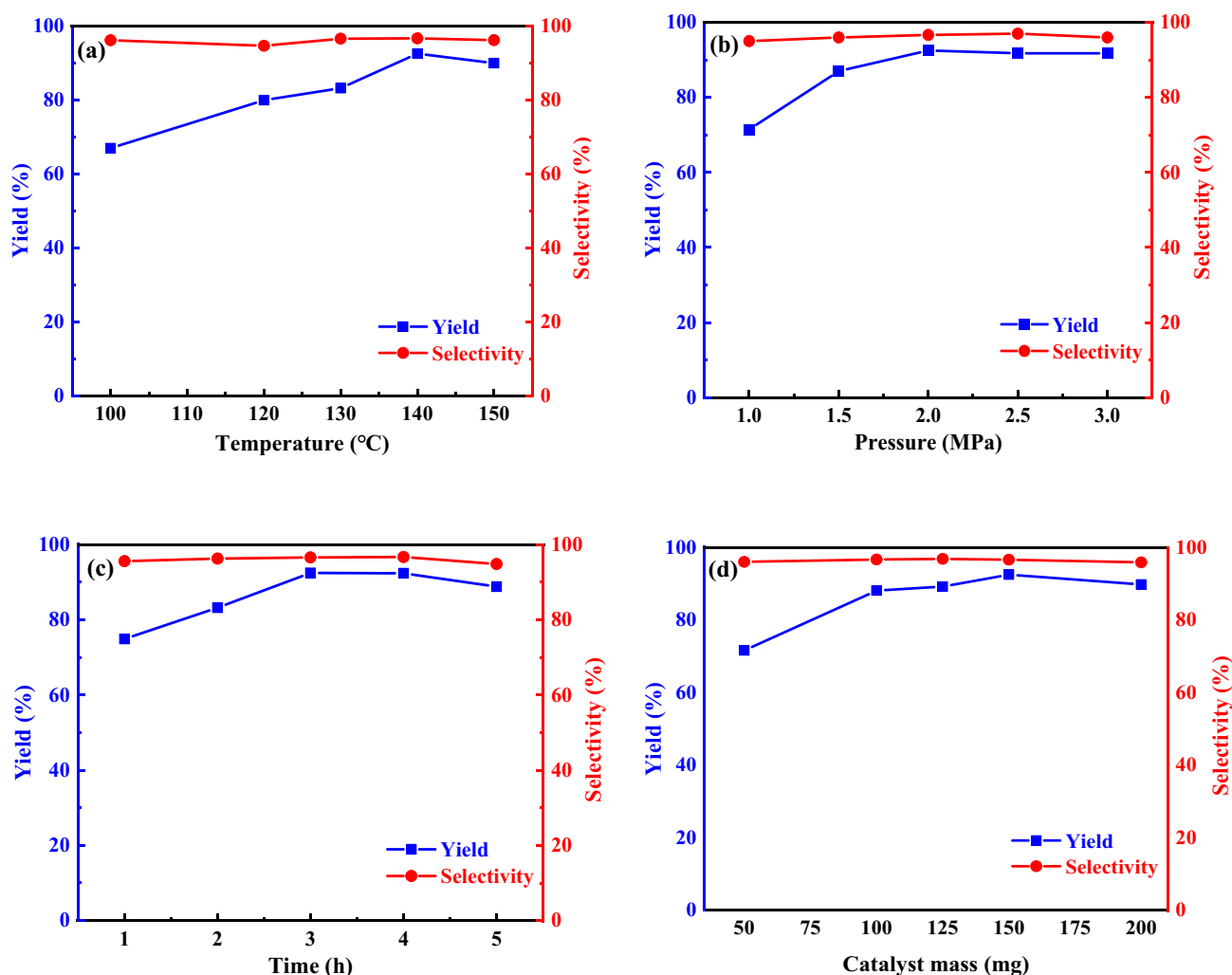
Fig. 8 Influences of reaction conditions on the catalytic activity for the cycloaddition reaction of MCM-41-N/CH$_3$: **a** temperature (PO 17 mmol, catalyst 150 mg, 3 h, CO$_2$ 2.0 MPa), **b** CO$_2$ pressure (PO 17 mmol, catalyst 150 mg, 3 h, 140 °C), **c** time (PO 17 mmol, catalyst 150 mg, CO$_2$ 2.0 MPa, 140 °C), and **d** catalyst dosage (PO 17 mmol, 3 h, CO$_2$ 2.0 MPa, 140 °C)

3.2.3 Effect of CO$_2$ concentration

The actual concentration of CO$_2$ in the exhaust gas is relatively low, especially in the exhaust gas generated by the combustion of fossil fuels, which is about 20%, requiring a catalyst with the good catalytic activity to achieve the cycloaddition of CO$_2$ and epoxides at low CO$_2$ concentrations. To verify the availability of the prepared MCM-41-N/CH$_3$(1:3) catalyst at low concentrations of CO$_2$, the cycloaddition reaction between CO$_2$ and epoxide at low CO$_2$ concentrations was conducted. The pressure was 2.0 MPa for all the experiments, and the CO$_2$ concentrations were adjusted by adjusting the amounts of N$_2$ and CO$_2$. The added amount of PO was 10 mmol and the volume of the reactor was chosen to be 50 ml to ensure the CO$_2$ sufficient. As shown in Table 4, the yield of PC decreases with the reduction in the CO$_2$ concentration, and when the concentration of CO$_2$ is 50%, the yield of PC is 91.0%, only 1.5% lower than that when using pure CO$_2$. When the concentration of CO$_2$ is reduced to 20%, the yield of PC decreases to 78.8%. Moreover, the concentration of CO$_2$ has almost no effect on the selectivity of PC, which is higher than 96.0%. The above results show that the MCM-41-N/CH$_3$(1:3) has the excellent catalytic activity for the dilute CO$_2$ conversion to cyclic carbonates.

3.3 Reusability test

The recoverability of the MCM-41-N/CH$_3$(1:3) catalyst was evaluated under optimal conditions by the five consecutive reaction/regeneration cycles. As shown in Fig. 9, the PC yield decreases from 92.5 to 76.8% after first three cycles, which may be attributed to the unstable connection of a small portion of the quaternary ammonium ionic liquid immobilized on the

Table 4 Catalytic activity of MCM-41-N/CH$_3$(1:3) for low concentration of CO$_2$

CO$_2$ mole fraction (%)	Temperature (°C)	Pressure (MPa)	Time (h)	Yield[a] (%)	Selectivity[a] (%)
99.9999	140	2.0	3	92.5	96.6
50	140	2.0	3	91.0	96.9
40	140	2.0	3	89.9	96.8
30	140	2.0	3	88.1	96.0
20	140	2.0	3	78.8	96.5

Reaction conditions: PO 1.0 g (17 mmol), catalyst addition amount 150 mg

[a]Determined by GC analysis
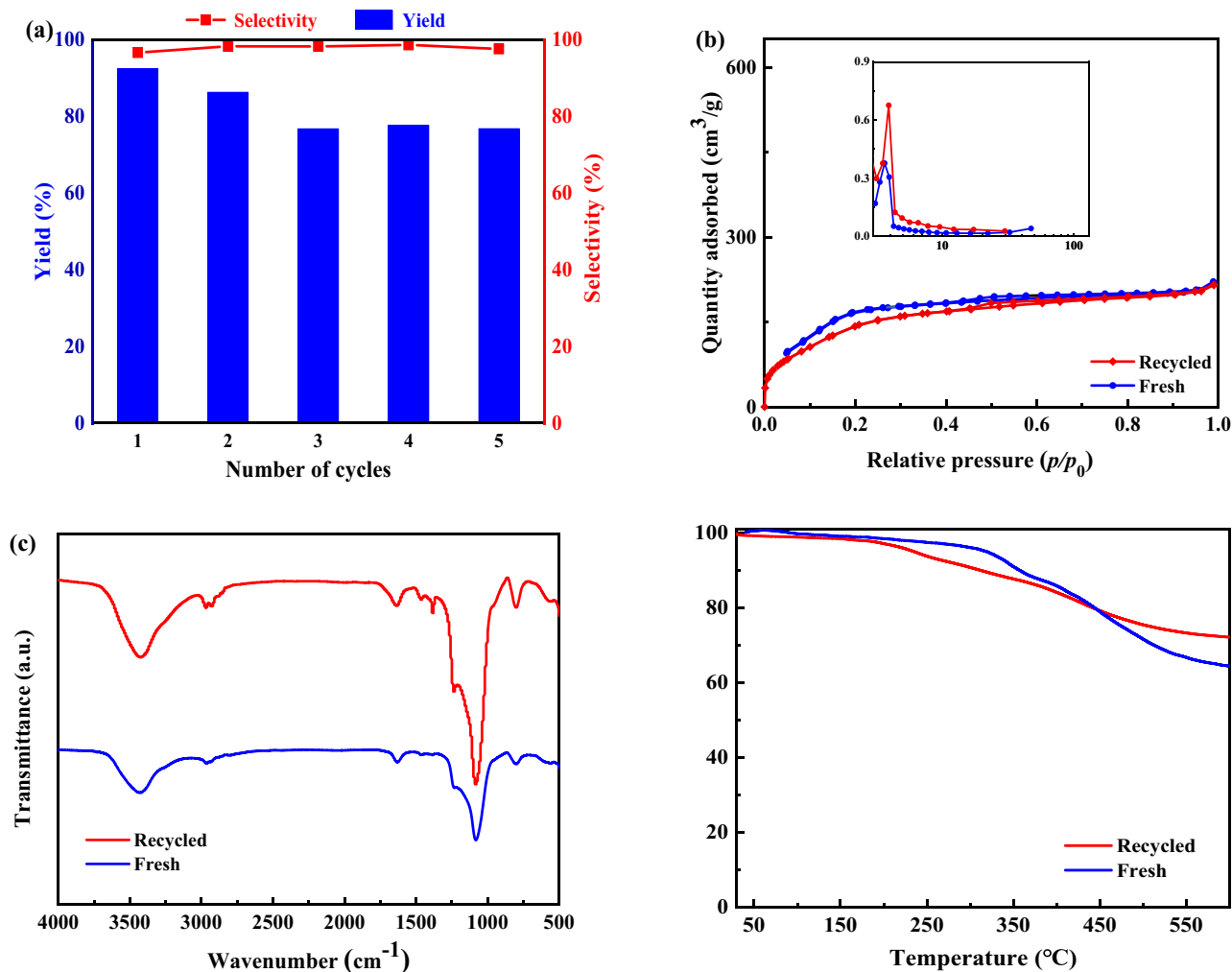
Fig. 9 **a** Effect of number of cycles on MCM-41-N/CH$_3$(1:3) catalytic performance for CO$_2$ cycloaddition. (Catalytic conditions: PO 1.0 g (17 mmol), 3 h, 2.0 MPa, 150 mg, 140 °C); **b** N$_2$ adsorption/desorption isotherms and pore distribution, **c** FT-IR spectra, and **d** TGA curves of fresh and recycled MCM-41-N/CH$_3$(1:3)

catalysts, resulting in the loss of active components. The PC yields remains almost unchanged in the last two cycles. In the five cycles, the selectivity of PC remains basically unchanged. In addition, the recovered MCM-41-N/CH$_3$(1:3) was further characterized by the N$_2$ adsorption–desorption test, FT-IR and

TGA. The recovered sample exhibits the similar pore structure characteristics (Fig. 9b), functional groups (Fig. 9c) and thermogravimetric behavior to the fresh catalyst, indicating the well maintenance of physicochemical properties of MCM-41-N/CH$_3$(1:3) after the catalytic reaction. Furthermore, in

order to evaluate the heterogeneous nature of the prepared catalyst, the leaching test was conducted. After 1 h of the catalytic reaction, the MCM-41-N/CH$_3$(1:3) catalyst was removed by the filtration, and the filtrate was further reacted at the same reaction conditions for another 4 h without the catalyst. After removing the catalyst, the yield of PC barely increases from 75 to 77%, indicating the heterogeneity and good stability of the MCM-41-N/CH$_3$(1:3) catalyst. The above results show that the MCM-41-N/CH$_3$(1:3) catalyst possess the excellent recoverability and potential for the industrial application.

3.4 Catalytic properties of other epoxy substrates

Table 5 shows the catalytic activity of catalyst MCM-41-N/CH$_3$(1:3) for different epoxides. Evidently, the catalyst MCM-41-N/CH$_3$(1:3) has excellent catalytic performance for the mono-epoxides (entries 1–5, PO, AGE, BO, ECH, SO) and di-epoxides (entries 6–8 DEDG, DLD and HDK), and all the epoxides can be converted to the corresponding cyclic carbonates with yields of higher than 90%. For cyclohexene oxide (CO) (entry 9), the catalytic activity is lower with the yield and selectivity of the target product of 22.9% and 67.7%, respectively. This is attributed to the larger steric hindrance of cyclohexene oxide, which hinders the nucleophilic attack of the catalyst and makes it difficult for cyclohexene oxide to open the ring [25, 45]. The above results indicate that MCM-41-N/CH$_3$(1:3) has the excellent generalization.

3.5 Possible reaction mechanism

Based on the characterization, catalytic reaction results and the previously reported works on the CO$_2$ cycloaddition reaction by quaternary ammonium ionic liquids [46–52], a feasible reaction mechanism for the CO$_2$ cycloaddition with PO by MCM-41-N/CH$_3$(1:3) catalyst was proposed in Fig. 10. The whole cycloaddition process consists of three processes: epoxide ring-opening, CO$_2$ insertion and ring-closing. In this catalytic system, the Br$^-$ ions and hydrogen bond donors (hydroxyl groups) synergistically catalyze the reaction. Firstly, the halogen Br$^-$ ions in the MCM-41-N/CH$_3$(1:3) catalyst nucleophilically attack the β-C atoms in the epoxide, and the –OH groups on the MCM-41 molecular sieve activate the oxygen atom in the epoxide through hydrogen bonds, and their synergistic effect causes the epoxide to open the ring, forming the haloalkoxy intermediate. Subsequently, haloalkoxy intermediate interacts with CO$_2$ to form an alkyl carbonate anion. Finally, an intramolecular ring-closure step by the nucleophilic attack of anionic oxygen atoms towards the carbon atoms bearing bromide achieves the formation of cyclic carbonates and catalyst regeneration.

4 Conclusions

A series of quaternary ammonium ionic liquids functionalized MCM-41 catalysts were successfully prepared using a post-synthetic modification method for catalyzing the CO$_2$ cycloaddition reaction. The prepared metal-free catalysts can effectively catalyze CO$_2$ conversion under cocatalyst-free and solvent-free conditions. Among them, the MCM-41-N/CH$_3$ (1:3) catalyst can achieve a yield of 92.5% and selectivity of 96.6% when reacting for 3 h at 2.0 MPa and 140 °C. Moreover, the catalyst can be easily recovered through the simple centrifugation, demonstrating the superior reusability. Additionally, the MCM-41-N/CH$_3$(1:3) can catalyze CO$_2$ cycloaddition reactions effectively of various epoxy substrates with excellent substrate compatibility. Furthermore, the MCM-41-N/CH$_3$ (1:3) catalyst exhibits outstanding catalytic properties for the dilute CO$_2$ conversion to cyclic carbonates. The excellent catalytic performance as well as the confirmed stability make the developed quaternary ammonium ionic liquids MCM-41 hybrid materials a promising heterogeneous catalyst for the CO$_2$ cycloaddition reaction, and the results of this work will provide some guidance for the development of metal-cocatalyst-solvent-free CO$_2$ cycloaddition catalysts and ionic liquid functionalized materials.

Table 5 Catalyst properties of MCM-41-N/CH$_3$(1:3) for the CO$_2$ cycloaddition with various epoxides substrates
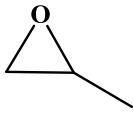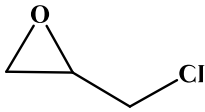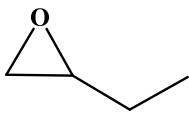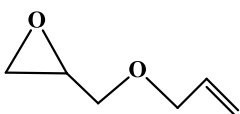
Entry	Epoxides	Yield (%)[a]	Selectivity (%)[a]
1	PO	92.5	96.6
2	ECH	91.0	94.0
3	BO	91.1	95.5
4	AGE	90.6	93.5
5	SO	90.0	95.0
6	BDE	90.6	94.5
7	DEDG	90.7	92.4
8	HDK	90.1	94.3
9	CO	22.9	67.7

Fig. 10 Feasible mechanism of cycloaddition catalyzed by MCM-41-N/CH$_3$(1:3)

Author contributions QL and SW wrote the main manuscript including text, tables and figures. CJ and JD conducted experiments. GC and FG contributed equally with conceptualization and supervision. All authors reviewed the manuscript.

Declarations

Competing interests The authors declare no competing interests.

Research involving human or animal rights This work does not contain any studies with human participants or animals performed by any of the authors.

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