RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2017, 7, 14721

Inclusion complexes of organic salts with β-cyclodextrin as organocatalysts for CO_2 cycloaddition with epoxides†

Kun Li, Xiaohui Wu, Qingwen Gu, Xiuge Zhao, Mingming Yuan, Wenbao Ma, Wenxiu Ni and Zhenshan Hou*

The inclusion complexes between β-cyclodextrin (β-CD) and the organic bases 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU)-based phenolates have been prepared by a simple method and also characterized by FT-IR, ^{1}H NMR, ^{19}F NMR, TGA *etc.* Among these inclusion complexes, DBU-based 2,3,4,5,6-pentafluorophenolate as a guest compound bound by β-CD ([DBUH][PFPhO]/β-CD) has been employed as an easily-separable organocatalyst for the cycloaddition of CO_2 into cyclic carbonate and exhibited the best catalytic performance. High conversion of epoxides and excellent selectivity to carbonates could be achieved at 130 °C and under the 3.0 MPa CO_2 without additional organic solvents or additives. Additionally, the organocatalyst [DBUH][PFPhO]/β-CD exhibited the better recycability in consecutive catalytic recycles, as compared with that of corresponding DBU-based phenolates. The β-CD played a crucial role in immobilizing catalytically active species and thus improving the recyclability of the present organocatalysts. The detailed characterization indicated that phenolate anions had been bound inside the cavity of β-CD, while the $[DBUH]^+$ cation was located outside of β-CD. More interestingly, it was observed that phenolate anions could dissociate from the β-CD cavity under the reaction temperature, but the inclusion compound could form on cooling the reaction mixture after reaction, which was extremely attractive for separation and recycling of the supramolecular organocatalysts. Finally, on the basis of the characterization above, a reaction mechanism for the present organocatalysts has been proposed.

Received 11th January 2017
Accepted 1st March 2017

DOI: 10.1039/c7ra00416h

rsc.li/rsc-advances

Introduction

Carbon dioxide (CO_2) is a greenhouse gas that induces global warming and climate change. Meanwhile, it always can be regarded as an easily available and renewable carbon resource, which is mainly due to its advantages of being abundant, cheap, non-toxic, and nonflammable in CO_2 capture and conversion.[1] Transformation of CO_2 into highly valuable chemicals is of great importance and has attracted increasing attention. One of the most attractive synthetic goals starting from carbon dioxide is the chemical fixation of CO_2 onto epoxide to afford the five-membered cyclic carbonates,[2] such products are among the most important feedstocks which have been extensively used as aprotic polar solvents, electrolyte components in lithium batteries, precursors for polycarbonates, and intermediates in organic synthesis.[3]

A broad variety of homogeneous catalysts for the synthesis of cyclic carbonates have been developed and reported so far, such as quaternary ammonium and phosphonium salts,[4] bromine,[5] ionic liquid,[6] triphenylphosphine-phenol,[7] metalloporphyrins[8] and polyoxometalate.[9] However, these catalysts generally suffer from low to moderate catalytic activity, selectivity and poor recyclability. Besides, a co-solvent/additive and harsh reaction conditions such as high pressure and/or high temperature are required in some cases. Meanwhile, the inherent corrosion, toxicity and environmental problems associated with metallic cations and halide anions are also concerned from the view-point of green chemistry. Thus, the development of a highly efficient, metal and halide ions-free environment-friendly catalytic system for the cycloaddition of carbon dioxide with epoxide are highly desirable.[10] Meanwhile, the recovery of homogeneous catalyst from products could also be a non-ignorable defect which may result in the difficulty for further product purification and catalyst reuses.[11]

By contrast, heterogeneous catalysts, due to its convenience of separation and recovery, have received more attention and extensive application than homogeneous analogues in the catalytic synthesis of cyclic carbonates. From this point, a series of inorganic oxides and organic polymers supported catalysts

---

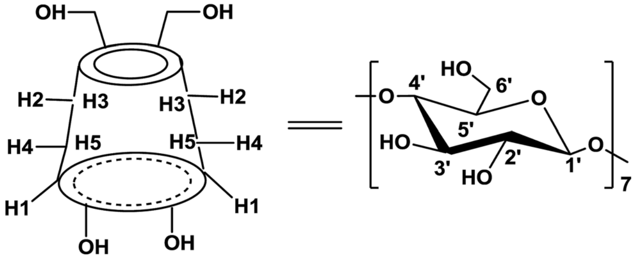
Key Laboratory for Advanced Materials, Research Institute of Industrial Catalysis, School of Chemistry & Molecular Engineering, East China University of Science and Technology, Shanghai 200237, People's Republic of China. E-mail: houzhenshan@ecust.edu.cn

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7ra00416h

have been developed. For examples, these supports include mesoporous silica,[12] polymers,[13] graphene oxide,[14] carbon nanotubes,[15] chitosan (CS)[16] *etc.* The synergistic effect of hydroxyl groups of solid materials on promoting the reaction has also been unveiled.

The supramolecular chemistry played a significant role in many fields, while the supramolecular catalysis has recently emerged and been well developed.[17] The main strategy is to assemble building blocks by weak interactions to elaborate new catalytic systems, which could avoid the modification of the catalyst backbone by means of multistep synthesis as usually required to improve the catalytic performance of covalent catalysts. Especially, β-cyclodextrin (β-CD) has been used as a host molecule to construct the supramolecular catalysts with the aid of the interactions of the host–guest type. β-CD are cyclic oligosaccharides connected by α-1,4 linkages (Scheme 1), frequently characterized as a doughnut-shaped truncated cone.[18] The primary hydroxy groups (OHs) of glucose units are located on the narrower rim of the cone, and the secondary OHs are on the wide one. The β-CD's external surface is hydrophilic to make them be soluble in water, while their hydrophobic cavity can host a variety of guest organo-molecules leading to the formation of guest/β-CD inclusion complexes. Actually, inclusion complexes between β-CD and various guest molecules have been employed as efficient catalysts and studied extensively.[19]

On the other hand, organic Lewis base like 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and 1,4-diazabicyclo[2.2.2]octane (DABCO), *etc.*, showed some activity for chemical fixation of CO_2 into cyclic carbonates and were regarded as an environmental-friendly catalysts due to the absence of halogen ions.[20,21] However, these organic base-derived materials normally acted as homogeneous catalysts, resulting in difficult recovery of the catalysts. Taking into account of the drawbacks of the homogeneous base catalysts, in our previous work, we have found that niobate salts of organic base were highly efficient catalysts for CO_2 cycloaddition, and the catalyst was stable in the consecutive recycles.[22] As far as we have known, the efficient synthesis of cyclic carbonate by using the metal-free heterogeneous catalysts still remains a huge challenge and is highly promising. Herewith, we attempted to prepare inclusion complexes of DBU-based phenolates with β-CD by a simple method and to use as heterogeneous organocatalysts for the cycloaddition of carbon dioxide with epoxide without additional solvents and additives. It was found that the β-CD played a crucial role in immobilizing catalytically active species and thus improving the recyclability of the supramolecular organocatalysts. Furthermore, the reaction mechanism over the present supramolecular catalysts has been proposed on the basis of the detailed characterization.



Scheme 1 Chemical structures of β-CD.

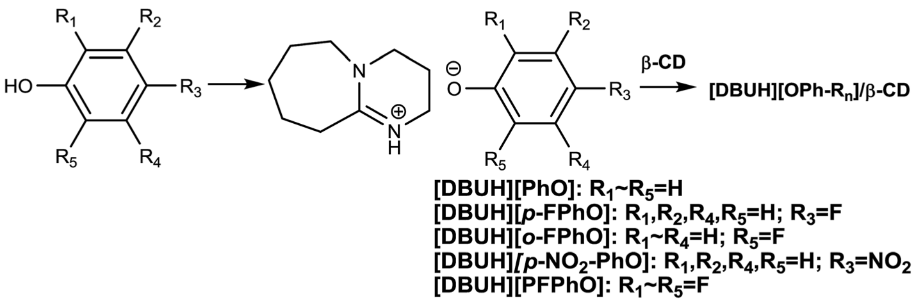
Results and discussion

Characterizations of catalysts

First, the different kinds of salts were synthesized by simply neutralizing phenol derivatives with DBU in tetrahydrofuran (THF). The β-CD was chosen as host molecules because it is highly thermally stable and owns abundant hydroxyl groups. Through the hydrogen bond interaction, DBU-based phenolates were thus included by β-CD in aqueous solution (Scheme 2).

In the first step, a series of DBU-based phenolate salts were firstly characterized by FT-IR spectra. As shown in Fig. 1b–f, after the neutralization reaction, the characteristic peaks at 3600 cm^{-1} of hydroxyl groups on phenol and other phenol derivatives disappeared, and the new peaks at 2935 cm^{-1} can be assigned to the stretching vibration of N^+–H.[22] The peaks at 1646 cm^{-1} and 2854 cm^{-1} could be attributed to C=N^+ and C–H vibration on protonated DBU, respectively. The peak at 1499 cm^{-1}, 1593 cm^{-1} could be assigned to C=C vibration on benzene ring.[22–24] ^1H NMR spectra of DBU-based phenolates have been depicted in Fig. S1,† the signal of hydroxyl hydrogen in phenol moved to downfield after the salts were formed (9–12 ppm). Additionally, the amidinium carbon in the DBU structure moved to downfield from 161.8 ppm to 178.5 ppm (^{13}C NMR spectra shown in Fig. S2†), as compared with that of free DBU (δ = 161.5 ppm),[25] revealing that DBU has been protonated after neutralization.[23] All these results proved that the different kinds of DBU-based salts have been attained unambiguously.

Because all these DBU-based phenolates served as homogeneous catalysts in cycloaddition reaction of CO_2 as shown from our experimental observation, we next have prepared the inclusion complexes of DBU-based salts and β-CD with the aid of the interactions of the host–guest type. The ^1H NMR spectra of all inclusion complexes was shown in Fig. S3.† Before the inclusion, the chemical shifts of H-3′ and H-5′ protons of β-CD were 3.60 and 3.56, respectively. Having included the DBU-based phenolates, the chemical shifts of H-3′ and H-5′ moved to 3.59 and 3.55. As shown in Scheme 1, the H-3′ and H-5′ were located inside the cavity of β-CD and formed the inner wall in it, when the guest molecules or the groups such as benzene rings on guest molecules were included in the cavity of β-CD, the shielding effect of these molecules could changed the chemical shifts of H-3′ and H-5′,[26] but the H-2′, H-4′ and H-6′ out of the cavity still remained unchangeable. It was worth noticing that the chemical shifts of all protons on $[DBUH]^+$ cation in all salts did not undergo any obvious changes, while the resonance signal from H6 protons in phenolates anions disappeared after inclusion (Fig. S1 *vs.* S3†). Moreover, the NMR signal from the protons of OH-2′ and OH-3′ in β-CD moved to higher field and became boarder after inclusion (Fig. S3a–S3f†), which might result from the hydrogen bonding interaction between the OH-2′ and OH-3′ protons and $[DBUH]^+$ cation. From these results



Scheme 2 The synthetic route of β-CD inclusion complexes.

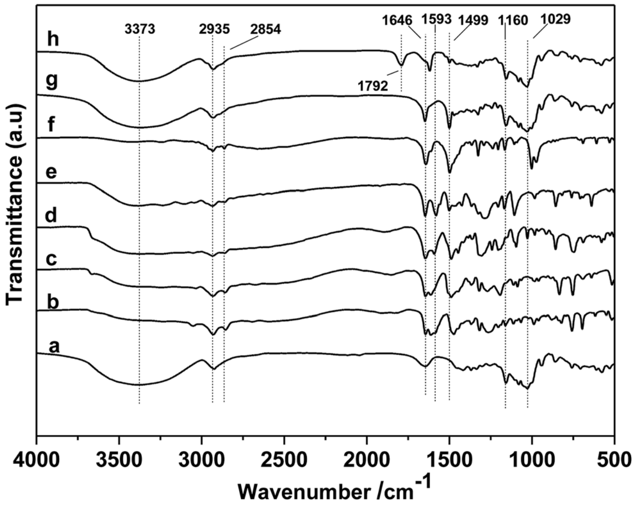


Fig. 1 The FT-IR spectra of (a) β-CD; (b) [DBUH][PhO]; (c) [DBUH][*p*-FPhO]; (d) [DBUH][*o*-FPhO]; (e) [DBUH][*p*-NO_2-PhO]; (f) [DBUH][PFPhO]; (g) [DBUH][PFPhO]/β-CD; (h) the recovered [DBUH][PFPhO]/β-CD organocatalyst after recycling.

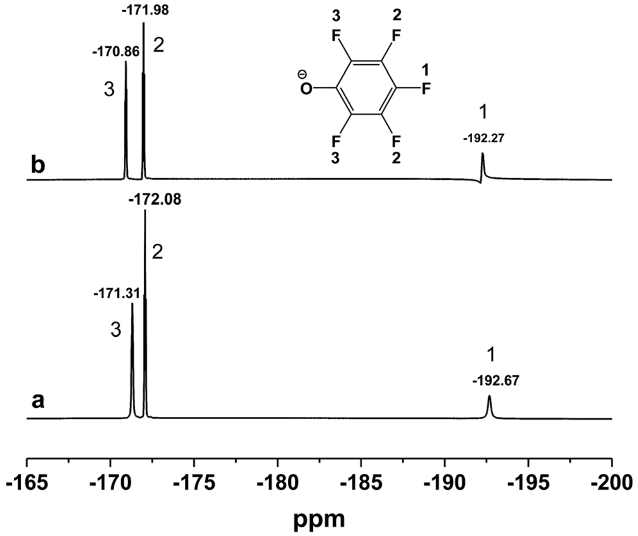


Fig. 2 ^{19}F NMR spectra of (a) [DBUH][PFPhO]; (b) [DBUH][PFPhO]/β-CD. The concentration of [DBUH][PFPhO] in d6-DMSO was 0.054 mmol mL^{-1}.

above, it suggested that the inclusion complexes between β-CD and DBU-based phenolates have been formed.

Sequentially, taking inclusion complexes formed between [DBUH][PFPhO] with β-CD as an example, FT-IR, ^{19}F NMR and ^{13}C NMR provided an additional evidence of inclusion compound formation. As shown in Fig. 1a, β-CD exhibited the characteristic peaks at 3373 cm^{-1} (–OH), 2926 cm^{-1} (C–H stretch) (too closing to overlapped with the peaks of N^+–H on protonated DBU), 1160 cm^{-1} (C–O–C stretch/O–H bend), 1250–1370 cm^{-1} (C–H bend), 1029 cm^{-1} (C–O stretch). After inclusion (Fig. 1f and g), the catalyst still remains the characteristic peaks of β-CD, which indicated that the skeleton structure of β-CD remained untouched. The peaks at 2935 cm^{-1} (N^+–H stretch) and 1646 cm^{-1} ($C{=}N^+$ vibration) on DBU seems unchanged after inclusion. It should be noted that the peak at 1593 cm^{-1} (C=C on benzene ring) disappeared and the peak at 1499 cm^{-1} (C=C on benzene ring) became weaker after inclusion. Meanwhile, ^{19}F NMR spectra (500 MHz) of [DBUH][PFPhO]/β-CD was shown in Fig. 2. It was found that the chemical shifts of fluorine atoms on the *para*, *ortho* and *meta* position changed from −192.67, −172.08 and −171.31 to −192.27, −171.98 and −170.86 respectively after inclusion, which suggested the deshielding effects of β-CD on [DBUH][PFPhO].[19b] What's more, from the ^{13}C NMR spectra (Fig. S4b and S4c†), after inclusion the ^{13}C NMR signals of guest anion $[PFPhO]^-$ increased varying from 0.3 ppm to 0.8 ppm. Furthermore, the *para* carbon signals of phenolate anions disappeared nearly (Fig. S4c†), while all protons in $[DBUH]^+$ did not show any obvious changes in chemical shifts after inclusion (Fig. S4b and S4c†). This had been explained in previous work that carbon atoms of guest molecules which are deeper in the cavity seem to undergo shielding effects with β-CD.[26] Additionally, if the concentration of [DBUH][PFPhO]/β-CD increased further, the ^{13}C NMR signals did not showed much change (Fig. S4d and S4e†), but the ^{19}F NMR signals of guest anion $[PFPhO]^-$ changed considerably (Fig. S5a and S5b†). All these results also suggested that the β-CD had included the [DBUH][PFPhO] successfully. Most likely, $[DBUH]^+$ cation was located outside of β-CD, while the hydrophobic phenol derivatives as the guest molecules was bound inside the cavity of β-CD.

The thermal stability of the β-CD and the inclusion complex catalysts [DBUH][PFPhO]/β-CD were investigated by TGA. As shown in Fig. S6,† β-CD showed a slightly weight loss below 100 °C, which could be attributed to the removal of the adsorbed H_2O on the surface of β-CD. The β-CD started to decompose after 300 °C, which indicated its highly thermal stability. The salt [DBUH][PFPhO] appeared an obviously weight loss at 150 °C, after inclusion with β-CD, the decomposition onset temperature was around 200 °C, indicating that the thermal stability of [DBUH][PFPhO] was improved due to the formation of inclusion complexes. Scanning electron microscopy (SEM) was also employed to observe the morphology of β-CD, [DBUH][PFPhO] and [DBUH][PFPhO]/β-CD, and their SEM images were shown in Fig. S7†. Compared with pure β-CD, the inclusion compounds have a lower dispersity (Fig. S7a and 7d *vs.* S7c and 7f†). Modification of crystals can be added as a proof of the formation of a solid inclusion complexes with hydrophobic cavity of β-CD.

Catalyst performance

In the previous work, DBU has been proved as a well homogeneous catalyst for the cycloaddition reaction of CO_2 with epoxides.[20] In this work, for the sake of comparison, we synthesized a serial of salts containing DBU and different kinds of phenol derivatives, and their inclusion complexes of β-CD, which all have been employed as our catalysts. The cycloaddition reaction of propylene oxide (PO) and CO_2 to propylene carbonate (PC) was chosen as a model reaction to evaluate the catalytic performance under the optimized reaction conditions. The catalytic activities over these catalysts have been displayed in Fig. 3. When only use the β-CD as catalyst, it can be seen that only PO conversion of 29.8% was attained and 1,2-propanediol was formed as a main product without any formation of cyclic carbonates. When DBU and phenol were used as homogeneous catalysts, the conversion of PO was 80% and 8.5%, respectively. However, it was found that the catalytic activity was improved considerably by using different DBU-based phenolates. Interestingly, with the decrease of pK_a value of the phenolate anions within catalysts (Table S1†), the catalytic activity was increased (Fig. 3). It indicated that the stronger acidity of phenol derivatives really benefits the reaction. Previous reports have suggested that the parallel requirement of both Lewis base and Lewis acid in the fixation of CO_2.[27] As a result, the increasing in acidity may promote the activation of CO_2.[28] From this standpoint, the salt [DBUH][PFPhO] formed with DBU and 2,3,4,5,6-pentafluorophenol owning the lowest pK_a value of 5.50 showed the highest catalytic activity under the present condition. On the other hand, it was worth noticing that 2,3,4,5,6-pentafluorophenol had CO_2-philic properties, which presumably facilitated CO_2 conversion with increasing activity.[29]

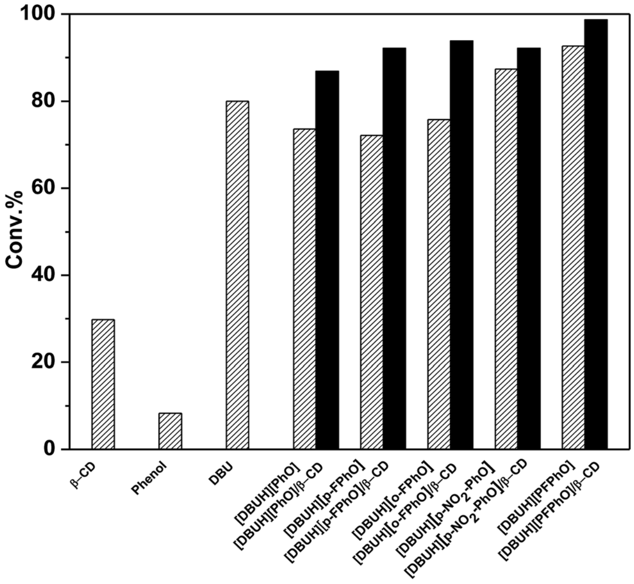


Fig. 3 The effect of different catalysts on the conversions of cycloaddition reaction. Reaction conditions: PO 0.7 mL (10 mmol), organocatalyst (1.5 mmol%), 130 °C, 3 MPa. All catalysts showed over 98% selectivities toward cyclic carbonates except that β-CD afford 1,2-propanediol as a main by-product.

Since the DBU-based phenolate catalyst was miscible with cyclic carbonate after reaction, leading to the deficient recovery of catalyst. In contrast, it was found that the inclusion complexes as organocatalysts not only were separated easily only by standing and filtration after reaction but also even afforded higher catalytic activity, in comparison with that of the corresponding DBU-based phenolate catalysts (Fig. 3), which was probably due to abundant hydroxyl on β-CD's surface.[30] Moreover, it has been reported that the acidity of guest molecules (here are phenol derivatives) bound to β-CD was considerably higher than that of the corresponding free one,[31] which could result in stronger acidity after inclusion in the present situation and thus benefits the reaction as well. Among all these organocatalysts, [DBUH][PFPhO]/β-CD was chosen as a main catalyst in the following investigation owing to its excellent catalytic performance.

Influence of reaction parameters

All probable effects of reaction condition (temperature, CO_2 pressure and reaction time and catalyst amount) were considered and investigated over the [DBUH][PFPhO]/β-CD catalyst. Firstly, the effect of the reaction temperature has been examined and the results were shown in Fig. 4a. With the increment of temperature from 90 °C to 130 °C, the conversion of PO increased significantly from 20% to 96%. However, the PO conversion leveled off under higher reaction temperature. Consequently, it was suggested that 130 °C was the appropriate temperature for the cycloaddition reaction.

Then the impact of the CO_2 pressure on cycloaddition reaction of PO was studied and depicted in Fig. 4b. The conversion of PO was increased in some extent with the reaction pressure changing from 1.5–3.0 MPa. It could possibly be explained that more CO_2 can be dissolved in PO as increasing reaction pressure,[6e] which facilitated the CO_2 cyclic addition reaction. However, when the reaction pressure continued to rise to 6.0 MPa, the conversion of PO has a slight decrease while the selectivity has no obvious change. This might be related to a dilution effect occurring that the excess CO_2 reduced the concentration of the catalyst in the vicinity or hinder the active mass transport, which was also be observed in our group's previous studies.[22,32,33] The impact of reaction time under the condition of 130 °C and 3.0 MPa can also be obtained in Fig. 4c.

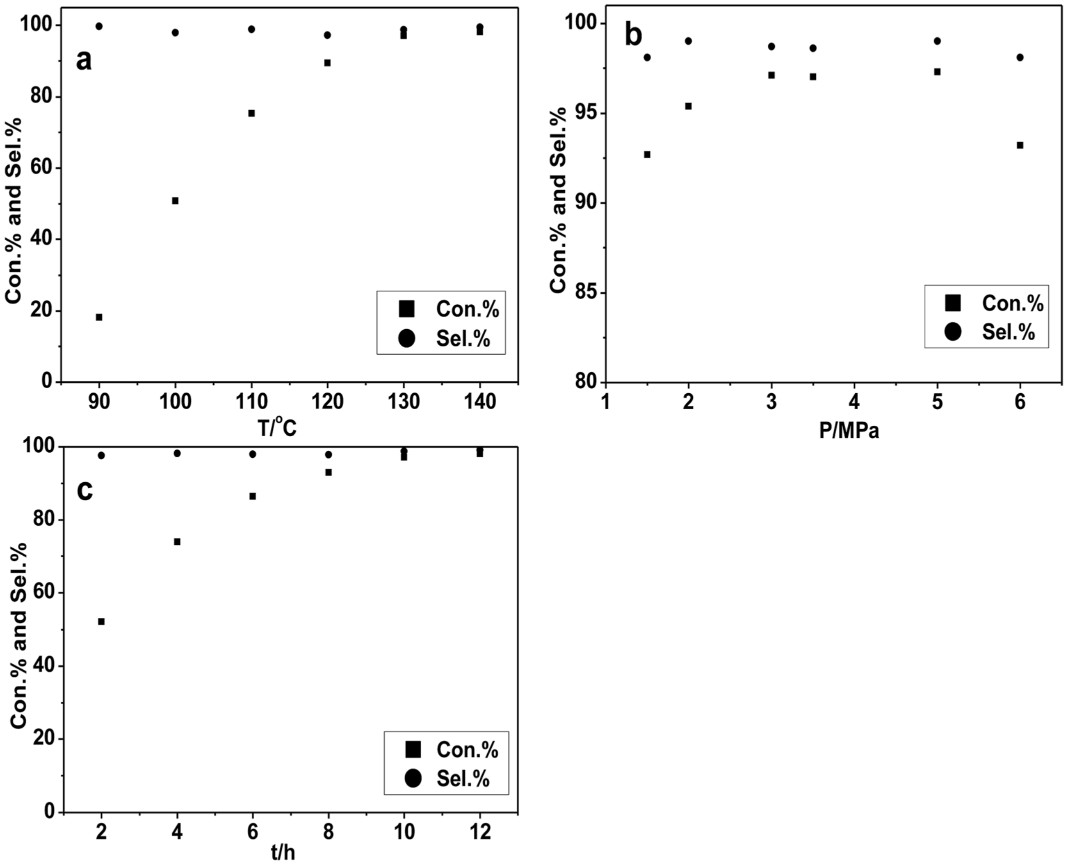


Fig. 4 The effects of reaction temperature, pressure and time on conversion and selectivity of cycloaddition reaction. Reaction condition: PO 0.7 mL (10 mmol); organocatalyst 1.5 mmol%. (a) CO_2 pressure 3 MPa; time 10 h; (b) temperature 130 °C; time 10 h; (c) temperature 130 °C; CO_2 pressure 3 MPa.

The conversion of PO had a gradual increasing from 2 to 10 h and then remained almost unchanged with high selectivity all time. The substrate was almost completely converted into PC within 10 h with high selectivity.

At last, we investigated the effect of the catalyst amount to the reaction and the results were shown in Table S2.† With the increasing of the catalyst amount from 1 mmol% to 1.5 mmol%, the conversion of PO had an obvious improvement. The possible explanation is that increasing the catalytic activity center indeed benefits a lot to the reaction. However, the further increasing of catalyst amount leads to a sharp descent. Due to the significant molecular weight of β-CD, the excessive amount of catalyst may be harmful to the mass transfer of the reactant and then decrease the conversion of PO. Thus, it was apparent that the appropriate catalyst amount was 1.5 mmol%.

Reaction kinetics

Sequentially, the reaction kinetics of catalysts [DBUH][PFPhO]/β-CD and [DBUH][PFPhO] was investigated respectively. The procedure for the studies of the kinetic parameters was similar to our group's previous work.[33] PO (0.7 mL, 10 mmol), catalysts (1.5 mmol%) was loaded into autoclave, CO_2 was introduced to the reaction and kept at 3.0 MPa under the reaction temperature. The rate constant was determined from the experimental data assuming pseudo-first order reaction kinetics. The kinetic parameters were studied over temperature ranged from 110 to 140 °C. The relationship of $-\ln(1 - \text{Con.})$ and PO remaining with reaction time at different temperature was shown in Fig. S8.† Finally, as shown in Fig. 5, the activation energy (E_a) for the process was calculated using the Arrhenius equation, where E_{a_1} of [DBUH][PFPhO]/β-CD was 43.1 kJ mol^{-1} while the E_{a_2} of [DBUH][PFPhO] was 59.9 kJ mol^{-1}. It can be seen that from this results that the inclusion of β-CD indeed owned lower E_a for the process and really benefited the cycloaddition reaction of CO_2 with epoxides. The activation energy under the present conditions is consistent with that of the other many reports, in which E_a was in the range of about 35–70 kJ mol^{-1}.[34]

The substrate scope of the catalyst

The results above demonstrated that the inclusion complexes of organic salt [DBUH][PFPhO] with β-CD was an highly efficient organocatalyst for the cycloaddition of CO_2 and PO without any organic solvents and additives. Thus, a series of epoxides were tested to synthesize the corresponding carbonates under optimized conditions to check the scope of the substrates over the present catalyst and the results were shown in Table 1. It was found that the organocatalyst was applicable to producing

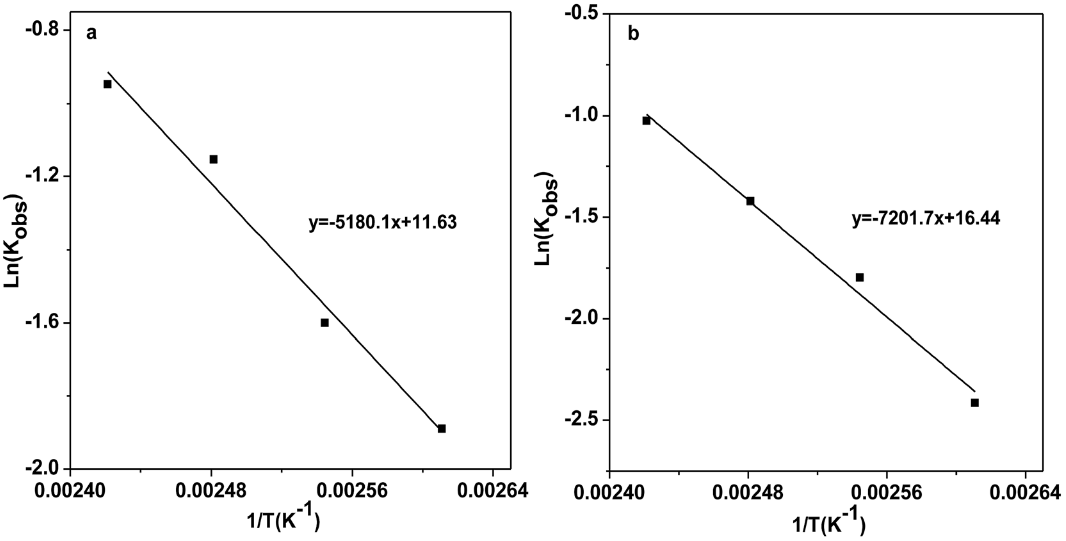
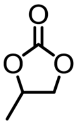
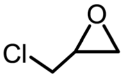
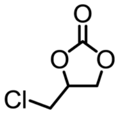
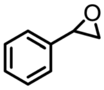
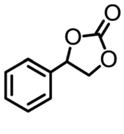
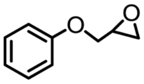
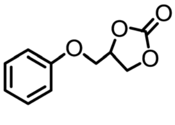
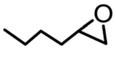
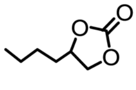
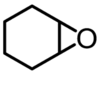
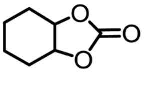


Fig. 5 Arrhenius plots for the CO_2 cycloaddition to PC catalyzed by (a) [DBUH][PFPhO]/β-CD; (b) [DBUH][PFPhO].

cyclic carbonates from CO_2 and various epoxides with high conversions and selectivities (Table 1, entries 1–6). Compared with other epoxides, 1,2-epoxyhexane and 1,2-epoxycyclohexane needed a longer reaction time to produce corresponding cyclic carbonates because of the higher steric hindrance (Table 1, entries 5 and 6).

Table 1 Different epoxides as substrates for the cycloaddition reaction with carbon dioxide catalyzed by [DBUH][PFPhO]/β-CD[a]

Entry	Substrates	Products	Con. (%)	Sel. (%)
1			98.7	99.1
2			98.8	97.9
3			95.6	99.8
4			99.5	99.2
5[b]			94.8	99.1
6[c]			81.7	76.8[d]

[a] Reaction conditions: PO 0.7 mL (10 mmol), organocatalyst (1.5 mmol%), 130 °C, 3 MPa, 10 h. [b] Reaction time: 30 h. [c] Reaction time: 45 h. [d] The main by-product was corresponding diol.

Catalyst stability

In the next step, the reusability of catalyst [DBUH][PFPhO]/β-CD was examined under the optimal conditions. After the reaction, the anhydrous ether was added to the reaction mixture. The catalyst was recovered by a simple standing and filtration, followed by washing with ethyl ether in 3 times and vacuum drying at 60 °C. Then the recovered catalyst can be reused for the next recycle. The reusability of [DBUH][PFPhO]/β-CD catalyst was shown in Fig. 6. It was found that the catalyst could be reusable for at least up to four times with high product selectivity, while the conversion of PO had a slight decrease in the consecutive recycles. Subsequently, the FT-IR of the reused [DBUH][PFPhO]/β-CD catalysts was displayed in Fig. 1h. Compared with the fresh catalyst, after recycling, the catalyst still remains the characteristic peaks of β-CD, which indicated that the skeleton

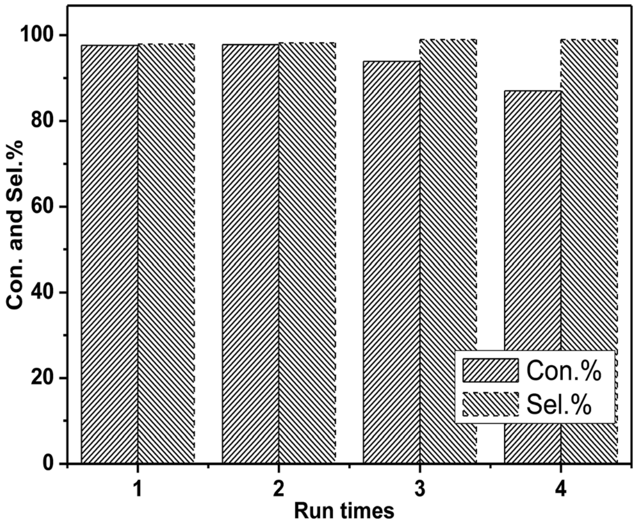


Fig. 6 Recyclability of [DBUH][PFPhO]/β-CD. Reaction conditions: PO 0.7 mL (10 mmol), organocatalyst (1.5 mmol%), 130 °C, 3 MPa.

structure of β-CD remained unchangeable. The peak at 1646 cm^{-1} ($C{=}N^+$ vibration) and the peak at 1499 cm^{-1} (C=C on benzene ring) were still visible in the spite of the intensity was decreased, which may caused by slightly leaching of [DBUH][PFPhO] from the cavity of β-CD. Additionally, the new band at 1792 cm^{-1} were assigned to the C=O stretching of the residual propylene carbonate over catalyst surface.[22,35]

Reaction mechanism

As we have mentioned above, the [DBUH][PFPhO] and β-CD can form the inclusion complexes by means of the host–guest interaction. In order to further investigate the chemical state of [DBUH][PFPhO] bound in the inclusion complexes during the reaction, the ^{19}F NMR spectra (500 MHz) of the [DBUH][PFPhO]/β-CD had been determined at elevated temperature by simulating reaction condition. The organocatalyst was dissolved in d6-DMSO, and then the ^{19}F NMR spectra was recorded in 25 °C, 50 °C and 70 °C in turn. After that, the solution was cooled down to 25 °C and recorded the spectra of the catalyst. The results were shown in Fig. 7. It was found that at 25 °C, the chemical shifts of fluorine atom on *para*, *ortho* and *meta* position was −192.27, −171.98 and −170.86, respectively (Fig. 7a). While the temperature was raised to 50 °C and 70 °C, the chemical shifts of all fluorine atoms moved slightly to the downfield, where was −192.94, −172.21, −171.17 and −192.98, −172.24 and −171.17, respectively (Fig. 7b and c). Increasing the concentration [DBUH][PFPhO]/β-CD in d6-DMSO, the chemical shifts of all fluorine atoms moved to the downfield more obviously (Fig. S5a *vs.* S5c†). When the solution cooled down back to 25 °C, the spectra of catalyst remain unchangeable, compared with its initial spectra in 25 °C (Fig. 7d). The change of chemical shifts in 50 °C and 70 °C may caused by the overflowing of guest [DBUH][PFPhO] from the β-CD's cavity. After cooled down the solution back to 25 °C, the [DBUH][PFPhO] moved into cavity and kept its initial state. This revealed that organic salt [DBUH][PFPhO] might dissociate from cavity of β-CD under the reaction temperature, but inclusion compound formed as cooling the reaction mixture after reaction, which was extremely attractive for separation and recycling of the supramolecular organocatalysts.

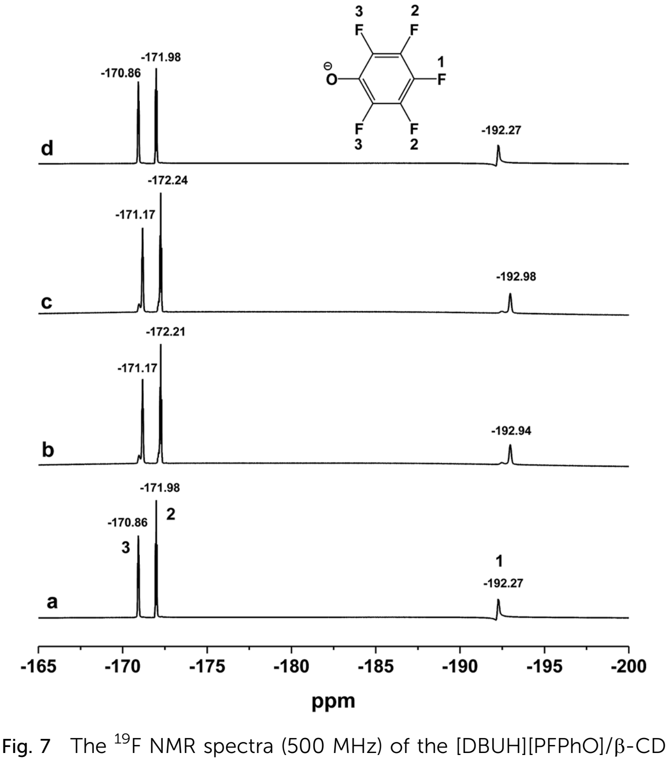


Fig. 7 The ^{19}F NMR spectra (500 MHz) of the [DBUH][PFPhO]/β-CD (0.054 mmol mL^{-1} in d6-DMSO) at different temperature. (a) 25 °C; (b) 50 °C; (c) 70 °C; (d) cooled down back to 25 °C.

In order to further gain a deeper insight into the reaction mechanism, DRIFTS of *in situ* PO adsorption was performed over the [DBUH][PFPhO]/β-CD in 298 K. As shown in Fig. 8a, the peaks at 1423, 1409 and 1399 cm^{-1} can be assigned to C–H bending vibration of gas-phase PO molecules.[33] After PO was introduced and purging with Ar, it was observed that the peaks of gas-phase PO molecules disappeared, and the new peaks at 1458 and 1452 cm^{-1} were formed (Fig. 8b and c). But these peaks were disappeared with keeping purging with Ar more longer time (Fig. 8d), indicating weak interaction of PO molecules with organocatalyst at room temperature. The new peaks could be assigned to C–O bending vibration of a probable intermediate species forming between PO and [DBUH][PFPhO] by hydrogen bond (species **2** in Scheme 3). This result suggested that the [DBUH][PFPhO] acted a crucial role in activating PO molecules. Next, the DRIFT of *in situ* CO_2 adsorption over the [DBUH][PFPhO]/β-CD was performed and the results have been listed in Fig. 9. The gas CO_2 exhibited its anti symmetric stretching vibration peaks at 2367 and 2344 cm^{-1} (Fig. 9a and b), respectively.[36] When the CO_2 was introduced on [DBUH][PFPhO]/β-CD, the peak intensity was increased. But with purging with Ar, no absorption peaks can be detected (Fig. 9h), which suggested that CO_2 could only physically absorbed on the [DBUH][PFPhO]/β-CD and showed weak absorption ability on catalyst at room temperature. Meanwhile, it should be noticed

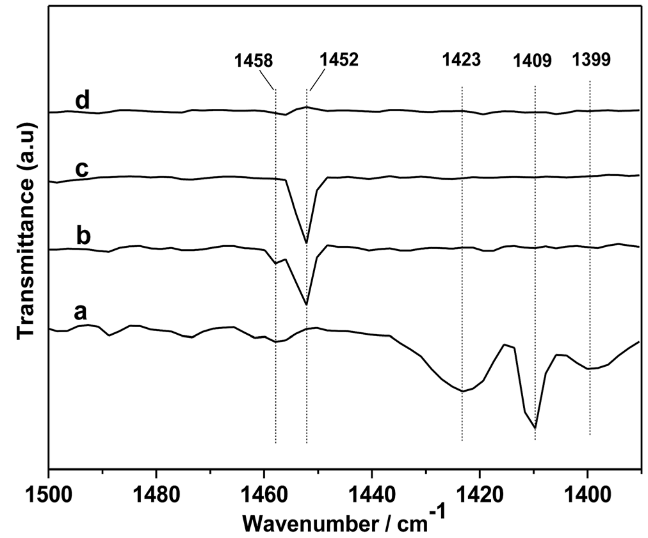
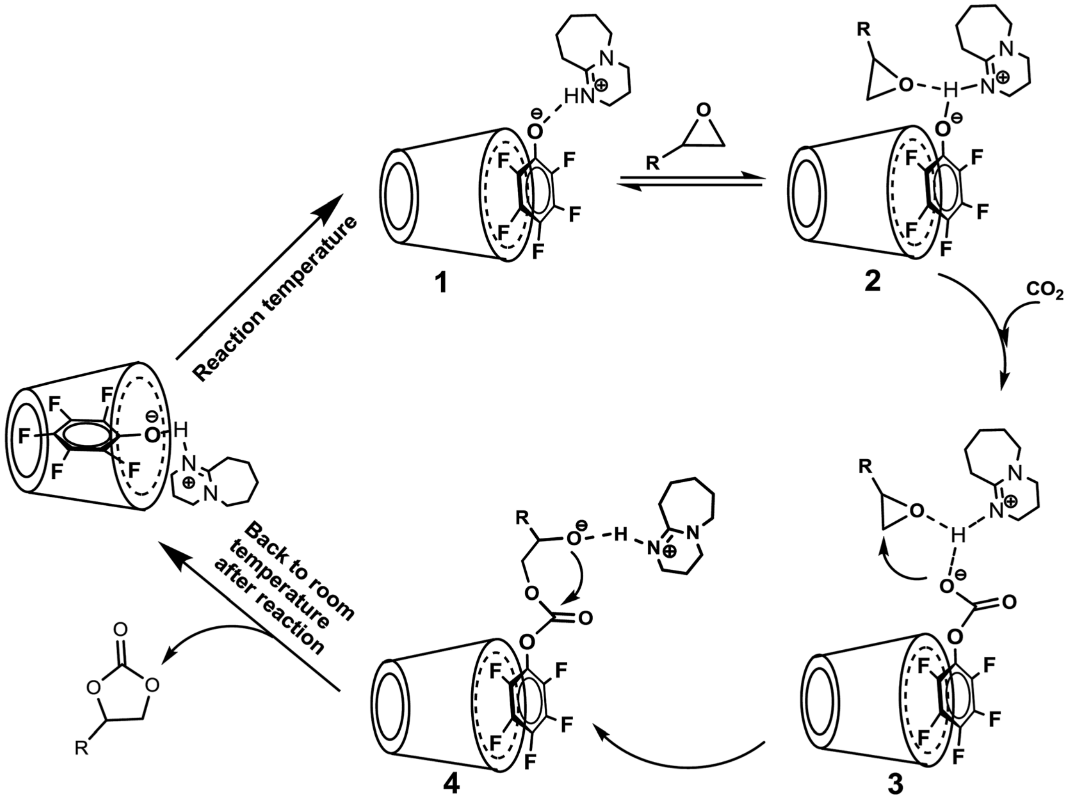


Fig. 8 DRIFT spectra of gas-phase PO (a) and *in situ* PO adsorbed on [DBUH][PFPhO]/β-CD samples followed purging with the flow of Ar (50 mL min^{-1}), (b) 3 min; (c) 6 min; (d) 9 min.



Scheme 3 The proposed reaction mechanism for cycloaddition of epoxide and CO_2 catalyzed by [DBUH][PFPhO]/β-CD catalyst.

that when we introduced the PO and CO_2 on [DBUH][PFPhO]/β-CD simultaneously, only CO_2 peaks could be observed and the peak from PO adsorption was too weak to be observable. Furthermore, we can easily found that the peak intensity became much stronger (Fig. 9d and e *vs.* g). From these results, it can be deduced that the existence of the adsorbed PO can promote the CO_2 absorption on [DBUH][PFPhO]/β-CD organocatalyst.

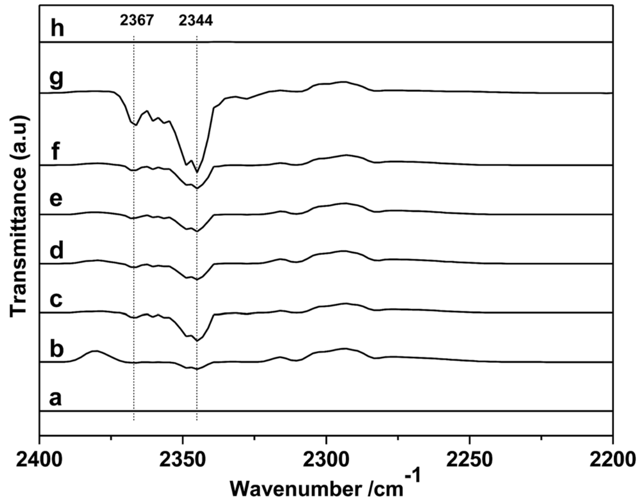


Fig. 9 DRIFT spectra of (a) baseline; (b) gas-phase CO_2; (c) gas-phase CO_2 on [DBUH][PFPhO]/β-CD; (d) *in situ* CO_2 adsorbed on [DBUH][PFPhO]/β-CD samples with purging CO_2 for 5 min; (e) for 15 min; (f) gas-phase CO_2 and PO on [DBUH][PFPhO]/β-CD; (g) *in situ* CO_2 and PO co-adsorbed on [DBUH][PFPhO]/β-CD samples with purging CO_2; (h) all samples purging with Ar (50 mL min^{-1}) for 5 min.

From what has been discussed above, we may draw the conclusion that 2,3,4,5,6-pentafluorophenol had CO_2-philic properties, and it may capture the CO_2 and forms a critical intermediate species during the reaction. Thus we attempted to characterize this probable critical intermediate species formed with $[PFPhO]^-$ anion and CO_2. A stainless autoclave was charged with [DBUH][PFPhO] (336 mg, 1.0 mmol) and CO_2 (1.0 MPa), and the mixture was stirred at a constant temperature (60 °C) for 24 h. Carefully release of CO_2 gave a white powder. The product was characterized by ^{13}C NMR spectra, a new signal at 159.2 ppm produced after the absorption of CO_2 (Fig. S9b†), which can be assigned to carbonate carbon.[37] Based on the previous reports, and observed product, a plausible intermediate species formed with $[PFPhO]^-$ anion and CO_2 can be proposed (Scheme S1†), which exhibits the interaction between the electronegative oxygen on $[PFPhO]^-$ and CO_2 to form the intermediate $[PFPhO\text{-}CO_2]^-$ in CO_2 cycloaddition reaction.[38] Another new signal at 129.4 ppm could be assigned to the gas CO_2 which was dissolved in DMSO.[39] The solvent of CO_2 adduction with [DBUH][PFPhO] was vacuumed and the ^{13}C NMR spectra was recorded again. As shown in Fig. S9c,† it was found that the peaks at 159.2 and 129.4 ppm disappeared completely, which indicated that the peaks at 129.4 ppm and 159.2 ppm were highly relevant to CO_2 adduction.

Based on the results we have obtained, we proposed a reasonable mechanism for this chemical fixation reaction of CO_2 (Scheme 3). As the temperature increasing, the guest compound [DBUH][PFPhO] dissociated from the cavity of β-CD under the reaction temperature, and could immobilize on the surface through the hydrogen bond. The proton in DBU-based salts was coordinated with the oxygen of the epoxide through a hydrogen bond, resulting in the activation of an epoxide,[2c,4h,12b,28] and this is followed by CO_2 insertion to form the intermediate species $[\text{PFPhO-CO}_2]^-$ bounding with the $[\text{DBUH}]^+$ and PO through the hydrogen bond. Simultaneously, the nucleophilic attack of $[\text{PFPhO-CO}_2]^-$ on the less sterically hindered β-carbon atom of the epoxide furnished the ring-opened intermediate species, and then the intermediate species made a subsequent intramolecular ring-closure, cyclic carbonate was formed. With the temperature cooled down after reaction, the guest compound [DBUH][PFPhO] could be back to the cavity of β-CD and the catalyst can be regenerated. It should be noticed that the hydroxyl groups of the glucopyranose monomers (such as cellulose and β-CD *etc.*) act as hydrogen bond donor and thus activate the ring-opening reaction of epoxides through the hydrogen bond on the oxygen atom of the epoxide.[20,30,40] In the present catalyst system, we could regard β-CD as an additional activator for the ring-opening of epoxide and thus promoted the cycloaddition of carbon dioxide with epoxide.

Conclusions

In summary, we have developed a series of DBU-based phenolates and their inclusion complexes with β-CD to act as the supramolecular organocatalysts in chemical fixation of CO_2 into cyclic carbonates. High epoxides conversion and excellent cyclocarbonates selectivity can be achieved under the optimal reaction conditions. Among these catalysts, the organocatalyst [DBUH][PFPhO]/β-CD afforded the best catalytic performance. Furthermore, it can be easily separated after reaction and reused with high activity and selectivity. Based on all characterization, we proposed a reasonable mechanism for this reaction, where β-CD played a crucial role in immobilizing catalytically active species and thus improving the recyclability of the supramolecular catalyst. This easily-prepared, metal and halogen ion-free, inexpensive and recyclable catalytic system has potential application for catalytically synthesizing cyclic carbonates from CO_2 and epoxides.

Experimental

Chemical materials

β-Cyclodextrins (β-CDs) was purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai. Organic bases 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) was also purchased from Sinopharm Chemical Reagent Co., Ltd., and directly used without any further purification. Phenol and its other kinds of substituted derivatives such as 2,3,4,5,6-pentafluorophenol, 4-fluorophenol, 2-fluorophenol and 4-nitrophenol were all purchased from Shanghai Macklin Biochemical Co., Ltd., and were also used without further purification. CO_2 was supplied by Shanghai Shangnong Gas Factory with a purity of >99.95%. All kinds of epoxides were analytic grade and were used directly without further purification. All solvents (analytic grade) were dried by using the methods that have been previously reported.

Characterizations

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 MHz instrument (400 MHz ^1H NMR), and ^{19}F NMR spectra were recorded on a Bruker AVANCE 500 MHz instrument (500 MHz ^{19}F NMR). The concentration of samples in deuterated solvent was 0.054 mmol mL^{-1}, unless indicated otherwise. The FT-IR spectra were recorded at RT on a Nicolet Magna 550 FT-IR spectrometer. The thermal stability of catalysts was determined by Thermogravimetry analysis (TGA) method (heating rate: 10 °C min^{-1}; N_2 flow: 100 mL min^{-1}) using Perkin Elmer Pyris Diamond Analyzer. The scanning electron microscopy (SEM) images were performed on JSM electron microscopes (JEOL JSM-6360LV, Japan). *In situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were conducted on a Nicolet 6700 FTIR fitted with a liquid nitrogen cooled mercury-cadmium-telluride detector (MCT). The DRIFTS cell (Harrick, HVC-DRP) fitted with CaF_2 windows were used as the reaction chamber that allowed samples to be heated to 150 °C. All the spectra were within the range of 4000–1200 cm^{-1} at the resolution of 4 cm^{-1} and 64 scans. Prior to the adsorption experiments, the samples were pretreated in Ar at 150 °C for 4 h. Then the samples were cooled down to 25 °C in order to remove the contaminants and the PO/CO_2-adsorbed FT-IR spectra of the samples (40 mg) were recorded at 25 °C.

Preparation of DBU-based phenolates

Preparation of [DBUH][PFPhO]. The DBU-based 2,3,4,5,6-pentafluorophenolate ([DBUH][PFPhO]) was prepared by neutralizing method. 1,8-Diazabicyclo-[5.4.0]undec-7-ene (DBU) (5 mmol, 0.75 mL) and 2,3,4,5,6-pentafluorophenol (5 mmol, 0.92 g) were solved in 15 mL dried THF and stirred at 40 °C for 4 h in 100 mL Schlenk flask equipped with a magnetic stirrer under N_2 atmosphere. After the mixture was cooled to room temperature under nitrogen atmosphere, the solvent in the resulting mixture was evaporated under vacuum and then dried under the vacuum at 60 °C for 2 h to obtain the white powder (Fig. S1, S4b,† and 2a). ^1H NMR (400 MHz, d6-DMSO): δ 1.63 (m, 6H), 1.91 (m, 2H), 2.70 (d, $J = 10.4$ Hz, 2H), 3.24 (t, $J = 5.7$ Hz, 2H), 3.47 (t, $J = 5.8$ Hz, 2H), 3.54 (m, 2H), 11.15 (s, 1H); ^{13}C NMR (100 MHz, d6-DMSO): δ 19.0, 23.5, 26.0, 28.3, 31.2, 37.7, 47.8, 53.1, 124.2, 126.4, 137.1, 139.5, 141.8, 146.0, 165.2; ^{19}F NMR (500 MHz, d6-DMSO): δ −192.67, −172.08, −171.31.

Preparation of [DBUH][PhO]. The DBU-based phenolate ([DBUH][PhO]) was prepared with the similar method but replacing the 2,3,4,5,6-pentafluorophenol with phenol (5 mmol, 0.47 g) to obtain the pale yellow liquid (Fig. S1 and S2†). ^1H NMR (400 MHz, d6-DMSO): δ 1.56 (m, 6H), 1.71 (m, 2H), 2.38 (m, 2H), 3.13 (t, $J = 5.3$ Hz, 2H), 3.24 (m, 4H), 6.59 (t, $J = 7.2$ Hz, 1H), 6.67 (d, $J = 8.1$ Hz, 2H), 7.06 (t, $J = 7.6$ Hz, 2H), 9.19 (s, 1H);

^{13}C NMR (100 MHz, d6-DMSO): δ 21.4, 25.1, 27.5, 28.8, 34.5, 41.6, 47.5, 52.1, 116.0, 116.2, 129.0, 160.6, 161.8.

Preparation of [DBUH][*p*-FPhO]. The DBU-based 4-fluorophenolate ([DBUH][*p*-FPhO]) was prepared with the similar method but replacing the 2,3,4,5,6-pentafluorophenol with 4-fluorophenol (5 mmol, 0.56 g) to obtain the pale yellow liquid (Fig. S1 and S2†). ^{1}H NMR (400 MHz, D_2O): δ 1.54 (m, 6H), 1.83 (p, $J = 5.8$ Hz, 2H), 2.44 (d, $J = 9.0$ Hz, 2H), 3.14 (t, $J = 5.5$ Hz, 2H), 3.35 (m, 4H), 6.41 (dd, $J = 7.5$, 5.6 Hz, 2H), 6.74 (t, $J = 8.9$ Hz, 2H), 10.73 (s, 1H); ^{13}C NMR (100 MHz, d6-DMSO): δ 21.2, 25.1, 27.4, 28.8, 34.2, 41.2, 47.6, 52.2, 115.1, 116.5, 152.8, 155.1, 157.7, 162.2.

Preparation of [DBUH][*o*-FPhO]. The DBU-based 2-fluorophenolate ([DBUH][*o*-FPhO]) was prepared with the similar method but replacing the 2,3,4,5,6-pentafluorophenol with 2-fluorophenol (5 mmol, 0.56 g) to obtain the deep yellow liquid (Fig. S1 and S2†). ^{1}H NMR (400 MHz, d6-DMSO): δ 1.53 (m, 6H), 1.77 (p, $J = 5.9$ Hz, 2H), 2.51 (d, $J = 9.7$ Hz, 2H), 3.16 (t, $J = 5.5$ Hz, 2H), 3.32 (m, 4H), 6.31 (m, 1H), 6.73 (m, 2H), 6.86 (m, 1H), 11.98 (s, 1H); ^{13}C NMR (100 MHz, d6-DMSO): δ 20.3, 24.4, 26.9, 28.6, 32.8, 47.7, 52.6, 112.8, 120.0, 119.4, 124.2, 152.5, 154.7, 163.4.

Preparation of [DBUH][*p*-NO$_2$-PhO]. The DBU-based 4-nitrophenolate ([DBUH][*p*-NO$_2$-PhO]) was prepared with the similar method but replacing the 2,3,4,5,6-pentafluorophenol with 4-nitrophenol (5 mmol, 0.70 g) to obtain the light yellow powder (Fig. S1 and S2†). ^{1}H NMR (400 MHz, d6-DMSO): δ 1.63 (m, 6H), 1.91 (m, 2H), 2.65 (d, $J = 8.0$ Hz, 2H), 3.25 (s, 2H), 3.47 (s, 4H), 6.06 (d, $J = 8.5$ Hz, 2H), 7.78 (d, $J = 8.5$ Hz, 2H), 10.10 (s, 1H); ^{13}C NMR (100 MHz, d6-DMSO): δ 18.9, 23.4, 25.9, 28.2, 31.6, 37.6, 47.8, 53.3, 118.7, 127.2, 129.6, 165.3, 178.5.

Purification of β-cyclodextrins. The commercial β-CD needs to be re-crystallization before it was used as the support. The method as followed have been reported previously: β-CD (10 g) was added in 50 mL deionized water and heated until the β-CD was completely solved. And then remove the impurities instantly by filtration, the filtrate was stirred vigorously in ice bath to get the hydrate β-CD. The above operation was repeated three times and dried the hydrate β-CD at 80 °C under the reduced pressure. The purified sample was stored in flask under the N_2 atmosphere (Fig. S3a and S4a†). ^{1}H NMR (400 MHz, d6-DMSO): δ 3.30 (m, 7H, H-2′), 3.35 (m, 7H, H-4′), 3.56 (m, 7H, H-5′), 3.60 (m, $J = 5.4$ Hz, 7H, H-3′), 3.65 (dd, $J = 10.1$, 7.5 Hz, 14H, H-6′), 4.47 (t, $J = 5.6$ Hz, 7H, OH-6′), 4.83 (d, $J = 3.4$ Hz, 7H, H-1′), 5.68 (d, $J = 2.3$ Hz, 7H, OH-3′), 5.74 (d, $J = 6.9$ Hz, 7H, OH-2′); ^{13}C NMR (100 MHz, d6-DMSO): δ 59.9, 72.0, 72.4, 73.0, 81.5, 101.9.

Preparation of inclusion complexes

The inclusion complexes were prepared by mixing the DBU-based phenolates (1 mmol) and β-CD (1 mmol, 1.135 g) in aqueous solution at 60 °C for 6 h under the N_2 atmosphere. After the solution was cooled to room temperature, the water was removed by rotary evaporation to get the solid powder. Then drying the powder at 70 °C for 2 h under the vacuum afforded the inclusion complexes as white powder (Fig. S3†).

[DBUH][PhO]/β-CD. ^{1}H NMR (400 MHz, d6-DMSO): δ 1.56 (m, 6H), 1.72 (m, 2H), 2.40 (m, 2H), 3.13 (t, 2H), 3.24–3.26 (m, 11H), 3.32 (m, 7H, H-4′), 3.55 (m, 7H, H-5′), 3.59 (m, 7H, H-3′), 3.65 (dd, 14H, H-6′), 4.82 (d, $J = 3.4$ Hz, 7H, H-1′), 5.1–5.5 (m, 14H), 6.66 (m, 2H), 7.10 (t, 2H).

[DBUH][*p*-FPhO]/β-CD. ^{1}H NMR (400 MHz, d6-DMSO): δ 1.57 (m, 6H), 1.73 (p, $J = 5.8$ Hz, 2H), 2.38 (d, $J = 9.0$ Hz, 2H), 3.12 (t, $J = 5.5$ Hz, 2H), 3.24–3.26 (m, 11H), 3.32 (m, 7H, H-4′), 3.55 (m, 7H, H-5′), 3.59 (m, 7H, H-3′), 3.65 (dd, 14H, H-6′), 4.82 (d, $J = 3.4$ Hz, 7H, H-1′), 5.1–5.5 (m, 14H), 6.63 (m, 2H), 6.90 (m, 2H).

[DBUH][*o*-FPhO]/β-CD. ^{1}H NMR (400 MHz, d6-DMSO): δ 1.57 (m, 6H), 1.82 (p, $J = 5.9$ Hz, 2H), 2.41 (d, $J = 9.7$ Hz, 2H), 3.18 (t, $J = 5.5$ Hz, 2H), 3.24–3.26 (m, 11H), 3.32 (m, 7H, H-4′), 3.55 (m, 7H, H-5′), 3.59 (m, 7H, H-3′), 3.65 (dd, 14H, H-6′), 4.82 (d, $J = 3.4$ Hz, 7H, H-1′), 5.1–5.5 (m, 14H), 6.41 (m, 1H), 6.64 (dd, $J = 12.9$, 4.7 Hz, 1H), 6.74 (m, 1H), 6.86 (m, 1H).

[DBUH][*p*-NO$_2$-PhO]/β-CD. ^{1}H NMR (400 MHz, d6-DMSO): δ 1.64 (m, 6H), 1.91 (m, 2H), 2.64 (d, $J = 8.0$ Hz, 2H), 3.24 (s, 2H), 3.30 (m, 7H, H-2′), 3.47 (s, 2H), 3.32 (m, 7H, H-4′), 3.55 (m, 7H, H-5′), 3.59 (m, 7H, H-3′), 3.65 (dd, 14H, H-6′), 4.47 (t, $J = 5.6$ Hz, 7H, OH-6′), 4.83 (d, $J = 3.4$ Hz, 7H, H-1′), 5.5–6.0 (m, 14H), 6.03 (d, $J = 8.5$ Hz, 2H), 7.76 (d, $J = 8.5$ Hz, 2H).

[DBUH][PFPhO]/β-CD. ^{1}H NMR (400 MHz, d6-DMSO): δ 1.64 (m, 6H), 1.91 (m, 2H), 2.64 (d, $J = 10.2$ Hz, 2H), 3.24 (t, $J = 5.7$ Hz, 2H), 3.47 (t, 2H), 3.53–3.55 (m, 9H), 3.59 (m, 7H, H-3′), 3.65 (m, 14H, H-6′), 4.48 (s, 7H, OH-6′), 4.83 (d, $J = 3.4$ Hz, 7H, H-1′), 5.73 (s, 7H, OH-3′), 5.79 (d, $J = 6.4$ Hz, 7H, OH-2′); ^{13}C NMR (100 MHz, d6-DMSO): δ 19.4, 23.9, 26.4, 28.7, 32.0, 38.1, 48.3, 53.8, 60.4, 72.5, 72.9, 73.6, 82.0, 102.4, 137.6, 139.9, 142.2, 146.1, 165.8; 19F NMR (500 MHz, d6-DMSO): δ −192.27, −171.98, −170.86 (Fig. 2b).

Reaction of cycloaddition from CO$_2$ and peroxides

The cycloaddition reaction of propylene oxide (PO) and CO_2 to propylene carbonate (PC) was used as a model reaction to evaluate the catalytic performance. The catalyst (0.15 mmol) and PO (10 mmol) were added into the glass bush, and then put the bush into the 50 mL stainless autoclave and then sealed it. The loading of supramolecular organocatalyst was based on that of DBU-based phenolates for the reaction. The reactor was purged with CO_2 for 3 times to remove the air into the reactor, and finally charged with CO_2 to the desired pressure. After the reaction, the reactor was cooled in ice-water bath immediately, and the CO_2 was slowly vented while anhydrous ether was as absorption liquid to absorb the PO and products entrained by CO_2. Then, the anhydrous ether in the trap was added to the reactor and washed the catalyst to extract products and substrate. The catalyst was separated simply by standing and filtration, and the filtrate was subjected to GC-MS and GC analysis. The catalyst was washed with anhydrous ether 3 times and dried in a vacuum at 60 °C to be used directly in next reaction.

Acknowledgements

The authors are grateful for support from the National Natural Science Foundation of China (21373082) and innovation Program of Shanghai Municipal Education Commission (15ZZ031), and the Fundamental Research Funds for the Central Universities.

Notes and references

1 (*a*) K. Thenert, K. Beydoun, J. Wiesenthal, W. Leitner and J. Klankermayer, *Angew. Chem., Int. Ed.*, 2016, **55**, 12266; (*b*) M. Aresta, A. Dibenedetto and E. Quaranta, *J. Catal.*, 2016, **343**, 2; (*c*) S. Wang and X. Wang, *Angew. Chem., Int. Ed.*, 2016, **55**, 2308; (*d*) J. Shi, Y. Jiang, Z. Jiang, X. Wang, X. Wang, S. Zhang, P. Han and C. Yang, *Chem. Soc. Rev.*, 2015, **44**, 5981; (*e*) G. Fiorani, W. Guo and A. W. Kleij, *Green Chem.*, 2015, **17**, 1375; (*f*) P. Lanzafame, G. Centi and S. Perathoner, *Chem. Soc. Rev.*, 2014, **43**, 7562; (*g*) G. Ji, Z. Yang, H. Zhang, Y. Zhao, B. Yu, Z. Ma and Z. Liu, *Angew. Chem., Int. Ed.*, 2016, **55**, 9685; (*h*) T. Sakakura and K. Kohno, *Chem. Commun.*, 2009, 1312; (*i*) M. Mikkelsen, M. Jørgensen and F. C. Krebs, *Energy Environ. Sci.*, 2010, **3**, 43; (*j*) M. Peters, B. Kohler, W. Kuckshinrichs, W. Leitner, P. Markewitz and T. E. Muller, *ChemSusChem*, 2011, **4**, 1216.

2 (*a*) P. Z. Li, X. J. Wang, J. Liu, J. S. Lim, R. Zou and Y. Zhao, *J. Am. Chem. Soc.*, 2016, **138**, 2142; (*b*) T. T. Liu, J. Liang, Y. B. Huang and R. Cao, *Chem. Commun.*, 2016, **52**, 13288; (*c*) M. Ding and H. L. Jiang, *Chem. Commun.*, 2016, **52**, 12294; (*d*) Y. Toda, Y. Komiyama, A. Kikuchi and H. Suga, *ACS Catal.*, 2016, **6**, 6906; (*e*) S. Verma, R. B. N. Baig, M. N. Nadagouda and R. S. Varma, *Green Chem.*, 2016, **18**, 4855; (*f*) X. Liu, S. Zhang, Q. W. Song, X. F. Liu, R. Ma and L. N. He, *Green Chem.*, 2016, **18**, 2871; (*g*) M. Aresta and A. Dibenedetto, *Dalton Trans.*, 2007, 2975; (*h*) M. North, R. Pasquale and C. Young, *Green Chem.*, 2010, **12**, 1514; (*i*) J. Sun, S. Zhang, W. Cheng and J. Ren, *Tetrahedron Lett.*, 2008, **49**, 3588; (*j*) D. H. Lan, F. M. Yang, S. L. Luo, C. T. Au and S. F. Yin, *Carbon*, 2014, **73**, 351.

3 (*a*) M. Liu, B. Liu, L. Liang, F. Wang, L. Shi and J. Sun, *J. Mol. Catal. A: Chem.*, 2016, **418–419**, 78; (*b*) T. Ema, Y. Miyazaki, S. Koyama, Y. Yano and T. Sakai, *Chem. Commun.*, 2012, **48**, 4489; (*c*) T. Sakakura, J. C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365; (*d*) M. Yoshida and M. Ihara, *Chem.–Eur. J.*, 2004, **10**, 2886.

4 (*a*) F. D. Bobbink and P. J. Dyson, *J. Catal.*, 2016, **343**, 52; (*b*) V. Besse, N. Illy, G. David, S. Caillol and B. Boutevin, *ChemSusChem*, 2016, **9**, 2167; (*c*) V. Butera, N. Russo, U. Cosentino, C. Greco, G. Moro, D. Pitea and E. Sicilia, *ChemCatChem*, 2016, **8**, 1167; (*d*) H. Yang, X. Wang, Y. Ma, L. Wang and J. Zhang, *Catal. Sci. Technol.*, 2016, **6**, 7773; (*e*) S. Liu, N. Suematsu, K. Maruoka and S. Shirakawa, *Green Chem.*, 2016, **18**, 4611; (*f*) V. Caló, A. Nacci, A. Monopoli and A. Fanizzi, *Org. Lett.*, 2002, **4**, 2561; (*g*) Y. Zhou, S. Hu, X. Ma, S. Liang, T. Jiang and B. Han, *J. Mol. Catal. A: Chem.*, 2008, **284**, 52; (*h*) N. Aoyagi, Y. Furusho and T. Endo, *Tetrahedron Lett.*, 2013, **54**, 7031.

5 J. A. Kozak, J. Wu, X. Su, F. Simeon, T. A. Hatton and T. F. Jamison, *J. Am. Chem. Soc.*, 2013, **135**, 18497.

6 (*a*) Q. He, J. W. O'Brien, K. A. Kitselman, L. E. Tompkins, G. C. T. Curtis and F. M. Kerton, *Catal. Sci. Technol.*, 2014, **4**, 1513; (*b*) H. Yang, Y. Gu, Y. Deng and F. Shi, *Chem. Commun.*, 2002, 274; (*c*) J. Sun, L. Han, W. Cheng, J. Wang, X. Zhang and S. Zhang, *ChemSusChem*, 2011, **4**, 502; (*d*) A.-L. Girard, N. Simon, M. Zanatta, S. Marmitt, P. Gonçalves and J. Dupont, *Green Chem.*, 2014, **16**, 2815; (*e*) L. Xiao, D. Su, C. Yue and W. Wu, *J. CO2 Util.*, 2014, **6**, 1; (*f*) J. Palgunadi, O. S. Kwon, H. Lee, J. Y. Bae, B. S. Ahn, N. Y. Min and H. S. Kim, *Catal. Today*, 2004, **98**, 511.

7 Y. M. Shen, W. L. Duan and M. Shi, *J. Org. Chem.*, 2003, **68**, 6705.

8 (*a*) T. Ema, Y. Miyazaki, S. Koyama, Y. Yano and T. Sakai, *Chem. Commun.*, 2012, **48**, 4489; (*b*) T. Ema, Y. Miyazaki, J. Shimonishi, C. Maeda and J. Y. Hasegawa, *J. Am. Chem. Soc.*, 2014, **136**, 15270; (*c*) C. Maeda, T. Taniguchi, K. Ogawa and T. Ema, *Angew. Chem., Int. Ed.*, 2015, **54**, 134; (*d*) Y. Qin, H. Guo, X. Sheng, X. Wang and F. Wang, *Green Chem.*, 2015, **17**, 2853.

9 H. Yasuda, L. He, T. Sakakura and C. Hu, *J. Catal.*, 2005, **233**, 119.

10 (*a*) H. Zhou, G. X. Wang, W. Z. Zhang and X. B. Lu, *ACS Catal.*, 2015, **5**, 6773; (*b*) L. Martinez-Rodriguez, J. Otalora Garmilla and A. W. Kleij, *ChemSusChem*, 2016, **9**, 749; (*c*) C. Kohrt and T. Werner, *ChemSusChem*, 2015, **8**, 2031; (*d*) D. H. Lan, N. Fan, Y. Wang, X. Gao, P. Zhang, L. Chen, C. T. Au and S. F. Yin, *Chin. J. Catal.*, 2016, **37**, 826.

11 (*a*) Y. Xie, T. T. Wang, X. H. Liu, K. Zou and W. Q. Deng, *Nat. Commun.*, 2013, **4**, 1960; (*b*) L. F. Xiao, F. W. Li, J. J. Peng and C. G. Xia, *J. Mol. Catal. A: Chem.*, 2006, **253**, 265; (*c*) D. H. Lan, L. Chen, C. T. Au and S. F. Yin, *Carbon*, 2015, **93**, 22; (*d*) D. H. Lan, H. T. Wang, L. Chen, C. T. Au and S. F. Yin, *Carbon*, 2016, **100**, 81.

12 (*a*) L. Han, S. W. Park and D. W. Park, *Energy Environ. Sci.*, 2009, **2**, 1286; (*b*) W. Cheng, X. Chen, J. Sun, J. Wang and S. Zhang, *Catal. Today*, 2013, **200**, 117; (*c*) A. S. Aquino, F. L. Bernard, J. V. Borges, L. Mafra, F. D. Vecchia, M. O. Vieira, R. Ligabue, M. Seferin, V. V. Chaban, E. J. Cabrita and S. Einloft, *RSC Adv.*, 2015, **5**, 64220.

13 (*a*) Z. Zhou, C. He, J. Xiu, L. Yang and C. Duan, *J. Am. Chem. Soc.*, 2015, **137**, 15066; (*b*) W. Wang, C. Li, L. Yan, Y. Wang, M. Jiang and Y. Ding, *ACS Catal.*, 2016, **6**, 6091; (*c*) Z. Dai, Q. Sun, X. Liu, C. Bian, Q. Wu, S. Pan, L. Wang, X. Meng, F. Deng and F.-S. Xiao, *J. Catal.*, 2016, **338**, 202; (*d*) A. H. Jadhav, G. M. Thorat, K. Lee, A. C. Lim, H. Kang and J. G. Seo, *Catal. Today*, 2016, **265**, 56; (*e*) W. Zhang, Q. Wang, H. Wu, P. Wu and M. He, *Green Chem.*, 2014, **16**, 4767.

14 W. H. Zhang, P. P. He, S. Wu, J. Xu, Y. Li, G. Zhang and X. Y. Wei, *Appl. Catal., A*, 2016, **509**, 111.

15 L. Han, H. Li, S. J. Choi, M. S. Park, S. M. Lee, Y. J. Kim and D. W. Park, *Appl. Catal., A*, 2012, **429–430**, 67–72.

16 J. Sun, J. Wang, W. Cheng, J. Zhang, X. Li, S. Zhang and Y. She, *Green Chem.*, 2012, **14**, 654.

17 M. Raynal, P. Ballester, A. Vidal-Ferran and P. W. van Leeuwen, *Chem. Soc. Rev.*, 2014, **43**, 1660.

18 (*a*) J. Szejtli, *Chem. Rev.*, 1998, **98**, 1743; (*b*) M. V. Rekharsky and Y. Inoue, *Chem. Rev.*, 1998, **98**, 1875.

19 (*a*) F. Hapiot, H. Bricout, S. Menuel, S. Tilloy and E. Monflier, *Catal. Sci. Technol.*, 2014, **4**, 1899; (*b*) A. H. Karoyo, P. S. Sidhu, L. D. Wilson, P. Hazendonk and A. Borisov, *J. Phys. Chem. C*, 2015, **119**, 22225.

20 J. Sun, W. Cheng, Z. Yang, J. Wang, T. Xu, J. Xin and S. Zhang, *Green Chem.*, 2014, **16**, 3071.

21 Y. M. Shen, W. L. Duan and M. Shi, *Adv. Synth. Catal.*, 2003, **345**, 337–340.

22 A. Chen, C. Chen, Y. Xiu, X. Liu, J. Chen, L. Guo, R. Zhang and Z. Hou, *Green Chem.*, 2015, **17**, 1842.

23 (*a*) L. Branco, G. Carrera, A. Costa and M. da Ponte, *Synlett*, 2013, **24**, 2525; (*b*) B. Wang, Z. Luo, E. H. M. Elageed, S. Wu, Y. Zhang, X. Wu, F. Xia, G. Zhang and G. Gao, *ChemCatChem*, 2016, **8**, 830; (*c*) I. Cota, R. Chimentao, J. Sueiras and F. Medina, *Catal. Commun.*, 2008, **9**, 2090.

24 (*a*) Y. Xie, R. Parnas, B. Liang, Y. Liu, C. Tao and H. Lu, *Chin. J. Chem. Eng.*, 2015, **23**, 1728; (*b*) L. Mino, A. Zecchina, G. Martra, A. M. Rossi and G. Spoto, *Appl. Catal., B*, 2016, **196**, 135.

25 J. W. Wiench, L. Stefaniak, E. Grech and E. Bednarek, *J. Chem. Soc., Perkin Trans.*, 1999, **2**, 885.

26 (*a*) H. J. Schneider, F. Hacket and V. Rudiger, *Chem. Rev.*, 1998, **98**, 1755; (*b*) K. Srinivasan, K. Sivakumar and T. Stalin, *Carbohydr. Polym.*, 2014, **113**, 577.

27 (*a*) H. S. Kim, J. J. Kim, B. G. Lee, O. S. Jung, H. G. Jang and S. O. Kang, *Angew. Chem., Int. Ed.*, 2000, **39**, 4096; (*b*) K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida and K. Kaneda, *J. Am. Chem. Soc.*, 1999, **121**, 4526.

28 Y. M. Shen, W. L. Duan and M. Shi, *Eur. J. Org. Chem.*, 2004, 3080.

29 (*a*) Y. Zhao, K. X. Yao, B. Teng, T. Zhang and Y. Han, *Energy Environ. Sci.*, 2013, **6**, 3684; (*b*) Z. Z. Yang, Y. Zhao, G. Ji, H. Zhang, B. Yu, X. Gao and Z. Liu, *Green Chem.*, 2014, **16**, 3724.

30 J. Song, Z. Zhang, B. Han, S. Hu, W. Li and Y. Xie, *Green Chem.*, 2008, **10**, 1337.

31 (*a*) K. Srinivasan, T. Stalin and K. Sivakumar, *Spectrochim. Acta, Part A*, 2012, **94**, 89; (*b*) R. Rajamohan, S. Kothai Nayaki and M. Swaminathan, *J. Solution Chem.*, 2011, **40**, 803.

32 B. Song, L. Guo, R. Zhang, X. Zhao, H. Gan, C. Chen, J. Chen, W. Zhu and Z. Hou, *J. CO2 Util.*, 2014, **6**, 62.

33 X. Wu, M. Wang, Y. Xie, C. Chen, K. Li, M. Yuan, X. Zhao and Z. Hou, *Appl. Catal., A*, 2016, **519**, 146.

34 S. Supasitmongkol and P. Styring, *Catal. Sci. Technol.*, 2014, **4**, 1622.

35 R. Srivastava, D. Srinivas and P. Ratnasamy, *Catal. Lett.*, 2003, **91**, 133.

36 (*a*) S. Chen, T. Cao, Y. Gao, D. Li, F. Xiong and W. Huang, *J. Phys. Chem. C*, 2016, **120**, 21472; (*b*) J. Yu and S. S. C. Chuang, *Energy Fuels*, 2016, **30**, 7579.

37 (*a*) X. Luo, Y. Guo, F. Ding, H. Zhao, G. Cui, H. Li and C. Wang, *Angew. Chem., Int. Ed.*, 2014, **53**, 7053; (*b*) C. Wang, H. Luo, H. Li, X. Zhu, B. Yu and S. Dai, *Chem.–Eur. J.*, 2012, **18**, 2153; (*c*) C. Wang, H. Luo, D. E. Jiang, H. Li and S. Dai, *Angew. Chem., Int. Ed.*, 2010, **49**, 5978.

38 Y. Tsutsumi, K. Yamakawa, M. Yoshida, T. Ema and T. Sakai, *Org. Lett.*, 2010, **12**, 5728.

39 S. Morooka, C. Wakai, A. Nobuyuki Matubayasi and M. Nakahara, *J. Phys. Chem. A*, 2005, **109**, 6610.

40 (*a*) K. R. Roshan, G. Mathai, J. Kim, J. Tharun, G. A. Park and D. W. Park, *Green Chem.*, 2012, **14**, 2933; (*b*) S. Liang, H. Liu, T. Jiang, J. Song, G. Yang and B. Han, *Chem. Commun.*, 2011, **47**, 2131.