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Metal-free imidazolium hydrogen carbonate ionic liquids as bifunctional catalyst for the one-pot synthesis of cyclic carbonates from olefins and CO_2

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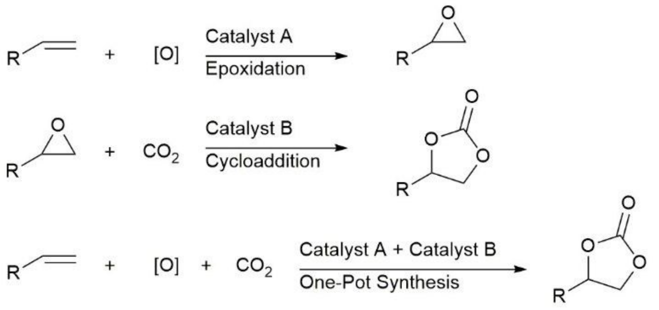
A direct route for the synthesis of cyclic carbonates from olefins and CO_2 has been achieved by using an imidazolium hydrogen carbonate ionic liquids ($[C_nC_mIm][HCO_3]$) as bifunctional catalyst in the absence of solvent. $[C_nC_mIm][HCO_3]$ can convert into carbene-CO_2 adduct spontaneously. The HCO_3^- anion and carbene-CO_2 can serve as the catalysts of olefins epoxidation and CO_2 cycloaddition respectively, which obviously simplify the synthesis of cyclic carbonates. The reaction performs quite well at mild conditions. This cheap and simple method can be applied to various olefins with good to excellent yield of cyclic carbonates. The catalyst can be easily recycled at least four times without significant losing its catalytic activity.

Introduction

Carbon dioxide (CO_2) is one of the main greenhouse gases. The reduction of CO_2 concentration in atmosphere, which is regarded as an important way to slow down the greenhouse effect, has got a lot of attention[1-4]. On the other hand, CO_2 is also an abundant, renewable, nontoxic and economical carbon source[5]. In this sense, using CO_2 as an eco-friendly feedstock to synthesize industrial products is an ultimate solution that has become one of the most important branches of green chemistry and chemical engineering. Until now, many useful chemicals have been synthesized from CO_2, such as formic acid[3,5-7], methanol[6-8], carboxylic acid[9, 10], ketone[11, 12], oxazolidinones[13], amides[14], methyl compounds[15], imines[16], dimethyl carbonate[17], salicylic acid[18], urea, and others[1, 3].

Cyclic carbonates are important industrial products that have been widely applied as polar aprotic solvent, organic synthesis intermediates, electrolytes in lithium-ion batteries and monomers of polymer[1, 19]. In recent decades, a number of syntheses of cyclic carbonates from CO_2 have been described. Among them, a classical and industrial way is the cycloaddition of CO_2 with epoxides. Until now, many catalytic systems have been developed for the cycloaddition of CO_2 with epoxides, such as ionic liquid with halogen as anion[20-25], metal halides[26-28], organic-metal complexes[1, 29-31], metal oxides[32], and immobilized molecular catalysts[33]. However, the complicated production and unstability of epoxides hamper the application of this process. Considering that epoxides are synthesized from olefins, [34] one-pot synthesis of cyclic carbonates from olefins and CO_2 has attracted many interestings, because the reaction uses readily available and low-priced chemicals olefins, and avoids the preliminary synthesis of epoxides. Most of the reported processes adopted the strategy using two different catalysts in the one-pot synthesis (Scheme 1). One of the catalyst (catalyst A) is for olefins epoxidation and another (catalyst B) is for CO_2 cycloaddition[35-44]. Though these reactions have achieved successes, the using of two different catalysts makes the processes quite complicated, especially for the catalyst recycling.



Scheme 1. Traditional strategy for one-pot synthesis of cyclic carbonates from olefins and CO_2

Obviously, developing single catalyst with both catalytic ability for olefins epoxidation and CO_2 cycloaddition is more attractive and challenging. However, only few examples were reported.[45-48] Dupont et al. reported the one-pot synthesis of cyclic carbonate from styrene and CO_2 at 150 ℃ using [BMim][Br] as catalyst and tert-butyl hydroperoxide (TBHP) as oxidant. 90% conversion of styrene and 40% selectivity of

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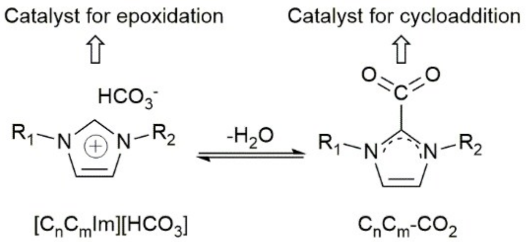
cyclic carbonate were obtained.[45] Sun et al. reported the synthesis of styrene carbonate from styrene and CO_2 catalyzed by basic resin R201 supported Au catalyst, using TBHP as oxidant under 4.0MPa CO_2. The best yield of styrene carbonate was obtained at 150℃ (yield: 50.6%).[46] Jain et al. reported the oxidative carboxylation of styrene catalyzed by Co(acac)$_2$-QPB@MCS which contains both cobalt(II) acetylacetonate complex and quaternary triphenylphosphonium bromide.[47] Duan et al. combined polyoxometalate ($[ZnW_{12}O_{40}]^{6-}$), Zn ion, amino bridge ligand and chiral functional group to produce a metal-organic framework catalyst (ZnW-PYIs). ZnW-PYIs can catalyze the oxidative carboxylation of styrene by using TBHP as oxidant at mild conditions.[48]

Some pioneer researches had suggested that bicarbonate may react with hyperoxide to produce peroxymonocarbonate which is known as the active intermediate of olefins epoxidation[49-52]. On the other hand, carbene-CO_2 adduct has shown catalytic ability for the CO_2 cycloaddition reaction[53-57]. In our previous research, we had reported that imidazolium hydrogen carbonate ionic liquids ($[C_nC_mIm][HCO_3]$ ILs) can convert into carbene-CO_2 adduct spontaneously[17]. It means that there has both HCO_3^- and carbene-CO_2 in $[C_nC_mIm][HCO_3]$, which provides an interesting chance to perform the one-pot synthesis of cyclic carbonates from olefins and CO_2 (Scheme 2). Herein, we report a simple direct synthesis of cyclic carbonates from olefins and CO_2 using a metal-free $[C_nC_mIm][HCO_3]$ as a bifunctional catalyst in the absence of solvent under mild reaction conditons. Good to excellent yield of cyclic carbonates were obtained and the catalyst $[C_nC_mIm][HCO_3]$ is easy to be recycled.



Scheme 2. The structure of catalyst used here, the equilibrium between $[C_nC_mIm][HCO_3]$ and carbene-CO_2 (C_nC_m-CO_2) derived from this IL is shown.

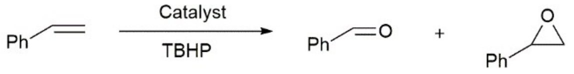
Results and discussion

Epoxidation of styrene catalyzed by the $[C_nC_mIm][HCO_3]$

Before the one-pot synthesis of cyclic carbonates from olefins and CO_2 was performed, it is necessary to investigate the catalytic ability of $[C_nC_mIm][HCO_3]$. The epoxidation of olefins to epoxides and the cycloaddition of CO_2 with epoxides to cyclic carbonates were separately investigated using $[C_nC_mIm][HCO_3]$ as catalyst.

The epoxidation of styrene was selected as a probe to investigate the reactivity of different catalysts (Table 1). The oxidation of styrene mainly produced styrene oxide (SO) and benzaldehyde (BA). Among the $[C_nC_mIm][HCO_3]$ catalysts investigated here, $[C_1C_4Im][HCO_3]$ shows the best catalytic reactivity (Table 1, Entries 1-4). Obviously, the conversion is quite low and no SO is produced in the absence of any catalyst (Entry 6). $KHCO_3$ can slightly catalyze the reaction and the selectivity of SO can reach 78.7% (Entry 7). This result agrees well with previous researches [49-52] and suggests that the active center of $[C_nC_mIm][HCO_3]$ for the epoxidation is the HCO_3^- anion. It is worth noticing that the cation also has non-negligible influence on the catalytic ability. $[C_nC_mIm]^+$ is better compared with K^+.

Table 1 The epoxidation of styrene catalyzed by the $[C_nC_mIm][HCO_3]$/THBP system[a]



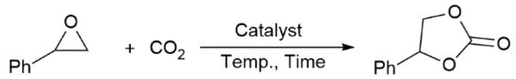
Entry	Catalysts	Conv.(%)[b]	Selectivity(%)[b]	
			BA	SO
1	$[C_1C_2Im][HCO_3]$	44.2	15.3	78.9
2	$[C_1C_4Im][HCO_3]$	53.5	13.3	77.6
3	$[C_1C_6Im][HCO_3]$	39.3	15.2	73.6
4	$[C_1C_{12}Im][HCO_3]$	33.6	15.6	74.9
5	$[C_1C_4Im][Br]$	40.7	22.5	70.2
6	None	12.5	41.0	0.0
7	$KHCO_3$	20.2	20.9	78.7
8[c]	$KHCO_3$	45.1	19.0	80.7

[a] Conditions: Styrene: 20mmol, Catalysts: 1.25mmol, Oxidants: TBHP 40mmol, Temp: 65℃, Time: 22h.

[b] Products were identified by GC and GC-MS.

[c] The reactor was pressurized with CO_2 up to 2.0 MPa.

Table 2 The cycloaddition of CO_2 and styrene oxide catalyzed by the $[C_nC_mIm][HCO_3]$[a]



Entry	Catalysts	Conv.(%)[b]	Sel.(%)[b]
1	$[C_1C_2Im][HCO_3]$	92.3	98.4
2	$[C_1C_4Im][HCO_3]$	94.5	99.2
3	$[C_1C_6Im][HCO_3]$	94.2	98.7
4	$[C_1C_{12}Im][HCO_3]$	94.2	98.5
5	$[C_1C_4Im][Br]$	72.4	98.7
6	None	0	-
7	$KHCO_3$	0	-
8[c]	SMes-CO_2	90.2	98.8

[a] Conditions: Styrene oxide: 20mmol, Catalyst: 1.25mmol, CO_2: 2.0MPa, Temp: 60℃, Time: 30h.

[b] Products were identified by GC and GC-MS.

[c] CO_2: 4.0MPa, Temp: 100℃

Cycloaddition of CO_2 and styrene oxide catalyzed by the $[C_nC_mIm][HCO_3]$

A series of imidazolium hydrogen carbonate ILs were used to catalyze the synthesis of styrene carbonate from CO_2 and styrene oxide. As shown in Table 2 (Entries 1-4), the conversions and the styrene carbonate selectivities were higher than 92% and 98% respectively. Further experiments revealed that no product was obtained in the absence of any catalyst (Entry 6).

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To find out the catalytic species in the cycloaddition reaction, some control experiments were further performed. No reaction happens when $KHCO_3$ was used alone (Entry 7), indicating that HCO_3^- anion is not the active center for the cycloaddition between CO_2 and styrene oxide. Previous researches have shown that carbene-CO_2 adduct can serve as catalyst for the CO_2 cycloaddition reaction[53-57]. Considering that $[C_nC_mIm][HCO_3]$ can transform quickly into a carbene-CO_2 adduct and there has about 35% carbene-CO_2 in the $[C_1C_4Im][HCO_3]$,[17] we rationalize that the carbene-CO_2 in the ILs should be the catalyst. Herein, when the SMes-CO_2, a well-known carbene-CO_2 adduct, was added into the reaction system, 90.2% conversion of styrene oxide and 98.8% selectivity of SC were obtained (Entry 8). Above results clearly reveal that the equilibrium coexistence carbene-CO_2 in the $[C_nC_mIm][HCO_3]$ catalyzes the cycloaddition between CO_2 and styrene oxide.

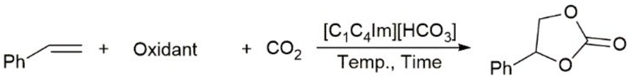
Oxidative carboxylation of styrene catalyzed by $[C_1C_4Im][HCO_3]$

According to above results, $[C_1C_4Im][HCO_3]$ showed good activity and selectivity for both epoxidation and cycloaddition reactions. Then, $[C_1C_4Im][HCO_3]$ was used as catalyst for the synthesis of styrene carbonate in one-pot process. It is exciting to find that good styrene conversion and styrene carbonate selectivity were obtained in the one-pot process (Table 3). Especially, the styrene conversion in the one-pot process is obviously higher than that in the epoxidation. For example, 53.5% conversion of styrene was obtained at 65 ℃ in the epoxidation reaction (Table 1, Entry 2), whereas the conversion is 91.2% at the same temperature in one-pot process (Table 3, Entry 4). To check the possible influence of CO_2 on the oxidation, the epoxidation reaction using $KHCO_3$ as catalyst was performed with and without CO_2 (Table 1, Entries 7 and 8). Higher conversion was obtained in the presence of CO_2, indicating that CO_2 can enhance the oxidation. [58, 59] From this viewpoint, the one-pot direct synthesis can not only simplify the process but also reduce the amount of oxidant for the epoxidation reaction.

Temperature has important influence on the styrene conversion and the styrene carbonate selectivity (Table 3). Low temperature is benefit for improving the selectivity. With the decreasing temperature in the oxidative carboxylation process from 70 to 50 ℃, the conversion of styrene gradually decreased from 92.8 to 56.4%, whereas the selectivity of styrene carbonate generally increased from 75.7 to 88.7%. The main byproduct is benzaldehyde which is produced in the epoxidation reaction.

$[C_1C_4Im][Br]$ has been reported as catalyst for the one-pot synthesis of cyclic carbonate from styrene and CO_2 at 150℃, which showed 90% conversion of styrene and 40% selectivity of cyclic carbonate. [45] At lower temperature, the performances of $[C_1C_4Im][Br]$ are poorer comparing with that of $[C_1C_4Im][HCO_3]$ in not only the epoxidation and cycloaddition, but also the one-pot process (Tables 1-3). Besides, the yield of cyclic carbonate using $[C_1C_4Im][HCO_3]$ as catalyst at 65℃ is also obviously higher than that using $[C_1C_4Im][Br]$ as catalyst at 150℃.[45]

Table 3 The oxidative carboxylation of styrene catalysed by $[C_1C_4Im][HCO_3]$[a]



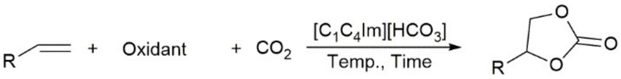
Entry	Temp(℃)	Conv.(%) [b]	Sel.(%) [b]	
			SC	BA
1	50	56.4	88.7	3.2
2	55	73.0	86.3	5.3
3	60	79.1	87.3	7.6
4	65	91.2	82.3	10.5
5	70	92.8	75.7	19.0
6[c]	65	79.4	64.7	15.3

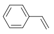
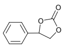
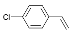
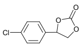
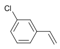
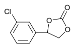
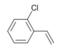
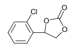
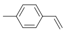
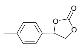
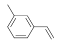
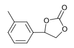
[a] One-pot single step process: Styrene: 20mmol, $[C_1C_4Im][HCO_3]$: 1.25mmol, Oxidants: TBHP 40mmol, CO_2: 2.0MPa, Time: 30h.

[b] Products were identified by GC and GC-MS.

[c] Catalyst: 1.25mmol $[C_1C_4Im][Br]$.

Table 4 The oxidative carboxylation of different olefins catalyzed by the $[C_1C_4Im][HCO_3]$.[a]



Entry	Substrate	Product	Conv.(%)[b]	Sel.(%)[b]
1			91.2	82.3
2			71.4	77.3
3			48.8	79.5
4			75.5	63.5
5			93.0	84.7
6			91.0	89.0

[a] Conditions: Substrate: 20mmol, $[C_1C_4Im][HCO_3]$: 1.25mmol, Oxidants: TBHP 40mmol, CO_2: 2.0MPa, Temp: 65℃, Time: 30h.

[b] Products were identified by GC and GC-MS.

Oxidative carboxylation of various olefins catalyzed by $[C_1C_4Im][HCO_3]$

To explore the substrate scope of this new one-pot process for the synthesis of cyclic carbonates, different olefins were investigated (Table 4). The catalyst is reactive for all the substrates presented in the table. However, the conversions and cyclic carbonates selectivities depend strongly on the olefin structures. For the oxidative carboxylation of 3-Methylstyrene and 4-Methylstyrene, the conversions are high (>91%), and the cyclic carbonates selectivities are 89.0 and 84.7% respectively, due to electron-donating effect of methyl (Table 4, Entries 5 and 6). Comparing with methylstyrenes, due to electron-withdrawing effect, the conversions of chlorostyrenes and the cyclic carbonates selectivities are lower (Table 4, Entries 2-4). The non-aromatic olefins have also been used as substrates, such as 1-hexene and 1-octene. However, no cyclic carbonates were obtained in the one-pot process.

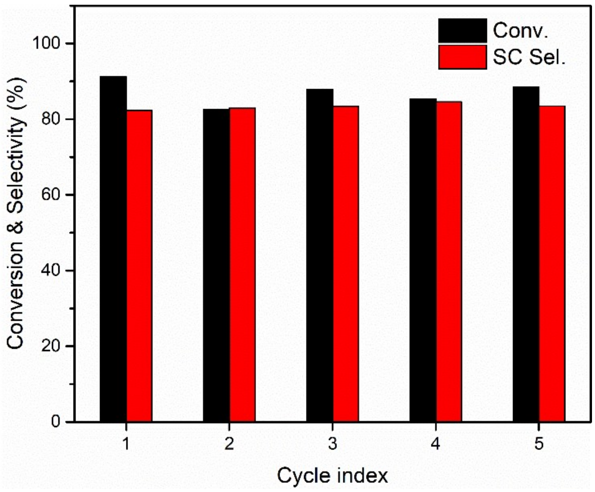


Fig. 1 Recycling of $[C_1C_4Im][HCO_3]$. Reaction conditions: Styrene (20mmol), $[C_1C_4Im][HCO_3]$ (1.25mmol), TBHP (40mmol), CO_2 (2.0MPa), Temp. (65℃), Time (30h).

Recycling of the catalyst

Recycling of the catalyst is very important for the large-scale application. Hence, the recycling studies of $[C_1C_4Im][HCO_3]$ were investigated in the oxidative carboxylation of styrene. After the reaction, the catalyst can be easily separated from the solution by extraction and reused without further treatment except drying under vacuum. The catalyst can be used at least five cycles without significantly losing its catalytic reactivity (Fig. 1).

Conclusions

We have demonstrated a direct one-pot synthesis of cyclic carbonates from olefins and CO_2 at mild conditions catalyzed by metal-free imidazolium hydrogen carbonates $[C_nC_mIm][HCO_3]$. The $[C_nC_mIm][HCO_3]$ are active not only for the epoxidation but also for the cycloaddition reaction. For the one-pot synthesis of styrene carbonate, good conversion of styrene and selectivity of styrene carbonate can be obtained at mild reaction conditions. The scope of this new catalytic system can be extended to other substrates. Compared with previous systems which contain two different catalysts, [35-44] the bifunctional catalyst reported here is easy to be reused without significantly losing its catalytic reactivity. From the viewpoint of green chemistry, the direct synthesis of cyclic carbonates from olefins and CO_2 catalyzed by the simple and cheap $[C_nC_mIm][HCO_3]$ system in the absence of solvent would have great application potential.

Conflicts of interest

There are no conflicts to declare.

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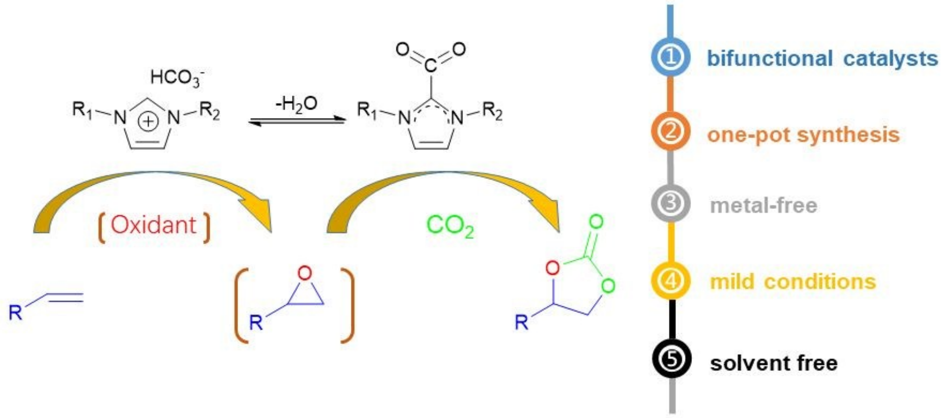

A direct route for the synthesis of cyclic carbonates from olefins and CO_2 has been achieved by using an imidazolium hydrogen carbonate ionic liquids as bifunctional catalyst in the absence of solvent.