

# Chemical Fixation of Carbon Dioxide Using a Green and Efficient Catalytic System Based on Sugarcane Bagasse—An Agricultural Waste

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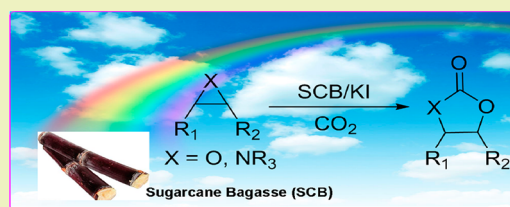
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## S Supporting Information

**ABSTRACT:** In this study, an efficient, reusable, and environmental catalytic system consisting of sugarcane bagasse (an agricultural and sugar mill waste material, SCB) and KI was applied to the cycloaddition of carbon dioxide (CO<sub>2</sub>) to epoxides or aziridines under mild conditions for the first time. Their catalytic cycloaddition activities were found to be well correlated with the large quantities hydroxyl groups in SCB, which had a synergetic effect with the halide anion of KI. The as-prepared catalytic system also exhibited excellent cycloaddition activities for various epoxide or aziridine substrates as well. Moreover, the catalyst could be recovered and reused multiple times without obvious loss in activity. The present method represents an integrated and ideal green process for the utilization of biomass and “carbon neutral” resources, which has a high potential for large-scale fixation of CO<sub>2</sub> into value-added chemicals.

**KEYWORDS:** Sugarcane bagasse, Carbon dioxide fixation, Cycloaddition reaction



## INTRODUCTION

Carbon dioxide chemistry (carbon capture, storage, and utilization) has attracted much attention from the scientific community due to growing concerns about the environmental impact of this greenhouse gas.<sup>1–3</sup> As an abundant, nonflammable, and renewable C1 building block, CO<sub>2</sub> can be converted into many useful chemicals, fuels, and materials.<sup>4–7</sup> In particular, the syntheses of five-membered cyclic carbonates from epoxides and CO<sub>2</sub> is one of the most important routes for the chemical fixation of CO<sub>2</sub> because this reaction has 100% atom economy and cyclic carbonate products are useful molecules in chemistry. For example, cyclic carbonate products can serve as excellent polar aprotic solvents, precursors for polymeric materials, and intermediates in the production of pharmaceuticals and fine chemicals.<sup>8–10</sup>

In the past decades, a wide range of catalyst systems have been developed for this transformation, including alkali metal halides,<sup>11,12</sup> metal oxides,<sup>13,14</sup> transition metal complexes,<sup>15,16</sup> quaternary ammonium and phosphonium salts,<sup>17,18</sup> organic bases,<sup>19,20</sup> and ionic liquids.<sup>21,22</sup> Although significant advantages have been made in these fields, most of them generally possess one or more problems, including low catalyst reactivity, long reaction time, and water or air sensitivity of the catalyst, along with requiring a large amount of toxic co-solvent, not conforming to the principles of green chemistry. Therefore, designing efficient, cheap, and eco-safe catalyst systems for cycloaddition under mild conditions is still an interesting topic.

In recent studies, it has been found that hydroxyl/carboxyl group-containing catalytic systems can coordinate with the

oxygen atom of epoxides and accelerate the cycloaddition of epoxides with CO<sub>2</sub>.<sup>23–25</sup> Thus, a series of catalytic systems possessing hydroxyl or carboxyl groups have been studied extensively.<sup>26–31</sup> Among these catalytic systems, biomass ( $\beta$ -CD,<sup>26</sup> cellulose,<sup>27,28</sup> lignin,<sup>29</sup> etc.) as the hydrogen bond donor in promoting the reaction was especially highlighted. The reasons are that biomass is widely available on Earth, contains abundant hydroxyl groups, and is chemically stable, biocompatible, and biodegradable.<sup>32</sup> However, many tedious processes are required to separate pure cellulose and lignin from a complicated biomass cell wall, and these processes require high energy input and cause environmental problems. Thus, appropriate raw biomass with the same active functional groups (hydroxyl and/or carboxyl) as contained in cellulose and lignin would be a perfect substituted biomass-based catalyst for catalytic cycloaddition of epoxides with CO<sub>2</sub>.

Sugarcane bagasse (SCB) is one of the largest agricultural residues derived from the sugar industry, and it has attracted extensive attention for obtaining environmentally friendly and biocompatible materials, chemicals, and fuels.<sup>33,34</sup> SCB is a complex biopolymer, mainly consisting of cellulose (40–50%), hemicelluloses (25–30%), and lignin (20–25%).<sup>35</sup> The electron-rich feature of hydroxyl and/or carboxyl groups in these components make them suitable for the preparation of novel catalytic materials. Extracting cellulose from SCB is a

**Received:** October 10, 2014

**Revised:** November 13, 2014

**Published:** November 17, 2014

strenuous process<sup>36,37</sup> and will result in other components in SCB not being fully utilized (lignin and hemicelluloses will be seriously degraded into small fractions). Therefore, utilization of lignocellulosic components in SCB by directly exploiting their inherent functionalities for green chemistry is urgent from the viewpoints of both sustainability and environmental protection.

Herein, we highlight the direct use of SCB as a novel cooperative catalytic system (in the presence of KI) for catalytic carboxylation of various epoxides and aziridines with CO<sub>2</sub> under solvent-free conditions. It was found that the catalytic system was very active, selective, stable, and easily recyclable. This established process opens a new way for rational utilization of waste biomass, with the benefit of making green catalytic materials.

## EXPERIMENTAL SECTION

**Chemicals.** CO<sub>2</sub> was supplied from Guangzhou Zhuo Zheng Gas Co., Ltd. with a purity of >99.999%. Aziridines were prepared according to the reported method.<sup>38</sup> All the other reagents were purchased from commercial suppliers (Aldrich, U.S.A. and J&K Scientific Ltd., China) and used without further purification. Sugarcane bagasse was obtained from a local factory (Guangzhou, China), milled into powder, and screened to 80–100 mesh (150–180 μm). The grinding bagasse was dewaxed in a Soxhlet extractor with toluene ethanol (2:1, v/v) for 12 h and then dried under vacuum at 60 °C.

**Instrumentation.** FTIR spectra were recorded on a Nicolet 6700 FTIR spectrophotometer by using KBr pellets. TGA was performed on a TGA Q500 (TA Instruments) at a heating rate of 20 °C min<sup>-1</sup> with a nitrogen flow (25 mL min<sup>-1</sup>). <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded on a Bruker FT-NMR spectrometer. NMR chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as the internal standard. GC analyses were performed on a Shimadzu GC-2014, equipped with a capillary column (RTX-5, 30 m × 0.25 μm) using a flame ionization detector (FID).

### General Procedure for Cycloaddition of Epoxides with CO<sub>2</sub>

All the reactions were conducted in a 25 mL Hastelloy reactor equipped with a magnetic stirrer and automatic temperature control system. Epoxide (20 mmol), SCB (100 mg), and KI (0.5 mmol) were added into the reactor and then purged with CO<sub>2</sub> several times. The reactor was sealed and pressurized with 2.0 MPa CO<sub>2</sub> at room temperature (RT). Next, the reactor was placed in a constant-temperature air bath at the desired temperature, and the stirrer was started. After completion of the reaction, the autoclave was cooled in an ice water bath, and the excess CO<sub>2</sub> was vented slowly. The reaction mixture was then dissolved in ethyl acetate (10 mL) and filtered to remove the catalyst. The catalyst was washed with ethyl acetate (2 × 10 mL) and dried under vacuum. The selectivity was determined by GC/GC-MS. Isolated yields were obtained via column chromatography using a mixture consisting of petroleum ether (PE) and ethyl acetate (EA) as the eluents to obtain the desired product. The products were further confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectra.

### General Procedure for Cycloaddition of Aziridines with CO<sub>2</sub>

Aziridine (10 mmol), SCB (50 mg), and KI (0.25 mmol) were added into the reactor and then purged with CO<sub>2</sub> several times. The reactor was sealed and pressurized with 2.0 MPa CO<sub>2</sub> at RT. Next, the reactor was placed in a constant-temperature air bath at the desired temperature, and the stirrer was started. After completion of the reaction, the autoclave was cooled in an ice water bath, and the excess CO<sub>2</sub> was vented slowly. The reaction mixture was then dissolved in ethyl acetate (10 mL) and filtered to remove the catalyst. The catalyst was washed with ethyl acetate (2 × 10 mL) and dried under vacuum. The selectivity was determined by GC/GC-MS. Isolated yields were obtained via column chromatography using a mixture consisting of PE/EA as the eluents to obtain the desired product. The products were further confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectra.

## RESULTS AND DISCUSSION

The activity of –OH groups in SCB and the catalytic performance of alkali halides were first examined in the cycloaddition reaction of CO<sub>2</sub> with propylene oxide (PO) to produce propylene carbonate (PC), and the corresponding results were summarized in Table 1. It is shown in Table 1 that

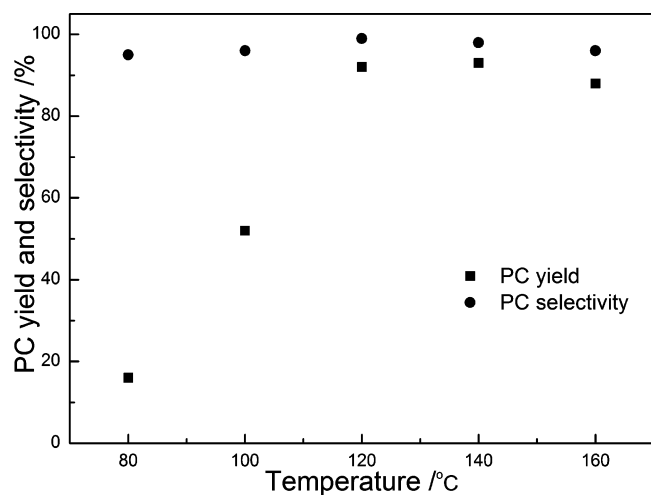
Table 1. Synthesis of PC Catalyzed by Different Catalysts<sup>a</sup>

entry	catalyst	potassium halide	PC yield (%) <sup>b</sup>	PC selectivity (%) <sup>c</sup>
1	SCB	None	trace	–
2	None	KCl	3	97
3	None	KBr	5	98
4	None	KI	18	98
5	SCB	KCl	15	98
6	SCB	KBr	32	99
7	SCB	KI	92	99
8 <sup>d</sup>	SCB	KI	86	99
9 <sup>e</sup>	SCB	KI	78	98
10 <sup>f</sup>	SCB	KI	93	99

<sup>a</sup>Typical reaction conditions: PO (20 mmol), SCB (100 mg), potassium halide (0.5 mmol), CO<sub>2</sub> (initial pressure 2.0 MPa), 120 °C, and 6 h. <sup>b</sup>Isolated yield. <sup>c</sup>Determined by GC/GC-MS. <sup>d</sup>KI/SCB = 0.42:1 (w/w). <sup>e</sup>KI/SCB = 0.21:1 (w/w). <sup>f</sup>KI/SCB = 1.66:1 (w/w).

the activity of SCB depends strongly on the potassium halide used. Nearly no product was detected when SCB was used as the catalyst alone (entry 1). Potassium halide could also catalyze this cycloaddition reaction in the absence of SCB, but the yield of PC was very low (entries 2–4). In contrast, the catalyst was active in the presence of potassium halide, and the yield of PC increased with the increasing ion radii of the halogen ion (entries 5–7). Obviously, the combination of KI with SCB exhibited the best effect in the aspect of catalytic activity; this could probably result from the cooperation of the relatively strong nucleophilicity and leaving ability of I<sup>-</sup> relative to Cl<sup>-</sup> and Br<sup>-</sup>, which is consistent with previous publications.<sup>11,23</sup> The above results elucidated the respective roles of the –OH group and halide ion in the complex catalyst system for accelerating the reaction. The mass ratio of KI to SCB was also screened. When the ratio was increased from 0.21:1 to 0.84:1, the PC yield increased from 78% to 92%. However, a further increase in the ratio to 1.66:1 did not result in a significant change in PC yield. The PC selectivity was almost independent of the mass ratio change of KI to SCB within the range from 0.21:1 to 1.66:1 (always above 98%). Therefore, the optimum ratio of KI to SCB was 0.84:1, which was identified as the most effective catalyst system and was used to optimize other reaction parameters (e.g., temperature, CO<sub>2</sub> pressure, and time).

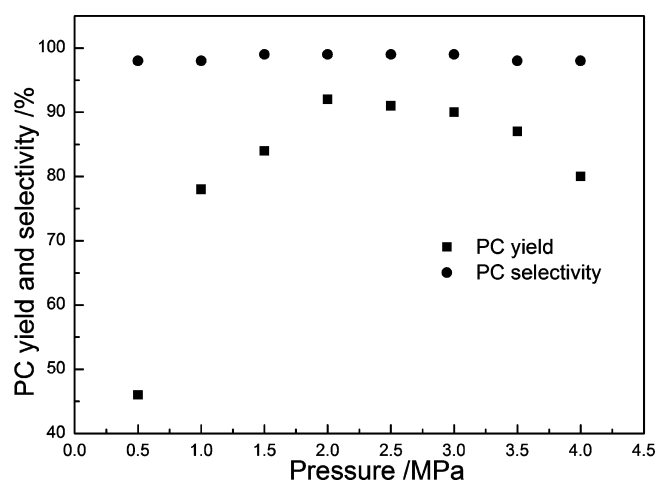
Figure 1 shows the effect of temperature on the yield of PC. It is clear that the catalytic activity is sensitive to the reaction temperature. The yield of PC increased sharply when the temperature increased from 80 to 120 °C and then underwent no significant change from 120 to 140 °C. Further increasing the temperature caused a slight decrease in both the PC yield and selectivity, which is possibly due to the formation of a small amount of byproducts such as polymerized PC at a higher



**Figure 1.** Dependence of the PC yield and selectivity on reaction temperature. Reaction conditions: PO (20 mmol), SCB (100 mg), KI (0.5 mmol), CO<sub>2</sub> (initial pressure 2.0 MPa), and 6 h.

temperature.<sup>39</sup> Therefore, 120 °C was the optimum temperature in this reaction.

Subsequently, we also investigated the effect of reaction pressure on the cycloaddition reaction at 120 °C. As shown in Figure 2, the CO<sub>2</sub> pressure had a great influence on the yield of

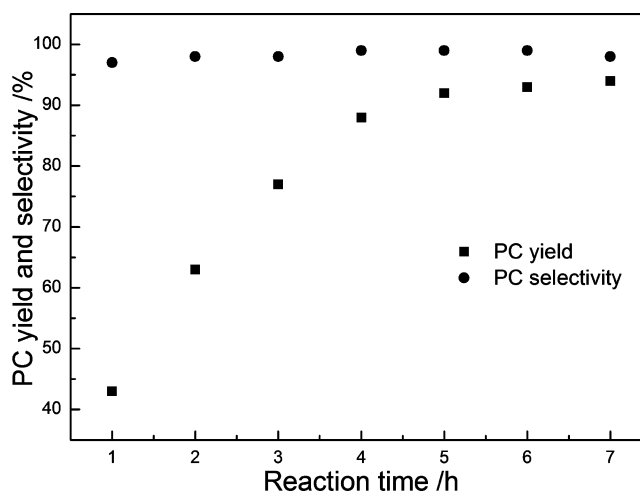


**Figure 2.** Effect of CO<sub>2</sub> pressure on the PC yield and selectivity. Reaction conditions: PO (20 mmol), SCB (100 mg), KI (0.5 mmol), 120 °C, and 6 h.

PC. The yield initially increased with pressure in the low pressure range of 0.5–2.0 MPa, and a maximum PC yield could be obtained at about 2.0 MPa and then showed little change in the range of 2.0–3.0 MPa. However, further increasing the pressure led to a decrease in PC yield. This phenomenon can be explained by a pressure effect on the concentrations of CO<sub>2</sub> and epoxides in the two phases, which has been observed in other catalytic systems.<sup>40,41</sup> As shown from the phase behavior of the reaction through an autoclave equipped with a sapphire window, the gas phase was the CO<sub>2</sub>-rich phase and the liquid phase was the PO-rich phase. When the reaction was carried out in the low CO<sub>2</sub> pressure region (0.5–2.0 MPa), the PC yield increased due to a high concentration of CO<sub>2</sub> in the liquid phase. However, high CO<sub>2</sub> pressure caused a low concentration of PO in the vicinity of the catalyst with an increasing

concentration of CO<sub>2</sub>, thus leading to a low PC yield. The competition of these opposite factors resulted in a maximum yield of PC, and the optimum CO<sub>2</sub> pressure was 2.0 MPa. It is noted that PC selectivity fluctuation is relatively small always above 98%.

The dependence of PC yield on the reaction time was also evaluated. As shown in Figure 3, the reaction proceeded rapidly

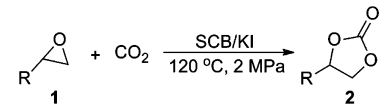





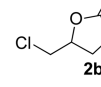

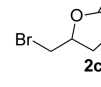

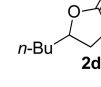

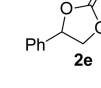
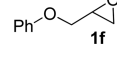
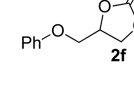
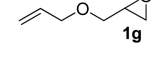
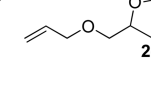

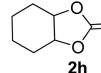
**Figure 3.** Influence of reaction time on PC yield and selectivity. Reaction conditions: PO (20 mmol), SCB (100 mg), KI (0.5 mmol), CO<sub>2</sub> (initial pressure 2.0 MPa), and 120 °C.

within the first 4 h, and 92% PC yield with 99% selectivity could be achieved in 6 h. Prolonging the reaction time did not increase the PC yield. Hence, 6 h was chosen as the optimum reaction time in this study.

To survey the scope of substrates, a series of epoxides were explored for the synthesis of the corresponding cyclic carbonates in the presence of SCB and KI under the optimum reaction conditions, and the results are summarized in Table 2. The SCB/KI catalytic system was found to be applicable to a variety of terminal epoxides that contain electron-withdrawing and electron-donating substituents, producing the corresponding cyclic carbonates in excellent yields (82–96%) with high selectivity (Table 2, entries 1–7). Besides terminal epoxides, internal epoxide **1h** was also examined in this cycloaddition reaction. However, a relatively lower yield was obtained, and even the reaction time was prolonged to 12 h, which was presumably due to the higher steric hindrance of cyclohexene oxide.

Encouraged by the successful results of CO<sub>2</sub> fixation using epoxides as substrates, we further explored the scope of this carboxylation by reaction of *N*-substituted aziridines with CO<sub>2</sub>. As depicted in Table 3, the SCB/KI catalytic system had a good catalytic activity, high selectivity, and excellent regioselectivity for oxazolidinones synthesis. It is worth mentioning that 5-aryl-2-oxazolidinones were preferentially formed under identical reaction conditions. The reaction of 1-methyl-2-phenylaziridine (**3a**) and 1-ethyl-2-phenylaziridine (**3b**) with CO<sub>2</sub> afforded medium yields of the desired products probably due to the formation of self-oligomers (Table 3, entries 1 and 2). The aziridines bearing benzyl at the nitrogen atom provided the corresponding oxazolidinones in good yields, and 5-substituted oxazolidinones were the major isomer (Table 3, entry 3). Unfortunately, 3-cyclohexyl-5-phenyloxazolidin-2-one (**3d**) afforded low activity under the same experimental conditions,

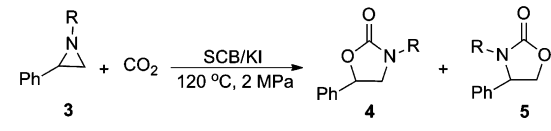
Table 2. Cycloaddition of CO<sub>2</sub> to Terminal Epoxides Catalyzed by SCB/KI<sup>a</sup>






Entry	Substrate	Product	Yield (%) <sup>b</sup>	Selectivity (%) <sup>c</sup>
1			92	99
2			82	95
3			85	93
4			90	98
5			87	99
6			96	99
7			94	99
8 <sup>d</sup>			28	96

<sup>a</sup>Reaction conditions: epoxide (20 mmol), SCB (100 mg), KI (0.5 mmol), CO<sub>2</sub> (initial pressure 2.0 MPa), 120 °C, and 6 h. <sup>b</sup>Isolated yield. <sup>c</sup>Determined by GC/GC-MS. <sup>d</sup>12 h.

which may result from the high steric hindrance of nitrogen atom.<sup>38</sup>

Furthermore, to test the recyclability and stability of the SCB/KI catalytic system in this study, the cycloaddition of PO with CO<sub>2</sub> was investigated as a model reaction under the optimum conditions. In each cycle, the catalyst was recovered via distillation under vacuum and then reused directly for the next cycle without any further purification. As shown in Figure 4, the yield and selectivity of the PC obtained from the second to fifth runs were similar to those obtained with the fresh catalyst. After five times, a 85% PC yield with 99% selectivity could be obtained, indicating that the catalytic activity of the catalyst could be kept. The excellent stability was also supported by FTIR and TGA analysis. The FTIR shown in Figure 5 revealed that the structure of SCB after the fifth reuse was not significantly changed as compared to the fresh SCB. A new weak absorption at 1778 cm<sup>-1</sup> was observed, which may be due to C=O in the accumulated carboxylic acid groups because of the potential carboxylation of -OH groups in SCB by CO<sub>2</sub>.<sup>42</sup> The TGA showed that the decomposition of the catalyst occurred at 220 °C, which was much higher than the reaction temperature (120 °C) in our experiments (Figure 6).

Table 3. Cycloaddition of CO<sub>2</sub> to N-substituted aziridines catalyzed by SCB/KI<sup>a</sup>


Entry	Substrate	Yield (%) <sup>b</sup>	Selectivity (%) <sup>c</sup>	Regioselectivity <sup>d</sup> (4:5)
1		60	95	95:5
2		67	93	98:2
3		80	98	100:0
4		10	92	99:1

<sup>a</sup>Reaction conditions: aziridines (10 mmol), SCB (25 mg), KI (0.25 mmol), CO<sub>2</sub> (initial pressure 2.0 MPa), 120 °C, and 10 h. <sup>b</sup>Total yield of 4 and 5. <sup>c</sup>Total selectivity of 4 and 5, determined by GC/GC-MS. <sup>d</sup>Molar ratio of 4:5, determined by <sup>1</sup>H NMR.

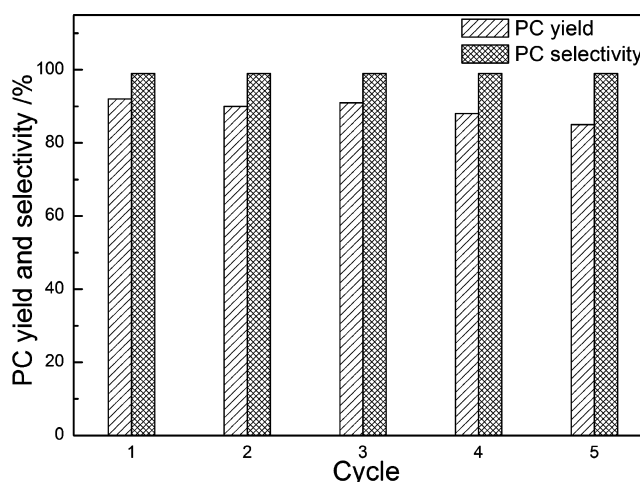
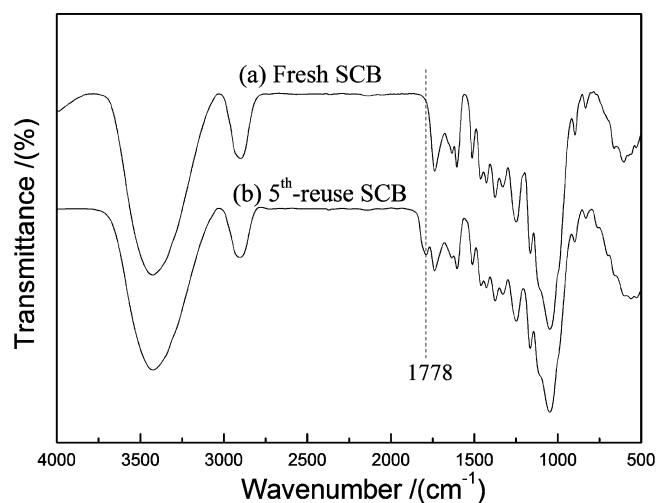


Figure 4. Reuse of the catalyst. Reaction conditions: PO (40 mmol), SCB (200 mg), KI (1.0 mmol), CO<sub>2</sub> (initial pressure 2.0 MPa), 120 °C, and 6 h.

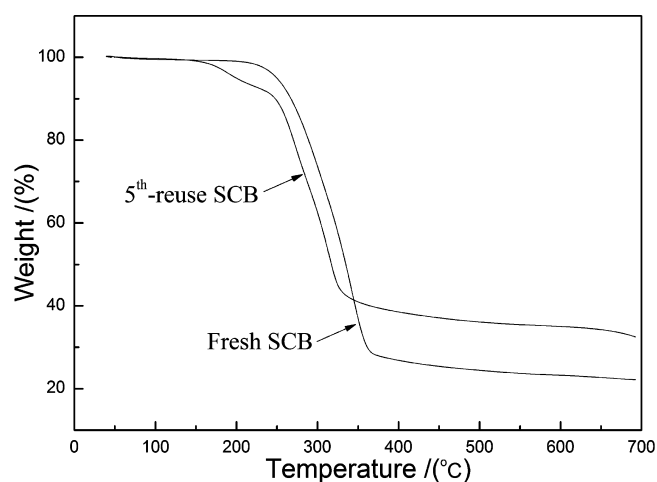
To demonstrate the synthetic utility of this cycloaddition reaction, a large-scale experiment was performed with 500 mmol PO in a 100 mL stainless steel reactor under optimum reaction conditions. A 81% yield of PC with a 99% selectivity was obtained in this large-scale test. This result implied that our catalytic system can serve as a guide for the preparation of PC in industrial applications, and further researches are under investigation in our lab.

It has been known that a hydrogen-bonding donor can activate the ring-opening reaction through the hydrogen bond on the oxygen atom of the epoxides.<sup>23–25</sup> In our catalytic system, SCB is a complex biopolymer containing abundant hydroxyl groups in its structure, which can be used as a hydrogen bonding donor. On the basis of the previous reports<sup>27,30,41,43,44</sup> and the results discussed above, we proposed



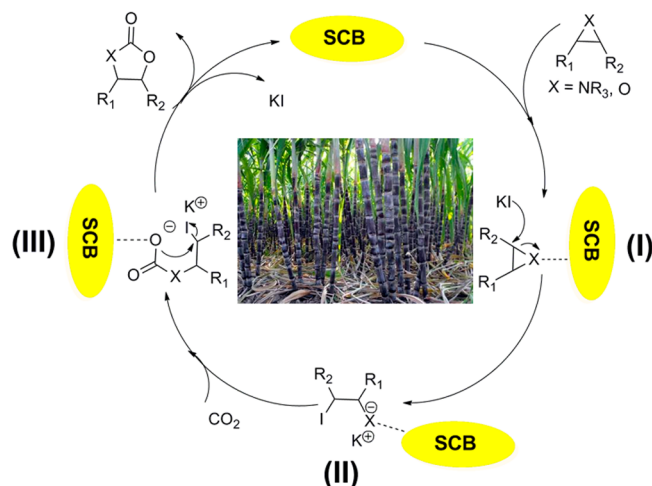


**Figure 5.** FTIR spectra of the two SCB samples: (a) fresh SCB and (b) reused SCB after five cycles.



**Figure 6.** TG curves of (a) fresh SCB and (b) SCB recycled after five cycles.

### Scheme 1. Plausible Reaction Mechanism



a plausible mechanism for this chemical fixation reaction of  $\text{CO}_2$ . As shown in Scheme 1, the coordination of the hydroxyl groups in SCB with the O atom of epoxide or the N atom of aziridine through a hydrogen bond resulted in the activation of

the ring of epoxide or aziridine, and simultaneously, the  $\text{I}^-$  anion made a nucleophilic attack on the less sterically hindered carbon atom of the epoxide or aziridine ring to form the intermediate (I), by which the ring of epoxide or aziridine was opened easily. Then, the interaction occurred between the intermediate (II) and  $\text{CO}_2$  to produce a new intermediate (III). Finally, the final product could be formed via an intramolecular cyclic elimination, and the catalyst was regenerated.

### CONCLUSIONS

In summary, we developed a facile, reliable, and efficient catalytic protocol for the carboxylation of various epoxides and aziridines using SCB and KI as a binary system catalyst under solvent-free conditions. The hydroxyl groups in SCB acted as hydrogen-bonding donors to accelerate the ring-opening reaction and showed a synergistic effect with halide anions. This binary catalytic system can be extended to the synthesis of many cyclic carbonates and 5-substituted-2-oxazolidinones with high activity and selectivity. Moreover, the catalytic system can be recycled and reused multiple times without significant loss of its catalytic activity. This study opens a new way for simple and highly efficient utilization of waste biomass as a potential alternative in green organic synthesis and catalysis.

### ASSOCIATED CONTENT

#### Supporting Information

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for all products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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#### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

The project is supported by the National Natural Science Foundation of China (21404043, 21336002, 31430092), Research Fund for the Doctoral Program of Higher Education (20130172120024), Guangdong Natural Science Foundation (S2013040015055), Science and Technology Project of Guangzhou City in China (2014J2200063), and Fundamental Research Funds for the Central Universities.

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