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Recyclable Bifunctional Polystyrene and Silica Gel-Supported Organocatalyst for the Coupling of CO_2 with Epoxides

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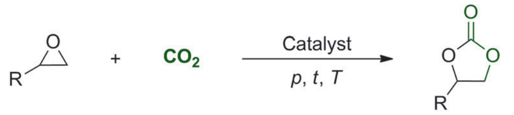
Dedicated to Prof. Dr. Detlef Heller on the occasion of his 60th birthday.

A bifunctional ammonium salt covalently bound to a polystyrene or silica support proved to be an efficient and recyclable catalyst for the solvent-free synthesis of cyclic carbonates from epoxides and CO_2. The catalyst can be easily recovered by simple filtration after the reaction and reused in up to 13 consecutive runs with retention of high activity and selectivity even at 90 °C. The scope and limitations of the reaction has been evaluated in terms of reaction conditions and substrate scope.

The development and design of sustainable synthetic methods as well as environmentally benign products and processes is guided by the general principles of green chemistry.[1] One major scientific challenge in this context is the efficient utilization of CO_2 for the sustainable development of our society.[2] The principle limitation to the use of CO_2 as a C_1 building block originates from its inherent kinetic and thermodynamic stability.[3] Thus, chemical processes utilizing CO_2 as a feedstock usually require high-energy starting materials and/or elevated operating temperatures, which hampers the overall sustainability of those processes. However, ideally such a process should emit less CO_2 than it uses. The atom-economic addition of CO_2 to epoxides yielding cyclic carbonates is an interesting and frequently studied reaction as those products might be utilized as green solvents, synthetic building blocks, or plasticizers (Scheme 1).[4]



1 **2**

Scheme 1. Atom-economic conversion of epoxides **1** to cyclic carbonates **2** with CO_2.

Numerous catalytic systems able to mediate this reaction have been reported.[5] However, most of them require unfavorable elevated temperatures. Recently, metal-based as well as organocatalytic systems have been evolved, permitting the use of more sustainable reaction conditions.[6] A crucial point in the development of environmentally benign processes is the catalyst separation and recycling. Besides many other possibilities for green separation techniques, the immobilization of catalysts permits both facile separation from the product avoiding tedious purification and isolation steps as well as easy recycling of the catalyst.[7] In this context, amongst others, there have been reports on immobilized catalysts for the conversion of epoxides with CO_2 on various inorganic supports, for example, silica[8] as well as organic supports such as polyethylene glycol,[9] various synthetic polymers,[8a,10] and even natural occurring polymers.[11] Even though there are examples on immobilized metal-based catalysts,[12] the majority of those reports are on immobilized organocatalysts. However, most of those systems usually require harsh reaction conditions, for example, reaction temperatures >100 °C, need reactivation, or loose activity during the recycling processes, thus hampering the overall sustainability.

Earlier, we developed homogeneous two-component catalyst systems operating at favorable reaction temperatures of 45 °C.[13] Moreover, we described the straight forward synthesis and utilization of functionalized phosphonium and ammonium salts as very efficient homogeneous one-component organocatalysts for the conversion of epoxides **1** to cyclic carbonates **2**.[14] Herein, we report the synthesis of a silica- as well as polystyrene-supported ammonium salt as recyclable and sustainable immobilized organocatalyst that shows high activity even at reaction temperatures <100 °C. Both catalysts were prepared by the conversion of readily available supported amines **3a** or **3b** with iodoethanol (Scheme 2). Complete alkylation was achieved after 4 days at 60 °C. Scheme 2 shows the synthesis of catalyst **4a** and **4b**, their respective SEM images are shown in Figure 1.

The coupling of butylene oxide (**1a**) and CO_2 served as a model reaction to determine the catalytic activity of the prepared catalysts **4** and was performed in a batch-wise operation (Table 1). Initial experiments were performed under identical conditions (90 °C, 5 MPa, 2 h) in the presence of 1 mol% catalyst based on the nitrogen content of **4** and with respect to **1a**. It is worthwhile to mention that the supporting materials **3a** and **3b** showed no conversion under the chosen conditions (entries 1 and 2). In contrast to **3a** and **3b**, the supported

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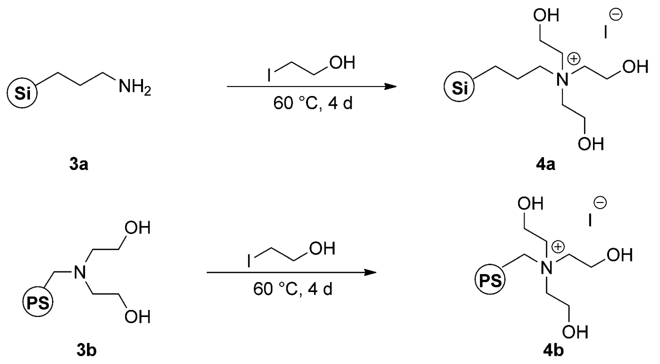


Scheme 2. Synthesis of silica-supported catalyst **4a** (top) and polystyrene-bound catalyst **4b** (bottom).

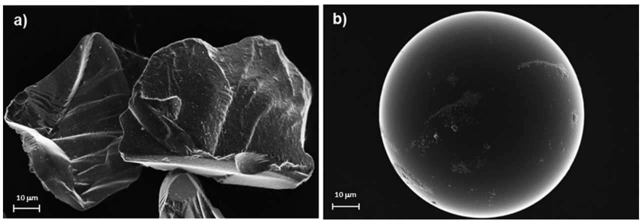
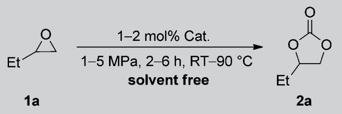


Figure 1. SEM images of **4a** (a) and **4b** (b) on 10 µm scale.

Table 1. Synthesis of butylene carbonate **2a** under various conditions.



Entry	Cat.	mol%[a]	*p* [MPa]	*T* [°C]	*t* [h]	Yield [%][b]
1	**3a**	1	5	90	2	0
2	**3b**	1	5	90	2	0
3	**4a**	1	5	90	2	40
4	**4b**	1	5	90	2	82
5	**4b**	2	1	90	2 (4)	93 (99)
6	**4a**	2	1	90	2 (6)	67 (98)
7	**4c**	2	1	90	2	19
8	**4d**	2	1	90	2	96
9	**4b**	2	1	45	4	23
10	**4b**	2	1	RT	4	8

[a] Catalyst amount with respect to **1a** calculated from the N-content. [b] Isolated yields are given. The selectivity to **2a** was $\geq$98%.

catalysts **4a** and **4b** resulted in moderate to good yields under these conditions (entries 3 and 4). Interestingly, polystyrene-bound catalyst **4b** showed significantly higher activity. Under modified reaction conditions (2 mol% **4b**, 1 MPa, 4 h), quantitative conversion of **1a** to **2a**was observed even at 90 °C (entry 5). The desired product **2a** was obtained in 99% isolated yield after simple filtration. Similar results were obtained in the presence of silica-supported catalyst **4a** by extending the reaction time to 6 h (entry 6). Compared to simple tetrabutylammonium iodide (**4c**) as homogeneous catalyst, both **4a** and **4b** show much higher activity (entries 5 and 6 vs. 7). The need of the hydroxyl function to achieve good results can be emphasized by comparing the results for the simple salt **4c** with tri-*n*-butyl-(2-hydroxyethyl)ammonium iodide (**4d**) as bifunctional organocatalyst (entry 8).[14a] The activation of the epoxide in this reaction either by Lewis acids or hydrogen bonding has been frequently reported.[4] The reaction temperature had a significant impact on the yields (entries 5 vs. 9 and 10). Remarkably, the supported catalyst **4b** is even active at 45 °C and room temperature even though only low yields were obtained after 4 h reaction time (entries 9 and 10).

The facility of recycling catalysts **4** is one of the key advantages of these systems. Our main aim was to develop a recyclable catalyst system that efficiently operates at temperatures <100 °C. Hence, we utilized both silica-supported catalyst **4a** as well as polystyrene-bound ammonium salt **4b** in multiple consecutive runs to convert the model substrate **1a** to the corresponding carbonate **2a** (Figure 2). We employed 2 mol% **4a** or **4b** under solvent-free conditions and at 1 MPa CO_2 pressure at 90 °C to achieve full conversions in a reasonable time frame. The catalytic activity of **4a** remained constant for 13 cycles. In each cycle full conversion was achieved and excellent isolated yields $\geq$93% were obtained. Similar results were achieved using polystyrene-bound catalyst **4b** for five cycles. However, conversion and yield dropped below 60% in the eighth cycle most probably due to mechanical stress caused by the stirring during the reaction. Hence, the recycling was stopped after the eighth cycle. The FTIR spectra of **4a** exhibited a very strong O–H stretch band between 3000 and 3400 cm^{-1}, which was absent after the eighth cycle.

The scope of the substrates was further explored as shown in Table 2. Several terminal epoxides **1** were converted under the conditions of the recycling experiments in the presence of both immobilized catalysts **4a** and **4b**. As expected from the initial experiments, the polystyrene-supported organocatalyst

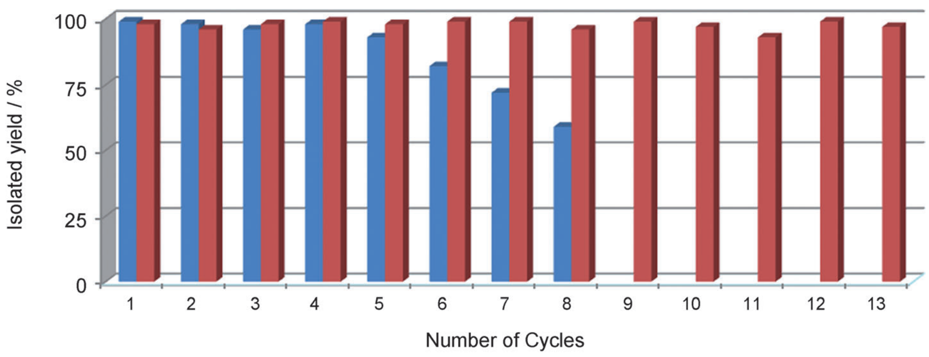
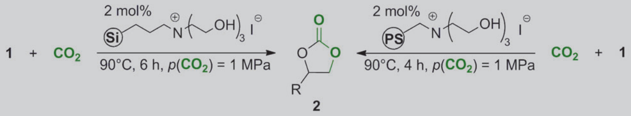
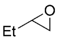
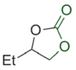
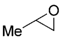
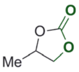
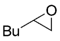
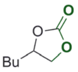
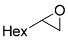
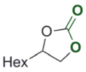
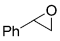
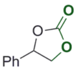
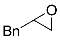
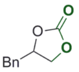
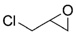
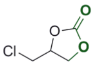
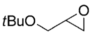
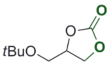
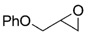
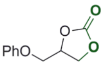


Figure 2. Catalyst recycling of the immobilized catalysts **4a** (red) and **4b** (blue). Reaction conditions: 2 mol% **4**, 90 °C, 1 MPa; 6 h reaction time for **4a** and 4 h for **4b**. Isolated yields are given.

Table 2. Conversion of various terminal epoxides **1** with CO_2 using the silica-supported catalyst **4a** or the polystyrene-supported catalyst **4b**.[a]



Entry	Epoxide **1**	Product **2**	Cat. **4**	*t* [h]	Yield[b] [%]
1	 **1a**	 **2a**	**4a**	6	99
2			**4b**	4	98
3	 **1b**	 **2b**	**4a**	6	86
4			**4b**	4	93
5	 **1c**	 **2c**	**4a**	6	87
6			**4b**	4	94
7	 **1d**	 **2d**	**4a**	6	67
8			**4b**	4	88
9	 **1e**	 **2e**	**4a**	6	85
10			**4b**	4	93
11	 **1f**	 **2f**	**4a**	6	88
12			**4b**	4	99
13	 **1g**	 **2g**	**4a**	6	83
14			**4b**	4	97
15	 **1h**	 **2h**	**4a**	6	91
16			**4b**	4	95
17	 **1i**	 **2i**	**4a**	6	97
18			**4b**	4	98

[a] Reaction conditions: 2 mol% **4a**, 90 °C, 1 MPa, 6 h, solvent-free or 2 mol% **4b**, 90 °C, 1 MPa, 4 h, solvent-free. [b] Isolated yields are given; selectivity to **2** was ≥98%.

4b led in all cases to excellent yields after 4 h. Catalyst **4a,** which proved to be slightly less active compared to **4b** but showed much higher stability in the recycling experiments, gave slightly lower yields. It should be mentioned that in all cases the selectivity to corresponding cyclic carbonates was ≥98%. A feasible mechanism for the polystyrene-supported **4b** as well as the silica-supported bifunctional ammonium salt **4a** catalyzed coupling of epoxides with CO_2 in this study would be similar to that of ammonium/phosphonium salt catalysis.[9a,15] The proposed mechanism involves activation of the epoxide by the ammonium cation and hydrogen bonding, ring opening of the epoxide via nucleophilic attack of the iodide at the least hindered carbon followed by CO_2 insertion, and subsequent ring closure via intramolecular nucleophilic substitution, simultaneously regenerating the catalyst.

In conclusion, polystyrene- and silica-supported triethanolammonium iodide represents a sustainable and easily recyclable class of immobilized organocatalysts for the reaction of CO_2 with epoxides. Remarkably, those catalysts are highly active at reaction temperatures <100 °C. A variety of epoxides were converted to the corresponding cyclic carbonates under mild and solvent-free conditions in the presence of those catalysts. The desired products were obtained in excellent selectivities and isolated yields. Moreover, we demonstrated that the silica-supported catalyst could be recycled 13 times without loss of activity and selectivity, yielding the desired carbonate in ≥93% yield in each step.

Experimental Section

Typical procedure for the preparation of silica supported catalyst **4a**: A mixture of aminopropyl-functionalized silica gel **3a** (1.00 g, 1 mmolg^{-1} N-loading) and 2-iodoethanol (5.00 g, 29.1 mmol) were mixed in a shaking device at 60 °C under argon for 4 d. The obtained solid was filtered off, washed with Et_2O (8×20 mL), and dried in vacuum to yield **4a** (1.24 g, 0.79 mmolg^{-1} N-loading) as a yellow solid.
General procedure for the coupling of epoxides with CO_2: A 25 mL autoclave was charged with silica gel-supported catalyst **4a** (0.02 equiv based on 0.79 mmolg^{-1} N-loading) and epoxide **1** (1 equiv). The reactor was purged once with CO_2, pressurized with CO_2 to 1.0 MPa, and heated to 90 °C. After 6 h the reactor was cooled using an ice bath and CO_2 was released slowly. The catalyst was removed by filtration and washed with Et_2O (3×10 mL). After removal of all volatiles, the cyclic carbonates **2** were obtained.

Preparation of 4-ethyl-1,3-dioxolan-2-one (**2a**): According to the general procedure, 1,2-epoxybutane (**1a**, 3.45 g, 47.8 mmol) was converted with CO_2 in the presence of silica gel-supported catalyst **4a** (1.20 g). **2a** (5.55 g, 47.8 mmol, 99%) was obtained as a colorless oil.

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Keywords: carbon dioxide · catalyst immobilization · cyclic carbonates · organocatalysis · recycling

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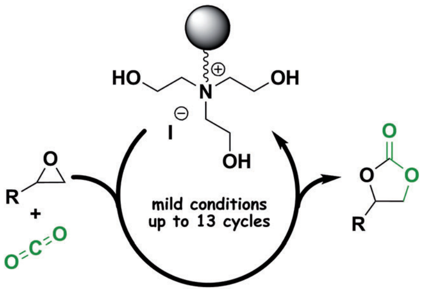
Do it again: Polystyrene and silica-supported bifunctional ammonium salts catalyze the addition of carbon dioxide to epoxide under mild and solvent-free reaction conditions. Those catalysts can be recycled up to 13 times without loss of activity. Moreover, a wide array of cyclic carbonates can be prepared in excellent yields utilizing those immobilized metal-free catalyst.



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Recyclable Bifunctional Polystyrene and Silica Gel-Supported Organocatalyst for the Coupling of CO_2 with Epoxides