RESEARCH ARTICLE

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Exploring the Immobilization Strategies of Lewis Bases on Lignocellulosic Bamboo Shavings and their Applications in Cycloaddition of CO_2 and CO_2 Derivatives

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For the first time, the immobilization of Lewis base molecular catalysts is demonstrated on lignocellulosic bamboo shavings for synthetic applications, focusing on the valorization of CO_2 and its derivatives. Two types of catalysts are immobilized on bamboo shavings: covalent functionalization using isocyanate chemistry is employed to prepare Bamboo supported Hexaethylenedicarbamate ethyl methyl imidazolium iodide [Bamboo@HMEMIM][I], while a silane-based approach is applied to obtain Bamboo supported 1,5,7-Triazabicyclo[4.4.0]dec-5-ene [Bamboo@TBD]. Both materials are fully characterized through elemental analysis, FT-IR, TGA, and Scanning Electron Microscopy (SEM). The first catalyst, [Bamboo@HMEMIM][I], promoted the cycloaddition of CO_2 with epoxide, achieving 100% conversion and complete selectivity toward cyclic carbonates under optimized conditions (2.8 mol% catalyst, 10 bar CO_2, at 70 °C for 16 h). This catalyst also demonstrates good recyclability, showing a decrease in activity only after four consecutive cycles (74% yield in the fourth cycle, 61% in the fifth). The reaction scope demonstrates its broad applicability for other epoxides (Y = 86–100%). The second catalyst is applied to the synthesis of glycerol carbonate through cycloaddition between dimethyl carbonate (DMC) and glycerol. Optimized conditions (5 mol% catalyst, 10:1 DMC:glycerol ratio, at 100 °C for 16 h) achieves 100% conversion and 69% selectivity for glycerol carbonate. In this case the degradation of catalysts by *Phanerochaete chrysosporium* is investigated.

1. Introduction

Integrating biobased side-products from natural sources into catalytic frameworks is becoming an appealing approach for advancing greener applications in heterogeneous catalysis.[1–3] Chemical functionalities of some biopolymers like cellulose, lignin, and some fibrous proteins can be adopted as catalytic sites and/or provide grafting points for immobilization of privileged molecular catalysts.[4] Semi-processed waste which incorporates the mentioned biopolymers represents a huge resource in this regard, and bamboo is nowadays one of the most interesting sources of lignocellulose due to its low-cost, quick harvesting and large abundance in all tropical and subtropical zones in the world.[5] These lands are characterized by extreme climatic conditions that make cultivation for food impossible, thereby avoiding the use of potential land for global food supply.[6] China represents the largest producer of bamboo, with around 40 million tons produced annually, and a well-managed bamboo grove can produce ≈20 to 40 tons per acre annually everywhere. Moreover, selected species like Guadua or Phyllostachys can yield even higher amounts in some circumstances.[7–9] In addition, maintaining and renewing bamboo forest bring benefits to the ecosphere of the planet, because an average plantation can absorb up to 12 tons of carbon dioxide per hectare every year and produce 35% more oxygen than an equivalent area of trees.[10] Semi-processed wood from

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bamboo covers important applications in unconventional building for low-income housing and sustainable urban architecture. Furthermore, in line with the purpose to conserve biodiversity, many countries have started to reduce timber harvesting, replacing classical wood furniture with bamboo counterparts, due to its rapid growth cycle.[11] In this case, the turning process involved in the semi-processing of wood produces a large amount of wood powder as waste, which should be utilized in other technological applications according to the principles of a circular and sustainable economy.[12,13] According to its botany, Bamboo is not a tree but a giant grass with a rigid cylinder shell named "culm" divided by transversal diaphragms at the nodes. In terms of chemical composition, bamboo is composed of fibers of cellulose, which represent the most abundant part (55%), followed by lignin (25%) and hemicellulose (20%).[14] Cellulose, lignin, and hemicellulose compose the sclerenchyma of the plant, which is the hard wall that supports tissues and is responsible for bamboo's mechanical strength. When bamboo shavings are treated and washed to remove everything except lignin, cellulose, and hemicellulose, the sclerenchyma structure forms small cavities (diameter 3–25 μm) with thick walls (5–8 μm). This characterizes bamboo as a hierarchical natural material, combining macro-, meso-, and microporous structures.[15–17] This characteristic results in a higher surface area compared to other natural amorphous materials such as wool and cotton,[18] enhancing reactant adsorption and improving mass transfer efficiency both have significant implications for catalytic performance. Additionally, the increased surface area promotes better dispersion of active catalytic species, reducing agglomeration, and contributing to more uniform and sustained catalytic activity.[19] Thus, due to its chemical composition, surface morphology, and mechanical properties, bamboo represents an interesting alternative to standard supports used in heterogeneous catalysis.[20] Furthermore, lignocellulosic composition makes the bamboo suitable for biodegradation when reuse is no longer feasible; this is a valuable characteristic compared to standard inorganic and polymeric matrix such as polystyrene and SiO_2.[21]This holistic approach underscores the transformative potential of heterogeneous catalysis in fostering a more sustainable and responsible chemical industry, where innovation and ecological stewardship converge to address global environmental challenges.[22] However, the use of bamboo as a support in heterogenous catalysis remains underexplored. In literature, it has primarily been employed as a support for immobilization of nanoparticles used in reduction reactions and for enzymes anchoring. To best of our knowledge, its utilization as support for organic base has not been reported.[23,24] Herein, we demonstrate the immobilization of two molecular catalysts on bamboo shavings for synthetic applications. Both the catalysts were investigated in reaction of interest for the valorization of CO_2 and CO_2 derivates according to the holistic approach aforementioned, where covering more sustainable aspects in the same scientific designed studies can boost the research toward the highly ambitious purposes on climate change actions and all correlated scientific tasks.

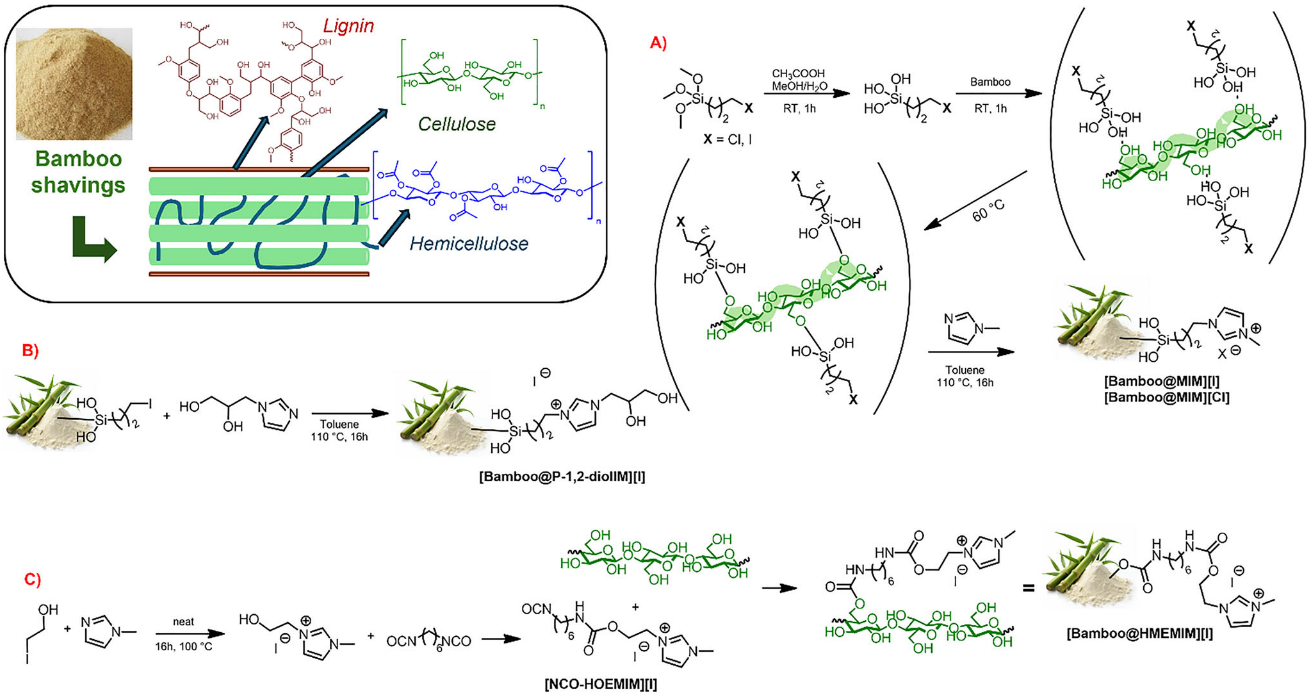
2. Results and Discussion

Our study commenced investigating the immobilization of selected catalysts. We have chosen some privileged structures according to the recent reports on topic of cycloaddition of CO_2 with epoxides.[2,25,26] Two strategies have been explored in this regard; first, we attempted the standard approach employed to functionalize cellulosic-based material via condensation of hydroxy silanes in acid condition. By following the general procedure, both (3-chloropropyl)trimethoxysilane and (3-iodopropyl)trimethoxysilane were hydrolyzed under controlled acidic conditions for 1 hour in a mixture of H_2O/MeOH/AcOH. The resulting hydrolyzed silanes were then allowed to interact with bamboo by promoting noncovalent bonding between the hydroxyl groups of saccharide fraction and hydroxy silane groups. Furthermore, to strengthen the resulting moieties onto the matrix, avoiding leaching during the catalytic conditions, neat condensation at high temperature (60 °C) were performed in this regard. The so-called iodide and chloride bamboo derivatives were employed in the quaternarization of 1-methyl-1H-imidazole, affording bamboo-imidazolium iodide **[Bamboo@MIM][I]** and bamboo-imidazolium chloride **[Bamboo@MIM][Cl]** both with a loading of 0.55 mmol g^{-1} (**Scheme** 1A). Because we were interested in understanding even the effect of the linker on the catalytic performance, we brough variety to the pool of catalysts in terms of hydrogen bond donor (HBD) ability and length of the spacer. HBD groups such as hydroxyl and carbamate moieties installed close to the Lewis basic site have proven to increase the activity of resulting catalyst in the cycloaddition of CO_2 to epoxide.[25] Thus, we prepared the polyhydroxylated **[Bamboo@P-1,2-diolIM][I]**, with a loading of 1.2 mmol g^{-1} via quaternarization of 3-(1H-imidazol-1-yl)propane-1,2-diol with iodide bamboo derivative as shown in Scheme 1B.

According to previous results published by our group on keratin-based imidazolium catalysts, we envisaged the opportunity to exploit hydroxyl groups of saccharides fraction in lignocellulosic moiety of bamboo, to intercept the isocyanate functional group forming a new carbamate bond that can be employed to covalently functionalize the material.[2] Thus, instead of preparing a matrix bearing isocyanate functional groups, we synthetized the hexamethylene isocyanate oxyethyl-1-methyl-1H-imidazol-3-ium iodide **[NCO-HOEMIM][I]**, by treating the hexamethylene diisocyanate HDI with 3-(2-hydroxyethyl)-1-methyl-1H-imidazol-3-ium iodide under controlled conditions (See Supporting Information for details). Finally, we obtained the resulting **[Bamboo@HMEMIM][I]**, with a loading of 0.33 mmol g^{-1} by treating the resulting **[NCO-HOEMIM][I]** with dried pretreated bamboo in DMSO for 16 h at 50 °C (Scheme 1C).

The cycloaddition of CO_2 to styrene oxide was selected as the benchmark reaction, and all the catalysts synthesized were tested by varying pressure, temperature and catalyst loading to find the optimal conditions, as reported in **Table** 1.

We started the optimization study investigating the effect of the counter anion by moving from the hard chloride anion to the softer and more nucleophilic iodide, testing **[Bamboo@MIM][Cl]** and **[Bamboo@MIM][I]**, respectively. Iodide shows a sort of reactivity (entry 4, Yield = 5%) at 70 °C, whereas no conversion has been observed in the same conditions with chloride (Entry 2, Yield = 0). Latter results are in line with findings reported in literature; in fact, according to the model of epoxide activation via halogen catalysis, iodide is more reactive than chloride as leaving group in the key intermediate α-halo-alkoxide, which represents the species generated in situ by the epoxide



Scheme 1. A) preparation of catalysts **[Bamboo@MIM][I]** and **[Bamboo@MIM][Cl]**. B) preparation of catalyst **[Bamboo@P-1,2-diolIM][I]**. C) preparation of **[Bamboo@HMEMIM][I]**. see Supporting Information for details on the synthesis and catalysts loading estimated by elemental analysis.

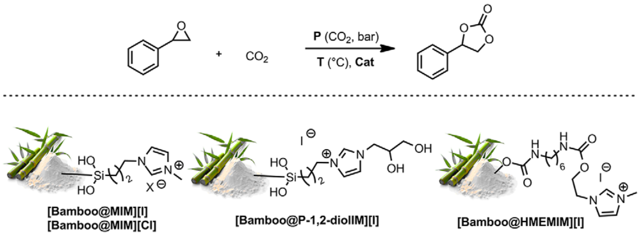
opening (see Supporting Information for the mechanism).[27] Continuing the screening of conditions, within silane-based imidazolium catalysts, acceptable results have been observed only increasing pressure of CO_2 until 10 bar, and moles of catalyst up to 10% (Entry 5, Yield = 32%). Moreover, increasing the reaction temperature to 70 °C seems to be detrimental for both conversion and yield (Entry 6, Conversion = 17%, Yield = 17%). Due to the lack of potential enhancements in the optimization using **[Bamboo@MIM]I]**, we proceeded to explore alternative synthetic catalysts. According to our previous work on CO_2 cycloaddition to epoxide in continuous flow,[25] the polyhydroxylated analogue **[Bamboo@P-1,2-diolIM][I]** was tested because the installed hydroxyl groups can stabilize the α-iodo-alkoxide intermediate through hydrogen bonding interactions, increasing the reactivity observed in catalysis. Disappointingly, this catalyst produced poor results at 1 bar (Entry 7, Yield = 3%) and 10 bar (Entry 8, Yield = 13%), thus not allowing further optimization. Finally, we moved to test **[Bamboo@HMEMIM][I]**, which was prepared by grafting bamboo with imidazolium iodide functionalized with an isocyanide moiety as anchoring group. This strategy offers two more features respect to **[Bamboo@MIM][I]**, a different HBD group, named carbamate, and a lengthier spacer between the matrix (lignocellulose) and the active site (imidazolium moiety). Pleasantly, we observed encouraging results working at 1 bar with a 2.8 mol% at high temperature (Entry 10, yield = 22% and Entry 11 yield = 51%, at 70 and 90 °C, respectively). Finally, we optimized the reaction conditions by varying temperature, pressure, and catalyst loading obtaining full conversion and complete selectivity with 2.8 mol% at 10 bar and 70 °C (Entry 18, yield = 100%). For all entries, selectivity toward the formation of cyclic carbonate, and conversion refers to consumption of epoxide, match because we did not observe typical by-products of this reaction in the crude. With the optimal conditions in hand, we moved to investigate the reaction scope, summarized in **Table 2**.

In this brief study of the reaction scope, epoxides **1b–g** were employed under the optimal conditions described in Table 1, Entry 18. The excellent results demonstrated the efficiency of **[Bamboo@HMEMIM][I]** in the cycloaddition process. Indeed, besides the styrene oxide analogue **1d**, the epoxides containing an alkyl chain can also be transformed into the corresponding cyclic carbonates in excellent yields (86–100%).

The recyclability of **[Bamboo@HMEMIM][I]** was tested under the optimized conditions employing the benchmark reagents. It was observed a decrease of the overall activity only after four consecutive cycles (fourth cycle yield = 74%; fifth cycle yield = 61% **Figure 1**), confirming the immobilization strategy onto bamboo as useful approach for recyclability of imidazolium catalysts applied to carbonation of epoxides. Elemental analysis of nitrogen and iodine, both performed on the spent **[Bamboo@HMEMIM][I]**, indicated that the reduced performance cannot be attributed to either catalyst leaching due to hydrolysis of carbamate functionality or loss of the halogen nucleophile. Therefore, a reasonable explanation for the deactivation is chemical modification of the catalyst under the reaction conditions or due to deposition of substances on the active surface.

Diols, and in general polyols, are other important building blocks for the synthesis of cyclic carbonates. Besides being easier to handle than epoxides, several platform chemicals belong to this class, making new synthetic protocols for their elaboration of great interest for sustainable chemistry. Among them, glycerol is one of the most important biobased molecules; it is the main by-product of biodiesel production and covers important

Table 1. Optimization of cycloaddition between CO_2 and styrene epoxide.

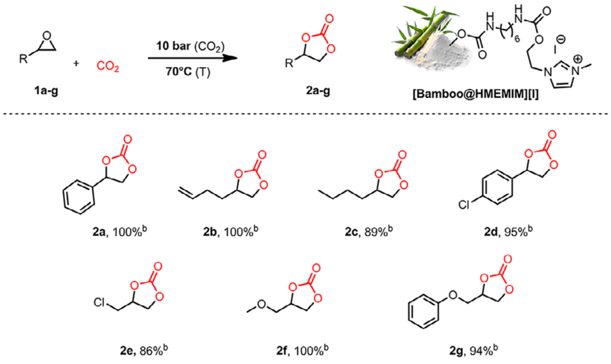


Entry[a)]	Cat	Cat [mol%]	P [bar]	*T*[°C]	Conv [%]	Y[%]
1	**[Bamboo@MIM][Cl]**	2.8	1	55	0	0
2	**[Bamboo@MIM][Cl]**	2.8	1	70	0	0
3	**[Bamboo@MIM][I]**	2.8	1	55	0	0
4	**[Bamboo@MIM][I]**	2.8	1	70	5	5
5	**[Bamboo@MIM][I]**	10	10	55	32	32
6	**[Bamboo@MIM][I]**	10	10	70	17	17
7	**[Bamboo@P-1,2-diolIM][I]**	10	1	55	3	3
8	**[Bamboo@P-1,2-diolIM][I]**	10	10	55	13	13
9	**[Bamboo@HMEMIM][I]**	2.8	1	55	7	7
10	**[Bamboo@HMEMIM][I]**	2.8	1	70	22	22
11	**[Bamboo@HMEMIM][I]**	2.8	1	90	51	51
12	**[Bamboo@HMEMIM][I]**	10	1	90	34	34
13	**[Bamboo@HMEMIM][I]**	2.8	3	55	56	56
14	**[Bamboo@HMEMIM][I]**	10	10	55	44	44
15	**[Bamboo@HMEMIM][I]**	10	10	55	43	43
16	**[Bamboo@HMEMIM][I]**	10	10	55	43	43
17	**[Bamboo@HMEMIM][I]**	2.8	10	55	48	48
18	**[Bamboo@HMEMIM][I]**	2.8	10	70	100	100

[a)] To a glass vial (5 mL) was added bamboo powder (supported catalyst) and 61 µL of styrene oxide. Then the vial was put inside a steel stainless autoclave that was sealed and filled with CO_2 (pressure in table). After three cycles of vacuum/CO_2 the autoclave was heated, and the system was kept under the reported conditions for 16 h. Then, the system was allowed to cool at RT and the resulting mixture was extracted with 1 mL of $CDCl_3$ and the conversion and yield were measured by ^{1}H-NMR, employing durene as external standard.

industrial applications in cosmetics, food, pharmaceuticals, and in fuel additive. Transformation of glycerol into glycerol carbonate represents one of the most important strategies to valorize it as chemical feedstock for production of bulk compounds such as polyurethane, polycarbonates, polyesters, and polyamides.[28–30] However, using CO_2 for synthesis of glycerol carbonate remains a challenging task.[31] Dimethyl carbonate (DMC) has emerged as a sustainable alternative for the synthesis of glycerol carbonate; furthermore, it can be obtained easily from carbon dioxide and methanol in controlled reaction conditions, opening new routes for the indirect valorization of CO_2.[32] Nitrogen bases as 1,5,7-Triazabicyclo[4.4.0]dec-5-ene TBD have proven to be active in

Table 2. Reaction scope.[a,b)]



[a)] 1 (1.00 mmol); see the Supporting Information for details. [b)] Isolated yield.

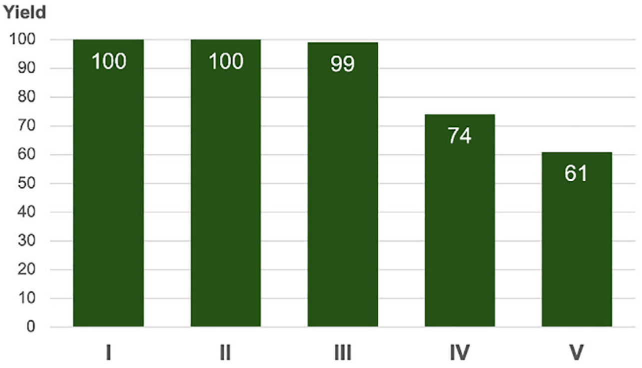
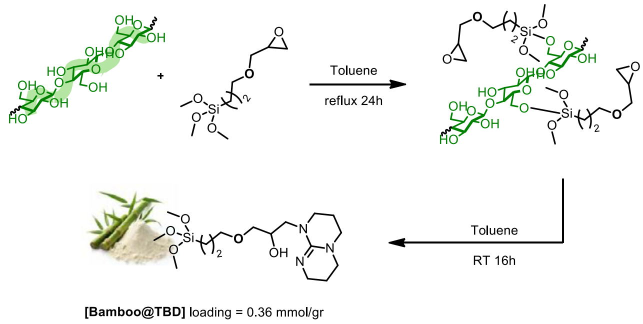


Figure 1. Recycling experiments (optimized conditions of Entry 18, Table 1).

DMC activation;[33] thus, we envisaged the opportunity to exploit the strategy described above to support the TBD onto the bamboo in this regard. Inspired by the strategies already reported to functionalized other inert matrixes such as silica and polystyrene, we designed, and then developed, the synthesis of the resulting bamboo supported TBD **[Bamboo@TBD]** as reported in **Scheme 2**.

Grafting of the epoxide derivative onto pre-treated bamboo support has been performed by mixing them and reflux the suspension in toluene for 24 h. We adopted this strategy instead of the previous one, which involves the hydrolyzed analogue of silane, because epoxide functional group is not compatible with acidic conditions required for hydrolysis.[34] Epoxide functionalization (0.36 mmol g^{-1}) has been determined by checking the residual silane after concentration of supernatant. Finally, the resulting TBD functionalized bamboo **[Bamboo@TBD]** has been obtained via epoxide opening by treating the epoxide functionalized bamboo with TBD in toluene at reflux for 16 h. Thus, **[Bamboo@TBD]** was tested in the synthesis of glycerol carbonate **5A** through the cycloaddition between DMC and glycerol as summarized in **Table 3**.

We commenced our optimization study by performing the reaction at 80 °C employing 2 %mol of [**Bamboo@TBD**] and with a ratio of DMC:glycerol 5:1, obtaining 62 % of the target product **5A**. We observed an increase of yield and still complete selectivity with 5 %mol of catalyst (entry 2, Y = 71%); interestingly, increasing the temperature to 90 °C, we observed an erosion of reactivity (entry 3, **5A** = 20%), probably due to the partial evaporation of DMC; this hypothesis was corroborated by the excellent conversion (entry 4 and 5, conv = 100%) observed performing the reaction at higher temperatures (100 and 120 °C, respectively) but with an additional excess of DMC (10:1). However, the reaction conditions reported in entries 4 and 5 determined the formation of the methyl carbonate O-protected glycerol carbonate **5B**, which was the main product at 120 °C. Compound **5B** is formed sequentially after **5A** via nucleophilic substitution of DMC with the secondary hydroxyl group of **5A**; this substitution is less favorable than the double substitution which leads to the kinetic product (the 5-membered ring). Thus, more energy is required to raise the activation barrier, which explains the formation of this side product upon increasing the temperature. Bamboo stem is a lignocellulosic material principally consisting of lignin, cellulose and hemicellulose. Lignin is a highly irregular insoluble polymer that is chemically bonded by covalent linkages with hemicellulose and represents the most difficult fraction to biodegrade. Among the methods available, biological treatments using lignin-degrading microorganisms is said to be superior to the current chemical and thermochemical methods in terms of energy intensity, environmental impact and process costs.[35] White-rot fungi are known as the most efficient lignin degraders, in which the representative species *Phanerochaete chrysosporium* has been most extensively studied due to its ability to efficiently depolymerize polysaccharides in plant biomass by using a battery of cellulolytic enzymes (i.e., peroxidases and laccases). Those enzymes are constitutive and continue to be produced during the different phases of fungal growth that can be accompanied by the degradation of several contaminants present in industrial waters, for purification purposes.[36] In our case, the inoculation of *P. chrysosporium* on spent **[Bamboo@TBD]** powder has demonstrated the capability to achieve an increase in fungal biomass of ≈60% (on dry weight) within a 7-day period, comparable to its growth on raw virgin bamboo. Furthermore, a biodelignification of ≈25% was observed, indicating that the fungus can utilize lignin as a substrate even after chemical treatment. The results suggest that, at the current substrate-to-fungus ratio, any toxic or inhibitory effects of chemical catalyst residues on bamboo powder is absent (See Supporting Information for details on lignin fraction and biodelignification).

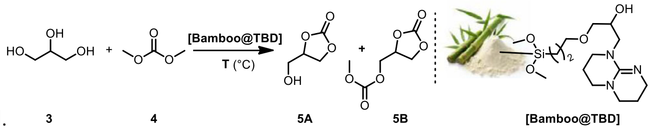


Scheme 2. Synthesis of **[Bamboo@TBD]** by functionalization of cellulose fraction with epoxide group followed by coupling with TBD via epoxide opening.

The characterization of each catalyst was performed by elemental, FT-IR, TGA analyses and Scanning Electron Microscopy (SEM). Catalyst loading was measured by quantification of nitrogen by elemental analysis (see Supporting Information for details). FTIR spectra have been recorded for each catalyst and compared with the pristine bamboo (**Figure 2A**). **Table 4** summarizes the most relevant vibration frequencies and band assignments lignocellulose polymer and its derivatives. In particular, the carbonyl stretching ν(C═O) at 1735 cm^{-1} remains unaffected in the **Bamboo@TBD**, while the **Bamboo@HMEMIM[I]** presents a broadening to lower wavelengths characteristic of the ν(C═O) of the carbamate groups (—COONH—). The ν (CN) vibration at 1356 cm^{-1} is covered into the complex fingerprint vibration of lignocellulose.[37]

The DRIFT spectra of the **Bamboo@TBD** present sharp bands at 736, 837, 890, and 1067 cm^{-1}, which correspond to organic siloxane (Si—O—C) or condensate silica network (Si—O—Si)

Table 3. Optimization of cycloaddition between DMC and glycerol.



Entry[a]	Cat [%mol]	DMC:Gly [V:V]	T [°C]	5A+5B [%]	5A:5B [%]
1	2	5:1	80	62	100:0
2	5	5:1	80	71	100:0
3	5	5:1	90	20	100:0
4	5	10:1	120	94	27:67
5	5	10:1	100	100	69:31

[a] A 5 mL vial was charged with 139 mg or 56 mg of **[Bamboo@TBD]** (0.36 mmol g^{-1}, 5% mol or 2% mol respectively) and 92 mg (1 mmol) of glycerol. After 3 cycles of vacuum/argon 421 µL (450 mg, 5 mmol) of DMC were added and the reaction was left at the reported temperature for 16 h. After that, the suspension was extracted with methanol (3 x 1.5 mL) in a sonicator. NMR yield was calculated by recording a ^{1}H-NMR spectrum employing DMC as external standard (64 µL, 1 mmol).

networks. The last band at 1067 cm^{-1} overlaps with the broadband of cellulose and hemicellulose's ν(C—O—C) $b_{1\rightarrow4}$ glycosidic bond. The new sharp peak at 1650 cm^{-1}, corresponding to the aliphatic C=N vibrations, confirms the covalent bonding of the TBD moiety.[38]

SEM analysis shows that the hierarchical structure is maintained for all the functionalized materials (Figure 2B–E).

Furthermore, **Figure 3** shows the TGA curves for **Bamboo**, and the immobilized catalysts. At the first stage from RT to 150 °C, all the samples have lost the moisture content of ≈2%. The complete thermal degradation in N_2 atmosphere from 150 to 800 °C is attributed sequentially to hemicellulose (from 230 to 340 °C), cellulose (from 340 to 370 °C) and lignin (from 370 to 700 °C). In the case of **Bamboo** the total weight loss is ≈90%, the remaining 8% of biochar is totally burned in oxygen atmosphere. **Bamboo@TBD** and **Bamboo@HMEMIM[I]** show similar TGA curves, but compared to the Bamboo, the curves are shifted to the left and decomposition started at 150 °C, suggesting a lower thermal stability of the lignocellulose biomass. The total deposition till 800 °C, in N_2 atmosphere, led to a total weight loss of around 82%. We attribute the higher degradability of **Bamboo@TBD** and **Bamboo@HMEMIM[I]** to the chemical

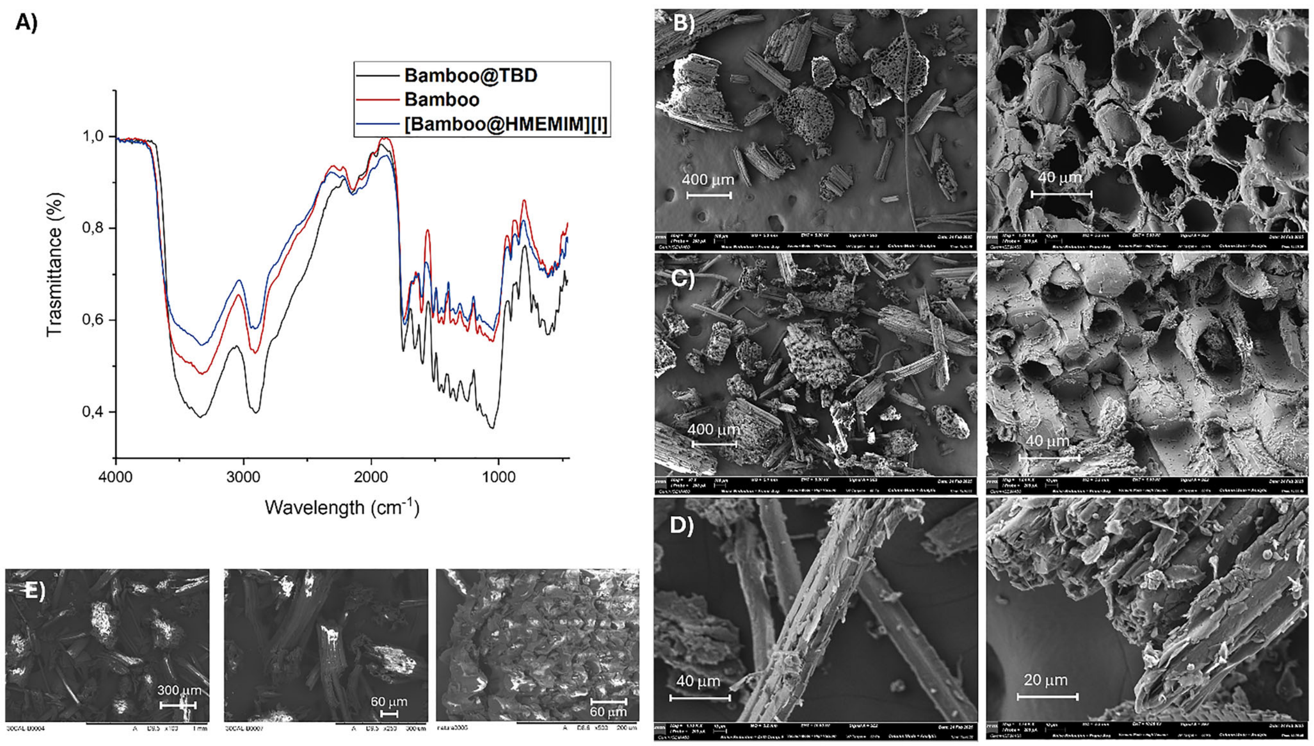


Figure 2. A) DRIFTS of Bamboo washed with SDS (pre-treated before functionalization), **[Bamboo@MIM][I]**, **[Bamboo@TBD]** and **[Bamboo@HMEMIM][I]**; SEM image of B) **[Bamboo@MIM][I]**, C) **[Bamboo@HMEMIM][I]**, D) **[Bamboo@TBD]**, E) unfunctionalized Bamboo. All images show the main macroporous structure of Bamboo functionalized catalysts.

Table 4. FT-IR frequencies and band assignments for natural **Bamboo** and the functionalized **Bamboo@TBD** and **Bamboo@HMEMIM[I]**.

Frequency [cm^{-1}]	Characteristic vibration and functional group
3422	n(O—H) Aromatic and aliphatic hydroxyl group H-bonded
2940-2906	$n_{asym\text{-}sym}$(C$_{sp3}$-H) stretching of aliphatic C—H
2000-1600 (several)	Aromatic combination bands of lignin
1735	Aromatic carbonyl n(C═O) of lignin and hemicellulose
1722	Carbammate of [Bamboo@HMEMIM][I], shoulder of the n(C═O band at 1735 cm^{-1}
1650	nC═N of **Bamboo@TBD**
1600, 1513, 1425	n(C=C) of Aromatic skeletal vibration of lignin
1100 (broad band)	n(C—O—C) $b_{1\rightarrow 4}$ glycosidic bond of cellulose and hemicellulose
898 and 840	d(C—H)$_{oop}$ Aromatic C—H out-of-plane bend of lignin
890, 837, and 736	Organic siloxane and Silicon network for **Bamboo@TBD**
720–590	d(O—H)$_{oop}$ Alcohol O—H out-of-plane bend

treatment that were submitted. Alternatively, the cellulose can be degraded by a grafted base catalyst which increases the reactivity of the glycosidic bond and its cleavage. Finally, in O_2 atmosphere the remaining biochar (16%) is completely burned. Acid catalysts generally improves the biochar yield, while basic catalyst tend to reduce it, but this depends on the pyrolysis condition, feedstock type, concentration, pH and presence of labile organic substrate.

3. Conclusion

In conclusion we successfully demonstrated the potential of bamboo shavings as a sustainable support for immobilizing Lewis base catalysts in the cycloaddition of CO_2 and its derivatives. In particular, the isocyanate derivate **[Bamboo@HMEMIM][I]** showed high efficiency in converting various epoxides into cyclic carbonates, achieving up to 100% yield under optimized conditions. The latter catalyst exhibited good recyclability, maintaining significant catalytic activity over multiple cycles, which is crucial for sustainable industrial applications. Furthermore, the study also explored the synthesis of glycerol carbonate using a bamboo-supported TBD catalyst **[Bamboo@TBD]**, achieving high yields and demonstrating the versatility of bamboo-based catalytic systems. Furthermore, later, after its use in catalysis, it was found to serve as feedstock for mycobacteria in applications involving fungal-mediated decontamination.

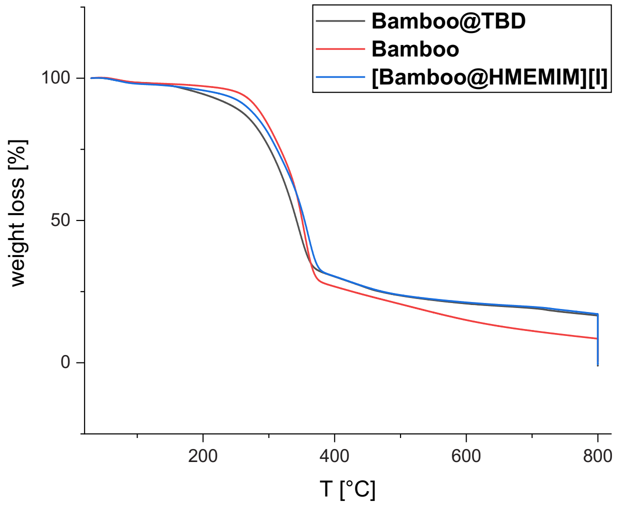


Figure 3. TGA curves of **Bamboo** biomass, **Bamboo@TBD** and **Bamboo@HMEMIM[I]**.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

bamboo, catalyst immobilization, CO_2 valorization, cycloaddition, glycerol carbonate, heterogeneous catalysis, lignocellulose

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[1] S.-Z. Zhang, Z.-S. Cui, M. Zhang, Z.-H. Zhang, *Curr. Opin. Green Sustainable Chem.* **2022**, *38*, 100713.
[2] M. Bottin, C. De Risi, G. Sotgiu, S. Buoso, O. Ginoble Pandoli, L. Poletti, G. Di Carmine, C. D'Agostino, D. Ragno, A. Massi, *ACS Sustainable Chem. Eng.* **2024**, *12*, 12482.
[3] X. Zhang, M. Jiang, N. Niu, Z. Chen, S. Li, S. Liu, J. Li, *ChemSusChem* **2018**, *11*, 11.
[4] A. Shetty, V. Molahalli, A. Sharma, G. Hegde, *Catalysts* **2022**, *13*, 20.
[5] R. Wang, Z. Guo, C. Cai, J. Zhang, F. Bian, S. Sun, Q. Wang, *Clean Technol. Environ. Policy* **2021**, *23*, 1687.
[6] A. Ickowitz, S. McMullin, T. Rosenstock, I. Dawson, D. Rowland, B. Powell, K. Mausch, H. Djoudi, T. Sunderland, M. Nurhasan, A. Nowak, V. Gitz, A. Meybeck, R. Jamnadass, M. R. Guariguata, C. Termote, R. Nasi, *Lancet Planet. Health* **2022**, *6*, 632.
[7] Y. Li, N. Wang, A. R. A. Latiff, *Adv. Bamboo Sci.* **2025**, *11*, 100130.
[8] P. K. Virtanen, F. Apurinã, K. Ruokolainen, L. Manchineri, *Hum. Ecol.* **2022**, *50*, 1077.
[9] M. Chen, L. Guo, M. Ramakrishnan, Z. Fei, K. K. Vinod, Y. Ding, C. Jiao, Z. Gao, R. Zha, C. Wang, Z. Gao, F. Yu, G. Ren, Q. Wei, *Plant Cell* **2022**, *34*, 3577.
[10] X. Song, G. Zhou, H. Jiang, S. Yu, J. Fu, W. Li, W. Wang, Z. Ma, C. Peng, *Environ. Rev.* **2011**, *19*, 418.
[11] M. Yadav, A. Mathur, *Mater. Today Proc.* **2021**, *43*, 2872.
[12] M. Hossain, S. Park, N. Suchek, M. Pansera, *Business Strategy Environ.* **2024**, *33*, 7077.
[13] J. C. Slootweg, *Curr. Opin. Green Sustainable Chem.* **2020**, *23*, 61.
[14] N. A. Siam, A. S. Yusoh, M. K. A. Uyup, in *Multifaceted Bamboo*, Springer Nature Singapore, Singapore, **2023**, pp. 43–51.
[15] M. L. Testa, O. G. Pandoli, C. Cecone, E. Laurenti, V. La Parola, C. Vineis, M. L. Tummino, *Adv. Sustainable Syst.* **2025**, *9*, 2400710.
[16] B. G. Palma, R. A. C. Leão, R. O. M. A. de Souza, O. G. Pandoli, *Catal. Today* **2021**, *381*, 280.
[17] D. S. de Sá, R. de Andrade Bustamante, C. E. Rodrigues Rocha, V. D. da Silva, E. J. da Rocha Rodrigues, C. Djenne Buarque Müller, K. Ghavami, A. Massi, O. G. Pandoli, *ACS Sustainable Chem. Eng.* **2019**, *7*, 3267.
[18] S. J. McNeil, M. R. Sunderland, S. J. Leighs, *Appl. Catal., A* **2017**, *541*, 120.
[19] S. Sun, H. Li, Z. J. Xu, *Joule* **2018**, *2*, 1024.
[20] J. Li, R. Ma, Y. Lu, Z. Wu, R. Liu, M. Su, X. Jin, R. Zhang, Y. Bao, Y. Chen, D. Qin, D. Yang, Z. Jiang, *Appl. Catal. B* **2022**, *310*, 121297.
[21] A. A. El-Gammal, Z. Kamel, Z. Adeeb, S. M. Helmy, *Polym. Degrad. Stab.* **1998**, *61*, 535.
[22] C. R. McElroy, A. Constantinou, L. C. Jones, L. Summerton, J. H. Clark, *Green Chem.* **2015**, *17*, 3111.
[23] Y. Ren, L. Zhang, T. Sun, Y. Yin, Q. Wang, *ACS Sustainable Chem. Eng.* **2022**, *10*, 6244.
[24] J. Li, R. Ma, Y. Lu, Z. Wu, R. Liu, M. Su, X. Jin, R. Zhang, Y. Bao, Y. Chen, D. Qin, D. Yang, Z. Jiang, *Appl. Catal. B* **2022**, *310*, 121297.
[25] L. Poletti, C. Rovegno, G. Di Carmine, F. Vacchi, D. Ragno, A. Brandolese, A. Massi, P. Dambruoso, *Molecules* **2023**, *28*, 1530.
[26] A. Rehman, F. Saleem, F. Javed, A. Ikhlaq, S. W. Ahmad, A. Harvey, *J. Environ. Chem. Eng.* **2021**, *9*, 105113.
[27] V. Butera, H. Detz, *ACS Omega* **2020**, *5*, 18064.
[28] G. Fiorani, A. Perosa, M. Selva, *Green Chem.* **2023**, *25*, 4878.
[29] D. Wang, D. Bai, J. Xiong, Z. Chen, X. Zhao, H. Wu, J. Shan, S. Wei, X. Zhang, *Appl Catal., A* **2023**, *665*, 119370.
[30] C. Terazzi, A. Spannenberg, J. von Langermann, T. Werner, *ChemCatChem* **2023**, *15*, 202300917.
[31] F. Della Monica, A. Brandolese, G. Di Carmine, M. Selva, G. Fiorani, L. Izzo, *ChemSusChem* **2025**, *18*, 202500030.
[32] S.-H. Pyo, J. H. Park, T.-S. Chang, R. Hatti-Kaul, *Curr. Opin. Green Sustainable Chem.* **2017**, *5*, 61.
[33] H. Mutlu, J. Ruiz, S. C. Solleder, M. A. R. Meier, *Green Chem.* **2012**, *14*, 1728.
[34] X. Lin, G. K. Chuah, S. Jaenicke, *J. Mol. Catal., A Chem.* **1999**, *150*, 287.
[35] I. Gugel, D. Summa, S. Costa, S. Manfredini, S. Vertuani, F. Marchetti, E. Tamburini, *Fermentation* **2024**, *10*, 80.
[36] D. Konan, A. Ndao, E. Koffi, S. Elkoun, M. Robert, D. Rodrigue, K. Adjallé, *AIMS Microbiol.* **2024**, *10*, 1068.
[37] K. Ravishankar, S. Muthusamy, S. K. Durai, G. Murugan, A. V. V. Koushik, N. Thirumal, S. N. Bhaskar, S. N. Jaisankar, *ACS Sustainable Resour. Manage.* **2024**, *1*, 2203.
[38] B. Karmakar, R. Nandi, *Res. Chem. Intermed.* **2021**, *47*, 2161.