



Plant-based Basic Carbocatalyst for Lactone Ring-Opening Polymerization and Isosorbide Transesterification with High Efficiency

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Basic carbocatalyst made of simple natural precursors using environmentally friendly processes are eagerly required for a wide range of chemical processes. This work is devoted to a carbocatalyst with base functionality from soybean flour as a nitrogen-rich carbon source. This metal-free basic carbocatalyst showed a density of basic sites of 0.165 mmol g⁻¹ as quantified via CO₂-TPD. The activity of the prepared basic carbons was successfully confirmed in two industrially important base-catalyzed reactions of green chemistry, namely, ring-opening

polymerization (ROP) of ϵ -caprolactone and transesterification of isosorbide with dimethyl carbonate. Utilizing the prepared basic carbon in the ROP reaction of ϵ -caprolactone, gave a white polymer with high molecular weight ($M_w = 30000 \text{ g mol}^{-1}$), which is comparable to industrial products. Moreover, a yield of 79% of isosorbide bismethyl carbonate was obtained using the prepared basic carbon in isosorbide transesterification with dimethyl carbonate at 493 K for 6 hours.

Introduction

Of the primary four heterogeneous catalytic operations (acid, base, oxidation, reduction), base catalysis is the least covered, and industrial chemistry is in eager need of it. The number of available heterogeneous bases is very limited, and this is why mostly still molecular bases are applied.^[1,2] This comes with the known disadvantages of molecular catalysts, e.g. contamination of the product and demanding separation processes. Biorefinery, which is mostly working in water and in the presence of organic functionalities,^[3-9] is in high demand for such solid base catalysts, as not only transesterification reactions^[10-13] or lactone ring-opening polymerization (ROP),^[14] but also carbon-carbon coupling via e.g. Aldol condensation^[15] or Knoevenagel reaction^[16] are to be realized. Among these reactions, the ϵ -caprolactone ROP to poly(ϵ -caprolactone) (PCL), and isosorbide transesterification to isosorbide bis(methyl carbonate) abbreviated as (ISBMC) have recently gained attention.

PCL is a biodegradable bio-based polymer that can be applied in multiple applications such as biomedical, pharmaceutical, and for packaging.^[17] Traditionally, PCL can be

synthesized via ROP, mostly using homogenous catalysts, with tin octoate being the most often applied catalyst.^[18] Recently, heterogeneous catalysts were also applied for this ROP, such as microporous polymer and double metal cyanide.^[19,20]

Isosorbide is a unique bio-based monomer that has the potential to be applied for the production of green polymers, mostly polycarbonate.^[21,22] To date, this is generally done with polycondensation of isosorbide with phosgene or other metal halides, which are not green.^[23] However, a green alternative methodology is via the transesterification of isosorbide with dimethyl carbonate (DMC) to produce ISBMC. Nowadays, few catalysts are employed for this reaction with a reasonable yield, mostly with homogeneous catalysts (K₂CO₃, Cs₂CO₃, and Li-(Acaq)) or ionic liquids.^[23,24] However, to the best of our knowledge, no basic heterogeneous catalyst has been reported for this reaction.

Known and currently applied heterogeneous systems include BaO or MgO, CsOH supported on silica or zeolites, ZnO, or layered metal hydroxides, but all of these systems suffer from partial water solubility and comparably quick leaching in water. Heterogeneous organocatalysts, based on polymer resins, covalent frameworks, or modified carbons, are less sensitive to leaching problems. Relevant to the present contribution, there is a primary, and old observation that charcoal can be base activated when treated at 1173 K in the presence of N₂O, NH₃, or ZnCl₂-NH₄Cl-CO₂.^[25] Active base sites were later introduced by functionalizing the carbonaceous network with heteroatoms such as nitrogen and oxygen,^[26,27] and N-doped carbon nanotubes are a reference system for that type of approach.^[26,27] Most of these structures are however comparably weak, i.e., the base strength is along typical tertiary amines. However, the chemical nature of nitrogen atoms in well-established super bases such as 8-diazabicyclo[5.4.0]undec-7-ene (DBU) or 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) could inspire chemistry of heterogeneous catalyst to obtain strong

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basicity beyond current limits. Different nitrogen-rich carbonaceous materials with similar structures have been used as base heterogeneous catalysts. For instance, Makowski et al.^[28] reported that cross-linked mesoporous poly(benzimidazole) was able to catalyze a variety of Knoevenagel condensation reactions, providing that the catalyst was porous and deprotonated after synthesis. We also reported the catalytic activity of deprotonated mesoporous graphitic carbon nitride for different Knoevenagel condensation and transesterification reactions.^[29] Despite being catalytically active, the as-prepared mpg-C₃N₄ still exhibited unsatisfactory results, and chemical activation with tBuOK, KOH, and K₂CO₃ was performed.^[29] In the model Knoevenagel reaction of benzaldehyde with malonitrile, such activated samples gave a conversion of 89% after 2 h at 343 K and a selectivity of 98%. However, substrate variation to the less reactive ketones resulted only in low conversion (30% conversion after 19 h), reflecting again the relatively low basicity of the materials. Furthermore, Titirici et al.^[30] reported the preparation of mesoporous and highly functionalized biochar via hydrothermal carbonization of glucose and vinyl imidazole.^[30] These materials were not only active for Knoevenagel condensation of benzaldehyde with malonitrile (yielding over 98% at 353 K after 12 h), but were also moderately active in transesterification reactions (yielding over 50% at 423 K after 72 h), without being neither structurally nor chemically affected.^[30] In related work, covalent triazine frameworks as catalysts were used in the cycloaddition of CO₂ to epichlorohydrin obtaining the full conversion of the initial epoxide and up to 95.8% selectivity at 403 K when the sample exhibited a

larger surface area and a high density of basic sites brought in by pyridine units.^[31]

So-called “basic carbons” are well known in the community of sorption materials,^[32] and they were empirically optimized as they are mandatory in air cleaning and gas mask applications to remove acidic impurities. In many cases, basicity is coming from including alkali and earth alkali oxides and hydroxides, but strong interaction with the carbon support gave them robust and less water sensitive. Interestingly, some authors give evidence for aromatic carbon-oriented basic sites on the basal planes.^[32] As such, the high acid affinity of basic sites is applied in gas masks, to capture acids of very low concentrations, which is a matter of survival in such cases. Details on the nature of basicity in carbon materials can be found in the literature.^[33]

Not only sorption but also catalysis can be an attractive platform for basic carbon applications. Perozo-Rondon et al exhibit the usage of basic carbons for the synthesis of dihydropyridine, and the performance of the heterogeneous catalyst was comparable to homogeneous ones.^[34] Additionally, Rubio Gomez et al employed activated basic carbons for the synthesis of alpha-beta-unsaturated nitriles.^[35] One can conclude that the selectivity and yield of the previous basic carbocatalysts are already more than only promising.

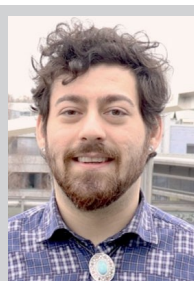
In the present paper, we will follow and extend one of the most simple approaches to carbon functionalization: for centuries, animal blood or bones were carbonized to create “bone char” or “carbo animalis”, and the products were applied from medieval times to modern age to cure a broad range of diseases, especially detoxification of the intestine. We however



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Prof. Dr. Markus Antonietti is the director of the Max Planck Institute of Colloids and Interfaces and has worked in the field of functional materials for 30 years. His current scientific interests include green chemistry and material solutions for energy change, porous polymers, artificial photosynthesis, as well as the chemistry of cooking.

Table 1. Elemental composition, <i>i.e.</i> , C, S, H, O, N, K, Mg and Zn of the basic carbocatalyst.							
	C [wt.%] ^[a]	N [wt.%] ^[a]	H [wt.%] ^[a]	O [wt.%] ^[a]	K [wt.%] ^[b]	Mg [wt.%] ^[b]	Zn [wt.%] ^[b]
Basic Carbon	68.4	5.5	2.0	23	0.2	0.3	< 0.1

[a] Obtained from combustion elemental analysis. [b] Obtained from ICP-OES.

will replace animal products with a more timely “vegan” choice by using a plant-based, protein-rich starting product (soybean flour) which is then carbonized and functionalized towards a porous carbocatalyst with basic functionality. After broad characterization, the superior base activity is confirmed in two industrially important base-catalyzed reactions of green chemistry, namely ring-opening polymerization of ϵ -caprolactone and transesterification of isosorbide with dimethyl carbonate.

Results and Discussion

We choose Soybean flour as a sustainable, regrowing starting product, as it is rich with protein 49.3 wt.% that serves as a nitrogen source. The composition of the soybean flour as received is described in Table S1 at electronic supporting information (ESI). As a binder, we added a liquid eutectic urea-glucose mixture, which also enables water-poor processing and homogenization of the catalyst green body. ZnO nanoparticles ($d=20$ nm) were added as a sacrificial hard template to establish mesoporosity, as previously reported.^[7,36] Then, the precursor was homogenized by kneading, pelletized, and carbonized at 1223 K for 2 h. The catalyst preparation, carbonization procedure, as well as washing is described in detail in the ESI. The catalyst after carbonization is named basic carbon (BC) for the rest of the manuscript.

The BC pellets were characterized by combustive elemental analysis and inductively coupled plasma optical emission spectroscopy (ICP-OES), X-ray diffraction (XRD), N_2 sorption, thermogravimetric analysis (TGA), temperature programmed desorption of carbon dioxide (CO_2 -TPD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM).

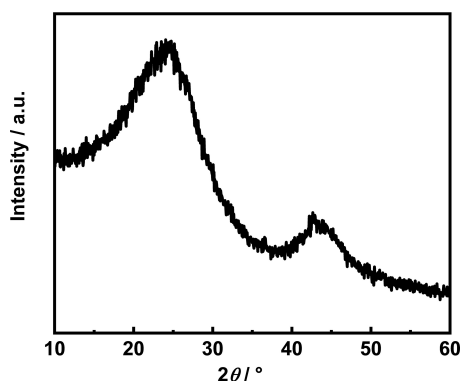


Figure 1. XRD diffraction pattern for the basic carbon.

The elemental composition of the basic carbon upon the carbonization procedure showed that the N content is 5.5 wt.%. This is an unusually high N content for carbon material that condensed at 1223 K. Furthermore, elemental analysis via ICP-OES showed the presence of traces of K (0.2 wt.%) and Mg (0.3 wt.%) in the carbonized sample. The detailed chemical composition of basic carbon is presented in Table 1. XRD pattern showed the typical peaks of weakly ordered carbon at 2θ of 24° and 44° (Figure 1). Furthermore, the basic carbon possesses high thermal stability, *i.e.*, 823 K in air and 1073 K under N_2 , confirmed via TGA analysis (Figure 2). A high content of N in the final carbonized sample leads to a change in the electron density of the carbonized material and contributes to increasing the oxidation stability/nobility.^[26,27]

N_2 physisorption (Figure 3) indicates the coexistence of micro- and mesopores with a specific surface area of $707\text{ m}^2\text{ g}^{-1}$,

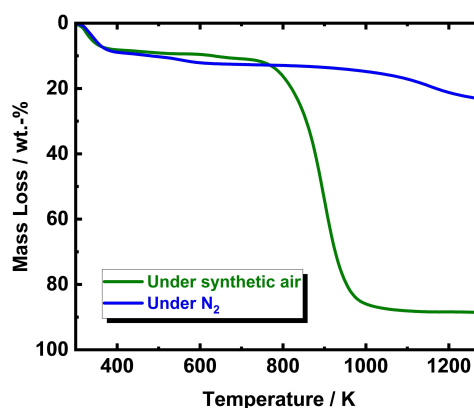


Figure 2. TGA profile for the basic carbon measured under synthetic air and N_2 atmospheres.

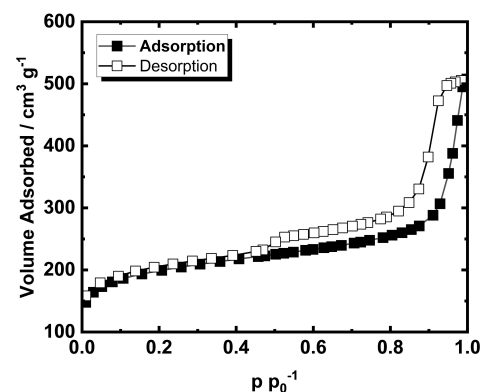


Figure 3. N_2 sorption isotherm recorded at 77 K for the basic carbon.

specific pore volume of 0.5 and pore width between 2.0–6.0 nm (Figure 3 and Table 2). It is to be underlined that the mesoporosity is due to the ZnO template which was applied to enable access to a larger number of active sites to reaction mixtures in catalysis.

CO₂-TPD indicated the presence of two different base sites, one with an adsorption peak maximum at 443 K, and the other with a peak at 553 K (Figure 4). By comparison with similar systems, we attribute the first peak to the N-sites in carbon (amine-basidity), while the second peak is bigger and similar to weaker metal hydroxides. A similar peak was however already described by Kuang et al.^[37] and was related to small micropores being capable to bind CO₂ with multiple O and N binding sites. The total amount of basic sites is 1.088 mmol g⁻¹, and 0.928 mmol g⁻¹ (measured via CO₂-TPD and acid-base titration), which is in the typical range of heterogeneous base catalysts.^[38,39]

XPS indicates the sole presence of carbon, nitrogen, and oxygen (Figure 5). It is important to state that we have significant amounts of negatively charged or polarized nitrogen in the sample, i.e., the also second base peak is potentially related to multiple binding with nitrogen involved. We also find about 0.2 wt.% of K and 0.3 wt.% of Mg from the soybean flour in the carbonized material, which are assigned as counter ions of the potential charged organic base or helper bases.

In line with N₂ physisorption, scanning electron microscopy (SEM) images (Figure 6) indicate a highly open texture, where a hierarchical porous structure on the macro-level supports the micro- and mesopores.

To evaluate the activity of the prepared basic carbons, two different reactions with importance in the field of sustainable chemistry were targeted. These reactions are: 1) synthesis of biodegradable polycaprolactone (PCL) by ring-opening poly-

Table 2. Textural properties, namely specific surface area (A_{BET}), pore volume (V_p) and pore diameter (D_p), as well as the density of basic sites represented by CO₂ uptake in the basic carbon.

	A_{BET} [m ² g ⁻¹]	V_p [cm ³ g ⁻¹]	D_p [nm]	CO ₂ Uptake [mmol g ⁻¹]	N Titration [mmol g ⁻¹]
Basic Carbon	707	0.5	2.0–6.0	1.088	0.928

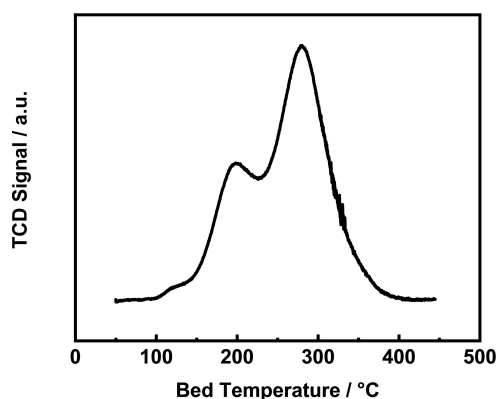


Figure 4. CO₂-TPD profile for the basic carbon.

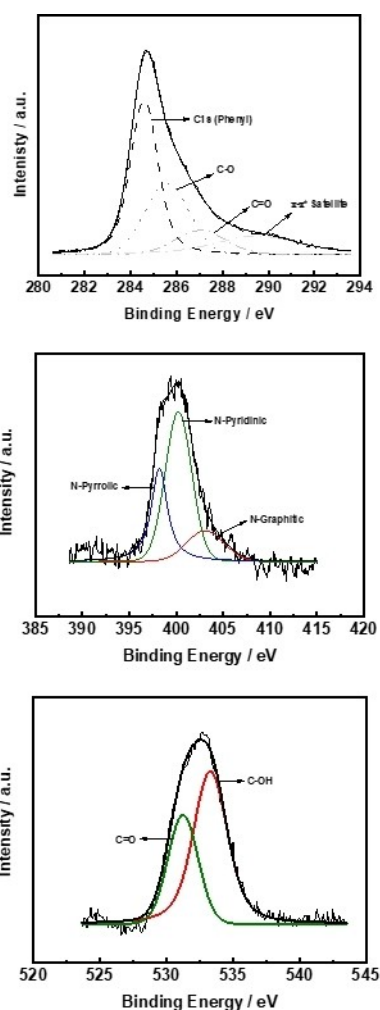


Figure 5. XPS spectra (C1s, N1s and O1s) for basic carbon.

merization (ROP) of ϵ -caprolactone (ϵ CL), 2) transesterification of isosorbide (IS) to isosorbide bis(methyl carbonate) abbreviated as “ISBMC” for sustainable polycarbonate synthesis. It is noteworthy to be mentioned here that experiments performed in absence of basic carbocatalyst for both reactions show no products and conversion of ϵ CL and IS.

The white and dense precipitate indicated the successful ROP of ϵ CL using the basic carbon as a heterogeneous catalyst at 413 K after 24 h of reaction time almost with quantitative conversion (Figures 7 and 8), whereas no precipitate was observed by performing the experiment in absence of catalyst under aforementioned conditions. The so-formed polymer showed standard chemical shifts at 1.3 ppm for methylene group that constitutes the backbone of the PCL structure (labeled as “c”). This methylene group at 1.3 ppm is proof of the formation of a polymer as does not exist in the pure monomer (Figure 8), i.e., ϵ CL. 1.5–1.7 ppm for the overlapped methylene groups due to the similar chemical environment (labeled as “b + b” in the PCL structure). SEC analysis of the formed PCL showed a molecular weight (M_w) of 30000 g mol⁻¹ with number average molecular weight (M_n) of 19500 g mol⁻¹ with a poly-

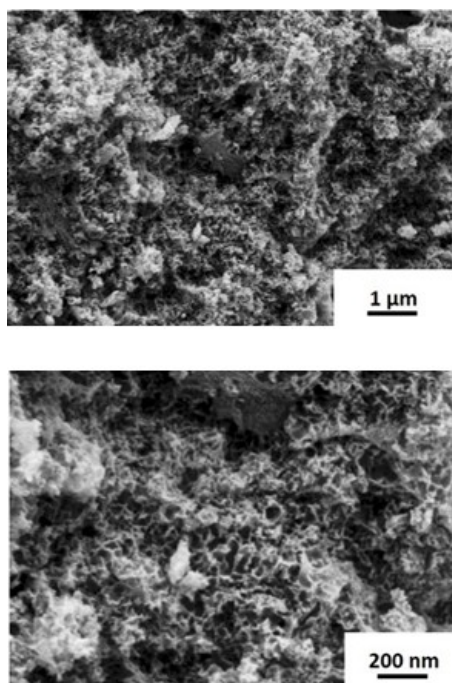


Figure 6. SEM images for the basic carbon with a magnification of x15 k (up) and x30 k (down).

dispersity (\bar{D}) of 1.2, which indicates a living mechanism (All the properties of the formed polymer are presented in Table 3), while standard commercial PCL has a smaller molecular weight (Table 3). Additionally, this performance compares nicely with modern homogenous and heterogenous catalysts.^[18–20] When compared with the heterogeneous In addition, DSC analysis showed that the synthesized polymer possesses a melting temperature (T_m) of 338 K.

The second reaction is the transesterification of isosorbide (IS) with dimethyl carbonate (DMC) in the presence of basic carbon to isosorbide bismethyl carbonate (ISBMC) via isosorbide monomethyl carbonate (ISMMC) intermediate (Figure 9). The reason we aimed for this particular product, ISBMC, is due to its employment in the synthesis of alternative biodegradable rigid polymers such as non-isocyanate-based polyurethanes and bisphenol A/phosgene-free polycarbonates.

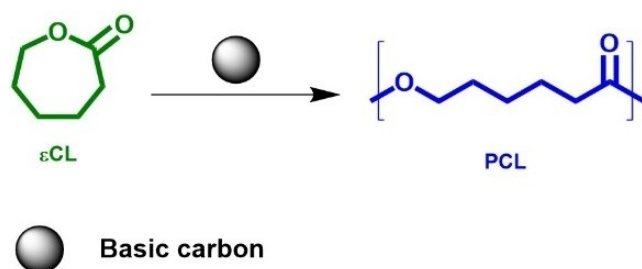


Figure 7. Chemical Structures of monomer and polymer as well as a digital image of the obtained polymer product, indicating also a full separation of the black carbon catalyst.

The catalyst shows high catalytic performance with 98% conversion of IS with a yield of 79% of ISBMC and 19% of ISMMC after 6 h of reaction time at 423 K (Figure 10). These results can be nicely compared to similar studies reported in the presence of a homogenous catalyst such as triazabicyclodecene or a standard basic catalyst such as K_2CO_3 , LiOH or KOH.^[40,41] In these reported studies in which homogenous catalysts were utilized, a thorough purification process afterward to separate the reaction products from the homogenous catalyst is required. To the best of our knowledge, this is the first time that a heterogeneous catalyst is applied in this reaction.

Conclusion

A simple, cheap, sustainable, scalable, and efficient basic carbon in pellet shape was produced as a heterogeneous catalyst for base-catalyzed reactions. This simple approach is based on the utilization of a plant-based protein-rich carbon source (soybean flour) and cross-linking of the system preceding carbonization (through glucose/urea eutectics), ZnO ($d=20$ nm) as a hard templating agent and a “pasta” technology for shaping the mixture.

The as-prepared catalyst exhibits high catalytic performance in two different base-catalyzed reactions that are usually performed using homogenous catalysts, i.e., ring-opening polymerization of ϵ -caprolactone and transesterification of isosorbide with dimethyl carbonate. The high activity in these reactions points to the strong basic sites (amine-basicity), as well as the high specific surface area (combining micro-mesopores) of the prepared basic carbon. Filtering off the basic carbon catalyst gave white (polycaprolactone) or transparent (isosorbide bismethyl carbonate) products with neutral pH, underlining the ease of catalyst/products separation. Finally, this catalyst is the 1st generation of such a plant-based carbocatalyst with basic functionality which can replace many homogenous catalysts due to its high activity and thermal stability.

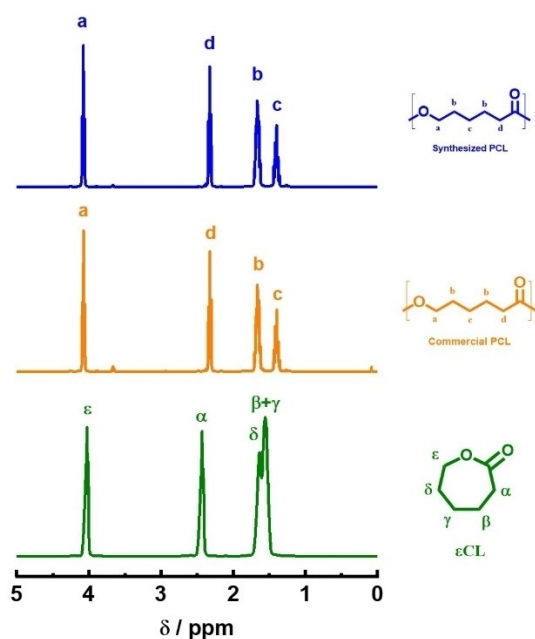


Figure 8. $^1\text{H-NMR}$ spectra of ϵCL , commercial PCL, and synthesized PCL obtained in CDCl_3 .

	M_w [g mol^{-1}]	M_n [g mol^{-1}]	\bar{D}	T_m [K]
Commercial PCL	35000	22600	1.5	338
PCL	30000	19500	1.2	338

Experimental Section

Catalyst preparation and characterization

The basic carbocatalyst was synthesized according to our standardized approach that we have previously reported. However, the details of the synthesis of the basic carbocatalyst are described in detail at ESI. The prepared basic carbocatalyst was characterized by elemental analysis via combustion analysis and inductively coupled plasma optical emission spectroscopy (ICP-OES), X-ray diffraction (XRD), N_2 sorption, thermogravimetric analysis (TGA), temperature programmed desorption of carbon dioxide (CO_2 -TPD), X-ray photo-

electron spectroscopy (XPS) and Scanning electron microscopy (SEM). The experimental procedure is described in detail at the ESI.

Catalytic experiments and products analysis

ϵ -Caprolactone (ϵCL) ring-opening polymerization

ϵ -caprolactone (ϵCL) ring-opening polymerization to polycaprolactone (PCL) was performed in a 250 cm^3 round bottom flask equipped with a condenser with a stirring plate and heating mantle. Prior to the experiment, the air was purged from the flask with a continuous flow of N_2 ($20\text{ cm}^3\text{ min}^{-1}$), then the system was closed and connected balloon filled with N_2 to guarantee that the experiments is performed under N_2 atmosphere (Figure S1 at ESI). In a typical experiment, 5.0 g of ϵCL and 0.3 g of basic carbon with a magnetic stirrer were introduced to the round bottom flask. Then, the flask was heated to 413 K with continuous stirring (600 min^{-1}) under N_2 atmosphere for 24 h. Upon the completion of the reaction, 10 cm^3 of THF was added to the formed viscous liquid, which dissolves the PCL and allows simple separation of the catalyst pellets from the viscous liquid via centrifugation with 9500 rmin^{-1} . After centrifugation, the dissolved polymer was precipitated in 30 cm^3 of pre-cooled methanol and resulted in a clean white polymer. Finally, the polymer was separated from methanol via centrifugation with 9500 rmin^{-1} and dried at 323 K in a vacuum oven. The reaction setup are shown in Figure S1 at ESI. The product analysis is described in detail at ESI.

Isosorbide transesterification with DMC

The catalytic transesterification of isosorbide (IS) to isosorbide bis(methyl carbonate) (ISBMC) was carried out in a 300 cm^3 stainless steel batch reactor with a head stirrer (Model # 4566), as well as an external temperature, pressure, and stirring speed monitor (Model # 4848) from Parr Instruments Company (Figure S2 at ESI). Typically, for the catalytic experiments, 0.5 g of basic carbon and 5.0 g of IS, and 100 cm^3 of dimethyl carbonate (DMC) were loaded into the reactor. After the reactor was sealed, the air was purged out of the reactor by flowing 3.0 MPa of Ar in the system for 15 min. The experiments were then carried out at 393 K, 600 rmin^{-1} under autogenous pressure for 2 h. Upon the completion of the reaction, the reactor was cooled down to room temperature, then the liquid sample was taken and analyzed via gas chromatography coupled with MS and FID (GC-MS and GC-FID), cf. ESI.

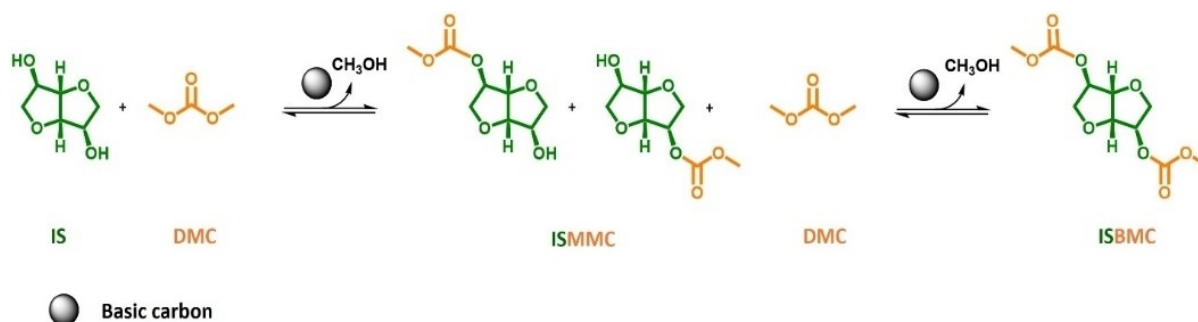


Figure 9. Synthetic pathway for the production of ISBMC via IS and DMC in the presence of basic carbon.

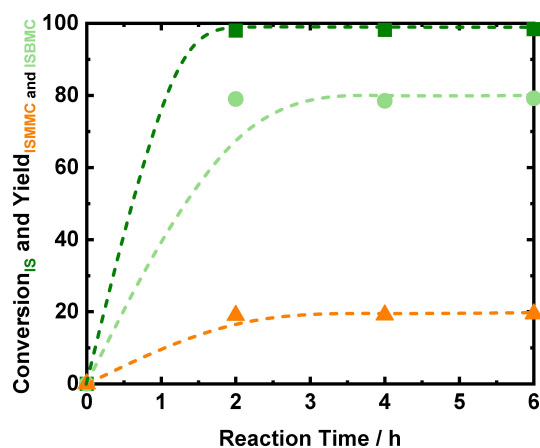


Figure 10. The conversion of isosorbide (IS) in dimethyl carbonate (DMC) as a solvent, as well as the yield of isosorbide monomethyl carbonate (ISMMC) and isosorbide bismethyl carbonate (ISBMC) over the prepared basic carbon as a function of reaction time; reaction conditions: $m_{IS} = 1$ g, $V_{DMC} = 100$ cm³, $m_{Catalyst} = 0.3$ g, $T = 493$ K, $n = 600$ min⁻¹, autogenous pressure.

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Conflict of Interest

The authors have no conflicts of interest.

Data Availability Statement

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

Keywords: bio-based building blocks · carbocatalysis · heteroatom-doped carbon · heterogeneous base catalysts · sustainable polymers

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