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Amine-grafted heterogeneous catalysts from waste for diols conversion into cyclic carbonates

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Keywords

Biomass waste valorization - renewable feedstock - thermochemical process - catalyst synthesis - pyrolysis - biochar - amine grafted biochar - heterogeneous catalysts - diols to cyclic carbonates - dimethyl carbonate - sustainability.

Abstract

The valorization of cellulose- and starch-based wastes has been investigated through a two-step methodology, aiming at the synthesis of amine grafted chars, tested as catalysts in the synthesis of cyclic carbonates from diols and dimethyl carbonate. Catalysts were prepared by subjecting the starting material to mild pyrolysis for obtaining biochars, followed by anchoring of 1,6 diamino-hexane on the surface of the char, performed in H_2O. This protocol has been applied to three different pristine polysaccharides (starch, cellulose and cellulose acetate) and wastes containing the same (post use starch-based plastics, fir sawdust and post use cigarette filters). The successfulness of the derivatization method was confirmed by XPS and elemental analyses. The obtained catalysts were effective and did not show any significant difference in terms of catalytic activity. Broad investigation on the reaction scope has been conducted on several mono- and di- substituted, aliphatic and aromatic 1,2 and 1,3 diols, giving carbonates in high yields and selectivity (up to 96% and 99%, respectively). Quantification of the active sites' density has been also performed, allowing to calculate TONs, TOFs and productivity values for each catalyst. The recyclability of the heterogenous catalysts has been also proved and characterization of the recycled materials confirmed this behaviour.

Introduction

Cyclic carbonates (CCs) are important molecules widely used in industry as they find application as polymer precursors (e.g. polycarbonates), fuel additives, aprotic high-boiling point solvents and ions carrier inside lithium batteries.[1] Although their synthesis starting from epoxides and CO_2 is very advantageous from various points of view (e.g. 100% atom economy reaction, use of CO_2),[2] some epoxides (i.e. ethylene oxide, propylene oxide, glycidol) have high toxicity, making the synthesis process poorly sustainable and less safe.[3] The carbonate interchange reaction (CIR), the trans-carbonation of a diol with a cyclic or linear carbonate,[4] is an interesting alternative for the synthesis of CCs. In fact, diols are usually less toxic than their epoxide

equivalents; moreover, the most used linear carbonate, dimethyl carbonate (DMC), is considered a green solvent, both for its properties and synthesis.[5] Since DMC can be potentially obtained from CO_2 and MeOH, the carbonate interchange reaction virtually consumes CO_2 and releases MeOH that can be cycled back to DMC from CO_2 process (Fig 1).[6–9] CIR can be catalysed using both acids or bases, however alkaline catalysts have demonstrated to be the most effective ones in terms of reaction rate and catalyst loadings.[10] Typical homogenous catalysts for CIRs with DMC include amines, amidines, guanidines, N-heterocyclic carbenes, phosphazenes, enzymes, organic salts, metal complexes and ionic liquids.[11–13] However the use of heterogenous catalysts should be prioritized over homogenous ones since their use allows simpler work up saving energy and material consumption. The heterogenous version of CIRs is poorly reported in literature, main examples are applied only for glycerol carbonate synthesis and include the use of metal oxides, zeolites or hydrotalcites;[14–16] while polystyrene-supported (PS) organic superbases of the amidine, guanidine and phosphazene-types represent an effective heterogenous system applied to a broader range of 1,2 diols.[17]

This evidence combined with our interest in the development of alternative ways for the recycling and valorisation of waste and biomass, the use of which could be beneficial to mitigate the enormous pollution and devastating climate consequences that our society is already experiencing, lead us to investigate a way to produce active heterogenous catalysts starting from several sources of waste polysaccharides for CIRs. Thermo-chemical processes (e.g., pyrolysis or hydrothermal conversion) are industrially growing technologies that play a significant role in waste recycling and valorization.[18] Specifically, pyrolysis process of biomass produces condensable volatiles (bio-oil, whose composition depends on the input biomass), non-condensable gases and a carbon rich solid (i.e. char or biochar) via externally supplied heat under an inert atmosphere.[19] Biochar is a carbon-rich material with varying physicochemical properties depending on the feedstock, the conditions adopted (e.g. time temperature, gradient), and the pre- and post- treatments applied.[20] A wide range of application is reported for these materials comprising carbon sequestration agents, activated carbons, adsorbents for pollutants and heavy metal removal and soil amendments.[21,22] Moreover, when properly functionalized through the grafting of specific functional groups, they can turn into versatile catalysts and/or catalyst supports active in several chemical reactions, such as CO_2 conversion into cyclic carbonates,[23] or biofuels production.[24–26]

To this purpose, we synthesized catalysts from three different polysaccharides (starch, cellulose and cellulose acetate) and corresponding wastes (starch-based plastics, fir sawdust and post-use cigarette filters) by adopting a two-step pyrolysis-based process. In the first step the materials were pyrolyzed to produce a char, enriched in surface functional groups; in the second step such functional groups were exploited to introduce amine functionalities and obtain amine grafted biochars that can act as basic catalysts. Such catalysts were then investigated in the synthesis of cyclic carbonates through the CIR of diols and DMC, and their recyclability was evaluated (figure 1). Characterization of the chars, the final catalysts and the recycled catalysts was also reported.

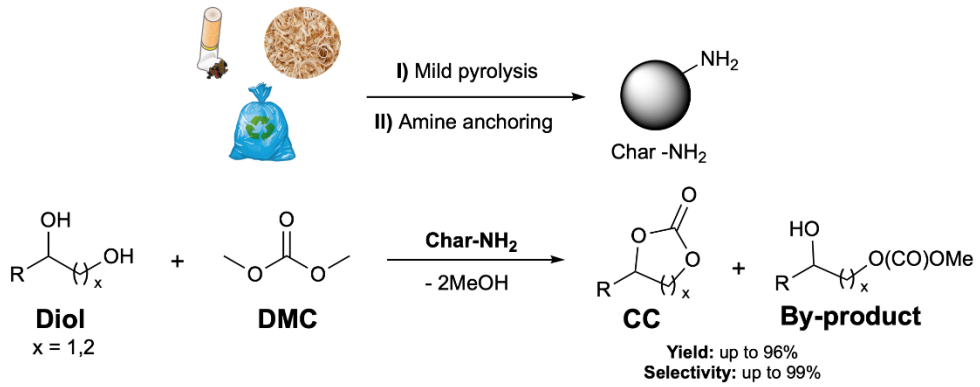


***Figure 1**. Synthesis of amine-grafted chars from cellulose and starch-based waste materials and their use in the CIR of diols with DMC.*

Experimental Section

Materials

All chemicals were purchased from Sigma-Aldrich and used without further purification. Starch-based plastics (SBP) were obtained from a local supermarket (Ravenna, Italy). Fir Sawdust (FSD) was purchased by a woodworking company (Salati e Montepietra s.r.l., Reggio Emilia, Italy). Post-use cigarette filters (PUCF) were self-obtained after smoking cigarettes.

Catalysts synthesis procedure

The catalysts reported in this work were synthetized following the 2-steps procedure here reported:

1. *Pyrolysis of polysaccharide-based materials.* Cellulose acetate (CA), pristine cellulose (PC), potato starch (PS), SBP, PUCF or FSD were subjected to bench-scale pyrolysis, using an apparatus consisting of a sliding sample carrier placed in a heated quartz tube connected to ice traps. The quartz tube was pre-heated by a cylindrical co-axial furnace at the desired temperature and purged by 1.5 L min^{-1} N_2 flow. Samples were placed into the heated zone of the quartz tube and kept for 3 h at 350 °C (measured temperature) under N_2 flow. The resulting char (C) was collected, powdered in a mortar, and used for the next step without further purification. Yields are reported in ESI, table S1.
2. *Anchoring of the amine group.* Char (150 mg) was added to a solution of 1,6-diamino hexane (1,6-DH, 10 w/w %) in H_2O (1 mL) in a closed-cap glass reactor. The mixture was magnetically stirred at 130 °C (measured temperature, oil bath = 140 °C) for 15 h, then the solution was filtered, and the catalyst washed several times with H_2O (500 mL) to remove unreacted 1,6-DH, until the pH of the washing solution became neutral. The resulting amine-grafted char (AC) was dried overnight at 70 °C under reduced pressure (100 mbar).

Characterization techniques for chars and catalysts

Elemental Analysis. The elemental composition of the chars and the catalysts was determined using an elemental analyzer (Thermo Scientific, Flash 2000, Organic Elemental Analyzer) through the flash combustion

technique. Samples were prepared by weighing an exact amount of sample, ranging from 2 to 5 mg, into a tin capsule.

Surface analysis. The surface elemental composition of the samples was investigated by XPS. The XPS measurements were performed by using an ESCALAB MkII spectrometer (Vacuum Generator Ltd., Green East, UK), equipped with a monochromatic Al X-ray source (hν = 1486.6 eV) and five-channeltrons as a detection system. The spectra were acquired operating in constant pass energy of 50 eV, while the accuracy was ± 0.1 eV. The binding energy (BE) calibration was carried out positioning the contribution of aliphatic carbon at BE = 285.0 eV. All samples were mounted fixing the powder on Au foil by mechanical pressure. All data were collected and processed by Avantage v.5 (Thermo Fischer Scientific Ltd., Green East, UK).

Representative procedure for the synthesis of cyclic carbonates

In a typical experiment, the diol (1 mmol, 1 eq), the catalyst (5-10% w/w respect to the diol) and dimethyl carbonate (5-10 mmol, 5-10 eq) were weighed into a closed-cap glass reactor equipped with a magnetic stirring bar. The CIR was carried out under magnetic stirring at 130 °C for 3 h (oil bath = 140 °C, optimized reaction conditions). After reaction completion, the reactor was cooled to rt and the mixture was centrifuged at 4500 rpm for 5 min. The supernatant was analyzed by GC-MS after silylation with *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA, see below) to check conversion and then collected in a round-bottom flask while the solid catalyst was recovered and dried for analysis/recycle. The separated organic mixture (surnatant) was distilled to remove DMC and isolate the cyclic carbonate product for further characterizations.

All obtained carbonates are present in the literature; thus, they were recognized by comparison through NMR and mass spectra. [27–30] Selectivity was determined by ^{1}H-NMR spectroscopy and GC-MS. TONs have been calculated as mol of cyclic carbonate obtained over moles of active sites contained in the AC used. The moles of active amine on grams of ACs (mmol/g) have been determined through XPS analysis.

Catalyst recycling

The recycling of the catalysts in the conversion of 1,2-hexanediol (1,6-HD, 1 mmol) into the corresponding cyclic carbonate was tested using AC-FSD or AC-PS (10% w/w), 10 eq. DMC, 130 °C in 3 h. At the end of the reaction, the catalyst was separated by centrifugation and then washed twice with ethyl acetate. The collected organic phases were evaporated to isolate the product, while the solid catalyst was dried under reduced pressure. The recovered catalyst was weighed to check any mass loss and used for the next runs without further purification.

Analysis for reactions monitoring and product characterization

Sample derivatization. For GC-MS analysis, crude samples were silylated according to the following procedure: a sample aliquot (1− 2 mg) was treated at 70 °C for 30 min with 0.1 mL EtOAc, 0.08 mL

bis(trimethylsilyl)trifluoroacetamide containing 1% of trimethylchlorosilane, and 0.02 mL of pyridine and further diluted with 0.9 mL EtOAc prior to injection.

GC-MS analysis. *GC*-MS analyses were performed using an Agilent HP 6850 gas chromatograph connected to an Agilent HP 5975 quadrupole mass spectrometer. Analytes were separated on a HP-5MS fused-silica capillary column (stationary phase 5%-Phenyl)-methylpolysiloxane, 30 m, 0.25 mm i.d., 0.25 µm film thickness), with helium as the carrier gas (at constant pressure, 36 cm s^{-1} linear velocity at 200 °C). Mass spectra were recorded under electron ionization (70 eV) at a frequency of 1 scan s^{-1} within the 12–600 m/z range. The injection port temperature was 250 °C. The temperature of the column was kept at 50 °C for 5 min, then increased from 50 to 250 °C at 10 °C min^{-1} and kept at 250 °C for 10 min.

Nuclear Magnetic Resonance. ^{1}H NMR spectra were recorded on Varian 400 (400 MHz) spectrometers. ^{13}C NMR spectra were recorded on a Varian 400 (100 MHz) spectrometers. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (deuterochloroform: 7.26 ppm).

Results and Discussion

Synthesis of the catalysts (AC)

The heterogeneous catalysts were obtained following a 2-step synthetic pathway: a) low T pyrolysis of the starting material, obtaining a char (C); b) anchoring of 1,6-DH on the surface of the char, to give amine grafted char catalyst (AC). Preliminary experiments were performed on a char obtained from potato starch at 420°C for 15 h (C-420), already reported in previous works,[23,31] monitoring all the steps through elemental analysis (CHN). When direct functionalization of the char C-420 with 1,6-DH was performed, obtaining $AC_{no\text{-}ox}$, almost no nitrogen was detected by elemental analysis and no CIR was observed (Entry 2, Table 1). The same held for C-420 used as it is without any further treatment after pyrolysis (Entry 1, Table 1). However, when a char rich in oxygen functionalities, labelled OC, was obtained from C-420 upon mild oxidation with H_2O_2,[23] it was properly functionalized with 1,6-DH, resulting in an active catalyst (Entry 4, Table 1). The OC was also tested and it was not active (Entry 3, Table 1).

Table 1. *Elemental composition and activity of the functionalized chars obtained upon high T pyrolysis preliminary derivatization pathway of potato starch.*

Entry	Sample	Elemental composition [a]			H/C	CIR conversion (%) [b]
		N [%]	C [%]	H [%]		
1	C-420	/	82.8 ± 0.3	2.7 ± 0.1	0.39	0
2 [d]	$AC_{no\text{-}ox}$	0.4 ± 0.1	80.9 ± 0.3	3.7 ± 0.1	0.55	1
3 [c]	OC	/	63.8 ± 0.4	3.3 ± 0.1	0.62	0
4 [d]	AC_{ox}	4.2 ± 0.1	60.5 ± 0.2	4.7 ± 0.1	0.93	95

[a] Mean ± standard deviation of three independent replicates. [b] CIR conditions: Hexanediol (1 eq.), DMC (10 eq), 130 °C for 3h. [c] Oxidation conditions: C-420, H_2O_2, 80 °C for 17h. [d] Amination conditions: C-420 or OC, H_2O, 1,6-DH, 130 °C for 15h

Since the presence of oxygen functional groups was necessary for the anchoring of 1,6-DH on the char surface, a milder pyrolysis experiment was conducted on the starting material at 350 °C for 3h (Table 2). This was done to keep more functionalities on the char after the thermal treatment, avoiding performing the oxidation step. Indeed, when lower pyrolysis temperatures (< 400 °C) are applied for shorter time, a less aromatic char with higher amount of reactive C-C double bonds and oxygen groups is obtained. This results in higher H/C ratio and more carbonyl functionalities, that are lost when the temperature is above 350 °C.[32,33] The char obtained after the mild pyrolysis of potato starch (Entry 1, Table 2) showed lower carbon content (76.8 vs 82.8%) and higher H/C ratio (0.39 vs 0.5) than the one obtained using harsher pyrolysis conditions (Entry 1, Table 1); this corresponds to higher oxygen content and lower aromaticity of the former compared to the second, confirming the above mentioned behavior. When C-PS was subjected to the amination treatment with 1,6-DH, nitrogen content significantly increased (Entry 1, Table 2), attesting the successful anchoring of the amine functionality on the char surface, through the formation of C-N covalent bonds and ammonium carboxylates interactions (see next paragraph).

Table 2*. Elemental composition (expressed in wt%) of the chars derived from different materials after pyrolysis and after amination*

Entry	Char Source	After Pyrolysis (C) [a,b]				After amination (AC) [a,c]			
		N [%]	C [%]	H [%]	H/C	N [%]	C [%]	H [%]	H/C
1	Potato Starch (PS)	-	76.8 ± 0.2	3.2 ± 0.1	0.50	2.4 ± 0.1	70.9 ± 0.2	4.1 ± 0.3	0.70
2	Pristine Cellulose (PC)	-	75.6 ± 0.5	2.8 ± 0.2	0.45	2.2 ± 0.2	64.9 ± 0.4	4.5 ± 0.2	0.83
3	Cellulose Acetate (CA)	-	76.6 ± 0.3	3.1 ± 0.1	0.48	2.1 ± 0.1	64.4 ± 0.5	4.4 ± 0.1	0.83
4	Starch Based Plastics (SBP)	0.1 ± 0.1	55.8 ± 0.4	3.1 ± 0.1	0.66	1.5 ± 0.1	49.1 ± 0.2	3.4 ± 0.2	0.83
5	Fir Sawdust (FSD)	0.15 ± 0.1	79.7 ± 0.3	3.5 ± 0.2	0.53	2.1 ± 0.2	72.4 ± 0.4	4.8 ± 0.2	0.79
6	Post-Use Cigarette Filters (PUCF)	1.14 ± 0.2	71.3 ± 0.2	2.8 ± 0.1	0.48	3.4 ± 0.3	69.1 ± 0.3	4.1 ± 0.1	0.72

[a] Mean ± standard deviation of three independent replicates. [b] Pyrolysis conditions: N_2 flow, 350 °C for 3h. [c] Amination conditions: C, H_2O, 1,6-DH, 130 °C for 15h

The two-step optimized procedure was then applied to three different polysaccharides (Entries 1-3, Table 2) and the corresponding wastes (Entries 4-6, Table 2). The successfulness of the functionalization was monitored by elemental analysis (Table 2). While the overall composition could be considered similar, some differences appear in the carbon and nitrogen content of the chars depending on the starting material:

- SBP char shows a lower quantity of carbon than the other chars, already from the first pyrolysis step (Entry 4, Table 2). This behavior, already observed in other works,[23,31] may be due to the chemical composition of SBP: in addition to starch, corresponding to 28% of the total weight and responsible of the majority of the char produced, the main component is poly-(butylene adipate-co-terephthalate) (64%), PBAT, a co-polyester which, if subjected to pyrolysis, tends to form less amount of char than starch, as already observed and confirmed by the lowest pyrolysis yield respect to the other materials (see ESI, table S1); 4-6% of plasticizer (usually sorbitol); 2-4% of inorganic compounds

(including $CaCO_3$ and TiO_2 as major components), which are responsible for decreasing the carbon content as they remain in the char fraction.[34]

- PUCF char shows a higher N amount than the other chars (1.14 vs 0.1 %) due to the presence of amines, like nicotine and cotinine, adsorbed on post use cigarette filters, released upon tobacco combustion (Entry 6, Table 2).[35–37] Due to the presence of non-negligible nitrogen content, the C-PUCF was tested in the CIR, to verify if a further amination step was still necessary: no CC was observed, demonstrating the need to perform the second step.

Surface chemical characterization of the chars

The surface chemical composition of the chars after pyrolysis (C) and after amination (AC), was investigated by X-ray photoelectron spectroscopy (XPS), in order to identify the chemical state of the char atoms and to hypothesize the reactions that lead to the synthesis of AC. In agreement with the elemental analysis, ~~the~~ XPS measurements confirmed that the tested materials have similar composition after the derivatization process (see ESI, Tables S2-S9). As can be seen in figure 2, the survey scans of C-PS and AC-PS, reveal the presence of C 1s, O 1s, Ns 1s and Si 2p. The small amount of silicon is probably related to the surface contamination of samples due to laboratory glassware. On the other hand, the presence of N 1s signal in the AC samples testifies to the successful anchoring of 1,6-DH to the char, after the second reaction step and the washing of the catalyst with H_2O. The inset of figure 2, shows the high-energy resolution N 1s spectrum, that is characterized by two contributions assigned to C-N and C=N bonds (BE = 400 eV), and a smaller one assigned to ammonium bonds (BE = 402.0-403.0 eV). [38–41]

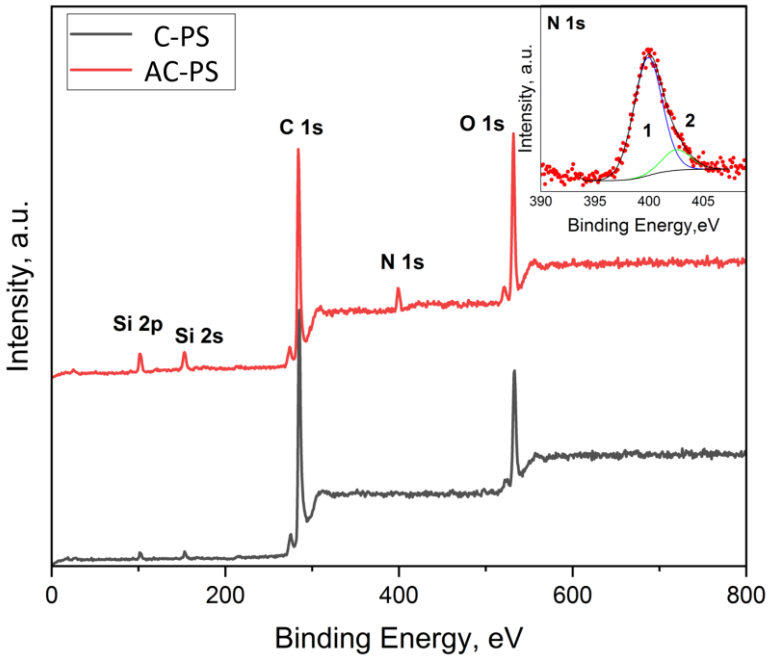


Figure 2. *Survey scans comparison of C-PS and AC-PS samples. In the inset figure is shown the high-energy resolution N 1s spectrum of AC-PS sample: component **1**. C-N and C=N bonds; component **2**. ammonium bond.*

The obtained results confirm that 1,6-DH is mostly grafted on the surface of the char covalently, probably through amidation, condensation, hydroamination and/or aza-Michael reactions (when α,β-unsaturated carbonyl are present), and, in a minor contribution, ionically, through ammonium carboxylates interactions (Figure 3). The C 1s signal of the chars after the first step of pyrolysis evidence the presence of three contributions positioned at BE = 285.0 eV, 287.0 eV and 289.0 eV, assigned to aliphatic carbon, C=O carbonyl bonds and C-O carboxylic functionalities, respectively.[40,42–44] The same contributions are found in the C 1s signals of the catalysts, since both the C-N amine, imine and amide bonds are characterized by similar binding energy values: 1) amines/imines - BE = 286.0 - 287.0 eV; 2) amides - BE = 289.0 eV (Figure 4). [40,41,44]

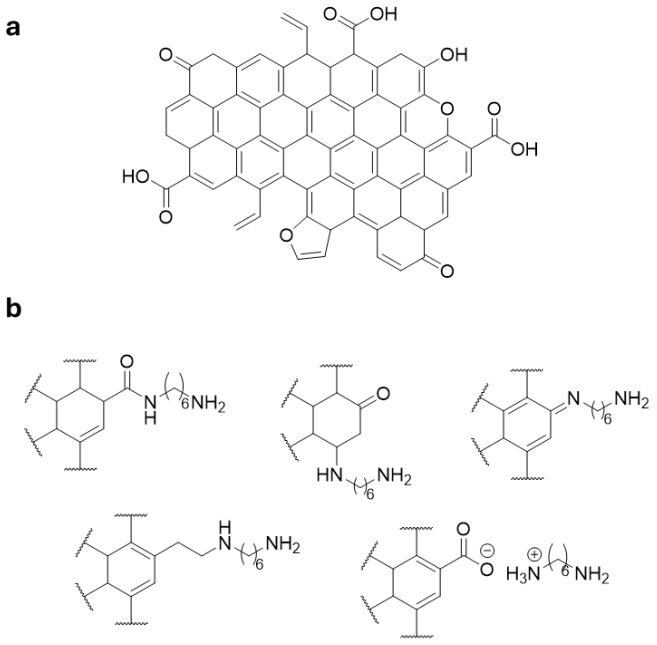


Figure 3. *Structure of the char and catalyst:* ***a****) A tentative model structure of the chars after pyrolysis was given, based on the characterization results (elemental analysis and XPS);* ***b****) possible bonds and interactions of 1,6-DH with the char surface, based on XPS results.*

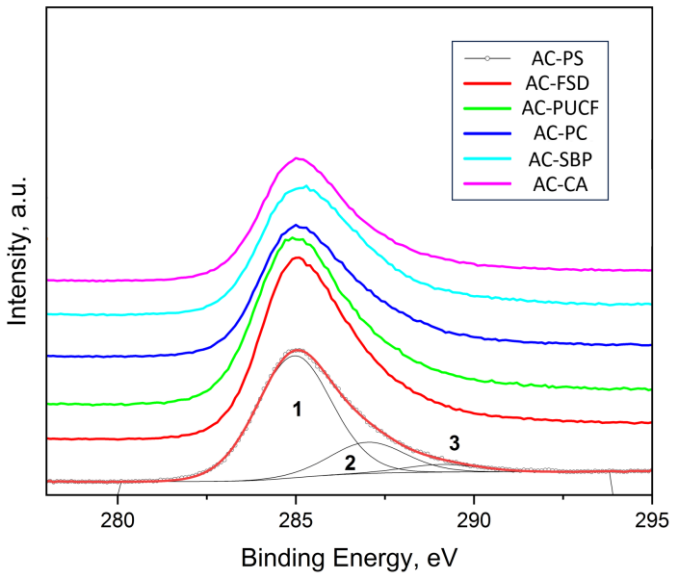


Figure 4. *Comparison of the C 1s signals for ACs:* ***1.*** *aliphatic carbon;* ***2.*** *C=O, C-N, C=N bond;* ***3.*** *carboxylic/amide group.*

The XPS results thus demonstrate the effectiveness of the two-step derivatization protocol and its versatility towards several polysaccharidic sources. XPS quantitative analysis allows to determine the N atomic concentration (at%) at the char surface, letting to quantify the N-containing groups concentration, and hence the catalytic performances. The concentration of the amine groups grafted on the surface of AC, reported in mmol/g, highlights that all synthetized catalysts have comparable number of active sites (Table 3).

Table 3*. Surface amine active sites quantification by XPS*

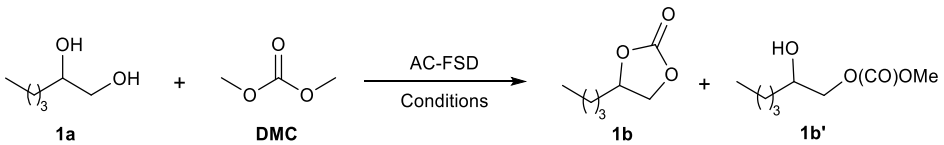
Entry	Catalyst	Active sites (mmol/g)
1	AC-PS	2.9
2	AC-PC	2.8
3	AC-CA	3.2
4	AC-SBP	1.2
5	AC-FSD	3.0
6	AC-PUCF	3.1

Only AC-SBP has lower amount of amine grafted (1.2 mmol/g, Entry 4, Table 3), as also evidenced by elemental analysis (Entry 4, Table 2): this could be due to the lower amount of carbon, given by the presence of other inorganic compounds (e.g. $CaCO_3$ or TiO_2), that decrease the amount of graftable 1,6-DH respect to other materials. To support this, the XPS measurement of AC-SBP shows the existence of Ca atoms given by the $CaCO_3$ used as additive. XPS quantitative analysis, BE value and comparison of all the AC samples are reported in ESI, tables S2-S9 and figure S1.

Synthesis of cyclic carbonates with the amine catalysts

The CIR between 1,2-hexanediol (1,2-HD, **1a**) and DMC to give 1,2-hexylene carbonate (1,2-HC, **1b**) catalyzed by the amine catalyst obtained from fir sawdust (AC-FSD) was chosen as a model reaction for the optimization of the reaction parameters (Table 4), and the comparison of the catalytic activities of all the synthetized materials (Table 5).

Table 4*. Screening of the reaction conditions for the CIR of 1,2-HD with DMC catalyzed by AC-FSD.*



Entry	Cat. Amount (% w/w)	DMC equivalents	T[a] (°C)	t (h)	Conversion[b] (%)	Selectivity[c] (%)
1	10	10	90	4	0	-
2	10	10	100	4	0	-
3	10	10	110	4	9	98
4	10	10	120	4	30	99
5	10	10	130	3	95	99
6	10	10	130	2	82	99
7	5	10	130	3	93	99
8	10	5	130	3	90	98

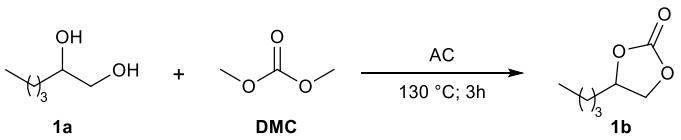
9	5	5	130	3	89	99
10	5	2.5	130	3	13	98
11	2.5	5	130	3	68	98

[a] When T > 90 °C autogenous pressure is present. [b] Conversion obtained by GC-MS analysis, expressed as mean of two independent replicates. [c] Selectivity toward 1b was calculated by GC-MS and ^{1}H-NMR on crude products.

When using 10% w/w of AC-FSD, the conversion of the diol to the corresponding cyclic carbonate started to be efficient at 130 °C with 10 equivalents of DMC (table 4, entry 5-6), while no or partial conversion was observed when testing lower temperatures (90-120 °C, table 4 entries 1-4). Decreasing the catalyst amount to 5% w/w or the DMC equivalents to 5, had a slightly hampering effect on the CIR conversion (table 4, entries 7-9), while when using 2.5 % w/w of catalyst or 2.5 equivalents of DMC the CIR conversion was significantly lower (table 4, entries 10-11). Using less DMC equivalents could be beneficial in order to let the process more easily scalable due to the halved volume of the reaction. Moreover, working with less catalyst could be beneficial for the work up procedure, letting to use less solvent to wash it. The selectivity of the CIR toward the cyclic product was always >98%, meaning that only negligible quantities of the open by-product (**1b'**) were formed during the reaction.

After the optimization of the reaction conditions for AC-FSD, the activity of all the other catalysts synthesized was explored (Table 5).

Table 5. *Results for the CIR of 1,2 HD and DMC catalyzed by all the ACs synthetized*



Entry[a]	Catalyst	Cat. Amount (% w/w)	DMC equivalents	Yield[b,c] (%)	TON[d]	TOF[e] (h^{-1})	Productivity[f] (h^{-1})
1	AC-FSD	10	10	95	26.4	8.8	4.3
2		5	5	89	49.4	16.5	8.1
3	AC-PUCF	10	10	92	24.7	8.2	4.2
4		5	5	88	47.3	15.8	8.0
5	AC-SBP	10	10	89	61.8	20.6	4.1
6		5	5	82	113.9	38.0	7.5
7	AC-PC	10	10	90	26.8	8.9	4.1
8		5	5	85	50.6	16.9	7.7
9	AC-CA	10	10	96	25.0	8.3	4.4
10		5	5	90	46.9	15.6	8.2
11	AC-PS	10	10	94	27.0	9.0	4.3
12		5	5	89	51.1	17.0	8.1

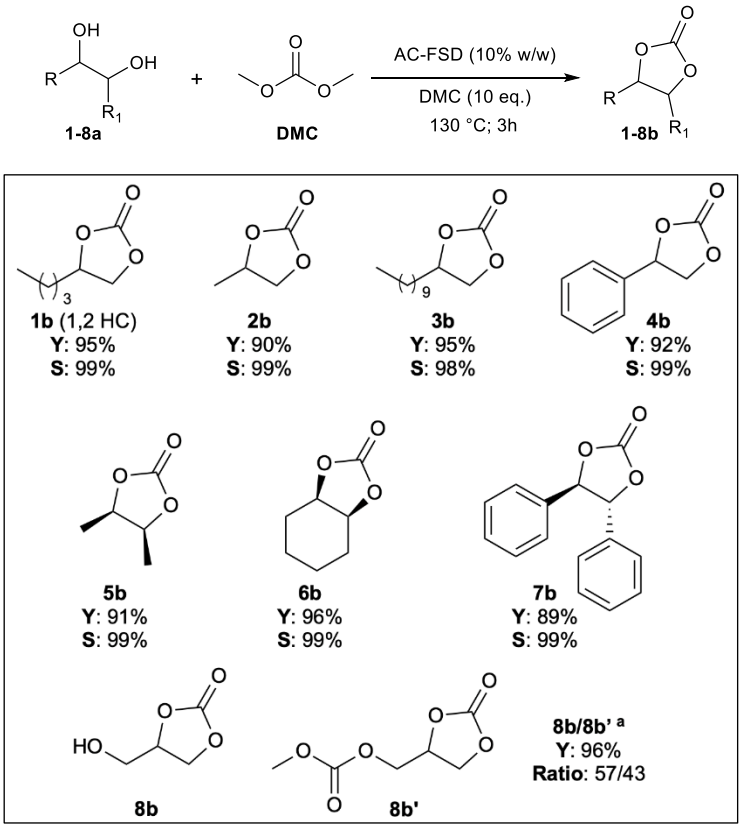
[a] Reaction conditions: 1 mmol 1,2-HD, 130 °C, 3h. [b] Yields of 1,2-HC are given as the average after two independent reactions. [c] Selectivity toward 1b was 99% for all entries. Selectivity was calculated by GC-MS and ^{1}H-NMR on crude products. [d] Turnover number, defined as mol_{SC}/mol_{Amine}. [e] TOF = TON h^{-1}. [f] Productivity=$[g_{sc}/(g_{cat}\ h^{-1})]$.

The amine grafted chars were tested at 5 and 10 % w/w with 5 or 10 equivalents of DMC, adopting the conditions optimized for AC-FSD (130 °C, 3h), all demonstrating similar and high activity in the conversion of 1,2-HD to 1,2-HC (table 5). This behavior is further confirmed by the similar chemical composition previously observed through XPS and elemental analysis, not showing significant differences between most of the ACs.

Only AC-SBP reported an active sites density of 1.2 mmol/g vs an average 3 mmol/g for other ACs (table 3). However, it still gave similar yields to other catalysts probably due to the presence of $CaCO_3$ that, even if characterized by a low activity alone,[10] in combination with the amine grafted char could promote to the CIR.

AC-FSD was then used to investigate the substrate scope under the previously described optimized reaction conditions (Figure 5). Both aromatic and linear mono-substituted 1,2-diols were efficiently converted to the corresponding cyclic carbonate with yields up to 95% and 99% selectivity (**1-4b,** Figure 5). The same was observed for di-substituted 1,2-diols: linear, aromatic and cyclic diols gave high yields, up to 96%, and selectivity of 99% (**5-7b**, Figure 5). This is of a great importance since 1,2-disubstituted cyclic carbonates are particularly challenging molecules to obtain starting from CO_2 and disubstituted epoxides, while the reported trans-carbonation of diols with DMC allows to easily obtain this class of compounds. Glycerol (**8a**) was also tested to obtain glycerol carbonate (1,2-GC, **8b**): high conversion was observed for the cyclic compound (96% yield), however, the reaction went further, since also the hydroxyl group of glycerol carbonate was partially carbonated, obtaining a mixture of 1,2-GC and methyl ((2-oxo-1,3-dioxolan-4-yl)methyl) carbonate (**8b** vs **8b'**, 57:43 Figure 5).

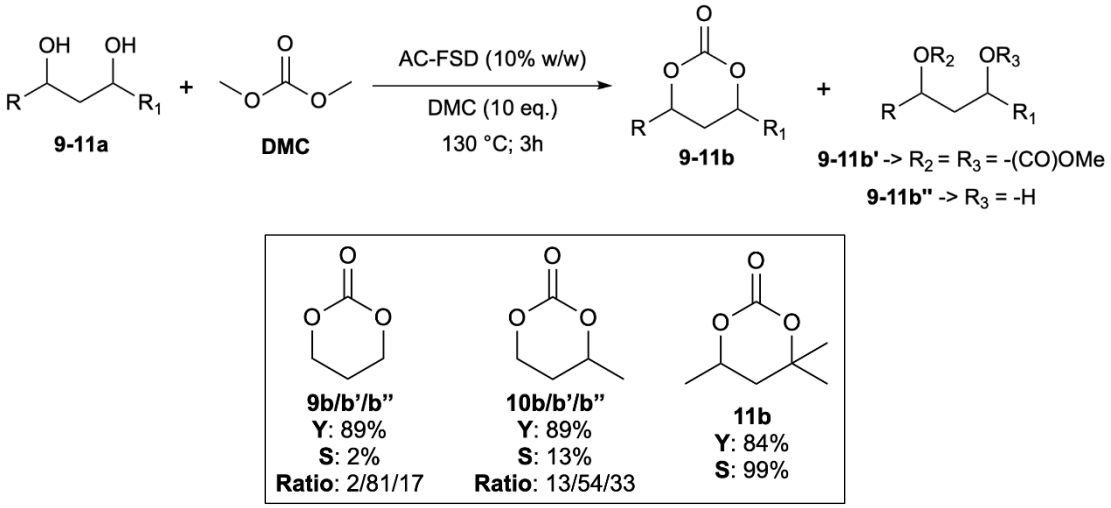
Figure 5. *CIR of different substituted 1,2-diols with DMC catalyzed by AC-FSD to form cyclic carbonates. Yield (**Y**) of the product and by-product together, isolated as a mixture, is given as the average after two independent reactions. Selectivity (**S**) toward **b** and ratio were calculated by GC-MS and ^{1}H-NMR on crude products.*



[a] The yield is expressed on the mixture 8b/8b'

When 1,3-diols are used, it was observed that less substituted one gave higher yields of open chain products, in agreement with the literature results:[27] 1,3-propanediol gave only 2 % of the cyclic compound (**9b**), with mono- and di- methyl open carbonates being the major products with 18% and 81% respectively (**9b''/9b'**, Figure 6); 1,3-butanediol gave only 13% of the cyclic product (**10b**) with 33% and 54% of mono- and di- methyl open carbonates respectively (**10b'/10b''**, Figure 6); 2-methyl-2,4-pentanediol gave the corresponding CC as the sole major product, with 84% yield and 99% selectivity (**11b**, Figure 6). This could be explained by the fact that less substituted 1,3-diols do not have steric hinderance: this reflects in longer distance between the two hydroxyl groups, respect to the more substituted 1,3-diols, that can rotate more easily on their bonds, not allowing stable cyclic intermediates, necessary for the ring closure.[27] This behavior allows the free hydroxyl group left on the linear mono-carbonate intermediate to interact more with other DMC molecules, reacting intermolecularly and giving the linear di-carbonate. On the other hand, more substituted 1,3-diols, due to the steric hinderance that hampers the free rotation, that favors more stable cyclic structure intermediates, are protected from interacting with other DMC molecules and react intramolecularly, with a slower rate, as evinced by the lower yield.

Figure 6. CIR of substituted 1,3-diols with DMC catalyzed by AC-FSD to form cyclic or linear carbonates. *Yield (**Y**) of the product mixture (b/b'/b''), isolated as a mixture, is given as the average after two independent reactions. Selectivity (**S**) toward **b** and ratio were calculated by GC-MS and ^{1}H-NMR on crude products.*



Finally, recyclability tests were performed on AC-FSD and AC-PS using the model reaction of 1,2-HD to 1,2-HC, in the previously described optimized reaction conditions (catalyst loading 10% w/w, 10 eq. DMC, 130 °C, 3h). At the end of the reaction, the catalyst was separated by centrifugation, washed twice with EtOAc and then dried under reduced pressure as described in the experimental section. Both AC-FSD and AC-PS resulted to be recyclable over 5 times, with no appreciable loss of catalytic activity (Figure 7).

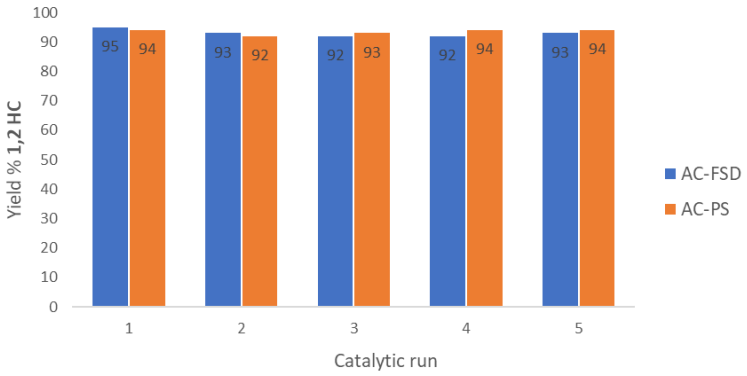


Figure 7. *Recycling catalytic test for the CIR of 1,2 HD and DMC catalyzed by AC-FSD and AC-PS. Reaction conditions: 1 mmol 1,2-HD, 10 eq. DMC, catalyst loading 10% w/w, 130 °C, 3h. Isolated yields are given as the average after two runs. Selectivity was 99% for all catalytic runs.*

Characterization of the recycled catalysts was also performed to check if significant changes in chemical composition happened during the CIR. Elemental analysis showed a slight decrease in nitrogen, carbon and hydrogen content after 5 cycles for both AC-FSD and AC-PS (Table 6). Same evidence was observed when the surface chemical composition analysis through XPS was performed (Figure 8) both AC-FSD and AC-PS showed a slight decrease in nitrogen content (avg. C/N ratio 22 vs 16) in favor of a slight increase in oxygen content (avg. C/O ratio 2.7 vs 3.5). Comparison of the intensity of C 1s peaks can be found in ESI, figure S1. This result could be explained by a minimal amount of DMC grafted on the catalyst under the reaction conditions adopted, since XPS shows a slight increase of the C=O contribution in the O 1s signal (BE = 533). Overall, the recycled catalysts showed negligible differences in comparison to the fresh ACs, as demonstrated by the unchanged catalytic activity and chemical composition.

Table 6. *Elemental composition of AC-FSD and AC-PS after 5 catalytic runs*

Catalyst	**Elemental composition**			
	N [%]	**C [%]**	**H [%]**	**H/C**
AC-PS$_r$	2.10	68.54	3.70	0.65
AC-FSD$_r$	1.90	69.95	4.40	0.75

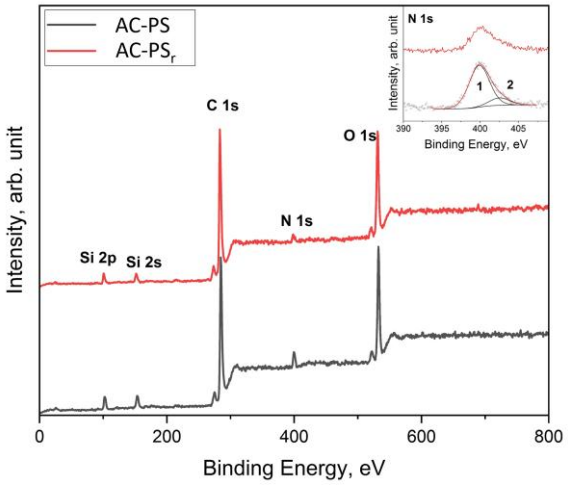
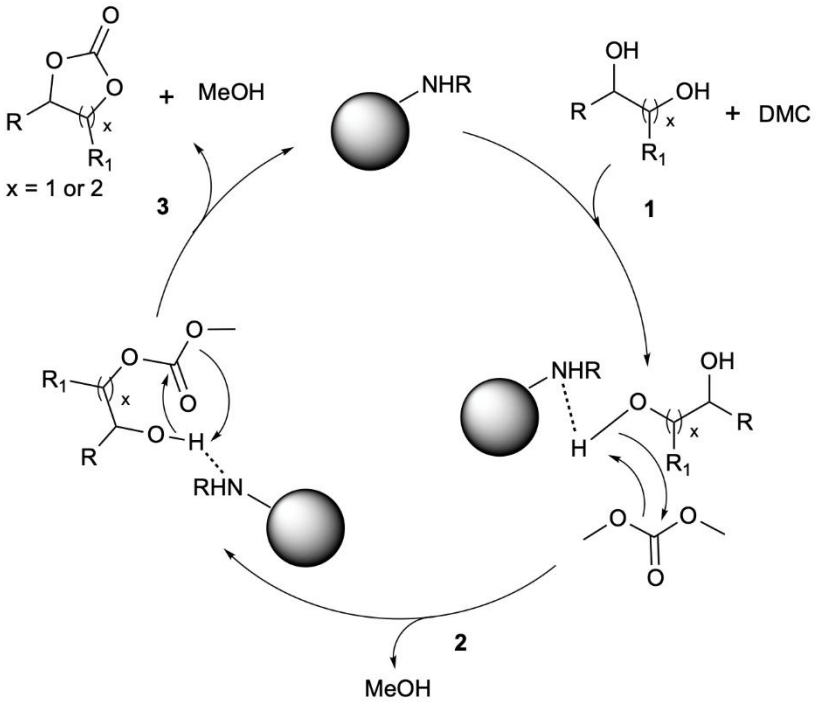


Figure 8. *AC-PS survey scans comparison of fresh catalyst and after 5 catalytic runs (AC-PS$_r$).*

Hypothesis of reaction mechanism

A reaction mechanism has been hypothesized for the studied reaction (Scheme 1). Since the trans carbonation is catalyzed by a mild base (i.e. amine), it is plausible that the free electron pair of nitrogen could interact with the hydrogens of the diol through H-bonding. This interaction would weaken the O-H bond that will be more favourable to the nucleophilic attack to the carbonyl group of DMC, giving the trans-carbonation reaction. During the reaction it is possible that the catalyst amine active site is slightly functionalized through amidation or methylation reaction operated by DMC, as already described elsewere,[5] hence R = -H, -Me or -CO)OMe.



Scheme 1. *Reaction mechanism hypothesis for the trans-carbonation of a diol with DMC catalyzed by amine grafted char,* R = -H, -Me or -(CO)OMe.

Conclusions

This work reports a novel versatile methodology for the synthesis of amine grafted chars, starting from pristine polysaccharides (PS, PC and CA) and waste materials (SBP, FSD and PUCF). The use of mild pyrolysis conditions (e.g. low T and short residence time) for the obtainment of a char that could be easily functionalized, constitute important finding for sustainability, since this can avoid additional energy and material consuming steps. The amine grafted chars were used as heterogenous catalysts for converting different substituted 1,2- and 1,3-diols into their corresponding cyclic or open carbonates with DMC, all demonstrating high catalytic activity. The catalysts were characterized through elemental analysis and XPS, showing similar functionalities and compositions in all the materials produced, further demonstrating high versatility of the AC synthesis protocol. Moreover, catalysts from sawdust and starch were easily and fully recyclable over five cycles with no appreciable activity loss, as also evinced by the chemical composition. These results show an example that meet the need of obtaining cyclic carbonates with safe reagents and

easy conditions through the virtuous use of DMC (potentially obtainable from CO_2), and valorising polysaccharidic wastes, that represent a significant part of the solid garbage and constitute a big concern for the waste management system.

Author contributions

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A. Parodi: conceptualization, investigation, methodology and validation of the work. Writing of original draft and visualization. M. Merendino: investigation. M. Vagnoni: preliminary conceptualization and investigation. A. Mezzi: investigation and review (concerning XPS analysis). C. Samorì and P.Galletti: review, funding acquisition.

Conflicts of interest

There are no conflicts to declare.

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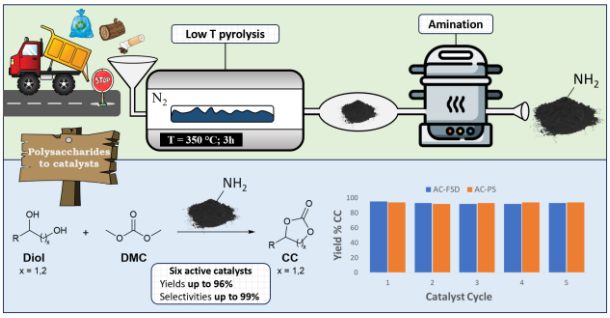
Synopsis: A novel and versatile protocol for the synthesis of recyclable heterogenous catalysts, active in the trans carbonation of a diol to cyclic carbonates, from several polysaccharidic waste sources.

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