ADVANCED SUSTAINABLE SYSTEMS

Supporting Information

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Upcycling Waste Biomass–Production of Porous Carbonaceous Supports from Paper Mill Sludge and Application to CO_2 Conversion

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Table of Contents

1. Experimental

1.1. Reagents

Commercially available reagents were used without any further purification. Chitosan (degree of deacetylation 76%, low molecular weight), poly(diallyldimethylammonium chloride) solution − 20 wt.% in H_2O, sodium dicyanamide 96%, styrene oxide 97%, anion exchange resin Amberlyst A-26 (OH^- form), potassium chloride, tetrabutylammonium chloride (TBACl) >97%, and 1-butyl-3-methylimidazolium chloride (ImCl) were all purchased from Sigma-Aldrich (St. Louis, MO, USA). 1-Butyl-4-methylpyridinium chloride (2PyCl), 1-butyl-2-methylpyridinium chloride (4PyCl, and 1-butyl-1-methylpyrrolidinium chloride (PyrCl) were purchased from Iolitec (Heilbronn, Germany). Chloroform-*d* and deuterium oxide were purchased from Euriso-top (Saint-Aubin, France). Ethanol 96%, acetone, and lithium chloride anhydrous were purchased from Honeywell (Charlotte, NC, USA). Trichloromethane was purchased from PanReac AppliChem ITW Reagents (Barcelona, Spain). Tetrabutylammonium bromide was purchased from TCI (Tokyo, Japan). Carbon dioxide (>99.9%) and compressed nitrogen (>99.8%) were obtained from Air Liquide. Vinylbenzyltriethylammonium chloride and poly(vinylbenzyltriethylammonium) chloride were synthesized and kindly provided by a member of this research team, Raquel Barrulas. Paper mill waste sludges − primary and biological sludge − and knots were kindly supplied by The Navigator Company (Setúbal, Portugal). The water used was MilliQ water.

1.2. Characterization

Nuclear magnetic resonance (NMR) spectra were recorded at room temperature on a Bruker Avance III 400 spectrometer operating at 400.15 MHz Larmor frequency for hydrogen and 100.61 MHz for carbon with a Bruker High-Resolution BBO probe. This spectrometer is equipped with a temperature control unit and a pulse field gradient unit capable of producing magnetic pulsed field gradients in the z-direction of 50.0 G/cm. ^{1}H NMR spectra were acquired with 64 K time domain points over a spectral window of 8012.820 Hz and with 16 scans per FID. Data processing was carried out using Bruker Topspin 3.5 software. Chloroform-*d* was used for NMR analysis of the catalytic conversion. Scanning electron microscopy was performed on a Carl Zeiss AURIGA CrossBeam workstation instrument equipped with an Oxford X-ray Energy Dispersive Spectrometer. The images were analyzed using ImageJ software (v1.50i). Raman spectra were collected using a Labram300 Jobin Yvon spectrometer, equipped with a HeNe laser 17 mW operating at 632.8 nm. The spectra were acquired in the range of 1800 to 100 cm^{-1}. Data processing was

carried out with Origin 9 software. Nitrogen adsorption/desorption experiments and CNHS elemental analysis were outsourced to LAQV/REQUIMTE – the Associated Laboratory for Green Chemistry at NOVA School of Science and Technology (FCT NOVA). Nitrogen adsorption/desorption isotherms were obtained from a gas porosimeter Micromeritics ASAP 2010 at 77 K. CNHS elemental analysis was carried out in an Elemental analyzer Thermo Finnigan-CE Instruments Flash EA

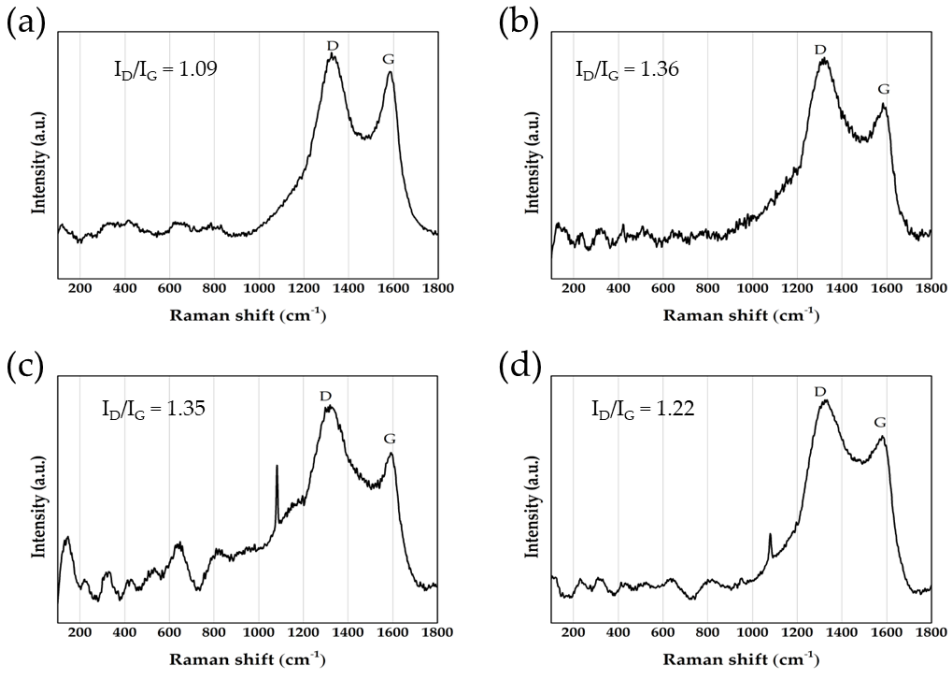

Figure S1. Raman spectra of starting materials: (a) Nod-0. (b) PriS-0 (c) BioS-0. (d) BioS-Im.

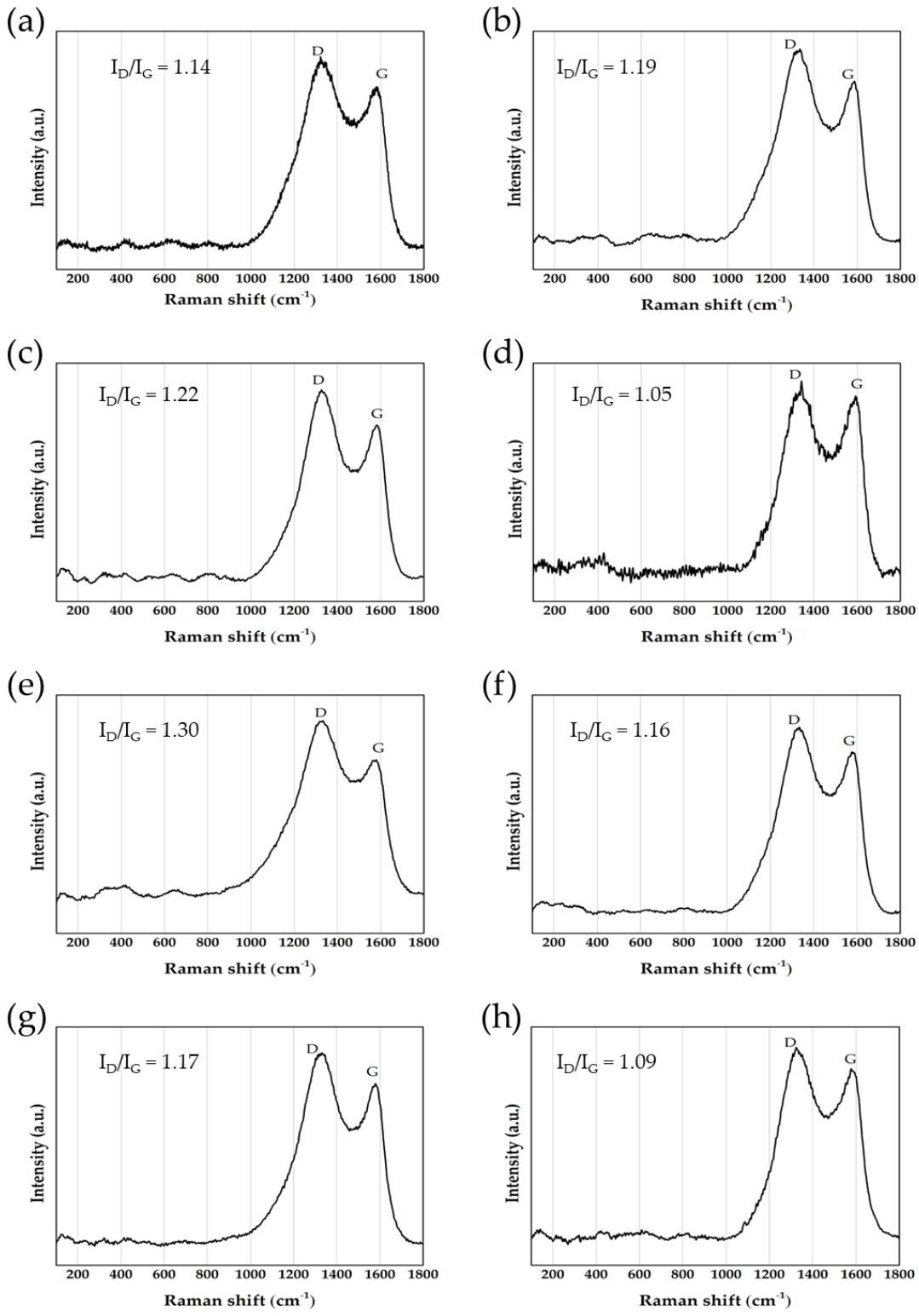

Figure S2. Raman spectra of prepared materials: (a) CHI-0. (b) CHI-Im. (c) CHI-Pyr. (d) CHI-DCA. (e) CHI-PIL. (f) CHI-2Py. (g) CHI-4Py. (h) CHI-DES.

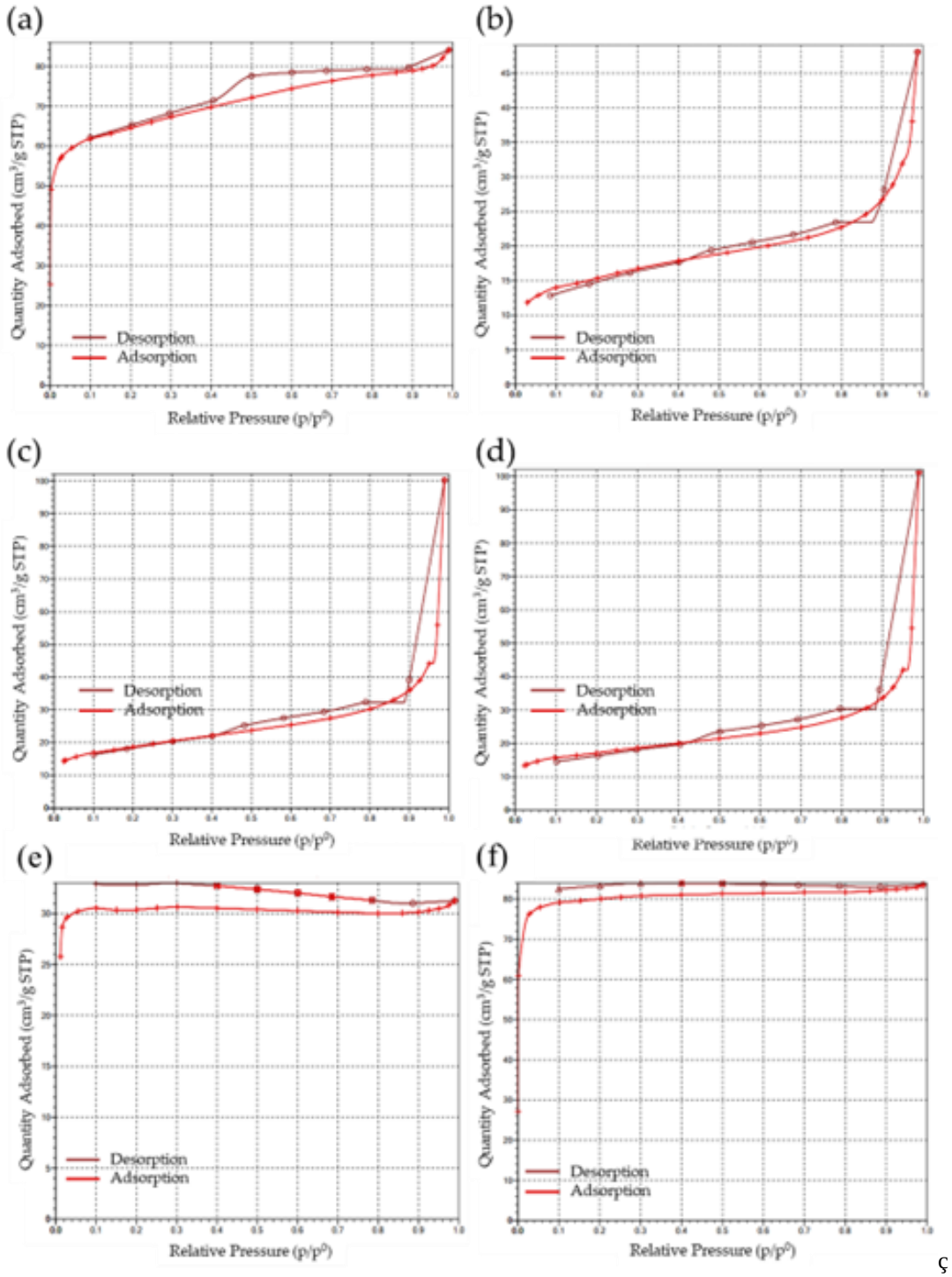

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Figure S3. N_2 adsorption/desorption isotherms of samples (a) Kno-0; (b) PriS-0 (c) BioS-0; (d) BioS-ImCl; (e) CHI-0; (f) CHI-PyrCl.

1.3. Prepared materials

Table S1. Materials used in all completed carbonizations.

Entry	Sample	Biomass	Additive
1	CHI-0	CHI	–
2	Kno-0	Knots	–
3	PriS-0	Primary sludge	–
4	BioS-0	Biological sludge	–
5	BioS-ImCl	Biological sludge	[Bmim]Cl
6	CHI-ImCl	CHI	[Bmim]Cl
7	CHI-PyrCl	CHI	[Bmpyr][Cl]
8	CHI-PyrDCA	CHI	[Bmpyr][DCA]
9	CHI-PDADMACl	CHI	PDADMACl
10	CHI-2PyCl	CHI	[2Bmpy]Cl
11	CHI-4PyCl	CHI	[4Bmpy]Cl
11	CHI-DES	CHI	LiCl/KCl[a]
13	CHI-DES-F[b]	CHI	LiCl/KCl[a]

[a] 45:55 by weight. [b] Carbon obtained from washing and filtering sample CHI-DES.

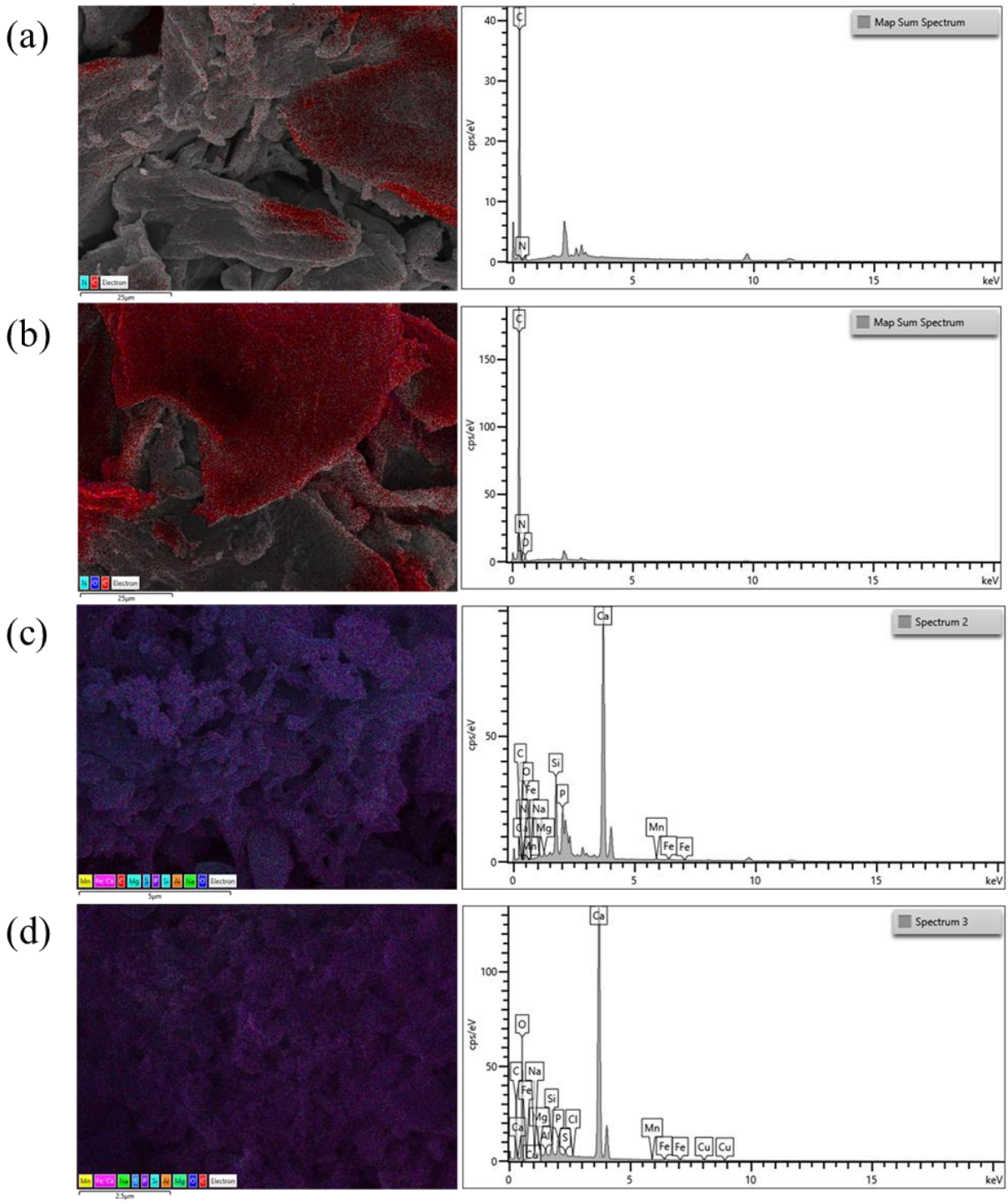

Figure S4. Scanning electron microscopy (SEM) images, energy dispersive X-ray spectroscopy (EDS) spectra and elemental mapping of CHI-0 (a); CHI-IM (b); BioS-0 (c) and BioS-IM (d).

CHI-0 Map Sum spectrum								
Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %	Standard Label	Factory Standard
C	K series	5.49	0.05488	89.61	1.77	90.95	C Vit	Yes
N	K series	0.22	0.00038	10.39	1.77	9.05	BN	Yes
Total:				100.00		100.00		

(a)

CHI-IM Map Sum spectrum								
Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %	Standard Label	Factory Standard
C	K series	24.48	0.24477	86.93	0.61	89.25	C Vit	Yes
N	K series	0.65	0.00116	6.11	0.64	5.38	BN	Yes
O	K series	0.81	0.00274	6.97	0.18	5.37	SiO2	Yes
Total:				100.00		100.00		

(b)

BioS-0 Map Sum spectrum								
Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %	Standard Label	Factory Standard
C	K series	1.69	0.01686	22.29	0.59	33.73	C Vit	Yes
N	K series	0.00	0.00000	0.00	1.52	0.00	BN	Yes
O	K series	5.80	0.01950	43.27	0.47	49.16	SiO2	Yes
Na	K series	0.30	0.00125	0.83	0.05	0.66	Albite	Yes
Mg	K series	0.12	0.00078	0.32	0.03	0.24	MgO	Yes
Si	K series	2.34	0.01851	4.36	0.06	2.82	SiO2	Yes
P	K series	2.03	0.01135	2.52	0.06	1.48	GaP	Yes
Ca	K series	16.04	0.14336	25.93	0.26	11.76	Wollastonite	Yes
Mn	K series	0.11	0.00113	0.22	0.05	0.07	Mn	Yes
Fe	K series	0.13	0.00129	0.25	0.05	0.08	Fe	Yes
Total:				100.00		100.00		

(c)

BioS-IM Map Sum spectrum								
Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %	Standard Label	Factory Standard
C	K series	4.53	0.04530	25.75	0.23	36.37	C Vit	Yes
O	K series	12.96	0.04361	49.91	0.21	52.93	SiO2	Yes
Na	K series	0.09	0.00038	0.15	0.02	0.11	Albite	Yes
Mg	K series	0.22	0.00147	0.36	0.02	0.25	MgO	Yes
Al	K series	0.25	0.00182	0.33	0.01	0.21	Al2O3	Yes
Si	K series	0.52	0.00410	0.57	0.01	0.34	SiO2	Yes
P	K series	1.09	0.00612	0.75	0.02	0.41	GaP	Yes
S	K series	0.24	0.00209	0.26	0.01	0.14	FeS2	Yes
Cl	K series	0.06	0.00052	0.06	0.01	0.03	NaCl	Yes
Ca	K series	23.20	0.20730	21.46	0.10	9.09	Wollastonite	Yes
Mn	K series	0.09	0.00095	0.11	0.02	0.03	Mn	Yes
Fe	K series	0.12	0.00123	0.14	0.02	0.04	Fe	Yes
Cu	K series	0.14	0.00136	0.15	0.03	0.04	Cu	Yes
Total:				100.00		100.00		

(d)

Figure S5. Elemental analysis from EDS of CHI-0 (a); CHI-IM (b); BioS-0 (c) and BioS-IM (d).

1.4. Cycloaddition of CO_2 and recyclability

Table S2. Screening of porous carbon supported IL catalytic performance in the reaction between SO and CO_2 to obtain SC[a].

Entry	Catalyst[a]	Conversion (%)
1	**Kno-0**	50
2	**PriS-0**	47
3	**BioS-0**	75
4	**BioS-ImCl**	**81**[c]
5	CHI-0	61
6	CHI-ImCl[b]	≈0
7	**CHI-ImCl**	**80**[c]
8	CHI-2PyCl	**77**
9	CHI-4PyCl	58
10	CHI-PyrCl	**74**
11	CHI-PDADMACl	56
12	CHI-PyrDCA	62
13	CHI-DES	**74**
14	CHI-DES-F	**74**
15	TBAB	62

[a] Reaction conditions: 100 ºC, 3 h, CO_2 (5 bar), SO (6.66 mmol), catalyst (10 mg), co-catalyst TBABr (7 mol% concerning SO), unless stated otherwise. [b] Without co-catalyst TBABr.[c] Performed in triplicate, deviation of 5% observed.

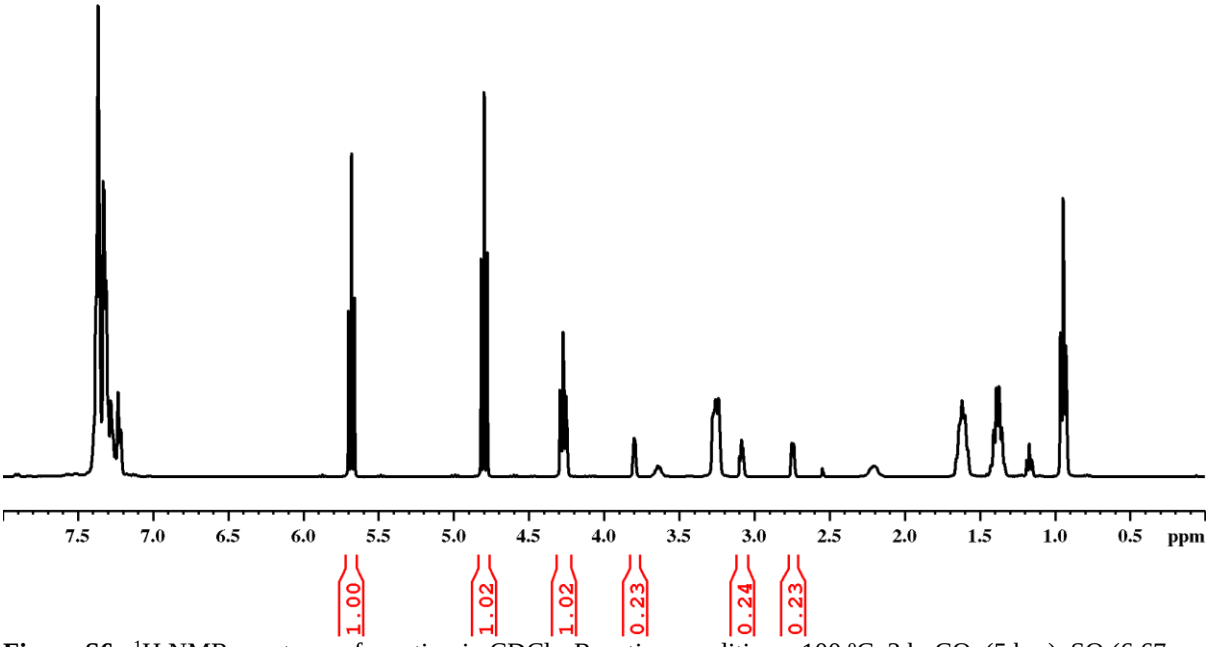

Figure S6. ^1H NMR spectrum of reaction in $CDCl_3$. Reaction conditions: 100 ºC, 3 h, CO_2 (5 bar), SO (6.67 mmol), TBABr (3.5 mol%), BioS-ImCl (10 mg).