

Electronic supplementary information

Process Systems for the Carbonate Interchange Reactions of DMC and Alcohols: Efficient synthesis of Catechol Carbonate

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Materials

Commercial grade reagents and solvents were used without further purification.

Instrumental analyses

GC-FID

The mixtures recovered from the transcarrbonation reactions were analysed by a gas-chromatograph Thermo Focus equipped with a capillary column HP-5 (25m x 320 μ m x 1.05 μ m). The following conditions were used. Carrier gas: N₂ (1.2 mL/min); split ratio: 30:1; initial T: 50 °C (2 min), ramp rate: 20 °C min⁻¹; final T: 280 °C (5 min); T_{inj.}=280°C. The volume of solution injected for each analysis was 0.5 μ L.

Each compound was calibrated in an appropriate range of concentrations, by using decane or octane as an external standard. The corresponding response factor was evaluated according to the following equation:

$$\frac{A}{A_{std}} = f * \frac{mol}{mol\ std}$$

GC-MS

The products isolated from the transcarrbonation reactions were analysed by electrospray ionization mass spectroscopy (ESI-MS) and GC-MS.

The GC-MS (EI, 70eV) was a 6890 GC coupled with a mass spectrometer 5973 (both from Agilent) equipped with a HP5 column (5% Phenyl - 95% methylsiloxane; 30m x 250 μ m x 1.05 μ m).

The following conditions were used. Carrier gas: He (1.0 mL/min); split ratio: 50:1; initial T: 50 °C (2 min), ramp rate: 20 °C min⁻¹; final T: 280 °C (5 min); T_{inj.}=250°C.

ESI-MS

ESI-MS spectra (positive or negative) were recorded using a Waters Micromass ZQ 4000, equipped with a capillary probe (3.54 kV), with a cone voltage of 20 volts and direct injection (20 μ L min⁻¹).

Infrared spectrometry

Catechol carbonate IR spectra were recorded between 4000 and 450 cm⁻¹ (NIR Near Infra-Red), using a Perkin Elmer Spectrum One FT-IR spectrometer.

X-ray diffraction analyses (XRD).

XRD powder patterns of the catalysts were recorded with a Ni-filtered Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$) on a Philips X'Pert vertical diffractometer equipped with a pulse height analyzer and a secondary curved graphite-crystal monochromator.

The analysis of the phases present in the patterns were performed using the Bragg's Law:

$$n\lambda = 2d\sin \theta$$

to calculate the crystalline d values, and compare them with those reported in the literature and collected in the ICDD database (International Centre for Diffraction Data).

^1H -NMR and ^{13}C -NMR

The ^1H and ^{13}C NMR spectra were recorded on a Bruker spectrometer at 400 MHz and 100 MHz, respectively.

The chemical shifts (δ) for ^1H and ^{13}C are given in δ values downfield from TMS; CDCl_3 or CD_3OD were used as solvent.

Thermogravimetric analysis (TGA)

TG/DT analyses of the molecular sieves were performed with a SDT Q 600 instrument, in order to evaluate their methanol adsorption capacity. 30 mg of the sample was typically employed for the measurement, at temperatures from room temperature up to 220 °C, with a heating rate of 2 °C/min, in a nitrogen flux.



Figure S1 Schematic representation of the reactive vapor adsorption system (RVA) with the selective adsorption of methanol inside molecular sieves.

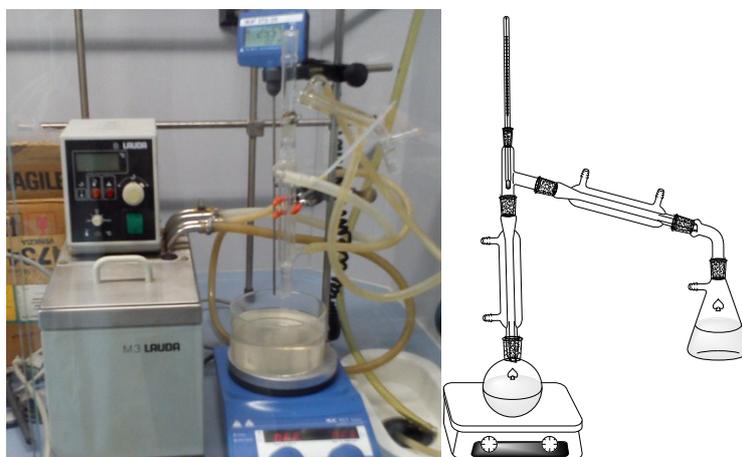


Figure S2: Reactive azeotropic distillation (RAD) setup

4A Molecular sieves TGA comparison

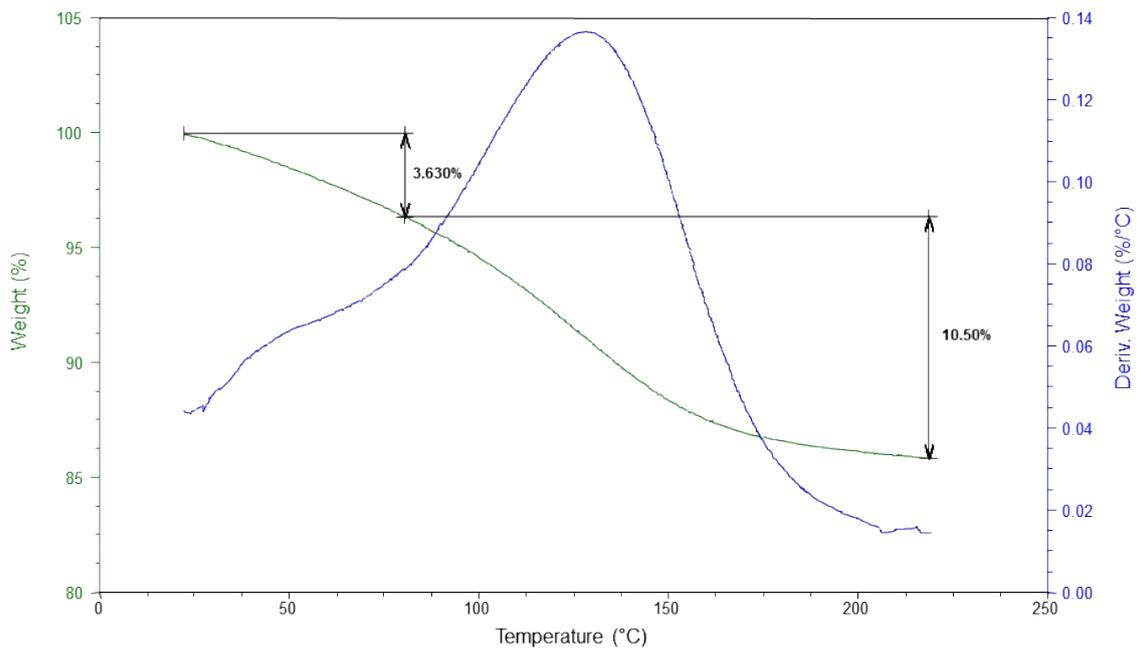


Figure S3: 4A molecular sieves TGA after one night in a DMC/methanol mixture

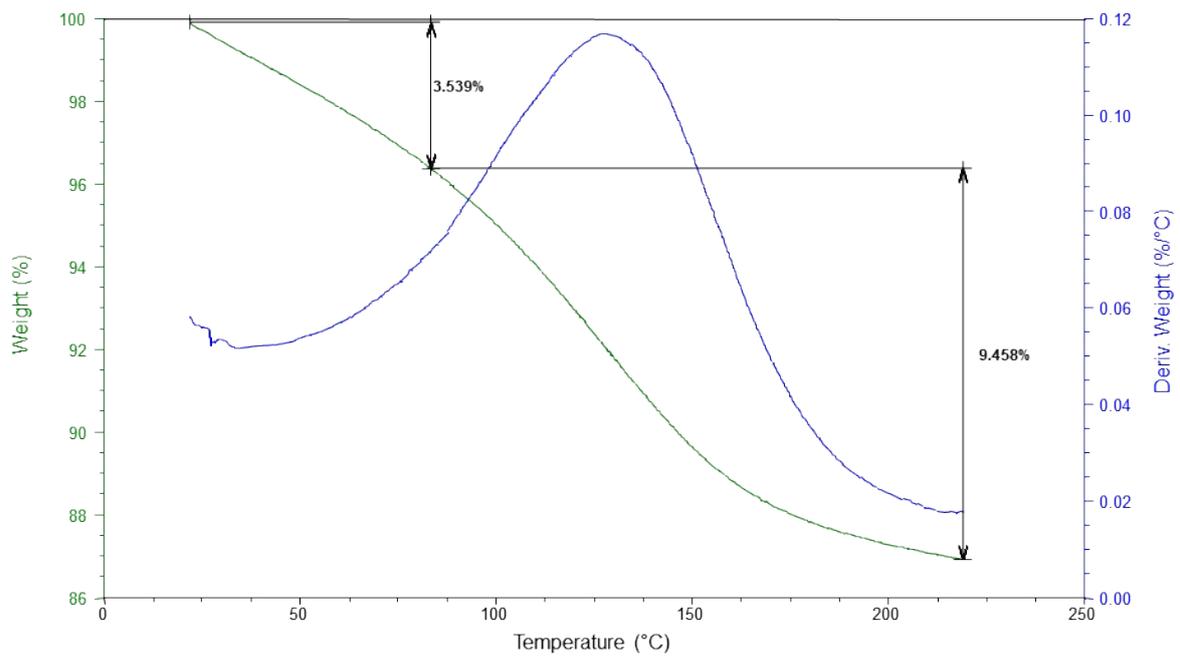


Figure S4: 4A molecular sieves TGA after 24 hours of reaction in the RVA system, starting from a mixture of DMC:Catechol=10:1

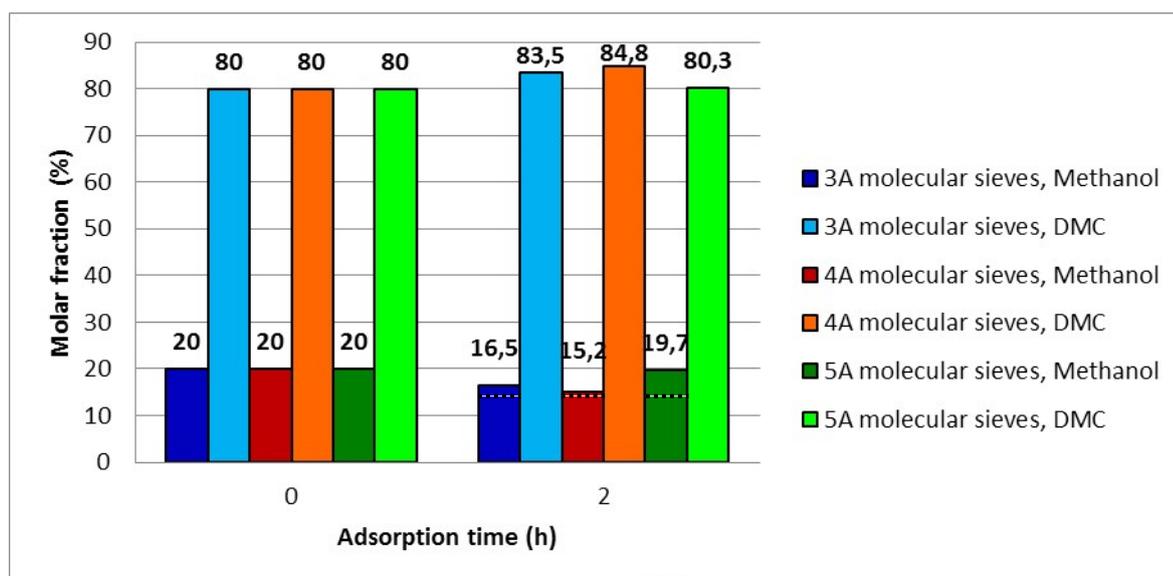


Figure S5: Adsorption test results for the different shapes molecular sieves, the dotted lines represents the theoretical adsorption capacity (15 grams of a mixture with a molar ratio of DMC:methanol = 4, 20% w/w of molecular sieves)

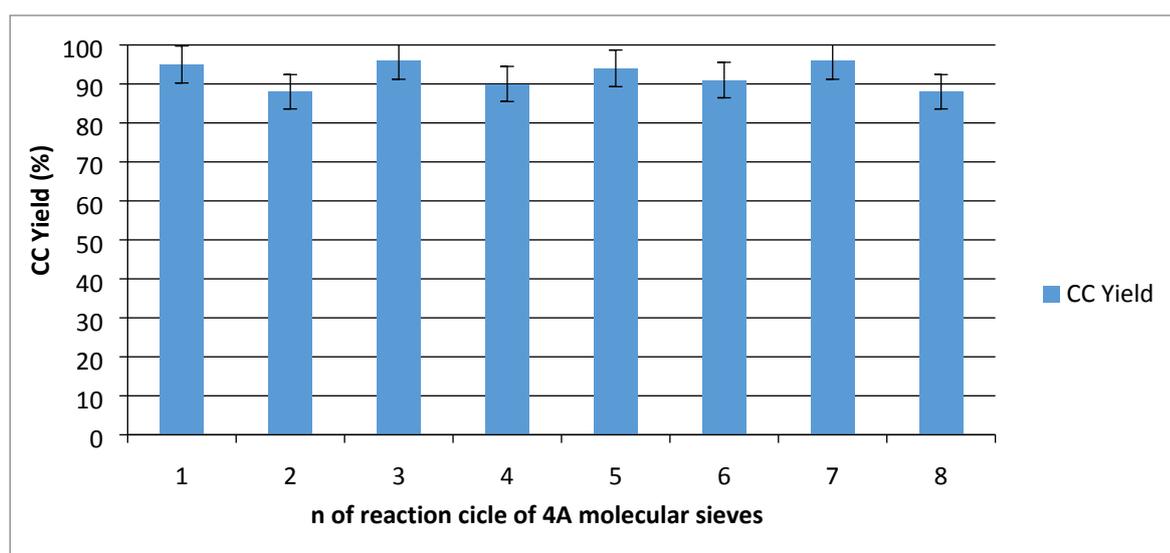


Figure S6: Recyclability test of the 4A molecular sieves for the synthesis of catechol carbonate (CC) in the presence of NaOMe with RVA system. (Conditions: DMC:catechol: NaOMe = 10:1:1/30; T≈90°C)

Reaction time (h)	Reactive mixture molar composition	Distilled (above sieves) mixture molar composition
6	DMC = 90,4% ; CH ₃ OH =9,6%	DMC = 81,9% ; CH ₃ OH =18.1%
24	DMC = 86,2% ; CH ₃ OH =13,8%	DMC = 39,8% ; CH ₃ OH =60,2%

Table S1: Composition of the lightest compound (DMC and methanol) in the mixtures inside the batch and the distilled one above the sieves in a typical test for the synthesis of catechol carbonate (CC). (Conditions: DMC:catechol: NaOMe = 10:1:1/30; T≈90°C)

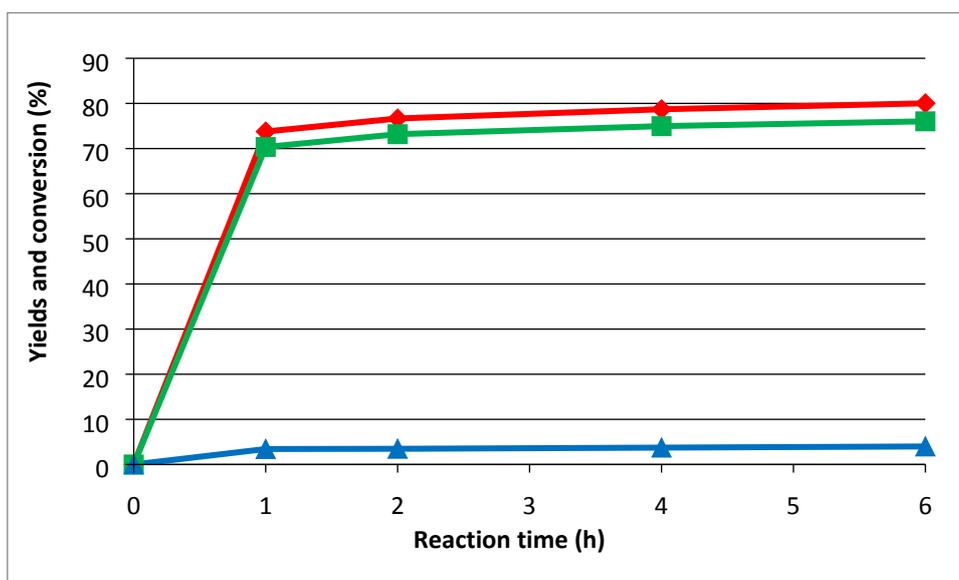


Figure S7: CIR of solketal (2,2-dimethyl-1,3-dioxolan-4-yl)methanol) and DMC, RVA system. (Conditions: DMC:solketal:NaOMe = 10:1:1/30; T≈90°C)

Green Metrics

For the estimation of the green parameters the following data were used

Methods	Catechol (g)	DMC (g)	Catalyst (g)	CC (g)	Molecular sieves (g)
RAD	2.4	39.6	0.303	2.8	/
RVA	2.4	19.8	0.04	2.8	8

Table S2: Data used for the calculation of the green parameters

The following equations were used for the calculation of the different green parameters:

$$AE = \frac{MW \text{ Product}}{\sum MW \text{ Reagents}}$$

$$SF = 1 + \frac{AE * \text{Mass of exceed material}}{\text{Mass of expected product}}$$

$$RME = \frac{\text{Mass of the product obtained}}{\sum \text{Mass of the reagents}}$$

$$MP = \frac{1}{MI} = \frac{\text{Mass of Product}}{\sum \text{Mass of all reagents, solvent, catalyst}}$$

FT-IR of catechol over MgO

The reaction of aromatic alcohols (phenol) and diols (catechol) did not proceed with MgO. This is due to the stronger interaction between these more acidic alcohols and the catalytic surface, with the formation of a strong adsorbed magnesium salt of the corresponding alcoholate. This hypothesis was confirmed by means of infrared spectroscopy characterisation. Firstly, the catechol spectra was registered (Figure S7) and the main bands were attributed to the vibrational mode of the molecule by matching experimental and calculated wavenumbers (Table S3).

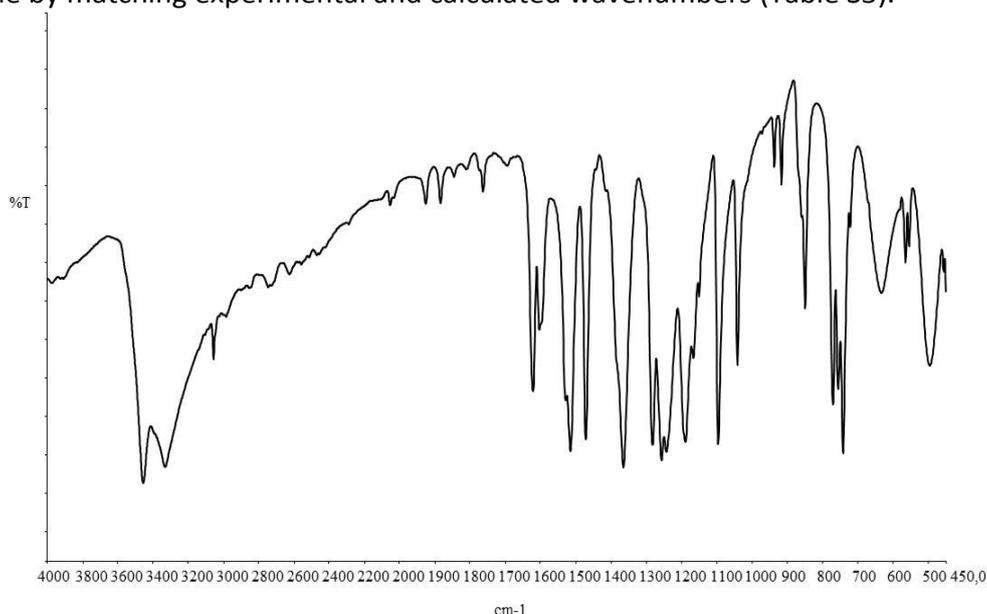


Figure S8: Catechol infra-red spectrum between 4000 and 450 cm^{-1} (transmittance mode)

Calculated Wavenumbers (cm^{-1})	Experimental Wavenumbers (cm^{-1})	Vibrational mode description
3898	3451	ν OH
3838	3327	ν OH
3239	3100	ν sym CH
3229	3080	ν asym CH
3216	3052	ν asym CH
3194	3043	ν asym CH
1668	1620	ν aromatic CC + δ OH
1664	1600	ν aromatic CC
1554	1596	ν aromatic CC + δ OH
1507	1528	ν aromatic CC
1482	1514	ν aromatic CC
1382	1470	ν aromatic CC + δ OH + δ CH
1324	1364	δ CH + δ OH + ν CO
1285	1281	ν CO (both) + δ OH
1231	1255	δ OH (both)
1184	1241	δ OH + ν CO + δ CH
1108	1187	δ CH + δ OH
1050	1165	δ CH
861	1149	δ CH
781	1096	δ CH
729	1040	δ CH

Table S3: Catechol main vibrational mode and related bands wavenumbers

Then, MgO was recovered after the reaction test with catechol, filtered and washed with dichloromethane in order to remove the weakly adsorbed organic molecule. Then the catalyst was dried and its IR spectrum was recorded.

The catechol spectrum and that one of the used catalyst are compared in the following figure (Figure S8).

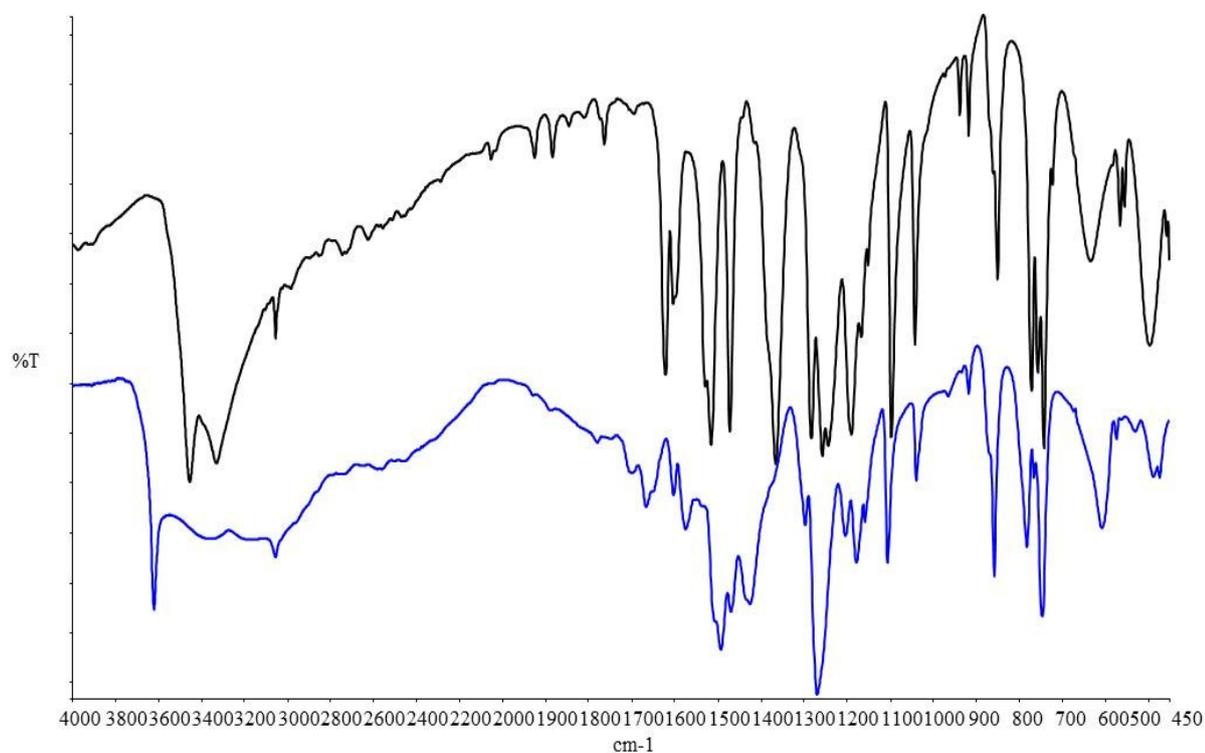


Figure S9: FT-IR spectra of catechol moiety (black) and of the used MgO after the reaction with catechol and DMC (blue). Spectra collected in transmittance mode between 4000 and 450 cm^{-1} .

Spectra clearly show that the aromatic species was adsorbed, and that the main bands were perturbed due to the formation of the catecholate magnesium salts. In particular, the -OH stretching bands at 3451 and 3327 cm^{-1} disappeared with the concomitant formation of the Mg-OH moiety vibrating at 3618 cm^{-1} .

Moreover, the band at 1363 cm^{-1} completely disappeared demonstrating the deprotonation of both -OH groups; in the CO stretching region (around 1200 cm^{-1}), the shift of the bands toward higher wavenumber and the corresponding formation of a strong band centred at 1268 cm^{-1} can be attributed to the CO stretching in the dissociated alcoholate.

Furthermore the bands at 1620 and 1596 cm^{-1} attributed to the C-C stretching bands, with a minor component of -OH bending were strongly perturbed and shifted toward 1663 and 1572 cm^{-1} , respectively, while the band centred at 1601 cm^{-1} was almost unperturbed.

A further proof for the formation of magnesium catecholate was achieved by reacting catechol with magnesium hydroxide (Mg(OH)_2), and comparing the spectrum of the obtained salt with that one of used MgO (Figure S9).

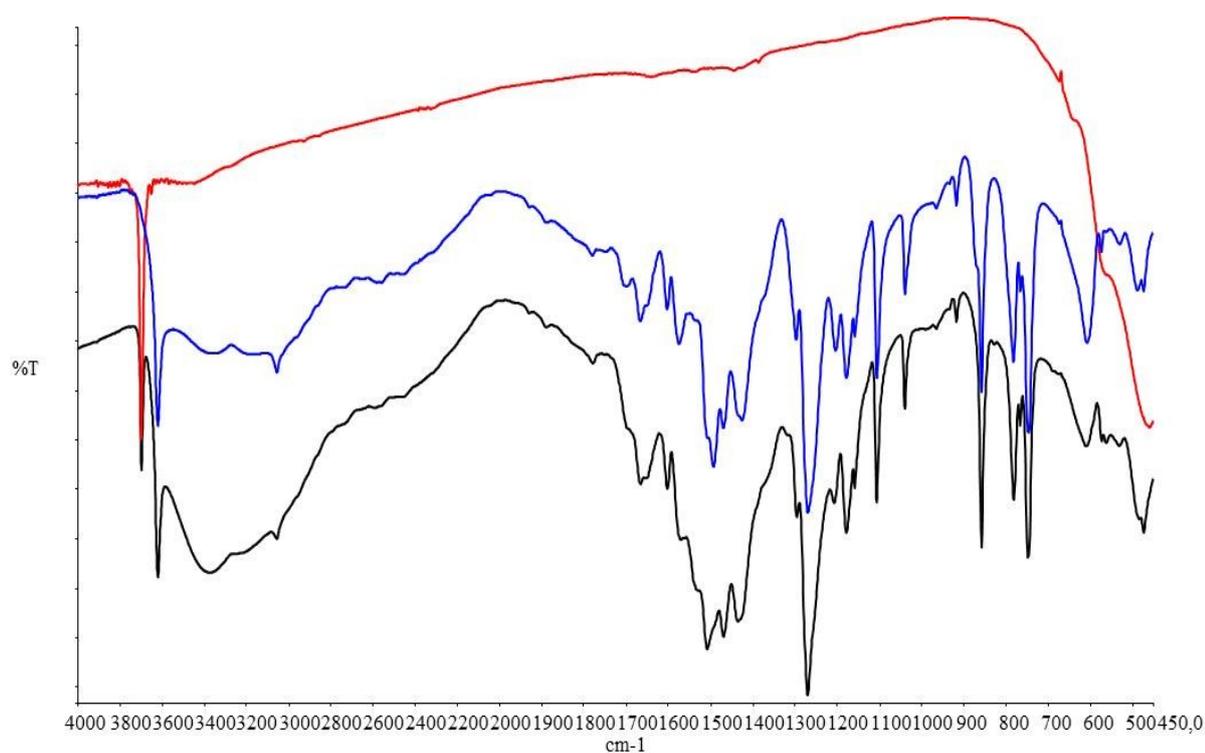


Figure S10: FT-IR spectra of the used MgO after the reaction with catechol and DMC (blue), of the catechol magnesium salt (black) and of the pure magnesium hydroxide (red). Spectra registered in the transmittance mode between 4000 and 450 cm^{-1} .

The spectra clearly show the similarity between the magnesium salt, obtained reacting catechol and $\text{Mg}(\text{OH})_2$, and the used MgO catalyst; the same bands were shown, which proved the formation of strongly adsorbed catecholate on MgO surface.

CO₂-TPD analysis: MgO

The characterisation of MgO's alkaline sites was performed by means of CO₂ Temperature Programmed Desorption (TPD) analysis. Firstly, the catalyst was pre-treated in He at 450°C for 1 hour to clean the catalytic surface. Then, the CO₂ adsorption was performed feeding a 30mL/min of 10% CO₂ in He, at 40°C for 1 h. Afterwards, the flux was switched to He only (30 mL/min) for one hour at 40°C to remove the physisorbed CO₂ and clean the lines. Finally, the desorption step was performed in He increasing the temperature to 500°C at 10°C/min.

The results are showed in Figure S11.

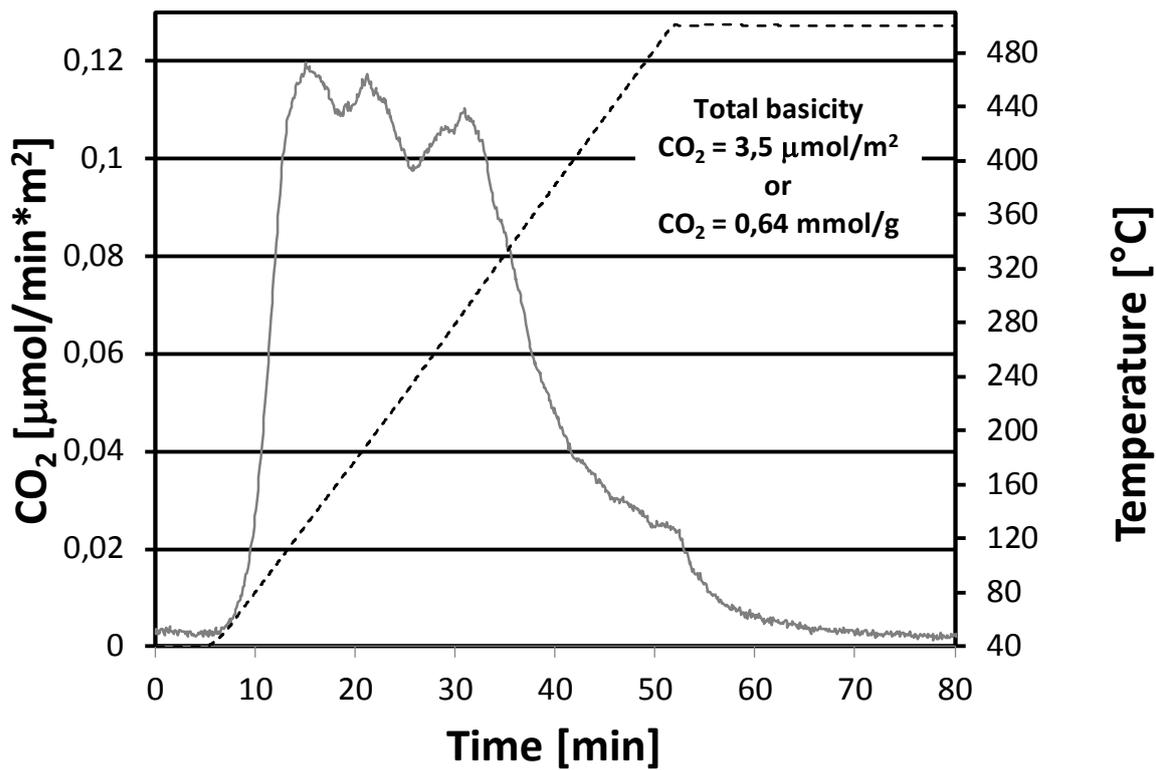
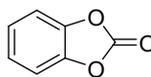


Figure S11: MgO CO₂-TPD profile in function of the time of analysis, correlated with the temperature.

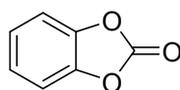
The results obtained shown a total basicity of the MgO catalyst equal to 0.64 mmol/g.

Catechol carbonate (CC) characterisation

IUPAC name	1,3-benzodioxol-2-one
Linear formula	C ₇ H ₄ O ₃
M.W.	136.1 g/mol
Physic state at RT	white cristalline solid
XRD pattern	See below
IR spectra	See below
Melting point	Calculated: 78°C ^a ; Sperimental: 116°C
Boiling point	Calculated: 181°C ^a
P (g/ml)	1.4 ^a

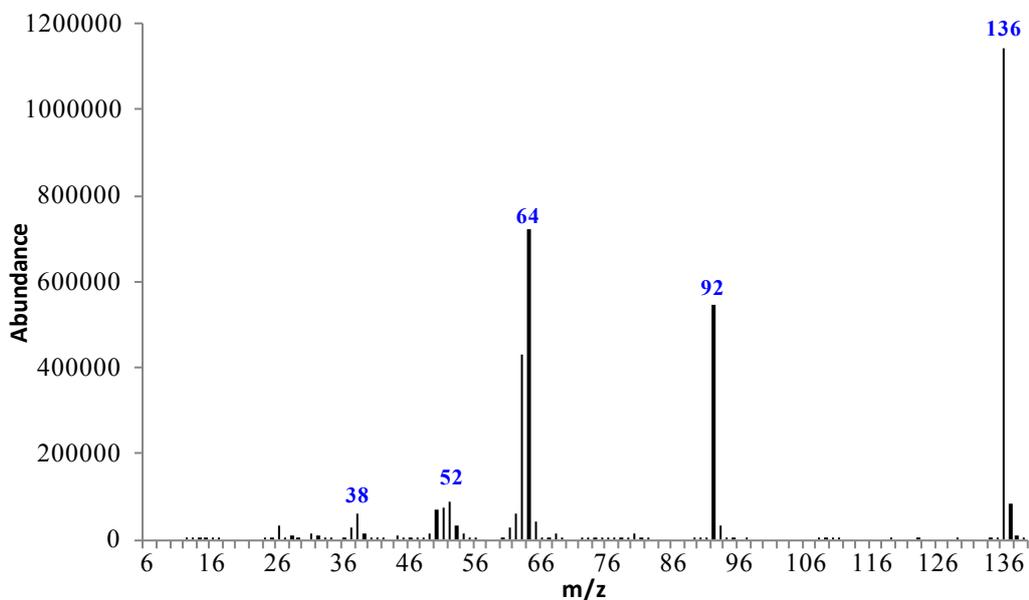


^a computational data ref: <http://www.scbt.it/datasheet-273562-1-3-benzodioxol-2-one.html>



CC

Mass Spectrum



GC-MS (relative intensity, 70eV) *m/z*: 136 (M⁺, 100), 92 (48), 64 (63), 63 (38), 52 (8), 38 (5), 26 (3).

Figure S12: GC-MS spectrum of catechol carbonate (CC)

IR Spectroscopy Data

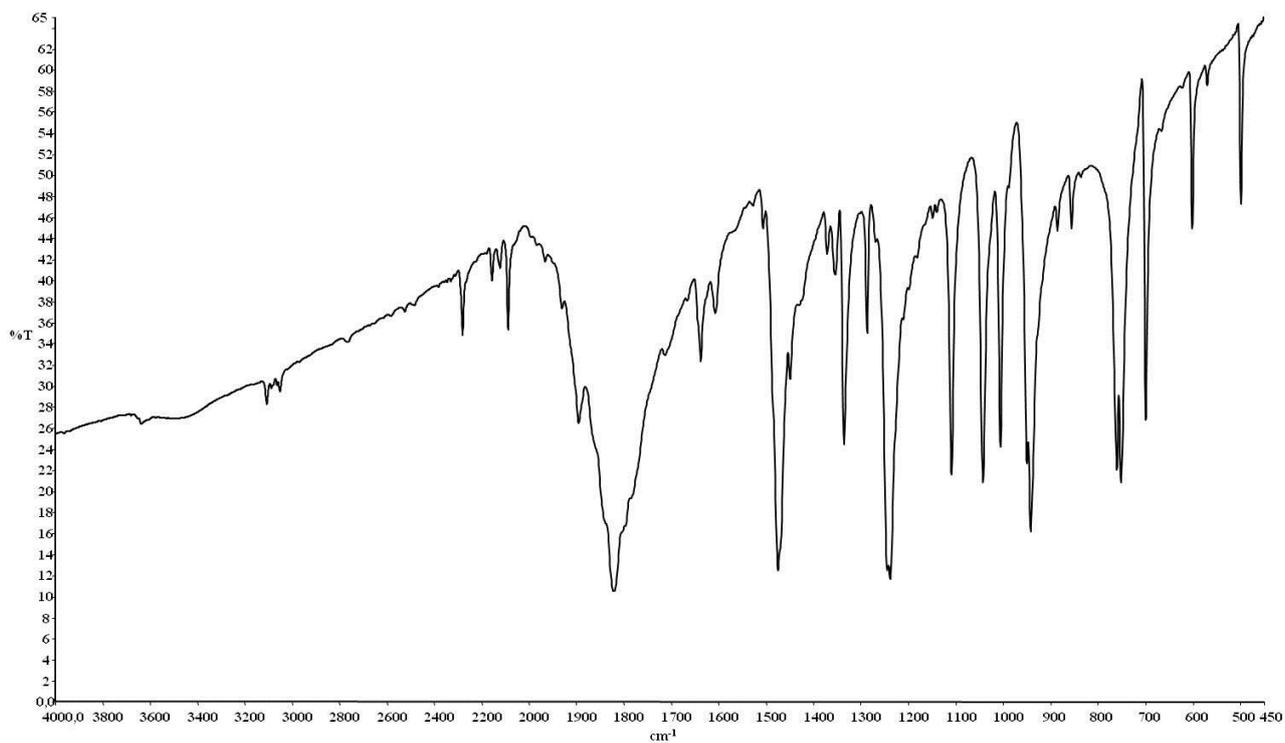


Figure S13: IR spectrum of catechol carbonate (CC)

Powder XRD pattern of catechol carbonate

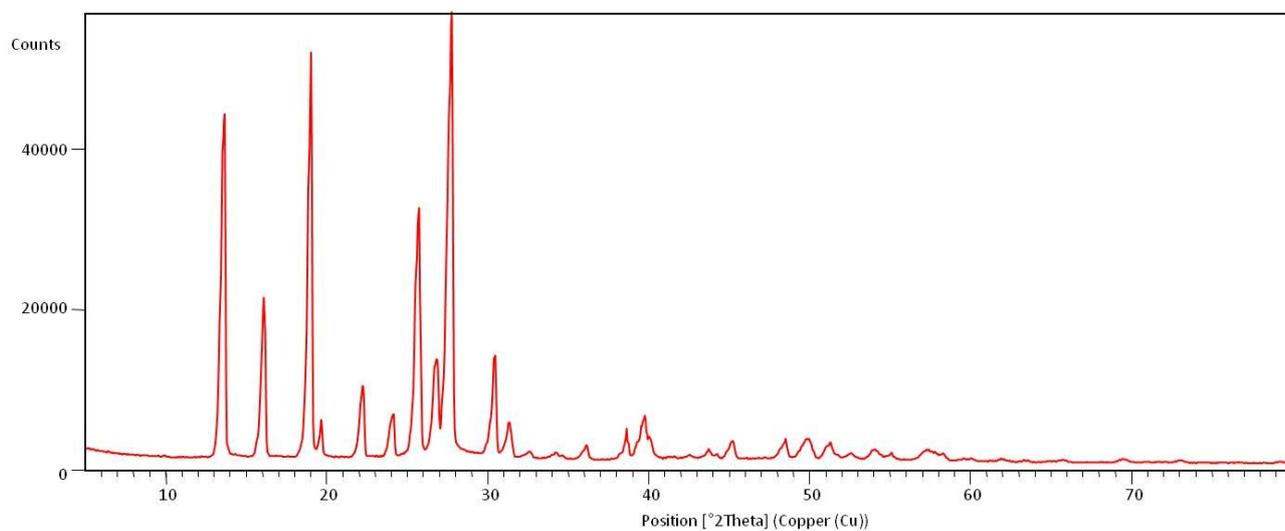


Figure S14: powder XRD pattern of catechol carbonate (CC)

NMR spectra

Catechol carbonate (CC)

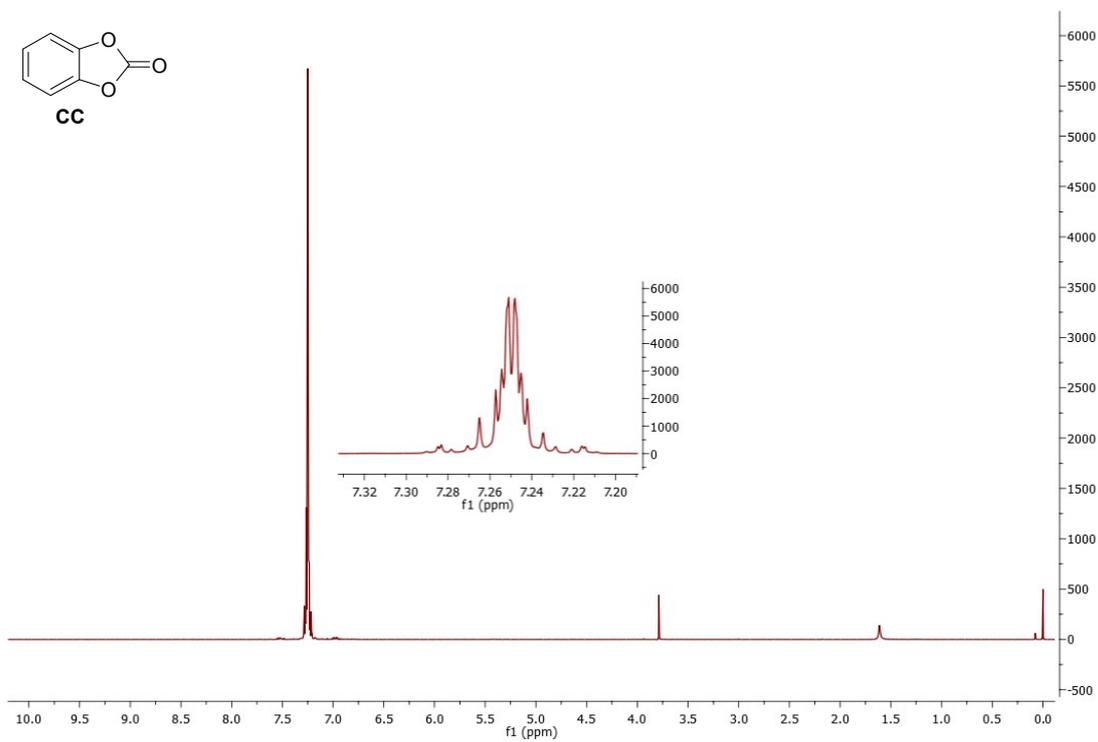


Figure S15: ¹H NMR spectrum of CC. ¹H NMR (CDCl₃, 400MHz) δ (ppm): 7.25 (m, 4H).

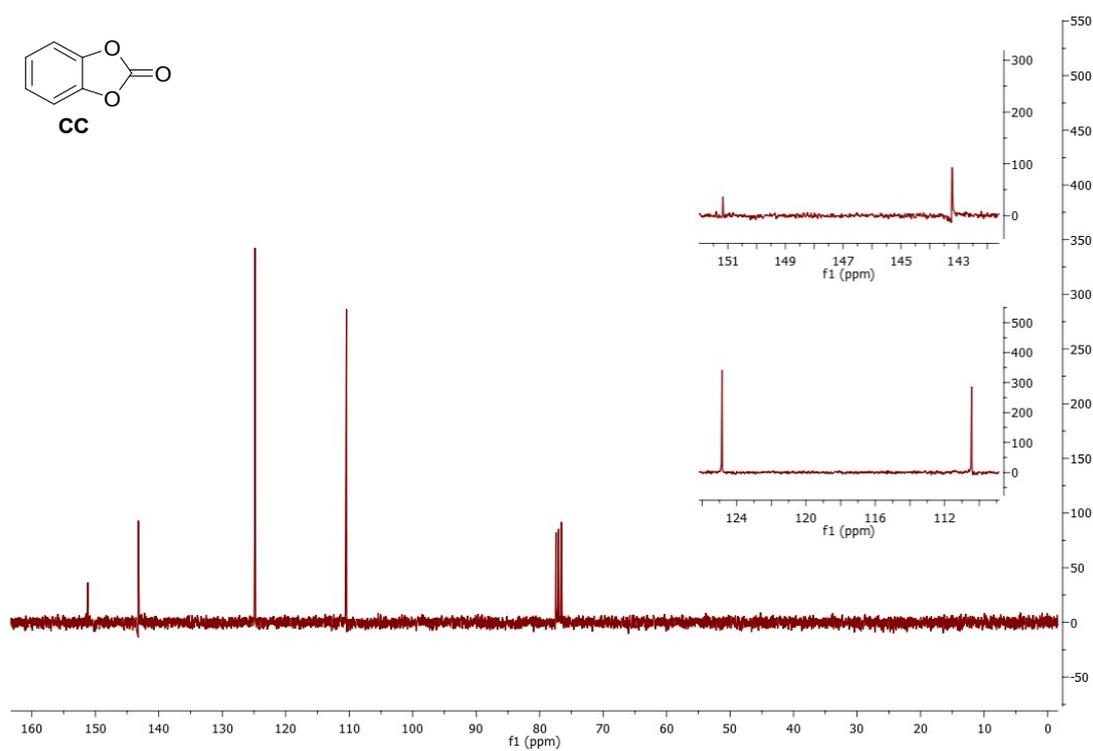
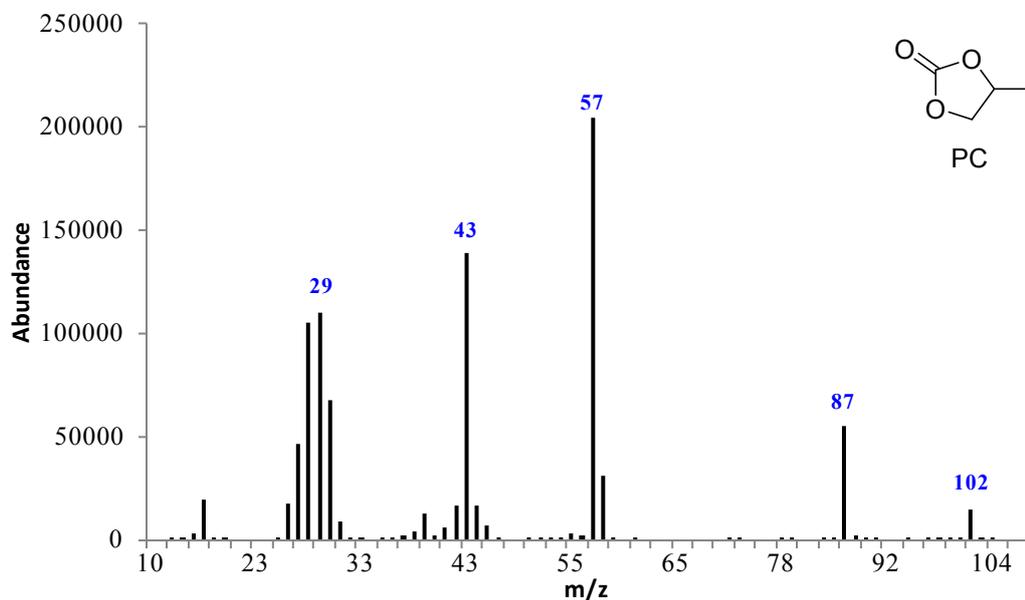


Figure S16: ¹³C NMR spectrum of CC. ¹³C NMR (CDCl₃, 100MHz) δ (ppm): 151.1, 143.2, 124.8, 110.4.

Characterisation of products

Mass Spectra

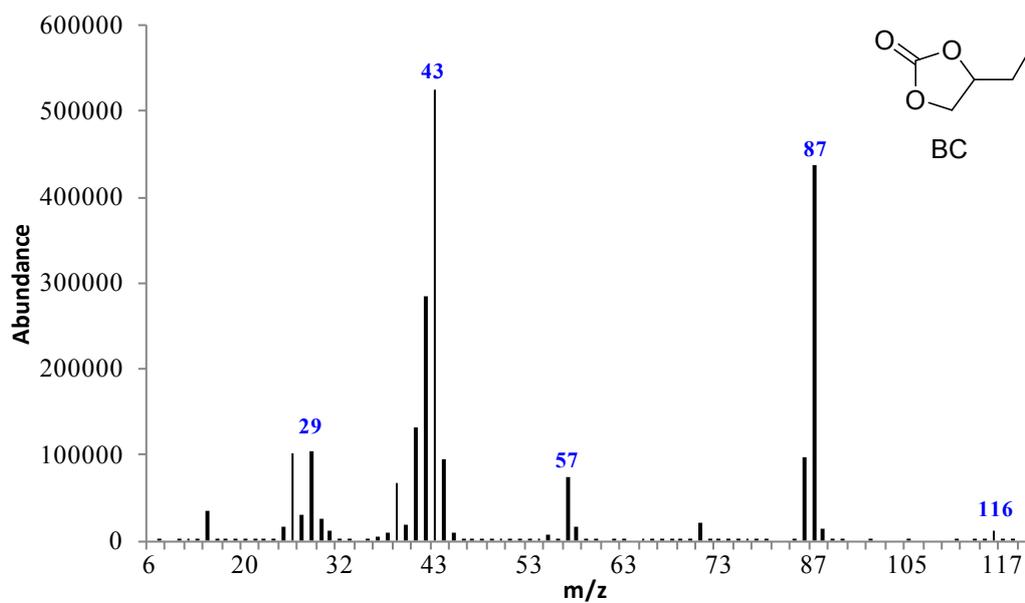
Propylene carbonate (PC)



GC-MS (relative intensity, 70eV) m/z : 102 (M^+ , 7%), 87 (27), 57 (100), 43 (68), 29 (54), 28 (51).

Figure S17: GC-MS spectrum of propylene carbonate (PC)

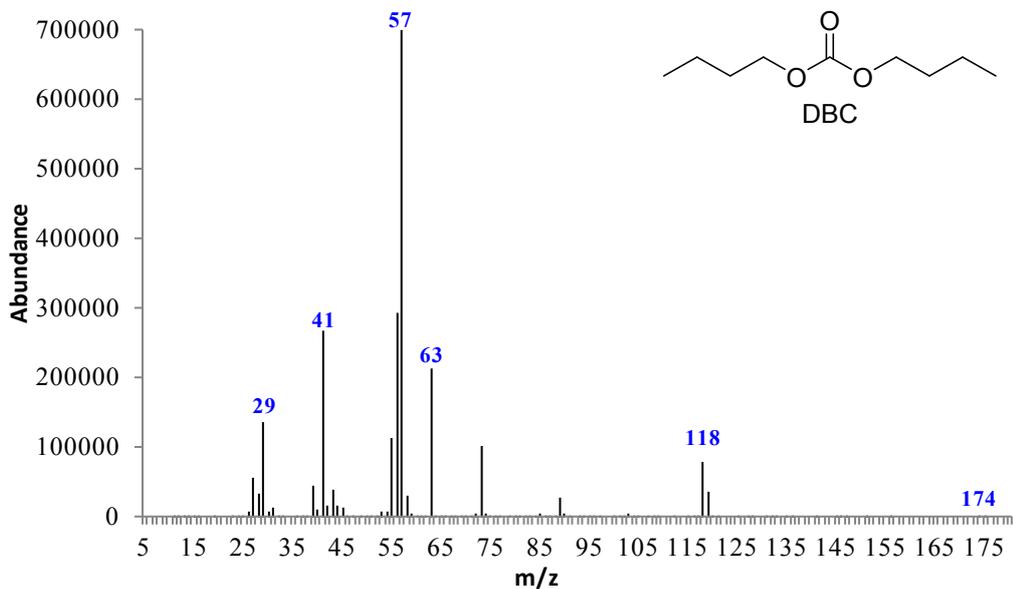
1,2-Butylene carbonate (BC)



GC-MS (relative intensity, 70eV) m/z : 116 (M^+ , 2%), 87 (83), 71 (4), 57 (14), 43 (100), 29 (20), 27 (20).

Figure S18: GC-MS spectrum of butylene carbonate (BC)

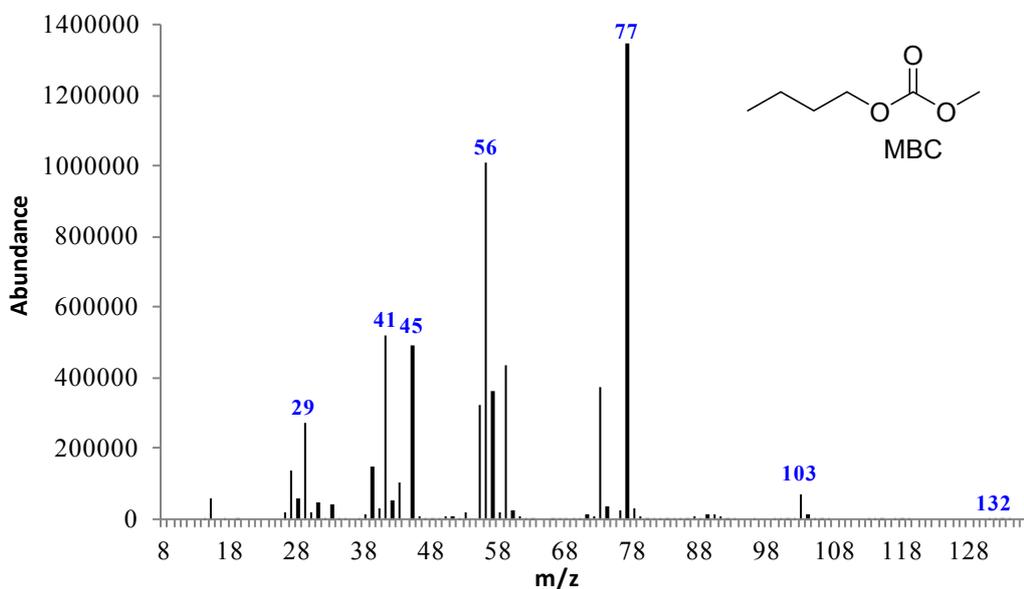
Dibutyl carbonate (DBC)



GC-MS (relative intensity, 70eV) m/z : 174 (M^+ , <1%), 118 (11), 89 (4), 73 (14), 63 (30), 57 (100), 56 (42), 41 (38), 29 (19).

Figure S19: GC-MS spectrum of dibutyl carbonate (DBC)

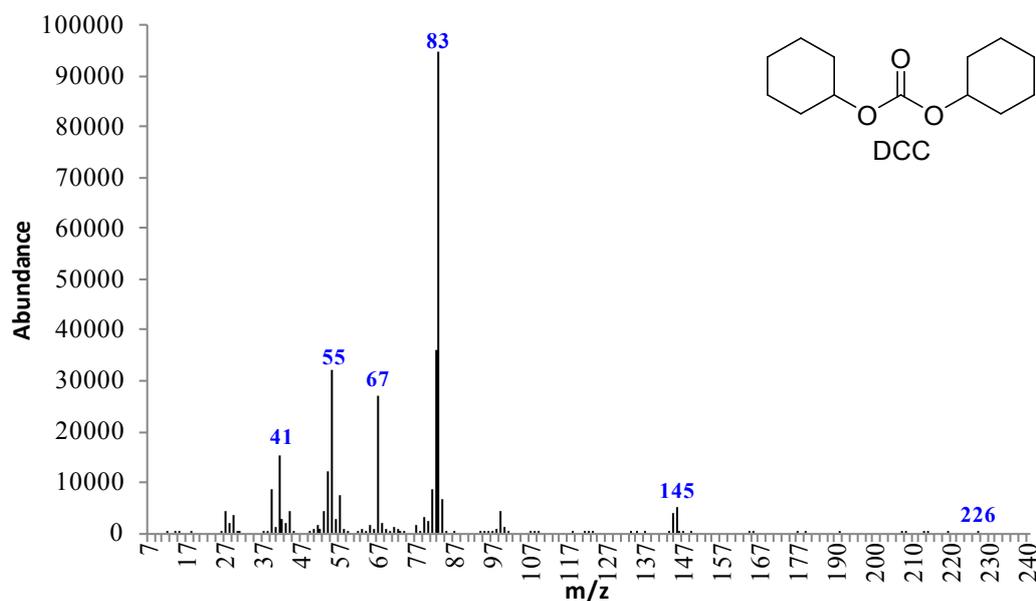
Methyl butyl carbonate (MBC)



GC-MS (relative intensity, 70eV) m/z : 132 (M^+ , <1%), 103 (5), 77 (100), 73 (28), 59 (32), 56 (75), 45 (36), 41 (39), 29 (20).

Figure S20: GC-MS spectrum of methyl butyl carbonate (MBC)

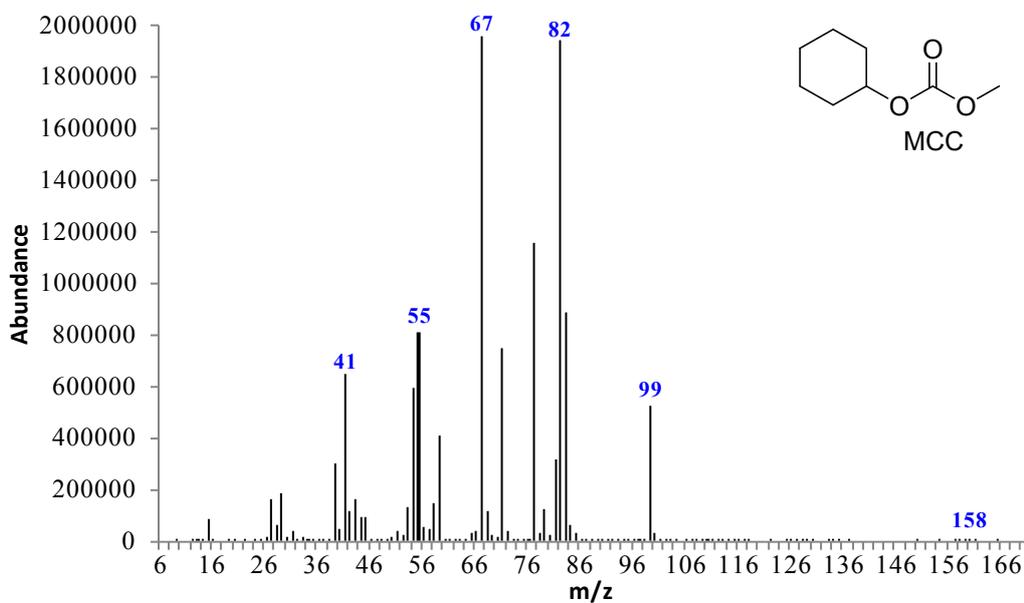
Dicyclohexyl carbonate (DCC)



GC-MS (relative intensity, 70eV) m/z : 226 (M^+ , <0.1%), 145 (6), 99 (5), 83 (100), 82 (38), 67 (28), 55 (34), 54 (13), 41 (16), 29 (4), 27 (4).

Figure S21: GC-MS spectrum of dicyclohexyl carbonate (DCC)

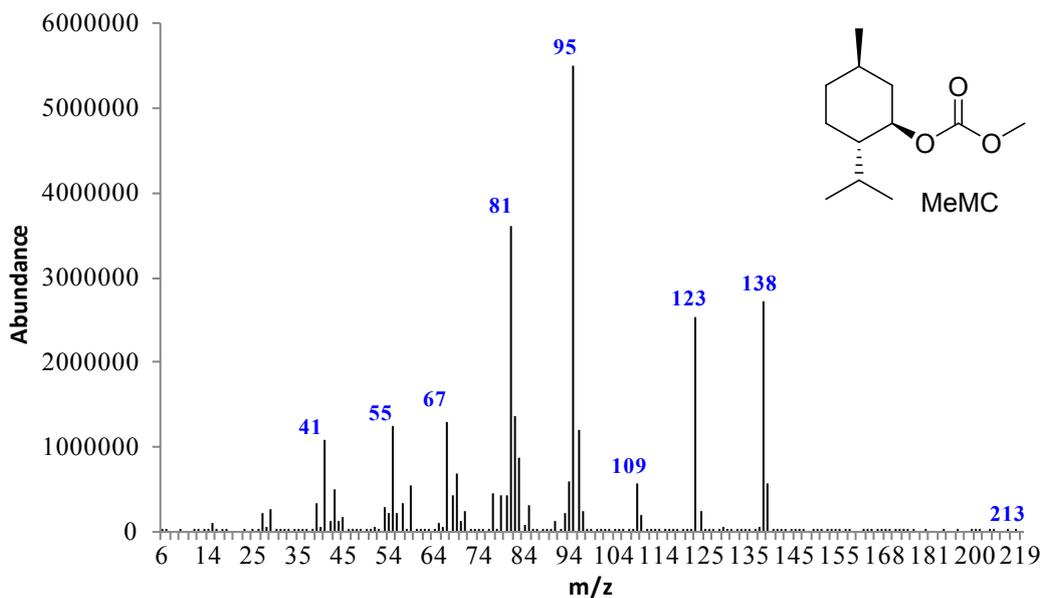
Methyl cyclohexyl carbonate (MCC)



GC-MS (relative intensity, 70eV) m/z : 158 (M^+ , <1%), 99 (27), 83 (45), 82 (99), 77 (59), 71 (38), 67 (100), 59 (21), 55 (41), 54 (30), 41 (33), 29 (9), 27 (8).

Figure S22: GC-MS spectrum of methylcyclohexyl carbonate (MCC)

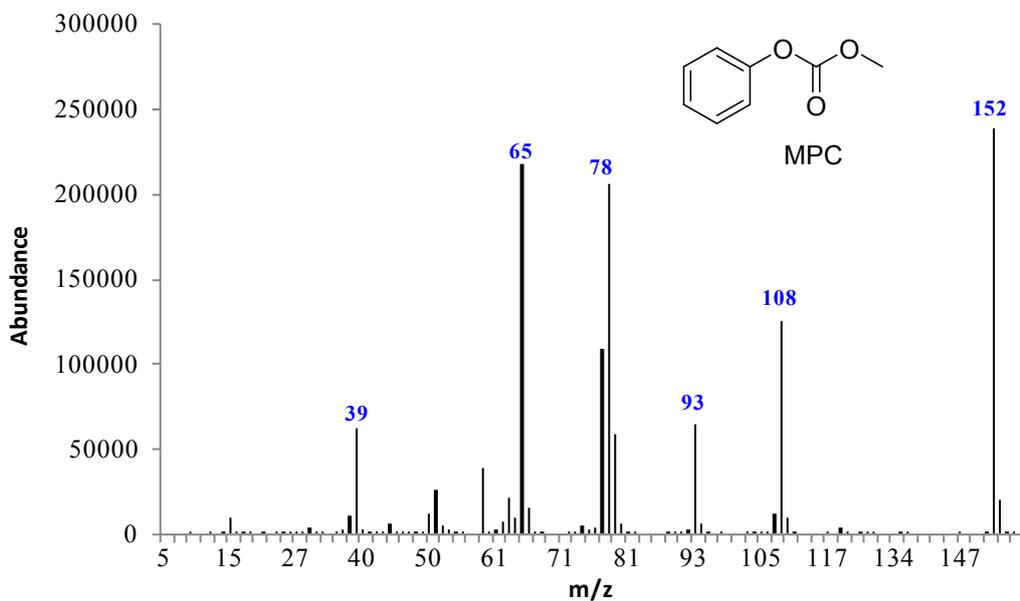
Methyl Menthyl Carbonate (MeMC)



GC-MS (relative intensity, 70eV) m/z : 214 (M^+ , <1%), 139 (10), 138 (50), 123 (46), 109 (10), 95 (100), 81 (66), 67 (24), 55 (24), 41 (20).

Figure S23: GC-MS spectrum of methyl menthyl carbonate (MeMC)

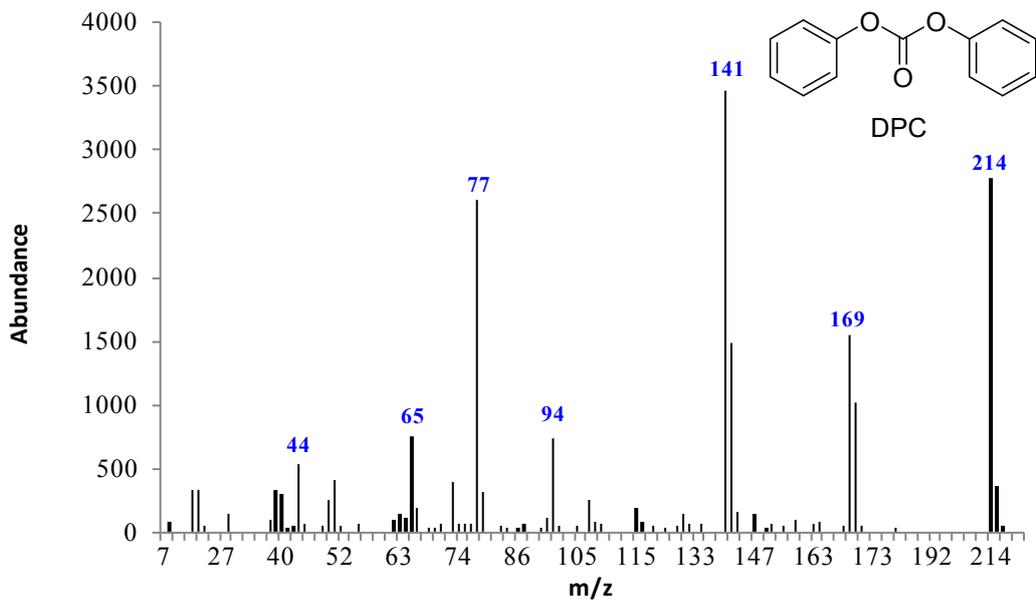
Methyl Phenyl Carbonate (MPC)



GC-MS (relative intensity, 70eV) m/z : 152 (M^+ , 100%), 108 (53), 93 (27), 78 (87), 65 (91), 59 (16), 51 (11), 39 (26).

Figure S24: GC-MS spectrum of methyl phenyl carbonate (MPC)

Diphenyl Carbonate (DPC)



GC-MS (relative intensity, 70eV) m/z : 214 (M^+ , 80%), 169 (45), 141 (100), 94 (21), 77 (75), 65 (22), 51 (12), 44 (15).

Figure S25: GC-MS spectrum of diphenyl carbonate (DPC)