CO_2 VALORIZATION – CATALYSIS – SUPPORTED IONIC LIQUIDS

CONTINUOUS FORMATION OF BIODERIVED CYCLIC CARBONATES USING SUPERCRITICAL CARBON DIOXIDE

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INTRODUCTION

We present a continuous flow method for the conversion of bioderived epoxides into cyclic carbonates using carbon dioxide in its supercritical state as reagent and solvent. Various ammonium-based ionic liquids were initially investigated in batch mode. For limonene oxides[1], tetrabutylammonium chloride turned out to be the best-performing and selective catalyst. In continuous flow, the ionic liquid was physisorbed on mesoporous silica as SILP catalyst. After optimization in short-term experiments, the long-term stability of the SILP system was studied for 48 h.

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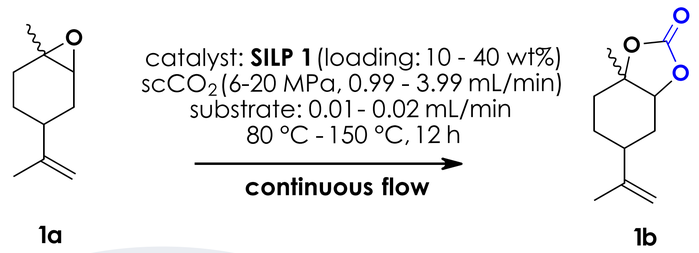
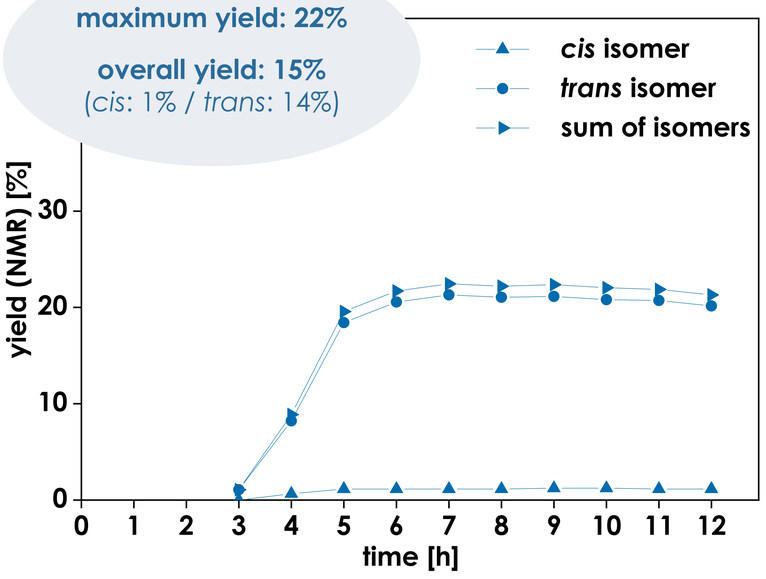
CONTINUOUS CONVERSION: LIMONENE OXIDE



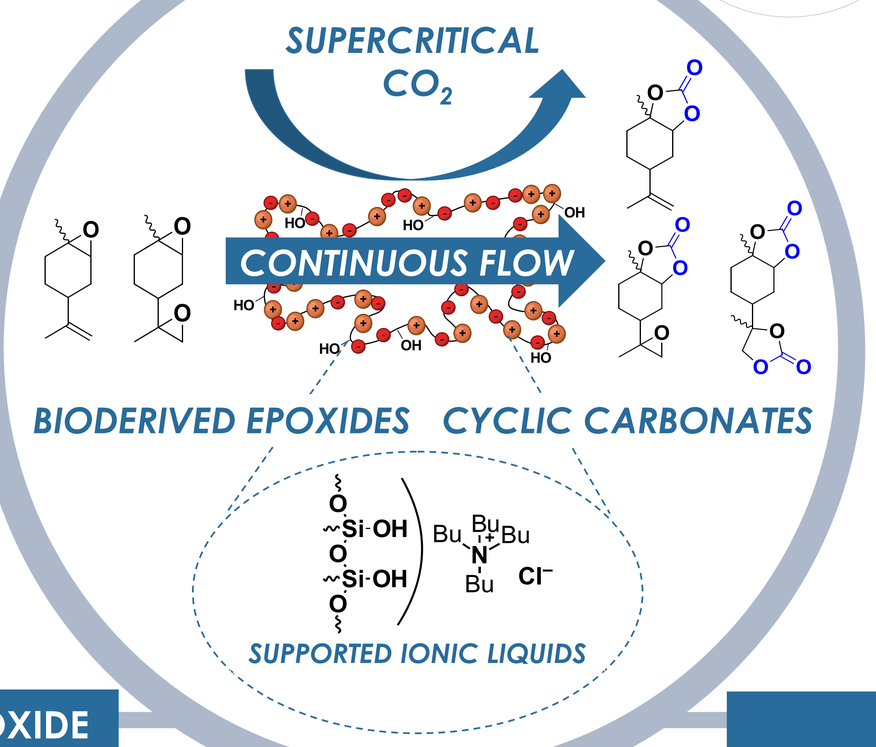


optimized conditions:

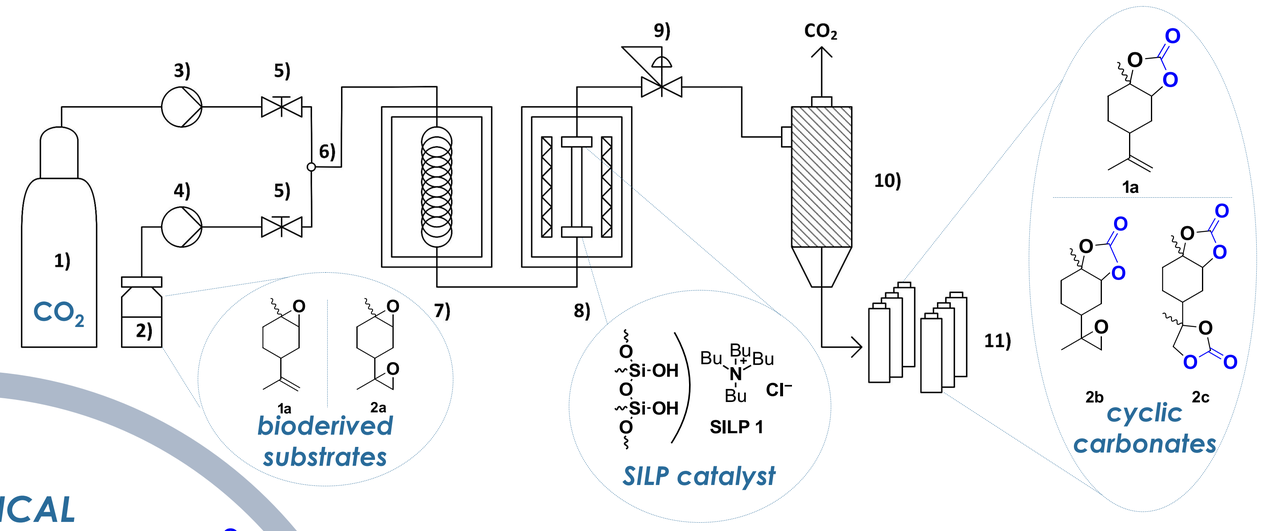
SILP 1 (30 wt% TBAC (**1**) on mesoporous silica),
CO_2: 1.99 mL/min, limonene oxide (**1a**): 0.01 mL/min,
15 MPa, 120 °C, 12 h

LONG-TERM STABILITY

- 48 h experiment
- maximum yield: 22%
- overall yield: 16%
- no leaching of catalyst



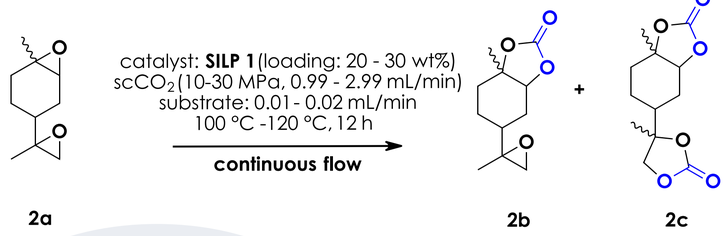
SET-UP FOR CONTINUOUS FLOW

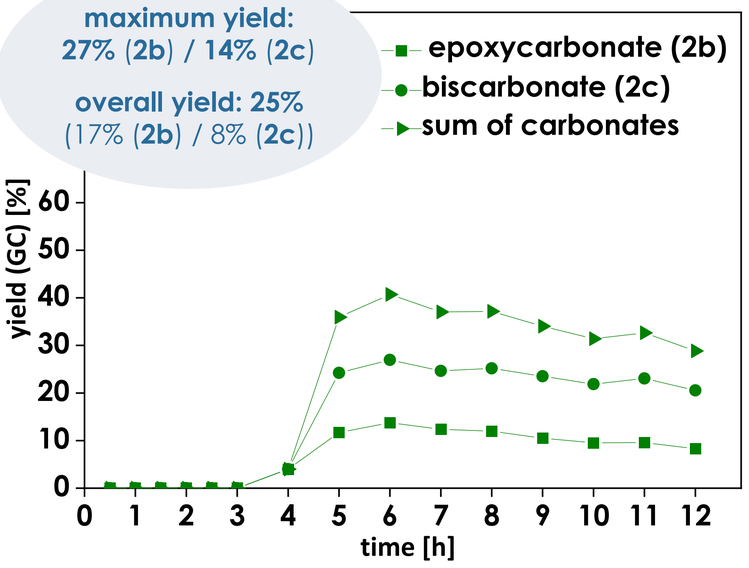


1) liquid CO_2 supply; 2) substrate supply; 3) CO_2 pump; 4) substrate pump; 5) hand operated valve; 6) T-piece; 7) oven with preheating coil (up to 80 °C); 8) oven with catalyst cartridge (up to 150 °C); 9) back-pressure regulator; 10) gas-liquid separator; 11) product collector

- $scCO_2$ and substrate (**1**) entered a thermostated unit where the catalyst cartridge, filled with SILP catalyst (**SILP 1**), was placed
- mixture of carbonates (**2**) and unconverted starting material (**1**) was collected in different fractions
- conversion and yields were determined *via* NMR and GC analysis

CONTINUOUS CONVERSION: LIMONENE DIOXIDE





optimized conditions:

SILP 1 (30 wt% TBAC (**1**) on mesoporous silica,
CO_2: 1.99 mL/min, limonene dioxide (**2a**): 0.01 mL/min,
20 MPa, 120 °C, 12 h

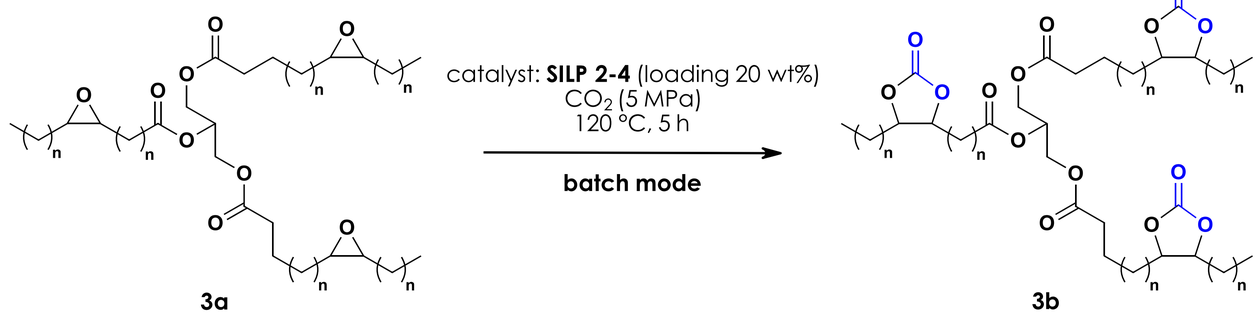
WHY CARBONATES ?

- biscarbonates:
  precursors for polymers such as isocyanate-free polyurethanes
- cyclic carbonates:
  aprotic polar solvents, e.g. in Li-ion batteries
- limonene carbonate:
  cheap and abundant feedstock (43 Mt/a)[2]

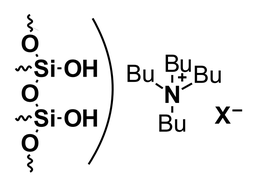
LONG-TERM STABILITY

- 48 h experiment
- overall yield: 17%
  (13% (**2b**) / 3% (**2c**))
- traces of leaching
  (15 wt% loading)

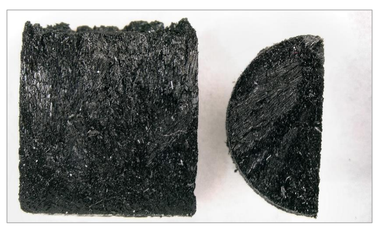
LINSEED OIL-BASED CARBONATES



X⁻	conversion [%] (NMR)
Cl⁻ (**SILP 2**)	31%
Br⁻ (**SILP 3**)	42%
I⁻ (**SILP 4**)	75%



silica supported ILs
before and after application in continuous flow



SiOC supported ILs
studies on tunable porosity and hydrophobicity

CONTINUOUS FLOW ?

- mesoporous silica as a commonly used support material not suitable due to agglomeration over time
- research on alternative supporting materials such as monolithic silicon oxycarbides (SiOC)[3] currently ongoing

References:
[1] Mikšovsky *et al.*, Organic Process and Research Development, **2022**, 26, 2799-2810.
[2] 360ResearchReports Global Limonene Market Research Report 2020, **2020**, https://www.360researchreports.com/global-limonene-market-15061488 (04/2023)
[3] Stabler *et al.*, Journal of the American Ceramic Society, **2018**, 101, 4817–4856.

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