

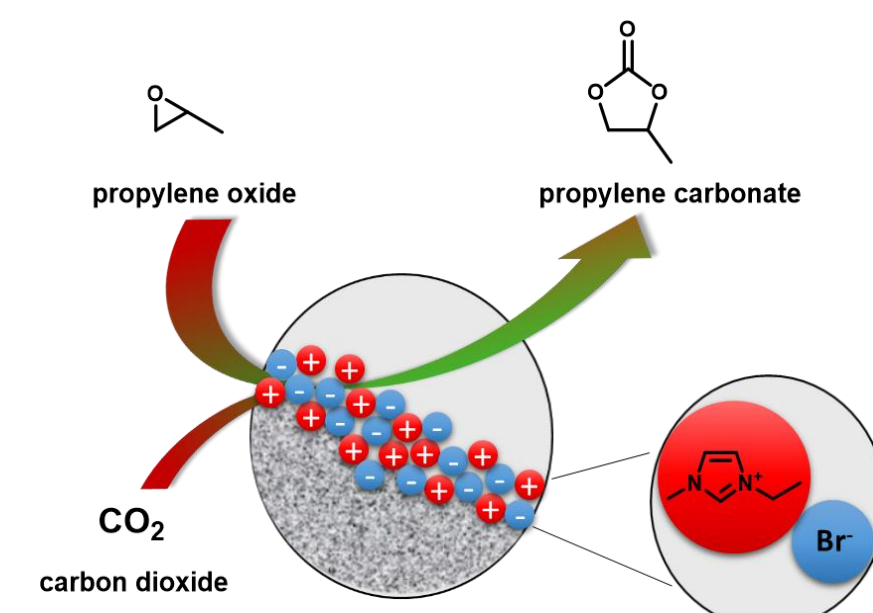
CONTINUOUS CONVERSION OF CARBON DIOXIDE WITH SUPPORTED IONIC LIQUIDS

Aitor Sainz Martinez, Apurba Ranjan Sahoo and Katharina Schröder

Institute of Applied Synthetic Chemistry, TUWien
Getreidemarkt 9/163, 1060 Vienna, Austria
aitor.martinez@tuwien.ac.at

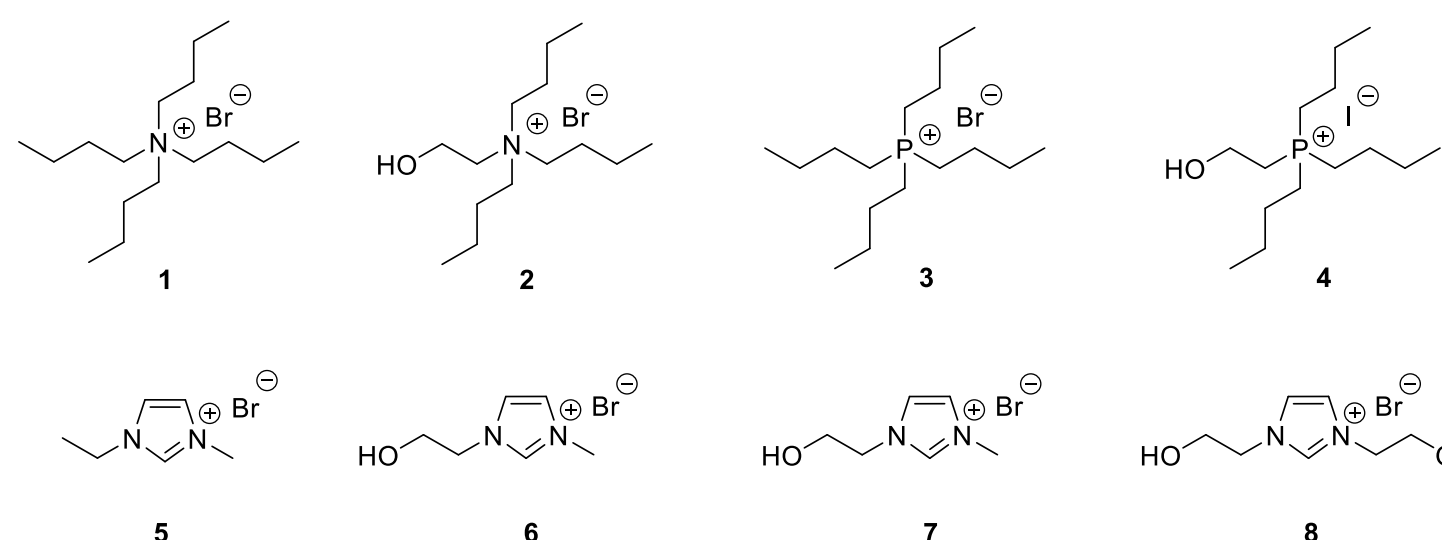
Introduction

The implementation of CO₂ capture from flue gases provides an enormous stream of potential raw materials for chemical production. Apart from their application in carbon capture and storage (CCS) technologies, ionic liquids have attracted considerable interest as tailored catalysts for the conversion of CO₂ to chemical feedstocks [1]. Among all potential products of CO₂, its conversion into cyclic carbonates via reaction with epoxides has received the most attention. Despite the fact that a large pool of catalytically active ionic liquids is available for this reaction, examples of the continuous conversion of CO₂ to cyclic carbonates are rare [2]. This lack of ionic liquid-based continuous flow processes for the conversion of epoxides with CO₂ is surprising, as the liaison of ionic liquids with (supercritical) CO₂ provides an ideal pre-requisite for this purpose. Herein, we present our investigation towards the use of supported ionic liquids as catalysts for the conversion of supercritical carbon dioxide, which acts both as solvent and reagent, aiming for the continuous production of propylene carbonate from propylene oxide and carbon dioxide [3].

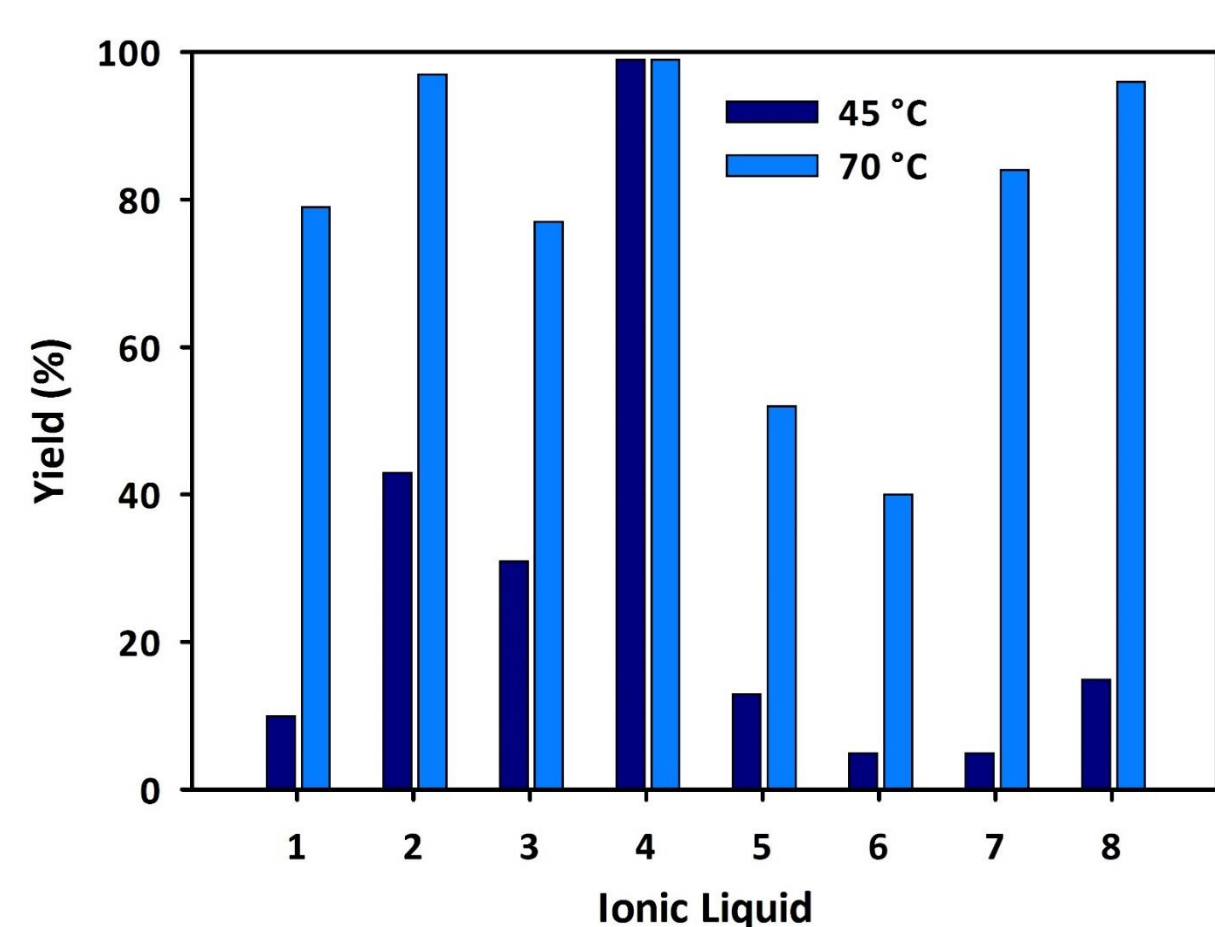


Selection of ionic liquids for batch processes

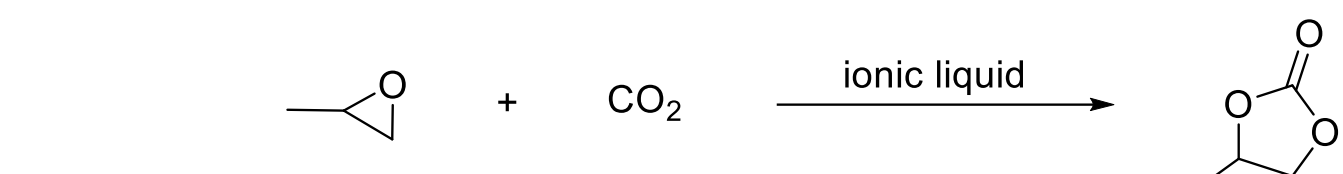
According to recent literature data, a set of eight ionic liquids based on imidazolium, ammonium or phosphonium core structures with halide anions and optional side chain functionalization was selected.



As reaction conditions in literature vary, the reaction of propylene oxide with carbon dioxide was initially performed in an autoclave under batch conditions to allow for a comparison of their catalytic properties.



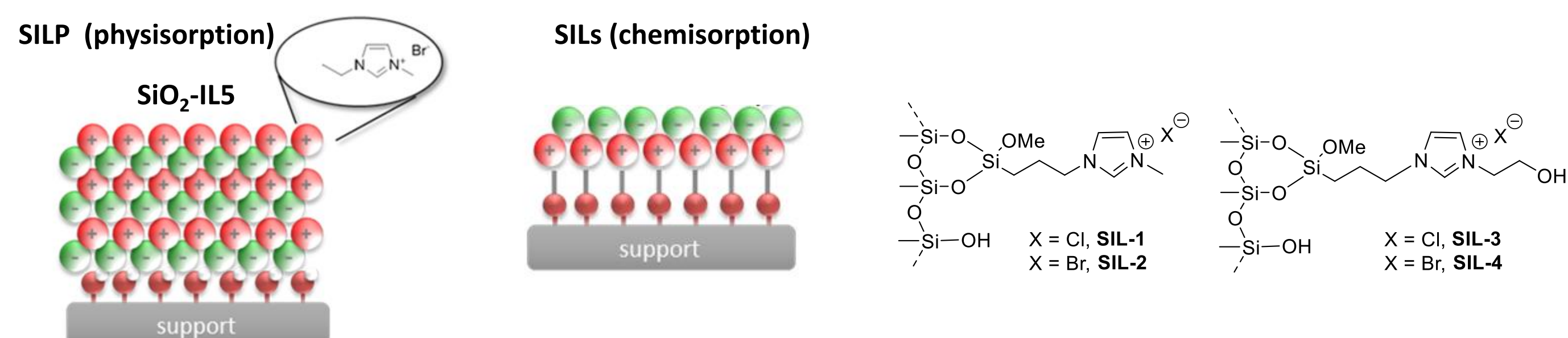
^[a] Reactions were conducted using 5 mol% ionic liquid as catalyst under subcritical conditions at 50 bar and 45 °C or 70 °C for 18 hours, using a 40 cm³ Berghof stainless steel autoclave. ^[b] Isolated yields after flash column chromatography.



As expected, all ionic liquids with a hydroxyl group as substituent demonstrated higher reactivity than those without. Similarly, the influence of the anion could be confirmed since ionic liquids with bromide as anion showed higher reaction rates following the order of nucleophilicity and size [4]. The highest catalytic activity was obtained with the phosphonium based ionic liquid **4**.

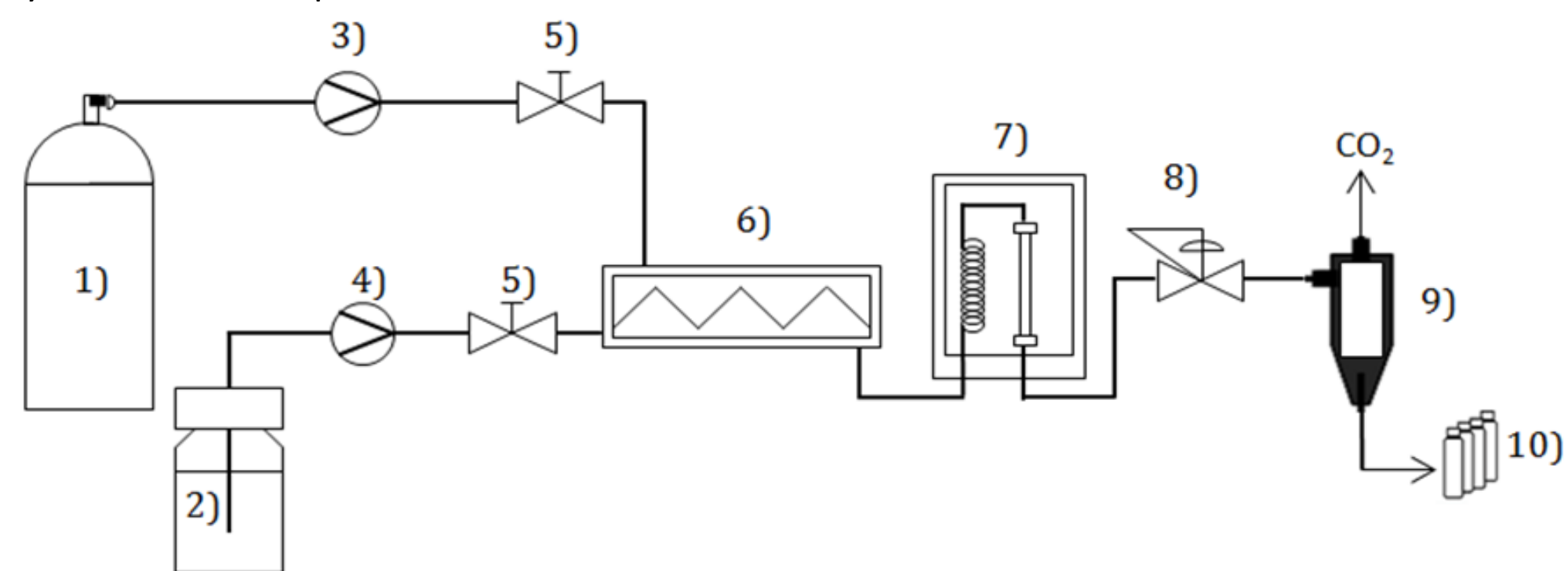
Synthesis of supported ionic liquids

Supported ionic liquid phases (**SILPs**) with physisorbed ionic liquids on silica support were prepared according to literature technologies, relying on the suspension of the ionic liquid and silica in a co-solvent, e.g. methanol, prior to evaporation of the solvent and removal of remaining volatile traces under vacuum. In parallel to the preparation of conventional supported ionic liquids, surface-modified silica (**SIL**) with a monolayer of ionic liquid covalently bound to the solid surface was prepared via reaction of siloxy-functionalized ionic liquids with the surface-OH groups of mesoporous silica.

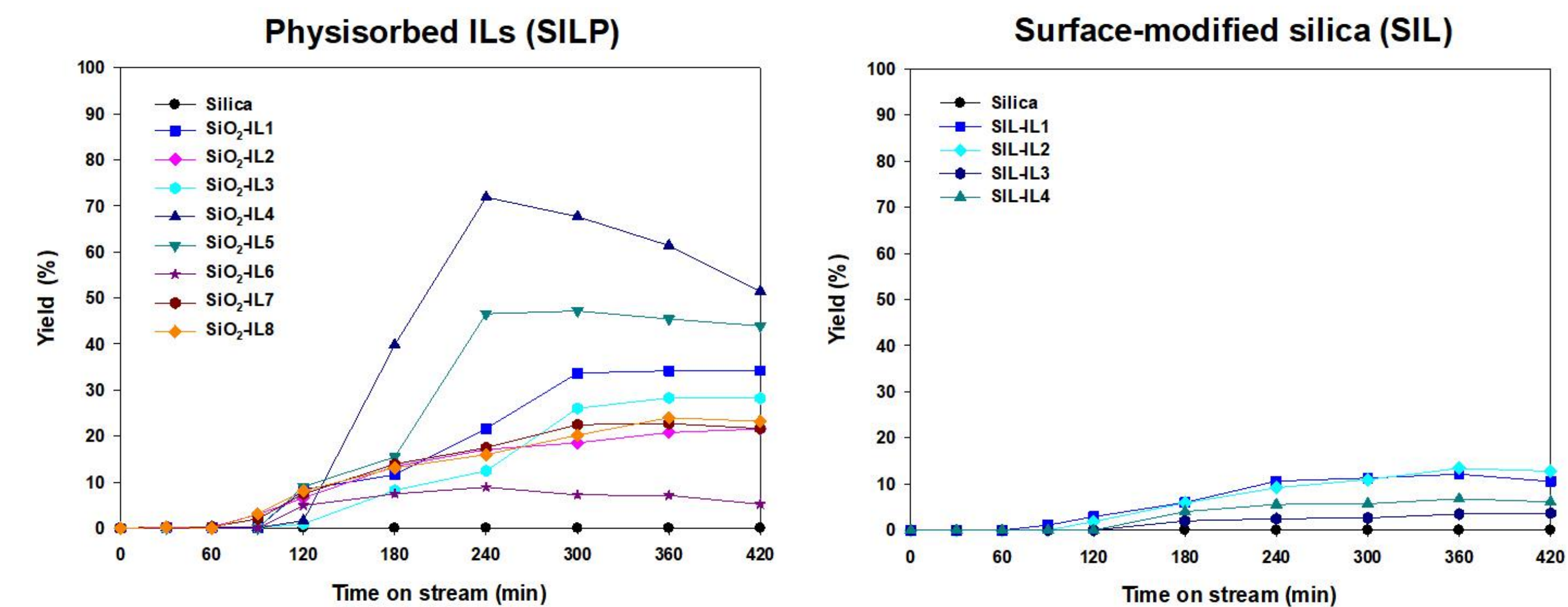


Towards a continuous process

After evaluation of different ionic liquids under batch conditions in an autoclave, the conversion of propylene oxide with carbon dioxide was further studied in continuous flow using supported ionic liquid phases (**SILPs**) and supported ionic liquid surface-modified silica (**SIL**). The employed reactor set-up is shown below.



General set-up for the continuous conversion of propylene oxide with scCO₂ using silica-supported ionic liquids. 1) Liquid CO₂ supply; 2) substrate supply; 3) CO₂ pump; 4) solvent pump; 5) manually operated valve; 6) inline mixer; 7) thermostated oven with preheating coil and catalyst cartridge; 8) back pressure regulator; 9) gas-liquid separator; 10) fraction collector.

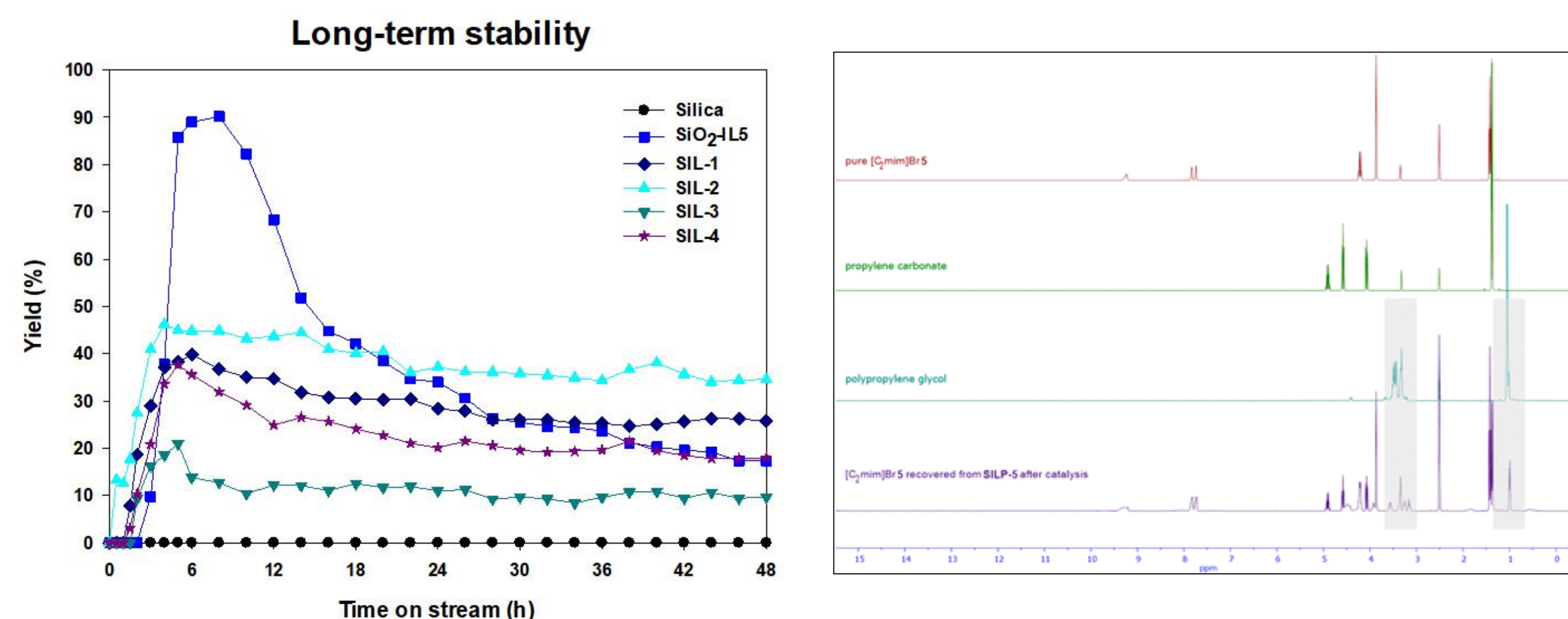


- Stable product output was observed for all SILP catalysts except the supported phosphonium-based ionic liquid **SiO₂-IL4**.
- The supported ionic liquid **SiO₂-IL5** without intermolecular hydroxyl groups present on the silica surface seemed to be the most efficient SILP under flow conditions.
- Considerably lower yield was observed with surface-modified silica (**SILs**) compared to physisorbed (**SILP**) species.
- This indicates a synergistic effect of surface hydroxyl groups present on the silica support material that outperforms the intramolecular hydroxyl groups in ionic liquids **7** and **8**.

Optimization and long-term stability

Based on all tested systems, the combination of [C₂mim]Br **5** and untreated silica as support material appeared to be the optimum system for the formation of propylene carbonate. Further optimization of the system parameters regarding catalyst loading, temperature, pressure and column length were performed.

- An increase in ionic liquid loading to 20 wt% did not improve the yield.
- Under optimized parameters (120 °C, 100 bar, 10 wt% IL loading), the process reached a maximum yield of 89% based on substrate input at 420 min.

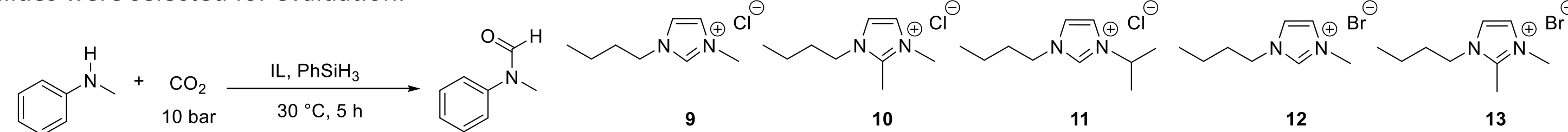


- Yields decreased drastically over time when studying long-term stability using **SiO₂-IL5** under optimized conditions.
 - Accumulation of polypropylene glycol as by-product in the ionic liquid layer was identified as the major cause.
- The formation of polypropylene glycol could be suppressed using surface-modified silica (**SIL**) with a monolayer of ionic liquid cation covalently bound to the solid surface.
- The influence of the anion was similar to the batch-wise processing, and best results were obtained with the bromide-based surface-modified silica **SIL-2**.
- A compromise between high activity and stability is the best solution with this particular catalyst system.

^[a] Experiments were performed on a scCO₂ extraction device by Jasco (Tokyo, Japan) using liquid CO₂ (> 99.995% purity; Messer Austria GmbH) equipped with two CO₂-pumps (PU2086) with recirculating cooler (FL300, JULABO GmbH) and an additional HPLC-pump (PU2082) to deliver substrates and solvents. Heating coil and HPLC column cartridges (50 mm, 150 mm and 250 mm x 4.5 mm ID) filled with catalyst material were equilibrated in a thermostated oven (CO-2060) to the desired temperature, followed by a back-pressure regulator (BP-2080), gas/liquid separator (HC-2086-01) and a product collector (SCF-Vch-Bp). Performed with a flow rate of 2 ml/min (1.98 ml/min scCO₂ and 0.02 ml/min propylene oxide)/n-hexane 1:1, column: 4.5 mm ID x 250 mm.

Next challenge: *N*-formylation of amines

After thorough investigation, we expanded the reaction scope towards the *N*-formylation of amines with CO₂ to produce formamides. The reductive functionalization of amines in the presence of CO₂ and ionic liquids as catalyst is a well-established route to access value-added chemicals [5]. Based on current literature data, a number of ionic liquids based on imidazolium core structure with halides were selected for evaluation.



Entry	Ionic Liquid	Conv. [%] ^c	Yield [%] ^c
1	9	100	90
2	10	100	>99
3	11	100	86
4	12	40	40
5	13	23	19

According to the obtained results, the chloride anion seems to play a pivotal role in enhancing this reaction, whereas the bromide anion is less efficient. Apart from that, the C-2 substitution in the imidazole core was found to be beneficial for this reaction. The highest catalytic activity was obtained with the imidazolium based ionic liquid **10**.

^[a] Reactions were conducted using a 40 cm³ Berghof stainless steel autoclave.
^[b] Reaction conditions: *N*-methylamine (1 mmol), IL (1 mmol), PhSiH₃ (2 mmol).
^[c] Conversion and yield were determined by GC using dodecane as internal standard.

To optimize this reaction system, the effect of temperature, pressure, PhSiH₃ amount and solvent volume was considered. 2-Methyltetrahydrofuran (2-mTHF) was chosen as a solvent. In the subsequent optimization step, the ionic liquid **10** supported on silica was used in a slurry-phase mode, prior to its application in a continuous flow.



Entry	T [°C]	P [bar]	PhSiH ₃ [mmol]	2-mTHF [mL]	Conv. [%] ^c	Yield [%] ^c
1	30	10	2	None	>99	95
2	30	10	1	None	92	89
3	30	10	2	2	55	53
4	80	40	2	2	>99	87
5	80	40	2	5	85	60
6	120	40	2	5	>99	86
7	120	40	1	5	72	55

Entry	IL loading [%]	T [°C]	P [bar]	PhSiH ₃ [mmol]	Conv. [%] ^c	Yield [%] ^c
8	10	120	40	2	37	20
9	10	120	40	1	12	9
10	20	120	40	2	46	38
11	20	120	40	1	24	13

^[a] Reactions were conducted using a 40 cm³ Berghof stainless steel autoclave.
^[b] Reaction conditions: *N*-methylamine (1 mmol), SILP [BdMim]Cl (1 mmol), 2-mTHF (5 mL).
^[c] Conversion and yield were determined in GC using dodecane as internal standard.

^[a] Reactions were conducted using a 40 cm³ Berghof stainless steel autoclave.
^[b] Reaction conditions: *N*-methylamine (1 mmol), [BdMim]Cl (1 mmol).
^[c] Conversion and yield were determined in GC using dodecane as internal standard.

Based on the positive outcome of these preliminary experiments, further attempts will be made for the implementation of *N*-formylation reactions in continuous flow.

References & Acknowledgments

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