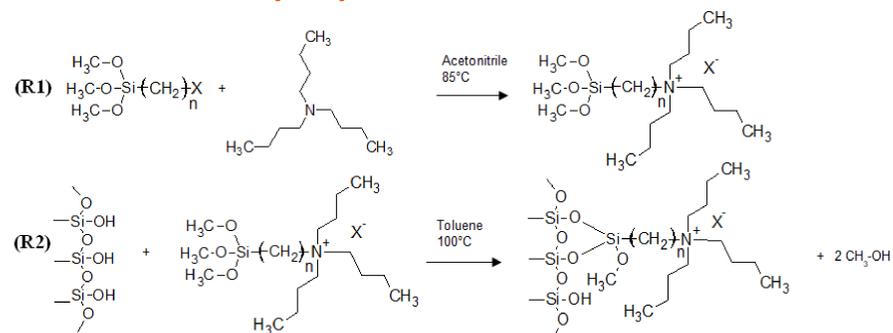


## Introduction

Different types of heterogeneous catalysts designed for a cyclocarbonation reaction between an epoxidized source and CO<sub>2</sub> under supercritical conditions have been synthesized. The process implied a quaternization step where a (haloalkyl)trimethoxysilane reacted with tributylamine (TBA) leading to a tributyl(trimethoxysilylalkyl)ammonium halide, with iodine and bromine as halogens. Then, a grafting step onto commercial fumed silica (EH-5) through condensation reaction between the silane part and Si-OH surficial groups provided the immobilized catalyst. The efficiency of grafting has been validated by liquid <sup>1</sup>H NMR, solid <sup>29</sup>Si NMR and TG-DSC-MS analyzes. The benchmark cyclocarbonation reaction of polyethylene glycol diglycidylether (PEG) at 80°C and 100bar during 4h showed that the best immobilized catalyst was tributylpropylammonium iodide

(IC3Q-EH5). It has also been shown that immobilization provided -surprisingly!- better conversions than the corresponding homogeneous catalysts: this phenomenon has been explained through an epoxide-ring-opening activating effect thanks to Si-OH surficial groups. Furthermore, kinetic studies performed by *in situ* Raman spectroscopy on IC3Q-EH5 showed that temperature had a strong influence on the yield of the reaction while CO<sub>2</sub> pressure had only a small effect. Recycling of the catalyst has also been considered, but no precise conclusions could be conducted because of the high catalyst dispersion. Finally, the addition of a fluorinated alcohol co-catalyst allowed obtaining a similar yield but at 80°C and 55bar during only 2,5h with IC3Q-EH5.

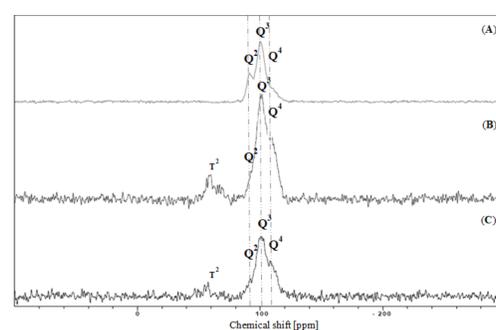
## Immobilized catalyst synthesis



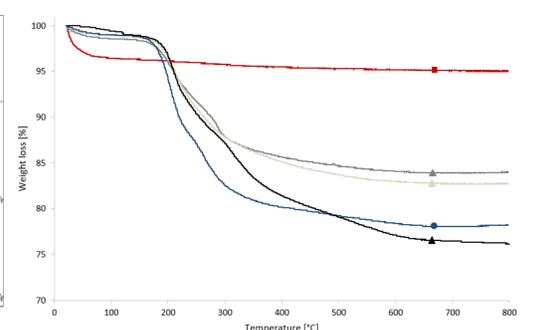
**(R1)** Quaternization reaction between IC3 (X=I and n=3), BrC3 (X=Br and n=3), BrC7 (X=Br and n=7), BrC11 (X=Br and n=11) and TBA to produce the corresponding hybrid catalysts IC3Q, BrC3Q, BrC7Q and BrC11Q in acetonitrile at 85°C.

**(R2)** Grafting of the hybrid catalyst on fumed silica EH-5 by condensation reactions with Si-OH surficial groups and -Si-(O-CH<sub>3</sub>)<sub>3</sub> silane methoxy groups in toluene at 100°C.

## Grafting characterizations

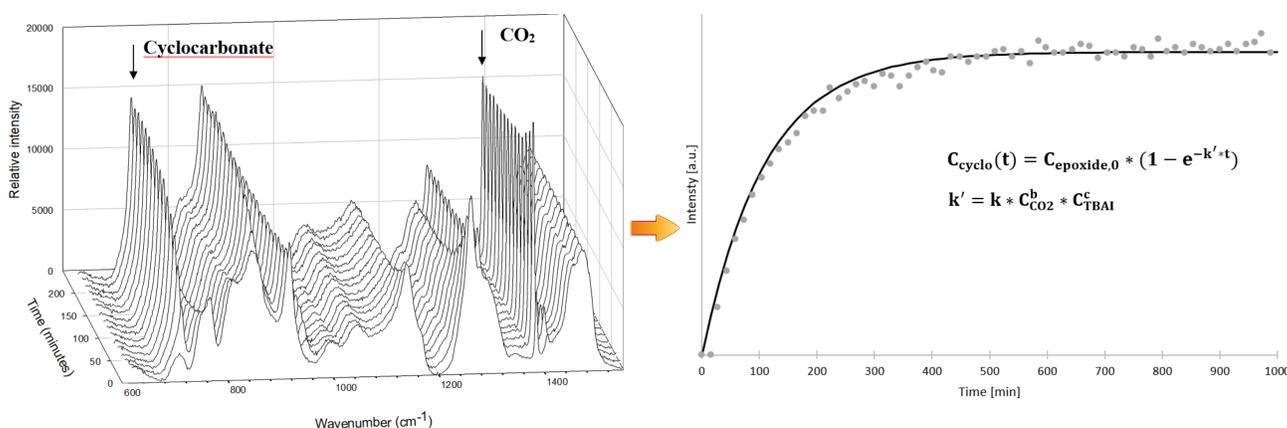


Solid state <sup>29</sup>Si NMR spectra of (A) EH-5, (B) BrC7Q-EH5 and (C) IC3Q-EH5. The capital letters correspond to the following chemical groups: Q<sup>2</sup> = Si(OSi)<sub>2</sub>(OH)<sub>2</sub>, Q<sup>3</sup> = Si(OSi)<sub>3</sub>(OH), Q<sup>4</sup> = Si(OSi)<sub>4</sub> and T<sup>2</sup>: N<sup>+</sup>Si(OSi)<sub>2</sub>(OH)



Weight losses of fumed silica EH-5 (■) and the immobilized catalysts IC3Q-EH5 (●), BrC3Q-EH5 (▲), BrC7Q-EH5 (▲) and BrC11Q-EH5 (▲). Plots were determined by TG-DSC measurements inside a 100μL platinum crucible (heat rate of 5°C/min).

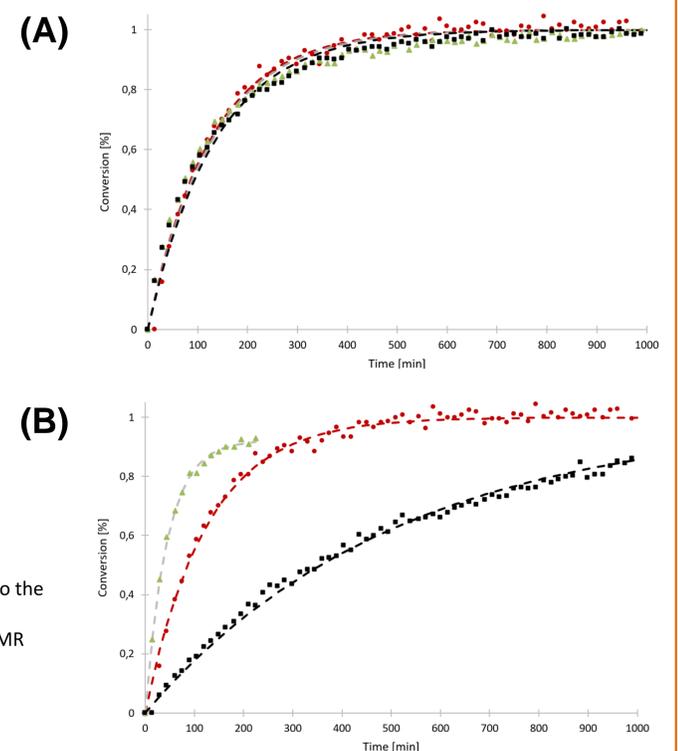
## In situ Raman spectroscopy



Evolution with time of the Raman scattering spectra ( $\lambda = 784,7\text{nm}$ , 300mW) of PEG during cyclocarbonation reaction. The peak at 714cm<sup>-1</sup> corresponds to the cyclocarbonate group and peak at 1388cm<sup>-1</sup> corresponds to CO<sub>2</sub> and is used as a control. The intensity of the 714cm<sup>-1</sup> peak is plotted against time and a pseudo-first order kinetic fit allows the calculation of the kinetic constant *k*. Conversion plots are obtained from intensity plots by additional liquid <sup>1</sup>H NMR measurements.

**(A)** Cycloaddition of CO<sub>2</sub> to epoxidized PEG with IC3Q-EH5 (2mol%) at 80°C and (■) 14bar, (▲) 59bar, (●) 100bar.

**(B)** Cycloaddition of CO<sub>2</sub> to epoxidized PEG with IC3Q-EH5 (2mol%) at 100bar and (■) 60°C, (●) 80°C, (▲) 100°C.



## Results

Sample	Grafting ratio [wt%]	Molar grafting ratio [mol <sub>CAT</sub> /g <sub>EH-5</sub> ]	Cyclocarbonation yield [%]
TBAI	-	-	76
TBABr	-	-	60
TBAI + EH-5	-	-	94
IC3Q	-	-	66
BrC3Q	-	-	64
BrC7Q	-	-	66
BrC11Q	-	-	55
IC3Q-EH5	21	5,8 * 10 <sup>-4</sup>	93
BrC3Q-EH5	16	5,2 * 10 <sup>-4</sup>	64
BrC7Q-EH5	14	3,7 * 10 <sup>-4</sup>	87
BrC11Q-EH5	21	5,0 * 10 <sup>-4</sup>	64

Grafting ratios and molar grafting ratios of catalysts immobilized on the fumed silica EH-5 (calculated from weight loss plots). Cyclocarbonation yields are evaluated by liquid <sup>1</sup>H NMR after reaction at benchmark experimental conditions (80°C and 100bar during 4h.) Rows colored in grey (■) correspond to homogeneous reactions since no silica is present. Tetrabutylammonium iodide/bromide (TBAI/TBABr) are the corresponding homogeneous catalysts. The best candidate identified is IC3Q-EH5. The activating effect coming from the silica matrix is clearly illustrated.

## Acknowledgments

The authors of Liège thank the "Région Wallonne" in the frame of the CO2Green.