

CHEMISTRY & SUSTAINABILITY

CHEM5USCHEM

ENERGY & MATERIALS

Accepted Article

Title: Plasma-assisted immobilization of a phosphonium salt and its use as a catalyst in the valorization of CO2

Authors: Yuya Hu, Sandra Peglow, Lars Longwitz, Marcus Frank, Jan Dirk Epping, Volker Brüser, and Thomas Werner

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemSusChem 10.1002/cssc.201903384

Link to VoR: http://dx.doi.org/10.1002/cssc.201903384



WILEY-VCH

www.chemsuschem.org

FULL PAPER

WILEY-VCH

Plasma-assisted immobilization of a phosphonium salt and its use as a catalyst in the valorization of CO₂

Yuya Hu,^[a] Sandra Peglow,^[b] Lars Longwitz,^[a] Marcus Frank,^[c, d] Jan Dirk Epping,^[e] Volker Brüser,^[b] Thomas Werner^{*[a]}

Dedication ((optional))

a]	Y. Hu, L. Longwitz and PD Dr. T. Werner Leibniz-Institute for Catalysis	
	Albert-Einstein-Straße 29a, 18059, Rostock, Germany	
	E-mail: Thomas.Werner@catalysis.de	
b]	Dr. S. Peglow and Dr. V. Brüser	
-	Leibniz-Institute for Plasma Science and Technology (INP)	
	Felix-Hausdorff-Straße 2, 17489, Greifswald, Germany	
[c]	PD Dr. M. Frank	
	Medical Biology and Electron Microscopy Center	
	University Medicine Rostock	
	Stremelstraße 14, 18057, Rostock, Germany	
d]	PD Dr. M. Frank	
	Department Life, Light & Matter	
	University of Rostock	
	Albert-Einstein-Straße 25, 18059, Rostock, Germany	
e]	Dr. J. Epping	
	Institute of Chemistry	
	Technical University of Berlin	
	Straße des 17 Juni 135, 10623 Berlin, Germany	

Supporting information for this article is given via a link at the end of the document. ((Please delete this text if not appropriate))

Abstract: Herein, we report the first plasma-assisted immobilization of an organocatalyst namely a bifunctional phosphonium salt in an amorphous hydrogenated carbon coating. This method makes the requirement of prefunctionalized supports redundant. The immobilized catalyst was characterized by solid state ¹³C and ³¹P NMR as well as SEM and EDX. The immobilized catalyst (1.0 mol%) was employed in the synthesis of cyclic carbonates from epoxides and CO₂. Notably, the efficiency of the plasma treated catalyst on SiO₂ was higher compared to SiO₂ support impregnated with the catalyst and even to the homogenous counterpart. After optimization of the reaction conditions 13 terminal and 4 internal epoxides were converted with CO2 to the respective cyclic carbonates in yields up to 99%. Furthermore, the possibility to recycle the immobilized catalyst was evaluated. Even though the catalyst could be re-used the yields gradually decreased from the third run. However, this is the first example of the recycling of a plasma immobilized catalyst which opens new possibilities in the recovery and reuse of catalysts.

Introduction

A crucial point in the development of sustainable catalytic processes is the separation and recycling of the catalysts.^[1] In contrast to many other separation techniques,^[2] the immobilization of catalysts allow the facile separations from the product avoiding tedious purification and isolation steps as well as easy recovery and reuse of the catalyst.^[3] Numerous

transformation can be catalyzed by organocatalysts which are typically readily available and nontoxic.^[4] A significant benefit of organocatalysts is the carbon-based scaffold which allows facile structural modification and catalyst tuning as well as catalyst immobilization.^[5]

Amorphous hydrogenated carbon (a-C:H) thin films generated with plasma techniques are promising materials due to their chemical inertness and interesting physical properties such as high density, thermal stability, low friction, high wear resistance, and hardness.^[6] These films are applied as protective coatings for optical windows^[7], antireflective coatings for crystalline silicon solar cells^[8], for biomedical applications^[9] and wear resistant coatings for tools^[10]. Due to their unique properties, amorphous hydrogenated carbon thin films, are highly attractive materials for the immobilization of catalysts. An additional advantage in the use of plasma generated a-C:H films is the direct attachment of the polymeric film to a desired surface without any pretreatment. Compared to other coating procedures it reduces preparative steps and allows in principle the direct incorporation of a functionalized catalyst.

So far, there are only a very limited number of reports regarding the immobilization of catalysts using plasma techniques. For example, Kruth et al. encapsulated Ru-,^[11] as well as Ir-dyes^[12] with plasma polyallylamine (PPAAm) onto TiO₂. The prepared stable TiO₂/N₃ (Ru dye complex)/PPAAm catalyst assemblies and encapsulated Ru sensitizer at the TiO₂ surface, showed improved catalytic performance in the visible-light-driven hydrogen evolution. Additionally, significant enhancement of photo

FULL PAPER

efficiency was observed with the PPAAm encapsulated Ir dye/titania catalyst assemblies. There are also some examples concerning plasma immobilization techniques in biology, for instance, the entrapment of enzymes. In this respect, the groups of Belhacene^[13] and Elagli^[14] reported the polymerization of tetramethyldisiloxane to immobilize β -galactosidase via plasma enhanced chemical vapor deposition. Furthermore, Heyse et al.^[15] described the simultaneous injection of an enzyme solution and acetylene or pyrrole to an atmospheric plasma to immobilize enzymes while preserving their bioactivity.

The atom economic addition of carbon dioxide to epoxides yielding cyclic carbonates is an interesting and frequently studied reaction (figure 1a).^[16] Lately, highly active systems based on OHfunctionalized organocatalysts were reported for the synthesis of cvclic carbonates.^[17] The superior activity of these catalysts is attributed to the epoxide activation and the stabilization of intermediates by hydrogen bonding.^[18] We are interested in development of bifunctional onium salt catalysts for synthesis of cyclic carbonates as well as their recovery and reuse.^[17a, 17b, 19] In this respect one strategy is the immobilization of the onium salt catalyst on organic or inorganic supports. The immobilization of monofunctional phosphonium salt catalysts was studied previously.^[20] Pioneering work on the immobilization of bifunctional structural motifs has been reported by the groups of Dai.^[21] and Liu.^[22] Recently, we reported the successful immobilization of a bifunctional phosphonium bromide bearing a phenol moiety utilizing functionalized polystyrene and silica supports (figure 1b).^[19b] Herein, we report the use of plasma techniques as strategy for the direct immobilization of P-based organocatalysts on unfunctionalized titanium dioxide, iron oxide and silica (figure 1c). Furthermore, the efficiency and recyclability of the immobilized catalysts were studied in the synthesis of cyclic carbonates.





(c) This work: Direct immobilization on unfunctionalized supports by plasma polymerisation



Figure 1. a) Synthesis of cyclic carbonates 2 from CO_2 and epoxides 1. b) Previous strategy for the immobilization of bifunctional phosphonium salts using functionalized supports. c) Concept for the immobilization of phosphonium salt catalysts in an amorphous hydrogenated carbon thin film using plasma polymerization techniques.



Bifunctional phosphonium salts bearing a hydroxyl group in the 2position proved to be a superior structural motif in the cycloaddition of CO₂ and epoxides to form cyclic carbonates.^[23] We envisioned that an allyl substituent might allow the subsequent immobilization in an amorphous hydrogenated carbon thin film generated with plasma techniques. Thus, bifunctional phosphonium salts **5a** and **5b** were synthesized by allylation of 2-(diphenylphosphanyl)phenol (**3**) with allyl bromide (**4a**) or allyl iodide (**4b**) (scheme 1a). The incorporation of **5a** and **5b** into the a-C:H films will most probably lead to saturated linkage in the immobilized catalyst **6** (scheme 1b). Hence, we additionally prepared salts **5c** and **5d** bearing a saturated side chain for comparison of the activity.

a) Synthesis of bifunctional phosphonium salts 5



b) Putative catalyst structure in the a-C:H film



Scheme 1. a) Synthesis of phosphonium salts 5. b) Putative structure 6 of the immobilized phosphonium salts 5a and 5b.

Subsequently, we tested catalysts **5** (1 mol%) in the model reaction of 1,2-butylene oxide (**1a**) with CO₂ to generate the cyclic carbonate **2a** (table 1). At 90 °C and a CO₂ pressure of 1.0 MPa the bromide **5a** and iodide **5b** showed similar activity, giving the desired carbonate **2a** after 2 h in 68% and 67%, respectively (table 1, entries 1 and 2). The propyl substituted phosphonium bromide **5c** gave **2a** only in 40% yield (entry 3). Notably, the iodide **5d** gave the best result under these reaction conditions and 1,2-butylene carbonate (**2a**) was obtained in 83% yield (entry 4). Based on these results, phosphonium salt **5b** was chosen for the immobilization in a-C:Hfilms on TiO₂, FeO and SiO₂.

Calbulate Za.					
	$Et \xrightarrow{O} + CO_2$	Catalyst 5	Et 2a		
Entry	Catalyst	Loading / mol%	Yield $2a$ / % ^[a]		
1	5a	1	68		
2	5b	1	67		
3	5c	1	40		
4	5d	1	83		

Table 1. Comparison of phosphonium salts 5 as catalysts in the synthesis of

Reaction conditions: Epoxide **1a** (13.9 mmol, 1.0 equiv), catalyst **5** (1 md%), 90 °C, 2 h, $p(CO_2)$ = 1.0 MPa solvent-free. [a] Yields determined by ¹H NMR with mesitylene as internal standard.

FULL PAPER

Initially, the supports were tested in the model reaction and proved not facilitate the conversion of 1a with CO₂ (table 2, entries 1-3). Subsequently, these supports were treated with low pressure plasma techniques, generating an a-C:H coating.^[24] Also, in the presence of the plasma treated supports, the formation of 2a was not observed (entries 4-6). Furthermore, the supports were impregnated with catalyst 5b and tested in the model reaction (entries 7-9). The catalyst retained its catalytic activity and all three samples 5b@TiO2, 5b@FeO as well as 5b@SiO2 gave 1,2-butylene carbonate (2a) in excellent yields of 87%, 78% and 88%, respectively (entries 7-9). Subsequently, the impregnated supports 5b@TiO₂, 5b@FeO and 5b@SiO₂ were treated with a low pressure plasma. The obtained catalyst samples 5bb@TiO2, 5bb@FeO as well as 5bb@SiO2 were tested in the model reaction (entries 10-12). Notably, with 1 mol% catalyst loading, TiO2 and SiO2 supported catalysts converted the 1,2-butylene oxide (1a) into the 1,2-butylene carbonate (2a) with 93% and 99% yields (table 2, entries 10 and 12), while with FeO supported catalyst, a moderate yield of 72% was obtained (table 2, entry 11). These yields were comparable to the results obtained with the impregnated samples (entries 7-9 vs. 10-12).

Table 2. Screening of supports and immobilized catalysts.					
		+ CO ₂ 90 °C,	Catalyst 6 h, <i>p</i> (CO ₂)= 1.0 MI	Pa Et	
Entry	1a Support	5b / mol%	Cat.	t / min ^[a]	Yield 2a / % ^[b]
1	TiO ₂	-		-	0
2	FeO	-		-	0
3	SiO ₂	-		-	0
4	TiO ₂	-		25	0
5	FeO	-		25	0
6	SiO ₂	-		25	0
7	TiO ₂	1	5 b @TiO ₂	-	87
8	FeO	1	5b@FeO	- L	78
9	SiO ₂	1	5b@SiO ₂		88 (65) ^[c]
10	TiO ₂	1	5bb®TiO ₂	25	93
11	FeO	1	5bb®FeO	25	72
12	SiO ₂	1	5bb®SiO ₂	25	99(77) ^[c]

Reaction conditions: Epoxide **1a** (13.9 mmol, 1.0 equiv), 500 mg of the support or catalyst, 90 °C, 6 h, $p(CO_2)$ = 1.0 MPa, solvent-free. [a] Plasma treating time. [b] Yield determined by ¹H NMR with mesitylene as internal standard. [c] 2 h reaction time.

The nominal layer thickness of the a-C:H coating is related to the plasma treating time. Longer treating time will result in a thicker film and better coverage of the particle. This might lead to a stronger catalyst binding to the surface, reducing catalyst leaching and enhancing its recyclability. The nominal layer thickness is determined by profilometry of an a-C:H coating deposited on planar glass plate.^[24] This is only an approximation for films on particles because the planar glass plate is

homogeneously coated while the deposition on particles takes place non-uniformly and partially. Profilometric measurements of the nominal layer thickness of a-C:H films obtained after 6.5, 25 and 39 min of plasma treatment gave layer thicknesses of 53.3, 136.8 and 190 nm, respectively. We studied the impact of different plasma treating times (6.5, 25 and 39 min) on the catalytic activity of 5b on TiO₂, FeO and SiO₂ and the effect of the catalyst recyclability in our model reaction. To reveal the effect of the plasma treatment, the recycling of the non-plasma treated impregnated catalysts 5b@TiO2, 5b@FeO and 5b@SiO2 were initially investigated (figure 2). In the model reaction all three catalyst samples gave good yields up to 88% after 6 h at 90 ℃ and 1.0 MPa CO₂ pressure in the first run. The product was obtained after simple filtration and the recovered catalyst was reused in a second run under the same reaction conditions. Notably, the yields dropped significantly. The best yield achieved in the second run was only 31% with 5b @SiO2. We assumed that the low yields can be explained by the leaching of catalyst 5b into the liquid phase. This is easily possible since the catalyst is not covalently bonding to the supports. The ³¹P NMR spectrum of the product mixture showed a signal at δ = 20.2 ppm which was assigned to the homogenous catalyst 5b. This consequently confirms the proposed leaching.



Evaluation of impregnated catalyst (
 1st run
 2nd run)



Figure 2. Recyclability evaluation of impregnated catalyst samples **5b**@TO₂. **5b**@FeO and **5b**@SiO₂. Reaction conditions: Epoxide **1a** (13.9 mmol, 1.0 equiv), immobilized catalyst (500 mg, 1 mol% catalyst loading in respect to **1a**), 90 °C, 6 h, $p(CO_2)$ = 1.0MPa, solvent-free. For the 1st runs isolated yields are given. For the 2nd runs the yield was determined by ¹H NMR with mesitylene as internal standard.

We studied the immobilized catalyst **5b** on different supports (TiO₂, FeO and SiO₂) after 6.5 min plasma treating time under the same conditions. Catalysts **5ba**®TiO₂, **5ba**®FeO and **5ba**®SiO₂ gave the desired carbonate **2a** in good to excellent yields up to 98% (figure 3a). Even though with catalysts **5ba**®TiO₂ and **5ba**®FeO the yields dropped significantly in the second run, in the presence of **5ba**®SiO₂ carbonate **2a** was obtained in >80%. These results might be explained by an insufficient immobilization due to the short plasma treating time. Nevertheless, compared to

FULL PAPER

the impregnated catalysts the plasma treatment led to a significant improvement of the yield (Figure 2 vs. Figure 3a).

a) Results for 6.5 min plasma treating time (= 1st run = 2nd run)







Figure 3. Recyclability evaluation of catalysts **5b** on TiO₂, FeO and SiO₂ with different plasma treating time (a) 6.5 min, b) 25 min c) 39 min plasma treating time). Reaction conditions: Epoxide **1a** (13.9 mmol, 1.0 equiv), immobilized catalyst (500 mg, 1 mol% catalyst loading in respect to **1a**), 90 °C, 6 h, $p(CO_2)$ = 1.0 MPa, solvent-free. For the 1st runs isolated yields are given. For the 2nd runs the yield was determined by ¹H NMR with mesitylene as internal standard.

Hence, the same set of experiments was repeated with catalysts (**5bb** $^{\odot}$ TiO₂, **5bb** $^{\odot}$ FeO and **5bb** $^{\odot}$ SiO₂) obtained after 25 min plasma treating time (figure 3b). In the first run, all three catalysts gave results comparable to **5ba** $^{\odot}$ TiO₂, **5ba** $^{\odot}$ FeO and **5ba** $^{\odot}$ SiO₂ (figure 3a vs. 3b, 1st run). The yields for **2a** were significantly increased in the case of the TiO₂ and SiO₂ supported catalysts (**5bb** $^{\odot}$ TiO₂ and **5bb** $^{\odot}$ SiO₂) in the second run (figure 3a vs. 3b, 2rd run). This indicates that the prolonged plasma treating time leads

to an improved catalyst binding to the a-C:H coatings. Finally, the plasma treating time was extended to 39 min and the prepared catalysts were tested under the standard conditions (figure 3c). In the case of **5bc**®TiO₂ the yields dropped in the first and second runs compared to the results with shorter treating times (figure 3a and 3b). In contrast **5bc**®FeO showed increased yields compared to the previous experiments. Again, the best result was obtained with **5bc**®SiO₂ giving yields of 99% for **2a** in the first and second runs.

As observed for **5bc**®TiO₂ longer plasma treating times might lead to a better recyclability most probably due to an improved immobilization (figure 3a and 3b). However, if the plasma treating time is too long, e.g. 39 min for **5bc**®TiO₂, this might lead to partial coverage of the catalyst and thus lower yields (figure 3c vs. 3a and 3b). In the case of **5bb**®FeO the yield and recyclability were enhanced by a plasma treating time of 39 min indicating a better immobilization of **5b** on the support. This suggests that not only the plasma treating time but also the nature of the support material is of crucial importance for the efficiency and recyclability of the catalyst.

Based on these results, 5bb®SiO2 was identified to be the most promising catalyst. Thus, 5bb@SiO2 was characterized with various analytical methods and compared to the homogenous catalyst 5b as well as 5b impregnated on SiO2, 5b@SiO2. As expected, the elemental analysis of both the impregnated catalyst 5b@SiO2 and the plasma treated catalyst 5bb@SiO2 showed the presence of phosphorus and iodine. The solid state ³¹PNMR spectrum of the plasma treated catalyst 5bb@SiO2 showed a broad signal at $\delta = 16.9 \text{ ppm}$ which is in the similar range as signal in the ³¹PNMR spectrum of homogenous catalyst **5b** (δ = 20.2 ppm), indicating the presence of the phosphonium motif. The solid state ¹³C NMR spectra of the impregnated **5b**@SiO₂ and the plasma treated sample 5bb®SiO₂ showed the expected signals compared to the ¹³C NMR spectrum of the homogeneous catalyst 5b (figure 4a-c). Notably, the characteristic signal for the phenolic carbon at δ = 161 ppm for **5b** can clearly be identified in the solid state NMR of **5b**@SiO₂ and **5bb**@SiO₂. This is of particular importance since it indicates that the bifunctional nature of the immobilized catalyst stays intact, which is crucial for its superior catalytic activity.

Furthermore, EDX measurements were performed on the impregnated 5b@SiO2 and plasma treated sample 5bb@SiO2 as well as on the SiO₂ support.^[24] The EDX spectrum of the SiO₂ support showed no signal in the range between 1.90 and 4.10 keV (figure 5a). In contrast the impregnated and plasma treated samples show signals at 2.04 keV (P K $_{\alpha}$) which indicates the presence of phosphorous (figure 5b and 5c). Notably, the impregnated sample 5b@SiO2 does not show an iodine signal (figure 5b) while the plasma treated sample has a low intensity signal at 4.07 keV (I $L_{\alpha 1}$ and $L_{\beta 1}$) which is characteristic for iodine (figure 5c). The absence of the signal for $IL_{\alpha 1}$ and $L_{\beta 1}$ in figure 5b and the low intensity of the signal in figure 5c can be explained by problems of detecting surface associated iodine, which is resulted from the high energy required for the excitation of the iodine L transitions. This can be overcome by changing the sample pretreatment, e.g., the EDX spectra of the impregnated sample 5b@SiO2 which was copper sputtered clearly showed the presence of iodide (figure 5d). The copper layer (z= 29, 10 nm) altered penetration and spreading of the electron beam within the sample surface compared to the rather electron transparent carbon coating (z=6, 10-15 nm). Notably, a comparable peak for

FULL PAPER

phosphorus is obtained under both pretreatment conditions (figure 5b and 5d).



Figure 4. a) ¹³C NMR spectrum of homogeneous catalyst **5b** in CDCl₃. b) Sold state ¹³C NMR spectrum of impregnated catalyst **5b**@SiO₂ and c) Solid state ¹³C NMR spectrum of plasma immobilized catalyst **5bb**@SiO₂.



Figure 5. Section of EDX spectra between 1.90 and 4.10 keV for a) the SO₂ support (black, carbon coated), b) the impregnated catalyst **5b**@SiO₂ (grey, carbon coated), c) the plasma treated catalyst **5bb**@SiO₂ (blue, carbon coated) and d) the impregnated catalyst **5b**@SiO₂ (red, Cu-sputtered).^[24]

Moreover, we studied the plasma treated sample **5bb**@SiO₂ by scanning electron microscopy (SEM) and EDX mapping in comparison to the neat support (figure 6). The SEM images of the silica support and **5bb**@SiO₂ are shown in figure 6, Ia and IIa. The carbon EDX mapping on these particles show clearly an increase of carbon surface coating due to the plasma treatment (figure 6, Ib vs. IIb). The mapping for phosphorus indicates that the catalyst is evenly distributed over the support as well as the absence of phosphorous on the neat support (figure 6, Ic and IIc).





Figure 6. SEM images of the silica support (Ia) and catalyst **5bb**®SiO₂ (Ila). EDX mapping with color coded intensity range of carbon (Ib) and phosphous (Ic) for the silica support. EDX mapping with colour coded intensity range of carbon (IIb) and phosphorus (IIc) for the immobilized catalyst **5bb**®SiO₂.^[24]

Subsequently we studied the performance of catalyst **5bb**®SiO₂ under different reaction parameters (table 3). Under the conditions of the catalyst screening the desired product **2a** was obtained in 99% yield (entry 1). A decrease of the reaction time to 3 h gave 1,2-butylene carbonate (**2a**) in 99% isolated yield (entry 2) and even after 1 h a yield of 57% was obtained (entry 3). The influence of the CO₂ pressure was also investigated. The reduction of the CO₂ pressure to 0.5 MPa led to a lower yield of 88% compared to the standard conditions (entry 1 vs. entry 4). Next, the reaction temperature was decreased to 45 °C. Even at 45 °C the immobilized catalyst **5bb**®SiO₂ led to full conversion and 99% yield after 6 h (entry 5). Notably, 21% yield of **2a** was still obtained after 3 h at this temperature (entry 6).

Table 3. Catalytic reaction conditions optimization for the conversion of 1,2- butylene oxide 1a.							
		1 mol% 5bb	\rightarrow				
	Et 4 002	45 or 90 °C, 1–6 h	solvent-free	Et			
	1a	p(CO2)= 0.5 01 1.0 MPa		2a			
Entry	T/ °C	p/ MPa	t/ h	Yield 2a / % ^[a]			
1	90	1.0	6	99			
2	90	1.0	3	99			
3	90	1.0	1	57			
4	90	0.5	6	88			
5	45	1.0	6	99			
6	45	1.0	3	21			

Reaction conditions: Epoxide **1a** (13.9 mmol, 1.0 equiv), immobilized catalyst **5bb**@SiO₂ (500 mg, 1 mol% catalyst loading in respect to **1a**), *T*, *t*, *p*, solvent-free. [a] Isolated yields are given.

Based on these results we determined reaction conditions (1 mol% catalyst **5bb** \mathbb{P} SiO₂, 45 °C, 6 h, $p(CO_2)=1.0$ MPa, solvent-free) suitable for the evaluation of the substrate scope. As shown in scheme 2, terminal aliphatic epoxides **1a–d** were converted into the respective carbonates **2a–d** in yields up to >99% under these conditions. In contrast styrene oxide (**1e**) showed only moderate conversion and **2e** was obtained in a yield of 61%. However, with a prolonged reaction time of 24 h, full conversion was achieved and the desired product was isolated in

FULL PAPER

92% yield. In this reaction acetophenone from a Meinwald rearrangement was observed as a by-product.^[25]



Scheme 2. Evaluation of the substrate scope using catalyst **5bb** $@SO_2$ Reaction conditions: Epoxide 1 (13.9 mmol, 1.0 equiv), **5bb** $@SO_2$ (500 mg, 1 mol% catalyst loading in respect to 1), 45 °C, 6 h, $p(CO_2)=1.0$ MPa, solvent-free. Isolated yields are given. [a] 24 h. [b] 90 °C. [c] 90 °C, 24 h. d 1.0 mL 1-BuOH was used as the solvent.

Glycerol has become widely available since it is the major byproduct in the manufacturing of biodiesel.[26] The so-called "biodiesel" is a popular term for the fatty acid methyl esters formed by transesterification of vegetable oils with methanol.^[27] It has been investigated that the use of glycerol as the feedstock for the synthesis of carbonates can lead to a significant reduction in the carbon footprint of their production compared to the use of fossil resources.^[28] Glycidol (1f), epichlorohydrin (1g) as well as their derivatives 1h-1m can be obtained from glycerol as renewable feedstock.^[29] The respective carbonates often show unique properties and are used as synthetic building blocks, monomers and solvents.^[30] Hence, we were particularly interested in the preparation of carbonates 2f-2m. Despite notable progress that was recently reported in the reaction of glycidol (1f) with CO₂ to carbonate 2f the conversion of 1f is challenging. [31] Especially for the use of heterogeneous catalysts in this reaction, it typically requires drastic reaction conditions such as high reaction temperatures (\geq 110 °C) and high CO₂ pressure (\geq 1 MPa).^[32] Under the standard reaction conditions 2f was obtained in a yield of 58% and in 85% when extending the reaction time. In contrast, epichlorohydrin (1g) and glycidyl ether 1h were isolated in 84 and 99% yield after 6 h. However, to achieve full conversion of the other glycidol derivatives 1i-1m, the reaction condition were adjusted and high yields up to 96% on the respective carbonates 2i-2m were achieved. Of particular interest are the products 2k which was obtained in 89% yield and is used as electrolyte in lithium ion batteries,^[33] as well as glycerol carbonate methacrylate

2I and siloxane **2m** which both were isolated in 95% yield and are used as monomers and adhesion promotors. ^[34]

We turned our attention to the conversion of internal epoxides with CO₂ which is in general more challenging. Under the standard conditions 2n was obtained only in 13% yield. At higher reaction temperatures of 90 °C carbon ate 2n was obtained in 61% yield after 24 h, which is a good result for an internal epoxide considering that a heterogeneous organocatalyst with low loading (1 mol%) was used. Full conversion was achieved for the reaction between 3,4-epoxytetrahedrofuran (10) and CO₂. However, due to partial polymerization only 31% of the desired product 20 were isolated. The conversion of cis-stilbene oxide (cis-1p) and epoxidized methyl oleate (cis-1q) gave the desired cyclic carbonates in yields of 13% and 30%, respectively. For the reaction of cis-1p a solvent was required since both the substrate and product are solid. In respect to the stereochemistry it has to be mentioned that, in the case of cis-1p the only product observed was the thermodynamically more stable trans-2p, which indicates that in this case the reaction proceeds via an cationic intermediate and an S_N1-type mechanism.^[35] Similarly, the conversion of biobased cis-1q led to 2q as a mixture of cis/transisomers (28:72). Finally, we studied the recyclability of the plasma treated catalyst on SiO2 in more detail. At first the impact of the different reaction parameters on the outcome of the model reaction over five runs using **5bb**[®]SiO₂ as the catalyst was evaluated. Under the standard conditions of the substrate screening the recycling experiments revealed that at 45 °C the yield decreased from >99% in the 1st run, 81% in the 2nd down to below 10% in the 5th run (figure7).



(= 45 °C, 6 h = 90 °C, 6 h = 90 °C, 3 h = 90 °C, 6 h, 2 mol^{%[a]})



Figure 7. Recyclability investigation for catalyst **5bb** $@SiO_2$ at different reaction temperatures and times. Reaction conditions: Epoxide **1a** (13.9 mmol, 1.0 equiv), immobilized catalyst (500 mg, 1 mol% catalyst loading in respect to **1a**), *T*, *t*, *p*(CO₂)= 1.0 MPa, solvent-free. Isolated yields are given for the 1st run. For run 2–5 the yields were determined by ¹H NMR with mesitylene as internal standard. [a] 2 mol% catalyst loading in respect to **1a**.

Improved yields were achieved at a higher reaction temperature of 90 °C. At this temperature **2a** was obtained in a yield of >99% in the 1st and 2nd run. In the subsequent runs the yield gradually decreased to 20%. We envisioned that catalyst leaching is responsible for yield decrease and postulated that the leaching might correlates to the reaction time. Thus, we reduced the reaction time to 3 h and repeated catalyst recycling (figure 7). Even though similar results were obtained in the 1st and 2nd run,

FULL PAPER

the yields in the following runs could not be improved. As expected with a higher catalyst loading of 2 mol%, the yields of **2a** were significantly improved in runs 3–5, though in this set of experiments the yield gradually decreased from 90% in the 3^{rd} run to 41% in the last run.

Due to these results we were especially interested on the impact of different plasma treating times (6.5 min for 5ba@SiO₂, 25 min for 5bb®SiO₂ and 39 min for 5bc®SiO₂, figure 8) on the recyclability of the respective catalysts. Full conversions and yields >99% were achieved in the 1st run for all three catalysts. The same results were achieved with catalyst 5bb@SiO2 and 5bc®SiO2 in the 2nd run while 5ba®SiO2 gave a lower yield of 82% which might be addressed to an insufficient immobilization due to the short treating time. In the 3rd run the yields in the presence of all three catalysts were decreased. 5bb@SiO2 led to the best result yielding 2a in 81% while 5ba®SiO2 and 5bc®SiO2 gave 2a in similar yields of 70 and 74% respectively. This trend further continued for all three catalysts whereby yields <20% were observed in the 5th run. Apparently, a plasma treating time of 25 min for 5bb®SiO2 led to a good balance between the binding to the a-C:H coating (compared to 5ba®SiO2) and its thickness, avoiding the coverage of the catalytically active species (compared to 5bc®SiO₂).

Recyclability of catalysts with different plasma treating times (6.5 min 25 min 39 min)



Figure 8. Recyclability investigation of SiO₂ supported catalyst **5b** with catalysts different plasma treating times **5ba**@SiO₂ (6.5 min), **5bb**@SiO₂ (25 min) and **5bc**@SiO₂ (39 min). Reaction conditions: Epoxide **1a** (13.9 mmol, 1.0 equiv), immobilized catalyst (500 mg, 1 mol% catalyst loading in respect to **1a**), 90 °C, 6 h, $p(CO_2)=1.0$ MPa, solvent-free. Isolated yields are given for the 1st run. For runs 2–5 the yields were determined by ¹H NMR with mesitylene as internal standard.

To get a better insight in the catalyst deactivation, **5bb**®SiO₂ was isolated after the 5th run and analyzed by solid state NMR, SEM, EDX and elemental analysis. Notably, the elemental analysis indicates that the phosphonium salt is detached from the surface of the SiO₂ support. This is supported by the ³¹P NMR spectrum which does not show the expected signals from the aryl substituents at the phosphorus in the aromatic region. In contrast the ³¹P NMR spectra of the product obtained in the 1st and 2nd run clearly indicate leaching of the catalyst into the product. Notably, the elemental analysis of the used catalyst showed a higher carbon and hydrogen content while solid state ¹³C NMR spectrum displayed several new multiplets between 0 and 80 ppm which indicates product deposition on the catalyst

surface. However, considering that the sample still showed catalytic activity, the concentration of the catalyst on the surface might be below the detection limit of these methods. In contrast the EDX mapping shows the presence of low amount evenly dispersed phosphorus compared to neat support (figure 9a vs. 9b). However, the concentration of phosphorus after the 5th run is still significantly lower compared to the fresh catalyst (figure 9a vs. 9c).



Figure 9. EDX mapping with color coded intensity range of phosphorus a) for 5bb@SiO₂ after 5 reaction cycles b) of the neat SiO₂ support and c) of immobilized catalyst 5bb@SiO₂.^[24]

Conclusion

In summary, we designed and synthesized a functionalized phosphonium salt suitable for plasma immobilization. The obtained catalysts were tested in the synthesis of 1,2-butylene carbonate from CO_2 and 1,2-butylene oxide as the model reaction. Among the three tested potential supports (TiO₂, FeO and SiO₂) SiO₂ proved to be the most suitable. In initial recycling experiments the support impregnated with the catalyst was compared to its plasma treated counterpart. These experiments revealed the clear advantage of the plasma treatment. Remarkably, the immobilized catalyst even showed similar (or higher) efficiency than its homogenous analogue. Furthermore, the impact of different plasma treating times on the efficiency and recyclability was investigated. The best catalytic material was characterized by solid state NMR, elemental analysis, SEM and EDX. The analysis revealed the formation of an amorphous hydrogenated carbon coating as well as the presence of the catalytically active species. After the optimization of the reaction conditions 13 terminal and 4 internal epoxides were converted with CO₂ to the respective cyclic carbonates in yields up to 99%. Special attention was paid to the conversion of 8 glycerol derivatives which can be obtained from the biodiesel production waste glycerol. Considering that a heterogeneous catalyst was used, it is noteworthy that most of the terminal substrates could be efficiently converted to the desired products under mild reaction conditions (45 °C, 6 h, $p(CO_2)$ = 1.0 MPa) with low catalyst loading of 1 mol%. Subsequently, we studied the recyclability of the catalyst for the model reaction in detail. Even though the catalyst was used in 5 consecutive runs, the yields gradually decreased from the second to the fifth run. The analysis of the produced cyclic carbonate as well as the characterization of catalyst after the fifth run revealed catalyst leaching into the product phase. The optimization of the coating process might allow the reduction of the catalyst leaching and is currently under investigation. To the best of our knowledge this is the first example on the successful recycling of a plasma immobilized catalyst. This prove of concept opens the opportunity for further studies on the application of plasma polymerization techniques in catalyst recycling.

FULL PAPER

Experimental Section

Preparation of bifunctional catalysts 5 (GP1)

A mixture of 1.0 equiv phosphane **3** and 5.0 equiv alkyl halides **4** were stirred 24 h at 23–102 °C under argon atmosphere. The crude product was washed with diethyl ether and dried in vacuo.

Procedure for the screening of homogeneous catalyst (Table 1)

A 45 cm³ stainless-steel autoclave was charged with catalyst **5** (1.0 mol%). Subsequently, 1,2-butylene oxide (**1a**, 1.00 g, 13.9 mmol, 1.0 equiv) was added. The autoclave was purged with CO₂ and heated to 90 °C for 2 h, while *p*(CO₂, 90 °C) was kept constant at 1.0 MPa. The reactor was cooled with an ice bath below 20 °C and CO₂ was released slowly. The conversion of the epoxide **1a** and yield of the carbonate **2a** were determined by ¹H NMR spectroscopy from the reaction mixture using mesitylene as internal standard.

Procedure for the impregnation of different supports with catalyst 5b

Phosphonium salt **5b** (119 mg, 0.278 mmol), was dissolved in CH₂Cl₂ (125 mL). The respective support (TiO₂, FeO or SiO₂, 1.00 g) was added to the solution. The suspension was shaken for 16 h at 23 °C. Subsequently all volatiles were removed in vacuo to obtain the support impregnated with catalyst **5b** (12 wt.% on TiO₂, FeO or SiO₂).

Procedure for the plasma assisted immobilization of catalyst 5b on different supports

Catalyst **5b** impregnated on TiO₂, FeO or SiO₂ (2.00 g, 12 wt.% **5b**) was dispersed on a sample holder in a vacuum chamber of the plasma deposition device. After a pumping time of about 2 hours, a gas mixture consisting of argon and methane in the ratio 1: 1 (40 sccm) was admitted. After a waiting period of 5 minutes the plasma power (600 W, 13.56 MHz) was switched on. The pressure of 15 Pa was controlled by pressure gauge and butterfly valve. The plasma treatment time was varied between 6.5, 25 and 39 min.

Catalyst and parameter screening (Table 2 and Table 3)

A 45 cm³ stainless-steel autoclave was charged with the impregnated or plasma treated catalyst (500 mg, 1.0 mol% or 2.0 mol%) and 1,2-butylene oxide (**1a**, 1.00 g, 13.9 mmol, 1.0 equiv). The autoclave was purged with CO₂ and the reactor was heated to 45 °C or 90 °C for 3–24 h, while $p(CO_2, 90 °C)$ was kept constant at 1.0 MPa. The reactor was cooled with an ice bath below 20 °C and CO₂ was released slowly. The conversion of the epoxide **1a** and the yield of the carbonate **2a** were determined by ¹H NMR spectroscopy from the reaction mixture using mesitylene as internal standard.

Protocol for the catalyst recycling experiments

A 45 cm³ stainless-steel autoclave was charged with the catalyst **5bb**@SiO₂ (500 mg, 1.0 mol% or 2.0 mol% loading), 1,2-butylene oxide (**1a**, 1.0 g, 13.9 mmol, 1.0 equiv). The autoclave was purged with CO₂ and heated to 45°C or 90 °C for 2 h or 6 h, while $p(CO_2, 90 °C)$ was kept constant at 1.0 MPa. Subsequently the reactor was cooled to ≤20 °C with an ice bath and CO₂ was released slowly. The reaction mixture was removed by extraction with Et₂O (3x30 mL). All volatiles were removed in vacuo to yield 1,2-butylene carbonate **2a**. The catalyst was dried in air overnight and reused. The conversion of the epoxide **1a** and yield of the desired carbonate were determined either with isolated product or by ¹H NMR spectroscopy using mesitylene as internal standard.

Acknowledgements ((optional))

This research was funded by the Leibniz Association within the scope of the Leibniz ScienceCampus Phosphorus Research Rostock (<u>www.sciencecampus-rostock.de</u>). We thank Dr. Armin Springer (Electron Microscopy Centre) for support during EDX analyses. Thomas Frankenberger (Dept. of Physics, University of Rostock) is acknowledged for helping with sample sputtering.

Keywords: CO₂ fixation • Plasma • Immobilization • Cyclic carbonates • Organocatalysts

- a) S. Hübner, J. G. de Vries, V. Farina, Adv. Synth. Catal. 2016, 358 3– 25; b) D. J. Cole-Hamilton, R. P. Tooze, Catalyst separation, recovery and recycling: chemistry and process design, Vol. 30, Springer Science & Business Media, 2006; c) V. S. Shende, V. B. Saptal, B. M. Bhanage, Chem. Rec. 2019, 19, 2022–2043.
- a) C. A. M. Afonso, J. G. Crespo, Green separation processes, Wiley-VCH, Weinheim, 2005; b) D. J. Cole-Hamilton, Science 2003, 299, 1702– 1706; c) I. V. Gürsel, T. Noël, Q. Wang, V. Hessel, Green Chem. 2015, 17, 2012–2026; d) Y. Brunsch, A. Behr, Angew. Chem. Int. Ed. 2013, 52, 1586–1589.
- [3] a) M. Benaglia, A. Puglisi, F. Cozzi, *Chem. Rev.* 2003, *103*, 3401–3430;
 b) A. Das, S. S. Stahl, *Angew. Chem. Int. Ed.* 2017, *56*, 8892–8897; c)
 A. R. Grimm, D. F. Sauer, T. Mirzaei Garakani, K. Rübsam, T. Polen, M. D. Davari, F. Jakob, J. Schiffels, J. Okuda, U. Schwaneberg, *Bioconjug. Chem.* 2019, *30*, 714–720; d) W. Leitner, *Pure Appl. Chem.* 2004, *76*, 635–644; e) M. Schreier, J. Luo, P. Gao, T. Moehl, M. T. Mayer, M. Grätzel, *J. Am. Chem. Soc.* 2016, *138*, 1938–1946; f) R. Zhong, A. C. Lindhorst, F. J. Groche, F. E. Kühn, *Chem. Rev.* 2017, *117*, 1970–2058.
- [4] a) A. Berkessel, H. Gröger, *Asymmetric Organocatalysis*, Wiley-VCH, Weinheim, **2005**; b) T. Werner, *Adv. Synth. Catal* **2009**, *351*, 1469– 1481; c) B. List, *Chem. Rev.* **2007**, *107*, 5413–5415.
- a) F. Cozzi, Adv. Synth. Catal. 2006, 348, 1367–1390; b) M. Gruttadauria,
 F. Giacalone, R. Noto, Chem. Soc. Rev. 2008, 37, 1666–1688.
- [6] a) J. M. Lackner, R. Major, L. Major, T. Schöberl, W. Waldhauser, *Suf. Coat. Technol.* 2009, 203, 2243–2248; b) D. Mansuroglu, K. Goksen, S. Bilikmen, *Plasma Sci. Technol.* 2015, *17*, 488–495.
- [7] J. Robertson, Mater. Sci. Eng. R: Rep. 2002, 37, 129–281.
- D. Silva, M. Namani, A. Côrtes, M. O. Jr, P. Mei, F. Marques, in 23rd European Photovoltaic Solar Energy Conference, Valencia, Spain, 2008.
 M. Santos, M. Bilek, S. Wise, Biosurf. Biotribol. 2015, 1, 146–160.
- [10] S. A. Bakar, A. A. Aziz, P. Marwoto, S. Sakrani, R. M. Nor, M. Rusop, in *Carbon and Oxide Nanostructures*, Springer, **2010**, pp. 79–99.
- [11] a) A. Kruth, S. Hansen, T. Beweries, V. Brüser, K. D. Weltmann, *ChemSusChem* **2013**, 6, 152–159; b) A. Kruth, A. Quade, V. Brüser, K.-D. Weltmann, *J. Phys. Chem.* C **2013**, *117*, 3804–3811.
- [12] A. Kruth, S. Peglow, N. Rockstroh, H. Junge, V. Brüser, K. D. Weltmann, J. Photochem. Photobiol. A 2014, 290, 31–37.
- [13] K. Belhacene, A. Elagli, C. Vivien, A. Treizebré, P. Dhulster, P. Supiot, R. Froidevaux, *Catalysts* 2016, *6*, 209.
- [14] A. Elagli, K. Belhacene, C. Vivien, P. Dhulster, R. Froidevaux, P. Supiot, J. Mol. Catal. B, Enzym. 2014, 110, 77–86.
- [15] P. Heyse, A. Van Hoeck, M. B. Roeffaers, J. P. Raffin, A. Steinbüchel, T. Stöveken, J. Lammertyn, P. Verboven, P. A. Jacobs, J. Hofkens, *Plasma Process Polym.* 2011, *8*, 965–974.
- [16] a) M. Cokoja, M. E. Wilhelm, M. H. Anthofer, W. A. Herrmann, F. E. Kuehn, *ChemSusChem* 2015, *8*, 2436–2454; b) G. Fiorani, W. Guo, A. W. Kleij, *Green Chem*. 2015, *17*, 1375–1389; c) C. Martín, G. Fiorani, A. W. Kleij, *ACS Catal.* 2015, *5*, 1353–1370; d) H. Büttner, L. Longwitz, J. Steinbauer, C. Wulf, T. Werner, *Top. Curr. Chem*. 2017, *375*, 50; e) A. W. Kleij, M. North, A. Urakawa, *ChemSusChem* 2017, *10*, 1036–1038.
- [17] a) J. Großeheilmann, H. Büttner, C. Kohrt, U. Kragl, T. Werner, ACS Sustainable Chem. Eng. 2015, 3, 2817–2822; b) C. Koht, T. Werner, ChemSusChem 2015, 8, 2031–2034; c) M.H. Anthofer, M. E. Wilhelm, M. Cokoja, M. Drees, W. A Herrmann, F. E. Kühn, ChemCatChem 2015, 7, 94–98; d) M. Ding, H.-L. Jiang, Chem. Commun. 2016, 52, 12294–

FULL PAPER

12297; e) S. Liu, N. Suematsu, K. Maruoka, S. Shirakawa, *Green Chem* **2016**, *18*, 4611–4615; f) X. Meng, H. He, Y. Nie, X. Zhang, S. Zhang, J. Wang, *ACS Sustainable Chem. Eng.* **2017**, *5*, 3081–3086; g) V. B. Saptal, B. M. Bhanage, *ChemSusChem* **2017**, *10*, 1145–1151.

- [18] J. Steinbauer, C. Kubis, R. Ludwig, T. Werner, ACS Sustainable Chem Eng. 2018, 6, 10778–10788.
- [19] a) W. Desens, C. Kohrt, M. Frank, T. Werner, *ChemSusChem* 2015, 8, 3815–3822; b) J. Steinbauer, L. Longwitz, M. Frank, J. Epping, U. Kragl, T. Werner, *Green Chem.* 2017, *19*, 4435–4445.
- [20] a) T. Takahashi, T. Watahiki, S. Kitazume, H. Yasuda, T. Sakakura, *Chem. Commun.* 2006, 1664–1666; b) J.-S. Tian, C.-X. Miao, J.-Q. Wang, F. Cai, Y. Du, Y. Zhao, L.-N. He, *Green Chem.* 2007, *9*, 566–571; c) T. Sakai, Y. Tsutsumi, T. Ema, *Green Chem.* 2008, *10*, 337–341; d) Y. Xiong, F. Bai, Z. Cui, N. Guo, R. Wang, *J. Chem.* 2013, *2013*; e) Q.-W. Song, L.-N. He, J.-Q. Wang, H. Yasuda, T. Sakakura, *Green Chem.* 2013, *15*, 110–115; f) J. Wang, J. G. W. Yang, G. Yi, Y. Zhang, *Chem.* 2015, *51*, 15708–15711.
- [21] W. Dai, Y. Zhang, Y. Tan, X. Luo, X. Tu, Appl. Catal., A 2016, 514, 43– 50.
- [22] Y. Liu, W. Cheng, Y. Zhang, J. Sun, S. Zhang, Green Chem. 2017, 19, 2184–2193.
- [23] H. Büttner, J. Steinbauer, C. Wulf, M. Dindaroglu, H. G. Schmalz, T. Werner, ChemSusChem 2017, 10, 1076–1079.
- [24] More details see Supporting Information.
- [25] M. W. Robinson, A. M. Davies, R. Buckle, I. Mabbett, S. H. Taylor, A E. Graham, Org. Biomol. Chem. 2009, 7, 2559–2564.
- [26] a) F. Ma, M. A. Hanna, *Bioresour. technol.* **1999**, *70*, 1–15; b) M. R. Monteiro, C. L. Kugelmeier, R. S. Pinheiro, M. O. Batalha, A. da Siva César, *Renew. Sustain Energy Rev.* **2018**, *88*, 109–122.
- [27] a) M. A. Meier, J. O. Metzger, U. S. Schubert, *Chem. Soc. Rev.* 2007, 36, 1788–1802; b) A. B. Leoneti, V. Aragão-Leoneti, S. V. W. B. De Oliveira, *Renew. Energy* 2012, 45, 138–145; c) P. Okoye, B. Hameed, *Renew. Sustain. Energy Rev.* 2016, 53, 558–574; d) A. Rodrigues, J. C. Bordado, R. G. d. Santos, *Energies* 2017, 10, 1817.
- [28] H. Büttner, C. Kohrt, C. Wulf, B. Schäffner, K. Groenke, Y. Hu, D. Kruse, T. Werner, *ChemSusChem* 2019, 12, 2701–2707.
- [29] a) B. M. Bell, J. R. Briggs, R. M. Campbell, S. M. Chambers, P. D. Gaarenstroom, J. G. Hippler, B. D. Hook, K. Kearns, J. M. Kenney, W. J. Kruper, *Clean Soil, Air, Water* **2008**, *36*, 657–661; b) R. M. Hanson, *Chem. Rev.* **1991**, *91*, 437–475; c) M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi, C. Della Pina, *Angew. Chem. Int. Ed.* **2007**, *46*, 4434–4440; d) K. Urata, *PharmaChem* **2010**, *9*, 7–10; e) M. Sutter, E. D. Silva, N. Duguet, Y. Raoul, E. Métay, M. Lemaire, *Chem. Rev.* **2015**, *115*, 8609–8651.
- [30] a) A.-A. G. Shaikh, S. Sivaram, *Chem. Rev.* **1996**, *96*, 951–976; b) B. Schäffner, F. Schäffner, S. P. Verevkin, A. Börner, *Chem. Rev.* **2010**, *110*, 4554–4581; c) M. O. Sonnati, S. Amigoni, E. P. T. de Givenchy, T. Darmanin, O. Choulet, F. Guittard, *Green Chem.* **2013**, *15*, 283–306; d) D. C. Webster, *Prog. Org. Coat.* **2003**, *47*, 77–86.
- [31] a) R. Huang, J. Rintjema, J. González-Fabra, E. Martín, E. C. Escudero-Adán, C. Bo, A. Urakawa, A. W. Kleij, *Nature Catal.* 2019, *2*, 62–70; b)
 S. Sopeña, M. Cozzolino, C. Maquilón, E. C. Escudero - Adán, M. Martínez Belmonte, A. W. Kleij, *Angew. Chem. Int. Ed.* 2018, *57*, 11203– 11207; c) J. Rintjema, R. Epping, G. Fiorani, E. Martín, E. C. Escudero -Adán, A. W. Kleij, *Angew. Chem. Int. Ed.* 2016, *55*, 3972–3976.
- [32] a) L. Han, H.-J. Choi, S.-J. Choi, B. Liu, D.-W. Park, *Green Chem.* 2011, 13, 1023–1028; b) J. Sun, J. Wang, W. Cheng, J. Zhang, X. Li, S. Zhang, Y. She, *Green Chem.* 2012, 14, 654–660; c) C. Qi, J. Ye, W. Zeng, H. Jiang, *Adv. Synth. Catal.* 2010, 352, 1925–1933; d) K. R. Roshan, G. Mathai, J. Kim, J. Tharun, G.-A. Park, D.-W. Park, *Green Chem.* 2012, 14, 2933–2940.
- [33] a) N. Ohmi, T. Nakajima, Y. Ohzawa, M. Koh, A. Yamauchi, M. Kagawa, H. Aoyama, *J. Power Sources* **2013**, *221*, 6–13; b) D. Nishikawa, T. Nakajima, Y. Ohzawa, M. Koh, A. Yamauchi, M. Kagawa, H. Aoyama, *J. Power Sources* **2013**, *243*, 573–580.
- [34] a) S. Jana, A. Parthiban, C. L. L. Chai, *Chem. Commun.* 2010, 46, 1488–1490; b) M. Wehbi, S. Banerjee, A. Mehdi, A. Alaaeddine, A. Hachem, B. Ameduri, *Macromolecules* 2017, *50*, 9329–9339.

[35] J. Steinbauer, A. Spannenberg, T. Werner, Green Chem. 2017, 19, 3769–3779.

9 This article is protected by copyright. All rights reserved.

FULL PAPER

Entry for the Table of Contents

In sert graphic for Table of Contents here. ((Please ensure your graphic is in one of following formats))



Plasma polymerization has been employed as a strategy for the immobilization of an organocatalyst on unfunctionalized supports $(SiO_2, TiO_2 \text{ and FeO})$. The catalytic material was used in synthesizing cyclic carbonates from epoxides and CO_2 . Under the optimized conditions 17 cyclic carbonates were synthesized in up to 99% yield under mild conditions. Furthermore, the unprecedented recycling of a catalyst immobilized by plasma techniques was investigated.

Institute and/or researcher Twitter usernames: ((optional))