

# Final Report

## Immobilization of P-based organocatalysts by plasma techniques

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Funding number:	SAS-2015-IOW-LWC
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Cooperation partner:	Prof. M. Beller (LIKAT) Prof. Dr. U. Kragl (UoR, MNF) Dr. J. von Langermann (UoR, MNF) Prof. Dr. A. Schulz (UoR, MNF)
Project title:	Immobilization of P-based organocatalysts by plasma techniques/ H-POP
Project duration:	1 <sup>st</sup> of August 2017 till 31 <sup>st</sup> of June 2018
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\* z.B. Conference contributions, publications (with status), funding applications (with status)

## 1 Summary

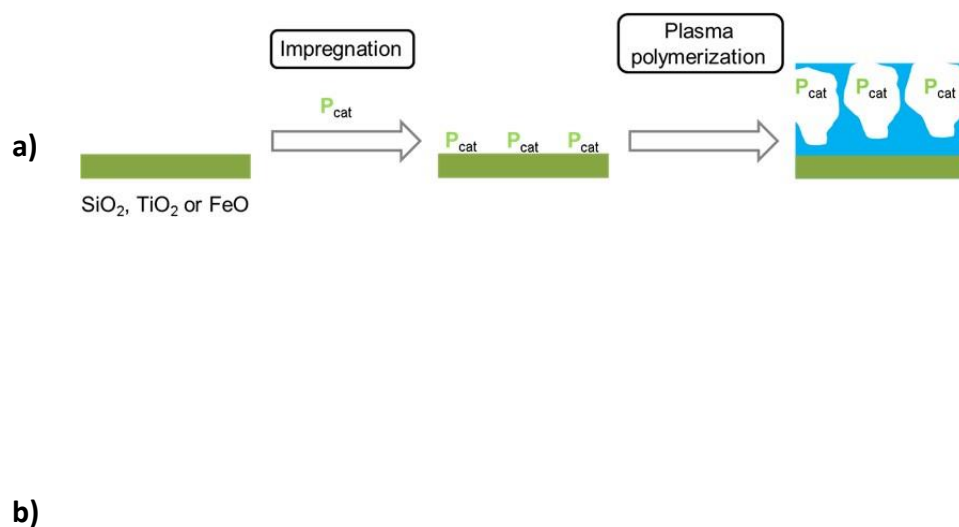
The immobilization of catalysts permits both facile separations from the product avoiding tedious purification as well as easy recycling of the catalyst. The plasma-assisted catalyst immobilization has drawn significant attention due to its coating with the direct attachment on the surface without the need of supported substrates. So far, there is only a limited number of research done with immobilization of catalysts using plasma techniques.

In the last decade the valorization of CO<sub>2</sub> into useful products gained much interest and therefor the synthesis of cyclic carbonates from epoxides and CO<sub>2</sub> is a prominent example. In this context we designed and synthesized phosphonium salts, and immobilized them on the surface of TiO<sub>2</sub>, FeO and SiO<sub>2</sub> by using amorphous hydrogenated carbon thin films generated from plasma techniques. After preliminary study, SiO<sub>2</sub> was found to be the best support, the heterogeneous catalyst was prepared with plasma treatment, and analysed with elemental analysis, solid state NMR, SEM and EDX. The immobilized phosphonium salt catalyst showed very good activity in the cycloaddition of CO<sub>2</sub> to epoxides, and offered a variety of substrate scope for the conversion of epoxides under mild conditions. Furthermore, the catalyst recycling was achieved for the first time in the plasma-assisted immobilization of catalysts. In conclusion we developed an efficient immobilized catalytic system operating under mild conditions for terminal and internal epoxides, and succeeded in the recycling of the catalyst, which was immobilized with plasma techniques for the first time.

## 2 Introduction and aim of the project

Amorphous hydrogenated carbon (a-C:H) thin films generated with plasma techniques are very attractive due to their chemical inertness, high density, thermal stability, low friction, high wear resistance, high electrical resistivity and hardness.<sup>1-2</sup> They are investigated as protective coatings for windows<sup>3</sup>, antireflective coatings for crystalline silicon solar cells<sup>4</sup>, for biomedical applications<sup>5</sup> and wear resistant coatings for tools<sup>6</sup>. Interestingly, an alternative application of the amorphous hydrogenated carbon thin films could be the immobilization of catalysts. The biggest advantage of this process is, that polymers can be directly attached to a desired surface while the chains are growing, which reduces steps necessary for other coating processes. So far, there is only a limited number of research done regarding immobilization of catalysts using plasma polymers.<sup>7-8, 9</sup> And there are also several examples concerning plasma immobilization techniques in biology.<sup>10,11,12</sup> A crucial point in the development of environmentally benign processes is the catalysts separation and recycling. Beside many other possibilities for green separation techniques, the immobilization of catalysts permits both facile separations from the product avoiding tedious purification and

isolation steps as well as easy recycling of the catalyst.<sup>13-15</sup> Organocatalysts are cheap, nontoxic, and bench-stable organic molecules that do not necessarily require inert reaction conditions.<sup>16</sup> A significant benefit of organocatalysts is undoubtedly the carbon-based scaffold associated with high potential of structural modification and catalyst tuning, especially in terms of catalyst immobilization.<sup>17-19</sup> The atom economic addition of carbon dioxide to epoxides yielding cyclic carbonates is an interesting and frequently studied reaction since those products might be utilized as green solvents, synthetic building blocks or plasticizers.<sup>20-22</sup> Lately, highly active OH-functionalized organocatalysts have been reported for the synthesis of cyclic carbonates.<sup>23-27</sup> The superior activity of these catalysts is attributed to the epoxide activation and the stabilization of intermediates by hydrogen bonding. The development of bifunctional P-based catalyst systems has been intensively studied in our group.<sup>28-31</sup> We are especially interested in the design and application of bifunctional phosphonium salts as recyclable catalysts. One method for obtaining reusable catalyst systems is the immobilization of the phosphonium salt on an organic or inorganic support. Herein, we report our studies on the use of plasma techniques for polymerizing and thus immobilizing suitable P-based organocatalysts on titanium dioxide, iron oxide and silica (Fig. 1, a), as well as on immobilized catalysts activity investigation and recyclability evaluation.

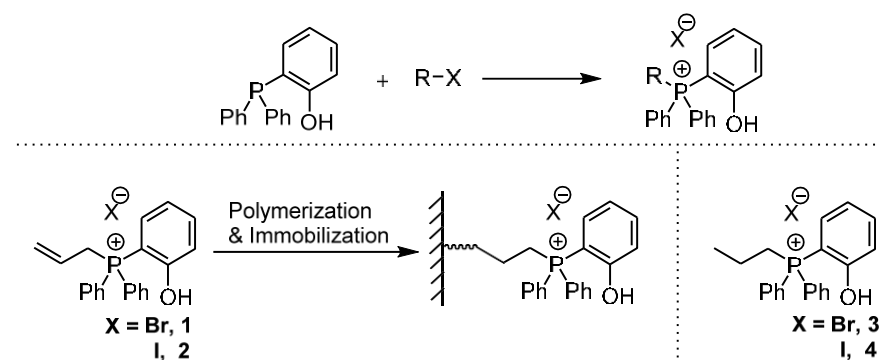


**Figure 1.** a) Concept of immobilization of phosphonium salt catalyst using plasma techniques. b) Prepared homogeneous v.s. heterogeneous catalysts.

The goal of the kickoff project H-POP is to prepare heterogeneous phosphorus based organocatalysts by using plasma techniques, and test the activities of immobilized catalysts, as well as the recycling. The homogeneous catalysis is often highly efficient, however, the separation and recovery of the catalyst from the product is usually difficult. The heterogeneous catalysis offers the possibility of catalyst recover with general separation processes, for instance, the filtration, and then the catalyst could be reused in the catalytic system. In this context, novel suitable P-based organocatalysts were designed and synthesized for the polymerization and immobilization by using plasma techniques.

### 3 Results and discussion

Bifunctional phosphonium salt bearing a hydroxyl group in the 2-position proved to be a superior structural motif in the cycloaddition of CO<sub>2</sub> and epoxides to form cyclic carbonates. We envisioned that an allyl substituent might allow the subsequent immobilization using plasma-enhanced polymerization. In this case, we designed and synthesized bifunctional phosphonium salt catalysts **1** and **2** by allylation of 2-(diphenylphosphanyl)phenol with allylic halides. Based on our previous study, the bromide and iodide catalysts represent the basic bifunctional structures, the –OH functional group may facilitate the activation of the epoxide by the additional hydrogen bonding. Since after the polymerization of the catalysts, the alkyl substituted phosphonium salts will be obtained, **3** and **4** were also synthesized for comparison of the activity. (**Scheme 1**)

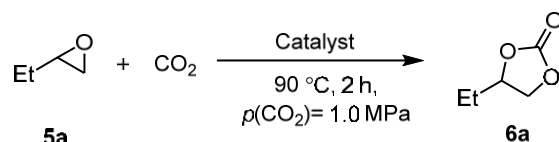


**Scheme 1.** Synthesis of phosphonium bromide and iodide catalysts.

The four catalysts were tested in the model reaction of 1,2-butylene oxide with CO<sub>2</sub> to generate the cyclic carbonate with 1 mol% catalyst loading at 90 °C for 2 h ( $p(\text{CO}_2) = 1.0$  MPa). The allyl-substituted phosphonium salts (either the anion is bromide or iodide) showed similar activity, with the generation of 68% (**3**) and 67% (**4**) (**Table 1**, entries 1 and 2) yield of 1,2-butylene carbonate. The propyl bromide phosphonium salt was slightly less active, 40% yield of 1,2-butylene carbonate was obtained (**Table 1**, entry 3). The propyl iodide catalyst was proved to be the best under these reaction conditions, 1,2-butylene

carbonate was converted with 83% yield (**Table 1**, entry 4). With these preliminary results, phosphonium salt **2** was chosen as the model catalyst to employ in the polymerization, thus immobilization with plasma techniques.

**Table 1** Catalyst screening and parameter optimization for the conversion of 1,2-butylene oxide in homogeneous system.



Entry	Catalyst	Cat. Loading / mol%	Yield <b>6a</b> <sup>a</sup> / %
1	<b>1</b>	1	68
2	<b>2</b>	1	67
3	<b>3</b>	1	40
4	<b>4</b>	1	83

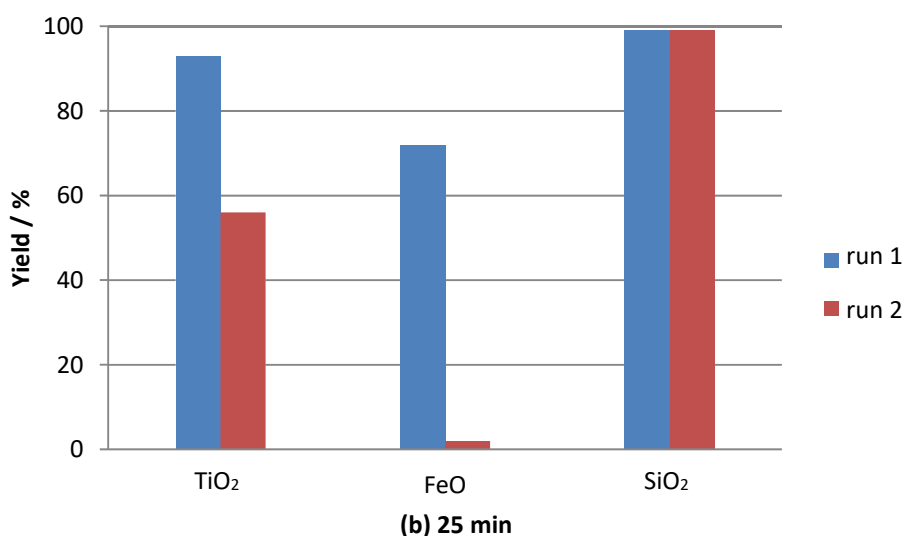
Reaction conditions: 45 cm<sup>3</sup> stainless-steel autoclave, 1 equiv **5a** (13.9 mmol), 1 mol% catalyst, solvent-free.

<sup>a</sup>Yields were determined by <sup>1</sup>H NMR with mesitylene as internal standard.

TiO<sub>2</sub>, FeO and SiO<sub>2</sub> were chosen as potential supports. Initially we tested the activities of supports and the impregnated catalysts in the model reaction by using 1,2-butylene oxide. To our delight, no activity was observed with pure supports, and moderate to good yields of 1,2-butylene carbonate were obtained with impregnated catalyst. Subsequently we tested the plasma immobilized catalyst under the standard reaction conditions. Also in this case very nice activities were obtained with those three supports. (More details see in Appendix table A1.) To evaluate the recyclability of these three plasma immobilized catalysts, after the first run, the catalysts were simply filtered off and reused in the second run. As shown in **Figure. 2**, for the first run, catalysts **16** and **18** converted 1,2-butylene oxide into the 1,2-butylene carbonate in more than 93% yield, **17** also gave 72% yield. With the second run, **16** gave 1,2-butylene carbonate with 56% yield, **17** only generated the product with 2% yield, and **18** still gave quantitative yield, extraordinarily.

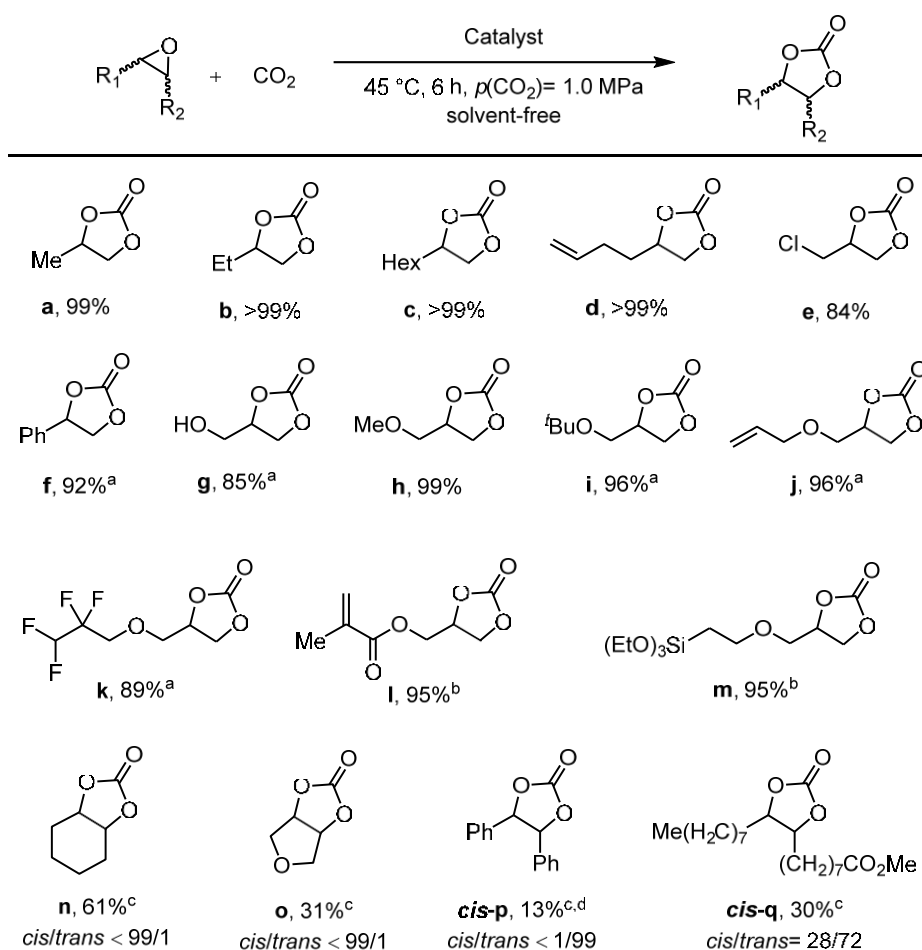
After we had the optimized catalyst preparation conditions, more catalyst were prepared supported by SiO<sub>2</sub> and employed in the model catalytic reaction condition optimizations. A variety of epoxides were tested in this reaction conditions. As shown in **Scheme 2**, the aliphatic substituted terminal epoxides were converted into the carbonates with quantitative yields (**a–d**). Epichlorohydrin (**e**) was converted to the respective carbonate **e** in a good yield of 84%. With 24 h, 92% yield was obtained when the aryl substituted styrene

oxide was employed, and acetophenone was observed as the byproduct, which comes from the Meinwald rearrangement.<sup>32</sup>



**Fig. 2** Preliminary recyclability evaluation of plasma immobilized catalysts based on TiO<sub>2</sub>, FeO and SiO<sub>2</sub>. Reaction conditions: 45 cm<sup>3</sup> stainless-steel autoclave, 1 equiv **5a** (13.9 mmol), 0.5 g of immobilized catalyst (1 mol% catalyst loading), solvent-free. Yield of 1<sup>st</sup> run was isolated yield, from the 2<sup>nd</sup> run, yields were determined by <sup>1</sup>H NMR with mesitylene as internal standard.

Glycidol<sup>33-34</sup> and its derivatives bearing high functionality (**g-i**) were also converted into corresponding carbonates in excellent yields, though most of them need 24 h to complete the conversion. Glycidyl methacrylate<sup>35</sup> (**l**) was also transformed to its carbonate at 90 °C without polymerization, in 95% yield. The organosilane substrate **m** could be obtained in 95% yield, which serve as effective adhesion promoters in paints, inks, coatings and sealants.<sup>36</sup> Notably, the catalytic protocol tolerates alkyl, halide, alkene, ether, ester, silyl and aryl groups. Our immobilized catalyst was also engaged in the more challenging cycloaddition of internal epoxides with CO<sub>2</sub>. The cyclic carbonates could be isolated with stereoselectivity as high as 99%, with only 1 mol% catalyst loading, the reaction of internal epoxides took place at 90 °C with 24 h. The cyclohexene oxide was converted into the corresponding carbonate in 61% yield. Only 31% yield of product was obtained from 3,4-epoxytetrahydrofuran, the unidentified brown sticky liquid covered on the surface of the catalyst, which comes from the decomposition of the substrate. The conversion of more challenging *cis*-stilbene oxide led selectively to *trans*-product in isolated yield of 13%, with a *cis/trans* ratio <1/99.



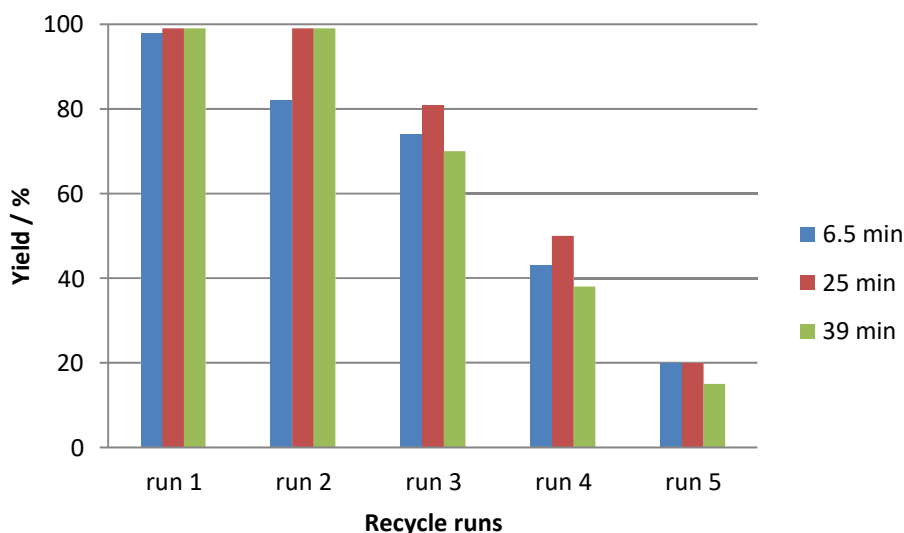
**Scheme 2** Catalytic suitability for various epoxides. Reaction conditions: 45 cm<sup>3</sup> stainless-steel autoclave, 1.0 equiv **1** (13.9 mmol), 0.5 g of immobilized catalyst (1 mol% catalyst loading), solvent-free. Isolated yield. <sup>a</sup> 24 h. <sup>b</sup> 90 °C. <sup>c</sup> 90 °C, 24 h. <sup>d</sup> 1.0 mL 1-BuOH was used as the solvent.

Since the substrate was the solid, 1.0 mL 1-butanol was added as the solvent. The epoxidized methyl oleate **cis-q** derived from the renewable feedstocks was also investigated under the respective reaction conditions, 30% yield of the carbonate could be isolated with a *cis/trans* ratio of 28/72. The reversion of stereochemistry could be explained that, in the presence of substituents, the reaction proceeded through the S<sub>N</sub>1-pathway and led to the *trans*-product, which is more thermodynamically preferred.<sup>37</sup>

The reaction with plasma treated catalyst went smoothly, various functionalized epoxides were converted to the corresponding carbonates under relatively mild conditions. Then, to evaluate the recyclability of our immobilized catalyst, recycling experiments were conducted with 1,2-butylene oxide as the substrate under 90 °C, 6 h and  $p(\text{CO}_2) = 1.0 \text{ MPa}$ . After each reaction Et<sub>2</sub>O was added, the dissolved product was separated from the catalyst, then the catalyst was dried and employed in next run under the standard reaction conditions. Based



on previous results, SiO<sub>2</sub> was chosen as the model support. The standard catalyst treated by plasma with 25 min was firstly investigated. Quantitative yields were obtained for the 1<sup>st</sup> and 2<sup>nd</sup> runs, then 81% with the 3<sup>rd</sup> run, 50% for the 4<sup>th</sup>, and 20% yield could be observed even after the 5<sup>th</sup> run. (Fig. 7) In the end, the mass of recovered catalyst was 85% of the original weight. To the best of our knowledge, this is the first report of success in recycling immobilized catalyst treated with plasma techniques.



**Figure 3** Recyclability investigation with immobilized catalysts treated with various plasma treating time. Reaction conditions: 45 cm<sup>3</sup> stainless-steel autoclave, 1.0 equiv **5a** (13.9 mmol), 1.0 g of immobilized catalyst (0.010 equiv catalyst loading), solvent-free. Yield of 1<sup>st</sup> run was isolated yield, from the 2<sup>nd</sup> run, yield was determined by <sup>1</sup>H NMR with mesitylene as internal standard.

Since the immobilization condition will be different according to the plasma treatment time, the recyclability of immobilized catalysts with 6.5 min and 39 min plasma treatment were also studied. As shown in **Fig. 3**, the recyclabilities were similar with different plasma treating time, the activity of the catalyst treated with 6.5 min was slightly lower may due to not enough fixation with plasma treatment.

#### 4 Further achievements/ benefit from the project

##### Poster presentation:

“Immobilization of P-based organocatalysts by plasma techniques”, Y. Hu, , S. Peglow, R. Eckelt, A. Schulz, J. von Langermann, V. Brüser, M. Beller, U. Kragl, T. Werner\*, 3. Internes P-Campus Symposium, 8.-9. November **2017**, Rostock, Deutschland.

“Immobilization of P-based organocatalysts by plasma techniques”, Y. Hu, , S. Peglow, R. Eckelt, A. Schulz, J. von Langermann, V. Brüser, M. Beller, U. Kragl, T. Werner\*, 51. Katalytiker Konferenz Weimar 2018, 14.–16. März **2018**; Weimar, Deutschland.

**Oral presentation:**

"Plasma based immobilization of catalysts for chemical synthesis", V. Brüser, S. Peglow, Y. Hu, T. Werner, M. Beller, A. Kruth, IX International Conference on Plasma Physics and Plasma Technology PPPT-9, 17.-21. September **2018**; Minsk/Weißrussland.

“Immobilization of P-based organocatalysts by plasma techniques”, Y. Hu, , S. Peglow, R. Eckelt, A. Schulz, J. von Langermann, V. Brüser, M. Beller, U. Kragl, T. Werner\*, Internal PCampus Symposium, Dummersdorf, 19.–20. November **2018**, FBN, Deutschland.

**Publication:**

"Plasma based immobilization of catalysts for chemical synthesis", V. Brüser, S. Peglow, Y. Hu, T. Werner, M. Beller, A. Kruth, Proceedingband IX International Conference on Plasma Physics and Plasma Technology PPPT-9, 17.-21. September **2018**; Minsk/Weißrussland.

A publication entitled “Plasma-assisted immobilized Phosphonium Salts as Recyclable Catalysts for the Valorization of CO<sub>2</sub>” is currently finalized.

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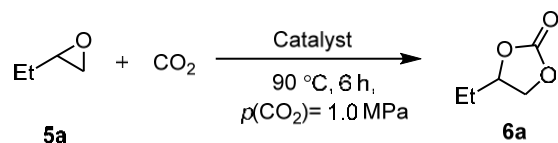
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## 8 Appendix

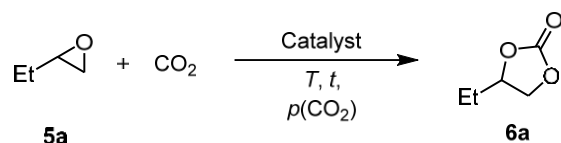
**Table A1** Screening of immobilized catalyst on different supports for the conversion of 1,2-butylene oxide in heterogeneous system.



Entry	Catalyst	Support	Impregnated cat. Loading / mol%	Plasma treating time / min	Yield <b>6a</b> <sup>a</sup> / %
1	<b>7</b>	TiO <sub>2</sub>	-	-	0
2	<b>8</b>	FeO	-	-	0
3	<b>9</b>	SiO <sub>2</sub>	-	-	0
4	<b>10</b>	TiO <sub>2</sub>	-	25	0
5	<b>11</b>	FeO	-	25	0
6	<b>12</b>	SiO <sub>2</sub>	-	25	0
7	<b>13</b>	TiO <sub>2</sub>	1	-	87
8	<b>14</b>	FeO	1	-	78
9	<b>15</b>	SiO <sub>2</sub>	1	-	88
10	<b>16</b>	TiO <sub>2</sub>	1	25	93
11	<b>17</b>	FeO	1	25	72
12	<b>18</b>	SiO <sub>2</sub>	1	25	90

Reaction conditions: 45 cm<sup>3</sup> stainless-steel autoclave, 1.0 equiv **5a** (13.9 mmol), 0.5 g of support, solvent-free. <sup>a</sup>Yields were determined by <sup>1</sup>H NMR with mesitylene as internal standard.

**Table A2** Catalytic reaction conditions optimization for the conversion of 1,2-butylene oxide.



Entry	T / °C	p / MPa	t / h	Yield <b>6a</b> / %
1	90	1.0	6	99
2	90	1.0	3	99
3	90	0.5	6	88
4	45	1.0	6	99

Reaction conditions: 45 cm<sup>3</sup> stainless-steel autoclave, 1 equiv **5** (13.9 mmol), 0.5 g of immobilized catalyst (1 mol% catalyst loading), solvent-free. Isolated yield.