One-pot Fixation of CO₂ into Glycerol Carbonate using Ion-Exchanged Amberlite Resin Beads as Efficient Metal-free Heterogeneous Catalysts

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The one-pot synthesis of glycerol carbonate from carbon dioxide and glycerol was achieved using ion-exchanged Amberlite resin beads as metal-free heterogeneous catalysts. Two commercially available Amberlite resin beads consisting of polystyrene cross-linked with divinylbenzene and functionalized with either trimethyl ammonium chloride (IRA-900) or dimethyl ethanol ammonium chloride (IRA-910) groups were used as starting materials to prepare the catalysts. These polymeric beads were transformed into their iodide (Amb-900-I, Amb-OH-910-I) or hydroxide (Amb-900-OH and Amb-OH-910-OH) counterparts through straightforward ion-exchange reactions. First, the two resin bead catalysts in hydroxide form were tested in the base-catalyzed transcyanation reaction of glycerol with propylene carbonate. Both resin bead catalysts were more active compared to benchmark basic catalysts as hydrotalcites employed as catalysts. Although Amb-OH-910-I alone is poorly active in the transcyanation reaction, it showed the highest catalytic activity in the one-pot cascade reaction, surprisingly surpassing the performance of the Amb-OH-910-I/Amb-OH-910-OH mixtures and reaching high yields of glycerol carbonate (81 %, 115 °C, 4 h). These findings led to proposing a mechanism for the one-pot reaction using the Amb-OH-910-I catalyst. The bead format led to easy recovery of the catalyst, which displayed good reusability in consecutive runs.

Introduction

Carbon dioxide is as an attractive and inexpensive carbon-based feedstock due to its renewability and widespread availability as end-product from fuel combustion, cement manufacture and other industrial processes.[1–4] Its conversion into useful compounds represents a desirable and sustainable alternative to emission of this greenhouse gas into the atmosphere. However, the utilization of CO₂ as building block in the production of useful chemicals is a challenging task due to its high thermodynamic stability. This limitation can be overcome by the reaction of CO₂ with compounds that have high free energy, such as epoxides.[5–8] The chemical fixation of CO₂ with epoxides to produce cyclic carbonates has been widely investigated (Scheme 1), because of the extensive range of applications found by cyclic carbonates, e.g. in electrolyte formulations for Li-ion batteries, as green aprotic solvents, and as intermediates in the production of fine and bulk chemicals.[9–11]

Glycerol is another interesting, renewable, abundant and cheap raw material since it is generated in large amounts as the main by-product of biodiesel manufacturing.[12,13] In order to prevent glycerol over-supply from hindering the development of the biodiesel industry, the conversion of glycerol into valuable products is highly desirable, and many approaches have been developed for this purpose.[12–16] Among these options, the transformation of glycerol into glycerol carbonate (GC) has drawn increasing attention in recent years.[12] The obtained glycerol carbonate is non-toxic, non-flammable, water soluble and biodegradable. These features lead to proposing a

![Scheme 1. Synthesis of propylene carbonate (PC) from CO₂ and propylene oxide (PO).](image-url)
wide range of potential industrial applications as component in lubricants, adhesives, surfactants and personal care products. It has also been proposed as a monomer in polymer synthesis and as an alternative green solvent in Li-ion batteries.\textsuperscript{12,14,17} The synthesis of glycerol carbonate can be achieved through the reaction of glycerol with different compounds acting as carbonyl sources, such as carbon monoxide,\textsuperscript{18,19} phosgene,\textsuperscript{20} carbon dioxide,\textsuperscript{18,21} urea,\textsuperscript{22,23} and organic carbonates.\textsuperscript{13,24,25} However, most of these routes present major issues such as: (i) the toxicity of the reagents, as in the case of phosgene and carbon monoxide;\textsuperscript{12,15} (ii) the thermodynamic limitation associated with direct reaction with carbon dioxide, which can be only partially mitigated using sacrificial dehydrating agents (e.g. 2-cyanopyridine and acetonitrile)\textsuperscript{21,26} or adsorbents (e.g. zeolites)\textsuperscript{27} to remove the water product; and (iii) the need to carry out the reaction at reduced pressure to remove the produced ammonia to shift the equilibrium concentrations towards the product side, as in the case of using urea as reactant.\textsuperscript{18,28,29} Conversely, the transcarbonation reaction of glycerol with organic carbonates is considered the most viable route for the synthesis of glycerol carbonate due to its environmental friendliness, mild operation conditions, high yield and selectivity.\textsuperscript{12,14} This reaction has been broadly studied with dimethyl carbonate\textsuperscript{17,30} or diethyl carbonate\textsuperscript{31,32} as reactants, while only a few works reported the reaction with propylene carbonate (PC).\textsuperscript{13,34} The synthesis of dimethyl or diethyl carbonate from CO$_2$ requires stoichiometric amounts of a drying agent to achieve acceptable products yields,\textsuperscript{33} or can be achieved with high yields through a greener path involving a transcarbonation reaction from propylene carbonate.\textsuperscript{34} Based on these considerations, the direct reaction of glycerol with propylene carbonate (Scheme 2) is preferable in the context of sustainability compared to the routes involving dimethyl or diethyl carbonate. The catalysts that have been investigated for these transcarbonation reactions include homogeneous ones as organic bases\textsuperscript{35,36} and ionic liquids,\textsuperscript{37,38} or heterogeneous basic catalysts such as metal oxides (e.g. MgO, CaO and MgO@ZIF-8)\textsuperscript{39,40,42} and hydroxalates.\textsuperscript{43,44} Based on these previous studies, the presence of a basic catalytic site is crucial to initiate this reaction by abstracting a proton from glycerol, which results in the formation of the glycerol oxide ion, thus enhancing the nucleophilicity in the attack on the carbonyl group of propylene carbonate.\textsuperscript{12,25} Moreover, this reaction is a reversible process, meaning that the molar ratio between the organic carbonate and glycerol plays a critical role in determining the equilibrium concentrations of reactants and products.\textsuperscript{13,34}

The transcarbonation route can be made even more attractive from the point of view of green chemistry and sustainability by combining it with the synthesis of propylene carbonate by reaction of CO$_2$ with propylene oxide (PO) in a one-pot process (Scheme 3).\textsuperscript{45} This approach has several assets in the context of sustainability: (i) it allows converting two renewable compounds for which there is an oversupply as CO$_2$ and glycerol into useful chemical products as glycerol carbonate and propylene glycol (the latter can find applications in food, liquid detergents, health care products, paints and adhesives)\textsuperscript{33,46} (ii) it can reach high product yields as both the cycloaddition reaction of CO$_2$ with propylene oxide to produce propylene carbonate (Scheme 1), and the transcarbonation reaction of propylene carbonate with glycerol (Scheme 2) are thermodynamically viable; (iii) by combining the two reactions in one pot, the process would require a single reactor and the intermediate separation and purification of propylene carbonate would be avoided. The transcarbonation of propylene carbonate with glycerol is generally a fast reaction, meaning that the cycloaddition reaction of CO$_2$ to propylene oxide is expected to be the rate-determining step in the one-pot process (Scheme 3).\textsuperscript{47}

Although this one-pot conversion of CO$_2$, glycerol and propylene oxide into glycerol carbonate and propylene glycol represents an alternative, promising approach to other routes for the synthesis of glycerol carbonate, it has been rarely investigated.\textsuperscript{48} The first report of this one-pot approach employed KI as a homogenous catalyst and achieved 77% yield of glycerol carbonate (115 °C, 1.5 h, 20 bar CO$_2$, catalyst loading 0.75 mol%, PO/glycerol molar ratio of 2).\textsuperscript{47} However, this homogeneous catalytic system suffers from the difficulty of recycling it, which limits its large-scale applicability. This issue was overcome in a recent work, in which a heterogeneous catalyst was developed by copolymerization of imidazole-based ionic liquids with divinylbenzene (DVB). Among the prepared catalysts, PDVB-(vIm-BuBr) showed the highest activity, reaching 81% yield of glycerol carbonate (100 °C, 4 h, 20 bar CO$_2$, catalyst loading 0.64 mol%, PO/glycerol molar ratio of 4), and could be reused in five consecutive runs without significant loss in activity.\textsuperscript{49} However, the two-step, relatively expensive synthesis method of this catalyst can represent a limiting factor for its large-scale application. In this work, we focused on designing and developing an affordable and efficient catalytic system to

\begin{equation}
\text{PC} + \text{GLY} \rightarrow \text{GC} + \text{PG}
\end{equation}

Scheme 2. Transcarbonation reaction of glycerol (GLY) with propylene carbonate (PC) yielding glycerol carbonate (GC) and propylene glycol (PG).
enable the one-pot cascade reaction that would allow converting glycerol, propylene oxide and CO\(_2\) into glycerol carbonate and propylene glycol (Scheme 3). Our initial reasoning was that the overall efficiency would improve if we employed a combination of two catalysts, of which the first one would be tuned for promoting the cycloaddition of CO\(_2\) to propylene oxide, and the second one would be tailored towards the transcarbonation of the formed propylene carbonate with glycerol. For catalyzing the reaction of CO\(_2\) with propylene oxide, we selected two Amberlite polymeric beads in iodide-form (Amb-900-I, Amb-OH-910-I, see top part of Scheme 4), which were recently identified by our group as highly active metal-free heterogeneous catalysts in the presence of hydrogen bond donor groups (e.g. water) for the synthesis of cyclic carbonates from CO\(_2\) and a variety of epoxides.\(^{[49]}\) These polymeric resins also exhibited other advantages such as low-cost preparation, easy separation (stemming from their macroscopic bead format), and good reusability. For the second step, i.e. the transcarbonation of propylene carbonate with glycerol, we selected and screened a broader scope of heterogeneous catalysts. Since this reaction is base-catalyzed, we prepared and tested the OH-form of the resin beads mentioned above (Amb-900-OH and Amb-OH-910-OH, see bottom part of Scheme 4). Their catalytic performance was compared to that of the Amberlite polymeric beads in halide-form and to a set of commercial hydrotalcites as benchmark catalysts. Finally, we combined the best catalyst for each of the two separate reactions in different relative ratios and tested these catalytic systems in the one-pot process to convert CO\(_2\), glycerol and propylene oxide into glycerol carbonate and propylene glycol. This allowed achieving high yield of the desired glycerol carbonate product with an affordable and reusable catalytic system. Additionally, the results of our catalytic study provided new insights in the mechanism of the one-pot reaction.

**Results and discussion**

**Screening of catalysts for the transcarbonation reaction**

The main target of this work was to develop an efficient and affordable catalytic system that can catalyze both the cycloaddition and the transcarbonation reactions in order to convert carbon dioxide, glycerol and propylene oxide into glycerol carbonate and propylene glycol (Scheme 3). In our recent work, we identified Amb-900-I and Amb-OH-910-I polymeric beads as active, selective and easily separable heterogeneous catalysts for the cycloaddition reaction of CO\(_2\) with a variety of epoxides, including propylene oxide.\(^{[49]}\) With the purpose of combining these catalysts with a suitable catalyst for the transcarbonation reaction, we sought an optimum catalyst for the latter reaction by defining, preparing and screening a library of catalysts with basic behavior. The first type of basic catalysts that we selected was prepared starting from the same commercially available Amberlite polymeric beads that we used to prepare Amb-900-I and Amb-OH-910-I. The parent macroscopic resin beads have an approximate size distribution between 500 and 800 \(\mu\)m and consist of polystyrene crosslinked with divinylbenzene, containing either trimethyl ammonium chloride groups (IRA 900) or dimethyl ethanol ammonium chloride groups (IRA 910). In order to obtain catalysts with basic sites, the two resin beads were

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**Scheme 4.** Preparation method of Amb-900-I, Amb-OH-910-I, Amb-900-OH and Amb-OH-910-OH through ion-exchange reactions of the commercial IRA-900 and IRA-910 resin beads in chloride form.
ion-exchanged with aqueous NaOH (Scheme 4). The molar loadings of OH anions in the two prepared resin beads in OH-form were determined by ion chromatography to be 2.14 mmol/g for Amb-900-OH and 2.58 mmol/g for Amb-OH-910-OH (see Experimental Section for details). The thermal stability of the newly prepared polymeric beads in OH-form was studied by thermogravimetric analysis (Figure S1). The TGA data show a gradual weight loss in the 50–200 °C range attributed to removal of adsorbed water, followed by a steepening of the curve above 200 °C, attributed to the combustion of the organic polymer structure of these materials. Compared to the same beads in iodide-form, these data suggest that Amb-900-OH and Amb-OH-910-OH display higher hydrophilicity, as indicated also by their FT-IR spectra (Figure S2), which display the same characteristic peaks observed for the beads in iodide-form, but with a broader and more intense band in the region where both the stretching of C–C in aromatic groups and the bending mode of H2O (~1625 cm⁻¹) are found. SEM analysis of Amb-OH-910-OH showed a similar inner porous structure to that previously reported for the beads in iodide-form, characterized by pores with irregular shapes in the meso- and macropore scale (Figure 1).

The second type of catalysts that we chose to investigate in the transcarnation reaction are hydrotalcites (HT), which are a well-known class of basic catalysts that has been reported to be active in the transcarbonylation of organic carbonates (e.g. dimethyl carbonate) with glycerol.[33,44,50] Hydrotalcites are layered double hydroxides with general formula [MgAl(OH)₆CO₃·4H₂O].[51] Each magnesium cation is coordinated to six hydroxyl anions, leading to stacks of edge-shared layers of octahedra. In this structure, some of the Mg²⁺ ions are substituted by Al³⁺ ions, resulting in positively charged layers, in which the charge is balanced by interlayer anions such as carbonates. The interlayer anions in hydrotalcites can act as weak basic sites.[50,54] The thermal decomposition of hydrotalcites leads to the formation of mixed Mg–Al oxides with an increase in surface area and the generation of stronger basic sites (i.e. Mg/Al–O pairs with intermediate basicity and O²⁻ sites acting as strong basic sites).[33,50,51,54] Four types of hydrotalcites were employed in this work, which were kindly provided by Kisuma Chemicals B.V.. These hydrotalcites have different properties in terms of surface area, Mg/Al ratio and basicity (see Table S1 for more details). To investigate the effect of calcination on the catalytic behavior of these materials, all the hydrotalcites were calcined at 300 °C for 3 h. The parent and calcined hydrotalcites were then employed as catalysts for the synthesis of glycerol carbonate from glycerol and propylene carbonate.

In this first part of our study, the activity of the two newly prepared resin beads in OH-form as metal-free heterogeneous catalysts for the transcarnation of propylene carbonate with glycerol to produce glycerol carbonate and propylene glycol (80 °C, 5 h) was compared to that of their counterparts resin beads in iodide- or chloride-form and to the selected set of hydrotalcites (Table 1). Among the metal-free catalysts in resin bead format, the Amberlite materials in OH-form (Amb-900-OH and Amb-OH-910-OH) showed significantly higher catalytic activity in the target transcarnation reaction (Table 1, entries 5 and 6), compared to their iodide and chloride counterparts (Table 1, entries 1–4). This trend in activity is ascribed to the stronger basicity of OH⁻ compared to Cl⁻ and I⁻.[33] The hydroxide ion can promote this reaction by abstracting a proton from glycerol, leading to the formation of a nucleophilic alkoxo ion, which facilitates the nucleophilic attack on the carbonyl group of propylene carbonate.[31] As a consequence, a carbonate intermediate ion is formed, which undergoes ring closure, yielding glycerol carbonate.[33] Remarkably, the Amb-900-OH and Amb-OH-910-OH proved to be much more active catalysts compared to the benchmark hydrotalcites (Table 1, entries 5 and 6 compared with entries 7–16). Among the hydrotalcites, a general trend in catalytic behavior was observed: the calcined materials displayed higher catalytic activity compared to the uncalcined counterparts (Table 1,

![Figure 1. SEM images of the Amb-OH-910-OH polymeric beads (A: the whole beads, B: the surface).](image)

**Table 1. Screening of Amberlite resin beads and hydrotalcites as heterogeneous catalysts in the transcarnation of propylene carbonate with glycerol to produce glycerol carbonate and propylene glycol.**

| Entry | Catalyst      | Yield [%] PG | Yield [%] GC |
|-------|---------------|--------------|--------------|
| 1     | Amb-900-Cl    | 2            | 1            |
| 2     | Amb-OH-910-Cl | 1            | 1            |
| 3     | Amb-900-I     | 8            | 6            |
| 4     | Amb-OH-910-I  | 6            | 5            |
| 5     | Amb-900-Cl    | 50           | 37           |
| 6     | Amb-OH-910-Cl | 51           | 38           |
| 7     | HT-4A         | 21           | 10           |
| 8     | HT-4B         | 18           | 16           |
| 9     | HT-4C         | 10           | 9            |
| 10    | HT-4S         | 23           | 14           |
| 11    | HT-6          | 22           | 17           |
| 12    | HT-4A-calcined| 31           | 28           |
| 13    | HT-4B-calcined| 28           | 27           |
| 14    | HT-4C-calcined| 33           | 30           |
| 15    | HT-4S-calcined| 35           | 28           |
| 16    | HT-6-calcined | 34           | 31           |

Reaction conditions: PC (12 mmol), glycerol (12 mmol), catalyst (95 mg), mesitylene (1.5 mmol) as NMR internal standard, 80 °C, 5 h (all tests were carried out in duplicate; the average value of each product yield is reported). [a] The yields of PG and GC were calculated based on ¹H-NMR analysis of the reaction mixture. [b] Relative to the initial amount of PC and PG at the end of the test. [c] Relative to the initial amount of glycerol.
entries 7–11 vs. entries 12–16). This result is in line with previous reports, which proved that the calcination of hydro-
talcites generates mixed Mg and Al oxides, with higher surface
area and stronger basic sites, leading to higher activity than
with the parent, uncalcined materials. All the uncalcined
hydrotalcites displayed similar, moderate activity with the
exception of HT-4C, i.e. the material with the lowest basicity
and the lowest surface area (Table S1), which was significantly
less active. Among the calcined hydrotalcites, no major differ-
cence in catalytic activity was observed.

In all the transcarbonation tests, the yield of propylene
glycol was higher compared to that of glycerol carbonate,
whereas a 1:1 ratio would be expected based on the stoichiom-
etry of the reaction (Scheme 2). This suggests the
formation of propylene glycol through the hydrolysis of
propylene carbonate as a side reaction, as a consequence of the
2–3 wt% water content of the used glycerol (as determined by
Karl Fischer titration). This hypothesis was supported by a
control experiment in which propylene carbonate was allowed
to react with water in the presence of the Amb-OH-910-OH
catalyst (Table S3 in the SI), leading to a moderate conversion
of propylene carbonate into propylene glycol (9%).

This initial study allowed us to identify Amb-900-OH and
Amb-OH-910-OH as highly active heterogeneous catalysts for
the transcarbonation reaction yielding glycerol carbonate. Since
no significant difference was observed between the activities of
these two catalysts, only one of the two resin beads (Amb-OH-
910-OH) was chosen for the continuation of this work. The next
step in our study was an investigation of the effect of the molar
ratio between glycerol and propylene carbonate on the
products yields of the transcarbonation reaction, with the
selected Amb-OH-910-OH as catalyst (Figure 2 and Table S2).
These tests were carried out at 115 °C for 2 h. If the target is to
maximize the yield of glycerol carbonate, the best results were
obtained with the highest molar ratio of propylene carbonate
to glycerol (4:1), leading to a high yield of glycerol carbonate
(80%, relative to glycerol) but a low yield of propylene glycol
(23%, relative to propylene carbonate). On the other hand, if
equimolar amounts of glycerol and propylene carbonate were
employed, a higher yield of propylene glycol was achieved
(55%) but at the expenses of the yield of glycerol carbonate
(48%). It is worth noting that when the results of the catalytic
tests with different molar ratios between glycerol and
propylene carbonate are analyzed based on the moles of each
product obtained instead of the products yields (while employing
always the same amount of catalyst), the results with
equimolar amount of the reactants represent the optimum,
leading to higher number of moles of each of the two products
(Table S2).

One-pot synthesis of glycerol carbonate from CO₂, glycerol
and propylene oxide

After having identified the most promising heterogeneous
catalyst for the transcarbonation reaction (Amb-OH-910-OH),
we moved on to the main goal of this work, which was to find
the optimum catalytic system for the overall one-pot process, in
which the cycloaddition and transcarbonation reactions are
combined in a cascade reaction (Scheme 3). For this purpose,
we investigated combinations of the two best catalysts
identified for each of the two separate reactions, i.e. Amb-OH-
910-I (cycloaddition of CO₂ to propylene oxide) and Amb-OH-
910-OH (transcarbonation). The tests were performed keeping
the total catalyst mass constant and using different relative
amounts of the two catalysts. The idea behind this strategy was
to optimize the overall catalytic performance by tuning the
relative amount of catalyst promoting each of the two
reactions. The one-pot tests were performed employing a 1:1
ratio between glycerol and propylene oxide, 20 bar CO₂ at
115 °C for 2 h (Table 2 and Table S4). Remarkably, the highest
yields of propylene carbonate and glycerol carbonate were
obtained when the Amb-OH-910-I catalyst was used as a single

![Figure 2](image_url)  
Figure 2. Effect of the molar ratio between glycerol and propylene carbonate (PC) on the transcarbonation reaction using Amb-OH-910-OH as catalyst. Reaction conditions: glycerol (5, 10 or 20 mmol), PC (20 mmol), Amb-OH-910-OH catalyst (95 mg). The yields of propylene glycol (PG) and glycerol carbonate (GC) were calculated by 

| Entry | Catalytic system | Catalysts ratio | Yield [%] | PG [%] | GC [%] |
|-------|-----------------|-----------------|-----------|--------|--------|
| 1     | Amb-OH-910-I/OH | 100:0           | 33        | 37     | 27     |
| 2     | Amb-OH-910-I/OH | 75:25           | 27        | 36     | 23     |
| 3     | Amb-OH-910-I/OH | 50:50           | 20        | 31     | 21     |
| 4     | Amb-OH-910-I/OH | 25:75           | 14        | 28     | 15     |
| 5     | Amb-OH-910-I/OH | 0:100           | 5         | 17     | 6      |

Reaction conditions: PO (20 mmol), glycerol (20 mmol), catalyst (95 mg), mesitylene (1.5 mmol) as NMR internal standard, 115 °C, 20 bar CO₂, 2 h. [a] The yields were calculated by 

[b] H-NMR analysis of the reaction mixture. [b] Relative to the total amount of PC, PG and unreacted PO at the end of the test. [c] Relative to the initial amount of glycerol.

Table 2. One-pot synthesis of glycerol carbonate from CO₂, glycerol and propylene oxide over a catalytic system consisting of Amb-OH-910-I and Amb-OH-910-OH (in different ratios).
catalyst (Table 2, entry 1) and not, as we anticipated, with a combination of the two catalysts. This is rather surprising when we consider that Amb-OH-910-I displayed much lower activity compared to Amb-OH-910-OH in the transcarboxylation reaction (Table 1, compare entries 4 and 6). The presence of Amb-OH-910-OH in the catalytic system proved detrimental, as shown by the gradual decrease in the yields of propylene carbonate, propylene glycol and glycerol carbonate with the increase in the amount of Amb-OH-910-OH employed (Table 2, entries 2–4). When the Amb-OH-910-OH catalyst was used alone, the products yields were the lowest in this set of tests (Table 2, entry 5). Notably, the yields of propylene glycol were higher than the yields of glycerol carbonate in all tests, which is the same trend observed in the transcarboxylation reactions (vide supra). The latter result is ascribed to the hydrolysis of propylene oxide generating propylene glycol (Scheme 3), as a consequence of the presence of water as an impurity of the highly hygroscopic glycerol (2–3 wt%). In order to investigate further this hypothesis, the hydrolysis of propylene oxide was studied in the presence of either Amb-OH-910-I or Amb-OH-910-OH under the same reaction conditions described in Table 2 but in the presence of water (20 mmol) instead of glycerol (and with no CO₂). These catalytic tests proved that the hydrolysis of propylene oxide indeed occurs (Table S3, entries 1 and 2), and that this happens to a much larger extent with the hydrolysis of propylene oxide (Scheme 3) and thus hinders the formation of propylene carbonate, in this way limiting the transcarboxylation of propylene carbonate with glycerol. It should be noted that the possible hydrolysis reaction of the formed propylene carbonate contributes to a much lesser extent to the formation of propylene glycol compared to the hydrolysis of propylene oxide, as proven by specific control tests (Table S3, entries 3 and 4). Additionally, we carried out another study with the same combinations of the Amb-OH-910-I and Amb-OH-910-OH catalysts and under the same conditions described in Table 2 but in the presence of glycerol with a higher water content (13–14 wt% based on Karl Fischer titration). The same trend of activity was observed, with the highest yield of glycerol carbonate being achieved with Amb-OH-910-I alone (Table S5). Also in this case, the yields of glycerol carbonate decreased with increasing relative amount of Amb-OH-910-OH in the catalytic system. The yield of propylene glycol was higher than that of glycerol carbonate in each test, but the difference between the yields of these two products was much more pronounced compared to the tests with the glycerol with a lower water content (compare each entry in Table S5 with the corresponding entry in Table 2). This strongly supports our hypothesis that the presence of water in glycerol promotes the hydrolysis of propylene oxide, leading to the observed high yields of propylene glycol. Notably, this competitive reaction also implies a lower efficiency in the synthesis of glycerol carbonate, as indicated by the systematically lower yields of this compound obtained when using the aqueous glycerol as substrate (compare each entry in Table S5 with the corresponding entry in Table 2). A deeper understanding of the results of the catalytic tests presented in Table 2 (and Table S5) can be achieved by comparing the yield of glycerol carbonate relative to that of propylene carbonate while taking into account the observations made above. The GC/PC relative yield increases with the relative amount of Amb-OH-910-OH that is employed (Table 2). This is in line with logical expectations, as Amb-OH-910-OH is a better catalyst than Amb-OH-910-I for the transcarboxylation of propylene carbonate leading to the formation of glycerol carbonate (see Table 1). Therefore, the fact that the presence of Amb-OH-910-OH is detrimental to the overall glycerol carbonate yield should be attributed to the observed higher activity of Amb-OH-910-OH in catalyzing the competitive hydrolysis of propylene oxide (Table S3), thus preventing the formation of the propylene carbonate that is necessary for the transcarboxylation reaction. Based on these results, it can be concluded that the Amb-OH-910-I catalyst alone is a more effective system for the one-pot reaction compared to any of the combinations of Amb-OH-910-I and Amb-OH-910-OH.

The study of the one-pot process was continued by investigating the effect of the molar ratio between propylene oxide and glycerol with the best catalytic system, i.e. Amb-OH-910-I (Table 3 and, for more detailed information, Table S6). If the reaction was carried out in the absence of glycerol, propylene carbonate was obtained with high yield (76%, Table 3, entry 1) and full selectivity, in agreement with the previously reported excellent activity of the Amb-OH-910-I catalyst in the cycloaddition of CO₂ to epoxides. When a low relative amount of glycerol was employed (5 mmol vs. 20 mmol of PO), high yields of propylene carbonate (67%) and glycerol carbonate (69%) were reached (Table 3, entry 2). Under these conditions, the number of moles of propylene glycol formed is only slightly higher than those of glycerol carbonate (Table S6), indicating that the hydrolysis of propylene oxide to the glycol becomes less prominent, in line with the lower amount of water impurity that would be introduced into the mixture when a lower relative amount of glycerol is used. The yields of

| Entry | Catalyst          | Glycerol [mmol] | Yield [%] | PG [g] | GC [g] |
|-------|-------------------|----------------|-----------|--------|--------|
| 1     | Amb-OH-910-I      | 0              | 76        | 0      | 0      |
| 2     | Amb-OH-910-I      | 5              | 67        | 23     | 69     |
| 3     | Amb-OH-910-I      | 10             | 51        | 33     | 50     |
| 4     | Amb-OH-910-I      | 20             | 0          | 0      | 0      |
| 5     | Amb-OH-910-I      | 20             | 0          | 0      | 0      |

Reaction conditions: PO (20 mmol), catalyst (95 mg), mesitylene (1.5 mmol) as NMR internal standard, 115 °C, 20 bar CO₂, 2 h. [a] The yields were calculated by 1H-NMR analysis of the reaction mixture. [b] Relative to the total amount of PC, PG and unreacted PO at the end of the test. [c] Relative to the initial amount of glycerol. [d] The reaction was performed for 4 h.
propylene carbonate and glycerol carbonate gradually decreased by increasing the relative amount of glycerol from 5 to 20 mmol (while keeping the moles of PO constant at 20 mmol), while the yields of propylene glycol increased (Table 3 entries 2 to 4). The decrease in glycerol carbonate yield is a logical consequence of the decrease in PO/glycerol molar ratio, which affects the equilibrium concentrations of the transcarbonation step according to Le Chatelier’s principle. The decrease in propylene carbonate yield and the concomitant increase in propylene glycol yield with decreasing PO/glycerol ratio are attributed to the increased competition of the hydrolysis of propylene oxide into its glycol, which is expected to be related to the amount of water in the reaction mixture. Since water is present as impurity in the highly hygroscopic glycerol, the probability of the hydrolysis reaction to take place becomes higher with an increase in the glycerol concentration. When the same test was performed using the Amb-900-I catalyst in the presence of glycerol (20 mmol), the propylene carbonate yield was slightly higher compared to the result obtained in the absence of glycerol (Table 3, entry 7 vs. entry 6). This increase in the activity towards the formation of propylene carbonate can be explained by the presence of glycerol in the reaction mixture, which enhances the cycloaddition reaction of CO₂ to propylene oxide through its three —OH groups that can act as hydrogen bond donors that activate the epoxide, as reported in previous works. This result showed that glycerol plays two roles: as a hydrogen bond donor acting as co-catalyst, and as a reactant. The yield of propylene carbonate obtained with the Amb-900-I catalyst was lower than with Amb-OH-910-I when the same amount of glycerol was employed (20 mmol), but nearly the same yields of propylene glycol and glycerol carbonate were attained with both catalysts (Table 3, entry 7 vs. entry 4), indicating that both polymeric bead catalysts have potential applicability for the one-pot synthesis of glycerol carbonate from CO₂, glycerol and propylene oxide. In line with logical expectations, when we increased the reaction time to 4 h, we could increase the yield of glycerol carbonate, achieving a notable 81% with Amb-OH-910-I (Table 3, entry 5).

Mechanism for the one-pot reaction

Interestingly and surprisingly, the Amb-OH-910-I catalyst gave a much lower yield of glycerol carbonate when it was tested in the transcarbonation reaction with either 5 or 20 mmol of propylene carbonate as reactant (Table S2, entries 4 and 5), compared to the corresponding one-pot cascade reaction with either 5 or 20 mmol of propylene oxide as reactant (Table 3, entry 2 and 4), under the same reaction conditions (115 °C, 2 h, 95 mg of catalyst). This is remarkable, because the one-pot reaction is expected to proceed through the formation of propylene carbonate as intermediate (Scheme 3) and it would be natural to expect a higher yield of glycerol carbonate when starting the reaction from this intermediate. The fact that this is not the case, strongly suggests a concerted mechanism for the one-pot reaction catalyzed by Amb-OH-910-I, in which species formed from propylene oxide are involved in promoting the transcarbonation step. Based on these observations, we propose a possible mechanism for the one-pot reaction of CO₂, glycerol and propylene oxide leading to the formation of glycerol carbonate, propylene carbonate and propylene glycol using Amb-OH-910-I as catalyst (Scheme 5). This mechanism consists of three combined cycles: (A) is the catalytic cycle for the cycloaddition of CO₂ to propylene oxide; (B) is the cycle involving the formation of basic intermediates, which in turn are involved in catalyzing the transcarbonation reaction from propylene carbonate to glycerol carbonate (cycle C). In cycle (A), the cycloaddition reaction of CO₂ to propylene oxide takes place as the first step in the overall one-pot reaction. The mechanism for this reaction was proposed according to previously published work for this reaction. First, the hydrogen bond donor group in Amb-OH-910-I (I) activates the oxygen of the epoxide through hydrogen bonding interactions, thus promoting the nucleophilic attack by iodide (2), which results in the ring-opening of the epoxide with formation of an alkoxide anion (3a). Then, the insertion of CO₂ occurs, generating a carbonate anion intermediate (4), which undergoes intramolecular ring closure (5), leading to the formation of propylene carbonate (6) and the restoring of the catalytic site (1). The obtained propylene carbonate can undergo a transcarbonation reaction with glycerol to yield glycerol carbonate (cycle C). This reaction has been rarely discussed in the literature with propylene carbonate as substrate (Scheme 2), whereas the same reaction with other organic carbones has been widely studied. According to these previous reports, the key step that initiates this reaction is the presence of a basic catalyst, which can form a glyceroxide anion (7) by the deprotonation of glycerol, thus facilitating the nucleophilic attack on the carbonyl group of propylene carbonate, which leads to the formation of intermediate carbonate anion species (8a & 8b). Intermediate (8b) can undergo intramolecular ring closure resulting in glycerol carbonate (9) and in an alkoxide ion (10). In our work, we observed that the Amb-OH-910-I catalyst was less active than the Amb-OH-910-OH in the transcarbonation reaction. Conversely, this catalyst showed the highest activity during the one-pot reaction, achieving a high yield of glycerol carbonate (69%). This observation indicates that there is at least an intermediate formed during the cycloaddition reaction (cycle C) that initiates the further transcarbonation reaction (cycle C) by abstracting a proton from the glycerol resulting in the glyceroxide ion (7). We propose this intermediate to be the alkoxide ion (3a) formed upon ring opening of the epoxide. This is a basic species that can either attack CO₂ (4) to generate the carbonate ion (5) in cycle (A), or abstract a proton from glycerol to generate the glyceroxide anion (7) that initiates cycle (C). In the latter case, the alkoxide ion (3a) is converted into the 1-iodo-2-propanol intermediate (3b), which can react with the alkoxide ion (10) formed at the end of cycle (C), to yield propylene glycol as the final product (11) while restoring intermediate (3a), and thus closing the intermediate catalytic cycle (B).

Besides the alkoxide ion, another possible species that could act as a base to promote the formation of the glyceroxide anion is the iodide in Amb-OH-910-I. However, this is a weaker base
than the alkoxide ion, suggesting that the latter is more likely to be the main active species for this step. The formation of the glyceroxide anion from glycerol is in competition with other possible hydrogen bond donor groups present in our catalytic system, namely water and propylene glycol. The pKₐ of glycerol (14.15), water (14) and propylene glycol (14.47) are rather close to each other and the formation of the glyceroxide anion is therefore mainly attributed to the much larger (initial) concen-

Scheme 5. Proposed mechanism for the one-pot synthesis of glycerol carbonate from CO₂, glycerol and propylene oxide using Amb-OH-910-I as catalyst [X = I in the case of Amb-OH-910-I]. Note that glycerol can also play a role as hydrogen bond donor in cycle A; however, this was omitted from the scheme for the sake of readability.
tration of glycerol compared to the other two compounds. However, as the reaction proceeds the concentration of propylene glycol gradually increases, likely leading to competition with glycerol for the deprotonation step.

In the proposed mechanism, we did not include the formation of glycerol carbonate through the direct reaction of CO$_2$ with glycerol (in grey in Scheme 4), because a control test in which these two compounds were allowed to react under the same conditions specified in Table 3 in the presence of the Amb-OH-910-I catalyst (but without propylene oxide) gave no glycerol carbonate yield.

The observed higher activity of Amb-OH-910-I compared to any combination of Amb-OH-910-I and Amb-OH-910-OH, together with the above-proposed mechanism, are in agreement with the expectation that the cycloaddition of CO$_2$ to propylene oxide would be the rate-determining step in the one-pot process.

Catalyst reusability

Finally, we investigated the reusability of the Amb-OH-910-I catalyst in the one-pot cascade reaction (Figure 3). After each catalytic run, the bead format of the catalyst enabled the straightforward separation from the reaction mixture without the need for filtration or centrifugation (see Experimental section for further information). The results of the reusability tests revealed that the yields of glycerol carbonate and propylene glycol remained constant in four consecutive runs, though the yield of propylene carbonate slightly decreased upon recycling. This result is in line with the gradual, slight decrease in propylene carbonate yield that was observed with this catalyst in the cycloaddition reaction of CO$_2$ to propylene oxide in previous work from our group. This slight deactivation was attributed to the observed exchange of a small fraction (~1% per run) of the iodide in Amb-OH-910-I with other anions (e.g. OH$^-$), whereas FT-IR and SEM analyses proved that the polymeric structure of the catalyst did not undergo any detectable change during the catalytic tests. To counter the loss of iodide, the catalyst was regenerated by washing with an aqueous solution of KI (1 M) after the third run (see Experimental section for more details). This allowed to restore nearly the same yield of propylene carbonate as in the first run (Figure 3). Importantly, this regeneration protocol can be repeated in consecutive runs without requiring to substitute the aqueous solution of KI with a fresh one in each cycle.

Conclusion

Amberlite polymeric beads were demonstrated to be highly efficient metal-free heterogeneous catalysts for the synthesis of glycerol carbonate from glycerol, either through reaction with propylene carbonate in a transcarbonation reaction, or through reaction with CO$_2$ and propylene oxide in a one-pot cascade process. In the transcarbonation reaction, the highest activity was displayed by the two polymeric bead catalysts in hydroxide form (Amb-900-OH and Amb-OH-910-OH), which achieved significantly superior product yields compared to their counterparts in halide form (Amb-900-X and Amb-OH-910-X, with X=Cl, I) and to hydrotalcite benchmark catalysts. The yield of glycerol carbonate achieved after 2 h reaction at 115°C with Amb-OH-910-OH as catalyst was 48% when an equimolar amount of propylene carbonate and glycerol was used, and reached 80% if the molar ratio between propylene carbonate and glycerol was 4:1. The Amb-OH-910-OH catalyst was employed in combination with Amb-OH-910-I, which was previously proven to be highly active in the cycloaddition of CO$_2$ to propylene oxide, in the one-pot cascade reaction in which glycerol carbonate and propylene glycol are synthesized starting from CO$_2$, glycerol and propylene oxide. The combination of the optimum catalyst for the first step of the cascade reaction (Amb-OH-910-I) with that for the subsequent transcarbonation step (Amb-OH-910-OH) did not lead to the anticipated synergy and the highest catalytic activity was obtained when Amb-OH-910-I was employed alone, leading to high yield of glycerol carbonate (69% after 2 h at 115°C). This is a remarkable result, particularly when taking into account that Amb-OH-910-I displayed much higher glycerol carbonate yield in the one-pot process than when it was used for catalyzing the second step alone (i.e. the transcarbonation). The obtained catalytic results also provided a fundamental understanding of the one-pot process that allowed to shed light on the reaction mechanism. The Amb-OH-910-I catalyst could be recovered by a straightforward procedure owing to its bead format and was reused in four consecutive runs without decrease in the glycerol carbonate yield. For these catalytic results and for being easily prepared by ion-exchange from a commercial resin bead, Amb-OH-910-I represents an efficient, environmentally friendly, easily available, up-scalable, cost-effective metal-free heterogeneous catalyst for the synthesis of glycerol carbonate from carbon dioxide and glycerol in a one-pot process. Future research should aim at identifying the most suitable way to separate the reaction products. The high boiling point of propylene
carbonate and glycerol carbonate might represent a challenge for separation by distillation, but the biphasic reaction mixture obtained in our catalytic tests suggests that separation by liquid-liquid extraction might be a viable alternative.

### Experimental Section

#### Materials

Propylene oxide (PO, 99.5 % purity), propylene carbonate (PC, 99.5 % purity), glycerol (nominally > 99 % purity, but containing 2–3 wt% of water based on Karl Fischer titration), sodium hydroxide (> 98 % purity), potassium iodide (> 99 % purity), Amberlite IRA-900 in chloride form, Amberlite IRA-910 in chloride form, mesitylene (98 % purity), deuterated dimethyl sulfoxide-δ (DMSO-d₆, 99.5 atom %) as solvent for ²H-NMR, were purchased from Sigma-Aldrich. Acetone and ethanol were purchased from Boom B.V. (technical grade). Methanol (absolute) was purchased from Biosolve Chimie. Glycerol with lower purity (85 %) was purchased from Boom B.V. (containing 13–14 wt% of water based on Karl Fischer titration). All chemicals were used without further purification. The hydroxalite catalysts used in the transcarbonylation reaction were prepared and kindly provided by Kísuma Chemicals B.V. (see Table S1 for more information about these materials). To study the effect of calcination on their catalytic behavior, all the hydroxalites were thermally treated at 300 °C for 3 h in air.

#### Catalyst Preparation

The Amb-900-I, Amb-900-OH, and Amb-OH-910-OH resins were prepared by ion-exchange reactions with potassium iodide or sodium hydroxide. For preparing Amb-900-OH, 3.0 g of Amberlite IRA-900 resin beads were washed with water (4.83 mmol/g) and acetonitrile (2×20 mL, and dried for 48 h at 70 °C in an oven, to attain an Amberlite IRA-900 in hydroxide form (Amb-900-OH). Based on the elemental analysis of chlorine (6.52 wt%), the molar loading of OH (2.14 mmol/g) and CI (1.84 mmol/g) in Amb-900-OH were estimated. The Amb-900-I catalyst was prepared from the Amberlite IRA-910 resin beads in chloride form (3.39 mmol/g) following the same procedure described above. Based on the elemental analysis of chlorine (3.44 wt%), the molar loading of OH (2.58 mmol/g) and CI (0.97 mmol/g) in Amb-900-I were estimated. The Amberlite IRA-910-I resin beads were prepared by following our previously reported procedure, and the molar loading of these resins based on the elemental analysis of iodine were 3.03 mmol/g and 2.19 mmol/g, respectively.

### Catalyst Characterization

The elemental analysis of the prepared resin beads was carried out at Mikroanalytisches Laboratorium KOLBE using Metrohm ion chromatography model IC 883 Plus. Fourier-transform infrared (FT-IR) spectra were recorded on an IRTTracer-100 spectrometer by averaging 64 scans with a spatial resolution of 4 cm⁻¹. The surface morphology of the resin beads was analyzed by scanning electron microscopy (SEM) using a Philips XL30 ESEM FEG equipment. Owing to the non-conductive nature of the beads, the materials were coated by gold prior to the SEM measurement. Thermogravimetric analysis (TGA) of the resin beads was performed under air from 30 to 900 °C at 10 °C/min using a thermogravimetric analyzer TGA-4000. The water amount in glycerol was determined by Karl Fischer titration using a Metrohm 720-SM Titrino device.

### Catalytic tests

#### Transcarbonylation reactions

All transcarbonylation experiments were carried out using a 48-well reactor block equipped with a heating system and individual magnetic stirring. In a typical catalytic test, propylene carbonate (12–20 mmol, depending on the experiment), glycerol (5–20 mmol, depending on the experiment), catalyst (95 mg), mesitylene (1.5 mmol) as NMR internal standard, were added into a 10 mL glass vial equipped with a magnetic stirring bar and closed with a screw cap containing a silicone/PTFE septum. The reactor was heated up to the desired temperature (80 or 115 °C), and then the vials were placed in the reactor block and stirred at 600 rpm for the chosen reaction time. Next, the stirring was turned off, the vials were removed from the reactor block and allowed to cool down to room temperature (30 min). Then, 2 mL of methanol was added into each vial to achieve a monophasic solution (the reaction mixture at the end of the catalytic test is biphasic). After this step, an NMR sample was prepared by adding approximately 50 mg of the reaction mixture to 500 mg of DMSO-d₆. The yields of propylene glycol and glycerol carbonate were calculated based on ¹H-NMR spectra measured on a Varian Oxford 300 MHz or Varian Mercury 400 MHz.

#### One-pot reactions of CO₂, glycerol and propylene oxide

The catalytic tests were performed using a high-throughput reactor unit manufactured by Integrated Lab Solutions (ILS) and located at the University of Groningen (see previous work from our group for more information). The reactor unit contains a reactor block with 10 individually-stirred batch reactors, and a visualization reactor equipped with a window. In a typical experiment, glycerol (0–20 mmol), propylene oxide (20 mmol), the polymeric bead catalyst (95 mg), mesitylene (1.5 mmol) as NMR internal standard were placed into a glass vial (46 mL volume, 30 mm external diameter) equipped with a magnetic stirring bar and closed with a screw cap containing a silicone/PTFE septum (which was pierced with two needles to allow the CO₂ gas to enter and exit the vial). Next, the glass vial was placed into the selected reactor block of the high-throughput unit, and the reactor block was closed. Then, a software was employed to control the pressurization and heating steps needed to reach the desired reaction conditions. First, the reactor block was pressurized with 10 bar N₂, depressurized and then pressurized with 10 bar of CO₂ and depressurized again to remove air from the system. Then, the reactor block was pressurized with CO₂ (to a lower pressure compared to the target), heated up to the desired temperature and finally further pressurized with CO₂ (if required) to reach the selected pressure. Then, the reactor was left under the selected conditions for 2 h while stirring at 600 rpm. Next, the stirring was stopped and the reactor was cooled down to < 20 °C (to limit the loss of the highly volatile propylene oxide), and depressurized to < 1 bar. Finally, the lid of the reactor block was opened, and the glass vial was removed. Afterwards, 1–2 mL of methanol (based on the amount of glycerol) was added into the reaction mixture to achieve a monophasic solution (the reaction mixture is biphasic). Then, an NMR sample was prepared by adding
approximately 50 mg of the reaction mixture to 500 mg of DMSO-
\(d_6\). The amounts of propylene carbonate (PC), propylene glycol
(PG), glycerol carbonate (GC) and propylene oxide (PO, if employed)
at the end of each catalytic test were calculated by \(^1H\)-NMR
employing a Varian Oxford 300 MHz or Varian Mercury 400 MHz.

Note: the amount of glycerol could not be determined by \(^1H\)-NMR
due to overlapping peaks with other products (e.g. PG, GC, methanol and H\(_2\)O, see Figures S3 and S4). The moles of PC, GC, PG and PO (if used), were obtained based on the integration of the respective peaks relatively to the integration of the internal standard peaks. The use of an internal standard allowed to calculate the mass balance for all the catalytic tests. The mass balance was in the range of 98–100\% in all transcarbonation reactions, whereas
the mass balance was in the range of 85–91\% in the one-pot
reactions, in which propylene oxide was used as a substrate. This is
because propylene epoxide is highly volatile even at room temperature
and can thus partially evaporate during the purging of the reactor before the catalytic test and/or during the depressurization step at the end of the test (see the SI for the mass balances).

The yield of PG and the mass balance for the transcarbonation
reaction were calculated based on the following formulas [Eqs. (1)–
(6)]:

\[
\text{Yield}_{PC} (\%) = \frac{\text{mol}_{PC}}{\text{mol}_{PC} + \text{mol}_{\text{unreacted PC}}} \times 100 \%
\]

\[
\text{Mass balance} (\%) = \frac{\text{mol}_{PC} + \text{mol}_{\text{unreacted PO}}}{\text{mol}_{PC, \text{initial}}} \times 100 \%
\]

The yields of PC, PG and GC, and the mass balance for the one-pot
reaction were calculated based on the following formulas:

\[
\text{Yield}_{PG} (\%) = \frac{\text{mol}_{PG}}{\text{mol}_{PG} + \text{mol}_{\text{unreacted PC}}} \times 100 \%
\]

\[
\text{Yield}_{GC} (\%) = \frac{\text{mol}_{GC}}{\text{mol}_{\text{glycerol, initial}}} \times 100 \%
\]

\[
\text{Mass balance} (\%) = \frac{\text{mol}_{PG} + \text{mol}_{GC} + \text{mol}_{\text{unreacted PO}}}{\text{mol}_{PC, \text{initial}}} \times 100 \%
\]

\[
\text{Yield}_{GC} (\%) = \frac{\text{mol}_{GC}}{\text{mol}_{GC} + \text{mol}_{\text{unreacted PO}}} \times 100 \%
\]

\[
\text{Mass balance} (\%) = \frac{\text{mol}_{PC} + \text{mol}_{PG} + \text{mol}_{\text{unreacted PC}}}{\text{mol}_{PG, \text{initial}}} \times 100 \%
\]

Catalyst reusability tests

The reusability of the catalyst was investigated adapting a procedure previously reported by our group.\(^{[49]}\) In short, at the end of the catalytic test 20 mL of ethanol was added into the glass vial containing the reaction mixture, followed by stirring for 5 min to wash the resin beads catalyst. This washing step was carried out two times. Then, the reaction mixture was easily removed by a 150 mm capillary glass pipette. Next, the catalyst was washed with ethanol (2 \(\times\) 20 mL) and acetone (1 \(\times\) 20 mL) with a similar protocol
as the one described above, to remove possible residual impurities. After this, the resin beads catalyst was dried in a vacuum oven at 70 °C for 48 h and then was employed in the next recycling experiment.

Note: the catalyst was regenerated in the fourth run of the reusability test. After the first washing step with ethanol (20 mL)
and removal of the reaction mixture with a capillary glass pipette (see above), an aqueous solution of KI (1 M), which was prepared
by dissolving KI (0.5 g, 3 mmol) in water (3 mL), was added to the resin beads catalyst, followed by stirring for 4 h at 65 °C. Then, the resin beads catalyst was washed with water (3 \(\times\) 20 mL) and acetone (2 \(\times\) 20 mL). Finally, the catalyst was dried in a vacuum oven at 70 °C for 48 h and then was used in the next recycling experiment.

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Conflict of Interest

The authors declare no conflict of interest.

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