Cooperative NHC-based Catalytic System Immobilised onto Carbon Materials for the Cycloaddition of CO_2 to Epoxides.

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Abstract: New pyrene-tagged imidazolium salts and their corresponding carboxylates were synthesized and the latter tested as organocatalysts in the cycloaddition of CO_2 with epoxides. The best performing organocatalyst was then non-covalently immobilized onto carbon materials (carbon nanotubes (CNTs), reduced graphene oxide (rGO) and carbon beads (CBs)) via π-π stacking interactions and their activity and recoverability in the cycloaddition addition reaction were studied. The heterogenized catalyst onto reduced graphene oxide (**4a**@rGO) could be recycled up to 4 runs without relevant loss of activity and selectivity and was thus used for the transformation of a series of epoxides under mild conditions.

Introduction

The chemistry of carbon dioxide (CO_2) has attracted increasing interest given the disastrous consequences of its emissions.[1] In this context, an active goal is to transform this carbon trapped in this waste product into useful chemicals through catalytic processes.[2–5] To address this important issue, metal-based catalysts, as well as organocatalysts, have been reported.[6,7] This latter type often involves strong Lewis bases such as carbenes,[8] guanidines[9] and phosphines[10] able to reversible activate CO_2.

Since they were first investigated by Wanzlick in the early 1960s,[11] N-heterocyclic carbenes (NHCs) have attracted considerable interest due to their electron-rich character. In particular, Kuhn *et al.* described for the first time in 1999 the reaction between an NHC and CO_2 to form the corresponding imidazolium-2-carboxylate.[12] This NHC-CO_2 adduct is used as the active catalyst for the coupling reaction of CO_2 with epoxides to form cyclic carbonates (Scheme 1).[13] A convergent activation of the epoxide by adding a second co-catalyst was reported to increase the activity of the NHC based catalytic systems.[14] This type of reaction represents an interesting pathway for the chemical fixation of carbon dioxide as it does not involve the formation of any by-product and therefore is 100% atom economical (Scheme 1). Cyclic carbonates are useful products due to its applications,[15] e. g. as polar aprotic solvents,[16,17] electrolytes in lithium-ion batteries,[18] industrial lubricants,[19] monomers for polymer synthesis[20–22] and as useful intermediates for the preparation of a large variety of organic chemical products.[23]

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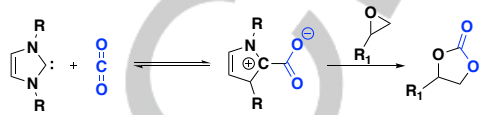


Scheme 1. Formation of NHC-CO_2 adduct followed by cycloaddition reaction of CO_2 with an epoxide.

Initial work related to the metal-free conversion of epoxides into cyclic carbonates used ammonium salts alongside phosphonium bromide (Bu_4PBr) as organocatalysts.[24] Their recycling was facilitated through their grafting on solid carriers with an optimal alkyl chain linker. However, conditions of temperature (120 - 150 ºC) and CO_2 pressure (20 bar - 40 bar) were required to achieve relevant activities.[25] Imidazolium-based organocatalysts containing hydroxyl substituents were also reported for the synthesis of cyclic carbonates from epoxides and CO_2.[26–28] Indeed, the advantage of such organocatalysts is the possibility to activate the epoxide by a hydrogen bond with the donor sites (HBD) thus, increasing the reaction rate. Their covalent immobilisation on various supports (polymer, silica, carbon surfaces) is well documented.[25] These systems were able to catalyze the reaction with high conversions under milder reaction conditions (T< 120 ºC, P< 20 bar of CO_2). Nevertheless, leaching issues were often observed, thus limiting their applicability. To date, only one system using imidazolium carboxylate covalently anchored onto silica was reported for this cycloaddition reaction.[29] Such organocatalyst can activate carbon dioxide, although it requires a large amount of volatile organic solvent and harsh reaction conditions (120 °C, 20 bar of CO_2 for 48 h in dichloromethane) to obtain high cyclic carbonate yields. Additionally, this immobilized organocatalyst suffers from a loss in activity after each run during the recycling. Therefore, the chemical transformation of CO_2 under an eco-friendly and efficient way remains an important challenge.

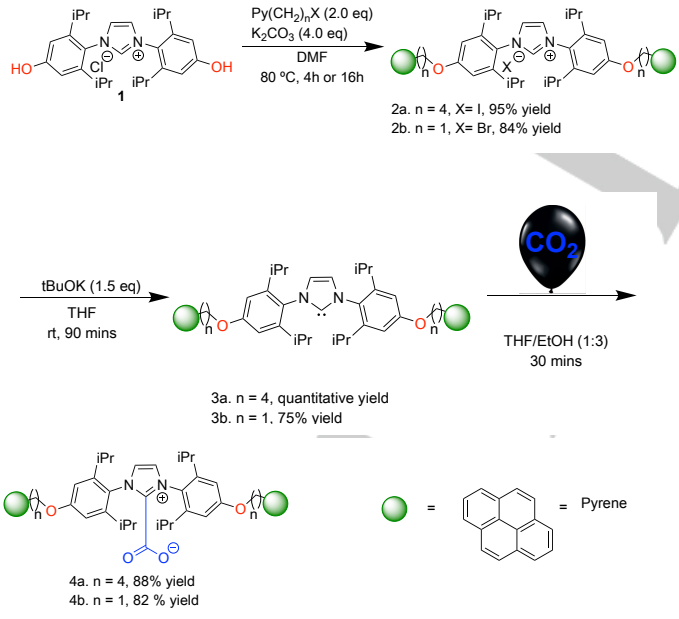
Translation of homogeneous catalysis into heterogeneous catalysis by supporting an active compound onto solid surfaces is a promising solution for the green and sustainable development in the chemical industry.[30] Indeed, “heterogenized” catalysts can solve catalyst separation issues common in homogeneous catalysis and allow catalyst recycling, thus, reducing the process cost.[31] The most used strategy to support a homogeneous catalyst is via the covalent anchoring of the ligand onto the solid support.[29] However, an important drawback of this method is the need for additional modification of the solid support and/or the ligand before the key covalent anchoring step which raises the cost of the catalyst and can also affect its chemical reactivity.[32] An alternative to this strategy is promoting non-covalent interactions that would avoid chemical modifications of the support. Among the reported materials for non-covalent

anchoring, carbon surfaces are interesting supports as they allow strong π-π stacking interactions between polycyclic aromatic hydrocarbons such as pyrene and graphitized surfaces such as carbon nanotubes (CNTs), reduced graphene oxide (rGO) and carbon beads (CBs).[33] Using this strategy, robust heterogenized catalysts were reported in various reactions with constant activity upon recycling up to 10 runs.[34]

Herein, we report the synthesis and characterization of pyrene-tagged organocatalysts and their immobilization onto carbon surfaces through π-π interactions. These hybrid materials were studied in the cycloaddition of epoxides with CO_2 to yield cyclic carbonates, and could be recycled up to 4 times without significant loss of activity.

Results and discussion

Our group recently reported the synthetic procedure for the preparation of hydroxy-functionalized imidazolium salt **1**[35] containing hydroxyl groups in *para* positions of the aryl rings that provide a flexible handle for the attachment of moieties through etherification. In this work, pyrene-tagged imidazolium salts were prepared by reaction of this compound with 2-(4-iodobutyl)pyrene and 2-(bromomethyl)pyrene under controlled reaction conditions. The carbenes **3a-b** were obtained by deprotonation with potassium *tert*-butoxide under inert atmosphere.[36] Subsequent addition of CO_2 (1 atm) to the carbene species provided the corresponding zwitterionic imidazolium carboxylates in high yields (Scheme 2).

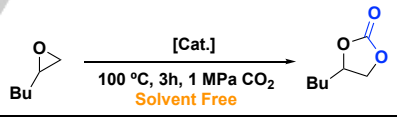


Scheme 2. Synthesis of pyrene tagged NHC-CO_2 adducts **4a-b**.

The pyrene-tagged imidazolium salts and carbenes were characterized by NMR spectroscopy and MS. The formation of the carbenes **3** was confirmed by ^{1}H NMR via the disappearance of the acidic signal of the imidazolium salts at δ 10.0-10.5 ppm and the detection by ^{13}C NMR of the characteristic signals of the $C_{carbene}$ at 220.6 ppm and 217.8 ppm for **3a** and **3b,** respectively. Upon reaction with CO_2, a new ^{13}C signal at *ca.* 153 ppm attributed to the carboxylate carbons of **4** was observed (See Supporting Information for more details). Moreover, thermogravimetric and FT-IR analysis provided further evidence of the CO_2 incorporation via the observation of a clean CO_2 loss between 100 °C and 250 ºC. In the IR spectra of **4a** and **4b**, stretching bands were readily detected at 1674 and 1671 cm^{-1}, respectively (see Supporting Information for more details)

To evaluate possible effects induced by the introduction of the pyrene group, the catalytic performance of the new organocatalysts **4a** and **4b** was evaluated and compared with that of 1,3-diisopropyl-imidazolium-2-carboxylate (IPr-CO_2)[36] in the cycloaddition reaction using 1,2-epoxyhexane as substrate (entry 1-3, Table 1). The pyrene-tagged imidazolium carboxylate **4a** exhibited similar performance than the IPr-CO_2 counterpart while **4b** provided lower activity. It was therefore concluded that the presence of the pyrene moiety could affect the catalytic performance of the corresponding organocatalysts depending on the linker length between the pyrene moiety and the aryl substituent of the carbene. The organocatalyst **4a** has further been compared to his carbene analogue and evaluated in the presence or not of additives. The best result was obtained while combining imidazolium carboxylate **4a**, KI and 18-crown-6 ether (18C6), in agreement with previously published results.[14,37–41]

Table 1. New pyrene-tagged imidazolium carboxylate activity in the cycloaddition reaction of 1,2-epoxyhexane with CO_2



Entry	Organocatalyst	Additives	Yield (%) [b]
1	iPr-CO_2	-	69
2	**4a**	-	57
3	**4b**	-	46
4	**-**	KI/18C6	37
5	**4a**	KI/18C6	87
6	**3a**	KI/18C6	73

[a] Reaction conditions: 12.3 mmol of 1,2-epoxihexane, 2 mol% of organocatalyst/KI/18C6 (1:1:1), 18C6= 18-crown-6 ether, P(CO_2)= 1 MPa, T= 100 °C, 3h, neat. iPr=1,3-diisopropyl-imidazolium-2-carboxylate [b] Isolated yield

In view of these results, the imidazolium carboxylate **4a** was supported onto three carbon supports MWCNTs, rGO and CBs (Table 2). For this purpose, the use of polar solvents is required due to the lipophilicity of both the carbon material and the pyrene moiety,[42] therefore ethyl acetate was selected.[43] The procedure for the immobilization included the dispersion of the carbon supports in ethyl acetate using an ultrasound bath for 1 h followed by addition of the organocatalyst. The mixture was then left stirring for 16 h at room temperature, the immobilised organocatalyst separated by filtration, and the non-immobilized catalyst recovered. The exact content of the organocatalyst on these hybrid materials was determined by TGA analysis. The

results obtained (Table 2) suggest that the organocatalyst is more easily anchored onto the flat structure of the rGO (25%, entry 3, Table 2) than onto the curved structure of the MWCNTs and CBs (16% and 13% respectively, entries 2 and 3, Table 2).

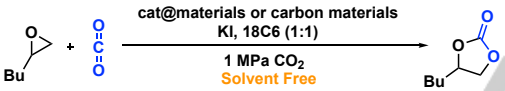
Table 2. Immobilisation of pyrene tagged imidazolium carboxylate **4a** onto MWCNTs, CBs and rGO and TGA analysis under N2 atmosphere

Entry	Carbon materials	wt%[b]
1	CBs	13
2	MWCNTs	16
3	rGO	25

[a] Reaction conditions: Commercial MWCNTS and rGO were dispersed in AcOEt and sonicated for 1h. The organocatalyst was then added to the suspension and stirred 16 h at r.t. [b] TGA analysis under N_2 atmosphere.

These hybrid materials were tested in the cycloaddition reaction of model 1,2-epoxihexane at 80 °C over 5 h in the presence of KI/18C6 and under solvent-free conditions. As shown in Table 3., the hybrid materials are highly selective in the cycloaddition reaction, and no by-product was formed. Similar yields to the unsupported catalytic system were obtained in all cases (Table 3).

Table 3. Cycloaddition of CO_2 into 1,2-epoxyhane using heterogenized catalysts **4a@MWCNTs, 4a@rGO**, **4a@CBs**



Entry	cat@materials	T °C/t (h)	Yield (%) [b]
1	**4a@MWCNTs**	80 °C / 5 h	78
2	**4a@rGO**	80 °C / 5 h	75
3	**4a@CBs**	80 °C / 5 h	73

[a] Reaction conditions: 12.3 mmol of 1,2-epoxihexane, 2 mol% of cat@materials/KI/18C6 (1:1:1), P(CO_2)= 1 MPa, [b] Isolated yield

At this stage, the recycling of the hybrid materials was probed using epichlorohydrin (ECH) as a substrate due to the important adsorption of 4-butyl-1,3-dioxolan-2-one (the cyclic carbonate obtained from 1,2-epoxyhexane) at the surface of the supports which made quantification extremely complex. After completion of each run, the reaction mixture was allowed to reach room temperature and the solid catalyst was separated by simple filtration, washed using EtOAc, dried and reused in the next run. The additives (KI/18C6) were only added in the 1st run. By following this procedure, only the supported organocatalyst onto rGO could be recycled up for 4 runs without significant loss of activity (Figure 2). These results suggested that the cooperative catalytic system involving epoxide and CO_2 activation is viable for a much longer period when rGO is used as support. Indeed, iodide ability to intercalate into carbon nanotubes has been previously reported[44] and rGO has a larger surface area compared to CBs and MWCNTs (500–400 m^2/g> 211 m^2/g> 80 m^2/g respectively) which is important for the catalytic application.[45] The drop in yield observed after each cycle is concomitant with catalyst deactivation *and/or* leaching (see Supporting Information for details).

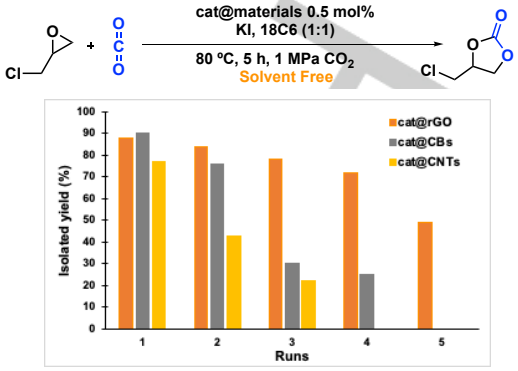
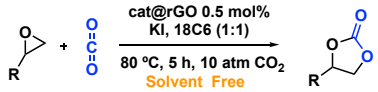
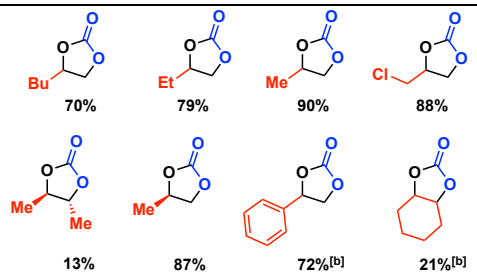


Figure 2. Recycling experiments using heterogeneous catalysts **4a@MWCNTs**, **4a@rGO** and **4a@CBs** for the cycloaddition of CO_2 with ECH

Based on these results, the imidazolium carboxylate supported onto rGO (**4a@rGO**) was selected to evaluate the scope of epoxides that could be efficiently transformed. The standard reaction conditions were set to 80 °C, 1MPa of CO_2 for 5h. The reactions were performed under solvent-free conditions and all products were obtained by simple filtration over silica gel. The results of the substrate screening are summarized in Table 5. The cooperative catalytic system consisting of **4a@rGO**/KI-18C6 was effective for monosubstituted terminal epoxides providing the corresponding carbonate products in yields from 70 to 90 % (Table 4). Furthermore, the substrate bearing aromatic groups 1,2-epoxyethylbenzene was transformed into carbonate with an isolated yield of 72%. The regiochemistry regarding the epoxide ring-opening in this reaction was further tested by the coupling reaction of (*R*)-propylene oxide with CO_2. The corresponding (*R*)-propylene carbonate was obtained in high yield with retention of stereochemistry. It confirms that the nucleophilic attack of the iodide occurs at the less sterically hindered carbon atom of the terminal epoxide through a SN_2 mechanisme.

Table 4. Evaluation of the substrate scope under standard reaction conditions





[a] Reaction conditions: 12.3 mmol of substrate, 0.5 mol% of KI/18C6 (1:1), P(CO_2)= 1 MPa, neat. Isolated yield, selectivities >99%. [b] Purification via column chromatography

For more challenging disubstituted epoxides such as cyclohexene oxide and *trans*-2,3-epoxybutane, low yields were obtained (21% and 13% respectively). It was thus concluded that the presence of an additional substituent at the epoxide hinders the nucleophilic attack of the cocatalyst, hence slowing down the ring-opening step. It was previously reported that for these more sterically hindered substrates, the use of smaller nucleophile such as bromide anion is more efficient.[18]

The generally accepted mechanism for the organocatalyzed cycloaddition of carbon dioxide to epoxides involves three basic steps namely ring-opening of the epoxide, insertion of carbon dioxide and ring-closure to form the cyclic carbonate. The activation modes may take place through epoxide and/or carbon dioxide activation.[46] According to the observations, in the pyrene tagged NHC-based catalytic systems, there is an increase of conversion when the carboxylate carbene adducts and KI are used in combination. Therefore and according to previously reported mechanisms,[14,46–48] we propose that the ring-opening of the epoxide may take place by nucleophilic atack of the iodide (Figure 3a) or carboxylate-NHC (Figure 3b) over the less hindered β-carbon of the epoxide. Carbon dioxide will be transfered from the carboxylated species **4a**@carbon material to the halohydrin (**aI**, Figure 3). The carbonaceous suport rGO acts a support to the carbene but also immobilises the iodide avoiding its leaching to maintain the catalytic activity after separation and recycling.

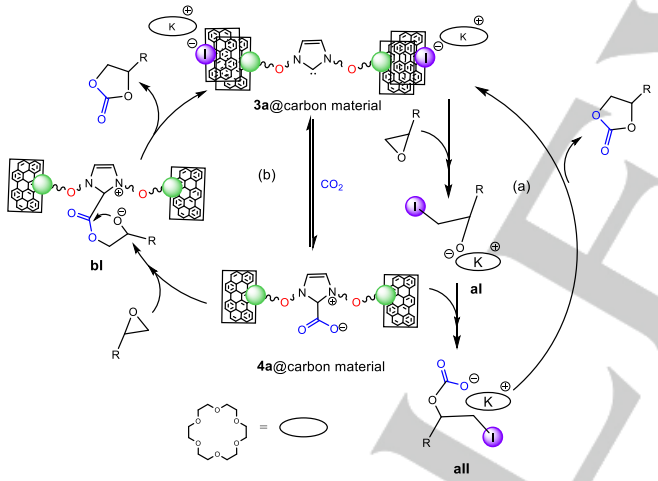


Figure 3. Proposed mechanism for the CO_2/epoxide cycloaddition catalyzed by **4a**@carbon materials.

Conclusions

In summary, pyrene-tagged imidazolium carboxylates have been designed for immobilization onto MWCNTs, rGO, CBs through π-π stacking interactions to give supported homogeneous catalysts. They remained intact on the carbon materials surface after immobilisation and their activity in the cycloaddition of epoxides with CO_2 were not affected. We have shown that the recycling is possible up to 4 runs using **4a@rGO** hybrid material with a strong "immobilisation" of the iodide additive. Its presence onto the solid support maintains a cooperative catalytic system where the epoxide and the CO_2 are activated, and thus results in higher production of cyclic carbonates. In comparison to existing report using covalently supported imidazolium carboxylate onto silica (2 MPa of CO_2 at 120 ºC for 48h in CH_2Cl_2), various substituted epoxides were converted to the corresponding cyclic carbonates under mild reaction conditions (1 MPa of CO_2 at 80 °C for 5h). Excellent isolated yields up to 90% could be achieved under solvent-free conditions after simple filtration.

Experimental Section

The synthesis of imidazolium carboxylates **2a-b, 3a-b, 4a-b** is described in the Supplentary Information.

General Procedure for the catalytic cycloaddition of CO_2 and epoxide. In a typical experiment, a 25 mL stainless steel autoclave equipped with a magnetic stirrer was charged with the corresponding quantities of potassium iodide, 18-crown-6 ether, imidazolium carboxylate or supported homogeneous catalyst and the epoxide. Then, the autoclave was sealed, purged with CO_2 at 0.3 MPa for three times and heated to the desired temperature. Subsequently, the reactor was pressurized with 1MPa of CO_2 for 3h or 5h with a stirring speed of 500 rpm. The autoclave was cooled in a liquid nitrogen bath below 0ºC and the CO_2 was slowly liberated from the vessel.

Work up using homogeneous catalysts: General procedure was followed. The crude reaction mixture was extracted with EtOAc and filtrated through a silica gel plug. After removal of all volatiles under reduced pressure the cyclic carbonates were obtained.

Work up using heterogenized catalysts: General procedure was followed. The crude reaction mixture was extracted with ethyl acetate and filtrated through a Büchner funnel with a filter plate. The black powder was washed thoroughly with EtOAc and the resulting filtrate collected and concentrated by rotavapor.

The recycling experiments were carried out under identical reaction conditions as described in the "using heterogenized catalysts". After completion of each run, the black powder was washed thoroughly with EtOAc, dried and reused as such in the following run.

Acknowledgements

The authors are grateful to the Ministerio de Economia y Competividad and the Fondo Europeo de Desarrollo Regional FEDER (CTQ2016-75016-R, AEI/FEDER,UE; PID2019-104427RB-I00) for funding and to the URV for PhD grant 2016-PMF-PIPF-47 to MS. The authors also gratefully acknowledge financial support from the Agencia de Gestio Ajusts Universitaris i de Recerca through the project 2017SGR1472.

Keywords: carbon materials • imidazolium carboxylates • carbon dioxide conversion • π interactions • supported organocatalyst

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