

Catalysis Science & Technology

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/catalysis

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Imidazolium Based Silica Microreactors for the Efficient Conversion of Carbon Dioxide

Mireia Buaki-Sogo^a, Hermenegildo Garcia^b and Carmela Aprile^{*a}

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

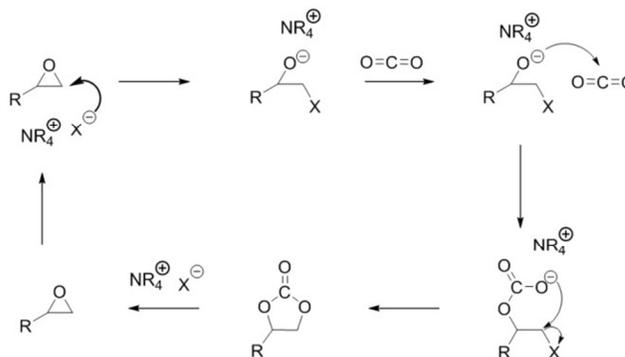
Imidazolium based silica microreactors were synthesized in a one-pot procedure. A straightforward synthesis approach was achieved through self-organization/polymerization of the amphipathic organic salts that behave as template for the construction of silica architecture and as catalytic active sites. The porous silica shell allowed the diffusion of reactants and products to/from the active sites and conferred stability to the polymeric matrix. The solid was extensively characterised by transmission and scanning electron microscopy, N₂ adsorption/desorption, X-ray diffraction, ²⁹Si solid state MAS-NMR and combustion chemical analysis. The material was tested as catalyst for the reaction of carbon dioxide with various epoxides to produce cyclic carbonates. The organic-inorganic hybrid microreactors displayed excellent performances in terms of both, yield and selectivity. Moreover it can be used in multiple catalytic cycles.

Introduction

Carbon dioxide is an easily available, inexpensive and non-toxic source of carbon. The transformation of carbon dioxide into cyclic carbonates, through its chemical fixation onto epoxides, is attracting a growing interest in the scientific community. The reasons of this great deal of attention, coming both from academic and industrial parties, stand mainly in the possibility to transform a “waste” (the CO₂) into useful products.¹ Cyclic carbonates may find applications in a broad variety of fields as aprotic polar solvents, electrolytes for lithium batteries, precursors for pharmaceuticals and intermediates for the synthesis of polycarbonates.² Moreover, the direct use of carbon dioxide as a reagent represents a sustainable alternative to the traditional synthesis route involving the use of phosgene and the opportune diols.² Despite all the previously mentioned advantages the route for what could seem a modern *lapis philosophicus* like process is far from completion. Carbon dioxide does not represent an easily reactive molecule, the main drawback being represented by its elevate thermodynamic and kinetic stability. The disadvantage linked to the high energy input required for its transformation may be, at least partially, overcome selecting high energy starting materials like epoxides or amines, and low energy target products such as carbonates, carbamates, ester, etc.² Of fundamental importance is the choice of an active catalyst able to promote the CO₂ conversion in an efficient way. Among the many catalysts that have been developed so far, in both homogeneous and heterogeneous conditions, metal halides, Lewis acid complexes, ammonium or phosphonium salts should be mentioned.³⁻⁵ The “activation mechanism” that makes possible the energetically unfavourable CO₂ conversion was extensively studied also by means of quantum mechanical investigations, and varies in function of the selected catalyst.^{6,7} In general when a nucleophile is involved the activation should proceed through the epoxide opening with consequent generation of a negatively charged oxygen,⁸⁻¹⁰ while

if a Lewis acid is present the first step is represented by the coordination of the oxygen at the three member ring.^{3,11}

The commonly accepted reaction mechanism for the synthesis of cyclic carbonates catalyzed by nucleophiles is reported in the following scheme.^{3,5-8,11}



Scheme 1. Proposed mechanism for the chemical fixation of CO₂ onto epoxides for its conversion into cyclic carbonates mediated by ionic liquid-based catalysts.

In the last years, imidazolium and ammonium based ionic liquid have been suggested as efficient (co)catalysts for the chemical fixation of carbon dioxide.^{5, 8-10, 12-21} Homogeneous catalysts based on ionic liquid moieties have been used with excellent results, both in terms of yield and selectivity for the synthesis of cyclic carbonates;^{5, 12, 22-24} some examples have been also reported in the polycarbonates production.^{3, 18, 25-29} Imidazolium based ionic liquids have been also immobilized onto various solid supports in order to combine the good catalytic performances of the active sites with the advantages of the heterogeneous systems.^{3-5, 30-40} The more frequently used solid supports are represented by silica based materials^{9, 10, 13-15, 17, 19, 41, 42} even if some application related to polymers can also be found.^{38, 39, 43, 44} In particular, mesoporous ordered silica solids such as MCM-41 and SBA-15 or high surface area non structured silica materials,

received considerable attention due to their large specific surface areas and accessible porosity.⁴⁵ However the grafting approach leading to the *heterogenized* catalyst is usually time-consuming, since the preparation of the support followed by a post-functionalization to create the appropriate anchoring site is required.^{9, 10, 19, 42, 46} The possible incorporation of the ionic liquid in the solid support through immobilization or co-synthesis procedure does not constitute a valid alternative due to possible leaching phenomena and/or the low degree of functionalization usually achieved.^{32, 47}

Very recently it was found that the proximity of the reactant, that plays a key role in all the catalytic processes, is even more important in the carbon dioxide conversion.^{3, 48}

Herein, we present a novel material based on polymerized imidazolium salts protected by a porous silica shell in a microreactors-like catalytic system. The idea was to use properly functionalized imidazolium salts as template for the generation of a silica architecture in order to obtain the final catalyst in a one-pot synthesis approach.⁴⁹⁻⁵² The solid combine the advantages of a *heterogenized* catalyst with a straightforward synthesis procedure. With our new catalyst improved performances derived from strict interaction between reactants and catalytic active sites inside a confined space were observed. The excellent activity was confirmed by the high turnover numbers (TON) obtained in several catalytic tests performed under different reaction conditions.

Results and Discussion

Synthesis of the hybrid silica microreactors

For the preparation of the hybrid imidazolium-silica microreactors, the *N,N'*-bis(10-undecenyl)-2-methylimidazolium bromide was synthesized by optimizing a previously reported procedure.^{53, 54} It is known, that under selected conditions this amphipathic organic salt with its polar head and double hydrophobic tail self-organizes in water simulating a liposome-like structure (Scheme 2).^{53, 54} The charged imidazolium heads face the aqueous phase protecting the hydrophobic hydrocarbon chains in the internal part of the bi-layered organization (Scheme 2). Here, this ionic liquid based bilayer was used as template to direct the formation of porous silica architecture. Since the terminal part of the long alkyl chain is represented by a vinyl group, the liposome-like structures may also be “frozen” in a stable spherical packing by radical polymerization of double

bond.

In order to study the influence of the polymerization of the alkyl tails on the final silica structure, two different methodologies were employed for the preparation of the micro-reactors (Scheme 2). The bipodal ionic liquid *N,N'*-bis(10-undecenyl)-2-methylimidazolium was self-organized in water⁵⁵ or treated with potassium persulfate as radical source for the polymerization reaction⁵⁵ (see experimental). The solution containing the liposomes either polymerized (Poly-Imi) or only self-organized (Self-Imi), was used as template for the synthesis of the mesoporous silica matrix through the classical sol-gel method in basic medium.^{45, 56, 57} After hydrothermal treatment at 100 °C, under static conditions, the suspension was filtered and the solids obtained exhaustively washed with water and ethanol. Moreover, to remove the possible traces of unreacted imidazolium salts adsorbed on the surface of the spheres, the solids were also submitted to soxhlet extraction. The residual solvent was evaporated and analyzed by ¹H NMR spectroscopy. This analysis allows evidencing a first difference between the two samples. For the solid obtained using the Poly-Imi template, no traces of organic species were found in the solvent coming from the first extraction. In contrast, the SiO₂ solid generated in presence of the self-Imi suffered of a small but constant leaching of imidazolium salts.

Transmission electron microscopy investigation performed on both samples allow evidencing a clear structural difference between the material obtained starting from Self-Imi (Figure 1 left) or Poly-Imi (Figure 1 right).

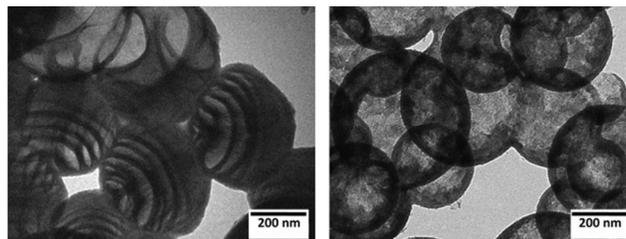
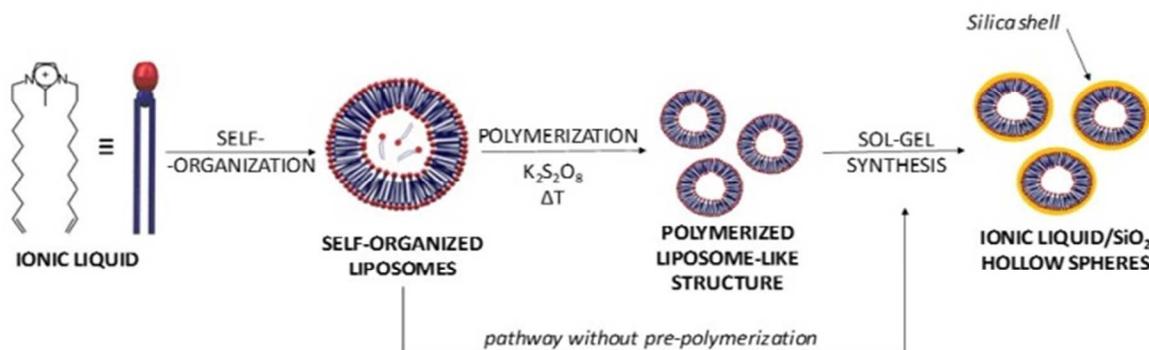


Figure 1. TEM images of the materials prepared using Self-Imi (left) or Poly-Imi (right) as template for the silica architecture.

The presence of a rigid polymeric bilayer (Poly-Imi) favored the formation of stable spherical silica shell, while in presence of self-Imi a structure constituted by concentric silica layers was obtained. This behavior can be explained taking into account the thermodynamics of liposome and vesicle formation.^{58, 59}



Scheme 2. General scheme for preparation of the imidazolium based silica sphere.

It is known that, the double tailed surfactants use to form bilayers or lamellar aggregates in aqueous media.^{57, 60} When these surfactants self-organize in water and in function of their concentration, the different bilayers give rise to sheet-like aggregates that solve their energy loss due to surface tension closing itself in a onion-like structure.⁵⁹ If a silica source is added in basic medium, an S^+I^- interaction (with S^+ being the cationic surfactant and I^- the anionic inorganic species) will occur.^{45, 56, 57} The condensation/polymerization of the silica precursor will occur between the bilayers resulting in the formation of concentric spheres.^{61, 62} When the pre-polymerization step is performed, the morphology of the materials obtained corresponds to a hollow sphere. In this case, the relatively high temperature of the polymerization (80°C), in combination with the curing time, causes the migration of the polymeric chains, and a fusion process between clusters of different size is favoured.^{53, 63, 64} This different mechanism led to the formation of a liposome like organization and the consequent generation of one external silica layer. It is not excluded that the internal part of this silica/imidazolium bilayer may be constituted by a mixture of solvent and residual organic monomers/oligomers.⁵³ From the preliminary transmission electron microscopy screening of the two solids, and taking into account the leaching of organic species observed in the case of self-assembled imidazolium salts, the silica spheres containing the polymerized liposome-like structure clearly represent the most promising material for catalytic applications. Therefore, Only the full characterization of the best material will be discussed.

The imidazolium based silica material prepared through the polymerization of the hydrocarbon chains (SImCat) was extensively characterized by transmission and scanning electron microscopy, N_2 adsorption/desorption, ^{29}Si solid state MAS-NMR and combustion chemical analysis.

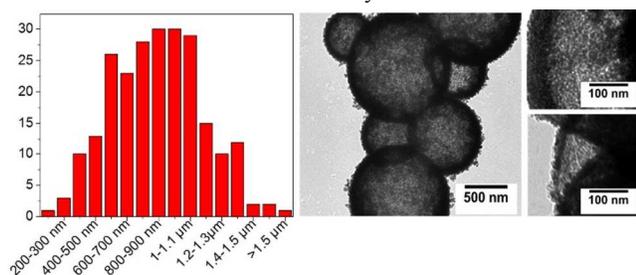


Figure 2. Particle size distribution of SImCat measured by TEM (left) and the high magnification TEM images (right) in which the porosity is clearly observed.

Transmission electron microscopy was used to determine the particle size distribution of the hybrid material. The results obtained from 200 measurements in different regions of the TEM grid are displayed in Figure 2 left. High resolution TEM images (Figure 2 right) revealed the presence of a mesoporosity in the silica shell. This finding allows ensuring the accessibility of the inner active sites through the external inorganic layer. Silica spheres of very small dimensions (<200 nm) can also be sporadically observed in some part of the sample.

Scanning electron microscopy (SEM) analysis of the SImCat confirms the spherical morphology of the solid (Figure 3). All the silica particles display a perfectly closed shape, the occasional

presence of few partially broken shells (representing the 1% of the entire sample) allows evidencing that the SImCat is constituted by hollow spheres (Figure 3b).

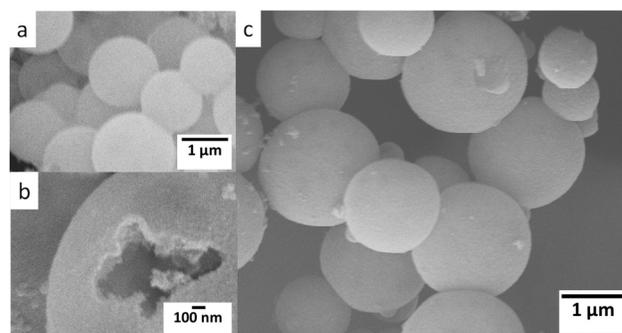


Figure 3. Selected SEM images of the SImCat solid.

The results of N_2 physisorption measurements are displayed in Figure 4 left. The Brunauer-Emmet-Teller (BET) specific surface area (180 m^2/g) as well as the absence of a narrow pore size distribution obtained for the SImCat, can be attributed to the presence of the organic polymeric matrix inside the solid. The observed BET value is similar to those reported for other porous silica architectures covered by polymeric cross-linked organic shell^{9, 10, 13, 17, 41, 65}. The type 3 hysteresis loop observed at high P/P_0 can be ascribed to a large meso-macro porosity arising from interparticles interaction.

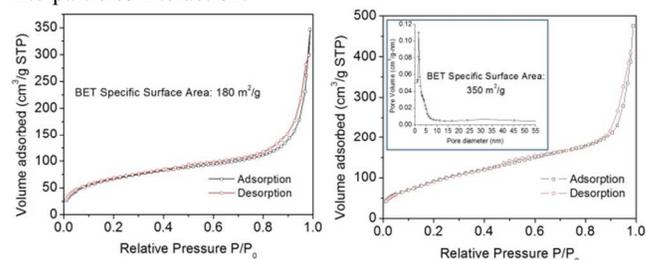


Figure 4. N_2 adsorption-desorption isotherms of the SImCat before (left) and after (right) thermal treatment.

In order to have a deeper understanding of the mesostructure generated under our synthesis conditions, the sample was submitted to a controlled thermal treatment (see experimental). To ascertain that the SiO_2 spherical architecture was preserved during this process, a TEM investigation prior to N_2 adsorption/desorption measurement was performed on the calcined sample. As expected, the sample submitted to thermal treatment displayed a higher specific surface area (350 m^2/g) and, in agreement with TEM observation, a pore size distribution centered at 2.4 nm (Figure 4, right). The large band between 25 and 50 nm, observed in the pore size distribution pattern, confirms the presence of an irregular porosity generated between the particle grains.

The X-ray diffraction pattern of the SImCat before calcination showed a broad signal at low 2θ (Figure 5, left). After thermal treatment the peak increased in intensity and the maximum shifted to higher 2θ values ($2\theta = 2.1^\circ$), in the typical region of MCM-41 like materials.

To check the good condensation degree of the Si-O-Si bonds, ^{29}Si solid state nuclear magnetic resonance was performed as well. The ^{29}Si -MAS-NMR (Figure 5, right) displayed two bands at -

113 ppm and -103 ppm corresponding respectively to the Q⁴ and the Q³ species. This result clearly indicates a good condensation of the inorganic precursor in the silica shell of the hybrid material. Due to the large dimension of the silica sphere, the relatively high Q³/Q⁴ ratio (0.3) may be justified in function of the presence of a silica layer with a double (external and internal) surface decorated with sylanol groups. In order to prove the reproducibility of the synthesis procedure, various SImCat solids were synthesized with similar results in terms of TEM and ²⁹Si NMR measurements. Moreover, combustion chemical analysis performed on each different batch gave also similar percentage of polymerized imidazolium salts (about 20 wt% in all samples with some exceptions in the range between 17 and 21%).

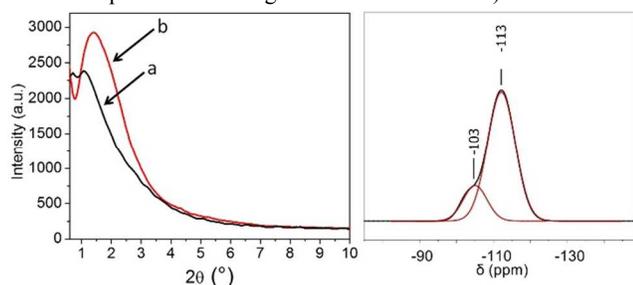


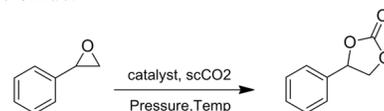
Figure 5. Left: XRD pattern of the microreactors before (a) and after (b) calcination. Right: ²⁹Si MAS NMR of the hybrid silica microreactors. The two fittings correspond to the Q³ (at -103 ppm) and Q⁴ (-113 ppm) species.

Catalytic tests

The presence of a porous shell (clearly observed in TEM measurements) ensuring the accessibility of the active sites together with the relatively high surface area and stability (absence of leaching) of the imidazolium/silica solid are interesting features for possible catalytic applications. The SImCat microreactor was tested as catalyst for the synthesis of cyclic carbonates *via* the chemical fixation of carbon dioxide. The catalytic tests were performed in a batch reactor under different conditions in terms of pressure, substrate to catalyst weight ratio and presence or not of solvent. The loading of imidazolium active sites remained constant since is dependent by critical concentration required for the formation of the liposome-like structures and for the consequent synthesis of the SImCat. A challenging substrate like the styrene oxide (SO) was selected as target starting material. One of the most used solvent for the synthesis of cyclic carbonates is the dichlorometane (DCM), this solvent was therefore selected for a first screening of the catalytic activity. In order to allow a meaningful comparison with literature data the temperature was maintained at 150°C since it is the value usually selected for imidazolium based systems, under heterogeneous condition and in absence of any further activation coming from co-catalyst with Lewis acid properties.^{9, 10, 17, 38, 44} Moreover turnover number (TON; defined as *moles of epoxide converted/moles of imidazolium active sites*) and turnover frequency (TOF; calculated as $TON \cdot h^{-1}$) were calculated as well. The results are summarized in Table 1. The first catalytic test was performed selecting the initial pressure of 50 bar. It is worth to underline that the TON value obtained under these conditions (TON = 136) is one of the highest reported in literature for supported heterogeneous systems⁹. An increase of the working

pressure to 70 bar, while keeping constant the temperature at 150 °C (Table 1, entry 2), did not substantially improve the catalytic performances. The conversion remained unchanged also under supercritical conditions (Table 1, entry 3). A prior purge of the reactor with N₂, in order to remove the eventual presence of air, resulted in a considerable increase of the carbonate yield (Table 1, entry 4). From this first results it appears evident that the SImCat is a promising catalyst, especially if we take into account that bromide (and not iodide) is present as imidazolium counterion⁹ and that the reaction is performed in presence of a considerable amount of solvent (19.2 ml DCM and 4.8 ml of epoxide). Moreover, no leaching of the ionic liquid occurred as confirmed by the absence of signals corresponding to imidazolium salt in the ¹H-NMR spectra. In addition, by-products were not observed during the reaction that always displayed very high selectivity, superior to 99%. A blank experiment with pure MCM-41 solid showed that no formation of carbonate occurred in absence of imidazolium based catalyst. Good conversions were also obtained for the reactions performed in presence of acetonitrile or acetone as solvents (Table 1, entries 5 and 6). However, under these conditions a lower selectivity was found. This behaviour can be ascribed to the presence of small amounts of water in the solvents, whose presence favoured the formation of the 1-phenyl-1,2-ethanediol as main by-product⁴⁰.

Table 1. Catalytic tests for chemical fixation of carbon dioxide onto styrene oxide.



Entry	P (bar)	Solvent	Carbonate yield (%)	Selectivity (%)	TON	TOF (h ⁻¹)
1	50	CH ₂ Cl ₂	27.1	~99	136	45
2	70	CH ₂ Cl ₂	25.6	~99	123	41
3	80	CH ₂ Cl ₂	23.1	~99	114	38
4 ^a	80	CH ₂ Cl ₂	33.3	~99	193	64
5 ^a	80	CH ₃ CN	21.1	76	156	52
6 ^a	80	CH ₃ COCH ₃	15.9	72	125	41
7	80	-	52.3	~99	305	102
8 ^a	80	-	56.3	~99	328	109

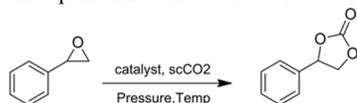
Ratio SO/catalyst = 28 in weight; T=150°C; superscript “a” refers to a previous N₂ purge of the reaction system; carbonate yield and TON obtained from ¹H-NMR data. The reaction time was of 3h for all catalytic tests. **Selectivity ~99%.**

It was recently proved by various research groups that the performance of a catalytic system may be substantially improved working under solvent free conditions due to the increased local concentration of substrate and/or carbon dioxide.^{9, 17, 48} To investigate whether the activity of the SImCat could further improve two additional tests in supercritical condition and in absence of solvent were performed. As it can be observed in Table 1 (entries 7 and 8), the performances of the system greatly improved, especially when the reaction mixture was previously purged with N₂ (TON =328). It should be noticed that the difference in the carbonate yield between entries 7 and 8 was not

as pronounced as in the test performed in the presence of solvent. Since the contact between the reactants and active sites is one of the key aspects of the catalysis in both homogeneous and heterogeneous conditions⁴⁸, the good catalytic performance of our solid compared to analogous imidazolium based materials may be justified by an increased interaction due to a confinement effect inside the SImCat microreactor⁴⁸. The mesoporosity of the silica shell, clearly visible in the TEM investigation of the sample (Figure 2, right) allows an easy diffusion of reactants/product to and from the active sites while the stability of the inorganic architecture, prevents the polymeric matrix from degradation or leaching. Moreover a possible active role of the surface hydroxyl groups present in the inner silica shell (hence in strict contact with the imidazolium units) can not be completely excluded.⁴⁶ It was proved, also *via* density functional theory (DFT) studies that the hydroxyl groups may activate the epoxide through a hydrogen bond interaction in the earlier step of the reaction mechanism favouring the ring opening by the nucleophile.^{24, 66} Quantum mechanical modelling was also used to evidence that hydrogen bond interactions could promote the stabilization of other intermediate species such as the anionic carbonate (scheme 1) whose ring closure through intramolecular SN2 leads to the formation of the cyclic carbonate.^{7, 24, 66}

In order to further understand the catalytic behaviour of the SImCat, more demanding conditions in terms of epoxide to catalyst weight ratio were selected (SO/SImCat = 56). These tests were performed with pure styrene oxide; no solvent was added to the reaction mixture. The results are presented in Table 2. Under these conditions, the carbonate yield was 24.8% when the test was performed at 80 bar and 150 °C (Table 2, entry 1); further increase in the working pressure until 90 bar lead to a small increase in the cyclic carbonate yield (Table 2, entry 2). When the system was purged with N₂, the carbonate yield increased to 40% with a corresponding TON of 388 mol converted/mol active site (see Table 2, entry 3). These data confirm the good catalytic activity of the material and prove that the amount of catalyst can be decreased without major drawbacks. It is worth to mention that in all the catalytic tests the selectivity of the reaction was high (~99%), with the cyclic carbonates as the sole quantifiable product.

Table 2. Catalytic tests for chemical fixation of carbon dioxide onto styrene oxide performed in absence of solvent.



Entry	P (bar)	Carbonate yield (%)	TON	TOF (h ⁻¹)
1	80	24.8	283	94
2	90	29.4	290	97
3 ^a	80	40.3	388	129
4 ^{a,b}	80	77	797	133

Ratio SO/catalyst = 56 in weight; T=150°C; superscript “a” refers to a previous N₂ purge of the reaction system; “b” reaction performed during 6 h; carbonate yield and TON obtained from ¹H-NMR data. **Selectivity ~99%.**

A further increase in the reaction time to 6 h (Table 2, entry 4) resulted in a higher carbonate yield (77 %) with an exceptionally high TON of 797.

When working in heterogeneous conditions, the catalytic behaviour of the catalyst in terms of yield and selectivity, are not the only parameters that should be considered. One important factor is represented by the possible use of the catalyst in multiple catalytic cycles. The reusability of the catalyst was tested selecting the best reaction conditions found in the last set of catalytic essays (entry 3 in Table 2). The results of these tests are presented in Figure 6 left. The catalytic activity of the material suffered of a decrease after the first run. However, it remained constant in the following two cycles and slowly increased in the successive ones, proving that the catalyst can be recycled. Characterization of the solid after the consecutive catalytic cycles (Figure 6 right) did not show any substantial structural change in the silica with regards to both, shape and porosity. The presence of possible leaching of low amount of imidazolium species in the reaction mixture too small to be detected by ¹H-NMR analysis was excluded by combustion chemical analysis performed after the fifth cycle. The percentages of nitrogen were of 1.36% for the fresh catalyst (after extraction) and of 1.35% after the fifth catalytic cycle. The difference in the activity between the first cycle and all the following could be tentatively attributed to a reorganization of the imidazolium bilayer inside the silica porous shell. A similar behavior is described in the literature when polymeric active layers are used.¹⁰ Another possible explanation could lie in a partial adsorption of small amount of substrate in the SImCat material resulting in a change of the local polarity and thus in a different solubility of CO₂. Future studies will be performed in order to better understand the nature of these modifications. It is worth to underline the high TON calculated after the fifth cycle (TON = 281 after reuse) compared to other heterogeneous catalytic systems. This result proves that the excellent performances of the solid are not strongly affected by this initial decrease.

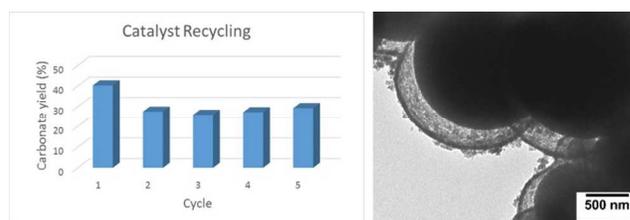
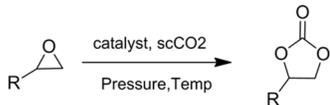


Figure 6. Left: recycling tests for styrene oxide (SO/Cat = 56; N₂; carbonate yield obtained from ¹H-NMR data). Right: TEM image of hollow sphere after reuse.

In order to check the versatility of the SImCat four additional epoxides were selected. The substrates chosen for this study were three monosubstituted aliphatic epoxides, the propylene oxide (PO), the epichlorohydrin (ECH) and the 1,2-Epoxybutane (EB) and a disubstituted compound, the cyclohexene oxide (CHO). The catalytic experiments were performed in presence of solvent selecting the conditions reported in Table 1, entry 4. As it can be observed in Table 3, the highly reactive ECH gave an almost quantitative conversion (higher than 94%) and a TON of 337.

The catalytic test performed using PO as starting material resulted in conversion of 58.7% with a corresponding TON of 275, thus further confirming the good performance of the heterogeneous catalyst. The EB gave a lower conversion with a carbonate yield of 15.2%. As expected, the more hindered epoxide (CHO) gave a lower (4.8 %) conversion as compared with previous compounds. The lower reactivity of CHO was previously observed and described in details also by means of density functional theory calculations.^{67, 68}

Table 3. Catalytic tests for chemical fixation of carbon dioxide onto different substrates



Substrate	Carbonate yield (%)	TON	TOF (h ⁻¹)
ECH ^a	94.4	491	163
PO ^a	58.7	275	92
EB	15.2	132	44
CHO	4.8	35	12

Ratio SO/catalyst = 28 in weight; T=150°C; P=80 bar; DCM; “a” refers to a molar ratio SO/catalyst of 1%; carbonate yield and TON obtained from ¹H-NMR data. **Selectivity ~99%.**

Conclusions

Herein, the synthesis of novel heterogeneous catalytic system was presented. An imidazolium based ionic liquid bearing two undecenyl chains was polymerized leading to a liposome-like structure. This polymeric matrix was used as template for the preparation of porous silica architecture. It is worth to highlight the straightforward preparation of the material in a one-pot procedure. The solid behave as an organic/inorganic hybrid microreactor with enhanced catalytic activity. The good performances were proved by the high TON and selectivity. Moreover, the activity was preserved in multiple catalytic cycles although a small decrease in the carbonate yield was observed after the first run.

Experimental Section

General

2-methylimidazole, 11-Bromo-1-undecene, triethylamine, tetraethyl orthosilicate (TEOS), NH₄OH 28 % solution, K₂S₂O₈ potassium persulfate, biphenyl, styrene oxide(SO), propylene oxide(PO), epichlorhydrin (ECH), 1,2-epoxybutane(EB) and cyclohexene oxide(CO) were purchased from Sigma Aldrich and used as received. Toluene, ethanol, absolute ethanol, acetonitrile, acetone and dichloromethane (DCM) were purchased from Fisher and used without further purification. ¹H-NMR spectroscopy and ¹³C-NMR spectroscopy were performed on a JEOL 400 and Bruker 500 spectrometers respectively. Combustion chemical analysis (C, H, N) were performed on a Thermo Finnigan-FlashEA 1112 apparatus. Transmission electron microscopy images were taken with a PHILLIPS TECNAI 10 instrument at

80 kV. Scanning electron microscopy images were taken with a JEOL JSM 7500-F instrument. MAS-²⁹Si-NMR spectrum was recorded on a Bruker 500 spectrometer operating at 5.5 kHz. XRD patterns were collected with a PANalytical X'pert diffractometer with Cu K_α radiation (k = 1.54178 Å). Isothermal nitrogen adsorption was carried out with at 77 K with a volumetric adsorption analyser (Micromeritics Tristar 3000) with a prior sample drying under vacuum at 120 °C.

Synthesis of the ionic liquid N,N'-bis(10-undecenyl)-2-methylimidazolium.

The ionic liquid N,N'-bis(10-undecenyl)-2-methylimidazolium was synthesized as previously reported^{53, 54}. In brief, 2-methylimidazole (1 equivalent) was allowed to react with 11-Bromo-1-undecene (2 equivalents) in the presence of 1.2 equivalents of triethylamine and toluene as solvent. The reaction was stirred for 48 h, at 90 °C under N₂ atmosphere. After removing the solvent under vacuum, the oily residue was exhaustively washed with hexanes until a yellowish-white powder was obtained, that was finally recovered by vacuum filtration and drying. ¹H-NMR: (400 MHz, DMSO): δ=7.733 (s, 2H), 5.877–5.716 (m, 2H), 5.024–4.878 (dd, J₁=5.017, J₂=4.952, 4H), 4.156–4.039 (t, J₁=4.138, J₂= 4.114, J₃=4.090 Hz, 4 H), 2.624 (s, 3 H), 2.069–1.952 (m, 4H), 1.775–1.658 (m, 4H), 1.363–1.128 ppm (m, 24H). ¹³C-NMR: (126 MHz, D₂O) δ= 143.27, 138.46, 121.45, 113.85, 47.95, 33.46, 29.32, 29.20, 29.16, 28.88, 28.60, 25.65, 9.39. ppm. **Elemental Analysis (%):** theoretical: C, 66.79; H, 10.13; N, 5.99; found: C 63.1; H 10.07; N 5.38. **Yield:** 53 %.

Synthesis of the non-polymerized hybrid silica microreactors.

The synthesis of the non-polymerized silica microreactors was carried out following the conventional sol-gel approach⁴⁵ and using the N,N'-bis(10-undecenyl)-2-methylimidazolium (Imi) as structure directing agent. The gel composition in weight % was 1 TEOS/8 NH₄OH/114 H₂O/0.12 Imi/8 EtOH. The receipt was as follows: 72.2 mg of N,N'-bis(10-undecenyl)-2-methylimidazolium were stirred in presence of a 28% aqueous solution of NH₄OH (4.816 g, 5.35 ml) and water (64.8 ml) during 1 h in a closed PP bottle. Then, the temperature was increased and stabilized to 50 °C and kept strictly above this value during the rest of the synthesis procedure. After this, 645 μl of TEOS (602 mg) dissolved in absolute ethanol (4.816 g, 6.1 ml) were slowly added to the reaction during 1 h and the mixture was stirred for 1 more hour at 50 °C. The reaction mixture was placed in the oven for 96 h at 100 °C. The solid obtained (~120 mg) was filtered and washed with water (200 ml) and ethanol (200 ml). To complete remove the traces of adsorbed imidazolium salts a soxlet extraction with DCM (200 ml) was performed as well.

Synthesis of the pre-polymerized hybrid silica microreactors.

For the synthesis of the pre-polymerized silica microreactors, first step was the polymerization of the precursor N,N'-bis(10-undecenyl)-2 methylimidazolium, accomplished as follows: in a 250 ml two-necked round bottom flask, 232.5 mg of N,N'-bis(10-undecenyl)-2-methylimidazolium were magnetically stirred in 150 ml of milliQ water during 1 h, at room temperature and under N₂ atmosphere. After 1 h, 90 mg of K₂S₂O₈ were added to the

reaction mixture and the temperature was increased to 80 °C. After 3 h, the reaction mixture was cooled down and all the flask content was transferred into a 250 ml PP closed container. NH₄OH (15.5 g, 17.22 ml) was added drop wise to the solution at a temperature of 50 °C and kept strictly above this value during the rest of the synthesis procedure; when the temperature was stable, TEOS (1.937 g, 2.076 ml) dissolved in 19.65 ml (15.5 g) of absolute ethanol was also added to the mixture during 1 h. The gel composition used in % weight was 1 TEOS/ 8 NH₄OH/ 83.84 H₂O/0.12 Imi/8 EtOH. The mixture was placed in the oven for 96 h at 100 °C. The solid obtained was filtered and washed with water (200 ml) and ethanol (200 ml). To ensure the complete removal of the traces of adsorbed imidazolium salts a soxhlet extraction with DCM (200 ml) was performed as well. The solid was again filtered and placed for 24 h in an oven at 40 °C. In order to prove the reproducibility of the synthesis procedure, this approach was repeated different times. Combustion analysis, performed on all the different materials (~530 mg) gave the following range of values: 1 - 1.3 %N, 13.1 – 14.8 %C, and 1.8 - 2.6 % H. The percentage of imidazolium in the samples was calculated from the Nitrogen content.

Catalytic tests.

All the catalytic tests were performed in a *Cambridge Design Bullfrog* batch reactor with individual temperature control and mechanical stirring, designed to operate at high temperature and pressures. The operating pressures of CO₂ ranged between 50 and 90 bar and other parameters like temperature and presence of solvent were also tested. In a common test: epoxide (24 ml in solvent-free condition or 4.8 ml if solvent was used), solvent if needed (19.2 ml), biphenyl (3.2375 g or 645 mg when solvent is present) as GC internal standard and the catalyst (180 mg when solvent was employed and 450 mg or 900 mg in solvent-free conditions depending on the ratio substrate/catalyst) were placed in the reactor connected to the heating block. The mechanical stirring was kept constant at 500 rpm. The closed reactor system was purged with N₂ (P =3.5 bars) for 10 min and then filled with a CO₂ selected pressure depending on the final desired value. The temperature was gradually increased from room temperature to 125 or 150 °C. Once the system reached the desired final temperature, the reaction was allowed to run for 3h. After this time, the heating block was removed (in order to allow a rapid cooling down of the system) and the system cooled to room temperature. When the temperature was about 28 °C, the mechanical stirring was stopped and the slow depressurization of the reactor was carried out. At 1 bar pressure, the system was opened and the reaction mixture submitted to a centrifugation step at 2000 rpm during 3 min. The supernatant was removed and analyzed by both, ¹H-NMR spectroscopy using d₈ toluene as solvent and gas chromatography with similar results. For the recycle experiments, the catalyst was placed in an ultrasound bath for 15 min, twice with toluene (35 ml) and once with ethanol (35 ml) and centrifuged after each washing step at 2000 rpm during 3 min. Then, it was placed in an oven at 80 °C overnight before being reused.

Acknowledgements

The authors acknowledge the FRS-FNRS funding. M.B-S is gratefully acknowledged for an Incoming Post-Doctoral Fellowship of the *Academie Universitaire de Louvain* co-funded by the Marie Curie Actions of the European Commission.

Notes and references

- ^a *University of Namur, Laboratory of Applied Materials Chemistry (CMA)*
⁶⁵ *Unit of Nanomaterial Chemistry (CNano)-Chemistry Department, 61 rue de Bruxelles B-5000 Namur, Belgium.*
 *E-mail: carmela.aprile@unamur.be
^b *Technical University of Valencia, Chemical Technology Institute (ITQ-CSIC) Camino de Vera s/n, 46022 Valencia (Spain)*
⁷⁰ † Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/
⁷⁵ ‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.
1. G. Centi, E. A. Quadrelli and S. Perathoner, *Energy Environ. Sci.*, 2013, **6**, 1711-1731.
 2. T. Sakakura, J.-C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365-2387.
 3. P. P. Pescarmona and M. Taherimehr, *Catal. Sci. Technol.*, 2012, **2**, 2169-2187.
 4. M. North, R. Pasquale and C. Young, *Green Chem.*, 2010, **12**, 1524-1539.
 5. F. Jutz, J.-M. Andanson and A. Baiker, *Chem. Rev.*, 2011, **111**, 322-353.
 6. H. Sun and D. Zhang, *J. Phys. Chem. A*, 2007, **111**, 8036-8043.
 7. S. Foltran, R. Mereau and T. Tassaing, *Catal. Sci. Technol.*, 2014, **4**, 1585-1597.
 8. V. Caló, A. Nacci, A. Monopoli and A. Fanizzi, *Org. Lett.*, 2002, **4**, 2561-2563.
 9. P. Agrigento, S. M. Al-Amsyhar, B. Sorée, M. Taherimehr, M. Gruttadauria, C. Aprile and P. P. Pescarmona, *Catal. Sci. Technol.*, 2014, **4**, 1598-1607.
 10. C. Aprile, F. Giacalone, P. Agrigento, L. F. Liotta, J. A. Martens, P. P. Pescarmona and M. Gruttadauria, *ChemSusChem*, 2011, **4**, 1830-1837.
 11. M. North and R. Pasquale, *Angew. Chem. Int. Ed.*, 2009, **48**, 2946-2948.
 12. J. Sun, S. Fujita and M. Arai, *J. Organomet. Chem.*, 2005, **690**, 3490-3497.
 13. J. Q. Wang, D. L. Kong, J. Y. Chen, F. Cai and L. N. He, *J. Mol. Catal. A: Chem.*, 2006, **249**, 143-148.
 14. M. Alvaro, C. Baleizao, D. Das, E. Carbonell and H. Garcia, *J. Catal.*, 2004, **228**, 254-258.
 15. A. Zhu, T. Jiang, B. Han, J. Zhang, Y. Xie and X. Ma, *Green Chem.*, 2007, **9**, 169-172.
 16. S. Zhang, Y. Chen, F. Li, X. Lu, W. Dai and R. Mori, *Catal. Today*, 2006, **115**, 61-69.
 17. J. Q. Wang, X. D. Yue, C. Fei and L. N. He, *Catal. Commun.*, 2007, **8**, 167-172.
 18. X. Xu, C. Wang, H. Li, Y. Wang, S. Weilin and Z. Shen, *Polymer*, 2007, **48**, 3921-3924.
 19. L. Han, H. J. Choi, S. J. Choi, B. Liu and D. W. Park, *Green. Chem.*, 2011, **13**, 1023-1028.
 20. J. Peng and Y. Deng, *New J Chem*, 2001, **25**, 639-641.

21. M. H. Anthofer, M. E. Wilhelm, M. Cokoja, I. E. Markovits, A. Pöthig, J. Mink, W. A. Herrman and F. E. Kühn, *Catal Sci Technol*, 2014, **4**, 1749-1758.
22. J. Sun, S. Zhang, W. Cheng and J. Ren, *Tetrahedron Lett.*, 2008, **49**, 3588-3591.
23. W. L. Wong, L. Yoon Suk Lee, K. P. Ho, Z. Y. Zhou, T. Fan, Z. Lin and K. Y. Wong, *Appl. Catal. A*, 2014, **472**, 160-166.
24. J. Q. Wang, W. G. Cheng, J. Sun, T. Y. Shi, X. P. Zhang and S. J. Zhang, *RSC Adv.*, 2014, **4**, 2360-2367.
25. D. W. Park, N. Y. Mun, H. Y. Ju, Y. Choe and S. W. Park, *Stud Surf Sci Catal*, 2006, **159**, 865-868.
26. D. W. Park, N. Y. Mun, E. H. Lee, Y. Choe and S. W. Park, *React. Kinet. Catal. Lett.*, 2006, **89**, 149-156.
27. I. Kim, M. J. Yi, S. H. Byun, D. W. Park, B. U. Kim and C. S. Ha, *Macromol. Symp.*, 2005, **224**, 181-191.
28. G. P. Wu, S. H. Wei, W. M. Ren, X. B. Lu, B. Li, Y. P. Zu and D. J. Darensbourg, *Energy Environ. Sci.*, 2011, **4**, 5084-5092.
29. M. Kember, A. Buchard and C. K. Williams, *Chem. Commun.*, 2011, **47**, 141-163.
30. P. Zhang, T. Wu and B. Han, *Adv. Mater.*, 2014, DOI: 10.1002/adma.201305448.
31. C. P. Mehnert, *Chem. Eur. J.*, 2005, **11**, 50-56.
32. F. Shi, Q. Zhang, D. Li and L. Deng, *Chem. Eur. J.*, 2005, **11**, 5279-5288.
33. Y. Gu and G. Li, *Adv. Synth. Catal.*, 2009, **351**, 817-847.
34. S. Udayakumar, S. W. Park, D. W. Park and B. S. Choi, *Catal Commun*, 2008, **9**, 1563-1570.
35. J. Sun, J. Wang, W. Cheng, J. Zhang, X. Li, S. Zhang and Y. She, *Green Chem.*, 2012, **14**, 654-660.
36. J. Wang, J. Leong and Y. Zhang, *Green Chem.*, 2014, **16**, 4515-4519.
37. R. A. Watile, K. M. Deshmukh, K. P. Dhake and B. M. Bhanage, *Green Chem.*, 2012, **2**, 1051-1055.
38. S. Ghazali-Esfahani, H. Song, E. Paunescu, F. D. Bobbink, H. Liu, Z. Fei, G. Laurenczy, M. Bagherzadeh, N. Yan and P. J. Dyson, *Green Chem.*, 2013, **15**, 1584-1589.
39. W. Zhang, Q. Wang, H. Wu, P. Wu and M. He, *Green Chem.*, 2014, **16**, 4767-4774.
40. A. J. R. Amaral, J. F. J. Coelho and A. C. Serra, *Tetrahedron Lett.*, 2013, **54**, 5518-5522.
41. X. Zhang, D. Wang, N. Zhao, A. S. N. Al-Arifi, T. Aouak, Z. A. Al-Othman, W. Wei and Y. Sun, *Catal. Commun.*, 2009, **11**, 43-46.
42. A. Barbarini, R. Maggi, A. Mazzacani, G. Mori, G. Sartori and R. Sartorio, *Tetrahedron Lett.*, 2003, **44**, 2931-2934.
43. S. R. Jagtap, V. P. Raje, S. D. Samant and B. M. Bhanage, *J. Mol. Catal. A: Chem.*, 2007, **266**, 69-74.
44. Y. Xiong, Y. Wang, H. Wang, R. Wang and Z. Cui, *J. Appl. Polym. Sci.*, 2012, **123**, 1486-1493.
45. R. Xu, W. Pang, J. Yu, Q. Huo and J. Chen, *Chemistry of zeolites and related porous materials*, Wiley, 2007.
46. T. Takahashi, T. Watahiki, S. Kitazume, H. Yasuda and T. Sakakura, *Chem. Commun.*, 2006.
47. N. Zhao, N. Yu, J. Wang, D. Zhuang, Y. Ding, R. Tan and D. Yin, *Microporous Mesoporous Mater.*, 2009, **122**, 240-246.
48. M. Taherimehr, A. Decortes, S. M. Al-Amsyhar, W. Lueangchaichaweng, C. Whiteoak, E. C. Escudero-Adán, A. W. Kleij and P. P. Pescarmona, *Catal. Sci. Technol.*, 2012, **2**, 2231-2237.
49. Y. Zhou and M. Antonietti, *Chem. Mater.*, 2004, **16**, 544-550.
50. Y. Zhou, J. H. Schattka and M. Antonietti, *Nano Lett.*, 2004, **4**, 477-481.
51. Y. Zhou and M. Antonietti, *Adv. Mater.*, 2003, **15**, 1452-1455.
52. T. Wang, H. Kaper, M. Antonietti and B. Smarsly, *Langmuir*, 2007, **23**, 1489-1495.
53. M. Buaki, C. Aprile, A. Dhakshinamoorthy, M. Alvaro and H. Garcia, *Chem. Eur. J.*, 2009, **15**, 13082-13089.
54. M. Buaki-Sogo, M. Alvaro and H. Garcia, *Tetrahedron Lett.*, 2012, **68**, 4296-4301.
55. Y. S. Choi, H. T. Ham and I. J. Chung, *Polymer*, 2003, **44**, 8147-8154.
56. Z. A. Allothman, *Materials*, 2012, **5**, 2874-2902.
57. N. Pal and A. Bhaumik, *Adv. Colloid Interface Sci*, 2013, **189**, 21-41.
58. D. E. Discher and A. Eisenberg, *Science*, 2002, **297**, 967-973.
59. M. Antonietti and S. Förster, *Adv. Mater.*, 2003, **15**, 1323-1333.
60. A. Sein and J. Engberts, *Langmuir*, 1995, **11**, 455-465.
61. A. Monnier, F. Schuth, Q. Huo, D. Kumar, D. Margolese, R. S. Maxwell, G. D. Stucky, M. Krishnamurthy, P. Petroff, A. Firouzi, M. Janicke and B. F. Chmelka, *Science*, 1993, **261**, 1299-1303.
62. C. X. Lin, P. Yuan, C. Z. Yu, S. Z. Qiao and G. Q. Lu, *Microporous Mesoporous Mater.*, 2009, **126**, 253-261.
63. H. Noguchi and M. Takasu, *Phys. Rev.*, 2001, **64**, 041913-041911.
64. R. Nagarajan and E. Ruckenstein, *Langmuir*, 1991, **7**, 2934-2960.
65. M. Buaki-Sogo, M. De Miguel, P. Atienzar, M. Alvaro and H. Garcia, *ChemPhysChem*, 2013, **14**, 618-626.
66. C. Whiteoak, A. Nova, F. Maseras and A. W. Kleij, *ChemSusChem*, 2012, **5**, 2032-2038.
67. C. Whiteoak, E. Martin, M. Martinez Belmonte, J. Benet-Buchholz and A. W. Kleij, *Adv Synth Catal*, 2012, **354**, 469-476.
68. M. Taherimehr, S. M. Al-Amsyhar, C. Whiteoak, A. W. Kleij and P. P. Pescarmona, *Green Chem.*, 2013, **15**, 3083-3090.