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Supported POSS Based Materials as Highly Active Organocatalysts for the Conversion of CO_2

Carla Calabrese,[a,b] Leonarda F. Liotta,[c] Francesco Giacalone,[a] Michelangelo Gruttadauria,*[a] and Carmela Aprile*[b]

Abstract: Very high turnover numbers (TON) and productivity values up to 7875 and 740 respectively have been obtained for the conversion of CO_2 into cyclic carbonates by using hybrid materials based on imidazolium modified polyhedral oligomeric silsesquioxanes (POSS-Imi) grafted on amorphous silica (SiO_2) and mesostructured SBA-15. The heterogeneous organocatalysts were easily prepared *via* a straightforward synthetic procedure allowing to generate high local concentration spots of imidazolium active sites surrounding the POSS core. This synthetic procedure is also a promising approach for the design of a wide library of hybrid functional materials. The materials do not possess other co-catalytic species with Lewis or Brønsted acid functionalities which still represents a challenging aspect for the outcome of the process. The recyclability of the catalysts was successfully verified for four consecutive runs. The catalytic versatility was proved with a wide range of epoxides and with the most challenging oxetane on large scale (105-210 mmol) showing higher performances in comparison with other unmodified imidazolium-based catalytic systems. The new hybrids based on supported POSS nanostructures allowed the sustainable conversion of carbon dioxide under solvents- and metal-free reaction conditions with a full selectivity toward cyclic carbonates.

Introduction

Nowadays, the development of new technologies able to reduce CO_2 emission coming from anthropogenic activities is a topic of growing interest from both academic and industrial parties. Carbon dioxide capture, utilization and storage processes are part of the challenging project to mitigate CO_2 environmental impact. The conversion of carbon dioxide into valuable chemical products is attracting the interest of the scientific community due to the possibility to use carbon dioxide as inexpensive, available, nontoxic, and renewable C1 feedstock.[1] In particular, one of the most interesting pathway to valorize CO_2 is represented by carbon dioxide fixation into epoxides for the production of cyclic carbonates.[2] Furthermore, cyclic carbonates are compounds of interest finding widespread applications as aprotic polar solvents, intermediates for the synthesis of fine or bulk chemicals, electrolyte for batteries.[3] According to green chemistry principles,[4] the synthesis of cyclic carbonates from CO_2 and epoxides is a productive catalytic process displaying an atom economy of 100%. In order to face the challenging thermodynamic stability of carbon dioxide, starting materials with a relatively high free energy, like epoxides, have to be used combined with a proper catalyst able to reduce the activation energy of the process. In the last decades, several catalytic systems, working under both homogeneous and heterogeneous conditions, have been developed for the conversion of CO_2 into cyclic carbonates by reaction with epoxides. In particular, metal oxides,[5] metal organic frameworks (MOF),[6] metal salts,[7] metal complexes,[8] Lewis base systems,[9] ionic liquids (ILs),[10] and organic polymers[10c, 11] have been proposed as catalyst for this process. Among them, ionic liquids stand out for their high efficiency.[12] Furthermore, it is well known that the design of heterogeneous catalysts is particularly envisaged from industrial parties because of their simple recovery from the reaction medium and the possibility of using them in fixed bed reactors. The evident advantages of heterogeneous catalytic systems encouraged the development of supported ionic liquids hybrids for the production of cyclic carbonates. In particular, imidazolium salts have been immobilized on several solid supports such as cross-linked polymers,[13] silicon-based main chain polyimidazolium salts,[14] silica,[15] and carbon nanostructures[16]. It is worth pointing out that, for a selected heterogeneous catalyst, the overall performance depends on several features such as chemical, thermal and mechanical stability, a good amount of functionalization active sites, fast mass transport of reactants and products to and from the active sites. Moreover, in the synthesis of cyclic carbonates the activity of ionic liquid based catalysts strongly depends on the nucleophilicity of the anionic species towards the attack into the epoxide as well as on its ability as leaving group.[17] Therefore, taking into account previously mentioned catalytic systems, imidazolium counterions play a key role in the reaction mechanism by promoting epoxide ring opening followed by the CO_2 insertion. Furthermore, the design of hybrid materials able to combine the high activity and selectivity achieved by homogeneous catalysts and the intrinsic advantages of heterogeneous ones is still a challenging task. A promising catalyst for the synthesis of cyclic carbonates is represented by imidazolium functionalized polyhedral oligomeric silsesquioxanes (POSS-Imi).[18] Polyhedral oligomeric silsesquioxanes (POSS)

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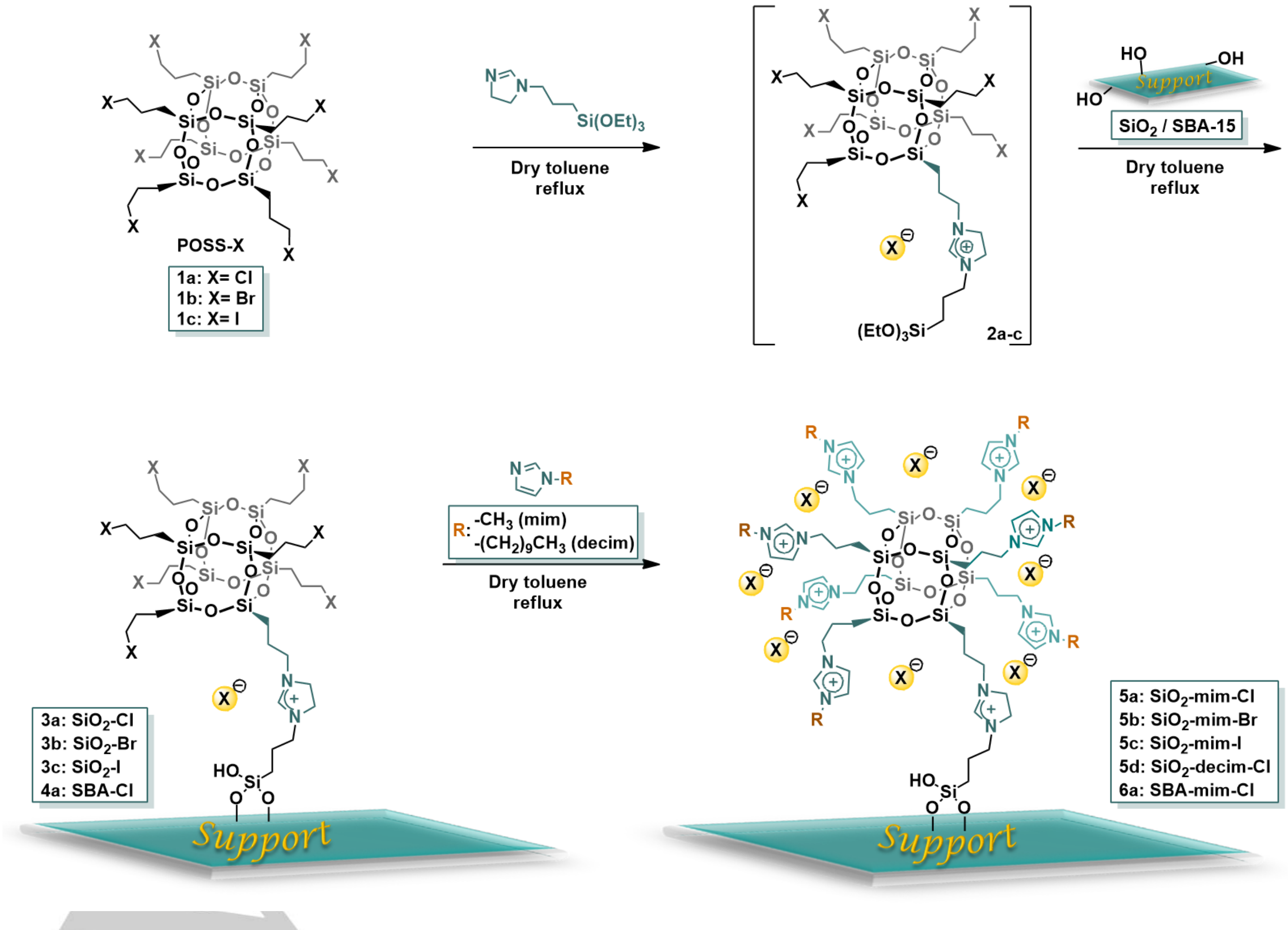
are usually considered as the smallest hybrid particles of silica.[19] POSS are a class of organic-inorganic hybrid molecules made up of an inorganic nanocaged silicate core surrounded by organic functional groups dangling in a three dimensional arrangement. The general formula of these hybrid molecules is $(R\text{-}SiO_{1.5})_n$, where n is commonly 6, 8, 10 and 12, the ratio O/Si is 1.5 and R is the vertex functional group (hydrogen, alkyl, alkene, aryl, arylene, etc.). POSS family is attracting the attention of the scientific arena owing to their wide range of applications in materials science ranging from soft electronics to nanomedicine.[1a, 20] The modular POSS molecular structure can be easily tuned to get a broad spectrum of properties.[21] In addition, POSS structures display high chemical and thermal stability together with a rigid molecular skeleton that can be functionalized with a plethora of organic side groups. Imidazolium modified POSS structures were used as homogeneous catalyst for the CO_2 conversion into cyclic carbonate showing improved catalytic performances compared to the unsupported 1-butyl-3-methylimidazolium salt. This behavior was ascribed to a proximity effect due to the higher local concentration of imidazolium active sites surrounding the inorganic silsesquioxane core. However, the recovery of the catalyst from the reaction mixture was tricky. Herein, in the light of the promising results achieved with imidazolium functionalized POSS molecules in terms of activity, we propose a broad series of heterogeneous catalysts based on imidazolium modified POSS units grafted into amorphous silica and mesostructured SBA-15. All the solids were extensively characterized and tested as the sole catalyst in the synthesis of cyclic carbonates by reaction between CO_2 and epoxides in solvent free reaction conditions. Moreover, the catalytic performances were stepwise improved, by finely tuning POSS-Imi units in terms of nucleophilic active species (Cl^-, Br^-, I^-) and imidazolium alkyl chain length.

Results and Discussion

A novel series of imidazolium modified POSS hybrids was designed and prepared to be applied as heterogeneous catalytic systems for the synthesis of cyclic carbonates from carbon dioxide and epoxides. In order to combine the proximity effect of imidazolium moieties surrounding the inorganic nanocage structure[18] together with the benefits of heterogeneous catalysis, functionalized POSS units were covalently grafted onto different solid supports, namely amorphous silica and mesostructured SBA-15.



Scheme 1. Synthesis of imidazolium functionalized POSS hybrids.

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A straightforward modular synthesis was developed using triethoxy-3-(2-imidazolin-1-yl)propylsilane as linker to connect POSS units to the solid support allowing to obtain dangling imidazolium modified supported nanostructures. In particular, the general synthetic route of these hybrids, reported in **Scheme 1**, started from the reaction between triethoxy-3-(2-imidazolin-1-yl)propylsilane and octakis(3-chloropropyl)-octasilsesquioxane (compounds **1a**, POSS-Cl) to give compound **2a** which was directly used for the grafting reaction onto two different supports to give materials **3a** (SiO_2-Cl) and **4a** (SBA-Cl). In this context, it is worth to observe that the above synthetic strategy represents a promising approach for the design of a wide library of hybrid functional materials. The latter materials were in turn reacted with 1-methylimidazole allowing to obtain the corresponding **5a** and **6a**. Materials **5a** and **6a**, endowed with chloride as counterion, were employed to study the effect of the solid supports on the catalytic performances. Then, amorphous silica was used, as support, to investigate the influence of the nucleophilic species in the final catalytic materials. For doing so, octakis(3-bromopropyl)-octasilsesquioxane (**1b**, POSS-Br) and octakis(3-iodopropyl)-octasilsesquioxane (**1c**, POSS-I) were prepared by halogen exchange reactions starting from POSS-Cl.[22] Then, both POSS-Br and POSS-I were grafted into amorphous silica to obtain the final imidazolium hybrids **5b** and **5c**. Moreover, in order to investigate the effect of the length of imidazolium alkyl side chain, a further hybrid was prepared *via* reaction between solid **3a** and 1-decylimidazole to give material SiO_2-decim-Cl (**5d**). The grafting of imidazolium modified POSS units into the solid support was proved by means of solid state NMR. Solid state ^{13}C and ^{29}Si cross polarization - magic angle spinning (CP-MAS) NMR experiments were carried out to characterize all the final hybrids (**Figure 1**).

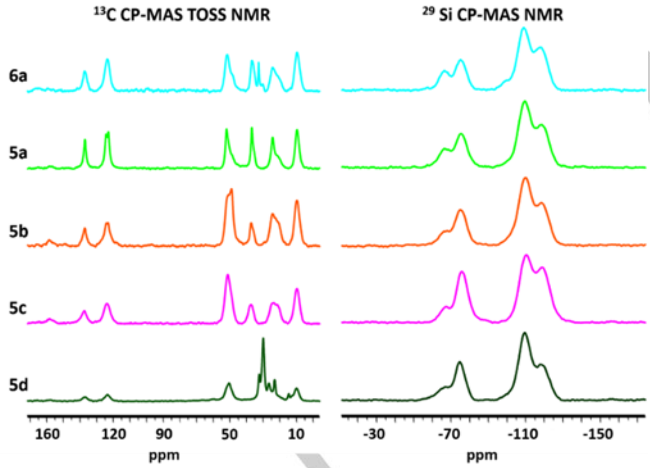


Figure 1. Solid state ^{13}C CP-MAS TOSS (on the left) ^{29}Si CP-MAS (on the right) NMR spectra of imidazolium functionalized POSS hybrids.

All the solid state ^{13}C CP-MAS NMR experiments were performed using the TOSS (total suppression side band) pulse sequence to remove the spinning side bands while leaving the isotropic signals. In CP-MAS ^{13}C NMR spectra the characteristic signals of the carbon atoms of imidazolium ring were observed in the range δ = 122-137 ppm, whereas the aliphatic ones resonated in the range δ = 10–52 ppm. The weak signal located at δ = ~158 ppm can be attributed to the C2 imidazolidinium carbon atom. CP-MAS ^{29}Si NMR spectra showed the presence of $Q^4[(SiO)_4Si]$ (δ = -118 ppm) and $Q^3[(SiO)_3SiOH]$ (δ = -110 ppm) units. The signal at δ = −75 ppm corresponded to the completely condensed T^3 silicon units $[R\text{-}Si(OSi)_3]$ of both POSS nanocage and the organosilane silicon acting as linker between the solid support and the POSS itself, whereas the signal at δ = −67 ppm was ascribed to T^2 $[R\text{-}Si(OSi)_2OR]$ silicon atoms bridging bulky silica to POSS units.

Combustion chemical analysis (C, H, N) allowed to estimate the catalyst loadings of all the solids, as showed in Table S1. Thermogravimetric analysis (TGA) allows to estimate the thermal stability of the hybrid materials (**Figure 2, Figure S1**). Moreover, from TGA data it is interesting to observe that the degradation of organic moieties starts at 250°C. On this ground, the good thermal stability of the solids emerged as promising feature for their repeated use under heating conditions.

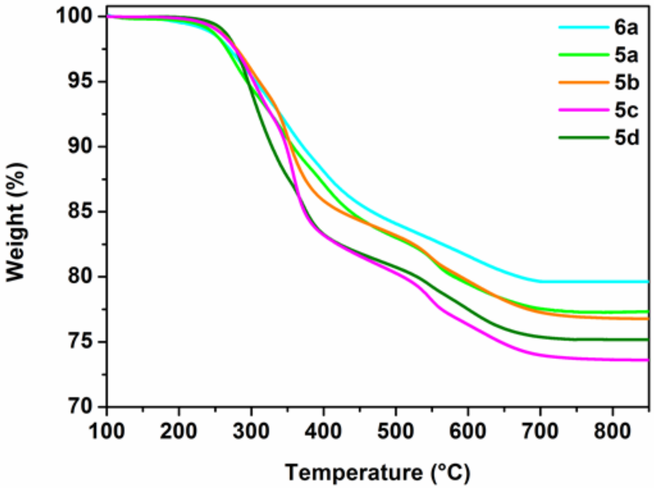


Figure 2. TGA profiles of imidazolium functionalized POSS hybrids.

Surface textural properties of the materials were investigated by means of N_2 adsorption/desorption measurements (**Table 1**). In particular, the specific surface area (SSA) was analyzed by Brunauer-Emmett-Teller (BET) method,[23] whereas pore volumes and pore size distributions (PSD) were estimated by applying Barrett-Joyner-Halenda (BJH) method[24] using the adsorption isotherms. A clear decrease in surface area and cumulative pore volume of amorphous silica and mesostructured SBA was observed after the grafting of imidazolium modified POSS units. All the supported POSS hybrids displayed a type IV isotherm (**Figure S2**) according to the IUPAC classification with a H_2 hysteresis loop.

Table 1. Textural properties of silica oxide and supported POSS hybrids.

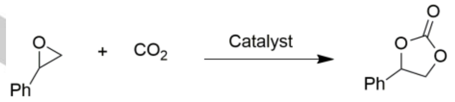
Material	BET[a] m^2/g	Pore Volume cm^3/g	PSD[b] nm
SiO_2	424	0.60	4.6
5a	250	0.28	3.7
5b	285	0.38	3.9
5c	279	0.37	3.5
5d	203	0.22	3.6
SBA-15	634	1.39	15.6
6a	272	0.87	14.3

[a] BET p/p^0 range: 0.05-0.3. [b] PSD calculated on the adsorption curve.

Materials **5a** and **6a** were analyzed by means of transmission electron microscopy (TEM) in order to collect morphological information. However, TEM pictures (**Figure S3**) did not reveal any appreciable difference compared to pristine solid supports. The amorphous morphology of SiO_2 and the bidimensional hexagonal mesostructure of SBA-15 were further observed for **5a** and **6a**, respectively.

Once characterized, imidazolium modified POSS hybrids were tested as catalysts for the synthesis of cyclic carbonates *via* reaction of CO_2 with epoxides under solvent free conditions, at 150 °C, and without using any co-catalytic species with Lewis acid properties. It is worth to mention that such reaction is highly exothermic. In this context, from an industrial point of view a reaction temperature around 150 °C could be evaluated as a beneficial condition allowing to recover the reaction heat as steam.[1b] To minimize the energy consumption, reaction temperatures <100 °C display indeed lower heat exchange efficiencies. The catalytic performances of the solids were evaluated in terms of turnover number (TON, defined as moles of epoxide converted/moles of supported imidazolium halide), productivity (P, calculated as grams of cyclic carbonates per grams of catalyst), recyclability and versatility. In order to study the effect of the solid support, two catalytic tests were carried out with materials **5a** and **6a** in the reaction between carbon dioxide and styrene oxide (**Table 2**, entries 1, 2). From this preliminary investigation, imidazolium modified POSS grafted into amorphous silica (**SiO_2-mim-Cl 5a**) resulted more active than the analogous material prepared by supporting POSS into SBA-15 (**SBA-mim-Cl 6a**). This behavior can be accounted to the specific textural properties of the final materials (**Table 1**). By comparison with **6a**, the solid **5a** displayed lower values in terms of both pore volume and pore size distribution, whereas it presented a higher catalyst loading (1.048 *vs* 0.753 mmol/g, **Table S1**). On this basis, the better catalytic activity of **5a** could be explained by a higher local concentration of imidazolium modified POSS units which resulted in improved intermolecular interactions. Both **5a** and **6a** showed competitive and higher performances in comparison with other catalytic systems recently reported in literature (**Table 2**) such as 1-butyl-3-methylimidazolium chloride (BmImCl)[12b, 18] or pyrazolium bromide (HEPzBr)[25] unsupported ionic liquids (entries 3,4), and heterogeneous catalysts based on polymer supported ammonium chloride salts (PSCQNCl),[26] imidazolium chloride[15b] and tetrafluoroborate[27] active sites supported onto silica (SiO_2ImCl, SiO_2ImBF_4), or imidazolium salts bearing bromide as counterion grafted onto carbon nanohorns (CNHsImBr),[16c] and benzyl chloride polymer (BCPImBr)[28] (entries 5-9). The above catalytic systems do not present other co-catalytic species with Brønsted or Lewis acid functionalities. High catalytic activity under such conditions is still challenging. On the other hand, much better performances can be obtained when co-catalytic species are present.[29] The higher catalytic activity of **5a** and **6a** can be ascribed to the proximity effect due to the increased local concentration of imidazolium moieties surrounding POSS nanocage skeleton. It is worth to note that supported POSS materials allowed to a good combination between the positive features of POSS nanostructures and the intrinsic advantages of heterogeneous catalytic systems such as their easy recovery from the reaction mixture together with the possibility to reuse them for consecutive runs.

Table 2. Conversion of styrene oxide into cyclic carbonate.



Entry	Catalyst	T [°C]	t [h]	TON	TOF[a]	Reference
1[b]	**5a**	150	3	477	159	This work
2[b]	**6a**	150	3	306	102	This work
3	BmImCl	150	3	326	109	Ref[18]
4	HEPzBr	140	4	68	17	Ref[25]
5	SiO_2ImCl	150	3	28	9	Ref[15b]
6	PSCQNCl	150	5	75	15	Ref[26]
7	SiO_2ImBF_4	160	4	53	13	Ref[27]
8	CNHsImBr	150	3	106	35	Ref[16c]
9	BCPImBr	140	5	323	65	Ref[28]

[a] Turnover frequency (TOF, calculated as TON/reaction time). [b] Reaction conditions: styrene oxide (172 mmol), CO_2 (P_i 4 MPa), catalyst **5a** and **6a**, 150 °C, 3h.

As a result of the higher activity of **5a** compared to **6a**, amorphous silica was selected as solid support in order to study the effect of the nucleophilic species. For doing so, materials **5b** and **5c**, bearing imidazolium bromide and iodide moieties respectively, were synthesized and tested. In order to compare the catalytic performances and investigate the recyclability of the solids **5a-c**, styrene oxide was selected as target substrate (**Figure 3**, **Table S2**). The effect of the nucleophilic species led to the overall order of activity $I^- > Br^- > Cl^-$ corresponding to **5c** > **5b** > **5a** hybrids. All the solid displayed promising turnover number and excellent selectivity. The recyclability of **5a**, **5b**, **5c** was studied for four consecutive runs without showing, in the case of **5a** and **5b**, any significant decrease in the catalytic activity. However, a progressive decrease was observed in the case of the most active **5c**.

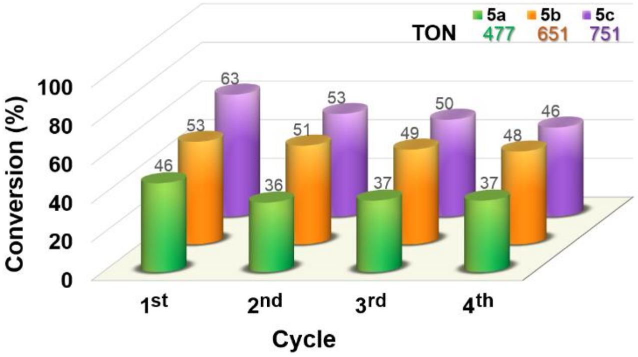


Figure 3. Recycling tests of materials **5a**, **5b**, **5c**. Reaction conditions: styrene oxide (172 mmol), CO_2 (P_i 4 MPa), 200 mg of catalyst (0.166 mmol of **5a**, 0.140 mmol of **5b**, 0.144 mmol of **5c**), 150 °C, 3 h. TON calculated on the first cycle.

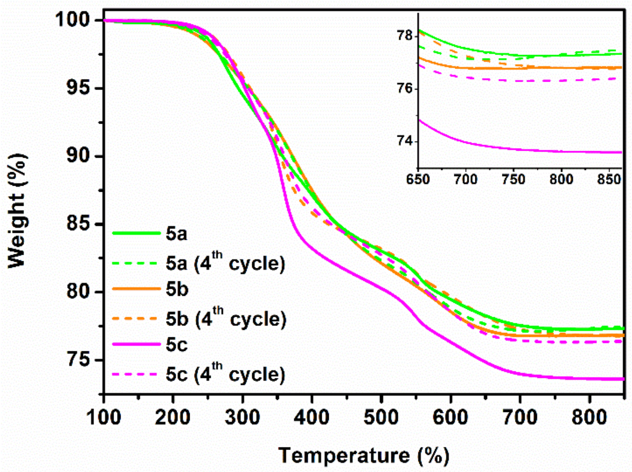
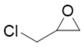
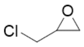
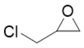
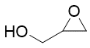
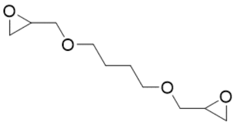
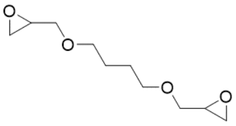
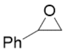
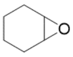


Figure 4. TGA profiles of as-synthesized and reused **5a-c**. Magnification of TGA curves (inset).

In order to check the thermal stability and the catalyst loading of reused solids, TGA measurements were performed on **5a-c** after the fourth catalytic cycle. Thermogravimetric analysis of reused catalysts confirmed the good robustness of materials **5a-b**. Indeed, TGA profiles of reused **5a-b** displayed the same weight loss compared to those of the as synthesized materials (**Figure 4**) leading to rule out the possibility of any leaching phenomena during the catalytic tests.

Conversely, TGA profile of **5c** reused for four cycles compared to that of the as-synthesized catalyst showed a loss in weight (~2.7%) allowing to justify the decrease in the catalytic activity during recycling experiments. Although the material **5c** proved to be the most active catalyst, the solid **5b** was selected for further investigations (**Table 3**) because of its higher stability after recycling compared to **5c** (**Figure 3**). Firstly, the potential influence of catalyst amount and operating CO_2 pressure was evaluated by using epichlorohydrin as target epoxide (entries 1-3). Material **5b**, tested at 0.022 mol%, displayed appealing performances in terms of TON, productivity and selectivity leading to 85% conversion into the desired product in 3 h. Furthermore, when the catalyst loading was scaled down to 0.006 mol%, **5b** showed an outstanding increased activity resulting in a turnover number of 7109 (entries 1-3). Such catalytic behavior could be ascribed to a better dispersion of the solid in the reaction medium when a decreased amount of **5b** was utilized. Furthermore, the overall versatility of **5b** was evaluated with a broad range of epoxides such as epichlorohydrin, propylene oxide, glycidol, 1,4-butanediol diglycidyl ether, and the less reactive cyclohexene oxide (entries 1-9). In all the catalytic tests, a full selectivity toward the corresponding cyclic carbonates was reached together with excellent TON and productivity. In particular, the reaction between CO_2 and 1,4-butanediol diglycidyl ether using 0.148 mmol/g of catalyst (entry 7) gave rise to a quantitative conversion. An additional catalytic test of **5b** was performed using the most challenging oxetane as substrate (entry 10). The synthesis of six membered cyclic carbonates by coupling of CO_2 and oxetane is challenging because of *i*) the lower reactivity of four membered ether rings compared to epoxides, and *ii*) a poor reaction selectivity as the six-membered cyclic carbonates is thermodynamically less stable than its corresponding co-polymer. Therefore, in the reaction with CO_2, oxetane ring opening step usually requires the use of an organometallic catalyst[30] or bicomponent catalysts composed of organometallic catalyst and ammonium salts[31]. A simple organocatalytic approach has been used only twice, using 2 mol% of tetraphenylstibonium iodide[32] or 3 mol% of TBAI and a hydrogen bond donor as co-catalyst[33]. In the latter case a mixture of oligocarbonate and six membered cyclic carbonate was formed. Nevertheless, in the reaction between carbon dioxide and oxetane ring, the catalytic performances of **5b** stand out from literature data in terms of TON. Then, the conversion of CO_2 and styrene oxide into styrene carbonate was chosen as benchmark reaction to check the influence of imidazolium alkyl chain length by comparison between the solids bearing imidazolium moieties with methyl and decyl alkyl side chain (**5a** and **5d**). Hybrid **5d** was tested for four consecutive runs and results compared with those of hybrid **5a** (**Figure 5**, **Table S2**).

Table 3. Synthesis of cyclic carbonates catalyzed by **5b**[a].

Entry	Substrate	Catalyst		Conv.	S	t	TON	P
		amt [mg]	[mol%]	[%]	[%]	[h]		
1		60	0.020	85	>99	3	4250	402
2		40	0.013	61	>99	3	4575	433
3		16	0.005	42	>99	3	7875	745
4		40	0.013	55	>99	3	4125	292
5[b]		40	0.013	51	>99	3	3825	313
6[c]		40	0.027	41	>99	16	3075	309
7[c]		200	0.133	99	>99	16	1485	149
8[d]		200	0.081	53	>99	3	651	74
9[e]		200	0.093	30	>99	16	321	32
10[f]		200	0.067	16	>99	16	240	19

[a] Conversion (Conv.), Selectivity (S), reaction time (t), Productivity (P, calculated as grams of cyclic carbonate/grams of catalyst). Reaction conditions: epoxide (210 mmol), CO_2 (P_i 4 MPa), catalyst **5b**, 150 °C. [b] Reaction conditions: glycidol (210 mmol), CO_2 (P_i 4 MPa), catalyst **5b**, 100 °C. [c] Reaction conditions: 1,4-butanediol diglycidyl ether (105 mmol), CO_2 (P_i 4 MPa), catalyst **5b**, 150 °C. [d] Reaction conditions: styrene oxide (172 mmol), CO_2 (P_i 4 MPa), catalyst **5b**, 150 °C. [e] Reaction conditions: epoxide (150 mmol), CO_2 (P_i 4 MPa), catalyst **5b**, 150 °C. [f] Reaction conditions: oxetane (210 mmol), CO_2 (P_i 4 MPa), catalyst **5b**, 150 °C.

Catalyst **5d** proved to be slightly less active than **5a** in terms of TON, indicating that the major role in the catalytic activity is probably played by the local arrangement due to the presence of the nanocage. In both **5a** and **5d** catalytic tests, the activity of the solid displayed a decreasing from the first to the second cycle followed by a stabilization in the next cycle. This behavior is

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probably due to thermal condensation phenomena that took place during the catalytic cycle.

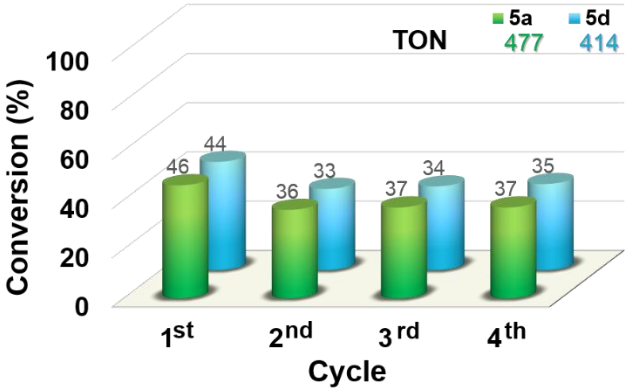

Figure 5. Recycling tests of materials **5a** and **5d**. Reaction conditions: styrene oxide (172 mmol), CO_2 (P_i 4 MPa), 200 mg of catalyst (0.166 mmol of **5a**, 0.183 mmol of **5d**), 150 °C, 3 h. TON calculated on the first cycle.

In order to verify such hypothesis, a ^{29}Si CP-MAS NMR experiment was carried out on the reused catalyst **5a** after the fourth cycle (**Figure S11**). The ^{29}Si spectrum of **5a** reused for four cycles compared to that of the as-synthesized catalyst showed an increase in the Q^4/Q^3 and T^3/T^2 ratio allowing to confirm a structural modification during the reaction.

Conclusions

In conclusion, we have prepared and characterized a series of hybrid materials based on imidazolium modified polyhedral oligomeric silsesquioxanes (POSS-Imi) in order to be employed as heterogeneous organocatalysts for the conversion of epoxides and CO_2 into cyclic carbonates in solvent-free reaction conditions. The main goal of this research was to maintain the high catalytic activity of unsupported imidazolium modified POSS, due to the proximity effect of the imidazolium units linked to the POSS nanocage, with the benefits of heterogeneous catalysis, in terms of recyclability, without the need of other co-catalytic species with Brønsted or Lewis acid functionalities. All the solids were easily prepared following tailored procedures designed to study the influence of the solid support (SiO_2 *vs* SBA-15) and the effect of both nucleophilic species (Cl^-, Br^-, I^-) and imidazolium alkyl side chain length. Such new hybrid materials were easily recyclable as well as highly active toward the formation of cyclic carbonates even with the less reactive oxetane, showing higher performances in terms of turnover number, productivity and selectivity in comparison with other unmodified imidazolium-based catalytic systems described in literature.[34] The combined features due to the good thermal stability of the solids and the local arrangement of the imidazolium units are, probably, the main reasons of the recyclability and high activity of such catalytic materials.

Experimental Section

Spectroscopic and analytical methods

Chemicals and solvents were purchased from commercial suppliers to be used without further purification. Combustion chemical analysis was carried out on a PerkinElmer 2400 Series II Elemental Analyzer. Thermogravimetric analysis was performed under oxygen flow from 100 to 1000°C with a heating rate of 10°C min^{-1} in a Mettler Toledo TGA STAR system. Solid state CP-MAS-TOSS ^{13}C-NMR spectra were recorded at room temperature, on a Bruker Avance 500 Spectrometer operating at 11.7 T, using a contact time of 2 ms, a spinning rate of 5 KHz and a Bruker probe of 4mm. CP-MAS ^{29}Si-NMR spectra were recorded at room temperature, on a Bruker Avance 500 Spectrometer operating at 11.7 T, using a contact time of 2ms, a spinning rate of 8 KHz and a Bruker probe of 4mm. Liquid state ^{1}H-NMR spectra were collected on a JEOL 400 spectrometer. TEM micrographs were taken on a Philips TECNAI 10 at 80-100 kV. N_2 adsorption–desorption measurements were carried out at 77 K by using a volumetric adsorption analyzer (Micromeritics Tristar 3000). Before the analysis, the samples were pretreated at 150°C for 16 h under reduced pressure (0.1 mbar). The BET method was applied in the p/p^0=0.05–0.30 range to calculate the specific surface area, whereas the pore size distributions were estimated from the adsorption isotherm using the BJH method.

Preparation of SBA-15

Mesoporous SBA-15 was prepared starting from tetraethyl orthosilicate (TEOS) as silica source, Pluronic P123 ($EO_{20}PO_{70}EO_{20}$) as template, and mesitylene as swelling agent, according to a published procedure.[35]

Synthesis of POSS 1a-c

POSS-Cl,[36] POSS-Br and POSS-I[22] were synthesized according to literature procedures.

Synthesis of materials 3a-c, 4a

A selected polyhedral oligomeric silsesquioxane (1 eq., 0.675 mmol of **1a-c**) was transferred in a two-necked round bottom flask. Anhydrous toluene (10 mL) and trethoxy-3-(2-imidazolin-1-yl)propylsilane (1.5 eq.) were added to POSS. The reaction mixture was refluxed under Argon atmosphere for 24 h. Then, the support (1.8 g of SiO_2 or SBA-15) was added to the reaction mixture without a prior isolation of intermediates **2a-c.** The obtained suspension was refluxed under Argon atmosphere for 72 h. The solids were recovered by centrifugation and washed with toluene, dichloromethane, and diethyl ether. The obtained materials (**3a-c**, **4a**) were dried at 60 °C under vacuum.

Synthesis of materials 5a-d, 6a

1-methylimidazole or 1-decylimidazole (15 eq. respect to halopropyl moieties of **3a-c** and **4a**) were added to a suspension of materials **3a-c** and **4a** (2.4 g) in toluene (25 mL). The reaction mixtures were refluxed for 72 h. The final solids **5a-d** and **6a** were recovered by centrifugation and washed with toluene, dichloromethane, hot methanol and diethyl ether. The final materials were dried at 60°C under vacuum.

Catalytic tests

The catalytic tests were carried out in a Cambridge Design Bullfrog batch reactor with temperature control and mechanical stirring, designed to operate at high temperature and pressures. A fine dispersion of the catalyst into the selected epoxide was transferred inside the reactor. Then, the reactor was closed and the mechanical stirring speed set at 500 rpm. The system was purged with N_2 for 10 min (0.4 MPa) and then, pressurized with CO_2. The temperature was increased to 150 °C with a rate of 5 °C min^{-1}. The reaction mixture was stirred at 150 °C for 3 h. Then, the reaction mixture was cooled down to room temperature and a slow depressurization of the reactor was carried out. The separation of the catalyst from the reaction mixture was easily performed by centrifugation (10 min at 4500 rpm). The supernatant solution was sampled and analyzed by ^1H-NMR.

Recycling tests

The recyclability of the materials was checked in the reaction between styrene oxide and CO_2. At the end of each catalytic test, the solids were recovered by centrifugation and washed with toluene (3x35 mL), methanol (30 mL) and diethyl ether. Moreover, the catalysts were previously sonicated in the washing solvent up to get a good dispersion. Then, the solids were dried under vacuum at 60 °C. Once dried, the materials were reused for the next cycle by tailoring epoxide amount in function of the recovered catalyst in order to maintain the ratio between moles of catalyst and moles of epoxides. The conversions of styrene oxide into cyclic carbonate was calculated by ^1H-NMR analysis.

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Keywords: CO2 conversion • cyclic carbonates • POSS • imidazolium catalyst • heterogeneous catalysis

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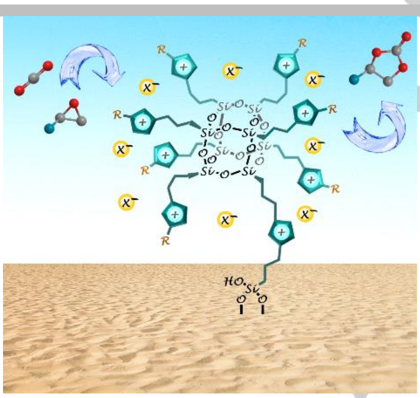
Entry for the Table of Contents

Layout 1:

FULL PAPER

PossAbility: POSS-based materials display great ability in the conversion of CO_2 into cyclic carbonates in terms of turnover number, productivity, selectivity and recyclability without the need of other co-catalytic species with Brønsted or Lewis acid functionalities.



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Supported POSS Based Materials as Highly Active Organocatalysts for the Conversion of CO_2