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Polyhedral Oligomeric Silsesquioxane Based Catalyst for the Efficient Synthesis of Cyclic Carbonates

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Polyhedral oligomeric silsesquioxane functionalized with imidazolium chloride peripheries (**POSS-Imi**) was successfully synthesized through a novel synthesis protocol. The solid was extensively characterized via ^{1}H, ^{13}C NMR and IR spectroscopy as well as via combustion chemical analysis, mass spectrometry and transmission electron microscopy. Moreover an in-depth investigation through ^{29}Si NMR was performed. The **POSS-Imi** was used for the first time as catalyst for the conversion of CO_2 and epoxides into cyclic carbonates with excellent results in both terms of yield and selectivity. The catalyst displayed improved catalytic performances with respect to the unsupported 1-butyl-3-methylimidazolium chloride. The enhanced activity was ascribed to the proximity effect generated by the increased local concentration of imidazolium species surrounding the inorganic silsesquioxane core.

Introduction

In recent years, the use of CO_2 as feedstock in chemical processes has attracted a considerable attention from the scientific community.[1, 2] Its low toxicity, along with its abundance and availability make of CO_2 an interesting molecule for sustainable applications. Carbon dioxide has been employed in different synthesis procedures as reagent, solvent and/or as extracting agent in purification processes.[2-5] One of the most studied reactions involving the use of CO_2 is represented by its fixation onto epoxides to produce cyclic carbonates and/or polycarbonates. Both classes of compounds are considered high added-value products widely used for different industrial and chemical applications.[2, 6-10] Among the possible active species able to catalyze the synthesis of cyclic carbonates,[6] imidazolium ionic liquids have shown excellent performances acting as catalysts or co-catalysts, for the latter usually in combination with organometallic complexes with Lewis acid properties.[11-19] When used as the sole catalysts, imidazolium salts display good catalytic performances in function of the selected counterion, however high temperatures (usually 150 °C) are required.[20-22] It is worth to be mentioned that, as highlighted by Sakakura,[3] a temperature of 150 °C does not represent necessarily a drawback in industrial applications. In particular, since the synthesis of cyclic carbonates from CO_2 and epoxides is an exothermic reaction, an efficient heat removal should be envisaged in large-scale applications in order to optimize the energy consumption. A reaction temperature of about 150 °C would allow recovering the reaction heat as steam. Different parameters including the working pressure or the presence of a co-solvent may greatly influence the performance of the selected catalyst. It is known that the close proximity of the reactants, achievable using various strategies, plays a positive effect on the catalytic activity.[11] Improved carbonate yield can be obtained in absence of solvent[11, 23, 24] or when the reaction takes place in a confined space or in a particular phase rich in catalytically active species.[21, 25, 26] Due to their excellent performances various imidazolium based catalysts working under both homogeneous and heterogeneous conditions have been proposed. However, the design of a catalyst displaying a perfect compromise between the excellent conversion and selectivity achieved with the homogeneous catalysts and the easy recovery of the heterogeneous ones, still represents a challenging objective. Polyhedral oligomeric Silsesquioxanes (POSS) is a family of organic-inorganic hybrids compounds characterized by an O/Si molar ratio of 1.5. Their structure can be expressed by the general formula T_nR_m , where T represent the number of Si and R the organic functionalities.[27-29] The most common of these compounds (T_8R_8) is the totally condensed POSS displaying an almost cubic structure. POSS nanostructures have attracted a growing interest during last decades due to their unique properties. Silsesquioxanes exhibit both organic and inorganic characteristics and a rigid cage-like core whose presence provides a high thermal and mechanical stability. Moreover, the organic peripheries can be easily functionalized allowing a facile tuning of the

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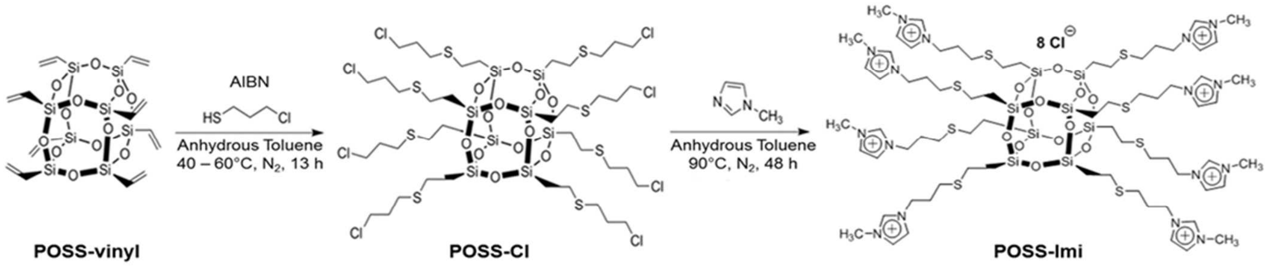


Scheme 1 Synthesis of the **POSS-Imi** catalyst

silsesquioxanes properties.[28, 30-33] Therefore, they have been widely used in different applications as the development of bio-inspired materials[34] and optic devices,[35, 36] as solid electrolytes,[37] additives in synthesis of periodic mesoporous organosilicas [38, 39] and composites,[40] and more recently in (photo)catalysis. [39, 41-47] Herein, we present a silsesquioxane based nanostructure functionalized with imidazolium chloride peripheries as efficient catalyst for the chemical fixation of carbon dioxide. Although similar POSS structures have already been reported,[31, 36] here we report a novel synthesis protocol. Moreover, to the best of our knowledge this is the first time that imidazolium substituted silsesquioxanes (**POSS-Imi**) have been used as catalysts for the synthesis of cyclic carbonates starting from CO_2 and epoxides. An in-depth investigation of the **POSS-Imi** nanocage via ^{29}Si NMR, never reported earlier, was also performed. The anchoring of the imidazolium moieties to the POSS nanocage produced a substantial improvement of the catalytic performances thus proving the importance of the silsesquioxane core.

Results and discussion

Polyhedral oligomeric silsesquioxane functionalized with imidazolium moieties was synthesized in a two steps procedure starting from the commercially available T_8R_8 octavinyl- substituted silsesquioxane (**POSS-vinyl**, Scheme 1). The **POSS-vinyl** was reacted with 3-chloro-1-propanethiol through a thiol-ene reaction in presence of 2,2-azobisisobutyronitrile (AIBN) as radical source to give the **POSS-Cl** (Scheme 1). The good performance of the thiol-ene reaction was confirmed by following, *via* ^{1}H-NMR spectroscopy, the disappearance of the vinyl signals in the region between 5.5 and 6.5 ppm (Figure S1). After purification, the product was also characterized by ^{13}C NMR and FT-IR spectroscopy as well as by combustion chemical analysis (Figures S2, S3 and experimental). The integrity of the nanocage was confirmed by the presence of only one signal in the ^{29}Si NMR spectrum typical of a T_8R_8 structure, corresponding to the T^3 silicon units (Figure 1b). For comparison, the ^{29}Si NMR spectrum of the **POSS-vinyl** is shown in Figure 1a. The **POSS-Cl** was used as starting material in the reaction with the 1-methylimidazole to produce the desired imidazolium functionalized silsesquioxane (**POSS-Imi**, Scheme 1). Different parameters, in terms of amount of 1-methylimidazole and reaction time, were tested in order to improve the yield of the target product. After optimization of the reaction conditions, the **POSS-Imi** was obtained in relatively high yield (85 %) *via* an easy purification from the unreacted precursors by precipitation and washing.

The imidazolium based organocatalyst was exhaustively characterized by ^{1}H-NMR, ^{13}C-NMR, ^{29}Si-MAS-CP-NMR and FT-IR spectroscopy (Figures S4 to S6). The degree of functionalization was proved by combustion chemical analysis, which revealed a high but not total degree of functionalization with a percentage of nitrogen corresponding to an average value of 7.2 imidazolium units per silsesquioxane nanocage and an amount of imidazolium unit of 39 wt%. In the ^{13}C NMR of the **POSS-Imi** a small signal at 43 ppm, corresponding to the unreacted chloropropyl branches can be also observed. The synthesis was repeated four times with highly reproducible results (%N = 9.15-9.35). Interestingly, solid state ^{29}Si-MAS-NMR (Figure 1c) performed on the **POSS-Imi** displayed two different bands, the most intense located at -70 ppm can be attributed to the T3 silicon units (compare Figures 1b and 1c) while the second at -60 ppm could be a consequence of a partial opening of the silsesquioxane nanocage via corner cleavage. Liquid state ^{29}Si NMR (Figure 1d) exhibited an even more complex pattern with the presence of one additional contribution (at -50 ppm) of minor but still appreciable relevance. The difference between solid and liquid state ^{29}Si NMR can be attributed to the better signal to noise ratio usually obtained in liquid state nuclear magnetic resonance experiments. Surprisingly, the liquid state spectrum of **POSS-Imi** still displayed the broad bands typical of the solid state patterns indicating that the broadening of the signals can not be completely attributed to the effect of chemical shift anisotropy or heteronuclear dipolar coupling. The presence of these large bands could be the consequence of various contributions due to silicon units with similar chemical environment. In order to understand the origin of these additional contributions an in-depth study on the stability and reactivity of the silsesquioxane nanocage through liquid state ^{29}Si NMR spectroscopy was performed.

All the experiments described below were carried out in a NMR tube and repeated twice.

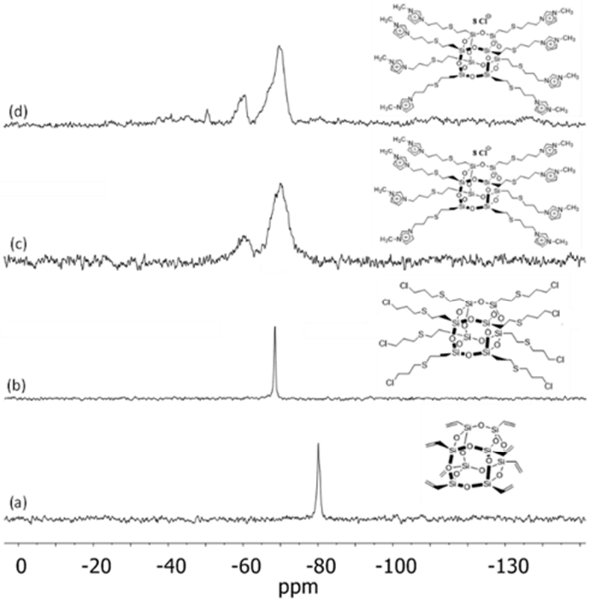


Fig. 1 Liquid state ^{29}Si NMR spectra of the **POSS-vinyl** in deuterated toluene (a), **POSS-Cl** in deuterated toluene (b), **POSS-Imi** in deuterated water (d) and solid state ^{29}Si MAS NMR of the **POSS-Imi** (c)

Control experiments in a round-bottom flask and under magnetic stirring were performed as well, and the NMR spectra, recorded for comparison at the final time (48 h), displayed similar results. Since the synthesis of the imidazolium derivative was performed in toluene, the stability of the **POSS-Cl** was tested by dissolving the solid in deuterated toluene in a NMR tube at 90°C and by following the evolution of the ^{29}Si NMR spectrum **in time**. A special NMR tube (see experimental) was used in order to avoid solvent evaporation. The final ^{29}Si NMR (Figure S10b) recorded after 48 h, did not show substantial differences proving that the selected silsesquioxane was stable under the reaction conditions. In order to simulate the possible influence of moisture a small amount of water (10 µL) was also added. The NMR spectrum is shown in Figure S10c. These experiments allow excluding the eventual partial decomposition of the **POSS-Cl** as consequence of the solvent and/or of the temperature. The presence of the additional bands in the ^{29}Si NMR of the **POSS-Imi** could be hence attributed to the reaction with the imidazole unit or to the presence of the imidazolium chloride salt. To exclude the possible interaction of imidazole and/or imidazolium with the silsesquioxane nanocage and remove any possible interference coming from other reactive groups, a silsesquioxane similar to **POSS-Cl** but bearing a terminal methyl group (**POSS-Me**) was synthesized (Figure 2). The ^{29}Si NMR of the fresh catalyst is reported in Figure 2 while the ^{1}H and ^{13}C NMR as well as the IR spectra were included in the supporting information material (Figure S7 to S9). The **POSS-Me** was reacted in presence of 1-Me-imidazole or 1-butyl-3-methylimidazolium chloride under the reaction conditions previously selected for the **POSS-Cl**. The final spectra after 48h displayed in both cases only one signal corresponding to the T^3 units (Figure S11).

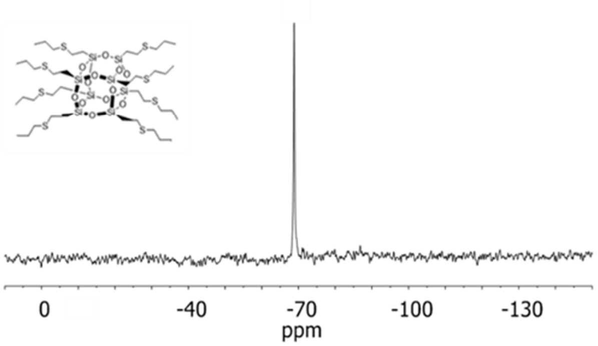
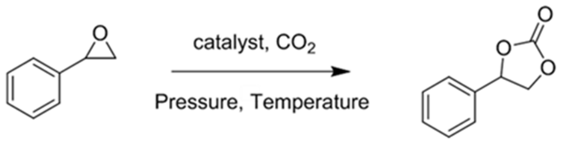


Fig. 2 ^{29}Si NMR spectrum of the **POSS-Me**

These experiments evidenced the absence of any detrimental effect of the reaction conditions as well as of the presence of the imidazolium chloride on the stability of the POSS nanocage. From the analysis of these data, the presence of the additional signals can not be clearly attributed to possible T^2, T^1 silicon units generated as consequence of the partial opening of silsesquioxane structure. The additional bands may be tentatively ascribed to the sensitivity of the ^{29}Si NMR chemical shift to the T-O-T angle. A total condensed and octa-functionalized silsesquioxane possesses a highly symmetric structure, which explains that the ^{29}Si NMR consists of a sole peak. On the other side, in hepta-functionalized nanocages the silicon atoms could not be chemically equivalent despite the similarity of the functional groups.[37] In the literature, difference in chemical shift of 10 ppm can be found only for POSS with T_8R_7R' structures where the R and R' have a very different nature (e.g. R = isobutyl and R' = vinyl [48]; R=cyclopentyl and R'= H [49]). In the present case the **POSS-Imi** is mainly a hepta-substituted silsesquioxane with similar R and R' functionalities, however the ionic nature and the aromatic character of the imidazolium moieties should not be underestimated. The interaction between the imidazolium functionalities could cause important distortions in the partially functionalized silica nanocage, which may display different O-Si-C angles. The polyhedral oligomeric silsesquioxane with its small silica unit surrounded by imidazolium peripheries represents a promising catalyst for the conversion of CO_2 and epoxides into cyclic carbonates. The broadly accepted reaction mechanism for this reaction is reported elsewhere. [50, 51] The presence of the functionalized nanocage could create an increased local concentration of catalytic active species where the CO_2 migrates preferentially due to the affinity and high solubility of this small molecule in imidazolium ionic liquids phases. Since the opening of the three membered ring is catalyzed by the imidazolium counterion, the close proximity of the CO_2 is expected to bring improved carbonate yield.[11]

In order to test the catalytic performances of the **POSS-Imi**, styrene oxide was selected as target starting material as well as solvent for the reaction. All the catalytic tests were performed in presence of a small amount of co-solvent (1.5 mL per 24 mL of styrene oxide) in order to favor a homogeneous dispersion of the **POSS-Imi** in the reaction mixture. In absence of an appropriate co-solvent the **POSS-Imi** macromolecules tend to assembly forming large visible aggregates probably as consequence of the inter-molecular interaction between the imidazolium moieties. Different parameters including the nature of the solvent, pressure and relative amount of catalyst were studied.

Table 1 Catalytic tests performed with **POSS-Imi** with different working pressures.[a]



Entry	Pressure (bar)	Temperature (°C)	Conversion (%)	TON
1	20	125	24	70
2	30	125	35	102
3	40	125	49	143
4	60	125	44	128
5	80	125	37	108
6	40	150	92	268

[a] Reaction conditions: 220 mg (0.10 mmol) of **POSS-Imi** (which corresponds to 0.72 mmol of Imi active sites), 24 mL (210 mmol) styrene oxide, 3 h and 1.5 mL of H_2O.

Due to the absence of additional co-catalysts with Lewis acid properties the selected range of studied temperature was maintained between **100°C and 150°C** (with the more reactive epoxides). It is known[21, 22] that without “co-activation”, good conversions at temperatures lower than 100 °C are difficult to achieve. In a first attempt, the reaction of CO_2 with styrene oxide was conducted at the fixed temperature of 125°C and in presence of water as co-solvent. The effect of different working pressures was studied and the results are summarized in Table 1 (entries 1-5). At low pressures (Table 1, entries 1 and 2) a relatively low epoxide conversion was obtained with a corresponding TON (calculated as *moles converted/moles of imidazolium active sites*) of 70 and 102. An increase in the working pressure to 40 bar led to enhanced conversion (Table 1, entry 3) while a further increase resulted in a slight reduction of the catalyst performance with a clear drop of the catalytic activity (Table 1, entry 5) under supercritical conditions. A similar trend was previously observed, in particular when heterogeneous catalysts with a multilayered ionic liquid like phase were used.[26] As expected, the increase of the temperature at 150 °C while keeping constant the pressure at 40 bar (Table 1, entry 6) caused a substantial improvement in the conversion (92%) with a corresponding TON of 268. The influence of the catalyst amount was also evaluated (Table 2). It was observed that the decrease of the catalyst amount to 110 mg did not strongly affected the performances of the **POSS-Imi** (Table 2, entries 1 and 2) suggesting that, at higher silsesquioxane concentration and despite the presence of co-solvent, small aggregates probably non completely accessible are still present in the reaction mixture.

Table 2 Catalytic tests performed with **POSS-Imi** varying the catalyst amount.[a]

Entry	Catalyst (mg)	Catalyst (mmol)	Active sites (mmol)	Conversion (%)	TON
1	220	0.100	0.72	92	268
2	110	0.050	0.36	71	414
3	55	0.025	0.18	47	548

[a] Reaction conditions: 40 bar, 150°C, 24 mL (210 mmol) styrene oxide, 3 h and 1.5 mL of H_2O.

A further decrease to 55 mg (Table 2 entry 3) **caused a substantial decrease in the epoxide conversion** indicating that a good balance between catalyst loading and dispersion was already obtained in the previous essay.

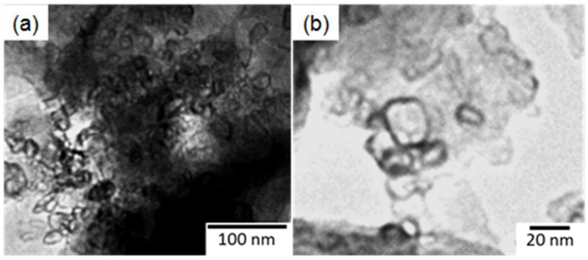


Fig. 3. TEM images of **POSS-Imi**

Transmission electron microscopy (TEM) investigation on the silsesquioxane based solid was performed as well. An aqueous solution of catalyst, with the same concentration of **POSS-Imi** used in the CO_2 conversion, was stirred for 1h and analyzed by TEM. The analysis of the sample revealed the presence of nano-organizations with distorted spherical shape (Figure 3). These irregular organizations **may explain the trend observed in table 2 thus confirming the previous hypothesis based on the formation of nanometric aggregates even if a possible role of the solvent evaporation can not be completely excluded.**

It should be noticed that in the previous analysis of catalyst performances, the selectivity through the synthesis of cyclic carbonates was not considered. The choice of water as co-solvent was dictated **by the objective to maintain a higher sustainability of the catalytic process**, moreover its use as efficient medium for the synthesis of cyclic carbonate was already reported.[52] Some of the most used co-solvents for the target reaction (eg: acetonitrile, dichloromethane, dioxane)[11, 12] are not recommendable from an environmental point of view.[53] However, the use of water as co-solvent, caused a lowering of the selectivity due to the formation of styrene glycol as main by-product. Separation of the products from the reaction mixture allowed the isolation and complete characterization of the by-product (figures S12 and S13). A blank test performed in absence of catalyst and with the corresponding amount of water produces styrene glycol as the sole product.

In order to improve the selectivity, the best conditions in terms of epoxide conversion where selected and the effect of different co-solvents (always considering their environmental impact) was studied.

A first screening of different polar solvents allows identifying the alcohols as the most suitable class of solvents. The evolution of TON and selectivity in function of methanol (MeOH), ethanol (EtOH) and isopropanol (^{i}PrOH) are shown in Table 3 (entries 1-4). The reactions performed in both EtOH and ^{i}PrOH displayed improved conversions with respect to the analogous test conducted in presence of water while similar results were obtained in MeOH (compare entries 1 to 4 in Table 3). An increased selectivity was observed with all the alcohols. The best co-solvent was clearly represented by the ^{i}PrOH, which exhibited an almost total conversion (94%) and complete selectivity. It is worth to underline the exceptionally high TON obtained under this reaction conditions (entry 4

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Table 3 Catalytic tests performed with different co-solvents.[a]

Entry	Catalyst	Co-solvent	Conversion (%)	Carbonate yield (%)	Selectivity (%)	TON
1	**POSS-Imi**	H_2O	71	51	72	410
2	**POSS-Imi**	MeOH	73	69	95	429
3	**POSS-Imi**	EtOH	85	81	95	499
4	**POSS-Imi**	^{i}PrOH	94	94	>99	553
5[b]	**BMim**	^{i}PrOH	98	98	>99	326
6	**POSS-Imi**	EtOH(abs)	84	84	>99	490

[a] Reaction conditions: 110 mg of catalyst (which corresponds to 0.36 mmol of imidazolium active sites in **POSS-Imi**), 40 bar, 150°C, 24 mL (210 mmol) styrene oxide, 3 h and 1.5 mL of solvent were used in all tests. [b] **BMim**, 0.63 mmol

The increased conversions in the series ^{i}PrOH>EtOH>MeOH≈H_2O can be related to the higher solvation of the chloride ions in water with respect to alcohols, especially ^{i}PrOH, that cause a decreased nucleophilicity. On the other hand, the lower reactivity of the chloride ions in water led to a lower selectivity because of the higher nucleophilicity of water. When the amount of water was decreased (entries 2-4) the selectivity was higher.

In order to highlight the importance of the silsesquioxane nanocage, an analogous catalytic test performed using the commercially available 1-butyl-3-methylimidazolium chloride (**BMIm**) in presence of isopropanol was performed as well. In order to allow a meaningful comparison and avoid the possible differences linked to the dispersion of the catalysts in the reaction mixture, the experiments were performed maintaining constant the amount of catalyst and comparing the results in terms of TON. The lower TON obtained in presence of **BMIm** (Table 3, entries 5) allows evidencing the positive role of the silsesquioxane. As previously described, the enhanced activity was ascribed to the proximity effect generated by the increased local concentration of imidazolium species surrounding the inorganic silsesquioxane core.

In an attempt to completely clarify the role of water in the formation of the by-product, absolute ethanol was also employed for the catalytic tests (Table 3, entry 6).

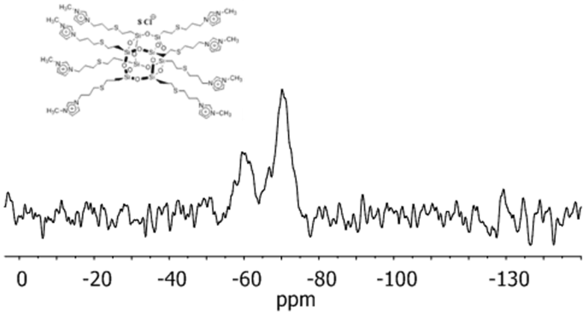

Fig. 4 ^{29}Si MAS-NMR spectrum of the **POSS-Imi after its use in catalysis.**

This test allows proving that an exceptional selectivity (> 99%) can be achieved in absence of water (compare entries 3 and 6 in table 3). The high selectivity represented an advantage not only from the point of view of the catalytic performances, but also because in absence of by-products the recovery of the catalyst after reaction was also accomplished by simple extraction of the reaction mixture. The ^{29}Si NMR spectrum of the recovered **POSS-Imi** catalyst is shown in Figure 4.

As can be clearly seen no major differences can be observed from the comparison of the ^{29}Si NMR before and after reaction proving that the **POSS-Imi** was stable under the reaction conditions.

From all these results emerged that **POSS-Imi** is a very promising catalyst, especially if we take into account that chloride is present as nucleophile and no additional expensive activating agents (e. g. Lewis acids) were added to the reaction mixture. In order to study the versatility of the catalyst, two aliphatic epoxides were also investigated and the results are collected in Table 4. Good conversion and selectivity were obtained in presence of 1-butene oxide (entry 2). With the more reactive epichlorohydrin a total conversion was obtained after 1h at 150 °C (entry 3). The decrease of the temperature at 125°C did not show substantial differences (compare entries 3 and 4) and an excellent conversion was also achieved at the challenging temperature of 100 °C (Table 4, entry 5). A further comparison with **BMim** at the temperature of 100 °C while keeping constant the amount of catalyst was performed as well (Table 4, entry 6). The lower TON obtained with unsupported imidazolium salt allows further highlighting the positive effect of the inorganic core.

Experimental

Materials and methods

1-Methylimidazole, 3-chloropropanethiol, propanethiol, 2,2’azobisisobutyronitrile (AIBN), POSS-octavinyl, anhydrous toluene, styrene oxide (SO), anhydrous ethanol and isopropanol (^{i}PrOH) were purchased from Sigma Aldrich. Toluene, hexane, diethyl ether, methanol (MeOH), ethanol (EtOH), and dichloromethane (DCM) were purchased from Fisher and used without further purification. All of the liquid-state NMR experiments were conducted using 5 mm NMR tubes. When indicated, a J. Young valve tube was used to prevent solvent evaporation. ^{1}H NMR and ^{13}C NMR spectra were performed on a JEOL ECX-400 MHz spectrometer operating at 9.4 T (399.9 MHz for ^{1}H and 100.5 MHz for ^{13}C).

Table 4 Catalytic tests performed with different substrates.[a]

Entry	Catalyst	Epoxide	Temperature (°C)	Reaction time (h)	Conversion (%)	Selectivity (%)	TON
1	**POSS-Imi**	Styrene oxide	150	3	88	>99	513
2	**POSS-Imi**	1-butene oxide	150	3	60	>99	416
3	**POSS-Imi**	Epychlorohydrin	150	1	>95	>99	722
4	**POSS-Imi**	Epychlorohydrin	125	1	93	>99	706
5	**POSS-Imi**	Epychlorohydrin	100	3	63	>99	479
6[b]	**Bmim**	Epychlorohydrin	100	3	79	>99	342

[a]Reaction conditions: Imi active sites catalyst to epoxide molar ratio = 0.15%, 40 bar, 1.5 mL of absolute ethanol were used in all tests. [b] Imi active sites catalyst to epoxide molar ratio = 0.23%

Their chemical shifts were referenced to the ^{1}H residual signals and ^{13}C signals of the deuterated solvents. ^{29}Si NMR spectra were recorded on a Bruker Avance-500 spectrometer operating at 11.7 T (99.3 MHz for ^{29}Si). Liquid-state experiments were conducted at 298 K using a Bruker broadband probe, while solid-state MAS experiments were recorded at room temperature, using a 3.2 mm Chemagnetics probe and a spinning frequency of 8 kHz. IR absorption spectra were obtained with a Perkin-Elmer Spectrum II. Combustion chemical analysis (C, H, N, S) were performed on a Thermo Finnigan Flash-45 EA 1112 apparatus. Melting points were performed on a Büchi Melting Point B-545. Transmission electron microscopy images were taken with a PHILIPS TECNAI 10 at 80 eV.

Synthetic procedures

General procedure for synthesis of propyl-thio-ethyl-octasilsesquioxane (POSS-Me): POSS-octavinyl (300 mg, 0.47 mmol) was dissolved in anhydrous toluene (1.6 mL) under N_2 atmosphere. The radical initiator AIBN (30 mg, 0.18 mmol) was added to POSS-octavinyl solution and the reaction mixture was heated to 40 °C. Then the linker 1-propanethiol (380 µl, 4.19 mmol, 8.2 eq.) was slowly added to the mixture and the reaction was stirred for 17 h at 60 °C. After cooling the reaction at room temperature, the gel was dried under reduced pressure to give the **POSS-Me**.

POSS-Me. Transparent viscous gel. Yield: 99 %. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 2.61 (t, 16H, J = 8.5 Hz); 2.51 (t, 16H, J = 7.3 Hz); 1.62 (m, 16H); 0.99-1.05 (br, 40H, J = 8.7 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm) = 34.2, 26.2, 23.1, 14.0, 13.4. MAS ^{29}Si-NMR (99 MHz) δ (ppm) = - 68.

General procedure for synthesis of chloropropyl-thio-ethyl-octasilsesquioxane (POSS-Cl): POSS-octavinyl (1.0 g, 1.58 mmol) was dissolved in anhydrous toluene (5.5 mL) under N_2 atmosphere. The radical initiator AIBN (100 mg, 0.61 mmol) was added to POSS-octavinyl solution and the reaction mixture was heated to 40 °C. Then the linker 3-chloropropanethiol (1.32 mL, 13.55 mmol, 8.8 eq.) was slowly added to the mixture and the reaction was stirred for 13 h at 60 °C. After cooling the reaction at room temperature, the supernatant was removed and the gel was solubilized in dichloromethane (2.5 mL) and precipitated with hexane (5 x 25 mL) at 0 °C. Finally, the gel was dried under reduced pressure to give the **POSS-Cl**.

POSS-Cl. Transparent viscous gel. Yield: 99 %. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 3.66 (t, 16H, J = 6.2 Hz); 2.68 (t, 16H, J = 8.7 Hz); 2.63 (t, 16H, J = 8.7 Hz); 2.04 (m, 16H); 1.04 (t, 16H, J = 8.7 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm) = 43.8, 32.4, 29.1, 26.3, 13.2. MAS ^{29}Si-NMR (99 MHz) δ (ppm) = - 68. Elemental analysis (%) for $C_{40}H_{80}Cl_8O_{12}S_8Si_8$; found: C = 32.09, H = 5.28, S = 16.27; calculated: C = 31.65, H = 5.31 S = 16.90.

General procedure for synthesis of POSS imidazolium chloride (POSS-Imi): **POSS-Cl** (1.30 g, 0.861 mmol) was dissolved in anhydrous toluene (16 mL) under N_2 atmosphere and 1-methyl-imidazole (3.294 mL, 41.32 mmol, 48 equiv.) was slowly added to the **POSS-Cl** solution. The reaction was stirred for 48 h at 90 °C resulting in the precipitation of a brown solid. Then, the reaction mixture was cooled down and the supernatant removed. The solid was dissolved in methanol (2 mL) and was precipitated with hexane (3 x 20 mL) and diethyl ether (3 x 20 mL) using a centrifuge (20 °C, 4500 rpm, 5 min). The purified solid was dried under reduced pressure and with vacuum pump. Finally it was lyophilized overnight by dissolving it in milliQ water (2 mL) to give the **POSS-Imi**.

POSS-Imi. Brown viscous solid. Yield: 85%. ^{1}H-NMR (500 MHz, D_2O) : δ (ppm) = 7.37 (d, 8H, J = 2.0 Hz); 7.31 (d, 8H, J = 2.0 Hz); 4.18 (t, 16H, J = 6.9 Hz); 3.75 (s, 24H); 2.54 (t, 16H, J = 8.9 Hz); 2.44 (t, 16H, J = 7.0 Hz); 2.03 (m, 16H); 0.86 (t, 16H, J = 7.0 Hz). ^{13}C-NMR (125 MHz, D_2O) δ (ppm) = 135.7, 123.4, 121.8, 47.9, 35.4, 28.4, 26.5, 25.2, 12.6. MAS ^{29}Si-NMR (99 MHz) δ (ppm) = - 60.7, -70.3. Elemental analysis (%) for $C_{72}H_{128}Cl_8N_{16}O_{12}S_8Si_8$; found: N = 9.33, C =

37.02, H = 6.22, S = 10.06; calculated: N = 10.31, C = 39.77, H = 5.93, S = 11.79.

General procedure for Extraction of the styrene glycol: After the catalytic test, the reaction mixture was dissolved in water (3 x 40 mL) and was placed in an ultrasound bath for 5 min resulting in the precipitation of the cyclic styrene carbonate. The aqueous phase was extracted and dried under reduced pressure. The resulting residue was dissolved in methanol (2 mL) and was precipitated with toluene (3 x 20 mL) using a centrifuge (20 °C, 4500 rpm, 5 min). The purified solid was dried under reduced pressure to give the styrene glycol.

Styrene glycol. White powder. ^{1}H-NMR (400 MHz, DMSO-d$_6$) δ (ppm) = 7.24-7.39 (m, 5H), 5.27 (s, 1H), 4.77 (s, 1H), 4.58 (t, 1H, J = 6.0 Hz), 3.46 (d, 2H, J = 6.0 Hz). ^{13}C-NMR (100 MHz, DMSO-d$_6$) δ (ppm) = 144.2, 128.6, 127.7, 127.1, 74.6, 68.3. Elemental analysis (%) for $C_8H_{10}O_2$; found: C = 69.55, H = 7.18; calculated: C = 69.55, H = 7.30. **Melting Point:** found (°C): 63; theorical (°C): 67.5.

General procedure for synthesis of cyclic carbonates: All the catalytic tests were performed in a *Cambridge Design* 25 *Bullfrog* batch reactor with individual temperature control and mechanical stirring, designed to operate at high temperature and pressures in the presence of different protic polar solvents (H_2O, MeOH, EtOH and ^{i}PrOH). In brief, the catalyst (110 mg, 0.05 mmol) dissolved in protic polar solvent (1.50 mL) was added to the epoxide (0.2 mol) into the reactor vessel and connected to the heating block. The reaction mixture was mechanically stirred at 500 rpm and the system was purged with N_2 for 5 min before to filling the reactor with CO_2 until the required pressure was reached (ranged between 20 and 80 bar). The temperature was raised stepwise from room temperature to 125 or 150 °C. Once reached the desired temperature, the reaction was allowed to proceed during 3 h. After that, the temperature was fixed at 0 °C, the heating block was removed and the reactor was cooled down until the temperature of 28 °C was reached. The depressurization of the reactor was carried out slowly and the reaction mixture was recovered in a flask and analyzed by ^{1}H NMR. Conversion and selectivity were calculated via ^{1}H NMR.

Conclusions

The synthesis of imidazolium functionalized polyhedral oligomeric silsesquioxanes was successfully achieved. The **POSS-Imi** nanostructure was extensively characterized in particular *via* ^{29}Si NMR spectroscopy and used as catalyst for the chemical fixation of carbon dioxide onto epoxides to give the corresponding cyclic carbonates. Different reaction conditions in terms of working pressure, temperature, amount of catalyst and nature of co-solvent were investigated. No additional co-catalyst with Lewis acid properties was added to the reaction mixture. The **POSS-Imi** displayed excellent catalytic performances in the synthesis of styrene carbonate. Under the best reactions conditions, using isopropanol as co-solvent, an almost total conversion and complete selectivity was obtained. Moreover the catalyst was recovered by simple extraction from the reaction mixture. The **POSS-Imi** displayed excellent performances also in presence of aliphatic epoxides. With the more reactive epichlorohydrin a remarkable TON of 476 was achieved at the challenging temperature of 100°C. Comparison with unsupported 1-butyl-3-methylimidazolium chloride allows highlighting the positive effect of the silsesquioxane core on the catalytic activity.

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