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**Imidazolium-based heterogeneous catalysts for the conversion of CO₂ into cyclic carbonates
from in-depth understanding of a synergistic activation to enhanced performances**

COMES, ADRIEN

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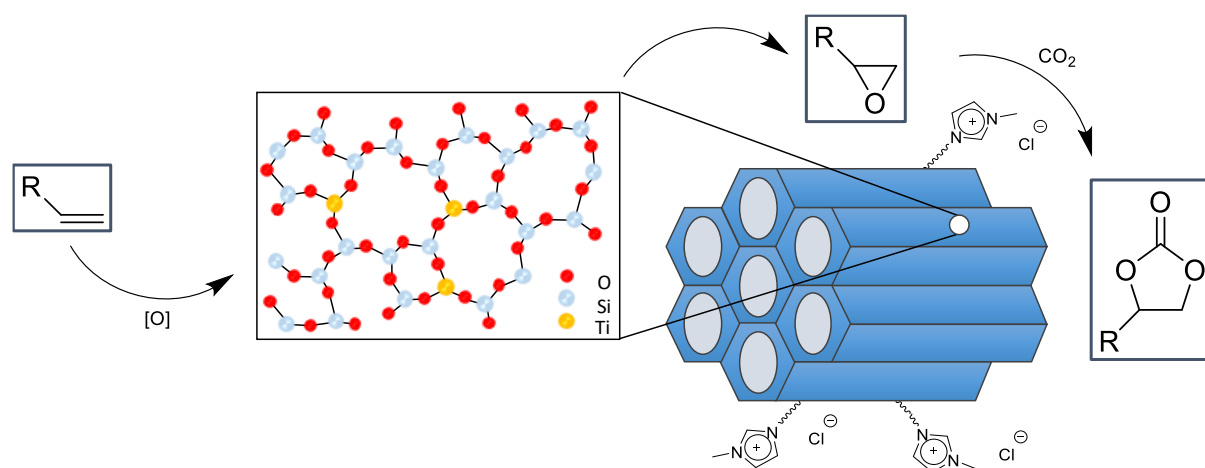
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Chapter III

Imidazolium-based titanosilicate nanospheres as active catalysts in carbon dioxide conversion: towards a cascade reaction from alkenes to cyclic carbonates



Abstract

Porous silica-based nanospheres bearing titanium centres as single site were successfully synthesized employing a time- and energy-efficient procedure. The influence of the post-synthesis treatment on the insertion of Ti was investigated via DR UV-Vis and XPS spectroscopy and the titanium content was quantified through ICP-OES analysis. The textural and structural properties of the different solids were evaluated via XRD, TEM and N₂ physisorption. The resulting materials were thereafter covalently functionalized with imidazolium chloride, followed by characterization via ²⁹Si and ¹³C solid-state NMR, N₂ physisorption and combustion chemical analysis. The bi-functional catalysts were tested in the challenging conversion of CO₂ with cyclohexene oxide to the corresponding cyclic carbonate as well as with various other epoxides with excellent results. The insertion of Ti as single site played a key role substantially improving the activity of the solids. The most active bi-functional material was successfully recovered and reused through multiple cycle without loss of the catalytic activity. Moreover, the cyclohexene epoxidation reaction, was tested as well employing the mono-functionalized Ti-based material. The catalytic mixture, composed by the mono-functional and bi-functional solids, was efficiently used to convert the cyclohexene into cyclohexene oxide and subsequently the cyclohexene oxide into the corresponding carbonate thus opening the prospect for a cascade reaction

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Introduction

In the previous chapters, the insertion of Sn and Zn as single site in the silica structure to induce a Lewis acid character to the solids was explored. These silica-based solids were post-functionalized with imidazolium salts and demonstrated an increased activity compared to the metal-free materials.

Herein, the attention was focused on one of the most studied transition metals: titanium. Due to their Lewis acid properties, Ti-based silicates are employed in a plethora of reactions [226, 227] including alkenes epoxidations,[40, 228-235] epoxide isomerization to aldehyde,[236] glycerol acetalization [237] or sugar isomerization.[238] Among the titanosilicate, the TS-1 is largely employed at industrial scale for the epoxidation of alkenes but it suffers from pore size limitation,[235, 239] while Ti-MCM,[228-230] Ti-SBA [40, 231, 232] or Ti-TUD, have larger pores that allow working with bulkier alkenes.

Herein, we report a fast and energy saving approach for the synthesis of porous titanosilicate nanospheres requiring only 1 h reaction time without additional hydrothermal treatment under static conditions. The post-synthesis treatment for removal of the template was also evaluated. The solids were decorated with imidazolium salts in order to generate a bi-functional heterogeneous catalyst able to efficiently promote the synthesis of cyclic carbonates via CO₂ conversion. Titanium is expected to be a better co-catalyst than the previously reported Sn- and Zn-based solids due to its higher affinity for the oxygen. The solids were extensively characterized via various techniques, including transmission electron microscopy (TEM), X-ray diffraction (XRD), N₂ physisorption, X-ray photoelectron spectroscopy (XPS), UV-Vis diffuse reflectance (DR UV-Vis), inductively coupled plasma optical emission spectroscopy (ICP-OES), ²⁹Si- and ¹³C-CP MAS NMR. Their catalytic performances were evaluated in the reaction between epoxides and CO₂ to form the corresponding cyclic carbonates. The materials revealed excellent catalytic performances displaying high turnover numbers and turnover frequencies even in the challenging synthesis of cyclohexene carbonate. Moreover, the unfunctionalized material was also active in the conversion of cyclohexene to cyclohexene oxide, thus proving the versatility of the synthesis approach.

Results and discussion

The synthesis of mesoporous titanosilicate nanospheres was accomplished via an optimized diluted protocol adapting a previously reported methodology.[16, 19] The material was

prepared using a co-synthesis strategy involving the hydrolysis and condensation of titanium and silicon alkoxides in basic medium and in the presence of cetyltrimethylammonium bromide (CTAB) as structure directing agent. It should be mentioned that the optimized procedure implies a short synthesis time (1 hour) and allows obtaining the porous solids without additional hydrothermal treatments under static conditions hence improving the sustainability of the whole procedure. After the synthesis, in order to ensure the removal of the surfactant and thus make the pores accessible, the solid was subjected to two different treatments: calcination or extraction in acidic ethanol.[240, 241] These two methods were selected to investigate the influence of the post-synthesis treatment on the insertion of titanium as single site. The two materials were respectively labelled as **Ti-SiO₂-C** (where C stands for calcined) and **Ti-SiO₂-E** (where E stands for extracted). The structural and textural properties of both materials were initially investigated through transmission electron microscopy (TEM) and X-Ray Diffraction (XRD). TEM analysis of the samples (Figure 1a and b) revealed that all the particles display an almost spherical shape with very small size (compared to standard MCM-41-like solids) and a narrow particle size distribution centred at 30 nm.

To the best of our knowledge this precise control of the size below 100 nm was never reported previously. The regular arrangement of the pores was assessed through low-angle XRD (Figure 1c). Both samples present a main contribution at c.a $2\theta = 2.1^\circ$ which can be assigned to a d_{100} diffraction.[16-18, 20] The broadness of the signal is not surprising and can be related to the small size of the particles and the consequent decrease of long-range order.[17, 19]

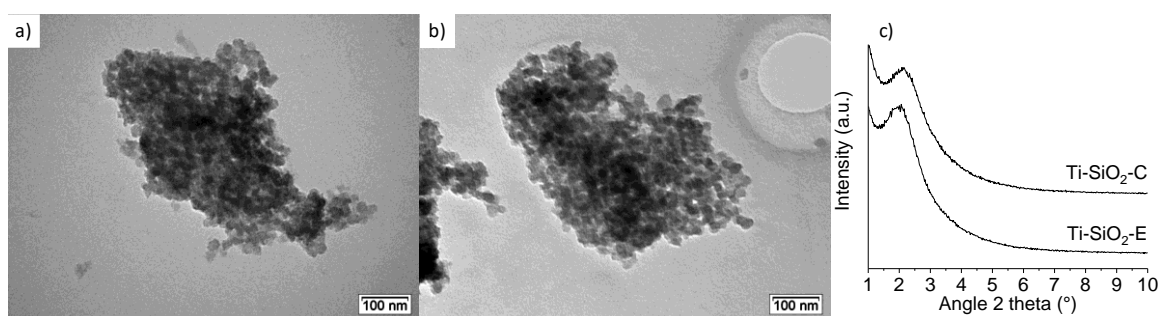


Figure 1: TEM pictures of Ti-SiO₂-E (a) and Ti-SiO₂-C (b) and the corresponding low-angle XRD (c).

Nitrogen physisorption analysis (isotherms presented in Figure 2) allows confirming the mesoporosity and the elevate surface area of the solids. Both **Ti-SiO₂-C** and **-E** display a high specific surface area of 1140 m²/g and 1198 m²/g, respectively. A deep investigation of the pore size distribution via both BJH (Figure 2) and DFT methods (Figure S1) showed the presence of a bimodal distribution. The first one, around 3.2 ± 0.2 nm as determined by DFT,[219] is characteristic of materials with small-mesopores like MCM-41. The second and

broader one, (centred at 13 nm) visible on the BJH pore size distribution, is the result of the reduced size of the particles and a consequence of the inter-granular space.[16, 17, 19] Combustion chemical analysis revealed that both extraction in HCl/EtOH and calcination procedures are efficient to ensure the complete removal of the templating agent. N₂ physisorption of the solid before calcination or extraction is presented in Supporting Information (Figure S2).

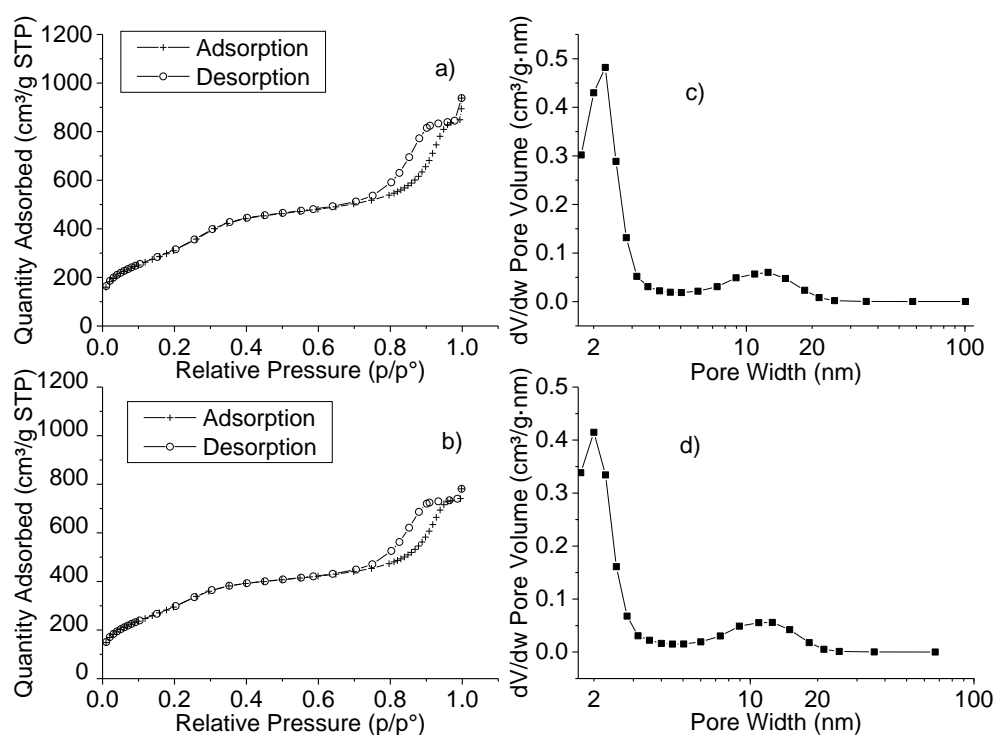


Figure 2: N₂ physisorption isotherms (left) and BJH pore size distribution (right) of Ti-SiO₂-E (a; c) and Ti-SiO₂-C (b; d). Pore size distribution are presented using a logarithmic scale.

The results discussed so far showed no relevant differences in textural and structural properties between the materials obtained via extraction or calcination procedure.

The amount of titanium in the materials was measured by ICP-OES analysis (Table 1, Entries 1-2) while its insertion as single site was assessed through both DR UV-Vis and XPS spectroscopies (Figure 3). ICP-OES analysis of the samples (Table 1, entries 1-2) allowed evidencing a first significant difference between the two solids. Ti-SiO₂-C displays a much higher titanium loading than the corresponding solid obtained via extraction.

DR UV-Vis analysis of titanosilicates are profusely described in literature. The different absorption bands are directly correlated to the isomorphic substitution of silicon with titanium in the SiO₂ architecture as well as to the formation of extra-framework domains. The bands between 215 and 230 nm are usually attributed to Ti species in a (distorted) tetrahedral environment, while a shift at higher wavelength (around 270 nm) is ascribed to

pentacoordinated surface species most probably in interaction with water molecules. A further shift towards the UV-A (290 nm) is associated to the formation of octahedral oligomeric chains and the contribution above 300 nm is attributed to TiO₂ domains. **Ti-SiO₂-E** displays a band centred at 230 nm corresponding to the expected tetrahedral environment.[229] The larger peak observed for **Ti-SiO₂-C** (ranging from 230 and 290 nm) suggests the presence of a combination of different Ti-based species, most probably as tetra-, penta- and hexa-coordinated sites.[26] From these results, it clearly emerged that the calcination used to remove the template has a detrimental effect on the insertion of Ti as single site. This behaviour could be ascribed to a migration (favoured by the high temperature) of the Ti species on the external surface with the consequent formation of a mixture of different extra-framework structures. It is possible that the small size of the particle contributes to the efficiency of the migration. In order to understand if the process could be at least partially reversible, the **Ti-SiO₂-C** solid was submitted to the same acid extraction applied to **Ti-SiO₂-E**. The resulting materials which underwent both calcination and extraction treatments was named **Ti-SiO₂-CE**. The full characterization of the solid can be found in Supporting Information (Figures S3). The UV-Vis spectrum is shown in Figure 3. As can be seen, the sample **Ti-SiO₂-CE** exhibits two more defined maxima (compared to **Ti-SiO₂-C**) at 230 nm and 300 nm. Moreover, the band at higher wavelength is less pronounced suggesting a partial conversion of the pentahedral or isolated octahedral species in tetrahedral sites.[40, 242-244] However, this modification of the UV-Vis pattern, could be also associated to a leaching of oligomeric surface titanium oxide chains in the acidic solution. In order to support or exclude this hypothesis, ICP-OES analysis of the **Ti-SiO₂-CE** solid was performed as well. The ICP-OES data (Table 1, Entry 3) showed a decrease in the amount of Ti corresponding to c.a. 25% of the initial value (determined for **Ti-SiO₂-C**) thus indicating a possible leaching in solution. These experiments were performed in duplicate with highly reproducible results, thus proving the robustness of the whole process of synthesis and templating agent removal.

The conclusions derived from the analysis of the DR UV-Vis spectra were supported by XPS analysis (Figure 3). The 2p core level XPS spectra on Figure 3 displays the typical doublets in the region between 455 and 470 eV (with a separation of 5.75 eV) which are assigned respectively to Ti_{2p3/2} and Ti_{2p1/2} components originating from the spin-orbit splitting effect contributions. It is known that TiO₂ in octahedral coordination displays a doublet in which the most intense contribution is located at 458.5 eV (Figure S4). As can be clearly seen in the Figure 3, the Ti_{2p3/2} contribution in **Ti-SiO₂-E** displays an evident shift (1.5 eV difference) at higher binding energy. According to literature, this shift can be attributed to a different

chemical environment of Ti that is mainly present in tetrahedral coordination.[245-247] The $Ti_{3/2}$ binding energy of **Ti-SiO₂-C** and **Ti-SiO₂-CE** present intermediate values between **Ti-SiO₂-E** and TiO_2 indicating that a combination of different Ti species is most probably present. These results are in agreement with the previous finding and allow confirming the detrimental effect of the calcination process on the insertion of Ti as single site in the silica network.

Table 1: Textural and structural properties of the synthesised titanosilicates

Entry	Material	BET Surface Area (m ² /g)	Pore Size (nm) ^[a]	Ti inserted (mg/g) ^[b]
1	Ti-SiO ₂ -C	1140	3.1	12.4
2	Ti-SiO ₂ -E	1198	3.3	7.7
3	Ti-SiO ₂ -CE	1204	3.0	8.8

[a] Determined by DFT method.

[b] Amount of Ti determined via ICP-OES and expressed in mg of Ti per gram of material

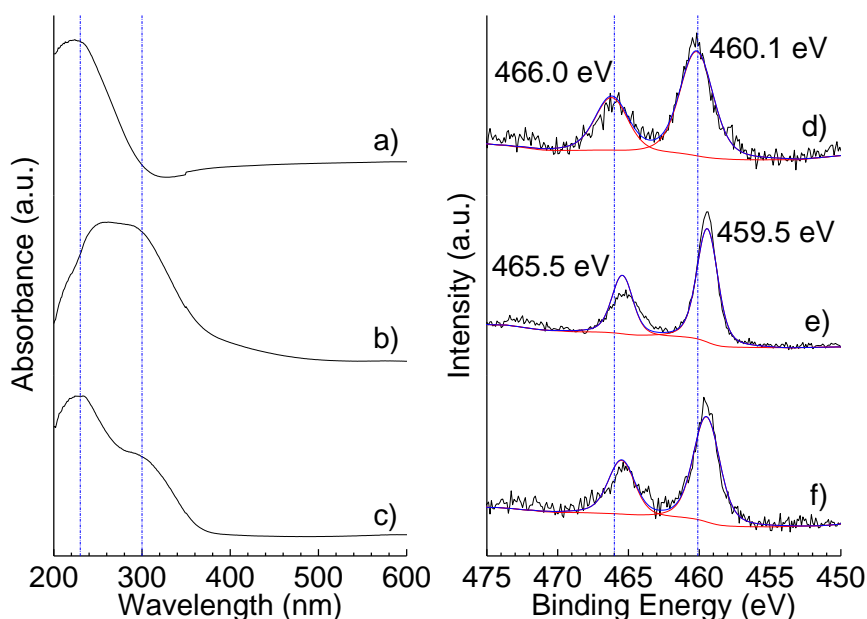


Figure 3: DR UV-Vis (left) and XPS (right) of Ti-SiO₂-E (a; d); Ti-SiO₂-C (b; e) and Ti-SiO₂-CE (c; f). Vertical guidelines in UV-Vis spectra are positioned at 230 nm and 300 nm. Vertical guidelines in XPS are centred on the peaks of Ti-SiO₂-E to underscore the shift of Ti-SiO₂-C and -CE.

From the previous characterization, **Ti-SiO₂-E** emerges as the most promising material for further functionalization. However, to go in depth in our analysis, all the Ti-based silicates were decorated with imidazolium moieties following a one-pot procedure previously described by us.[210] The presence of the organic moieties as well as the covalent nature of the

functionalization were addressed respectively via ^{13}C and ^{29}Si solid-state NMR. The two aromatic signals at 140 ppm and 125 ppm in the ^{13}C -CP-MAS-NMR spectra (Figure 4 left) are assigned to the imidazolium moiety.[210, 248] The four additional contributions in the aliphatic region can be attributed to the methyl group of the imidazolium moiety and to the propyl chain of the linker connecting the aromatic ring to the silica. ^{29}Si NMR spectra evidence the presence of two signals at -75 ppm and -60 ppm, which can be assigned to $-\text{CH}_2\text{-Si}(\text{OSi})_3$ (T^3) and $-\text{CH}_2\text{-Si}(\text{OSi})_2(\text{OH})$ (T^2) contributions respectively (Figure 4 right). These signals constitute the proof of the covalent nature of the organic functionalization. The broad band in the region comprised between -115 and -90 ppm can be deconvoluted into three different contributions at -112, -103 and -93 ppm corresponding respectively to $\text{Si}(\text{OSi})_4$ (Q^4), $\text{Si}(\text{OSi})_3\text{OH}$ (Q^3) and $\text{Si}(\text{OSi})_2(\text{OH})_2$ (Q^2) species. As expected, the materials submitted to the sole thermal treatment at 550 °C exhibit a higher degree of condensation of the silica network and, therefore, display a more relevant population of Q^4 species (See Figure S5 and Table S1).

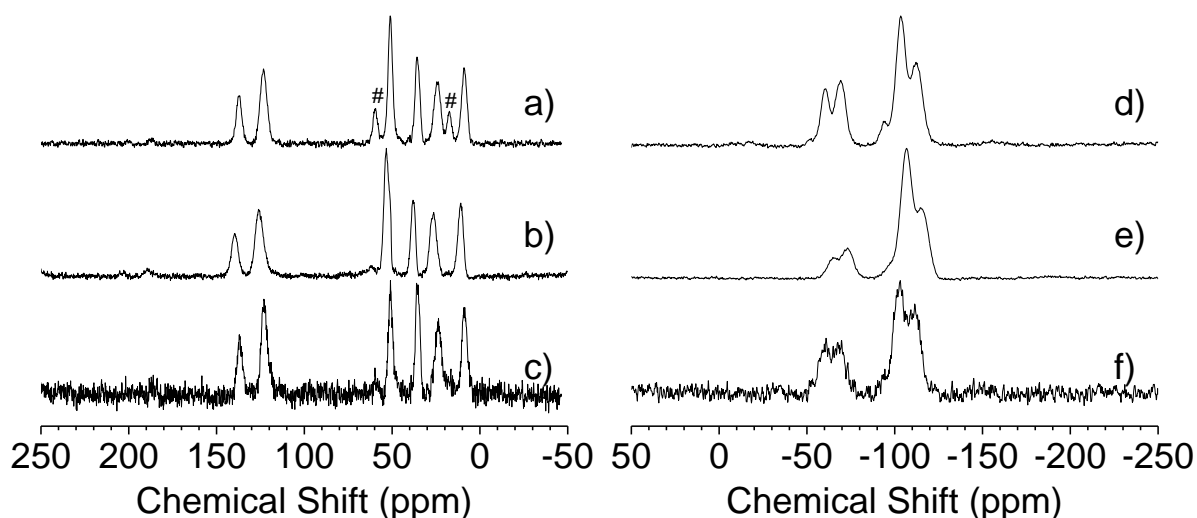


Figure 4: ^{13}C CP MAS NMR (left) and ^{29}Si CP MAS NMR (right) of $\text{Ti-SiO}_2\text{-E-imi}$ (a; d); $\text{Ti-SiO}_2\text{-C-imi}$ (b; e) and $\text{Ti-SiO}_2\text{-CE-imi}$ (c; f).

The textural properties of the imidazolium functionalized materials were determined using N_2 physisorption (Figure 5). As expected, the surface functionalization led to a decrease of the BET surface area. The materials treated by extraction (**Ti-SiO₂-E-imi** and **Ti-SiO₂-CE-imi**) exhibited similar specific surface area (Table 2), while the solid obtained via the sole calcination of the structure directing agent (**Ti-SiO₂-C-imi**) revealed a higher specific surface area. This result could be explained considering the higher amount of free Si-OH group at the surface of the extracted solids (as evidenced from the quantitative ^{29}Si NMR in Figure S5 and Table S1), which can be responsible for a more efficient anchoring of the siloxanes groups and

hence for a higher amount of imidazolium species. This hypothesis was confirmed by the quantification of the imidazolium moieties via combustion chemical analysis (Table 2).

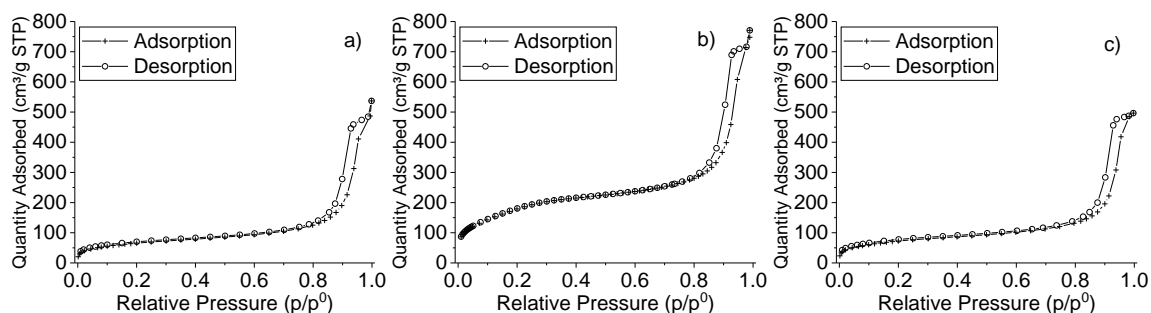


Figure 5: N_2 physisorption isotherms of Ti-SiO₂-E-imi (a); Ti-SiO₂-C-imi (b) and Ti-SiO₂-CE-imi (c).

Table 2: Textural and structural properties of the catalysts

Entry	Material	Amount of imidazolium (mmol/g) ^[a]	BET surface area (m ² /g)	Pore size distribution (nm) ^[b]
1	Ti-SiO ₂ -C-imi	1.04	669	2.7
2	Ti-SiO ₂ -E-imi	1.39	236	2.3
3	Ti-SiO ₂ -CE-imi	1.43	263	2.3

[a] Amount of imidazolium salt determined by combustion chemical analysis considering the nitrogen percentage.

[b] Determined by DFT method

All the prepared materials were tested as catalysts in the conversion of carbon dioxide into cyclic carbonates, selecting the challenging reaction between cyclohexene oxide (CHO) and CO₂ as target process. Due to different loading of Ti and imidazolium sites in each material and in order to allow a meaningful comparison between the catalysts, both conversion and turnover number (TON = moles converted / moles of imidazolium) were reported in Table 3 and Figure 6. Moreover, also turnover numbers calculated considering the Ti loading (TON_M = moles converted / moles of titanium) were included in the table. As can be clearly seen from the data reported in the Table 3, **Ti-SiO₂-E-imi** demonstrated better catalytic performance (entries 1-3) both in terms of conversion and TON and despite its lower specific surface area.[249] The difference in activity is even more pronounced if the TON are normalized through the BET surface area, as reported on the right part of Figure 6. This evidence highlights further the importance of the insertion of titanium as single site in the silica network.

Ti-SiO₂-E-imi revealed good activity also when tested over another challenging epoxide as styrene oxide (SO) (Entry 4). It is important to mention that the reaction was performed at a lower temperature (compared to standard tests usually employing 150 °C) and at a short reaction time (3h). A Ti-free material (Entry 5) was tested under the same condition exhibiting a conversion of 34 % and a TON of 94. It emphasizes once more the importance of the insertion of Ti in the structure. A test with the **Ti-SiO₂-E** is reported at Entry 6. No cyclic carbonate was detected using the ¹H-NMR and the monitoring of the pressure (Figure S6) revealed no consumption of the CO₂. These results evidence the imidazolium chloride is the main catalyst while the Ti is its co-catalyst. The activity of **Ti-SiO₂-E-imi** was also compared with literature data. For this purpose, it deserves to be mentioned that a direct comparison with reference catalysts is often hindered by the different reaction conditions in terms of pressure, temperature, reaction time, nature of the nucleophile and presence of solvents, among others. Moreover, many authors report the use of Lewis acid heterogeneous catalysts in presence of ammonium or imidazolium salts in homogeneous conditions. In Table 3, we compare our materials with other silica-based catalysts previously reported by us (hence tested exactly under the same reaction conditions) or some fully heterogeneous catalysts reported in literature. Importantly **Ti-SiO₂-E-imi** revealed improved catalytic performances in terms of TON compared to previously reported catalysts containing tin or zinc inserted as single sites in a mesoporous silica structure as Sn-SiO₂-imi [210] (compare entries 3 vs 7 and entries 4 vs 8) and Zn-SiO₂-imi [210] (compare entries 4 vs 9). More significantly, **Ti-SiO₂-E-imi** is more active than the multifunctional solid Sn-A-imi(II)-Cl [248] (compare entries 3-4 vs 10-11), which presents imidazolium chloride catalytic sites together with both Lewis acids sites and H-donor as co-catalysts. This demonstrates the important role of titanium as Lewis acid co-catalysts. Moreover, **Ti-SiO₂-E-imi** displayed higher TON and TOF than a MOF based system (Entry 12) functionalized with imidazolium moieties (hence fully heterogeneous). It should be noted that the catalyst reported in Entry 12 operates at slightly lower temperature (120 °C) and pressure (1 bar) but it presents a different nucleophile (iodide compared with chloride in our system). A similar strategy was employed by Liang et al., who reported the use of a bifunctional catalyst bearing Zn as Lewis acid and functionalized with imidazolium bromide (Entry 13). This last example displayed lower activity than our material despite the higher reaction temperature and the use of bromide as nucleophile.[183] The increased performance of the bifunctional MOF reported in Entry 14 can be attributed to the presence of the ammonium iodide as catalytically active specie together with the more elevated reaction temperature (140 °C compared with 125 °C in our case). As expected, Ti-SiO₂-E solid shows

better carbonate yield than some other highly performing catalysts presenting only imidazolium-based units and used in absence of co-catalytically active species (Entry 15).

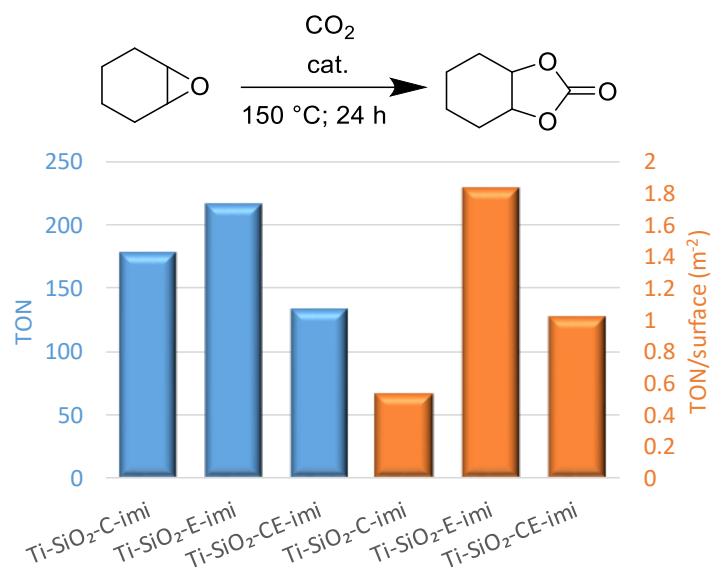


Figure 6: TON values (blue columns on the left) and TON values normalized by the specific surface area (orange columns on the right) in the catalytic conversion of CO₂ and cyclohexene oxide into the corresponding cyclic carbonate

Table 3: Catalytic tests of CO₂ fixation over cyclohexene oxide (CHO) and styrene oxide (SO).

Entry	Epoxide	Catalyst	Epoxide conversion (%)	Cyclic carbonate selectivity (%)	TON [a]	TOF [b]	TON _M [c]	TOF _M [b]
1 [d]	CHO	Ti-SiO ₂ -C-imi	39	> 95	178	7.4	1009	42
2 [d]	CHO	Ti-SiO ₂ -CE-imi	41	> 95	134	5.6	2260	94
3 [d]	CHO	Ti-SiO ₂ -E-imi	63	> 95	217	9.0	4685	195
4 [e]	SO	Ti-SiO ₂ -E-imi	42	> 95	127	42	938	313
5 [e]	SO	SiO ₂ -C-imi	34	> 95	94	31	-	-
6 [e]	SO	Ti-SiO ₂ -E	-	-	-	-	-	-
7 [d]	CHO	Sn-SiO ₂ -imi	26	> 95	90	3.8	532	22
8 [e]	SO	Sn-SiO ₂ -imi	32	> 95	96	32	826	275
9 [e]	SO	Zn-SiO ₂ -imi	32	> 95	98	33	1343	448

10 ^[d]	CHO	Sn-A-imi(II)-Cl	36	> 95	197	8.2	1341	56
11 ^[e]	SO	Sn-A-imi(II)-Cl	22	> 95	108	36	735	245
12 ^[f]	SO	(I-)Meim-UiO-66 [250]	46	71	63	2.6	n.d. ^[g]	n.d. ^[g]
13 ^[h]	SO	ZnTCPPc(Br-)Etim-UiO-66 [183]	53	n.d. ^[g]	56	4.0	n.d. ^[g]	n.d. ^[g]
14 ^[i]	SO	F-IRMOF-3-4d [154]	84	n.d. ^[g]	589	118	n.d. ^[g]	n.d. ^[g]
15 ^[j]	SO	bV-IMI-NT-2 [173]	22	> 95	103	34	-	-

[a] Turnover number (TON) calculated as moles of epoxide converted / moles of imidazolium sites. Amount of imidazolium salt quantified via combustion chemical analysis for each catalyst and based on %N.

[b] TOF and TOF_M (turn-over frequency) calculated respectively as TON and TON_M / reaction time.

[c] TON_M calculated as moles of epoxide converted / moles of metallic sites. Amount of Ti, Sn or Zn quantified via inductively coupled plasma optical emission spectroscopy (ICP-OES) for each catalyst

[d] Reaction conditions: Cyclohexene oxide CHO (24.0 mL; 237 mmol); mass of catalyst (500 mg); CO₂ initial pressure (25 bar); 150 °C; heating rate (1 °C/min); 24 h; 500 rpm.

[e] Reaction conditions: Styrene oxide SO (24.0 mL; 210 mmol); mass of catalyst (500 mg); CO₂ initial pressure (25 bar); 125 °C; heating rate (1 °C/min); 3 h; 500 rpm.

[f] Temperature (120 °C); CO₂ (1 bar); 24 h; TON calculated considering 46 % of conversion and 71 % of selectivity over 10 mmol of styrene oxide and 50 mg = 0.052 mmol of catalyst.[250]

[g] n.d. = not determined.

[h] Temperature (140 °C); CO₂ (constant 1 bar); 14 h; TON calculated considering 52.8 % of yield and 0.95 mol % imidazolium.[183]

[i] Temperature (140 °C); CO₂ (20 bar); 5 h; TON calculated considering 84 % of conversion and a total selectivity over 0.2 mol of styrene oxide and 0.17 g of catalyst with 21,3 wt% of iodine = 0.285 mmol.[154]

[j] Temperature (150 °C); CO₂ (40 bar); 3 h. [173]

The reusability of the **Ti-SiO₂-E-imi** catalyst was tested over several cycles in the presence of styrene oxide. The reaction conditions were selected in order to ensure a catalyst performance far enough from total conversion.[249] After each cycle, the material was washed with toluene and ethanol, dried and employed in a successive cycle without further activation. As can be seen in Figure 7, the activity of **Ti-SiO₂-E-imi** was preserved in consecutive runs, only a slight decrease was evidenced in the initial cycles followed by a stabilization (starting from the 3rd run).

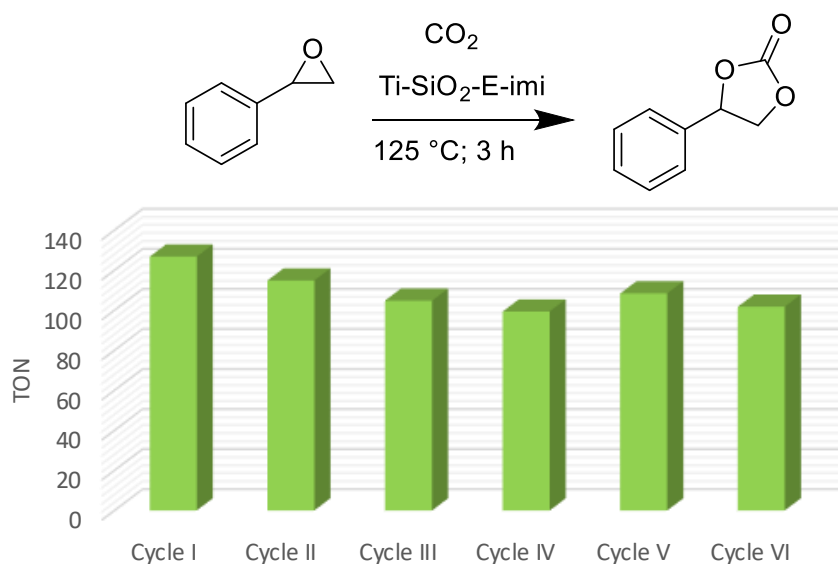


Figure 7: Recycling tests performed on **Ti-SiO₂-E-imi** over styrene oxide.

The wide applicability of the **Ti-SiO₂-E-imi** catalyst was evidenced by running the reaction in the presence of other epoxides (Table 4). An additional test over the 1,2-epoxybutane (Entry 2) was performed at 125 °C. This experiment further supports the ability of the Ti centre to activate the oxirane ring. As expected, lower temperatures can be used in presence of more reactive epoxides like epichlorohydrin (Entry 3) or glycidol (Entry 4). The use of glycidol allows decreasing the reaction temperature down to 50 °C (Entry 4). The same experiment was reproduced using a constant pressure of 5 bars (Entry 5) demonstrating only a minor influence of the CO₂ pressure on the conversion. It should be highlighted that the selectivity was always close to 100 % and no by-product was observed from ¹H NMR analysis of the reaction mixture.

The regular decrease of pressure in the reactor due to CO₂ consumption was monitored over the time (Figure 8).

Table 4: Conversion of various epoxides using Ti-SiO₂-E-imi

Entry	Substrate	Temperature (°C)	Time (h)	Conv. (%)	Sel. (%)
1	Styrene oxide	125	3	42	> 95
2	1,2-Epoxybutane	125	3	41	> 95
3	Epichlorohydrin	100	3	53	> 95
4	Glycidol	50	6	28	> 95
5 [a]	Glycidol	50	6	22	> 95

Reaction conditions: Substrate (24.0 mL); mass of catalyst (500 mg); CO₂ initial pressure (25 bar); heating rate (1 °C/min); 500 rpm.

[a] Constant pressure (5 ± 0.5 bar)

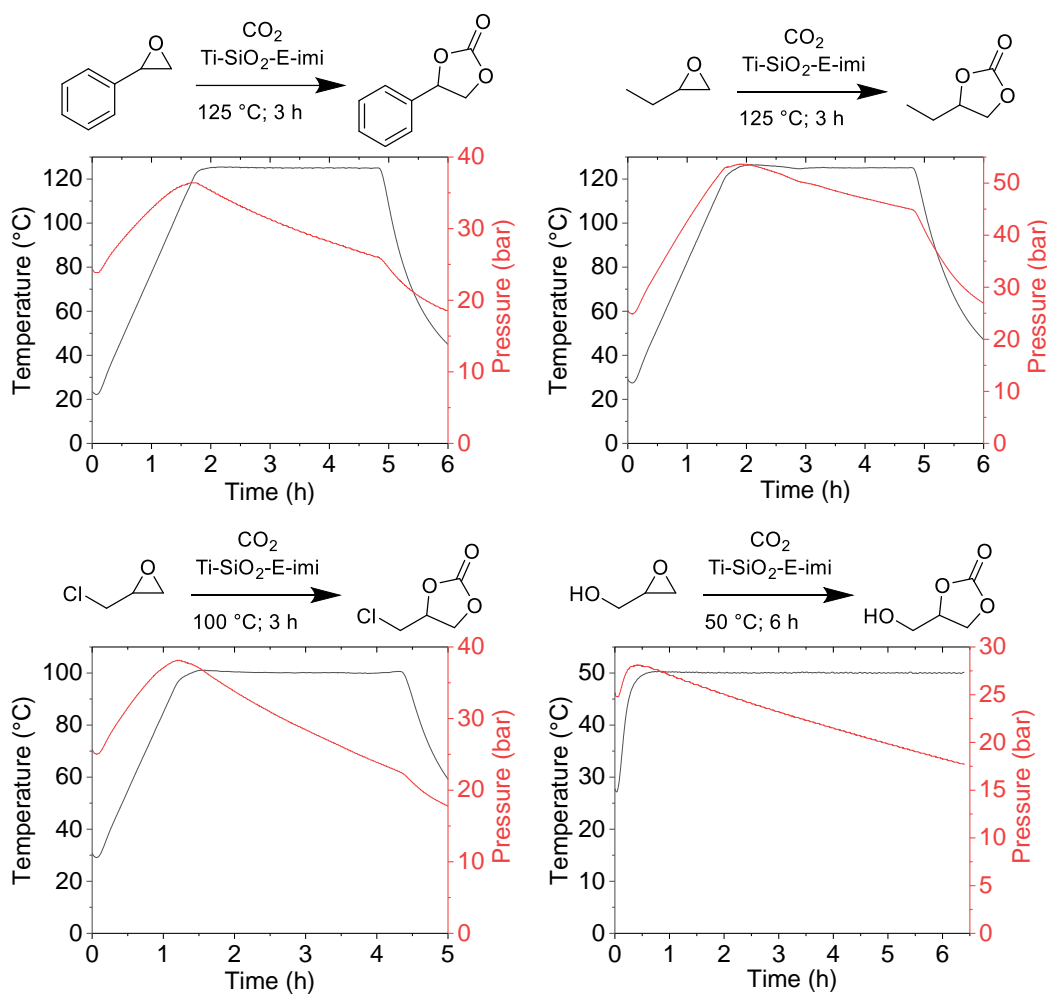


Figure 8: Temperature and pressure monitoring of the conversion of styrene oxide, 1,2-epoxybutane, epichlorohydrin and glycidol using **Ti-SiO₂-E-imi** as catalyst

These results prove that **Ti-SiO₂-E-imi** is an efficient and versatile catalyst in the CO₂ conversion, able to preserve its activity in multiple cycles. Moreover, the **Ti-SiO₂-E** matrix can be synthesized in aqueous medium with a short synthesis procedure not requiring thermal treatments under static conditions and the release of the porosity can be achieved via simple extraction. All these parameters contribute in making the entire process highly sustainable.

Moreover, the proposed solid could present other additional advantages. It is known that Ti-silicates are amongst the most active catalysts in epoxidation reactions. In this reaction, the Ti centres play the role of Lewis acids interacting with the peroxides. To prove that the efficiency of the materials synthesized can be dual, preliminary tests were performed selecting as target reaction the epoxidation of cyclohexene into cyclohexene oxide using *tert*-butyl hydroperoxide (TBHP) as oxidant (Figure 9). The best catalytic performance was achieved employing the **Ti-SiO₂-E** catalyst. This result is ascribed to the almost complete insertion of Ti in tetrahedral coordination. As expected, **Ti-SiO₂-C** showed poor activity and the main products obtained are side-products (identified as cyclohex-2-en-1-one and cyclohex-2-en-1-ol) while **Ti-SiO₂-CE** exhibits intermediate conversion.

Ti-SiO₂-E displayed good performances also when compared with other reference catalysts already reported in literature. A hybrid mesoporous titanosilicate (19%Me-Ti-MCM-41) prepared by Lin et al [26] demonstrated similar conversion (38.5 %) and a higher selectivity (94.1 %) after 5 h reaction, attributed to the more hydrophobic surface. Recently, Wang and Balkus [251] published interesting results combining a conversion of 22 % in 2 h with excellent selectivity (94 %) using reaction conditions close to the ones adopted by us. It should be noted that our best solid catalyst displays a twice higher conversion. Wang et al [252] also published the synthesis of an extra-large-pore zeolites Ti-SSZ-53 able to achieve competitive results with excellent selectivity (94.6 %) but lower conversion (12.2 %) after 4 h. It should be mentioned that the epoxidation reactions with **Ti-SiO₂-E** were always performed in presence of an aqueous solution of *tert*-butyl hydroperoxide (TBHP) while the other reported examples employ non-aqueous TBHP solution which can account for the higher selectivity.[41, 253, 254]

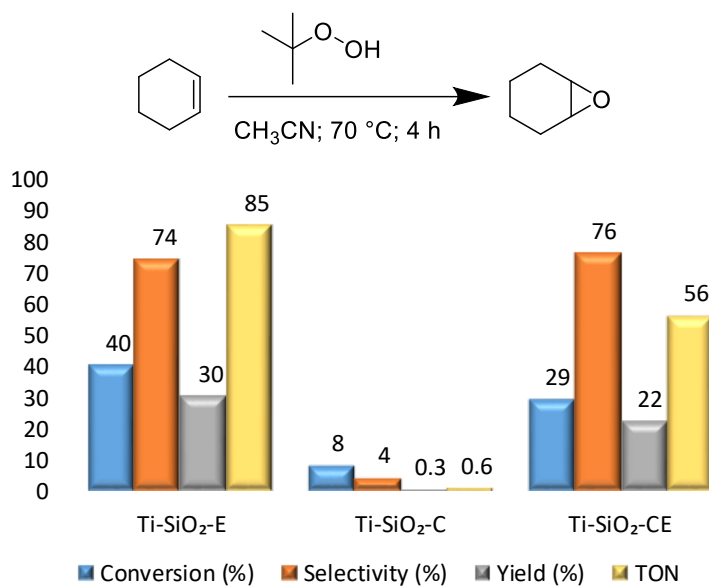


Figure 9: Catalytic results for the epoxidation of cyclohexene. Reaction conditions: alkene (4.5 mmol), TBHP_{aq} (4.5 mmol), catalyst (100 mg), acetonitrile as solvent (4.5 mL), temperature 70 °C.

The above described results demonstrated the efficiency of **Ti-SiO₂-E** and **Ti-SiO₂-E-imi** as catalysts in the epoxidation of cyclohexene to cyclohexene oxide and the carbonatation of cyclohexene oxide, respectively. Hence, to challenge even more our catalyst we decided to test them in the two consecutive reactions. Table 5 summarizes a series of preliminary tests performed as proof of principle. Entry 1 displays the CHO yield achieved in the presence of 100 mg of **Ti-SiO₂-E**. As expected, a decrease of the amount of catalyst (Entry 2) caused a lowering of the yield. This result was also accompanied by a decrease of the selectivity. A catalytic essay in the presence of **Ti-SiO₂-E-imi** revealed a drastic drop of the catalytic performance (Entry 3). No epoxidation product was observed even after 24 h reaction. The side products were identified as cyclohex-2-en-1-one and cyclohex-2-en-1-ol. This result could be ascribed to the hydrophilic nature of the imidazolium moieties, which can decrease the possibility of interaction with the hydrophobic cyclic alkene.[255] To circumvent this problem, a physical mixture of both **Ti-SiO₂-E** and **Ti-SiO₂-E-imi** (Entry 4) was employed. The idea is to have a solid with two components in which one partner can act as catalyst for the epoxidation while the second will convert the epoxide, as depicted in Scheme 2. Interestingly, the yield in CHO was slightly higher [26, 27, 255] thus proving that the presence of **Ti-SiO₂-E-imi** has no detrimental effect on the epoxidation reaction. The same catalysts mixture constituted by 50 wt% of **Ti-SiO₂-E** and 50 wt% of **Ti-SiO₂-E-imi** was successfully used in the conversion of carbon dioxide (reaction 2; Entry 5) and a result similar to the one obtained with the sole **Ti-SiO₂-E-imi** (Entry 6) proves that there is no detrimental effect in CO₂ conversion by using the mixture of both catalysts. The results obtained demonstrate that the catalytic mixture can be

used for both processes (reaction 1 and 2) without decreasing the overall catalysts performances. Moreover, these tests highlight the importance of the spatial proximity of the catalyst (imidazolium chloride) and the co-catalyst (Ti centre) in the formation of cyclic carbonates.

The difficulties related to direct conversion of cyclohexene to the corresponding cyclic carbonate when the sole **Ti-SiO₂-E-imi** is used, can be overcome employing a mixture of **Ti-SiO₂-E** and **Ti-SiO₂-E-imi** catalysts. The results summarized in the Table 5 represent a proof of concept of the above-mentioned strategy. The reasons of the limited activity of the **Ti-SiO₂-E-imi** solid in the first step of the cascade reaction (epoxidation) could be ascribed to the enhanced hydrophilic character of the surface decorated with imidazolium moieties which may hinder or strongly reduce the contact with the hydrophobic cyclohexene substrate. The importance of the hydrophilic/hydrophobic balance of the catalyst surface in many catalytic reactions including epoxidation, is a largely described topic in literature. An additional treatment of the surface with methylsilane or phenylsilane could improve the yield and selectivity of the first step. Moreover, the differences in reaction conditions with the previously reported epoxidation reactions should be also considered: reaction time, temperature and more importantly the presence or absence of solvent. A possible solution to these issues could stand in the utilization of flow chemistry. This would allow to physically separate the mixtures in cartridges and through membrane to eliminate the solvent.

Table 5: Cascade Reaction.

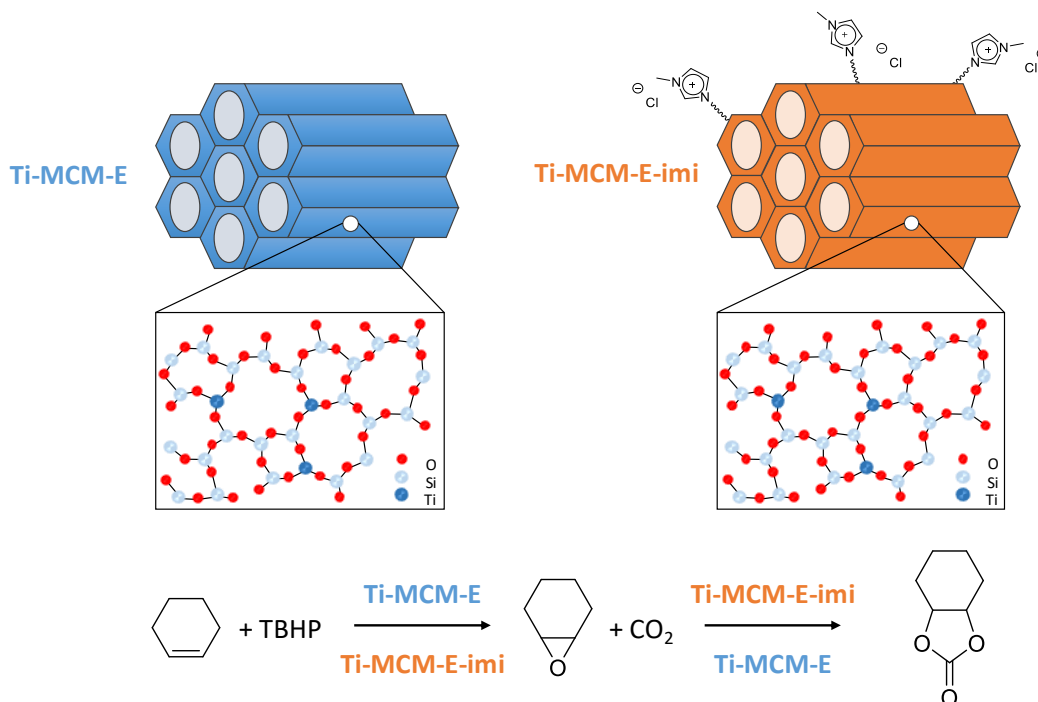
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Entry	Reaction	Catalyst	Conv. (%)	Sel. (%)	Yield (%)
1	1	Ti-SiO ₂ -E (100 mg)	45	74	33
2	1	Ti-SiO ₂ -E (50 mg)	30	47	14
3	1	Ti-SiO ₂ -E-imi (50 mg)	17	-	-
4 ^[a]	1	Ti-SiO ₂ -E-imi (50 mg)	33	79	26
5 ^[b]	2	Ti-SiO ₂ -E-imi (250 mg)	34	> 95	32
6	2	Ti-SiO ₂ -E-imi (250 mg)	33	> 95	31

Reaction 1: Cyclohexene (4.5 mmol); TBHP_{aq.} 70 % (4.5 mmol); acetonitrile (4.5 mL); mesitylene as internal standard (50 μ L); temperature (70 $^{\circ}$ C); 1 h.

Reaction 2: Cyclohexene oxide (24.0 mL; 237 mmol); CO₂ initial pressure (25 bar); 150 $^{\circ}$ C; heating rate (1 $^{\circ}$ C/min); 24 h; 500 rpm.

[a] reaction performed in presence of an equivalent amount of Ti-SiO₂-E (50 mg).

[b] reaction performed in presence of an equivalent amount of Ti-SiO₂-E (250 mg)



Scheme 1. Representation of the two catalysts reaction.

Conclusions

Porous titanasilicate nanospheres were efficiently prepared via a straightforward synthesis protocol requiring only 1h reaction and no hydrothermal treatment under static conditions thus strongly decreasing the energy consumption. The effect of the post-synthetic treatment on the insertion of titanium was investigated, proving that the pores can be freed from the template through an extraction in aqueous medium. The solids were functionalized with imidazolium moieties and thoroughly characterized via various techniques including transmission electron microscopy, N₂ physisorption, XPS, UV-Vis, ¹³C and ²⁹Si solid state NMR. The bifunctional particles were successfully employed as catalysts in the conversion of carbon dioxide with various epoxides to form the corresponding cyclic carbonates. The results obtained proved the added value of a titanium containing support which plays the role of Lewis acid enhancing the

overall catalytic performance. The best solid displayed better performances in terms of TON and TOF than other fully heterogeneous catalysts reported in literature. The catalytic performance correlate coherently with all the set of characterization data. Moreover, the catalyst was reused in multiple cycle without decrease of the catalyst performance. The bifunctional nature of the best solid was challenged testing the catalyst in the epoxidation reaction of cyclohexene. The same catalytic mixture, composed by the titanosilicate nanospheres and bi-functional solid, was used to convert the cyclohexene into cyclohexene oxide and subsequently the cyclohexene oxide into the corresponding carbonate. All these results prove the versatility of the catalysts and confirm the key role played by the Ti centre inserted in tetrahedral coordination.

Experimental

Materials and Methods

Ammonium hydroxide (30 %), fuming hydrochloric acid and acetonitrile were purchased from Carl Roth GmbH+Co. Cetylmethylammonium bromide (CTAB), tetraethylorthosilicate (TEOS), tetraisopropylorthotitanate, N-methylimidazole, (3-chloropropyl)trimethoxysilane, styrene oxide, cyclohexene oxide, epichlorohydrin and tert-butyl hydroperoxide (70% in water) and were purchased from TCI NV Europe. Glycidol, 1,2-epoxybutane, cyclohexene and mesitylene were purchased from Sigma-Aldrich. DMSO-d₆ was purchased from Eurisotop. All chemicals were used as received without further purification. Milli-Q water was 18.2 M Ω .cm.

Diffuse reflectance UV-Vis spectra were recorded with a Varian Cary 5000 UV-Vis-NIR Spectrophotometer.

Synthesis of Ti-SiO₂ solids

Mesoporous silica-based materials were prepared adapting a previously reported dilute route.[16, 19] Ammonium hydroxide (1.422 mL, 10.95 mmol) and CTAB (1.516 g, 4.16 mmol) were dissolved in 726 mL of distilled water. When a clear solution was obtained, TEOS (6.936 g, 33.29 mmol) and tetraisopropylorthotitanate (132 μ L, 0.45 mmol) were mixed together and added dropwise in the aqueous solution. After 1 h under vigorous stirring at room temperature, the solid was filtered and washed 3 times alternatively with water and ethanol. The solid was dried overnight at 65 °C. It was then submitted to calcination and/or extraction respectively described here after. The calcination was performed in a Nabertherm oven with heating and cooling rate of 120 °C/h under air for 8 h at 550 °C. The extraction was performed dispersing the solid (3g) in ethanol (200 mL) and adding HCl (24 mL) under stirring.[240] After 4 h under agitation at 50 °C, the solution was filtered and washed by ethanol until the pH of the filtrate was neutral. The recovered solid was dried at 100 °C.

Synthesis of Ti-SiO₂-imi

The Ti-SiO₂ solid was dried in oven at 100 °C overnight before functionalization. In a round bottom flask, the silica matrix (1.5 g) was suspended in 15 mL of dry toluene. Under agitation, N-methylimidazole (24 mmol) and (3-chloropropyl)trimethoxysilane (12 mmol) were added.

The mixture was stirred at reflux temperature for 24 h. After cooling, the material was washed with Soxhlet extractor using ethanol as solvent.

Catalytic tests: Epoxidation

All catalysts were dried overnight at 100 °C prior to catalytic test. In a typical test, the solid was weighted in a 20 mL glass vial. The solvent (4.5 mL acetonitrile), the internal standard (50 µL mesitylene), the alkene (4.5 mmol cyclohexene) and the oxidant (4.5 mmol TBHP) were added. The vial was closed with a silicon/PTFE screw cap and heated at 70 °C using dry heating block. The mixture was stirred at 500 rpm using cross-shaped PTFE-coated magnetic stirrer. The mixture was analysed on a Trace 1300 gas chromatograph from Thermo Scientific equipped with a Rt-Q-Bond column (15 m long, 0.25 mmID, 8 µm_df) from Restek. The inlet was preheated at 250 °C. The oven sequence was the following: 50 °C for 1 minute, heating ramp of 50 °C/min up to 250 °C and a plateau at 250 °C for 5 minutes. The carrier gas was N₂ flowing at 1 mL/min. The instrument was equipped with a flame ionization detector (FID) powered by a mixture of H₂ and dry air.

Supporting Information

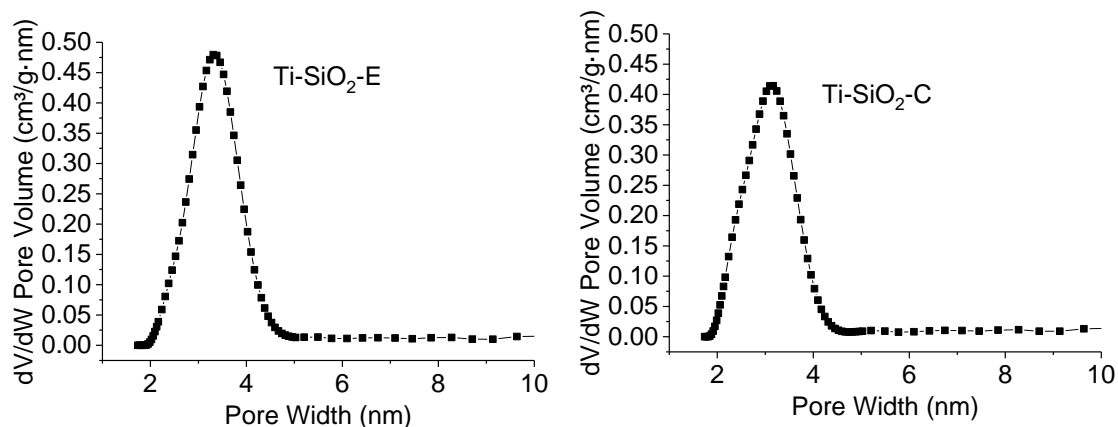


Figure S1: DFT pore size distribution of Ti-SiO₂-E (left) and Ti-SiO₂-C (right) and TEM images

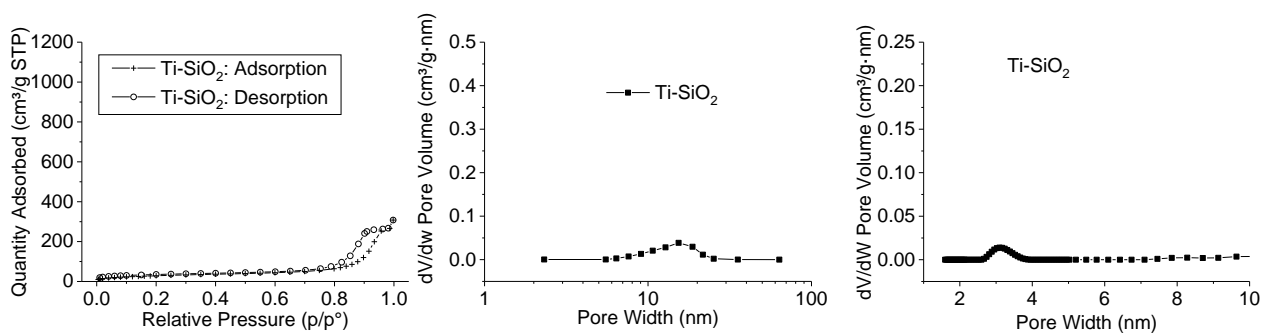
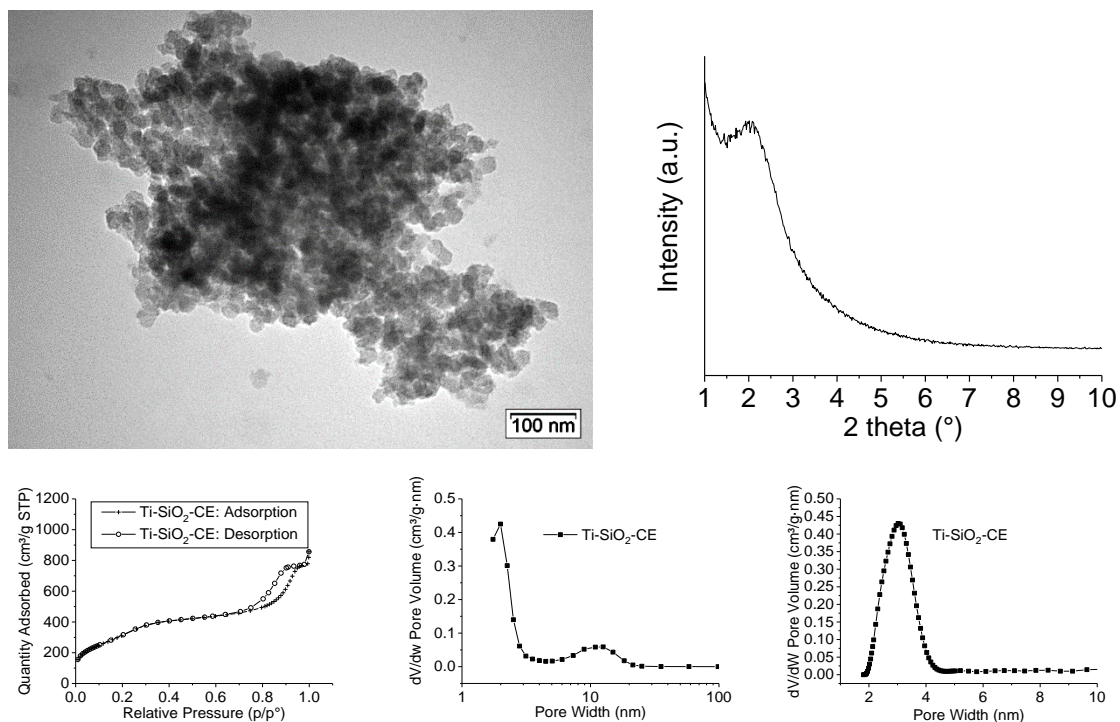


Figure S2: N₂ physisorption isotherm (left), BJH pore size distribution (middle) and DFT pore size distribution (right) of Ti-SiO₂ before calcination or extraction of the templating agent.



Figures S3: TEM (top left), low-angle XRD (top right), N₂ physisorption isotherm (bottom left), BJH pore size distribution (bottom middle) and DFT pore size distribution (bottom right) of Ti-SiO₂-CE

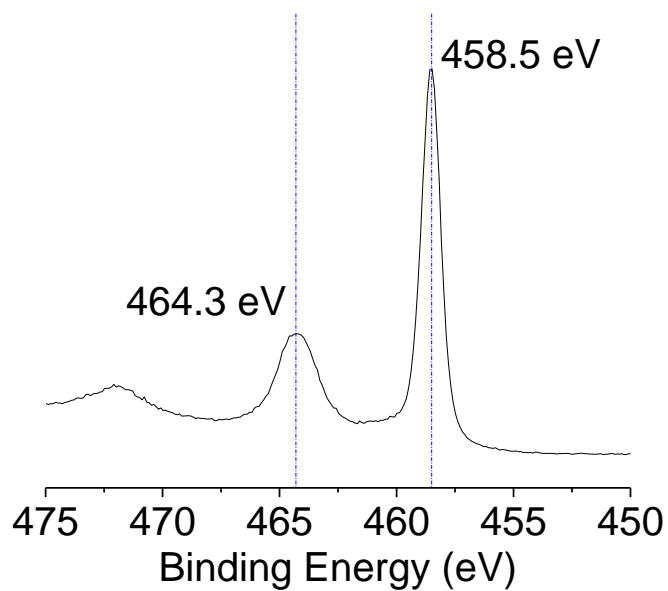


Figure S4: XPS of commercial TiO₂ (P25)

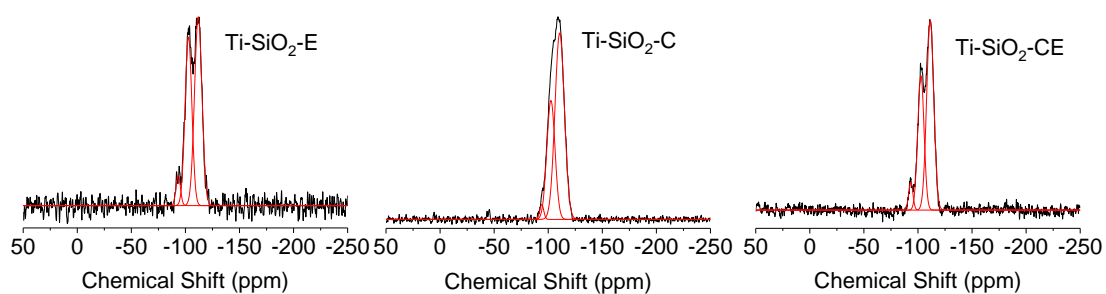


Figure S5: Direct excitation ^{29}Si MAS NMR of Ti-SiO₂-E (left); Ti-SiO₂-C (middle) and Ti-SiO₂-CE (right)

Table S1: Position and relative abundance of Q ⁴ ; Q ³ and Q ² species for Ti-SiO ₂ -E; Ti-SiO ₂ -C and Ti-SiO ₂ -CE materials			
	Peak centered at (ppm)	Relative peak area (%)	Degree of condensation ^[a]
Ti-SiO ₂ -E (Q ⁴)	-112	52	1.1
Ti-SiO ₂ -E (Q ³)	-103	42	
Ti-SiO ₂ -E (Q ²)	-93	5	
Ti-SiO ₂ -C (Q ⁴)	-111	63	1.7
Ti-SiO ₂ -C (Q ³)	-103	35	
Ti-SiO ₂ -C (Q ²)	-94	2	
Ti-SiO ₂ -CE (Q ⁴)	-111	58	1.4
Ti-SiO ₂ -CE (Q ³)	-103	37	
Ti-SiO ₂ -CE (Q ²)	-93	5	
^[a] Degree of condensation calculated as $Q^4/(Q^3+Q^2)$			

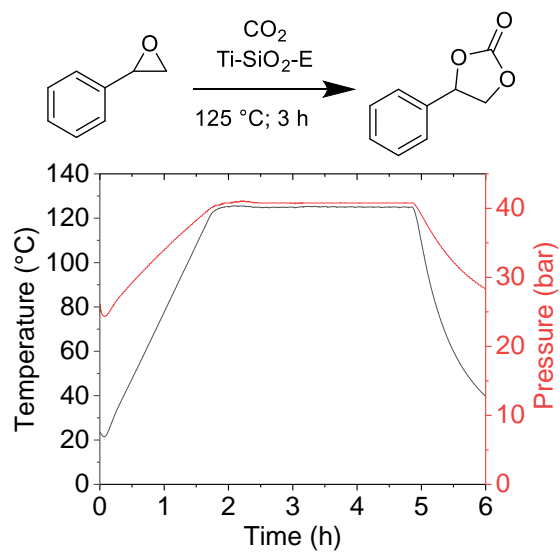


Figure S6: Temperature and pressure monitoring of the conversion of styrene oxide using **Ti-SiO₂-E**

