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Titanosilsesquioxane Anchored on Mesoporous Silicas: A Novel Approach for the Preparation of Heterogeneous Catalysts for Selective Oxidations

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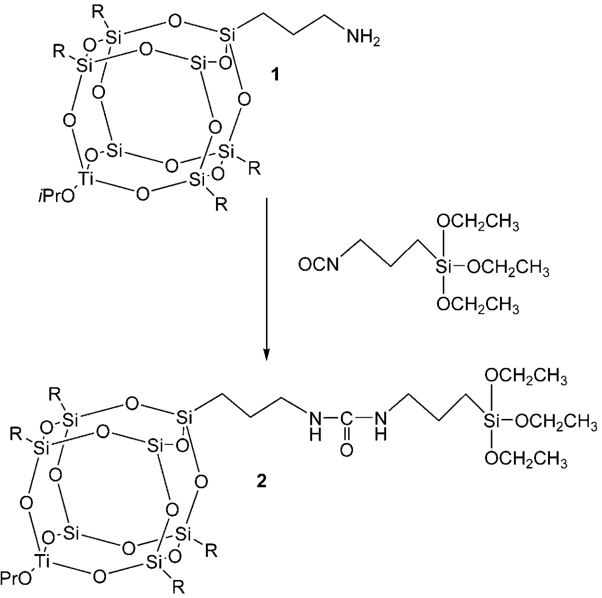
Polyhedral oligomeric silsesquioxanes (POSS) are a class of condensed three-dimensional organosiliceous compounds with cage frameworks that have different degrees of symmetry. These molecular materials have a general formula $R_8Si_8O_{12}$[1–3] and display silicon atoms bound to one-and-a-half oxygen atoms (sesqui), the remaining valence being saturated by organic entities (R). Numerous metals have been incorporated successfully into POSS cages with the aim to obtain either specific homogeneous catalysts,[4] or models for active sites of heterogeneous catalysts. For example, POSS cages with titanium(IV) complexes proved to be highly active in the epoxidation of olefins.[5–9]

Special attention was recently devoted to the heterogenisation of Ti–POSS compounds onto insoluble and easily recoverable supports. Interesting examples encompass the incorporation of Ti–POSS into mesoporous MCM-41, sol–gel matrices, polysiloxanes and the preparation of organic–inorganic hybrid materials and coatings based on polystyrene polymers containing Ti–POSS moieties.[9–14] However, the literature on the direct anchoring, through covalent bonding of preformed Ti–POSS cages onto silica supports is very poor.[14] The stabilisation of Ti–POSS compounds onto silica surfaces through covalent bonds is a relevant issue for obtaining heterogeneous catalysts with isolated active centres, because it may avoid metal leaching from the catalysts.

This work is focused on the preparation of Ti–POSS-based heterogeneous catalysts, by anchoring of a functional titanium-containing silsesquioxane on the surface of an ordered mesoporous silica (SBA-15) and of a non-ordered silica (SiO_2-Dav). An innovative bifunctional POSS, bearing in the structure both a Ti^{IV} metal centre and a triethoxy group for grafting on the silica surfaces, was specifically synthesised for this purpose and named Ti–POSS–TSIPI (Scheme 1, **2**).

Ti–POSS–TSIPI was prepared by an equimolar reaction between Ti–NH_2POSS (Scheme 1, **1**), the synthesis of which was reported by some of us,[15] and 3-isocyanatopropyl triethoxysilane (TSIPI) under basic conditions.

The product of the reaction was monitored by both IR (Figure 1) and ^{1}H NMR spectroscopy (see Experimental



Scheme 1. The reaction between Ti-NH_2POSS (**1**) and 3-isocyanatopropyl triethoxysilane for the preparation of Ti–POSS-TSIPI (**2**); R = isobutyl group.

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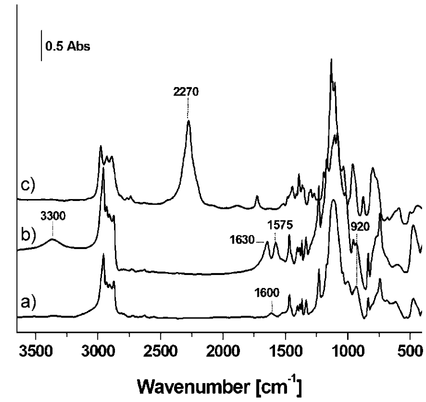


Figure 1. IR spectra in KBr matrix of a) Ti-NH_2POSS, b) Ti–POSS-TSIPI (**2**) and c) 3-isocyanatopropyl triethoxysilane.

Section). The absence of the IR absorption at 2270 cm^{-1}, due to the asymmetric stretching of N=C=O group, confirmed that the reaction between 3-isocyanatopropyl triethoxysilane and **1** was complete. Moreover, the IR spectrum of **2** (Figure 1, b) showed a wide band at about 3300 cm^{-1}, assigned to the NH stretching of ureic group. The success of the reaction was also confirmed by the absence of the band at 1600 cm^{-1}, due to a bending mode of the NH_2 group of **1**, which was replaced by two peaks at 1630 and 1575 cm^{-1} assigned to the C=O stretching and N–H bending of ureic group, respectively. It is worth noting that the Si-O-Ti stretching band at 920 cm^{-1} of both the reactant (**1**) and product (**2**) was not modified; this testifies the integrity of the Ti–POSS cage after reaction with the triethoxysilane.

Thanks to the presence of three ethoxy groups, compound **2** can be easily anchored onto the surface of porous silica SBA-15 and SiO_2-Dav, which are both rich in surface silanols (Si–OH). SBA-15 was prepared as previously described in the literature[16] and showed the typical X-ray diffraction pattern (Figure 2, curve a) with three distinct reflections at 0.9, 1.53 and 1.76° 2θ assigned to (100), (110), (200) planes of a hexagonal array of pores.[16] SiO_2-Dav is a commercial product delivered by Grace and it represents an easy available and cheap mesoporous silica support.

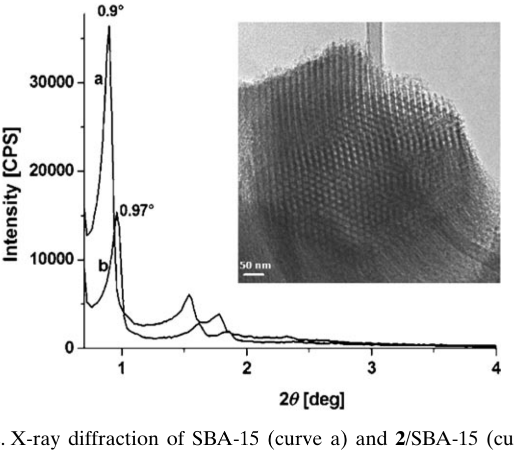


Figure 2. X-ray diffraction of SBA-15 (curve a) and **2**/SBA-15 (curve b). Inset: TEM micrograph of **2**/SBA-15.

The anchoring of **2** was carried out after evacuating both silica samples at 773 K for 4 h. The amount of **2** used in both syntheses was fixed to 20 wt % respect to the support. The final solids showed a titanium concentration of 0.26 and 0.33 wt. % for **2**/SBA-15 and **2**/SiO_2, respectively.

The anchoring process was followed by IR spectroscopy (see supporting information), which provided clear-cut evidences that condensation reactions occurred between surface silanols of silicas and ethoxy groups of **2**.

Relative to the parent SBA-15, the grafted sample displayed a decrease of the XRD peaks intensity (Figure 2, curve b), which is assigned to the modification of the scattering properties of the solid, for the presence of compound **2**. Structural order and morphology of SBA-15 were preserved after the grafting of **2**, as highlighted by the narrow and distinct XRD reflections and by TEM micrograph (Figure 2 inset). A clear shift to higher 2θ values of the XRD peaks was also found, which was assigned to the immobilisation of **2** on the surface of the SBA-15 channels, in agreement with IR spectroscopic results.

A textural analysis was performed by nitrogen adsorption (Table 1) to define specific surface area and specific pore volume. Both SBA-15 and SiO_2-Dav showed type IV isotherms, according to the IUPAC classification, and H1 hysteresis loops. In the case of SBA-15 the hysteresis loop is representative of structural mesoporous cylindrical or rod-like pores. The presence of **2** did not significantly modify the textural features of both silicas (Table 1). This suggests that **2** is evenly distributed on the surface of the silicas and that no pore blocking or hindering occurred upon anchoring.

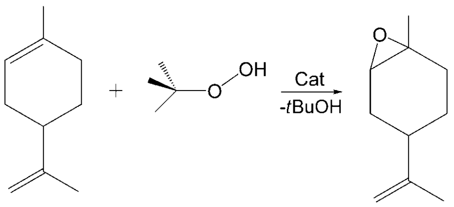
Table 1. Textural properties (measured by N_2 adsorption-desorption isotherms) of the porous materials studied in this work.

Material	*S*BET [$m^2 g^{-1}$]	Pore diameter [Å]	Pore volume [$cm^3 g^{-1}$]
SBA-15	650	88	1.04
2/SBA-15	547	85	0.91
SiO_2-Dav	290	221	1.3
2/SiO_2-Dav	265	206	1.2

Both titanium-containing materials, were used as catalysts for the epoxidation of limonene (1-methyl-4-(prop-1-en-2-yl)cyclohex-1-ene) with *tert*-butylhydroperoxide (TBHP; Scheme 2), which was chosen as a test reaction to verify whether the Ti^{IV} sites were accessible to the reactants and possessed catalytic activity.

The anchored materials were compared to widely studied titanium-containing heterogeneous catalysts obtained by grafting a similar loading of titanocene dichloride precursors onto mesoporous silica supports.[17]

The systems **2**/SBA-15 and **2**/SiO_2 are both active in the epoxidation of limonene and the specific activity values (turnover numbers; TONs) obtained on them are rather



Scheme 2. Limonene (1-methyl-4-(prop-1-en-2-yl)cyclohex-1-ene) epoxidation with TBHP.

similar (Table 2). Furthermore, the heterogeneous character of both catalysts was checked by removing the solid catalyst by centrifugation and testing the residual liquid mixture for further reaction. No significant loss of active species was detected (see Supporting Information). Thus, the immobilisation technique by covalent anchoring does not hinder the oxidising activity of the Ti^{IV} sites and, more significantly, it is not sensitive to the morphology of the support. When the epoxidation of limonene is considered, in fact, the choice of an ordered mesoporous silica with a marked confinement effect is not essential (this is not the case when simple immobilisation by impregnation is employed[10]) and non-ordered commercial silica with large mesopores can be used successfully.

Table 2. Catalytic performance of limonene epoxidation over Ti-containing catalysts.[a]

Catalyst	Ti content[b] [wt. %]	C[c] after 24 h [%]	TON[d] after 24 h	S[e] after 24 h [%]
2/SBA-15	0.23	25	95	88
2/SiO_2-Dav	0.33	39	108	85
Ti/SBA-15	0.24	48	192	78
Ti/SiO_2-Dav	0.29	60	198	82
no catalyst	–	4	–	n.d.[f]
SiO_2	–	5	–	n.d.

[a] Reaction conditions: glass batch reactor; 10 mL AcOEt solvent; 358 K; 24 h; 50 mg catalyst; 1.2 mmol TBHP; 1.0 mmol limonene; mesitylene internal standard. [b] Obtained by ICP-AES. [c] Limonene conversion after 24 h. [d] Turn-over Numbers after 24 h (mol converted substrate/mol Ti). [e] Selectivity to endocyclic limonene monoepoxide after 24 h. [f] Not detected.

Anchored catalysts show lower conversions with respect to reference materials (Ti/SBA-15 or Ti/SiO_2-Dav) simply prepared by direct grafting of titanocene on the same silica supports. This is likely due to the optimal site isolation achieved by grafting modest amount of titanocene over high-surface-area silica supports. However, in terms of selectivity, the anchored materials display slightly better results than those obtained over reference titanium–silica catalysts with comparable metal loading. In all cases, the major product is the endocyclic limonene epoxide (80–88 %). Virtually the only other product is the exocyclic epoxide (10–12 %) when anchored Ti–POSS-derived catalysts are used, whereas acid-derived by-products (9–14 %) are found when reference titanium catalysts are employed. This behaviour suggests that a similar reactivity takes place at the Ti^{IV} sites for the epoxidation reaction, but a more marked acidic character is present in the reference titanocene-derived catalysts with respect to the anchored ones.

A similar behaviour is observed in carveol (2-methyl-5-(prop-1-en-2-yl)cyclohex-2-enol) epoxidation. Anchored Ti–POSS-derived catalysts show TON values almost identical to reference Ti/SBA-15 catalyst (47, 52 and 48, for **2**/SBA-15, **2**/SiO_2 and Ti/SBA-15, respectively), but they display a remarkably higher selectivity to endocyclic epoxide than titanocene-derived systems (ca. 80 % vs. 60 %, respectively; see Supporting Information).

In conclusion, a novel approach for the preparation of heterogeneous catalysts based on an innovative and versatile functional titanosilsesquioxane (Ti–POSS-TSIPI; **2**) and mesoporous silicas (SBA-15 and non-ordered silica) is proposed. The spectroscopic characterisation showed that **2** was effectively anchored with good dispersion on the surface of both ordered and non-ordered silica supports. Preliminary catalytic tests in the epoxidation reaction of limonene and carveol showed that both hybrid materials (**2**/SBA-15 and **2**/SiO_2-Dav) display interesting catalytic activity that was not sensitive to the morphology of the support. Anchored catalysts showed, in terms of selectivity, good results comparable to those obtained over the reference titanocene-derived materials (Ti/SBA-15 and Ti/SiO_2-Dav). Finally, this new approach of functionalisation and immobilisation of Ti–POSS species may generate a wider interest, especially for mechanistic studies for which a thorough tuning and control of the chemical surroundings of the Ti active sites is crucial.

Experimental Section

Preparation of Ti–POSS-TSIPI (2): Ti-NH_2POSS (1 g, 1.1×10^{-3} mol)[15] was dissolved in chloroform (40 mL). An equimolar amount of 3-isocyanatopropyl triethoxysilane and triethylamine was added to the solution. The reaction was performed under inert conditions, using nitrogen flow, at room temperature for 20 h. Finally, the solvent was evaporated until a white powder was obtained. ^{1}H NMR (400 MHz $CDCl_3$): $\delta = 3.9$ (t, 2H; NH, ureic group), 3.7 (q, 6H; CH_2, O*Et*) ,3.6 (m, 1H; CH, O*iPr*), 2.9 (m, 4H; CH_2 of ureic group), 1.85 (m, 6H; CH), 1.20 (m, 15H; CH_3 of O*Et* and O*iPr* groups), 0.93 (d, 36H; CH_3 of isobutyl groups), 0.59 ppm (m, 20H; CH_2).

Preparation of SBA-15: Pluronic P123 (4.0 g, Sigma–Aldrich) was dissolved in water (30 g) and HCl (2N, 120 g) with stirring at 308 K. Tetraethoxysilane (8.5 g, Sigma–Aldrich) was added to the solution and stirred at 308 K for 24 h. The mixture was aged at 373 K in an autoclave for 24 h. The solid product was filtered and washed several times by water. Calcination was carried out increasing the temperature at 1 °C min^{-1} under air flow from room temperature to 823 K and heating the material at 823 K for 5 h.

Preparation of 2/SBA-15: SBA-15 (1 g) was evacuated at 773 K for 4 h in order to remove the adsorbed water and to activate the surface. Then the powder was dispersed in anhydrous THF (by Sigma–Aldrich) under vacuum. Compound **2** (20 wt % respect to the support) was added to the suspension. The reaction was stirred at 323 K for 24 h. The final product was filtered through a fine sintered glass funnel and washed several times by THF.

Preparation of 2/SiO_2: SiO_2-Dav (1 g, commercial silica, obtained from Grace) was treated at 773 K for 4 h in order to remove the adsorbed water and to activate the surface. Then, SiO_2 was dispersed in anhydrous THF (by Sigma–Aldrich) under vacuum. Compound **2** (20 wt % respect to the support) was added to the suspension. The reaction was stirred at

323 K for 24 h. The final product was filtered through a fine sintered glass funnel and washed several times by THF.

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