Mesoporous SiO$_2$–TiO$_2$ epoxidation catalysts: tuning surface polarity to improve performance in the presence of water

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Abstract

Herein, we present the preparation by the non-hydrolytic sol-gel route of a mesoporous SiO$_2$–TiO$_2$ epoxidation catalyst with high specific surface area and large pores. This catalyst is active in the catalytic epoxidation of cyclohexene with H$_2$O$_2$ in acetonitrile, showing performances comparable to a TS-1 catalyst. Yet, it is dramatically deactivated when water is used as a co-solvent, which represents an important limitation for the applicability of this catalyst. In order to circumvent the deactivation of the catalyst in the presence of water, we investigate the effect of surface hydrophobization with methyl groups on the catalytic activity and selectivity. Two functionalization methods are investigated: one-pot synthesis with methyltrichlorosilane and post-synthesis silanization with methyltrimethoxysilane. The catalytic performance of the materials are compared to the pristine catalyst and to TS-1 in the presence of an excess of water in the medium. On the one hand, we show that the one-pot methylation does not increase water resistance, in spite of an increased surface hydrophobicity. We interpret this result in the light of a poorer Ti dispersion and lower Ti$^{4+}$ surface content in these catalysts. On the other hand, post-synthesis grafting significantly improves the catalytic performances because it combines a hydrophobic surface with a high active site content. At the molecular level, we show that the direct epoxidation pathway is restored thanks to the surface functionalization.

Keywords
Olefin epoxidation ; Mesoporous mixed oxide ; Non hydrolytic sol-gel ; Surface hydrophobicity ; Catalyst deactivation.
1. Introduction

Olefin epoxidation is widely represented in the chemical industry, from the production of pharmaceuticals to the polymer industry, due to the extensive use of these reactions for the synthesis of active intermediates (e.g. ethylene and propylene oxide, epichlorhydrin, cyclohexene oxide, etc.) [1]. With the advent of green chemistry and its associated principles [2], industrially relevant chemical processes, including olefin epoxidation, have to be re-designed. Sustainable routes are highly sought-for, not necessarily to maximize conversion or yield, but rather to minimize energy consumption and waste [3,4]. In the field of heterogeneous catalysis, this trend fosters the emergence of a new class of materials with relatively high activity and selectivity under mild conditions, i.e. in water-based media at moderately low temperatures [5,6].

Among the available catalysts and oxidants, the combination of titanium-containing zeolite TS-1 and hydrogen peroxide H$_2$O$_2$ represents one of the success-story of industrial epoxidation reactions. First, the efficiency of TS-1 in terms of catalytic activity and selectivity to epoxidation products, even at low temperatures and in the presence of water, stems for its success as an oxidation catalyst [7]. Second, H$_2$O$_2$ is commonly considered as one of the greenest oxidants, since it produces water as the only by-product. In return, the atomic percentage of active sites in the MFI crystal structure is limited to a maximum of 2.5% (n Ti/ (n Ti + n Si)) [8]. Additionally, the intrinsic microporosity of TS-1 circumvents the use of this catalyst for the epoxidation of large olefins due to diffusional limitations. There is therefore a high demand for mixed oxides – either crystalline or amorphous – with larger pores and high surface area in order to extend the versatility of Ti-containing catalysts to a wider range of substrates [8–12]. Several challenges have to be addressed for the preparation of such materials, from the true incorporation of the active species (i.e. Ti$^{4+}$) by the levelling of the precursors reactivity (e.g. pre-hydrolysis of alkoxide precursors [13]) to the control over the texture by the choice of the templating agent, as well as proper drying conditions (e.g. supercritical drying [14]).

Sol-gel methods represent a versatile toolbox for the bottom-up preparation of heterogeneous catalysts [15]. Controlling the transition metal dispersion as well as the texture and functionalization of the catalyst surface, it is possible to obtain mesoporous silica-based epoxidation catalysts with high activity and selectivity. In particular, we put our focus on non-hydrolytic sol-gel (NHSG), which is currently emerging as a powerful preparation technique for mesoporous mixed oxide catalysts [16–19]. This approach allows reaching remarkable
specific surface area (ca. 1000 m².g⁻¹) and pore volume (ca. 1.0–1.5 cm³.g⁻¹), associated with a tunable pore size and a high active phase dispersion without the need for organic templating agent of for supercritical drying or pre-hydrolysis of the precursors [20,21]. In those conditions, catalysts with a high content of active sites can be obtained, with benefits for the catalytic performances compared to single TS-1 nanocrystals.

Despite the promising improvement brought by the fine control over the catalyst textural properties, amorphous SiO₂–TiO₂ mixed oxides are easily deactivated in water [22]. This issue has to be addressed when running epoxidation reactions with aqueous solutions of H₂O₂ (with final production of H₂O) and/or in the presence of large amounts of water in the solvent. An exception to deactivation by H₂O is provided by TS-1: its crystallinity and intrinsic hydrophobicity accounts for its good performance in aqueous media [22,23].

In order to circumvent the deactivation of the amorphous and mesoporous TiO₂–SiO₂ catalyst prepared by NHSG, we investigated the effect of surface hydrophobization on the catalyst activity in the presence of water for the epoxidation of cyclohexene [24,25]. The surface functionalization was achieved either in one-pot during the gel synthesis or by post-synthesis silanization with a methylated precursor.

Not only the activity but also the selectivity is expected to be influenced by the surface hydrophobization. Considering the reaction pathway for cyclohexene oxidation (Figure 1), the epoxide can be produced by two competitive paths, either by direct epoxidation of cyclohexene with H₂O₂ or by the formation of cyclohexenyl hydroperoxide responsible for the oxidation of the olefin through a radical mechanism called allylic oxidation [22,26]. The second path should be avoided since it leads to the concomitant formation of undesired side products (2-cyclohexen-1-ol and its oxidation product 2-cyclohexen-1-one [27]). The mechanism implies the formation of a radical species on the Ti active site (i.e. TiO-) due to the over-adsorption of H₂O₂ onto the catalyst surface, which is favoured by a high H₂O₂/Ti ratio [26,28,29]. We put forward that increasing the surface hydrophobicity would locally reduce this ratio by repelling H₂O₂ molecules from the surface and thus from Ti active sites. Consecutive to the formation of the epoxide, the ring opening of the epoxide to form a diol (cyclohexane diol) is another unwanted process (Figure 1). This hydrolysis reaction is promoted by the presence of H₂O [30,31] and therefore thought to be mitigated by surface hydrophobization.

2. Experimental

The catalysts were prepared with a 6% at. Ti loading (Ti/Ti+Si) according to the non-
hydrolytic sol-gel (NHSG) method, following a procedure described elsewhere [21]. Briefly, SiCl$_4$ (4.267 g, Acros Organics, 99.8%), iPr$_2$O (5.449 g, Acros Organics, 99%) and TiCl$_4$ (0.304 g, Acros Organics, 99.9%) were successively transferred into a 100 cm$^3$ teflon-lined stainless steel autoclave along with CH$_2$Cl$_2$ (8.867 g, VWR Chemicals, 99.8%) in a glovebox. Prior to use, iPr$_2$O and CH$_2$Cl$_2$ were dried using metallic sodium and P$_2$O$_5$, respectively, down to a water concentration below 15 ppm. The other reactants were used as received. The clear solution, with a molar composition of 1 SiCl$_4$: 0.064 TiCl$_4$: 2.127 iPr$_2$O: 4.165 CH$_2$Cl$_2$, was manually stirred for 10 min. The autoclave was subsequently sealed and kept in an oven at 150°C for 6 days. Afterwards, it was opened in the glovebox and the as-synthesized gel was ground and dried overnight under vacuum. The solid catalyst, in powder form, was obtained after calcination at 500°C for 5 h (10°C.min$^{-1}$). It is denoted “NHSG”. As a reference material, titanosilicalite-1 (TS-1) was synthesized with a Ti atomic content of 1.8% [32].

One-pot functionalization. The gel was obtained by the same method as depicted above, but replacing part of the SiCl$_4$ by MeSiCl$_3$ (Sigma-Aldrich, 99%) [24]. The catalysts are denoted “NHSG$_X$Me”, where “X” represents the nominal molar ratio MeSiCl$_3$/Si. The final composition was 1 SiCl$_4$: 0.111 SiCl$_3$: 0.071 TiCl$_4$: 2.309 iPr$_2$O: 4.628 CH$_2$Cl$_2$ (NHSG$_{0.3}$Me) and 1 SiCl$_4$: 0.429 SiCl$_3$: 0.091 TiCl$_4$: 2.825 iPr$_2$O: 5.950 CH$_2$Cl$_2$ (NHSG$_{0.3}$Me).

Two-step functionalization. The pristine NHSG catalyst (200 mg) was methylated by a dry impregnation method using methyltrimethoxysilane (MTMS) (0.206 g, TCI, > 98%) in water-saturated toluene (0.062 g, Sigma-Aldrich, ≥ 99.7%). The impregnation solution was mixed with the solid sample and the mixture was further homogenised by vortexing for 10 min in a closed vial. Afterwards, the solid was put to rest in a toluene saturated atmosphere for 48 h. Then, the solid was heated at 90°C for 1 h, washed successively with 50 ml toluene and 50 ml pentane, and dried overnight at 120°C under vacuum. The nominal methylation ratio (MeSi(OMe)$_3$/Si) was 30%, and the catalyst is denoted “NHSG@0.3Me”.

Textural properties were determined from N$_2$ adsorption/desorption isotherms at -196°C using a Tristar 3000 instrument (Micromeritics, USA). Prior to measurement, the samples were first degassed overnight under vacuum at 150°C. The pore size distribution was obtained from the desorption branch using the BJH method. The surface area was evaluated by the BET method in the relative pressure range of 0.05–0.30. Powder X-ray diffraction (PXRD) patterns were recorded at room temperature on a Siemens D5000 diffractometer equipped with a Ni filter using CuK$\alpha$ radiation (Bragg-Brentano geometry) operated at 40 kV and 40 mA. Diffractograms were taken between 5° and 80° (2θ) with a step size of 0.02° (2θ). Diffuse reflectance spectra (DRS) were obtained with an AvaSpec-2048-1-DT (Avantes) spectrometer,
equipped with a 300 lines/mm grating, a 100 μm slit size, a deuterium-halogen light source and a reflection probe with 6 illumination fibres and 1 read fibre. UV-visible spectra were recorded from 250 nm to 500 nm, with a 3 ms integration time of the CCD detector. Each spectrum was the average of 100 scans and smoothed using 3 pixels. The fluoropolymer Zenith® Ultrawhite (SphereOptics) was used as the white standard (> 99% reflectance). The Ti content of the materials was measured by ICP-AES on an ICP 6500 instrument (Thermo Scientific Instrument) after dissolution of the samples by sodium peroxide fusion. XPS experiments were carried out using an SSX 100/206 spectrometer (Surface Science Instruments, USA) with Al-Kα radiation operated at 10 kV and 20 mA. The C-(C, H) component of the C1s peak of carbon has been fixed to 284.8 eV to set the binding energy scale [33]. The quantification of Ti in Ti–O–Si and Ti–O–Ti was based on the decomposition of the 2p3/2 peak at approximately 460.0 and 458.5 eV, respectively [34,35]. Si was quantified on the basis of the Si 2p peak at 103.5 eV. FT-IR spectra were collected in the ATR mode using an Equinox 55 spectrometer (Bruker) equipped with a Platinum ATR cell. The spectra were recorded between 4000 and 800 cm⁻¹ with a resolution of 2 cm⁻¹. Each spectrum was the average of 100 scans. The organic content was determined by temperature-programmed oxidation (TPO) experiments carried out with a CATLAB-PCS (Hiden Analytical) instrument connected to a mass spectrometer. m/z = 15, 28, 29 and 44 were detected throughout the temperature program starting from 40°C to a final temperature of 800°C at a rate of 10°C/min. Surface hydrophobicity was evaluated from a water adsorption experiment by measuring the amount of water desorbed at 150°C under vacuum after 24 h storage in a humid environment [31].

The catalytic properties were investigated for the epoxidation of cyclohexene with hydrogen peroxide as the oxidizing agent. The reaction was carried out in a two-necked glass round-bottomed reactor at 60°C, equipped with a condenser, a magnetic stirrer and a rubber septum. In a typical run, 0.510 g (0.3 mol.l⁻¹) cyclohexene (Sigma-Aldrich, 99%), 0.092 g (0.05 mol.l⁻¹) toluene (Sigma-Aldrich, 99.7%) – used as the internal standard – and 120 mg (6 g.l⁻¹) catalyst were pre-mixed in 20 ml of AcN or AcN/H₂O 75:25 (v/v) under stirring. After 10 min, 0.136 g (0.06 mol.l⁻¹) of 30% (w/w) aqueous H₂O₂ was added and the mixture was allowed to react for 2 h. The product formation was followed by collecting aliquots at regular time intervals and by analysing them in gas chromatography, using a Varian CP-3800 chromatograph equipped with a FID detector and a capillary column (BR-5, 30 m, 0.32 mm i.d., 1.0 μm film thickness).
3. Results and discussion

The elemental analysis of the xerogels showed that the experimental Ti content was in the 5.53–6.11 at.% (95% confidence interval), and thus very close to the nominal one (6 at.%). This result demonstrates a good control over the bulk composition for all the catalysts, with a quantitative incorporation of both titanium and silicon species in the final material. However, PXRD and DRS UV-vis analysis revealed the presence of small amounts of crystalline anatase TiO$_2$ phase in all samples (see Supplementary Information, Fig. S1). The presence of extra-framework TiO$_2$ is attributed to the difference of solvolysis-condensation rates around Si and Ti centres during the gel formation.

XPS analyses were conducted in order to investigate the surface composition and the quality of the Ti dispersion at the surface (Table 1). For NHSG, the surface Ti concentration matched the bulk content, showing that the synthesis method leads to homogeneous mixed oxides. Yet the Ti surface concentration is markedly lower than the bulk concentration when MeSiCl$_3$ is used as an additional precursor in the one-pot methylation procedure (NHSG$_{0.1}$Me and NHSG$_{0.3}$Me). This indicates a lack of homogeneity, probably caused by the slower reaction rates around the methylated Si precursors, which results in Ti-richer cores and Ti-poorer surfaces.

Among the Ti detected at the surface of the catalyst by XPS, one can distinguish the fraction that is truly incorporated into the silica matrix (denoted “Ti-O-Si” in Table 1) from the fraction that is not dispersed and instead present as TiO$_2$ inclusions. The former is found at 460.0 eV and the latter is found at 458.5 eV [34,35]. In TS-1, as expected, almost all surface Ti atoms are incorporated in the well-defined crystalline titanosilicate matrix [36–38]. In the pristine NHSG catalyst, only a third of the surface Ti is in the highly dispersed form. This is consistent with the detection of small amounts of crystalline anatase by PXRD and DRS UV-vis. In the samples methylated via the one-step procedure, the amount of surface Ti is lower but the proportion of well-dispersed surface Ti atoms is higher.

N$_2$-physisorption isotherms are shown in Figure 2, along with the BJH pore size distribution. Textural data are summarized in Table 2. As expected, TS-1 solely displayed micropores and interparticular spaces which contribute to the total pore volume. In comparison, remarkably high pore volumes and surface areas were obtained by the non-hydrolytic sol-gel method. Figure 2 reveals the presence of mesopores with a distribution centred at ca. 9 nm in the pristine NHSG catalyst and in NHSG@0.3Me. On the opposite, the pore size distribution of NHSG$_{0.1}$Me shows small mesopores with diameter ca. 5 nm whereas NHSG$_{0.3}$Me does
not present any pores above \( ca. \ 3.8 \ \text{nm} \). The BET surface area is comparable for NHSG and the one-pot methylated catalysts NHSG\_0.1Me and NHSG\_0.3Me, whereas it is significantly lowered upon post-synthesis functionalization in NHSG@0.3Me (Table 2). Total pore volume is reduced by both methylation methods. The data indicate a lower impact of the post-synthesis grafting on the pore size, while decreasing both pore volume and surface area. Conversely, the one-pot methylation preserves the surface area while lowering the pore size and pore volume, which could be detrimental to the conversion of large molecules.

To probe the surface functionalization, the samples were analysed by FT-IR in ATR mode. The normalized spectra in the region 1300–900 cm\(^{-1}\) (Fig. 3) show the appearance of a vibration band at \( ca. \ 1280 \ \text{cm}^{-1} \) in NHSG\_0.1Me, NHSG\_0.3Me and NHSG@0.3Me. This band is characteristic of the Si–CH\(_3\) stretching vibration (\( \nu(\text{Si–CH}_3) \)) [39] and confirms the successful grafting of –CH\(_3\) moieties in all the samples. The spectrum of NHSG@0.3Me displays a reduction of the Si–O\(^-\) stretching vibration band (\( \nu(\text{Si–O}^-) \)) at \( ca. \ 950 \ \text{cm}^{-1} \). Since this region is governed by the absorption of both Si–O–Ti and Si–OH groups [20,40], this observation evidences the grafting of the methyl groups through condensation reactions with surface silanols.

The methyl content as well as the surface polarity have been approached by TPO and thermal analysis, respectively (Table 3). Crystalline TS-1 is classically more hydrophobic than amorphous xerogels [41]. This verifies in our study as TS-1 indeed demonstrated a lower amount of adsorbed water than for NHSG (Table 3). As expected, the presence of methyl groups correlated with a substantial decrease in the amount of water adsorbed on the solids, i.e. the higher the amount of methyl groups, the lower the adsorption of water. Interestingly, the NHSG\_0.1Me and NHSG@0.3Me samples – prepared by different methods – appear to have a similar –CH\(_3\) content and surface polarity.

The catalysts were tested in the epoxidation of cyclohexene at 60°C, first in AcN to verify their intrinsic epoxidation activity and then in an AcN/H\(_2\)O mixture (75:25 (v/v)) to test their resistance against water (Table 4). A hot filtration test was carried out in AcN/H\(_2\)O 75:25 (v/v), confirming that all the catalytic activity was attributable to the solid material (see Supplementary Information, Fig. S2).

NHSG exhibits almost the same performances as the reference catalyst TS-1 in acetonitrile (Entries 1 and 2). Epoxide ring opening occurs to a moderate extent, as shown by a high Epox./Diol value (81–84%), which is typically obtained when an aqueous solution of H\(_2\)O\(_2\) is used as the oxidant [31]. When the AcN/H\(_2\)O mixture was used as the solvent, TS-1 and NHSG catalysts behave very differently. On the one hand, the overall yield of TS-1 was barely affected
(Entry 3), albeit the production of diol increased at the expense of the epoxide. This is expected in the presence of higher amount of H$_2$O which favours epoxide ring opening. On the other hand, a drastic loss of activity was observed for the NHSG catalyst (Entry 4). In that case, both the overall product yield and the epoxide yield are low; the epoxide yield drops to 2.1% only. The % DE/AO value is approximately 50%, which is an indication that only the allylic oxidation routes is active and contributes to the formation of the epoxide [28].

This is attributed to the role played by water in the mechanism of direct epoxidation, as schematized in Figure 4. When H$_2$O adsorbs on the Ti active site, it hydrolyses one siloxane bridge, allowing titanium to release its internal tension by changing the coordination sphere from a tetrahedral to an octahedral configuration [22,42]. Classically, the coordination of a H$_2$O$_2$ molecule subsequently leads to the formation of the activated intermediate (i.e. Ti–OOH) that in turn oxidises the olefin via the direct epoxidation mechanism [36–38]. However, in amorphous materials such as NHSG, the system can undergo a second hydrolysis step that inactivates the complex and so prevents direct epoxidation. In crystalline TS-1, the formation of the inactive complex is hampered by the stable tripodal anchoring that maintains Ti–OOH in its activated form [22]; the latter is therefore available for direct epoxidation in the presence of the olefin. This partly explains the good performance of TS-1 even in the presence of water (Entry 3).

Nevertheless, it has been shown that tripodal Ti sites somehow favour the homolytic cleavage of the O–O bond of hydrogen peroxide compared to tetrahedral sites, thus leading to the formation of cyclohexenyl hydroperoxide (chhp, see Fig. 1) [27]. This explains the lower % H$_2$O$_2$ values for the catalysts tested in the presence of water, including TS-1, compared to acetonitrile.

The attractive performances of TS-1 in a water-containing medium, however, are also generally ascribed to the intrinsic hydrophobicity of this material [23]. On the one hand, hydrophobicity decreases the rate for epoxide ring opening, affecting positively the % Epox./Diol value [30,31]. On the other hand, the unwanted allylic oxidation is known to be favoured by a high H$_2$O$_2$/Ti ratio (where “Ti” represents the amount of available Ti sites at the surface of the catalyst) [26,28,29]. Surface hydrophobicity provokes the repelling of H$_2$O$_2$ molecules from the surface thereby decreasing locally the H$_2$O$_2$/Ti ratio close to the active sites. This is proposed to explain the relatively high DE/AO values obtained with TS-1. Nevertheless, TS-1 is microporous, which limits its value in a range of potential applications.

Consistent with the foregoing, we aimed at stabilizing the mesoporous but amorphous NHSG catalysts by tuning surface hydrophobicity. The idea is to benefit from the advantageous
open texture, while maintaining decent activity for the direct epoxidation in the presence of water (Entries 5-7, Table 4).

Despite its increased surface hydrophobicity, NHSG_0.1Me showed poor catalytic performance in AcN/H2O (Entry 6), similar to the pristine NHSG. A possible explanation is linked to the low concentration of dispersed surface Ti sites on the catalyst, resulting in a high H2O2/Ti ratio (45.4 for NHSG_0.1Me vs. 29.1 for NHSG). Possibly, the beneficial effect of surface hydrophobicity is counter-balanced by lower surface concentration of dispersed Ti. The coverage of some Ti species by methyl groups during the gel formation is another possible assumption to explain the reduction of the amount of available active sites in consequence of the steric hindrance. The situation is even worse for NHSG_0.3Me which has a three times higher methyl content; this catalyst was totally inactive (Table 3).

Compared to the pristine catalyst, NHSG@0.3Me shows the same total conversion (~13%) but a significant improvement in the epoxide yield (5.1% vs. 2.1% for the pristine NHSG catalyst). This is related to an increase in the % DE/AO value up to 77% and in the % Epox./Diol value with 48% of non-hydrolysed products (versus 28% for NHSG). As the yields of other co-products hardly varied, this result is a strong evidence of the re-activation of the direct epoxidation route. Since NHSG@0.3Me and NHSG have the same concentration of dispersed Ti surface sites, the overall H2O2/Ti ratio is the same. Thus, we attribute the amelioration of the production of epoxide on NHSG@0.3Me to the repelling of H2O and H2O2 molecules from the methyl-grafted surface and so to the stabilization of the active sites for the direct epoxidation route.

4. Conclusions

Titanosilicates prepared by the NHSG method present high surface areas and pore volumes, combined with the presence of large mesopores which makes them very attractive for the conversion of bulky olefins such as cyclohexene. While highly active in organic solvent (AcN), the catalysts showed poor epoxidation activity in the presence of water. In those conditions, only the unwanted radical allylic oxidation route is active. In an attempt to restore the epoxidation efficiency of such amorphous catalyst, we proposed to increase their surface hydrophobicity.

Methyl groups were successfully incorporated in the xerogels, in one-pot, and this was shown to increase the surface hydrophobicity. However, these catalysts suffered from a lack of homogeneity, which resulted in a lower concentration of surface active sites. In the presence of water, the epoxide yield remained very low. Methylation by post-grafting, on the other hand,
allowed to significantly restore the direct epoxidation mechanism in the presence of water. In this case, the concentration of active sites remained the same and the surface hydrophobicity appears to protect the active site from the inactivating effect of water.

This study gives promising insights into the understanding of the role played by water on the performances of amorphous TiO$_2$–SiO$_2$ and opens the way to the use of these materials for the conversion of larger molecules in the presence of water or in aqueous solutions.

5. Acknowledgments

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References


Figure 1. Reaction scheme for the epoxidation of cyclohexene via the *allylic oxidation* (up) or the *direct epoxidation* routes (bottom) [26].

Figure 2. $N_2$ adsorption-desorption isotherms of the catalysts. Pore size distributions (PSD) based on the desorption branch are shown in inset.
Figure 3. Normalized FT-IR spectra (ATR) of the methylated samples relative to the unmodified catalyst.

Figure 4. Mechanism of the inactivation of amorphous titanosilicate epoxidation catalysts in the presence of water.
Table 1. Atomic percentage of Ti species in the catalysts (bulk composition, ICP-AES) and at the catalysts surface (from XPS)

<table>
<thead>
<tr>
<th></th>
<th>Bulk Ti at.% a</th>
<th>Surface Ti at.%</th>
<th>Surface Ti-O-Si at.%</th>
<th>% Ti-Si b</th>
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<tbody>
<tr>
<td>TS-1</td>
<td>2</td>
<td>0.9</td>
<td>0.8</td>
<td>89</td>
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<tr>
<td>NHSG c</td>
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<td>1.9</td>
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<td>1.3</td>
<td>76</td>
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<tr>
<td>NHSG_0.3Me</td>
<td>6</td>
<td>0.9</td>
<td>0.8</td>
<td>89</td>
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</tbody>
</table>

a Nominal composition
b % Ti–Si = Surface at. % Ti–O–Si / Surface at. % Ti
c Two-step methylation (NHSG@0.3Me) did not affect the Ti quantification in bulk or at the surface

Table 2. Textural properties of the pristine and surface modified catalysts compared to the reference material TS-1

<table>
<thead>
<tr>
<th></th>
<th>S_{BET} \text{ (m}^2\text{.g}^{-1})</th>
<th>V_p \text{ (cm}^3\text{.g}^{-1}) a</th>
<th>V_{μ} \text{ (cm}^3\text{.g}^{-1}) b</th>
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<tr>
<td>TS-1</td>
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<td>0.11</td>
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<tr>
<td>NHSG</td>
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<tr>
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<tr>
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<td>–</td>
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<tr>
<td>NHSG_0.3Me</td>
<td>940</td>
<td>0.49</td>
<td>–</td>
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</tbody>
</table>

a Measured at P/P_0 max
b Micropore volume calculated from the t-plot
Table 3. Surface composition and water adsorptive properties of the pristine and surface modified catalysts compared to the reference material TS-1

<table>
<thead>
<tr>
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<th>–CH₃ (μmol.m⁻²)</th>
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<tr>
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<tr>
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Table 4. Results for cyclohexene epoxidation at 60°C (2 h) with 30% (w/w) aqueous H₂O₂ [29,43]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Catalyst</th>
<th>H₂O₂/Ti&lt;sup&gt;b&lt;/sup&gt;</th>
<th>% Yield&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Epoxide</th>
<th>Diol</th>
<th>Alcohol</th>
<th>Ketone&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Overall&lt;sup&gt;d&lt;/sup&gt;</th>
<th>% H₂O₂&lt;sup&gt;e&lt;/sup&gt;</th>
<th>% Epox./Diol&lt;sup&gt;f&lt;/sup&gt;</th>
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<td>4.8(1.5)</td>
<td>13.0(1.2)</td>
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<td>28(11)</td>
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<sup>a</sup> H₂O₂ is the limiting reagent. Yield for product i is defined as the ratio “amount of product i / amount of H₂O₂ introduced”

<sup>b</sup> Initial mol H₂O₂/mol Ti (deduced from “Surface at. % Ti –O–Si”, Table 1)

<sup>c</sup> This value takes into account the ketone produced by the radical mechanism as well as the possible minor contribution of the decomposition of chhp in the chromatograph injector

<sup>d</sup> Values do not take into account the presence of chhp (not quantified)

<sup>e</sup> % H₂O₂ is defined as the selectivity to oxidation products (excl. chhp); values identified with “*” are associated with a cyclohexene conversion higher than the maximal amount of H₂O₂ due to the role of O₂ as alternative initiator of the radical mechanism

<sup>f</sup> % Epox./Diol = Epoxide/Diol

<sup>g</sup> % DE/AO = (Epoxide + Diol)/(Alcohol + Ketone + Epoxide + Diol)

<sup>h</sup> Averaged on four identical tests; standard deviations are given in brackets
Additional figures

**Figure S1.** a) DRS UV-visible spectra of the catalysts TS-1, NHSG and NHSG_0.3Me. The spectra of NHSG and NHSG_0.3Me reveal the presence of anatase with a characteristic absorption band centered around 330nm depicted by the position of the arrow. b) PXRD patterns of the catalysts NHSG and NHSG_0.3Me. The presence of extra-framework TiO$_2$ anatase is evidenced by the characteristic peaks shown on the diffractogram of NHSG_0.3Me.

**Figure S2.** Leaching test on the catalyst NHSG. The kinetic data for the conversion of cyclohexene in AcN/H$_2$O 75:25 (v/v) are first collected for 2h (solid line). Then, the catalyst is removed from the reaction medium by hot filtration and the reaction followed for further 3h (dashed line). Experimental conditions: $T = 60^\circ$C, [CATA] = 6 g.l$^{-1}$, [Allyl alcohol] = 0.3 mol.l$^{-1}$, [H$_2$O$_2$] = 0.06 mol.l$^{-1}$. 