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### Hydrophobic titania-silica mixed oxides for the catalytic epoxidation of cyclooctene

Lucia E. Manangon-Perugachi<sup>a</sup>, Alvise Vivian<sup>b</sup>, Pierre Eloy<sup>a</sup>, Damien P. Debecker<sup>a</sup>, Carmela Aprile<sup>b</sup> and Eric M. Gaigneaux<sup>a</sup>\*

<sup>a</sup>Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, Place Louis Pasteur 1, box L4.01.09, 1348 Louvain-la-Neuve, Belgium

<sup>b</sup>Unit of Nanomaterial Chemistry, Department of Chemistry, University of Namur, Namur, Belgium \*corresponding author: eric.gaigneaux@uclouvain.be

#### **Graphical abstract**



#### Highlights

- Successful synthesis of hydrophobic TiO<sub>2</sub>-SiO<sub>2</sub> catalysts by one-pot sol-gel procedure.
- Hydrophobic TiO<sub>2</sub>-SiO<sub>2</sub> catalysts contain framework Ti species.
- Hydrophobic TiO<sub>2</sub>-SiO<sub>2</sub> catalysts performed better than hydrophilic TiO<sub>2</sub>-SiO<sub>2</sub>.
- An optimal methyl-functionalization degree improves the catalyst performance.

#### Abstract

Titania-silica (TiO<sub>2</sub>-SiO<sub>2</sub>) mixed oxides are known catalysts for the epoxidation of olefins. It has been demonstrated that their active sites consist in isolated framework Ti atoms. However, the latter species are only obtained when Ti loading is low, limiting the number of active sites and the catalytic performances. Thus, the need to search other approaches to boost them. We succeeded improving the catalytic activity of TiO<sub>2</sub>-SiO<sub>2</sub> mixed oxides in the epoxidation of cyclooctene with hydrogen peroxide by introducing hydrophobic organic moieties at their surface. Hydrophobic TiO<sub>2</sub>-SiO<sub>2</sub> mixed oxides were prepared through a one-pot sol-gel method. Titanium butoxide (TiBut) and tetraethoxy silane (TEOS) were used as the Ti and Si precursors respectively. Hydrophobization was achieved by substituting a fraction of TEOS in the synthesis by methyltriethoxy silane (MTES). The characterization of the Ti species was performed by FTIR, DRUV, and XPS, confirming the presence of significant amount of the active framework Ti. The methylation degree was evaluated by Solid State <sup>29</sup>Si-NMR and TGA-MS. Hydrophobic TiO<sub>2</sub>-SiO<sub>2</sub> performed better in the epoxidation reaction than a fully inorganic more hydrophilic TiO<sub>2</sub>-SiO<sub>2</sub> prepared without MTES. A too high methylation degree of the catalysts is however detrimental. Our contribution allows elucidating the debate in literature about the consequence of hydrophobization of epoxidation catalysts on their performance.

#### **Keywords**

Olefin epoxidation ; TiO<sub>2</sub>-SiO<sub>2</sub> mixed oxide ; One-pot hydrolytic sol-gel ; Methyl-functionalization ; Surface hydrophobicity ; Framework-Titanium

#### 1. Introduction

Epoxides are key molecules in many important organic transformation reactions. They are widely used in industry for manufacturing of a variety of valuable products ranging from perfumery chemicals to polymeric materials [1, 2]. Titania-silica (TiO<sub>2</sub>-SiO<sub>2</sub>) materials are widely used as catalysts for multiple reactions due to their high activity; for example they are common catalysts for isomerization of olefins, dehydration of alcohols, and selective oxidation [2,

3]. Titania-silica (TiO<sub>2</sub>-SiO<sub>2</sub>) mixed oxides are also well-known catalysts for the epoxidation of olefins, and it has been demonstrated that their active sites are isolated framework Ti atoms [1-9]. However, such active Ti species are only obtained at low Ti loadings, which limits the number of active sites and the corresponding catalytic performances. Thus the need to search other approaches to boost them. In most cases, researchers have explored the possibility to improve the epoxidation performance of the titania-silica system via an increase of the number of active Ti sites using innovative synthetic methods [10-12]. Attempts to boost catalytic activity via alternative ways, such as modification of reaction conditions or modification of catalyst hydrophobicity are much scarcer.

Some studies indeed found that depending on the catalyst structure, the hydrophobicity changes accordingly, affecting the activity and selectivity of Ti-silicalites. For example, the crystallinity of the defect-free TS-1 makes it more hydrophobic than Ti-Beta and Ti-MWW, which improves its catalytic behavior [13-15]. Figueras and Kochkar achieved higher epoxide yields with hydrophobic TiO<sub>2</sub>-SiO<sub>2</sub> in the epoxidation of cyclohexene with tert-butyl hydroperoxide (t-BHP) [16, 17] and Müller *et al.* found higher selectivity in the epoxidation of cyclohexenol with t-BHP using hydrophobic TiO<sub>2</sub>-SiO<sub>2</sub> [18, 19]. Klein *et al.* found higher activity for hydrophobic TiO<sub>2</sub>-SiO<sub>2</sub> mixed oxides in the epoxidation of cyclohexene with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) [20, 21]. Lin *et al.* also found improved catalytic behavior in the epoxidation of cyclohexene with both t-BHP and H<sub>2</sub>O<sub>2</sub> for hydrophobic Ti-containing silicates [22], and Brutchey *et al.* achieved higher yields in the epoxidation of cyclohexene with H<sub>2</sub>O<sub>2</sub> with mesoporous Ti-silicates functionalized with alkylsilyl groups [23]. Along the same line, Smeets *et al.* showed that, in the presence of water, the hydrophobization of titanosilicates promotes a direct epoxidation mechanism leading to higher catalyst stability and higher epoxide yields [24].

However at the same time, other studies – sometimes by the same authors – consider that there is a negative effect of hydrophobization on the epoxidation of olefins [13, 18, 19, 25]. Fan *et al.* found no significant effect of hydrophobization on the epoxidation of 1-hexene and cyclohexene with  $H_2O_2$  in the presence of silvlated TS-1 as catalyst[13]. Müller *et al.* found a negative effect of hydrophobic modification on the epoxidation of 1-hexene and cyclohexene with t-BHP[18]. Fraile *et al.* (2001) also found that silanization of silica-supported Ti catalysts, which increased the hydrophobic character of their surface, had little influence on their catalytic behavior [25].

Furthermore, hydrophobization can be achieved directly (one-pot, for example via sol-gel as done here) or by postgrafting, raising the question if the debate is only observed for one-pot synthesized materials; nevertheless, the debate is also present in materials synthesized by post-grafting [13, 18, 23, 24]. Considering the contradictions found in the

literature, one can only conclude that, currently the effect of hydrophobicity is not clear at all. Likely, such effect combines with impacts coming from other parameters, such as catalyst acidity, steric and solvent effects, which were hard to address in the cited works [26]. Moreover, several studies draw conclusions based on the nominal methylation degree and/or the nominal Ti loading, which does not necessarily represent the real content of methyl moieties and the real number of active Ti species. There is thus obviously room and necessity to address the effect of hydrophobization in a rigorous manner.

In this context, this contribution aims at elucidating the effect of hydrophobization of TiO<sub>2</sub>-SiO<sub>2</sub> mixed oxides and exploring its potential in epoxidation catalysis. In an attempt to improve the catalytic activity of TiO<sub>2</sub>-SiO<sub>2</sub> mixed oxides in the epoxidation of cyclooctene with hydrogen peroxide we incorporate organic moieties that modify the hydrophobicity of their catalytic surface. We have hypothesized that such modification of the catalyst hydrophobicity could improve the catalytic performance by favoring both the adsorption of the olefins, which are hydrophobic, and the desorption of the epoxides, which are less hydrophobic.

#### 2. Experimental

#### 2.1. Catalyst synthesis

The catalysts were prepared via one-pot sol-gel since this method allows to control the Ti loading and dispersion [3]. Hydrophobization was achieved in a one-pot manner, by substituting a fraction of the standard tetraethoxy silane precursor (TEOS, Sigma-Aldrich, 98%) by a more hydrophobic one, namely methyltriethoxy silane (MTES, Sigma-Aldrich, 99%). Titanium butoxide (TiBut, Sigma-Aldrich, 97% reagent grade) was used as the Ti precursor. Precisely, 20 mL ethanol (Normapur, absolute) and 12 mL distilled water were poured to a 250-mL round-bottom three-neck flask and stirred at 750 rpm at 40 °C (using an oil bath and cooling system). TEOS and MTES were added dropwise under continuous stirring. MTES molar ratios (as defined in eq (1)) between 0.1 and 0.4 were explored. After the addition of the Si precursors, concentrated HCl (Sigma-Aldrich, 37%) was added to catalyze the hydrolysis. The Ti precursor (TiBut) was added dropwise after 25 minutes of the addition of HCl, at a nominal molar ratio of 0.025 (as defined in eq (2)). After gelation, the gel was recovered in a crystallizer and dried in air overnight. Later, the gel was dried under vacuum (300 mbar) at 140 °C for 3 hours. The dried solid was slightly grinded and calcined following a ramp from room temperature to 500 °C at 1 °C min<sup>-1</sup> and then a dwell for 3 hours at the set temperature. Finally, the

solid was removed from the furnace after cooling down for about 4 hours, and it was stored in a desiccator. Additionally, samples with only TEOS and only TiBut were prepared following a similar procedure as described above to obtain silica (SiO<sub>2</sub>) and titania (TiO<sub>2</sub>) as reference materials. The whole synthetic protocol is summarized on Scheme 1.

$$Molar \ ratio_{MTES} = \frac{mol_{MTES}}{mol_{TEOS} + mol_{TiBut} + mol_{MTES}}$$
(1)  

$$Molar \ ratio_{TiBut} = \frac{mol_{TiBut}}{mol_{TEOS} + mol_{TiBut} + mol_{MTES}}$$
(2)  

$$\int \int Gelation \int Ge$$

Scheme 1. Representation of the sol-gel synthesis method

#### 2.2. Characterization techniques

Solid State <sup>29</sup>Si magic angle spinning nuclear magnetic resonance (<sup>29</sup>Si-MAS-NMR) spectra were recorded at room temperature on a Bruker Avance-500 spectrometer operating at 11.7 T (99.3 MHz for <sup>29</sup>Si) using a 4 mm cross polarization-magic angle spinning (CP-MAS) Bruker probe. The sample was packed in a 4 mm zirconia rotor (around 100 mg) and measured with a spinning frequency of 8000 Hz. Direct excitation-magic angle spinning (DE-MAS) <sup>29</sup>Si spectra were recorded using the following acquisition parameters: 300 s relaxation delay, 3 µs (90°) excitation pulse, 52 ms acquisition time. CP-MAS spectra were recorded using a 5 s relaxation delay and 5 ms contact time. The processing comprised exponential multiplication of the free induction decay (FID) with a line broadening factor of 30 Hz, zero-filling, Fourier transform, phase and baseline corrections performed on the Bruker TopSpin v2.1 software. The chemical shifts were calibrated with respect to tetramethylsilane (fixed at 0 ppm). Thermogravimetric analysis

(TGA-MS) was performed in a Mettler Toledo TGA/SDTA 851 apparatus. The samples were analyzed by different methods. A typical method was a ramp from 30 °C to 900 °C at 10 °C min<sup>-1</sup> under air flow (50 mL min<sup>-1</sup>, 80% N<sub>2</sub> and 20% O<sub>2</sub>, Air Liquide). Temperature Programmed experiments were performed using a Catlab-PCS Hiden Analytical equipped with a QGA mass spectrometer with 70 mg of catalyst. A typical temperature program applied is i) plateau at 40 °C under air (30 mL min<sup>-1</sup>) for 10 minutes; ii) heating to 800 °C at 5 °C min<sup>-1</sup> under air flow (30 mL min<sup>-1</sup>). Followed mass to charge ratios were: 2 (H<sub>2</sub>), 15 (CH<sub>3</sub>), 17 and 18 (H<sub>2</sub>O), 28 (N<sub>2</sub>), 29 (methanol), 31 (ethanol), 40 (Ar), 44 (CO<sub>2</sub>) and 56 (butanol). To determine the real amount of Ti loading, the titania-silica samples were analyzed by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). The samples were calcined at 550 °C to remove the organic matter and then were decomposed by sodium peroxide fusion in carbon crucibles. The instrument was an ICAP 6500 from Thermo Scientific. Fourier transform infrared spectroscopy (FTIR) was used in transmission and attenuated reflectance modes using an IFS55 Equinox spectrometer (Bruker) equipped with a DTGS detector. The spectra were obtained by recording 100 scans in the range from 400 to 4000 cm<sup>-1</sup> with a 4 cm<sup>-1</sup> resolution. For transmission mode, wafers were prepared by diluting the sample in KBr (Janssens Chimica,  $\geq$ 99%) with a 2.5 % dilution factor. The spectra were analyzed using the software OPUS. X-ray diffraction (XRD) measurements on solid samples were performed with a Siemens D5000 diffractometer using the K $\alpha$  radiation of Cu ( $\lambda$ =1.5418 Å). The small 2 $\theta$  range (10 – 80°) was recorded at a rate of 0.01° s<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) analyses were performed on a SSX 100/206 photoelectron spectrometer from Surface Science Instruments (USA) equipped with a monochromatized micro focused AI X-ray source (powered at 20 mA and 10 kV), a 30° solid angle acceptance lens, a hemispherical analyzer and a channel plate detector. The sample powder, pressed in small stainless steel troughs of 6 mm diameter, were placed on a ceramic carousel. The pressure in the analysis chamber was around 10<sup>-6</sup> Pa. The angle between the surface normal and the axis of the analyzer lens was 55°. The analyzed area was approximately 1.4 mm<sup>2</sup> and the pass energy was set at 50 eV. In these conditions, the full width at half maximum (FWHM) of the Au 4f7/2 peak of a clean gold standard sample was about 1.1 eV. A flood gun set at 8 eV and a Ni grid placed 3 mm above the sample surface were used for charge stabilization. The following sequence of spectra were recorded: survey spectrum, C 1s, O 1s, Ti 2p, Si 2p, and C 1s again to check the stability of charge compensation with time and the absence of sample degradation. The C-(C,H) component of the C 1s peak of carbon has been fixed to 284.8 eV to set the binding energy scale. Data treatment was performed with the CasaXPS program (Casa Software Ltd, UK). Some spectra were decomposed with the least squares fitting routine provided by the software with a Gaussian/Lorentzian (85/15) product function and after subtraction of a non-linear Shirley baseline. Molar fractions were calculated using peak areas normalized on the basis of acquisition

parameters and sensitivity factors provided by the manufacturer. Diffuse reflectance spectroscopy UV-Vis (DRUV) spectra were recorded in a spectral range from 200 nm to 800 nm using the Cary Win UV software package and a CARY 5000 Agilent spectrometer equipped with a Praying Mantis. A BaSO<sub>4</sub> pellet was used as a blank, and the Kubelka-Munk function F(R) was calculated using the reflectance (R). Specific surface area and pore size were determined by N<sub>2</sub> adsorption-desorption at 77 K experiments performed using a Micromeritics Tristar 3000. Before the analysis, the samples were degassed overnight under vacuum (6.7 Pa) at 150 °C. The specific surface area was calculated from the adsorption isotherm using the Brunauer-Emmet-Teller (BET) method. Having replicated some of the analysis three times, we know the uncertainty of the specific surface area is 10 %. Water vapor adsorption isotherms were acquired at 295 K, using a 3Flex instrument from Micromeritics. Before the analysis, the samples were degassed overnight under vacuum (6.7 Pa) at 180 °C.

#### 2.3. Catalytic tests

The performance of the synthesized catalysts was measured in the epoxidation of cyclooctene (Fluka, >90%) with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, Sigma-Aldrich, 30%), as defined in eq (3). The reaction temperature was 60 °C, the initial concentration of cyclooctene was 0.1 M, the initial concentration of  $H_2O_2$  was 0.5 M and the catalyst addition was 10 g L<sup>1</sup>. 8.5 mL of the solvent, acetonitrile (VWR Chemicals, >99.9%), was added to a 10-mL batch reactor immersed in an oil bath and equipped with a reflux condenser. The internal standard was dibutyl ether (DBE, TCI, >99%) and its concentration was 0.1 M. In a typical test, acetonitrile, cyclooctene, DBE and the catalyst were added to the reactor and heated to 60 °C. The reaction started when H<sub>2</sub>O<sub>2</sub> was added to the solution. The reaction time was 10 hours and 100-µL aliquots were sampled every hour with a syringe through a septum fitted to the reactor. The aliquots were diluted in acetonitrile and filtered through a 0.2 µm syringe filter. The cyclooctene and epoxy cyclooctane concentrations were measured with gas chromatography (GC). The GC instrument was a SHIMADZU GC-2010 Plus equipped with a capillary column Shimadzu SH-RTX-5 column with a Crossbondx 5% diphenyl/95%dimethyl polysiloxane composition, 30 m, 0.25 mm ID, 0.10 µm film thickness and a theoretical maximum temperature of 330 °C. The temperature program was composed of two segments: a first ramp from 60 to 100 °C at 7.5 °C min<sup>-1</sup> and a second one from 100 to 240 °C at 30 °C min<sup>-1</sup>. The temperature of the injector was 270 °C and the temperature of the FID detector was 275 °C. Helium (Praxair, quality 5.0) was used as carrier gas at flow rate of 20 mL min<sup>-1</sup>. 1-µL aliquot was injected into the GC column with a split ratio (SR) of 20. Initial reaction rates were calculated from the derivative of

the cyclooctene concentration as a function of time and the error bars were calculated based on the triplication of the

(3)

catalytic tests.



3. Results and discussion

#### 3.1. Assessing the degree of methylation and the corresponding hydrophobicity using NMR and TGA-MS

The degree of methyl-functionalization (%Me) of calcined TiO<sub>2</sub>-SiO<sub>2</sub> samples was addressed by quantitative solid state <sup>29</sup>Si magic-angle-spinning (MAS) NMR investigation. The NMR spectra are reported for all the solids in Figure 1. <sup>29</sup>Si direct excitation (DE) MAS spectra shows for all solids the presence of a broad band centered at -100 ppm, assigned to Q<sup>n</sup> contributions. The deconvolution analysis by using Gaussian functions allows to distinguish different contributions centered at -109 ppm, -100 ppm and -91 ppm which can be attributed to Q<sup>4</sup> (Si(OSi)<sub>4</sub>), Q<sup>3</sup> (Si(OSi)<sub>3</sub>OH) and Q<sup>2</sup> (Si(OSi)<sub>2</sub>(OH)<sub>2</sub>) species respectively. For methylated TiO<sub>2</sub>-SiO<sub>2</sub> samples, an additional broad signal centered at -60 ppm reveals the presence of T<sup>3</sup> (Si(OSi)<sub>3</sub>Me) and T<sup>2</sup> (Si(OSi)<sub>2</sub>(OH)Me) contributions (detailed deconvolution analysis shown in ESI). The presence of methyl moieties was confirmed also by performing cross-polarization (CP) experiments. Titania-silica samples exhibited four degrees of methylation: 0%, 1%, 5%, and 14%, determined from direct excitation NMR experiments by the following formula::  $%Me = 100 \cdot (T^{i} / \sum_{i} (Q^{i} + T^{i}))$ . As Solid State NMR provides an accurate quantification of the degree of methyl-functionalization, from now all the samples will be compared considering the effective degree of methylation found via Solid State NMR analysis. Hereafter our samples will be noted as TS-x%Me, where x represents the effective percentage of methyl-functionalization. The presence of methyl groups after the calcination at 500°C might appear surprising, but in previous studies methyl groups strongly bonded to Si have been shown to remain in the catalyst even after calcination at temperatures close to 500 °C [18, 19], which is in agreement with our observations.



Figure 1. Solid state <sup>29</sup>Si MAS NMR spectra of calcined TS-x%Me, direct excitation measurements (bottom) and cross polarization measurements (top). TS-0%Me (a), TS-1%Me (b), TS-5%Me (c), TS-14%Me (d)

TGA-MS analysis were performed mainly to evaluate the hydrophobicity of the samples (via the quantification of the physisorbed water desorbing in the low temperature range).



Figure 2. TGA analysis of calcined TS-x%Me

The totally inorganic sample (TS-0%Me, ie produced with only TEOS as Si precursor) and samples with the three increasing degrees of methylation (TS-1%Me, TS-5%Me, TS-14%Me) were analyzed. Three mass losses are observed in respectively the range 40-200 °C, the range 200-500 °C, and above 500°C (Figure 2). Reproducing in the CatLab instrument exactly the same temperature program as that applied in the TGA, MS analysis of the gases vented from the reactor along the temperature program indicates that the first mass loss is due to physisorbed water (m/z=18) (Figure 3). The second mass loss is related to low combined MS signals of water (m/z=18) and carbon dioxide (m/z=44). As this second mass loss is observed for all four samples, whatever MTES was used in their synthesis or not, it can be attributed to organic contamination frequently found in such sol-gel samples, as for example traces of precursors or solvents not totally evacuated during calcination. The mass loss above 500 °C is also related to a combined release of water (m/z=18) and carbon dioxide (m/z=44), indicating it also corresponds to a combustion event. This third mass loss is strongly displayed by the methylated samples, suggesting this thermal event is due to methyl groups coming from the use of MTES in the synthesis. However, this mass loss is also present in smaller degree in the non-methylated catalyst. In this case, the mass loss probably corresponds to the OH groups chemically bonded to the material [27]. This makes the exploitation of this third mass difficult as resulting from at least two different entangled events. Thus on the main basis of the mass losses in the lower temperature range, one can conclude (i) that our protocol aiming at the incorporation of methyl moieties in the samples was successful, and (ii) that these methylated samples are more hydrophobic (than the not methylated one) as they desorb lower contents of physisorbed water.



Figure 3. TGA-MS analysis of calcined TS-0%Me (a) and calcined TS-14%Me (b)

A more precise quantification of the mass losses corresponding to physisorbed water and methyl content was then performed (Figure 4). A valid comparison of physisorbed H<sub>2</sub>O and methyl contents among the samples must be performed after normalization to the final mass at 900 °C, which is the exact mass of the inorganic content whatever the sample. This normalization avoids the misleading interpretation that the inverse dependence of physisorbed H<sub>2</sub>O and methyl contents could have induced. The totally inorganic sample (TS-0%Me) has the highest content of physisorbed water, whereas the methylated samples display a decrease of the amount of physisorbed H<sub>2</sub>O going gradually with their increasing content of methyl groups. The evolution of the methyl content for our four samples showed a similar trend as the one observed from NMR analysis.



Figure 4. Quantification of methyl moieties and physisorbed water

The difference of physisorbed H<sub>2</sub>O content from one sample to another could be an effect of the difference of their respective surface area; so we have used N<sub>2</sub> physisorption to obtain information about the textural properties of the inorganic and methylated catalysts (Table 1). These results show that the specific surface areas vary from one sample to another in a much lesser extent than the methyl content. The difference of texture alone can thus not explain the gradual decrease of physisorbed H<sub>2</sub>O content in the methylated samples, ascertaining the effect of hydrophobization due to the methyl content.

	S <sub>BET</sub> ,	Pore	Pore size,
Sample	m²g⁻¹	Volume,	nm
		cm³g⁻¹	
TS-0%Me	550	0.28	2.5
TS-1%Me	501	0.32	3.4
TS-5%Me	445	0.31	3.3
TS-14%Me	620	0.34	2.8

Table 1. Textural properties of inorganic and methylated  $TiO_2$ -SiO<sub>2</sub>

3.2. Identification and quantification of Ti species using ICP-AES, FTIR, DRUV and XPS

ICP-AES analysis allowed quantifying the total content of Ti in our samples (Table 2). For all samples, the real amount

of Ti is very close to the nominal one (TiBut nominal molar ratio = 0.025).

Sample	Ti wt% (ICP)	Si wt% (ICP)	Ti/(Si+Ti) Molar ratio (ICP)
TS-0% Me	1.75	40.3	0.025
TS-1% Me	2.11	42.6	0.029
TS-5% Me	2.27	42.5	0.031
TS-14% Me	1.65	42.4	0.023

Table 2. ICP-AES analysis of inorganic and methylated  $TiO_2$ -SiO<sub>2</sub>



Figure 5. IR spectra of inorganic and methylated TiO<sub>2</sub>-SiO<sub>2</sub>

Previous studies revealed that the presence of Ti active species can be followed by FTIR detection of the Si-O-Ti bridge [2, 3, 6-8, 15, 28, 29]. On Figure 5, the band of Si-O-Si at 1080 cm<sup>-1</sup> can be observed. The band at 950 cm<sup>-1</sup> can be attributed to silanol groups, but it can also be attributed to the Si-O-Ti bridges [29, 30]. Additionally, the IR spectra of TS-5% Me and TS-14% Me samples showed the presence of the methyl groups bonded to silicon ( $\nu$ (Si-C)) at 1279 cm<sup>-1</sup>. Due to the low methyl content in TS-1% Me, only a faint shoulder at this wavenumber was observed for this sample.



Figure 6. DRUV spectra of inorganic and methylated TiO<sub>2</sub>-SiO<sub>2</sub>

Furthermore, diffuse reflectance UV spectroscopy was exploited to identify framework Ti (FW-Ti) in the range 200-240 nm, and extraframework Ti (EFW-Ti) in the range of 240-330 nm. DRUV also allows detecting the presence of anatase (crystalline TiO<sub>2</sub>) in the range 310-330 nm [8, 31, 32]. Inorganic and methylated TiO<sub>2</sub>-SiO<sub>2</sub> catalysts both exhibit FW-Ti and EFW-Ti species (Figure 6). It seems that the use of MTES as a synthesis co-precursor, not only modifies the surface polarity but also the catalyst structure by promoting the formation of EFW-Ti and anatase in the catalyst. Anatase was not detected by XRD analysis (shown in ESI), probably due to the very small size of anatase domains formed. Nevertheless, this structure modification might have an effect on the catalytic activity that should be considered.

XPS was performed on TiO<sub>2</sub>-SiO<sub>2</sub> catalysts to quantify the Ti surface content. Interestingly, according to literature [12, 33-37], XPS allows distinguishing and quantifying FW-Ti and EFW-Ti species. Thus, the binding energy of Ti 2p was compared among the inorganic TiO<sub>2</sub>, TiO<sub>2</sub>-SiO<sub>2</sub> and the methylated TiO<sub>2</sub>-SiO<sub>2</sub>. The Ti 2p spectrum is composed of a doublet of Ti  $2p_{3/2}$  and Ti  $2p_{1/2}$  peaks, which are separated by 5.7 eV [38]. Previous works studied the different species of Ti in titanosilicates, and they agreed that the binding energy of FW-Ti is 460.0 eV [33, 34, 36, 37]. However, the same studies have found different binding energy for EFW-Ti due to the diversity of EFW-Ti species that can be found on the catalyst surface. For example, the binding energy of Ti  $2p_{3/2}$  in pure titanium dioxide is 458.5 eV [33, 38]. Hasegawa *et al.* found that the Ti  $2p_{3/2}$  peak shows a shoulder centered at 457.8 eV, corresponding to the EFW-Ti

species in TS-1 [37], and Tyablikov *et al.* found BEs of 457.7-458.2 eV [12]; but Langerama *et al.* reported BEs of 458.4-458.9 eV for the EFW-Ti species [34]. For similar Ti loadings, the inorganic and methylated mixed oxides in our own work do not show the shoulder for Ti  $2p_{3/2}$ . However, they exhibit a peak shifting and broadening, suggesting the presence of different Ti species.

The peak decomposition of Ti 2p from our samples was therefore performed under certain constraints (Figure 7). After screening several hypotheses, the most consistent decomposition method was as follows. The binding energy of Ti  $2p_{3/2}$  can be explained as corresponding to a system containing two kinds of Ti species: FW-Ti and EFW-Ti. The FW-Ti species fall at the binding energy of 460.0 eV in agreement with the literature [33, 34, 36, 37], whereas the EFW-Ti species fall at 458.5 eV, which also agrees with previous studies [34].



Figure 7. Normalized XPS spectra of Ti 2p for inorganic and methylated TiO<sub>2</sub>-SiO<sub>2</sub>

Table 3 shows the surface elemental quantification estimated under this hypothesis. Increasing the methylation degree gradually diminishes the fraction of FW-Ti species on the surface. This corroborates the same effect of methylation that DRUV revealed on the evolution of the different Ti species population.

Sample	C (of which C-H) (mole %)	O (mole %)	Ti (of which FW-Ti) (mole %)	Si (mole %)	Ti/(Si+Ti) molar ratio	FW-Ti/(Si+Ti) molar ratio
TS-0% Me	2.2 (1.2)	67.6	0.6 (0.4)	29.6	0.020	0.014
TS-1% Me	3.1 (1.9)	70.8	0.5 (0.3)	25.6	0.018	0.013
TS-5% Me	7.5 (5.1)	66.9	0.4 (0.3)	25.1	0.017	0.011
TS-14% Me	6.6 (5.5)	68.5	0.3 (0.2)	24.7	0.011	0.009

Summarizing, by combining the results from XPS and ICP-AES, it turns out that for similar bulk Ti content, the methylated mixed oxides exhibit a lower Ti total content on their surface and also a smaller FW-Ti fraction of this total content. According to this observation, one could expect that the catalytic activity gradually decreases for the methylated samples.

### 3.3. Assessing the role of hydrophobicity on the catalytic epoxidation of cyclooctene

Inorganic and methylated catalysts were compared in the epoxidation of cyclooctene with H<sub>2</sub>O<sub>2</sub> (Figure 8). The initial reaction rates were calculated and normalized to specific surface area to better recognize an effect of hydrophobicity.



Figure 8. Initial reaction rates normalized to specific areas for inorganic and methylated  $TiO_2$ -SiO<sub>2</sub>

Hydrophobic  $TiO_2$ -SiO<sub>2</sub> with effective methyl content of 1 % and 5 % achieved higher epoxidation rates than the totally inorganic one. In this case, hydrophobization had a positive impact on the catalytic activity, which agrees with our

initial working hypothesis that the cyclooctene adsorption and the epoxide desorption are facilitated by a more hydrophobic TiO<sub>2</sub>-SiO<sub>2</sub> catalyst. However, the methylated sample with 14% as effective methyl content showed lower performance. This sounds more in line with the negative effect of methylation contrarily observed by Müller *et al.* in the epoxidation of 1-hexene and cyclohexene, where the nominal degree of methylation varied from 10 % to 30 % [18]. Conversions, yields and selectivities measured after 8 hours of reaction were compared for the inorganic and methylated samples (Table 4). Similarly to what was observed when comparing the rates, the performances of the methylated samples TS-1%Me and TS-5%Me are higher than for the purely inorganic one, and they are by far higher than the TS-14%Me sample presenting the highest methylation degree.

Table 4. Conversions, yields and selectivities after 8 hours of reaction for the inorganic and methylated catalysts

Sample	Conversion <sup>a</sup>	Yield <sup>a</sup>	Selectivity <sup>a</sup>
	(%)	(%)	(%)
TS-0% Me	38	18	47
TS-1% Me	45	25	56
TS-5% Me	48	31	65
TS-14% Me	20	6	33

<sup>a</sup>Uncertainties are ±3 % and were determined from triplicates of the catalytic tests.

At this stage, possible explanation for the loss of performance for TS-14%Me not aligning with the tendency observed for TS-0%Me to 1%Me and 5%Me could be that the methylation degree of 14% is too high, causing: i) strong adsorption of cyclooctene that stabilizes it excessively on the surface and prevents it from reacting, ii) reduced adsorption of H<sub>2</sub>O<sub>2</sub> due to the too hydrophobic catalyst character, iii) low content of FW-Ti species available at the surface that affects the catalytic activity.

Further isolating the effect of hydrophobicity required normalization to the Ti content since methylation affects not only the surface polarity but also the catalyst structure. DRUV and XPS analysis indeed showed that by increasing the methylation degree, the FW-Ti molar ratio decreases, which could be detrimental to the catalytic activity. Therefore, the catalytic activity was normalized to bulk Ti, surface Ti and surface FW-Ti, so the hydrophobicity effect can be better identified (Figure 9). The initial rate from Figure 8 was normalized to the bulk Ti molar fraction, calculated from ICP-AES, as well as to the total Ti and FW-Ti molar fractions at the surface, which were determined by XPS analysis.



Figure 9. Initial reaction rates normalized to different Ti states<sup>a</sup> in the inorganic and methylated TiO<sub>2</sub>-SiO<sub>2</sub> <sup>a</sup>The normalization was performed based on the Ti molar fraction Ti/(Ti+Si) of the different Ti species. Bulk Ti molar fraction is shown in table 2. Surface Ti and surface FW-Ti molar fractions are shown in table 3.

Figure 9 shows that the rates were higher for the 1% and 5% methyl content whatever the normalization. Actually, the trend observed in Figure 7 is reinforced by the normalization to the Ti content, which establishes that there is an optimal methylation degree that improves the catalytic performance. An excessive methylation degree seems to be detrimental to the catalytic activity, not only due to the lower FW-Ti content it induces but also to the hydrophobic character it brings. To support this hypothesis, water vapor sorption experiments were performed at 295 K for all the samples (Table 5). According to literature, the affinity of the catalyst surface with water is featured at low relative pressures of the adsorption isotherm [39, 40]. The adsorption isotherm of TS-14%Me displays a reduced affinity for water, thus a more hydrophobic character, compared to the rest of the samples. The adsorption isotherms are shown in Figure ESI3. For comparison between samples, the water uptake at a selected relative pressure ( $p/p_0= 0.1$ ) was normalized by the specific surface area (shown in table 1). These results confirm that TS-14%Me is too hydrophobic likely decreasing its affinity for H<sub>2</sub>O<sub>2</sub>.

Table 5.  $H_2O$  uptake at a relative pressure  $p/p_0=0.1$  of inorganic and methylated TiO<sub>2</sub>-SiO<sub>2</sub>

Sample	H <sub>2</sub> O uptake at p/p <sub>o</sub> =0.1, $\alpha/100q_{cat}$	H <sub>2</sub> O uptake, mg <sub>H2O</sub> m <sup>-2</sup>
TS-0%Me	<u>9.2</u>	0.17
TS-1%Me	7.1	0.14
TS-5%Me	7.6	0.17
TS-14%Me	3.6	0.06

#### 4. CONCLUSIONS

We succeeded synthesizing hydrophobic TiO<sub>2</sub>-SiO<sub>2</sub> mixed oxide catalysts through one-pot sol-gel procedure with significant amount of the active framework isolated Ti species and different degrees of hydrophobicity. The effective methylation degree and the content of active Ti species were quantified thanks to a combination of multiple analytical techniques, which made possible to isolate the hydrophobic effect on the catalytic epoxidation performance. Increasing the degree of methyl-functionalization during synthesis was detrimental to the formation of framework Ti in the catalyst. Nevertheless, hydrophobic TiO<sub>2</sub>-SiO<sub>2</sub> performed much better in the epoxidation of cyclooctene with hydrogen peroxide than inorganic more hydrophilic TiO<sub>2</sub>-SiO<sub>2</sub>. However, this tendency only verifies at low methylation degree and thus hydrophobicity. Too high degree of methylation and thus hydrophobicity led to diminished catalyst performance, likely due to a too low affinity of H<sub>2</sub>O<sub>2</sub> with the too hydrophobic catalytic surface, as proved by water vapor sorption experiments.

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