Université catholique de Louvain

Faculty of Bioscience Engineering

Hydrophobized Ti-SiO₂ catalysts for the liquid phase epoxidation of olefins

Thèse présentée en vue de l'obtention du grade de docteur en sciences agronomiques et ingénierie biologique

By Lucia E. Manangon-Perugachi

Supervisor: Prof. Eric Gaigneaux Co-supervisor: Prof. Damien Debecker

March 2023

Composition du Jury:

Président:	Prof. Yann Garcia (UCLouvain)	
Promoteur:	Prof. Eric M. Gaigneaux (UCLouvain)	
Co-promoteur:	Prof. Damien Debecker (UCLouvain)	
Lecteurs:	Prof. Patricia Luis Alconero (UCLouvain), secretary	
	Prof. Carmela Aprile (UNamur)	
	Prof. Pegie Cool (UAntwerp)	
	Prof. Paolo Pescarmona (University of Groningen, NL)	

A mis padres.

Acknowledgements

Tout d'abord, je voudrais remercier mon promoteur, le professeur Eric Gaigneaux. Il m'a ouvert les portes du laboratoire de catalyse et m'a donné l'opportunité d'apprendre la catalyse hétérogène. J'apprécie votre patience et votre soutien tout au long de la réalisation de cette thèse. Merci de croire dans les capacités des étudiants équatoriens Vous êtes le catalyseur qui accélère l'amélioration de l'éducation en Equateur.

Merci également à Professor Debecker, le co-promoteur de cette thèse. Il a eu toujours des excellents conseils scientifiques et des mots d'encouragement. Je remercie aussi aux membres de mon comité d'accompagnement, les Professeurs Carmela Aprile et Michel Devillers. Particularly, I would like to thank Professor Aprile as well as Luca Fusaro and Alvise Vivian for their collaboration with the solidstate NMR analyses.

I also thank Professors Patricia Luis Alconero, Carmela Aprile, Pegie Cool, Paolo Pescarmona and Yann Garcia for being part of this doctoral committee, for their time invested in reviewing this work, and for your valuable feedback.

I would like to acknowledge the collaboration to this work from Institute Paul Lambin and UCLouvain students through their rapport de stage and mémoire: Vincent Demesmacre, Charles Cassou-Mounat and Corentin Dubois.

Deseo agradecer a mis padres, quienes son un ejemplo de fortaleza y bondad, quienes me enseñaron que el esfuerzo y la educación son el camino para alcanzar mis sueños. Vengo de una familia humilde pero muy trabajadora que siempre me ha motivado a dar lo mejor de mi. Agradezco a mi tía y mi prima que viven en Roma, con quienes pude disfrutar del aire familiar durante mi estadía en Europa. Agradezco a mi hermano Pedrito, abuelita, tías, tíos, primas y primos por el apoyo familiar.

Agradezco a mis mentores, la Dra. Alicia Guevara y el Dr. Ernesto de la Torre. Mi vida cambió desde el momento en que me uní al Departamento de Metalurgia Extractiva. Ellos me han motivado y apoyado desde que me conocieron cuando era estudiante de pregrado.

Life during the PhD was a learning experience not only in the academic field, but also in the cultural and personal aspects. For this, I would like

to thank all the colleagues and great researchers I met during my four years in the lab at UCLouvain: Ara, Anna, Chiara, Ludivine, Josefine, Solène, William, Ramesh, Palraj, Vijay, Yaqi, Gabriel, Isaac, Charlotte, Arnaud, Paulina, Weiyi, Aleš, Itika, Valeria, Margot, Sebastian and Valentin. En particulier, je tiens à remercier Valentin pour les conseils par rapport à l'utilisation du system aerosol. Un merci spécial aussi a mes amies Solène et Charlotte avec qui j'ai eu des chouettes conversations et voyages.

Merci au personnel du laboratoire pour tout l'expertise technique, scientifique et logistique : Françoise Somers, Pierre Eloy, François Devred, Nathalie Blangenois, et Audrey Dejean. Je voudrais remecier aussi à Anne Iserentant. Elle est une grande amie des étudiants équatoriens. Merci pour tout.

I have no words to thank my dear friends Eva, Aga and Carlitos. They were my family in Belgium, and my source of strength and fun. They were there for the movings, the health issues, the good and the bad times. We shared many great moments and I just hope our friendship will last beyond distance and time. Gracias querido Isaac por tu amistad, apoyo y enseñanzas durante la realización de esta tesis. Gracias a tu familia, Nathie y Emilio, ustedes han sido un pedacito de Ecuador en Bélgica y esto ha sido muy importante para mi. Gracias queridos amigos!!

During my stay in Belgium, I met great people and friends outside of the Catalysis field, with whom I shared important moments: Sabrina, Lena (thank you for sharing with me these last steps of the PhD), Yenny, Anita, Cyrille, Fabian, Marinho, Pablo, José, Louise, Anne Marie, Yoly, Elena. Gracias a Dianita y Mari, amigas ecuatorianas que conocí en Bélgica y que me ofrecieron su apoyo en momentos difíciles.

Feri y Cari, amigas queridas, ustedes fueron un apoyo gigante durante el periodo de escritura de esta tesis. Gracias totales!

A mis queridos colegas del DEMEX, quienes más que colegas, son mi segunda familia: Eve, Dianita, Carlitos, Sra. Verito, Eddy, Dra. Diaz, Kleberito, Sra. Betty, Wilmerito. Gracias por el cariño y apoyo. Mi Eve querida, gracias por tu amistad y companía. Gracias a todos los estudiantes y profesores que han formado y forman parte del gran DEMEX.

A mi regreso a Ecuador, pude conocer a Anibelen, estudiante de maestría, quien se arriesgó a trabajar y colaborar conmigo en mis primeros proyectos de investigación en Ecuador. Gracias por tu colaboración y sobre todo por tu amistad.

Currently, I am an assistant professor in Escuela Politecnica Nacional in Ecuador and I want to thank all my students who have motivated me to continue my preparation in the field of heterogeneous catalysis. I look forward to being part of the growing research in this field in my country and to strengthening the collaborations with UCLouvain.

Finally, I thank Escuela Politécnica Nacional, a public university, who gave me a special license and economic support to pursue my doctoral studies abroad. I acknowledge Secretaría de Educación Superior, Ciencia Tecnología e Innovación (Senescyt) and IFTH, governmental institutions in Ecuador, for my PhD grant. I would like to thank as well the 'Communauté française de Belgique' for the financial support for this work through the ARC programme.

Abstract

Titanosilicates (Ti-SiO₂) are well-known catalysts for the epoxidation of olefins. Isolated Ti inserted in tetrahedral coordination of the silica framework are the active species. The present thesis proposes the hydrophobization of Ti-SiO₂ by organic-functionalization in a one-pot manner as a strategy to boost the catalytic performance in the epoxidation of olefins in liquid phase. First, the synthesis conditions, such as precursor type and molar ratios were optimized to obtain hydrophobic Ti-SiO₂ catalysts via one-pot sol-gel procedure. Methvlfunctionalized Ti-SiO₂ were active, but a positive effect on the catalytic activity could not be totally attributed to hydrophobicity. Second, hydrophobic Ti-SiO₂ were produced under the optimized conditions and displayed better performance in the epoxidation reaction than the pristine analogous except at high degrees of methyl-functionalization. Third, the Ti molar ratio was further tuned to prevent the loss of active Ti sites due to methylfunctionalization. However. adjusting the hydrophobic/hydrophilic balance via a one-pot classical sol-gel generally led to detrimental decrease of the Ti dispersion and/or collapse of the pore network. Therefore, mesoporous Ti-SiO₂ were synthesized by aerosol-assisted one-pot sol-gel to control the number of Ti active sites, degree of methyl-functionalization, and textural properties simultaneously. These materials exhibited positive effect of adjusting а the hydrophobic/hydrophilic balance on their performance as epoxidation catalysts.

TABLE OF CONTENTS

General Introduction	1
1. Research context	
2. Generalities about titanosilicates	5
3. Epoxidation of olefins over titanosilicates	7
4. Hydrophobization of titanosilicates	9
4.1 Methodologies to hydrophobize titanosilication	ates9
4.2. Characterization of hydrophobicity in titar	າosilicates 11
4.3. Review on the catalytic epoxidation perfond hydrophobized titanosilicates	ormance of 17
5. Objectives and strategy	
6. Structure of the thesis	22
Naterials and Methods	
1. Catalyst synthesis	27
1.1 Classical one-pot sol-gel synthesis proced	dure 27
1.2 Aerosol assisted one-pot sol-gel	27
2. Catalyst characterization	
3. Catalytic tests	
CHAPTER 1: Optimizing the conditions toward SiO₂ catalysts via one-pot sol-gel chemistry	s hydrophobic Ti- 35
Abstract	
1.1. Introduction	
1.2. Experimental section	
1.2.1 One-pot sol-gel synthesis procedure of functionalized SiO ₂ , Ti-SiO ₂ , methyl-, propyl- a functionalized Ti-SiO ₂	methyl- and octyl- 36
1.2.2. Catalyst characterization	

1.2.3. Catalytic tests	38
1.3. Results and discussion	39
1.3.1. One-pot sol-gel synthesis of methyl-functionalized SiO_2 and Ti-SiO_2	39
1.3.2. One-pot sol-gel synthesis of methyl-, propyl-, and octyl- functionalized Ti-SiO ₂	43
1.3.3. Synthesis and characterization of methyl-functionalized SiO ₂	Гі- 44
1.4. Conclusions	68

	Abstract	73
	2.1. Introduction	73
	2.2. Experimental section	74
	2.2.1 One-pot sol-gel synthesis towards methyl-functionalized SiO ₂	Ti- 74
	2.2.2. Catalyst characterization	76
	2.2.3. Catalytic tests	78
	2.3. Results and discussion	79
	2.3.1. Assessing the degree of methyl-functionalization and the corresponding hydrophobicity using NMR and TGA-MS	e . 79
	2.3.2. Identification and quantification of Ti species using ICP- AES, FTIR, DRUV and XPS	. 84
	2.3.3. Assessing the role of hydrophobicity on the catalytic epoxidation of cyclooctene with hydrogen peroxide as oxidant.	89
	2.4. Conclusions	94
C fu c	HAPTER 3: Optimizing the Ti molar ratio in methyl- Inctionalized Ti-SiO₂ catalysts for the epoxidation of yclooctene with tert-butyl hydroperoxide	97
	Abstract	97
	3.1. Introduction	97

3.2. Experimental section
3.2.1 One-pot sol-gel synthesis towards methyl-functionalized Ti-SiO $_2$
3.2.2. Catalyst characterization
3.2.3. Catalytic tests 100
3.3. Results and discussion 102
3.3.1. Optimizing the calcination temperature
3.3.2. Assessing the degree of methyl-functionalization and the corresponding hydrophobicity
3.3.3. Identification and quantification of Ti species 111
3.3.4. Assessing the role of hydrophobicity on the catalytic epoxidation of cyclooctene with tert-butyl hydroperoxide as
oxidant 114
3.3.5. Leaching tests and recyclability evaluation 116
3.4. Conclusions 122

Abstract 12
4.1. Introduction 12
4.2. Experimental section 12
4.2.1 One-pot aerosol-assisted sol-gel synthesis towards methy functionalized Ti-SiO ₂ 12
4.2.2. Catalyst characterization13
4.2.3. Catalytic tests13
4.3. Results and discussion13
4.3.1. Assessing the degree of methyl-functionalization and
4.3.2. Quantification of Ti dispersion
4.3.3. Catalytic performance of hydrophobic mesoporous Ti-SiO on the epoxidation of cyclooctene
4.4. Conclusions 15

General Conclusions and Future Work	153
Appendix	159
References	171
Publications	187

General Introduction

1. Research context

Catalysis plays an important role in sustainable chemistry since it has demonstrated to make processes more efficient in the use of energy and resources [1]. This has led to the development of the area of green catalysis which additionally looks for minimizing the production of undesirable by-products [2]. Both homogeneous and heterogeneous catalysis have enabled the chemical industry from refineries to pharmaceuticals [3]. However, heterogeneous catalysts are preferred for some reaction systems due to their potential to be separated from the reaction medium and recycled. For this reason, the design and synthesis of heterogeneous catalysts for different applications has been the main interest of several researchers.

To improve heterogeneous catalyst performance, different approaches have been proposed, such as tuning the catalyst texture, controlling the nature and dispersion of the active sites, and optimizing the reaction conditions. Another interesting approach is the adjustment of the hydrophobic/hydrophilic balance of the catalyst surface, which regulates the interaction between the catalyst and the reactants and products and, if well-adjusted, leads to more efficient adsorption of the reactants and desorption of the products, improving the catalyst performance.

Adjusting the hydrophobic/hydrophilic balance of the catalyst surface has proven to enhance catalytic activity. For example, Fidalgo et al. showed that alkyl-functionalized sol-gel catalysts with higher hydrophobicity performed better than less hydrophobic ones in oxidation of alcohols [4]. Swalus et al. observed that more hydrophobic hybrid peroxotungstophosphate organized catalysts achieved higher conversions in the epoxidation of cyclooctene than their hydrophilic analogous [5]. Cordon et al. measured higher rates of isomerization of glucose to fructose with Ti-beta zeolites where the active sites were confined in hydrophobic pores [6]. Vivian et al. showed that methylfunctionalization, which modified the hydrophobic/hydrophilic balance of Sn-silicates, enhanced the catalytic activity and selectivity in the production of ethyl lactate from dihydroxyacetone [7]. There are also cases of successful adjustment of the hydrophobic/hydrophilic balance of metal-organic frameworks (MOFs) [8-10]. All these studies demonstrate that the adjustment of the hydrophobic/hydrophilic balance has a great potential as a tool to boost catalytic performances making these reactions sustainable thanks to more efficient catalysts.

The epoxidation of olefins is an important reaction in the fine and bulk chemical industry [11, 12]. Epoxides are key intermediates in organic reactions, and they are widely used in the manufacture of a variety of valuable products, such as epoxy resins, pharmaceutical products, sweeteners, perfumery chemicals and polymeric materials [13, 14].

The scale of production of different types of epoxides ranges from a few grams to millions of tons per year [11]. For example, ethylene oxide and propylene oxide are the two most utilized epoxides in large-scale chemical production. The worldwide production of ethylene oxide was 20 million tons in 2009, and the worldwide production of propylene oxide surpassed 9 million tons in 2013 [15].

The ethylene oxide market size was estimated at over 30 million tons in 2020 [16]. The global market of propylene oxide was valued at USD 22.5 billion in 2021 [17]. For example, Shell has coproduced propylene oxide (PO) and styrene using its styrene monomer propylene oxide (SMPO) process for three decades. The core of this process is the catalytic epoxidation of propylene with ethylbenzene hydroperoxide using a silica-supported titanium catalyst (Ti/SiO₂), a type of Ticontaining catalysts, which was first synthesized by Shell researchers in the 1970s [18]. Many other epoxide compounds are produced in smaller scale for specialized and important applications in the polymeric and pharmaceutical industry [11].

The study of the epoxidation mechanism with Ti-containing catalysts has been performed not only for technological improvement, but also for the advance in fundamental knowledge in the area of chemistry. The level of understanding has advanced, but further study is required to reach improved catalytic epoxidation systems [11]. In fact, intense work has been put forward to improve the catalytic activity of Ticontaining catalysts, mostly by improving the textural properties and controlling the nature of the Ti active sites, but the effect of the hydrophobic/hydrophilic balance remains challenging.

Thus, this work was focused on improving the catalytic epoxidation performance of titanosilicates (Ti-SiO₂) by adjusting their hydrophobic/hydrophilic character. Isolated Ti inserted in the silica framework in tetrahedral coordination are the active species for epoxidation. However, the Ti content in these catalysts is limited due to the trend of TiO₂ to crystallize at high loadings, which diminishes the catalytic performance. Tuning the hydrophobic/hydrophilic balance of such catalysts has appeared as a promising tool to further boost their

performance, leading to greener epoxidation processes. This paradigm will be at the core of this thesis as will progressively be built in the following paragraphs and explained in more detail in section 4.3 of this chapter.

2. Generalities about titanosilicates

In this work, titanosilicates (Ti-SiO₂) are considered materials that contain titanium atoms inserted in a silica matrix that can be either crystalline (zeolitic framework) or amorphous.

Titanosilicates, both crystalline and amorphous are important materials with fast development from the first time they were synthesized in 1983 [19-22]. The importance of these materials lies in their remarkable catalytic activity in selective oxidation reactions, isomerization of olefins, and dehydration of alcohols [23].

Various types of titanosilicates with zeolitic as well as amorphous structure have been synthesized. All titanosilicates contain Ti(IV) species. A variety of zeolites containing atoms other than AI^{3+} (i.e. heteroatoms) as Ti(IV), Sn(IV), Ga(III) have been created and used in acid-catalyzed reactions with higher performance than the traditional SiO₂-AI₂O₃ catalysts [24].

Ti atoms were introduced into the silica matrix by isomorphous substitution of Si(IV) by Ti(IV) [25]. The substitution of Si(IV) by heteroatoms in the crystalline lattice has been extensively studied since this replacement can produce important effects on the physical, chemical, and catalytic properties [25]. An important parameter to be considered is that Ti can be inserted into the silica structure in tetrahedral and/or octahedral coordination. The ionic ratio (cation radius/anion radius) of Ti-O bond corresponding to 0.515 exceeds the range of 0.225 to 0.414 to produce tetrahedral coordination. Thus, the isomorphous substitution of Si(IV) by Ti(IV) seemed improbable [26].

The substitution of Si(IV) by Ti(IV) in the TS-1 titanosilicate was verified by modification of the unit-cell parameters as a function of the substitution degree and the difference between Si-O and Ti-O bond distances. No substantial changes were detected in XRD spectra of TS-1 compared with silicalite-1, and the minor changes were attributed to the formation of titanium dioxide which corresponds to octahedral coordination (extraframework titanium, EFW-Ti (Figure I-1b)). This means that the isomorphous substitution cannot be perfect. Subsequent studies reached great reproducibility of the TS-1 synthesis in industrial laboratories. According to TS-1 characterization, it was possible to determine that Si(IV) was mainly substituted by Ti(IV) in tetrahedral coordination (framework titanium, FW-Ti (Figure I-1a)) [24]. In the case of TS-1, the substitution limit based on the lattice constants is around 2.5% (Ti/(Ti+Si)). Above this value, EFW-Ti appears [27]. There is not a theoretical substitution limit for all types of titanosilicates since it depends on the structure of each material [28].



Figure I-1 Titanium species in titanosilicates: a) Framework titanium (FW-Ti) and b) Extraframework titanium (EFW-Ti).

Different analytical techniques were developed for characterization of Ti sites in titanosilicates such as Fourier transform infrared spectroscopy (FTIR), Raman vibrational spectroscopies, Electron Paramagnetic Resonance (EPR), X-Ray Absorption Fine Structure (EXAFS), X-Ray Absorption Near Edge Structure (XANES), and Diffuse Reflectance DRUV-Vis. Specifically, tetrahedral titanium can be detected by UV peak at 210 nm (absorption in 330 nm discloses the presence of octahedral Ti). An interesting compilation of these analytic procedures was presented by Vayssillov in 2008 [19].

In this work, we focused on Ti-SiO₂ with amorphous structure, also known as titania-silica (TiO_2 -SiO₂) mixed oxides, since these catalysts have been used in the epoxidation of cyclohexene, limonene, styrene

and even larger olefins due to their large pore sizes and high number of Ti active sites [29-31].

3. Epoxidation of olefins over titanosilicates

A wide variety of Ti-containing materials, such as TS-1 [25, 32-34], Tibeta [35, 36], Ti-SBA-15 [37-39], Ti-MCM-41 [40-43], Ti/SiO₂ [35, 42, 44, 45], and Ti-SiO₂ [30, 31, 46-49] have been studied as heterogeneous catalysts for the epoxidation of olefins. Ti in tetrahedral coordination inserted as single atoms in the silica framework (FW-Ti) forms strong Lewis acid species due to electron withdrawal by the silanoxy ligands, and appears as their active sites [11, 23, 31, 32, 50-53]. The Lewis acid strength has been correlated positively to higher epoxidation rates and selectivities in simulations [54] and experimentally [53, 55, 56].

The epoxidation mechanism of olefins has been extensively studied, and it was found that epoxides can be produced by two competitive routes: direct epoxidation and allylic oxidation (Figure I-2). When H_2O_2 is used as the oxidant, the direct epoxidation is mediated by the titanium-hydroperoxo complex (Ti-OOH). However, the presence of water in this reaction mixture promotes undesired epoxide ring opening which produces the corresponding diol. Diol can be also generated by the presence of Bronsted acid sites on the catalysts surface [56, 57]. The allylic route is mediated by radicals (Ti-O' and HO') which are formed by the homolysis of Ti-OOH. This route generates oxygenated products including epoxides, alcohols and ketones through consecutive reactions [258]. The mechanism of the direct epoxidation, which is our route of interest, has been studied and widely accepted to follow an Eley-Rideal mechanism [53, 58, 59]. In this mechanism the oxidant (hydrogen peroxide or organic peroxide) adsorbs on the titanium active sites forming active intermediate species (Ti-OOR, where R=H or alkyl). These species react with the olefin producing the epoxide that is later desorbed from the catalyst surface.



Figure I-2 Direct epoxidation and allylic route for cyclohexene oxidation. Adapted from [45].

Choice of the olefin, oxidizing agent and solvent

Cyclic olefins have been used as common olefins to study the catalytic performance of titanosilicates. In this work, cyclooctene epoxidation was selected as model reaction since it has been previously used to study the effect of hydrophobization of other catalysts with positive results [5]. Additionally, cyclic olefins are studied due to their molecule size. It has been shown that the epoxidation rates and yields decrease for olefins whose kinetic diameter is c.a. 6 Å [60, 61]. Thus, it was important to synthesize a catalyst with improved textural properties.

Two widely used oxidizing agents in epoxidation were used in the experimental work: hydrogen peroxide (H_2O_2) and tert-butyl hydroperoxide (TBHP). Since the polarities of the reactant and oxidant are different, a solvent was necessary to guarantee a good miscibility. Acetonitrile, methanol, toluene, and chloroform have been used as solvent for the epoxidation reaction. However, acetonitrile has been commonly used for cyclooctene epoxidation either with hydrogen peroxide or organic peroxides [62-65].

The catalytic performances of titanosilicates for the epoxidation of cyclooctene are summarized in Table I-1. A direct comparison of the catalytic indicators is not possible due to different reaction conditions and different reaction times, but the highest conversion registered was achieved with a Ti-beta after 5 h, and the highest TOF was obtained with a hierarchical Ti-beta.

Catalyst	Oxidant	Temp. °C	Conversion % ^b	Yield %	TOF h⁻¹	Ref.
Ti-MCM-41	TBHP	70	24.9 (at 10 h)	-	18	[62]
Hierarchical Ti-beta	H_2O_2	40	-	26 (at 8 h)	42	[63]
Ti-beta	TBHP	50	58 (at 5 h)	40	17	[64]
Ti-beta	H_2O_2	50	88 (at 5 h)	65	35	[64]
Pillared TS-1	H_2O_2	60	21 (at 4 h)	16.9	-	[65]

Table I-1. Catalytic performance of titanosilicate in the epoxidation of cvclooctene

4. Hydrophobization of titanosilicates

4.1 Methodologies to hydrophobize titanosilicates

In general, two main approaches can be distinguished in the literature to tune the hydrophobicity of Ti-containing catalysts. The first approach is the control of the silanol surface density by improving the catalyst crystallinity, by preparing the catalysts in fluoride (F⁻) medium instead of OH⁻ medium, or by incorporating Ti on terminal silanols. It is known that defect-free siliceous surfaces formed by Si-O-Si bonds are hydrophobic [66], whereas surfaces with hydroxyl groups (Si-OH) and bridging hydroxyl groups (i.e., Si-OH-Ti, Si-OH-AI) are hydrophilic [67].

Crystallization of titanosilicates is more complex than crystallization of aluminosilicates because Ti(IV) insertion is more difficult than that of AI^{3+} . The Ti-O bond (1.80 Å) is longer than the Si-O bond (1.61 Å), which distorts the structure around Ti resulting in a limited insertion of Ti into the silica framework and in the formation of undesired phases [68]. Structure directing agents (SDAs), such as TEAOH and TPAOH improve Ti insertion [69]. Fan et al. demonstrated that (NH₄)₂CO₃ was an effective crystallization-mediating agent that improves the insertion of titanium into the silica framework and decreases the number of silanol defects [68]. Better crystallized TS-1 has less terminal silanols and appeared to be more hydrophobic than conventional TS-1 [68, 69].

Synthesis in F⁻ medium prevents the formation of anionic framework vacancy defects since the cationic charges of the structure directing

agents (SDAs, ie. NH₄OH, TPAOH) are counterbalanced by F⁻ forming strong ion-pairs [70, 71]. As shown in Figure I-3, anionic framework vacancy defects are produced in the presence of OH⁻ anions, and silanol nests are formed after the removal of SDA cations, which increases the hydrophilicity of the material, making that they adsorb more water [71]. Fluoride (F⁻) medium has been used to obtain more hydrophobic TS-1 [72] and Ti-beta [73-76]. The high epoxidation activity indeed displayed by these modified catalysts was attributed to their higher hydrophobic character [68, 73, 74].





Organometallic Ti precursors react with terminal silanols leading to Ti incorporation on the silica. In this way, the silanol surface density decreases. The control of hydrophobicity is more evident after the incorporation of Ti in dealuminated materials [77-80].

The second approach for hydrophobization is the functionalization of the catalyst surface with organic moieties by either post-grafting [12, 45, 81-85] or one-pot functionalization [86-92]. Post-grafting is based on the reaction between alkoxysilanes (most common), carboxylic acids, or isocyanates with the silanol groups present on the surface due to the silica synthesis procedure [93]. The process of silylation occurs on isolated (\equiv Si-OH) and geminal silanol (=Si(OH)₂) groups [94, 95]. However, hydrogen-bonded silanol groups form stable silanol nests among themselves, limiting the functionalization [94, 95]. A

drawback of post-grafting has been the lack of homogeneity in surface coverage given that silanols located on the external surface of pores are more available for grafting than the ones on the internal surface [95]. This promotes an accumulation of the organic moieties and consequently pore blockage. Post-grafting of organosilanes has been used to produce hydrophobic Ti-MCM-41 [82], Ti-SBA-15 [12, 82], Ti/SiO₂ [83, 84], and Ti-SiO₂ [96]. The low silanol density of these materials was mainly attributed to the substitution of Si-OH groups by organic moieties and this was confirmed by IR spectroscopy and ²⁹Si NMR analysis [82, 84].

Direct hydrophobization through one-pot synthesis methods is less time-consuming and can be more efficient than post-modification. Additionally, the functionalization is controlled by the chemistry of the precursors, guaranteeing the functionalization of the desired atoms. The one-pot synthesis method facilitates a homogeneous distribution of organic groups on the entire inner pore surfaces without shrinkage or pore-blockage problems [94, 95]. One-pot functionalization has been used to hydrophobize Ti-MCM-41 and Ti-SiO₂ [87-89, 91, 92, 96]. The presence of the organic moieties was confirmed by IR spectroscopy and ²⁹Si NMR analysis [97, 98].

Regarding the textural properties, both functionalization procedures diminished the specific surface area and pore size, and this difference in textural properties can affect the catalytic performance of functionalized catalysts [95, 96]. For this reason, it is necessary to develop a functionalization procedure that is efficient and does not affect the catalyst texture. This is one of the objectives of the current work.

4.2. Characterization of hydrophobicity in titanosilicates

The analytical techniques applied to characterize this property in solids differ particularly regarding the experimental method and the physical/chemical properties considered for the evaluation of the porous solid surface [99].

The term hydrophobicity/philicity refers to the affinity that exists between a solid surface and water. A hydrophobic surface can be defined similarly as a hydrophobic substance. Nonpolar substances are hydrophobic and have low solubility in water at room temperature. The accumulation of the nonpolar molecules in aqueous media produces a high cohesive energy density of water that decreases the interface between the nonpolar substance and water, explaining the hydrophobic effect. Therefore, to transfer nonpolar molecules into an aqueous medium, the enormously stable hydrogen bond among water molecules must be disrupted [99, 100].

The characterization of the hydrophobicity in titanosilicates has been studied with TGA, IR spectroscopy, vapor-water adsorption, calorimetric techniques and solid-state NMR.

TGA is a common analytical technique used to measure the water capacity that is the quotient between the mass loss due to the water desorption by the mass of dry solid [101]. TGA measurements provide information about the water adsorbed physically and chemically depending on the temperature range. For example, Mueller et al. found that physisorbed water mass loss occurred at temperatures below 120 °C in pure silica [102]. In fact, Anderson and Klinowski introduced the term hydrophobicity (h) as the ratio of mass loss due to physisorbed water at temperatures below 150 °C and the final mass loss at 400 °C [103]. Some works have evaluated the hydrophobicity of titanosilicates by measuring the mass loss due to physisorbed water [12, 68, 78, 82, 85, 92, 98]. However, this model is not always useful to evaluate the hydrophobicity/philicity of all zeolites [104]. Textural properties, sample preparation and storage have an impact over the measurement of physisorbed water and could lead to imprecise conclusions about the hydrophobicity/philicity of a material. Thus, comparison of the hydrophobicity of materials should be performed carefully since the measurement of physisorbed water is indeed related to the affinity for water, but it is also influenced by the textural properties (e.g. pore volume, specific surface area). To prevent the influence of the sample storage and ambient conditions, samples are generally saturated in NH₄Cl or MgCl₂ solutions to reach a maximum level of water adsorption [82, 88, 103].

TGA has been also used to study water affinity of solids through the quantification of hydroxyl surface density which is an indirect way to quantify the water affinity of solid surfaces [102, 105]. For example, Mueller found that the presence of OH groups on the SiO₂ surface can be measured in the temperature range of 120-800°C, and the OH content was normalized to the specific surface area to be able to compare the OH/m² of each material [102]. Guidotti and coworkers measured surface silanol density of Ti-MCM-41 and Ti-SiO₂ by TGA in the temperature range between 150 °C and 900 °C [106].

In the case of organically-functionalized titanosilicates, TGA under air atmosphere has also allowed the quantification of their organic content based on the mass loss above 400°C. A mass spectrometer has been coupled to TGA to detect the mass to charge ratios (m/z) related to CO_2 and H_2O , and fragments of other organic groups such as ethyl and phenyl [12, 78, 90-92].

IR spectroscopy is a popular technique to obtain structural and surface information of crystalline and non-crystalline solids [107-109]. Polar and non-polar groups on the solid surface can be directly quantified by IR spectroscopy, providing information about the surface polarity [105]. In comparison with TGA, IR spectroscopy provides more information about the distinction between physically adsorbed and chemically bound water [110, 111]. Water affinity has been studied by identifying the types of hydroxyl groups on the surface and the types of sorbed water molecules [72, 76, 77]. For example, the band at 3750 cm⁻¹ of the IR spectra of silica is assigned to isolated Si-OH groups [110, 112]. A close-lying band (a tail) formed by the weakly Hbonded -OH groups, appears in the 3600-3750 cm⁻¹ region [112]. The band of strongly H-bonded -OH groups and/or desorbed water appears in the 3400-3500 cm⁻¹ region [112, 113]. The band of -OH groups that belong to sorbed water appears at 1630 cm⁻¹ (water deformation) [111, 113]. As vacancy defects also called silanol nests (Si(OH)₄) stabilize H-bonded networks of water [76, 114] and isolated silanols adsorb water weakly [114], distinction between them is important to understand the hydrophobic/philic character of materials. In order to compare the hydrophobicity of metal-substituted zeolites, some researchers have normalized the different silanol IR signals by the band of v(Si-O-Si) at 1990 and 1865 cm⁻¹ (assuming this band is constant) [72, 76, 115]. The interest in the identification of types of silanols on micro to mesoporous materials has increased lately, so research articles and reviews dedicated to this study have been published recently [101, 105, 116].

The OH region of the IR spectra of titanosilicates generally displays two intense bands centered at 3750 and ~3500 cm⁻¹ corresponding to isolated silanols and H-bonded silanols at defect sites and/or desorbed water, respectively [73, 76, 81, 117].

Quantification of non-polar groups on the solid surface can be also performed by IR spectroscopy. Metal-substituted zeolites and silicabased materials functionalized either by the one-pot method or by postgrafting have been characterized by transmission, ATR or DRIFT modes of IR spectroscopy. C-H stretching and bending vibration bands that reflect the incorporation of alkyl groups appear at 2850-2985 cm⁻¹ and 1460 cm⁻¹ [118].

Water affinity can be understood by recording the **water vapor adsorption isotherms**. A hydrophobic material displays low affinity for water and low water adsorption capacity. In contrast, a hydrophilic material displays high affinity for water, but does not necessarily exhibit a high water adsorption capacity since the latter depends on the pore volume [101]. Therefore, to know if a material is more hydrophobic or hydrophilic, it is necessary to determine the amount of adsorbed water per unit area or mass in the range of low relative pressures [119]. In fact, the measurement of water adsorption capacity at higher relative pressures does not provide information about water affinity since the adsorbate–adsorbate interactions result in a multilayer adsorption and/or pore condensation. To solve this drawback, the water adsorption capacity must be analyzed at low loading (low amount of water adsorbed), without surpassing the monolayer adsorption, to minimize the influence of adsorbate–adsorbate interactions [99].

Figure I-4 illustrates three water adsorption isotherms of zeolitic materials with different hydrophobicity degrees and with the same pore volume [120]. Curve (a) is a type I isotherm in which the sorption equilibrium in the material is reached after the adsorption of high amount of water at very low relative pressures (P/Po), curve (b) is also a type I isotherm in which the sorption equilibrium is reached at higher P/Po, the curve (c) corresponds to a type V isotherm where just a small amount of water is adsorbed at low P/ Po until the sorption capacity is reached, this is a hydrophobic or weakly hydrophilic solid, and curve (d) represents a type VII isotherm where a very small amount of water is adsorbed for material is considered highly hydrophobic. According to the adsorption isotherms of materials (a) and (b) at low loading, the material with steeper slope is defined as more hydrophilic [101, 120].



Figure I-4 Water adsorption isotherms for ideally hydrophobic and hydrophilic zeolitic materials normalized to pore volume. Copied from Ref [101].

Some titanosilicates have been studied by using vapor-water sorption. Igarashi et al (2005) synthesized Ti-MCM41 by methyl-, phenyl-, vinyl-, and pentyl-functionalization and used water sorption to measure the water uptake [97]. Ti-Beta zeolites were also characterized by this technique, the water adsorption isotherms showed that Ti-Beta zeolites synthesized in F^- medium displayed lower water uptake (mmol g⁻¹) than Ti-Beta (OH⁻) [73, 80].

Calorimetric techniques have been used to study the solid surface of solids in liquid medium. For example, the solid surface affinity for water is characterized by the measurement of the heat of immersion, also called heat of wetting or immersion enthalpy, which is the energy change at constant pressure and temperature when a solid is immersed in a liquid. The heat of immersion depends on both the chemical interactions of the liquid with the solid surface and the textural properties of the solid [99, 101, 121]. Silvestre-Alveró and co-authors used calorimetry of immersion to compare the hydrophobic character between Ti-MCM-41 and silylated Ti-MCM-41. They used different liquids as probe molecules, ranging from non-polar (i.e., hydrocarbons)

and polar molecules (i.e., water, alcohols). According to their results, silylated Ti-MCM-41 demonstrated a hydrophobic character since the heat of immersion in water decreased for increasing silylation degrees. On the other hand, silylation displayed a lower effect on the heat of immersion measured in cyclohexane, indicating that the interactions between a hydrophobic surface with a non-polar liquid are smaller and likely also affected by the textural properties [121].

Solid-state NMR can be used to evaluate the hydrophobic character of solids since the presence of hydrophilic sites (-OH) and organic moieties bonded to Si atoms can be determined by this analytical technique. For example, the intensity of hydroxyl groups and molecular water signals can be measured from ¹H NMR spectroscopic data at low temperature [101]. Additionally, some previous studies have used solid-state NMR to describe the degree of condensation of silicates by deconvoluting the ²⁹Si NMR spectrum using the contributions of Q⁴ ((Si(OSi)₄)), Q³ ((Si(OSi)₃OH)), and Q² ((Si(OSi)₂(OH)₂)) (Figure I-5) [76, 90]. Besides the condensation degree, this analysis is strongly related to the hydrophobicity/philicity of the material since silanols (Si-OH) are hydrophilic sites, so a higher fraction of Q³ and Q² relative to Q⁴ would indicate a more hydrophilic character.

In addition to Q species, there are other siloxane species that can be identified in a ²⁹Si NMR spectrum, such as M, D, and T species. These species correspond to R₃SiO_{0.5}, R₂Si(O_{0.5})₂, RSi(O_{0.5})₃ units, respectively, where R represents aliphatic and/or aromatic substituents or H [122, 123]. Solid-state NMR has been also used to characterize titanosilicates hydrophobized by organic functionalization [82, 84, 91, 117, 121]. For example, certain researchers determined the fraction of Si bonded to methyl groups $(T^i/\sum_i (Q^i + T^i))$, in order to evaluate the effective methyl-functionalization of zeolitic and amorphous titanosilicates [90, 97, 124].

There are two modes for the experimental approaches of solid-state NMR. The cross-polarization mode allows to transfer polarization from abundant spins like ¹H to more diluted spins like ²⁹Si to enhance signal/noise ratio [125]. In this case, the signals of the contributions of Q^2 , Q^3 , T^2 and T^3 increase, so T^2 and T^3 are better appreciated even at low organic content. Indeed, some previous studies have used cross-polarization to verify the surface functionalization of titanosilicates [84, 90]. Nevertheless, this method cannot be used for quantification of each resonance. The direct excitation mode is applied for

quantification, and once the spectrum is recorded, contributions are quantified by deconvolution of peaks using Gaussian functions.

Solid-state NMR cannot be used to study the Ti nucleus at very low Ti molar ratios [28]. Another nucleus that can be followed by solid-state NMR is ¹³C [91]. In this case, the analysis provides information about organic functionalization or the degree of removal of the templating agents [7].



Figure I-5. Typical types of resonance contributions of a solid-state ²⁹Si NMR spectrum. Adapted from [90].

4.3. Review on the catalytic epoxidation performance of hydrophobized titanosilicates

Tuning the hydrophobic/hydrophilic balance of the catalyst surface which regulates the interaction between the catalyst and the reactants and products leads to more efficient adsorption of the reactants and desorption of the products. This approach has proven to enhance catalytic activity, limit side reactions, and improve the stability of diverse catalysts in diverse model reactions [4-10, 126]. Specifically, it was shown that hydrophobic catalysts displayed better reactivity and stability than their hydrophilic analogous in reactions occurring in the presence of water [67, 96, 127-129]. In this line, this work aimed to elucidate the effect of hydrophobizing titanosilicates over their catalytic performance in olefin epoxidation.

Olefin epoxidation allows to study the effect of adjusting the catalyst hydrophobic/hydrophilic balance due to the difference in hydrophobicity between the olefin and the epoxide. As explained previously in section 3 of the General Introduction, the accepted mechanism for the catalytic epoxidation of olefins with heterogeneous Ti-based catalysts is the Eley-Rideal mechanism [53, 58, 59], in which the oxidant adsorbs on the Ti active site and forms active intermediate species [53], which then react with the olefin to produce the epoxide that finally desorbs from the catalyst. Hence, hydrophobized heterogeneous catalysts should display higher affinity for the olefin, allowing it to get close of the active sites (or at least of the active surface), and lower affinity for the epoxide, favoring desorption and preventing ring opening reactions.

In fact, various attempts have been made to boost the catalytic epoxidation performance of Ti-containing catalysts [36, 46, 68, 81, 130-132], but only recently more attention has been paid to the effect of adjusting the hydrophobic/hydrophilic balance and the environment surrounding the active sites on the catalyst surface. Even though the epoxidation mechanism does not require the olefin to adsorb on the catalyst, some affinity is desired so that the olefin can approach the Ti active species on the catalyst surface. It has been indeed shown that hydrophobic Ti-zeolites displayed higher affinity for olefins than hydrophilic ones [133]. Conversely, affinity between the catalyst surface and the epoxide should decrease so that the epoxide desorbs immediately avoiding undesired consecutive oxidation or ring opening.

As described in section 4.1 of the General Introduction, titanosilicates can be hydrophobized either by the control of the silanol surface density or by organic functionalization. A discussion about the catalytic performance of the hydrophobized titanosilicates will be described in the following paragraphs.

The **control of the surface silanol density** was studied as an alternative to modify the hydrophobicity of titanosilicates. For example, the use of $(NH_4)_2CO_3$ (crystallization-mediating agent) improved the crystallization process of TS-1. This facilitated the insertion of Ti into the zeolite framework and lowered the number of defect sites (Si-OH), increasing the hydrophobicity of TS-1. The more hydrophobic TS-1 displayed a higher resistance to water attack and better catalytic activity (TON and conversion) in the epoxidation of 1-hexene and styrene using H_2O_2 as oxidant [68]. However, in this case, the positive catalytic effect cannot be totally attributed to hydrophobicity

considering that the crystallization process increased the incorporation of FW-Ti which could be the main reason for the enhanced catalytic activity.

Ti-SiO₂ hydrophobized by **post-grafting** achieved higher yields in the epoxidation of cyclohexene with H_2O_2 or 1-octene with tert-butyl hydroperoxide (TBHP), and some of them even demonstrated higher stability in the presence of water [84, 96]. In contrast, hydrophobization by silylation had no significant effect on the epoxidation of 1-hexene and cyclohexene with H_2O_2 catalyzed by either silylated Ti/SiO₂ [45] or silylated TS-1 [81]. Moreover, silylated Ti-beta displayed lower catalytic activity in the epoxidation of 1-hexene with H_2O_2 than the pristine Ti-beta [81]. Markedly, the effect of surface functionalization by post-grafting is different for each Ti-based catalyst. This is explained by the fact that post-grafting procedure tends to also modify the catalyst structure, texture, and the nature of the active sites.

Some reports have utilized the **one-pot approach** to test the effect of adjusting the hydrophobic/hydrophilic balance of Ti-containing catalysts. For example, Ti-MCM-41 was hydrophobized by one-pot functionalization with methyl [88, 97, 134], phenyl [97], vinyl [97] and pentyl [97] organo-alkoxysilanes. These modified catalysts were used on the oxidation of cyclohexene using TBHP and H_2O_2 as oxidants. A significant improvement on the activity was observed with the methyl-functionalized Ti-MCM-41 [88, 97, 134].

Amorphous titanosilicates Ti-SiO₂ were also modified by one-pot functionalization with phenyltrimethoxysilane (PHTMS) (nominal 30%). The epoxidation of cyclohexene using both modified and unmodified Ti-SiO₂ was compared, and the initial epoxide production rate and yield (after 2 hours) were higher for the functionalized materials compared with the pristine samples. This was attributed to the presence of nonpolar organic groups on the modified surface catalyst which increased the hydrophobic character and improved the selectivity to epoxide [91]. This positive effect of the hydrophobization of Ti-SiO₂ in a one-pot approach was also observed by other researchers [86, 87, 89].

As described in the previous paragraphs, hydrophobic titanosilicates achieved higher rates and yields in the epoxidation of cyclohexene. Contrarily, in other studies, a negative effect of one-pot hydrophobization on the epoxidation of 1-hexene and cyclohexene with TBHP [90, 91] was found due to lower surface area, diminished Ti dispersion and excessive surface functionalization. In addition, one-pot methyl-functionalized Ti-SiO₂ catalysts exhibited similar catalytic performance as their hydrophilic analogues in the epoxidation of cyclohexene in the presence of water [96]. The negligible effect of hydrophobization was attributed to the lower concentration of surface active sites resulted from the one-pot methylfunctionalization [96].

Table I-2 summarizes some of the catalytic indicators of titanosilicates hydrophobized using the one-pot approach over the epoxidation of cyclohexene.

Catalyst Oxidant Tomp Conversion Viold TOE Bof						Pof
Galaryst	Oxidant	°C	%	%	h ⁻¹	itel.
Ti-MCM-41 (pristine)	H ₂ O ₂	70	39 (at 3 h)	-	-	[97]
Methyl-Ti- MCM-41	H_2O_2	70	67 (at 3 h)	-	-	[97]
Phenyl-Ti- MCM-41	H_2O_2	70	72 (at 3 h)	-	-	[97]
Ti-MCM-41 (pristine)	TBHP	60	16.3 (at 5 h)	-	33.8	[88]
Methyl Ti- MCM-41	TBHP	60	38.5 (at 5 h)	-	62.7	[88]
Ti-SiO ₂ (pristine)	H_2O_2	75	65	29	0.06*	[87]
Phenyl-Ti- SiO ₂	H_2O_2	75	97	41	0.07*	[87]
Ti-SiO ₂ (pristine)	TBHP	60		45 (at	2.02*	[135]
Methyl-Ti- SiO ₂	TBHP	60		2 ii) 16 (at 2 h)	0.34*	[135]

Table I-2. Catalytic performance of hydrophobized titanosilicates in the epoxidation of cyclohexene

*the units are mmol g⁻¹ min⁻¹

As shown in the previous paragraphs, some research works have found a positive effect of hydrophobization, but others have found a negative or negligible effect. This diversity in the points of view can be justified because there is a considerable number of variables influencing the catalytic performance of titanosilicates in oxidation reactions. The physical/chemical properties of each type of titanosilicate and the methodologies for hydrophobization affect their interactions with the reactants, products, intermediate species, and solvent.

Specifically, the results obtained by one-pot functionalization are difficult to compare, and not much research has gone into evaluating the catalytic performance per active Ti site and per accessible surface area, so more exploration is necessary to clarify the effect of adjusting the hydrophobic/hydrophilic balance on the epoxidation of olefins. There is thus obviously room and necessity to address the effect of hydrophobization in a rigorous and systematic manner, which is the main objective of this work.

Furthermore, evaluating and comparing the hydrophobic character of Ti-SiO₂ are still a challenge due to the variety of analytical techniques applied to measure this property in different works, making complex any comparison. The hydrophobic character of the modified titanosilicates originates from different chemical properties. In some cases, the hydrophobicity is related to the silanol surface density and the type of silanol (isolated or hydrogen-bonded silanols), whereas in other cases, the hydrophobicity is related to the functionalization degree with organic moieties. Therefore, there is not a specific characterization technique to measure the hydrophobicity of a catalyst. In fact, analytical techniques have ranked a given set of porous solids according to their hydrophobic character, but a quantitative assessment remains a challenge. Also, it is important to keep in mind that the conditions under which the experimental analysis is carried out not always correspond to the conditions in the application, especially in the case of catalysts. In addition, the applicability of the characterization techniques depends on each type of porous solid [99].

5. Objectives and strategy

Four main objectives were proposed to evaluate the effect of hydrophobizing Ti-SiO₂ over their catalytic performance in liquid-phase epoxidation reaction. The first three objectives were related to the optimization of the one-pot synthesis of hydrophobized Ti-SiO₂ by classical sol-gel. The last objective was devoted to reach a better control of the textural properties and dispersion of Ti active sites and methyl moieties through the use of aerosol-assisted sol-gel in a one-pot manner. The details of each objective are described as follows:

The **first objective** was related to finding the optimal conditions to prepare hydrophobic Ti-SiO₂ catalysts via a classical one-pot sol-gel. The molar ratio of the Ti precursor will affect the incorporation of Ti and the number of active Ti sites. Regarding the hydrophobization of Ti-SiO₂, the functionalization by the one-pot approach must consider the choice of the alkyl alkoxysilane precursor and the degree of functionalization needed to modify the hydrophobic/hydrophilic balance of the catalyst surface. Additionally, some characterization techniques were applied and adapted to: i) identify the Ti active species, and ii) assess the degree of surface functionalization and the corresponding hydrophobicity.

Once the optimal range of molar ratios of Ti and organic precursors was determined, the **second objective** was to evaluate the effect of hydrophobization over the catalytic activity of catalyst with a better Ti dispersion and different degrees of methyl-functionalization in the epoxidation of cyclooctene with hydrogen peroxide as oxidant.

Two hypotheses were proposed to explain the lower catalytic performance of the Ti-SiO₂ with the highest methyl-functionalization degree. Therefore, the **third objective** was proposed to evaluate if the Ti dispersion was still the reason for the lower catalytic performance or if it was the high degree of hydrophobization that prevented the oxidant to interact with the catalyst surface. Thus, an organic oxidant, tetrabutyl hydroperoxide (TBHP) was used as the oxidant.

After the effect of hydrophobization by methyl-functionalization was confirmed to be positive even for Ti-SiO₂ with limited textural properties, and limited Ti sites (due to the negative effect of methyl-functionalization over Ti dispersion), the **fourth objective** was related to improve these properties. Therefore, the aerosol-assisted sol-gel (AASG) method was proposed as an alternative to tackle this problematic, since AASG is known to improve textural properties and active sites dispersion.

6. Structure of the thesis

This thesis structure was organized as follows. First, a general introduction including the research context of olefin epoxidation and fundamentals of titanosilicates as well as their use as a catalyst in the epoxidation of olefins is shown. A literature review of the methodologies to hydrophobize Ti-SiO₂, the analytical techniques
applied to characterize the hydrophobic/philic properties of Ti-SiO₂, and the catalytic performance of hydrophobic Ti-SiO₂ in olefin epoxidation is also included. The final sections of the general introduction were devoted to the description of the objectives, strategy and thesis structure. The next chapter is related to the materials and methods used during the experimental work. The last four chapters are dedicated to fulfill the goals of the specific objectives of this research work. Each chapter contains an abstract, introduction, experimental section, results and discussion and conclusions. The general conclusions and perspectives of future work are found at the end.

Materials and Methods

This section describes the materials and methods for the catalyst synthesis, catalyst characterization and the evaluation of the catalytic performance in the liquid phase epoxidation of olefins. Essentially, only materials and methods common to all the chapters of this thesis are described here, additional details related to more specific materials and methods being described in the corresponding chapters.

1. Catalyst synthesis

Catalysts were synthesized by classical and aerosol-assisted sol gel in a one-pot manner.

1.1 Classical one-pot sol-gel synthesis procedure

The following synthesis procedure was used for the synthesis of functionalized Ti-SiO₂ unless indicated otherwise. Hydrophobization was achieved in a one-pot manner, by substituting a fraction of tetraethoxy silane precursor (TEOS, Sigma-Aldrich, 98%) by a more hydrophobic alkyl alkoxysilane. Titanium butoxide (TBOT, Sigma-Aldrich, 97% reagent grade) was used as the Ti precursor. Several molar ratios of the alkyl alkoxysilane and the Ti precursor were evaluated through the Chapters of this thesis, according to Equation 1. 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). The alkoxysilanes were added dropwise and prehydrolized before the addition of the Ti precursor. Once the gel was obtained, it was dried and calcined at the desired temperature. Specific details of the synthesis procedure are provided in each Chapter.

$$Molar \ ratio_{alkyl \ alkoxysilane} = \frac{mol_{alkyl \ alkoxysilane}}{mol_{TEOS} + mol_{TBOT} + mol_{alkyl \ alkoxysilane}}$$
(1)

1.2 Aerosol assisted one-pot sol-gel

The procedure for the catalyst synthesis was adapted from Smeets et al. [46]. The precursor solution was prepared by adding TBOT (Sigma-Aldrich, 98% reagent grade) dropwise to tetrapropyl ammonium hydroxide (TPAOH, Merck, 40%). After 10 min stirring, distilled water was poured and stirred for additional 10 min. TEOS and the alkyl alkoxysilane (methyltriethoxy silane, MTES, Sigma-Aldrich, 99%) were successively added and the final mixture was stirred overnight at room temperature in a closed vessel to hydrolyze the precursors. Afterwards, the solution was aged in the oven at 70 °C for 15 h. Pluronic F127 (F127, BASF) was added and the solution was stirred for 1 h prior to atomization. The final molar composition of the precursor solution was x MTES : 1-x (TEOS + TBOT) : 0.15 TPAOH : 0.005 F127 : 19.6 H₂O, where "x" represents the molar fraction of MTES used in the synthesis of the hydrophobic samples, as defined in Equation 1.

The clear precursor solution was sprayed by a Büchi Mini Spray Drier B-290 (Büchi Labortechnik AG, Flawil, Switzerland) with a liquid flow rate of 5 mL min⁻¹ and an air pressure of 4 bars. The atomized sol was dried by traveling through a glass reactor fed with air heated at 220 °C. Under these conditions, the exit gas had a temperature of 120 °C. The powder was collected and aged at 70 °C overnight in a static oven. After aging, the powder was calcined in static air along a temperature program that started with a ramp of 1 °C min⁻¹ from room temperature to 350 °C and followed by a dwell step at the final temperature for 10 h. After cooling down inside the furnace for around 3 h, the calcined solids were stored in a desiccator. Specific details of the synthesis procedure are provided in Chapter 4.

2. Catalyst characterization

Fourier Transform Infrared (FTIR) spectroscopy was performed in attenuated total reflectance (ATR) and transmission modes using an IFS55 Equinox Bruker spectrometer equipped with a DTGS detector. The spectra were obtained by recording 100 scans in the range from 400 to 4000 cm⁻¹ at a resolution of 4 cm⁻¹. For transmission mode, the pellets were prepared by diluting the sample in KBr (Janssens Chimica, \geq 99%) with a 2.5 wt% dilution factor. The spectra were analyzed using the software OPUS.

Thermal Gravimetric Analysis (TGA) was performed in a Mettler Toledo TGA/SDTA 851 apparatus. A typical method consisted in a ramp from 30 °C to 900 °C at 10 °C min⁻¹ under air flow (50 mL min⁻¹, 80% N₂ and 20% O₂, Alphagaz Air Liquide). TGA profiles were also obtained with the instrument Mettler Toledo TGA/DSC 3+ STAR System.

Temperature-programmed oxidation (TPO) experiments were performed with a Catlab-PCS (Hiden Analytical) equipped with a QGA mass spectrometer. A typical temperature-program under air flow (30 mL min⁻¹) included two stages: i) plateau at 40 °C for 10 minutes and ii) heating to 800 °C at 5 °C min⁻¹. The sample mass was 70 mg and the detected mass to charge ratios (m/z) were: 2 (H₂), 15 (CH₃), 17 and 18 (H₂O), 28 (N₂), 29 (methanol), 31 (ethanol), 40 (Ar), 44 (CO₂) and 56 (butanol).

X-ray diffraction (XRD) measurements on solid samples were performed with a Siemens D5000 diffractometer using the K α radiation of Cu (λ =1.5418 Å) operated at 40 mA and 40 kV. The small 2 θ range (10 – 80°) was recorded at a rate of 0.01° s⁻¹.

Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) was performed by Anne Iserentant on an ICAP 6500 Thermo Scientific instrument at the Earth and Life Institute (ELI). Prior analysis, the samples were calcined at 550 °C for 24 h to remove the organic matter, and then they were decomposed by sodium peroxide fusion in carbon crucibles.

X-ray photoelectron spectroscopy (XPS) experiments were performed on a SSX-100/206 photoelectron spectrometer from Surface Science Instruments (USA) equipped with a monochromatized micro focused Al X-ray source (powered at 10 kV and 20 mA), a 30° solid angle acceptance lens, a hemispherical analyzer and a channel plate detector. Samples were pressed into clean stainless-steel troughs of 6 mm diameter and placed on a ceramic carousel. Samples were degassed inside the sample introduction chamber overnight and transferred to the analysis chamber where pressure was around 10⁻⁶ Pa. The angle between the surface normal and the axis of the analyzer lens was 55°. The area of analysis was approximately 1.4 mm² and the passing energy was set at 50 eV. Under 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. Charging effects were stabilized using a flood gun set at 8 eV and a fine-meshed Ni grid placed 3 mm above the sample surface. The following sequence of spectra was 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 binding energy scale was referenced to the C-(C,H) component of the C 1s peak of carbon fixed at 284.8 eV. Peak decomposition was performed with the CasaXPS processing software (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. Surface elemental composition was calculated using peak areas normalized on the basis of acquisition parameters and sensitivity factors provided by the manufacturer.

Diffuse reflectance UV-Vis (DRUV) spectra were recorded in a typical spectral range from 200 nm to 800 nm using a CARY 5000 Agilent spectrometer or a Shimadzu UV-vis-NIR spectrometer, both equipped with a Praying Mantis. A $BaSO_4$ or a Spectralon® pellet was used to measure the background spectrum, and the Kubelka-Munk function F(R) was calculated based on the reflectance (R).

 N_2 adsorption-desorption experiments were performed at -196 °C using a Micromeritics Tristar 3000 instrument. Before the analysis, the samples were degassed overnight under vacuum (6.7 Pa) at 180 °C. The Brunauer-Emmet-Teller (BET) method was applied to the adsorption isotherm to calculate the specific surface area. For certain samples, the pore size distribution was determined from the desorption isotherms applying the BJH method.

Solid-State ²⁹Si magic angle spinning nuclear magnetic resonance (²⁹Si-MAS-NMR) was performed by Luca Fusaro in the laboratory of Prof. Carmela Aprile at the University of Namur. Spectra were recorded at room temperature on a Bruker Avance-500 spectrometer operating at 11.7 T (99.3 MHz for ²⁹Si) 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) ²⁹Si 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).

Scanning electron micrographs were obtained with a JEOL 7600F (JEOL, Belgium) operated at 15.0 kV. Samples were placed on a piece of carbon black tape on an aluminum stub. A chromium coating of 10 nm was sputtered with a Sputter Metal 208 HR (Cressington, UK).

Water vapor adsorption isotherms were acquired at 22 °C, using a 3Flex instrument from Micromeritics. Before the analysis, the samples were degassed overnight under vacuum (6.7 Pa) at 180 °C, and distilled water was purified applying freeze-pump-thaw cycles.

3. Catalytic tests

The performance of the synthesized catalysts was measured in the epoxidation of cyclooctene (Fluka, >90% or TCI, >90%) with two types of oxidants: hydrogen peroxide (H₂O₂, Sigma-Aldrich, 30%) and *tert*-butyl hydroperoxide (TBHP, Sigma-Aldrich, 30%). The reaction temperatures tested were 60 °C and 70 °C, and the stirring was set at 700 rpm. The initial concentration of cyclooctene was 0.1 M or 0.5 M, whereas the initial concentration of the oxidant was 0.5 M and 0.25 M.

The catalyst addition was 10 g L⁻¹. The solvent was acetonitrile (VWR Chemicals, >99.9%) which was added to the 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 the selected reaction temperature. The reaction started when the oxidant was added to the reactor. The reaction time was 8 h or 10 h, and 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 μ m syringe filter. Cyclooctene and epoxy cyclooctane concentrations were measured by gas chromatography (GC). Further details about the catalytic tests are shown in each Chapter of this thesis.

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 μ m 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⁻¹ and a second one from 100 to 240 °C at 30 °C min⁻¹. 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⁻¹. 1- μ L aliquot was injected into the GC column with a split ratio (SR) of 20.

The catalytic performance was evaluated by different indicators, and more details about the calculation are provided in each Chapter:

Conversion of a reactant i was calculated as follows:

Conversion
$$\% = \frac{n_{ir}}{n_{io}} = \frac{n_{io} - n_i}{n_{io}} \cdot 100$$

Where n_{ir} is the number of moles of i that reacted at a given reaction time, n_{io} is the number of initial moles, and n_i is the number of moles of the reactant at a given reaction time.

Yield of a product j with respect to a reactant i was calculated as follows:

$$Yield \ \% = \frac{n_j}{n_{io}} \cdot \ 100$$

Where n_j is the number of moles of the product j at a given reaction time.

Selectivity to a product j was calculated as follows:

Selectivity % =
$$\frac{n_j}{n_{ir}} \cdot 100 = \frac{n_j}{n_{io} - n_i} \cdot 100$$

Initial reaction rate is the number of moles of reactant converted per liter, per hour. Additionally, the initial reaction rate was normalized by the specific surface area of each catalyst.

Epoxide production is the number of moles of the epoxide product normalized by the specific surface area or by the number of active Ti sites.

The **Turn Over Frequency (TOF)** was calculated as the initial reaction rate normalized by the number of active Ti sites.

Chapter 1

CHAPTER 1: Optimizing the conditions towards hydrophobic Ti-SiO₂ catalysts via one-pot sol-gel chemistry

Abstract

The successful synthesis of hydrophobic titanosilicates (Ti-SiO₂) by classical sol-gel requires the meticulous optimization of the experimental conditions. The one-pot approach is a further challenging strategy considering the different hydrolysis-condensation rates of the silicon and titanium precursors, but after optimization, the method becomes less time-consuming. In addition, a proper selection of the alkyl alkoxysilane allows to control the atom that will be functionalized (i.e. here, made hydrophobic) easily. In this chapter, one-pot sol-gel was used to synthesize functionalized silica, non-functionalized (pristine) Ti-SiO₂, and functionalized Ti-SiO₂ with Ti molar ratios (Ti/(Ti+Si)) varying from 0.025 to 0.20. The alkyl alkoxysilane for the functionalization was varied among three precursors: methyl triethoxy silane (MTES), propyl triethoxy silane (PTES) and octyl triethoxy silane (OTES) to target variable hydrophobicity in the final materials. The synthesized materials were characterized by IR spectroscopy, XRD, TGA-MS, ICP-OES, XPS, DRUV, and N₂ physisorption. The catalysts were tested in the epoxidation of cyclooctene with hydrogen peroxide as oxidant. The synthesis of functionalized Ti-SiO₂ catalysts was possible under certain limits of the molar ratios of silicon and titanium precursors. Among the alkyl alkoxysilanes tested in this work, MTES was the precursor that allowed the widest range of molar ratios without affecting the gel homogeneity. Hydrophobic characteristics were detected in methyl-functionalized Ti-SiO₂ (lower OH density and less physisorbed water) compared to the pristine one. Low Ti molar ratios were most favorable for the formation of active framework-Ti (FW-Ti) species. Methyl-functionalized Ti-SiO₂ were active in the epoxidation of cyclooctene, but a positive effect of hydrophobicity on the catalytic activity was detected only for certain MTES molar ratios.

1.1. Introduction

The sol-gel procedure has been extensively used and adapted to synthesize pristine and functionalized titanosilicates $(Ti-SiO_2)$ [20]. However, some conditions of the sol-gel synthesis procedure and specifically of the one-pot approach must be considered and optimized. For example, it is known that for certain zeolitic Ti-SiO₂, such as TS-1, there is a maximum Ti molar content that can be incorporated into the

silica matrix [136]. Thus, the molar ratio of the Ti precursor will affect the incorporation of Ti and the number of active Ti sites. Regarding the hydrophobization of Ti-SiO₂, the functionalization by the one-pot approach must consider the choice of the alkyl alkoxysilane precursor and the degree of functionalization needed to modify the hydrophobic/hydrophilic balance of the catalyst surface.

In this chapter, several molar ratios of titanium butoxide (TBOT) and alkyl alkoxysilanes were tested to select the best precursors and optimal molar ratios for the synthesis of hydrophobic Ti-SiO₂. Some characterization techniques were applied and adapted to reach two main objectives: i) identification of the Ti actives species, and ii) assessment of the degree of surface functionalization and the corresponding hydrophobicity. These first experiments marked the guidelines for the experimental conditions of the catalyst synthesis in the following chapters. Furthermore, the understanding about the characterization techniques achieved in this chapter led to explore complementary techniques to elucidate the effect of hydrophobization in the following chapters. The catalytic tests showed the first hints of improvement of the catalytic activity due to functionalization of the Ti-SiO₂ catalysts.

1.2. Experimental section

1.2.1 One-pot sol-gel synthesis procedure of methylfunctionalized SiO₂, Ti-SiO₂, methyl-, propyl- and octylfunctionalized Ti-SiO₂

The one-pot sol-gel synthesis procedure used in this work was adapted from the method reported by Kukovecz et al. in 2002 [137]. The synthesis of the alkyl-functionalized materials was achieved by the replacement of a fraction of tetraethoxy silane (TEOS, Sigma-Aldrich, 98%) by an alkyl alkoxysilane, namely methyl triethoxy silane (MTES, Sigma-Aldrich, 99%), propyl triethoxy silane (PTES, Sigma-Aldrich, ≥98%) or octyl triethoxy silane (OTES, Sigma-Aldrich, 97%). Several molar ratios of the alkyl alkoxysilanes were explored (as defined in Equation 1.1): MTES molar ratios ranged from 0.1 to 0.6, PTES molar ratios ranged from 0.2 to 0.4, and OTES molar ratios ranged from 0.05 to 0.2. Precisely, 20 mL ethanol (Normapur, absolute) and 12 mL distilled water were poured into a 250-mL round-bottom three-neck flask and stirred at 750 rpm at 40 °C (using an oil bath and a cooling system) until the gel formed. TEOS and the alkyl alkoxysilane (MTES, PTES or OTES) were added dropwise under continuous stirring. Later, concentrated HCI (Sigma-Aldrich, 37%) was added to catalyze the

precursors hydrolysis. In the case of titanosilicate samples, titanium butoxide (TBOT, Sigma-Aldrich, 97% reagent grade) was added dropwise 25 minutes after HCl addition. TBOT molar ratios ranged from 0.025 to 0.20 according to Equation 1.2. The formed gel was recovered and dried under vacuum (300 mbar) and 140 °C for 3 hours. The dried solid was slightly grinded and calcined in static air following a ramp from room temperature to 500 °C at 1 °C/min and then a dwell for 3 hours at the set temperature. This calcination temperature was selected based on works that showed that methyl-functionalization resists temperatures as high as 500 °C [90, 91]. Finally, the solid was removed from the furnace after cooling down for about 4 hours, and it was stored in a desiccator.

The alkyl alkoxysilanes molar ratios were calculated according to Equation 1.1:

$$Molar \ ratio_{alkyl \ alkoxysilane} = \frac{mol_{alkyl \ alkoxysilane}}{mol_{TEOS} + mol_{TBOT} + mol_{alkyl \ alkoxysilane}}$$
(1.1)

The TBOT molar ratios were calculated according to Equation 1.2:

$$Molar \ ratio_{TBOT} = \frac{mol_{TBOT}}{mol_{TEOS} + mol_{TBOT} + mol_{alkyl \ alkoxysilane}}$$
(1.2)

1.2.2. Catalyst characterization

Samples were characterized by FTIR in ATR and transmission modes, TGA, Temperature-programmed oxidation (TPO) experiments, ICP-AES, XRD, XPS, DRUV, and N₂ adsorption-desorption experiments, as described in section 2 of Materials and Methods. Specific analysis conditions used in this Chapter are described hereafter.

In this Chapter, X-ray photoelectron spectroscopy (XPS) analyses were performed as described in the section of Materials and Methods, except for the sequence of spectra, which were recorded as follows: survey spectrum, C 1s, O 1s, Ti 2p, Cl 2p, Si 2p, and C 1s again to check the stability of charge compensation with time and the absence of sample degradation.

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 $BaSO_4$ pellet was used as a blank, and the Kubelka-Munk function F(R) was calculated using the reflectance (R).

Specific surface areas were determined by N_2 adsorption-desorption experiments performed at -196 °C (77 K) with a Tristar 3000 instrument (Micromeritics). Before the analysis the samples were degassed overnight under vacuum (50 mtorr) at 150 °C. The specific surface areas were calculated from the adsorption isotherm using the Brunauer-Emmet-Teller (BET) method.

1.2.3. Catalytic tests

The activity of the synthesized catalysts was tested in the epoxidation of cyclooctene (C_8H_{14} , Fluka, 90%,) with hydrogen peroxide (H_2O_2 , SigmaAldrich, 30% w/w) as oxidant, as defined in Equation 1.3. The reaction temperature was kept at 60 °C. The initial concentration of C_8H_{14} , was 0.1 M, the initial concentration of H_2O_2 was 0.5 M, and the catalyst addition was 10 g L⁻¹. 8.5 mL of the acetonitrile (CH₃CN, VWR Chemicals, >99.9%) as solvent 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. The reaction time was 8 h and 100 µL aliquots were sampled every hour with a syringe through a septum fitted to the reactor. The aliguots were diluted in acetonitrile and filtered through a 0.2 μ m syringe filter. The cyclooctene (C₈H₁₄) and epoxy cyclooctane (C₈H₁₄O) concentrations were monitored with gas chromatography (GC). The GC instrument was a SHIMADZU GC-2010 Plus equipped with a capillary column Shimadzu SH-RTX-5 column with Crossbondx 5% diphenyl/95% dimethyl а polysiloxane composition, 30 m, 0.25 mm ID, 0.10 µm film thickness and a theoretical maximum temperature of 330 °C. 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⁻¹. 1 μ L aliquots were 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 catalytic tests.

$$+ \frac{H}{2} + \frac{H}{2} + \frac{TI-SIO_2}{Acetonitrile, 333 K} + H^{O} + H^$$

1.3. Results and discussion

1.3.1. One-pot sol-gel synthesis of methyl-functionalized SiO_2 and Ti-SiO_2

First, methyl-functionalization of silica (no addition of TBOT) was performed in a one-pot procedure to synthesize methyl-SiO₂. A set of methyl-SiO₂ with different molar ratios of MTES (0.1, 0.2, 0.4 and 0.6) were synthesized according to a procedure adapted from Fidalgo et al. [4]. The presence of the methyl moieties in the silica matrix was verified by IR spectroscopy in ATR mode.

The IR spectra of methyl-SiO₂ in ATR mode (Figure 1.1) showed the presence of the methyl moiety bound to silicon (v(Si-C)) at 1279 cm⁻¹. This band increased for increasing nominal molar ratios of MTES. Likewise, the band corresponding to the asymmetrical vibration of methyl groups ($v_{as}(Si-CH_3)$) at 2973 cm⁻¹ increased with higher molar ratios of MTES. In fact, the bands at 1279 cm⁻¹ and 2973 cm⁻¹ were observed better in ATR mode than in transmission mode likely because of the sample dilution in a pellet that the latter mode required. The band at 1080 cm⁻¹ that corresponds to the asymmetrical vibration of Si-O-Si (v_{as}(Si-O-Si)), shifted to lower wavenumber values when methyl moieties were present in the structure. This shifting was previously observed by Fidalgo et al. [4], and it was attributed to a structural change in the silica network. Fidalgo and co-workers found that pure silica structure is dominated by four-member siloxane rings, whereas methyl-functionalized silica network is mostly formed by six-member siloxane rings which are larger and less tensioned structures that can better allocate the methyl moiety [4]. However, the sample with 0.6 MTES molar ratio exhibited visible heterogeneities during and after the gel formation, indicating that excessive methyl-functionalization affects the homogeneity of the synthesized catalysts. The band at 945 cm⁻¹ that is attributed to hydrophilic residual silanol groups, decreased when MTES was added to the silica structure. Consistent with this behavior, the band that corresponds to v(O-H) (centered at 3300 cm⁻¹) decreased when more MTES was added, supporting the hydrophobization effect of methyl-functionalization of silica.



Figure 1.1. ATR-IR spectra of SiO₂ and methyl-functionalized SiO₂. Two regions of the spectra are shown: i) left: 900 to 1350 cm⁻¹ and ii) right: 2625 to 3625 cm⁻¹

A series of titanosilicates (Ti-SiO₂) with Ti molar ratio ranging from 0.025 to 0.20 were also synthesized and characterized by FTIR spectroscopy in transmission mode to evaluate the effect of varying the Ti molar ratio on the catalyst structure (Figure 1.2). In this case, the transmission mode provided semi-quantitative comparison among the samples with different Ti molar ratios.

The band of Si-O-Si (v_{as}(Si-O-Si)) at 1080 cm⁻¹ slightly shifted to lower wavenumbers due to the substitution of the Si atom by a larger Ti atom, which probably promoted a different configuration of the siloxane ring in the silica structure, similar to the structure change observed for the addition of MTES. The band at 950 cm⁻¹ is attributed to silanol groups [4], and a close band at 960 cm⁻¹ is attributed to the Si-O-Ti bridges [19]. It is known that the Si-O-Ti bridges are required in the formation of the active sites for epoxidation; however, not all Ti involved in the Si-O-Ti bridges are active. Only isolated framework-Ti (FW-Ti) ones are active and Ti bound to one (or more) O-Ti form other Ti species which are not active. As shown in Figure 1.2, the higher absorbance at 960 cm⁻¹ detected in the IR spectra of Ti-SiO₂ materials compared to the SiO₂ spectrum could be related to the presence of the Si-O-Ti bridges. However, a clear relation between the molar ratio of the titanium precursor (TBOT) and the absorbance at this wavenumber was not found in this section of our work. This band did not increase according to the increasing Ti nominal molar ratio. This indicated that only a certain number of Ti atoms can be accommodated in the network to form Si-O-Ti entities. In fact, Stakheev et al. (1993) and Greegor et al.

(1983), found that there is a maximum Ti loading (10 wt%) up to which a homogeneous solid solution forms [138, 139]. Therefore, at too high Ti molar ratios, total incorporation of Ti is not possible, as confirmed here.



Figure 1.2. Transmission-FTIR spectra of SiO_2 and Ti- SiO_2 at Ti molar ratios ranging from 0.025 to 0.20. Two regions of the spectra are shown in the wavelength range from 1600 to 850 cm⁻¹

The IR spectra of Ti-SiO₂ with Ti molar ratios up to 0.15 exhibited the presence of the same bands (same fingerprint), and the intensities of the Si-O-Si and Si-O-Ti bands decreased for increasing Ti molar ratios. In contrast, the IR spectrum of SiO₂-0.20 Ti displayed bands slightly shifted and the intensity of the Si-O-Si band at 1080 cm⁻¹ increased. This could be attributed to the difficulty to allocate Ti atoms in the network leading to a higher content of Si-O-Si bridges. At this point, Ti molar ratios up to 0.15 were apparently able to allocate Ti atoms in the network without causing large differences in the structure. Samples with lower Ti molar ratios displayed larger peak areas for the band corresponding to the Si-O-Ti bridges.

A sample with Ti molar ratio of 0.25 was also synthesized, but after the sol-gel synthesis, two phases were visually distinguished, showing no homogeneity of the sample due to the different hydrolysis and condensation rates of Si and Ti precursors [140]. Furthermore, after calcination, XRD analysis showed presence of anatase (Figure A-1,

Appendix). The latter result agrees with the findings of Stakheev *et al.* and Greegor *et al.* [138, 139].

The band at 950-960 cm⁻¹ corresponds to both silanol and Si-O-Ti bridge. In order to discriminate the contribution only due to the Si-O-Ti bridge, a pellet of SiO₂-0.15 Ti was prepared and heated at 400 °C inside a cell with a NaCl window under vacuum for 4 h. After recording the IR spectrum of the dehydrated sample, it was exposed to atmospheric conditions and more spectra were recorded at different times to monitor the evolution of the band with the progressive sample rehydration.

Figure 1.3 shows that the OH band centered at 3400 cm⁻¹ increases according to the exposure time to atmospheric conditions, indicating the hydration due to water affinity, but the band at 950-960 cm⁻¹ did not increase. Therefore, this band corresponds mostly to the Si-O-Ti bridge. The dehydration treatment allowed to identify the band corresponding to isolated OH at 3750cm⁻¹ and the band corresponding to hydrogen-bonded OH at 3400-3750 cm⁻¹ [112].



Figure 1.3. Transmission-FTIR spectra of hydration during 220 minutes of the Ti-SiO₂ with Ti molar ratio of 0.15 after being vacuumed at 400 $^{\circ}$ C for 4 h.

1.3.2. One-pot sol-gel synthesis of methyl-, propyl-, and octyl-functionalized Ti-SiO $_2$

Three types of alkyl alkoxysilanes (MTES, PTES, and OTES) were used for the synthesis of functionalized Ti-SiO₂. We hypothesized that longer alkyl chains would increase the hydrophobic character of the titanosilicates. In addition, two Ti nominal molar ratios (0.05 and 0.15) were tested to explore the effect of the simultaneous addition of the alkyl alkoxysilane and the Ti precursor during synthesis.

The previous section dedicated to the synthesis of methylfunctionalized silica showed that the maximum MTES molar ratio that allowed to obtain a homogenous gel was 0.4, so two methylfunctionalized samples with Ti nominal molar ratios of 0.05 and 0.15 were synthesized: 0.4MTES-0.05Ti and 0.4MTES-0.15Ti.

In the case of propyl-functionalized Ti-SiO₂, three PTES nominal molar ratios were tested (0.2, 0.3 and 0.4) in combination with a Ti nominal molar ratio of 0.15, but during the synthesis, a biphasic gel was obtained with PTES molar ratios of 0.3 and 0.4. Therefore, only two propyl-functionalized Ti-SiO₂ were studied by IR spectroscopy: 0.2PTES-0.05Ti and 0.2PTES-0.15Ti. Similarly, octyl-functionalized Ti-SiO₂ were synthesized with three different OTES molar ratios (0.05, 0.1, and 0.2) in combination with a Ti molar ratio of 0.15, but during the synthesis, a biphasic gel was formed with 0.1 and 0.2 molar ratios. Thus, only two octyl-functionalized Ti-SiO₂ samples were studied by IR spectroscopy: 0.05OTES-0.05Ti and 0.05OTES-0.15Ti.

The IR spectra in ATR mode of the alkyl-functionalized Ti-SiO₂ are shown in Figure 1.4. Samples with longer alkyl chains displayed a stronger band at 2980 cm⁻¹ which corresponds to the asymmetrical vibration of CH₃ [4, 141] despite the lower nominal molar ratios of PTES and OTES compared to the molar ratio of MTES. A previous work found that larger areas of the band at 2980 cm⁻¹ are related to lower sol-gel efficiency caused by alkyl chains longer than methyl [4]. The OH band, centered at 3260 cm⁻¹, was stronger in the octylfunctionalized Ti-SO₂ than in the propyl- and methyl-functionalized Ti-SiO₂, indicating that the hydrophobic character did not increase with the length of the alkyl chain, contrarily to what we had hypothesized. In fact, alkoxysilanes with longer alkyl chains affected the efficiency of the hydrolysis-condensation reactions during sol-gel synthesis and produced catalysts with higher hydrophilicity. This behavior was previously observed for ethyl- and propyl-functionalized silicas [4]. Additionally, the simultaneous addition of the Ti precursor decreased even more the efficiency of the sol-gel synthesis, leading to biphasic systems in the case of too high molar ratios of alkyl alkoxysilanes. Moreover, the samples functionalized with PTES and OTES, exhibited a brown color after calcination, indicating that the propyl and octyl moieties were burned. Ti-SiO₂ functionalized with MTES did not change their color after the calcination treatment. These observations strongly suggested that the molar ratios of the precursors must be optimized and that the MTES precursor allows to explore a wider range of molar ratios combined with the addition of Ti precursor.



Figure 1.4. ATR-IR spectra of methyl-, propyl-, and octyl-functionalized $Ti-SiO_2$ with Ti molar ratios of 0.05 and 0.15. The alkyl alkoxysilanes used for the synthesis were MTES, PTES and OTES, respectively. The spectra were vertically offset for clarity.

1.3.3. Synthesis and characterization of methyl-functionalized Ti-SiO $_{2}$

According to the previous results of non-functionalized $Ti-SiO_2$ samples, both TBOT and MTES molar ratios cause structural changes, so two sets of samples were synthesized to study the effect of methyl-functionalization of $Ti-SiO_2$. One of the sets was synthesized with different Ti molar ratios and constant MTES molar ratio, and the other set was synthesized with different MTES molar ratios and constant Ti molar ratio. For the first set of samples, the MTES molar ratio was

selected based on the previous section of this work which showed that MTES molar ratios up to 0.4 produced homogeneous catalysts. For the second set, the selected Ti molar ratio was 0.15 based on the maximum amount of Ti that can be allocated in the silica network according to a previous section of this work. These two sets of samples were characterized to assess their effective degree of methyl-functionalization, their hydrophobic character, and their number of Ti active sites. Finally, the effect of adjusting the hydrophobic character of Ti-SiO₂ catalysts was studied in the epoxidation of cyclooctene with hydrogen peroxide.

1.3.3.1. Assessing the degree of methyl-functionalization and hydrophobic character by FTIR spectroscopy and TGA-MS

The transmission spectra of Ti-SiO₂ with constant MTES molar ratio of 0.4 but increasing Ti molar ratio is shown in Figure 1.5. The bands at 1279 cm⁻¹ and 2973 cm⁻¹ corresponding respectively to carbon bound to silicon (v(Si-C)) and to methyl moieties bound to silicon (v(Si-C)) and to methyl moieties bound to silicon (v(Si-CH₃)) are present. These samples were expected to contain the same amount of methyl moieties, but a rough estimation (peak areas) indicated that there is not the same amount of methyl moieties in all the samples. The area of the OH band (3400 cm⁻¹) decreased for samples with increasing Ti molar ratios. This pointed out a possible hydrophobic effect correlated to increasing Ti molar ratios. A plausible explanation was that higher Ti molar ratios could promote formation of TiO₂ domains that diminished the oxidative potential of Ti-SiO₂, leading to more methyl moieties remaining after calcination.



Figure 1.5. Transmission-FTIR spectra of methyl-functionalized Ti-SiO₂. Two regions of the spectra are shown: i) left: 1600 to 850 cm⁻¹ and ii) right: 4000 to 2500 cm⁻¹

Moreover, a negative correlation between the Ti molar ratio and the absorbance for the Si-O-Ti band at 950-960 cm⁻¹ was observed, similar to what was shown for inorganic (i.e. non-methyl-functionalized) Ti-SiO₂. Too high Ti molar ratios hinder the formation of Si-O-Ti bridges likely favoring the formation of TiO₂ domains. Still, XRD analyses did not indicate any crystalline phase of TiO₂ in the samples. This is explained by the formation TiO₂ nanodomains difficult to be detected by XRD.

ATR-FTIR spectra were also collected for Ti-SiO₂ synthesized with a constant Ti molar ratio of 0.15 and MTES molar ratios varying from 0.1 to 0.4 (Figure 1.6). The Si-O-Si band at 1080 cm⁻¹ shifted slightly to lower wavenumbers in the case of the methyl-functionalized samples compared to pure SiO₂ (reference sample). This behavior was also observed for methyl-functionalized SiO₂ samples shown previously, which corroborates a structure modification due to the formation of sixmember siloxane rings instead of four-member siloxane rings.



Figure 1.6. ATR-FTIR spectra of SiO₂, Ti-SiO₂ and methyl-functionalized Ti-SiO₂. The Ti molar ratio of all Ti-SiO₂ samples was 0.15. Two regions of the spectra are shown: i) left: 1400 to 900 cm⁻¹ and ii) right: 3750 to 2750 cm⁻¹

Figure 1.6 shows that the intensity of the band for the Si-O-Ti bridge at 950-960 cm⁻¹ decreased for higher degrees of nominal methyl-functionalization despite the constant Ti molar ratio. The Si-O-Ti band in the sample with 0.4 MTES molar ratio exhibited the lowest intensity.

Additionally, the band that corresponds to the vibration of Si-C (v(Si-C)) at 1279 cm⁻¹ increased for higher MTES molar ratios.

FTIR spectroscopy provided some insights about the effect of methylfunctionalization over the hydrophobic character of the samples. However, it was required to quantify the methyl moieties and the corresponding hydrophobic character, so TGA analyses were performed for the two series of samples.

The TGA profiles for the set of samples with constant MTES nominal molar ratio and increasing Ti molar ratios are given in Figure 1.7. Two main mass losses were observed: the first one was attributed to physisorbed water, and the second one to combustion of methyl moieties. From the derivative curves in Figure 1.7, the first mass loss in all samples occurred in the temperature range of 80-100 °C, whereas the second mass loss was centered in the temperature range 590-610 °C. A fraction of the methyl moieties remained in the catalyst and this amount was estimated by the mass losses measured by TGA.



Figure 1.7. TGA profiles (dashed lines) of calcined methylfunctionalized Ti-SiO₂ catalysts with Ti molar ratios from 0.025 to 0.20. All measurements were performed under air flow (50 mL/min). Solid lines are the derivative of the TGA profiles.

A comparison between the mass losses corresponding to physisorbed water and organic content is shown in Figure 1.8. These samples should contain the same amount of organic content since the nominal MTES molar ratio was set constant at 0.4. However, after calcination,

a lower remaining content of methyl moieties was recorded for samples with lower Ti molar ratios. This was in line with FTIR characterization that showed that Ti molar ratio affected the remaining amount of methyl moieties after calcination. Moreover, samples with higher methyl content exhibited less physisorbed water, displaying a correlation between the catalyst hydrophobic character and the methyl content.



Figure 1.8. Water mass loss as a function of methyl mass loss. Mass losses were estimated from TGA analysis of $Ti-SiO_2$ catalysts with a nominal MTES molar ratio of 0.4 and Ti molar ratios varying from 0.025 to 0.20. The dashed line represents a linear fit.

The hydrophobic effect was evaluated by comparing the TGA profiles of methyl-functionalized samples in the range from 0.1 to 0.4 (Figure 1.9). At constant Ti molar ratio of 0.15, being the maximum Ti molar ratio achievable according to our first observations, increasing MTES molar ratios leads to lower physisorbed water contents. In fact, the derivative profiles show that the water desorption process occurs at lower temperatures as the MTES molar ratio increases.



Figure 1.9. TGA profiles (dashed lines) of calcined methylfunctionalized Ti-SiO₂ catalysts with MTES molar ratios varying from 0.1 to 0.4. All measurements were performed under air flow (50 mL·min⁻¹). Solid lines correspond to the derivative of the TGA curve (dTG).

Based on the TGA data, the physisorbed water (40-200 °C) and methyl (>500 °C) contents were calculated (Figure 1.10).

To identify the sources of the mass losses recorded by TGA, TPO experiments were carried out under conditions similar to the ones used in TGA. The furnace was coupled to a mass spectrometer (MS) detector. The profiles of dried and calcined Ti-SiO₂ were compared to evaluate the effect of calcination over the removal of unreacted precursors or solvent (Figure 1.11).

Calcination is a crucial step in catalyst synthesis that allows the removal of precursor residues prior to catalytic experiments. However, in this case, calcination should not remove the methyl moieties on the catalyst surface. Therefore, this study was performed to determine the effect of calcination at 500 °C on both the preservation of methyl moieties and removal of precursor residues.



Figure 1.10. Physisorbed water and methyl content estimated from TGA data for Ti-SiO₂ catalysts with Ti molar ratio of 0.15 and MTES molar ratios from 0.1 to 0.4.

Figure 1.11 shows that there is agreement between the TGA profiles and the mass to charge ratios (m/z) detected by MS even though these analyses are performed separately. The first mass loss detected in the temperature range 40-180 °C corresponds to physisorbed water (m/z=18) in dried and calcined samples. Methyl-functionalized samples exhibited lower physisorbed water content than the pristine sample, confirming TGA observations about the catalyst hydrophobicity induced by higher methyl content.



Figure 1.11. dTG-MS profiles of 0.15Ti, 0.15Ti-0.2MTES and 0.15Ti-0.2MTES after drying and after calcination at 500 °C under air flow.

The second mass loss detected at 180-500 $^{\circ}$ C in TGA and MS profiles of the dried samples is related to water (m/z=18) and carbon dioxide (m/z=44), probably due to burning of unreacted precursors. This mass loss is barely detected in the calcined samples, demonstrating that calcination was successful at removing the unreacted precursors.

The mass loss detected after 500 °C is also related to water (m/z=18) and carbon dioxide (m/z=44), likely formed due to methyl combustion. Indeed, only methyl-functionalized samples displayed water and carbon dioxide signals above 500 °C in both dried and calcined samples. Additionally, intensity of these signals increased accordingly to the nominal MTES molar ratios. These results confirm that methyl moieties remain on the catalyst even after calcination.

Interestingly, methyl (m/z=15) and hydrogen (m/z=2) were detected consistently in methyl-functionalized samples at temperatures above 500 °C. This is probably due to removal of unburned methyl moieties, which in contact with water might have generated hydrogen.

To sum up, methyl moieties remaining after calcination induced a hydrophobic character on the catalyst and this was consistent with the nominal MTES molar ratio. The methyl content was better preserved during calcination in catalyst with higher Ti molar ratios. TGA-MS provided an estimation of the amount of methyl moieties remaining; however, a better analytical technique to quantify the effective methylfunctionalization degree is still missing at this stage.

1.3.3.2. Detection and quantification of active sites on the catalyst by FTIR, ICP-AES and XPS

As reported in the literature, FTIR spectroscopy allows identifying the presence of the Si-O-Ti bridge [19] which provides information about the incorporation of Ti into the silica matrix as required (although not sufficient) to obtain the active sites in Ti-SiO₂ catalysts. FTIR spectra of the two series of Ti-SiO₂ catalysts, the one with increasing Ti molar ratios and the second one with increasing MTES molar ratios, were recorded. As observed in Figures 1.5 and 1.6 (previous section), the presence of the Si-O-Ti bridge was detected in all catalysts, indicating the incorporation of Ti into the silica matrix which increases the likelihood of the presence of active sites for epoxidation. However, this analysis did not allow the quantification of Ti species and specially the active ones on the catalyst surface. Therefore, XPS and ICP-AES analyses were performed to quantify the surface and bulk Ti content (Table 1.1), respectively. The atomic percentage of oxygen is high

compared to the atomic percentage of silicon. This occurs due to hydroxyl groups on the catalysts surface that remain even after degassing the sample before XPS analysis.

Table 1.1. Bulk and surface elemental composition of Ti-SiO₂ with MTES molar ratio of 0.4 and increasing Ti molar ratio from 0.025 to 0.20

Sampla	Bulk Ti	Bulk Si	Surf. Ti	Surf. Si	Surf. C	Surf. O
Sample	wt.% ^a	wt. % ^a	at.% ^b	at.% ^b	at.% ^b	at.% ^b
0.025 Ti-0.4 MTES	1.7	42.4	0.3	24.7	6.6	68.4
0.05 Ti-0.4 MTES	3.2	40.6	0.4	27.3	11.5	60.8
0.10 Ti-0.4 MTES	6.0	38.2	1.5	24.1	9.4	65.0
0.15 Ti-0.4 MTES	10.4	35.8	1.3	22.5	11.6	64.6
0.20 Ti-0.4 MTES	11.7	32.4	2.8	23.3	10.7	63.2

^aBulk composition was determined by ICP-AES. ^bSurface elemental composition was determined by XPS.

Bulk and surface atomic Ti/(Ti+Si) ratios were calculated based on the ICP-AES and XPS results obtained for the series of samples with MTES molar ratio of 0.4 and increasing Ti molar ratio from 0.025 to 0.20 (Table 1.2).

Table 1.2. Bulk and surface atomic Ti/(Ti+Si) ratios of Ti-SiO₂ with MTES molar ratio of 0.4 and increasing Ti molar ratio from 0.025 to 0.20

		Nominal	Bulk	Surf.
	Sample	Ti/(Ti+Si)) Ti/(Ti+S	i) Ti/(Ti+Si)
_		at. ratio	at. ratio	^a at. ratio ^b
_	0.025 Ti-0.4 MTES	0.025	0.023	0.011
	0.05 Ti-0.4 MTES	0.05	0.044	0.015
	0.10 Ti-0.4 MTES	0.10	0.084	0.059
	0.15 Ti-0.4 MTES	0.15	0.145	0.055
	0.20 Ti-0.4 MTES	0.20	0.175	0.108
	^a determined from bulk	composition	(ICP-AES).	^b determined from

surface elemental composition (XPS).

Bulk atomic Ti/(Ti+Si) ratios were slightly lower than the nominal Ti/(Ti+Si) ratios which indicated that the incorporation of the Ti precursor was slightly affected by its fast hydrolysis-condensation rate. Bulk and surface atomic ratios of pristine Ti-SiO₂ catalysts are shown in Table 1.3 as reference, and they were calculated based on the bulk and elemental composition (Table A-1, Appendix). Comparison of bulk Ti ratios in methyl-functionalized samples against the pristine ones showed that the addition of the methyl precursor (MTES) at a molar ratio of 0.4 led to similar bulk Ti molar ratios.

Comparison of bulk and surface atomic Ti/(Si+Ti) ratios showed that there was an enrichment of Ti in the bulk that could lead to formation of TiO_2 domains. This showed that Ti was heterogeneously incorporated in the methyl-functionalized catalysts, and only a fraction of Ti atoms was found at the surface.

with increas	sing it mola	a rado from C	1.025 10 0.20	
	Nominal	Bulk	Surf.	
Sample	Ti/(Ti+Si)	Ti/(Ti+Si)	Ti/(Ti+Si)	
	at. ratio	at. ratio ^a	at. ratio ^b	
0.025 Ti	0.025	0.025	0.020	
0.05 Ti	0.05	0.042	0.032	
0.10 Ti	0.10	0.081	0.066	
0.15 Ti	0.15	0.137	0.060	
0.20 Ti	0.20	0.184	0.100	
adotorminod	from bulk	composition		

Table 1.3. Bulk and surface atomic Ti/(Ti+Si) ratios of pristine Ti-SiO₂ with increasing Ti molar ratio from 0.025 to 0.20

^adetermined from bulk composition (ICP-AES). ^bdetermined from surface elemental composition (XPS).

Bulk and surface elemental composition were also measured for the series of Ti-SiO₂ with Ti molar ratio of 0.15 and increasing MTES molar ratios (Table 1.4). Bulk and surface atomic Ti/(Ti+Si) ratios were calculated as well (Table 1.5).

Table 1.4. Bulk and surface elemental composition of Ti-SiO₂ with Ti molar ratio of 0.15 and increasing MTES molar ratios

Sampla	Bulk Ti	Bulk Si	Surf. Ti	Surf. Si	Surf. C	Surf. O
Sample	wt.% ^a	wt. % ^a	at.% ^b	at.% ^b	at.% ^b	at.% ^b
0.15 Ti	9.3	34.4	2.2	24.6	3.4	69.8
0.15 Ti-0.1 MTES	10.6	36.3	1.9	23.5	6.3	68.4
0.15 Ti-0.2 MTES	10.2	36.0	1.3	24.9	5.3	68.5
0.15 Ti-0.4 MTES	10.4	35.8	1.3	22.9	11.8	64.0

^aBulk composition was determined by ICP-AES. ^bSurface elemental composition was determined by XPS.

Table 1.5. Bulk and surface atomic ratios of methyl-functionalized Ti-SiO₂ catalysts with Ti molar ratio of 0.15

_					
		Nominal	Bulk	Surf.	
	Sample	Ti/(Ti+Si)	Ti/(Ti+Si)	Ti/(Ti+Si)	
		at. ratio	at. ratio ª	at. ratio ^b	
	0.15 Ti	0.15	0.137	0.084	
	0.15 Ti-0.1 MTES	0.15	0.147	0.074	
	0.15 Ti-0.2 MTES	0.15	0.142	0.050	
	0.15 Ti-0.4 MTES	0.15	0.145	0.055	
		141 /1			

^adetermined from bulk composition (ICP-AES). ^bdetermined from surface elemental composition (XPS).

Similar to what was observed for the catalysts functionalized at constant MTES molar ratio, bulk atomic Ti/(Ti+Si) ratios were slightly lower than the nominal Ti/(Ti+Si) ratios, which indicated that the Ti precursor was incorporated successfully.

Comparison of bulk and surface atomic Ti/(Si+Ti) ratios showed once more that there was an enrichment of Ti in the bulk. Moreover, surface Ti/(Ti+Si) ratios were lower in catalysts with higher MTES molar ratios, pointing out an effect of the one-pot addition of the methylfunctionalized precursor over the Ti content on the catalyst surface. This trend was consistent with the FTIR spectra which showed that the band corresponding to the Si-O-Ti bridge decreased at higher MTES molar ratios. In an attempt to differentiate Ti incorporated as epoxidation active sites and Ti forming TiO₂ (not active for epoxidation), the XPS O 1s, Ti 2p and Si 2p spectra were studied and compared among pure SiO₂, pure TiO₂, Ti-SiO₂ and methyl-functionalized Ti-SiO₂.

As shown in Figure 1.12, the binding energy (BE) of O 1s in SiO₂ is centered at 533 eV, whereas the BE of O 1s in TiO₂ is centered at 530 eV. Moreover, the O 1s spectra of the pristine and methyl-functionalized Ti-SiO₂ displayed a shoulder that is centered in the range 530-533 eV, demonstrating the presence of other species than O-Si or O-Ti. In fact, this difference in BEs allowed distinguishing the contributions of the O-Si, O-Ti, and Si-O-Ti bridges by peak decomposition.

The Ti 2p spectrum is composed of two spin-orbit components (Ti $2p_{3/2}$ and Ti $2p_{1/2}$) which are separated by 5.7 eV [142]. The typical binding energy of Ti $2p_{3/2}$ in TiO₂ is 458.5 eV [138, 143-147]. As shown in Figure 1.12, the BE of the Ti doublet in Ti-SiO₂ was shifted by 0.7 eV to a higher BE, which indicated that other Ti species different from the octahedral ones (typical of TiO₂) were present on the catalyst surface, likely Si-O-Ti bridges.

The BE of Si 2p in SiO₂ is centered at 104 eV, whereas in Ti-SiO₂, it is slightly shifted to a lower value.



Figure 1.12. XPS O 1s, Ti 2p, and Si 2p spectra for SiO₂ (green line), TiO₂ (black line), Ti-SiO₂ with Ti molar ratio of 0.2 (blue line), and Ti-SiO₂ with Ti molar ratio of 0.2 and MTES molar ratio 0.4 (red line).

In order to confirm the presence of the Si-O-Ti bridge, the peak decomposition of XPS O 1s spectra was attempted under various hypotheses. The first hypothesis was that the system was composed of only two chemical environments: O-Si and O-Ti, which would correspond to the case where no Si-O-Ti bridge is present. The second hypothesis was that the system was composed of three chemical environments: O-Si, O-Ti and Si-O-Ti. The third one was that the system was composed of two chemical environments: O-Si and Si-O-Ti, which would correspond to the case where Ti is totally incorporated in the silica matrix. XPS spectra of pure SiO₂ and pure TiO₂, synthesized with the same sol-gel method used for the synthesis of Ti-SiO₂ catalysts, were used as references for peak decomposition.

After screening the three hypotheses, it was found that the binding energy of O 1s was better fitted by a trimodal system of O-Si, O-Ti and Si-O-Ti (Figure 1.13). The decomposition showed that samples with higher Ti molar ratios consistently displayed a higher fraction of Ti-O (TiO₂), as well as a higher fraction of Si-O-Ti (Table 1.6). In fact, the sample with Ti molar ratio Ti/(Si+Ti)=0.20 displayed the largest O-Ti and Si-O-Ti components.



Figure 1.13. Decomposition of XPS O 1s spectra of a) 0.05 Ti-0.4 MTES, b) 0.10 Ti-0.4 MTES, c) 0.15 Ti-0.4 MTES, and d) 0.20 Ti-0.4 MTES. Si-O (blue line), Ti-O (light blue line) and Si-O-Ti (red line) were considered as components. The measured spectra are represented by the gray line and the corresponding fit is represented by the black solid line (sum of the three components).

	Surf.	Surf.	Surf.
Sample	Si-O-Ti	Si-O-Ti/O	O-Ti/O
-	% ^a	% ^b	%°
0.025 Ti-0.4 MTES	n.d. ^d	n.d. ^d	n.d. ^d
0.05 Ti-0.4 MTES	0.5	0.9	0.9
0.10 Ti-0.4 MTES	1.5	2.3	2.1
0.15 Ti-0.4 MTES	1.6	2.5	1.9
0.20 Ti-0.4 MTES	4.1	6.5	3.7

Table 1.6. Surface ratio of Si-O-Ti determined from the decomposition of XPS O 1s spectra of methyl-functionalized Ti-SiO₂ catalysts

^adetermined from the decomposition of XPS O 1s spectra. ^bdetermined from the fraction of O as Si-O-Ti. ^c determined from the fraction of O as O-Ti. ^dnot determined.

These results contradicted the trend observed in the transmission-FTIR spectra (Figure 1.5), in which the sample with the highest content of Ti active species was the one with the lowest nominal Ti molar ratio (Ti/(Si+Ti)= 0.025). Even though transmission-FTIR is a bulk technique and XPS is a surface one, there should be certain agreement on the assessment of the presence of the active species. The decomposition of XPS O 1s spectra, assuming a trimodal system, was challenging and probably led to an overestimation of the number of active sites since the Ti in the Si-O-Ti bridge could be as well bound to O-Ti which does not correspond to the Ti active species. Moreover, the decomposition of O 1s spectra was limited by the Ti molar ratio. In fact, the decomposition result reached the XPS detection limit for the catalyst with Ti molar ratio lower than 0.05. Same trends were observed for pristine and methyl-functionalized Ti-SiO₂ samples. Supplementary XPS spectra for pristine Ti-SiO₂ are provided in Appendix (Figures A-2).

The O 1s XPS decomposition suggested the presence of different Ti species, and even though the quantification was challenging, it pointed out the possibility of identifying and quantifying Ti active species on the catalysts through the decomposition of the XPS Ti 2p spectra directly.

Quantification of the active Ti species was attempted by studying the Ti 2p spectra of the catalysts. As shown in Figure 1.14, the shift and peak broadening of Ti 2p XPS spectra of the Ti-SiO₂ samples compared to pure TiO₂ (formed by extra-framework Ti) were attributed to the presence of FW-Ti together with EFW-Ti [138, 143-147]. Thus, decomposition and quantification were attempted on the basis of these two Ti species.
First the series of samples with Ti molar ratios ranging from 0.025 to 0.20 and constant MTES molar ratio at 0.4 were studied. The decomposition was performed under the following constraints: i) the Ti 2p spectrum is formed by two components which are FW-Ti and EFW-Ti, ii) the separation of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ for each component is 5.7 eV [142], and iii) the area of Ti $2p_{1/2}$ corresponds to half of the area of Ti $2p_{3/2}$. The decomposition successfully distinguished the FW-Ti and EFW-Ti components; however, the binding energy of each component varied among the samples. Thus, to perform a consistent quantification of Ti species in all samples, a fixed difference between the Ti species was set until the best fit would be attained. The difference that best fitted all the samples was 1.2 eV and quantification of the Ti species was performed.

Figure 1.14 shows that the fraction of active Ti species (FW-Ti) is lower than the one of EFW-Ti in all methyl-functionalized Ti-SiO₂. Even though, noise to signal ratio is high in samples with low Ti molar ratios, quantification of the Ti species was possible due to the significant difference of binding energies. As shown in Table 1.7, the sample with highest percentage of active species (and lowest percentage of EFW-Ti) is the sample with the lowest nominal Ti molar ratio (0.025). This was consistent with FTIR observations that exhibited that the intensity of the Si-O-Ti bridge decreased for increasing Ti molar ratios, confirming that XPS Ti 2p spectrum decomposition allows identifying and quantifying the Ti active sites on the catalyst surface.



Figure 1.14. Decomposition of XPS Ti 2p spectra of: (a) 0.025 Ti-0.4 MTES, (b) 0.05 Ti-0.4 MTES, (c) 0.10 Ti-0.4 MTES, (d) 0.15 Ti-0.4 MTES, and (e) 0.20 Ti-0.4 MTES. FW-Ti (green line) and EFW-Ti (red line) were considered as components. The measured spectra are represented by the gray line and the corresponding fit is represented by the black solid line (sum of the components).

	Surf.	Surf.		
Sample	FW-Ti/(Ti+Si)	FW-Ti/Ti		
	at. ratio ^a	% a		
0.025 Ti-0.4 MTES	0.004	35		
0.05 Ti-0.4 MTES	0.003	20		
0.10 Ti-0.4 MTES	0.010	17		
0.15 Ti-0.4 MTES	0.005	10		
0.20 Ti-0.4 MTES	0.014	13		
adatormined from the fraction of Tilds EW/ Tilded the surface				

Table 1.7.	Surface ratio of FW-Ti determined from the decompositio	n
of XPS	Ti 2p spectra of methyl-functionalized Ti-SiO ₂ catalysts	

^adetermined from the fraction of Ti as FW-Ti and the surface elemental composition.

Furthermore, quantification of the active Ti species on the catalysts with Ti molar ratio of 0.15 and MTES molar ratios from 0.1 to 0.4 was also attempted under the same constraints applied for the previous series of samples.

Figure 1.15 and Table 1.8 show that the FW-Ti/(Ti+Si) ratio slightly decreased in samples with higher methyl-functionalization degree, which indicated that methyl-functionalization slightly affected the formation of the active Ti species at a nominal Ti molar ratio of 0.15. This was attributed to the higher hydrolysis-condensation rate of the Ti precursor (TBOT) compared to the one of the methylated precursor (MTES) [97, 140], which can affect the insertion of Ti in the methyl-functionalized silica framework, particularly, at high molar ratios of MTES.



Figure 1.15. Decomposition of XPS Ti 2p spectra of methyl-functionalized Ti-SiO₂ with Ti molar ratio of 0.15 and different MTES molar ratios: (a) 0.15 Ti, (b) 0.15 Ti-0.1 MTES, (c) 0.15 Ti-0.2 MTES, and (d) 0.15 Ti-0.4 MTES.

Table 1.8. Surface ratio of FW-Ti determined from the decompositions
of XPS Ti 2p spectra methyl-functionalized Ti-SiO2 with Ti molar ratio
of 0.15 and MTES molar ratio ranging from 0.1 to 0.4

	Surf.	Surf.
Sample	FW-Ti/(Ti+Si)	FW-Ti/Ti
	at. ratio ^a	% ª
0.15 Ti	0.013	16
0.15 Ti-0.1 MTES	0.011	15
0.15 Ti-0.2 MTES	0.007	14
0.15 Ti-0.4 MTES	0.005	10

^adetermined from the fraction of Ti as FW-Ti and the surface elemental composition.

At this stage, studying the effect of the Ti molar ratio as well as of the degree of methyl-functionalization over the formation of active Ti sites was necessary. Therefore, diffuse reflectance UV (DRUV) spectroscopy was used to distinguish active Ti species from the oligomeric Ti species (inactive ones). Previous DRUV characterization of titanosilicates have reported that framework Ti (FW-Ti) appears in the range 200-240 nm, whereas extra-framework Ti (EFW-Ti) is found in the range of 240-330 nm [23, 148-150].

Non-functionalized and methyl-functionalized samples with three Ti molar ratios were first studied: 0.025, 0.15 and 0.25. Here, the sample with Ti molar ratio of 0.25 was known from previous XRD analysis to exhibit anatase domains, whereas the other samples did not exhibit this crystalline phase. As shown in Figure 1.16, the sample with Ti molar ratio of 0.25 displayed the highest signal at wavelengths above 310 nm, confirming the presence of TiO₂ domains. The samples with Ti molar ratio of 0.15 also exhibited the presence of EFW-Ti, although in lower intensity than the samples at Ti molar ratio of 0.25. In general, catalysts with lower Ti molar ratios induced less EFW-Ti. The 0.025 Ti sample displayed the strongest signal in the wavelength range assigned to FW-Ti, while the 0.025 Ti-0.4 MTES exhibited an increment of EFW-Ti species compared to the pristine analogous. At low Ti molar ratios, the effect of methyl-functionalization over Ti speciation became stronger. This observation agrees with FTIR and XPS characterization.



Figure 1.16. DRUV spectra of pristine and methyl-functionalized (MTES molar ratio =0.4) Ti-SiO₂ catalysts at three Ti molar ratios: 0.025, 0.15, and 0.25.

As DRUV successfully distinguished FW-Ti from EFW-Ti species, the series of samples at constant Ti molar ratio of 0.15 and MTES molar ratio of 0.1-0.4 were studied as well. As observed in Figure 1.17, the pristine and methyl-functionalized samples with Ti molar ratio of 0.15 exhibited stronger signal in the EFW-Ti region than in the FW-Ti region, showing that Ti is mostly present as inactive Ti species. Methyl-functionalization did not exhibit a significant effect in the EFW-Ti wavelength range, but it did weaken the intensity of the FW-Ti signal. These qualitative results are consistent with the quantification of Ti species by XPS (Table 1.8).



Figure 1.17. DRUV spectra of pristine and methyl-functionalized Ti- SiO_2 catalysts at Ti molar ratio of 0.15 and MTES molar ratios varying from 0.1 to 0.4.

1.3.3.3. Evaluating the catalytic activity of methyl-functionalized catalysts in the epoxidation of cyclooctene with H_2O_2

The aim of this work was to study the effect of hydrophobization of Ti-SiO₂ catalysts over their catalytic activity. Therefore, the series of Ti-SiO₂ catalysts with Ti molar ratio of 0.15 and different MTES molar ratios were tested in the epoxidation of cyclooctene (C₈H₁₄) with H₂O₂. The products of the reaction are cyclooctane epoxide and water. Initial epoxidation rates of the methyl-functionalized catalysts were compared to the non-functionalized (pristine) catalyst. The rates were calculated based on the C₈H₁₄ consumption rate.

Conversions and C-balance were calculated at 8 hours of reaction (Table 1.9). The pristine and methyl-functionalized $Ti-SiO_2$ catalysts were active and conversions for the methyl-functionalized samples were higher than that for the pristine one. The selectivity of cyclooctene to epoxide was 100%, since no other product appeared in the chromatogram. This high selectivity was in agreement with the literature and was explained by the conformation of cyclooctene which disfavors the allylic route and the formation of allylic byproducts [151].

The C-balance was around 90 %. Mass losses were attributed to the experimental procedure (sampling) after excluding adsorption to the catalyst and other by-product formation.

Sample	Conversion	C-balance	SSA	
	%	%	m²∙g⁻¹	
0.15Ti	22	87	438	
0.15Ti-0.1MTES	28	88	411	
0.15Ti-0.2MTES	43	93	433	
0.15Ti-0.4MTES	17	92	477	

Table 1.9. Conversions, C-balance and specific surface areas (SSA) of the pristine and methyl-functionalized Ti-SiO₂

Reaction conditions: 0.1M [C₈H₁₄], 0.5M [H₂O₂] in CH₃CN with 10 g·L⁻¹ of catalyst, 60 °C, 8 h.

Figure 1.18 shows the initial epoxidation rates of the series of $Ti-SiO_2$ catalysts with Ti molar ratio of 0.15 and MTES molar ratios of 0.1, 0.2 and 0.4, which were normalized by the specific surface areas (SSA) of each catalyst. This normalization was performed to compare the catalytic performance among the samples considering the effect of the different values of SSA of each sample. Methyl-functionalized catalysts exhibited higher rates than the pristine catalyst, except for the sample with the highest nominal MTES molar ratio (0.4 MTES).



Figure 1.18. Initial epoxidation rates normalized by the specific surface areas of the series of Ti-SiO₂ catalysts with Ti molar ratio of 0.15 and MTES molar ratios of 0.1, 0.2 and 0.4. All reactions were run at 60 °C, 0.1M [C₈H₁₄], 0.5M [H₂O₂] in CH₃CN with 10 g·L⁻¹ of catalyst. Error bars were estimated from 3 replicates of the catalytic tests.

The initial rates were also normalized considering Ti speciation obtained by XPS, as depicted in Figure 1.19. This normalization allowed to compare the samples by isolating the effect of MTES molar ratio from the Ti speciation. Hydrophobic Ti-SiO₂ with MTES molar ratios of 0.1 and 0.2 kept achieving higher epoxidation rates than pristine 0.15Ti, regardless of Ti normalization. The epoxidation rate of 0.15Ti-0.2MTES catalyst was ~4 times higher than the one of the pristine sample (Figure 1.18); however, after normalization to the number of FW-Ti, the epoxidation rate of 0.15Ti-0.2MTES was ~8 times higher than the one of the pristine catalyst. In contrast, the sample with the highest nominal MTES molar ratio (0.15Ti-0.4MTES) displayed the lowest epoxidation rate per specific surface area, but after normalization to FW-Ti, the rate was similar to the one of 0.15Ti-0.1MTES. Apparently, there is an optimum MTES molar ratio that leads to an effective degree of methyl-functionalization and improves the catalytic activity of Ti-SiO2. However, isolating the effect of hydrophobicity, originated from the presence of methyl moieties on the catalyst surface, cannot be separated from the effect of the FW-Ti content at this Ti molar ratio. Indeed, XPS characterization showed that

0.15Ti-0.4MTES contained the lowest amount of FW-Ti compared to the rest of the catalysts of the series with nominal Ti/(Ti+Si) molar ratio=0.15. Moreover, the incorporation of Ti as FW-Ti was below 20% for all samples, indicating that a great fraction of the Ti precursor forms non-active Ti species. Thus, catalysts with lower Ti molar ratios should be prepared and tested. As observed in Figure 1.16, Ti-SiO₂ with Ti molar ratios of 0.025 exhibit better incorporation of Ti as FW-Ti.



Figure 1.19. Epoxidation rates normalized to Ti speciation of the series of Ti-SiO₂ catalysts with Ti molar ratio of 0.15 and MTES molar ratios of 0.1, 0.2 and 0.4. All reactions were run at 60 °C, 0.1M [C₈H₁₄], 0.5M [H₂O₂] in CH₃CN with $10g \cdot L^{-1}$ of catalyst. Error bars were estimated from triplicates of catalytic tests.

1.4. Conclusions

The synthesis of Ti-SiO₂ catalysts with different degrees of hydrophobicity by one-pot sol-gel was possible under a limited range of molar ratios of the precursors. The MTES precursor produced the most stable samples compared to the ones synthesized with PTES and OTES. The maximum MTES and TBOT molar ratios up to which a homogeneous gel was obtained during the synthesis were 0.4 and 0.2, respectively. Methyl-functionalization was preserved after calcination

at 500 °C, and methyl moieties were better preserved in samples with high Ti molar ratios. Methyl-functionalized catalysts exhibited less physisorbed water, indicating a hydrophobic effect due to the presence of methyl moieties on the catalyst surface. Ti active sites were successfully identified by a combination of IR, XPS and DRUV spectroscopies. Analyses of the Ti 2p XPS spectra showed that the efficiency of Ti incorporation as active species on the catalyst surface was higher for the samples with low Ti molar ratios. Methylfunctionalized Ti-SiO₂ were more active (higher reaction rates) for the epoxidation of cyclooctene than the pristine sample. However, this positive effect was hindered by the low content of FW-Ti on the catalyst induced by the high Ti molar ratio. DRUV showed that the sample with Ti/(Si+Ti)=0.025 is a promising sample due to its higher fraction of FW-Ti compared to the samples with higher Ti molar ratios. Further characterization and quantification of methyl-functionalization and hydrophobicity are required to relate the catalyst performance to its hydrophobic character. In this chapter samples were compared based only on the nominal MTES molar ratio.

The understanding achieved in this Chapter about the molar ratios of the sol-gel precursors allowed the optimization of the synthesis conditions as they will be applied in the next Chapter. Furthermore, the need of analytical techniques for the characterization of Ti active sites, effective methyl-functionalization and hydrophobicity, identified in this Chapter, led to explore complementary techniques to propose an even more rigorous comparison among samples in the following Chapters. As the first hints of an improvement of the catalytic performance of hydrophobic Ti-SiO₂ were observed, in the next Chapter, another series of methyl-functionalized Ti-SiO₂ was synthesized under optimized conditions and tested catalytically to elucidate the effect of hydrophobization.

Chapter 2

CHAPTER 2: Methyl-functionalized Ti-SiO₂ catalysts for the epoxidation of cyclooctene with hydrogen peroxide

Published Article Title: "Hydrophobic titania-silica mixed oxides for the catalytic epoxidation of cyclooctene"

Abstract

Having found that a Ti molar ratio Ti/(Si+Ti) of 0.025 allowed a better incorporation of isolated framework-Ti (active sites) than higher Ti molar ratios, a series of methyl-functionalized Ti-SiO₂ at this Ti molar ratio was synthesized to elucidate the effect of hydrophobization of Ti- SiO_2 over its catalytic performance in olefin epoxidation. Given that the active sites for epoxidation are obtained at low Ti molar ratios, limiting their number, other approaches to boost the catalytic performance are needed. In the current Chapter, we succeeded improving the catalytic activity of Ti-SiO₂ in the epoxidation of cyclooctene with hydrogen peroxide by methyl-functionalization in a one-pot approach. Titanium butoxide (TBOT) 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 active Ti sites. In this chapter, the methyl-functionalization degree was evaluated by Solid-State ²⁹Si-NMR in addition to TGA-MS. Hydrophobic Ti-SiO₂ performed better in the epoxidation reaction than a fully inorganic more hydrophilic Ti-SiO₂ prepared without MTES. A too high methyl-functionalization degree of the catalysts was however detrimental.

2.1. Introduction

As explained in the General Introduction, isolated framework-Ti atoms (FW-Ti) are the active sites for epoxidation [11, 23, 29-32, 50-52]. In most cases, researchers have explored the possibility to improve the epoxidation performance of Ti-containing materials via an increase of the number of active Ti sites using innovative synthetic methods [68, 77, 130, 144]. In Chapter 1, it was found that the highest incorporation of active sites was achieved at a Ti molar ratio (Ti/(Ti+Si)) of 0.025 compared to the one obtained at Ti molar ratios of 0.05-0.20.

Therefore, in this Chapter, a series of Ti-SiO₂ with Ti molar ratio of 0.025 was synthesized varying the nominal MTES molar ratio from 0.1 up to 0.4 (range determined as optimal in Chapter 1).

In Chapter 1, samples were compared based only on the nominal MTES molar ratio. However, a key factor to evaluate the effect of hydrophobization on the catalytic performance is the measurement of the effective methyl-functionalization degree, which in the current Chapter, was quantified by Solid-State ²⁹Si magic angle spinning nuclear magnetic resonance (²⁹Si-MAS-NMR) in addition to TGA-MS. Furthermore, methyl-functionalization modifies the hydrophobic/philic balance of the catalyst surface. This property is the focus of this thesis, so water vapor sorption was selected as a suitable technique to quantitatively compare this property among samples in the current Chapter.

As discussed in Chapter 1, the effect of hydrophobicity, originated from the presence of methyl moieties on the catalyst surface, was not isolated from the effect of the low incorporation of FW-Ti induced by one-pot methyl-functionalization. Some studies drew conclusions about the catalytic performance based on the nominal methylfunctionalization degree and did not characterize the hydrophobic/philic balance of the catalyst surface. Thus, there is room and need to address the effect of hydrophobization in a more rigorous manner.

In this context, the present Chapter aimed at elucidating the effect of hydrophobization of Ti-SiO₂ and its potential in epoxidation catalysis. Additionally, the understanding about the techniques for the characterization of hydrophobicity achieved - led to quantitatively prove that methyl-functionalization indeed induces a hydrophobic character on the catalyst surface.

2.2. Experimental section

2.2.1 One-pot sol-gel synthesis towards methyl-functionalized Ti-SiO $_{2}$

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 (TBOT, 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 250mL round-bottom three-neck flask and stirred at 750 rpm at 40 °C (using an oil bath and cooling system) until the gel formed. TEOS and MTES were added dropwise under continuous stirring. MTES molar ratios (as defined in eq (2.1)) between 0.1 and 0.4 were explored. After the addition of the Si precursors, concentrated HCI (Sigma-Aldrich, 37%) was added to catalyze the hydrolysis. The Ti precursor (TBOT) was added dropwise after 25 minutes of the addition of HCl, at a nominal molar ratio of 0.025 (as defined in eq (2.2)). 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⁻¹ 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 TBOT were prepared following a similar procedure as described above to obtain silica (SiO₂) and titania (TiO_2) as reference materials. The whole synthetic protocol is summarized on Scheme 2.1.

 $Molar \ ratio_{MTES} = \frac{mol_{MTES}}{mol_{TEOS} + mol_{TBOT} + mol_{MTES}}$

(2.1)

 $Molar \ ratio_{TBOT} = \frac{mol_{TBOT}}{mol_{TEOS} + mol_{TBOT} + mol_{MTES}}$

(2.2)



Scheme 2.1. Representation of the sol-gel synthesis method

2.2.2. Catalyst characterization

Solid-State ²⁹Si magic angle spinning nuclear magnetic resonance (²⁹Si-MAS-NMR) spectra were recorded at room temperature on a Bruker Avance-500 spectrometer operating at 11.7 T (99.3 MHz for ²⁹Si) 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) ²⁹Si spectra were recorded using the following acquisition parameters: 300 s relaxation delay. 3 us (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 with 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⁻¹ under air flow (50 mL min⁻¹, 80% N₂ and 20% O₂, 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⁻¹) for 10 minutes; ii) heating to 800 °C at 5 °C min⁻ ¹ under air flow (30 mL min⁻¹). Followed mass to charge ratios were: 2 (H₂), 15 (CH₃), 17 and 18 (H₂O), 28 (N₂), 29 (methanol), 31 (ethanol), 40 (Ar), 44 (CO₂) and 56 (butanol). To determine the real Ti content, the Ti-SiO₂ 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⁻¹ with a 4 cm⁻¹ 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 Ka radiation of Cu $(\lambda = 1.5418 \text{ Å})$. The small 20 range $(10 - 80^{\circ})$ was recorded at a rate of 0.01° s⁻¹. 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 10⁻⁶ Pa. The angle between the surface normal and the axis of the analyzer lens was 55°. The analyzed area was approximately 1.4 mm² 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 was 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 BaSO₄ 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 N₂ 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.

2.2.3. Catalytic tests

The performance of the synthesized catalysts was measured in the epoxidation of cyclooctene (Fluka, >90%) with hydrogen peroxide (H₂O₂, Sigma-Aldrich, 30%), as defined in eq (2.3). The reaction temperature was 60 °C, the initial concentration of cyclooctene was 0.1 M, the initial concentration of H₂O₂ was 0.5 M and the catalyst addition was 10 g L⁻¹. 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 H₂O₂ 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⁻¹ and a second one from 100 to 240 °C at 30 °C min⁻¹. 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⁻¹. $1-\mu$ L aliquots were 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 catalytic tests.



2.3. Results and discussion

2.3.1. Assessing the degree of methyl-functionalization and the corresponding hydrophobicity using NMR and TGA-MS

The degree of methyl-functionalization (%Me) of calcined Ti-SiO₂ samples was addressed by guantitative solid state ²⁹Si magic-anglespinning (MAS) NMR investigation. The NMR spectra are reported for all the solids in Figure 2.1. ²⁹Si direct excitation (DE) MAS spectra show for all solids the presence of a broad band centered at -100 ppm, assigned to Qⁿ 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^4 (Si(OSi)₄), Q^3 (Si(OSi)₃OH) and Q^2 (Si(OSi)₂(OH)₂) species respectively. For methyl-functionalized Ti-SiO₂ samples, an additional broad signal centered at -60 ppm reveals the presence of T³ (Si(OSi)₃Me) and T² (Si(OSi)₂(OH)Me) contributions (detailed deconvolution analysis shown in Figure A-3, Appendix). The presence of methyl moieties was confirmed also by performing cross-polarization (CP) experiments. Ti-SiO₂ samples exhibited four degrees of methylfunctionalization: 0%, 1%, 5%, and 14%, determined from direct excitation NMR experiments by the following formula:: % Me = 100.

 $\binom{T^{i}}{\sum_{i}(Q^{i}+T^{i})}$. 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 methyl-functionalization 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 [90, 91], which is in agreement with our observations.



Figure 2.1. Solid-state ²⁹Si 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 analyses were performed mainly to evaluate the hydrophobicity of the samples (via the quantification of the physisorbed water desorbing in the low temperature range). The totally inorganic sample (TS-0%Me, ie produced with only TEOS as Si precursor) and samples with the three increasing degrees of methyl-functionalization (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 2.2).



Figure 2.2. TGA profiles of calcined TS-x%Me

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 2.3). 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 methyl-functionalized 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 nonfunctionalized catalyst. In this case, the mass loss probably corresponds to the OH groups chemically bonded to the material [102]. 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 methyl-functionalized samples are more hydrophobic (than the not methyl-functionalized one) as they desorb lower contents of physisorbed water.



Figure 2.3. 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 2.4). A valid comparison of physisorbed H₂O 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 H₂O and methyl contents could have induced. The totally inorganic sample (TS-0%Me) has the highest content of physisorbed water, whereas the methyl-functionalized samples display a decrease of the amount of physisorbed H₂O 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 2.4. Quantification of methyl moieties and physisorbed water.

The difference of physisorbed H_2O content from one sample to another could be an effect of the difference of their respective surface area; so we have used N_2 physisorption to obtain information about the textural properties of the inorganic and methyl-functionalized catalysts (Table 2.1). 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_2O content in the methyl-functionalized samples, ascertaining the effect of hydrophobization due to the methyl content.

	TI-SIO	2	
Sample	S_{BET} , $m^2 g^{-1}$	Pore Volume, cm ³ g ⁻¹	Average Pore Diameter, nm
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 2.1. Textural properties of inorganic and methyl-functionalized

2.3.2. 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 2.2). For all samples, the real amount of Ti is very close to the nominal one (TBOT nominal molar ratio = 0.025).

	TI-5102		
			Ti/(Si+Ti)
Sampla	Ti wt%	Si wt%	Molar
Sample	(ICP)	(ICP)	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 2.2. ICP-AES analysis of inorganic and methyl-functionalized

Previous studies revealed that the presence of Ti active species can be followed by FTIR detection of the Si-O-Ti bridge [23, 29-31, 49, 51, 132, 133]. On Figure 2.5, the band of Si-O-Si at 1080 cm⁻¹ can be observed. The band at 950 cm⁻¹ can be attributed to silanol groups, but it can also be attributed to the Si-O-Ti bridges [49, 139]. Additionally, the IR spectra of TS-5% Me and TS-14% Me samples showed the presence of the methyl groups bonded to silicon (v(Si-C)) at 1279 cm⁻¹. Due to the low methyl content in TS-1% Me, only a faint shoulder at this wavenumber was observed for this sample.



Figure 2.5. IR spectra of inorganic and methyl-functionalized Ti-SiO₂.

Furthermore, diffuse reflectance UV spectroscopy was exploited to identify isolated 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 TiO₂) in the range 310-330 nm [31, 148, 150]. Inorganic and methyl-functionalized Ti-SiO₂ catalysts both exhibit FW-Ti and EFW-Ti species (Figure 2.6). 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 Appendix), 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.



Figure 2.6. DRUV spectra of inorganic and methyl-functionalized Ti-SiO₂.

XPS was performed on Ti-SiO₂ catalysts to quantify the Ti surface content. Interestingly, according to literature [138, 143-147], XPS allows distinguishing and quantifying FW-Ti and EFW-Ti species. Thus, the binding energy of Ti 2p was compared among the inorganic TiO₂, Ti-SiO₂ and the methyl-functionalized Ti-SiO₂. The Ti 2p spectrum is composed of a doublet of Ti 2p3/2 and Ti 2p1/2 peaks, which are separated by 5.7 eV [142]. Previous works studied the different species of Ti in titanosilicates, and they agreed that the binding energy of FW-Ti is 460.0 eV [138, 143, 145, 147]. 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 2p3/2 in pure titanium dioxide is 458.5 eV [138, 142]. Hasegawa et al. found that the Ti 2p3/2 peak shows a shoulder centered at 457.8 eV, corresponding to the EFW-Ti species in TS-1 [147], and Tyablikov et al. found BEs of 457.7-458.2 eV [144]; but Langerama et al. reported BEs of 458.4-458.9 eV for the EFW-Ti species [145]. For similar Ti loadings, the inorganic and methyl-functionalized Ti-SiO₂ catalysts in our own work do not show the shoulder for Ti 2p3/2. 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 2.7). 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 [138, 143, 145, 147], whereas the EFW-Ti species fall at 458.5 eV, which also agrees with previous studies [145].



Table 2.3 shows the surface elemental quantification estimated under this hypothesis. Increasing the methyl-functionalization degree gradually diminishes the fraction of FW-Ti species on the surface. This corroborates the same effect of methyl-functionalization that DRUV revealed on the evolution of the different Ti species population.

Sample	TS-0% Me	TS-1% Me	TS-5% Me	TS-14% Me
C (of which C-H) (mole %)	2.2 (1.2)	3.1 (1.9)	7.5 (5.1)	6.6 (5.5)
O (mole %)	67.6	70.8	66.9	68.4
Ti (of which FW-Ti) (mole %)	0.6 (0.4)	0.5 (0.3)	0.4 (0.3)	0.3 (0.2)
Si (mole %)	29.6	25.6	25.1	24.7
Ti/(Si+Ti) molar ratio	0.020	0.018	0.017	0.011
FW-Ti/(Si+Ti) molar ratio	0.014	0.013	0.011	0.009

Table 2.3. XPS surface elemental quantification

Summarizing, by combining the results from XPS and ICP-AES, it turns out that for similar bulk Ti content, the methyl-functionalized Ti-SiO₂ catalysts 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 methyl-functionalized samples.

2.3.3. Assessing the role of hydrophobicity on the catalytic epoxidation of cyclooctene with hydrogen peroxide as oxidant

Inorganic and methyl-functionalized catalysts were compared in the epoxidation of cyclooctene with H_2O_2 (Figure 2.8). The initial reaction rates were calculated and normalized to specific surface area to better recognize an effect of hydrophobicity.



Figure 2.8. Initial reaction rates normalized to specific areas for inorganic and methyl-functionalized Ti-SiO₂. Error bars were estimated from triplicates of catalytic tests

Hydrophobic Ti-SiO₂ 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 Ti-SiO₂ catalyst. However, the methyl-functionalized sample with 14% as effective methyl content showed lower performance. This sounds more in line with the negative effect of methyl-functionalization contrarily observed by Müller et al. in the epoxidation of 1-hexene and cyclohexene, where the nominal degree of methyl-functionalization varied from 10 % to 30 % [90]. Conversions, yields and selectivities measured after 8 hours of reaction were compared for the inorganic and methyl-functionalized samples (Table 2.4). Similarly, to what was observed when comparing the rates, the performances of the methyl-functionalized 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 methylfunctionalization degree.

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

Table 2.4. Conversions, yields and selectivities after 8 hours of reaction for the inorganic and methyl-functionalized catalysts

^aUncertainties 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 methyl-functionalization 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_2O_2 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 methyl-functionalization affects not only the surface polarity but also the catalyst structure. DRUV and XPS analysis indeed showed that by increasing the methyl-functionalization 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 2.9). The initial rate from Figure 2.8 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 2.9. Initial epoxidation rates normalized to Ti speciation^a of the inorganic and methyl-functionalized Ti-SiO₂. ^aThe normalization was performed based on the Ti molar ratio Ti/(Ti+Si) of the different Ti species. Bulk Ti molar ratio is shown in Table 2.2. Surface Ti and surface FW-Ti molar ratios are shown in Table 2.3. Error bars were estimated from replicates of catalytic tests

Figure 2.9 shows that the rates were higher for the 1% and 5% methyl content whatever the normalization. Actually, the trend observed in Figure 2.8 is reinforced by the normalization to the Ti content, which establishes that there is an optimal methyl-functionalization degree that improves the catalytic performance. An excessive methylfunctionalization degree seems to be detrimental to the catalytic activity, not only due to the lower FW-Ti content it induces but also to the too hydrophobic character it brings. To support this hypothesis, water vapor sorption experiments were performed at 295 K for all the samples (Table 2.5). According to literature, the affinity of the catalyst surface with water is featured at low relative pressures of the adsorption isotherm [101, 120]. 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 2.10. For comparison between samples, the water uptake at a selected relative pressure (p/po= 0.1) was normalized by the specific surface area (shown in Table 2.1). These



results confirm that TS-14%Me is too hydrophobic likely decreasing its affinity for H_2O_2 .

Figure 2.10. Water vapor adsorption isotherms of TS-0%Me, TS-1%Me, TS-5%Me and TS-14%Me at 295 K (low relative pressures). For comparison between samples, the water uptake was normalized by the specific surface area of each sample (shown in Table 2.1). The normalized water uptake values are depicted on the curve and the shaded regions denote the estimated error.

Sample	H ₂ O uptake at p/p _o =0.1, g/100g _{cat}	H ₂ O uptake, mg _{H20} m ⁻²
TS-0%Me	9.2	0.16
TS-1%Me	7.1	0.14
TS-5%Me	7.6	0.17
TS-14%Me	3.6	0.06

Table 2.5. H₂O uptake at a relative pressure p/p_0 = 0.1 of inorganic and methyl-functionalized Ti-SiO₂

2.4. Conclusions

We succeeded synthesizing hydrophobic Ti-SiO₂ catalysts through one-pot sol-gel procedure with significant amount of the active isolated framework-Ti species and different degrees of hydrophobicity. The effective methyl-functionalization degree and the content of active Ti species were quantified thanks to a combination of analytical techniques, which made possible to isolate the hydrophobic effect on the catalytic epoxidation performance. Increasing the degree of methylfunctionalization during synthesis was detrimental to the formation of isolated framework-Ti in the catalyst. Nevertheless, hydrophobic Ti-SiO₂ performed much better in the epoxidation of cyclooctene with hydrogen peroxide than inorganic more hydrophilic Ti-SiO₂. However, this tendency only verifies at low methyl-functionalization degree and thus hydrophobicity. Too high degree of methyl-functionalization and thus hydrophobicity led to diminished catalyst performance, likely due to a too low affinity of H_2O_2 with the too hydrophobic catalytic surface, as proved by water vapor sorption experiments.

Having understood that methyl-functionalization diminished the incorporation of Ti active species, a much lower Ti molar ratio combined with a lower MTES molar ratio was chosen as a strategy for the next Chapter since it proved successful at favoring the presence of FW-Ti in this Chapter. Indeed, in Chapter 3, hydrophobic Ti-SiO₂ catalysts were synthesized with a nominal Ti molar ratio of 0.015 and MTES molar ratios ranging from 0.05 to 0.4. To further elucidate the effect of hydrophobization on the catalytic activity, an organic peroxide (tert-butyl hydroperoxide) was tested instead of hydrogen peroxide. The hypothesis was that tert-butyl hydroperoxide (TBHP) would have a higher affinity for the methyl-functionalized catalyst surface than hydrogen peroxide, which would clarify and confirm the previously observed effect of hydrophobization.
Chapter 3

CHAPTER 3: Optimizing the Ti molar ratio in methylfunctionalized Ti-SiO₂ catalysts for the epoxidation of cyclooctene with tert-butyl hydroperoxide

Abstract

In the present chapter, Ti-SiO₂ catalysts were synthesized at a Ti molar ratio of 0.015 to improve their activity for the epoxidation of cyclooctene with tert-butyl hydroperoxide (TBHP). The first objective was to increase the amount of active titanium species, called isolated framework titanium (FW-Ti) and decrease the amount of inactive titanium species, such as extra-framework titanium (EFW-Ti). For this purpose, we used an even lower Ti molar ratio (Ti/(Ti+Si)=0.015) compared to the one used in Chapter 2 ((Ti/(Ti+Si)=0.025)). According to the literature, a lower Ti molar ratio indeed promotes the formation of FW-Ti. The second objective was to increase the catalytic activity by modifying the hydrophobicity of the catalyst surface with an optimized methyl-functionalization thanks to the adjustment of the calcination temperature. The calcined solids were characterized by TGA. IR-ATR and ²⁹Si NMR to confirm the presence of methyl groups and quantify them. Titanium species were analyzed thanks to DRUV and XPS. It was observed that FW-Ti was mainly formed and that the residual amount of EFW-Ti was not influenced by the methyl-functionalization degree, contrarily to the case of the samples with higher Ti molar ratio studied in Chapter 2. Moreover, N₂ physisorption highlighted the fact that Ti-SiO₂ catalysts are highly microporous. Finally, catalytic, recyclability and leaching tests were performed to study the impact of methyl-functionalization on the catalytic activity and catalyst stability. The most efficient catalyst was obtained with an intermediate degree of methyl-functionalization and no Ti leaching was detected during reactions.

3.1. Introduction

The first objective in Chapter 3 was to synthesize Ti-SiO₂ catalysts containing a high molar fraction of isolated FW-Ti, namely of Ti active species, and consequently a small molar fraction of EFW-Ti (if present at all). Chapter 2 showed that samples with Ti molar ratio of 0.025 still exhibited the presence of EFW-Ti. Therefore, in this Chapter, a Ti molar ratio of 0.015 was evaluated to further reduce the formation of EFW-Ti and to form preferentially isolated FW-Ti. However, a low Ti molar ratio also implies a lower number of active sites, so the second

objective was to modify the hydrophobic character of the catalyst to boost the catalytic activity and tackle the constraint of the low number of active sites. Additionally, surface hydrophobization should also have a good impact on the stability of the catalyst by preventing water to adsorb and deactivate the active sites. However, Chapter 2 showed that increasing the degree of methyl-functionalization of the catalyst promoted the formation of EFW-Ti. Indeed, the methyl-alkoxy Si precursor (MTES) is less likely to form Si-O-Ti bridges (needed for the formation of FW-Ti) than classical silica precursor (TEOS). Therefore, different molar ratios of MTES were tested to optimize methylfunctionalization, so a hydrophobic catalyst with reduced EFW-Ti would be obtained.

Moreover, a hydrophobic surface could also offer an advantage via its affinity for the oxidizing agent used in the epoxidation reaction. In this purpose in this Chapter, an organic peroxide will be used rather than hydrogen peroxide (H_2O_2). Chapter 2 indeed indicated that H_2O_2 offered poor results when a catalyst with a too hydrophobic character was used. Consequently, *tert*-butyl hydroperoxide (TBHP), being more hydrophobic than H_2O_2 , could be a good candidate for these experiments. The hypothesis is that this organic peroxide would be more likely to adsorb on the catalyst surface even at a high degree of methyl-functionalization. Among organic peroxides, TBHP is one of the smallest, so it will still be able to reach a maximum of active sites, eventually located in the porosity of the material. Finally, catalytic epoxidation tests were performed with cyclooctene and TBHP. The stability of the catalyst was also investigated with recyclability and leaching tests.

3.2. Experimental section

3.2.1 One-pot sol-gel synthesis towards methyl-functionalized Ti-SiO_2 $\ensuremath{\mathsf{SiO}_2}$

First, ethanol (VWR, 99.9%) and water were poured into a 250-mL round-bottom three-neck flask. The mixture was heated at 40°C while stirring at 750 rpm using an oil bath and a reflux condenser. Then, a mixture of tetraethylorthosilicate (Aldrich 98%) (TEOS) and triethoxymethylsilane (Aldrich 99%) (MTES) was added dropwise using a dropping funnel. MTES molar ratios (as defined in Equation (3.1)) between 0.05 and 0.4 were explored. 16 ml hydrochloric acid (ROTH, 37%) (HCI) was added to catalyze the hydrolysis. After 25 minutes, the titanium (IV) butoxide (Aldrich, 97%) (TBOT) was added dropwise at a nominal molar ratio of 0.015 (as defined in Equation (3.2)), and the

system was mixed until the gel forms. The gel was then left to cool all night and it was then dried using the vacuum oven at 140°C at around 300 mbar for 3 hours. The material was then grinded, transferred to a ceramic container and calcined at the desired temperature with the following method: ramp to the desired calcination temperature at 1°C/min and dwell for 3 hours. Two calcination temperatures were applied: 480 °C and 425 °C.

$$Molar \ ratio_{MTES} = \frac{mol_{MTES}}{mol_{TEOS} + mol_{TBOT} + mol_{MTES}}$$
(3.1)

$$Molar \ ratio_{TBOT} = \frac{mol_{TBOT}}{mol_{TEOS} + mol_{TBOT} + mol_{MTES}}$$

(3.2)

3.2.2. Catalyst characterization

Solid-State ²⁹Si magic angle spinning nuclear magnetic resonance (²⁹Si-MAS-NMR) spectra were recorded at room temperature on a Bruker Avance-500 spectrometer operating at 11.7 T (99.3 MHz for ²⁹Si) 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) ²⁹Si 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).

Furthermore, samples were characterized by TGA-MS, ICP-AES, FTIR in transmission and ATR modes, XRD, XPS, DRUV and N₂ adsorptiondesorption experiments. Specific analysis conditions used in this Chapter are described hereafter.

In this Chapter, 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⁻¹ under air flow (50 mL min⁻¹, 80% N₂ and 20% O₂, 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⁻¹) for 10 minutes; ii) heating to 800 °C at 5 °C min⁻¹ under air flow (30 mL min⁻¹). Followed mass to charge ratios were: 2 (H₂), 15 (CH₃), 17 and 18 (H₂O), 28 (N₂), 29 (methanol), 31 (ethanol), 40 (Ar), 44 (CO₂) and 56 (butanol).

Diffuse reflectance UV-Vis (DRUV) spectra were recorded on a Shimadzu UV-vis-NIR spectrometer equipped with a Praying Mantis in a spectral range from 200 to 600 nm.

Specific surface area and pore size were determined by N₂ adsorptiondesorption at -196 °C (77 K) experiments performed using a Micromeritics Tristar 3000. Before the analysis, the samples were degassed overnight under vacuum (6.7 Pa) at 180 °C. Adsorptiondesorption isotherms were obtained and the micropore volume was determined from the t-plot constructed based on the adsorption data. The intercept of the best tangent drawn on the t-plot in the range corresponding to partial pressures between 0.05 and 0.30 of the t-plot was used to determine the micropore volume, which was then subtracted from the N₂ volume adsorbed at each data point to construct a second adsorption isotherm. The Brunauer-Emmet-Teller (BET) method was applied to this second isotherm to calculate the specific surface area excluding the consumption of nitrogen corresponding to micropore filling, and it was called specific surface area corrected (SSA_{corrected}). Having replicated the analysis three times for one of the samples, we know the uncertainty of the measurement of SSAcorrected is ca. 5%.

3.2.3. Catalytic tests

The epoxidation reaction was carried out in a 10-mL batch reactor equipped with a reflux condenser at 70 °C using an oil bath. Cyclooctene (TCI, 95%) and dibutyl ether (DBE, TCI, 99%) as internal standard were mixed in acetonitrile (VWR, 99.9%) which was the solvent. 100 mg of catalyst (the fraction was between 100 and 200 microns, obtained after grinding and sieving) were added to the mixture. The reaction started when *tert*-butyl hydroperoxide (TBHP, Aldrich, 5-6 M in decane) was added to the reactor (Equation 3.3). The concentrations in the reactor were 0.5 M for cyclooctene, 0.1 M for DBE, and 0.25 M for TBHP. 100- μ l aliquots were taken as a function

of time through a septum (commonly at 0, 1, 2, 4, 6, 8, 9 and 24 hours). The aliquots were filtered using a 0.2 μ m syringe filter and diluted in 900 μ l of acetonitrile before being injected into the gas chromatograph device (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 μ m 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⁻¹ and a second one from 100 to 240 °C at 30 °C min⁻¹. 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⁻¹. 1- μ L aliquot was injected into the GC column with a split ratio (SR) of 20.



Leaching tests

The leaching test starts similarly as a catalytic test, but a hot filtration was performed after 3.5h of reaction. The reaction medium with the catalyst is precisely transferred into a falcon tube and centrifuged with a Multifuge X1R centrifuge (Thermo Fisher Scientific) at 10 000 rpm (around 11200 g) for 10 min. The medium is then filtered with a 0.2 μ m syringe filter to remove the remaining particles. The filtrate is added to the reactor and heated again at the reaction temperature. Aliquots were taken as in classical reaction tests.

Recyclability tests

In order to determine if the catalyst is reusable for several reactions, 3 consecutive runs were operated with the same catalyst. A first method consisted in decanting the catalyst from a catalytic run of 8 h as described above, rinsing it with 10 mL acetonitrile for two days at room temperature under stirring, drying it at 60 °C for 6 h then calcining it at 350 °C for 3 h. A second method consisted in washing the recovered catalyst with 2 volumes of 10 ml acetonitrile, decanting and drying at 60 °C before the next run.

3.3. Results and discussion

3.3.1. Optimizing the calcination temperature

As observed in Chapter 1, the effective degree of methylfunctionalization (%Me) that remained after calcination decreased with the increment of active Ti sites, whose number depends on the Ti molar ratio. Thus, an optimization of the calcination temperature was performed considering that a new Ti molar ratio (Ti/(Ti+Si)) was here used, being 0.015.

A hypothesis has been put forward to explain the differences of temperature at which the removal of the methyl groups for samples with different Ti molar ratios: as the Ti molar ratio is lower in the present samples (Ti/(Ti+Si)=0.015) than in the ones studied in Chapter 2 (Ti/(Ti+Si)=0.025), the formation of isolated framework-Ti (FW-Ti) is expected to be favored. Therefore, there would be more active sites on the catalyst that would increase the oxidizing power of the samples. Precisely this would promote the elimination of CH₃ preferentially in samples with more FW-Ti than in samples with less FW-Ti. The texture of the catalysts with Ti molar ratio of 0.015 may also be different than that of the Ti molar ratio of 0.025 because of the different reactant ratios used during the synthesis of the catalyst.

In order to optimize the calcination temperature, the first derivative of the TGA curves of non-calcined samples was calculated (Figure 3.1). Three main mass losses were observed: i) the first one in the range 30-175 °C attributed to the desorption of physisorbed water, ii) the second one in the range 300-425 °C attributed to the removal of the precursor residues, and iii) the third one in the range 425-535 °C attributed to methyl loss by combustion. According to these observations, the optimal calcination temperature was 425 °C in order to eliminate the residues and prevent methyl groups loss. As hypothesized, the optimal calcination temperature for samples with Ti molar ratio of 0.015 was lower than the one used in Chapter 2 for the samples with Ti molar ratio of 0.025.



Figure 3.1. TGA profiles (dashed lines) of non-calcined methylfunctionalized Ti-SiO₂ catalysts with Ti molar ratio of 0.015 and MTES molar ratios from 0.05 to 0.4. A pristine sample (non-functionalized) was also analyzed as reference. All measurements were performed under air flow (50 mL/min). Solid lines are the derivative of the TGA profiles.

The TGA equipment was coupled to a mass spectrometer (TGA-MS) in order to study the mass loss stages previously identified. The samples analyzed were non-calcined 0.015Ti-0.1MTES and 0.015Ti-0.4MTES. The mass loss in the range 30-175 °C was confirmed to be related to physisorbed water (Figure 3.2). The mass loss in the range 300-425 °C corresponds to two processes, the removal of butanol and the burning of unreacted precursors. Butanol signal (m/z=56) was observed at 200-375 °C; this product formed during the syntheses (from Ti precursor, TBOT). Carbon dioxide (m/z=44) and water (m/z=18) were also detected in the range 275-400 °C and confirmed

the burning of un-reacted precursors in this temperature range. Carbon dioxide (m/z=44) and water (m/z=18) were as well detected in the range 425-535 $^{\circ}$ C, confirming the third mass loss was related to the burning of methyl groups.



Figure 3.2. dTG-MS profiles of non-calcined methyl-functionalized Ti-SiO₂ catalysts, 0.015Ti-0.1MTES (left) and 0.015Ti-0.4MTES (right). All measurements were performed under air flow (50 mL/min).

3.3.2. Assessing the degree of methyl-functionalization and the corresponding hydrophobicity

As confirmed in Chapter 2, measuring the effective degree of methylfunctionalization (%Me) is required for a precise comparison among samples. Thus, NMR analyses were performed first in semiquantitative mode (cross polarization experiments) in order to select the samples for the quantitative method (direct excitation experiments).

According to the semi-quantitative results (Figure 3.3), samples with higher nominal MTES molar ratios generally exhibited a more intense signal centered at c.a. -65 ppm. This signal corresponded to T^3 (Si(OSi)₃Me) and T^2 (Si(OSi)₂(OH)Me) contributions and indicated higher methyl content (after calcination at 425 °C) at higher MTES molar ratios. However, it was observed that the samples with nominal MTES molar ratios of 0.1, 0.2 and 0.3 were practically identical in terms of effective methyl-functionalization. Thus, the samples selected for the quantitative NMR analysis (direct excitation experiments) were the ones with nominal MTES molar ratios of 0.05, 0.2 and 0.4 (Figure 3.4). These results showed that calcination had indeed a significant impact on the effective methyl-functionalization.



Figure 3.3. Solid state ²⁹Si cross polarization MAS NMR spectra of calcined pristine (0.015 Ti) and methyl-functionalized Ti-SiO₂ catalysts with nominal MTES molar ratios varying from 0.05 to 0.4. Spectra are normalized to the Q⁴ contribution and are vertically offset for clarity.

²⁹Si direct excitation (DE) MAS spectra showed the presence of a broad band centered at -110 ppm, assigned to Qⁿ contributions. The deconvolution of this signal by using Gaussian functions allows to distinguish different contributions centered at -109 ppm, -100 ppm and -91 ppm which can be attributed to Q⁴ (Si(OSi)₄), Q³ (Si(OSi)₃OH) and Q² (Si(OSi)₂(OH)₂) species respectively. For methyl-functionalized Ti-SiO₂ samples, an additional broad signal centered at -65 ppm reveals the presence of T³ (Si(OSi)₃Me) and T² (Si(OSi)₂(OH)Me) contributions (detailed deconvolution analysis shown in Figure A-3, Appendix). Ti-SiO₂ samples exhibited three degrees of methyl-functionalization as molar percentages: 3%, 5%, and 10%, determined from direct excitation NMR experiments by the following formula:: % Me = 100. $\left(\sum_{i}(Q^{i}+T^{i})\right) = 100 \cdot (Si - CH_{3}/Si)$. As Solid-State NMR provides (T^i) an accurate quantification of the degree of methyl-functionalization, from now all the samples will be compared considering the effective degree of methyl-functionalization found via Solid-State NMR analysis. Hereafter our samples will be noted as 0.015Ti-x%Me, where x represents the effective molar percentage of methyl-functionalization.



Figure 3.4. Solid-state ²⁹Si direct excitation MAS NMR spectra of calcined methyl-functionalized Ti-SiO₂ catalysts. Spectra are normalized to the Q⁴ contribution and are vertically offset for clarity.

The quantitative method showed that the effective degree of methylfunctionalization (%Me) did follow a logical trend according to the MTES molar ratio incorporated in the synthesis, but the effective %Me were lower than the nominal MTES molar ratios. The semi-quantitative and quantitative results are summarized in Table 3.2.

Table 3.2: Summary of NMR results. Degree of methyl-functionalization (%Me) for all the Ti-SiO₂ samples

	Nominal	%Me by	%Me by
Sample	%Me	semi-quantitative	quantitative
		method	method
0.015 Ti	0%	0%	0%
0.015 Ti - 0.05MTES	5%	9%	3%
0.015 Ti - 0.10MTES	10%	13%	-
0.015 Ti - 0.20MTES	20%	12%	5%
0.015 Ti - 0.30MTES	30%	13%	-
0.015 Ti - 0.40MTES	40%	21%	10%

FTIR-ATR spectra were also collected for the series of methylfunctionalized Ti-SiO₂ synthesized with a Ti molar ratio of 0.015 (Figure 3.5). The peak at 1083 cm⁻¹ corresponds to Si-O-Si asymmetric vibrations and the peak at 950-960 cm⁻¹ corresponds to the band for the Si-O-Ti bridge which decreased for higher degrees of nominal methyl-functionalization despite the constant Ti molar ratio. This trend was observed in Chapter 2 as well.

The presence of methyl moieties on the methyl-functionalized samples was confirmed thanks to the band detected at 1279 cm⁻¹, which corresponds to the vibration of Si-C (v(Si-C)) (Figure 3.5, inset). This band followed the trend of the degree of methyl-functionalization determined by ²⁹Si solid-state NMR. Similarly, the band at 2975 cm⁻¹, corresponding to C-H stretching vibrations, agreed with the NMR results. The pristine sample (0.015Ti) did not show the methyl associated bands.

On the other hand, the OH band at 3350 cm⁻¹ decreased in the samples with higher degree of methyl-functionalization, suggesting that methyl-functionalization indeed reduced the affinity for water, so less water adsorbed on the catalyst surface. In fact, the pristine sample (0.015Ti) exhibited the largest amount of physisorbed water.





TGA profiles and the derivative curves of the calcined pristine catalyst, namely Ti0.015, and calcined methyl-functionalized catalysts (Ti0.015-3%Me, Ti0.015-5%Me, Ti0.015-10%Me) showed two main mass

losses (Figure 3.6). The first mass loss, observed in the range 40-165 °C, was associated with physisorbed water. The second mass loss, observed in the range 475-505 °C, was related to the effective methyl content combustion. In this Chapter, the calcination temperature was optimized to remove the unreacted precursors while preserving the methyl-functionalization. Hence these TGA results confirmed that the chosen calcination temperature effectively led to remove unreacted precursors (no thermal event at 300-425 °C anymore) while preserving a certain degree of methyl-functionalization (event at 475-505 °C for calcined methyl-functionalized catalysts, and absent for calcined pristine one).



Figure 3.6. TGA profiles (dashed lines) of calcined methylfunctionalized Ti-SiO₂ catalysts with Ti molar ratio of 0.015. A pristine sample (non-functionalized) was also analyzed as reference. All measurements were performed under air flow (50 mL min⁻¹). Solid lines are the derivative of the TGA profiles.

Based on the TGA profiles, the mass losses attributed to physisorbed water and methyl content were calculated to evaluate the relationship

between the degree of methyl-functionalization and physisorbed water (Figure 3.7). The methyl content calculated by TGA followed the trend established by NMR analyses. The amount of physisorbed water decreased in samples with higher methyl content, except for the sample 0.015Ti-3%Me. Our hypothesis is that there is an effect of the specific surface area which influences the amount of physisorbed water.



Figure 3.7. Physisorbed water and methyl content estimated from TGA data for Ti-SiO₂ catalysts with Ti molar ratio of 0.015.

The difference of physisorbed H₂O content from one sample to another could originate from the difference of their respective specific surface area (SSA), so N₂ physisorption was used to obtain information about the textural properties of the pristine and methyl-functionalized catalysts (Table 3.3). The adsorption isotherms for the pristine sample, namely 0.015 Ti, and for the methyl-functionalized one, 0.015Ti-10% Me are shown in Figure 3.8. The SSA determined by applying the BET model (SSA_{BET}) for the pristine sample is much lower than the SSA determined for the methyl-functionalized samples. This could be attributed to the addition of the MTES precursor during the synthesis that favored the generation of porosity. The SSA_{BET} was strongly influenced by the micropore volume, so the former value was corrected by excluding the N₂ uptake due to micropores filling (SSA_{corrected}). These results showed that the corrected specific surface area values varied from one sample to another in a much lesser extent than the

methyl content, except for the sample with the highest degree of methyl-functionalization. The difference of texture alone can thus not explain the gradual decrease of physisorbed H_2O content in the methyl-functionalized samples, ascertaining the effect of hydrophobization due to the methyl content.

SIO ₂ with 11 molar ratio of 0.015				
			Pore	Micropore
Sample	SSABET	SSA _{corrected} ^a	volume ^b	volume ^c
Gample	m²g-1	m²g⁻¹	(77 K)	(77 K)
			cm³g⁻¹	cm³g⁻¹
0.015Ti	462	226	0.22	0.10
0.015Ti-3% Me	645	222	0.27	0.18
0.015Ti-5% Me	666	250	0.33	0.17
0.015Ti-10% Me	697	413	0.37	0.12

Table 3.3. Textural properties of pristine and methyl-functionalized Ti-SiO₂ with Ti molar ratio of 0.015

^aCorrected specific surface area (SSA_{corrected}) by excluding the N₂ uptake due to micropores corrected filling. ^b N₂ volume uptaken at 77 K and relative pressure of 0.99. ^c Determined from the intercept of the best tangent drawn in the t-plot in the relative pressure range of 0.05-0.30.



Figure 3.8. $N_{\rm 2}$ physisorption isotherms of 0.015 Ti and 0.015 Ti-10%Me.

The difference in SSA_{corrected} between the pristine sample and the one with the 10%Me is c.a. $100 \text{ m}^2 \text{ g}^{-1}$. In addition, the pore volume increased for samples with higher %Me. The structure is surely influenced by CH₃ groups inducing the network to organize around them with more defects, thereby impacting the texture and increasing the specific surface area. The trend of the micropore volume apparently does depend on the %Me. These observations showed that one-pot methyl-functionalization affected not only the surface chemistry of the catalyst, but also the textural properties. Therefore, any catalytic effect of methyl-functionalization should consider the possibility that it is also due (at least in part) to difference of textural properties among the compared samples.

3.3.3. Identification and quantification of Ti species

Bulk Ti content, determined by ICP-AES, varied slightly among the samples, but in all samples, it was close to the nominal value (Ti/(Si+Ti)) 0.015 (Table 3.4). The surface elemental composition and Ti speciation was evaluated by XPS. The peak decomposition of Ti 2p from our samples was therefore performed under certain constraints (Figure 3.9) similar to the ones applied in Chapter 2. 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 fell at the binding energy range 460.1-460.6 eV in agreement with the literature that assigns 460.0 eV for these Ti species [138, 143, 145, 147], whereas the EFW-Ti species fell at 458.6-459.1 eV, which also agrees with previous studies [145]. In contrast to the peak decomposition in Chapter 2, this analysis was more challenging given that the nominal Ti molar ratio was lower in this Chapter. For this reason, a larger variation of the binding energies was detected.

In Chapter 2, the surface total Ti and FW-Ti molar ratios decreased due to methyl-functionalization. Thus, in this chapter, the hypothesis was that a lower nominal Ti molar ratio would allow to prevent the effect of methyl-functionalization observed in Chapter 2. In fact, in Chapter 3, surface Ti molar ratios were similar in all the samples, except for the one with 10% degree of methyl-functionalization, demonstrating that our hypothesis was valid until a maximum value. A similar trend was observed for the surface FW-Ti molar ratio. Both surface total C and C-H molar ratios were consistent with the increasing degree of methyl-functionalization in the samples.

Sample	0.015Ti	0.015Ti-3% Me	0.015Ti-5% Me	0.015Ti-10% Me
Bulk Ti/(Si+Ti) at.ratio	0.014	0.018	0.016	0.014
Surf. Ti/(Si+Ti) at. ratio	0.014	0.013	0.013	0.010
Surf. FW-Ti/(Si+Ti) at. ratio	0.011	0.011	0.010	0.007
Surf. FW-Ti/Ti at. ratio	0.77	0.84	0.73	0.73
Surf. C/(Si+Ti) at. ratio	0.132	0.155	0.156	0.204
Surf. C-H / Si at. ratio	0.103	0.119	0.121	0.171

 Table 3.4 Bulk atomic ratios based on ICP-AES and surface atomic

 ratios based on XPS elemental quantification



Figure 3.9. Decomposition of XPS Ti 2p spectra with two components FW-Ti (green solid line) and EFW-Ti (red solid line). The measured spectra are represented by the gray solid line and the corresponding fit is represented by the black solid line (sum of FW-Ti and EFW-Ti components). The BE of FW-Ti $2p_{3/2}$ is represented by the green dashed line and the BE of EFW-Ti $2p_{3/2}$ is represented by the red dashed line.

Furthermore, diffuse reflectance UV spectroscopy allowed to study the type of titanium species present on the catalyst surface. In Chapter 2, it was observed that methyl-functionalization increased the number of EFW-Ti even though the nominal Ti molar ratio used in the synthesis was constant at 0.025. For this reason, in this chapter, the Ti molar ratio was lowered to 0.015. Figure 3.10 shows the DRUV spectra of methyl-functionalized Ti-SiO₂ with Ti molar ratio of 0.015.

Comparison of the DRUV spectra from Chapter 2 (Figure 2.6) and from this Chapter (Figure 3.9) shows that the impact of methyl-

functionalization over the formation of EFW-Ti was less significant at lower Ti molar ratios such as 0.015. Contrarily to the impact observed for Ti-SiO₂ samples with Ti molar ratio of 0.025, where the amount of extra-framework-Ti increased with the methyl-functionalization degree. This was also confirmed by comparing the values of the band gaps (Eg) as shown in Figure 3.11.



Figure 3.10. DRUV spectra of pristine and methyl-functionalized Ti- SiO_2 with nominal Ti molar ratio of 0.015.

3.3.4. Assessing the role of hydrophobicity on the catalytic epoxidation of cyclooctene with tert-butyl hydroperoxide as oxidant

In Chapter 2, methyl-functionalization proved to be beneficial for the catalytic activity until a maximum degree above which hydrophobicity was too high and started to decrease the affinity for H_2O_2 , according to the water vapor sorption experiments. For this reason, in this Chapter, an organic peroxide such as *tert*-butyl hydroperoxide (TBHP), which as being more hydrophobic should display more affinity for a methyl-functionalized surface than H_2O_2 . Table 3.5 summarizes the catalytic

results, showing that the samples with an intermediate degree of methyl-functionalization perform better.

Table 3.5. Conversions, yields and carbon balance after 8 hours of reaction for pristine and methyl-functionalized Ti-SiO₂

nple	Conversion ^a	Yield ^a	Carbon Balance ^a
-	(%)	(%)	(%)
5Ti	33	32	98
- 3% Me	37	36	99
- 5% Me	41	39	98
10% Me	34	33	99
	nple 5Ti - 3% Me - 5% Me 10% Me	nple Conversion ^a (%) 5Ti 33 - 3% Me 37 - 5% Me 41 10% Me 34	Conversion ^a Yield ^a (%) (%) 5Ti 33 32 - 3% Me 37 36 - 5% Me 41 39 10% Me 34 33

Reaction conditions: 0.5M [C₈H₁₄], 0.25M [TBHP] in CH₃CN with 10 g·L⁻¹ of catalyst, 70 °C, 8 h.

 a Uncertainties are ±4 % and were determined from quadruplicates of the catalytic tests.

The carbon balance was close to 100% for all the experiments and no other product than the epoxide was detected, so the selectivity was 100% towards the epoxide.

In order to determine the best methyl-functionalization degree, catalytic tests with each of the methyl-functionalized samples were performed. The respective epoxide yield is shown in Figure 3.11. The sample with an effective 5% degree of methyl-functionalization performed the best. The uncertainties were calculated from tests with two samples (3%Me and 10%Me) repeated 4 times. The sample with the highest degree of methyl-functionalization showed once more the lowest activity of all the methyl-functionalized samples.



Figure 3.11. Kinetic data in terms of epoxide yield for the reaction of cyclooctene with TBHP with pristine and methyl-functionalized Ti-SiO₂ with Ti molar ratio of 0.015. Reaction conditions: 0.5 M [C₈H₁₄], 0.25 M [TBHP] in CH₃CN with 10 g·L⁻¹ of catalyst, 70 °C, 8 h.

3.3.5. Leaching tests and recyclability evaluation

The catalyst stability was studied by leaching tests. After 3.5 hours of reaction, the reaction medium was centrifuged at 10000 rpm for 10 minutes and then filtered through a 0.2 μ m filter. The filtered solution was refluxed again, and samples were collected regularly to follow the evolution of the reaction. In case of catalyst leaching, cyclooctene would continue reacting due to leached titanium species present in the solution as they would continue to catalyze the reaction as homogeneous catalyst. In Figure 3.12, the evolution of the concentration of the epoxycyclooctane is represented as a function of time. It was observed that as soon as the catalyst was removed from the reaction medium, the epoxide concentration remained constant during 24 hours of test. This indicated that the reaction was no longer catalyzed and therefore the catalyst did not leach or at least that it doesn't leach active species.



Figure 3.12. Hot filtration tests with 0.015 Ti and 0.015 Ti 3%Me as catalysts for the epoxidation of cyclooctene with TBHP.

The catalyst stability is also studied by recyclability tests. Two procedures were applied to recover the used catalysts, one involving a calcination and one where the samples were only rinsed with excess of solvent.

For the first procedure, the reactions were performed with two different catalysts, the pristine Ti-SiO₂ (0.015 Ti) and one of the methylfunctionalized ones (0.015 Ti 3% Me). After 8 hours, the solutions were centrifuged, and the catalyst was recovered for recycling. The catalysts were rinsed with acetonitrile at room temperature for two days (with agitation). They were then dried in a vacuum oven at 60 °C and calcined at a 350 °C for 5 hours. Previous recyclability tests for similar samples indicated that calcination under these conditions was enough to remove any reactant or solvent residues present on the catalyst. In the current case, after calcination, the catalyst was brown, indicating that coke was trapped in the solid. The original color of the powder was white. The infrared spectrum of this sample (Figure 3.13) indicated a signal at 1636 cm⁻¹. According to the literature, this band corresponds to the C=C aromatic bond, which was attributed to the presence of residues from the catalytic test trapped in the porosity of the recovered catalyst after drying and calcination [152].

The brown catalysts were re-calcined at 400 $^{\circ}$ C in order to try to eliminate the coke without burning the methyl moieties (which burn around 425 $^{\circ}$ C) but the visual result was identical to the first calcination, as well as the IR spectra.



Figure 3.13. FTIR-ATR spectrum of the catalyst calcined at 425 °C after the catalytic test. The peak at 1636 cm⁻¹ corresponds to the C=C band, probably due to residues from the catalytic test. This peak was absent in the IR spectra of the just synthesized catalysts.

Finally, calcination at 425°C was tested, but the catalyst appearance was still not satisfactory. In addition, the catalyst texture changed, becoming much harder to grind for IR analysis. This probably indicates sintering. Considering this result and the difficulties during calcination, the calcined used catalysts were not used in a second run since it would be difficult to identify the real cause of an eventual loss of activity. The risk of methyl loss caused by the high calcination temperature or the modification of the texture indeed becomes significant.

A second procedure was developed to recycle the catalyst. Instead of calcining the catalyst, a simple rinse with acetonitrile between consecutive catalytic runs was performed. The advantages of this procedure were that the visual appearance was similar to a fresh catalyst and catalyst loss during transfer was prevented. The pristine catalyst (0.015 Ti) and the methyl-functionalized one (0.015 Ti-3%Me) were tested (Figures 3.14 and 3.15, respectively). Between each catalytic run, the catalyst was washed with an excess of acetonitrile

and stirred at 60 °C. Later the catalyst was recovered and dried at 60 °C overnight. The hot rinsing helped to remove all the possible compounds adsorbed on the catalyst. The catalyst was weighed in its reactor before each new run, and the catalyst loss was negligible (0.1%), which implies that any difference of activities between runs could not be attributed to catalyst mass loss.



Figure 3.14: Recyclability test of the pristine Ti-SiO₂ (0.015 Ti), the catalyst is washed with acetonitrile and dried between each reaction.



Figure 3.15: Recyclability test of the 3% methyl-functionalized Ti-SiO₂ (0.015 Ti 3%Me), the catalyst is washed with acetonitrile and dried between each reaction.

It was observed that for the pristine Ti-SiO₂ (0.015 Ti), the activity decreased after the first cycle, and this activity then seemed identical at the third cycle. On the other hand, the activity of the methylfunctionalized catalyst (0.015 Ti 3%Me) also decreased after the first cycle, but it increased again during the third cycle. Several hypotheses were drawn to explain this. There was a difference in drying time between runs 1 and 2 and between runs 2 and 3. The first drying lasted all night before launching the second reaction and the second drying lasted a whole weekend before the third reaction. Therefore, it is possible that a longer drying allowed a better regeneration of the catalyst after reaction. If this is the case, methyl-functionalization could help the catalyst to regenerate, which would explain why the methylfunctionalized sample displayed a higher reactivation capability than the pristine sample. Consequently, a second test was performed with a longer drying time (2 days). The results are shown in Figures 3.16 and 3.17 for the pristine and methyl functionalized samples, respectively. It was observed that even with the repetition of the same drying conditions, the deactivation still occurs. Therefore, the drying time does not help to recover the initial catalytic activity. In the case of 10%MTES sample, a long drying of 4 days was applied, and a third run was accomplished. The activity increased compared to the second cycle but not as high as the activity in the first cycle.



Figure 3.16: Repetition of the recyclability test of the pristine Ti-SiO₂ (0.015 Ti), the catalyst was washed with acetonitrile and dried between each reaction.



Figure 3.17: Repetition of the recyclability test of the 3% methylfunctionalized Ti-SiO₂ (0.015 Ti 3%Me), the catalyst is washed with acetonitrile and dried between each reaction.

In order to determine if the difference of activity comes from the standard error, the two recyclability tests were overlaid for the sample 3%Me (Figure 3.17).



Figure 3.17: Superposition of the two catalytic tests (blue for the first and green for the second) of the 3% methyl-functionalized $Ti-SiO_2$ (0.015 Ti 3%Me), including the error bars.

The first runs from the two recyclability tests are the same, considering the standard deviation. The second and the third runs are also the same, considering the standard deviation. After the first run, the activity decreased and remained stable for runs 2 and 3. This is similar in the case of the pristine sample where the second and third runs were almost the same (Figure 3.17). The decrease of activity was around 10% for the 3%Me sample whereas it was around 20% for the pristine sample.

3.4. Conclusions

The synthesis of the methyl-functionalized Ti-SiO₂ catalyst with Ti molar ratio of 0.015 was slightly different than in Chapter 2. During the calcination, the methyl moieties of the 0.015Ti sample were lost by calcining at a lower temperature than the one used in Chapter 2. This relation between Ti molar ratio and calcination temperature was also observed in Chapter 1. This result may be explained by the higher molar fraction of isolated framework-Ti present in the catalyst, which are known to be sites capable of oxidation catalysis.

Regarding the distribution of Ti species, the series of samples in this Chapter were different from the ones in Chapter 2. Samples with a Ti molar ratio of 0.025 contained a larger molar fraction of EFW-Ti when the methyl-functionalization degree increased. In this Chapter, DRUV and XPS showed that methyl-functionalization influenced in a lesser extend the amount of EFW-Ti compared to the samples in Chapter 2.

The catalytic tests showed there is an optimal degree of methylfunctionalization, which is an intermediate and not the most hydrophobic one. This result partially agrees with Chapter 2, and the hypothesis that more hydrophobic catalysts would exhibit a higher activity. However, a too high degree of methyl-functionalization still diminishes it. All the samples contained almost the same ratio of Ti species and therefore, this parameter is not the only one explaining the different catalytic activities. N₂ physisorption indicated that the catalysts are highly microporous. Only active sites located on the external surface would be effective for the epoxidation reaction. The external surface area estimated does not indicate either a relation with the catalytic activity. Samples with higher external surface are not the most efficient for the epoxidation reaction.

The recyclability tests showed that the catalysts lost activity after the first reaction, but they were still active in the second and third runs. This loss of activity is about 10% and 20%, respectively for a methyl-

functionalized and the pristine catalyst. The leaching tests showed that Ti active species did not leach.

Nevertheless, adjusting the hydrophobic/hydrophilic balance via a onepot classical sol-gel generally led to a decrease of the Ti dispersion and/or collapse of the pore network. Thus, controlling the textural properties was required, so aerosol-assisted one-pot sol-gel appeared as an alternative to be evaluated in Chapter 4.

Chapter 4

CHAPTER 4: Hydrophobic effect of the mesoporous methyl-functionalized Ti-SiO₂ catalysts synthesized by aerosol-assisted sol-gel on the catalytic epoxidation of olefins

"Mesoporous methyl-functionalized titanosilicate produced by aerosol process for the catalytic epoxidation of olefins"

Abstract

Previous chapters studied the one-pot hydrophobization of Ti-SiO₂ via classical sol-gel and the catalytic performance of these synthesized materials in the epoxidation of cyclooctene with H₂O₂ or TBHP as oxidants. However, N₂ physisorption showed that hydrophobic Ti-SiO₂ catalysts were microporous, and the specific surface areas varied greatly depending on the degree of methyl-functionalization, complicating the comparison of catalytic activities. To overcome this limitation, hydrophobic mesoporous Ti-SiO₂ were here synthesized by aerosol-assisted one-pot sol-gel, which allowed the simultaneous control of their Ti loading, degree of methyl-functionalization, and textural properties. Similarly to previous chapters, methylfunctionalization was achieved by a partial substitution of tetraethoxy silane (TEOS) by methyltriethoxy silane (MTES) in different ratios. Solid-State ²⁹Si-NMR, FTIR, TGA and vapor-phase water adsorption showed that methyl moieties were effectively incorporated, conferring a hydrophobic character to the Ti-SiO₂ catalysts. ICP-AES, DRUV, XPS, and N₂ physisorption demonstrated that Ti dispersion and textural properties were both successfully preserved upon the incorporation of the methyl moieties. In the epoxidation of cyclooctene with tert-butyl hydroperoxide as oxidant, the hydrophobic Ti-SiO₂ showed higher catalytic performance than pristine Ti-SiO₂ prepared without MTES. In addition to disentangling the positive effect of adjusting the hydrophobic/hydrophilic balance of epoxidation catalysts on their performance, this chapter highlights the advantages of the aerosol procedure to synthesize mesoporous functionalized catalysts with very high dispersion of active sites.

4.1. Introduction

Chapters 2 and 3 showed that one-pot methyl-functionalization was successful at producing hydrophobic $Ti-SiO_2$ catalysts that reached higher epoxidation rates and yields than pristine ones in the

epoxidation of cyclooctene, proving the concept that adjusting the hydrophobicity of Ti-SiO₂ catalysts by methyl-functionalization increases their catalytic activity [153]. However, the addition of the methyl alkoxysilane precursor disturbed the Ti dispersion and diminished the number of active sites in the catalyst. This was clearly observed for the catalyst with the highest methyl content, which exhibited the lowest number of active sites compared to the other methyl-functionalized catalysts. Hence, there is a limitation for the degree of methyl-functionalization that can be achieved by this method. Additionally, the specific surface area of the samples was strongly influenced by the degree of methyl-functionalization, which added another variable to be accounted to compare the catalysts performance. These co-dependent variables make the elucidation of functionalization effects challenging, thus there is a demand for an innovative synthesis procedure that allows controlling Ti dispersion, textural properties and surface functionalization simultaneously.

A method that has demonstrated to produce catalysts with tailored texture and well-dispersed active species is aerosol-assisted sol-gel (AASG), which is emerging as a practical method to synthesize tailormade mesoporous catalysts [46, 154-160]. The high dispersion of Ti active sites is achieved thanks to the fast drying of the atomized precursor mixture which quenches the condensation kinetics and leads to the synthesis of materials with homogeneous composition [154]. Besides, a large variety of templates can be used so as to finely tune the textural properties. In a previous study, we demonstrated that mesoporous Ti-SiO₂ catalysts prepared by AASG are highly effective for the epoxidation of bulky olefins in organic conditions [46].

In this Chapter, AASG process was applied to synthesize methylfunctionalized Ti-SiO₂ catalysts. We envisage that the high Ti dispersion achievable with the aerosol method will promote the formation of more numerous active Ti species. In this sense, we hypothesize that methyl-functionalized Ti-SiO₂ catalysts synthesized by AASG will exhibit superior Ti and methyl dispersion as well as higher mesoporosity than previous analogous catalysts synthesized by conventional sol-gel. Such aerosol-synthesized materials are good materials to studv the effect model of adiusting the hydrophobic/hydrophilic balance achieved by one-pot surface functionalization on the catalytic epoxidation of cyclooctene with tertbutyl hydroperoxide as oxidant since the textural properties are not affected by the functionalization. Thus, it should be possible to isolate the effect of the hydrophobic/hydrophilic balance thanks to an extended characterization of the catalyst that allows normalizing the catalytic activity per specific surface area and per Ti active site.

4.2. Experimental section

4.2.1 One-pot aerosol-assisted sol-gel synthesis towards methyl-functionalized Ti-SiO_2

The catalysts were prepared via one-pot aerosol-assisted sol-gel to achieve good Ti and methyl dispersion as well as good textural properties. A fraction of tetraethoxy silane precursor (TEOS, Sigma-Aldrich, 98%) was substituted by a more hydrophobic alkyl silane, namely methyltriethoxy silane (MTES, Sigma-Aldrich, 99%) to obtain hydrophobic methyl-functionalized mesoporous catalysts with Ti incorporated by the addition of titanium butoxide (TBOT, Sigma-Aldrich, 97% reagent grade) in Ti/(Si+Ti) molar ratio equal to 0.02 in all samples.

The procedure for the catalyst synthesis was adapted from Smeets et al. [46]. Precisely, the precursor solution was prepared by adding 0.6 mmol TBOT dropwise to 79 mmol tetrapropyl ammonium hydroxide (TPAOH, Merck, 40%). After 10 min stirring, 513.6 mmol distilled water were poured and stirred for an additional 10 min. 29.4 mmol TEOS and MTES were successively added and the final mixture was stirred overnight at room temperature in a closed vessel to hydrolyze the precursors. Afterwards, the solution was aged in the oven at 70 °C for 15 h. 0.2 mmol Pluronic F127 (F127, BASF) was added and the solution was stirred for 1 h prior to atomization. The final molar composition of the precursor solution was x MTES : 1-x (TEOS + TBOT) : 0.15 TPAOH : 0.005 F127 : 19.6 H₂O, where "x" represents the molar fraction of MTES used in the synthesis of the hydrophobic samples, as defined in Equation 4.1. In the case of the pristine sample, no MTES was added to the mixture (*i.e.*, x = 0). For the methylfunctionalized samples, the MTES molar ratios used were 0.05, 0.10 and 0.20 as defined in Equation (4.1).

$$Molar \ ratio_{MTES} = \frac{mol_{MTES}}{mol_{TEOS} + mol_{TBOT} + mol_{MTES}}$$
(4.1)

The clear precursor solution was sprayed by a Büchi Mini Spray Drier B-290 (Büchi Labortechnik AG, Flawil, Switzerland) as described in the section 1.2 of Materials and methods. The collected powder was aged at 70 °C overnight in a static oven, and then it was calcined in static air along a temperature program that started with a ramp of 1 °C min⁻¹ from room temperature to 350 °C and followed by a dwell step at the final temperature for 10 h. After cooling down inside the furnace for around 3 h, the calcined solids were stored in a desiccator.

4.2.2. Catalyst characterization

Solid-state ²⁹Si direct excitation magic-angle spinning nuclear magnetic resonance (²⁹Si-DE-MAS-NMR) spectra were recorded as described in detail in the Materials and Methods section. Samples were also characterized by FTIR in ATR mode, TGA, DRUV, ICP-AES, XPS, SEM, N₂ adsorption-desorption experiments and vapor-phase water adsorption experiments. Specific analysis conditions used in this Chapter are described hereafter.

In this Chapter, Thermal Gravimetric analyses (TGA) were performed on a Mettler Toledo TGA/DSC 3⁺ STAR System instrument. Diffuse reflectance UV-Vis (DRUV) spectra were recorded on a Shimadzu UVvis-NIR spectrometer equipped with a Praying Mantis in a spectral range from 200 to 600 nm using the Shimadzu UV software package. A Spectralon pellet was used to measure the background spectrum, and the Kubelka-Munk function F(R) was calculated based on the reflectance (R). The band gap energy value (Eg) was calculated from the optical absorption edge in the DRUV spectra using the Tauc method [161]. Moreover, C 1s and Ti 2p XPS 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.

N₂ adsorption-desorption experiments were performed at -196 °C using a Micromeritics Tristar 3000 instrument. Before the analysis, the samples were degassed overnight under vacuum (6.7 Pa) at 180 °C. Adsorption-desorption isotherms were obtained and the micropore volume was determined from the t-plot constructed based on the adsorption data. The intercept of the best tangent drawn on the t-plot in the range corresponding to partial pressures between 0.05 and 0.30 of the t-plot was used to determine the micropore volume, which was then subtracted from the N₂ volume adsorbed at each data point to construct a second adsorption isotherm. The Brunauer-Emmet-Teller (BET) method was applied to this second isotherm to calculate the specific surface area excluding the consumption of nitrogen corresponding to micropore filling, and it was called specific surface area corrected (SSA_{corrected}). Having replicated the analysis three times for one of the samples, we know the uncertainty of the measurement of SSA_{corrected} is ca. 5%. The pore size distribution was determined from the desorption isotherms applying the BJH method.
4.2.3. Catalytic tests

The catalytic performance of the synthesized Ti-SiO₂ was evaluated in the epoxidation of cyclooctene (TCI, >90%) with *tert*-butyl hydroperoxide (TBHP, Sigma-Aldrich, 30%), as defined in equation 4.2. The initial concentrations of cyclooctene and TBHP were of 0.5 and 0.25 M, respectively, whereas the catalyst concentration was of 10 g L⁻¹. The reactants were successively added to a 10-mL reactor with 7.8 mL of acetonitrile (VWR Chemicals, ≥99.9%) in the presence of 0.1 M dibutyl ether (DBE, TCI, >99%) used as internal standard. The reaction temperature was set at 70 °C (343 K), and the reaction time was 8 h. 100-µL aliquots were sampled every hour (an aliquot taken at 0.5 h) with a syringe through a septum fitted to the reactor. The reactant consumption and product formation were followed by gas chromatography (GC) as explained in the Materials and Methods section.



4.3. Results and discussion

4.3.1. Assessing the degree of methyl-functionalization and hydrophobicity

Quantitative solid-state ²⁹Si magic-angle spinning (MAS) NMR spectroscopy was used to examine the degree of methyl-functionalization (%Me) of Ti-SiO₂ catalysts (Figure 4.1). In the ²⁹Si direct excitation (DE) MAS spectra of all Ti-SiO₂ samples, a broad band, assigned to Qⁿ contributions typical of an amorphous silica matrix was observed. A deconvolution analysis using Gaussian functions allows to assign the different contributions centered at -112 ppm, -102 ppm and -92 ppm which are attributed to Q⁴ (Si(OSi)₄), Q³ (Si(OSi)₃OH) and Q² (Si(OSi)₂(OH)₂) species, respectively. In methyl-functionalized Ti-SiO₂ samples, an additional broad signal centered at -60 ppm revealed the presence of T³ (Si(OSi)₃Me) and T² (Si(OSi)₂(OH)Me) contributions (deconvolution analysis shown in Figure 4.2). After calcination at 350 °C, Ti-SiO₂ samples exhibited

three degrees of methyl-functionalization: 3%, 9%, and 14%, determined from direct excitation NMR experiments by the following formula: $\% Me = 100 \cdot {T^i / \sum_i (Q^i + T^i)}$. Previous studies have reported that methyl groups strongly bonded to Si were largely preserved upon calcination temperatures as high as 500 °C [90, 91, 153], which is in agreement with our own observations. Hereafter our samples will be named TS_Aer-x%Me, where "x" represents the effective percentage of methyl-functionalization found via quantitative solid-state NMR.



Figure 4.1. Solid state ²⁹Si direct excitation MAS NMR spectra of calcined TS_Aer-x%Me. Spectra are normalized to the Q⁴ contribution and are vertically offset for clarity.



Figure 4.2. Deconvolution of ²⁹Si DE MAS NMR spectra of TS_Aer-14%Me

Furthermore, FTIR-ATR spectra of the methyl-functionalized samples confirmed the presence of methyl moieties bonded to silicon (v(Si-C)) at 1279 cm⁻¹, whereas this band was absent in the pristine sample (Figure 4.3). Qualitatively, the IR spectra of the methyl-functionalized samples follow the same trend as observed by ²⁹Si NMR, with the v(Si-C) band intensity increasing when increasing the MTES/TEOS ratio in the precursor solution.



Figure 4.3. FTIR-ATR spectra of the TS_Aer-x%Me catalysts

TGA analyses of the pristine catalyst, namely TS Aer-0%Me (produced only with TEOS as Si precursor), and methyl-functionalized catalysts (TS Aer-3%Me, TS Aer-9%Me, TS Aer-14%Me) were performed to: i) further verify the presence of methyl moieties, ii) to evaluate the removal of residual templating agents, and iii) to assess the hydrophobic character by quantification of the physisorbed water (water desorbing in the low temperature range). Three main mass losses were observed in the ranges of 40-180 °C, 180-500 °C and 500-600 °C (Figure 4.4). The first mass loss was associated with physisorbed water whereas the second mass loss was present equally in the four samples and it was presumably related to small amounts of organic contaminants, frequently found in such sol-gel samples, that were still present after the calcination (e.g., traces of precursors, solvents and templating agents). In this Chapter, a mild calcination temperature of 350 °C was selected to remove the templating agents while preserving the methyl-functionalization. Previous works successfully removed from silicalites templating agents such as Pluronic at calcination temperatures lower than 600 °C [7, 162]. Inspired by these works, the sample with a nominal MTES molar ratio of 0.20 was calcined at 250, 350, and 450 °C in order to select the best calcination temperature. At 250 °C, the incomplete removal of the templating agents was noticed based on the brown color of the sample

(see Table A-2, Appendix). At higher calcination temperatures, the sample color was beige, suggesting that the removal of the templating agents improved. At this point, the selection of the calcination temperature was based on the difference in the preservation of the methyl-functionalization. This was determined by following the band corresponding to v(Si-C) at 1279 cm⁻¹ by FTIR-ATR. As depicted in Figure 4.4, almost all the methyl moieties were lost due to calcination at 450 °C, and the best compromise between templating agents removal and methyl content preservation was found at 350 °C. Therefore, the calcination temperature selected for all the samples was 350 °C. Interestingly, the third mass loss was only observed in the methyl-functionalized samples. From the derivative curves in Figure 4.5, this mass loss occurred around 530 °C, and presented a direct correlation with the degree of methyl-functionalization, thereby suggesting a correspondence with the degradation of the methyl groups as previously reported in the literature [90, 91, 153].



Figure 4.4. FTIR-ATR spectra of the sample with nominal MTES molar ratio of 0.20 calcined at 350 °C and 450 °C in static air.



Figure 4.5. TGA analysis profiles (dotted lines) and derivative curves (solid lines) obtained under air flow for the TS Aer-x%Me catalysts.

The water desorbed in the 40-180 °C range was quantified to assess the degree of hydrophobicity. The derivative curves in Figure 4.5 suggest that the pristine sample TS_Aer-0%Me desorbed a higher amount of water compared to the methyl-functionalized samples. Nevertheless, a valid comparison of physisorbed H₂O among the samples must be performed after proper normalization to the specific surface area.

 N_2 physisorption analyses were performed to properly address the degree of hydrophobicity as well as to understand the effect of the methyl precursor addition on the texture of the catalysts. The N_2 adsorption-desorption isotherms of all samples featured a Type IV isotherm typically associated to mesoporous materials (Figure 4.6) [163-165]. The specific surface area, excluding the surface area of micropores, was quantified following the strategy described in the Experimental section. T-plots for all samples, shown in Figure 4.7, were used to determine their micropore volume from the intercept of the linear fit in the thickness range corresponding to relative pressures between 0.05 and 0.30. As shown in Table 4.1, the samples with higher degree of methyl-functionalization, exhibited higher specific surface areas and lower micropore volumes. All samples had the same pore

volume, close to 1.0 cm³g⁻¹, related with the templating effect of the surfactant (Table 4.1). The pore size distributions (PSD) determined from the BJH method did not vary significantly despite the addition of the methyl precursor, as the mesopores distribution remained centered at ca. 12 nm (Figure 4.4, inset). These results demonstrate that, unlike Ti-SiO₂ prepared by conventional sol-gel techniques in the previous chapters [90, 91, 96], the catalysts prepared by aerosol-assisted sol-gel show no alteration of their mesostructure upon the incorporation of methyl groups during the synthesis.



Figure 4.6. N_2 physisorption isotherms of TS-Aer x%Me catalysts. Pore size distributions (PSDs) based on the desorption branch of the isotherms are shown in inset.



Figure 4.7. t-plots constructed based on the N_2 adsorption data for the TS_Aer-x%Me catalysts.

Table 4.1. Textural properties of the TS_Aer x%Me catalysts.						
	SSV , a	Pore volume	Micropore			
Sample	m ² g ⁻¹	(77 K) ^b	volume (77 K) ^c			
		cm³g⁻¹	cm³g⁻¹			
TS_Aer-0%Me	360	1.00	0.21			
TS_Aer -3%Me	364	1.00	0.20			
TS_Aer -9%Me	402	0.98	0.18			
TS Aer-14%Me	462	0.99	0.16			

^aSpecific surface area corrected by excluding the N₂ uptake due to micropores filling. ^b N₂ volume uptaken at 77 K and relative pressure of 0.99. ^c Determined from the intercept of the best tangent drawn in the t-plot in the relative pressure range of 0.05-0.30.

Additionally, SEM images of TS_Aer-0%Me and TS_Aer-9%Me, given in Figure 4.8), showed that pristine and methyl-functionalized catalysts are formed of microspheres with similar size in the range 1 to 20 µm.



Figure 4.8. SEM images of TS_Aer-0%Me (a) and TS_Aer-9%Me (b)

The degree of hydrophobicity was then assessed by three different approaches (Table 4.2). First, the amount of physisorbed water (calculated from TGA data) was normalized by the specific surface area SSA_{corrected} to get rid of textural differences from one compared sample to another. As expected, the pristine sample TS_Aer-0%Me presented the biggest evolution of physisorbed water during the analysis, whereas the methyl-functionalized samples desorbed smaller amounts of physisorbed water per unit of surface area (Table 4.2). In general, methyl-functionalized catalysts exhibited a stronger hydrophobic character than the pristine one. Yet, this approach did not allow to properly correlate the methyl content with the degree of hydrophobicity since all methyl-functionalized catalysts displayed similar amounts of physisorbed water.

Therefore, in a second approach, the fraction of Si atoms coordinated to –OH groups (hydrophilic sites) was estimated from the contributions of Q³ and Q² species in ²⁹Si solid-state MAS NMR spectra (that correspond to Si atoms existing as $(OSi)_3SiOH$ and $(OSi)_2Si(OH)_2$. This strategy has been used previously to assess the degree of hydrophobicity of a material based on the quantification of the fraction of Si atoms existing as distinct silanol species [73, 76]. As shown in Table 2, this analysis showed that the fraction of Si as $(OSi)_3SiOH$ and $(OSi)_2Si(OH)_2$ decreased with increasing amount of methyl content.

Third, in order to allow a better comparison of the hydrophilic/hydrophobic character of the catalysts, water vapor sorption experiments were performed at 22 °C. Figure 4.9 shows the vapor water adsorption isotherms normalized to the specific surface

area (SSA_{corrected}) at low relative pressures. The affinity of the catalyst surface for water is featured at low relative pressures of the adsorption branch of the isotherm [101, 120]. The adsorption isotherms in the whole relative pressure range are shown in Figure A-3 (Appendix). The normalized water uptake at selected relative pressures of p/po= 0.1 and 0.2 are displayed in Table 4.2. A reduced affinity for water was featured by TS Aer-9%Me and TS Aer-14%Me compared to the pristine TS_Aer-0%Me, thus confirming the results from TGA analysis. Interestingly, the water sorption isotherms revealed that the TS Aer-14%Me catalyst was more hydrophobic than the TS_Aer-9%Me catalyst, regarding its lower H₂O uptake, which is in agreement with its methyl content. Notably, at relative pressures lower than 0.15, a difference in hydrophobicity between TS Aer-0%Me and TS Aer-9%Me is not marked due to the normalization to SSAcorrected, which has an associated uncertainty in the measurement of 5% and does not account for micropores filled at low relative pressures. The difference of hydrophobicity becomes clearer at relative pressures higher than 0.15.

Table 4.2. Physisorbed water per specific surface area, fraction of Si atoms existing as Q^3 (Si(OSi)₃OH) or Q^2 (Si(OSi)₂(OH)₂), and water uptake at p/p_o = 0.1 and p/p_o = 0.2 for TS_Aer x%Me.

	Phys	Fraction of Si	H₂O untake	H₂O untake
Sample	H ₂ O/SSA _{corr}	as Q ³ and Q ²	at $p/p_0 = 0.1^{\circ}$.	at $p/p_0 = 0.2^{\circ}$.
	ected ^a	species⁵	$mol_{\mu_{20}} m^{-2}$	$molupo m^{-2}$
	mol _{H2O} m ⁻²	mole %	molinzo m	
TS_Aer-0%Me	22.3	32.1	5.1	11.6
TS_Aer-3%Me	13.2	31.5	n.m. ^d	n.m. ^d
TS_Aer-9%Me	9.3	30.7	5.1	9.1
TS_Aer-14%Me	13.1	24.2	3.4	6.1

^aDetermined from the TGA analysis and the specific surface area corrected (SSA_{corrected}) given in Table 4.1. ^bDetermined from ²⁹Si solid-state direct excitation MAS NMR by the formula : $\%SiOH = 100 \cdot \left(\frac{Q^3 + Q^2}{\sum_i (Q^i + T^i)}\right)$ (Figure 4.1). ^cDetermined from the vapor water sorption analysis. ^dNot-measured.



Figure 4.9. Vapor water adsorption isotherms normalized by the specific surface area (SSA_{corrected}) at low relative pressures. The normalized water uptake values are depicted on the curve and the shaded regions denote the estimated uncertainty of 5% due to the N₂ physisorption measurement of SSA_{corrected}.

In summary, one can infer from the characterization presented above that (i) our aerosol protocol was successful at incorporating of methyl moieties in the samples, in particular that a large proportion of the methyl moieties survived the thermal treatment applied after synthesis, (ii) that all aerosol-made samples exhibit a very similar mesoporous texture featuring more accessible surfaces for the epoxidation reaction than the ones obtained by conventional sol-gel, and (iii) that the methylfunctionalized samples are more hydrophobic than the pristine one.

4.3.2. Quantification of Ti dispersion

Diffuse reflectance UV-Vis (DRUV) spectroscopy was performed to distinguish framework Ti (FW-Ti) in the range 200-240 nm, from extra-framework Ti (EFW-Ti) in the range of 240-330 nm [23, 148-150]. While FW-Ti corresponds to Ti atoms in tetrahedral coordination, EFW-Ti corresponds to Ti atoms in higher coordination numbers such as pentahedral or octahedral coordination [23, 148, 166]. The latter

species are the same Ti species found in anatase (crystalline TiO₂), and their presence can be detected by DRUVS in the range 310-330 nm [23, 148, 149]. Pristine and methyl-functionalized catalysts exhibit both FW-Ti and EFW-Ti species (Figure 4.10). The contribution of FW-Ti species is significantly higher than the one of EFW-Ti, and no contribution above 310 nm was detected, excluding the formation of TiO₂ nanodomains. This is an evidence of the high Ti dispersion that was achieved by the aerosol synthesis method. The samples TS_Aer-9% Me and TS_Aer-14% Me exhibit slightly higher amounts of EFW-Ti than the TS_Aer-3% Me and this should be kept in mind when discussing their catalytic activity.



Figure 4.10. DRUV spectra of the TS_Aer-x%Me catalysts. The white region corresponds to the FW-Ti species and the red region corresponds to the EFW-Ti species.

The difference of Ti dispersion among the samples was quantified by calculating the band gap energy values (Eg) for each sample. The Eg value has been used in several studies to follow the evolution of the structure/coordination of titanium at different loadings [35, 167]. In this study, Eg was calculated from the optical absorption edge in the DRUV spectra using the Tauc method [161]. The calculated Eg was plotted

as a function of the methyl-functionalization degree (Figure 4.11). The calculation of the Eg value for each sample is shown in Figure 4.12.



Figure 4.11. Influence of the methyl-functionalization degree on the band gap energy values (Eg) for TS_Aer-x%Me catalysts.



Figure 4.12. Eg calculation from the optical absorption edge in the DRUV spectra for the TS_Aer-x%Me catalysts using the Tauc method.

Higher Eg values are due to the presence of tetrahedral Ti (FW-Ti) corresponding to a higher Ti dispersion, whereas poorly dispersed species in octahedral coordination spheres (EFW-Ti) generate a lower Eg value. The value calculated for TS_Aer-0%Me fell in the range of the Eg values calculated for other Ti-SiO₂ catalysts synthesized by Smeets et al. [46] and De Clercq et al. [167]. As shown in Figure 4.11, TS_Aer-0% Me and TS_Aer-3% Me exhibited higher Eg values than TS_Aer-9%Me and TS_Aer-14%Me. This was attributed to the presence of EFW-Ti in the samples with higher methyl-functionalization degree. This trend was also observed in Chapter 2, where methyl-functionalization via one-pot synthesis contributed to the formation of EFW-Ti in the attempt to diminish this detrimental effect on the catalyst homogeneity. After comparing the Eg values range (4.03 -

4.65 eV) measured for similar pristine and methyl-functionalized Ti-SiO₂ catalysts synthesized by conventional sol-gel method in Chapter 2 [153] against the Eg values range (4.79 - 4.87 eV) measured for the aerosol catalysts in this Chapter, it is clear that the aerosol synthesis procedure allowed preserving the dispersion of the Ti active sites in the presence of the MTES co-precursor. The calculations of the Eg values for the conventional sol-gel samples can be found in Figure 4.13).



Figure 4.13. Eg calculation from the optical absorption edge in the DRUV spectra for pristine and methyl-functionalized Ti-SiO₂ catalysts synthesized by conventional sol–gel method (Chapter 2) [153] using the Tauc method.

To further evaluate the homogeneity and the Ti surface dispersion in the TS_Aer-x%Me catalysts, bulk and surface atomic Ti/(Si+Ti) ratios were determined by ICP-AES and XPS, respectively. Bulk atomic Ti/(Si+Ti) ratios were found to be equal to the nominal Ti/(Ti+Si) molar

ratio (0.020) in all samples (Table 4.3), meaning that the composition of the catalysts is well-controlled in the aerosol process, both in the presence or absence of the methyl-functionalized precursor. Surface atomic Ti/(Si+Ti) ratios for all catalysts were calculated based on the decomposition of the XPS Ti 2p spectra and the XPS elemental quantification, which is shown in the Table 4.4. The Ti 2p spectrum is composed of two spin-orbit components (Ti $2p_{3/2}$ and Ti $2p_{1/2}$) which are separated by 5.7 eV [142]. While the Ti 2p_{3/2} binding energy of pure TiO_2 is 458.5 eV (octahedral coordination) [138, 142], it is known that Ti in titanosilicate displays peak broadening and shift to higher binding energy (BE) [46, 144, 146, 153, 167]. In fact, the Ti 2p_{3/2} peak can be decomposed considering two kinds of Ti species: FW-Ti (460.0 eV) [138, 143, 145, 147] and EFW-Ti (458.5 eV) [138, 142]. As shown in Figure 4.14, the binding energy values of the Ti doublet of the TS Aerx%Me catalysts were shifted to values higher than 458.5 eV and exhibited peak broadening, suggesting the presence of FW-Ti species. Therefore, the Ti 2p peak decomposition of our catalysts was performed, and further details on the peak decomposition are included in the Appendix. Here we found that the FW-Ti species fell at the binding energy of 460.0 eV, whereas the EFW-Ti species fell at 458.5 eV, consistent with the literature [46, 138, 143, 145, 147, 168]. As indicated in Table 4.3, the Ti surface content increased slightly in more methyl-functionalized samples. On the contrary, the atomic fraction of FW-Ti over total Ti on the surface gradually diminished in more methyl-functionalized samples. These results reveal some heterogeneity in the TS Aer-x%Me catalysts due to the presence of the methyl precursor that caused slight Ti enrichment on the catalyst surface and affected its dispersion. This supports DRUVS observations. Even though small heterogeneities were detected in the aerosol samples, the Ti dispersion was superior to the one reached by conventional sol-gel method (Surf. FW-Ti/Ti of around 0.70) in Chapter 2 [153]. Additionally, XPS confirms that more methyl-functionalized samples have higher content of C and specifically higher content of the C-(C,H) component per Si atom, which is likely related to the presence of methyl moieties on the catalyst surface. This result is consistent with NMR, FTIR and TGA characterization of the methyl-functionalization degree in the TS Aer-x%Me catalysts.

Sample	TS_Aer-0%Me ⁻	TS_Aer-3%Me	TS_Aer-9%Me	TS_Aer-14%Me
Bulk Ti/(Si+Ti) at.ratio	0.020	0.020	0.020	0.020
Surf. Ti/(Si+Ti) at. ratio	0.015	0.016	0.017	0.019
Surf. FW-Ti/(Si+Ti) at. ratio	0.013	0.013	0.014	0.014
Surf. FW-Ti/Ti at. ratio	0.85	0.83	0.79	0.77
Surf. C/(Si+Ti) at. ratio	0.227	0.282	0.306	0.383
Surf. C-H / Si at. ratio	0.133	0.191	0.205	0.273

 Table 4.3. Bulk atomic ratios based on ICP-AES and surface atomic ratios based on XPS elemental quantification

Table 4.4. XPS surface elemental quantification.

Sampla	C (of which C–H)	0	Ti (of which FW-Ti)	Si
Sample	at.%	at.%	at.%	at.%
TS_Aer-0%Me	5.1 (3.0)	72.2	0.34 (0.29)	22.3
TS_Aer-3%Me	6.3 (4.2)	71.4	0.36 (0.30)	21.9
TS_Aer-9%Me	7.0 (4.7)	69.9	0.40 (0.32)	22.6
TS_Aer-14%Me	8.5 (6.0)	69.3	0.41 (0.32)	21.8



Figure 4.14. Decomposition of XPS Ti 2p spectra with two components FW-Ti (green solid line) and EFW-Ti (red solid line). The measured spectra are represented by the gray solid line and the corresponding fit is represented by the black solid line (sum of FW-Ti and EFW-Ti components). The BE of FW-Ti $2p_{3/2}$ is represented by the green dashed line and the BE of EFW-Ti $2p_{3/2}$ is represented by the red dashed line.

Summarizing, the combination of results from XPS, DRUV, and ICP-AES revealed that one-pot methyl-functionalized samples with identical bulk Ti content (0.020) exhibited higher Ti total content on their surface along with a slightly lower proportion of FW-Ti species as compared to the pristine one. Further comparison among the samples is required by determining their respective number of atoms of Ti and FW-Ti per unit of surface area. As depicted in Table 4.5, all catalysts exhibited similar Ti and FW-Ti surface density, except for the sample TS_Aer-14%Me that seemed to have a smaller surface density of FW-Ti species as compared to the others.

Table 4.5. Ti and FW-Ti surface density on the catalysts TS_Aer-x%Me.

Sample	Ti atoms nm⁻² *	FW-Ti atoms nm⁻² *
TS_Aer-0%Me	0.37	0.32
TS_Aer -3%Me	0.40	0.32
TS_Aer -9%Me	0.37	0.31
TS_Aer-14%Me	0.37	0.27

* An example of the calculation is shown in the Appendix.

4.3.3. Catalytic performance of hydrophobic mesoporous Ti-SiO₂ on the epoxidation of cyclooctene

Pristine and methyl-functionalized mesoporous catalysts were compared in the epoxidation of cyclooctene with *tert*-butyl hydroperoxide as oxidant. The catalytic activity was assessed by following the epoxide production as a function of the reaction time (Figure 4.15). The epoxide production was normalized by the specific surface area (SSA_{corrected}, see Table 4.1) to discriminate the detected effect of methyl-functionalization on the catalyst texture. The effect of the pore size was not taken into account as all catalysts displayed similar pore size distributions (see Figure 4.6, inset).



Figure 4.15. Kinetic data in terms of epoxide production per unit of surface area (SSA_{corrected}) for the reaction of cyclooctene with TBHP. Error bars are shown for TS_Aer-14%Me (n = 3).

As shown in Figure 4.15, hydrophobic catalysts with effective methylfunctionalization of 3 % and 9 % produced more epoxide per unit of surface area than the pristine catalyst, displaying a positive effect of hydrophobization on the catalytic activity. This is in agreement with our initial hypothesis that the high affinity of a hydrophobized catalyst for the olefin facilitates the olefin approaching to the active epoxidation sites on the catalyst surface. Yet, the methyl-functionalized sample with 14% as effective methyl content showed lower performance. This result is similar to the ones observed in Chapters 2 and 3 about the effect of methyl-functionalization over the catalytic performance of hydrophobized Ti-SiO₂.

The carbon balance was close to 100% for all the experiments and no other product than the epoxide was detected, so the selectivity was 100% towards the epoxide. TBHP conversions measured during reaction experiments are shown in the Appendix (Figure A-4). Methyl-functionalized samples reached TBHP conversions higher than the one reached with the pristine sample.

Further discussion of the effect of hydrophobicity on the catalytic activity requires consideration of the Ti surface density since the catalyst characterization indicated that methyl-functionalization affects not only the surface polarity but also the number of the Ti atoms present at the surface. The pristine catalyst TS Aer-0%Me contained as many FW-Ti species per unit of surface area as TS Aer-3%Me and TS Aer-9%Me, so their epoxide production should be similar if assumed on the basis of this criterion only. Inversely, TS Aer-3%Me and TS Aer-9%Me produced more epoxide per unit of surface area as compared to TS Aer-0%Me, confirming the positive effect of methylfunctionalization. The loss of performance for TS Aer-14%Me, unlike the tendency observed for TS Aer-3%Me and TS Aer-9%Me, could be explained by its lower content of active FW-Ti species available at the surface. Indeed, after normalization to the number of FW-Ti species (Figure 4.16), the epoxide production of TS Aer-14%Me reached those of TS Aer-3%Me and TS Aer-9%Me. An excessive methylfunctionalization degree induces a lower content of FW-Ti that diminishes the catalytic activity. Notably, all methyl-functionalized samples displayed better catalytic activity than TS Aer-0%Me. This was also verified in terms of TOF for TBHP conversion at initial stage of the reaction (30 min) over TS_Aer-x%Me. Estimated TOF values were 44, 45 and 57 h⁻¹ over TS Aer-3%Me, TS Aer-9%Me and TS Aer-14%Me, respectively. TOF over methyl-functionalized catalysts were higher than the one over TS Aer-0%Me (38 h⁻¹). An example of TOF calculation is shown in the Appendix. These results methyl-functionalization prove that and its corresponding

hydrophobicity improved the catalytic performance in the epoxidation of cyclooctene. This positive effect of hydrophobization agrees with the observations of Lin and co-workers [88], who reported that methylfunctionalization in a one-pot approach improved the TOF of Ti-MCM-41 in cyclohexene epoxidation, as described in Table I-2 of the General Introduction section. Comparing the TOF values of TS_Aer-x%Me obtained in this work to the TOF of pristine titanosilicates reported in the literature [62-65] (Table I-1 of the General Introduction), all TS_Aerx%Me are more active in cyclooctene epoxidation.



Figure 4.16. Epoxide production normalized by the number of FW-Ti species on the surface of the TS_Aer-x%Me catalysts. Error bars are shown for TS_Aer-14%Me.

4.4. Conclusions

The synthesis of hydrophobic mesoporous Ti-SiO₂ catalysts with effective methyl-functionalization, controlled texture and improved Ti dispersion through aerosol-assisted one-pot sol-gel procedure was successful. Tuning the right methyl precursor (MTES) molar ratio in the catalyst synthesis is crucial to obtain hydrophobized mesoporous Ti-SiO₂ catalysts, but also to prevent the detrimental effect of the addition of this methyl precursor over Ti dispersion and/or textural properties. The increment of the degree of methyl-functionalization of the aerosol-

catalysts achieved synthesized Ti-SiO₂ higher degrees of hydrophobicity, while maintaining constant their mesoporosity and pore size distributions. Beyond the control of the textural properties such as specific surface area and pore size distribution, the aerosol route proved its superiority at obtaining high Ti dispersion, maximizing the amount of the catalytically active Ti species (FW-Ti), despite the addition of the methyl precursor. This was confirmed by the comparison of the Ti dispersion in methyl-functionalized catalysts synthesized by aerosol-assisted sol-gel in this Chapter with those prepared by conventional sol-gel from Chapter 2. Hydrophobic Ti-SiO₂ samples perform much better in the epoxidation of cyclooctene with tert-butyl hydroperoxide than the pristine more hydrophilic Ti-SiO₂. This tendency was verified after normalization by the specific surface area and by the number of active framework Ti (FW-Ti) species. Excessive degree of methyl-functionalization diminishes the catalyst performance due to lower Ti dispersion. Overall, a right balance of the degree of methyl-functionalization and hydrophobicity of the Ti-SiO₂ allows improving their catalytic performance. All in all, it was demonstrated that the aerosol route is more advantageous than the conventional solgel route to prepare functionalized Ti-SiO₂ porous catalysts with improved catalytic properties.

General Conclusions and Future Work

Tuning the hydrophobic/hydrophilic character of heterogeneous catalysts has recently shown to have a great impact over their performance. In this context, this thesis aimed at improving the catalytic performance of Ti-SiO₂ for the epoxidation of olefins in liquid-phase by hydrophobization of such catalyst. Our working hypothesis has been that such improvement would be gained via the increase of affinity that the olefin would have with a more hydrophobic Ti-SiO₂. Previous works on this matter had reached contradicting catalytic results raising the question of the real effect of modifying the hydrophobic character of Ti-SiO₂. To elucidate this effect, it was required to consider a complete catalyst characterization to compare the catalytic performance in terms of specific surface area and number and nature of active sites. This has been our strategy during the thesis.

In our thesis, hydrophobization by methyl-functionalization indeed consistently improved the catalytic performance of Ti-SiO₂ in the liquidphase epoxidation of olefins. This was featured in superior initial reaction rates and higher epoxide production of hydrophobic Ti-SiO₂ compared to the pristine Ti-SiO₂ synthesized by either classical sol-gel or the novel aerosol-assisted sol-gel procedures. This agreed with the hypothesis proposed in this thesis that a more hydrophobic Ti-SiO₂ surface would display more affinity for the olefin, which is hydrophobic, and less affinity for the epoxide, which is more hydrophilic, so it desorbs immediately.

Nevertheless, the degree of methyl-functionalization reached in a onepot approach must be optimized to prevent the formation of inactive Ti species. Together all chapters and particularly Chapter 2 showed how methyl-functionalization affected the formation of Ti active sites. Ti-SiO₂ samples with the highest degrees of methyl-functionalization displayed higher intensities in the wavelength range corresponding to inactive Ti species in DRUV, lower band gap energy values and lower fraction of active Ti species, according to XPS. These results revealed the detrimental effect of excessive methyl-functionalization and occurred due to different hydrolysis-condensation reaction rates of the synthesis precursors and particularly of the methyl alkoxysilane added at the highest molar ratios during the synthesis.

Aerosol-assisted sol-gel (AASG) demonstrated to be more successful than conventional sol-gel in the one-pot synthesis of hydrophobic Ti-SiO₂ since the obtained catalysts displayed higher mesoporosity and higher Ti dispersion. The high Ti dispersion was evident at comparing the bang gap energy values which were higher for the AASG Ti-SiO₂ studied in Chapter 4 than for the conventional sol-gel analogous synthesized in Chapters 2 and 3. The excellent properties of these materials was achieved thanks to the fast drying of the atomized precursor mixture, which quenches the condensation kinetics and leads to the synthesis of materials with good dispersion of both Ti and methyl moieties.

Characterization of the hydrophobic character of porous solids such as Ti-SiO₂ is not totally straightforward. In this work, it was achieved by a combination of multiple techniques that consistently demonstrated the successful organic-functionalization and its effect over the hydrophobicity of the samples. Successfully functionalized Ti-SiO₂ synthesized in this thesis displayed the following characteristics: increasing infrared bands related to the presence of organic moieties and decreasing bands attributed to physisorbed water, decreasing mass losses due to physisorbed water while increasing mass losses due to organic content (TGA-MS) and higher peaks for the of T³ (Si(OSi)₃Me) and T² (Si(OSi)₂(OH)Me) contributions (²⁹Si solid-state NMR). Furthermore, vapor water sorption revealed an increment of hydrophobicity when the water uptake normalized to the specific surface area decreased in samples with higher degrees of organic-functionalization.

Isolating the effect of hydrophobization of Ti-SiO₂ was only achieved by carefully considering other factors that affect the catalytic performance such as the textural properties and the nature of the active sites. The textural properties included not only specific surface area but also pore size distribution. As discussed in the literature review, a rigorous and more complete characterization was required to conclude that hydrophobic Ti-SiO₂ performed better than pristine in the epoxidation of cyclooctene.

The positive effect of hydrophobization over the catalytic epoxidation performance of titanosilicates, elucidated in this thesis, highlights the benefits of adjusting the hydrophobic/philic balance of catalysts, encouraging more research in this direction. However, only rigorous studies will be able to assess the fundamental consequences of hydrophobization.

The **future work** proposed is related to reaching further understanding of the effect of hydrophobization of Ti-SiO₂. This work demonstrated that methyl-functionalization of Ti-SiO₂ improved the catalytic performance in the epoxidation of cyclooctene, but it would be interesting to understand which hydrophobization methodology impacts in a higher degree the catalytic performance. Thus, a comparison of organic-functionalized Ti-SiO₂ against less-defected Ti SiO_2 (Ti-SiO₂ with lower hydroxyl surface density) as well as the combination of methyl-functionalization with lower hydroxyl surface density could be evaluated. Less-defected Ti-SiO₂ can be synthesized in fluoride medium instead of the conventional hydroxide medium.

Moreover, characterization of the types of hydroxyls present on the Ti-SiO₂ surface can be performed to better understand the hydrophobic/hydrophilic character of the synthesized materials. Indeed, some recent studies have proposed that the catalytic epoxidation performance of Ti-SiO₂ can be improved by tuning the type of hydroxyl groups between isolated hydroxyls versus hydrogenbonded ones (silanol nests). The latter display a character more hydrophilic since they better stabilize water molecules.

In the same line, comparison of the catalytic performance of hydrophobized Ti-SiO₂ and hydrophobized crystalline titanosilicates, such as Ti-Beta, Ti-SBA-15 and Ti-MCM-41 after complete characterization of their hydrophobicity, textural properties and Ti active sites could provide more information about the effect of hydrophobization of Ti-containing materials.

Investigation of the Lewis acidity strength of the Ti sites could shed light on the impact of the hydrophobization methodology over the formation of the active Ti sites. From this thesis, we found that methylfunctionalization affected the formation of active Ti sites which are Lewis acid sites, but it would be interesting to study if the strength of these sites is influenced by the different hydrophobization strategies.

All these perspectives of future work could be evaluated for other reactions in which tuning the hydrophobic/hydrophilic character might play an important role on the reaction mechanism as in the case of olefin epoxidation such as glucose isomerization, Baeyer-Villiger oxidation, glycerol acetylation, as well as reactions in presence of water like biomass conversion reactions.

Appendix

CHAPTER 1: Optimizing the conditions towards hydrophobic Ti-SiO₂ catalysts via one-pot sol-gel chemistry



Figure A-1. XRD patterns of methyl-functionalized Ti-SiO₂ catalysts

Table A-1. I	Bulk and	surface e	elemental	composition	of pristine	Ti-SiO ₂
with increas	sing Ti m	olar ratio	from 0.02	5 to 0.20		

nan meredening	I I III eiai I			0.20		
Comula	Bulk Ti	Bulk Si	Surf. Ti	Surf. Si	Surf. C	Surf. O
Sample	wt.% ^a	wt. % ^a	at.% ^b	at.% ^b	at.% ^b	at.% ^b
0.025 Ti	1.75	40.3	0.6	29.6	2.2	67.6
0.05 Ti	2.80	37.3	0.8	23.8	3.6	71.9
0.10 Ti	5.41	35.9	1.6	22.5	10.2	65.7
0.15 Ti	9.29	34.4	1.6	24.4	5.1	68.9
0.20 Ti	11.89	30.9	2.6	23.0	10.3	64.1

^aBulk composition was determined by ICP-AES. ^bSurface elemental composition was determined by XPS.



Figure A-2a. Decomposition of XPS O 1s spectra of pristine Ti-SiO₂: 0.20Ti. Si-O (red line), Ti-O (blue line) and Si-O-Ti (purple line) were considered as components. The measured spectra are represented by the black line and the corresponding fit is represented by the brown solid line (sum of the three components).



Figure A-2b. Decomposition of XPS O 1s spectra of pristine Ti-SiO₂: 0.15Ti. Si-O (red line), Ti-O (blue line) and Si-O-Ti (purple line) were considered as components. The measured spectra are represented by the black line and the corresponding fit is represented by the brown solid line (sum of the three components).



Figure A-2c. Decomposition of XPS O 1s spectra of pristine Ti-SiO₂: 0.10Ti. Si-O (red line), Ti-O (blue line) and Si-O-Ti (purple line) were considered as components. The measured spectra are represented by the black line and the corresponding fit is represented by the brown solid line (sum of the three components).



Figure A-2d. Decomposition of XPS O 1s spectra of pristine Ti-SiO₂: 0.05Ti. Si-O (red line), Ti-O (blue line) and Si-O-Ti (purple line) were considered as components. The measured spectra are represented by the black line and the corresponding fit is represented by the brown solid line (sum of the three components).

CHAPTER 2: Methyl-functionalized Ti-SiO₂ catalysts for the epoxidation of cyclooctene with hydrogen peroxide



Figure A-3. Deconvolution analysis using Gaussian functions on TS-14%Me to correctly assign the chemical shift of the different contributions (i.e. Q^4 , Q^3 , Q^2 ...)

CHAPTER 4: Hydrophobic effect of the mesoporous methylfunctionalized Ti-SiO₂ catalysts synthesized by aerosol-assisted solgel on the catalytic epoxidation of olefins



Table A-2. Ti-SiO₂ sample with MTES molar ratio of 0.20 calcined at 250, 350, and 450 $^{\circ}$ C


Figure A-3. Water vapor adsorption isotherms for TS_Aer-0%Me, TS_Aer-9%Me, and TS_Aer-14%Me at 295 K. a) Water uptake in grams of water per gram of catalyst. b) For comparison among samples, the water uptake was normalized by the specific surface area corrected (SSA_{corrected}). The normalized water uptake values are depicted on the curve and the shaded regions denote the estimated uncertainty (5%) due to the N₂ physisorption measurement.

Description of the peak decomposition of Ti 2p XPS spectra for the samples TS_Aer-x%Me

In this work, the shift and peak broadening of Ti 2p XPS spectra of the samples TS_Aer-x%Me compared to the spectrum of pure titanium dioxide (TiO₂) are attributed to the presence of FW-Ti together with EFW-Ti [138, 143-147]. The quantification of these two Ti species was performed after some decomposition trials.

The first decomposition trial was performed under the following constraints: i) the spectrum is formed by two components which are FW-Ti and EFW-Ti, ii) the separation of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ for each component is 5.7 eV [142], and iii) the area of Ti $2p_{1/2}$ corresponds to half of the area of Ti $2p_{3/2}$. This attempt showed that the binding energy of the FW-Ti $2p_{3/2}$ component falls at 460.0-460.1 eV, which is in agreement with the literature [138, 143, 145, 147]. On the other hand, the binding energy of the EFW-Ti $2p_{3/2}$ component falls at 458.0-

458.5 eV, showing different binding energy values for the same component in each sample. This difference does not allow comparison of the quantification of FW-Ti and EFW-Ti species among the samples, so another constraint was added to set the difference of the two components as constant in all the samples. This value was selected based on the difference in binding energies of FW-Ti and EFW-Ti found in the literature, which is 1.5 eV [46, 145, 168]. Thus, the described constraint was included to perform the decomposition and quantification for all the samples.

Calculation of Ti surface density on the catalysts TS_Aer-x%Me

An example of the calculation of Ti surface density was performed for the sample TS Aer-14%Me. The same calculation was performed for all the samples for the estimation of the Ti and FW-Ti surface density.

 $Ti \ surface \ density =$

 $\frac{0.019 \text{ mol } Ti}{\text{mol } (Si+Ti)} \cdot \frac{0.015 \text{ mol } (Si+Ti)}{g_{catalyst}} \cdot \frac{g_{catalyst}}{462 \text{ } m^2} \cdot \frac{6.022 \text{ E23 } \text{ atoms } Ti}{\text{mol } Ti} \cdot \frac{m^2}{1\text{ E18 } nm^2}$ $g_{catalyst}$ $=\frac{0.37 atoms Ti}{nm^2}$

where

 $\frac{0.019 \text{ mol Ti}}{\text{mol (Si+Ti)}}$ was determined from XPS analysis (Table 4.3);

 $\frac{0.015 \text{ mol } (Si+Ti)}{g_{catalyst}}$ was determined from ICP-MS analysis;

 $\frac{g_{catalyst}}{462 m^2}$ is the inverse of the SSA_{corrected} for the sample TS_Aer-14%Me;

 $\frac{6.022E23 \ atoms \ Ti}{mol \ Ti}$ is the Avogadro number.

TBHP conversions of the TS_Aer-x%Me catalysts



Figure A-4. TBHP conversion as a function of reaction time of the TS_Aer-x%Me catalysts. Error bars are shown for TS_Aer-14%Me.

Calculation of the Turnover Frequency values (TOF) for the TS_Aer-x%Me catalysts

An example of the calculation of Turnover Frequency values (TOF) was performed for the sample TS_Aer-14%Me. The same calculation was performed for the rest of the samples.

$$TOF = \frac{\frac{0.0118 \ mol_{TBHP}}{h \ g_{catalyst}}}{\frac{0.014 \ mol \ FW - Ti}{mol \ (Si + Ti)} \cdot \frac{0.015 \ mol \ (Si + Ti)}{g_{catalyst}}} = 57 \ h^{-1}$$

where

 $\frac{0.0118 \ mol_{TBHP}}{h \ g_{catalyst}}$ number of mol of TBHP converted at 0.5 h reaction time per gram of catalyst;

 $\frac{0.014 \text{ mol FW}-Ti}{\text{mol (Si+Ti)}}$ was determined from XPS analysis (Table 4.3);

 $\frac{0.015 \text{ mol } (Si+Ti)}{g_{catalyst}}$ was determined from ICP-AES analysis.

References

- 1. Lamb, A.C., A.F. Lee, and K. Wilson, *Recent Advances in Heterogeneous Catalyst Design for Biorefining*. Australian Journal of Chemistry, 2020. **73**(10): p. 832-852.
- 2. Ross, J.R.H., Chapter 1 An Introduction to Heterogeneous Catalysis and Its Development Through the Centuries— Chemistry in Two Dimensions, in Contemporary Catalysis, J.R.H. Ross, Editor. 2019, Elsevier: Amsterdam. p. 3-38.
- 3. de Vries, J.G. and S.D. Jackson, *Homogeneous and heterogeneous catalysis in industry.* Catalysis Science & Technology, 2012. **2**(10): p. 2009-2009.
- 4. Fidalgo, A., et al., *Role of the Alkyl–Alkoxide Precursor on the Structure and Catalytic Properties of Hybrid Sol–Gel Catalysts*. Chemistry of Materials. 2005. **17**(26); p. 6686-6694.
- 5. Swalus, C., et al., *Hybrid peroxotungstophosphate organized catalysts highly active and selective in alkene epoxidation.* Catalysis Communications, 2013. **37**: p. 80-84.
- Cordon, M.J., et al., *Dominant Role of Entropy in Stabilizing Sugar Isomerization Transition States within Hydrophobic Zeolite Pores*. Journal of the American Chemical Society, 2018. **140**(43): p. 14244-14266.
- Vivian, A., et al., Mesoporous Methyl-Functionalized Sn-Silicates Generated by the Aerosol Process for the Sustainable Production of Ethyl Lactate. ACS Sustainable Chemistry & Engineering, 2018. 6(11): p. 14095-14103.
- 8. Chen, X., et al., *Catalyst surfaces with tunable hydrophilicity and hydrophobicity: metal–organic frameworks toward controllable catalytic selectivity.* Chemical Communications, 2018. **54**(32): p. 3936-3939.
- 9. Shi, W., et al., Surface Modification of Two-Dimensional Metal–Organic Layers Creates Biomimetic Catalytic Microenvironments for Selective Oxidation. 2017. **56**(33): p. 9704-9709.
- 10. Sun, Q., et al., *Imparting amphiphobicity on single-crystalline porous materials.* Nature Communications, 2016. **7**(1): p. 13300.
- 11. Oyama, S.T., Chapter 1 Rates, Kinetics, and Mechanisms of Epoxidation: Homogeneous, Heterogeneous, and Biological Routes, in Mechanisms in Homogeneous and Heterogeneous Epoxidation Catalysis. 2008, Elsevier: Amsterdam. p. 3-99.
- Brutchey, R.L., et al., *Influence of Surface Modification of Ti-SBA15 Catalysts on the Epoxidation Mechanism for Cyclohexene with Aqueous Hydrogen Peroxide.* Langmuir, 2005. **21**(21): p. 9576-9583.

- 13. Kholdeeva, O.A., Selective Oxidations Catalyzed by Mesoporous Metal Silicates, in Liquid Phase Oxidation via Heterogeneous Catalysis. 2013. p. 127-219.
- 14. Laha, S.C. and R. Kumar, *Selective Epoxidation of Styrene to Styrene Oxide over TS-1 Using Urea–Hydrogen Peroxide as Oxidizing Agent.* Journal of Catalysis, 2001. **204**(1): p. 64-70.
- Consulting, M.R. World Propylene Oxide (PO) Market to See Sustained Growth in Years Ahead. 2014 October 17, 2014; Available from: <u>https://mcgroup.co.uk/news/20141017/propylene-oxide-po-</u> market-sustained-growth-years.html.
- 16. Intelligence, M. *Ethylene Oxide Market Growth, Trends, Covid-19 Impact, and Forecasts (2021-2026.* 2020; Available from: <u>https://www.mordorintelligence.com/industry-</u> <u>reports/ethylene-oxide-market</u>.
- 17. MarketsandMarkets. *Propylene Oxide Market*. July, 2021; Available from: <u>https://www.marketsandmarkets.com/Market-Reports/propylene-oxide-market-55659975.html?gclid=CjwKCAjwhuCKBhADEiwA1HegOez50FlAKuV9wjOZNxl4rX7_pj-3EQdWYifprAPoioRQNPzW1amffxoCHtkQAvD_BwE.</u>
- 18. Sheldon, R.A., *Synthetic and mechanistic aspects of metalcatalysed epoxidations with hydroperoxides.* Journal of Molecular Catalysis, 1980. **7**(1): p. 107-126.
- 19. Vayssilov, G.N., *Structural and Physicochemical Features of Titanium Silicalites.* Catalysis Reviews, 1997. **39**: p. 209-251.
- Přech, J., Catalytic performance of advanced titanosilicate selective oxidation catalysts a review. Catalysis Reviews, 2018. 60(1): p. 71-131.
- Hutter, R., et al., Novel mesoporous titania–silica aerogels highly active for the selective epoxidation of cyclic olefins. Journal of the Chemical Society, Chemical Communications, 1995(2): p. 163-164.
- 22. Keshavaraja, A., et al., *Synthesis, Characterization, and Catalytic Properties of Micro-Mesoporous, Amorphous Titanosilicate Catalysts.* Journal of Catalysis, 1995. **157**(2): p. 501-511.
- Gao, X. and I.E. Wachs, *Titania–silica as catalysts: molecular structural characteristics and physico-chemical properties.* Catalysis Today, 1999. **51**(2): p. 233-254.
- 24. Notari, B., *Microporous Crystalline Titanium Silicates*, in *Advances in Catalysis*, D.D. Eley, W.O. Haag, and B. Gates, Editors. 1996, Academic Press. p. 253-334.

- 25. Taramasso, M., G. Perego, and B. Notari, *Preparation of porous crystalline synthetic material comprised of silicon and titanium oxides*. 1983, Google Patents.
- Ione, K.G., L.A. Vostrikova, and V.M. Mastikhin, *Synthesis of crystalline metal silicates having zeolite structure and study of their catalytic properties.* Journal of Molecular Catalysis, 1985.
 31(3): p. 355-370.
- 27. Millini, R., et al., *Framework composition of titanium silicalite-1.* Journal of Catalysis, 1992. **137**(2): p. 497-503.
- 28. Ratnasamy, P., D. Srinivas, and H. Knözinger, *Active Sites and Reactive Intermediates in Titanium Silicate Molecular Sieves*, in *Advances in Catalysis*. 2004, Academic Press. p. 1-169.
- 29. Dutoit, D.C.M., M. Schneider, and A. Baiker, *Titania-Silica Mixed Oxides: I. Influence of Sol-Gel and Drying Conditions on Structural Properties.* Journal of Catalysis, 1995. **153**(1): p. 165-176.
- Hutter, R., T. Mallat, and A. Baiker, *Titania Silica Mixed* Oxides: II. Catalytic Behavior in Olefin Epoxidation. Journal of Catalysis, 1995. 153(1): p. 177-189.
- Beck, C., et al., Nature of Active Sites in Sol–Gel TiO2–SiO2 Epoxidation Catalysts. Journal of Catalysis, 2001. 204(2): p. 428-439.
- 32. Notari, B., *Synthesis and Catalytic Properties of Titanium Containing Zeolites*, in *Studies in Surface Science and Catalysis*, P.J. Grobet, et al., Editors. 1988, Elsevier. p. 413-425.
- Clerici, M.G., *The activity of titanium silicalite-1 (TS-1): Some considerations on its origin.* Kinetics and Catalysis, 2015.
 56(4): p. 450-455.
- Signorile, M., et al., Effect of Ti Speciation on Catalytic Performance of TS-1 in the Hydrogen Peroxide to Propylene Oxide Reaction. The Journal of Physical Chemistry C, 2018. 122(16): p. 9021-9034.
- 35. Bregante, D.T., et al., *Consequences of Confinement for Alkene Epoxidation with Hydrogen Peroxide on Highly Dispersed Group 4 and 5 Metal Oxide Catalysts.* ACS Catalysis, 2018. **8**(4): p. 2995-3010.
- Corma, A., P. Esteve, and A. Martínez, Solvent Effects during the Oxidation of Olefins and Alcohols with Hydrogen Peroxide on Ti-Beta Catalyst: The Influence of the Hydrophilicity– Hydrophobicity of the Zeolite. Journal of Catalysis, 1996.
 161(1): p. 11-19.
- 37. Cordeiro, P.J. and T.D. Tilley, *Enhancement of the Catalytic Activity of Titanium-Based Terminal Olefin Epoxidation*

Catalysts via Surface Modification with Functionalized Protic Molecules. ACS Catalysis, 2011. **1**(5): p. 455-467.

- Wu, P., et al., Postsynthesis, Characterization, and Catalytic Properties in Alkene Epoxidation of Hydrothermally Stable Mesoporous Ti-SBA-15. Chemistry of Materials, 2002. 14(4): p. 1657-1664.
- 39. Chiker, F., et al., *Green and selective epoxidation of alkenes catalysed by new TiO2–SiO2 SBA mesoporous solids.* Green Chemistry, 2003. **5**(3): p. 318-322.
- 40. Blasco, T., et al., *Synthesis, Characterization, and Catalytic Activity of Ti-MCM-41 Structures.* Journal of Catalysis, 1995. **156**(1): p. 65-74.
- 41. Corma, A., et al., *Strategies to improve the epoxidation activity and selectivity of Ti-MCM-41.* Chemical Communications, 1998(20): p. 2211-2212.
- 42. Fraile, J.M., et al., *Is MCM-41 really advantageous over amorphous silica? The case of grafted titanium epoxidation catalysts.* Chemical Communications, 2001(16): p. 1510-1511.
- 43. Yu, J., et al., *Ti–MCM-41 Synthesized from Colloidal Silica* and *Titanium Trichloride: Synthesis, Characterization, and Catalysis.* Chemistry of Materials, 2001. **13**(3): p. 994-998.
- 44. Fraile, J.M., et al., *Silica-Supported Titanium Derivatives as Catalysts for the Epoxidation of Alkenes with Hydrogen Peroxide: A New Way to Tuneable Catalytic Activity through Ligand Exchange.* Journal of Catalysis, 2000. **189**(1): p. 40-51.
- 45. Fraile, J.M., et al., *Effect of the Reaction Conditions on the Epoxidation of Alkenes with Hydrogen Peroxide Catalyzed by Silica-Supported Titanium Derivatives.* Journal of Catalysis, 2001. **204**(1): p. 146-156.
- 46. Smeets, V., et al., *Aerosol Route to TiO2–SiO2 Catalysts with Tailored Pore Architecture and High Epoxidation Activity.* Chemistry of Materials, 2019. **31**(5): p. 1610-1619.
- Beck, C., T. Mallat, and A. Baiker, On the Limited Selectivity of Silica-Based Epoxidation Catalysts. Catalysis Letters, 2001. 75(3): p. 131-136.
- 48. Hutter, R., et al., *Titania-silica aerogels with superior catalytic performance in olefin epoxidation compared to large pore Ti-molecular sieves.* Topics in Catalysis, 1996. **3**(3): p. 421-436.
- 49. Dutoit, D.C.M., et al., *Titania–Silica Mixed Oxides: IV. Influence of Ti Content and Aging on Structural and Catalytic Properties of Aerogels.* Journal of Catalysis, 1996. **161**(2): p. 651-658.
- 50. Bordiga, S., et al., XAFS Study of Ti-Silicalite: Structure of Framework Ti(IV) in the Presence and Absence of Reactive

Molecules (H2O, NH3) and Comparison with Ultraviolet-Visible and IR Results. The Journal of Physical Chemistry, 1994. **98**(15): p. 4125-4132.

- 51. Clerici, M.G. and O.A. Kholdeeva, *Liquid phase oxidation via heterogeneous catalysis: organic synthesis and industrial applications*. 2013: John Wiley & Sons.
- 52. Thomas, J.M., et al., *The Identity in Atomic Structure and Performance of Active Sites in Heterogeneous and Homogeneous, Titanium–Silica Epoxidation Catalysts.* The Journal of Physical Chemistry B, 1999. **103**(42): p. 8809-8813.
- 53. Bregante, D.T. and D.W. Flaherty, *Periodic Trends in Olefin Epoxidation over Group IV and V Framework-Substituted Zeolite Catalysts: A Kinetic and Spectroscopic Study.* Journal of the American Chemical Society, 2017. **139**(20): p. 6888-6898.
- 54. Boronat, M., et al., *Predicting the Activity of Single Isolated Lewis Acid Sites in Solid Catalysts.* 2006. **12**(27): p. 7067-7077.
- 55. Thornburg, N.E., A.B. Thompson, and J.M. Notestein, *Periodic Trends in Highly Dispersed Groups IV and V Supported Metal Oxide Catalysts for Alkene Epoxidation with H2O2.* ACS Catalysis, 2015. **5**(9): p. 5077-5088.
- 56. Bu, J., S.-H. Yun, and H.-K. Rhee, *Epoxidation of n-hexene and cyclohexene over titanium-containing catalysts*. Korean Journal of Chemical Engineering, 2000. **17**(1): p. 76-80.
- Li, K.-T., C.-C. Lin, and P.-H. Lin, Chapter 14 Propylene Epoxidation with Ethylbenzene Hydroperoxide over Ti-Containing Catalysts Prepared by Chemical Vapor Deposition A2 - Oyama, S. Ted, in Mechanisms in Homogeneous and Heterogeneous Epoxidation Catalysis. 2008, Elsevier: Amsterdam. p. 373-386.
- 58. Liang, X., et al., *Kinetics of epoxidation of propylene over TS-1 in isopropanol.* Reaction Kinetics and Catalysis Letters, 2003. **80**(2): p. 207-215.
- 59. Ruddy, D.A. and T.D. Tilley, *Kinetics and Mechanism of Olefin Epoxidation with Aqueous H2O2 and a Highly Selective Surface-Modified TaSBA15 Heterogeneous Catalyst.* Journal of the American Chemical Society, 2008. **130**(33): p. 11088-11096.
- 60. Takashi, T., et al., *Shape Selective Epoxidation of Alkenes Catalyzed by Titanosilicate*. Chemistry Letters, 1990. **19**(2): p. 297-298.
- 61. Clerici, M.G. and P. Ingallina, *Epoxidation of Lower Olefins* with Hydrogen Peroxide and Titanium Silicalite. Journal of Catalysis, 1993. **140**(1): p. 71-83.

- Gallo, J.M.R., I.S. Paulino, and U. Schuchardt, *Cyclooctene* epoxidation using Nb-MCM-41 and Ti-MCM-41 synthesized at room temperature. Applied Catalysis A: General, 2004.
 266(2): p. 223-227.
- 63. Werner, A., et al., *Hierarchical Ti-Beta Obtained by Simultaneous Desilication and Titanation as an Efficient Catalyst for Cyclooctene Epoxidation.* 2017. **9**(20): p. 3860-3869.
- 64. Krijnen, S., et al., A controlled post-synthesis route to welldefined and active titanium Beta epoxidation catalysts. Microporous and Mesoporous Materials, 1999. **31**(1): p. 163-173.
- 65. Přech, J., et al., *Epoxidation of bulky organic molecules over pillared titanosilicates.* Catalysis Today, 2015. **243**: p. 134-140.
- 66. Young, G.J., *Interaction of water vapor with silica surfaces.* Journal of Colloid Science, 1958. **13**(1): p. 67-85.
- Gounder, R., Hydrophobic microporous and mesoporous oxides as Brønsted and Lewis acid catalysts for biomass conversion in liquid water. Catalysis Science & Technology, 2014. 4(9): p. 2877-2886.
- 68. Fan, W., et al., *Synthesis, Crystallization Mechanism, and Catalytic Properties of Titanium-Rich TS-1 Free of Extraframework Titanium Species.* Journal of the American Chemical Society, 2008. **130**(31): p. 10150-10164.
- Parker, W.O. and R. Millini, *Ti Coordination in Titanium Silicalite-1.* Journal of the American Chemical Society, 2006.
 128(5): p. 1450-1451.
- Camblor, M.A., A. Corma, and S. Valencia, *Spontaneous* nucleation and growth of pure silica zeolite-β free of connectivity defects. Chemical Communications, 1996(20): p. 2365-2366.
- 71. Gounder, R. and M.E. Davis, *Beyond shape selective catalysis with zeolites: Hydrophobic void spaces in zeolites enable catalysis in liquid water.* AIChE Journal, 2013. **59**(9): p. 3349-3358.
- Bregante, D.T., et al., Effects of Hydrofluoric Acid Concentration on the Density of Silanol Groups and Water Adsorption in Hydrothermally Synthesized Transition-Metal-Substituted Silicalite-1. Chemistry of Materials, 2020. 32(17): p. 7425-7437.
- Blasco, T., et al., Direct Synthesis and Characterization of Hydrophobic Aluminum-Free Ti-Beta Zeolite. The Journal of Physical Chemistry B, 1998. 102(1): p. 75-88.

- 74. Blasco, T., et al., *Unseeded synthesis of Al-free Ti-β zeolite in fluoride medium: a hydrophobic selective oxidation catalyst.* Chemical Communications, 1996(20): p. 2367-2368.
- 75. Bregante, D.T. and D.W. Flaherty, *Impact of Specific Interactions Among Reactive Surface Intermediates and Confined Water on Epoxidation Catalysis and Adsorption in Lewis Acid Zeolites.* ACS Catalysis, 2019. **9**(12): p. 10951-10962.
- 76. Bregante, D.T., et al., *Cooperative Effects between Hydrophilic Pores and Solvents: Catalytic Consequences of Hydrogen Bonding on Alkene Epoxidation in Zeolites.* Journal of the American Chemical Society, 2019.
- Hoeven, N., et al., Design of Ti-Beta zeolites with high Ti loading and tuning of their hydrophobic/hydrophilic character. Microporous and Mesoporous Materials, 2019. 288: p. 109588.
- Ruddy, D.A., R.L. Brutchey, and T.D. Tilley, *The Influence of* Surface Modification on the Epoxidation Selectivity and Mechanism of TiSBA15 and TaSBA15 Catalysts with Aqueous Hydrogen Peroxide. Topics in Catalysis, 2008. 48(1): p. 99-106.
- 79. Grosso-Giordano, N.A., et al., *Dynamic Reorganization and Confinement of TiIV Active Sites Controls Olefin Epoxidation Catalysis on Two-Dimensional Zeotypes*. Journal of the American Chemical Society, 2019. **141**(17): p. 7090-7106.
- Bregante, D.T., et al., Cooperative Effects between Hydrophilic Pores and Solvents: Catalytic Consequences of Hydrogen Bonding on Alkene Epoxidation in Zeolites. Journal of the American Chemical Society, 2019. 141(18): p. 7302-7319.
- Fan, W., P. Wu, and T. Tatsumi, Unique solvent effect of microporous crystalline titanosilicates in the oxidation of 1hexene and cyclohexene. Journal of Catalysis, 2008. 256(1): p. 62-73.
- 82. Tatsumi, T., K. A. Koyano, and N. Igarashi, *Remarkable activity enhancement by trimethylsilylation in oxidation of alkenes and alkanes with H2O2 catalyzed by titanium-containing mesoporous molecular sieves.* Chemical Communications, 1998(3): p. 325-326.
- 83. Li, S., et al., *Fabrication of Super-Hydrophobic Titanosilicate Sub-micro Sphere with Enhanced Epoxidation Catalytic Activity.* Catalysis Letters, 2019. **149**(5): p. 1396-1402.
- 84. Guo, Y., S.-J. Hwang, and A. Katz, *Hydrothermally robust Ti/SiO2 epoxidation catalysts via surface modification with oligomeric PMHS.* Molecular Catalysis, 2019. **477**: p. 110509.

- 85. B. D'Amore, M. and S. Schwarz, *Trimethylsilylation of ordered and disordered titanosilicates: improvements in epoxidation with aqueous H2O2 from micro- to meso-pores and beyond[dagger]*. Chemical Communications, 1999(2): p. 121-122.
- 86. Figueras, F. and H. Kochkar, *Effects of hydrophobicity on the epoxidation of cyclohexene by tert-butyl hydroperoxide on TiO2–SiO2 mixed oxides.* Catalysis Letters, 1999. **59**(1): p. 79-81.
- Kochkar, H. and F. Figueras, Synthesis of Hydrophobic TiO2– SiO2Mixed Oxides for the Epoxidation of Cyclohexene. Journal of Catalysis, 1997. 171(2): p. 420-430.
- Lin, K., et al., Direct room-temperature synthesis of methylfunctionalized Ti-MCM-41 nanoparticles and their catalytic performance in epoxidation. Journal of Catalysis, 2009.
 263(1): p. 75-82.
- 89. Klein, S. and W.F. Maier, *Microporous Mixed Oxides Catalysts with Tunable Surface Polarity*. Angewandte Chemie International Edition, 1996. **35**(19): p. 2230-2233.
- 90. Müller, C.A., et al., Organically Modified Titania–Silica Aerogels for the Epoxidation of Olefins and Allylic Alcohols. Journal of Catalysis, 1999. **184**(1): p. 280-293.
- 91. Müller, C.A., et al., *Hydrophobic titania–silica aerogels:* epoxidation of cyclic compounds. Topics in Catalysis, 2000.
 11(1): p. 369-378.
- 92. Manangon-Perugachi, L.E., et al., *Hydrophobic titania-silica mixed oxides for the catalytic epoxidation of cyclooctene.* Catalysis Today, 2019.
- Tiemann, M. and C. Weinberger, Selective Modification of Hierarchical Pores and Surfaces in Nanoporous Materials. Advanced Materials Interfaces, 2021. 8(4): p. 2001153.
- 94. Huang, Y., Functionalization of mesoporous silica nanoparticles and their applications in organo-, metallic and organometallic catalysis. 2009, Iowa State University.
- 95. Pednekar, P.P., et al., *Chapter 23 Mesoporous silica nanoparticles: a promising multifunctional drug delivery system*, in *Nanostructures for Cancer Therapy*, A. Ficai and A.M. Grumezescu, Editors. 2017, Elsevier. p. 593-621.
- 96. Smeets, V., et al., *Mesoporous SiO2-TiO2 epoxidation catalysts: Tuning surface polarity to improve performance in the presence of water.* Molecular Catalysis, 2018. **452**: p. 123-128.
- 97. Igarashi, N., et al., *Direct organic functionalization of Ti–MCM-*41: Synthesis condition, organic content, and catalytic activity.

Microporous and Mesoporous Materials, 2005. **81**(1): p. 97-105.

- Manangon-Perugachi, L.E., et al., *Mesoporous Methyl-Functionalized Titanosilicate Produced by Aerosol Process for the Catalytic Epoxidation of Olefins.* Catalysts, 2021. 11(2): p. 196.
- 99. Gläser, R. and J. Weitkamp, *Surface Hydrophobicity or Hydrophilicity of Porous Solids*, in *Handbook of Porous Solids*. 2002. p. 395-431.
- Blokzijl, W. and J.B.F.N. Engberts, *Hydrophobic Effects. Opinions and Facts.* Angewandte Chemie International Edition in English, 1993. **32**(11): p. 1545-1579.
- Ng, E.-P. and S. Mintova, *Nanoporous materials with* enhanced hydrophilicity and high water sorption capacity. Microporous and Mesoporous Materials, 2008. **114**(1): p. 1-26.
- 102. Mueller, R., et al., *OH Surface Density of SiO2 and TiO2 by Thermogravimetric Analysis.* Langmuir, 2003. **19**(1): p. 160-165.
- Anderson, M.W. and J. Klinowski, *Zeolites treated with silicon tetrachloride vapour. Part 1.—Preparation and characterisation.* Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases, 1986. **82**(5): p. 1449-1469.
- 104. Giaya, A., R.W. Thompson, and R. Denkewicz Jr, *Liquid and* vapor phase adsorption of chlorinated volatile organic compounds on hydrophobic molecular sieves. Microporous and Mesoporous Materials, 2000. **40**(1): p. 205-218.
- 105. Cavuoto, D., F. Zaccheria, and N. Ravasio, *Some Critical Insights into the Synthesis and Applications of Hydrophobic Solid Catalysts.* Catalysts, 2020. **10**(11): p. 1337.
- Guidotti, M., et al., *The effect of silylation on titanium-containing silica catalysts for the epoxidation of functionalised molecules*. Microporous and Mesoporous Materials, 2008.
 111(1): p. 39-47.
- 107. Condrate, R.A., *Vibrational spectra of structural units in glass.* Journal of Non-Crystalline Solids, 1986. **84**(1): p. 26-33.
- 108. Nakamoto, K., *Applications in Inorganic Chemistry*, in *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. 2008. p. 149-354.
- 109. Ryczkowski, J., *IR spectroscopy in catalysis*. Catalysis Today, 2001. **68**(4): p. 263-381.
- 110. Fripiat, J.J. and J. Uytterhoeven, *HYDROXYL CONTENT IN SILICA GEL "AEROSIL"*. The Journal of Physical Chemistry, 1962. **66**(5): p. 800-805.

- 111. Hambleton, F.H., J.A. Hockey, and J.A.G. Taylor, Investigation by infra-red spectroscopic methods of deuterium exchange properties of aerosil silicas. Transactions of the Faraday Society, 1966. **62**(0): p. 801-807.
- 112. Peri, J.B., *Infrared Study of OH and NH2 Groups on the Surface of a Dry Silica Aerogel.* The Journal of Physical Chemistry, 1966. **70**(9): p. 2937-2945.
- 113. Jentys, A., et al., *Adsorption of water on ZSM 5 zeolites.* The Journal of Physical Chemistry, 1989. **93**(12): p. 4837-4843.
- 114. Paukshtis, E.A., et al., *A FTIR study of silanol nests over mesoporous silicate materials.* Microporous and Mesoporous Materials, 2019. **288**: p. 109582.
- 115. Conrad, S., et al., *Influence of Hydrophilicity on the Snβ-Catalyzed Baeyer–Villiger Oxidation of Cyclohexanone with Aqueous Hydrogen Peroxide.* 2017. **9**(1): p. 175-182.
- 116. Medeiros-Costa, I.C., et al., *Silanol defect engineering and healing in zeolites: opportunities to fine-tune their properties and performances.* Chemical Society Reviews, 2021. **50**(19): p. 11156-11179.
- Igarashi, N., K. Hashimoto, and T. Tatsumi, *Catalytical studies* on trimethylsilylated Ti-MCM-41 and Ti-MCM-48 materials. Microporous and Mesoporous Materials, 2007. **104**(1): p. 269-280.
- 118. Li, X., et al., Synthesis of highly ordered alkyl-functionalized mesoporous silica by co-condensation method and applications in surface coating with superhydrophilic/antifogging properties. Journal of Porous Materials, 2015. **22**(1): p. 201-210.
- 119. Pires, J., et al., *Characterization of the hydrophobicity of mesoporous silicas and clays with silica pillars by water adsorption and DRIFT.* Journal of Colloid and Interface Science, 2008. **317**(1): p. 206-213.
- Olson, D.H., W.O. Haag, and W.S. Borghard, Use of water as a probe of zeolitic properties: interaction of water with HZSM-5. Microporous and Mesoporous Materials, 2000. 35-36: p. 435-446.
- 121. Silvestre-Alberó, J., et al., *Spectroscopic, calorimetric, and catalytic evidences of hydrophobicity on Ti-MCM-41 silylated materials for olefin epoxidations.* Applied Catalysis A: General, 2015. **507**: p. 14-25.
- Engelhardt, G. and H. Jancke, *Structure investigation of organosilicon polymers by silicon-29 NMR*. Polymer Bulletin, 1981. 5(11): p. 577-584.
- 123. Protsak, I.S., et al., A 29Si, 1H, and 13C Solid-State NMR Study on the Surface Species of Various Depolymerized

Organosiloxanes at Silica Surface. Nanoscale Research Letters, 2019. **14**(1): p. 160.

- 124. Lin, K., et al., Synthesis and catalytic activity of Ti-MCM-41 nanoparticles with highly active titanium sites. Journal of Catalysis, 2008. **254**(1): p. 64-70.
- 125. Singh, S.S., D.R. Salem, and R.K. Sani, *Chapter 17 -Spectroscopy, microscopy, and other techniques for characterization of bacterial nanocellulose and comparison with plant-derived nanocellulose*, in *Microbial and Natural Macromolecules*, S. Das and H.R. Dash, Editors. 2021, Academic Press. p. 419-454.
- Li, L., et al., Boosting selective oxidation of cyclohexane over a metal–organic framework by hydrophobicity engineering of pore walls. Chemical Communications, 2017. 53(72): p. 10026-10029.
- 127. Khouw, C.B., et al., *Studies on the Catalytic-Oxidation of Alkanes and Alkenes by Titanium Silicates.* Journal of Catalysis, 1994. **149**(1): p. 195-205.
- 128. Zapata, P.A., et al., *Hydrophobic Zeolites for Biofuel Upgrading Reactions at the Liquid–Liquid Interface in Water/Oil Emulsions.* Journal of the American Chemical Society, 2012. **134**(20): p. 8570-8578.
- 129. Zapata, P.A., et al., *Silylated hydrophobic zeolites with enhanced tolerance to hot liquid water.* Journal of Catalysis, 2013. **308**: p. 82-97.
- 130. Thangaraj, A. and S. Sivasanker, *An improved method for TS-1 synthesis: 29Si NMR studies.* Journal of the Chemical Society, Chemical Communications, 1992(2): p. 123-124.
- Notestein, J.M., E. Iglesia, and A. Katz, *Grafted Metallocalixarenes as Single-Site Surface Organometallic Catalysts.* Journal of the American Chemical Society, 2004.
 126(50): p. 16478-16486.
- 132. Fraile, J.M., et al., *Optimization of cyclohexene epoxidation with dilute hydrogen peroxide and silica-supported titanium catalysts.* Applied Catalysis A: General, 2003. **245**(2): p. 363-376.
- 133. Langhendries, G., et al., *Quantitative Sorption Experiments on Ti-Zeolites and Relation with α-Olefin Oxidation by H2O2.* Journal of Catalysis, 1999. **187**(2): p. 453-463.
- 134. Roy, S.K., D. Dutta, and A.K. Talukdar, *Highly effective methylated Ti MCM-41 catalyst for cyclohexene oxidation.* Materials Research Bulletin, 2018. **103**: p. 38-46.
- 135. Müller, C.A., et al., *Titania–Silica Epoxidation Catalysts Modified by Polar Organic Functional Groups*. Journal of Catalysis, 2000. **189**(1): p. 221-232.

- 136. Millini, R., et al., *Framework composition of titanium silicalite-1.* Journal of Catalysis;(United States), 1992. **137**(2).
- 137. Kukovecz, Á., et al., *Synthesis, characterisation and catalytic applications of sol–gel derived silica–phosphotungstic acid composites.* Applied Catalysis A: General, 2002. **228**(1): p. 83-94.
- Stakheev, A.Y., E.S. Shpiro, and J. Apijok, XPS and XAES study of titania-silica mixed oxide system. The Journal of Physical Chemistry, 1993. 97(21): p. 5668-5672.
- Greegor, R.B., et al., *Investigation of TiO2 · SiO2 glasses by X-ray absorption spectroscopy*. Journal of Non-Crystalline Solids, 1983. 55(1): p. 27-43.
- Brinker, C.J. and G.W. Scherer, CHAPTER 2 Hydrolysis and Condensation I: Nonsilicates, in Sol-Gel Science, C.J. Brinker and G.W. Scherer, Editors. 1990, Academic Press: San Diego. p. 20-95.
- 141. Peña, M.L., et al., *Elucidating the local environment of Ti(IV)* active sites in *Ti-MCM-48: a comparison between silylated* and calcined catalysts. Microporous and Mesoporous Materials, 2001. **44-45**: p. 345-356.
- 142. Wagner, C., et al., *Handbook of X-ray Photoelectron Spectroscopy*. 1979, Eden Prairie, MN, USA: Perkin-Elmer Corporation, Physical Electronics Division.
- 143. Vetter, S., et al., On the para/ortho product ratio of phenol and anisole hydroxylation over titanium silicalite-1. Chemical Engineering & Technology: Industrial Chemistry-Plant Equipment-Process Engineering-Biotechnology, 1994. 17(5): p. 348-353.
- 144. Tyablikov, I.A., et al., *Formation of active sites in titaniumcontaining zeolites with MFI structure in propylene epoxidation with hydrogen peroxide*. Petroleum Chemistry, 2016. **56**(3): p. 267-274.
- 145. Langerame, F., et al., *XPS characterization of a synthetic Ticontaining MFI zeolite framework: the titanosilicalites, TS-1.* Surface and Interface Analysis, 2008. **40**(3-4): p. 695-699.
- Yamashita, H., et al., Characterization of titanium- silicon binary oxide catalysts prepared by the sol- gel method and their photocatalytic reactivity for the liquid-phase oxidation of 1-octanol. The Journal of Physical Chemistry B, 1998.
 102(30): p. 5870-5875.
- 147. Hasegawa, Y. and A. Ayame, *Investigation of oxidation states of titanium in titanium silicalite-1 by X-ray photoelectron spectroscopy*. Catalysis Today, 2001. **71**(1): p. 177-187.

- 148. Zecchina, A., et al., *Framework and Extraframework Ti in Titanium-Silicalite: Investigation by Means of Physical Methods*, in *Studies in Surface Science and Catalysis*, P.A. Jacobs, et al., Editors. 1991, Elsevier. p. 251-258.
- Klein, S., et al., Homogeneity of Titania-Silica Mixed Oxides: On UV-DRS Studies as a Function of Titania Content. Journal of Catalysis, 1996. 163(2): p. 489-491.
- Ikeue, K., et al., Elucidation of the local structure of active titanium (IV) sites on silica-based phase-boundary catalysts for alkene epoxidation with aqueous hydrogen peroxide. Physical Chemistry Chemical Physics, 2004. 6(9): p. 2523-2528.
- 151. Neuenschwander, U. and I. Hermans, *The Conformations of Cyclooctene: Consequences for Epoxidation Chemistry*. The Journal of Organic Chemistry, 2011. **76**(24): p. 10236-10240.
- 152. Zhang, Y., et al., *Functionalization of Petroleum Coke-Derived Carbon for Synergistically Enhanced Capacitive Performance.* Nanoscale Research Letters, 2016. **11**(1): p. 163.
- 153. Manangon-Perugachi, L.E., et al., *Hydrophobic titania-silica mixed oxides for the catalytic epoxidation of cyclooctene.* Catalysis Today, 2021. **363**: p. 128-136.
- 154. Debecker, D.P., et al., *Aerosol processing: a wind of innovation in the field of advanced heterogeneous catalysts.* Chemical Society Reviews, 2018. **47**(11): p. 4112-4155.
- 155. Godard, N., et al., *High-Yield Synthesis of Ethyl Lactate with Mesoporous Tin Silicate Catalysts Prepared by an Aerosol-Assisted Sol–Gel Process.* ChemCatChem, 2017. **9**(12): p. 2211-2218.
- Kim, A., et al., Mesoporous TiO2 Support Materials for Ru-Based CO2 Methanation Catalysts. ACS Applied Nano Materials, 2019. 2(5): p. 3220-3230.
- 157. Wang, C.Y. and H. Bai, *Aerosol processing of mesoporous* silica supported bimetallic catalysts for low temperature acetone oxidation. Catalysis Today, 2011. **174**(1): p. 70-78.
- 158. Pega, S., et al., *Direct Aerosol Synthesis of Large-Pore Amorphous Mesostructured Aluminosilicates with Superior Acid-Catalytic Properties.* Angewandte Chemie International Edition, 2009. **48**(15): p. 2784-2787.
- Maksasithorn, S., et al., *Preparation of super-microporous* WO3–SiO2 olefin metathesis catalysts by the aerosol-assisted sol–gel process. Microporous and Mesoporous Materials, 2015. 213: p. 125-133.
- 160. Oveisi, H., et al., *Aerosol-assisted fabrication of mesoporous titania spheres with crystallized anatase structures and*

investigation of their photocatalitic properties. Journal of Sol-Gel Science and Technology, 2010. **56**(2): p. 212-218.

- 161. Viezbicke, B.D., et al., *Evaluation of the Tauc method for optical absorption edge determination: ZnO thin films as a model system.* 2015. **252**(8): p. 1700-1710.
- 162. Grudzien, R.M., B.E. Grabicka, and M. Jaroniec, *Effective* method for removal of polymeric template from SBA-16 silica combining extraction and temperature-controlled calcination. Journal of Materials Chemistry, 2006. **16**(9): p. 819-823.
- 163. Liu, Z., et al., *Recent progress in the direct synthesis of hierarchical zeolites: synthetic strategies and characterization methods.* Materials Chemistry Frontiers, 2017. **1**(11): p. 2195-2212.
- Ghosh, M., et al., *Mesoporous Titanium Dioxide Nanofibers* with a Significantly Enhanced Photocatalytic Activity. 2016. 8(15): p. 2525-2535.
- Sing, K.S., et al., *Reporting physisorption data for gas/soils* systems with special reference to the determination of surface area and porosity. Pure and Applied Chemistry, 1985. 57(4): p. 603-619.
- 166. On, D.T., L.L. Noc, and L. Bonneviot, *Electron transfer bands* of titanium sites in dehydrated silicalites and in TiO2–SiO2 gel. Chemical Communications, 1996(3): p. 299-300.
- 167. De Clercq, R., et al., *Titania-Silica Catalysts for Lactide Production from Renewable Alkyl Lactates: Structure–Activity Relations.* ACS Catalysis, 2018. **8**(9): p. 8130-8139.
- Erdem, B., et al., XPS and FTIR Surface Characterization of TiO2 Particles Used in Polymer Encapsulation. Langmuir, 2001. 17(9): p. 2664-2669.

Publications

Articles

Manangon-Perugachi, Lucia E., Smeets, Valentin, Vivian, Alvise, Kainthla, Itika, Eloy, Pierre, Aprile, Carmela, Debecker, Damien P. and Gaigneaux, Eric M. (2021). *Mesoporous Methyl-Functionalized Titanosilicate Produced by Aerosol Process for the Catalytic Epoxidation of Olefins*. Catalysts, 11(2), 196. DOI: https://doi.org/10.3390/catal11020196

Manangon-Perugachi, L. E., Vivian, A., Eloy, P., Debecker, D. P., Aprile, C., and Gaigneaux, E. M. (2021). *Hydrophobic titania-silica mixed oxides for the catalytic epoxidation of cyclooctene*. Catalysis Today, 363, 128-136. DOI: <u>https://doi.org/10.1016/j.cattod.2019.05.020</u>

Oral communications

L.E. Manangon-Perugachi, V. Smeets, A. Vivian, C. Aprile, D.P. Debecker and E.M. Gaigneaux. *Elucidating the effect of hydrophobicity of methyl-functionalized mesoporous titanosilicate in the epoxidation of olefins*. 9th World Congress on Oxidation Catalysis (WCOC 2022), Cardiff (United Kingdom), September 4-8, 2022.

L.E. Manangon-Perugachi, and E.M. Gaigneaux. *Hydrophobic titaniasilica mixed oxides for the catalytic epoxidation of olefins with hydrogen peroxide*. PhD. Students's Day 2018 (PhD Day 2018), Louvain-la-Neuve (Belgium), May 25, 2018.

L.E. Manangon-Perugachi, and E.M. Gaigneaux. *Sol-gel synthesis of hydrophobic titania-silica mixed oxides for the catalytic epoxidation of olefins*. 19th International Sol Gel Conference (SOL-GEL 2017), Liege (Belgium), September 3-8, 2017.

Poster communications

L.E. Manangon-Perugachi, A. Vivian, P. Eloy, C. Aprile, D.P. Debecker and E.M. Gaigneaux. *Elucidating the effect of hydrophobicity of methyl-functionalized titania-silica mixed oxides in the catalytic epoxidation of olefins*. 14th European Congress on Catalysis (EuropaCat 2019), Aachen (Germany), August 18-23, 2019.

L.E. Manangon-Perugachi, A. Vivian, P. Eloy, C. Aprile, D.P. Debecker and E.M. Gaigneaux. *Synthesis of hydrophobic titania-silica mixed oxides for the catalytic epoxidation of olefins with hydrogen*

peroxide. 12th International Symposium on the Scientific Bases for the Preparation of Hetrogeneous Catalysts (PREPA 2018), Louvainla-Neuve (Belgium), July 8-12, 2018.

L.E. Manangon-Perugachi, and E.M. Gaigneaux. *Hydrophobic titaniasilica mixed oxides for the epoxidation of cyclooctene with hydrogen peroxide*. 13th European Congress on Catalysis (EuropaCat 2017), Florence (Italy), August 27-31, 2017.

L.E. Manangon-Perugachi, and E.M. Gaigneaux. *Hydrophobic titaniasilica mixed oxides for the catalytic epoxidation of olefins*. Chemical Engineering & Material in Wallonia (GREENWIN 2017), Mons (Belgium), May 22-23, 2017.

L.E. Manangon-Perugachi, and E.M. Gaigneaux. *Hydrophobic titaniasilica mixed oxides for the epoxidation of cyclooctene with hydrogen peroxide*. PhD Day 2017, Louvain la Neuve (Belgium), May 24, 2017.

Student supervision

Corentin Dubois (UCLouvain, 2019), Master thesis: *"Cyclooctene epoxidation with methylated titania-silica catalysts*". Supervisor: Eric M. Gaigneaux, Co-supervisor: Lucia Manangon

Charles Cassou-Mounat (Institute Paul Lambin (IPL), 2016), Research Report: *"Modification du caractère hydrophobe/hydrophile d/un mélange silice/dioxyde de titane par chimie sol/gel"*. Supervisor: Eric M. Gaigneaux, Co-supervisor: Lucia Manangon

Vincent Demesmacre (Institute Paul Lambin (IPL), 2016), Research Report: "Oxydes mixtes de Si et Ti préparés par sol-gel comme catalyseurs d'époxydation à hydrophobicité contrôlée". Supervisor: Eric M. Gaigneaux, Co-supervisor: Lucia Manangon

Congresses, Symposia, Conferences

9th World Congress on Oxidation Catalysis (WCOC 2022), Cardiff (United Kingdom), September 4-8, 2022.

14th European Congress on Catalysis (EuropaCat 2019), Aachen (Germany), August 18-23, 2019.

12th International Symposium on the Scientific Bases for the Preparation of Heterogeneous Catalysts (PREPA 2018), Louvain-la-Neuve (Belgium), July 8-12, 2018.

19th International Sol Gel Conference (Sol-Gel 2017), Liege (Belgium), September 3-8, 2017.

13th European Congress on Catalysis (EuropaCat 2017), Florence (Italy), August 27-31, 2017.

Chemical Engineering & Material in Wallonia (GREENWIN 2017), Mons (Belgium), May 22-23, 2017.

PhD Day 2017, Louvain la Neuve (Belgium), May 24, 2017.

PhD Day 2016, Louvain la Neuve (Belgium), May 20, 2016.

PhD Day 2015, Louvain la Neuve (Belgium), May 22, 2015.

School of Catalysis at the University of Lyon (ELITECAT 2015), Lyon (France), July 6-10, 2015.