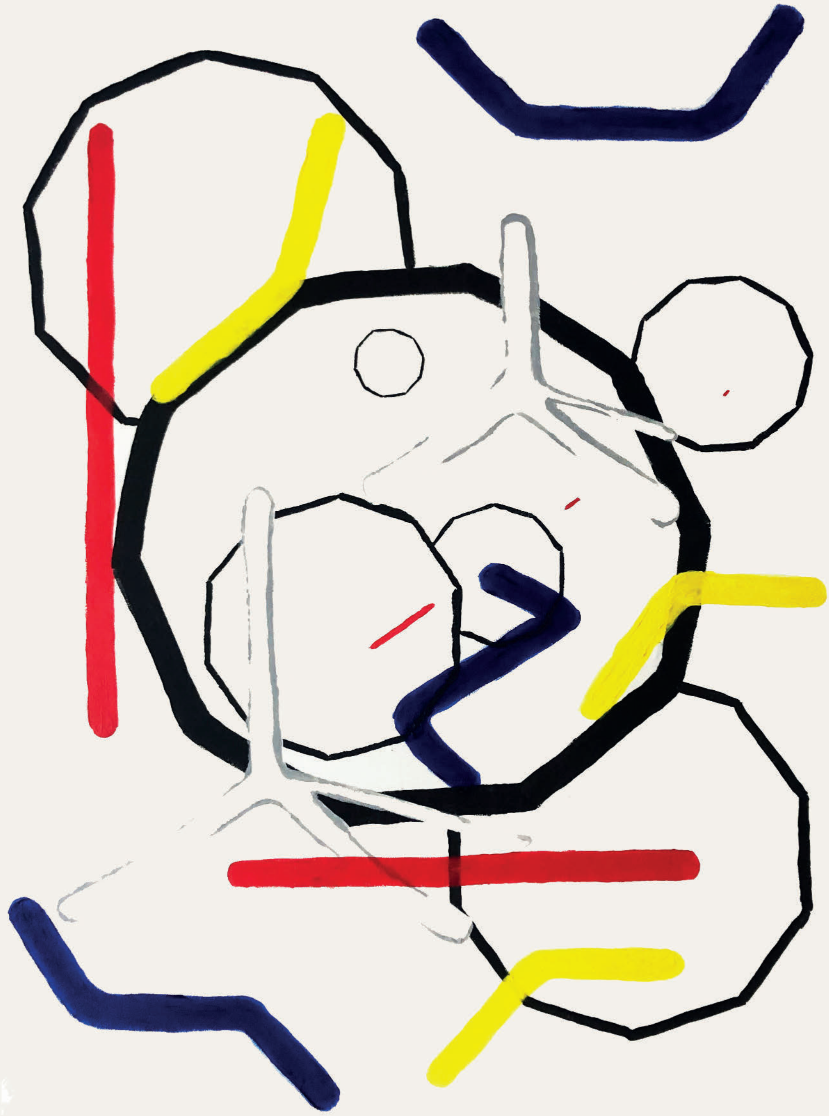
EPOXIDATION OF LIGHT OLEFINS ON TITANIUM SILICATES

MATIAS IGNACIO ALVEAR CABEZÓN



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“Be curious, not judgmental.”

Walt Whitman

Preface

The journey I embarked on to reach this stage was intricate and lengthy. However, with teamwork and the support of others, I successfully completed it. These past four years have been an incredible adventure, filled with ups and downs. Yet, I can confidently say that I have lived a profoundly joyful trip, and I wish the same happiness for all those who supported me along their own paths.

I want to sincerely appreciate the time, patience, support, and friendship of my supervisor, Tapio Salmi. I am incredibly grateful for his unwavering dedication, both professionally and personally. Throughout these four years, we embarked on numerous adventures, and I am truly thankful for his valuable advice. Most importantly, I am deeply grateful for the life-shaping opportunity he gave me.

I cannot proceed without expressing my heartfelt gratitude to Kari Eränen. He stood by my side, patiently listening to my unconventional ideas and assisting me in overcoming challenges. I know it was not an easy task, but I sincerely appreciate his relentless commitment to pushing the project forward and supporting me. I am deeply grateful for his dedicated work, benefiting not only our laboratory but also the wider community.

I am indebted to Dmitry Murzin for granting me access to the laboratory during my master's thesis. His patience and willingness to teach me invaluable lessons have been truly priceless. I am grateful for his genuine and authentic approach, which I believe serves as a role model for many.

A significant part of my journey was the time I spent in Madison. I am immensely grateful to Ive Hermans' group for the invaluable experience I gained there. During those intense five months, I underwent significant personal and professional growth. Ive, in particular, played a crucial role in pushing me to strive for better, and for that, I am deeply thankful.

To my dear students, Michele, Federica, and Marie, I express my gratitude for your invaluable assistance throughout this research. Each of you played a crucial role in its success, and observing the progress of your individual projects brought me immense joy. I extend my heartfelt appreciation to all my collaborators and supporters for their unwavering help. To everyone who has been or continues to be a part of the TKR family, I offer my sincerest thanks. Your comments, smiles, and constructive criticism have been instrumental in making this endeavor possible.

Lastly, I express my heartfelt gratitude to my beloved family, who have taught me invaluable lessons and continue to guide me. Your unshakable support keeps me grounded, and I am eternally grateful. To my friends, who have been by my side every day, please remember that I am here for you as well. Thank you for your patience, the cherished moments we've shared, and the love you've shown me.

The past four years have truly transformed my life, and I am grateful beyond words for the support I received along the way. I want to express my heartfelt thanks to all those who stood by me. Every little detail and act of kindness remains cherished in my heart.

Abstract

The topic of present work was the epoxidation of light olefins on titanium silicate catalysts. Epoxidation of single olefins (ethene, propene, 1-butene and iso-butene) and mixtures of them were investigated. A material study allowed an extensive comparison of titanium silicate catalysts (TS-1 and Ti-MWW) and active sites, revealing the reactant-catalyst interactions present in the activation of the active titanium sites.

The epoxidation of olefins was performed in a laboratory-scale trickle bed reactor operating under transient and stationary states. An extensive set of conditions was screened for each case in these gas-liquid-solid systems. Hydrogen peroxide was the epoxidation agent, while methanol and acetonitrile were used as solvents. The reactants and products were analyzed by gas chromatography. The single olefin epoxidation experiments in the trickle bed reactor revealed the changes in the dynamic behavior depending of the alkene chain length and the molecular structure. The epoxidation of olefin mixtures demonstrated to improve the catalyst stability. Nonetheless, the product selectivity was strongly affected by the number of olefins in the mixtures. Ternary mixtures displayed to be highly selective compared to binary olefin mixtures.

The comparison of titanium silicates demonstrated important differences between these otherwise similar materials. Both materials displayed to be active under comparable mild conditions. However, Ti-MWW exhibited a better performance as acetonitrile was used as solvent, allowing a higher selectivity to the epoxide. TS-1 displayed to be more active, nevertheless, the utilization of methanol as the solvent generated a higher concentration of methoxy species as by-products. The analysis of the synthesis conditions of Ti-MWW demonstrated important changes with the calcination temperature. The acidity and surface areas demonstrated to be affected by this synthesis parameter.

The analysis of reactant-catalyst interactions indicated differences in the titanium active site response depending on the material. The spectroscopic analysis of the materials was carried out in an ATR-FTIR system allowing the contact of the reactants and the catalyst under controlled conditions. The ex-situ analysis allowed the observation of changes in the framework titanium vibration, and the utilization of in-situ modulation excitation spectroscopy permitted the observation of changes in the vibration due to time dependent concentration gradients.

The present study is a broad approach to the epoxidation on titanium silicates, being the reactants, materials and active sites studied. The utilization of transient techniques as step responses demonstrated to be a highly valuable tool to understand the behavior of reactive systems.

Resumen

El tema del presente trabajo fue la epoxidación de olefinas ligeras sobre catalizadores de titanosilicato. Se investigó la epoxidación de olefinas individuales (eteno, propeno, 1-buteno e iso-buteno) y mezclas de ellas. Un estudio de materiales permitió una comparación exhaustiva de los titanosilicatos (TS-1 y Ti-MWW) y sus sitios activos, revelando las interacciones reactivo-catalizador presentes en la activación de los sitios activos de titanio.

La epoxidación de olefinas se realizó en un reactor trickle-bed a escala de laboratorio que operaba en estados transientes y estacionarios. Se evaluó un amplio conjunto de condiciones para cada caso en estos sistemas gas-líquido-sólido. El peróxido de hidrógeno fue el agente de epoxidación y se utilizaron metanol y acetonitrilo como disolventes. Los reactivos y productos se analizaron por cromatografía de gases. Los experimentos de epoxidación de olefinas individuales en el reactor trickle-bed revelaron los cambios en el comportamiento dinámico en función de la longitud de la cadena del alqueno y la estructura molecular. La epoxidación de mezclas de olefinas mejoró la estabilidad del catalizador. No obstante, la selectividad del producto se vio fuertemente afectada por el número de olefinas en las mezclas. Las mezclas ternarias mostraron ser altamente selectivas en comparación con las mezclas de olefinas binarias.

La comparación de silicatos de titanio demostró diferencias importantes entre estos materiales por lo demás similares. Ambos materiales mostraron ser activos en condiciones comparables. Sin embargo, Ti-MWW exhibió un mejor desempeño ya que se usó acetonitrilo como solvente, lo que permitió una mayor selectividad al epóxido. TS-1 mostró ser más activo, sin embargo, la utilización de metanol como solvente generó una mayor concentración de especies metoxi como subproductos. El análisis de las condiciones de síntesis de Ti-MWW demostró cambios importantes con la temperatura de calcinación. La acidez y las áreas superficiales demostraron verse afectadas por este parámetro de síntesis.

El análisis de las interacciones reactivo-catalizador indicó diferencias en la respuesta del sitio activo de titanio según el material. El análisis espectroscópico de los materiales se realizó en un sistema ATR-FTIR que permite el contacto de los reactivos y el catalizador en condiciones controladas. El análisis ex-situ permitió la observación de cambios en la vibración de titanio presente en la estructura de la zeolita, la utilización de espectroscopia de excitación de modulación in situ permitió la observación de cambios en la vibración debido a gradientes de concentración dependientes del tiempo.

El presente estudio es un análisis amplio de la epoxidación sobre titanosilicatos, siendo analizados los reactivos, materiales y sitio activo. La utilización de técnicas transitorias como respuestas escalon demostró ser una herramienta muy valiosa para comprender el comportamiento de los sistemas reactivos.

Referat

Temat för detta doktorsarbete är epoxiderig av lätta olefiner på titansilikatkatalysatorer. Epoxidering av enskilda olefiner (eten, propen, 1-buten och isobuten) samt blandningar av dem studerades ingående. Undersökning av katalytiska material möjliggjorde en omfattande jämförelse av titansilikatkatalysatorerna TS-1 och Ti-MWW inklusive aktiva säten i dessa material. Dessa studier avslöjade växelverkningar mellan reaktanterna och de aktiva sätena på katalysatorytan.

Epoxidering av olefinerna genomfördes i en tricklebäddreaktor som arbetade i laboratorieskala under transienta och stationära betingelser. En omfattande kartläggning gjordes för det komplicerade gas-vätske-fastfassystemet. Alkenerna epoxiderades i metanol- och acetonitril-lösningar, där väteperoxid användes som epoxideringsmedel. Reaktanterna och produkterna analyserades med gaskromatografi. Epoxideringsexperimenten av enskilda olefiner i tricklebädd-reaktorn visade förändringar i det dynamiska beteendet beroende på alkenens kedjelängd och molekylstruktur. Närvaron av nya produkter bekräftades med hjälp av kromatografisk analys. Epoxidering av olefinblandningar förbättrade katalysatorns stabilitet. Produktselektiviteten påverkades dock starkt av antalet olefiner i reaktionsblandningen. Trekomponentblandningar av olefiner visade sig vara mera selektiva än binära blandningar.

En jämförelse av titansilikater avslöjade väsentliga skillnader mellan dessa till synes liknande material. Båda materialen var aktiva under jämförbara milda reaktionsbetingelser. Ti-MWW presterade dock bättre, då acetonitril användes som lösningsmedel och gav en högre selektivitet av epoxider. TS-1 var mera aktiv men användningen av metanol som lösningsmedel ledde till ökad bildning av metoxikomponenter som biprodukter. En analys av syntesbetingelserna för Ti-MWW visade väsentliga förändringar beroende på kalcineringstemperaturen. Katalysatorns surhet och specifika ytarea påverkades av denna syntesparameter.

En analys av växelverkningarna mellan reaktanterna och den fasta katalysatorn indikerade skillnader mellan responser som härstammade från aktiva titansäten på katalysatormaterialet. Spektroskopisk analys genomfördes i ett ATR-FTIR-system, vilket möjliggjorde en kontakt mellan reaktanterna och katalysatorn under välkontrollerade betingelser. Med in situ –analys kunde förändringar i vibrationerna i titanramverket observeras och utnyttjandet av modulerings-excitationsspektroskopi avslöjade förändringar i vibrationerna p.g.a. tidsberoende koncentrations-gradienter.

Detta arbete är en bred analys av alkenepoxidering på titansilikater genom att reaktanter, katalysatormaterial och aktiva säten studerades med olika metoder. Användningen av transienta experimentella metoder i form av stegsvar visade sig vara ett synnerligen värdefullt verktyg för en djupare förståelse av reaktiva system.

List of publications

I. Matias Alvear, Michele Fortunato, Vincenzo Russo, Kari Eränen, Martino Di Serio, Juha Lehtonen, Sari Rautiainen, Dmitry Murzin, Tapio Salmi, Continuous liquid-phase epoxidation of ethylene with hydrogen peroxide on a titanium-silicate catalyst, Industrial & Engineering Chemistry Research, 2021, 60 (26), 9429–9436.

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IV. Matias Alvear, Michele Emanuele Fortunato, Vincenzo Russo, Tapio Salmi, Martino Di Serio, Modelling of transient kinetics in trickle bed reactors: Ethylene oxide production via hydrogen peroxide, Chemical Engineering Science, 248, 2022, 117156.

V. Matias Alvear, Federica Orabona, Kari Eränen, Juha Lehtonen, Sari Rautiainen, Martino Di Serio, Vincenzo Russo, Tapio Salmi, Epoxidation of light olefin mixtures with hydrogen peroxide on TS-1 in a laboratory-scale trickle bed reactor: Transient experimental study and mathematical modelling, Chemical Engineering Science, 269, 2023,118467.

VI. Matias Alvear, Michele Fortunato, Kari Eränen, Juha Lehtonen, Sari Rautiainen, Martino Di Serio, Vincenzo Russo, Tapio Salmi, Epoxidation of light olefin mixtures with hydrogen peroxide on TS-1 catalyst, Catalysis Letters (Accepted).

VII. Matias Alvear, Christoph Schmidt, Ole Reinsdorf, Edgard Lebron-Rodrigez, Abdullah Al Abdulghan, Ive Hermans, Markus Peurla, Mika Lastusaari, Kari Eränen, Dmitry Yu. Murzin, Narendra Kumar, Tapio Salmi, Ti-MWW catalyst a solution for propylene oxide production: Influence of Si/Ti ratio and calcination conditions, Catalysis Letters, 2023.

VIII. Matias Alvear, Zhuoqun Zhang, Ive Hermans, Tapio Salmi, Ti-MWW: Similar to TS-1 but not quite the same (submitted for publication).

Patents

I. Sari Rautiainen, Juha Lehtonen, Tapio Salmi, Matias Alvear and Michele Fortunato. Epoxidation of olefin mixture, International Patent Application, FI20216175 (A1) — 2023-05-17.

Matias I. Alvear Cabezon's contributions to articles I-VIII

I	Conceptualization, methodology, formal analysis, writing (original draft, review & editing) and supervision.
II	Conceptualization, methodology, formal analysis, writing (original draft, review & editing) and experimental work.
III	Conceptualization, methodology, formal analysis, writing (original draft, review & editing), supervision and experimental work.
IV	Conceptualization, methodology, formal analysis, writing (original draft, review & editing), supervision, RTD experiments and kinetic analysis.
V	Conceptualization, methodology, formal analysis, writing (original draft, review & editing), supervision and RTD experiments.
VI	Conceptualization, methodology, formal analysis, writing (original draft), supervision.
VII	Conceptualization, methodology, formal analysis, writing (original draft, review & editing), synthesis and experimental work.
VIII	Conceptualization, methodology, formal analysis, writing (original draft) and experimental work.

Conference publications related to the topic

I. **Matias Alvear**, Kari Eränen, Dmitry Yu. Murzin, Tapio Salmi. Towards a deeper understanding of propene oxide synthesis in a trickle bed reactor through transient experiments, 25th International Congress of Chemical and Process Engineering (CHISA 2021). Oral presentation.

II. **Matias Alvear**, Michele Fortunato, Kari Eränen, Vincenzo Russo, Dmitry Yu. Murzin, Tapio Salmi, Transient study of light olefins epoxidation in a trickle bed reactor, 13th European Congress of Chemical Engineering (ECCE 2021). Oral presentation.

III. **Matias Alvear**, Michele Fortunato, Marie-Louis Reich, Stefan Haase, Vincenzo Russo, Kari Eränen, Dmitry Murzin, Tapio Salmi, Transient investigation of the carbon chain length and molecular structure effect on the epoxidation of light olefins over TS-1 catalyst on a trickle bed reactor, SmartBIO Young Researcher Symposium 2021. Oral Presentation.

IV. **Matias Alvear**, Michele Emanuele Fortunato, Federica Orabona, Marie-Louis Reich, Vincenzo Russo, Martino Di Serio, Stefan Haase, Tapio Salmi, Transient behaviour and modelling of trickle bed reactors: alkene epoxidation with hydrogen peroxide, 26th International Congress of Chemical and Process Engineering (CHISA 2022). Oral presentation.

V. **Matias Alvear**, Christoph Schmidt, Ole Reinsdorf, Kari Eränen, Dmitry Murzin, Narendra Kumar, Tapio Salmi, Ti-MWW catalyst a solution for propylene oxide production: Influence of Si/Ti ratio and calcination conditions, 26th International Congress of Chemical and Process Engineering (CHISA 2022). Oral presentation.

VI. Ole Reinsdorf, **Matias Alvear**, Christoph Schmidt, Narendra Kumar, Tapio Salmi, Investigating the solvent effect in the epoxidation of propene using hydrogen peroxide over Ti-Silicalite materials with in-situ FTIR-ATR Spectroscopy and TPD, 26th International Congress of Chemical Process Engineering (CHISA 2022). Oral Presentation.

VII. **Matias Alvear**, Michele Fortunato, Marie-Louis Reich, Stefan Haase, Vincenzo Russo, Kari Eränen, Dmitry Murzin, Tapio Salmi, Transient investigation of the carbon chain length and molecule structure effect over the epoxidation of light olefins over TS-1 catalyst on a trickle bed reactor, Gas-Liquid-Solid Reactor Engineering 2022 (GLS-15). Oral Presentation.

VIII. **Matias Alvear**, Zhuoqun Zhang, Edgard Lebron-Rodrigez, Abdullah Al Abdulghani, Michele Fortunato, Marie-Louis Reich, Stefan Haase, Vincenzo Russo, Kari Eränen, Dmitry Murzin, Ive Hermans, Tapio Salmi, Transient study of light olefin epoxidation on titanium silicates. 28th Biennial ORCS Conference 2022. Oral Presentation.

IX. **Matias Alvear**, Michele Fortunato, Marie-Louis Reich, Stefan Haase, Vincenzo Russo, Kari Eränen, Dmitry Murzin, Tapio Salmi, Transient investigation of the carbon chain length and molecule structure effect over the epoxidation of light olefins over TS-1 catalyst on a trickle bed reactor, 55. Jahrestreffen Deutscher Katalytiker 2022. Oral Presentation.

X. **Matias Alvear**, Zhuoqun Zhang, Edgard Lebron-Rodrigez, Abdullah Al Abdulghani, Tapio Salmi, Ive Hermans, Reactant-catalyst interactions in the hydrogen peroxide activation over titanium silicates, International Symposium on Activation of Dioxygen and Homogeneous Oxidation Catalysis (ADHOC 2022). Poster Presentation.

XI. **Matias Alvear**, Zhuoqun Zhang, Edgard Lebron-Rodrigez, Abdullah Al Abdulghani, Tapio Salmi, Ive Hermans, Reactant-catalyst interactions in propylene epoxidation on TS-1, Johan Gadolin Process Chemistry Centre Annual Meeting 2022. Poster Presentation and Poster Award

XII. **Matias Alvear**, Michele Fortunato, Marie-Louis Reich, Kari Eränen, Vincenzo Russo, Stefan Haase, Dmitry Yu. Murzin, Tapio Salmi, Epoxidation of light olefins on titanium silicate catalyst, 14th European Congress of Chemical Engineering (ECCE 2023). Oral Presentation.

XIII. Tapio Salmi, **Matias Alvear**, Michele Fortunato, Ole Reinsdorf, Christoph Schmidt, Mouad Hachhach, Kari Eränen, Johan Warna, Vincenzo Russo, Application of transient techniques in the investigation of complex three-phase reaction systems: from experiments to modelling, from laboratory to computing, 14th European Congress of Chemical Engineering (ECCE 2023). Oral Presentation.

XIV. **Matias Alvear**, Kari Eränen, Dmitry Murzin, Narendra Kumar, Tapio Salmi, Epoxidation of light olefins on titanium silicate catalyst, 15th European Congress on Catalysis (EUROPACAT 2023). Poster Presentation.

XV. Krista Kuutti, **Matias Alvear**, Federica Orabona, Tapio Salmi, Sari Rautiainen, Juha Lehtonen, Epoxidation of CO_2-based light olefins as a key step to fossil-free polycarbonate polyols, 15th European Congress on Catalysis (EUROPACAT 2023). Oral Presentation.

XVI. **Matias Alvear**, Michele Emanuele Fortunato, Federica Orabona, Marie-Louis Reich, Vincenzo Russo, Martino Di Serio, Stefan Haase, Tapio Salmi, Transient investigation of the epoxidation of light olefins over titanium silicate catalyst, World Congress of Chemical Engineering (WCCE11 2023). Oral Presentation.

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1. Introduction

Propene epoxidation on titanium silicate catalysts is a system that has experienced a big development during the last 40 years [1–10], because it is possible to perform direct and selective epoxidation of propene with hydrogen peroxide [3,11–14]. The discovery of titanium silicate 1 (TS-1) has even allowed the development of a sustainable technology known as the hydrogen peroxide propylene oxide (HPPO) process [3–5]. Nonetheless, still after all the effort and advances, many questions remain open until nowadays.

As every heterogeneously catalyzed reaction, the system displays three basic elements, namely reactants, catalyst and reactor. During this work, the emphasis was focused on the reactants and the catalytic materials. The survey of reactants was based on the epoxidation of light olefins (ethene, propene, 1-butene and iso-butene) as single molecules and mixtures of them. The investigation of catalytic materials consisted of two main parts. A comparison of titanium silicate materials (TS-1 and Ti-MWW) was carried out as well as a spectroscopic study of the active sites on titanium.

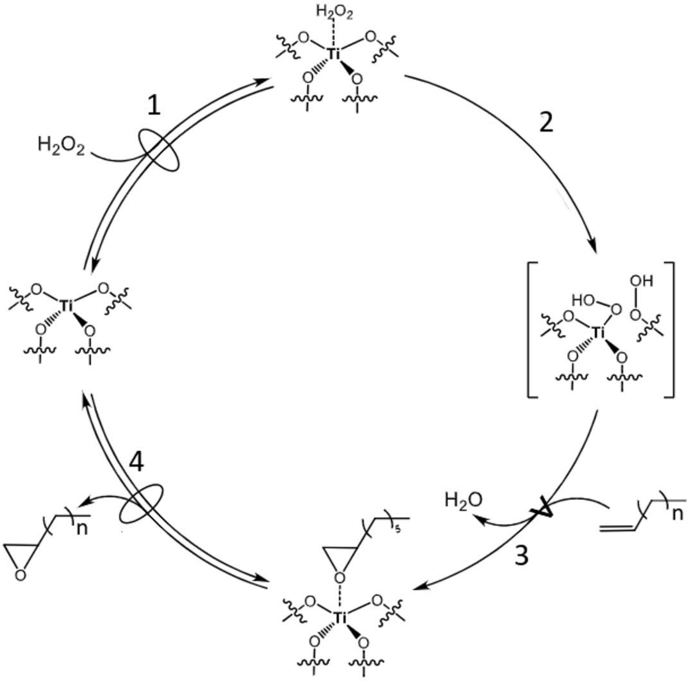
1.1. Titanium silicates

Titanium silicate is a material containing highly dispersed tetrahedral titanium (Ti(IV)) either as a heteroatom in the framework of a silica matrix or supported on a silica carrier [4]. The development of these materials started in 1970s by Shell with their patent for epoxidizing olefins with organic hydroxides on silica-supported titanium [15]. Nonetheless, it was the discovery of TS-1 by ENI [1], which allowed the development of several new technologies for propene epoxidation. Therefore, this work is focused on titanium that is embedded in a silica matrix as TS-1.

The research concerning the active site has been broad and many methods have been applied, such as spectroscopy [16–20], NMR [21,22], DFT [23–28], among others. During many years, the active site has been defined as a single atom of titanium in the silica framework. Nonetheless, recently the utilization of NMR has revealed the position of the titanium atoms suggesting a dinuclear site being highly possible [21]. This observation correlates with a work on neutron powder diffraction [29]. However, these studies have been performed on TS-1 only. Thus, still the question remains whether all the titanium silicates have the same active site, particularly because many titanium silicates behave differently under similar conditions [12,30–35].

1.2. Epoxidation reaction over titanium silicate

The epoxidation of olefins can be described in four steps. First, the hydrogen peroxide is adsorbed on the titanium site as a reversible step. Second, the hydrogen peroxide reacts with the titanium producing a hydroperoxo species. Third, the olefin approaches the hydroperoxo species reacting to produce propene oxide and water, water is desorbed and released. Fourth, the peroxide is released from the titanium active site in order to come back to the basal state. The epoxidation mechanism is illustrated in Scheme 1.



Scheme 1. Reaction mechanism on active site.

As it is possible to observe in Scheme 1, it is presumed that no direct interaction is taking place between the olefin and the titanium silicate material [12]. Nonetheless, recent literature describes a decrease in the activity with the time-on-stream for the 1-butene epoxidation over 10 hours of reaction [36–39] and catalyst deactivation caused by propene oxide adsorption [2]. Therefore, it is important to understand if all the molecules interact in the same way with the reaction system and if the mixture of olefins could affect the behavior of the reaction system.

1.3. Transient techniques

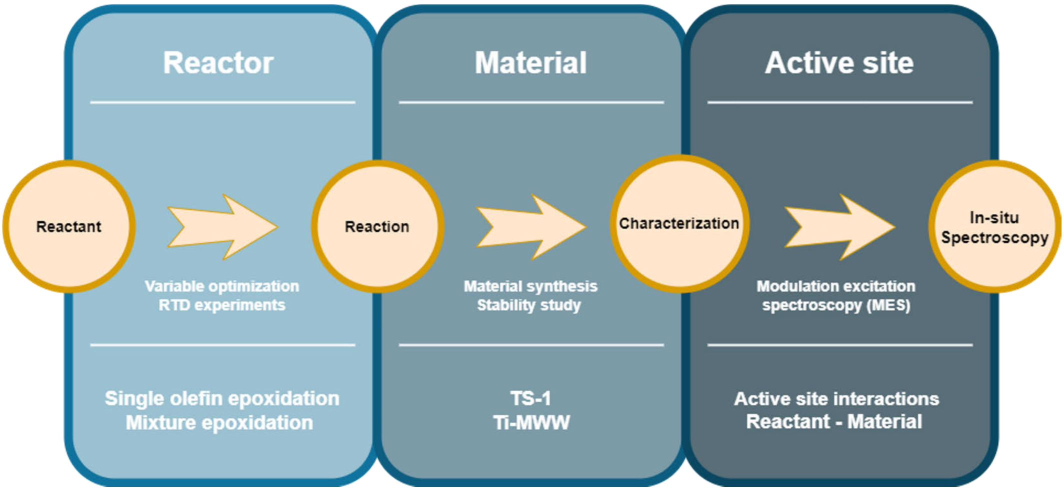
During the early research dedicated to TS-1, many molecules were screened and analyzed [1,40–42]. From these studies it was possible to see the decrease of the activity with the alkene chain length and the molecular structure [40]. However, these studies were performed in batch reactors and therefore it was not possible to observe the transient behavior of the system. The utilization of transient experiments allows the observation of how the activity change with the time-on-stream and changes in the parameters controlling the reaction affect the stability and the formation of the products and by-products [43].

During the present research, two kinds of transient techniques were used. The first one was the utilization of step response experiments in a laboratory scale trickle bed reactor. These experiments allowed to observe the behavior and production of different side products with time-on-stream.

The second transient technique was FT-IR modulation excitation spectroscopy; this technique enables to observe the interactions between the catalyst and the reactant over a stimulus (change in concentration in this case), and thanks to the modulation it is possible to eliminate passive signals and observe the active species in the system [44,45].

1.4. Aim of the research

The present work utilized transient and stationary techniques to analyze the behavior of several chemically relevant epoxidation systems. As it is illustrated in Scheme 2, three areas were developed. The reactor study was devoted to the epoxidation of single olefins and mixtures of them, the material study allowed an extensive comparison of titanium silicate catalysts and active sites revealing the reactant-catalyst interactions present in the activation of the titanium sites.



Scheme 2. Research structure and strategy.

The research on the trickle bed reactor system provided an advance in understanding the dynamic behavior of the olefins, epoxides and by-products thanks to the registration of the transient behavior of the system and the study of the by-products due to the changes in the reactivity of the epoxide related the molecule structure. The study of olefin mixtures was pursued to analyze the feasibility of a simultaneous epoxidation process. The epoxidation experiments were conducted for binary and ternary mixtures of olefins in order to understand how the olefin behavior is related to the number of olefins in the mixture.

The investigation of the Ti-MWW material was aimed to characterize and analyze the performance of this material after different synthesis procedures. The results were compared with commercial TS-1 in order to analyze and understand the reactivity and the selectivity of both materials.

The spectroscopic study of active sites revealed similarities and differences between the reactant-catalyst interaction of different titanium silicate materials. This approach can be identified as an exploratory study to understand if the titanium active site is the same in the family of materials.

2. Experimental methods

2.1. Chemicals [I–VIII]

The gases were nitrogen (AGA), ethene (AGA), propene (AGA), iso-butene (AGA) and 1-butene (Linde). Aqueous solutions of hydrogen peroxide (>30 w/v from Fisher Chemicals and 50 w/v from Sigma Aldrich), highly pure methanol (>99.9 wt%, Sigma Aldrich), acetonitrile >99.9% (Supelco), dichloromethane 99.9% (Sigma Aldrich), 1-methoxyethanol (>99.5 wt%, Sigma Aldrich), ethene glycol (>99.5 wt%, Fluka), propene glycol (<99.5%, Sigma Aldrich), propene oxide (99.9%, Sigma Aldrich), 1-methoxy-2-propanol (>99.5%, Sigma-Aldrich), 1,2-epoxybutane (99%, Sigma Aldrich), 1,2-epoxy-2-methylpropane (97%, Sigma Aldrich), isobutyraldehyde (99,9%, Sigma Aldrich), 2-methyl-2-propen-1-ol (98%, Sigma Aldrich), 1-methoxy-2-methyl-2-propanol (99,9%, Sigma Aldrich), 2-methyl-1,2-propanediol (99.71%, BLDpharm), 1-methoxy-2-butanol (97%, Sigma Aldrich), 1,2-butanediol (>98%, Sigma Aldrich), ferroin indicator (0.1wt%, Sigma Aldrich) and cerium sulphate solution (0.1 M, Honeywell) were used without further purification. Commercial titanium-silicalite (TS-1) of ACS material type B was employed as the heterogeneous catalyst: CAS No 13463-67-7 (titanium dioxide)/7621-86-9 (silicon dioxide).

The chemicals used for the Ti-MWW catalyst synthesis were fumed silica CAB-O-SIL® (CABOT GmbH), tetrabutyl orthotitanate (TBOT) (Sigma-Aldrich, 97 %), boric acid (Merck) as a crystallization agent, piperidine (PI) (Sigma-Aldrich, 99 %) as a template while deionized water was utilized as a solvent.

2.2. Catalyst characterization [VII–VIII]

The physico-chemical properties of the catalysts were characterized with several methods. The morphological features were studied with scanning electron microscopy (SEM, Zeiss Leo Gemini 1530) and transmission electron microscopy (TEM, JEOL JEM-1400Plus) was used to determine the crystal size. The obtained images were processed and analyzed by the software ImageJ to determine the crystal size of the Ti-MWW catalyst. The catalyst structure, phase purity and crystallinity were investigated by powder X-ray diffraction (XRD) characterization using a PANalytical Empyrean diffractometer with a five-axis goniometer. The incident beam optics consisted of Bragg-Brentano HD X-ray mirror, fixed 1/4 ° divergence slit, 10 mm mask, 0.04 rad soller slit and 1 ° antiscatter slit. The diffracted beam optics consisted of a 7.5 mm divergence slit, 0.04 rad soller slit and PIXcel detector array. The used X-ray tube was Empyrean Cu LFF. The X-ray radiation was filtered to include only Cu $K_{\alpha 1}$ and Cu $K_{\alpha 2}$ components. The results were analyzed with MAUD (Material Analysis Using Diffraction) software [46]. The instrumental broadening was evaluated with a Si standard sample. The results were obtained with 2θ scan range from 5° to 120°.

The surface area, pore size distribution, pore volume and adsorption-desorption isotherms were obtained by nitrogen physisorption (Micrometrics 3Flex-3500) using the Dubinin-Radushkevich method for calculating the specific surface area and the density functional theory (DFT) was used for the determination of the pore volume and pore size distribution. Before the measurements, the samples were exposed to ex-situ degassing, by treating them under vacuum at 180°C for 24 h. The acidities of the synthesized materials were measured by temperature programmed desorption (TPD) using ammonia as the probe molecule. The samples were pre-treated with the following program: approaching 500 °C with a heating rate of 25 K/min and keeping the temperature for 60 min and He flow of 30 mL/min, cooling down to 100 °C and switching to a gas mixture comprising 7.5 % NH_3/He for 30 min. The sample was flushed with He for 60 min and cooled down to 50 °C. The target temperature for desorption was set to 600 °C with a heating rate of 10 ºC/min. The target temperature was kept for 20 min. The outlet gases were monitored by a thermal conductivity detector (TCD) to analyze the adsorbed NH_3.

2.3. Experimental set-up

2.3.1. Catalytic experiments [I-VIII]

The set-up utilized in the laboratory scale reactor work is illustrated in the Figure 1. A solution comprising acetonitrile or methanol, water and hydrogen peroxide was fed along with nitrogen and an olefin or a mixture of olefins through the packed reactor with an internal diameter of 1.5 cm and length of 34 cm. The catalyst bed contained 0.15 to 1 g of TS-1 or Ti-MWW and quartz beads in a weight proportion of 1:20 and particle sizes between 125 and 250 µm. An HPLC pump (Agilent 1100 Series) was utilized for the liquid-phase feed while the gas phase was fed into the reactor system through a mass flow controller (MFC-1) from Brooks instruments. A pressure controller (PC-1) Equilibar (U3L Ultra Low Flow Back Pressure Regulator) was utilized downstream the reactor, followed by a gas-liquid separator at room temperature and atmospheric pressure. Gas chromatography (Agilent 6890N) was utilized to analyze the liquid (off-line) samples collected from the separator. The analysis of the gas phase (on-line) was performed with a Micro GC (Agilent 490) in order to prevent clogging of the gas chromatograph, the gas phase passed through a condenser.

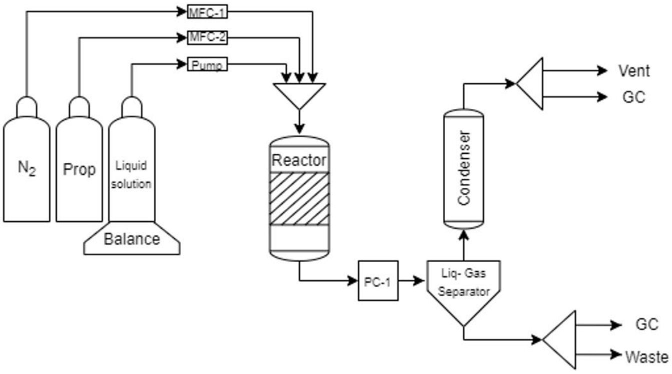


Figure 1. Experimental set-up for alkene epoxidation.

2.3.2. Modulation excitation spectroscopy [VIII]

Figure 2 illustrates the modulation excitation spectroscopy set-up. The catalyst layer was prepared by adding 10 mL of diethyl ether to 100 mg of the catalyst. The resulting suspension was sonicated for 30 min in an ice bath. One milliliter of this solution was deposited onto a ZnSe crystal (in 100 microliter intervals) and dried in the oven at 100 °C overnight. The ATR-IR measurements were conducted on a Bruker Vertex 70 spectrometer equipped with a liquid nitrogen cooled MCT detector. Typically, 16 scans with a resolution of 8 cm^{-1} were co-added to produce a spectrum. The switching between the two liquid reservoirs was accomplished through air-actuated valves (Parker). The ATR accessory was a Pike ATR cell. The liquids were drawn by a peristaltic pump (Ismatec) at flow rates of 5 mL/min. The absorbance is given in arbitrary units for all the spectra in the phase-domain.

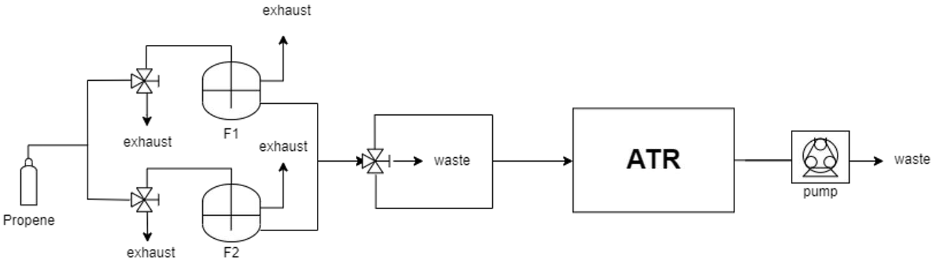


Figure 2. Set-up for modulation experiments.

3. Results and discussion

3.1. Epoxidation of individual olefins [I-IV]

The epoxidation of light olefins (ethene, propene, 1-butene and isobutene) with hydrogen peroxide was investigated in a broad range of experimental conditions. Temperature, total pressure, olefin partial pressures, water concentration, hydrogen peroxide concentration and liquid flow rate were the experimental parameters studied.

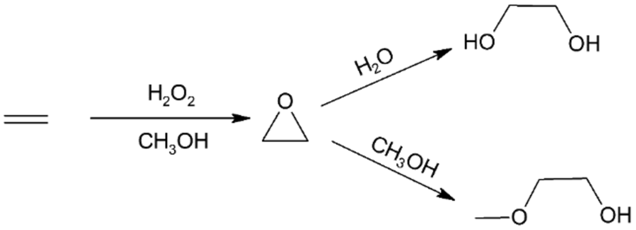
The results exhibited a molecular structure dependency. The epoxide selectivity increased as the carbon chain became longer. However, as the carbon chain was longer, the reactor stability versus the time-on-stream (TOS) decreased. At the same time as the carbon chain length affected the stability and selectivity, the double bond position influenced the activity and selectivities. Epoxidation experiments of isomers allowed to observe the important differences between the behaviors of 1-butene and isobutene. 1-butene epoxidation had shown high selectivity and important changes in activity with time-on-stream (TOS), while isobutene epoxidation displayed a lower selectivity but a better catalyst stability.

During this work, step-response experiments were carried out under different operation conditions with the purpose of reveal the epoxidation kinetics of light olefins with hydrogen peroxide as the oxidizing agent and TS-1 as the heterogeneous catalyst in a laboratory-scale three-phase fixed bed reactor operating in a trickle flow regime.

A dynamic isothermal reactor model was proposed and developed by considering the physical and chemical phenomena appearing in the reactor. The trickle bed reactor (TBR) model was based on dynamic mass balances and the fluid dynamics was expressed in terms of axial dispersion. The proposed kinetic model does not include any steady-state assumption, so it can be regarded as a dynamic kinetic model. The transient kinetic data obtained from the step-response experiments were modelled mathematically and the model was used in the parameter estimation. The model utilized the kinetic data for the epoxidation of ethene as a representative case of study. Nonetheless, this approach can be easily expanded to other olefins such as propene and isobutene, due to similar elementary steps present in for the olefins. In case of 1-butene, the addition of active site deactivation steps because of by-products clogging the zeolite structure are necessary.

3.1.1. Ethene epoxidation [I, IV]

The overall reaction network for ethene epoxidation is presented in Scheme 3. A detailed analysis of the gas and liquid phases was performed and it displayed the presence of ethene oxide as the main product as well as two secondary ring-opening products namely 2-methoxyethanol and ethene glycol.



Scheme 3. Reaction network for ethene epoxidation.

The catalyst stability experiments are illustrated in the Figure 3. The results suggest a highly stable and selective system. The dominating by-product was 2-methoxyethanol. The steady state was reached after 2.5 hours.

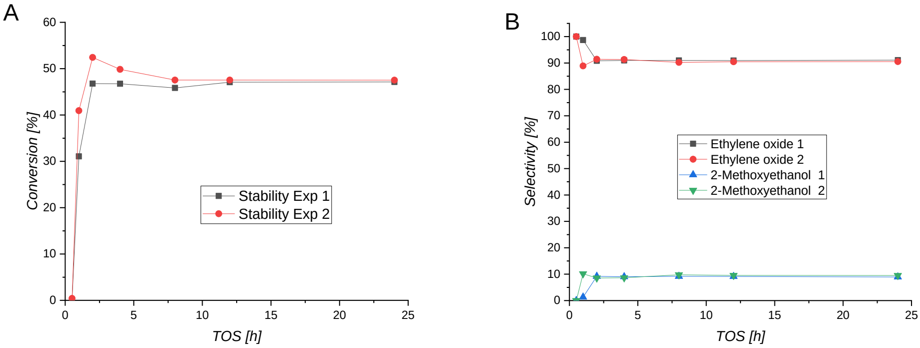
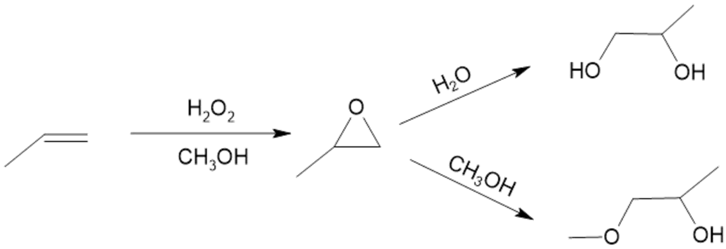


Figure 3. Dependence of the ethene a) conversion and b) selectivity during long-term stability experiments at 4.5 bar and 45 °C. The ethene flow was 0.22 mmol/min and the liquid comprised of 2 wt% H_2O_2 (0.24 mmol/min), 5 wt% H_2O and 93 wt% of methanol.

In general, the ethene oxide selectivities were high, exceeding 90%. The temperature increase gave a higher ethene conversion at 15 - 55 °C, while, as 60 °C was exceeded, the ethene conversion was affected negatively due to the increase of the hydrogen peroxide decomposition rate, which is highly temperature-dependent. The increase in the total pressure affected positively the ethene conversion but negatively the ethene oxide selectivity. Changes in the liquid-phase composition had a large impact on the reaction system. An increase of the hydrogen peroxide concentration had a positive effect on both the conversion and the selectivity. However, changes in the water amount had a varying effect on the reaction system, depending on the water concentration. An increase in the liquid residence time promoted the formation of the secondary product, 2- methoxyethanol.

3.1.2. Propene epoxidation [II]

Besides the main reaction of propene epoxidation, secondary reactions with methanol and water can appear leading to the ring-opening products 1-methoxy-2-propanol and propene glycol as is illustrated in the Scheme 4. The results exhibited to be similar to ethene epoxidation. However, the propene epoxidation displayed to be more active than ethene epoxidation.



Scheme 4. Reaction scheme for propene epoxidation.

The catalyst durability was investigated in two experiments of 24h time-on-stream (TOS). As can be seen from Figure 4, the catalyst displayed an excellent stability ensuring the reproducibility of the experiments over 150 hours (37 experiments from experimental matrix and two experiments of 24 hours) without any changes in the activity and selectivity.

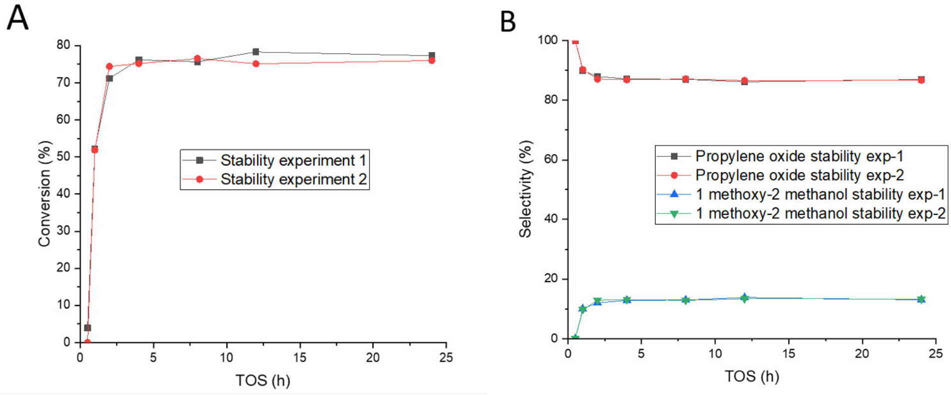


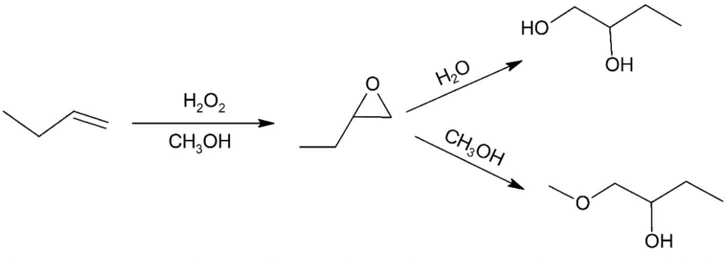
Figure 4. Catalytic behavior vs time-on-stream in propene epoxidation. Experiments were conducted at 40°C and 4.5 bar. The flow of propene was 0.22 mmol/min and the liquid was composed of 2 wt% H_2O_2 (0.24 mmol/min), 5 wt% H_2O and 93 wt% of methanol.

The reaction system was sensitive to the experimental parameters studied. The changes in the total pressure displayed the presence of a maximum in the conversion of propene at 4.5 bar. The maximum of the rates as a function of the reaction temperature was obtained at 40 °C, while the maximum in the selectivity towards propene oxide was observed at the lowest temperature (25 °C). The results were strongly related to the hydrogen peroxide decomposition. An increase in the concentration of hydrogen peroxide improved the propene conversion, but decreased the selectivity to propene oxide. However, an increase in the water content gave a decrease in the conversion, accompanied by changes in the selectivity because of propene glycol formation.

Even if the ethene and propene system were similar, they displayed to be affected in different ways by the same variables. Increasing temperate displayed to decrease the epoxide selectivity in both systems, however, for propene, the production of methoxy species was more important than for ethene. This observation can be strongly related by the phase distribution; ethene oxide being predominantly in the gas phase, while, most of the propene oxide remained in the liquid phase. The increase in the water concentration displayed to be negative for propene due to the increase in the of by-products, i.e. the production of propene glycol, while an increase in the conversion and selectivity was observed by the rise of the water content in the ethene epoxidation. The liquid flow rate had an opposite behavior between ethene and propene. As the flow rate was increased, the conversion of propene increased, while, the conversion of ethene decreased. Nonetheless, both systems displayed an increase in the selectivity with the increase of the liquid flow rate.

3.1.3. 1-Butene epoxidation [III]

Scheme 5 illustrates the overall reactions proposed for the 1-butene epoxidation [37,39,40]. According to this scheme, 1-butene is transformed to 1,2-epoxybutene after which the epoxide can react further with methanol or water through ring-opening and nucleophilic substitution to generate 1-methoxy-2-butanol and 1,2-butanediol as secondary ring-opening products. As expected for this epoxidation system, the results are similar to ethene and propene epoxidation.



Scheme 5. Proposed overall reaction scheme for 1-butene epoxidation.

To confirm the reaction scheme, the catalyst stability and selectivity were monitored with prolonged (24h) experiments time-on-stream (TOS). The results are displayed in Figure 5. During the three successive experiments performed, changes in the catalyst activity with the time-on-stream were noticed. At the start-up of the experiment, the 1-butene conversion increased reaching a maximum, after which it decreased gradually towards a steady state. However, even if the activity change with the time was observed, an excellent reproducibility of the experiments was confirmed as shown in Figure 5. The catalyst was fully regenerated in the one-hour cleaning with methanol. Even though the 1-butene conversion declined, the selectivity of 1,2-epoxybutane was well preserved, the only by-product being 1-methoxy-2-butanol, evidently formed from a reaction between methanol and 1,2-epoxybutane. In contrast to Scheme 5, no 1,2-butanediol was detected. The standard deviation in the conversion measurements were higher during the first four hours but it was defined be less than 5% after this period, whereas for the selectivity, the deviations were less than 0.1%. The TOS behaviour of 1-butene epoxidation displayed from be different to ethene (Figure 3) and propene (Figure 4) epoxidation. For ethene and propene epoxidation, the steady state was reached after 2.5 hours. However, 1-butene reached the stability after 12 h almost five times longer than the shorter olefins. The epoxide selectivities for ethene and propene were stable, around 90%, while for 1-butene the selectivity increased with the time on stream (Figure 5). Nevertheless, the selectivity always exceeded 98%.

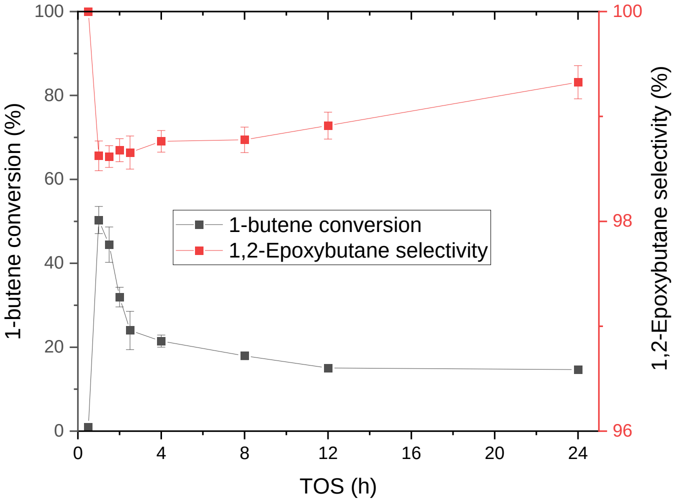


Figure 5. Long-term experiments for 1-butene epoxidation conducted at 40°C and 1 bar. 0.22 mmol/min of 1-butene (0.5 bar) was fed along with the liquid phase composed of 2 wt% H_2O_2 (0.24 mmol/min), 5 wt% H_2O and 93 wt% CH_3OH. The liquid flow rate was 0.5 ml/min.

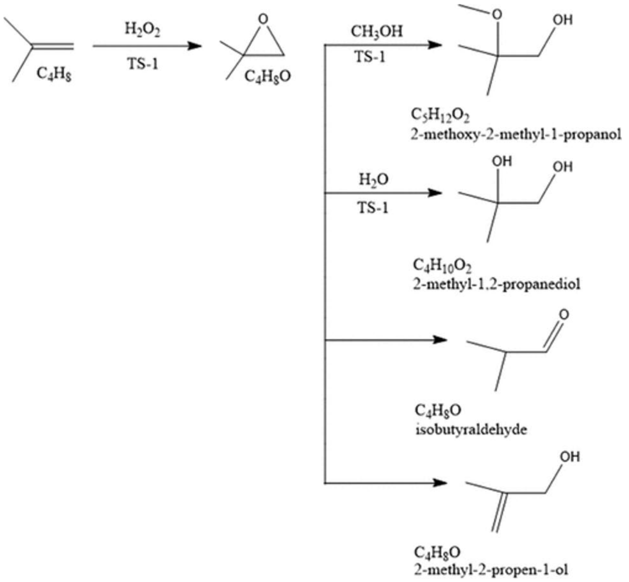
This system has previously been reported from the 10 h to the 350 h [37,39]. Therefore, the first 10 hours of the reaction were always excluded. This was the first time where the first 10 hours of TOS are reported. With the addition of this interval, it is possible to observe a correlation between the increase in the product selectivity and the decrease of the catalyst activity [37,39], because, how it is described in the literature, the decrease in the conversion can be correlated to the higher concentration of by-products during this transition time.

The 1-butene system displayed a different behaviour compared with the epoxidation of propene carried out previously by us under similar conditions [47]: the transient response of the propene oxide increased monotonically during the experiment. The reason for the behaviour of 1,2-epoxybutane response with the time-on-stream might be due to the capture of reactants and products in the catalyst structure, which was confirmed by the high amounts of reactants and products identified during the flushing the reactor with methanol after each experiment.

Most of the experimental conditions screened did not affect the principal transient behavior of the system. However, the experiment with 1 wt% of hydrogen peroxide suggested an opportunity to decrease the amplitude of the change with the time-on-stream to decrease the clogging of the catalyst. The selectivity of the desired product, 1,2-epoxybutane was very high, exceeding 98% in most experiments. Minor amounts of 1-methoxy-2-butanol were detected as the by-product, evidently formed from 1,.2-epoxybutane and methanol. The role water in the ring-opening process was negligible, practically no 1,2-butanediol was detected among the reaction products.

3.1.4. Epoxidation of iso-butene [III]

The epoxidation process of iso-butene resulted in the highly reactive 1,2-epoxy-2-methylpropane as the primary product and in various secondary by-products. In addition to the main reaction, ring-opening reactions with water and methanol took place, as confirmed by gas chromatography, leading to the secondary products isobutyraldehyde, 2-methyl-2-propen-1-ol, 1-methoxy-2-methyl-2-propanol, 2-methoxy-2-methyl-1-propanol and 2-methyl-1,2-propanediol as well. The results suggest a consecutive-parallel stoichiometric pattern as displayed in Scheme 6.



Scheme 6. Confirmed overall reaction scheme for iso-butene epoxidation.

The important issue is whether the secondary products displayed in Scheme 6 are formed from the epoxide or not. Therefore, an additional experiment was carried out to confirm the reaction scheme.

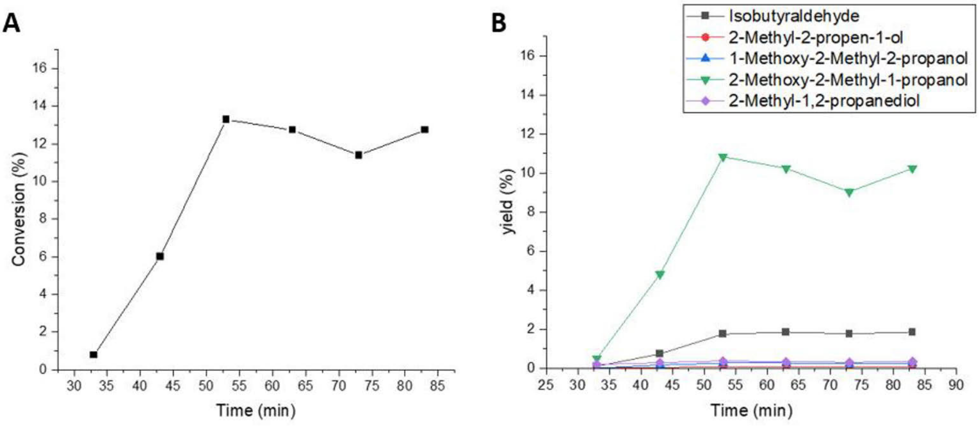


Figure 6. Ring opening experiment of 1,2-epoxy-2-methylpropane. Conversion of 1,2-epoxy-2-methylpropane (A) and by-product yields (B) in the epoxidation of iso-butene. The liquid flow was 0.5 ml/mim of 2 wt% 1,2-epoxy-2-methylpropane in methanol at 40ºC and 1 bar.

The reactor was fed with a liquid phase contained 2 wt% 1,2-epoxy-2-methylpropane, the primary reaction product, diluted in methanol with a flow of 0.5 ml/min at 1 bar. The gas phase was composed of 10 ml/min nitrogen and the temperature was maintained at 40 °C. Figure 6B shows the secondary products as a function of time and Figure 6A represents the achieved conversions. The results indicate that all the secondary products were formed parallelly from the epoxide and that the reaction network for the epoxidation of iso-butene (Scheme 6) is valid.

The catalyst stability was investigated at three 12 h time-on-stream (TOS) experiments conducted at 1 bar. The reaction temperature was maintained constant at 15 °C. The gas phase consisted of a constant flow of 9 ml/min iso-butene with an equal amount of inert gas and, the liquid flow contained of 2 wt% hydrogen peroxide, 5 wt% water and 93 wt% methanol with a volumetric flow rate of 0.5 ml/min. Figure 7 represents the selectivity of 1,2-epoxy-2-methylpropane and 2-methoxy-2-methyl-1-propanol as well as the conversion over 12 h time-on-stream.

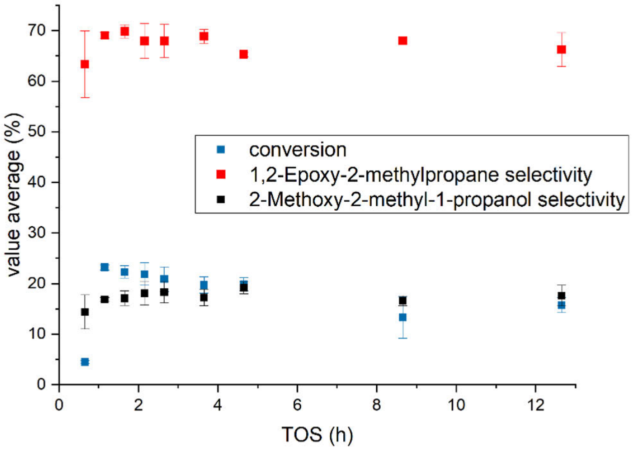


Figure 7. Long-term experiments for iso-butene epoxidation conducted at 15°C and 1 bar.

The selectivity of the epoxy species was c.a. 67 ± 2.7%. Furthermore, the 1-methoxy-2-methyl-2-propanol selectivity with an average of 17 % remained stable with a standard deviation less than 2 % (Figure 7). On one hand, the results demonstrate a good catalyst stability and an experimental repeatability over 113 h. Nonetheless, the system displayed to be sensitive because of a high number of by-products. The differences in the behaviors between 1-butene (Figure 5) and iso-butene epoxidation are remarkable. 1-butene being more selective, however, less stable with the time on stream. The behavior was closer to the shorter olefins, i.e. ethene (Figure 3) and propene (Figure 4) reaching the steady state in shorter times. Nonetheless, the selectivity of iso-butene epoxidation is clearly lower reaching a stability at 67%. These results suggest a strong molecular structure effect on the behavior of the system. The double bond position is an important element to be considered due the behavior of changes in the reactivity and selectivity. It is important to notice that these experiments were performed at 15 ºC, while, in all the other olefins the experiments were carried out at 40 ºC. The reason was that a high amount of 1,2-epoxy-2-methylpropane reacted at 40 ºC.

Different from 1-butene, the behavior of isobutene was affected by most of the experimental variables studied. Among the results it is possible to be outline the effect of the water and hydrogen peroxide; both of them displayed to be tunable in order to increase the selectivity of the system. Nevertheless, the best parameter to increase the selectivity displayed to be the residence time. Decreasing the residence time, it was possible to increase the selectivity to the epoxide by suppressing the consecutive ring opening reactions.

3.2. Epoxidation of olefin mixtures [V–VI]

The literature devoted to titanium silicate catalysts indicates that the activity decreases as the olefin chain length increases [40]. Nevertheless, the most active single α-olefin reaction between two to four carbons at the steady state is reported to be propene [47], followed by ethene [48,49]. However, as the chain becomes longer than the propene chain the activity drops [36–39]. Nonetheless, the epoxide selectivity increases as the olefin chain length increases [37,47–49].

The epoxidation of the α-olefin mixtures exhibits a different behavior. The epoxidation of a binary mixture of propene and 1-butene displayed a higher activity for longer α-olefins [50] and the same was observed in the case of propene and ethene, where, propene turned out to be more active than ethene. Moreover, the study of ternary mixtures displayed a high activity for 1-butene followed by propene and ethene [50].

The behavior of the mixture experiments indicates a trend towards the epoxidation of longer carbon chains. This behavior is independent of the number of α-olefins in the mixture (binary or ternary) or the reaction conditions. The reaction systems (ethene/propene, propene/1-butene [50] and ethene/propene/1-butene [50]) have been screened within a broad set of conditions confirming that the longest chain is the most active one.

A relevant element to be considered is the epoxide selectivity in these systems. The ethene-propene system exhibited lower epoxide selectivities compared to their single olefin epoxidation experiments. For the propene-1-butene system, the selectivity was similar to the propene epoxidation with a 90% selectivity [50]. The ternary mixture exhibited almost a complete selectivity to epoxides [50].

The conversion of the epoxidation mixture seems to behave closer to the longest olefin in the system, which can be observed for binary and ternary mixtures. The observation can be related to two elements: The increase of the solubility of the α-olefin in methanol as the chain becomes longer or to the interactions of reactants and products with the surface of the material is increased.

The encapsulation of 1-butene products in the pores of TS-1 has been discussed in literature [37–39] as the catalyst deactivation caused by products such as propene oxide plays an essential role on the titanium silicate material [2]. Nonetheless, the study of binary mixtures could indicate a decrease in these negative interactions, because, it is not possible to observe important deactivation as it is reported for these molecules. However, the presence of a second molecule competing for the epoxidation suggests a decrease in the epoxide selectivity. For ethene and propene and for propene and 1-butene, these two systems exhibited lower epoxide selectivities than observed in the corresponding single molecule epoxidation experiments. However, the catalyst stability was better for binary mixtures. On the contrary, in the ternary experiments, both the selectivity and stability were improved compared to the systems of single olefins. Therefore, it is highly probable that the presence of a second or a third molecule can affect the concentrations on the surface of the titanium silicate catalyst, by decreasing the deactivation by encapsulation.

The isothermal reactor model proposed and developed for single olefin epoxidation was simplified to considering the physical and chemical phenomena occurring in these cases. The change in this model is the addition of steady-state assumption. The steady state kinetic data obtained from step-response experiments have been modelled mathematically and were used in the parameter estimation. The model utilized the kinetic data for the epoxidation of ternary mixture (ethene, propene and 1-butene) as example. Nonetheless, this can be easily expanded to other mixtures, thanks to the similar reactor behavior of all the mixtures studied.

3.2.1. Binary mixtures

3.2.1.1. Ethene – propene epoxidation [V]

In the experimental work, the reactions displayed in Schemes 3 and 4 were expected to be present in the ethene and propene reaction networks in similar ways. Nonetheless, in this work, the presence of glycols was not observed as ring-opening products, while the ring-opening products were always the methoxy species.

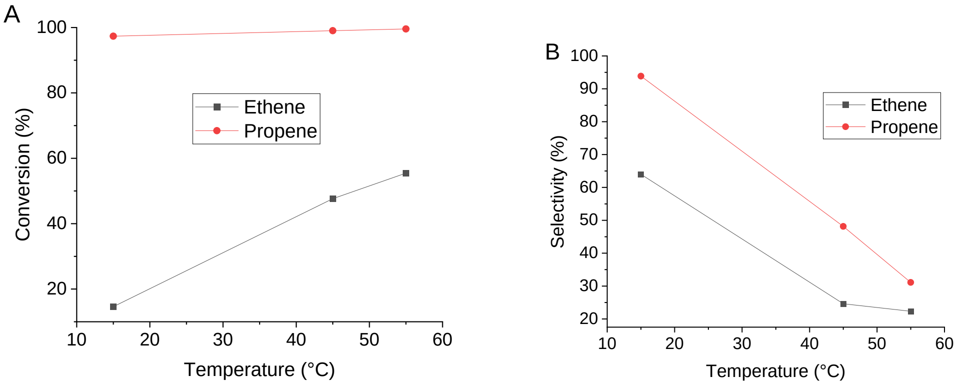


Figure 8. Conversion (a) and selectivity (b) of a mixture of ethene and propene at different temperatures and 4.5 bar. The flow of ethene and propene was 0.11 mmol/min each and the liquid consisted of 2 wt% H_2O_2, 5 wt% H_2O and 93 wt% of methanol.

The temperature effect on the reactant conversion and the product distribution was studied at 15-55°C (Figure 8). The temperature domain was selected, because the decomposition of hydrogen peroxide is enhanced at temperatures exceeding 55°C [47]. The pressure was kept constant during the experiments carried out at 4.5 bar. The results suggest a high activity of propene, while the conversion of ethene displayed to be similar to the previously reported studies [48,49]. An explanation to this observation could be the low partial pressure of propene in the gas mixture. Important changes in the activity for propene with the change in the partial pressure has been reported [47], where the conversion of ethene has displayed to be constant at different partial pressures [49].

3.2.1.2. Propene – 1-butene epoxidation [VI]

The effect of the reaction temperature on propene and 1-butene conversions and product selectivities are displayed in Figures 9 -10, respectively. Propene oxide and 1,2-epoxybutane were always the main products, whereas 1-methoxy-2-propanol and 1-methoxy-2-butanol were the secondary products formed via ring opening caused by methanol. By increasing the reaction temperature, both propene and 1-butene conversions were considerably enhanced, and the dynamics of the step responses became faster, but kept similar forms. The step responses of the main products, the epoxides are very similar, thus indicating that they are formed in parallel, in analogous surface reaction steps. A maximum of the epoxide concentration was observed in most experiments. In case of competitive adsorption of reactants, such a maximum in the product concentration is expected, if some of the reactants or products have clearly stronger adsorption affinity and start to dominate on the surface at steady state.

Ring opening reactions of propene oxide and 1,2-epoxybutane to 1-methoxy-2-propanol and 1-methoxy-2-butanol were not detected at 15°C but they became relevant at 45 and 55°C. After the initiation period, the propene oxide and 1,2-epoxybutane selectivities remained on constant levels, but diminished with temperature, from 100% at 15°C to approximately 90 % at 55 °C. As the main and side reactions are irreversible and consecutive, the selectivity to the desired product decreases, while that of the undesired product increases with the alkane conversion. The increase of the by-product formation with increasing temperature indicates that the activation energies of the ring opening reactions are higher than the activation energies of epoxidation. At 55°C, the hydrogen peroxide decomposition becomes important as has been reported in our previous work; therefore, the highest experimental temperature was fixed at 55°C.

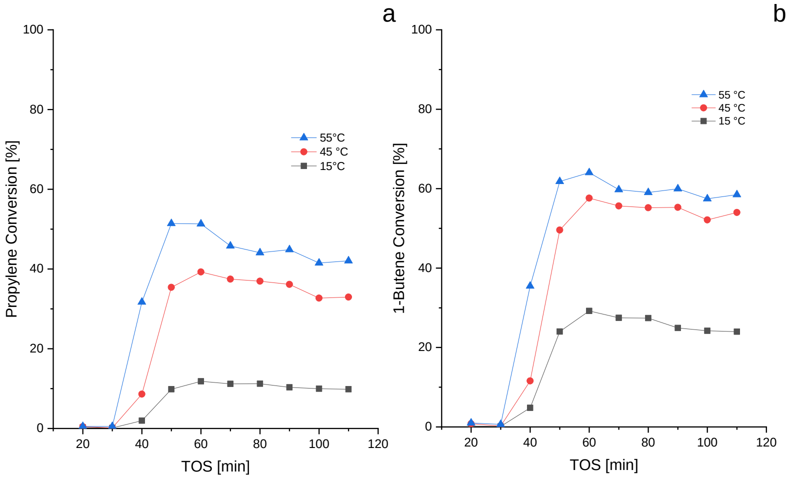


Figure 9. Effect of the reaction temperature on propene (a) and 1-butene conversion (b). Reaction conditions: Pressure (P) = 1 bar; Liquid flow rate (LFR) = 0.5 mL/min; Gas flow rate (GFR) = 0.446 mmol/min; wt% H_2O_2 =2

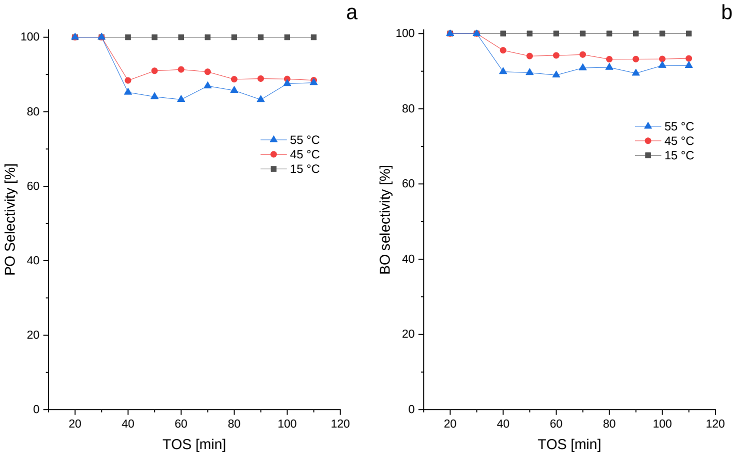


Figure 10. Effect of reaction temperature on propene oxide selectivity (a) and 1,2-epoxybutane selectivity (b). Reaction conditions: P=1 bar; LFR=0.5 mL/min; GFR=0.446 mmol/min; wt% H_2O_2 =2.

The epoxidation of binary mixtures exhibited to be strongly affected by the olefins in the mixtures. The ethene – propene mixture displayed a low selectivity in all the conditions screened, while propene – 1-butene mixture were highly selective in all the conditions even in those where propene had a relatively low selectivity.

3.3. Epoxidation of ternary mixtures [VI]

The conversions of ethene, propene and 1-butene are shown in Figure 11, while the epoxide selectivities are displayed in Figure 12. Similarly, to the binary mixture, the propene, 1-butene and ethene conversions were improved by increasing the reaction temperature. At the same time, the propene oxide and 1,2-epoxybutane selectivities remained stable at 100% from 15 to 35 °C, but decreased to approximately 90 % from 45 to 55 °C. For ethene oxide, a 100% selectivity was detected in all the experiments. The transient behaviors of the epoxides showed an interesting behavior: the step response of ethene oxide was monotonic, whereas profound maxima were noticed for the propene oxide and 1,2-epoxybutane responses. This can be due to the presence of 1,2-epoxybutane side products in the pores affecting the accessible active titanium sites for butene epoxidation.

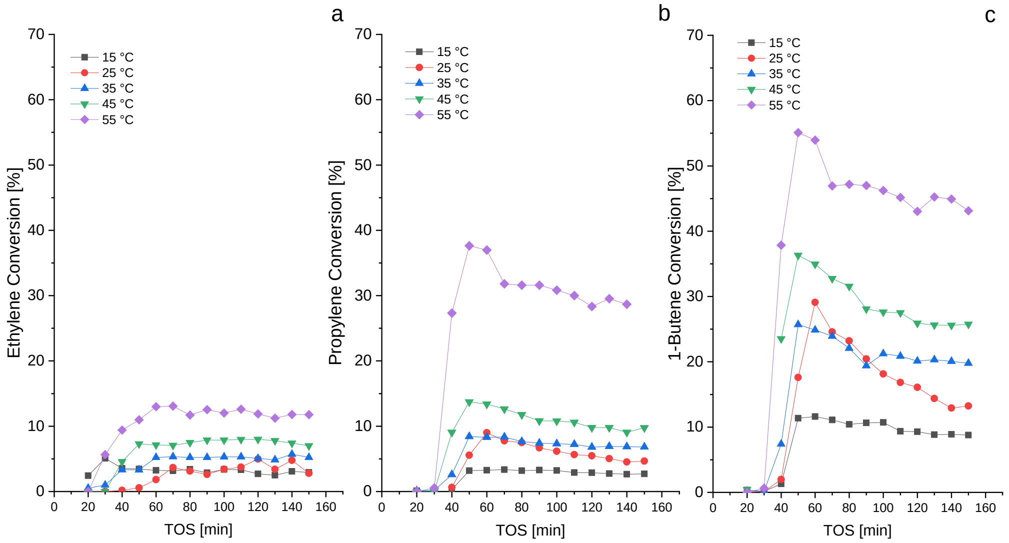


Figure 11. Effect of reaction temperature on ethene (a), propene (b) and 1-butene (c) conversions. Reaction conditions: P=1 bar; LFR=0.5 mL/min; GFR=0.446 mmol/min; wt% H_2O_2 =2.

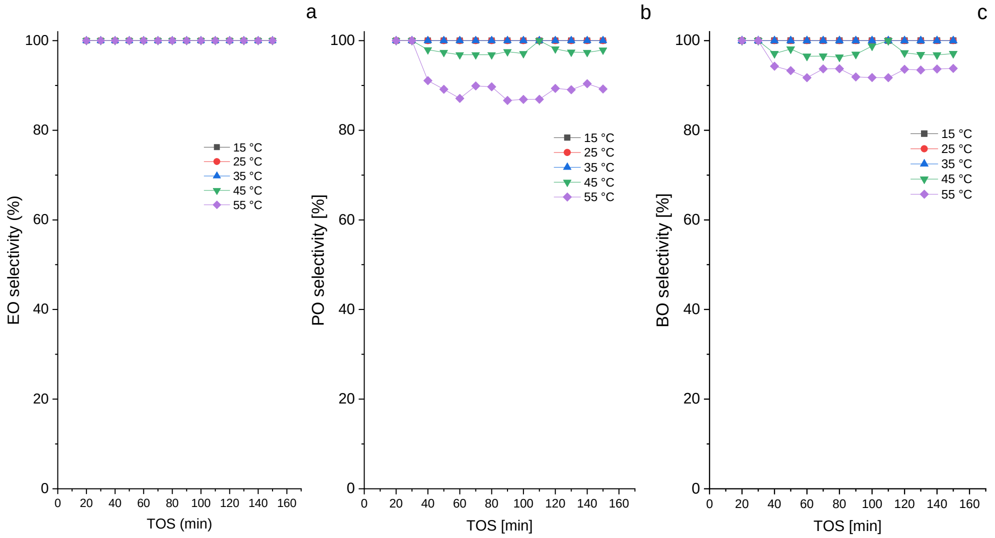


Figure 12. Effect of reaction temperature on ethylene oxide (a), propylene oxide (b) and 1,2-epoxybutane (c) selectivity. Reaction conditions: P=1 bar; LFR=0.5 mL/min; GFR=0.446 mmol/min; wt% H_2O_2 =2.

The epoxidation of ternary mixture implies a step forward due the process intensification. The elimination of the olefin separation could be useful when a low flow of olefin is produced e.g. via the Fischer-Tropsch process. The high selectivities to epoxides observed in this work encourages the efforts on mixture epoxidation.

3.4. Titanium silicate materials [VII-VIII]

3.4.1. Catalyst characterization [VII]

The hydrothermal synthesis resulted in a highly crystalline Ti-MWW catalyst, whereas boric acid acts as a structure-supporting agent to stabilize the structure in the absence of alkali-cations and to incorporate a high content of Ti. The crystallinity of all the synthesized materials was confirmed by XRD [51].

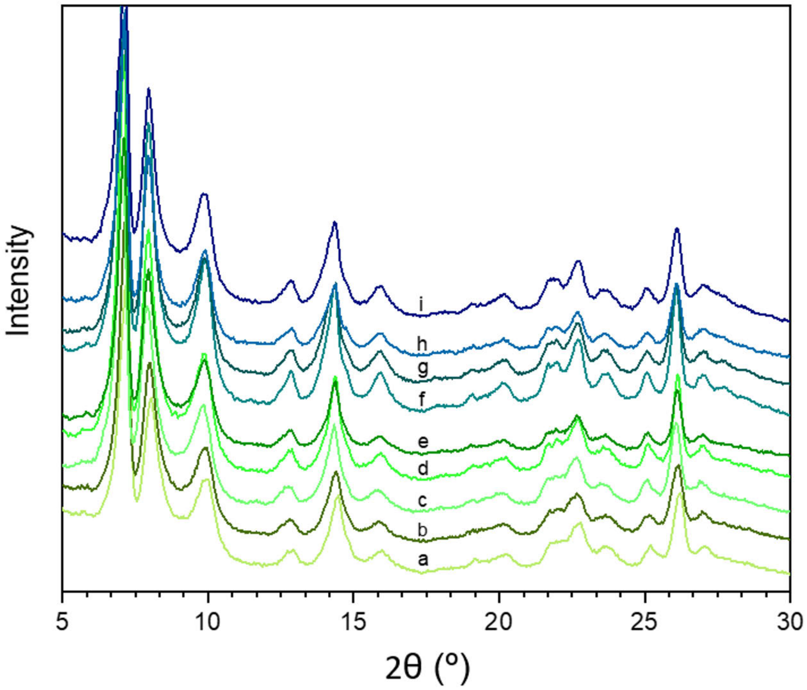


Figure 13. XRD patterns of synthesized Ti-MWW structures: (a) -1.6-530-6, (b) -1.6-550-6, (c) -3-530-10, (d) -3-530-6, (e) -3-550-6, (f) -4.5-530-6, (g) -4.5-550-6, (h) -6-530-6 and (i) -6-550-6.

The XRD patterns of the synthesized Ti-MWW structures are shown in Figure 13. All the samples had the typical MWW signals obtainable from the database, thus confirming the topology. Furthermore, the crystallinity judging from the shape of the reflexes was high. The Ti-MWW structure is mainly characterized by the intralayer orientation in the *c*-direction and the sheets in the *ab*-plane. The signals at 2Θ = 7.1 ° (100), 25.1 ° (220) and 26.2 ° (310) can be assigned to the layered structure of the stacked sheets [52]. All other signals originate from the typical platelets at the *ab*-plane. However, a small amount of impurities is present in the samples, suppressing the reflexes in the low region of the 2θ signals, like at 19.1 °, which was only observed in one of the samples (Figure 13f).

The images, obtained by TEM, confirmed the layered structure of the single platelets. On the micrographs, the platelets are visible as their orientation is along the ab-plane according to Figure 14a. The upright standing platelets reveal the stepwise changing thickness. Particularly towards the edges, a splitting of the single platelets is observed, clearly indicating the laminar morphology of the material. The platelets were 50 – 300 nm in length and 3 – 45 nm in thickness. Figure 14a is representative for all the Ti-MWWs materials. No visible effects of the calcination temperature or duration could be found. However, for a higher Ti content, non-laminated 3D structures were present to a certain extent (Figure 14b) but no agglomerate sheets, where the crystal growth took place in one orientation only, were observed (Figure 14c). This effect is produced by the crystallization on the walls and corners of the inner teflon vessel in the rotating autoclave. In contrast, the smaller and better defined crystals are obtained, which are mainly created due to the dynamic crystallization from the constantly rotating autoclave and the motion of the reacting gel [53]. Furthermore, in some places, an additional growth of the titanium silicate in the typical crystal shape was observed, which appears as blossoms at the outer shell of the agglomerated platelets (Figure 14d).

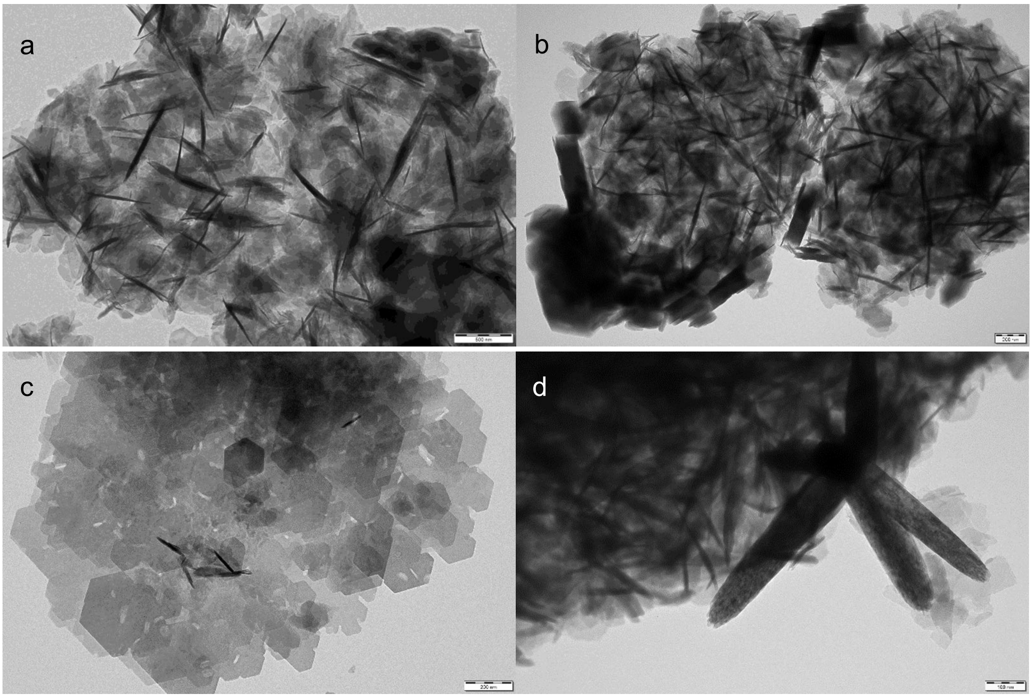


Figure 14. Transmission electron micrographs of Ti-MWW-1.6-550-6 (a) and Ti-MWW-3-530-6 (b), (c) and (d).

The scanning electron micrographs of Ti-MWW exhibited the presence of typical platelet shaped crystals of the MWW type microporous materials. The morphological features of the Ti-MWW were clearly observed in all the samples studied, since the surface of the material and not the transmission was imaged. Some findings from the TEM images are supported by the SEM micrographs displayed in Figure 15. The platelets are present as spherically shaped agglomerates with diameters of 2 – 4 µm. Moreover, the mentioned non-laminated 3D crystals with a hexagonal shape can be seen in Figure 15a. At a higher magnification, the characteristic well-defined hexagonal sheets of the synthesized material are visible. At a lower magnification, it can be found intact and partially broken larger spheres with the diameter of 15 – 35 µm. From the micrograph displayed in Figure 15c, it is inferred that larger particles break apart forming smaller agglomerates, indicated by cracking of the hollow particles. Hereby the fraction of the small agglomerates is significantly larger than the bigger particles. As already observed from the TEM images, the images are representative for all the synthesized materials. Neither the duration nor the temperature of the calcination procedure affected the morphology. As the ratio of Si/Ti is shifted towards a higher Ti content, the contribution of the planar shaped crystals increases compared to the agglomerates of single platelets. This fact indicates a higher mechanical stability of the titanium silicates, despite using the same dynamic crystallization process. This phenomenon was visible especially for Ti-MWW-4.5 and -6 samples and only in small amounts in TiMWW-3 materials. These crystal shapes were not observed in the Ti-MWW-1.6 silicates.

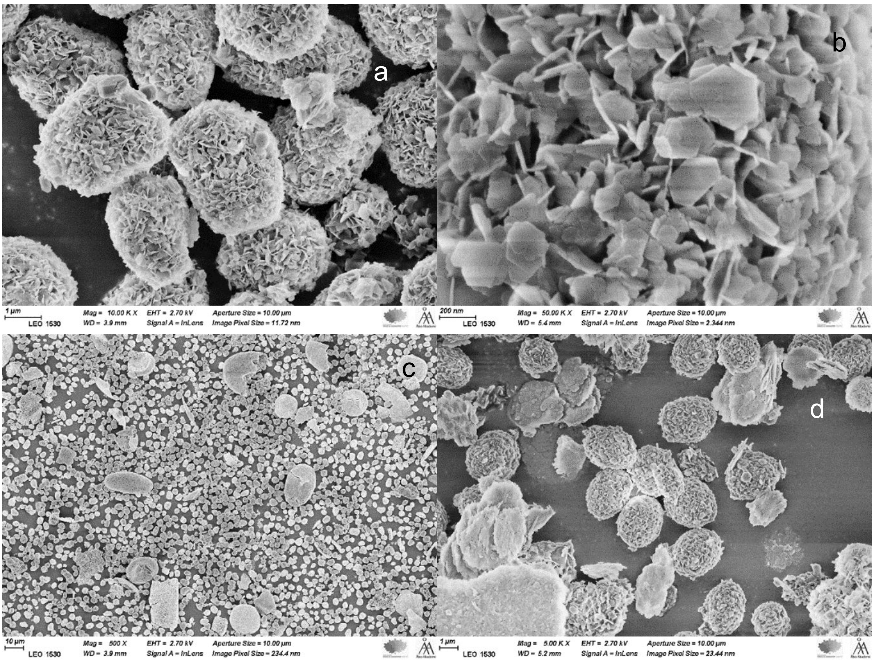


Figure 15. Scanning electron micrographs of (a) Ti-MWW-3-550-6, (b) Ti-MWW-6-530-6, (c) Ti-MWW-3-530-6, (d) Ti-MWW-4.5-530-6.

Nitrogen physisorption was carried out to investigate the textural properties, i.e. the surface area, pore volume, pore size distribution and adsorption-desorption isotherms of the Ti-MWWs materials. The results were compared with the properties of the commercial TS-1 titanium silicate. High surface areas were found for the synthesized catalysts, ranging from 420 to 480 m^2/g. An exception among the prepared catalysts was Ti-MWW-3-550-6 with 371 m^2/g; the decrease in the surface area can be attributed to the distortion of the structure of this catalyst. However, all the Ti-MWW materials displayed higher specific surface areas in comparison to TS-1 being 319 m^2/g. Moreover, the prepared titanium silicates had ca. two-fold higher pore volumes compared to the commercial reference material. A closer look on the porosity reveals that additional mesopores contribute to the microporosity in case for the Ti-MWW catalyst. In contrast, TS-1 mainly exhibits microporosity. Since the Ti-MWW and TS-1 crystals themselves contain micropore channels only, the mesoporosity originates from a secondary structure formed by the calcination of the 2D MWW precursor, leading to a partial condensation of the single sheets. As Figure 15b shows, the agglomerates form cavities between the single sheets, thus creating the mesoporosity. The second reason for a higher pore volume can be found in their different topologies. The framework of the MWW structure contains large internal supercages, which are not present in the MFI framework of TS-1 [54]. The microporous volumes of the synthesized titanium silicates are up to 40 % higher than those determined for TS-1.

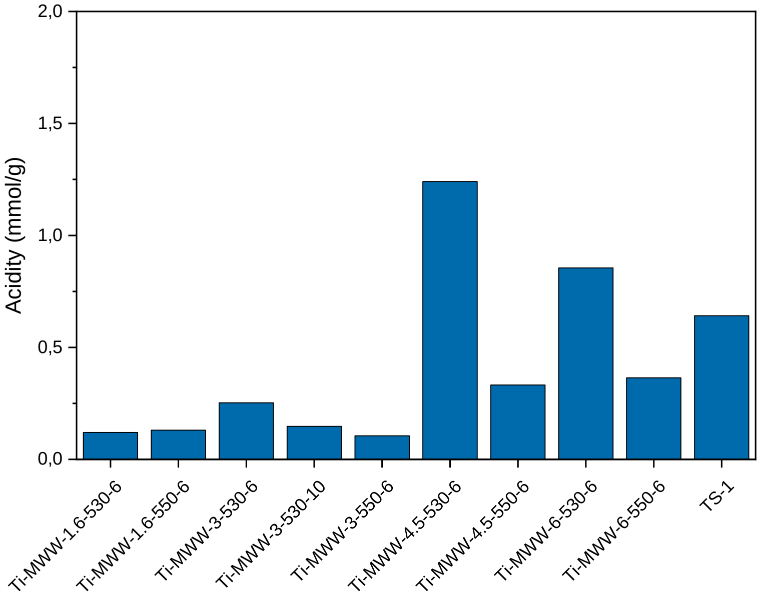


Figure 16. Acidities of the Ti-MWW materials and TS-1.

Table 1. Textural properties of Ti-MWW, TS-1 catalysts and the element analysis of Si and Ti. Legend: SSA – specific surface area, V_{pores} – pore volume and d_{pores} – average pore size.

Catalyst	SSA[a]	V_{pores} [cm^3/g]			d_{pores}[b]	Si	Ti	Atomic Si/Ti Ratio
	[m^2/g]	V_{micro}	V_{meso}	V_{tot}	[nm]	[wt%]		nominal
Ti-MWW-1.6-530-6	481	0.21	0.19	0.40	0.66	46.3	1.2	50
Ti-MWW-1.6-550-6	434	0.19	0.13	0.32	0.65	-	-	-
Ti-MWW-3-530-6	464	0.21	0.27	0.48	0.66	48.1	1.7	25
Ti-MWW-3-530-10	424	0.17	0.32	0.49	0.65	-	-	-
Ti-MWW-3-550-6	371	0.16	0.25	0.41	0.66	-	-	-
Ti-MWW-4.5-530-6	459	0.20	0.28	0.49	0.66	47.5	2.6	19
Ti-MWW-4.5-550-6	423	0.19	0.21	0.40	0.66	-	-	-
Ti-MWW-6-530-6	470	0.21	0.19	0.39	0.66	48.6	4.8	12
Ti-MWW-6-550-6	449	0.20	0.18	0.38	0.66	-	-	-
TS-1	319	0.15	0.04	0.19	0.63	-	-	-

[a] Calculated with the Dubinin-Radushkevich method.

[b] Calculated with the Horvath-Kawavoe method.

The two types of channel systems also result in different average pore sizes. For Ti-MWWs an almost constant value of ca. 0.66 nm was found, indicating the uniform channel system for all the synthesized materials, whereas the average pore size of TS-1 is 0.63 nm. One of the main objectives of the work was to study the influence of different Ti contents on the MWW framework. For the determination of the composition, ICP-OES was used for the elemental analysis. One sample of each synthesis batch was measured with a theoretical Si/Ti ratio of 50, 25, 19 and 12. The obtained weight percentages of Si and Ti are summarized in Table 1. From these values, the atomic ratios were determined to 65.7, 47.2, 31.4 and 17.2, respectively, being higher than the nominal values. Due to the acid treatment aimed at the removal of the extra framework Ti-species, which are not incorporated in the MWW structure, a 24 – 47 wt% shortage of Ti was found. This loss of Ti results in defects in the structure, confirmed by XRD, where smaller signals are poorly recognizable.

Titanium silicates had been characterized as purely Lewis acid materials [55]. The acidity was determined by ammonia TPD, for which the results show the important role of the Si/Ti ratio for the acidity of the material. The acidities are displayed in Figure 16. Here, a clear decrease of the acidity from Ti-MWW-4.5 and -6 to -3 and 1.6 was found, compared with the materials, which were treated under identical calcination conditions. The acidity drop is specifically pronounced for the materials treated at 530 °C. It is evident that the materials with higher Ti contents can also contain potentially more acid sites. It is noteworthy to mention that despite a higher Si/Ti ratio of TS-1, which is ≥ 25 according to the supplier, this material has an acidity lower than the Ti-MWW-4.5-530-6 with a ratio of c.a. 31. Moreover, the change of the calcination temperature had an impact on the acidity of the material, where particularly the Ti-MWW-4.5 and -6 materials with higher Ti content calcined at higher temperature possess significant a lower acidity. It is possible that the condensation of tetrahedral to octahedral non-acidic Ti-species is more probable at higher temperatures. The coordination of the Ti-species is decisive for acidic properties [56]. Unsaturated tetrahedral TiO_4 is able to accept electrons and therefore exhibits acidity, whereas saturated TiO_6 octahedra are non-acidic [57]. Consequently, Ti-MWW-4.5 possesses a higher amount of tetrahedral coordinated Ti than Ti-MWW-6, despite a higher Ti content. These observations are coherent with the results obtained by IR-spectroscopy as illustrated in Figure 17. The band at 960 cm^{-1} is the characteristic stretching vibration band of tetrahedral Ti-species, which is considered to be the active species in the epoxidation of olefins, at the bond Si-O-Ti [58]. The infrared spectra reveal an increase at the Ti content leading to a more intense band. However, both bands from Ti-MWW-6 display lower intensities than the ones from Ti-MWW-4.5 indicating less tetrahedral coordinated Ti-species and supporting the conclusions from the acidity measurements. An increase of the intensity is especially remarkable for Ti-MWW-1.5 and -3 materials, considering similar calcination conditions. Moreover, it was found that a lower calcination temperature of all the catalysts, particular by for the Ti-MWW-1.6 and -3, results in a more distinct band at 960 cm^{-1}. A negative effect on the amount of tetrahedral Ti-species was observed for a longer duration of the calcination treatment, as can be seen by comparing the spectra of Ti-MWW-3-530-6 and -10. The coordination of titanium can also be investigated with UV-vis spectroscopy. In the literature, the band at 220 nm is assigned to the tetrahedral, 260 nm to octahedral and 330 nm to anatase Ti-species in the extraframework. The displayed spectra in Figure 18 show a peak at 230 – 237 nm and for a higher Ti content a broad band around 319 nm. The positions of the obtained bands in the spectra is different from previous reports [59][51][60], however, judging from the shape of the curves, the former signal can be assigned to the desired tetragonal Ti-species and the latter broad band at ca. 319 nm to the anatase-like species. The UV-vis spectra suggest an increase in the concentration of extra-framework titanium with an increase in the titanium loading.

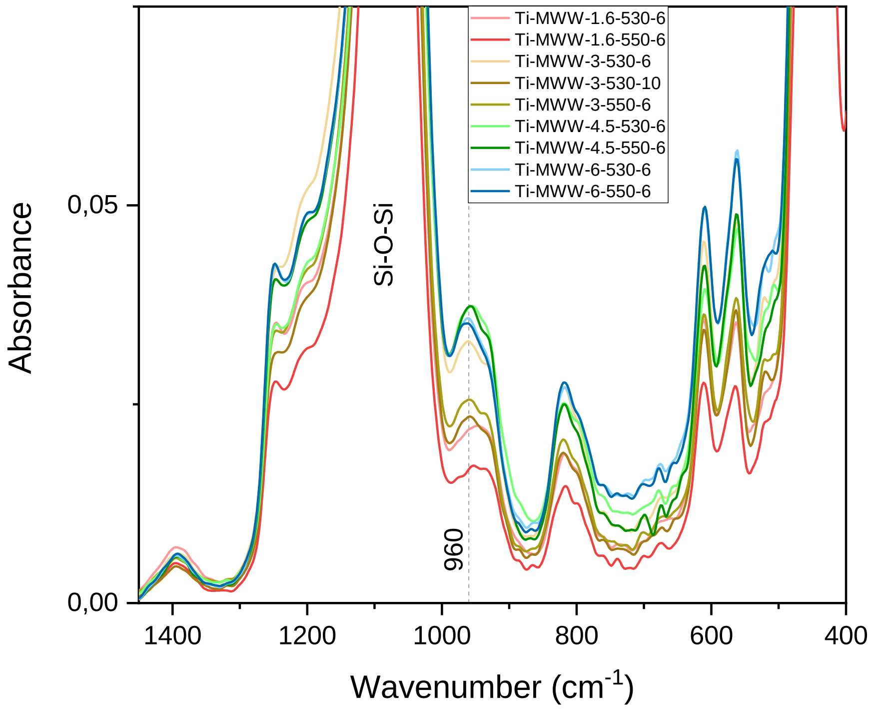


Figure 17. IR-spectra of synthesized Ti-MWW materials.

The IR-spectra reveal the increased formation of anatase-like species when the material contains more Ti, which is in a good agreement with the SEM images. Ti-MWW-3 and -4.5 show similar absorbances at this wavelength, whereas Ti-MWW-6 displays a significate increase of the absorbance. Hence, introducing of more titanium leads to the formation of undesired anatase-like species. The results are consistent with the IR-spectra, where Ti-MWW-6 exhibits even less absorbance at 960 cm^{-1} than Ti-MWW-4.5, despite a higher content of Ti. The recorded spectra from the UV-vis measurement are reproducible, confirmed by using another measuring instrument.

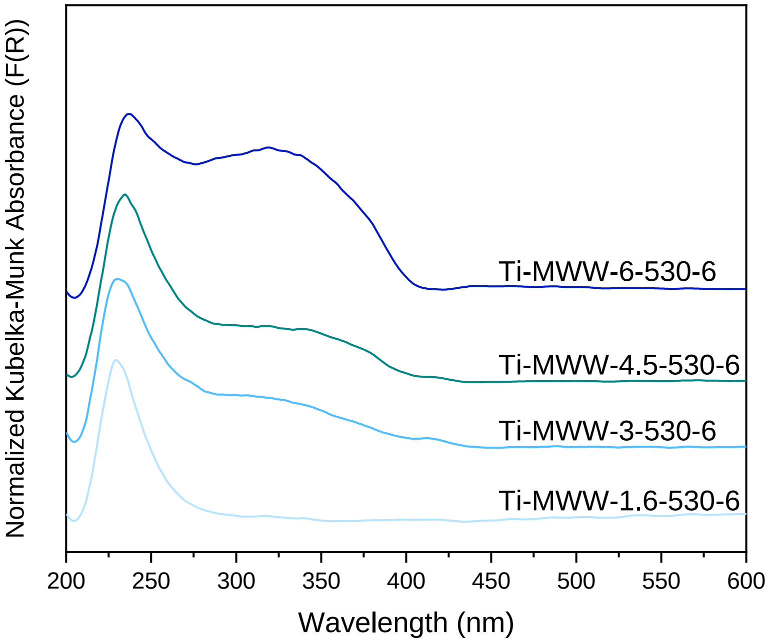


Figure 18. UV-vis-spectra of synthesized Ti-MWW materials.

3.4.2. Catalytic behaviour of Ti-MWW [VII –VIII]

The catalytic results from the trickle bed experiments are displayed in Table 2. One of the most important results is the superior conversion of propene in acetonitrile (MeCN), being up to 3.5 times higher for Ti-MWW catalysts compared to TS-1 in the same conditions. The epoxide selectivity was for all the catalysts close to 100 %. In the methanol (MeOH) solvent, the opposite behaviour was found: when a larger conversion with TS-1 was achieved, the selectivity decreased. Interestingly, switching the solvent from acetonitrile to methanol displays a considerable increase of the propene conversion in case of TS-1 and a slight decrease in case of the Ti-MWW materials. This behaviour has been previously reported by Tong et al. [59], where the phenomenon was explained by different adsorption strengths of the solvents on Ti-MWW. MeCN is an aprotic solvent, while MeOH is a protic one adsorbing more strongly in the channels of the MWW structure, and hindering diffusion of the reactants, which results in a lower activity. However, it is still under investigation, why the conversion in methanol is significantly higher using TS-1 instead of Ti-MWW, while the opposite results were observed for acetonitrile. It is widely reported that the solvent has a strong influence on the activity and selectivity on the propene epoxidation process, since many factors, such as the reactant solubility, the protonation ability of the solvent and the hydrophilic-hydrophobic interactions with the catalyst can affect the reaction system [61], giving a lower selectivity in methanol than in acetonitrile. Herein, TS-1 exhibits among the screened catalysts the lowest selectivity of 92.4 %. All the prepared Ti-MWW catalysts afforded higher selectivities and even for Ti-MWW-1.6-530-6 and Ti-MWW-3-550-6 no by-products were detected. The enhanced selectivity of the epoxidation process in acetonitrile compared to methanol has been reported previously [62]. The use of acetonitrile as a solvent did not result in any by-products formation. On the other hand, a lower selectivity in methanol is caused by a consecutive reaction of the solvent itself with the epoxide because a nucleophile attack of methanol leads to ring opening. Contrary to methanol, acetonitrile is not able to perform a nucleophilic addition of the epoxide ring.

Table 2. Conversion and selectivity of the synthesised Ti-MMW and TS-1 as a reference in MeOH and MeCN as solvents.

	Conversion [%]		Selectivity [%]		TOF [s^{-1}]	
	MeCN	MeOH	MeCN	MeOH	MeCN	MeOH
Ti-MWW-1.6-530-6	5.0	3.4	100	100	0.30	0.20
Ti-MWW-1.6-550-6	4.9	2.7	100	95.0	0.29	0.16
Ti-MWW-3-530-6	7.3	4.4	100	94.8	0.30	0.18
Ti-MWW-3-530-10	7.1	4.4	100	98.8	0.29	0.18
Ti-MWW-3-550-6	5.1	2.6	100	100	0.21	0.11
Ti-MWW-4.5-530-6	16.3	8.2	100	96.0	0.45	0.23
Ti-MWW-4.5-550-6	15.5	8.9	100	94.8	0.43	0.25
Ti-MWW-6-530-6	17.6	10.0	100	95.1	0.26	0.15
Ti-MWW-6-550-6	14.9	8.9	100	96.2	0.22	0.13
TS-1	4.8	23.2	100	92.4	0.10	0.47

The durability of the Ti-MWW catalyst durability was checked by performing four consecutive experiments of 24 h duration. The results are shown in Figure 19. The catalyst displayed an excellent stability over 180 h (total hours of the experimental campaign) and the system typically reached the steady state after 2.5 h. No propene glycol was detected, which implies that ring opening caused by water was excluded. Ti-MWW displayed a complete selectivity to the epoxide, while, TS-1 exhibited a ca. 90% selectivity to propene oxide under similar conditions in methanol.

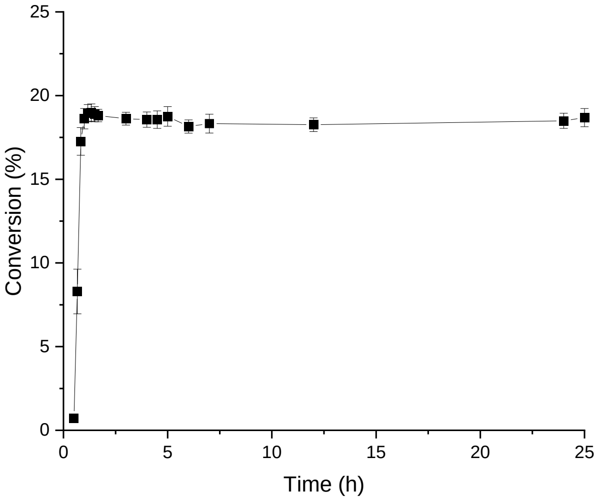


Figure 19. Stability experiments of Ti-MWW conducted at 40°C and 4.5 bar total pressure. The flow of propene was 0.22 mmol/min and the liquid phase included 2 wt% H_2O_2 (0.24mmol/min), 5 wt% H_2O, and 93 wt% acetonitrile

After investigating the catalyst stability, the catalyst was studied in a broad range of experimental conditions. The most remarkable in the differences in the behaviors of Ti-MWW catalyst and TS-1 was the effect of the reaction temperature and the water concentration. The increase of the reaction temperature improved the reaction rate without decreasing the propene oxide selectivity. At 60 ºC, the epoxide selectivity remained higher than 99%. Similar experiments performed in the presence of TS-1 revealed a decrease in the activity at temperatures exceeding 40 ˚C. At 60 ˚C, the propene oxide selectivity on TS-1 was around 60% [47], while, Ti-MWW displayed a selectivity equal to 99.4% ± 0.2% at the same temperature. In case of the water concentration. they indicated an increase in the activity with the growth of the water concentration until 35 wt%, but the epoxide selectivity was not affected by the water concentration. These results antagonize with results obtained with TS-1; the epoxidation on TS-1 in methanol is affected negatively by the presence of water in the system [47]. The opposite behavior can be related to the need of a protic molecule to activate the active site of titanium [63]. In this case, the protic solvent helps to stabilize the hydrogen peroxide and the titanium active site interaction with the creation of a five-member ring [12,63,64]. Nonetheless, recent literature proposes that the positive effect of water originate from interactions with the silanol groups in the hydrophilic pores [34], as the effect of this molecule on the outer sphere of the titanium active site [30].

3.5. Titanium active site [VIII]

The reactor studies revealed important differences between the Ti-MWW and TS-1 catalysts both systems displayed to be active under comparable conditions. Nevertheless, it has been demonstrated that differences in the activity appears between solvents [11,30,34,63–66]. TS-1 is more active in methanol, while, Ti-MWW exhibits a higher activity in acetonitrile. However, both systems are active at the same ranges of temperature, pressure, flow rates and concentrations. The systems however display different responses to these parameters: e.g. water has a negative interaction with TS-1 decreasing the activity, while for Ti-MWW the increase of the water concentration indicates an increase in the activity. These different behaviors between titanium silicate catalysts invites to speculate whether the active sites of both materials are similar or not. Even if the titanium silicates can be synthetized in different ways as hydrothermal and grafting. They can have different structures as MFI, MWW, BEA, among others, titanium silicates are usually treated and analyzed as a group of materials behaving in the same way. In order to observe similarities and differences in the behaviors, extensive ex-situ and an in-situ spectroscopic studies were performed in this work. However, the ex-situ technique lacks flexibility to unveil interactions between the catalyst and the reactants. Therefore, it is important to analyze the system under dynamic conditions. In order to do this, in-situ modulation excitation ATR-FTIR spectroscopy was utilized. Specifically, modulation excitation infrared spectroscopy was a flexible tool being able to deliver real-time information of the reactant-catalyst interactions in the system.

Characterization of catalytic materials is usually performed ex-situ and in dry conditions. One of the important characterizations for our case is recording infrared spectra of the titanium silicates. The peak at 960 cm^{-1} indicates the presence of titanium in the framework (Figure 20A), more precisely the Ti-O-Si asymmetric vibration, which suggests that the differences in the structures observed between the MFI and MWW does not influence the basic vibration of the system. The MFI (TS-1) structure is shaped by a 10-member ring, while MWW displays a mix of 10- and 12-member ring structures.

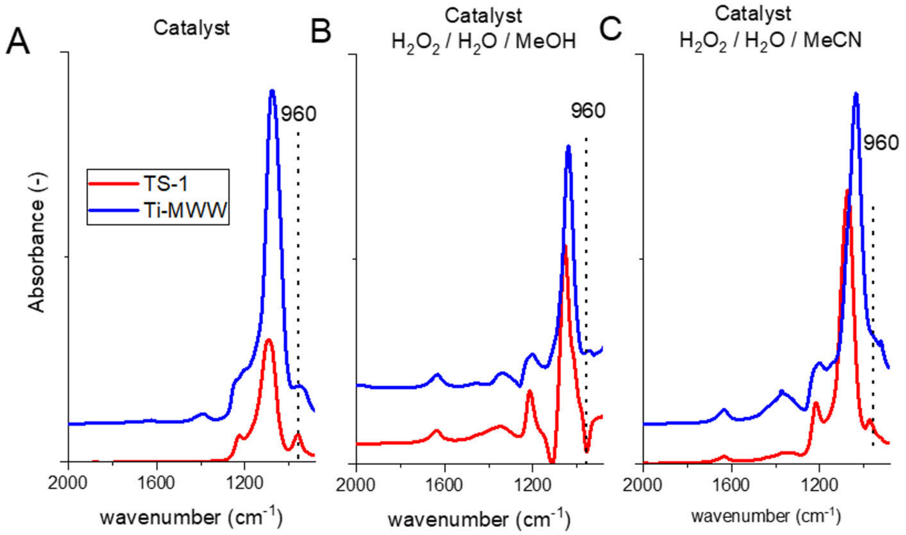


Figure 20. Ex-situ ATR-FTIR, catalyst (a), catalyst and 0.1 M H_2O_2 (50 w/v H_2O_2) in solvent (methanol (b) and acetonitrile (c)) 25 °C and 1 bar.

The study of the samples with ex-situ ATR-FTIR spectroscopy gave different results. Figure 20 shows the 960 cm^{-1} band ascribed for each catalyst as the Ti-O-Si asymmetric one. In order to observe this band, the catalyst was dried and measured under an inert atmosphere (Nitrogen). Figures 20B and 20C display the results when the same catalyst after been dried is humected with a mixture of hydrogen peroxide, water and solvent. When the solvent is methanol, it is possible to observe a decrease in the intensity of the 960 cm^{-1} band. However, Ti-MWW displayed a small shift to lower frequencies to c.a. 940 cm^{-1}. If the solvent is acetonitrile, these materials display a different behavior. TS-1 displays a shift of higher bands to 975cm^{-1}, while Ti-MWW exhibited a shift down to 925 cm^{-1}. The ATR-FTIR study shows changes in the peaks related to the Ti-O-Si vibration for each catalyst. The differences between the methanol and acetonitrile samples suggest interactions between the materials and the solvents.

Modulation excitation spectroscopy (MES) can be understood as a technique to obtain vibrational spectra of excited electronic states by modulating the reactant concentration and recording the transient infrared behavior. During an MES experiment, a reactant in a low and high concentration is modulated while the spectrometer is acquiring the spectra. As result of the response to the modulation, it is possible to classify the species as spectators and active species on the solid surface. Spectators are not affected by the stimulation while the active species are affected by the modulation. Active species follow the modulation with a time delay. The modulation data are obtained after the system has reached a quasi-steady state. The raw data are averaged in order to suppress the signal-to-noise ratio. These data sets are transformed from the time domain to the domain of the phase angle. Only signals following the fundamental vibration will display up in the phase-domain allowing to separate the active the spectator species. The time delay present in the active species is transformed to a phase delay, which allows to follow the elementary steps on the catalyst surface.

In order to perform the in-situ experiments, titanium silicate samples were deposited over a ZnSe crystal at room temperature (10 μm width). Each material was studied by using the in-situ ATR-FTIR spectroscopy modulating two solutions of different concentrations to observe the interactions of the compounds at different concentrations with the catalyst layer. This technique allows the observation of changes in the vibration of the titanium sites (~960 cm^{-1}) due the interaction of the site with the different reactants modulated. The phase angle consents the observation of the dynamic interaction of each compound in the reaction with the titanium site.

The methanol and acetonitrile interactions were analyzed due to the differences in the performances for TS-1 and Ti-MWW catalysts. The study of the solvent was performed modulating the protic (methanol) and the aprotic solvent (acetonitrile) in the presence of the apolar (dichloromethane) solvent. Dichloromethane was chosen as an apolar solvent due to viscosity, dielectric constant and low interactions with titanium silicates.

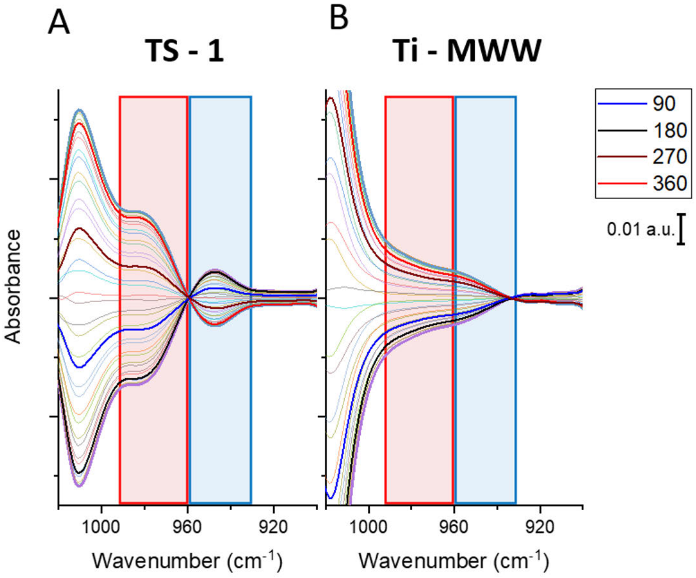


Figure 21. Methanol-solvent interaction MES experiments. 1wt%MeOH/DCM vs DCM over A) TS-1 B) Ti-MWW at 30 °C and 1 bar.

Figure 21 illustrates the different behaviors of the titanium silicates. The Ti-MWW catalyst displayed a passive behavior in the presence of methanol, while TS-1 exhibited different behaviors; it is possible to observe the two maxima in the TS-1 spectrum, the first one appearing at 950 cm^{-1} in the 180° phase angle, and the second one at 980 cm^{-1}. This observation indicates a clear interaction of methanol with the active titanium site, as the system reaches a quasi-steady state. First the vibration at 960 cm^{-1} is displaced to a lower frequency (950 cm^{-1}) when the concentration of methanol is at a maximum, but the concentration of methanol decreases, it is possible to see an increase in the vibration (980 cm^{-1}).

These results suggest a degeneration of the Ti-O-Si bond (950cm^{-1}) [18,19,67], which is can be related to a hydrogen bonding between the methanol and the Ti-O-Si bond. However, the presence of excitation of 980 cm^{-1}, suggests the subsequent production of O_3Si-OH groups, accordingly to titanium silicate catalyst [18,19,67]. This observation could be strongly related to the surface reaction mechanism proposed by Russo et al. [12]. In that mechanism, the reaction between methanol and the titanium site is contemplated. If we correlate the interpretation of the vibration observed with the phase modulation, it is possible to observe a two-step process, where the Ti-O-Si bridges are degenerated to react further with methanol.

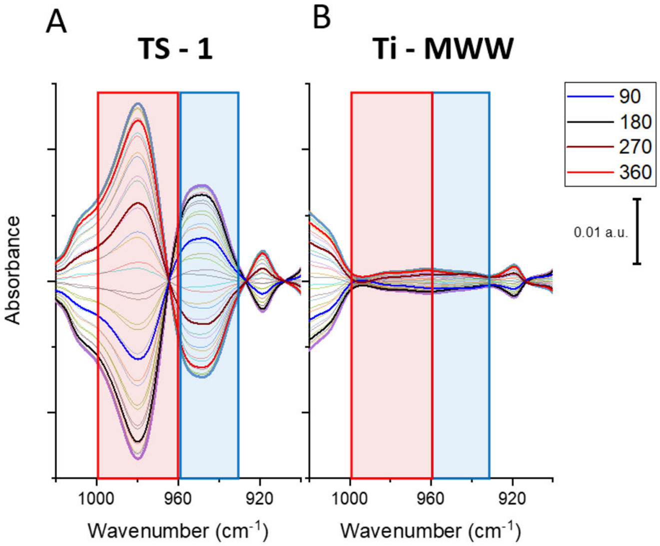


Figure 22. Solvent interaction of acetonitrile in MES experiments. 1wt%MeCN/DCM vs DCM over A) TS-1 and B) Ti-MWW at 30 °C and 1 bar.

The results from the modulation of the acetonitrile concentration are displayed in the Figure 22. The results indicate a clear interaction between the solvent and the TS-1 catalyst. The Ti-MWW exhibited changes during the modulation, however, the changes are not big, probably the interactions of acetonitrile and the titanium sites are weak.

As in the previous solvent experiment, TS-1 presented the peak at ~950 cm^{-1} suggesting the degeneration of the asymmetrical Ti-O-Si. Nevertheless, the presence of the ~980 cm^{-1} vibration is a controversial element, because, acetonitrile cannot deliver a hydrogen like methanol to produce silanols. Nevertheless, this vibration has been defined as [Si-O$^{\delta-}$...Ti$^{\delta+}$] previously [68,69]. This interpretation brings a general explanation to the methanol and acetonitrile observation ~980 cm^{-1} band as [Si-O$^{\delta-}$...Ti$^{\delta+}$] and suggest a driving force to produce the hydroperoxo species between hydrogen peroxide and the active titanium site. The absence of interactions between Ti-MWW and the solvents (methanol and acetonitrile) suggests differences in the structures of the active sites.

After the solvent study, the next step was the investigation of water-catalyst interactions, because the recent literature emphasizes the importance of water on the reaction mechanism [30,32]. The effect of water was studied in each catalyst modulating 2 wt% H_2O/MeCN vs 1 wt% H_2O/MeCN. The primary results are displayed in Figure 23. It is possible to extract from the phase graph the presence of water-catalyst interactions for both the titanium silicates studied. TS-1 and Ti-MWW displayed the ~980 and the ~950 cm^{-1} vibration bands, however, and TS-1 displayed an extra band at ~970 cm^{-1}, which can be related to the presence of a terminal silanol involved in the hydrogen bonding [67].

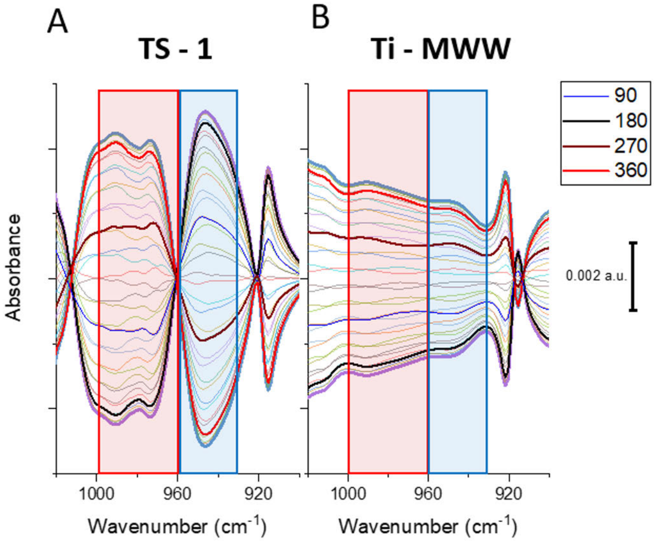


Figure 23. Water interaction MES experiments. 2wt%H_2O/MeCN vs 1wt%H_2O/MeCN over A) TS-1 and B) Ti-MWW at 30 °C and 1 bar.

After the water modulation the hydrogen peroxide study was performed. The modulation program of hydrogen peroxide was 2wt% H_2O_2/2wt% H_2O/MeCN vs 1wt% H_2O_2/2wt% H_2O/MeCN. The results indicate that the interaction between the hydrogen peroxide and the active titanium site is very much material dependent, against the recent literature that claims that the reversibility of the hydrogen peroxide-titanium interaction is dependent on the solvent [30]. However, as shown in Figure 24, the TS-1 catalyst structure displayed modulation in the presence of the hydrogen peroxide indicates reversibility. Figure 24 shows the presence of an opposite behavior compared to the previous modulation experiments. In this case, the ~970 cm^{-1} band indicates the production of silanol groups, while the concentration of hydrogen peroxide is high, followed by an increase in the degenerated Ti-O-Si, as the concentration of hydrogen peroxide decreases. Therefore, the system generates silanol groups as the concentration increases and as the concentration of hydrogen peroxide decreases, the Ti-O-Si groups are form again. For Ti-MWW, the modulation is not present suggesting an irreversible hydrogen peroxide interaction.

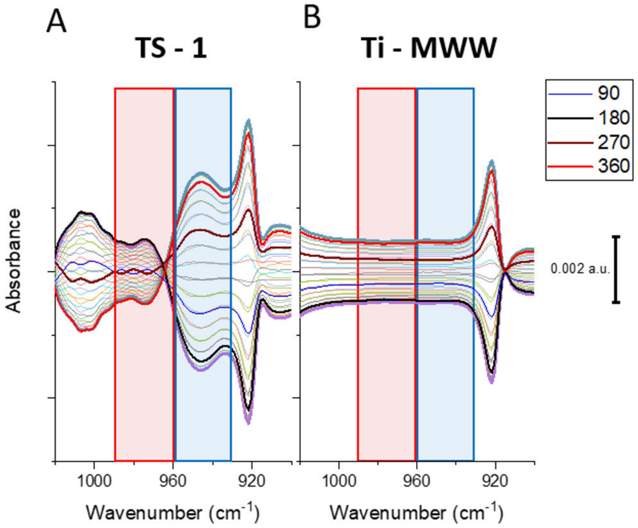


Figure 24. Hydrogen peroxide interaction MES experiments. 2wt%H_2O_2/2wt%H_2O/MeCN vs 1wt%H_2O_2/2wt%H_2O/MeCN over A) TS-1 and B) Ti-MWW at 30 °C and 1 bar.

The results from the spectroscopic studies suggest multiple interactions between TS-1 and the solvents. The larger amplitude of acetonitrile compared to methanol indicates more interactions between the Lewis base and the Lewis acid centra (titanium active site). However, even if Ti-MWW displayed to be more active in acetonitrile, the catalyst-solvent interaction in this material was not observed. The study in the presence of water indicated interactions of TS-1 and Ti-MWW with water. During the water experiments, the structure of the Ti-MWW signals observed were the closest to the TS-1 signal structures. This can be correlated to the positive interaction effect of increasing the water concentration in the epoxidation system in the presence of Ti-MWW. Moreover, the interactions between hydrogen peroxide and the titanium silicates are different. TS-1 presents reversibility, due the oscillations observed, while Ti-MWW interacted in an irreversible manner with the oxidant. All the results in the laboratory reactor level presented in the actual work and the previous work performed with TS-1, along with the spectroscopy studies suggest that the structures of the titanium active sites in TS-1 and Ti-MWW are different.

4. Conclusions

The epoxidation of light olefins on titanium silicates was studied in a broad range of conditions for single olefins and olefin mixtures. The observations on the reactor level were combined with a study of the catalyst materials. Due to the different behaviors observed for titanium silicates, a study of the active sites was performed to analyze the reactant-catalyst interactions.

The results of single olefin epoxidation were affected by the molecular structure. Ethene and propene behaved similarly with a high stability and epoxide selectivity; nonetheless, 1-butene displayed a higher selectivity than the shorter olefins but a lower activity. Isobutene displayed a better stability than 1-butene, however, the epoxide displayed to be highly reactive, giving secondary by-products. Therefore, the chain length of the olefin affects the stability of the system, however, increasing the selectivity and the double bond position can increase the epoxide reactivity.

The epoxidation of olefin mixtures was affected by the number of olefins in the mixture. The binary mixtures of ethene-propene exhibited low epoxide selectivities, while the propene-1-butene mixtures displayed higher selectivities but lower than 1-butene. The ternary mixtures (ethene, propene and 1-butene) were highly selective to the epoxides. It was observed that in all the mixtures with 1-butene present, the stability of the catalyst was improved. The increase in the stability was related to changes in the concentrations of the compounds on the catalyst surface. The utilization of olefin mixtures gives an opportunity for process intensification, because a separation step is eliminated and a more selective epoxidation is achieved in this way.

The study of titanium silicate materials showed the differences among this family of materials. TS-1 demonstrated to be more active in methanol, while Ti-MWW performed better in acetonitrile. Nevertheless, even working with different solvents, both catalysts were stable and selective under comparable conditions. Moreover, the investigation of TS-1 and the Ti-MWW materials demonstrated that it is possible to perform the epoxidation of propene with similar activities but without by-products on Ti-MWW. The use of acetonitrile allowed a more selective epoxidation process due to the elimination of the methoxy compounds formed in the reaction with methanol as the solvent.

From the studies of TS-1 and Ti-MWW it was possible to identify differences in how the systems were affected by the reaction and reactor parameters. These observations were correlated with a spectroscopic study to observe the interactions of the reactants with the catalyst. The adsorption of hydrogen peroxide in modulation experiments revealed that it is a reversible process depending on the material rather than the solvent as has been suggested in the literature. Nonetheless, the interactions exhibited to be different between TS-1 and Ti-MWW, because of that, it is highly probable that the active sites of titanium are different in these materials.

5. Future perspectives

The results achieved through this endeavor possess the potential for significant expansion, yet I find it crucial to underscore the specific domains in which this project could be extended in future, thereby amplifying the importance of the diligent work conducted.

A notably substantial outcome of the comprehensive effort of this thesis resides in the assembly of an extensive repository of experimental conditions encompassing four distinct olefins (ethene, propene, 1-butene, and isobutene), complemented by an impeccably developed trickle bed reactor model. Capitalizing on these amassed datasets to forge a comprehensive reaction mechanism stands as a pivotal contribution to the scientific landscape, aiming to pinpoint the utmost precision in elucidating complex reaction pathways. This endeavor could be further bolstered by harnessing the potential of linear free energy relationships, which could emerge as a pivotal component in this overarching pursuit.

In order to fortify and round out the proposed mechanisms, subjecting it to rigorous scrutiny through spectroscopic data becomes imperative. The broad-spectrum application of modulation excitation spectroscopy, involving all the reactants at the laboratory reactor scale, followed by judicious employment of Density Functional Theory (DFT) calculations, holds promise in elevating the level of confidence in the proposed mechanism.

Lastly, a notable avenue for exploration involves delving into shaped catalysts, a prospect ripe for investigating the influence of additives on the reaction system. The observed dip in activity and selectivity stemming from the adoption of pellets or extrudates could potentially be mitigated through the strategic incorporation of additives. Experimental and modelling activities devoted to pellets and extrudates would reveal the interaction of reaction kinetics and mass transfer, thus contributing to process scale-up.

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