



MAX-PLANCK-GESellschaft



- Master Thesis -

Synthesis and characterization of silica-supported vanadium oxide catalysts for oxidative dehydrogenation of propane

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Preface and Acknowledgement

The work presented in this report was carried out from February to June 2014 at the Department of Inorganic Chemistry at the Fritz-Haber-Institut der Max-Planck-Gesellschaft in Berlin. Herein I would like to give thanks to the people who have helped me and made this internship very interesting and rewarding.

Firstly, I would like to thank Professor Dr. Robert Schlögl for giving me the opportunity to carry out my internship in this prestigious institute. I would also like to thank my two supervisors, Dr. Annette Trunschke and Pia Kjør Nielsen, for helping and guiding me during these 5 months and for making me want to do a PhD thesis in catalysis. I would also like to thank the people who have helped me in the characterization of my samples: Jasmin Allan (XRD and TGA), Dr. Frank Girgsdies (XRD), Maike Hashagen (BET), Achim Klein-Hoffmann (XRF), Elif Ider (XRF), Dr. Johannes Noack (Raman spectroscopy), Jutta Kröhnert (IR spectroscopy), Gisela Weinberg (SEM and EDX). Thanks to Dr. Gregor Wowsnick who has helped me in my several syntheses and more particularly with the Schlenk line. Not forgetting all people working in the FHI for their kindness and for making this internship a great and rewarding experience.

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Chapter 1.

General Introduction

1.1 The Fritz-Haber-Institute ^[1, 2]



The Fritz Haber Institute (FHI) is a science research institute with focus on physical chemistry and chemical physics. The FHI was founded in 1911 in Berlin (Germany), firstly under the name the Kaiser Wilhelm Institute for Physical Chemistry and Electrochemistry. In 1953, the institute was incorporated in the Max-Planck-Gesellschaft (MPG) and renamed for its founding director, Fritz Haber. The FHI is the oldest and also the most distinguished institute of the MPG with 7 affiliated Nobel Prize laureates (Max von Laue, Fritz Haber, James Franck, Ernst Ruska, Heinrich Wieland, Eugene Wigner and Gerhard Ertl). For 100 years of research, a lot of topics were covered by the FHI: chemical kinetics, reaction dynamics, colloid chemistry, atomic physics, spectroscopy, surface chemistry, surface physics, chemical and molecular physics, theoretical chemistry and material science. Today, the FHI, directed by the board of directors (Prof. Martin Wolf is currently the chairman of the board), is composed of 5 departments. One of them is the Inorganic Chemistry (Anorganische Chemie; AC) department directed by Prof. Robert Schlögl where several topics are studied by six research groups.

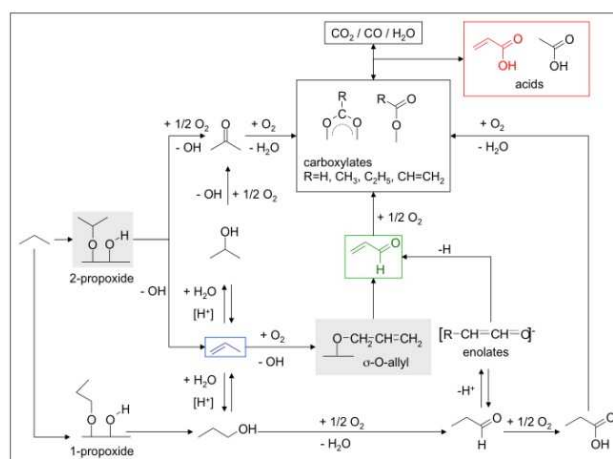
1.2 Background and scope of work

The activation of small alkane molecules extracted from natural gas or renewable resources regains higher scientific interest since it offers a promising alternative to produce high value chemicals without the use of petroleum.^[3] For instance, oxidative dehydrogenation (ODH) of light alkanes (C1 to C4) is an attractive alternative to the conventional cracking and dehydrogenation pathways to produce olefins. Today, the catalyzed ODH plays a leading role in the production of intermediates and monomers for the polymer industry (Table 1).^[3] However, ODH of alkanes to the corresponding olefins or selective oxidation to functionalized monomers generally suffer from insufficient selectivity due to consecutive and parallel reactions (Scheme 1). To find new approaches to improve ODH reaction efficiency, knowledge about the involved reaction mechanism is required. The purpose is to convince companies to abandon well-established technologies (steam cracking, fluid-catalytic-cracking, catalytic dehydrogenation) which are more energy-demanding, less selective and quickly deactivated (coking).^[4] Vanadium oxide species supported on silica have been frequently studied as model catalysts in ODH. In

previous studies, silica-supported vanadium oxide catalysts show good results despite a low activity which is needed to facilitate mechanistic studies: high yield and good selectivity to propene and oxygenates have been reported.^[5, 6]

Chemical	Capacity [Mt a ⁻¹]	Oxidant					
		Air	O ₂	HNO ₃	Cl ₂	ROOH	H ₂ O ₂
Terephthalic acid	44	X					
Formaldehyde	19	X					
Ethene oxide	18		X				
1,2-Dichloroethane	18	X	X		X		
Propene oxide	8				X	X	X
Cyclohexanone	6		X	X			
Vinyl acetate	6		X	X			
Acrylonitrile	6		X				
Styrene (ex PO/SM) ^[a]	5		X	X			
Phenol/acetone	5		X				
Phthalic anhydride	5		X				
Acrylic acid	5		X				
MTBE (ex PO/TBA) ^[a]	4			X			
Adipic acid	3				X		
Maleic anhydride	2		X				
Hydrogen cyanide	2		X				

Table 1. Chemicals produced by means of oxidation. Acrylic acid is an important monomer.



Scheme 1. Reaction network in selective oxidation of propane to acrylic acid.^[7]

The application of porous materials as supports for heterogeneous catalyst has been proven to be very useful.^[8] Although the chemical species at the support surface have an impact, another parameter has to be considered: the surface texture of the support. Indeed, according to the literature,^[9] experiments carried out and results presented in this report show that the texture also affects the types of dispersed catalytically active species in the resulting catalyst. Therefore, optimization and control of the surface morphology to obtain homogeneity of the surface are of high importance. SBA-15, a mesoporous silica material with a surface area up to 1000 m²/g and a considerable thermal stability is used. However, SBA-15 is known to contain micropores in the amorphous silica walls (more details in paragraph 1.3) causing inhomogeneity in the surface texture.^[10] The decrease of the microporosity results in a more uniform surface and a less complex final system, providing the opportunity to perform catalytic tests on the supported active vanadia species. Other studies highlighted the influence and the impact of the addition of molybdenum oxide as promoter on the catalytic activity of supported vanadium oxide catalysts.^[11, 12]

This Master Thesis project is comprised of two parts: the first one is about the preparation of SBA-15 with different textures and the second one is about the synthesis and characterization of silica-supported vanadium oxide catalysts. A third part had been started few weeks ago about silica-supported molybdenum oxide catalysts. It will be briefly described and the first results will be presented in the appendix (pages 9 and 10).

Two methods of deposition of vanadium on silica (SBA-15) are described in the literature: the ion exchange and the grafting. These two techniques are very different (Table 2) but no study to compare them directly has been made so far. During this project, ion exchange and grafting were done in parallel both on SBA-15 with different texture/porosity and the catalysts obtained were compared (structure, loading, catalytic activity).

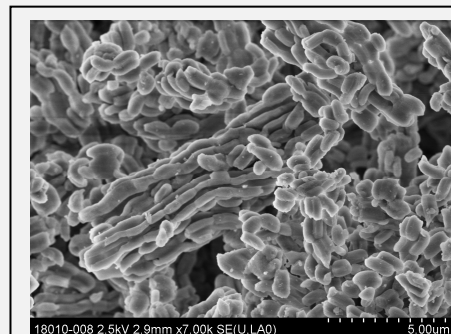
Through syntheses and characterization of several catalysts, impacts of surface morphology and method of deposition on silica-supported vanadia catalysts for ODH of propane have been highlighted.

1.3 Preparation of the support^[13]

SBA-15^[14]

SBA-15 (Santa Barbara Amorphous) is a mesoporous silica material generally used as catalysts support, absorbent, drug delivery material or for separation techniques. Several characteristics make this material very interesting: a large surface area, thick framework walls, a high thermal stability, highly uniform, cylindrical and ordered mesopores. The SBA-15 structure is composed of hexagonal pores (7-10 nm) in a 2D array with long 1D channels interconnected by small micropores. Modifications of this silica material (pore size, microporosity) can be controlled with the temperature, the synthesis time and the use of co-solvent or swelling agents.

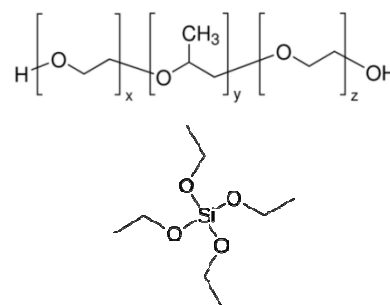
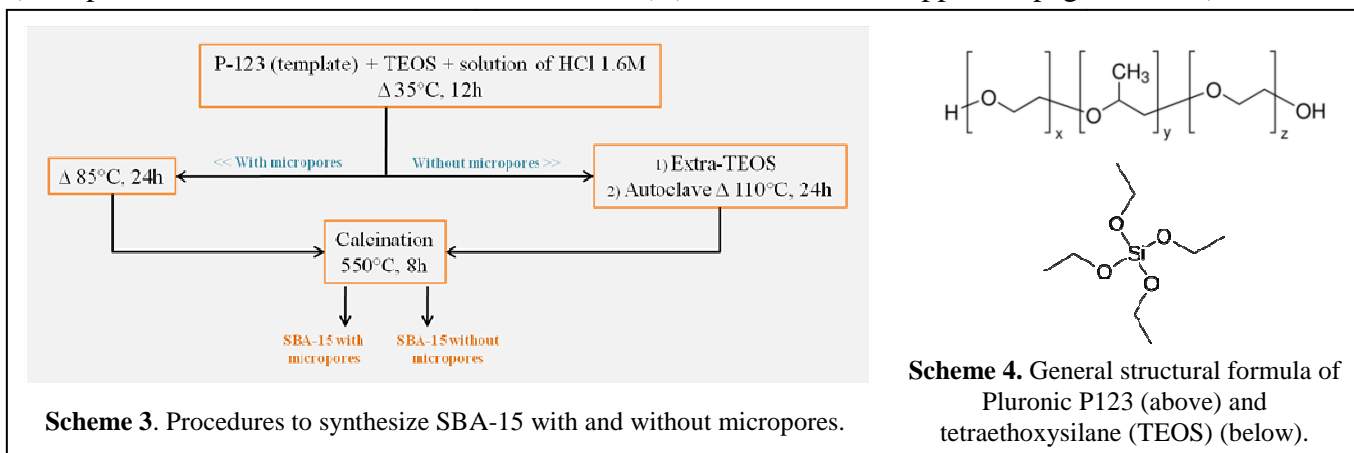
SBA-15 (Scheme 2) has been selected for this study because of these properties which are advantageous for catalytic reactions. Nevertheless, some drawbacks could be quoted. Firstly, SBA-15 is not perfectly stable in water and a slight dissolution may occur. Secondly, the synthesis requires advanced equipment and the mixture must be heated for several hours which could implicate problem in homogeneous heating for industrial scale synthesis. Thirdly, the material is very fluffy and electrostatic which makes it not very convenient to manipulate.



Scheme 2. SEM of SBA-15 with micropores (5.00 μm).

The preparation of the support was carried out in a LabMax Mettler-Toledo (see Appendix page 4) where were mixed Pluronic P123 (a triblock co-polymer $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ with EO for ethylene glycol and PO for propylene glycol) and TEOS (Scheme 4) as silica source in an acidic solution (further details in the Experimental Section). Then the calcination was undertaken with a rotating furnace at 550°C for 8h in O_2/Ar ratio 20/80. Concerning the SBA-15 without micropores, the heating step of the preparation

was achieved in several autoclave vessels placed in a furnace at 110°C under hydrothermal conditions (both procedures are described with the Scheme 3) (further details in Appendix pages 4 and 5).



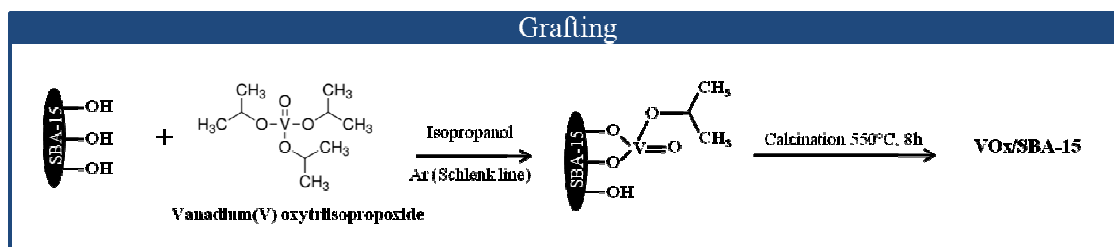
Scheme 4. General structural formula of Pluronic P123 (above) and tetraethoxysilane (TEOS) (below).

1.4 Deposition of vanadium oxide on SBA-15

Two (among others) methods of deposition are described in the literature and were used for the preparation of supported vanadium oxide catalysts: grafting^[15] and ion exchange.^[16, 17]

1.4.1 Grafting

This method (Scheme 5) takes only 2 days but requires more advanced equipment. Indeed, the use of air-sensitive precursor requires the use of a Schlenk line to work under inert atmosphere. See Experimental Section (page 19) for further details of the sample preparation.

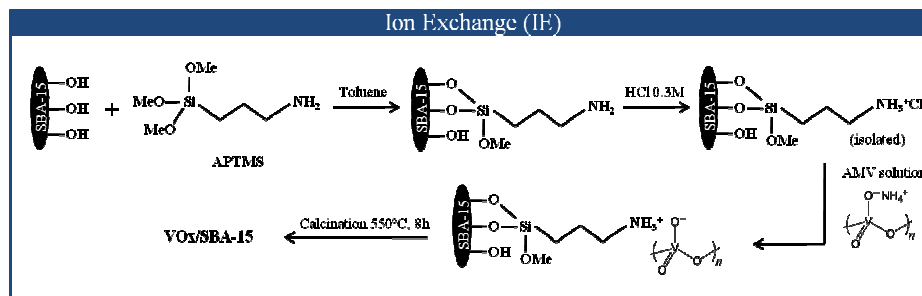


Scheme 5. Description of the grafting method to disperse vanadium on SBA-15.

1.4.2 Ion Exchange

This second method (Scheme 6) is rather easy to implement (no special vessel needed) but it takes one week of work. The first step is an organofunctionalization of SBA-15's hydroxyl groups using 3-aminopropyltrimethoxy-silane (APTMS). Then, the corresponding ammonium salt is formed using HCl treatment (protonation). Afterwards, ammonium metavanadate NH_4VO_3 (AMV) is incorporated to carry out the anion exchange reaction. Finally, the thermal treatment of the ionic species yields the final supported vanadia catalyst. During the calcination step, all organic residues and chlorine, sodium, NH_3 are completely removed from the pores and vanadia reacts with silanol groups to be anchored onto the

surface of the support. This technique is also valuable for the preparation of supported molybdenum oxide catalysts. See Experimental Section (page 19) for further details of the sample preparation.



Scheme 6. Description of the ion exchange method to load vanadium on SBA-15.

1.4.3 Comparison of these two methods

Herein below, a table sums up differences in procedures between these two deposition methods.

Parameter	ION EXCHANGE	GRAFTING
Solvent	Aqueous	Non-aqueous (isopropanol)
Duration	~1 week	~36h
Contact time between support and precursor	~20h	2h
Precursor	Inorganic non-air-sensitive precursor: ammonium metavanadate	Organic air-sensitive precursor: vanadium oxytriisopropoxide
Implementation	Classic vessels + rotary calciner	Schlenk line + rotary calciner

Table 2. Comparison of two procedures: ion exchange and grafting.

1.5 Characterization of the support and the catalysts

Various techniques brought different information on the properties of the support material and the final model catalysts (more details in Appendix pages 6 and 7).

- Physical properties: Homogeneity of pores structure and morphology
 - N₂ sorption isotherms with data analysis
 - X-ray Diffraction (XRD)
 - Electron Microscopy (SEM) (not systematic)
 - Thermogravimetric Analysis (TGA)
- Coordination environment of the metal oxide species
 - Infrared spectroscopy (IR)
 - Raman spectroscopy (Raman)
- Chemical contents: Elemental composition
 - X-ray Fluorescence (XRF)
 - Energy Dispersive X-ray spectroscopy (EDX) (not systematic)
- Catalytic performance in ODP (not systematic)

Chapter 2.

SBA-15: Results & discussion

The support synthesis is the first and one of the most important steps of the project. Several batches of SBA-15 were needed to prepare all catalysts. In order to avoid batch effect, the syntheses were carried out in large quantities in a reactor (Mettler-Toledo LabMax) where stirring, temperature and time of reaction were accurately controlled (see Experimental section p.19). Four syntheses were performed during this 5-month project: two syntheses of SBA-15 with micropores and two of SBA-15 without micropores. Characterization (BET, XRD, TGA) results of each sample prove a good reproducibility between these different batches (Table 3, Figure 1). Some distinct -and logical- differences between these two kinds of SBA-15 are also highlighted with characterization: a significant loss of total surface area and micropore-area is observed for the SBA-15 without micropores (N_2 adsorption isotherms analysis). However, the “SBA-15 without micropores” is not a good name and to be closer to reality it would be better to name it “SBA-15 with reduced micropores” (but the first name will be used in this report).

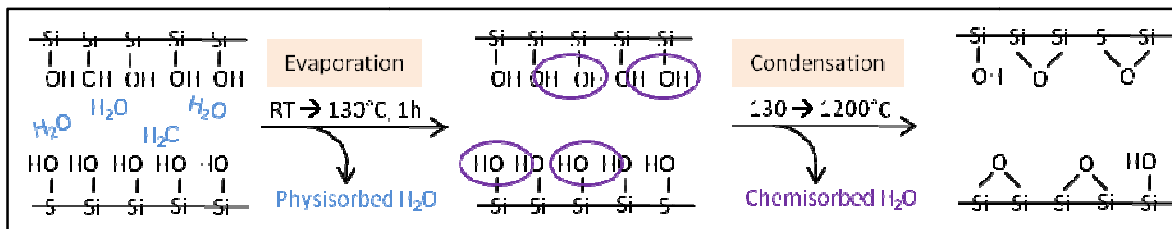
The XRD data (Figure 1a) show a peak at 1° on the abscise axis -for each sample- which indicates a very regular distance between mesopores of the support and allow to measure the distance between mesopores with Bragg’s law $2d\sin\theta = n.\lambda$ (*). The adsorption isotherms evidence the microporosity difference. At a same partial pressure of N_2 , more N_2 is adsorped in SBA-15 with micropores because of the filling of micropores with the gas (Figure 1b).

(*) d = the interplanar distance (distance between two crystallographic plans) ; θ = the scattering angle ; λ = X-ray wavelength ; n = an integer determined by the order given

	μ pores	Surface area (m^2/g)	μ pore surface area (m^2/g)	% of μ pores	Total pore volume (cm^3/g)	Si-OH groups (Si-OH/ nm^2)
SBA-15 S1	Yes	1044 (± 10)	358 (± 6)	34	1.24 (± 0.01)	2.9
SBA-15 S2	No	482 (± 12)	86 (± 6)	18	0.95 (± 0.06)	2.3
SBA-15 S3	Yes	1025 (± 3)	332 (± 0.4)	32	1.22 (± 0.01)	2.9
SBA-15 S4	No	502 (± 9)	101 (± 3)	20	0.97 (± 0.02)	2.7

Table 3. Prepared SBA-15.

TGA (Figure 1c) analysis allows quantification of Si-OH groups on SBA-15. The first step corresponds to heat until $130^\circ C$ for 1h to evaporate physisorbed water. Then, the temperature is increasing until $1200^\circ C$ to remove chemisorbed water resulting from Si-OH condensation (Scheme 7).



Scheme 7. Schematic presentation of what happened during TGA analysis.

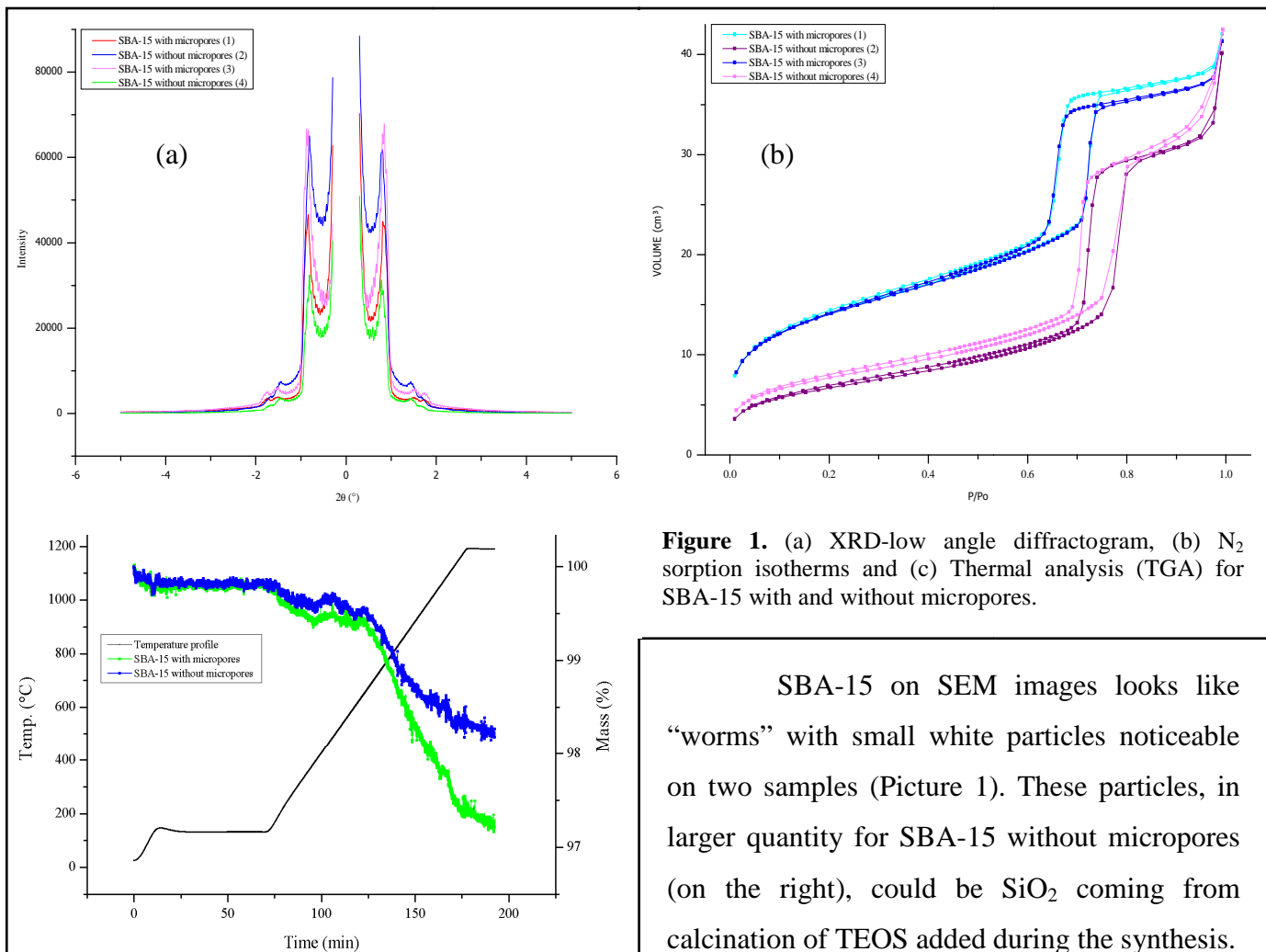
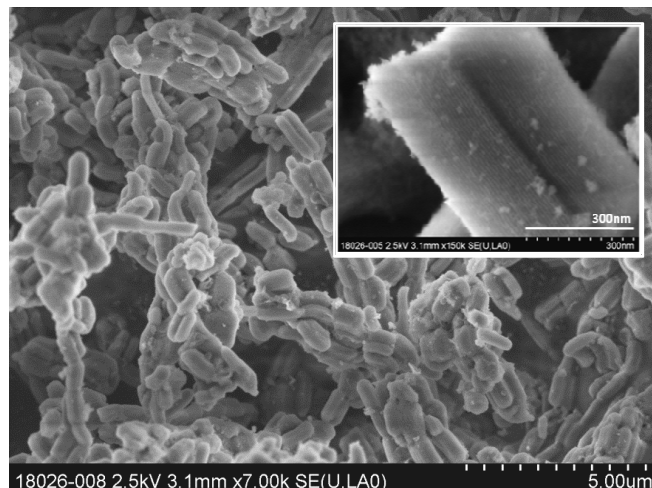
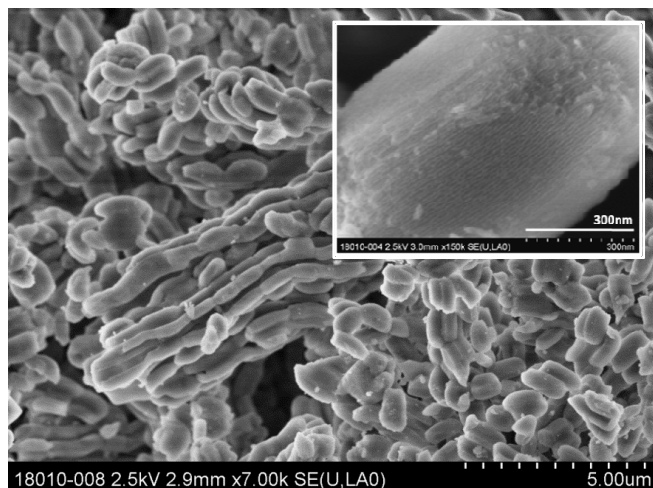


Figure 1. (a) XRD-low angle diffractogram, (b) N₂ sorption isotherms and (c) Thermal analysis (TGA) for SBA-15 with and without micropores.

SBA-15 on SEM images looks like “worms” with small white particles noticeable on two samples (Picture 1). These particles, in larger quantity for SBA-15 without micropores (on the right), could be SiO₂ coming from calcination of TEOS added during the synthesis.



Picture 1. SEM of SBA-15 with micropores (left) and SBA-15 without micropores (right).

Chapter 3.

Silica-supported vanadium oxide catalysts: Results & discussion

During this 5-month project 14 catalysts VO_x/SBA-15 were prepared but only 6 were selected to discuss the impact of texture and preparation procedure on the resulting catalysts.

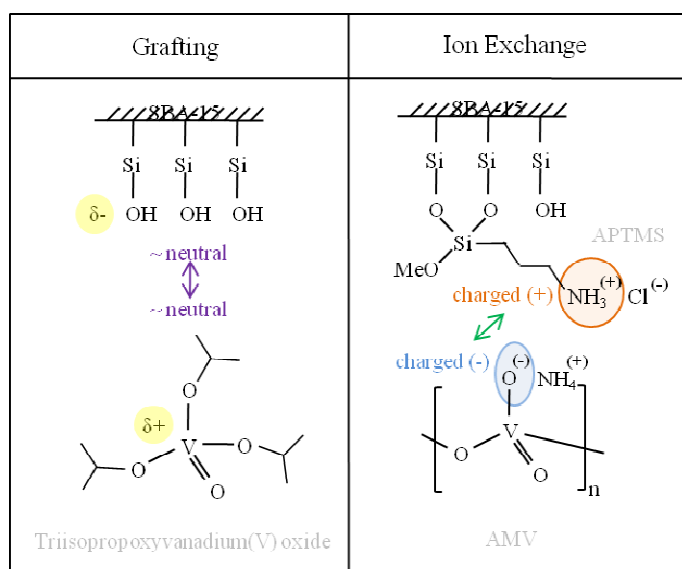
VO _x /SBA-15	μpores	Method of dispersion	V loading (wt %)	V loading (atoms/nm ²)	Surface area (m ² /g)	μpores area (m ² /g)	% of μpores	SBA-15 mother		
								Area (m ² /g)	μpores area (m ² /g)	% of μpores
(1)	Yes	Grafting	4.61	0.527	860.2	240.3	27.9	1044 (±10)	358 (±6)	34
(2)	Yes	Grafting	10.5	1.20	495.7	86.1	17.4	1044 (±10)	358 (±6)	34
(3)	No	Grafting	4.74	1.13	380.7	51.8	13.6	482 (±12)	86 (±6)	18
(4)	Yes	IE	7.85	0.881	524.4	128.9	24.6	1044 (±10)	358 (±6)	34
(5)	Yes	IE	5.12	0.574	559.5	149.4	26.7	1044 (±10)	358 (±6)	34
(6)	No	IE	4.12	1.04	367.6	53.8	14.6	482 (±12)	86 (±6)	18
(8)	No	IE	4.25	1.07	358.2	46.5	13	482 (±12)	86 (±6)	18
(9)	Yes	IE	7.94	0.891	490.5	114.9	23.4	1044 (±10)	358 (±6)	34

Table 4. Prepared VO_x/SBA-15 catalysts (more catalysts in Appendix page 8).

3.1 Influence of the solvent on the porosity

The analysis of adsorption isotherms of the catalysts (1) and (5) highlight a significant variance between total surface area and micropore area of both whereas these two catalysts (from the same SBA-15 mother) have micropores and the same vanadium surface density coverage (0.527 and 0.574 atoms/nm² respectively). The main difference between catalysts (1) and (5) is the method of preparation. The (1) was prepared by grafting whereas the (5) was prepared by ion exchange technique. There are several dissimilarities between these dispersion techniques but especially one could explain this variation of area and micropores area: the solvent. Previous studies showed that SBA-15 is quite unstable in water and, despite their thick walls, a slight dissolution of the SBA-15 could be observed.^[18] More than a real dissolution, a kind of homogenization happens in water i.e. results in a smoother support.^[19] The comparison of the experiments (1) and (5) tends to confirm that. Hence, a higher loss of (micro-)porosity is observed for the catalyst (5) prepared in water than the catalyst (1) prepared in isopropanol. Another factor could explain the decrease of micropore area; pore-blocking with vanadium species. With IE, the contact time between the support and the vanadium is higher (overnight for IE whereas only 2h for grafting), so vanadia species have more time to diffuse in micropores. Moreover, the presence of APTMS on the surface and in micropores may allow a better diffusion/attraction of vanadium thanks to the charged environment (Scheme 8).

However, the comparison of catalysts (3) and (6) shows that these observations are only valuable for catalyst formulated with SBA-15 with micropores. These two last catalysts, (3) and (6), are prepared on a support without micropores, have the same vanadium surface coverage (1.13 and 1.04 atoms/nm² respectively) and have the same surface area and micropore area, eventhough they were prepared with different dispersion techniques. This is expected since neither surface smothering nor (micro)pore blocking could play a role on a support without micropores.



These observations lead to the conclusion that the method of deposition has an impact on the microporosity and on the surface area of catalysts prepared on SBA-15 with micropores. Consequently, it is preferable to use SBA-15 without micropores in aqueous media to obtain a better stability of the support (Figure 2).

3.2 Variation of the vanadium dispersion depending on the preparation

The two methods of deposition of vanadia species are very different and their impact on the porosity has been discussed in the part above. Another impact of the applied technique was found on the vanadium species dispersed on the SBA-15 surface. *In situ* Raman spectroscopy was carried out at calcination temperature (550°C) to be sure there is no water and to study catalysts in their activation phase. Analysis of *in situ* Raman spectra (Figure 3) shows some differences between relatively similar

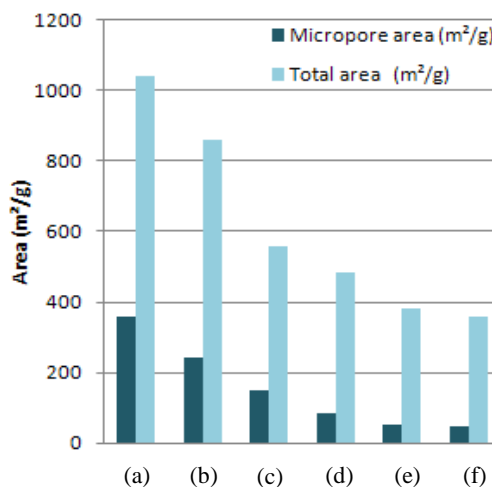


Figure 2. Ratio micropores area/total surface area for:

- (a) SBA-15 S1 with micropores (mother of 1 and 5)
- (b) VO_x/SBA-15 (1) with micropores and from grafting
- (c) VO_x/SBA-15 (5) with micropores and from IE
- (d) SBA-15 S2 without micropores (mother of 3 and 6)
- (e) VO_x/SBA-15 (3) without micropores and from grafting
- (f) VO_x/SBA-15 (6) without micropores and from IE.

Scheme 8. Schematic attraction of the precursor for the support in grafting (left side) and ion exchange (right side).

samples except the preparation method. Indeed, the comparison of Raman spectra of catalysts (3) and (6) at 550°C reveals a large domain of 2D species (at 158 and 272 cm^{-1}) for the $\text{VO}_x/\text{SBA-15}$ (3) prepared by grafting whereas there is no peak in this range for $\text{VO}_x/\text{SBA-15}$ (6) prepared by ion exchange. In comparison with V_2O_5 Raman reference spectrum, these two peaks correspond to skeleton bent vibration of V_2O_5 (at 142 cm^{-1} for pure V_2O_5) and bending vibration of O-V-O (2D) (at 282 cm^{-1} for pure V_2O_5).^[20] These peaks highlight a less homogeneous dispersion of vanadium species for the catalyst (3) prepared by grafting. The most important peak, proof of a good deposition and the presence of active species in catalysis, is situated at around 1038 cm^{-1} (991 cm^{-1} for pure V_2O_5) and corresponds to stretching vibration of vanadyl V=O bond. A slight shift between pure V_2O_5 and SBA-15-supported VO_x can be observed for each peak certainly due to interaction with the support.

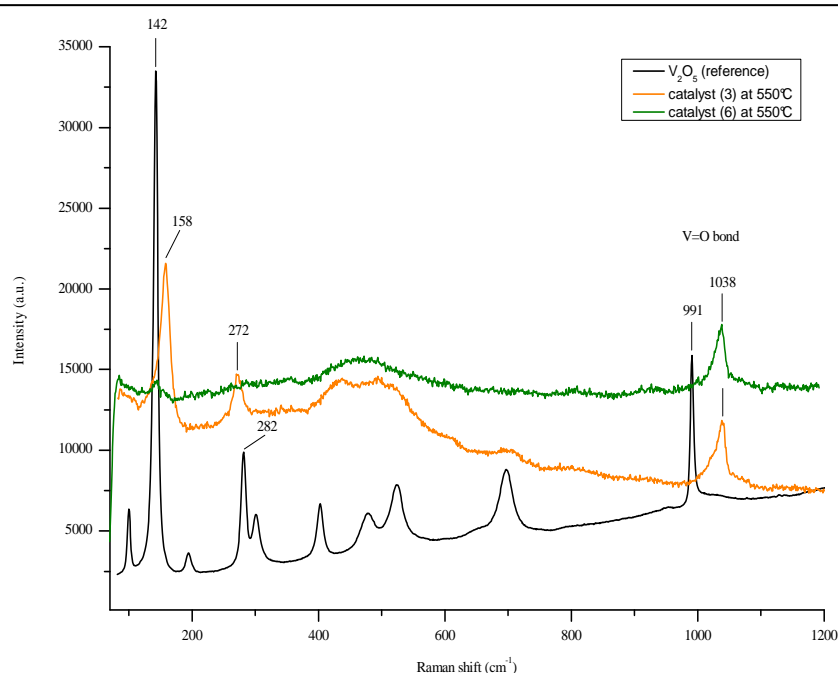
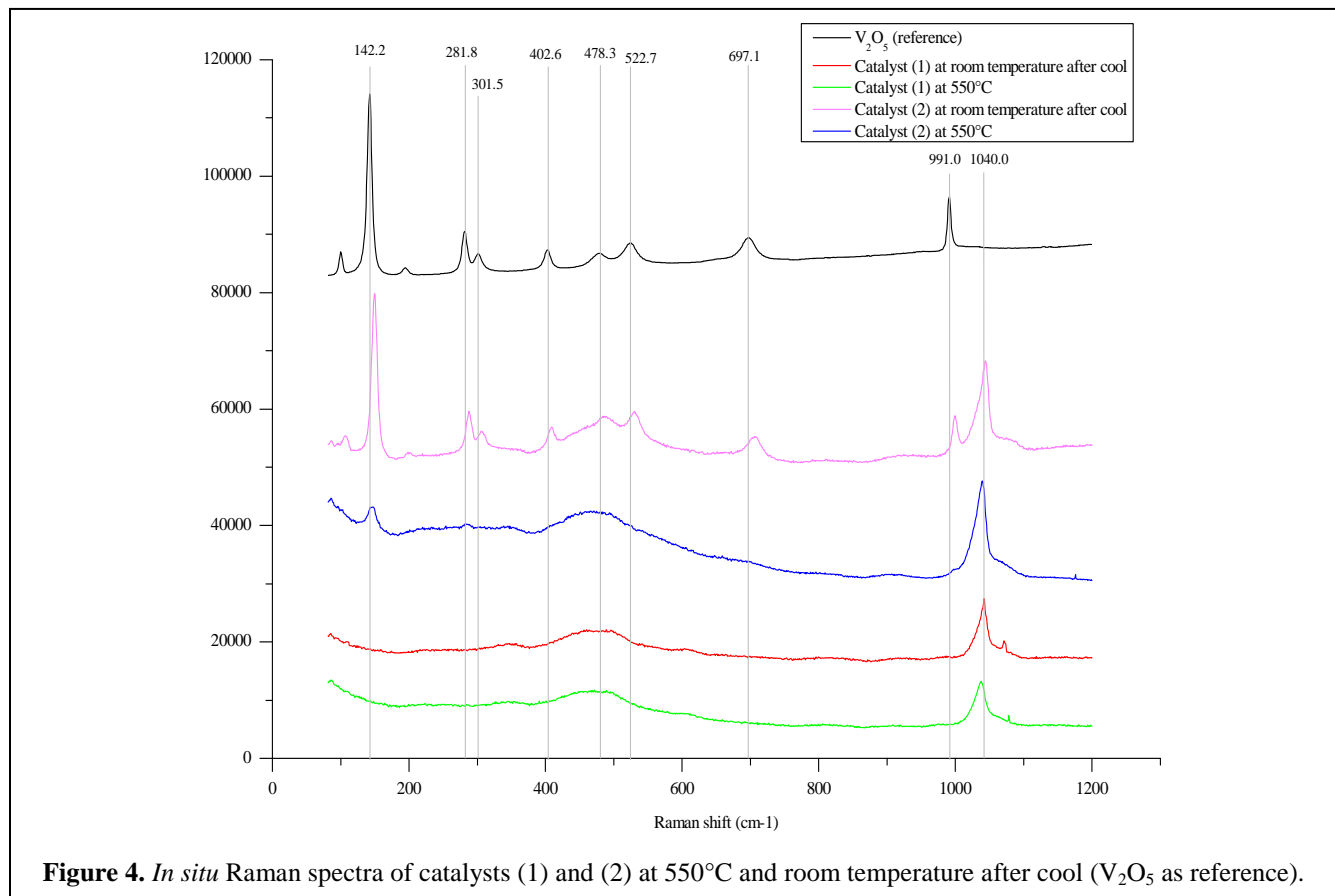


Figure 3. *In situ* Raman spectra of catalysts (3) (no micropores - grafting - 1.1 atoms/ nm^2) and (6) at 550°C (no micropores - IE - 1.0 atoms/ nm^2) with V_2O_5 as reference.

3.3 Variation of the vanadium dispersion depending on the loading

A first observation concerning the loading can be done by comparing the catalysts (1) and (2): pores are blocked if the loading is too high. The catalyst (2) has a loading more than twice as high as the (1) and its total surface area and micropore area are significantly reduced (by almost a factor two for the total surface area and more than two for the micropores area) (Table 4). Moreover, a too high loading (for instance, catalyst (2) with 10.5wt% of vanadium) is yielding of crystallization (“bulk”) of few vanadium species of V_2O_5 -like structure on the surface (Figure 4, pink line) and thus could lead to a change in catalytic activity. Nevertheless, the comparison of blue and pink lines of the catalyst (2) at 550°C and at room temperature after cool (Figure 4) shows the importance of studying and analyzing the

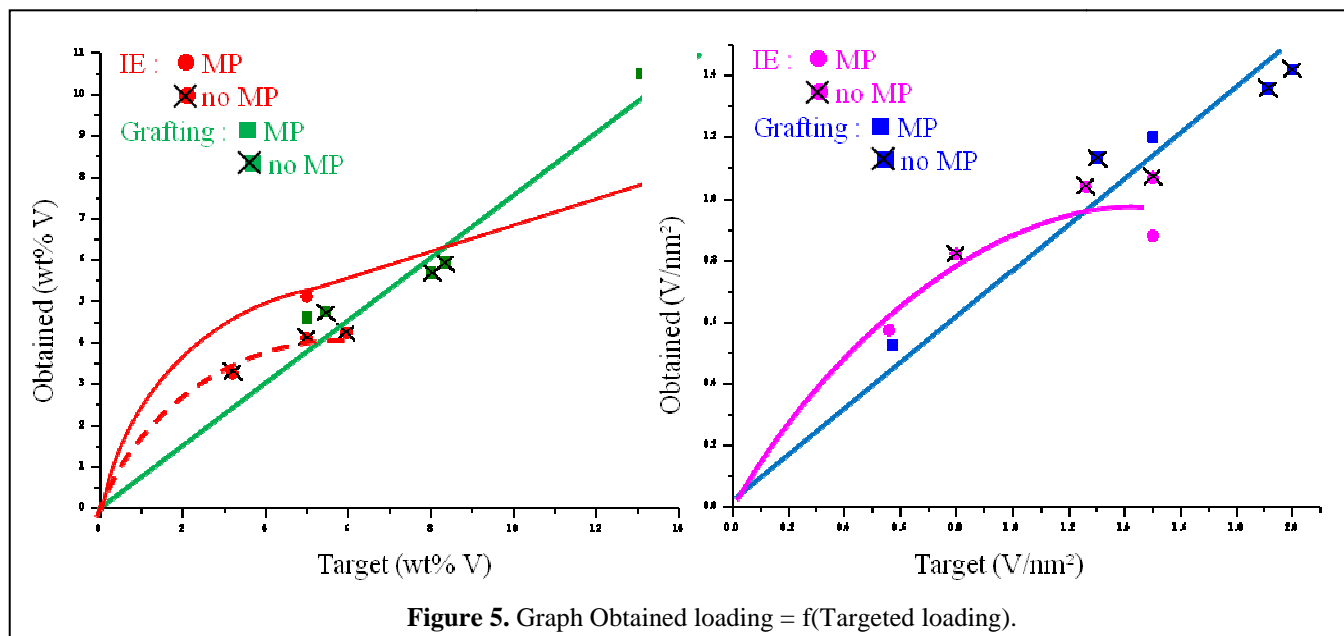
catalyst under experimental conditions (high temperature). Indeed, the Raman spectrum analysis at room temperature (pink) signals few crystallites of vanadia species whereas the Raman spectroscopy of the same sample analyzed at 550°C (blue) signals a catalyst without crystallites (vanadium well dispersed). Catalytic activity tests are needed to see if the high vanadium loading is a problem because of crystallization at room temperature or if the high loading results in a higher catalytic activity.



3.4 Comparison of IE and grafting according to the loading

Some differences between the targeted loading and the obtained loading (XRF measurement) exist for both techniques. Several factors could be responsible for these differences, for instance an error on the weigh-in of the silica-support because of a support incompletely dry, an inexact evaluation of the weight-percent of APTMS at the SBA-15 surface (5 wt% was considered), a source of error in the preparation of XRF samples. However, a graphical representation “loading obtained as a function of loading targeted” (Figure 5) was made and a tendency has been pointed out: for grafting (in wt% and atoms/nm²) an “almost-linear” curve was obtained which means the error of loading is quite constant and consequently predictable. This tendency is not as clear for IE method. This could be explained by the solvent used during the preparation (SBA-15 slightly unstable in water, paragraph 3.1), an incorrect estimation of weigh-percentage of APTMS of SBA-15, the purification of the sample (the filtration in IE

method could modify the vanadium content leading to further dissolution of SBA-15 and/or loss in AMV).



Comparison of XRF and EDX results: elemental composition

VO _x /SBA-15	Loading determined by XRF (wt %)	Loading determined by EDX (wt %)
(2)	10.5	12.85
(3)	4.74	5.36
(8)	4.25	4.24
(9)	7.94	8.64

Table 5. VO_x/SBA-15 catalysts loading determined by XRF and EDX.

These two techniques gave similar loading results. Nevertheless, EDX measurements are almost systematically higher than XRF (Table 5).

XRF analysis is carried out on the whole sample (“bulk” analysis). For EDX analysis, the sample is observed with a SEM microscope and several locations (5 here) on the sample are pointed out and the loading is measured only on these points (local analysis) (Table 6). Then, the loading is calculated with the average of these local measured loadings. The homogeneity of the sample can be estimated with these values.

VO _x /SBA-15	(2)	(3)	(8)	(9)
EDX values (vanadium content in wt%)	11.60	5.64	3.66	7.86
	14.21	5.56	4.95	9.03
	15.05	4.82	3.61	8.58
	11.89	5.50	4.94	10.88
	11.50	5.27	4.07	6.85
Dispersion of measurements (M-m)*	3.55	0.82	1.34	4.03

* M = Maximum ; m = minimum

Table 6. EDX measurements on 5 locations on 4 different catalysts.

A higher gap between the higher and the lower measurements can be observed for catalysts with SBA-15 microporous as support and a high loading ((2) and (9)). It appears that the vanadium dispersion is more homogeneous on SBA-15 without micropores and with a low loading ($M-m=0.82$ and 1.34 only).

3.5 Impact of the porosity/surface on the dispersion of vanadia species

The porosity of the support is a very important factor and must be taken in consideration for the dispersion of vanadia species. Several characterizations show a significant impact of the porosity on the catalyst preparation. Thus, for catalysts (2) and (3) prepared by grafting method (and a high loading at 1.1 atoms/nm^2), Raman spectra points out that SBA-15 with micropores (2) yields different vanadyl $V=O$ species than SBA-15 without micropores (3) (Figure 6 left). However, this observation cannot be done for the catalysts (6) and (4) prepared with ion exchange method (and a loading at around 1 atom/nm^2). In this last case (IE), there is no clear difference between supported-vanadium oxide on SBA-15 with or without micropores (Figure 6 right). These two observations could be interpreted with the links between preparation and porosity. The preparation technique has an impact on porosity and therefore an impact on dispersion. Indeed, with the first results, a decrease of the (micro)porosity had been observed with IE (aqueous media) because of the tendency to homogenize the support roughness and, as a result, vanadium species had another distribution on the surface (Schemes 9, 10 and 11).

Ion Exchange \rightarrow decrease of microporosity (smoother surface) \rightarrow homogeneity in vanadia species (Raman)

Grafting \rightarrow standard microporosity \rightarrow clusters of VO_x in micropores \rightarrow more different vanadia species (Raman)

Scheme 9. Summary of what could happen for SBA-15 with micropores.

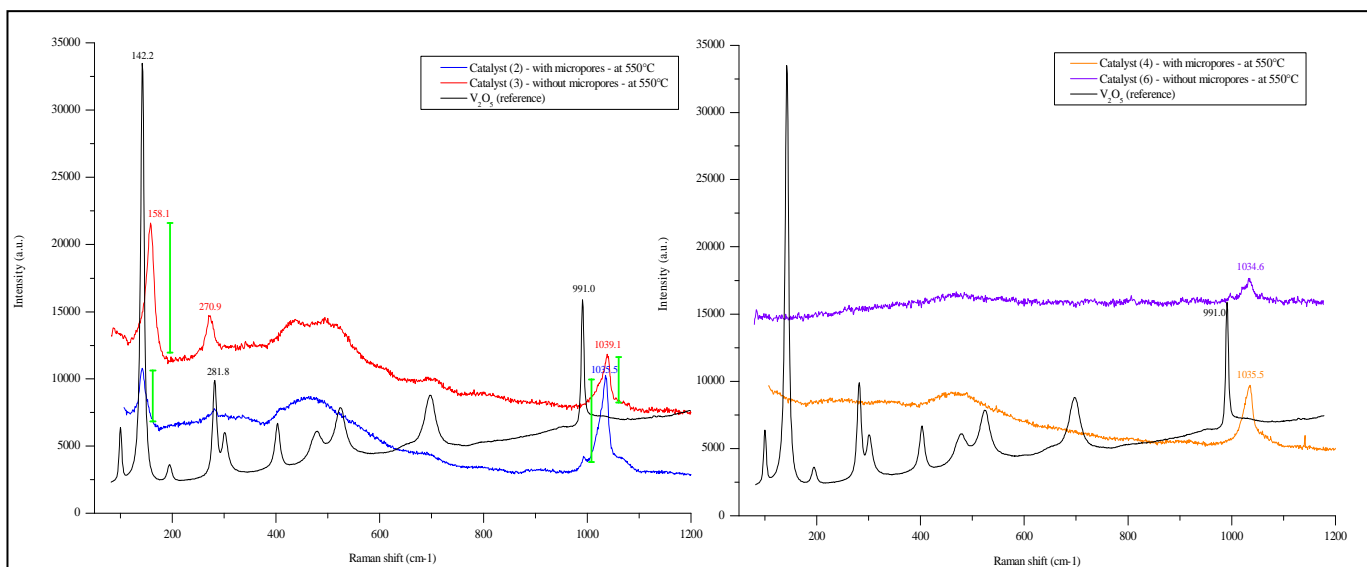
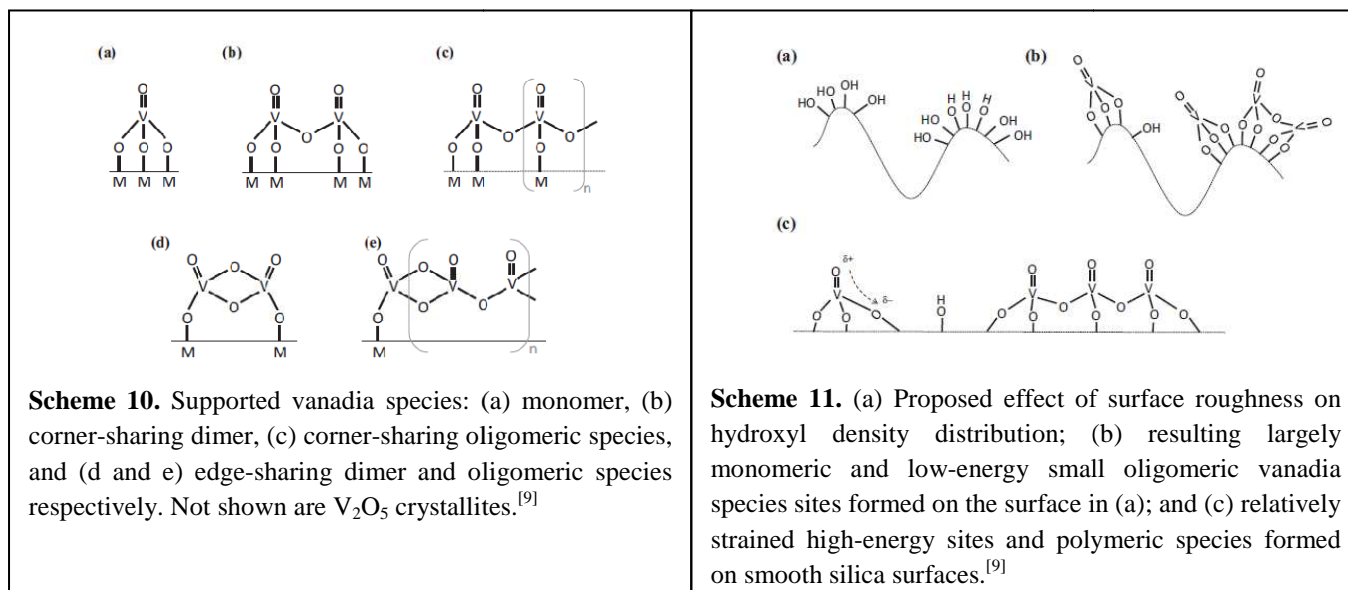
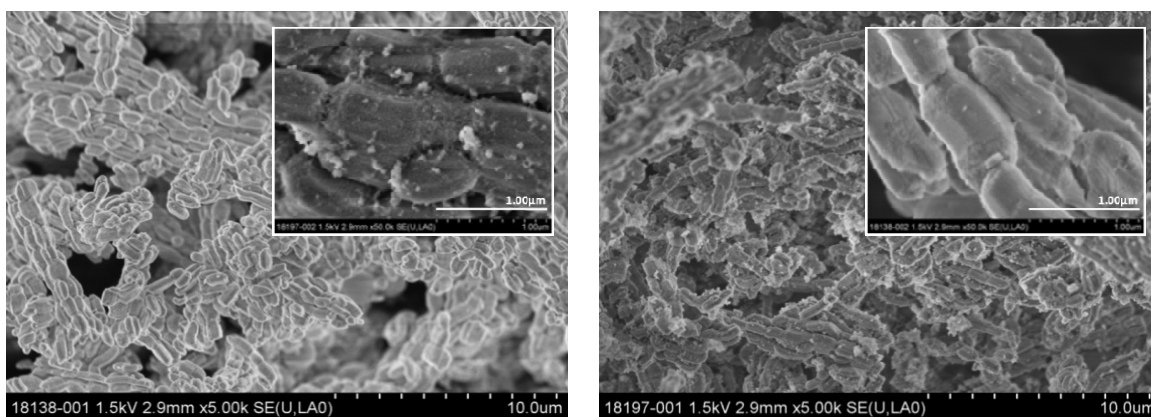


Figure 6. *In situ* Raman spectra of grafted samples at $1.1 - 1.2 \text{ atoms/nm}^2$ (left) and IE samples at $0.9 - 1 \text{ atoms/nm}^2$ (right).



3.6 Morphology of two $VO_x/SBA-15$ catalysts by SEM



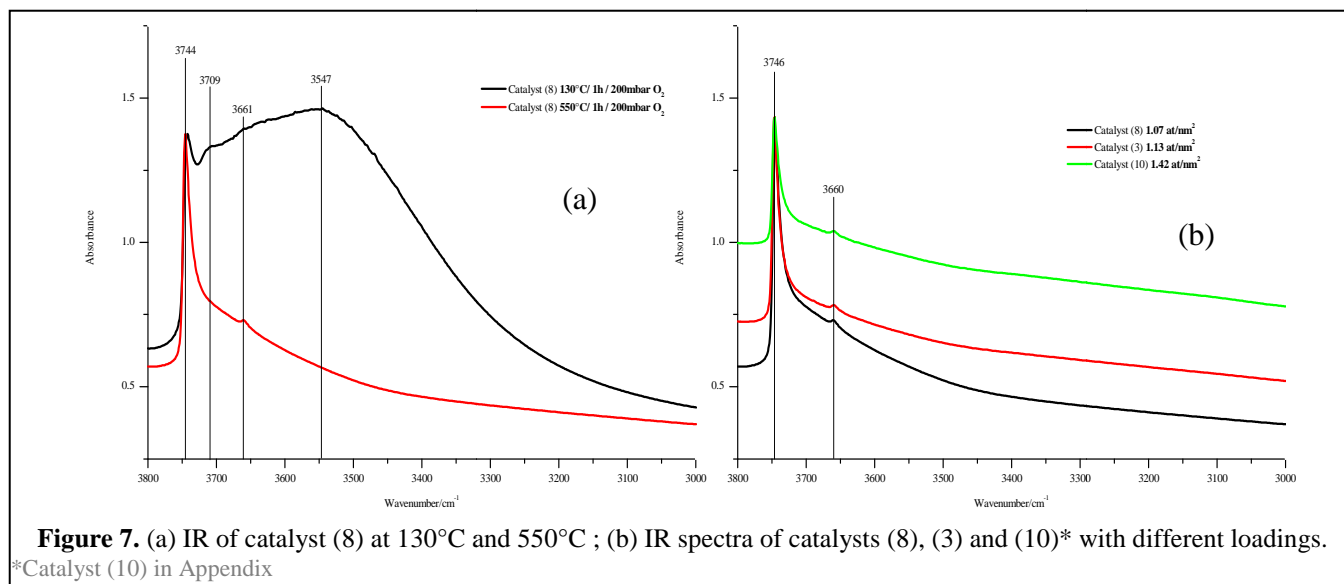
Picture 2. SEM of catalysts (2) (on the left) and (3) (on the right).

SEM images of samples (2) and (3) show two different catalysts. On the left, the SEM of catalyst (2) shows regular particles like “worms”. On the right, the SEM of catalyst (3) shows also these “worms” but partially covered with white and smaller particles. The only difference between these two samples is the microporosity: the (2) is with micropores while the (3) is without. These small white particles could be SiO_2 originating from the calcination of excess TEOS added during the support synthesis. There is more SiO_2 for the (3) because extra-TEOS is added to decrease microporosity.

3.7 First results of Infra-red spectroscopy

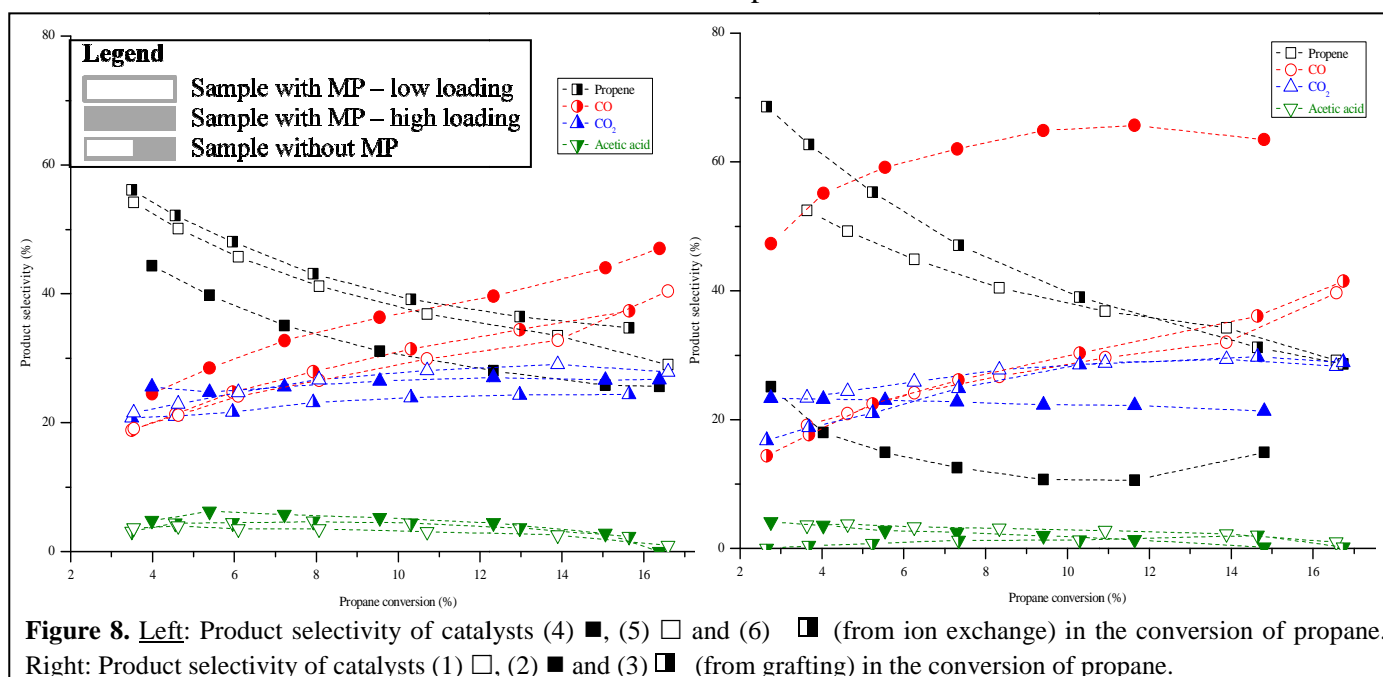
IR characterizations were carried out to briefly study Si-OH density still available after the loading on selected $VO_x/SBA-15$ catalysts. Figure 7a is the IR spectrum of the catalyst (8) (without micropores, prepared with IE and with a loading at 1.07 atoms/nm^2) studied at 130°C (black line) and 550°C (red line). According to the literature data^[21] the band at 3744 cm^{-1} corresponds to Si-O-H bond: this peak enables to determine the silanol density of the sample. The band at 3661 cm^{-1} is ascribed to

VO-H bond and peaks at 3709 and 3547 cm^{-1} are attributed to H_2O . The measurement after a heating at 130°C shows that the sample still contain water at these conditions. On the contrary, at 550°C all the water was removed and the catalyst is considered as “activated”. The superposition of IR spectra (Figure 7b) confirms that vanadium reacts on the O of the Si-OH groups, thus the higher the loading, the lower the SiO-H peak intensity.



3.8 Catalytic activity tests

To evaluate the effect of porosity and preparation procedure in the selective oxidation of propane, some catalytic tests were carried out with $\text{VO}_x/\text{SBA-15}$ catalysts (catalysts (1) to (6)). Measurement of selectivity towards propene, CO, CO_2 , and acetic acid were achieved to get an idea of catalysts efficiency. Conversion of propane and selectivity to oxidation products were calculated based on the number of carbon atoms and on the sum of found products.



Chapter 4.

Conclusion and outlook concerning VO_x/SBA-15 catalysts

A lot of catalysts were prepared during this 5-month project. First, two kinds of SBA-15 were synthesized as support materials: SBA-15 with a standard microporosity and SBA-15 with a reduced microporosity. These two textures were used to study the effects of micropores on catalyst's preparation, dispersion and arrangement of



Picture 3. VO_x/SBA-15 catalyst

vanadia species and eventually catalytic activity of VO_x/SBA-15 catalysts. SBA-15 supports were prepared with a good reproducibility (concerning synthesis and calcination) and expected properties (area, thermal stability, pores size...). SEM images of SBA-15 revealed the presence of small white particles on the surface (more on SBA-15 without micropores) which could correspond to SiO₂ species from the calcination of TEOS. To avoid this “pollution” some adjustments could be tried: more washes before calcination to remove TEOS excess, decrease the amount of extra-TEOS added in the synthesis of SBA-15 without micropores, etc.

The preparation technique and the texture of the support have impacts on the resulting catalysts. Several factors must be considered to prepare exactly a catalyst of desired properties. It has been shown with the comparison of two catalysts prepared with different procedures (IE and Grafting) that the SBA-15 with micropores is less stable in aqueous environment (IE) than SBA-15 without micropores. Another factor is the loading in vanadium on the catalyst: a too high loading could implicate a loss of porosity and the formation of some bulk of V₂O₅-like species (Raman) most likely responsible for a strong selectivity towards the total oxidation product CO in catalysis tests. The preparation method seems to have an impact on catalysts also. Indeed, even though the IE decreases the porosity of SBA-15 with micropores, this technique enables to obtain a more homogeneous dispersion of active vanadium species (Raman). More experiments could be useful to confirm the tendency already pointed out for grafted samples: with the graph obtained loading as a function of targeted loading, it will be easier to predict the error and correct it before starting the dispersion. Catalytic tests indicate that all tested catalysts had a low selectivity towards acetic acid and a selectivity of ~25% towards CO₂. More characterizations (UV-vis, SEM, EDX, IR, Raman) must be done on several VO_x/SBA-15 catalysts and more catalytic tests must be implemented to study the impact of porosity (and maybe preparation technique) on selectivity towards propene.

Experimental section

SBA-15 (with micropores) preparation.

In the reactor of the LabMax (Mettler-Toledo), 44.5g of Pluronic P-123 (poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol)) was combined with 1.6L of HCl 1.6M, stirred and heated at 35°C. After complete dissolution, 85.1g of TEOS was added. After 12h at 35°C, the temperature was increased to 85°C for 24h. Then, the solid was filtered and washed until the filtrate was neutral (approximately 5 times). The solid was dried in a furnace at 80°C overnight and then calcined in two batches at 550°C for 8h under O₂/Ar (20/80) (500mln/min) to obtain the final product.

SBA-15 (without micropores) preparation.

In the reactor of the LabMax (Mettler-Toledo), 44.8g of Pluronic P-123 (poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol)) was combined with 1.6L of HCl 1.6M, stirred and heated at 35°C. After complete dissolution, 85.1g of TEOS was added. After 12h at 35°C, 45g of TEOS was added. After stirring, the solution was heated in autoclaves at 110°C for 24h. Then, the solid was filtered and washed until the filtrate was neutral (approximately 5 times). The solid was dried in a furnace at 80°C overnight and then calcined in two batches at 550°C for 8h under O₂/Ar (20/80) (500mln/min) to obtain the final product.

SBA-15 functionalization with APTMS.

In a round flask, 9.5g of dry SBA-15 was dispersed in 380mL of toluene at 65°C. After complete dispersion, 25mL of APTMS was added within 5min. The solution is stirred overnight at 65°C. Then, the suspension was filtered and the solid was washed 5 times with toluene. The solid was dried in static air at room temperature overnight. After drying, the powder was dispersed in 600mL of HCl 0.3M and stirred overnight at room temperature. After filtration and 5 washes with water, the final product was dried overnight in static air at room temperature.

Grafting of vanadium on SBA-15.

In a Schlenk tube, 3g of dry SBA-15 and 110mL of dry isopropanol were combined and stirred 20min under Argon at room temperature. After dispersion, the vanadium triisopropoxide (volume depends on the expected loading) was added and the mixture was stirred for 2h under Argon at room temperature. Then, isopropanol was removed under reduced pressure and the resulting white powder was dried at 110°C overnight (and turned yellow). After that, the yellow powder was calcined at 550°C for 8h under O₂/Ar (20/80) (500mln/min).

Ion exchange with vanadium on SBA-15/APTMS.

In a round flask, 2g of SBA-15/APTMS (dried at 60°C overnight) was dispersed in 100mL of water at room temperature overnight. Then, AMV solution (AMV concentration depends on the expected loading) was added and the mixture was stirred at room temperature overnight. Then, the suspension was filtered and the solid was washed 5 times with distilled water. The product was dried in static air at room temperature overnight before calcination at 550°C for 8h under O₂/Ar (20/80) (500mln/min).

Ion exchange with molybdenum on SBA-15/APTMS.

Exactly the same procedure than ion exchange with vanadium. The AMV was replaced by AHM.

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1. List of abbreviations

AHM: Ammonium HeptaMolybdate tetrahydrate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$

AMV: Ammonium MetaVanadate NH_4VO_3

APTMS: 3-AminoPropyl-TriMethoxySiloxane $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$

BET: Brunauer, Emmett et Teller theory

EDX: Energy Dispersive X-ray spectrometry

FHI: Fritz-Haber-Institute

IE: Ion Exchange

IR: InfraRed

ODH: Oxidative DeHydrogenation

ODP: Oxidative Dehydrogenation of Propane

SA : Surface Area

SBA: Santa Barbara Amorphous

SEM: Scanning Electron Microscopy

TEOS: TetraEthOxySilane $\text{Si}(\text{C}_2\text{H}_5\text{O})_4$

TGA: ThermoGravimetric Analysis

UV-vis: UltraViolet-visible

XRD: X-Ray Diffraction

XRF: X-Ray Fluorescence

2. List of figures

2.1 Tables

Table 1. Chemicals produced by means of oxidation. Acrylic acid is an important monomer.

Table 2. Comparison of two procedures: ion exchange and grafting.

Table 3. Prepared SBA-15.

Table 4. Prepared $\text{VO}_x/\text{SBA-15}$ catalysts.

Table 5. $\text{VO}_x/\text{SBA-15}$ catalysts loading determined by XRF and EDX.

Table 6. EDX measurements on 5 locations on 4 different catalysts.

2.2 Schemes

Scheme 1. Reaction network in selective oxidation of propane to acrylic acid.

Scheme 2. SEM of SBA-15 with micropores (5.00 μm).

Scheme 3. Procedures to synthesize SBA-15 with and without micropores.

Scheme 4. General structural formula of Pluronic P123 and tetraethoxysilane (TEOS).

Scheme 5. Description of the grafting method to disperse vanadium on SBA-15.

Scheme 6. Description of the ion exchange method to load vanadium on SBA-15.

Scheme 7. Schematic presentation of what happened during TGA analysis.

Scheme 8. Schematic attraction of the precursor for the support in grafting and ion exchange.

Scheme 9. Summary of what could happen for SBA-15 with micropores.

Scheme 10. Supported vanadia species: (a) monomer, (b) corner-sharing dimer, (c) corner-sharing oligomeric species, and (d and e) edge-sharing dimer and oligomeric species respectively.

Scheme 11. (a) Proposed effect of surface roughness on hydroxyl density distribution; (b) resulting largely monomeric and low-energy small oligomeric vanadia species sites formed on the surface in (a); and (c) relatively strained high-energy sites and polymeric species formed on smooth silica surfaces.

2.3 Figures

Figure 1. (a) XRD-low angle diffractogram, (b) N_2 sorption isotherms and (c) Thermal analysis (TGA) for SBA-15 with and without micropores.

Figure 2. Ratio micropores area/total surface area.

Figure 3. *In situ* Raman spectra of catalysts (3) (no micropores - grafting - 1.1 atoms/ nm^2) and (6) at 550°C (no micropores - IE - 1.0 atoms/ nm^2) with V_2O_5 as reference.

Figure 4. *In situ* Raman spectra of catalysts (1) and (2) at 550°C and room temperature after cool (V_2O_5 as reference).

Figure 5. Graph Obtained loading= f(Targeted loading).

Figure 6. *In situ* Raman spectra of grafted samples at 1.1 – 1.2 atoms/ nm^2 and IE samples at 0.9 – 1 atoms/ nm^2 .

Figure 7. (a) IR of catalyst (8) at 130°C and 550°C ; (b) IR spectra of catalysts (8), (3) and (10) with different loadings.

Figure 8. Product selectivity of catalysts (4) ■, (5) □ and (6) ▣ (from ion exchange) in the conversion of propane. Product selectivity of catalysts (1) □, (2) ■ and (3) ▣ (from grafting) in the conversion of propane.

2.4 Pictures

Picture 1. SEM of SBA-15 with micropores and SBA-15 without micropores.

Picture 2. SEM of catalysts (2) and (3).

Picture 3. VO_x/SBA-15 catalyst.

3. Description of scientific material

3.1 Synthesis of supports and catalysts

3.1.1 Mettler-Toledo LabMax

The Mettler-Toledo Labmax is an automated laboratory reactor system where chemistry in solution and suspension can be done. The 2 liter reactor is monitored in-situ using probes for pH, conductivity, turbidity and UV-vis spectroscopy. The temperature and the stirring can be controlled via the computer using the software WinRC ALR. Through the process data recording, the effective duration and all parameters are measured for each steps of the reaction.

The Labmax was used to synthesize approximately 20g of SBA-15 in one batch with constant temperature and stirring. Thus, in order to avoid batch-effect, SBA-15 was synthesized in large amount and used to prepare catalyst series in sufficient quantities to do characterizations and catalysis tests.



Picture A1. Mettler-Toledo Labmax.



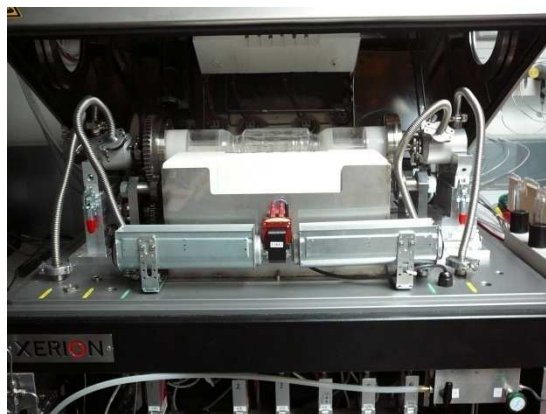
For the synthesis of SBA-15 without micropores, the heating at 110°C was carried out in autoclaves in a furnace at 110°C.

Picture A2. Autoclave.

3.1.2 Rotating furnace

The rotating furnace, or rotary calciner (Xerion) is a furnace where thermal treatments (drying, calcinations, etc.) are carried out under controlled atmosphere, temperature and heating rate. Two programs were used to control gas flows: Flow View V1.21 and Flow DDE V4.69 MBC FLOW-BUS host.

The rotary calciner was used to calcine SBA-15, $\text{VO}_x/\text{SBA-15}$ and $\text{MoO}_x/\text{SBA-15}$ at 550°C for 8h in 80% Ar and 20% O_2 (500 mln/min).



Picture A3. The rotary calciner.

3.1.3 Schlenk line

The Schlenk line is an apparatus which makes manipulation of air and water-sensitive materials possible and easy to perform. It consists in a dual manifold with several ports: one manifold is connected to a source of an inert gas and the other to a high-vacuum pump.

The Schlenk line was used to synthesize catalysts by grafting of vanadium on SBA-15. Indeed the starting reagent, vanadium triisopropoxide, is very oxygen-sensitive and can be deactivated by self-condensation if precautions are not taken.



Picture A4. The Schlenk line.

3.2 Characterization of supports and catalysts

3.2.1 Nitrogen sorption

Nitrogen sorption was performed at 77K on an AUTOSORB-6B analyzer (Quantachrome). Surface areas were determined using the isotherm method of Brunauer, Emmett, and Teller (BET). The microporous fraction of the surface area was determined using t-plot analysis and pore size distributions were calculated from the adsorption branch of the isotherms using an NLDFT method. All calculations were performed using the software package AUTOSORB-1 (Quantachrome, 1-software ASIWin V2.11).

3.2.2 X-ray diffraction

Small angle X-ray diffraction patterns were measured using a transmission diffractometer (STOE STADI P) equipped with a primary focusing Ge monochromator (Cu K α 1 radiation) and a scintillation counter.

3.2.3 FT-IR

FTIR spectra were collected using a Perkin-Elmer PE 100 spectrometer fitted with a deuterated triglycine sulfate (DTGS) pyroelectric detector (32 accumulated scans, 4 cm⁻¹ resolution). Self-supporting sample wafers with an areal density of ca. 10 mg.cm⁻² prepared by pressing at 13.5 MPa were located within a stainless steel infrared transmission cell fitted with CaF₂ windows. Samples were dehydrated at 723 K for a period of 1 h in 200 mbar of O₂. The oxygen atmosphere was exchanged several times during this procedure to remove evolved water.

3.2.4 Thermal analysis (TGA)

Thermal analyses were performed on a Netzsch Jupiter STA 449C thermobalance equipped with a Pfeiffer QMS200 OmniStar quadrupole mass spectrometer for analyzing the exhausted gases. Around 10 mg of SBA-15 were heated in corundum TG-DTA-crucibles under 100 ml.min⁻¹ Ar with a step-wise temperature program up to 1573 K. Desorption of physically adsorbed water occurs while heating from room temperature to 403 K with 5 K min⁻¹. After a holding time of 60 min no further mass loss was observed and the temperature program was allowed to continue with 10 K min⁻¹ to 1573 K and a final isothermal stage for 15 min.

3.2.5 *In situ* Raman spectroscopy

Raman spectra were recorded by using Raman microscope system (S&I Spectroscopy & Imaging GmbH) with a CCD camera (PyLoN: 2kBUV, Princeton Instruments) as the detector, attached to a confocal upright microscope (Olympus BX51, 10x objective) and monochromator with 750mm confocal length (Princeton Instruments), using an DPSS laser with 532 nm excitation wavelength (1 mW on the sample). The spectrometer was operated in triple subtractive mode and each spectrum was integrated for 10 min as required to produce spectra with an acceptable signal to noise ratio. Samples were loaded into Linkam CCR1000 in situ-cell, fixed bed in a flow of 20 mln/min synthetic air.

3.2.6 XRF

For chemical analysis, the samples and corresponding standards were mixed with lithiumtetraborate flux (FX-X100, Fluxana - 8.9 g of LTB and 100 mg of sample) and fused in a Vulcan Fusion Machine at 900°C (HD Electronic & Elektrotechnik GmbH) under formation of flat molten glass discs, which were analyzed by X-Ray Fluorescence spectroscopy using the spectrometer Pioneer S4 (Bruker AXS GmbH).

3.2.7 SEM & EDX

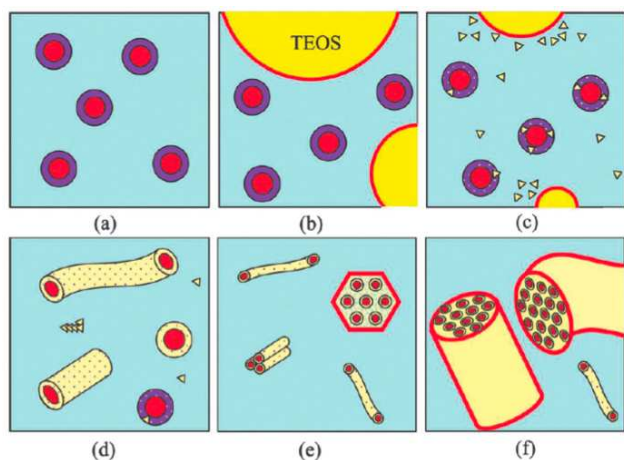
The morphology and local content of vanadium on SBA-15 was studied by scanning electron microscopy (SEM) coupled with energy-dispersive X-ray analysis (EDX) using a Hitachi S-4800 electron microscope operating at 2kV in secondary electron (SE) mode and backscattering electron (BSE) mode.

3.2.8 Catalytic tests

300mg of catalyst was pressed and sieved to 250-355µm and loaded into 6mm ID quartz reactor tubes with quartz wool to fix the bed. The reactors were equipped with individual thermocouples inserted into the catalyst bed and set into a parallel, 8-channel fixed bed reactor setup (Integrated Lab Solutions). Prior to catalytic measurements the catalysts were thermally pretreated in 20% O₂/N₂ at 550°C, overnight. The reactant feed was controlled by mass flow controllers (EL-FLOW, Bronkhorst) to give a C₃H₈/O₂/N₂ ratio = 10/5/85 at atmospheric pressure. Temperature was varied in 10K steps over the range 380°C-440°C. Reactants and products were analyzed with an online gas chromatograph (Agilent 7890). Quantity of CO, CO₂, N₂, O₂, propane and propylene was measured. Measurement of selectivity towards propene, CO, CO₂, and acetic acid were achieved to get an idea of catalysts

efficiency. Conversion of propane and selectivity to oxidation products were calculated based on the number of carbon atoms and on the sum of found products.

4. SBA-15: mechanism of preparation



Scheme A1. Formation mechanism of the 2D-hexagonal SBA-15.^[23]

- (a) Initial solution of P123 spherical micelles.
 (b) Addition of the TEOS silica precursor.
 (c) Hydrolysis step and beginning of condensation.
 (d) Shape transformation of the hybrid organic-inorganic micelles from spherical to rod-like.
 (e) Nucleation and (f) growth of the 2D-hexagonal phase.

5. Prepared VO_x/SBA-15 catalysts

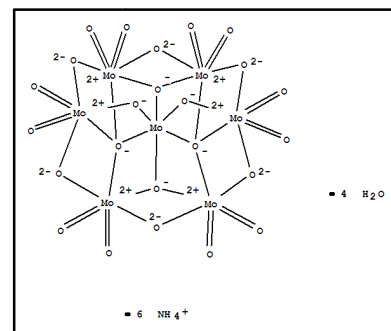
VO _x /SBA-15	μpores	Method of dispersion	V loading (wt %)	V loading (atoms/nm ²)	Area (m ² /g)	μpores area (m ² /g)	% of μpores	Area of SBA-15 mother (m ² /g)	% of μpores
(1)	Yes	Grafting	4.61	0.527	860.2	240.3	27.9	1044 (±10)	34
(2)	Yes	Grafting	10.5	1.20	495.7	86.1	17.4	1044 (±10)	34
(3)	No	Grafting	4.74	1.13	380.7	51.8	13.6	482 (±12)	18
(4)	Yes	IE	7.85	0.881	524.4	128.9	24.6	1044 (±10)	34
(5)	Yes	IE	5.12	0.574	559.5	149.4	26.7	1044 (±10)	34
(6)	No	IE	4.12	1.04	367.6	53.8	14.6	482 (±12)	18
(7)	Yes	IE	7.38	0.828	539.4	115.4	21.4	1044 (±10)	34
(8)	No	IE	4.25	1.07	358.2	46.5	13	482 (±12)	18
(9)	Yes	IE	7.94	0.891	490.5	114.9	23.4	1044 (±10)	34
(10)	No	Grafting	5.94	1.420	381.1	38.8	10.2	482 (±12)	18
(11)	No	Grafting	5.69	1.36	386.3	44.8	11.6	482 (±12)	18
(12)	No	IE	3.27	0.822	387.3	43.1	11.1	482 (±12)	18
(13)	Yes	IE	6.93	0.796	567.1	136.1	24	1025 (±3)	32
(14)	No	IE	4.30	1.03	383.1	56.9	14.8	502 (±9)	20

Table A1. All prepared VO_x/SBA-15 catalysts.

6. Silica-supported molybdenum oxide catalysts

6.1 Scope of work

The purpose on this part is to prepare different kinds of mixed MoO_x/VO_x on SBA-15 (Table A3). In this part, molybdenum is used as a promoter to increase catalytic properties of vanadia species. Indeed, isolated molybdenum has a very low activity for ODH of propane but promotes the adsorption of propane and improves activity and selectivity of vanadium-supported catalysts in propane ODH.^[11, 12, 22] In order to do that, the first step was to find the proper amount of precursor needed to obtain a full monolayer of MoO_x on the SBA-15 surface (Table A2, part 1). Subsequent to adjust the precursor quantity to get a submonolayer of MoO_x and then eventually fill the holes with VO_x species (Table A2, part 2). The deposition of Mo on SBA-15 was carried out with the ion exchange method because no precursor was available and compatible to do grafting. The precursor used for ion exchange was the ammonium heptamolybdate tetrahydrate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (AHM) (Scheme A2).



Scheme A2. AHM complex.

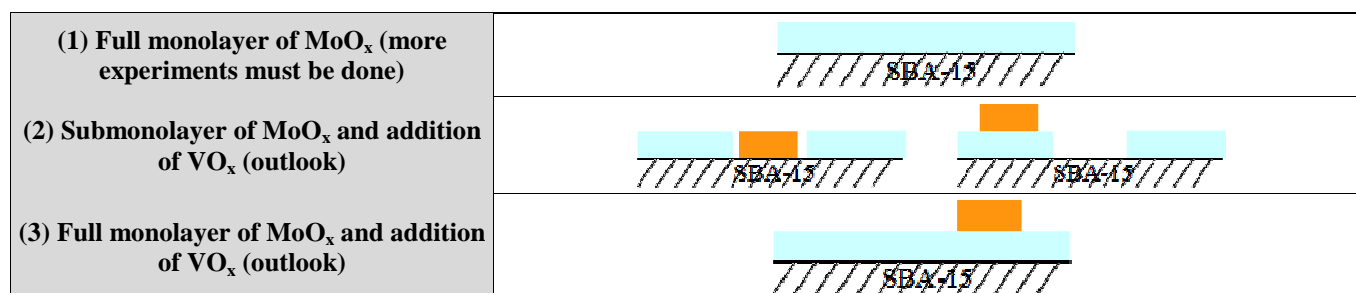


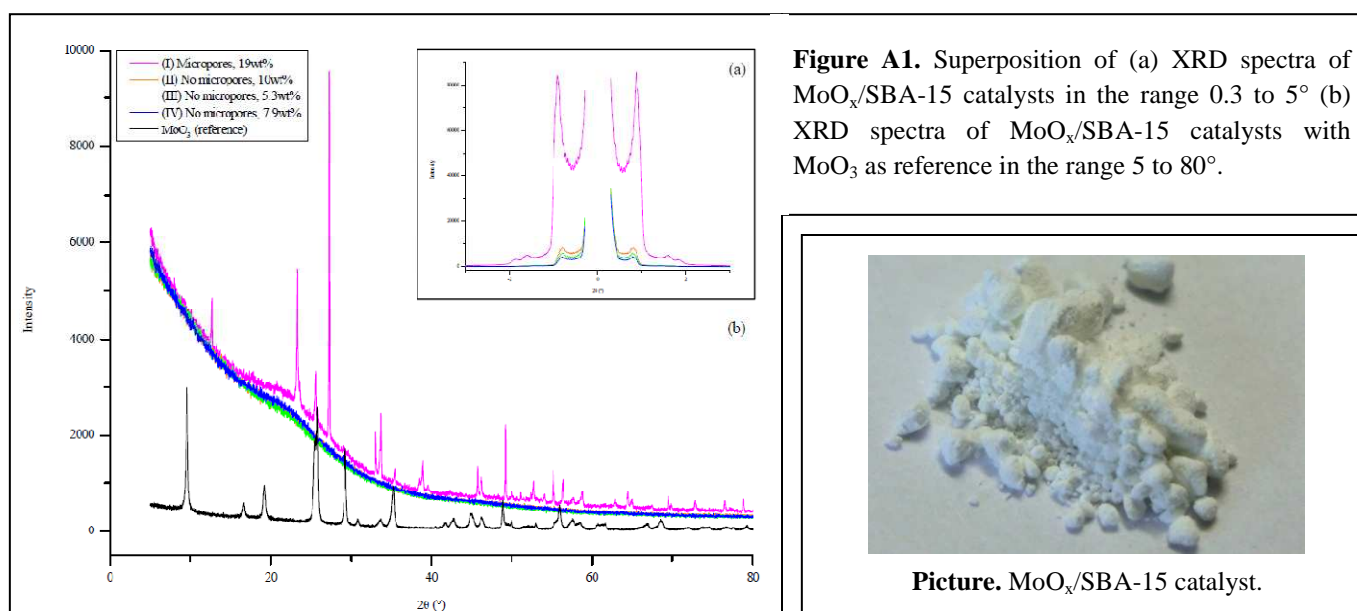
Table A2. Different kinds of surface coverage with VO_x (orange) and MoO_x (light blue).

6.2 First results & discussion

SBA-15/ MoO_x	μpores	Mo loading (wt %)	Mo loading (atoms/ nm^2)	Surface area (m^2/g)	μpores area (m^2/g)	% of μpores	SBA-15 mother		
							SA (m^2/g)	μpores area (m^2/g)	% of μpores
(I)	Yes	19	1.13	289.5	46.1	16	1044 (± 10)	358 (± 6)	34
(II)	No	10	1.28	377.9	60.3	16	502 (± 9)	101 (± 3)	20
(III)	No	5.3	0.67	414.2	71.6	17	502 (± 9)	101 (± 3)	20
(IV)	No	7.9	1.01	401.5	73.8	17	502 (± 9)	101 (± 3)	20

Table A3. Catalysts/Promoter $\text{MoO}_x/\text{SBA-15}$ prepared.

According to XRD diffractogram, there is no crystalline bulk of MoO_3 at the surface for the catalysts (II), (III) and (IV) whereas there is some for catalyst (I) (Figure – XRD spectra). At the same surface density (around 1 atom/ nm^2), there are MoO_x bulks on the catalyst (I) whereas none could be observed on the catalyst (IV): the decrease of the microporosity enables to put less Mo (7.9 wt% instead of 19 wt%) to obtain high surface density coverage without crystal formation. Nevertheless, the full monolayer of Mo species on SBA-15 without micropores was not achieved and more loadings (>10 wt% or >1.28 atoms/ nm^2) must be tried. Loadings targeted for catalysts (I), (II) and (III) were successfully achieved as the IE were carried out in order to obtain 10, 5 and 8wt% respectively. Moreover, the more molybdenum on the surface, the lower the total area, as expected. The decrease of the microporosity when the loading in Mo is higher indicates that MoO_x slot -partially- into the few micropores still present in SBA-15 without micropores. This is in agreement with the observations made from the $\text{VO}_x/\text{SBA-15}$ samples.



6.3 Conclusion and outlook

For now, only one observation has been done about $\text{MoO}_x/\text{SBA-15}$ catalysts: it is better to work with SBA-15 with less micropores because a high surface density coverage can be achieved without the formation of MoO_3 -like and other MoO_x crystallites bulk phases. The use of SBA-15 “without” micropores results in less AHM needed which means saving money and a reaction more in agreement with the Green Chemistry principles.

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Mots clés : catalyse hétérogène, oxyde de vanadium, SBA-15, ODH, porosité

Résumé :

Durant ce stage, une première partie consistait en la synthèse puis la caractérisation de SBA-15 (silice mésoporeuse) avec une porosité contrôlée. Dans un second temps, plusieurs catalyseurs à base d'oxydes de vanadium supportés sur SBA-15 ont été préparés et caractérisés par XRD, XRF, SEM, EDX, spectroscopie Raman, IR et isothermes d'adsorption du N₂. Plusieurs paramètres ont été modifiés et leurs impacts sur la morphologie du catalyseur et sur sa sélectivité pour la réaction de déshydrogénation oxydante du propane en propène ont été étudiés. Ces paramètres étaient : la texture du support, la méthode de préparation et la quantité de vanadium dispersé. Ceux-ci ont un impact sur le dépôt du vanadium sur le catalyseur. Une meilleure dispersion et une plus grande sélectivité ont été obtenues dans le cas d'une faible quantité de vanadium sur un support avec une porosité plus uniforme.

Summary :

During this internship, a first part focused on the synthesis and the characterization of SBA-15 (mesoporous silica) with a controlled porosity. The second part was the preparation of a number of SBA-15-supported vanadium oxide catalysts and the characterization of them by XRD, XRF, SEM, EDX, Raman and IR, N₂ sorption isotherms. Several parameters were modified and their impacts on the catalyst's morphology and on its selectivity towards propene for the ODH reaction of propane were studied. These parameters were: the texture of the support, the dispersion method used and the vanadium loading. All three parameters had an impact on the deposition and dispersion on the resulting catalysts. A better dispersion and higher selectivity towards propene were obtained by lower loading and more uniform porosity.