

Faculté des bioingénieurs

Postsynthetic Zr-Beta zeolites for the conversion of levulinic feedstock to γ -valerolactone

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Postsynthetic Zr-Beta zeolites for the conversion of levulinic feedstock to γ -valerolactone

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Abstract

With today's increasing environmental concerns, the development of sustainable materials and energy are of utmost importance. Working on the replacement of petroleum-based chemicals by biomass-derived chemicals can help reduce the consumption of fossil energy sources and lower our dependence to petroleum. This master thesis aims to help develop a new sustainable, safe and efficient process for the production of γ -valerolactone from biomass-derived levulinic acid by creating an efficient catalyst for this reaction.

Levulinic acid is a biomass-derived platform molecule that can be obtained from most plant-based resources, including lignocellulosic material. Lignocellulosic biomass is known for its hardness as plants have evolved this tissue to resist microbial and enzymatic degradation. Finding ways to exploit this biomass fraction is important, as it is most often discarded, wasted.

Gamma-valerolactone (GVL), can be used as the base chemical for a wide variety of applications, many of them being currently fulfilled by petroleum-based chemicals. It can be used as a solvent or fuel additive and even be transformed further to create synthetic fuels or polymers.

In this work, we have focused on making postsynthetic Zr- β zeolites, by removing the aluminum of commercial zeolite Beta and subsequently incorporating zirconium in the defect sites formed by the removal of Al. This allows to make Zr- β zeolites with controlled morphology, contrarily to its direct synthesis. Direct, hydrothermal synthesis of Zr- β yields large crystals in the micrometer range, as it is 20 days long, and requires the use of hydrofluoric acid which is harmful for the both the environment and for the operators.

Zr- β zeolites are microporous materials; only its external surface area is catalytically active, hence the need to improve their surface-to-volume ratio. We have proven that postsynthetic Zr- β zeolites can be used for the conversion of levulinic acid to γ -valerolactone under atmospheric pressure at 118°C by catalytic hydrogen transfer with 2-pentanol. The catalyzed reaction is the Meerwein-Ponndorf-Verley reduction of the ketone function of the substrate. When used with the ethyl ester of levulinic acid, ethyl levulinate, our catalysts have reached selectivities up to 96% for γ -valerolactone. We made highly active Zr- β zeolites with Si/Zr molar ratios down to 41 whereas hydrothermal synthesis does not work below a ratio of 75. We have also been able to prove that the zirconium was incorporated in the zeolitic framework, and not supported on its surface in the form of ZrO_2 .

With the knowledge gained from this master thesis, we will be working in the future on the creation of hierarchal Zr- β zeolites from nanozeolites pre-made in our lab.

Table of contents

Acknowledgments.....	I
Abstract	IV
Table of contents	VI
Table of figures	VII
Table of tables.....	IX
INTRODUCTION.....	X
1 Context	1
1.1 Levulinic acid as a platform molecule	2
1.2 Gamma-Valerolactone production and applications.....	3
1.3 MPV reduction mechanism	5
1.4 Zeolites, β -zeolites and Zr- β zeolites.....	7
1.5 Zr- β zeolites: syntheses and applications.....	11
1.6 Performance of Zr- β zeolites for MPV reduction.....	12
2 Objectives	13
3 Strategy.....	13
EXPERIMENTALS.....	16
4 Materials and method	18
4.1 Catalysts preparation	18
4.2 Catalytic testing.....	21
4.3 Characterization techniques.....	22
RESULTS AND DISCUSSION	26
5 Results and discussion.....	28
5.1 Dealumination of the parent H-beta zeolite	28
5.2 Catalytic tests.....	31
5.3 Characterization.....	52
CONCLUSIONS & OUTLOOK.....	68
6 Conclusion.....	70
7 Outlook and future research	72
References	73

Table of figures

Figure 1: Reaction pathway to produce levulinic acid from hexoses (adapted from [2])	2
Figure 2: Derivatives of levulinic acid (Adeleye et al., 2019).....	2
Figure 3: Catalytic upgrading of γ -valerolactone to fuels, fuel additives and value-added chemicals (Yan et Luo, 2017)	3
Figure 4: Conversion of LA to GVL (adapted from Wang et al., 2014).....	4
Figure 5: Simplified MPV reaction	5
Figure 6: Proposed mechanism for LA to GVL conversion via MPV reduction (Luo et al., 2014)	6
Figure 7: Stereographic drawings and perspective views of zeolite Beta viewed along axis (a) [010], (b) [100] and (c) [001]. Pore radii are showed in Å. In the stereographic drawings the spheres represent the oxygen atoms and the tetrahedron around which surround the T-site. The cylinders on the right represent the channels of the β zeolite. (Bárcia et al., 2005) ..	8
Figure 8: Schematic representation of the influence of external surface area	9
Figure 9: Catalytically active site for MPV reaction	10
Figure 10: SEM images of Zr-Beta zeolites made (a) hydrothermally and (b) postsynthetically (Wang et al., 2015).....	11
Figure 11: Schematic view of a silanol nest (Tang et al., 2014).....	12
Figure 12: Strategy organigram	13
Figure 13: GC temperature program	22
Figure 14: Adsorption and desorption isotherms comparison between parent and dealuminated β -zeolite.....	28
Figure 15: Powder XRD comparison of dealuminated sample and its parent zeolite ..	29
Figure 16: FT-IR spectra of the skeletal vibrations of the zeolites	30
Figure 17: 1-methylbutyl levulinate.....	31
Figure 18: Summary of catalytic tests using levulinic acid as a substrate	33
Figure 19: Performances of SSIE catalysts compared to the dealuminated zeolite.....	34
Figure 20: Summary of the performances of WIE catalysts.....	35
Figure 21: Selectivity vs activity of screened catalysts	36
Figure 22: Reaction kinetics for LA to GVL conversion using ONitr_WIE_1.....	37
Figure 23: Detailed reaction kinetics with Cl4_WIE_1.3 as catalyst. Concentrations expressed as internal standard equivalents. UC# are unidentified compounds.	37
Figure 24: Reaction kinetics of with Cl4_WIE_1.3 as catalyst. Missing carbon is calculated by difference	38
Figure 25: Detailed reaction kinetics with ONitr_WIE_1 as catalyst	38

Figure 26: Detailed kinetics with CL4_WI_1.3 as catalyst.....	39
Figure 27: Superimposed peaks of LA and EL from two catalytic tests. X axis is in minutes	40
Figure 28: Performances of catalysts tested in standard conditions with EL as substrate	42
Figure 29: Detailed kinetics of the conversion of EL to GVL using ONitr_WI_1 as catalyst	43
Figure 30: Initial rates of conversion of EL by various catalysts	43
Figure 31: Hypothetical difference between ZrO^{2+} and Zr^{4+} incorporation	44
Figure 32: Detailed kinetics of the conversion of EL to GVL using CL4_WI_1.3 as catalyst. Dotted line is the predicted concentration of EL using the mean value of the rate constants computed for each time interval	45
Figure 33: Performance of catalysts exposed to 0.4 mol/L of EL:	46
Figure 34: Detailed kinetics of the reaction using CL4_WIE_1.3 in presence of 0.4 mol/L of EL	47
Figure 35: Detailed kinetics of the reaction using ONitr_WI_1 in presence of 0.4 mol/L of EL	47
Figure 36: Performance of various ONitr_WI catalysts	48
Figure 37: Detailed reaction kinetics when using ONitr_WI_2 as catalyst with 0.2 mol _{EL} /L engaged	49
Figure 38: Detailed reaction kinetics when using ONitr_WI_4 as catalyst with 0.2 mol _{EL} /L engaged	49
Figure 39: Activity of ONitr_WI_1 after several uses. Third use is grayed as the reaction was set up with 0.4 mol/L of EL instead of 0.2 mol/L	50
Figure 40: Impact of the reactor on activity.....	50
Figure 41: XRD patterns of catalysts	54
Figure 42: Kubelka-Munk function of the DRUV spectra of the catalysts tested with LA, versus pure ZrO ₂ . “Parent” is the commercial zeolite as purchased, HBeta is after calcination to remove surface ammonia. Dashed lines are Zr-free materials. ZrO ₂ (dotted line) is on a higher scale	55
Figure 43: Normalized Kubelka-Munk function of the DRUV patterns of selected catalysts	56
Figure 44: N ₂ physisorption isotherms of catalysts of various loadings, precursors and impregnation methods	57
Figure 45: N ₂ adsorption and desorption isotherms for ONitr_WI_1	57
Figure 46: Focused FTIR-ATR spectra of various catalysts. Absorbance is normalized using the main peak around 1090 cm ⁻¹	59
Figure 47: FTIR spectra of ONitr_WI_1 after degassing at 350°C, and after adsorption and subsequent desorption of pyridine at increasing temperatures	60

Figure 48: FTIR-Pyridine adsorption results. a) Pyridine-bound Lewis acid sites after desorption at increasing temperatures. b), c) Quantity of Bronsted and Lewis acid sites calculated after desorption of pyridine at 100°C	61
Figure 49: XPS spectrum of ONitr_WI_4, zoom on the peak corresponding to Zr.....	62
Figure 50: Comparison of the Zr/Si ratio between Cl4_WIE catalysts.....	63
Figure 51: Turnover frequencies of the most active catalysts.	66

Table of tables

Table 1: Reported performances of Zr- β for GVL production under 1 atm. HT: hydrothermal, PS: postsynthetic, LA: levulinic acid, ML: methyl levulinate	12
Table 2: Summary of all prepared catalysts. The numbers in each cell are 100 times the nominal molar Zr/Si ratio.....	20
Table 3: Precursor masses used for a 1% loading.....	20
Table 4: Effect of dealumination on textural properties	29
Table 5: Summary of all non-standard tests.	31
Table 7: Comparison of our best catalyst and that of Wang et al., 2014	33
Table 8: Reaction rate constants $k(h^{-1})$ of two catalysts computed bihourly and their mean value.....	45
Table 9: Reaction rate constant k of catalytic tests displaying 1 st order kinetics	46
Table 10: Performance of catalysts tested with EL as a substrate. Mean conversion rate is calculated as the total substrate consumption divided by time and the amount of catalyst	51
Table 11: Summary of the N ₂ physisorption data.....	58
Table 12: 100*Zr/Si molar ratios as measured by XPS and ICP-AES.....	63
Table 13: Turnover frequencies of catalysts tested with EL, as calculated after 2h of reaction with 0.2 mol/L of EL	65
Table 14: Reported performances of Zr- β for GVL production under 1 atm. HT: hydrothermal, PS: postsynthetic, LA: levulinic acid, ML: methyl levulinate	71

INTRODUCTION

1 Context

This master thesis focuses on the conversion of levulinic acid (LA) or its esters into γ -valerolactone (GVL) using postsynthetic Zr-Beta zeolites, as opposed to the more widespread Zr-Beta synthesized hydrothermally.

With today's increasing environmental concerns, the development of sustainable materials and energy are of utmost importance. In this regard, we want to work on the replacement of petroleum-based chemicals by biomass-derived chemicals, to reduce the consumption of fossil energy sources. The extraction of these fossil fuels from the ground effectively increases the amount of carbon in the atmosphere and environment in general. Biomass on the other hand, uses carbon already present in the environment and stored in plants via photosynthesis, using energy from the sun. Using biomass-derived chemicals as a source of energy or materials equates to using solar energy stored in plants and the released CO₂ does not increase the total carbon in the environment, as it is stuck in a closed loop between the plants and the atmosphere.

To be used as a source of energy or base materials that can compete with petroleum-based chemicals, biomass needs to be chemically transformed, however. Catalysis is an important tool in this transformation, as it reduces the energetic costs of these transformations as well as increases the rate at which they can be performed, by reducing the energy barrier that needs to be crossed to perform the chemical reaction.

In this section, we will discuss the choice of levulinic acid as a starting material, and why we want to produce γ -valerolactone. We will also discuss the catalyst that we have chosen to perform the conversion; Zr-Beta zeolite.

1.1 Levulinic acid as a platform molecule

Levulinic acid (LA), or 4-oxopentanoic acid, is a white crystalline solid, with a pK_a of 4.64, a melting point of 33°C ¹ and is easily obtained from the hydrolysis of mono/poly-saccharides and lignocellulosic biomass.² The conversion of biomass into LA is an entire field of study in and of itself.² The reaction consists in dehydrating hexoses into 5-hydroxymethylfurfural which, through acid catalysis, hydrolyses into LA and formic acid.² This chain of reactions is shown in Figure 1 below.

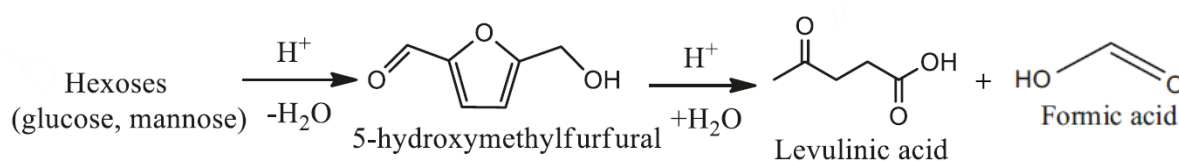


Figure 1: Reaction pathway to produce levulinic acid from hexoses (adapted from [2])

This synthesis can be carried out using a variety of catalysts, either homogeneous or heterogeneous², under relatively mild conditions (i.e. 1.7 wt% cellulose feed, H_2SO_4 1 mol/L, $\tau=2\text{h}$ at 150°C , 60 mol% yield in a CSTR³) and uses substrates that are widely available, renewable and abundant. Levulinic acid also has the great advantage of not competing with human or animal feedstock, as it can be extracted from untapped resources such as lignocellulosic biomass or starch waste.⁴ As such, it has been identified by the US Department of Energy as one of 12 platform molecules from biomass with high added value.⁵ A platform chemical is a molecule that can be further transformed in a variety of chemical products or intermediates; Figure 2 shows several routes through which LA can be transformed.

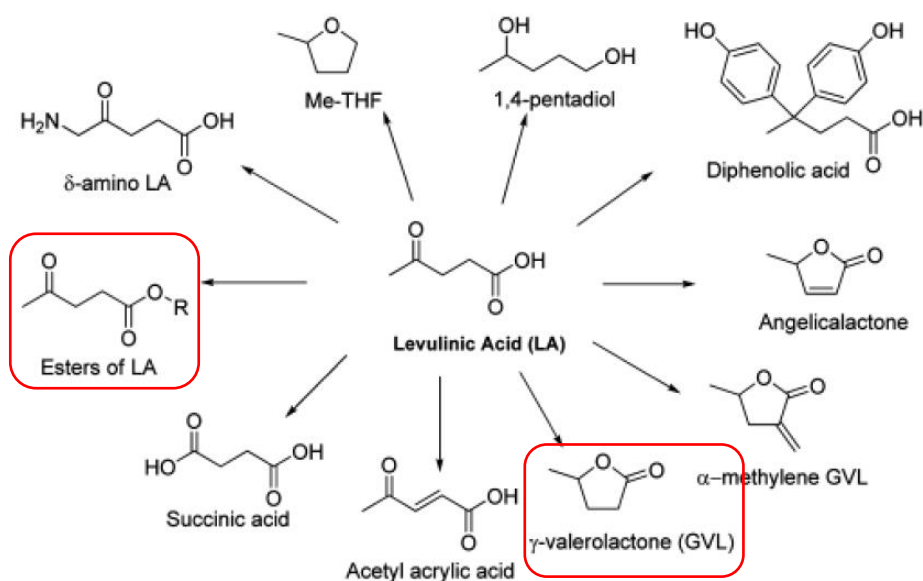


Figure 2: Derivatives of levulinic acid (Adeleye et al., 2019)

These products have a wide range of applications, from pharmaceuticals to polymers, flavoring agents, fuels, herbicides, solvents, and many more.⁶ Two of them will be relevant to the present work: γ -valerolactone (GVL, see 1.2), which we aim to produce, and the ethyl ester of LA, ethyl levulinate (EL) that will serve as an alternative substrate.

Ethyl levulinate, like levulinic acid, will serve as a substrate for the production of GVL. It can be synthesized either via the Fischer esterification of LA with ethanol, or directly from biomass by adding alcohol to the reaction mixture, resulting in the alcoholysis of 5-hydroxymethylfurfural (HMF) instead of its hydrolysis, which in turn yields the corresponding levulinate ester.² We thus deemed this alternative substrate to be just as legitimate as LA.

1.2 Gamma-Valerolactone production and applications

γ -valerolactone (GVL) is a faint yellow liquid, with a strong herbaceous scent.⁷ It has a high boiling point (207°C) with a low vapor pressure of 3.5 kPa at 80°C and is miscible with water up to 100mg/ml, making it a physically stable liquid, yet available for biodegradability⁸. By itself, it can be used as a fuel additive or a green solvent, but it can also be transformed into a variety of other compounds of great interest in other fields.⁹ For example, a 2019 study showed that GVL could be used as a wood pulping agent to extract nanocellulose of high quality and purity without the need of a bleaching process.¹⁰ As shown in Figure 3, GVL can be further transformed into a wide variety of other valuable compounds.

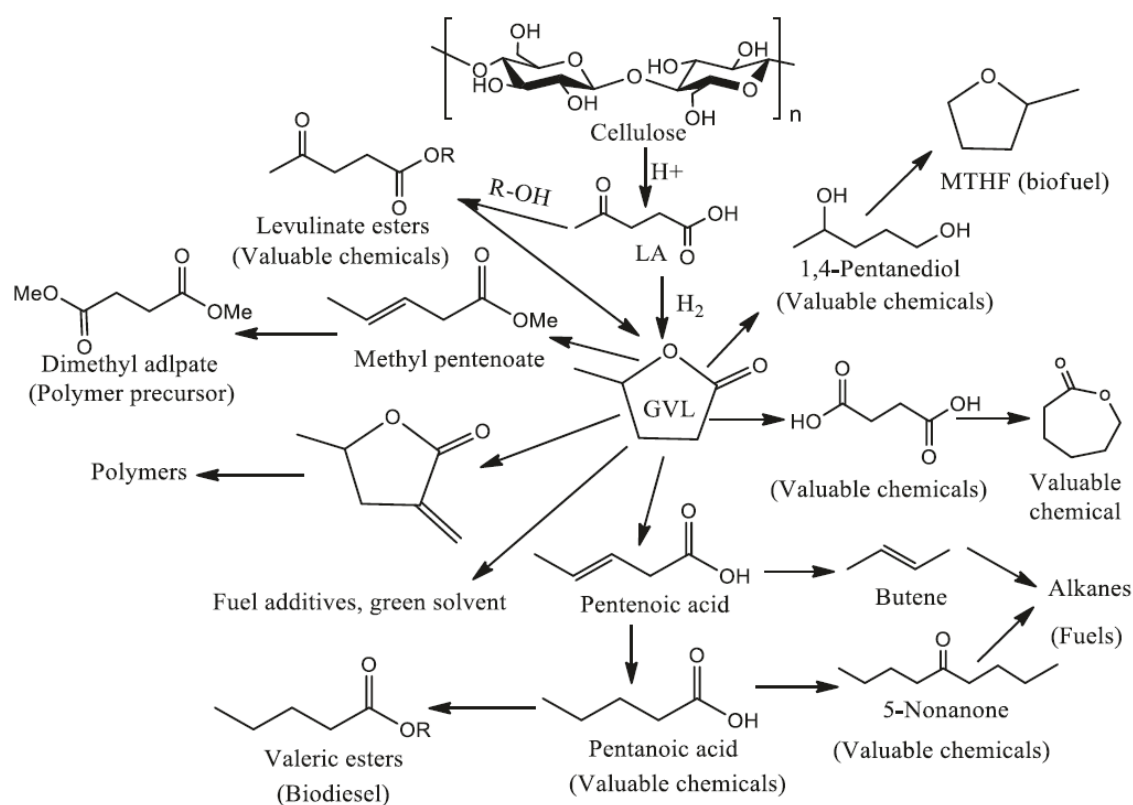


Figure 3: Catalytic upgrading of γ -valerolactone to fuels, fuel additives and value-added chemicals (Yan et Luo, 2017)

Very recently, GVL has also been used to create butenes under atmospheric pressure with a yield of >99%, using hetero-atomic MFI zeolite.¹¹ This is of great interest for our research group as we also work on the development of biomass derived butadiene.^{12,13}

As previously mentioned, GVL can be used as a fuel additive. In this regard, it displays great physical and chemical properties even when compared to ethanol⁸, which is the leading fuel source towards the post-petrol era.¹⁴ It does not form peroxides even when left under air for weeks, and does not hydrolyze under neutral conditions, making it safe for large scale use and storage.⁸ Though the combustion enthalpy of GVL is slightly lower than that of ethanol, its higher density (1.05 against 0.8) makes it energetically denser.⁹ For reference, in a mixture of 90% (v/v) conventional gasoline with either ethanol or GVL, both fuels show the same octane number as pure gasoline, while GVL does not display the volatility issues brought by ethanol. Finally, GVL has the advantage of not forming an azeotrope with water, making it much cheaper and energy-efficient to separate at high purity than ethanol, which requires azeotropic distillation or molecular sieves to purify above 95%.⁸

To synthesize GVL, the ketone function of LA (or any of its esters) must be hydrogenated to form an alcohol. Then, a spontaneous intramolecular lactonization occurs to form GVL and a molecule of water - or the corresponding alcohol if an ester is used as feedstock.¹⁵

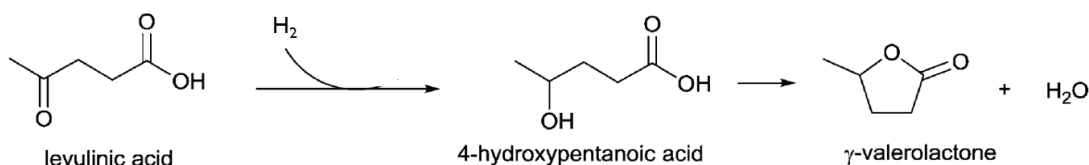


Figure 4: Conversion of LA to GVL (adapted from Wang et al., 2014)

Nowadays, this reaction is performed using high pressures of molecular hydrogen ranging from 34 to 100 bars, and using Ru, Pd or Pt based catalysts, making it a very expensive process.⁹ Besides the cost and availability of noble metals, the use of hydrogen as reducing agent also comes with several well-known issues such as transportation and storage difficulties and cost. Using H_2 thus causes problems in terms of EHS risk management (Environmental, Health and Safety). An alternative mechanism has been investigated since 2011, using an alcohol as a hydrogen source and non-noble metal based catalysts, thus aiming towards a cheaper and greener process.¹⁶ This other pathway is called the Meerwein-Ponndorf-Verley reaction (MPV) and is presented in detail in section 1.3. Compared to standard hydrogenation, it also has the advantage of being functional even under atmospheric pressure and in the liquid phase, drastically reducing the operational EHS risks associated with it.

1.3 MPV reduction mechanism

In organic chemistry, an MPV reaction is the catalyzed hydride shift from an alcohol to a ketone or aldehyde, involving a cyclic six-membered transition state (Figure 6). Through this reaction, the hydride donor is turned into a ketone and the recipient is transformed into an alcohol. Figure 5 shows a basic representation of the reaction. The term MPV reduction is used when the wanted final product is the alcohol.

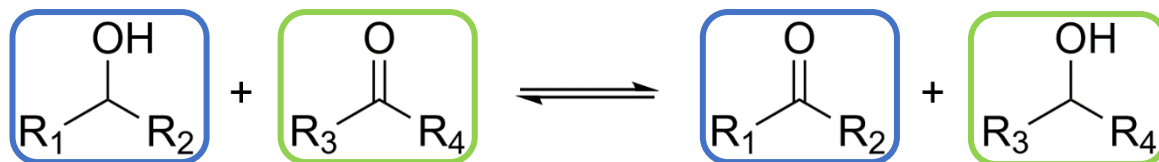


Figure 5: Simplified MPV reaction

Applied to conversion of LA to GVL, this mechanism can be broken down into a 6 steps reaction, illustrated in Figure 6 for the reaction of methyl levulinate (ML) with 2-butanol. (1) The sec-alcohol chemisorbs and deprotonates onto the partially hydrolyzed Lewis acidic site (detailed in section 1.4.2). (2) ML adsorbs via its ketone function. (3) The MPV reaction takes place, 2-butanol reduces ML through a six-membered transition state. (4) 2-butanone desorbs. (5) The newly formed 4-hydroxypentanoate receives the second proton left on the catalyst by 2-butanol then desorbs. The catalyst is ready for a new cycle. (6) 4-hydroxypentanoates spontaneously undergoes lactonization yielding GVL and methanol.¹⁷

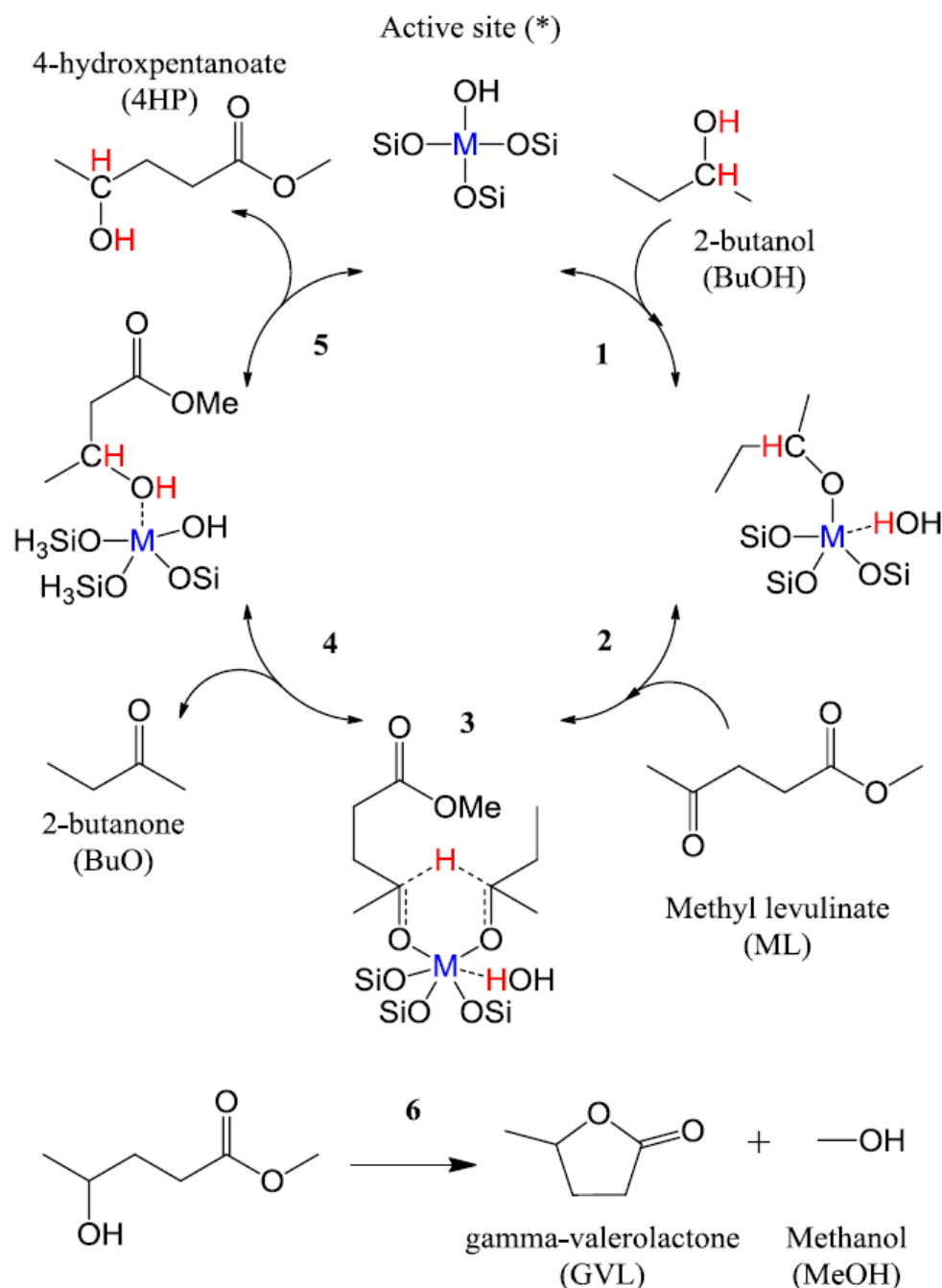


Figure 6: Proposed mechanism for LA to GVL conversion via MPV reduction (Luo et al., 2014)

Though any alcohol can be used for this reaction, it has been demonstrated that secondary alcohols are more active than primary alcohols, their activation energy being 20 kJ/mol lower.¹⁷ This difference in activation energy is most likely due to a higher stability of the α carbon during the hydride shift. Also, more polar hydrogen donors lead to decreasing activity as it affects the strength of solvation of ML and decrease the flexibility of the six-membered transition state.¹⁷

The kinetic study of this reaction showed a first order dependence on both substrates; however, when using one of them as the solvent (i.e. BuOH), it then constitutes the majority of bound species on the acid sites. This leads to an apparent reaction rate $r' = k_{shift}K_{ML}C_{ML}$ where k_{shift} is the forward rate constant of the hydride shift (s^{-1}), K_{ML} the bound-unbound equilibrium of ML and C_{ML} its concentration. This equation can be further simplified as $r' = k_{app}C_{ML}$ with k_{app} the apparent rate constant for the reaction with an excess of 2-butanol. This relation then shows a first-order reaction relative to the concentration of methyl levulinate.¹⁷ The limiting activation energy is that of the hydride shift, at about 52 kJ/mol.¹⁷

Historically, MPV reductions were carried out using aluminum alkoxides.¹⁸ In the specific case of the production of GVL, other oxide or supported metal catalysts have been investigated, such as ZrO_2 , MgO/Al_2O_3 , $CeZrO_x$, Al-Zr mixed oxides, $ZrO_2/SBA-15$, zeolite Beta and eventually Zr-Beta.⁹ Early on, Zr based catalysts showed the best results,¹⁶ hence its important presence in this field of research.

1.4 Zeolites, β -zeolites and Zr- β zeolites

Zeolites are a class of crystalline microporous aluminosilicates with a periodic three-dimensional framework characterized by structures with cavities in the form of channels or cages smaller than 20 Å in diameter.¹⁹ They are made of SiO_4 tetrahedra and, to a lesser extent AlO_4^- , crosslinked by the sharing of oxygen atoms.²⁰ Typically, these materials show Bronsted acidity (the ability to exchange protons), as the tetrahedral aluminum generates a negative charge available for the exchange of protons or cations.

More than 200 zeolite framework types have been identified to date. They vary in terms of structure, pore size and composition. A database containing all this information can be consulted online at <http://www.iza-structure.org/databases/>.

1.4.1 Structural and textural properties

β -Zeolites

Beta zeolites are a synthetic type of zeolites invented by Mobil Oil Corporation in 1967.²¹ However, their very intricate molecular structure was only described 1988 thanks to a combination of electron microscopy, electron diffraction, computer-assisted modelling and

powder X-ray diffraction²². This structure, proposed by Newsam et al. consists of “two sets of perpendicular channels, which intersect to form a three-dimensional array of cages that have three 12-ring apertures”²², these apertures have diameters of $5.6 \text{ \AA} \times 5.6 \text{ \AA}$ and $6.6 \text{ \AA} \times 6.7 \text{ \AA}$ ²³. Different representations of the beta structure are shown in Figure 7, T-sites are referred to as the location of a non-oxygen atom, usually Si or Al.

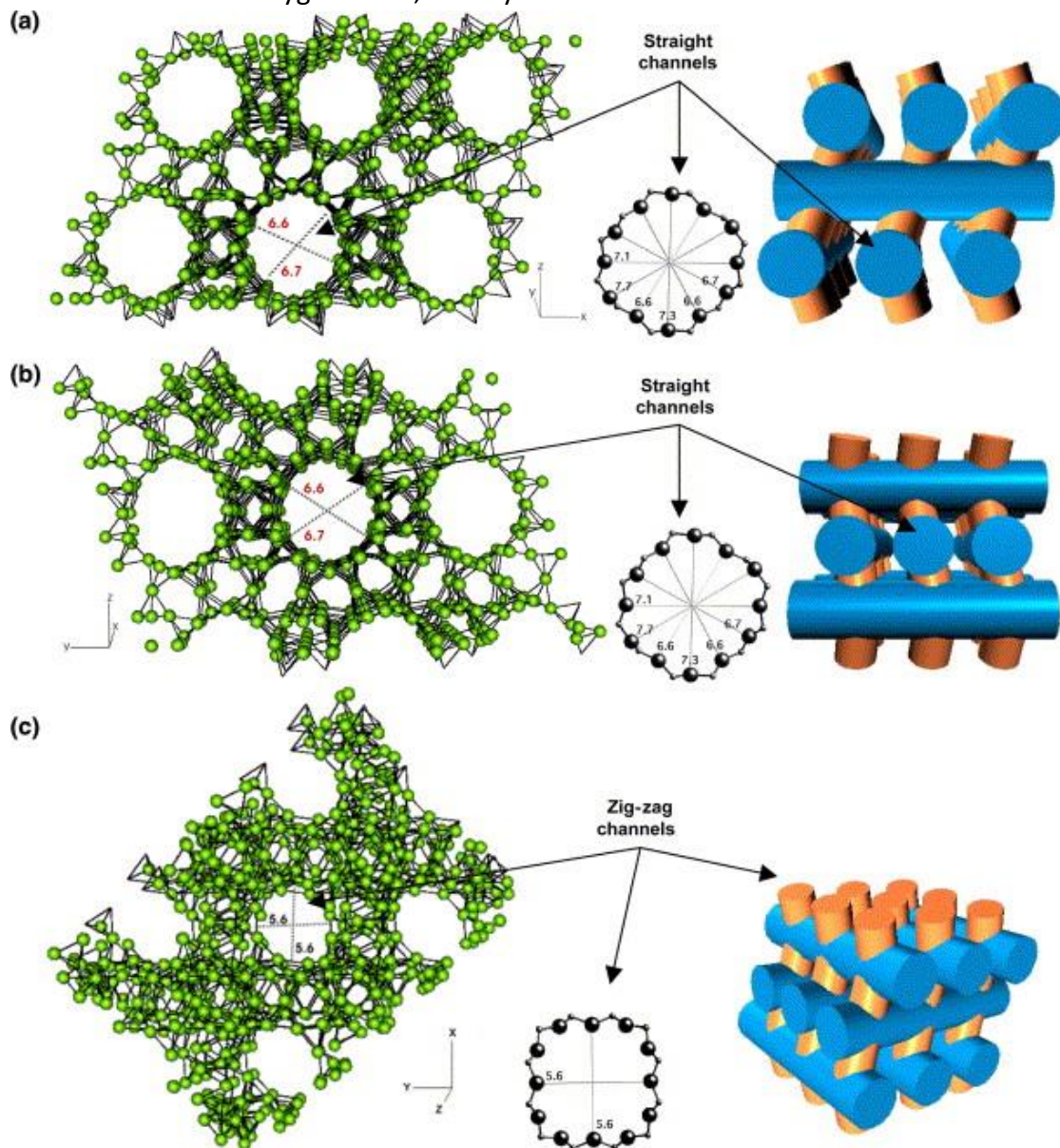


Figure 7: Stereographic drawings and perspective views of zeolite Beta viewed along axis (a) [010], (b) [100] and (c) [001]. Pore radii are shown in Å. In the stereographic drawings the spheres represent the oxygen atoms and the tetrahedron around which surround the T-site. The cylinders on the right represent the channels of the β zeolite. (Bárcia et al., 2005)

Three polymorph structures coexist in any beta zeolite and are called polymorphs A (chiral), B (achiral) and C (achiral), the first two being often present in similar proportion while the latter being almost absent.²⁰ Having different lattice energies, a variation in the relative presence of these polymorphs can yield information about the stress applied to the molecular structure of the zeolite, for example, the introduction of a new heteroatom in the lattice.

Theoretically, these two polymorphs have different responses in X-Ray diffractometry²⁰, meaning that it might be possible to detect a change in polymorphism of a zeolite beta²⁴, which could be of interest in this work.

Typical β zeolites have an impressive specific surface area ranging between 400 m²/g and 700 m²/g.^{25,26} Micropore volume is consistently estimated around 0.15-0.20 m³/g^{25,27,28}.

However, due to the very small size of those micropores (5-7 Å), little to none of this surface is available for catalytic activity. As depicted in Figure 8 the large molecules of substrate cannot diffuse through the small pores, rendering the internal surface area of the zeolite useless. This means that having smaller-sized particles would increase the available, external, surface area. It would not however increase the specific surface area as measured via N₂ physisorption, since nitrogen is small enough to diffuse through the micropores.

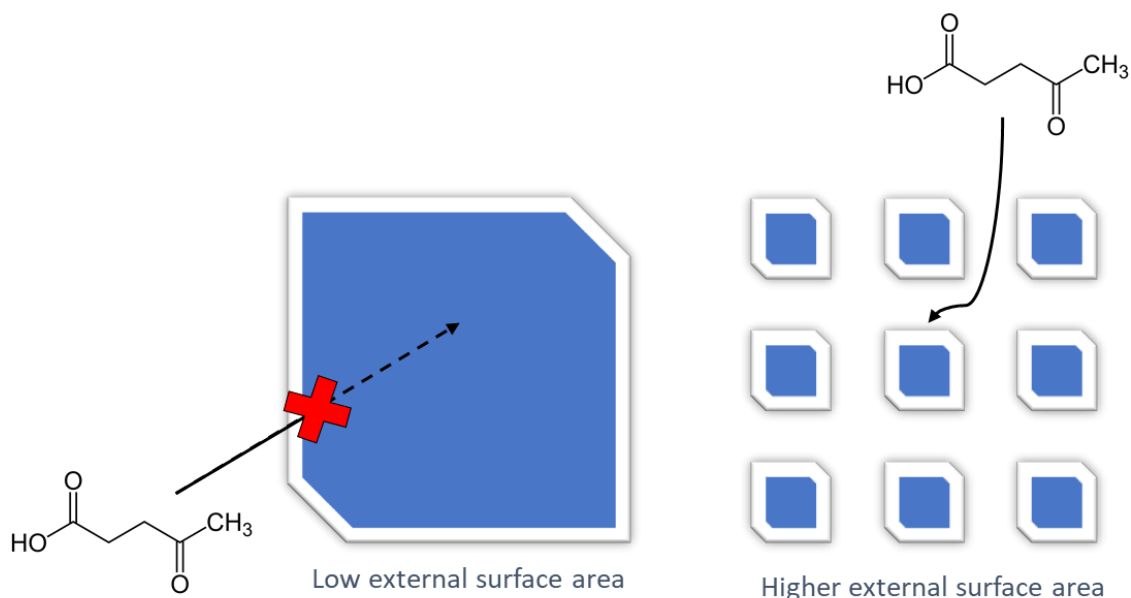


Figure 8: Schematic representation of the influence of external surface area

Zr- β zeolites

Zr- β zeolites are referred to as β zeolites in which a fraction of T-sites is occupied by zirconium. In this specific work, when talking about Zr- β we imply that these contain little to no aluminum (Si:Al >500). While Al- β zeolites can be found with Si:Al ratios going as low as 2.5²⁹, the synthesized Zr- β with the highest loading reported in the literature only has a Si:Zr ratio of 75.^{15,24,30} This limitation could be explained by structural limitations. In fact, the average distance between silicon and oxygen in a zeolite, $\langle\text{Si}-\text{O}\rangle$, is 1.6 Å, $\langle\text{Al}-\text{O}\rangle$ is 1.7 Å while $\langle\text{Zr}-\text{O}\rangle$ is 2.0 Å.^{31,32} Thus, the doping of the lattice with Zr^{4+} causes deviations to $[\text{TO}_4]$ tetrahedra and different degrees of T-O elongation³¹ which implies that above a certain proportion, the tetrahedra could be unable to organize in a crystalline fashion to form the beta zeolite. Some have also argued that this lattice distortion could favor the stacking sequence of the achiral polymorph B²⁴, which would be noticeable through X-ray diffraction. It must be noted however that this doping does not influence significantly the textural properties of the material.^{15,24,27,30}

1.4.2 Lewis acidity in Zr- β zeolites and active sites

The origin of the Lewis acidity in Zr- β zeolites is the Zr heteroatoms. A Lewis acid-base reaction is the coordination of the acid's Lowest Unoccupied Molecular Orbital (LUMO) and the base's Highest Occupied Molecular Orbital (HOMO). In the case of Zr- β , the LUMO is the d_z orbital of the zirconium atom, which can accept the electron density from a Lewis base molecule without increasing the basic character of the neighboring oxygen atoms.³³

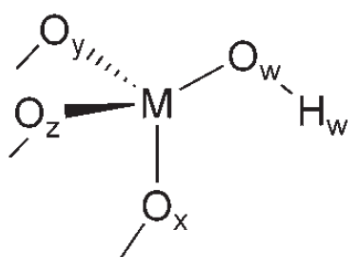


Figure 9: Catalytically active site for MPV reaction

Through density functional theory calculations (DFT) and catalytic tests, researchers have been able to prove that the active site for MPV reaction on a Zr- β is a partially hydrolyzed T site^{17,33,34} as depicted in Figure 9. However, when comparing various M- β zeolites, no direct correlation could be found between the activity and the LUMO energy of the active site.³⁴ The best descriptor for activity happens to be the ability of the metal to polarize the adsorbing carbonyl group³⁴, which

can only be theoretically computed. Though the proportion of Zr sites that are hydrolyzed is an important factor, there are no reports of it being quantified in the literature. In this work, we will refer to T-sites functionalized with Zr as either “Closed” or “Active” Zr T-sites.

1.5 Zr- β zeolites: syntheses and applications

Zr- β zeolites are referred to as beta zeolites in which T sites are occupied only by Si or Zr. Proper Al-free Zr-beta zeolites were first reported in the literature by Zhu et al. in 2003²⁴, thanks to the works of Corma et al. the year before, who pioneered the incorporation of transition metals in beta zeolites.²⁷ Both teams used these new materials as water-resistant catalysts for various MPV reactions, and zirconium immediately proved to be the most active and impervious to water of all tested metals (Zr, Sn, Ti, V, B).

Over the years, Zr-Beta zeolites have been tested for a wide range of applications: epoxidation, oxidation, Bayer-Villiger oxidation, etherification, intramolecular hydride shift, aldol condensation, Diels-Alder reaction and, of course, MPV hydride shift.^{34,35,36,37} In many of these works, Zr- β zeolites were compared with other M- β zeolites and showed to be best suited along with Hf- β for hydride shifts (such as MPV), etherifications and aldol condensations.³⁵ Though Hf- β zeolites show very similar results to those of Zr- β , they will not be investigated in this study as hafnium is ten times more expensive than zirconium with no significant advantage. The specifics and performances of Zr- β zeolites for the MPV reduction of levulinic acid are detailed in section 1.6.

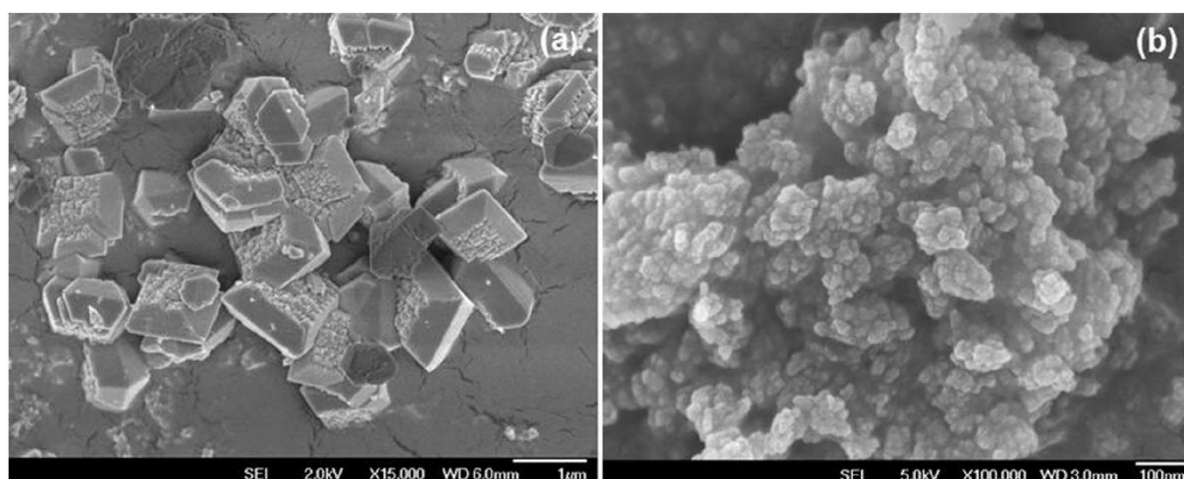


Figure 10: SEM images of Zr-Beta zeolites made (a) hydrothermally and (b) postsynthetically (Wang et al., 2015)

There are two main routes for synthesizing a Zr- β zeolites: the hydrothermal synthesis, and the postsynthetic approach. The hydrothermal route is the one paved by Corma and researchers in 2002 and applied to zirconium by Zhu et al. in 2003. In this method, silicon and zirconium precursor are dissolved in a hydrofluoric medium and set to crystallize under autogenous pressure at 140°C in an autoclave for 20 days.^{24,27} This yields zeolites with a well-dispersed metal content and a size in the micrometer range, as seen in Figure 10.³⁸

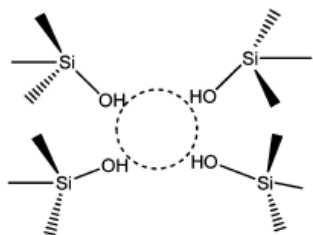


Figure 11: Schematic view of a silanol nest (Tang et al., 2014)

The second method is called postsynthetic as it consists in adding zirconium to a pre-made β -zeolite that has been dealuminated by acid treatment. This means that the zirconium is incorporated in the lattice by filling the defect sites, or silanol nests (see Figure 11), left after the removal of the aluminum; the metal is not simply deposited onto the surface.³⁸ This method allows for faster synthesis since Al-Si- β are much faster to crystallize than Zr- β and do not require hydrofluoric acid, a hazardous chemical both for the operator and the environment.^{38,39} Since the crystals' shape and size are those of the parent beta zeolite, of which the synthesis can be finely tuned, it is possible to obtain nanometric particles of postsynthetic Zr- β .

1.6 Performance of Zr- β zeolites for MPV reduction

Since 2003, Zr- β zeolites have been investigated for MPV reactions.²⁴ However, it is only in 2013 that its first use for the conversion of levulinic acid to GVL was reported.⁴⁰ Table 1 shows the results available in the literature for the reaction of interest. It should be noted, however, that different reaction conditions were used by different groups, notably in terms of substrate and catalyst concentration. TOF's were calculated at different reaction times; the reaction being of first order relative to substrate concentration, this may lead to further comparison issues. At the beginning of the present research project, no report mentioned the use of postsynthetic Zr- β for this reaction, and this prompted us to start investigating along that line. In the course of the project, a report by Morales et al. was published and showed such first example.⁴¹ These results will be discussed later in this manuscript, along with the data that we have acquired.

Table 1: Reported performances of Zr- β for GVL production under 1 atm. HT: hydrothermal, PS: postsynthetic, LA: levulinic acid, ML: methyl levulinate

Synthesis	Zr loading (Si:Zr molar)	T (°C)	Substrate	Initial TOF (s ⁻¹)	Selectivity (%)	Conversion	Ref
HT	127	120	LA	0.004	>99	98% (11 h)	Bui et al., 2013
HT	127	120	ML	0.026	>99	97% (5 h)	
HT	75	118	LA	-	93	88% (10h)	Wang et al., 2014
HT	100	118	LA	-	96	96% (10h)	
HT	150	118	LA	-	97	71% (10h)	
HT	200	118	LA	-	>99	27% (10h)	
PS	32	150 ^b	LA	0.008 ^a	85	99% (3h)	Morales et al., 2019

^a: approximation from available data, ^b: under autogenous pressure

2 Objectives

The main objective of this work is to investigate the potential of postsynthetic Zr- β zeolites for the production of GVL from levulinic feed. Particularly, we aim at evaluating the effectiveness different methods of metal (Zr) incorporation and of different Zr precursors in the perspective of optimizing catalytic performance.

In a broader perspective, our project aims at developing the expertise to carry out the postsynthetic approach on zeolites. Once these procedures are well mastered on the dealuminated commercial H- β zeolite, the method will be applied to nano-zeolites developed independently in the lab in the PhD thesis of Arnaud Dettaille. Ultimately, we plan to build hierarchal Zr- β zeolites similar to the hierarchical TS-1 zeolite catalysts reported by our group recently.⁴²

3 Strategy

To reach our objective, we will follow the strategy shown in Figure 12. The first step will be to synthesize the Zr- β zeolite, starting from commercial Si-Al- β zeolites. The aluminum will thus be removed before incorporating the zirconium. The choice of incorporation method will be related to the chosen precursor's characteristics: state of matter, solubility, nature of the counter-ion.

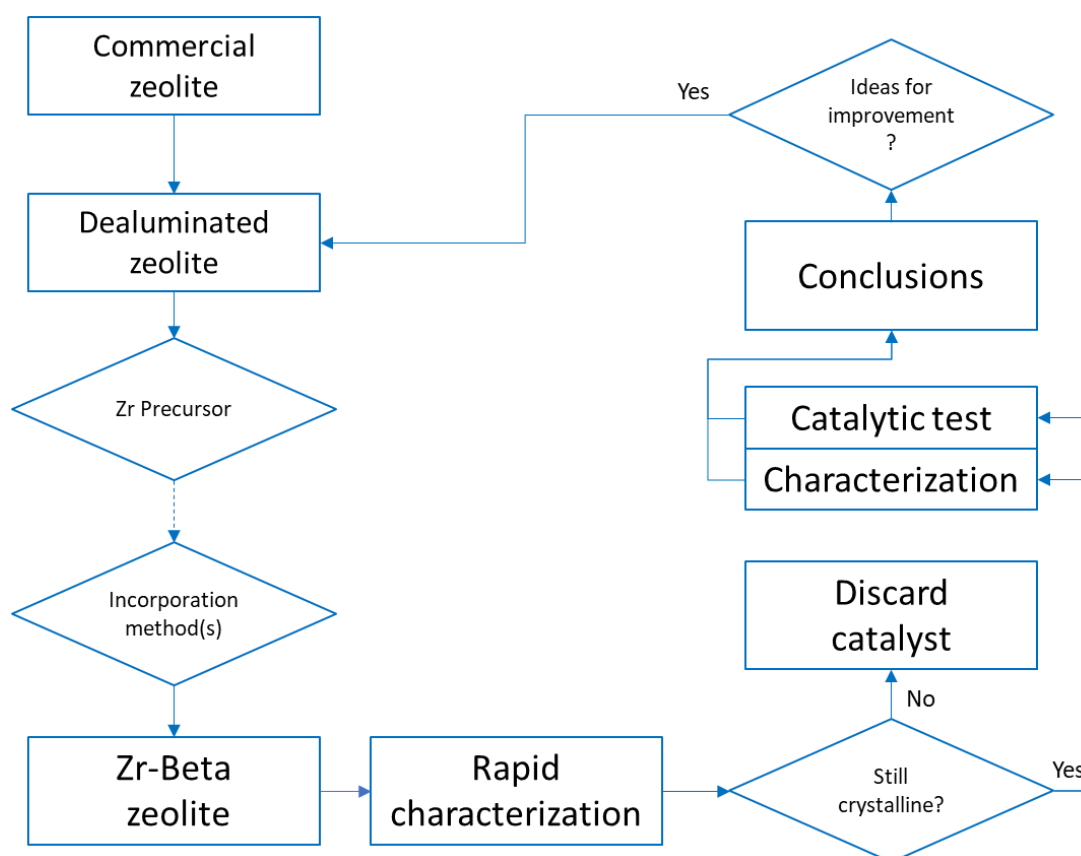


Figure 12: Strategy organigram

After the synthesis is complete, the powders will be characterized via X-Ray Diffractometry (XRD) and Fourier Transform Infrared spectroscopy – Attenuated Total Reflectance (FTIR-ATR), to ensure we still have a crystalline and aluminum free beta zeolite. In practice, the FTIR-ATR was not performed systematically, as the dealumination step is the same across all catalysts.

Catalysts passing this stage will be tested and further characterized (N_2 physisorption, diffuse reflectance UV spectroscopy (DRUV) and, depending on performance, IR-Pyridine adsorption, inductively coupled plasma-atomic emission spectroscopy (ICP-AES), X-ray Photoelectron Spectroscopy (XPS). The catalytic tests are carried out against a variety of blanks to assess the relevance of the results. These blanks include tests using commercial parent zeolite, dealuminated zeolite, no catalyst at all, a different substrate, no substrate, homogeneous Lewis or Bronsted catalyst. This will be done in an effort to isolate the effect of the Zr- β zeolite on the reaction.

Finally, the resulting information will be used to try to tweak the synthesis method and improve the catalyst.

EXPERIMENTALS

4 Materials and method

4.1 Catalysts preparation

4.1.1 *Starting materials*

Zr- β zeolites were postsynthetically prepared using commercial NH_4 - β zeolites with an Si/Al ratio of 12.5 from Zeolyst International (CP-814E). Before use, the NH_4 - β zeolites are calcined under static air at 550°C for 6 hours (5 K.min⁻¹ ramp) to obtain H- β zeolites.

4.1.2 *Dealumination*

Dealumination was carried out following a standard procedure as reported by Wang et al. in 2015³⁸. Briefly, the powder is suspended in 65% nitric acid (20mL_{HNO₃}/g_{cat}) for 20 hours at 80°C. The suspension is then quenched and centrifugated (14,000 rpm, 5 min). Finally, the resulting solid is washed with deionized water through repeated suspension and centrifugation until the supernatant reaches a pH of at least 6.

After washing and separation, the dealuminated beta zeolite is dried overnight in the oven at 100°C.

4.1.3 *Incorporation methods*

The following Zirconium precursors were used: Zr chloride (anhydrous powder, 99.5+%, Alfa Aesar), Zr oxychloride hydrate (powder, 98%, Sigma-Aldrich), Zr oxyacetate (powder, MEL[®] Chemicals), Zr oxynitrate hydrate (powder, 99%, Sigma-Aldrich), Zr propoxide (70% solution in 1-propanol, Sigma-Aldrich).

All resulting powders are dried overnight in the oven at 100°C then calcined at 550°C for 6 hours (5 K.min⁻¹ ramp) and stored in a desiccator.

4.1.3.1 *(Wet) Ion exchange*

This metal incorporation method is adapted from Kant et al. (2017)²⁵. The requested amount of metal precursor is dissolved in deionized water (25mL per gram of zeolite). After complete dissolution of the precursor, the dealuminated beta zeolite is added to the solution, then stirred at room temperature for 5 hours at 500rpm. The solution is then separated by centrifugation and, when applicable, the solid is washed three times with deionized water to remove chlorine.

4.1.3.2 *Solid state ion exchange*

Solid state ion exchange (SSIE) is performed by simply thoroughly grinding the appropriate amount of precursor with the dealuminated beta zeolite for 20 minutes to obtain a homogeneously dispersed powder. The incorporation of the metal is completed by the calcination.⁴³

4.1.3.3 Incipient wetness or dry impregnation

In this standard impregnation method, the required amount of metal is supplied to the dealuminated beta zeolite by adding a volume of precursor solution equal to that of the free pore volume of the powder, as calculated via nitrogen physisorption. The required volume of the solution is added dropwise to the powder while thoroughly mixing until it appears dry again.

4.1.3.4 Wet impregnation

The procedure for wet impregnation is adapted from Wang et al. (2015)³⁸. The requested amount of metal precursor is dissolved in deionized water (25mL per gram of zeolite). After complete dissolution of the precursor, the dealuminated beta zeolite is added to the solution, then stirred at 100°C in an oil bath until complete evaporation of the solvent.

4.1.4 Prepared catalysts

The details of the prepared catalysts are shown in Table 2 and Table 3. The nomenclature for the naming of the catalysts is “Counter-Ion_Method_100*Loading”, i.e.: Cl4_WIE_1.5 for a catalyst prepared via wet ion exchange using ZrCl_4 with a nominal Zr/Si molar ratio of 0.015. Different batches of a same catalyst are differentiated with a lower-case letter in the name code (Cl4_WIE_1.3b). For simplicity, the metal loading (%) will be referred to as the molar Zr/Si ratio multiplied by 100.

Table 2: Summary of all prepared catalysts. The numbers in each cell are 100 times the nominal molar Zr/Si ratio

Precursor \ Method	Wet ion exchange (WIE)	Solid state ion exchange (SSIE)	Dry impregnation (DI)	Wet impregnation (WI)
ZrCl_4	1, 1.3, 1.5, 2, 2.77			1
$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$	1			
Zr oxyacetate	0.75	0.75		0.75
Zr Propoxide		1	1	
$\text{ZrO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1	1		1,2,4

Table 3: Precursor masses used for a 1% loading

Precursor	Mass used ($g_{\text{precursor}}/g_{\text{dealuminated zeolite}}$)
ZrCl_4	0.0388
$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$	0.0536
Zr oxyacetate	0.0283 (0.75%) ^a
Zr Propoxide	0.0545
$\text{ZrO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	0.0565

^a: Value is wrong and leads to a 0.75% loading

4.2 Catalytic testing

Catalysts are tested in conditions similar to those reported by Wang et al. (2014)¹⁵ for comparison purposes. Two round-bottom glass flasks were used as reactors; reactor A: 50 mL and reactor B: 10 mL.

4.2.1 Standard tests

0.4 g of catalyst is weighted in a round-bottom flask and 454 μL of dodecane (>99%, VWR Chemicals) are added as an internal standard (IST). The substrate is then added to the flask, either 0.2322 g of levulinic acid (98%, Sigma-Aldrich) or 280 μL of ethyl levulinate (99%, Sigma-Aldrich). 2-Pentanol (99%, Alfa Aesar) is used both as a solvent and as reagent for a total volume of 10 mL. The concentrations of catalyst, dodecane and substrate are respectively 40 $\text{g}\cdot\text{L}^{-1}$, 0.2 $\text{mol}\cdot\text{L}^{-1}$ and 0.2 $\text{mol}\cdot\text{L}^{-1}$. Each compound is weighted individually in the flask for precise determination of its concentration.

The reaction is carried out in an oil bath at reflux temperature (118°C in the flask) under atmospheric pressure. The total reaction time is 10 hours, 200 μL samples are taken after homogeneous dispersion of the catalyst and then after 0.5, 2, 4, 6, 8 and 10 hours to plot a kinetic curve. Each sample is taken using a disposable syringe and needle (VWR) then filtered through a PTFE membrane with 0.2 μm pore size (VWR) and stored in a glass vial for GC analysis.

4.2.2 Recyclability tests

After a standard test run, the catalytic medium is recovered from the flask and centrifugated at 14,000 rpm for 4 minutes. The solid is then washed 3 times with deionized water. It is then dried overnight under air at 100°C and 2 hours under vacuum at 60°C.

The reaction is carried out in the same conditions as a standard test (4.2.1), adjusting the amount of both reactant and standard with respect to the remaining mass of powder. To reduce the losses of catalyst, samples are only taken 3 times: at $t=0$, $t=2$ hours and $t=10$ hours (after separation). To alleviate any risk of external factors of variation, the exact same reactor, refrigerant and magnetic stir bar are used for each run.

4.2.3 Gas Chromatography

GC analysis of the samples is carried out on a Bruker SCION 456-GC, equipped with an Agilent DB-5 (30mx0.32mmx1 μm) column, a split/splitless injector at 250°C set to a split ratio of 1:20 and an automatic sampler injecting precisely 1 μL . It has an FID detector at 250°C using 300 $\text{mL}\cdot\text{min}^{-1}$ of air, 30 $\text{mL}\cdot\text{min}^{-1}$ of H_2 and 25 $\text{mL}\cdot\text{min}^{-1}$ of helium as make-up gas.

Pressure is kept constant in the column at 11 psi, and oven temperature follows the profile shown in Figure 13.

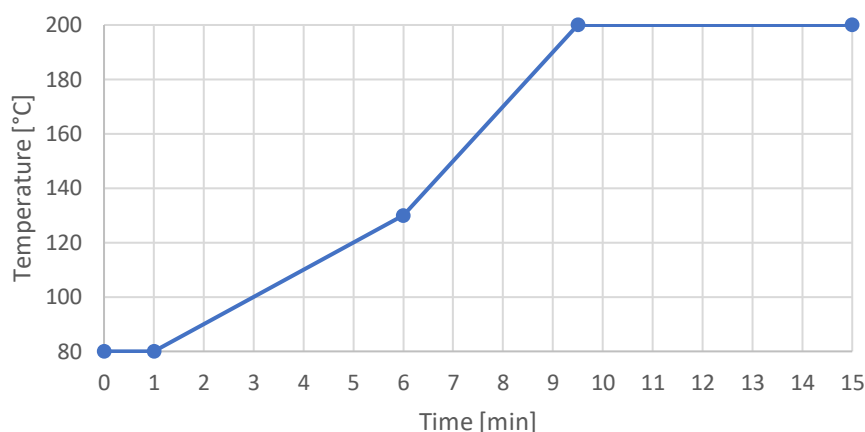


Figure 13:GC temperature program

4.3 Characterization techniques

4.3.1 N_2 physisorption

Nitrogen physisorption is a technique used to characterize the textural properties of the catalyst, such as specific surface area, pore volume, and average pore size. About 50 mg of power is precisely weighted for analysis and degassed under vacuum at 150°C overnight using a Micromeritics VacPrep 061. The samples are weighted again after degassing. Nitrogen physisorption isotherms are measured at 77K in a liquid nitrogen bath using a Micromeritics TriStar 3000.

4.3.2 X-Ray Diffractometry (XRD)

X-Ray diffractometry relies on the elastic diffusion of photons through the crystalline planes of the sample. This technique allows the identification of crystalline phases through the equation of Bragg and crystallite size using the equation of Scherrer. In practice, the sample is sprinkled on a sample holder coated with Nivea cream, which is then inserted in a Druker-D8 Advance diffractometer with a Bragg-Brentano geometry. X-Ray radiation ($K\alpha=0.154$ nm) is produced by a copper anode under 40 kV, 30 mA. Detection is performed using LynxEye XE-T technology, between $2\theta = 5^\circ$ and 80° at a speed of $5.93^\circ/\text{min}$, with a total of 5051 steps of 0.015° . The resulting data is treated using the PDF2-2004 database.

4.3.3 Diffuse reflectance UV-Vis spectroscopy (DRUV)

UV-Vis spectroscopy uses the property of atoms or molecules to undergo electronic transition when exposed to certain wavelengths of light and therefore absorb these photons. In DRUV, photons are captured by an integrating sphere after hitting the powder and scattering on the surface of its grains. This allows for an absorbance reading without having

to transmit through a thick, solid sample. DRUV is especially useful to look for extra-framework heteroatoms.⁴⁴

In practice, samples are prepared using a Harrick Praying Mantis™ Sampling kit (DRP-SAP); the powder is placed in a cylindrical sample holder and packed to obtain a relatively smooth surface. After running a Spectralon® blank from the kit, the sample can be inserted in the chamber for analysis. This is carried out with a Shimadzu UV-3600 Plus Series spectrometer, wavelength range is set from 190 to 350 nm, with a sampling interval of 0.1 nm. Acquired absorbance data is then transformed via the Kubelka-Munk function using Shimadzu's proprietary software UVProbe 2.62.

4.3.4 *Infrared spectroscopy*

4.3.4.1 FT-IR ATR

Fourier Transform Infrared spectroscopy – Attenuated Total Reflectance is a surface characterization technique used to determine the nature of the species on the sample, by analyzing the vibrational modes of molecules excited by the IR spectrum, which serve as the “fingerprint” of the different chemical species. In practice, a small quantity of sample is deposited on the surface of a highly refractive crystal, as to cover as much of its surface as possible. The IR beam goes through the crystal, reflects onto the sample, creating an evanescent wave, and is then caught by the detector.

The analysis is carried out using a Bruker EQUINOX IFS55 equipped with a DTGS detector. Each sample is scanned 100 times against air as background, in the wavelength range of 800 to 4000 nm with a sampling interval of 2 nm. Acquired data is normalized using the software OPUS.

4.3.4.2 Pyridine adsorption and temperature-programmed desorption (Pyr-IR)

This technique is used to characterize surface acidity of the catalyst, quantifying Lewis and Brønsted acidity. This is done by quantifying the absorption bands at 1455 cm⁻¹ (Lewis) and 1551 cm⁻¹ (Brønsted) caused by vibrational modes of pyridine that are specific to it being adsorbed on a certain type of acidic site.

In practice, about 15 mg of sample are pressed into a thin wafer and placed inside a sample holder in a Pyrex chamber equipped with a NaCl window for IR analysis. The sample can be moved in the chamber for either IR analysis or thermal treatment without breaking the vacuum. Typically, the sample is degassed under vacuum (10⁻⁵ mbar) at 350°C for 3 hours and analyzed. Then, 1000 Pa of Pyridine at room temperature is allowed in the cell for adsorption (30 minutes). The IR spectrum of the sample is taken again. Finally, desorption is carried out at 100°C, 10⁻⁵ mbar for 1 hour for and then sequentially by steps of 50°C until total desorption or up to 250°C. IR spectra are taken after each desorption steps, and in the same conditions

as in the FTIR-ATR method, with the exception being that the blank is taken on the NaCl window.

The molar absorption coefficients for protonated pyridine and coordinated pyridine are respectively 1.67 and 2.22 $\text{cm} \cdot \mu\text{mol}^{-1}$ as reported in the literature.⁴⁵

4.3.5 *X-ray Photoelectron Spectroscopy*

An incoming monochromatic X-ray beam induces the ejection of photoelectrons from the sample surface on a depth of around 10 nm. These emitted photoelectrons have a specific kinetic energy depending on their binding energy. They are filtered and analyzed to deduce this binding energy. The binding electron energy is specific for each orbital of a certain element. In this work, an SSX 100/206 Photoelectrons Spectrometer from Surface Science Instruments equipped with an Al RX monochromatic and a micro-focused source. Pressure inside the analysis chamber is about 10^{-6} Pa, the analysis angle is 55 °C and the pass energy is fixed at 150 eV. Data was processed with CasaXPS from Casa Software Ltd, UK. To calibrate the binding energy scale, the Si 2p peak has been set at 103.5 eV.. Spectra are then decomposed, and molar fractions can be obtained based on the acquisition parameters and sensitivity factors provided by the manufacturer.

4.3.6 *Inductively coupled plasma-atomic emission spectroscopy (ICP-AES)*

This analysis gives the elemental content of a sample. More specifically, Si, Al and Zr were analyzed. The device used is a Thermo Scientific ICP 6500. The calcined samples were solubilized by sodium peroxide fusion in carbon crucibles. Plasma is generated via inductive currents and produce excited atoms and ions, which in turn emit electromagnetic radiation at wavelengths characteristic of a particular element.⁴⁶

The analysis was carried out by the Mineral & Organic Chemical Analysis (MOCA) platform of the Earth and Life Institute (ELI) at UCLouvain.

RESULTS AND DISCUSSION

5 Results and discussion

This section will be organized following the strategy of the study. First, the quality of the dealumination process will be assessed. Then, the catalytic performances of the catalysts samples will be presented. Finally, the characterization of the samples will be used in an attempt to interpret their catalytic behavior as well as to assess the incorporation of zirconium in the zeolite structure.

5.1 Dealumination of the parent H-beta zeolite

The dealumination of β -zeolites is a well-documented simple process that poses little challenge. However, early characterization of this powder is necessary before starting the incorporation of the zirconium; a failure to dealuminate the zeolite would render the incorporation impossible.

After dealumination, the powder must be checked for textural and structural integrity, via N_2 physisorption and XRD by comparison with the parent H-Beta zeolite. FTIR-ATR is used to assess the removal of aluminum from the lattice.

5.1.1 N_2 Physisorption

The dealuminated zeolite will be compared to the parent zeolite to ensure the textural properties of the material remain unchanged. N_2 physisorption (Figure 14 and Table 4) revealed that the dealuminated zeolite display a combination of the type I and type IV isotherms, with a small H4-type hysteresis loop. Though a type I isotherm is to be expected from a microporous material, the hysteresis observed at higher relative pressure is not. It is reported in the literature however that this mesoporosity is often displayed by microporous

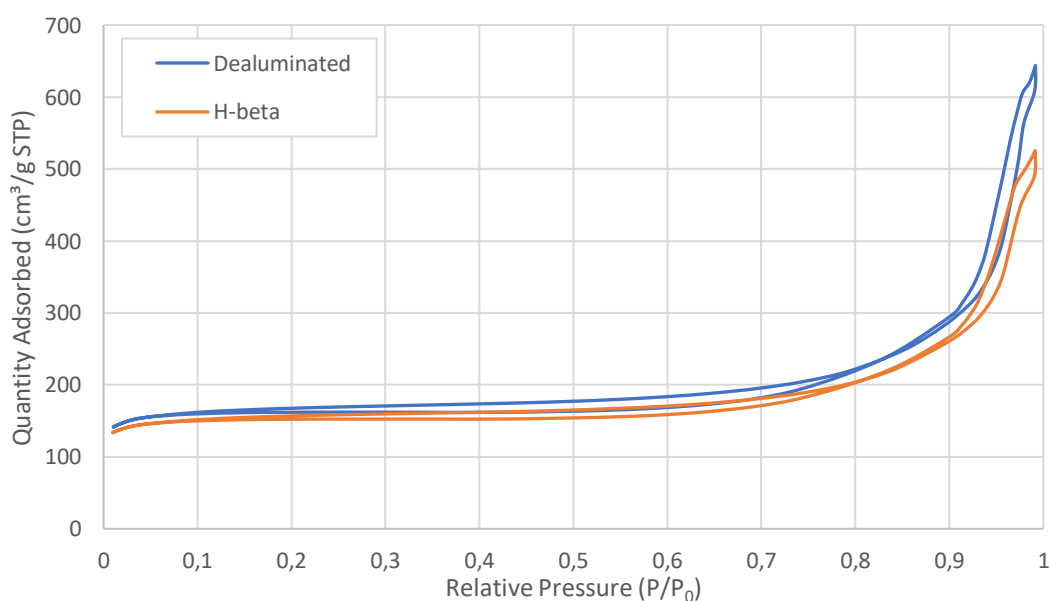


Figure 14: Adsorption and desorption isotherms comparison between parent and dealuminated β -zeolite

zeolites as a result of crystal aggregation.⁴⁷ Considering the 10% margin of error generally accepted for the method, we do not consider the dealumination process to have an impact on the textural properties of the material.

Table 4: Effect of dealumination on textural properties

Sample	S_{BET} (m ² /g)	t-Plot external surface area (m ² /g)	t-Plot micropore volume (cm ³ /g)	Cumulative pore volume (cm ³ /g)	BJH mesopore size (nm)
H-Beta	610	100	0.2	0.6	21
Dealuminated	650	110	0.2	0.8	23

5.1.2 XRD

The X-ray diffractogram of the dealuminated zeolites is compared to that of the parent zeolite beta in Figure 15. No significant phase change can be observed. There is however a slight shift to higher angles for the peaks after 20° as seen with the dotted lines on the diffractogram.

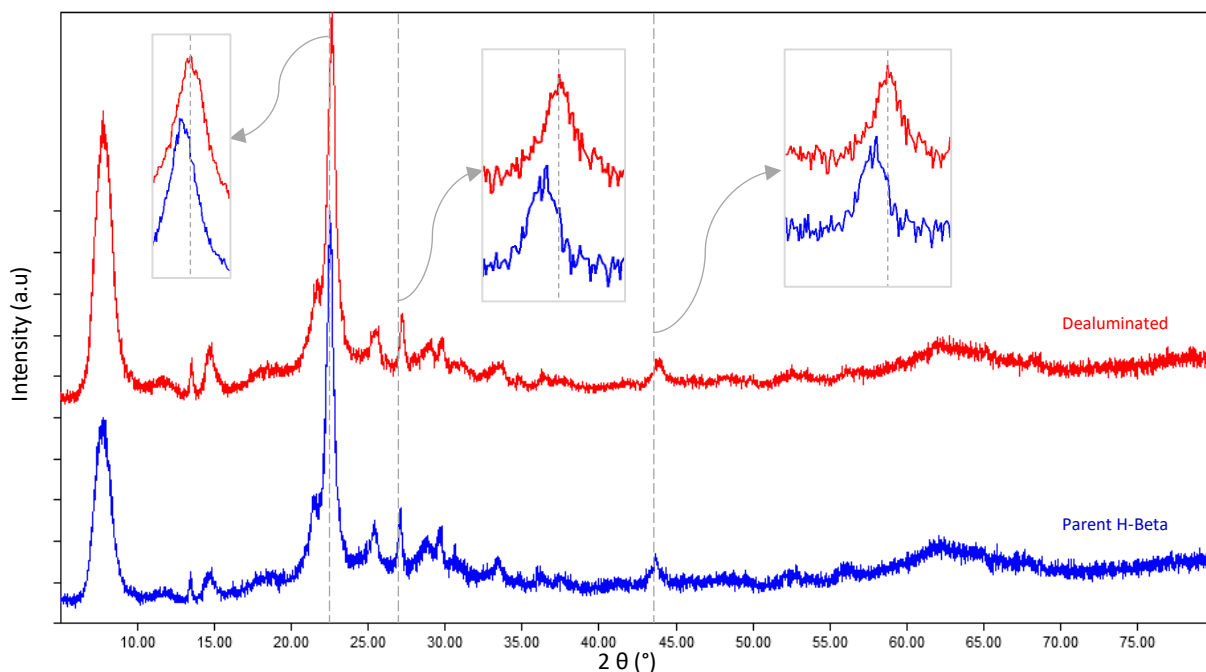


Figure 15: Powder XRD comparison of dealuminated sample and its parent zeolite

This shift implies a decrease of the d spacings, which corresponds to a smaller average bond length in the lattice. The Al—O bond being 0.1 Å longer than the Si—O bond, this could be the sign of the removal of aluminum from the zeolitic structure.

The X-ray diffraction data shows that the structural properties of the zeolite remain otherwise unchanged.

5.1.3 FT-IR

Analysis of the zeolites by IR spectroscopy allows to probe the vibrational modes of the silicon lattice. In Figure 16, we see the clear impact of dealumination on the sample. A new peak appears at 950 cm^{-1} , caused by Si—OH stretching, which can be related to the presence of a large amount of defect sites in the lattice.²⁸ The shift to higher wavenumbers of the large peak at 1090 cm^{-1} , the O—T—O asymmetric stretch, is reportedly a sign of a decreased content of aluminum.⁴⁸ The shoulder at 1230 cm^{-1} decreases upon dealumination which has also been reported, though not commented, in previous studies.²⁸

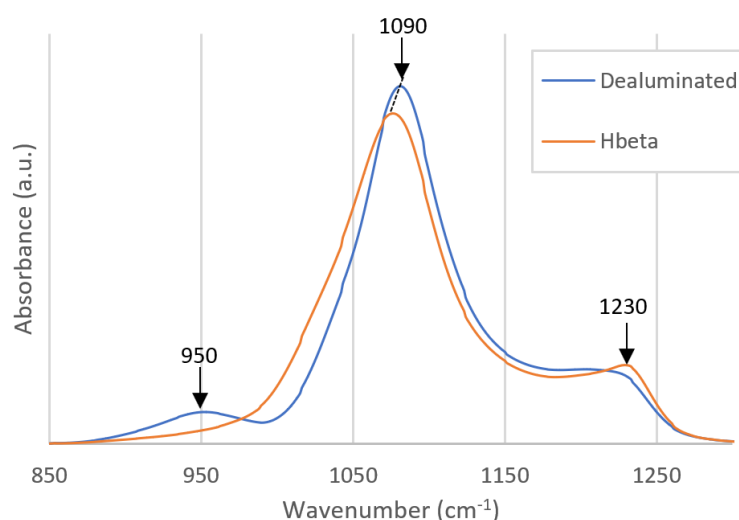


Figure 16: FT-IR spectra of the skeletal vibrations of the zeolites

Through this analysis, we have been able to confirm the removal of aluminum from the zeolitic material. However, the qualitative nature of the information makes it impossible to quantify to which extent the aluminum was removed.

5.1.4 Elemental analyses: ICP-AES and XPS

Elemental analysis was carried out on several finished catalysts to quantify the removal of aluminum from the lattice. The mean Si/Al molar ratio of our catalysts measured via ICP-AES is approximately 400 ± 100 (mean value of 7 samples). Starting from a Si/Al molar ratio of 12.5, we see that we have effectively removed about 97% of the aluminum.

Note that due to the sodium peroxide solubilization method, the limit of quantification for aluminum is quite high; we cannot precisely quantify a Si/Al molar ratio above 200.

Aluminum was below the limit of detection in XPS and could not be characterized.

5.1.5 Summary

Nitrogen physisorption has shown the retention of textural properties and infrared analysis the apparition of silanol nests as well as a qualitative decrease of aluminum. Through XRD, we saw no change of phase in the material. These results indicated an adequate dealumination process, allowing us to carry on with the incorporation of zirconium. The ensuing elemental analysis has confirmed the proper removal of aluminum.

5.2 Catalytic tests

5.2.1 Non-standard tests (NST)

A series of 7 non-standard tests, or NST, has been performed and are reported in Table 5. Some of them served as blanks and others were used to properly identify peaks appearing during GC analysis.

Table 5: Summary of all non-standard tests.

Experiment name #	Variation from standard test	Goal	GVL selectivity ^a	LA consumption (Time)
BLK 1	Absence of catalyst	Isolate the effect of the catalyst	0	3% (4h)
CH 2	Cyclohexanone as substrate	Confirm GC peak identification	N/A	100% (<2h)
HA 3	H ₂ SO ₄ as catalyst	identification of MBL GC peak	0	97% (3h20)
HBEA 4	H-Beta as catalyst	Isolate the effect of the catalyst	14%	29% (6h)
DEAL 5	Dealuminated zeolite as catalyst	Isolate the effect of Zr in the catalyst	0	7% (6h)
LEW 6	AlCl ₃ as catalyst	Isolate the effect of any Lewis acid	0	27% (9h)
CML 7	2-Pentanone as substrate	Identification of a ghost GC peak	N/A	N/A

a: GVL selectivity is calculated as mol_{GVL}/mol_{LA consumed}

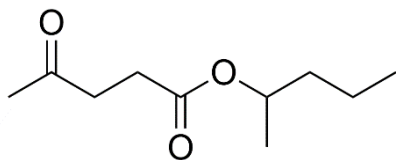


Figure 17: 1-methylbutyl levulinate

As expected, only the parent H-Beta zeolite showed some activity for the conversion of LA to GVL, though the conversion of LA and the selectivity for GVL were low. For NST that contained LA or EL, the main product observed was 1-methylbutyl levulinate (MBL), formed through the (trans)esterification of LA/(EL) by 2-pentanol. HA 3 and HBEA 4 have allowed us to compute the FID response coefficient of MBL which is not commercially available.

The last NST, CML 7, allowed us to confirm a certain unidentified peak appearing in GC was not directly related to the reaction of interest. Indeed, in all catalytic tests, an unknown compound's concentration rose significantly with respect to the consumption of LA. However, it did not appear to compete with GVL in terms of selectivity of the catalysts, as the carbon balance was not impacted by this compound. The compound also appeared when using cyclohexanone as substrate, but its concentration did rise more in presence of LA than EL. It was also most pronounced in presence of H-Beta than the dealuminated zeolite. This has led us to believe that the production of the compound was catalyzed by Bronsted acidity, and that it may come from the solvent. To test this hypothesis, we introduced Cl4_WIE_1.3 in a 50% v/v solution of 2-Pentanol and 2-Pentanone (the byproduct of the MPV reduction) and heated until reflux. The unknown compound was the only product of reaction, though in the exact same quantities as in a standard catalytic test of Cl4_WIE_1.3 with EL as substrate. We thus concluded that the compound was a product of the reaction of 2-pentanol and 2-pentanone catalyzed by Bronsted acidity, both that of the catalyst and that of the levulinic acid (pK_a 4.6). It was therefore not competing with the MPV reduction either in terms of selectivity or specificity, we decided to disregard this compound. We did note however that it may become a practical issue when it comes to separation, as its volatility is very close to that of GVL.

5.2.2 Screening on the Zr-beta catalysts for the conversion of LA to GVL

5.2.2.1 Overview

A total of 14 catalysts were tested for the conversion of LA to GVL (Figure 18). The activity is showed through the levulinic acid converted after 10 hours (full bar), with the blue part being the GVL yield which is directly measured by GC-FID, and the remaining orange part being the side products (mainly MBL), calculated by difference. For comparison, the scale of the graph goes to $5 \cdot 10^{-4}$ mol/h.g_{cat}, which is the 10h-specific activity achieved by Wang and researchers in 2014 with their hydrothermal Zr-β.

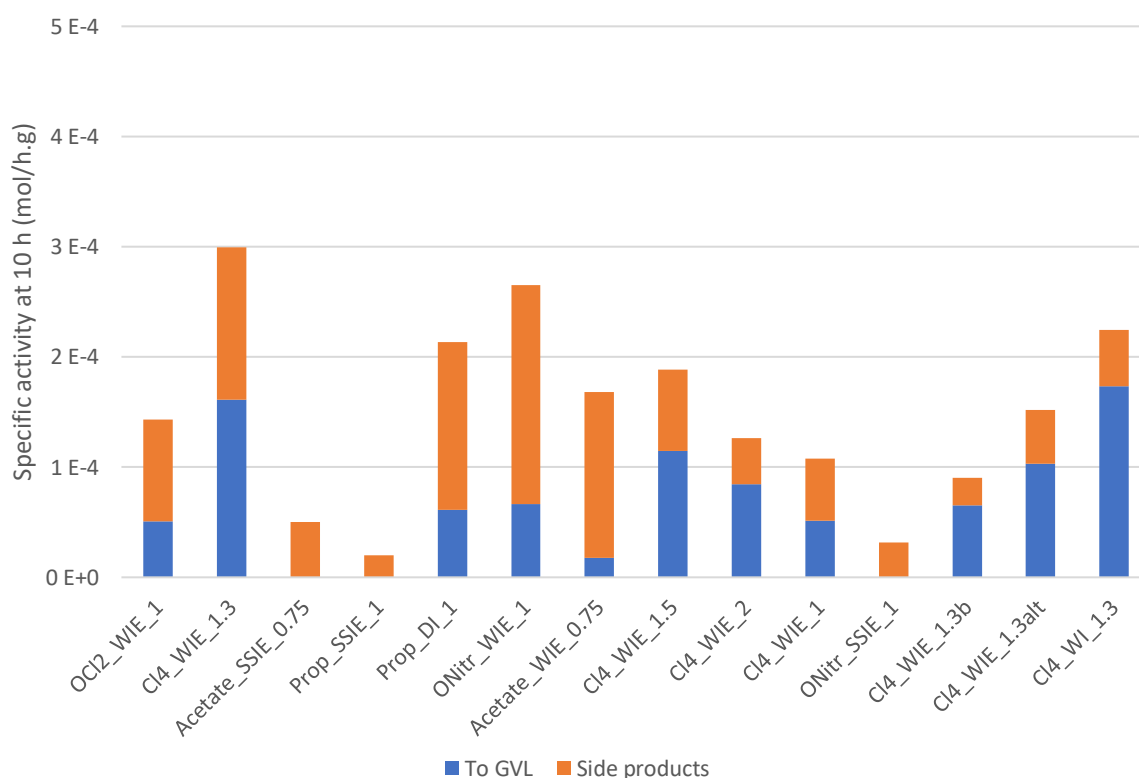


Figure 18: Summary of catalytic tests using levulinic acid as a substrate

In general, our catalysts do not perform as well as those reported by Wang and researchers, in the same conditions (Table 6). In the following sections, we will be discussing the different precursors, incorporation methods, as well as the reaction kinetics in an effort to understand the issues of our catalysts and improve them.

Table 6: Comparison of our best catalyst and that of Wang et al., 2014

Catalyst	GVL produced (mol/L)	LA consumed (mol/L)	MBL produced (mol/L)	LA conversion (%)	GVL selectivity (%)
Cl4_WI_1.3	0.067	0.087	0.009	46%	77%
Zr-Beta-100 (Wang et al.)	/	/	/	100%	96%

5.2.2.2 Discussion of the impact of different incorporation methods

All catalysts prepared via the SSIE method are close to inactive. We can even see in Figure 19 that these catalysts perform worse than the dealuminated parent zeolite and yield no GVL at all. The only plausible hypothesis for this failure is the improper grinding of the powders and thus poor distribution of the metal precursor.

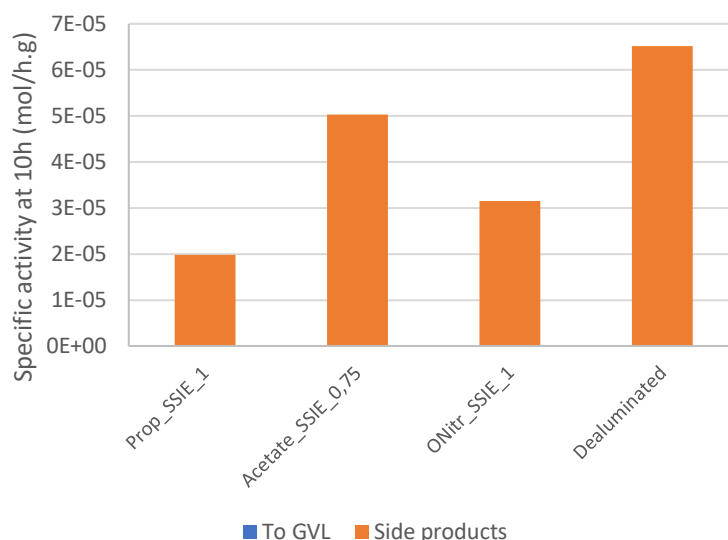


Figure 19: Performances of SSIE catalysts compared to the dealuminated zeolite

However, we could not hypothesize that the method was inappropriate for the incorporation of the zirconium in a dealuminated zeolite, as it has been successfully reported several times in the literature, with various precursors.^{28,43,49} Through characterization, we will discuss further the reasons behind poor activity of our SSIE catalysts, but we can already hypothesize that no Zr was incorporated in the framework of these catalysts.

The WIE method offered more promising results (Figure 20), though the activity of those catalysts depends vastly on the precursors; their effect will be discussed in section 5.2.2.3. We can however draw conclusions about the method itself if we compare the performances of the various Cl4_WIE catalysts. We see in Figure 20 that Cl4_WIE_1.3 and Cl4_WIE_1.3b have significantly different activities and selectivities even though they were prepared via the same procedure. This leads us to believe that the WIE method is not very repeatable.

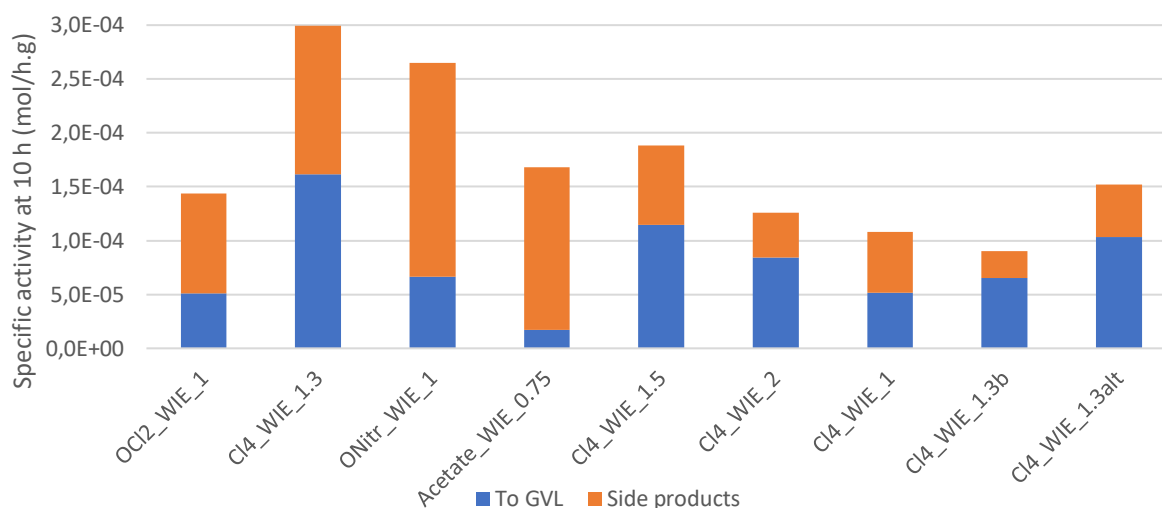


Figure 20: Summary of the performances of WIE catalysts

Similarly, we notice from the Cl4_WIE catalysts that using increased loadings of Zr (with this method) does not consistently increase the performance of the catalysts. We suspect this to be another result of the unreliability of this incorporation method; it appears we have little control on the actual quantity of Zr inserted in the catalyst. Our initial hypothesis was that the ion exchange of Zr with only 12.5% of the vacant sites left after removal of Al (for a 1% molar loading) could be done in a single step; this hypothesis is now threatened and will be challenged again through ICP-AES and XPS in section 5.3.5.

Cl4_WIE_1.3alt was made from the same batch as Cl4_WIE_1.3b but they were separated after ion exchange; the latter being thoroughly washed (similarly to all other WIE samples) and the former being dried immediately after centrifugation. This shows that the washing procedure not only removes the counter-ions of the precursors, but also a portion of the zirconium itself. This would explain the lower activity of the washed catalyst. Washing should thus be done only when the counter-ion does not vaporize through calcination (i.e. halogens).

The dry impregnation method was only used with Zr propoxide. The reason is that it is the only precursor we had in liquid form, which could then be diluted to the desired concentration. All other precursors are solids and were too difficult to solubilize at high concentrations. The performances of this catalyst were very similar to those of ONitr_WIE_1, so we have decided to focus our efforts on the latter, which appears more promising through characterization (see 0).

Finally, the wet impregnation method yielded the catalyst with the highest selectivity, which we thus deemed to be our best catalyst at this point. This method will be more thoroughly used in the second part of the catalytic testing.

5.2.2.3 Discussion of the impact of precursors choice

On Figure 21, we see that ZrCl_4 yielded the catalysts with the highest selectivity for GVL. This is probably due to it being a strong electrolyte in water and the metal ion being Zr^{4+} as opposed to ZrO^{2+} . Zr^{4+} with its higher charge and smaller size might interact more strongly with the silanol nests and diffuse more easily through the porosity of the zeolite.

$\text{ZrO}(\text{NO}_3)_2$, while not very selective, did show a high conversion rate, and has an advantage on ZrCl_4 in terms of synthesis of the catalysts, as it does not contain halogens. The nitrate anions can be removed through calcination and, as discussed in the previous section, this allows us to eliminate the washing step after ion exchange in the WIE method. This alleviates the risk of accumulating potentially poisonous and/or leaching species at the surface of the material in the other incorporation methods.

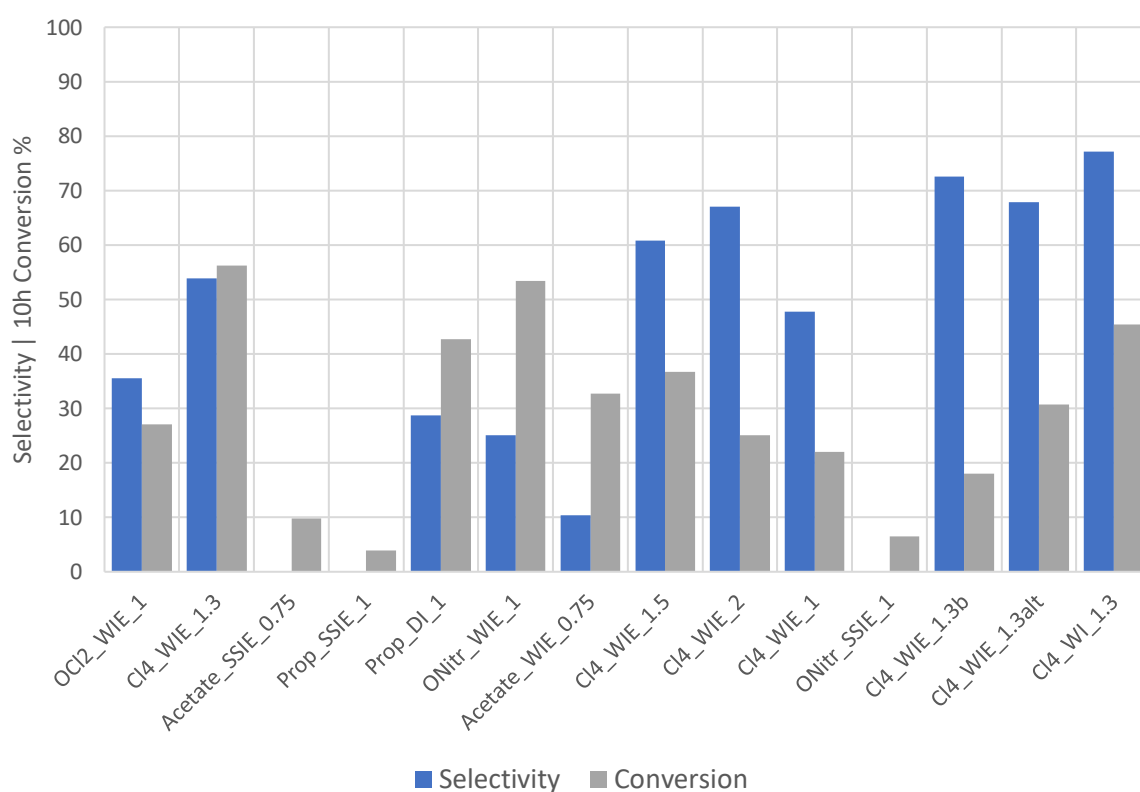


Figure 21: Selectivity vs activity of screened catalysts

ZrOCl_2 has been put aside due to its low availability and average performance not justifying its price. Zr propoxide being insoluble in water, it could only be used in solid form and by dry impregnation in an organic solvent. Its unpractical nature, along with the poor results of these catalysts, have led us to put it aside as well.

Finally, Zr oxyacetate will still be kept in the roster for further syntheses in spite of its poor results, as it has the same advantages in terms of synthesis as Zr oxynitrate.

5.2.2.4 Kinetics

When looking at the reaction kinetics shown in Figure 22, several issues can be pointed out. First, the reaction appears to follow a zero-order relationship to LA, which is contrary to the first order reported in the literature. Secondly, the concentration of LA varies erratically. These observations are true for all catalysts.

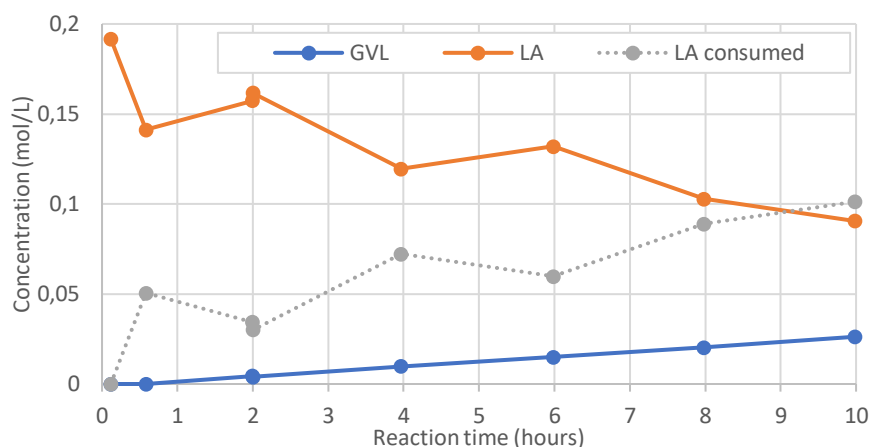


Figure 22: Reaction kinetics for LA to GVL conversion using ONitr_WIE_1

The same problems arise when looking at the more detailed kinetics of Cl4_WIE_1.3 in Figure 23. Though the quantity of GVL formed is almost equal to the quantity of LA consumed, a non-negligible quantity of other compounds was formed; notably MLB which has a response coefficient of about twice that of GVL. Considering only GVL, MLB and LA, the amount of carbon in the reactor increases by 11.5% from start to finish. The problem with LA concentration we saw in Figure 22 is here less erratic and easier to numerically isolate.

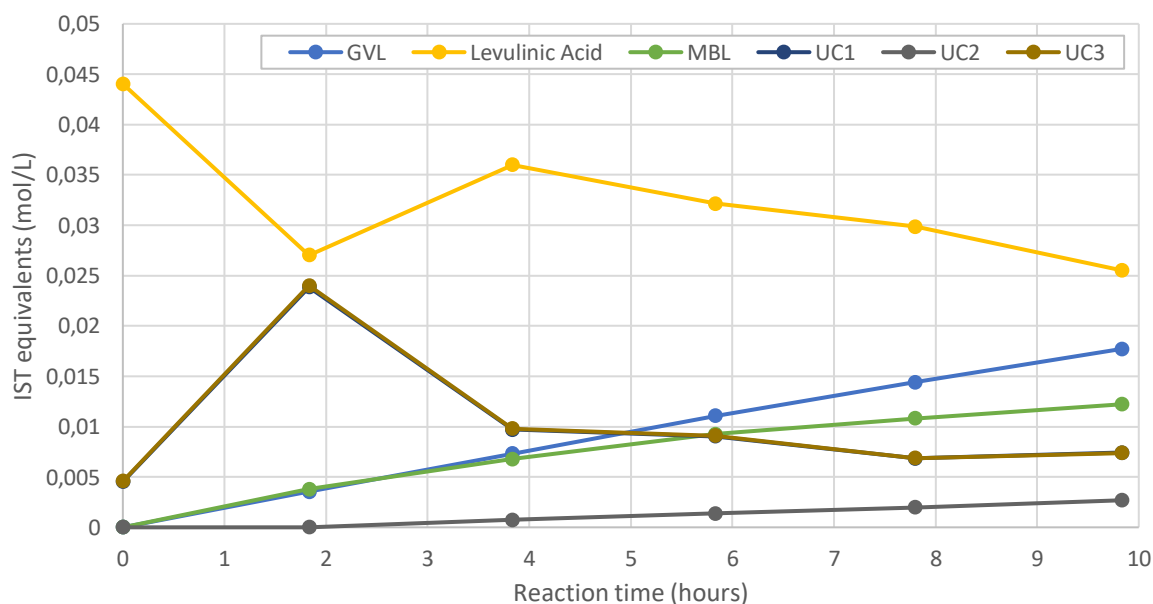


Figure 23: Detailed reaction kinetics with Cl4_WIE_1.3 as catalyst. Concentrations expressed as internal standard equivalents. UC# are unidentified compounds.

To further investigate the problem, we have plotted in Figure 24 the actual concentrations of the compounds of which we have the FID response coefficient. It appears that at the start of the reaction, about 25% of the engaged LA (0.19 mol/L) has spontaneously transformed into two other compounds (UC1 and UC3 in Figure 23). The evolution of their concentration seems to correspond to the deficit in the carbon balance (Figure 24). We can also see that these compounds can be transformed back into LA, as their concentration decreases over time. This also explains why LA seems to be consumed at a rate slower than the production rates of GVL and MBL combined.

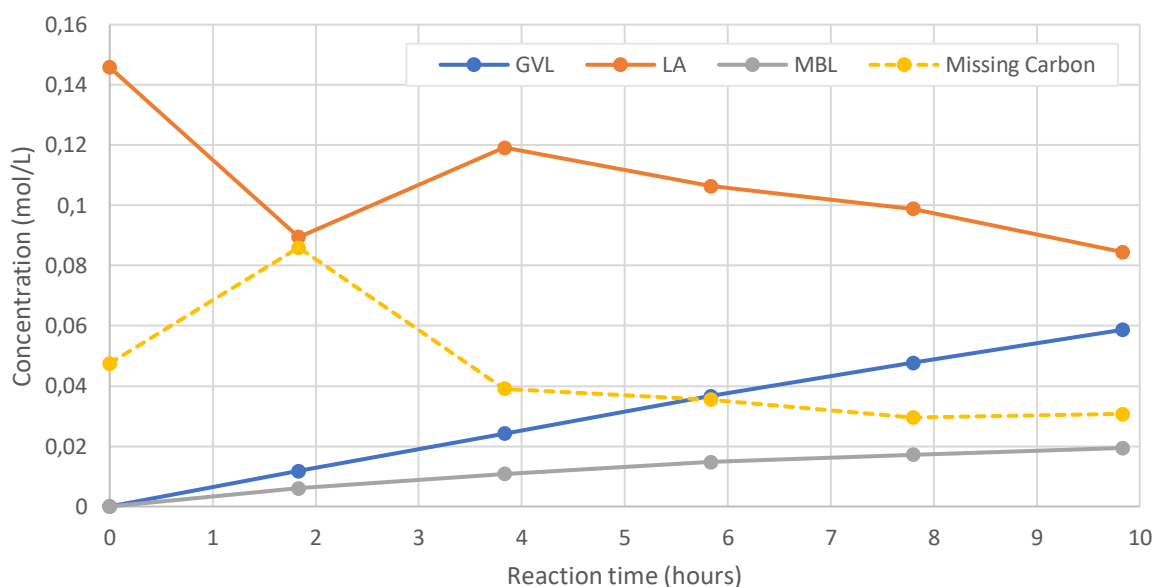


Figure 24: Reaction kinetics of with Cl4_WIE_1.3 as catalyst. Missing carbon is calculated by difference

Looking back at the detailed kinetics of ONitr_WIE_1 (Figure 25) will reveal the that UC1 and UC3 are also the cause of the erratic variation of LA concentration.

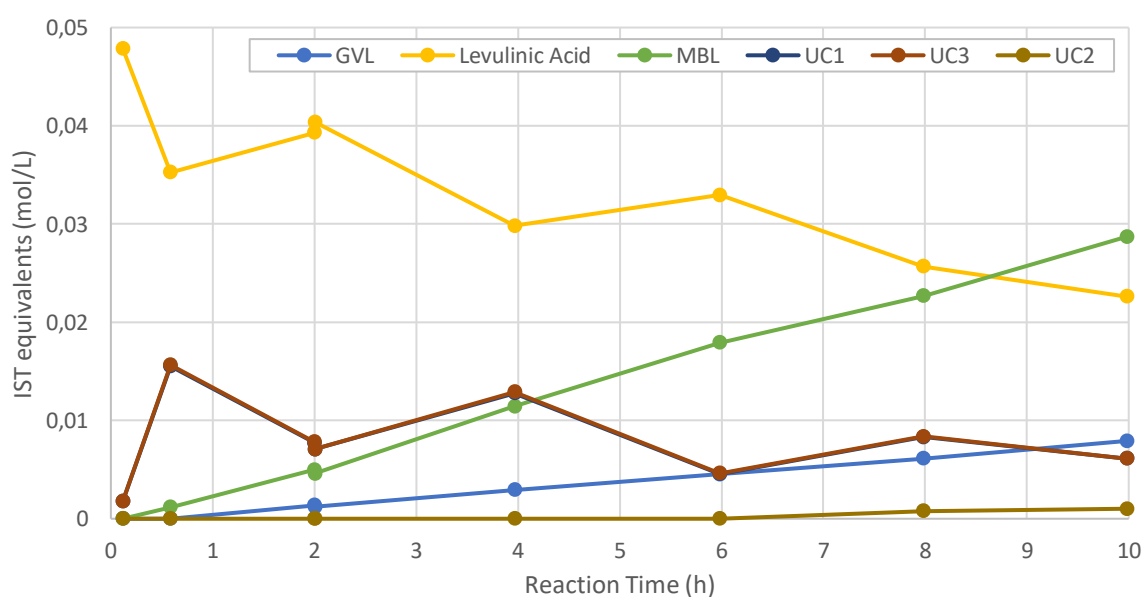


Figure 25: Detailed reaction kinetics with ONitr_WIE_1 as catalyst

Finally, for the catalyst that gave the best results for the conversion of LA to GVL, CL4_WI_1.3, we saw little production of UC1/3. Figure 26 shows the much lower concentration of unwanted compounds when using this catalyst.

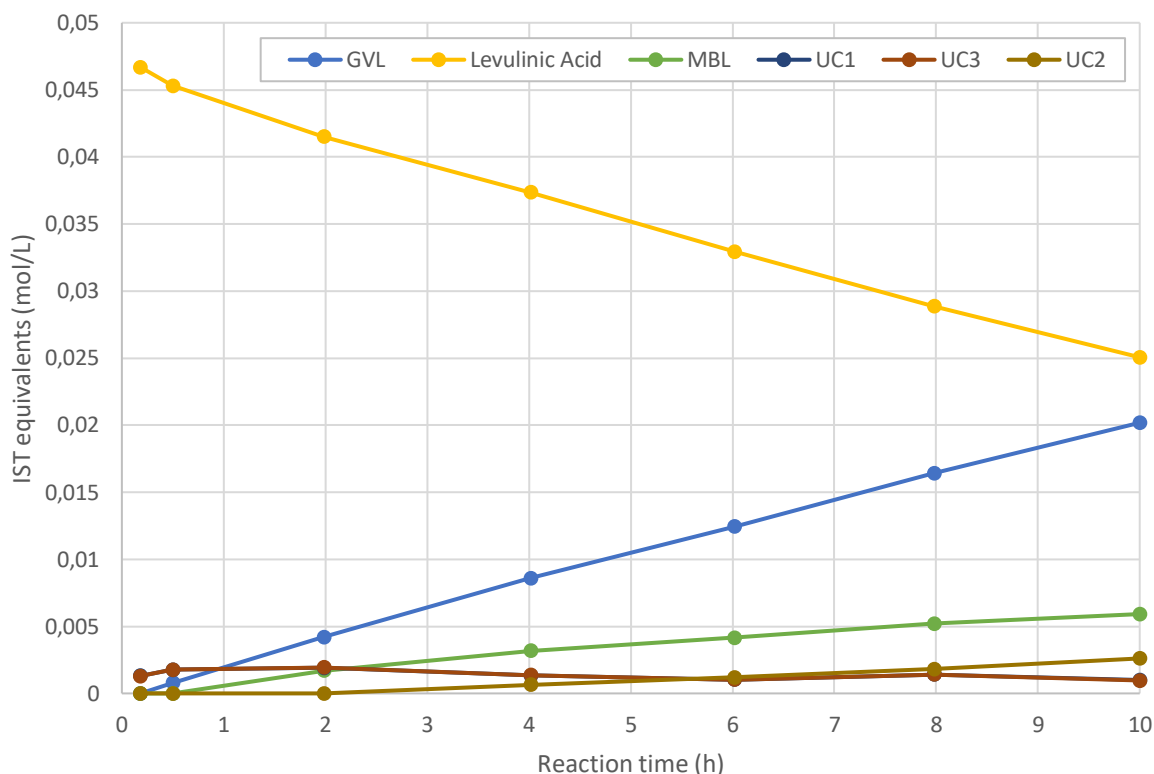


Figure 26: Detailed kinetics with CL4_WI_1.3 as catalyst

The last issue that has to be addressed in terms of kinetics is the zero-order reaction rates of the catalysts. Zero-order kinetics on a reaction where we should see first-order kinetics imply that the concentration of the reactive species is constant over time in the direct vicinity of the active sites.

The typical explanation for the constant local concentration is a diffusion hindrance. There are two types of diffusion; external and internal.

The first hypothesis is an external diffusion limitation on a macroscopic scale. Poor agitation of the medium was immediately put aside, as the reactor is both magnetically stirred and boiling. We do note however that it would have been wiser to repeat a catalytic test at various agitation speeds to verify the absence of a laminar layer of immobile molecules, which would be a hindrance to diffusion.

An explanation for internal diffusion hindrance is the presence of large aggregates of powder. Indeed, macroscopic aggregates of catalyst (up to 0.5 mm in size) can be observed in the powder. However, those aggregates can form after sieving the powder, and tend to

disappear in the reactor after 30 minutes to 2 hours of agitation; they cannot be avoided and could not be the source of constantly poor diffusion for 10 hours.

Similarly, the microscopic aggregates of powder are a plausible source of poor internal diffusion. We saw through N_2 physisorption in section 5.1.1 that the aggregation of the crystals of zeolite generates mesopores (≈ 20 nm, Table 4). If diffusion of the substrate through the mesopores (intragranular diffusion) is slower than the turnover frequency of the catalyst, the active sites will only be fed a constant amount of substrate and thus be exposed to a constant concentration of substrate.

Moreover, this internal diffusion hypothesis can be further backed up by a potential issue related to an adsorption phenomenon. Since our zeolites have been dealuminated, they contain a non-negligible amount of free silanol groups which could potentially increase the hydrophilicity of the material. As such, LA containing two hydrophilic carbonyl groups could interact more strongly with the non-active surface of the catalyst. This interaction would then in turn reduce further the mobility of the substrate in the intragranular porosity. If the aggregates of crystals are larger than the crystals made via hydrothermal synthesis, the intragranular diffusion hindrance could explain why we seem to have worse diffusion than what is seen in the literature.

A simple way to go around the hydrophilicity problem would be to switch to a more hydrophobic substrate like ethyl levulinate. Breaking down the aggregates is the other solution around the diffusional limitations. In this work, we have investigated the former.

5.2.2.5 Issues with the use of levulinic acid

The potential problem of the hydrophilicity of LA has already been discussed.

Another issue with levulinic acid is its quantification. In GC analysis, LA generates a fronting peak which could potentially be a problem in terms of resolution (Figure 27). This issue has been tackled early on by tuning the pressure and temperature parameters of the GC to increase resolution, as well as by reducing the injection volume and increasing split ratio. However, this could only be taken so far, as we started reaching a point where sensitivity became limiting for other compounds.

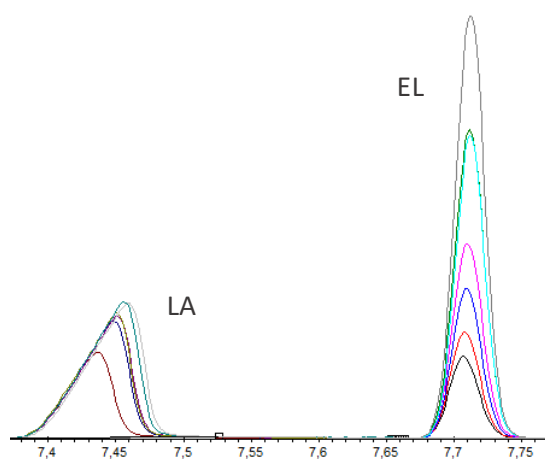


Figure 27: Superimposed peaks of LA and EL from two catalytic tests. X axis is in minutes

Also, the coefficient of determination R^2 of the calibration of LA was only 0.88, whereas those of GVL and EL reaches 0.9996 and 0.99995; this makes the concentration of LA somewhat unreliable to quantify.

Finally, LA being a crystalline solid at room temperature, it is unpractical to handle, and weigh for testing.

For all these reasons, it has been decided to no longer work with LA but instead use liquid ethyl levulinate (EL) which is just as easy to produce than LA (see section 1.1) and has often been used in the literature with success.⁹

5.2.2.6 Summary

In summary, several catalysts have been investigated, the best ones being those using $ZrCl_4$ as a precursor and the best incorporation method being the wet impregnation. We only reached a low conversion of 46% and have decided to switch to a more hydrophobic, practical substrate: ethyl levulinate. More catalysts remain to be made via wet impregnation, with Zr oxynitrate and Zr oxyacetate. The most promising catalyst will again be tweaked with increasing metal loadings to try to further improve catalytic performances.

5.2.3 Conversion of ethyl levulinate to GVL

In this section, new catalysts are tested, and variations in reaction conditions are investigated: substrate concentration, catalyst concentration, reactor size. It is also at this point that the recyclability of the catalysts will be addressed.

5.2.3.1 Standard conditions

The tests carried out in standard conditions with EL as a substrate are summarized in Figure 28. The two best catalysts identified in the screening on LA (Cl4_WIE_1.3 and Cl4_WI_1.3) were tested along with ONitr_WI_1 which we expected to be promising due to the volatility of the precursors' counter-ion. Activity levels were much higher than in the case of LA, where no catalyst would reach more than $3 \cdot 10^{-4}$ mol/h.g_{cat}. The selectivity of the catalyst is also much higher, ranging between 86 and 89% (up to 77% for LA).

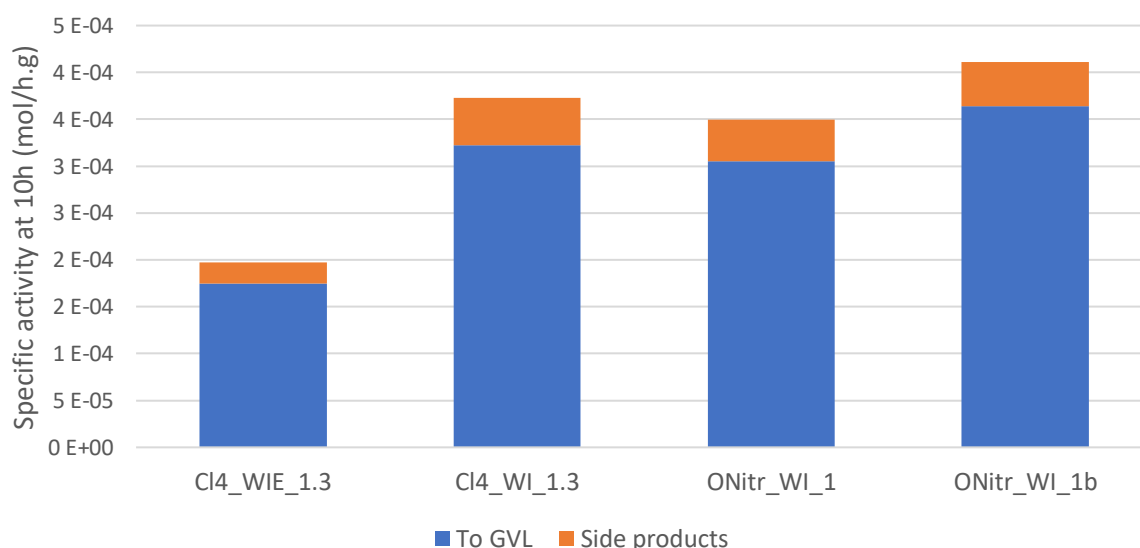


Figure 28: Performances of catalysts tested in standard conditions with EL as substrate

When looking at ONitr_WI_1 and ONitr_WI_1b, the repeatability of the wet impregnation method appears to be better than that of the wet ion exchange, as the catalysts have similar performances. We can also see that the WI catalysts perform better than the Cl4_WI_1.3, all three with similar results. This seems to indicate that the WI method allows a better incorporation of the zirconium than WIE. This will be verified through characterization.

With this higher activity, the reaction now accurately displays first order kinetics (see Figure 29) relative to ethyl levulinate with a reaction constant $k = 0.14 \text{ h}^{-1}$. Also, MBL is no longer the primary side product; the UC2 compound could however not be identified. It may also be noted that the concentration of ethyl levulinate is much more precisely measured than that of levulinic acid, with less than 1% difference between the concentration measure via GC and the concentration engaged in the reactor. Thus, no carbon balance issues arise. Notice in

Figure 29 that UC1 and UC3 are no longer produced, and MBL is almost negligible. The main byproduct is now UC2, however in small quantities. The apparition of first-order kinetics seems to confirm our hypothesis that diffusion limitations were increased by the hydrophilic interaction between LA and the material.

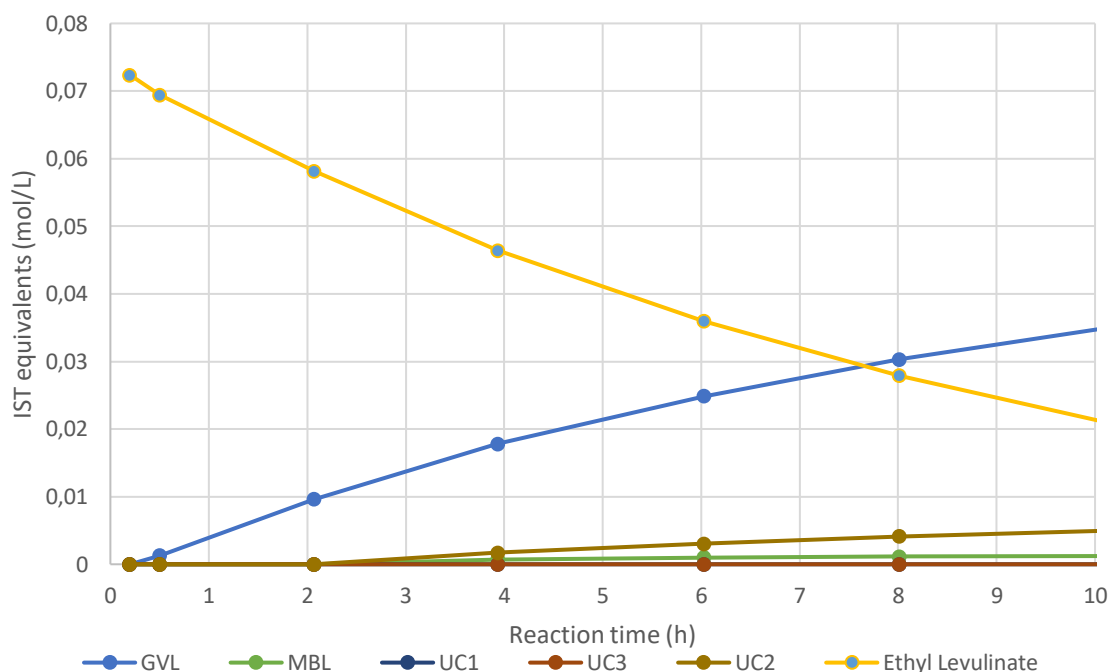


Figure 29: Detailed kinetics of the conversion of EL to GVL using ONitr_WI_1 as catalyst

With these first-order kinetics, it is now more relevant to display the initial specific activities rather than the global conversion after 10h; they are reported in Figure 30. Here we see that Cl4_WIE_1.3 is beaten by far by the WI catalysts, but also that ONitr_WI_1.3 performs worse than ONitr_WI_1. Adding to this difference, the Zr loading of Cl4_WI_1.3 is theoretically 30% higher than that of ONitr_WI_1, making the latter much more promising.

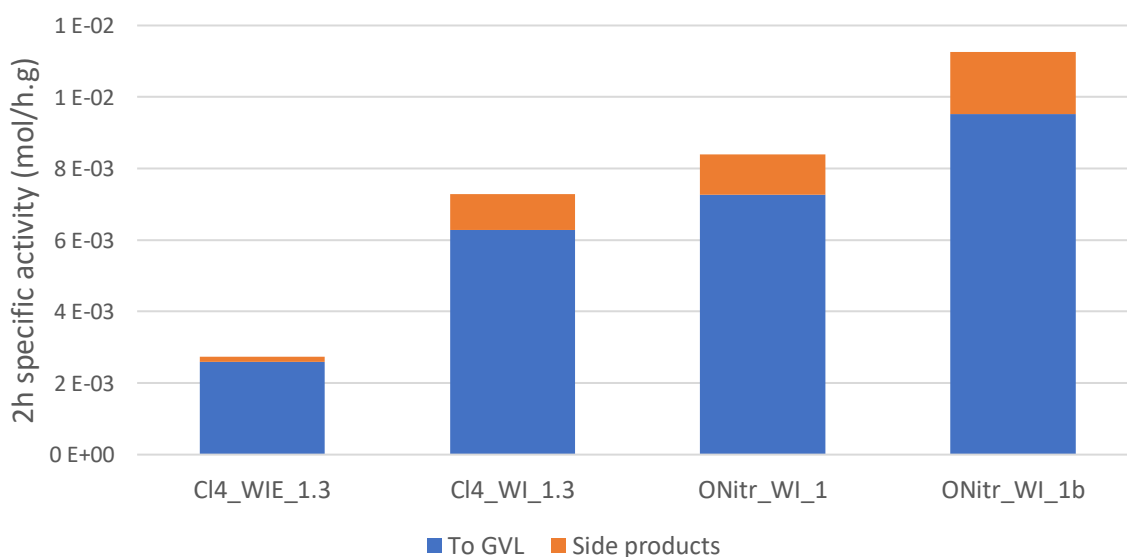


Figure 30: Initial rates of conversion of EL by various catalysts

The lower specific activity of Cl4_WI_1.3 leads us to believe that the precursor ZrCl_4 might not generate active sites as effectively as $\text{ZrO}(\text{NO}_3)_2$ does. While we have suspected that the Zr^{4+} ion may be better for incorporation than ZrO^{2+} with its better mobility and reactivity, we now have reasons to believe that ZrO^{2+} might form a higher proportion of active sites. Remember that for a site to be active, it must be partially hydrolyzed. A hypothesis is that ZrO^{2+} interacts with the silanol nests without bonding with each silanol groups because of its oxygen atom. Figure 31 illustrates this hypothesis which would explain a higher specific activity for the catalysts made from $\text{ZrO}(\text{NO}_3)_2$ compared to ZrCl_4 that would be caused by a higher proportion of active Zr sites.

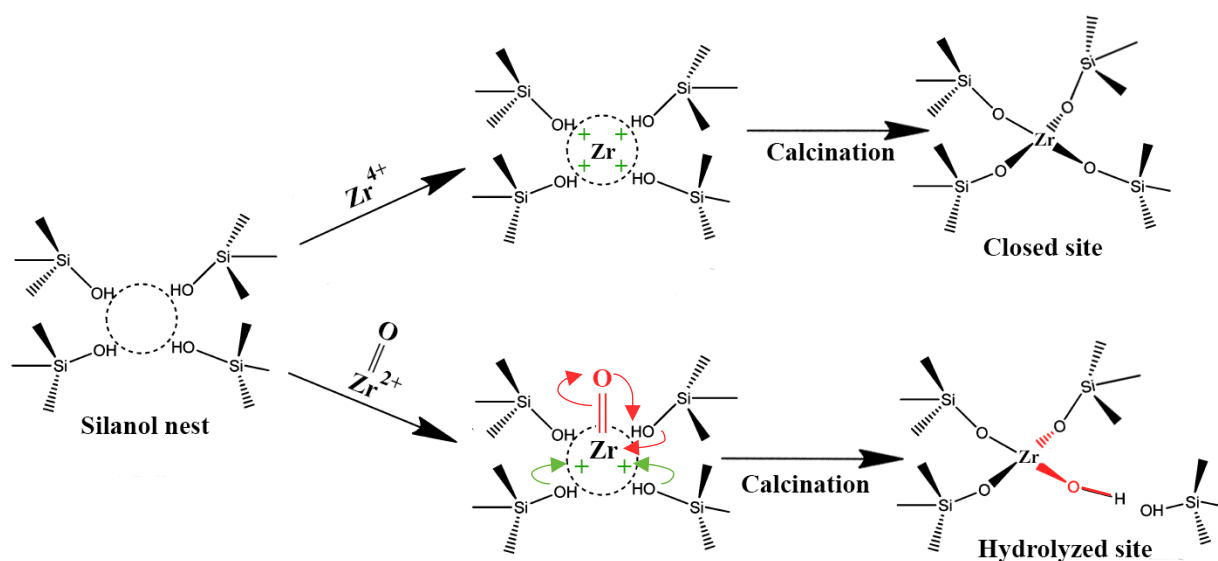


Figure 31: Hypothetical difference between ZrO^{2+} and Zr^{4+} incorporation

The kinetics of Cl4_WI_1.3 are peculiar as it seems to show a first order reaction at first glance, but the calculations prove otherwise. In Figure 32 we see that the concentration of ethyl levulinate does not exactly follow an exponential curve but rather decreases linearly for the first few hours before seeing a decrease in the conversion rate. This means that at higher concentrations, either diffusion is limiting again, or we have reached the maximal turnover frequency of Cl4_WI_1.3. Unless characterization shows that Cl4_WI_1.3 differs significantly from ONitr_WI_1 in terms of textural properties, the diffusion hypothesis is not receivable in this case, since the other WI catalysts do not suffer from it and there is no reason to suspect that hydrophobicity is significantly different between these WI catalysts.

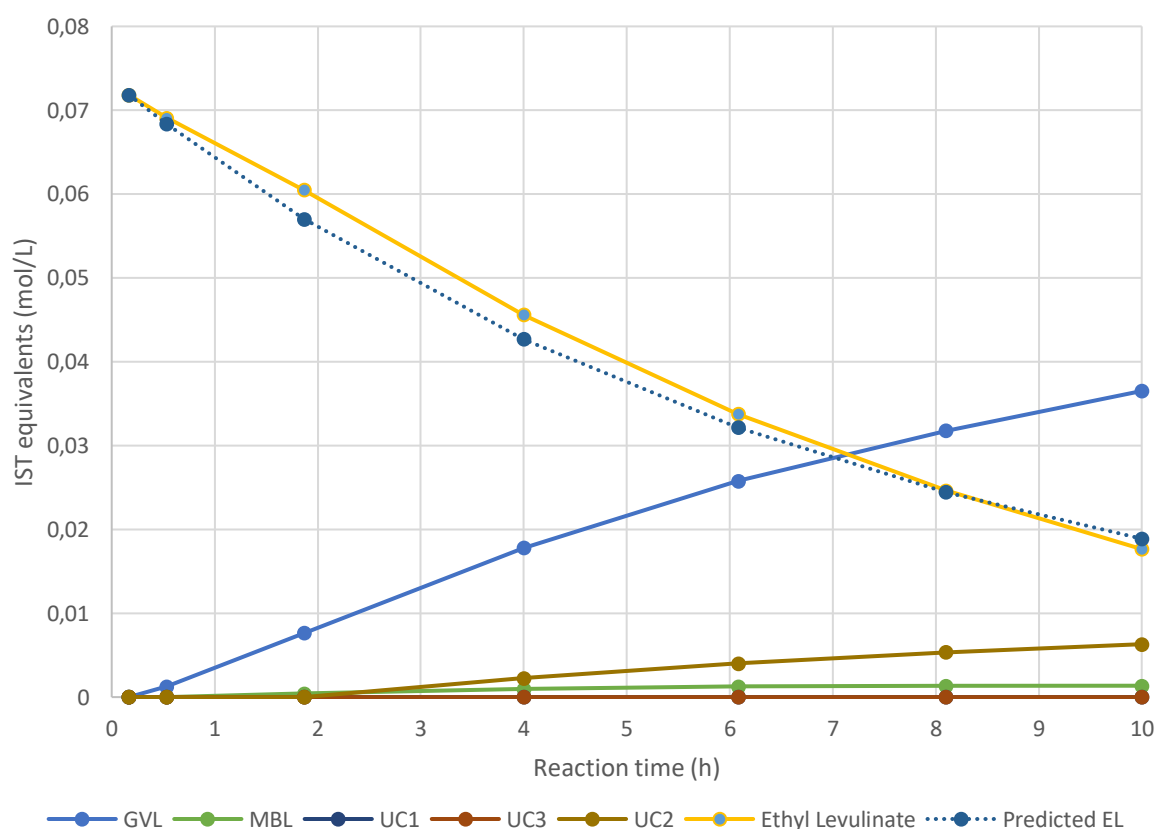


Figure 32: Detailed kinetics of the conversion of EL to GVL using Cl4_WI_1.3 as catalyst. Dotted line is the predicted concentration of EL using the mean value of the rate constants computed for each time interval

In Table 7, we clearly see that the reaction rate constant is thus not constant over time. On the other hand, the reaction rate constant of ONitr_WI_1 (which does display first-order kinetics) is steady.

Table 7: Reaction rate constants $k(h^{-1})$ of two catalysts computed bihourly and their mean value

Catalyst	$k_{0-10'}$	$k_{10'-2h}$	k_{2-4h}	k_{4-6h}	k_{6-8h}	k_{8-10h}	$\bar{k}$
Cl4_WI_1.3	0.107	0.100	0.132	0.144	0.157	0.175	0.136
ONitr_WI_1	0.139	0.113	0.121	0.122	0.128	0.135	0.126

We computed the rate constants relative to substrate concentration for the two ONitr_WI_1 catalysts. Table 8 shows these values computed via two different methods: first via the linearization of the concentration curve and linear regression, and secondly by taking the mean of 6 values as shown earlier.

Table 8: Reaction rate constant k of catalytic tests displaying 1st order kinetics

Catalyst	k (h^{-1})	$\bar{k} \pm s$ (h^{-1})
	Linearization	6 points mean value
ONitr_WI_1	0.126	0.126 ± 0.010
ONitr_WI_1b	0.163	0.164 ± 0.008

We can see that the three catalyst display values of k that are quite similar, with that of the second batch being a bit higher, as it did perform better.

5.2.3.2 Higher substrate concentration tests

These tests were carried out using double the usual amount of substrate, 0.4 mol/L. Besides increasing the conversion rate, it surprisingly led to a seemingly perfect selectivity for ONitr_WIE_1 and Acetate_WI_0.75. The former displaying less than 25% selectivity for GVL when used with levulinic acid.

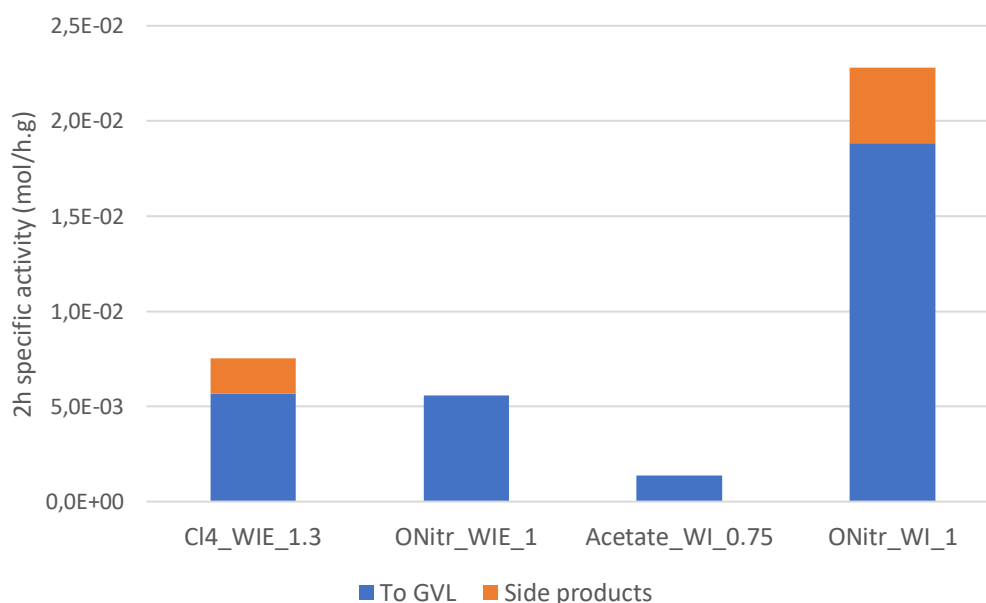


Figure 33: Performance of catalysts exposed to 0.4 mol/L of EL:

For the three less active catalysts (Cl4_WIE_1.3, ONitr_WIE_1, Acetate_WI_0.75), the kinetics resemble those in section 5.2.2.4, with a zero-order relation to the concentration of the substrate as shown in Figure 34, but the most active one, ONitr_WI_1 does follow the expected first-order kinetics, with a rate constant $k = 0.08 h^{-1}$ (Figure 35).

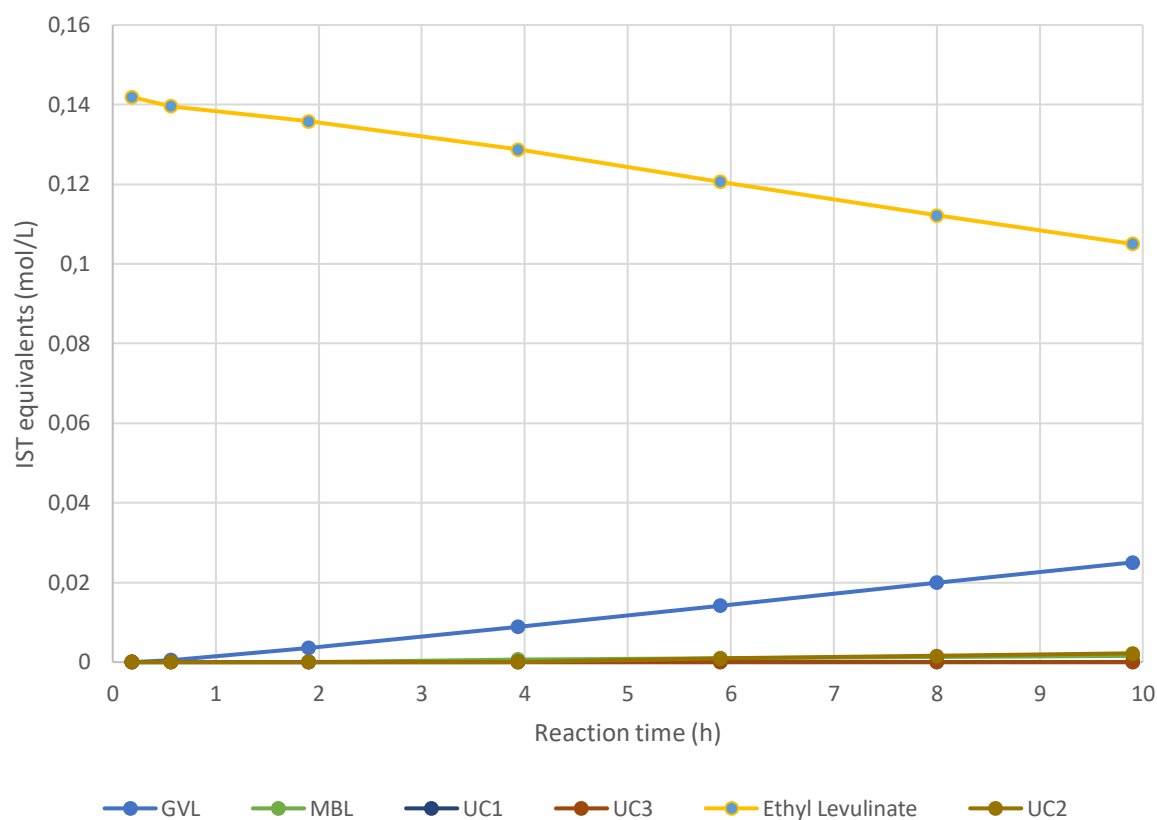


Figure 34: Detailed kinetics of the reaction using Cl4_WIE_1.3 in presence of 0.4 mol/L of EL

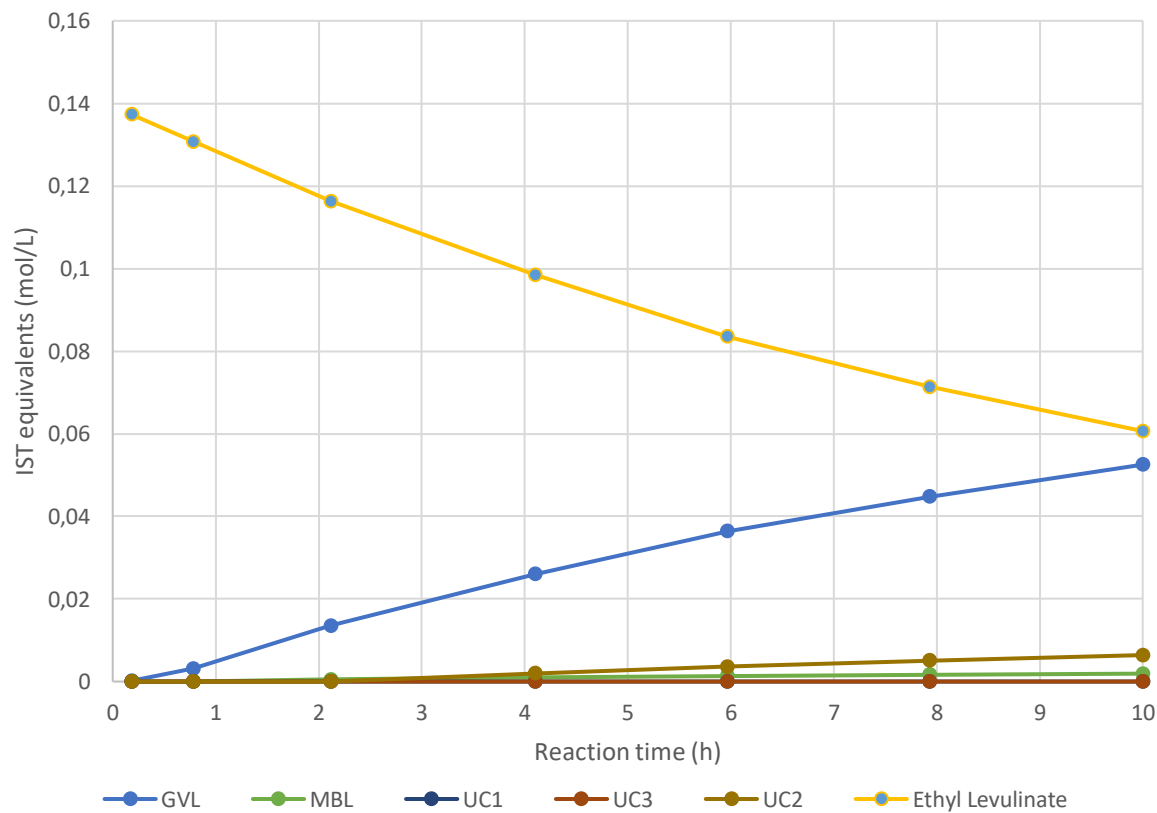


Figure 35: Detailed kinetics of the reaction using ONitr_WI_1 in presence of 0.4 mol/L of EL

5.2.3.3 Increased Zr loading

As ONitr_WI_1 and ONitr_1b showed the best catalytic performances, we have chosen to use the WI method with Zr oxynitrate to make catalysts with a higher loading of zirconium. We thus synthesized ONitr_WI_2 and ONitr_WI_4 with respectively 2 and 4 times the amount of zirconium in the initial catalyst (performances reported in Figure 36). This would fill at most half the silanol nests, so we do not believe this quantity of zirconium to be too high to be incorporated in the lattice.

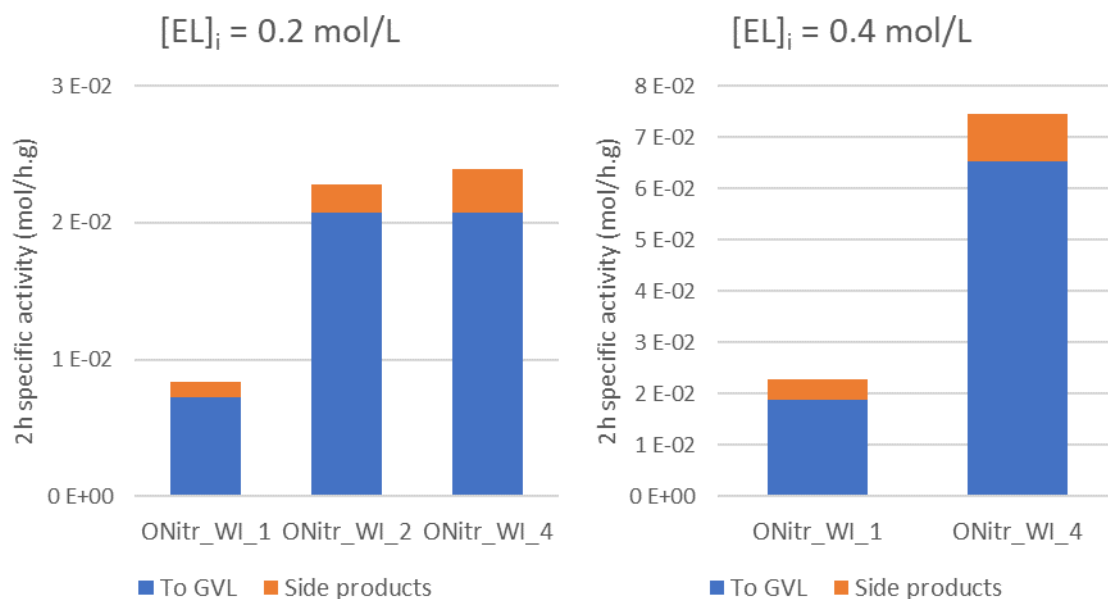


Figure 36: Performance of various ONitr_WI catalysts

Here we see that ONitr_WI_2 has double the activity of ONitr_WI_1, as we would expect if we do have twice the amount of active sites. ONitr_WI_4 does not have 4 times the activity of ONitr_WI_1 in standard conditions, but it does reach a much higher activity when engaged with 0.4 mol/L of EL. The elemental analyses in section 5.3.5 will allow us to compute the turnover frequencies (TOF) to more accurately compare those catalysts. The rate constants of ONitr_WI_2 and ONitr_WI_4 are respectively 0.5 and 0.4 h^{-1} .

Their selectivities do not vary much, as they consistently remain above 86%. We see in Figure 38 however that ONitr_WI_4 does produce more of UC2 than ONitr_WI_2 (Figure 37) and ONitr_WI_2 (Figure 29) in the same conditions. We can thus correlate a higher proportion of UC2 with a higher loading of zirconium; this can be taken further as we notice that UC2 is less present in WIE samples, which we suspect to contain less zirconium than what is engaged during synthesis (see comparison between Cl4_WIE_1.3b and Cl4_WIE_1.3alt in section 5.2.2.2).

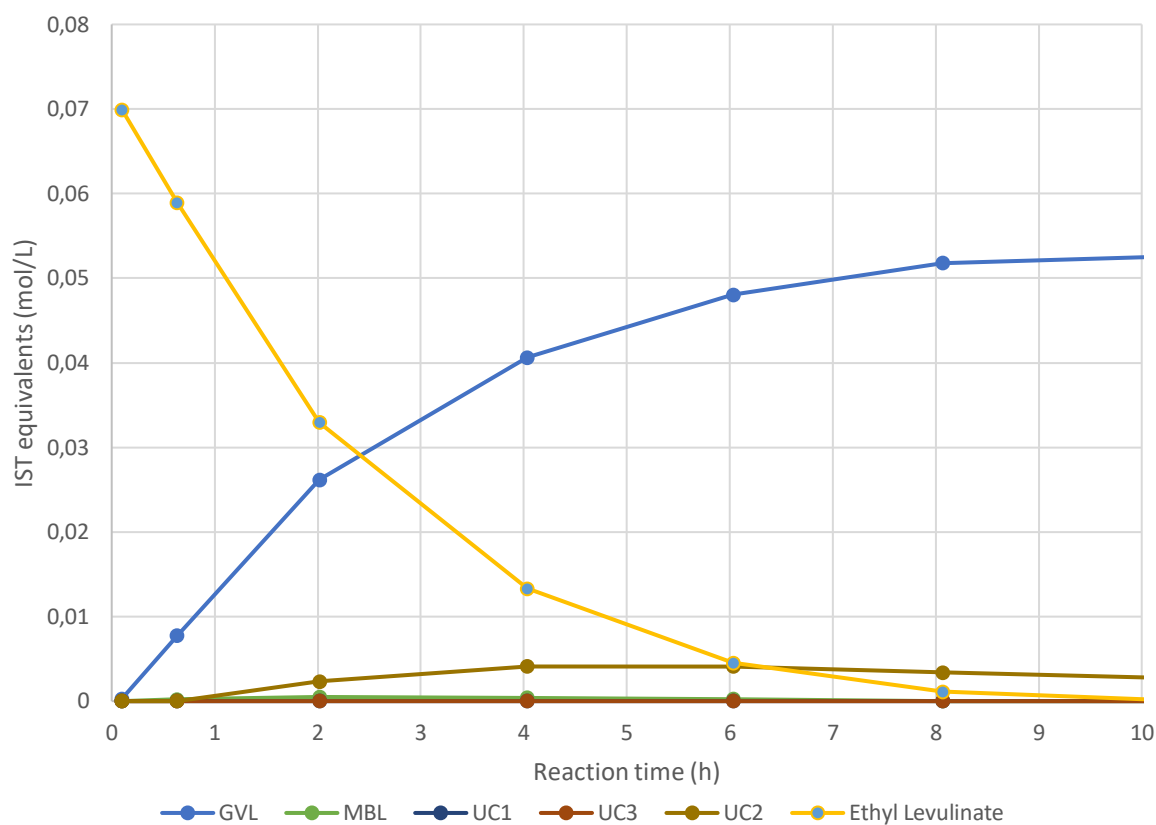


Figure 37: Detailed reaction kinetics when using ONitr_WI_2 as catalyst with 0.2 mol_{EL}/L engaged

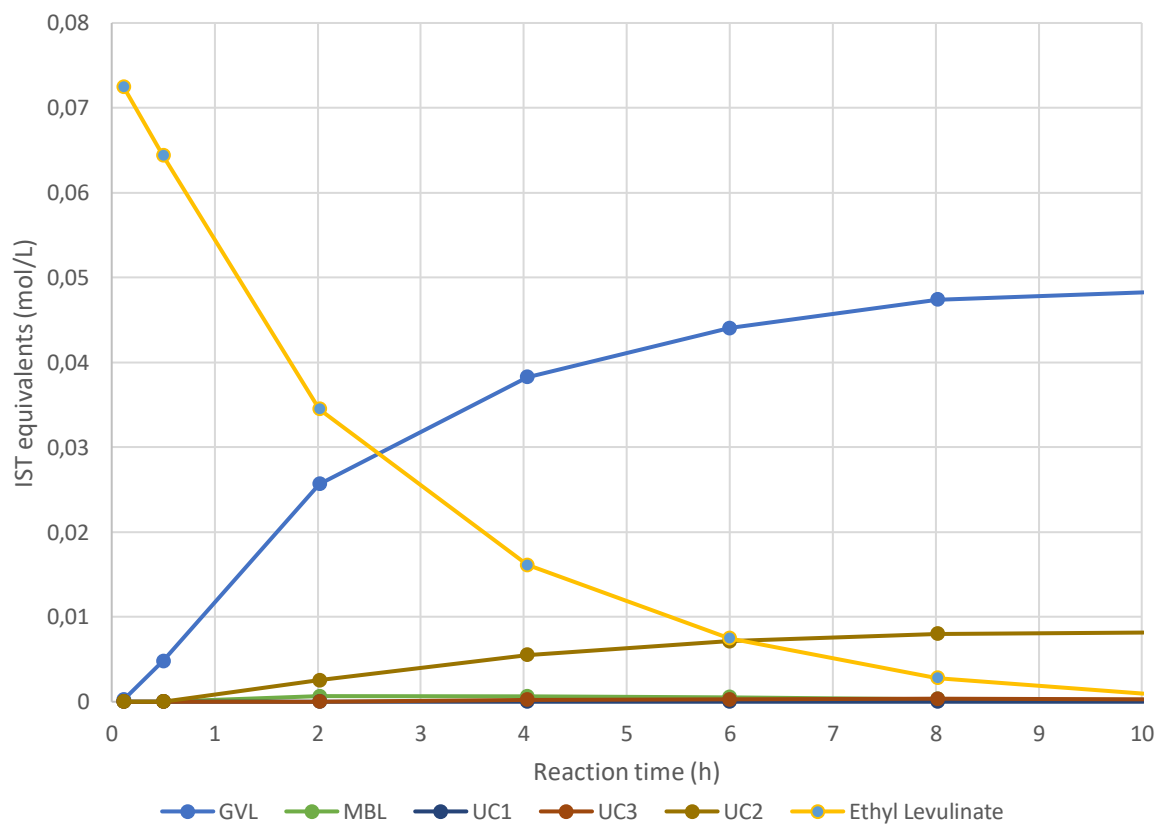


Figure 38: Detailed reaction kinetics when using ONitr_WI_4 as catalyst with 0.2 mol_{EL}/L engaged

5.2.3.4 Reusability and reactor influence

The catalyst used for the reusability test is ONitr_WI_1 as it is the most active. Figure 39 below shows no significant loss of activity after several uses of the catalyst; on the contrary, it appears to be even more active after regeneration at 550 °C than on its first use. The fresh and regenerated catalyst do appear to be a little more active than the spent one, though this effect is minor and only shows over longer batch times. The third run cannot be displayed due to experimental errors; the catalyst was however used for the intended 8 hours so that the subsequent runs remained relevant.

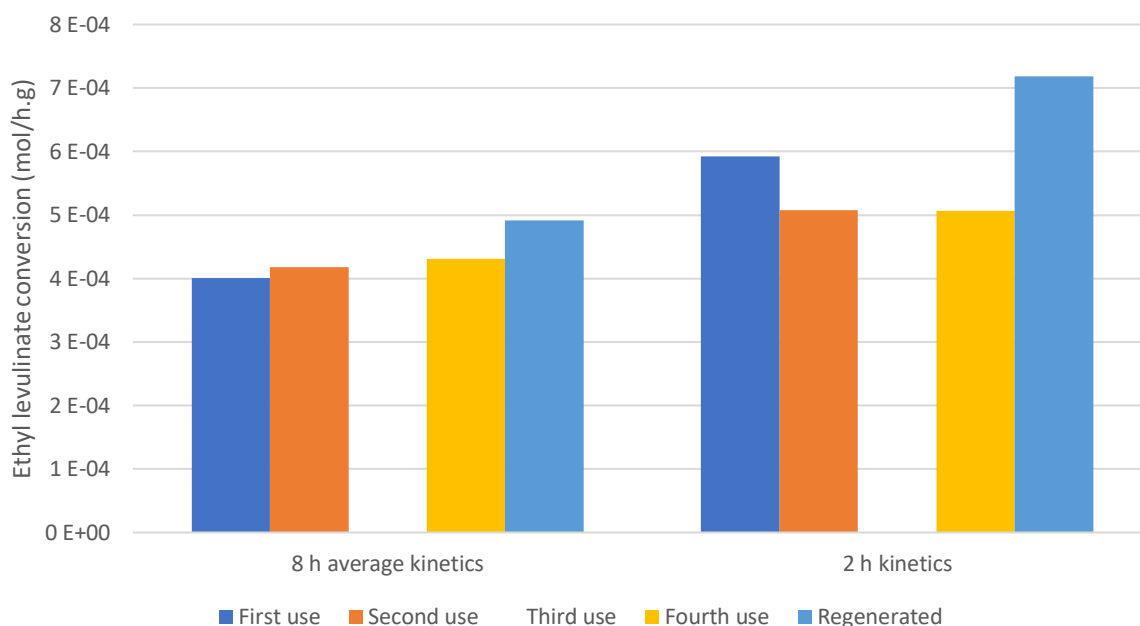


Figure 39: Activity of ONitr_WI_1 after several uses. Third use is grayed as the reaction was set up with 0.4 mol/L of EL instead of 0.2 mol/L

The reusability test of our catalyst was a success. It showed no major deactivation upon reuse even though the powder was only washed with water, and the regeneration was successful, as the catalyst appeared even more active than before. This however could be simply due to the fact that upon regeneration, the catalyst was tested immediately, as opposed to the “fresh” catalyst, which has sat for several days in the desiccator and may have adsorbed some contaminants. For this reason, we do not believe this increase to be relevant.

To evaluate the influence of the reactor, the same fresh catalyst was used in both available reactors. The results are shown in Figure 40. There seems to be a variation in activity resulting to a change of reactor, however the small sample size only allows for a qualitative evaluation of the effect.

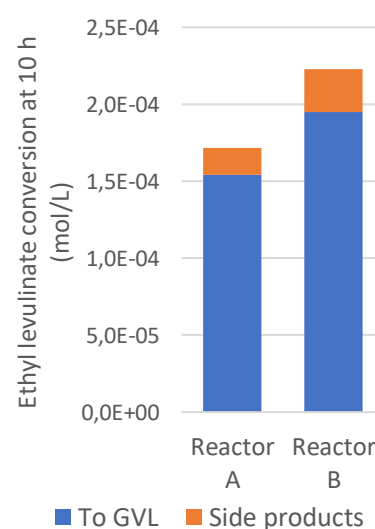


Figure 40: Impact of the reactor on activity

5.2.3.5 Summary and discussion of tests with ethyl levulinate

The catalysts all work better with ethyl levulinate rather than levulinic acid as substrate. With the appearance of the first order kinetics, it would seem that the diffusion issue has been resolved for some of the catalysts. For some (WIE catalysts and Acetate_WI_0.75) we still see zero-order kinetics though we suspect that this is simply an apparent zero-order; if their maximal conversion rate is very low, the first order would only be visible at lower concentrations.

Zirconium oxynitrate is deemed as a more suitable precursor than ZrCl_4 as it yields catalysts with overall better performances.

Conversion rates can be pushed higher with increased substrate concentrations, meaning we have not reached the limits of our catalysts in terms of specific activity. They can also be reused at least 3 times without any significant loss of activity, and regeneration at 550°C was not detrimental to the catalyst either.

The best catalysts are ONitr_WI_1/2/4 both in terms of activity and selectivity as seen in Table 9. Notice that no other catalyst has reached the same levels of selectivity besides the very little active ONitr_WIE_1 and Acetate_WI_0.75.

Table 9: Performance of catalysts tested with EL as a substrate. Mean conversion rate is calculated as the total substrate consumption divided by time and the amount of catalyst

Catalyst	Initial EL concentration (mol/L)	GVL produced (mol/L)	EL consumed (mol/L)	Initial conversion rate (10^{-3} mol/h.g _{cat})	GVL selectivity (%)
Cl4_WI_1.3	0.19	0.12	0.14	7.3	86%
	0.19	0.05 ^a	0.05 ^a	2.4	90%
Cl4_WIE_1.3	0.19	0.06 ^a	0.07 ^a	2.4	88%
	0.36	0.08	0.10	7.5	87%
ONitr_WI_1	0.19	0.12	0.13	8.4	87%
	0.36	0.17	0.20	22.8	88%
ONitr_WI_1b	0.20	0.14	0.15	11.3	87%
	0.18	0.08 ^b	0.09 ^b	7.1	92%
ONitr_WI_2	0.19	0.17	0.18	22.8	97%
ONitr_WI_4	0.19	0.16	0.18	23.9	87%
	0.36	0.29	0.33	73.4	88%
ONitr_WIE_1	0.36	0.08	0.08	1.7	>99%
Acetate_WI_0.75	0.36	0.03	0.03	1.2	>99%

^a: Over 8 hours instead of 10. ^b: 20g/L of catalyst instead of 40 g/L

5.3 Characterization

After a screening of different catalysts' performance, we have identified which catalysts work and which do not. We will now characterize these catalysts to try to understand the parameters that dictate the catalytic behavior of the zeolite. The reports in the literature have shown characterizations of catalysts, but mainly to confirm the catalysts were Beta zeolites and, subsequently, confirm the absence of bulk ZrO_2 . They also often show data on acidity and elemental composition. However, these studies have not correlated the activity of the catalysts to their intrinsic properties. We will thus try to do so after going through all of our selected characterization technique.

5.3.1 XRD

The powder X-Ray diffractograms were taken for each sample to ensure the beta topology was retained. As expected, across all catalysts, no change of phase was observed. Though the length of the Zr—O bond is longer than that of Si—O, we could not observe a shift reversing the one caused by the dealumination. This is however not surprising for most catalysts as the loading of zirconium is extremely low; an effect on the whole lattice would be surprising. For ONitr_WI_4 a shift could have been expected, as the quantity of Zr added is theoretically half that of the removed Al; it is however not the case either.

The shift to lower angles of the peak at about 8° that was expected from the change of polymorph A to B ^{20,24}(see Figure 41) is also non-present.

Qualitatively, no peak broadening can be observed. Thus, we do not suspect a loss of crystallinity in the material from the incorporation of zirconium.

Another investigated factor is the height and/or surface ratio between peaks A and B, but no correlation could be found between these ratios and activity. As an example, Acetate_SSIE_0.75 and Cl4_WIE_1.3 have similar ratios but have polar opposite results in terms of activity.

Finally, we do not observe the appearance of any new peak after addition of zirconium, no peak could be attributed to ZrO₂. This information however cannot rule out its formation on the surface of the catalyst as the loading is too small to actually have a chance to observe such particles. To check for ZrO₂ formation we must use other characterization techniques, notably DRUV.

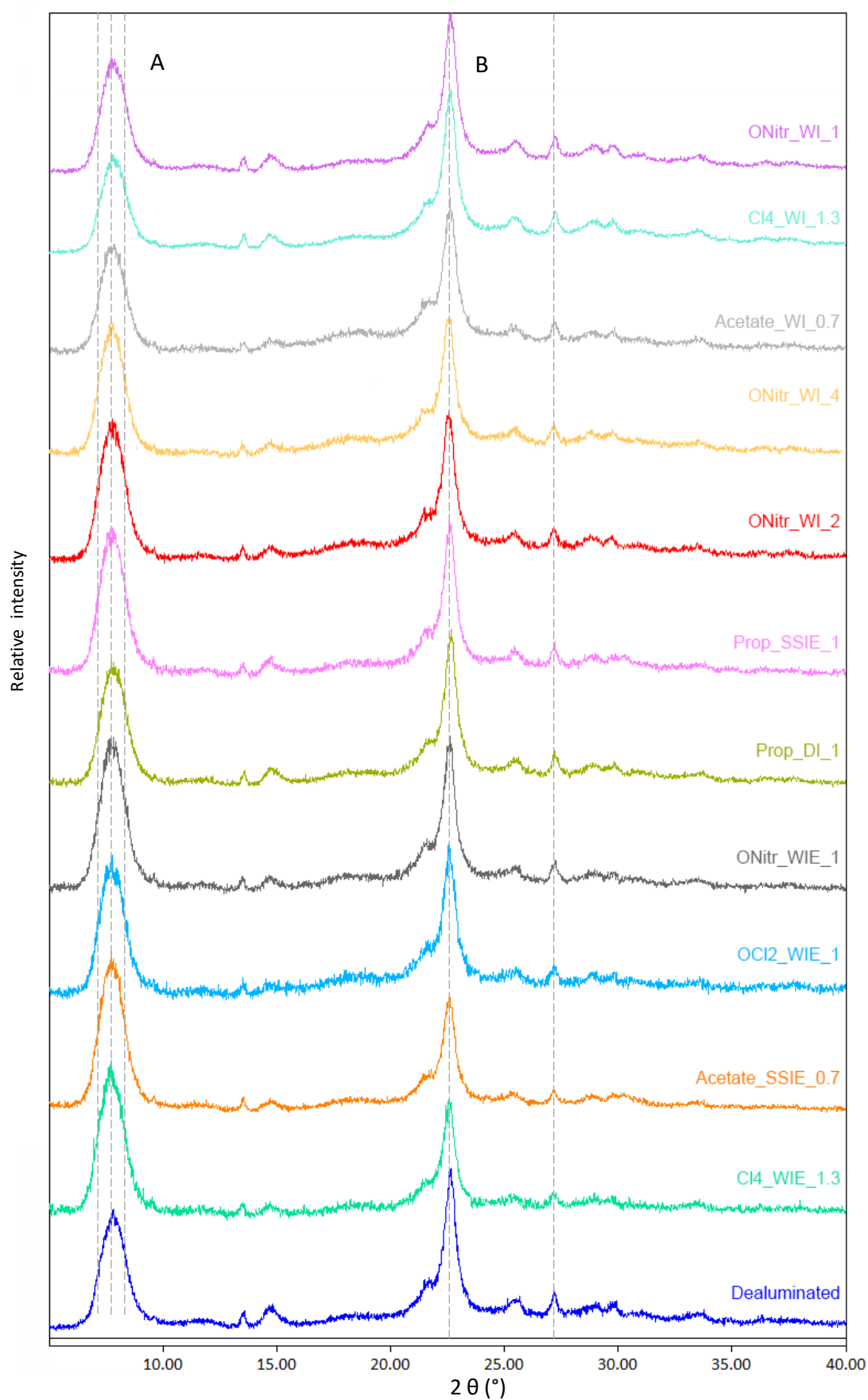


Figure 41: XRD patterns of catalysts

5.3.2 DRUV

The diffuse reflectance UV spectroscopy data (Figure 42 and Figure 43) can provide qualitative information about the presence or not of ZrO_2 at the surface of the material. In Figure 42 we see the spectra for the catalysts used in the tests with LA compared to those of the pristine H-beta zeolite, the dealuminated zeolite and pure zirconium oxide. As expected from the spectrum of ZrO_2 and according to literature reports^{38,43}, we expect catalysts with extra-framework zirconium to display a broadening of the peak at the lowest wavelengths to up to 250 to 300 nm.⁴³

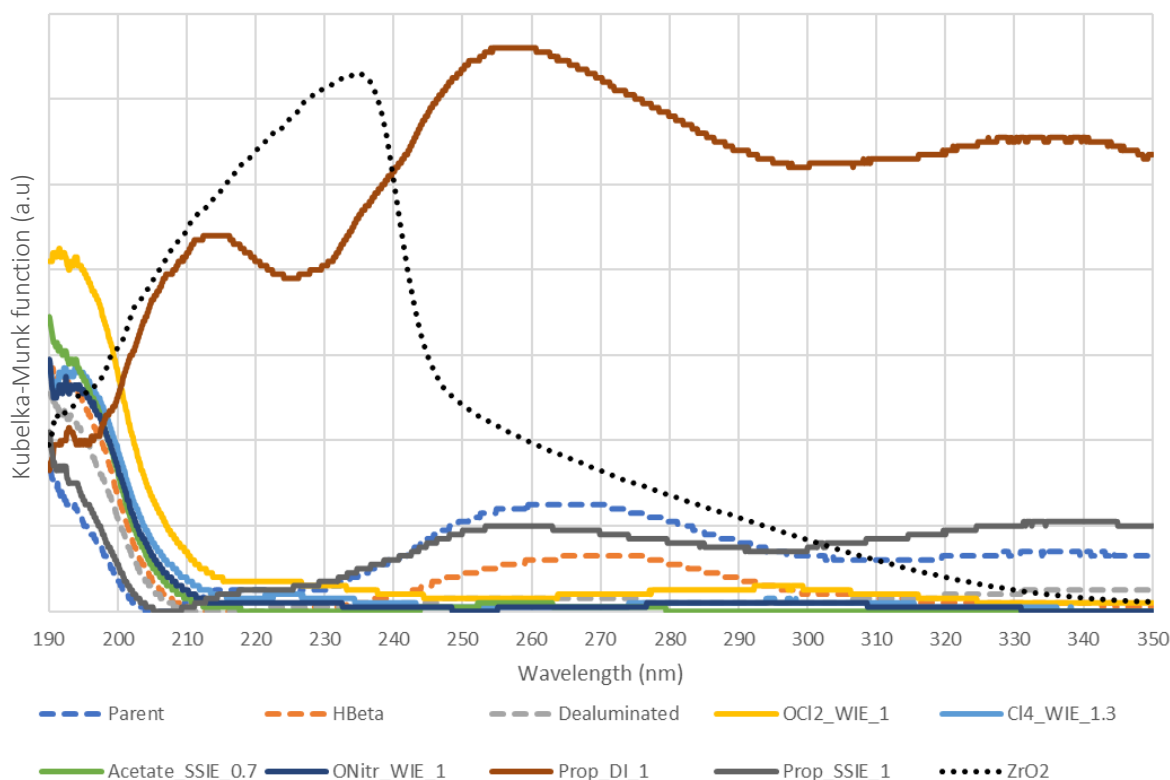


Figure 42: Kubelka-Munk function of the DRUV spectra of the catalysts tested with LA, versus pure ZrO_2 . "Parent" is the commercial zeolite as purchased, HBeta is after calcination to remove surface ammonia. Dashed lines are Zr-free materials. ZrO_2 (dotted line) is on a higher scale

Of all these catalysts, only Prop_DI_1 showed a spectrum that could be associated with ZrO_2 . Prop_DI_1 produces a very distinct pattern that appears to partially align with that of the oxide. This could explain its lack of selectivity, as ZrO_2 is reportedly a poor catalyst for the reaction of interest.¹⁵ Prop_SSIE_1 is surprisingly similar to the parent H-beta zeolite, indicating it may actually contain no Zr at all.

Figure 43 shows WI catalysts along with the high-load Cl4_WIE_2.77, compared to the dealuminated zeolite and pure ZrO_2 . We see that all WI catalysts show a peak about 30 nm broader than the dealuminated sample or the WIE catalyst. This might indicate the presence of small amounts of oxide on these catalysts. Acetate_WI_0.7 also shows a shoulder around 225 nm that is most likely due to more visible noticeable ZrO_2 .

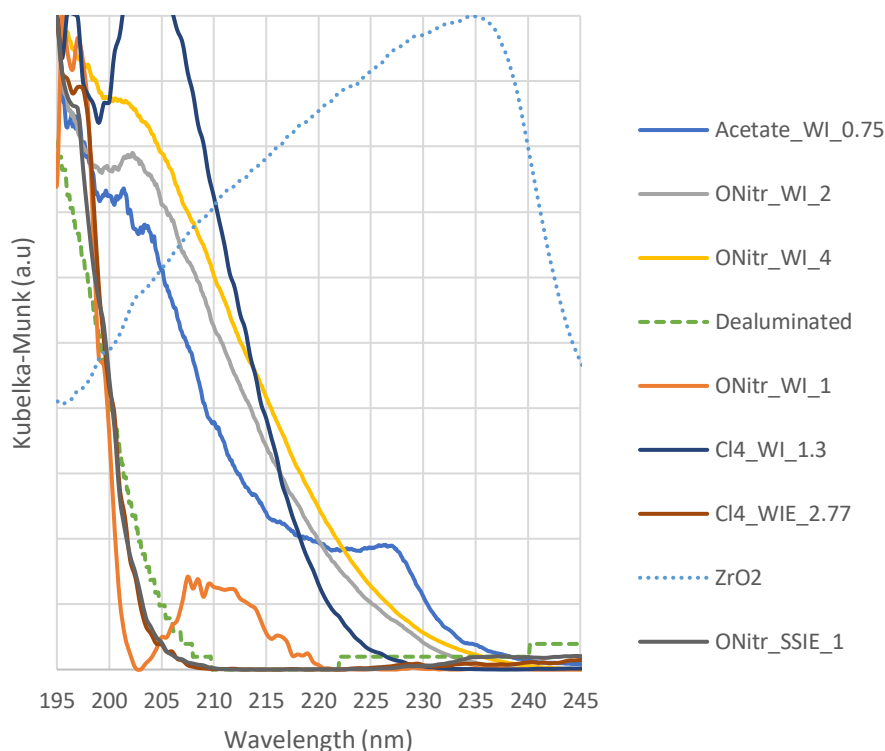


Figure 43: Normalized Kubelka-Munk function of the DRUV patterns of selected catalysts

In general, only Prop_DI_1 and Acetate_WI_0.7 have shown concerning signs of ZrO_2 . In the case of Prop_DI_1, it shows that the dry impregnation method leads to a poor dispersion of the metal, as it tends to agglomerate and form particles of ZrO_2 . This however might not be inherent to the method itself, but to the way it was performed; operational parameters may have been inadequate.

5.3.3 N_2 physisorption

As expected, all catalysts displayed similar isotherms and textural properties to those of the parent material. These results are summarized in Table 10 and several adsorption and desorption isotherms are shown in Figure 44 and Figure 45 for reference.

Notice that while the external surface area appears to vary from one precursor to another, they do not correlate with activity; one of the most active catalysts, ONitr_WI_1, has a smaller external surface area than CL4_WI_1.3 which is less active and contains more zirconium.

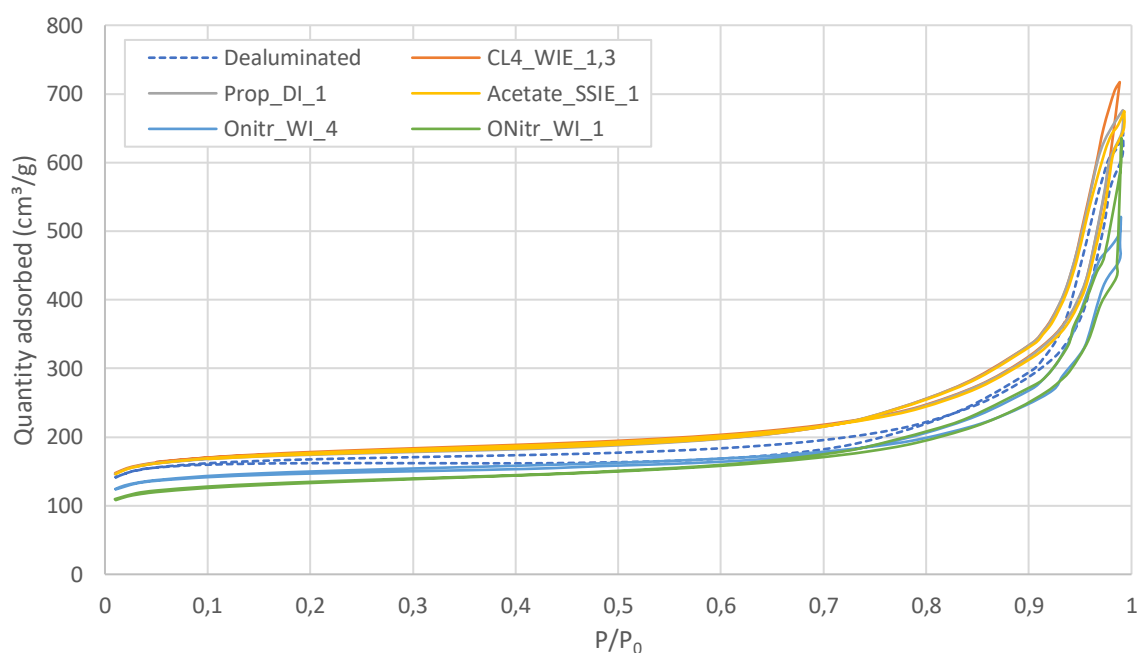


Figure 44: N_2 physisorption isotherms of catalysts of various loadings, precursors and impregnation methods

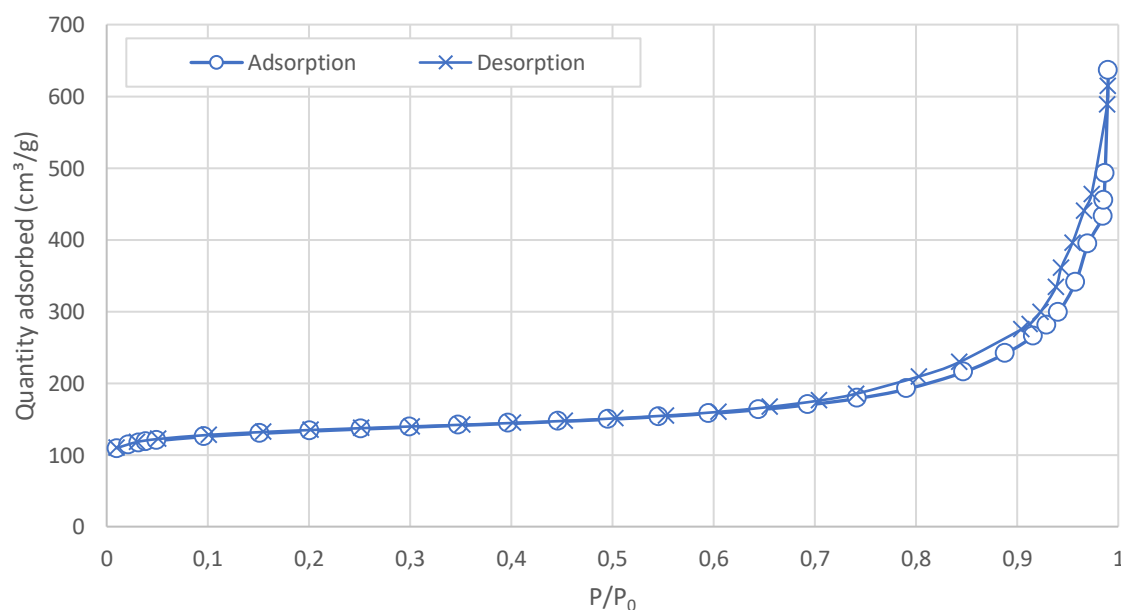


Figure 45: N_2 adsorption and desorption isotherms for ONitr_WI_1

Table 10: Summary of the N_2 physisorption data

Sample	S_{BET} (m^2/g)	t-Plot external surface area (m^2/g)	t-Plot micropore volume (cm^3/g)	Cumulative pore volume (cm^3/g)	BJH mesopore size (nm)
H-Beta	610	100	0.2	0.6	5
Dealuminated	650	110	0.2	0.8	6
Cl4_WIE_1.3	670	170	0.2	0.9	6
Cl4_WI_1.3	650	200	0.2	1.1	6
OC12_WIE_1	640	150	0.2	0.8	6
ONitr_WIE_1	600	130	0.2	0.8	6
ONitr_WI_1	500	150	0.1	0.9	6
ONitr_WI_2	600	140	0.2	0.8	6
ONitr_WI_4	560	140	0.2	0.6	5
Prop_DI_1	680	160	0.2	0.9	6
Prop_SSIE_1	600	150	0.2	0.8	6
Acetate_WI_0.75	680	170	0.2	0.9	6
Acetate_SSIE_0.75	680	170	0.2	0.9	6

5.3.4 Infrared spectroscopy

5.3.4.1 FTIR-ATR

Observing the peak at 950 cm^{-1} as described in section 5.1.3, we expect to observe a diminution of the signal corresponding to the silanol nets upon incorporation of zirconium. We also expect the appearance of a peak centered around 965 cm^{-1} caused by the asymmetric stretching mode of a silicon T site bonded to zirconium ($\text{O}_3\text{-Si-O-Zr}$)²⁸.

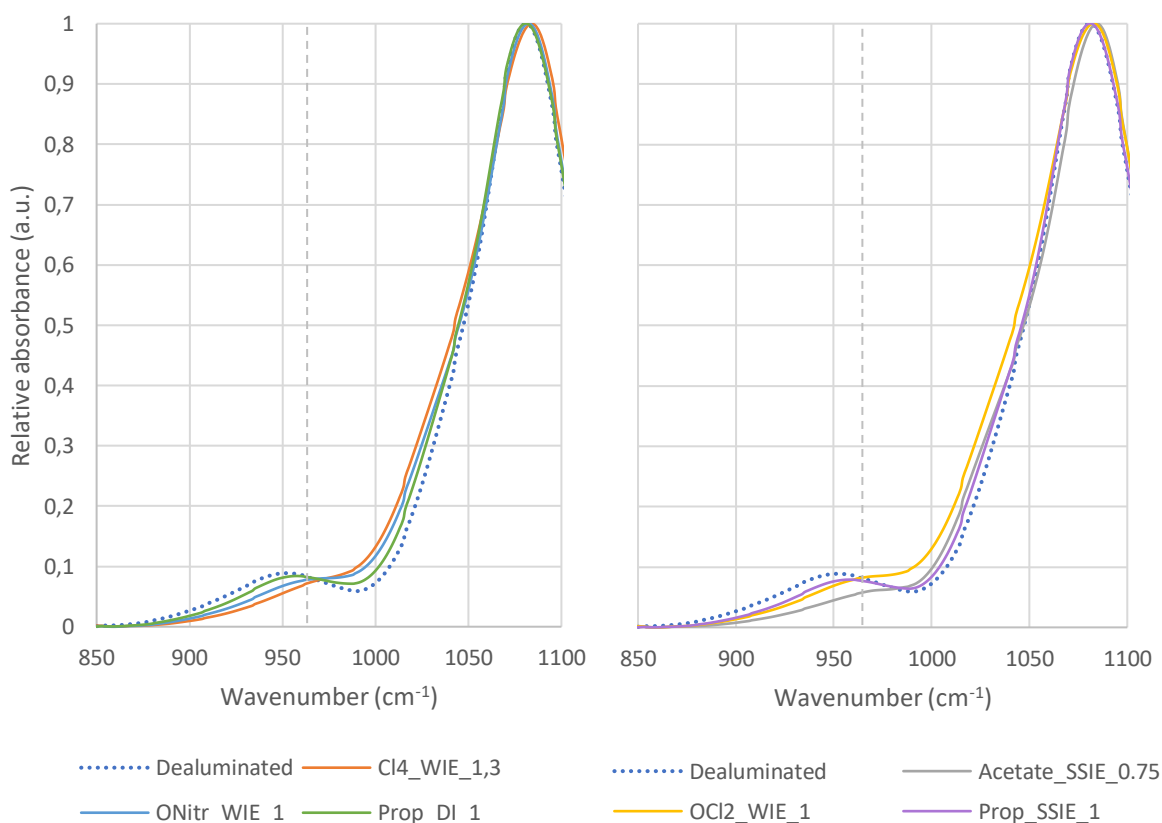


Figure 46: Focused FTIR-ATR spectra of various catalysts. Absorbance is normalized using the main peak around 1090 cm^{-1}

In Figure 46, we see the expected changes in the spectra of the active catalysts: OCI2_WIE_1, Cl4_WIE_1.3 and ONitr_WIE_1. Their spectra accurately show the decrease to the 950 cm^{-1} band as well as a shouldering around 965 cm^{-1} . We can also notice an asymmetric broadening of the peak at 1090 cm^{-1} towards the lower wavenumbers. All those changes combined point to an effective incorporation of the zirconium in the lattice.

Acetate_SSIE_0.75, Prop_SSIE_1 and Prop_DI_1, however, do not display significant changes from the dealuminated sample, which means the incorporation of zirconium was probably unsuccessful for these catalysts.

5.3.4.2 Pyridine adsorption

Due to the complexity and the time-consuming nature of this analysis, only a few select catalysts could undergo this analysis: the parent materials HBeta and Dealuminated-Beta, two good catalysts with different levels of activity (Cl4_WIE_1.3 and ONitr_WI_1), and Acetate_WI_0.75 as an example of a poor catalyst.

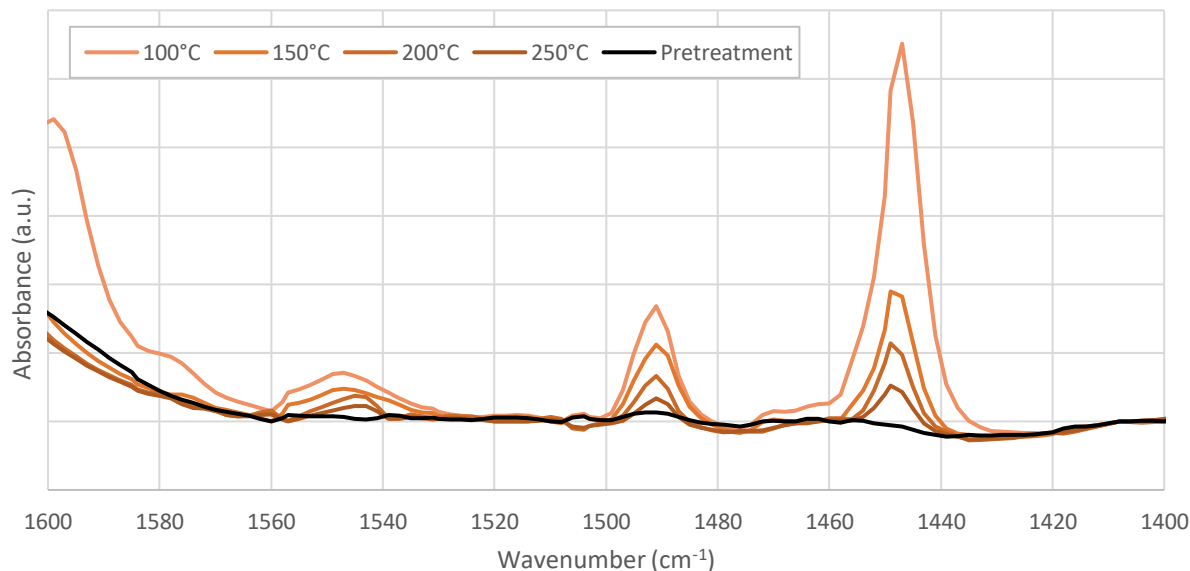


Figure 47: FTIR spectra of ONitr_WI_1 after degassing at 350°C, and after adsorption and subsequent desorption of pyridine at increasing temperatures

Figure 47 shows the typical spectra obtained via this method. We clearly see the typical peaks at 1551 cm⁻¹ and 1455 cm⁻¹ indicating pyridine chemisorbed on, respectively, Bronsted and Lewis acid sites.

With the total area of each peak, we can calculate the concentration of acid sites using the following equation:⁵⁰

$$n_T[\mu\text{mol}.g^{-1}] = n_L + n_B = \frac{A_L S_W}{\varepsilon_L m_W} + \frac{A_B S_W}{\varepsilon_B m_W}$$

Where A_L and A_B are the area of the peak corresponding to Lewis and Bronsted sites, S_W is the surface of the catalyst wafer, m_W its mass, and ε_L and ε_B the molar extinction coefficients of pyridine bound to each type of acid site documented in section 4.3.4.2.

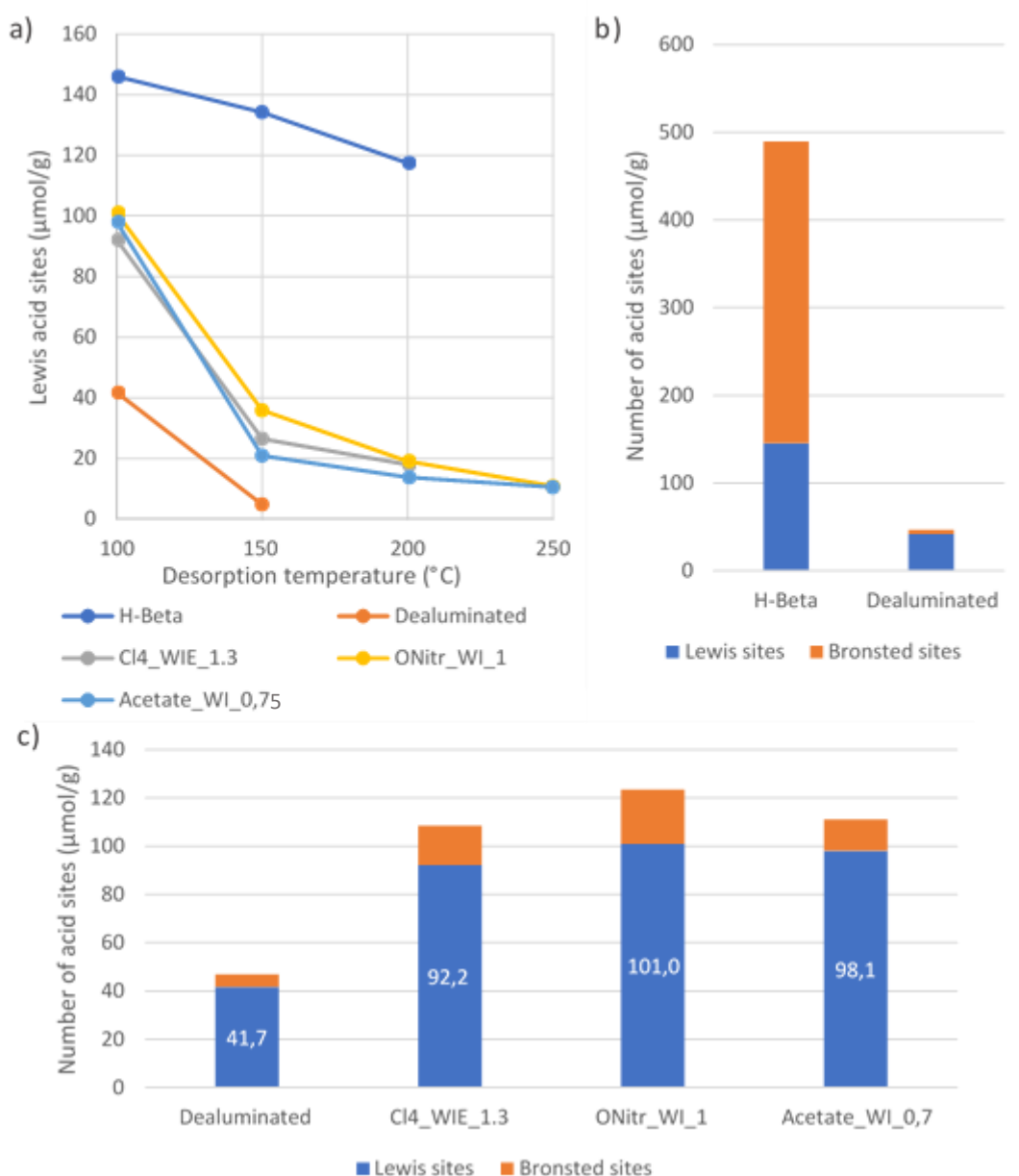


Figure 48: FTIR-Pyridine adsorption results. a) Pyridine-bound Lewis acid sites after desorption at increasing temperatures. b), c) Quantity of Bronsted and Lewis acid sites calculated after desorption of pyridine at 100°C

When looking at Figure 48, we can clearly see the impact of dealumination and subsequent incorporation of zirconium on the acidity of the zeolite. As expected, the parent H-Beta zeolite is highly acid, with a large quantity of Bronsted sites and a fair amount of Lewis acidity. The removal of aluminum seems to be effective, as little to no Bronsted acidity remains upon dealumination. The subsequent addition of zirconium then noticeably increases the amount of Lewis acid sites, though it is still lower than that of the parent H-Beta.

Unfortunately, when comparing the different catalysts, the amount of acid sites does not appear to correlate directly with their efficacy. The difference between the samples is too small to conclude that the better results of ONitr_WI_1 are due to a higher concentration of

Lewis acid sites. Moreover, Acetate_WI_0.75, which was close to inactive, shows quite similar results in terms of acidity. Even if we see in Figure 48a) that the sites of ONitr_WI_1 seem a little stronger than those of the other samples, we do not believe that this can be taken as an indicator of a good catalyst either since this difference is also quite small.

5.3.5 Elemental analyses: ICP-AES and XPS

Both methods of elemental analysis will be discussed in this same section, as their results are complementary. ICP-AES quantifying the bulk of the sample and XPS its surface, combining this information allows us to evaluate the homogeneity of the metal incorporation and make sure we did not form an external shell of zirconium.

Figure 49 shows the typical XPS spectrum obtained for our catalyst. Some catalysts showed a peak at 75.2 eV related to the presence of Al, however too small to be exploited as mentioned in section 5.1.4. The peak related to Zr 3d was consistently centered at 183.2 eV and had the profile shown in Figure 49, the only information that could be retrieved from it was thus quantitative.

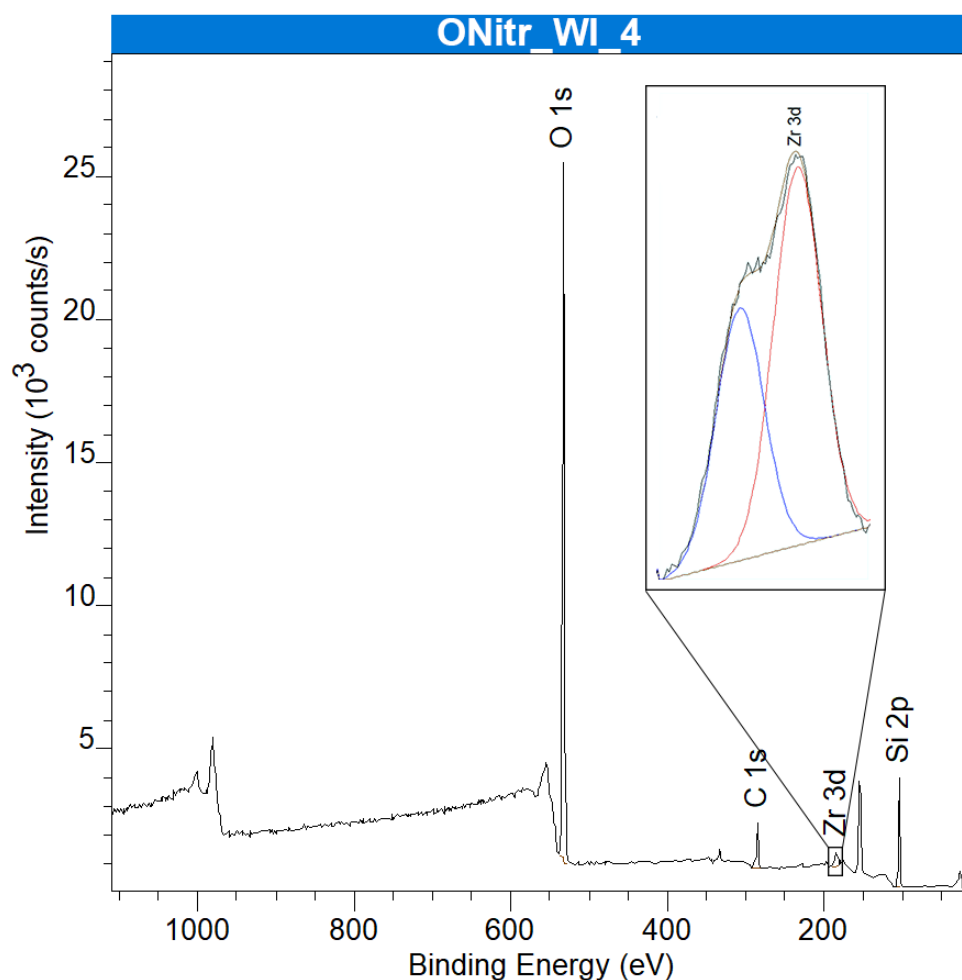


Figure 49: XPS spectrum of ONitr_WI_4, zoom on the peak corresponding to Zr

Because ICP-AES could not be carried out in our lab, only a few selected samples have been analyzed. The combined results of XPS and ICP-AES are shown in Table 11.

Table 11: 100*Zr/Si molar ratios as measured by XPS and ICP-AES

Catalyst	XPS	ICP-AES
Cl4_WIE_1.3	0.7	0.52 – 0.51 ^a
Cl4_WIE_1		0.52
Cl4_WIE_2.77	1.1	0.74
Cl4_WIE_2	1.0 – 1.1 ^a	0.69
Cl4_WIE_1.3alt	0.7	0.65
ONitr_WI_1	1.0	1.00
ONitr_WI_2	1.7	
ONitr_WI_4	2.5	
Prop_SSIE_1	0.0	
Prop_DI_1	2.0	
Acetate_WI_0.75	1.6	

^a: Measured twice

Notice the complete absence of Zr in Prop_SSIE_1, confirming the failure of the SSIE method that was already suspected. In general, all WIE method display a lower loading than expected. We had suspected in section 5.2.2.2 that we had reached a plateau of single-step ion exchange incorporation of Zr. This is now confirmed (Figure 50), as there is no significant difference in the quantity of zirconium detected between Cl4_WIE_2 and Cl4_WIE_2.77, which barely contain more Zr than Cl4_WIE_1.3 and Cl4_WIE_1.

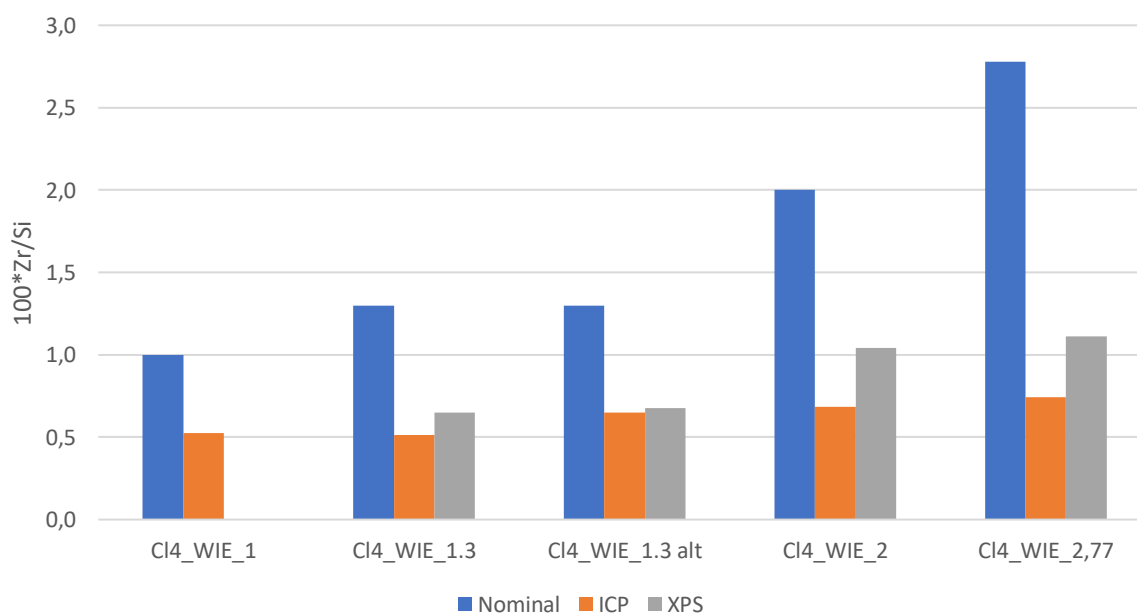


Figure 50: Comparison of the Zr/Si ratio between Cl4_WIE catalysts

The dispersion of the metal appears to be inadequate with this method, as the surface concentration (XPS) of Zr is consistently higher than the bulk concentration (ICP). There is also more zirconium in Cl4_WIE_1.3alt than in Cl4_WIE_1.3, as suspected.

Finally, Prop_DI_1 and Acetate_WI_0.75 both display a surface concentration of Zr that is double the intended, indicating a very poor distribution of the metal. In the case of Prop_DI_1, this information further feeds our suspicions that ZrO_2 was formed at the surface of the catalyst.

Now that we have access to the actual quantity of zirconium in the lattice, we can compute the TOF of our catalysts. Those will be discussed in the next section, where we will correlate the results from characterization to activity.

5.3.6 *Correlations between activity and physico-chemical properties*

Now that the catalysts have been characterized, we will try to make sense of the properties of the catalysts and see what fundamentally differentiates a good catalyst from a bad catalyst. Note that all conclusions taken here are specific to our catalyst, and for the conversion of LA/EL to GVL, they are not receivable for other applications of these characterization methods.

First, we can put aside the data from XRD, as we already discussed the absence of link between the efficacy of a catalyst and its response to this technique. The same can be said about pyridine-adsorbed infrared analysis. We have shown that neither the amount of Lewis acid sites nor their strength appear to be good descriptors of catalytic activity. Nitrogen physisorption cannot help us differentiate a good from a bad catalyst either.

Note however that N_2 physisorption and XRD are not completely irrelevant, as they allow confirmation of the Beta topology of the zeolitic material.

Pyr-IR on the other hand, does not offer any relevant information on the efficacy of the catalyst; only that a Lewis acid has been added to the catalyst. In the case of our catalysts, we cannot even correlate the amount of acid sites with the loading of Zr: Cl4_WIE_1.3 contains 30% (surface) to 50% (bulk) less Zr than ONitr_WI_1 yet in Figure 48c) we saw that it contained only 10% less Lewis acid sites. Acetate_WI_0.75 has a surface concentration of Zr double that of ONitr_WI_1 but displays about as many Lewis acid sites. Another information that may be exploited from Pyr-IR is the amount of Bronsted sites; qualitatively, it seems like the most active catalyst (ONitr_WI_1) contains more, while the least active (Acetate_WI_0.75) contains less. This could make sense, as the Zr T sites need to be partially hydrolyzed to be active (see section 1.4.2). However, we do not deem the data from only 3 catalysts to be sufficient to draw such farfetched conclusions from a small variation in Bronsted acidity. We cannot confirm the causality behind this correlation, more samples would need to be screened.

DRUV yields qualitative information; no quantitative correlation could be found between peak morphology (height, slope) and either zirconium loading (both via XPS and ICP) or the specific activity of the catalysts. What we see however is that the inactive catalysts (SSIE catalysts) display lower Kubelka-Munk functions than the dealuminated zeolite, and inactive ZrO_2 can be detected, as we have seen with Prop_DI_1 and to a lesser extent, Acetate_WI_0.75. On the downside, we have noticed some inconsistencies in the response of the samples to the method, as the repeatability is not good, and some samples (notably ONitr_WI_1) required several tries before giving a readable spectrum. We thus deem DRUV to be a good troubleshooting technique, but not a prediction tool in terms of specific activity.

FTIR-ATR is a useful technique in terms of characterization of the catalysts and approximate prediction of activity. We have noticed that a lower absorption at 950 cm^{-1} , along with an increase of absorption around 960 cm^{-1} and the asymmetric broadening of the 1090 cm^{-1} band on the lower wavelength side correlated was directly related to the correct incorporation of zirconium in the lattice, and subsequently good activity. A sample where the Zr was poorly incorporated in the form of ZrO_2 , such as Prop_DI_1, does not display these changes in its spectrum. This is also true for Prop_SSIE_1 which does not contain any zirconium according to XPS data. It would have been interesting to have FTIR-ATR data from the more active WI catalysts to see if we can observe different magnitudes of the changes in absorption that would relate to the level of activity of the catalysts.

The elemental analysis of the samples is what gives us most information on the catalysts. The absolute value of Zr concentration in the sample allows us to assess the maximal number of active sites present in the catalysts. Comparing the values from both XPS and ICP-AES yields even more information, as we can assess the homogeneity of the metal incorporation; a high XPS/ICP-AES Zr concentration ratio is a good sign of the presence of ZrO_2 at the surface of the catalyst, and a ratio slightly above 1 could simply be a sign that the Zr precursor cannot easily diffuse through the porosity of the zeolite.

With the elemental composition of our catalysts, we can compute the turnover frequency of the active sites. Since structure of the catalyst and of the active sites is, theoretically, the same in all samples, the turnover frequency is expected to be the same across all catalysts. However we see in Table 12 that catalysts made from ZrCl_4 have lower frequencies than those made from $\text{ZrO}(\text{NO}_3)_2$, and the different ONitr_WI catalysts have very different TOFs as well.

Table 12: Turnover frequencies of catalysts tested with EL, as calculated after 2h of reaction with 0.2 mol/L of EL

Catalyst	Cl4_WIE_1.3	Cl4_WI_1.3	ONitr_WI_1	ONitr_WI_2	ONitr_WI_4
TOF ($\text{mol}_{\text{EL}}/\text{mol}_{\text{Zr}}\text{ s}^{-1}$)	$7.6 \cdot 10^{-3}$	$9.5 \cdot 10^{-3}$ ^a	$14.3 \cdot 10^{-3}$	$23.6 \cdot 10^{-3}$	$16.6 \cdot 10^{-3}$

^a: Supposing the same level of incorporation than ONitr_WI_1

These results are represented graphically in Figure 51, along with the TOF of Cl4_WIE_1.3 and Cl4_WI_1.3 when tested with LA. We see once again the leap in activity when using EL over LA.

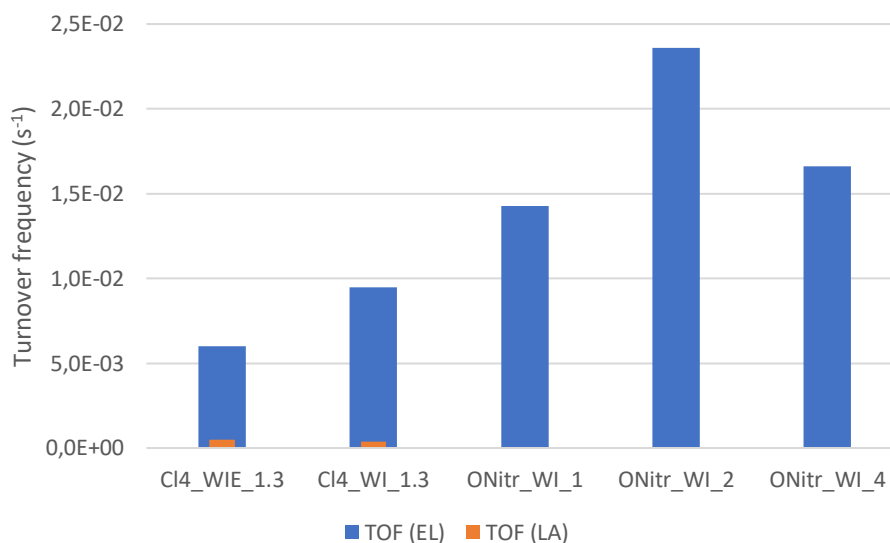


Figure 51: Turnover frequencies of the most active catalysts.

The differences in TOF between catalysts can be explained by the way it is computed:

$$TOF [s^{-1}] = \left. \frac{dC_{EL}}{dt} \right|_{2h} [mol.L^{-1}.s^{-1}] * \frac{1}{C_{cata}} [L.g^{-1}] * \left(\frac{n_{Zr}}{g_{cata}} \right)_{XPS}^{-1} [g.mol^{-1}]$$

TOF is calculated using the Zr content as measured from XPS, and not the actual number of active sites, which is not directly measurable. The differences in TOF are thus most likely due to different ratios of hydrolyzed over closed Zr T-sites (section 1.4.2).

We have chosen to work with the surface concentration of Zr as measured via XPS, since EL/LA cannot diffuse through the microporosity of the catalyst;

The higher TOF of ONitr_WI_1 compared to Cl4_WI_1.3 reinforces the hypothesis formulated in section 5.2.3.1, where we suspected that the ion ZrO^{2+} proportionally generates more active sites than Zr^{4+} . There also appears to be a sweet spot of turnover frequency somewhere between ONitr_WI_1 and ONitr_WI_4, so between Si/Zr ratios of 100 and 25, with the ratio of 50 (ONitr_WI_2) being the most effective one we have tried.

CONCLUSIONS & OUTLOOK

6 Conclusion

This master thesis aimed at mastering the production of postsynthetic Zr- β zeolite catalysts for the conversion of levulinic platform molecules to γ -valerolactone. We started from commercial β -zeolites with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 25 that we have dealuminated under acid conditions to generate defects in the lattice, or silanol nests, in which we can then incorporate zirconium. We screened various Zr precursors and impregnation methods to optimize catalytic activity. We have observed a strong impact of both these parameters on the catalytic performance of the catalyst.

The screened precursors were ZrCl_4 , $\text{ZrO}(\text{NO}_3)_2$, $\text{ZrO}(\text{CH}_3\text{COO})_2$, $\text{Zr}(\text{OCH}_2\text{CH}_2\text{CH}_3)_4$ and ZrOCl_2 . The metal organic compounds yielded catalysts close to inactive as they seem to favorize the formation of ZrO_2 outside the zeolitic framework. While we suspect Zr^{4+} precursors such as ZrCl_4 to be more effective than ZrO^{2+} precursors for ion exchange in liquid phase, they seem to generate a smaller proportion of active sites. The incorporation techniques used were dry impregnation, wet impregnation, wet ion exchange, and solid-state ion exchange. We have not been able to successfully perform the solid-state method reported in the literature^{39,43,49}. Dry impregnation was only performed with Zr propoxide and led to the formation of ZrO_2 , as mentioned. Wet ion exchange generally yielded active catalysts, though the metal loading was lower than expected, leading to lower specific activity but also fewer active sites per mole of Zr than wet impregnation. This is most likely due to the ion exchange nature of the method, which favors the complete tetrahedral incorporation of Zr in the lattice, while for a site to be active, it requires the metal to be bound to at least one hydroxyl group. Wet impregnation was thus more effective, as it led to both a higher metal loading and higher turnover frequencies than ion-exchanged catalysts.

The best catalysts synthesized were made via wet impregnation, using zirconium oxynitrate as precursor, with a nominal Si/Zr molar ratio of 100, 50 and 25. Their actual molar ratios as determined via XPS were respectively 100, 58 and 41. These catalysts display first-order kinetics relative to the concentration of ethyl levulinate with turnover frequencies around 0.02 s^{-1} in presence of $0.2 \text{ mol}_{\text{substrate}}/\text{L}$. One has been tested for reusability and did not display any significant loss activity of activity after 4 consecutive runs of 8 hours. Leaching of the active the active species was consequently ruled out. All catalysts retained the textural and structural properties of the parent zeolite.

We have also identified the most important descriptive factor of activity through characterization. Via Fourier transformed infrared spectroscopy, and when comparing the catalyst to the dealuminated zeolite, a diminution of the peak assigned to silanol groups needs to be visible at 950 cm^{-1} , as well as the increase in absorption between 960 and 1090 cm^{-1} , associated with the asymmetric stretching of the $\text{Zr}-\text{O}-\text{SiO}_3$ link, indicating the incorporation of Zr in the zeolitic framework.²⁸

Through other characterization methods, the catalyst needs to display the retention of the β -zeolite topology (XRD), as well as its textural properties (N_2 physisorption).

Finally, we can compare our results to those found in the literature. Our best catalyst, ONitr_WI_2 (Si/Zr = 58 in Table 13), is on par with the TOF obtained by Bui and researchers who used a hydrothermally synthesized Zr- β . The 97% selectivity is also competitive with what most hydrothermal Zr- β can offer, and higher than what Morales and researchers have reported with their postsynthetic Zr- β . ONitr_WI_2 has not been tested with LA, nor at 150°C however, so its TOF cannot be compared with that of the other postsynthetic Zr- β , and we also acknowledge that when using LA, selectivity is lower with our catalysts. The difference in selectivity may come from this difference in substrate.

Table 13: Reported performances of Zr- β for GVL production under 1 atm. HT: hydrothermal, PS: postsynthetic, LA: levulinic acid, ML: methyl levulinate

Synthesis	Zr loading (Si:Zr molar)	T (°C)	Substrate	Initial TOF (s ⁻¹)	Conversion	Selectivity (%)	Ref
HT	127	120	LA	0.004	98% (11 h)	>99	Bui et al., 2013
HT	127	120	ML	0.026	97% (5 h)	>99	
HT	75	118	LA	-	88% (10h)	93	Wang et al., 2014
HT	100	118	LA	-	96% (10h)	96	
HT	150	118	LA	-	71% (10h)	97	
HT	200	118	LA	-	27% (10h)	>99	
PS	32	150 ^b	LA	0.008 ^a	99% (3h)	85	Morales et al., 2019
PS	100	118	EL	0.014	69% (10h)	87	Our work
PS	58	118	EL	0.024	95% (10h)	97	
PS	41	118	EL	0.017	96% (10h)	87	

^a: approximation from available data, ^b: under autogenous pressure

In conclusion, we have successfully produced postsynthetic Zr-Beta zeolites from commercial H-Beta zeolites, that adequately perform the conversion of levulinic feedstock to γ -valerolactone. We have shown that the postsynthetic approach for Zr-Beta production, which is safer and faster than the hydrothermal synthesis, yields catalysts with similar performance but will allow a greater variety of textural properties in the future.

7 Outlook and future research

To further improve the postsynthetic production of Zr- β zeolites, the dry impregnation method needs to be investigated further, as is a much more energy-efficient incorporation method than wet impregnation, which requires the evaporation of a non-negligible amount of water. In a context of sustainable development, implementing more energy efficient unit operation is of great importance.

It would also be of interest to investigate to optimal loading of zirconium, as there appears to be a maximum of TOF comprised between Si/Zr molar ratios of 100 and 41.

More catalysts have to be analyzed via pyridine-adsorbed infrared spectroscopy, to investigate the link between activity and both Lewis and Bronsted activity. As the active sites are Lewis acid sites that also display Bronsted acidity, the simple quantification of either type of sites is not adequate to quantify the active sites.

Another interesting characterization of the catalyst would be their hydrophobicity. The difficulty to obtain a high activity with levulinic acid points to an issue with the hydrophobicity, or lack thereof, of the catalysts. Investigating the effect of this factor on activity and how different precursors and incorporation methods can tune this parameter could help us create more effective catalysts.

Once the postsynthesis of the Zr- β zeolites is mastered, the next step will be to apply this method to nano-zeolites developed in the lab in the PhD thesis of Arnaud Detaille, with the goal of building hierarchal Zr- β zeolites. Similar work has been reported by our group with TS-1 zeolite.⁴²

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Postsynthetic Zr-Beta zeolites for the conversion of levulinic feedstock to γ -valerolactone

Presented by Marty Kinnaer

With today's increasing environmental concerns, the development of sustainable materials and energy are of utmost importance. Working on the replacement of petroleum-based chemicals by biomass-derived chemicals can help reduce the consumption of fossil energy sources and lower our dependence to petroleum. This master thesis aims to help develop a new sustainable, safe and efficient process for the production of γ -valerolactone from biomass-derived levulinic acid by creating an efficient catalyst for this reaction.

Levulinic acid is a biomass-derived platform molecule that can be obtained from most plant-based resources, including lignocellulosic material. Lignocellulosic biomass is known for its hardness as plants have evolved this tissue to resist microbial and enzymatic degradation. Finding ways to exploit this biomass fraction is important, as it is most often discarded, wasted.

Gamma-valerolactone (GVL), can be used as the base chemical for a wide variety of applications, many of them being currently fulfilled by petroleum-based chemicals. It can be used as a solvent or fuel additive and even be transformed further to create synthetic fuels or polymers.

In this work, we have focused on making postsynthetic Zr- β zeolites, by removing the aluminum of commercial zeolite Beta and subsequently incorporating zirconium in the defect sites formed by the removal of Al. This allows to make Zr- β zeolites with controlled morphology, contrarily to its direct synthesis. Direct, hydrothermal synthesis of Zr- β yields large crystals in the micrometer range, as it is 20 days long, and requires the use of hydrofluoric acid which is harmful for the both the environment and for the operators.

Zr- β zeolites are microporous materials; only its external surface area is catalytically active, hence the need to improve their surface-to-volume ratio. We have proven that postsynthetic Zr- β zeolites can be used for the conversion of levulinic acid to γ -valerolactone under atmospheric pressure at 118°C by catalytic hydrogen transfer with 2-pentanol. The catalyzed reaction is the Meerwein-Ponndorf-Verley reduction of the ketone function of the substrate. When used with the ethyl ester of levulinic acid, ethyl levulinate, our catalysts have reached selectivities up to 96% for γ -valerolactone. We made highly active Zr- β zeolites with Si/Zr molar ratios down to 41 whereas hydrothermal synthesis does not work below a ratio of 75. We have also been able to prove that the zirconium was incorporated in the zeolitic framework, and not supported on its surface in the form of ZrO₂.

With the knowledge gained from this master thesis, we will be working in the future on the creation of hierarchal Zr- β zeolites from nanozeolites pre-made in our lab.

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