

Faculté des bioingénieurs

Shaping of Zr- β zeolite nanocrystals through spray drying for the upgrading of levulinates to γ -valerolactone

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Année académique 2020-2021

Mémoire de fin d'études présenté en vue de l'obtention du diplôme de
Bioingénieur : chimie et bio-industries

Acknowledgments

I would particularly like to thank Pr. Damien Debecker for welcoming me in his research laboratory and for his regular follow-up throughout the year. I would like to underline his contagious positive attitude, which we actually all need, and his incredible management of the lab despite all that was going on outside the work environment.

Then, I would like to thank the one who called me "cincle plongeur", "perdreau" or "rousserolle effarvate" during a whole year. I am of course talking about Arnaud Detaille, who I am still not sure knows my real name. Anyway, I would like to thank him for his support on this project and for having shared with me all his rich knowledge on beta zeolites. I would also like to thank him for risking his life more than once with hydrogen fluoride. It was worth it!

Of course, this master thesis would not have been possible without the help of Margot, Fanny, Marty, Hippolyte and especially François without whom the lab would probably not be running. They all repeatedly helped and advised me during this year, for which I am very grateful.

I am also very honored for Pr. Eric Gaigneaux and Pr. Aurore Richel to have accepted to read my master thesis and to be part of my jury.

On a more personal note, I would like to thank my parents for giving me the possibility to pursue such exciting studies during the past five years. And finally, I would like to thank all my fellow students who kept working hard and persevering this year, together giving courage to each other to keep giving the best of us. Life lessons were learned this year for sure!

Abstract

This master thesis focusses on the upgrading of levulinate esters to γ -valerolactone, a green solvent and fuel additive, using Zr-beta zeolite *nanocrystals*. These *nanocrystals* were shaped into *microparticles* by spray drying to overcome practical issues related to the colloidal size of the nanocrystals (handling, recovery, reuse, ...). Three features of the catalyst were extensively studied during this master thesis.

First, screening of Zr loadings was performed to enhance the catalytic activity. Zr-beta *nanocrystals* with a molar Si/Zr ratio of 26 obtained the highest productivity with 4.05 ± 0.55 mmol_{GVL}/h.g_{cat}. Overall, the productivity of the catalyst is among the highest reported in the literature.

Second, the potential of Zr-beta *microparticles* obtained by spray drying of Zr-beta *nanocrystals* was investigated. A 78 % decrease in productivity was observed, which could be associated with the use of a binder covering the surface and blocking the pores of the catalyst, preventing subsequent impregnation of active Zr species.

Third, the potential issue of internal diffusional limitations was studied to demonstrate whether the levulinate esters mostly react on the *surface* of the catalyst or rather in the *micropores*. Based on the conducted experiments and on the literature, the levulinate ester should not cause diffusion limitations in the micropores. However, the catalytic results suggested potential mass transport limitations to some extent due to the diffusion of γ -valerolactone in the micropores.

In summary, this work enabled us to showcase the high catalytic activity of Zr-beta nanocrystals and to demonstrate potential issues regarding the spray drying process of nanocrystals and the diffusion of γ -valerolactone in micropores.

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1. Introduction

1.1. Background and problem statement

The chemical industry currently faces the important challenge to substitute its fossil-based energy sources with renewable feedstocks, as it is pressured by environmental policies to lower carbon dioxide emissions and confronted by the undeniable fact that fossil fuel reserves will one day be depleted due to a global increase in energy demand.^{1 2}

By definition, renewable feedstocks are natural resources which are limitless in supply or can be restored in a limited amount of time on a human time scale, preferably within a few month or years.³ Therefore, biomass can be considered a renewable feedstock as it is referring to non-fossilized organic matter, mostly derived from plant-based materials. Biomass feedstocks have the advantage to be abundant worldwide, to produce lower CO₂ emissions and to reinforce supply security by increasing the global feedstock availability and by decreasing the import dependence.^{4 5}

On the contrary, petroleum, natural gas or coal are considered non-renewable feedstocks due to their limited supply as they are coming from fossilized carbon, fixed by plants via photosynthesis millions of years ago. Currently, seven simple and low-cost chemicals (ethene, propene, butadiene, benzene, toluene, xylene and methanol) produce the vast majority of chemicals. These chemicals are mostly produced from crude oil and natural gas by cracking, reforming, distillation and fractionation processes. Further functionalization which increases the complexity of the base chemicals gives access to a large set of valuable chemicals (Figure 1).³

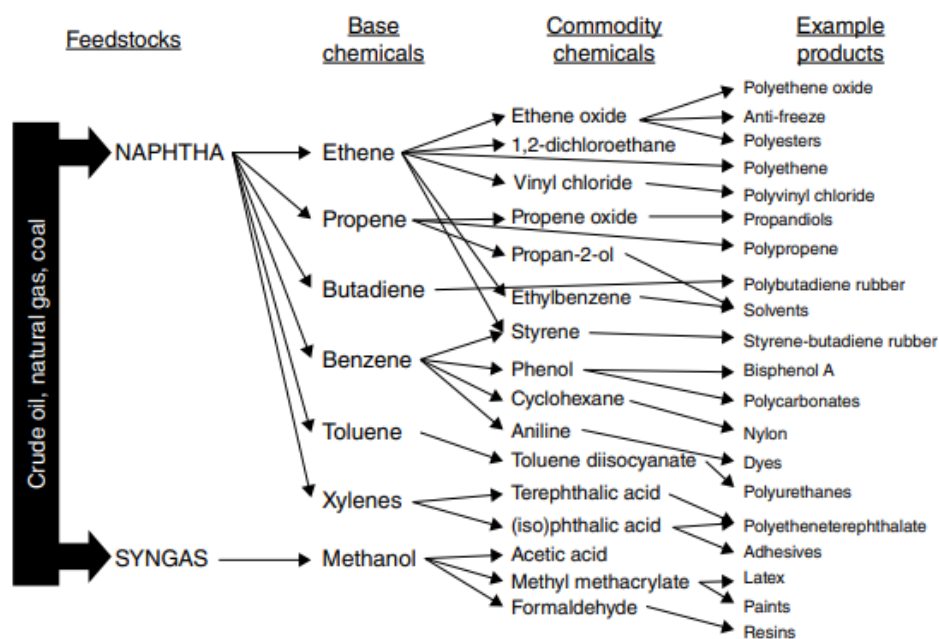


Figure 1. Simplified flowchart of applications from the seven based chemicals by Farmer and Pascal (2015).³

In order to switch from a fossil based chemical industry to a biomass-based counterpart, equivalent chemicals to these seven base chemicals, called platform molecules, are needed. Platform molecules are derived from harvested or waste biomass feedstocks (polysaccharides, mono/disaccharides, lignin, proteins, triglycerides, ...) at a competitive cost and used as intermediate building blocks to produce a broad range of products like polymers (plastics, synthetic textiles, ...) and highly valuable chemicals (pharmaceuticals, care products, ...).⁶ Hence, platform molecules are the key for the green transition of the chemical industry.

Most scientific articles and reviews refer to the Platform Chemical List of the Department of Energy (DOE) of the United States to explain the importance of platform chemicals, as this list aims to identify biomass-derived chemicals which should be prioritized for further research endeavors. This list was last updated in 2010 and contains the following chemicals: ethanol, furfural, hydroxymethylfurfural, 2,5-furandicarboxylic acid, glycerol, isoprene, succinic acid, 3-hydroxypropionic acid/aldehyde, levulinic acid, lactic acid, sorbitol, and xylitol.⁷ These chemicals made it to the DOE list as they have a potential lower cost, would they be produced from biomass feedstocks on a large scale.⁸

In spite of an increasing urge to use platform molecules as feedstocks, these alternative industrial processes are not yet sufficiently competitive compared to fossil-based counterparts. The main reason is linked to the complexity of the chemical pathways to produce high-value added chemicals from these platform chemicals.⁸

However, emerging market's interest in platform molecules challenges the chemical industry to upscale the bio-based processes. In this context, research on alternative reaction pathways, highly effective catalysts and new production strategies is crucial to increase production yields and meet the demand.^{9 10}

This master thesis took part in the PhD research of Arnaud Detaille and aimed to participate in the simplification and optimization of production processes of value-added chemicals produced from platform molecules. More specifically, the heterogenous catalyst consisting of Zr-beta zeolites was studied and optimized for the production of γ -valerolactone, a green solvent and fuel additive, from levulinate esters which in turn are easily obtained from levulinic acid, one of the twelve platform molecules listed by the US DOE.

1.2. Levulinic acid (LA) and ethyl levulinate (EL) as substrates for biomass valorization

Levulinic acid (LA) or 4-oxopentanoic acid is a C5 organic compound which contains a carboxylic acid and ketone group. These two functional groups enable to obtain a multitude of derivatives including levulinate esters and γ -valerolactone (Figure 2). LA and its derivatives find applications as fuel additives, food additives, solvents, surfactants, biodegradable herbicides, pharmaceuticals, polymers, flavoring agents, ...^{11 12}

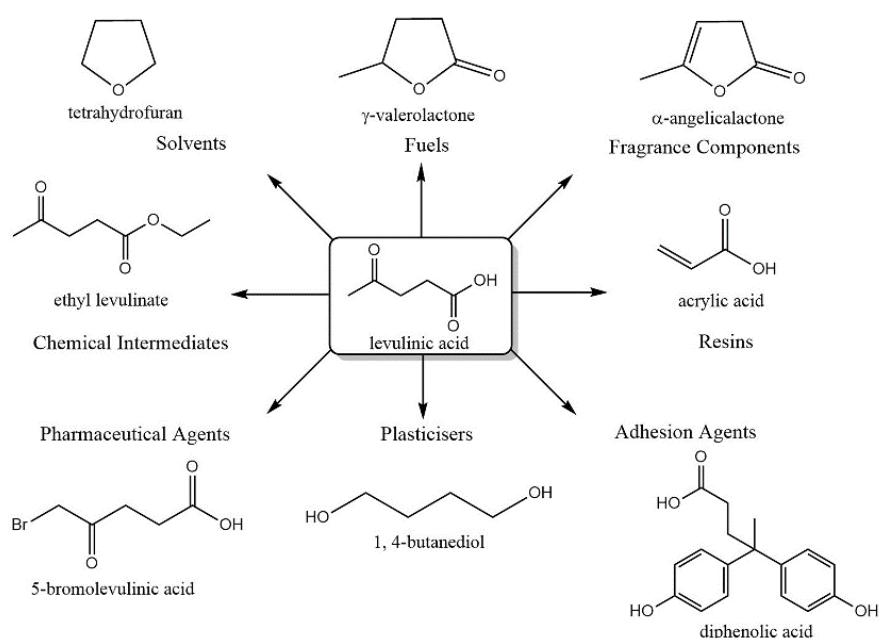


Figure 2. Main derivatives obtained from LA, by Liu et al. (2020).¹¹

LA can be produced from a variety of feedstocks like cellulose, sucrose, starch and multiple biomass residues such as crops and timber which undergo acid-catalyzed hydrolysis to obtain hexoses. Hexoses like fructose and glucose undergo tautomerization to form 1,2-enediol. Hydroxymethylfurfural (HMF) is then obtained through an acyclic dehydration of 1,2-enediol or through a cyclic dehydration directly from fructose. LA and formic acid are then obtained from HFM through a sequence of three hydrations and one dehydration (Figure 3).¹²

In this master thesis, ethyl levulinate (EL), which is easily obtained from LA, was used as the main reactant for the production of γ -valerolactone. Previous research in the PhD research of Arnaud Demaille demonstrated lower reaction yields with LA compared to EL, when Zr-beta zeolites are used as heterogeneous catalyst.¹³ Li *et al.* made a comparable observation when Zr-based metal organic frameworks (MOF) were used as catalyst (Table 3, entry 7). It could be that LA yielded lower catalytic activity than EL due to the carboxylic group of LA that has a strong inhibiting binding ability to the active sites.¹⁴

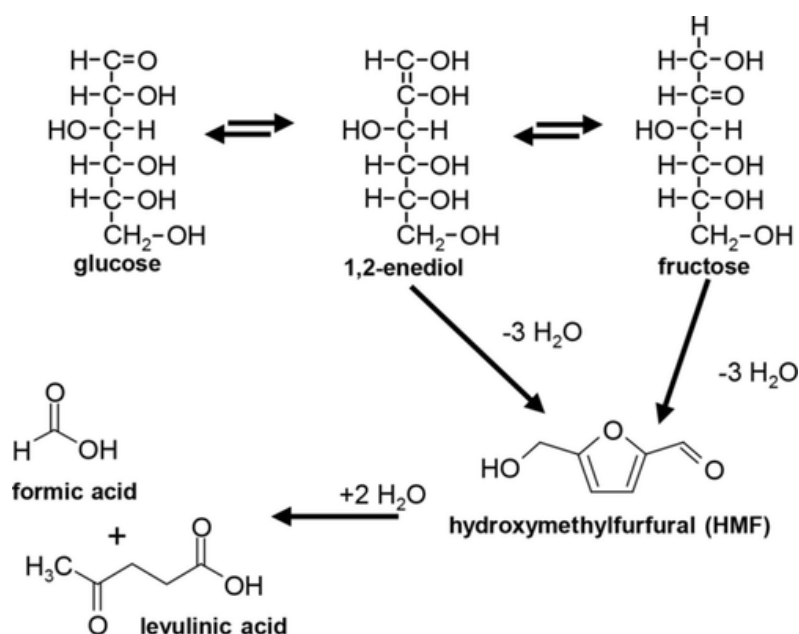


Figure 3. Synthesis route for the production of LA from hexoses, by Lea Silva et al. (2018).¹²

In Table 1, the physicochemical properties of LA and three levulinate esters (methyl-, ethyl- and butyl levulinate) are presented. The calculations of the approximative length of the molecules are made for a 1.43 Å C-O bond, a 0.97 Å O-H bond, a 1.54 Å C-C bond and an angle between bounded carbons of 109.5°.¹⁵

Table 1. Physicochemical properties of levulinic acid (LA), methyl levulinate (ML), ethyl levulinate (EL) and butyl levulinate (BL).

Properties of pure compounds	LA	ML	EL	BL
Boiling point [°C] at p_{atm} ¹⁶	245	196	205	238
Density [kg/m] at 363.15 K ¹⁷	1080	980	940	910
Viscosity [mPa.s] at 363.15 K ¹⁷	3.45	0.71	0.72	0.87
Approximative length [Å]	6	6	7	8

Levulinate esters are obtained through an esterification reaction between LA and an alcohol (i.e. methanol, ethanol, butanol) using acids such as HCl, H₂SO₄ or H₃PO₄ (Figure 4).¹⁹ The reaction is limited by an equilibrium and water must be removed or the alcohol must be present in excess to obtain higher levulinate yields.¹²

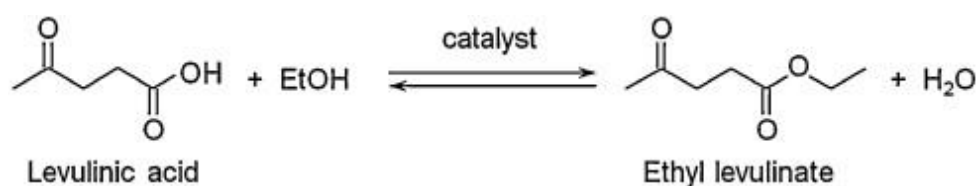


Figure 4. Reaction for the production of EL from LA, by Kuwahara et al. (2014).¹⁹

1.3. Alcohol as a hydrogen donor and a solvent

The upgrading of the levulinate platform molecule towards GVL implies the reduction of the ketone function by hydrogenation. Thus, a hydrogen donor is necessary to convert the ketone function of the levulinate ester to an alcohol and subsequently obtain γ -valerolactone. In most cases, molecular hydrogen gas is used under harsh conditions of approximately 14 bar and 180 °C or 30 bar and 150 °C, generally with noble metal catalyst.²⁰ Formic acid can also be used and is very interesting as it is produced during the synthesis of LA in an equimolar concentration. However, it also requires harsh conditions or noble metal catalysts.²⁰

An attractive alternative is to use an alcohol as reductant. The catalytic transfer hydrogenation (CTH) between the alcohol and the ketone of EL via the Meerwein-Ponndorf-Verley (MPV) reaction (see Chapter 1.5.) can lead to γ -valerolactone. This process enables working at temperatures as low as 110 °C and under atmospheric pressure, hence avoiding the use of noble-metal catalysts or harsh conditions. In addition, it enables using the alcohol as solvent and avoiding the use of water (which causes leaching problems of the active metal) or industrial solvents (with higher toxicity to human health and the environment) such as 1,4-dioxane and tetrahydrofuran (THF).²¹

Primary alcohols have been reported to obtain lower yields and selectivity than secondary alcohols.²² Luo *et al.* demonstrated experimentally that primary alcohols have higher activation energies (73.5 kJ/mol for 1-butanol compared to 52.5 kJ/mol for 2-butanol on Hf-beta zeolite) and thus a higher activation barrier resulting in a slower tendency to give an hydrogen atom, therefore retarding the hydrogenation.^{23 24}

Among secondary alcohols, a positive correlation has been established regarding the reducing capacity (oxidation enthalpies) and the MPV reduction. In a study conducted by Tang *et al.*, 2-butanol and 2-propanol, which have comparable reducing capacities, demonstrated considerably high yields in γ -valerolactone production. Yields were lower when ethanol was used, and even lower when methanol was used, in correlation with their lower reducing capacities. This correlation is not necessarily observed at low temperature due to the steric hindrance. For example, at 200 °C, a 62 % yield was achieved for 2-propanol, whereas a 27.5 % yield was observed for 2-butanol using the same reaction conditions (1 h, HCl/ZrO(OH)₂). However at 240 °C, the steric hindrance was overcome and both alcohols enabled to obtain a 84.5 % yield.²⁵

In this master thesis, 2-pentanol is used as the standard hydrogen donor but it is also compared with 2-propanol and 2-butanol. In Table 2, the physicochemical properties of the reductants are presented.

Table 2. Physicochemical properties of 2-propanol (2-PrOH), 2-butanol (2-BuOH) and 2-pentanol (2-PeOH).

Properties of pure compounds	2-PrOH	2-BuOH	2-PeOH
Boiling point [°C] at p_{atm}	82.3	99.5	119
Density relative to water [-] at 363.15 K	0.79	0.81	0.82
Viscosity [mPa.s] at 363.15 K	2.04	4.21	5.3
Standard heat of alcohol oxidation [kJ/mol] ²⁴	70.2	69.4	69.1
Approximative length [Å]	3	4	5

1.4. γ -Valerolactone (GVL) as a product

γ -Valerolactone (GVL) is a C5 organic saturated heterocyclic molecule with an ester and methyl group, naturally occurring in fruits. It has a high boiling point of 207 °C, a low melting point of -31 °C, a low vapor pressure of 3500 Pa at 80 °C and it is miscible with water.²⁶ Recently, GVL has drawn a considerable interest as a value-added chemical, thanks to its production from biomass and its multiple applications.²¹

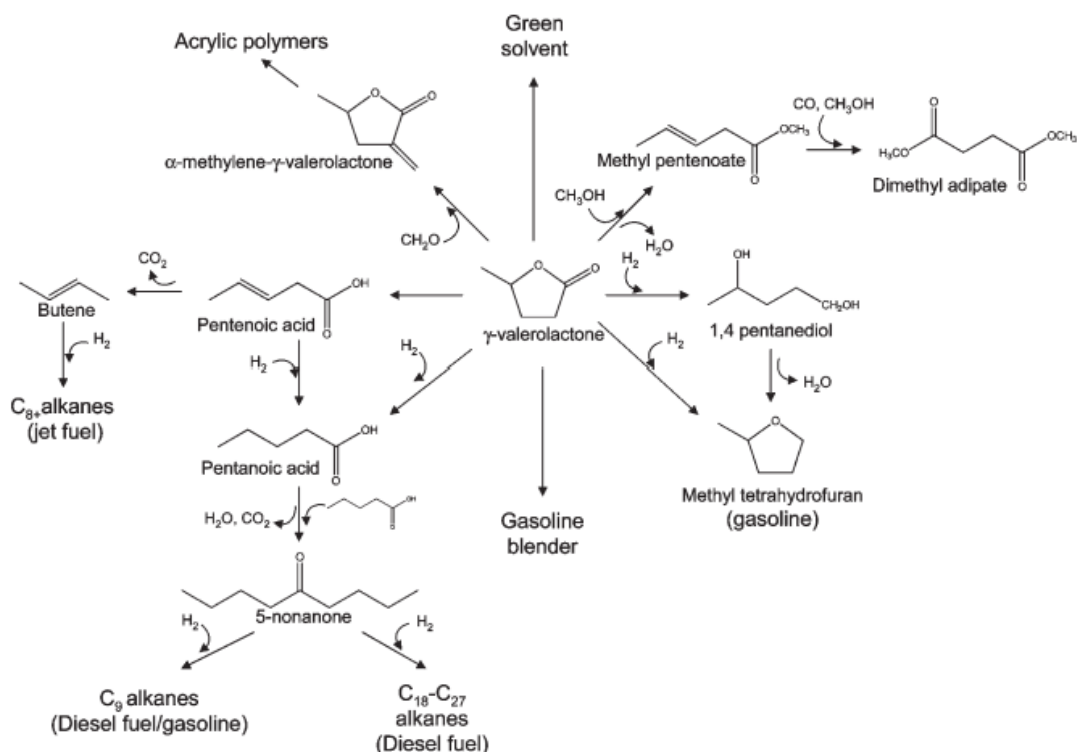


Figure 5. Main applications of GVL, by Bond et al. (2010).²⁶

GVL has applications as biodegradable food additive, green solvent to process biomass and fuel additive (prevents engine damages, improves overall performance of the engine, lowers greenhouse gas and particulate emissions). GVL could also be used as a biofuel as it demonstrates similar properties to (bio)ethanol. In fact, it retains 97 % of the energy of the glucose from which it is produced, it has a similar combustion energy to that of ethanol (29.7

MJ/kg) and it is relatively cheap (0.5-0.8 USD/liter). In addition, GVL can be further transformed to obtain multiple derivatives including long-chained alkanes that are used in diesel fuels (Figure 5).^{21 27}

GVL is mostly produced by hydrogenation of LA, in the liquid or in the gas phase. Two reactions pathways are possible (Figure 6): (1) the ketone group of LA is first hydrogenated, leading to the formation of 4-hydroxypentanoic acid, and the latter is then dehydrated (lactonization) to produce GVL; (2) LA is first dehydrated to obtain α -angelic lactone which is then dehydrogenated to obtain GVL.²¹ Abdelrahman *et al.* established that the former pathway was thermodynamically favored and was the most followed pathway at low temperature.²⁸ Similarly, Wise and Williams demonstrated neither LA nor its esters require to be present in excess, as the fast lactonization of 4-hydroxypentanoic acid into GVL drives the equilibrium.²⁹ In addition, when GVL is produced by MPV reduction, the hydrogenation step is catalyzed by Lewis acidity, whereas the dehydration step is catalyzed by Brønsted acidity.⁵

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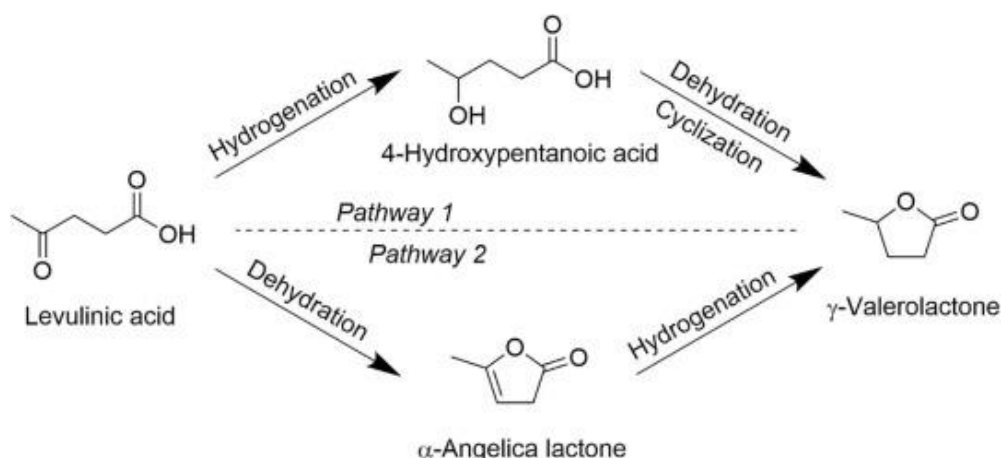


Figure 6. Two possible reaction pathways for the production of GVL from LA, by Dutta *et al.* (2019).²¹

1.5. Meerwein-Ponndorf-Verley (MPV) reaction mechanism

The conversion of EL into GVL is performed by the MPV mechanism whenever an alcohol is used to donate a hydride to the ketone.

The hydrogenation of alkyl levulinate through the MPV reaction has been divided into six steps by Luo *et al.* (see Figure 7). In this case, it is illustrated using methyl levulinate (ML) and 2-butanol as the hydrogen donor. (1) The secondary alcohol undergoes chemical adsorption and one deprotonation on a Lewis acid site of a metal, in this case Zr. The Zr atom is partially coordinated to three O atoms linked to a Si tetrahedra and one O atom from a hydroxyl group. (2) The levulinate ester undergoes chemical adsorption. All the adsorption and desorption steps are assumed to be in equilibrium. (3) A hydride transfer from the secondary alcohol to the ketone group of the levulinate ester takes place by the formation of

a six-membered transition state. The secondary alcohol becomes a secondary ketone. This hydride transfer is assumed to be the slowest step and thus the rate-determining step of the reaction mechanism. (4) The secondary ketone (2-butanone) desorbs. (5) The formed intermediate, 4-hydroxypentanoate, receives a second hydrogen atom. (6) Finally, 4-hydroxypentanoate undergoes a ring closing lactonization which produces GVL and releases an alcohol (here, methanol).²⁴ The 4-hydroxypentanoate intermediate is undetectable at high temperatures (above 323 K). As a consequence, the lactonization is assumed to be spontaneous and irreversible. Additionally, it has been demonstrated that Brønsted acidity leads to a higher lactonization rate and GVL selectivity.²⁸

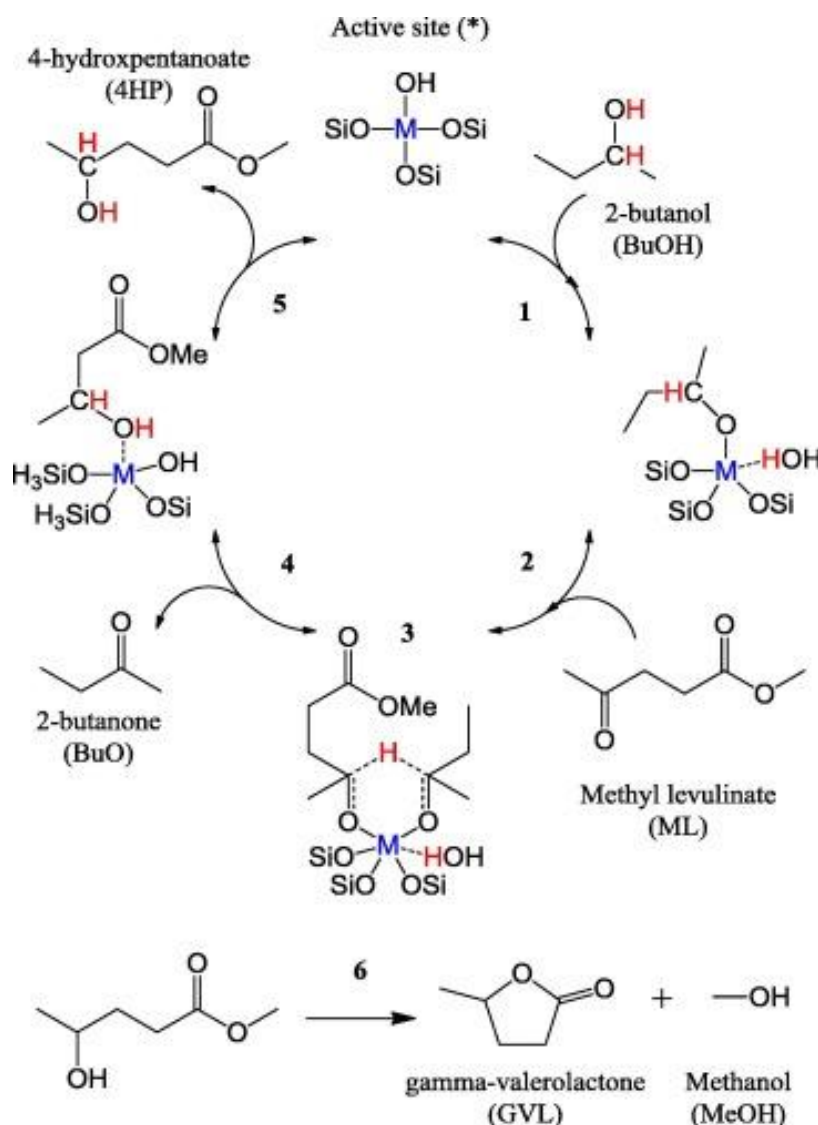


Figure 7. MPV reduction of ML on metal atom with Lewis acidity using 2-butanol as reductant, by Luo et al. (2014).²⁴

1.6. Heterogeneous catalysts for the upgrading of LA to GVL

1.6.1. Overview of catalysts reported for the upgrading of LA to GVL

GVL is mostly produced from LA using noble metal catalysts such as Ru, Ir, Pd and Pt. For illustration, a TiO₂ supported Ru (1 wt%) catalyst achieved a high GVL yield of 99.9 % and a 0.10 s⁻¹ turnover frequency (TOF) at full conversion within 3 h at 150 °C using H₂ (30 bar).³⁰

Alternatively, more earth-abundant and economically sustainable non-noble metals are preferred as catalyst, using H₂, formic acid or secondary alcohols as hydrogen donors. Mostly Cu, Ni, Fe, Al or Mg supported on SiO₂, Al₂O₃, ZrO₂ or ZnO are used. Overall, non-noble metals demonstrate a lower activity despite their high recyclability and low deactivation over successive runs thanks to their stable surface composition.²¹

Among non-noble metals, Zr-based catalyst have the advantage to demonstrate high conversion and high selectivity toward GVL using secondary alcohols as hydrogen donor, which is preferred over H₂ or formic acid. Bulk ZrO₂ was first used, followed by ZrO₂ supported on SBA-15 silica (ZrO₂/SBA-15; SBA = Santa Barbara Amorphous) and Zr-beta zeolites (Table 3, entries 1-3).^{22 32 33} Then, an organic-inorganic hybrid catalyst was developed using seeds to synthesize zirconium phosphonate (Zr-PhyA) in addition to a HCl/ZrO(OH)₂ catalyst which demonstrated very high productivity (Table 3, entries 4-5).^{34 21} More recently, a catalyst based on Zr and humic acid (HA-Zr) also demonstrated high efficiency (Table 3, entry 6).³¹ Finally, polyoxometalate Zr-based metal–organic frameworks (MOFs) have been used as catalyst (Table 3, entry 7).¹⁴

Table 3. Summary of Zr-based catalysts for the conversion of LA or EL to GVL.

Entry	Catalyst	LA conversion [%]	GVL yield [%]	GVL selectivity [%]	Productivity [mmol _{GVL} /g _{Zr} .h]	Solvent and H donor	Temperature, time
1	ZrO ₂ ²²	99.9	-	71	-	2-BuOH	220 °C, 16 h
2	ZrO ₂ /SBA-15 (9.8 wt% ZrO ₂) ³²	99.9	90	90	-	2-PrOH	150 °C, 3 h
3	Zr-beta zeolites (Si/Zr 107) ³³	100	96	96	30 (after 2 h)	2-PeOH	118 °C, 10 h
4	Zr-PhyA ³⁴	100	98.7	-	-	2-PrOH	130 °C, 2 h
5	HCl/ZrO(OH) ₂ by ZrOCl ₂ ·8H ₂ O ²¹	99.9	-	65.5	65 (after 2 h)	2-BuOH	240 °C, 2 h
6	HA-Zr ³¹	99.5	84.2	84.6	-	2-PrOH	150 °C, 11 h
7	H ₃ PW ₁₂ O ₄₀ Zr-based MOF ¹⁴	99	86	87	-	2-PrOH	160 °C, 6 h

In this master thesis, the focus is entirely on Zr-beta zeolites as they recently demonstrated relatively high catalytic activity in the production of GVL under mild conditions and are since decades highly used in industrial processes for their acidic properties and thermal stability. However, further research is necessary in order to understand how the catalyst functions and to consider future upscaling.

1.6.2. Zeolites and beta (BEA) zeolites

1.6.2.1. Definition, properties and applications

Zeolites are a type of crystalline aluminosilicates (SiO_4^{4-} and AlO_4^{5-} tetrahedra sharing oxygen atoms) characterized by a given framework of micropores.³⁵ Although the first zeolite was described 250 years ago, as they occur naturally as minerals, the last 60 years experienced a surge in research and applications of synthetic zeolites used for catalysis and adsorption processes. To each one of the 200 zeolite types, the IZA Structure Commission assigned a three-letter code based on their name. In the case of beta zeolites, the code BEA is used.³⁶

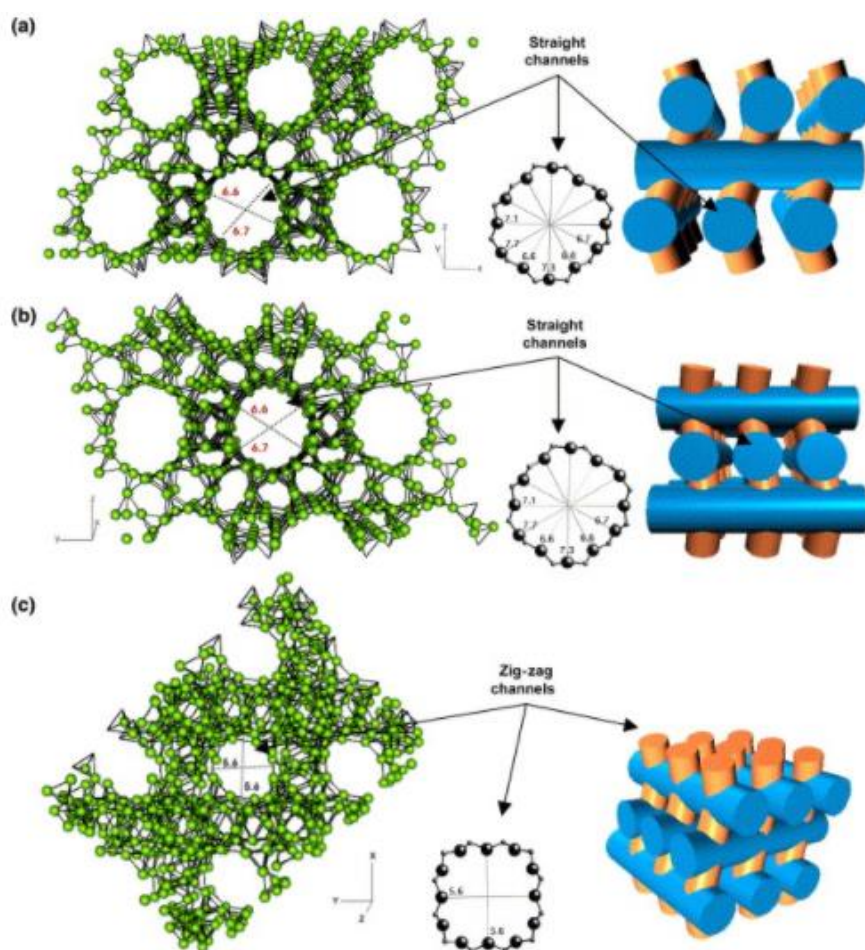


Figure 8. Stereographic drawings and perspective views of the beta zeolite structure along axis (a) $[0\ 1\ 0]$, (b) $[1\ 0\ 0]$ and (c) $[0\ 0\ 1]$, by Barcia et al. (2005).³⁷

The beta zeolite is one of the most used zeolites. It was first developed by Mobil in 1967, but its complex structure was only characterized in 1988. It has a three-dimensional system of ordered and disordered frameworks coexisting with three intersecting channels. In comparison to other zeolites, it has large pores made of two types of 12-atoms ring channels: 5.6 x 5.6 Å zigzag channels along axis [0 0 1] and 6.6 x 6.7 Å straight channels along axis [1 0 0] and axis [0 1 0] (Figure 8).³⁷

In addition, the beta zeolite varies according to the Al content incorporated in the framework (Si/Al ratio). Because tetravalent Si(IV) atoms are substituted by trivalent Al(III) atoms, the Al atom is negatively charged and compensated by a cation, in most cases a proton which gives the material its typical Brønsted acidity.³⁸ The catalyst is then referred to as H-beta zeolite. If Lewis acidity is desired, the Al atoms can be substituted by tetravalent metal atoms. If Zr is used as metal, the catalyst is referred to as Zr-beta.

Because beta zeolites demonstrate high acidity, good accessibility to these acid sites and high thermal stability, it is an excellent catalyst for multiple industrial processes such as hydro-alkylation of aromatics and alkanes, Friedel-Crafts acylation, catalytic cracking and decontamination processes (NO_x adsorption).³⁹ It demonstrates many potential applications in biomass valorization, confirming its tremendous potential in green chemistry.

1.6.2.2. Crystallization and synthesis process

Zeolites are formed through the rearrangement of precursor molecules (Si and Al precursors and structure-directing agents) into clusters which together irreversibly adopt the crystalline structure. This process is called primary nucleation and can be further separated into homogeneous and heterogeneous primary nucleation. The former occurs when the solution is impurity free and the latter when inert particles induce the nucleation. Secondary nucleation occurs when the process is induced by crystals (such as seeds) already present in the suspension.⁴⁰ The nucleation process is quantified by the nucleation rate (Figure 9), defined as the number of nuclei formed per time unit per volume and expressed by an Arrhenius-type equation.³⁶

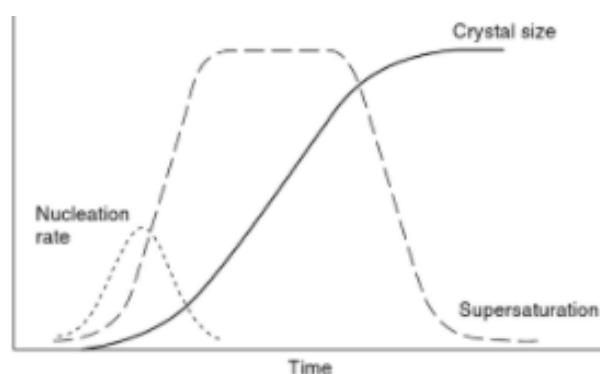


Figure 9. Evolution of the nucleation rate, the crystal size and the supersaturation as a function of time for the crystallization process of zeolites, by Ceika et al. (2010).³⁶

The thermodynamic driving force of the nucleation is the supersaturation, defined as the difference in chemical potential between a crystallizing compound in a supersaturated solution and that in the crystal phase. A solution is supersaturated when the concentration in solute is higher than the predicted value of the equilibrium solubility. This metastable state of the solution will cause crystallization until the solution reaches back the equilibrium solubility.⁴¹

Beta zeolites are usually synthesized through hydrothermal crystallization of an alkaline silico-alumina reaction mixture containing an organic structure-directing agent (SDA) such as tetraethylammonium hydroxide (TEAOH). The crystallization is conducted in an autoclave at 130-150 °C under autogenous pressure. A high content in TEOH is necessary to enable the formation of numerous zeolitic nuclei.³⁹ Moreover, beta zeolites can be synthesized as individual micro- or nanocrystals, as aggregated polycrystals and also as hierarchical nanocrystals with micropores connected to mesopores.³⁹

1.6.3. Zr-beta zeolite and postsynthetic Zr-beta nanocrystals

1.6.3.1. Properties

In this master thesis, Zr-beta zeolite nanocrystals are synthesized for the conversion of EL to GVL. Two properties of the material are tuned in comparison to conventional beta zeolites: the crystal size and the acidity of the material. Regarding the size, beta nanocrystals are synthesized instead of beta microcrystals to obtain a higher external surface, as the size of the reactant could be quite large in comparison to the pore diameter, which could potentially make it difficult for EL to access inner catalytic sites. Regarding the acidity, Al is removed from the framework by acid dealumination and replaced by various loadings of Zr to obtain Zr-beta zeolites with different Si/Zr ratios. Zr enables to replace the Brønsted acidity of the negatively charged Al with Lewis acidity.³⁸

1.6.3.2. Synthesis

Zr can be added into the framework of beta zeolites directly via the hydrothermal synthesis steps (Zr is incorporated during crystallization instead of Al) or via post-synthesis steps (Zr is incorporated after crystallization after the removal of Al). Direct incorporation of Zr through hydrothermal synthesis of Zr-beta zeolites has the inconvenience to lead to relatively large microcrystals of 1-10 µm (featuring very low external surface area) in addition to requiring long synthesis procedures (up to 12 days of crystallization) and HF which is toxic both for humans and the environment.⁴² Previous work in the PhD research of Arnaud Detaille demonstrated that postsynthetic commercial Zr-beta zeolites could have controlled incorporation of Zr and high catalytic activity.¹³

1.6.3.3. Performances of Zr-beta zeolites for MPV reduction

Since 2013, Zr-beta zeolites have been studied for the conversion of LA to GVL. In order to improve the catalyst or the reaction conditions, multiple parameters are optimized such as the synthesis method (hydrothermal or postsynthetic), the initial molar Si/Al ratio, the molar Si/Zr ratio, the nature of the hydrogen donor, the solvent, the synthesis temperature, the operating temperature, ...

Wang *et al.* (Table 4, entries 1-4) was the first to study Zr-beta zeolites on LA using very small amounts of Zr (molar Si/Zr = 75-200). The catalyst was synthesized through the hydrothermal method.³³

Simultaneously, Buit *et al.* (Table 4, entries 5-7) reported that Zr-beta showed the highest catalytic activity among the tested Lewis acid zeolites (Sn-Beta, Al-Beta, Ti-Beta, Al-MFI-n, ZrO₂).²⁰

More recently, Morales *et al.* (Table 4, entries 8-9) studied postsynthetic Zr-beta zeolites and demonstrated that higher temperatures enabled higher productivity, but caused a decrease in selectivity.⁵

Table 4. Summary of reported Zr-beta zeolites performances in the literature for batch reactors (HT: hydrothermal, PS: postsynthetic, LA: levulinic acid, ML: methyl levulinate)

Entry	Synthesis	Si/Zr ratio	Substrate	Conversion [%]	GVL yield [%]	GVL selectivity [%]	TOF [s ⁻¹]	Productivity [mmol _{GVL} /g _{Zr} ·h]	Solvent and H donor	Temp. Time
1	HT ³³	75	LA	88	82	93	-	19 (after 2 h)	2-PeOH	118 °C, 10 h
2	HT ³³	100	LA	100	96	96	-	30 (after 2 h)	2-PeOH	118 °C, 10 h
3	HT ³³	150	LA	71	69	97	-	31 (after 2 h)	2-PeOH	118 °C, 10 h
4	HT ³³	200	LA	27	27	>99	-	16 (after 2 h)	2-PeOH	118 °C, 10 h
5	HT ²⁰	100	LA	-	>99	-	-	90 (after 2 h)	2-PrOH	250 °C, 1 bar (gas-phase)
6	HT ²⁰	127	LA	98	-	>99	0.004	99 (-)	2-BuOH	120 °C, 11 h
7	HT ²⁰	127	ML	97	97	>99	0.026	213 (-)	2-BuOH	120 °C, 5 h
8	PS ⁵	32	LA	100	96	70	-	80 (after 6 h)	2-PrOH	190 °C, 6 h
9	PS ⁵	32	LA	99	84	85	0.008	60 (after 6 h)	2-PrOH	150 °C, 3 h

Morales *et al.* further studied their catalyst (not reported in Table 4) under continuous flow of LA (220 g/L for a flow rate of 0.025 mL/min) and obtained a yield of 65 %, a selectivity of 76 % and a high productivity of 44.4 g_{GVL}/g_{cat}.h in the catalytic bed. Small activity losses were observed but were easily recovered through calcination with an air flow at 550 °C, demonstrating the potential of Zr-beta zeolites in continuous industrial processes.⁴³

1.6.3.4. Reaction order and diffusional limitations in Zr-beta zeolites

According to Luo *et al.*, the conversion of a levulinate esters to GVL follows a first-order dependence to the levulinate ester concentration if the alcohol is present in excess. Similarly, a first-order dependence is observed to the alcohol when the levulinate ester is present in excess. This supports the mechanism discussed in Chapter 1.5., where both the alcohol and the levulinate are coordinated to the Lewis acid site.²⁴ These findings are confirmed by computational studies performed with density functional theory.^{44 45}

However, the reaction rate could be of an apparent first-order dependence if the diffusion of the reactants to the active acid sites is limited by the pore size. Therefore, Luo *et al.* conducted further research on external and internal heat and mass transport limitations using methyl levulinate and 2-butanol on Hf-beta zeolites in liquid phase packed-bed reactors pressurized under nitrogen at 15 bar. Similar results are expected for Zr-beta zeolites as Hf and Zr have similar electronic properties and atomic sizes.²⁴ First, external diffusion limitations were ruled out by changing the linear velocity but maintaining the space velocity (residence time) at different temperatures (393, 423 and 453 K). They observed no change in GVL production rates at different linear velocities in the given temperature range. However, it does not exclude external diffusion limitations in batch reactors, which depend on other parameters such as agitation. Second, internal diffusional limitations were also ruled out. They studied Hf-beta zeolites with different Si/Hf ratios (Si/Hf = 200, 300) at different temperature (same range) and observed constant TOFs (production rate normalized per total metal site). They concluded internal heat and mass transport limitations were non-existent because Hf-beta zeolites satisfied the Koros-Nowak criterion (constant TOF while diluting the concentration of active metal) for this particular reaction.²⁴ This criterion is based on the fact that the conversion is only limited by the amount of active sites (proportional relation) and not by the internal diffusion.⁴⁶ However, if we assume only the external active sites are in contact with the reactant and no internal diffusion occurs, then changing the number of total metal sites would change the number of active sites on the external surface and would also lead to a constant TOF.

Moreover, H-beta zeolites were used as catalyst for reactions using similar molecules such as the hydrolysis of ethyl acetate. Mowla *et al.* demonstrated an absence of external and internal mass transfer limitations by respectively changing stirring rates (in a liquid-phase batch reactor) and by using zeolites with different sizes. They also estimated the Thiele

modulus ϕ to characterize the internal diffusion limitations. ϕ is proportional to the particle diameter, the intrinsic diffusion velocity constant, the density of the catalyst (with pores), the specific surface area and is inversely proportional to the diffusion coefficient of the reactant in the pores. When ϕ is large, internal diffusion limits the rate of reaction, but when ϕ is small, the reaction is rate-limiting. They obtained values smaller than 0.4, indicating negligible internal mass transfer limitations. Similar observations were made when bigger molecules were used such as oleic acid, a fatty acid with a 18 carbon long chain.⁴⁷ The internal diffusional limitations of the oligomerization of butene with H-beta zeolites was also studied by Wulfers and Lobo. They treated external acid-sites with n-octyltrichlorosilane to reduce their contribution to the catalytic activity. They observed no significant drop in activity which indicates the reaction does not majorly takes place on the surface, but mostly in the micropores.⁴⁸

In contrast, Salzinger *et al.* tested three H-beta zeolites (Si/Al = 25, 35 and 150) for the conversion of formaldehyde and aniline into methylenedianiline. They demonstrated upon alkaline leaching with NaOH, the activity of the H-beta zeolites was significantly increased by the formation of additional micropores (from $V_{\text{micro}} = 0.09$ to $0.13 \text{ cm}^3/\text{g}$) and mesopores ($V_{\text{meso}} = 0.21$ to $0.32 \text{ cm}^3/\text{g}$). They also observed the TOF was affected by internal diffusional limitations because it was still increasing at increasing pore volume.⁴⁹ Additional studies demonstrated diffusion limitations of beta zeolites, mostly on cyclic molecules.^{50 51 52}

In view of the above findings in diffusional studies of beta zeolites, the conversion of EL to GVL by Zr-beta zeolites should neither be limited by external nor by internal mass transfers of the reactants (alcohol and levulinate). However, considering the fact that some larger cyclic molecules present diffusional limitations and considering the small size difference between the micropores (5-6 Å) and EL (approximately 7 Å), additional studies specifically for the conversion of EL into GVL using Zr-beta zeolites are required.

1.6.4. Shaping of Zr-beta zeolite nanocrystals and microparticles

One way to increase the external specific surface area of zeolite crystals (and potentially to boost their catalytic performance) is to decrease the size of the crystals towards the nanoscale. However, this comes with practical issues related to this colloidal size (handling, recovery, reuse, ...). In order to overcome these practical issues, small catalyst particles can be aggregated to obtain larger particles which would be easier to recover through filtration, sedimentation or centrifugation. The material would then demonstrate inter-crystallite mesoporosity (pore diameter comprised between 2 nm and 20 nm) in addition to microporosity (diameter < 2 nm). These zeolites could also have the advantage to limit pressure drops issues in fixed bed reactors compared to zeolite nanoparticles.⁵³ When spherical aggregated molecules are produced, they also tend to have a better resistance to

attrition which would make them very attractive for use in fluidized bed as they have a better resistance to a rapid flow.⁵⁴ Beta zeolite nanoparticles already present some mesoporosity due to the random aggregation of the nanocrystals occurring during drying and calcination. However, there is a lack of control on the parameters which effect this mesoporosity resulting in a very large pore diameter distribution.³⁹

In order to control the aggregation of zeolite nanocrystals, aerosol processing methods have been suggested.⁵⁵ These methods involve the atomization of a suspension resulting in a mist of droplets which can be transformed through processes such as spray drying, spray pyrolysis, flame spray pyrolysis, thermal decomposition, ... In the literature, aerosol processing techniques are mostly discussed as a synthesis process to obtain hierarchical porosity in zeolites, in order to overcome diffusion and steric limitations.^{56 57 58} This is not the case in this master thesis as mesoporosity is obtained after the synthesis of highly efficient nanozeolites with the goal to obtain bigger, more easily recyclable zeolites.

In this master thesis, the Zr-beta nanocrystals are assembled through an aerosol-assisted self-assembly technique called spray drying (Figure 10). In this case, referred to as a “Type I aerosol process”, a zeolite nanocrystals (material A) suspension is atomized in the form of microscale droplets followed by rapid drying of these droplets to obtain cohesive aggregates.⁵⁴ In order to modulate the aggregation process, compounds called binders (material B) are used.^{54 59}

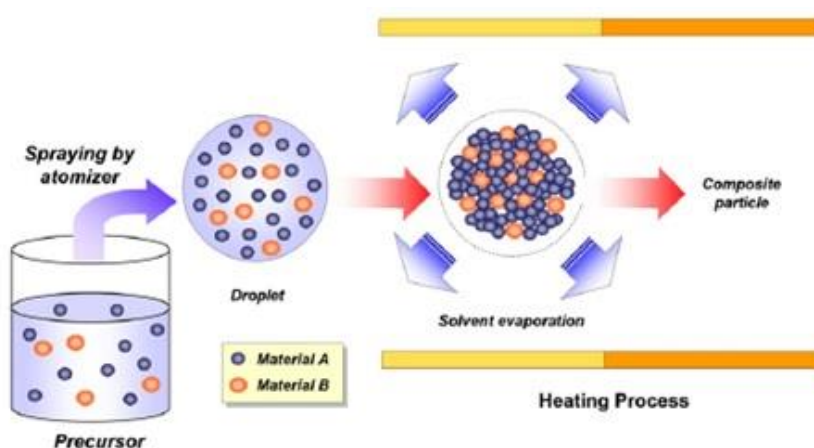


Figure 10. Scheme of spray drying mechanism, by Nandiyanto and Okuyama (2011).⁵⁹

The aggregated zeolites retain the same chemical composition and nature as the nanoscale Zr-beta zeolites, but have a different aggregation form and size. The size of the aggregated zeolites primarily depends on the size of the aerosol droplets, on the ratio of volatile solvents and non-volatile species in the starting suspension, and on the nature and amount of binder. Thus, the amount of precursor used has a significant impact on the size of the particle. The morphology, the porosity and other textural properties of the aggregated

particles can be tuned by multiple parameters including the inlet temperature, the spraying nozzle aperture, the rate of mass and heat transfer of the drying. Sphere, doughnut, encapsulated, porous, hollow and hairy particles are all possible morphologies of spray dried particles (Figure 11).^{59 53}

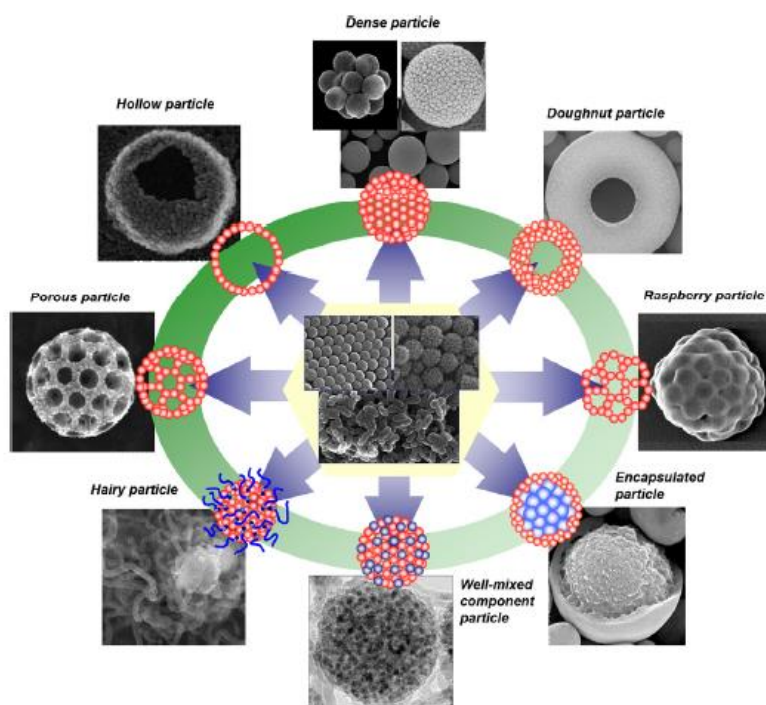


Figure 11. Multiple morphologies of particles obtained by spray drying, by Nandiyanto and Okuyama (2011).⁵⁹

1.7. Objectives and strategy

1.7.1. Objectives

The overall objective of our research is to shape highly active Zr-beta zeolite nanocrystals through spray drying to obtain structured microparticles, which retain high activity for the upgrading of levulinates to GVL and are easier to handle than the starting colloids. Ideally, the spray dried zeolites should demonstrate similar activity to the optimized nanoscale Zr-beta zeolites.

To further our understanding on the catalyst, three features of the catalyst are investigated in this master thesis. First, we aim to optimize the Zr loading to enhance the catalytic activity of the zeolite nanocrystals. Then, we investigate the potential of spray dried Zr-beta microparticles for the production of GVL. Finally, we study the potential issue of diffusion limitations in nanocrystals, spray dried microparticles and microcrystals in order to demonstrate whether EL mostly reacts on the surface of the catalyst or rather in the micropores.

1.7.2. Strategy

The strategy to reach the three objectives relied on an iterative three-step methodology. The first step consisted in the synthesis of the catalyst, the second step in its characterization and the third step involved catalytic testing for the production of GVL.

Regarding the first step, four catalysts were synthesized. First, the beta nanocrystals were synthesized, dealuminated and impregnated with different amounts of Zr in a search for the optimal Si/Zr ratio. Second, beta zeolite nanocrystals were shaped in the form of microparticles through spray drying. Third, commercially available beta zeolites were impregnated (after dealumination) with variable amounts of Zr in order to be used as benchmark. Fourth, a beta zeolite with microcrystals was synthesized, dealuminated and loaded with Zr to serve as a benchmark with very low external surface area. This catalyst was also ball milled to modify the crystal size and the external surface area.

The second step consisted in the characterization of the prepared catalysts. Practically, the catalysts were characterized at every major step of their synthesis process to investigate possible consequences of particular treatments (i.e. dealumination, impregnation, ...). First, X-Ray Diffraction (XRD) was performed to verify whether the synthesized catalysts had the crystalline beta zeolitic structure. Second, other properties of the catalysts were investigated such as the texture (N_2 physisorption), the morphology (transmission electron microscopy (TEM), scanning electron microscopy (SEM)), the elemental composition (X-ray photoelectron spectroscopy (XPS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES)) and the acidity (NH_3 -temperature programmed desorption (NH_3 -TPD), pyridine adsorption and temperature-programmed desorption (Pyridine-IR)).

The third step consisted in the investigation of the catalytic performances of the synthesized catalysts. The GVL production of the four catalysts were therefore compared for the conversion of EL to GVL using 2-pentanol as hydrogen donor. In addition, in order to study the diffusion limitations and steric hindrance of the catalyst, additional reactants (methyl levulinate, butyl levulinate, 2-propanol and 2-butanol) were used.

2. Experimental

2.1. Materials

Nitric acid (HNO_3 ; 60 %) was purchased from Carl Roth, aluminum isopropoxide ($\text{Al}(\text{OCH}(\text{CH}_3)_2)_3$; 98 %) was purchased from Arcos Organics, Ludox As-40 (Colloidal silica; 40 % in H_2O), anhydrous sodium aluminate (NaAlO_2 ; 50-56 % of Al_2O_3 and 40-45 % of Na_2O), zirconium(IV) oxynitrate hydrate ($\text{ZrO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99 %), methyl levulinate ($\text{C}_6\text{H}_{10}\text{O}_3$; 98 %), ethyl levulinate ($\text{C}_7\text{H}_{12}\text{O}_3$; 99 %) and 2-propanol ($\text{C}_3\text{H}_8\text{O}$; 99.5 %) from Sigma-Aldrich, tetraethyl orthosilicate (TEOS) ($\text{Si}(\text{C}_2\text{H}_5\text{O})_4$; 98 %), tetraethylammonium hydroxide (TEAOH) ($(\text{C}_2\text{H}_4)_4\text{N}(\text{OH})$; 35 % in H_2O), n-butyl levulinate ($\text{C}_9\text{H}_{16}\text{O}_3$; 98 %), 2-pentanol ($\text{C}_5\text{H}_{12}\text{O}$; 99 %) and hydrogen fluoride (HF ; 39 %) from Alfa Aesar, dodecane ($\text{C}_{12}\text{H}_{26}$; 100 %) from VWR Chemicals and 2-butanol ($\text{C}_4\text{H}_{10}\text{O}$; 99.5 %) from Honeywell. Commercial NH_4 -beta zeolites with a Si/Al ratio of 12.5 were purchased from Zeolyst International (CP-814E).

2.2. Methods

2.2.1. Catalyst preparation

2.2.1.1. Preparation of Zr-beta nanocrystals (Zr-BEA_nano and Zr-BEA_comm)

Preparation of beta zeolites

Zr-beta zeolite nanocrystals (Zr-BEA_nano) with a Si/Al ratio of 12.5 were synthesized based on the recipe proposed by Arnaud Detaille in his PhD research. The dealumination and impregnation steps were also applied to the commercial Zr-beta nanocrystals (Zr-BEA_comm) and the Zr-beta microcrystals (Zr-BEA_micro) which are discussed further in this chapter.

The first step in the procedure to synthesize beta nanocrystals was to dissolve 2.0424 g of the aluminum precursor (aluminum isopropoxide) in 29 mL of the organic structure-directing agent (TEAOH) under continuous stirring (500 rpm) during one hour. When the solution was translucent, 14.5 mL of the colloidal silica suspension (Ludox As-40) and 6 mL of deionized water were added. The resulting gel was then transferred into a 50 mL stainless-steel autoclave with a Teflon cup. Crystallization took place at 140 °C under autogenous pressure during at least 160 hours.

The second step was to wash the resulting suspension with deionized water by six consecutive centrifugation cycles at 14 000 rpm during one hour. The liquid was replaced each time by deionized water and the bottom was resuspended. As the Al atoms are negatively charged, they are counterbalanced by tetraethylammonium cations (TEA^+). These zeolites are therefore called TEA-BEA_nano. When the zeolites are calcined, the TEA^+ burns. The resulting sample is therefore denoted as calci_non-deal-BEA_nano.

Preparation of dealuminated beta zeolites

The zeolites are dealuminated before impregnation based on the protocol proposed by Wang *et al.*³³ First, TEA-BEA_nano is recovered by centrifugation. Second, the TEA-BEA_nano zeolites were suspended in nitric acid (20 mL of 60 % HNO₃ per gram of catalyst) during 20 hours at 80 °C. The zeolites were then cooled and washed six times with deionized water by centrifugation (13 000 rpm, 10 minutes), until the pH is higher than 6. Between each centrifugation cycle, the solid was resuspended with deionized water. The resulting sample was denoted as deal-BEA_nano.

The same protocol is performed for the commercial benchmark, starting with NH₄-beta zeolites purchased from Zeolyst International.

Preparation of Zr-beta zeolites

The zeolites were impregnated with Zr based on the postsynthetic approach which is inspired from the wet impregnation method of Wang *et al.*³³ The required amount of Zr is weighted to obtain a given Si/Zr ($M_{\text{SiO}_2} = 60.08 \text{ g/mol}$, $M_{\text{Zr precursor}} = 339.22 \text{ g/mol}$). The Zr precursor was added to the zeolitic suspension under agitation and the result was heated at 250 °C until total evaporation of the liquid. The resulting sample was called imp-Zr-BEA_nano_XX. The last two digits of the name of the sample refers to the Si/Zr ratio.

As a last step, the Zr-loaded zeolites were calcined during 6 hours at 550 °C (heating ramp of 3 °C per minute, cooling ramp of 2 °C per minute). The resulting sample was called Zr-BEA_nano or Zr-BEA_comm (for the commercial benchmark).

2.2.1.2. Preparation of Zr-beta microcrystals (Zr-BEA_micro)

Zr-beta zeolite microcrystals were synthesized using a recipe from Xia *et al.*⁶⁰ Hydrogen fluoride was used as a mineralizing agent as it is known to produce zeolites with large crystal sizes. The protocol was adapted to obtain a Si/Al ratio of 12.5 instead of 20.

First, a mixture of 21 mL TEAOH, 23 mL TEOS, 4 mL water and 0.6558 g NaAlO₂ was stirred overnight at room temperature to obtain a homogeneous sol. The morning after, 2.4 mL HF was added dropwise under vigorous stirring to obtain a gel. The gel was then crushed and transferred into a 50 mL stainless-steel autoclave with a Teflon cup for crystallization at 140 °C for 12 days. The autoclave was then quenched in cold water and the solid was washed in 80 mL tubes and resuspended with deionized water six times.

Second, the obtained zeolites were dealuminated and impregnated following the previously discussed protocols applied on the nanocrystals. The obtained sample was denoted as Zr-BEA_micro.

In order to obtain smaller sized Zr-BEA_micro through the top-down approach, the sample was ground using the Fritsch Planetary Micro Mill Pulverisette 7 during 5, 15 and 30 minutes at 500 rpm. A metal tungsten carbide bowl and 3 mm tungsten balls were used. The obtained samples were respectively called Zr-BEA_micro_BM5, Zr-BEA_micro_BM15 and Zr-BEA_micro_BM30.

2.2.1.3. Preparation of spray dried Zr-beta microparticles (Zr-BEA_SD)

Spray dried zeolite microparticles were obtained following postsynthetic manipulations of dealuminated nanocrystals. Spray drying was performed after dealumination as the nitric acid could impact the structure of the spray dried zeolites. The overall approach remained the same except between the dealumination and the impregnation steps, where the zeolites were spray dried.

First, the deal-BEA_nano were re-suspended in deionized water with additional Ludox (5 wt% of the resulting suspension) and were subsequently spray dried by a Büchi Mini Spray Dryer B-290. The suspension was pumped (8 mL/min pump rate) to a spray nozzle and then atomized following contact with the air flow. The obtained aerosol was then dried (inlet temperature of 175 °C, outlet temperature of approximately 75 °C) and separated through a cyclone (aspirator at 80 %).

Second, the obtained spray dried zeolites were impregnated and calcined according to the previously discussed protocol applied on Zr-BEA_nano and Zr-BEA_comm. The obtained sample was denoted as Zr-BEA_SD.

2.2.1.4. Summary of prepared catalysts

Four types of zeolites were synthesized: Zr-beta nanocrystals developed by Arnaud Demaille in his PhD research, commercial Zr-beta nanocrystals, Zr-beta microcrystals and spray dried Zr-beta microparticles. The synthesis steps of the Zr-BEA_nano were extensively characterized and the samples were given different names according to the synthesis step. Moreover, as some unfinished catalysts were analyzed by N₂ physisorption, NH₃-TPD and XPS, they sometimes needed to be calcined to avoid any damages to the machinery by volatile species or to avoid any misinterpretation. Specific names were given to these samples. Their names are written between brackets (Table 5).

In addition to the above catalysts, two catalysts were synthesized as additional benchmarks. First, a non-dealuminated TEA-BEA_nano was impregnated (Si/Zr = 18) to compare catalytic performances with dealuminated Zr-BEA_nano. The given benchmark was denoted as non-deal-Zr-BEA_nano_18. Second, a Zr-BEA_nano was ball milled 15 minutes to check whether the ball milling procedure affected its performance. The sample was denoted as Zr-BEA_nano_BM15.

Table 5. Summary of synthesized catalysts during this master thesis.

Zeolite type	Synthesis steps	Sample	Initial Si/Al ratio	Si/Zr ratio
Zr-beta nanocrystals	After crystallization	TEA-BEA_nano (calci_non-deal-BEA_nano after calcination)	12.5	-
	After dealumination	deal-BEA_nano (calci_deal-BEA_nano after calcination)	12.5	-
	After impregnation	imp-Zr-BEA_nano	12.5	-
	After calcination	Zr-BEA_nano	12.5	14, 18, 22, 26, 30, 35
commercial Zr-beta nanocrystals	After calcination	Zr-BEA_comm	12.5	14, 18, 22, 26, 30, 35
Zr-beta microcrystals	After calcination	Zr-BEA_micro	12.5	26
	After ball milling (5')	Zr-BEA_micro_BM5	12.5	26
	After ball milling (15')	Zr-BEA_micro_BM15	12.5	26
	After ball milling (30')	Zr-BEA_micro_BM30	12.5	26
spray dried Zr-beta microparticles	After calcination	Zr-BEA_SD	12.5	26

2.2.2. Catalyst characterization

2.2.2.1. X-ray diffraction (XRD)

X-ray diffraction measurements were performed to characterize the crystalline framework of a sample and to identify the synthesized material. Practically, the spatula tip of the sample is deposited on a sample holder coated with Nivea cream. It is then inserted into the Druker-D8 Advance diffractometer with Bragg-Brentano geometry where X-rays of a $K\alpha$ wavelength (0.154 nm) are produced by a copper anode (40 kV, 30 mA). LynxEye XE-T technology is used for detection in a 2θ range of 5° to 80° at a speed of $5.93^\circ/\text{min}$, with a total of 5051 steps of 0.015° . PDF2-2004-database is used to treat the resulting data.

2.2.2.2. N_2 physisorption

Nitrogen physisorption was used to characterize textural properties such as specific surface area (micropore and external surface area), pore volume and average pore size. Prior to the analysis, about 50 mg of catalyst were weighted before degassing under vacuum at 150

°C using Micromeritics VacPrep 061. The sample was again weighted after degassing. Nitrogen was physically adsorbed on the surface of the material at low temperature (77 K) using Micromeritics TriStar 3000.

Regarding the data treatment, textural properties were calculated using the BET theory developed by Brunauer, Emmett and Teller in 1938.⁶¹ It is preconized to only use values in the P/P_0 range between 0.0 and 0.05 to calculate the BET surface area in microporous materials. Microporous volume and external surface area were calculated using the t-plot statistical thickness method, respectively from the intercept and the slope of the t-plot. Only the values between a statistical thickness range of 3.5-5 Å are used for the regression.

N₂ physisorption has limited applications in microporous materials as the calculated BET surface area is essentially erroneous. This surface area is calculated based on the assumption a monolayer of nitrogen is formed in the pores. However, when micropores are present, it is not possible to discern monolayers from the filling of micropores which takes place below a relative pressure (P/P_0) of 0.15.⁶⁵ Although the calculated BET surface area has no physical meaning, it can nevertheless still be used to compare among samples of the same material.^{66 67}

2.2.2.3. NH₃ temperature-programmed desorption (NH₃-TPD)

Ammonia temperature-programmed desorption was measured to probe the acid properties of the catalyst. It is based on the quantification of the amount of chemically adsorbed ammonia molecules on the acids sites which provides the number of acid sites. The major inconvenient is the impossibility to distinguish Brønsted from Lewis acid sites.⁶²

Approximatively 50 mg of sample were weighted and introduced into the Hiden CATLAB-PCS microreactor equipped with a mass spectrometer which contains a quadrupole separator. The following temperature program was applied: first the sample was degassed with a 25 mL/min Ar flow at 500 °C, second the ammonia was adsorbed using He as carrier gas (5 % of ammonia) at 100 °C for 55 minutes followed by a 30 minutes purge and third, the temperature was increased until 700 °C at a 10 °C per minute rate to desorb the ammonia which was quantified.

2.2.2.4. Pyridine adsorption and temperature-programmed desorption (Pyr-IR)

Pyridine adsorption and temperature-programmed desorption were measured to characterize the acid properties of a catalyst, differentiating Lewis from Brønsted acid sites. The Brønsted acid sites give rise to a 1551 cm⁻¹ adsorption band due to coordination of pyridine with Al, while the Lewis acid sites correspond to the 1455 cm⁻¹ adsorption band linked to the coordination of pyridine with Zr atoms.⁶³

Approximatively 20 mg of catalyst were weighted and transformed into a thin wafer which was placed into a sample holder. The sample holder was then carefully transferred into a Pyrex chamber with a NaCl chamber for Infrared analysis. The sample was first degassed under vacuum (10⁻⁵ mbar) at 350 °C for three hours and analyzed. Second, 1000 Pa of pyridine at room temperature enabled pyridine to adsorb on the sample during 30 minutes. The sample was again analyzed by IR spectroscopy. Third, the pyridine was desorbed by treatment of the sample at 100 °C during one hour and again analyzed. This step was repeated at 150 °C, 200 °C and 250 °C to measure the strength of the acid sites. Quantification of the number of acid sites was performed using 1.67 and 2.22 cm²/μmol as molar extinction coefficients for respectively protonated pyridine (Brønsted acid sites) and coordinated pyridine (Lewis acid sites).⁶³

2.2.2.5. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy was used to characterize the composition of solid materials as far as 10 nm below the surface. Prior to the analysis, a spatula tip of the sample was deposited on a sample holder and analyzed in the SSX 100/206 Photoelectrons Spectrometer from Surface Science Instruments. It was equipped with an Al Kα monochromatic and micro-focused source. A 55° analysis angle and 150 eV pass energy were used. CasaXPS from Casa Software Ltd was used to process the data. For calibration, the Si 2p peak had been fixed at 103.5 eV.

2.2.2.6. Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

Inductively coupled plasma-atomic emission spectroscopy was performed to characterize the elemental content of a sample, using the Thermo Scientific ICP 6500. Analysis was carried out by the Mineral & Organic Chemical Analysis (MOCA) platform of the Earth and Life Institute (ELI) at UCLouvain. Beforehand, about 100 mg of a sample were placed in contact with 2 g of sodium peroxide Na₂O₂ and 1 g of sodium hydroxide NaOH in carbon crucibles. The sample was then heated until fusion of the mixture, which was then cooled and soaked in an acid solution (30 mL of HCl 37 % and 100 mL water). The mixture was then diluted to a final volume of 1 L and injected in a plasma of Ar.

2.2.2.7. Scanning electron microscopy (SEM)

Scanning electron microscopy images of the samples were obtained to study the morphology of materials, using the Field Emission Scanning Electron Microscope LEO 982 GEMINI apparatus (UCLouvain) or using the JEOL 7600F microscope at a 15 kV voltage (Sorbonne Université). Before analysis, the samples were pre-treated with a 15 nm layer of chrome under vacuum with a Sputter Metal 208 HR (Cressington) to increase the contrast.

2.2.2.8. Transmission electron microscopy (TEM)

Transmission electron microscopy images were obtained to study the morphology of materials which are not distinguishable in SEM. TEM was carried out using the LEO 922 Omega Energy Filter operated at 120 kV. To prepare the samples, a spatula tip of sample was suspended in hexane and dispersed using ultrasounds before being placed on a carbon-coated copper grid and dried.

2.2.3. Catalyst testing

2.2.3.1. Standard test conditions

The liquid-phase MPV reduction of the levulinate esters into GVL was performed into a round-bottom flask placed in an oil bath at reflux temperature (118 °C in the flask) under atmospheric pressure.

Typically, 285 µL of ethyl levulinate (244 µL for methyl levulinate, 349 µL for butyl levulinate corresponding to 0.002 mol), 454 µL of internal standard (dodecane) and 0.4 g of catalyst were introduced in the reactor. Then, 10 mL of 2-pentanol, which was used both as the hydrogen donor and as the solvent, were added. The concentrations of the catalyst, dodecane and the levulinate esters were respectively 40 g/L, 0.2 mol/L and 0.2 mol/L.

At 0 min, 30 min, 1 h, 2 h, 4 h and 6 h, a 300 µL sample was taken and analyzed by gas chromatography to obtain a kinetic curve. The sample was taken using a disposable syringe and needle, filtered through a PTFE membrane with a 0.2 µm pore size and stored in a glass vial with an additional 800 µL of 2-pentanol.

2.2.3.2. GC analysis

Samples were analyzed through gas chromatography (GC) using a Bruker SCION 456-GC equipped with an Agilent DB-5 (30 m x 0.32 mm x 1 µm) column, a split/splitless injector at 250 °C (split ratio of 1:20), an automatic sampler injecting 1 µL and a FID detector at 250 °C (300 mL/min of air, 30 mL/min of H₂ and 25 mL/min of He as make-up gas). The temperature program of the column was as follows: 110 °C for 5 minutes, increases to 150 °C at a 10 °C/min rate and 150 °C for 5 minutes.

The identified compounds were GVL, EL, methyl levulinate, butyl levulinate, 2-pentanone. By-products of the reaction were not specifically identified. Product quantification was based on previously available response coefficients (EL, GVL) or on new calibration done in the context of this master thesis (methyl levulinate, butyl levulinate).

2.2.3.2. Indicators of catalytic performances

Catalytic tests were run to assess the catalytic performances of a given catalyst. Different indicators such as the conversion (1), yield (2), selectivity (3), specific productivity (4) and turnover frequency (5) were used to compare catalysts among them and are defined below (LE = levulinate ester).

$$x_{LE} [\%] = \frac{n_{LE \text{ converted}}}{n_{LE \text{ introduced}}} \cdot 100 \% \quad (1)$$

$$y_{LE} [\%] = \frac{n_{GVL \text{ produced}}}{n_{LE \text{ introduced}}} \cdot 100 \% \quad (2)$$

$$S_{GVL} [\%] = \frac{y_{LE}}{x_{LE}} = \frac{n_{GVL \text{ produced}}}{n_{LE \text{ converted}}} \cdot 100 \% \quad (3)$$

$$P_{GVL} \left[\frac{\text{mmol}_{GVL}}{\text{g}_{cata} \cdot \text{h}} \right] = \frac{n_{GVL \text{ produced}} \cdot 10^3}{m_{catalyst} \cdot \text{time}} \quad (4)$$

$$TOF [s^{-1}] = \frac{n_{EL \text{ consumed}}}{n_{active \text{ sites}} \cdot \text{time}} \quad (5)$$

3. Results

3.1. Characterization of the synthesized catalysts

3.1.1. XRD

XRD was performed to confirm whether Zr-BEA_nano_26 featured the desired beta matrix and to investigate the effects of dealumination, Zr impregnation and calcination (Figure 12). The XRD patterns were compared to the commercial benchmark Zr-BEA_comm_26.

Overall, the XRD patterns of Zr-BEA_nano_26 and the commercial benchmark present similar peaks, which indicates the beta matrix was successfully obtained, although a slight change in peak shape is present around 30°, of unknown origin.

The obtained diffraction peaks for Zr-BEA_nano at different synthesis steps display similar shapes, although a small increase in peak width is observed between TEA-BEA_nano and deal-BEA_nano, which could indicate a small loss in crystallite quality due to the dealumination. In addition, slight shifts are observed between the main diffraction peaks, indicated with dotted lines. Regarding the peak with the highest intensity, a 0.11° shift is observed between TEA-BEA_nano (22.45°) and deal-BEA_nano (22.56°) caused by the dealumination, a 0.14° shift between deal-BEA_nano (22.56°) and imp-Zr-BEA_nano (22.70°) due to the Zr impregnation and a 0.04° shift between imp-Zr-BEA_nano (22.70°) and Zr-BEA_nano (22.66°) due to the calcination. These small shifts could be related to relaxation and contraction effects that occur when removing Al and replacing it with Zr. However, it is assumed the desired beta zeolite framework is conserved as the XRD patterns display all the peaks from a beta matrix and no additional crystalline phases are observed.

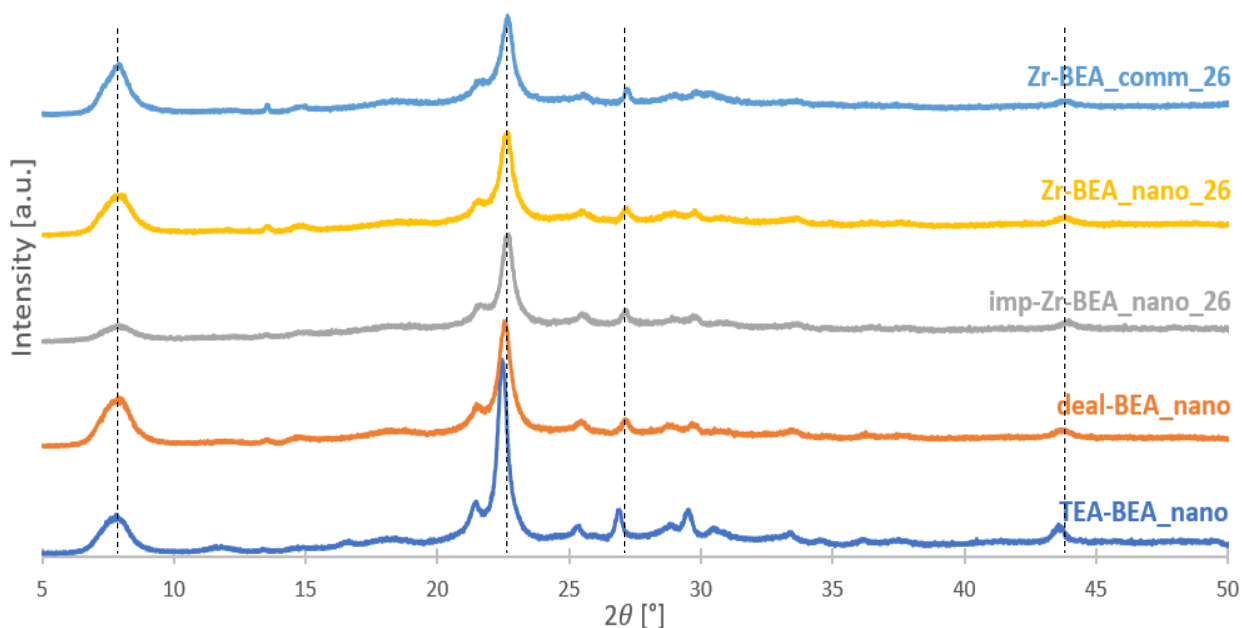


Figure 12. XRD comparison of Zr-BEA_comm_26 and Zr-BEA_nano_26 at different synthesis steps (TEA-BEA_nano, deal-BEA_nano, imp-Zr-BEA_nano_26, Zr-BEA_nano_26). The dotted lines represent the angle values of the main peaks of Zr-BEA_nano_26.

Then, XRD was performed to assess the effect of different Zr loadings (Si/Zr = 14, 26, 35) on the beta matrix (Figure 13). The obtained XRD patterns demonstrate highly similar peak shapes and identical peak positions. Hence, no effect of the Zr loading on the beta matrix is suspected.

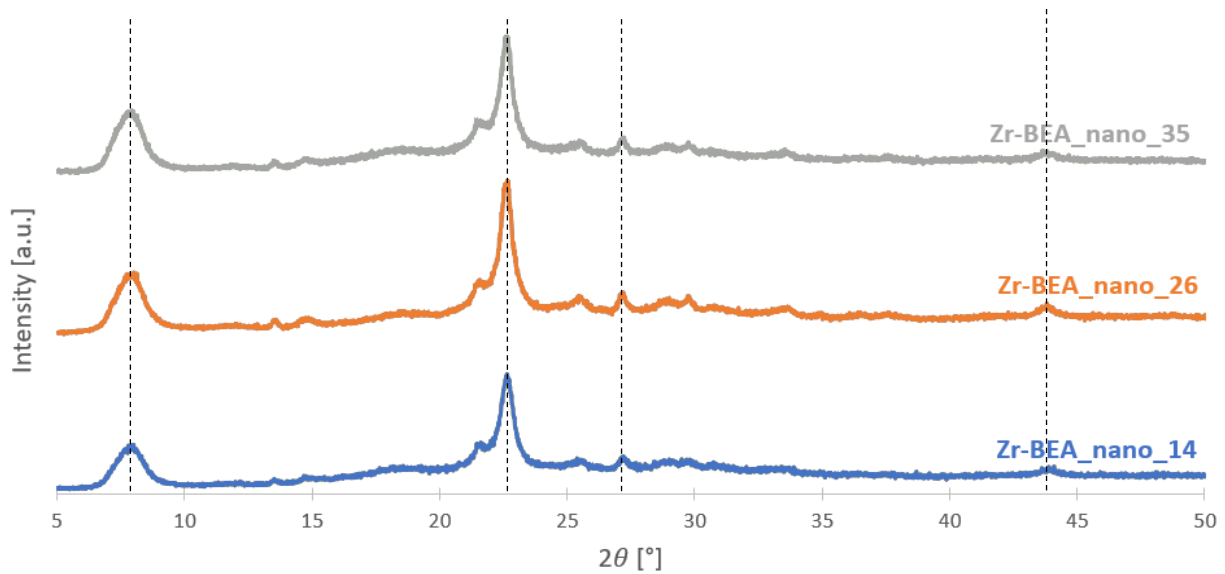


Figure 13. XRD comparison of Zr-BEA_nano with different Zr loadings (Zr-BEA_nano_14, Zr-BEA_nano_26, Zr-BEA_nano_35). The dotted lines represent the angle values of the main peaks of Zr-BEA_nano_14.

XRD was also performed to ensure the crystallite structure of Zr-BEA_nano was maintained after the spray drying step (Figure 14).

The XRD patterns demonstrate the global shape and position of the peaks is conserved before and after spray drying. No additional crystalline phase appears following the use of a binder that gives mechanical strength to the sample. However, a decrease in peak intensity is observed, especially visible at 15° and 22°, which could possibly indicate slight deterioration of the beta matrix or just that fewer catalyst was loaded on the sample holder of the DRX apparatus.

The crystal size was calculated using the Sherrer equation (6), where β refers to the peak full width at half maximum. Zr-BEA_nano_26 and Zr-BEA_SD_26 display similar crystal sizes, respectively 18.1 and 22.6 nm. In comparison, the commercial benchmark Zr-BEA_comm_26 displays a 17.8 nm crystal size.

$$D = 0.89 \frac{\lambda}{\beta(\cos\theta)} \quad (6)$$

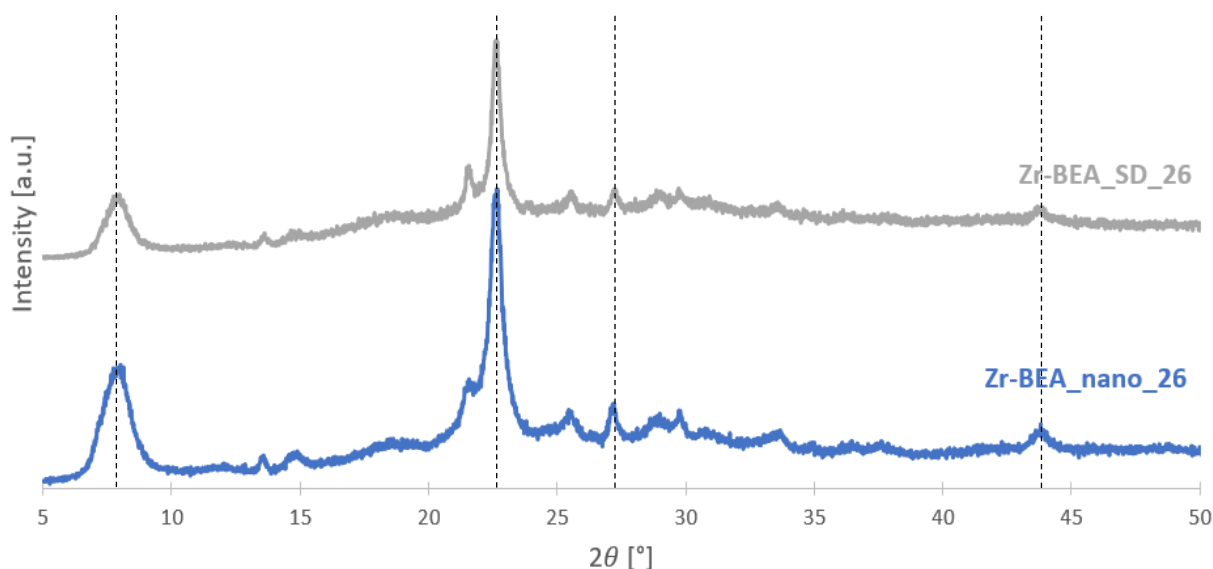


Figure 14. XRD comparison of Zr-BEA_nano_26 and Zr-BEA_SD_26. The dotted lines represent the angle values of the main peaks of Zr-BEA_nano.

Finally, XRD was performed to confirm whether Zr-BEA_micro_26 had been successfully synthesized and to investigate the effects of ball milling on the sample (Figure 15).

The obtained diffraction peaks for Zr-BEA_micro_26 display similar shapes to Zr-BEA_nano_26, although smaller peak widths are observed, which could indicate a bigger crystal size. The crystal size of the samples was estimated to be about 60 nm using the Scherrer equation, which is only 40 nm bigger than Zr-BEA_nano_26. It was expected to be ranging between 1-2 μm based on the performed protocol.

Moreover, a greater background is observed which could indicate the sample is partially amorphous. A loss in peak intensity is also present which can also be linked to a lower amount of crystallized material in the sample. Finally, the main peak presents a peak shift of 0.09° to lower values of 2θ in comparison to Zr-BEA_nano_26, which should however not affect the beta matrix. Based on the above observations, Zr-BEA_micro_26 successfully obtained the beta matrix although a non-negligible portion of the sample is probably amorphous.

Regarding the ball milled samples, they demonstrate similar shapes of peaks, but a contamination (possibly a scandium oxide) is observed for Zr-BEA_micro_BM5_26 and Zr-BEA_micro_BM30_26 around 31° , which could be related to insufficient cleaning of the ball milling apparatus. No shift in 2θ angle is present, but changes in peak intensity are observed in comparison to Zr-BEA_nano_26. In addition, no significant crystal size changes, using the Scherrer equation, are observed at different ball milling times. Hence, the ball milling does not seem to modify the beta matrix of Zr-BEA_micro_26 (abstraction made of the contamination).

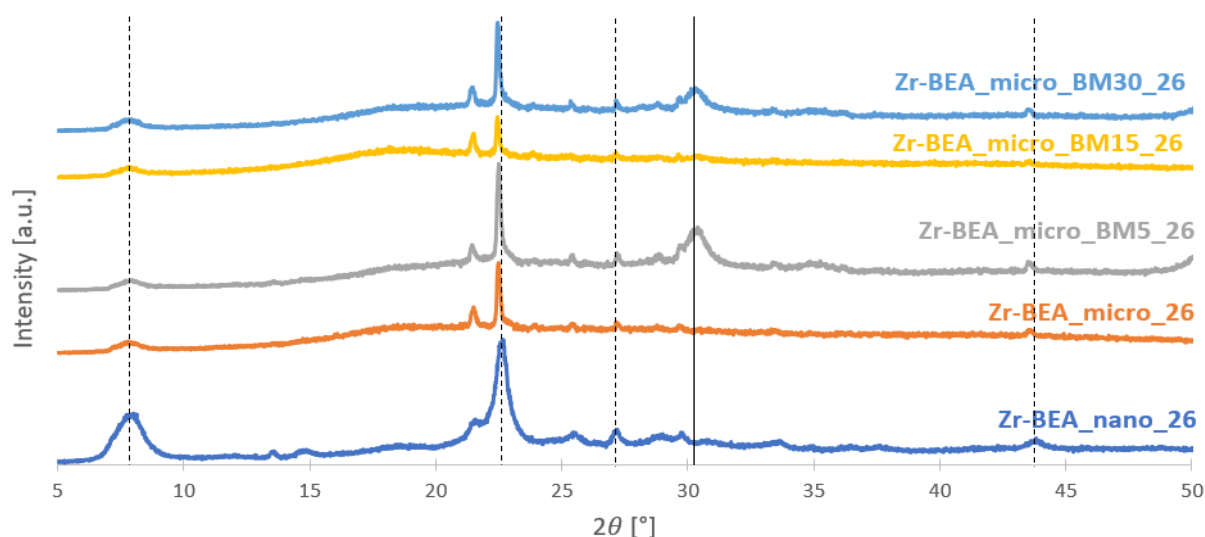


Figure 15. XRD comparison of Zr-BEA_nano_26 with Zr-BEA_micro_26 and the ball milled samples (after 5, 15 and 30 minutes). The dotted lines represent the angle values of the main peaks of Zr-BEA_nano_26. The solid line refers to the contamination peak.

3.1.2. N₂ physisorption

N₂ physisorption was performed to assess the effects of dealumination, Zr impregnation and different Zr loadings on Zr-BEA_nano_26 (Figures 16, 17, 18 and 19).

All samples display similar isotherms resulting in the combination of type I isotherms (due to the important uptake at P/P_0 lower than 0.05) and type IV isotherms (characterized by the hysteresis between adsorption and desorption curves) (Figures 16 and 18). Type I and type IV isotherms are respectively characteristic of micro- and mesoporosity. Zr-BEA_nano_26 only contain intra-particle micropores and the observed mesoporosity is generated by the aggregation of the nanoparticles which creates inter-particle mesopores.

The average pore size distribution was calculated using the Barret, Joyner and Halenda (BJH) model applied at the desorption. The pore distribution is quite dispersed from unquantifiable micropores sizes (< 2 nm) to mesopores of 50 nm (Figures 17 and 19). No significant differences are observed between the samples.

Regarding the BET surface area, an increase from 600 m²/g before dealumination to 680 m²/g after dealumination is observed (Table 6). After Zr impregnation, the BET surface area decreases, but no correlation between Zr loading and BET surface area is observed.

Table 6. Summary of textural properties obtained via N_2 physisorption of Zr-BEA_nano_26 at different synthesis steps (calci_non-deal-BEA_nano, calci_deal-BEA_nano, Zr-BEA_nano_26) and at different Zr loadings (Zr-BEA_nano_14, Zr-BEA_nano_26, Zr-BEA_nano_35). Values are rounded to two significant figures.

Sample	BET surface area [m ² /g _{cat}]	T-plot external surface area [m ² /g _{cat}]	T-plot micropore volume [cm ³ /g _{cat}]
calci_non-deal-BEA_nano	600	210	0.20
calci_deal-BEA_nano	680	280	0.21
Zr-BEA_nano_14	520	170	0.18
Zr-BEA_nano_26	610	220	0.20
Zr-BEA_nano_35	560	190	0.21

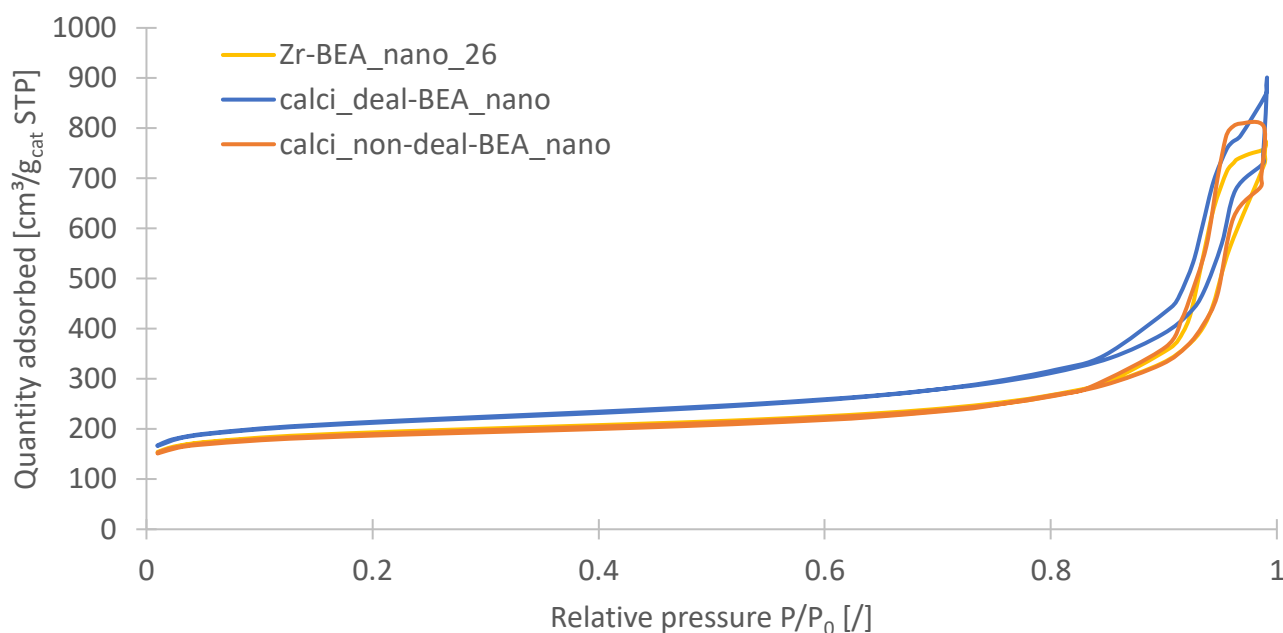


Figure 16. N_2 physisorption isotherms (adsorption and desorption) of Zr-BEA_nano_26 at different synthesis steps (calci_non-deal-BEA_nano, calci_deal-BEA_nano, Zr-BEA_nano_26).

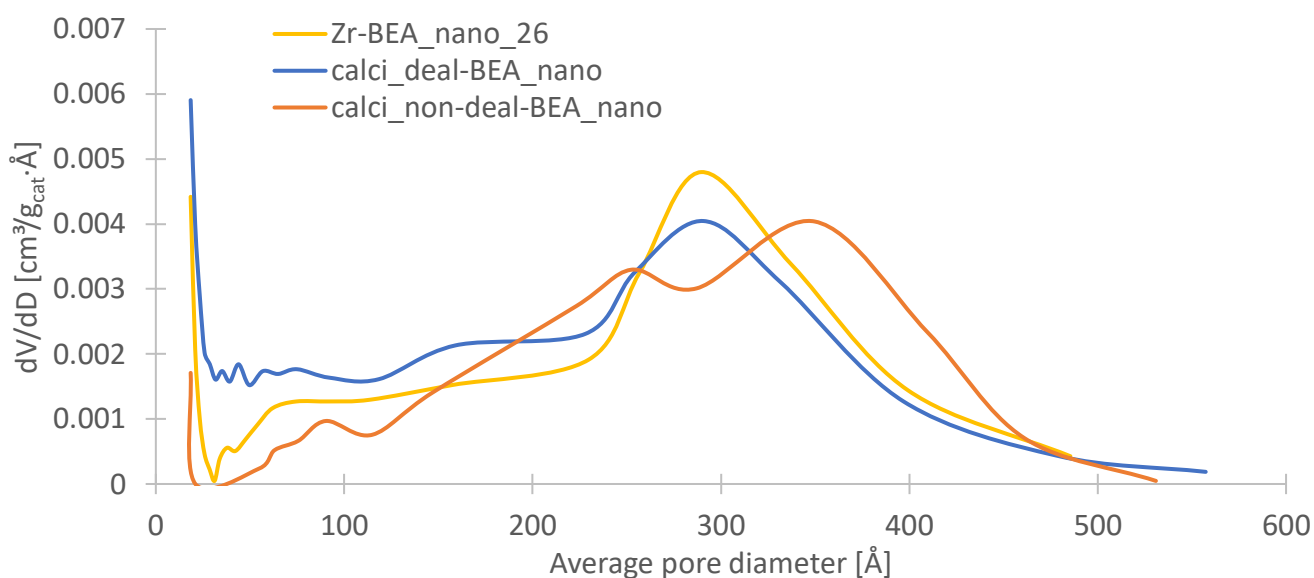


Figure 17. BJH desorption curves of Zr-BEA_nano_26 at different synthesis steps (calci_non-deal-BEA_nano, calci_deal-BEA_nano, Zr-BEA_nano_26).

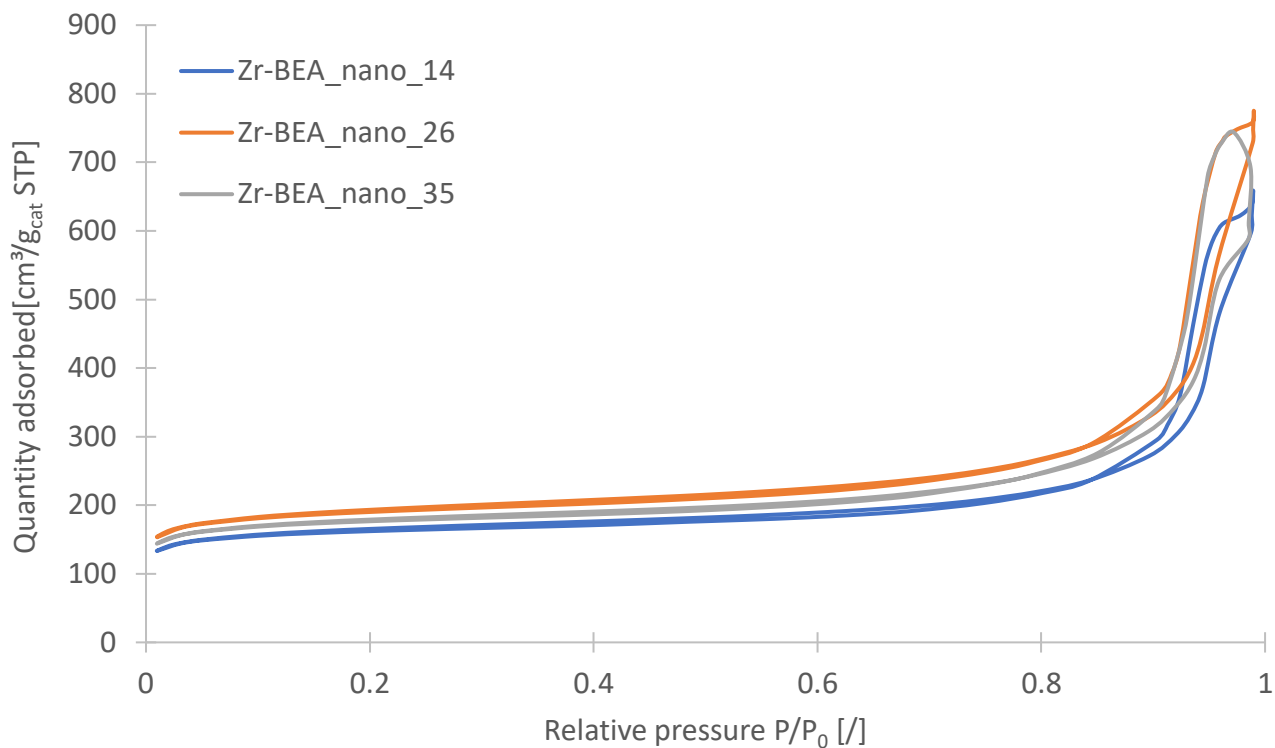


Figure 18. N_2 physisorption isotherms (adsorption and desorption) of Zr-BEA_nano with different Zr loadings (Zr-BEA_nano_14, Zr-BEA_nano_26, Zr-BEA_nano_35).

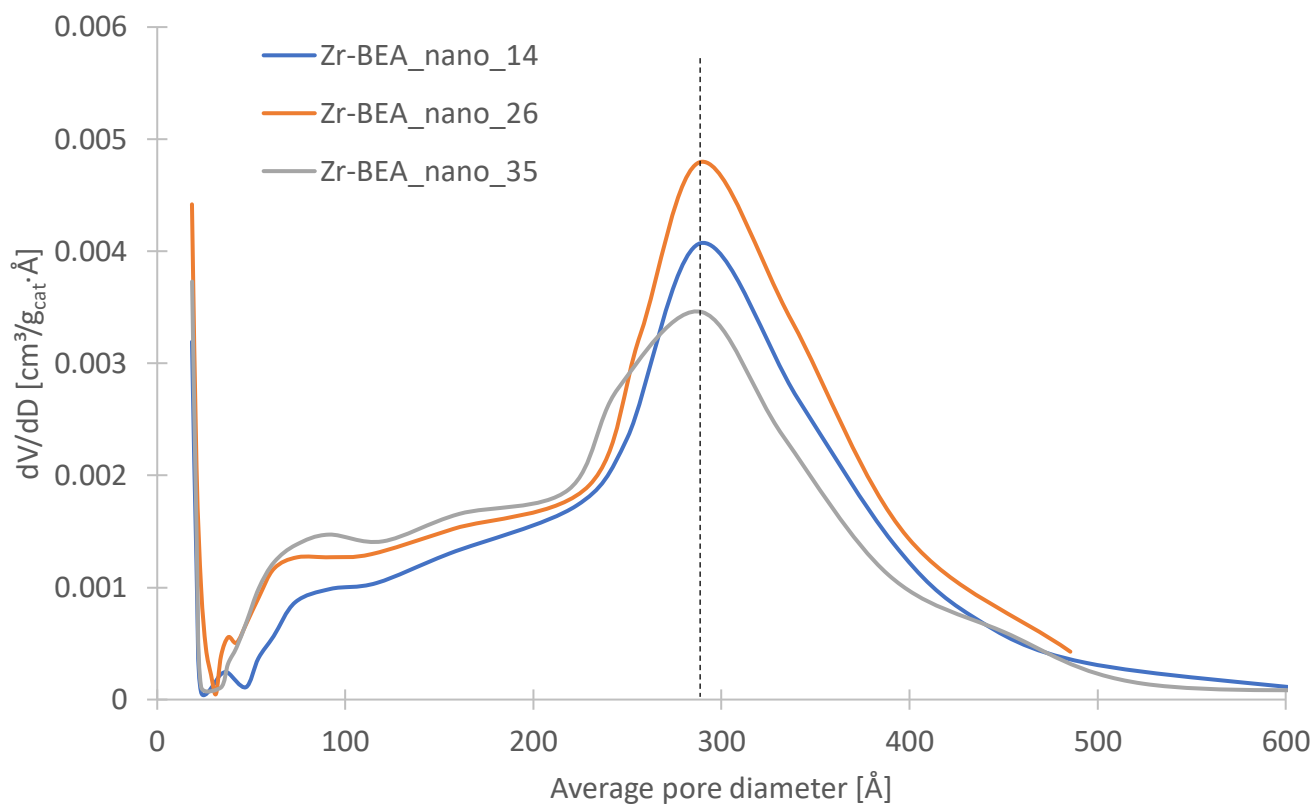


Figure 19. BJH desorption curves of Zr-BEA_nano with different Zr loadings (Zr-BEA_nano_14, Zr-BEA_nano_26, Zr-BEA_nano_35). The dotted lines represent the optimum pore diameter size.

Then, N₂ physisorption was performed to characterize the effects of spray drying on the textural properties of Zr-BEA_nano (Figures 20 and 21). The samples are compared to the commercial benchmark.

The samples display similar isotherms made of the combination of type I and IV isotherms (Figure 20). Regarding the BJH average pore diameter, a lower centered mesoporosity is observed for Zr-BEA_SD_26 (22 nm) than for Zr-BEA_nano_26 (29 nm) (Figure 21; see dotted lines). Regarding Zr-BEA_comm_26, a lower quantity of mesopores, centered at a diameter of 9 nm, is observed. The decrease in mesoporosity correlates with the decrease in external surface area. The significant decrease in external surface observed between Zr-BEA_nano_26 and Zr-BEA_comm_26 is probably related to the aggregation of the nanocrystals of the commercial benchmark. Regarding Zr-BEA_SD_26, the lower external surface area could be due to the use of a binder. Finally, as expected for beta zeolites, the micropore volume is constant for the three samples (Table 7).

Table 7. Summary of textural properties obtained via N₂ physisorption of Zr-BEA_nano_26, Zr-BEA_comm_26 and Zr-BEA_SD_26. Values are rounded to two significant figures.

Sample	BET surface area [m ² /g _{cat}]	T-plot external surface area [m ² /g _{cat}]	T-plot micropore volume [cm ³ /g _{cat}]
Zr-BEA_nano_26	610	220	0.20
Zr-BEA_comm_26	440	95	0.21
Zr-BEA_SD_26	490	93	0.20

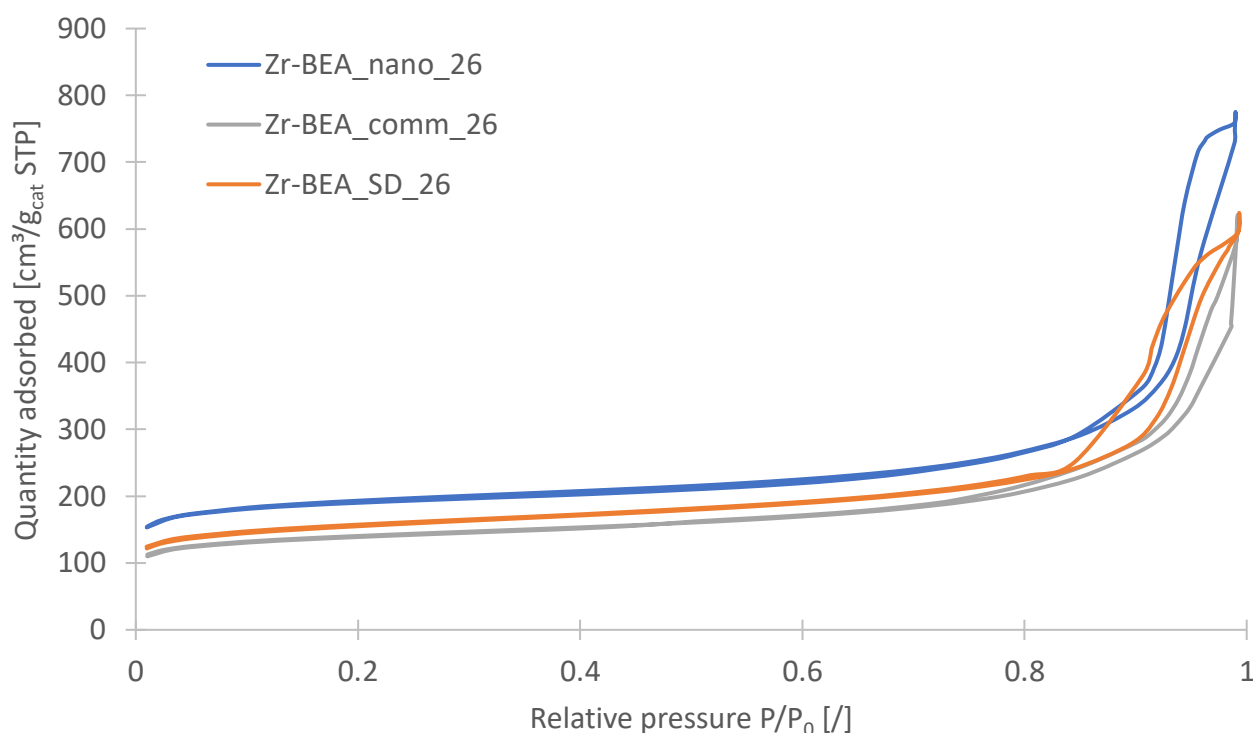


Figure 20. N₂ physisorption isotherms (adsorption and desorption) of Zr-BEA_nano_26, Zr-BEA_comm_26 and Zr-BEA_SD_26.

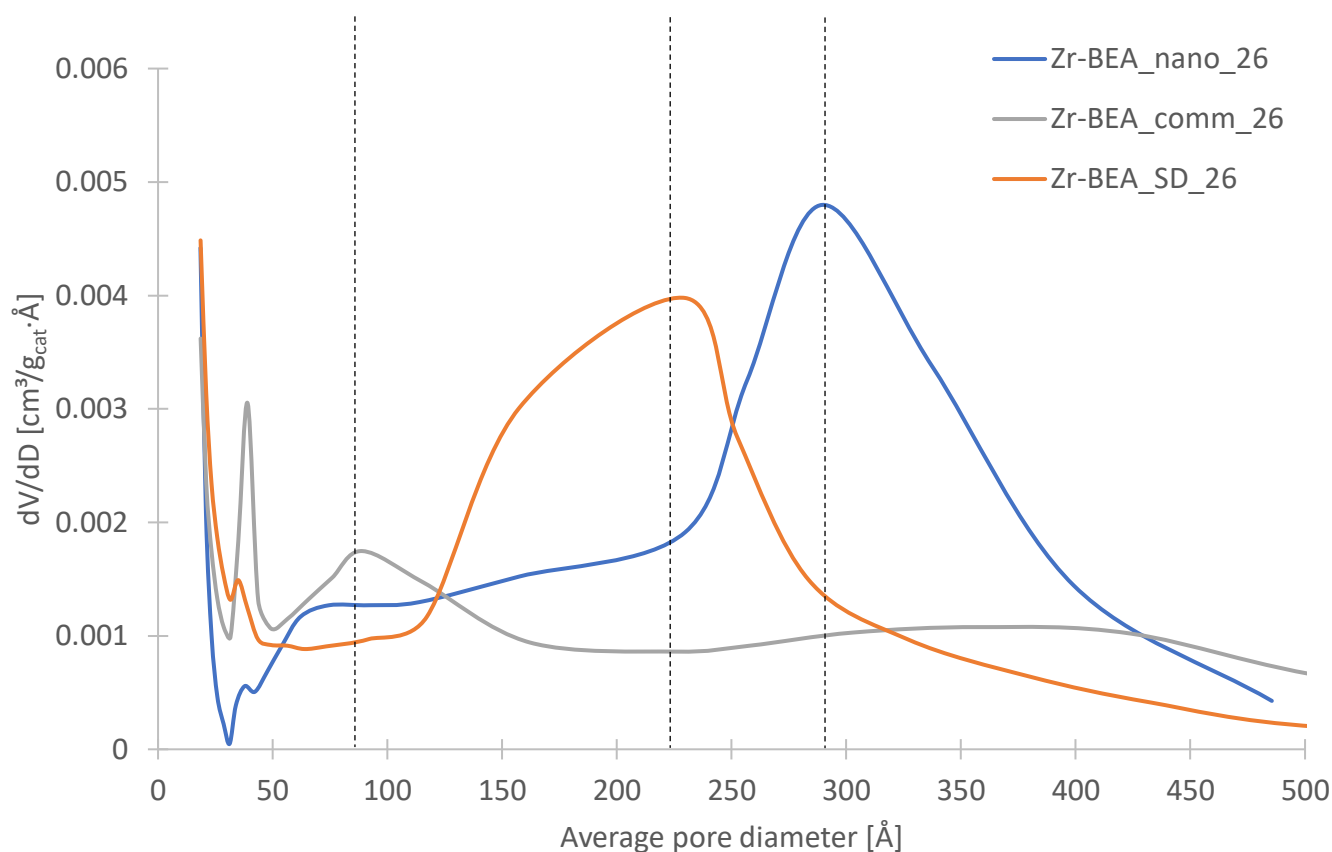


Figure 21. BJH desorption curves of Zr-BEA_nano_26, Zr-BEA_comm_26 and Zr-BEA_SD_26. The dotted lines represent the optimum pore diameter sizes.

N₂ physisorption was also performed to characterize the textural properties of Zr-BEA_micro_26 and the ball milled samples (Figures 22, 23 and 24). The adsorption curves of the samples suggest the presence of micropores (type I isotherms) (Figure 22), which is also suggested by the t-plot (Figure 24; see dotted lines). The isotherms of Zr-BEA_micro_26 and the ball milled samples also indicate an absence of mesopores due to a non-significant hysteresis loop between the adsorption and the desorption isotherms and the absence of a plateau (typical when mesopores are filled) at high P/P_0 values. Instead, an asymptomatic increase of the adsorbed volume is observed, which is characteristic for type II isotherms. The t-plot also suggests the absence of mesopores (Figure 24).

Regarding the BJH average pore diameter (Figure 23), only the presence of narrow mesoporosity is observed (3-4 nm), which typically does not lead to a hysteresis loop in N₂ physisorption isotherms. It is however not clear whether this mesoporosity originates from the crystalline or the amorphous phase.

As expected, ball milling increases the external surface area of Zr-BEA_micro_26 and its increase correlates with the ball milling time (Table 8). Regarding the micropore volume, it is relatively constant with a slight decrease after 30 minutes of ball milling, which could

indicate the crushing of the pores. However, the difference is rather low and not necessarily significant.

Table 8. Summary of textural properties obtained via N_2 physisorption of Zr-BEA_micro_26 at different ball milling times (Zr-BEA_micro_BM5_26, Zr-BEA_micro_BM15_26, Zr-BEA_micro_BM30_26). Values are rounded to two significant figures.

Sample	BET surface area [m^2/g_{cat}]	T-plot external surface area [m^2/g_{cat}]	T-plot micropore volume [cm^3/g_{cat}]
Zr-BEA_micro_26	220	16	0.11
Zr-BEA_micro_BM5_26	210	18	0.10
Zr-BEA_micro_BM15_26	230	25	0.11
Zr-BEA_micro_BM30_26	240	70	0.09
Zr-BEA_nano_BM15_26	390	55	0.15

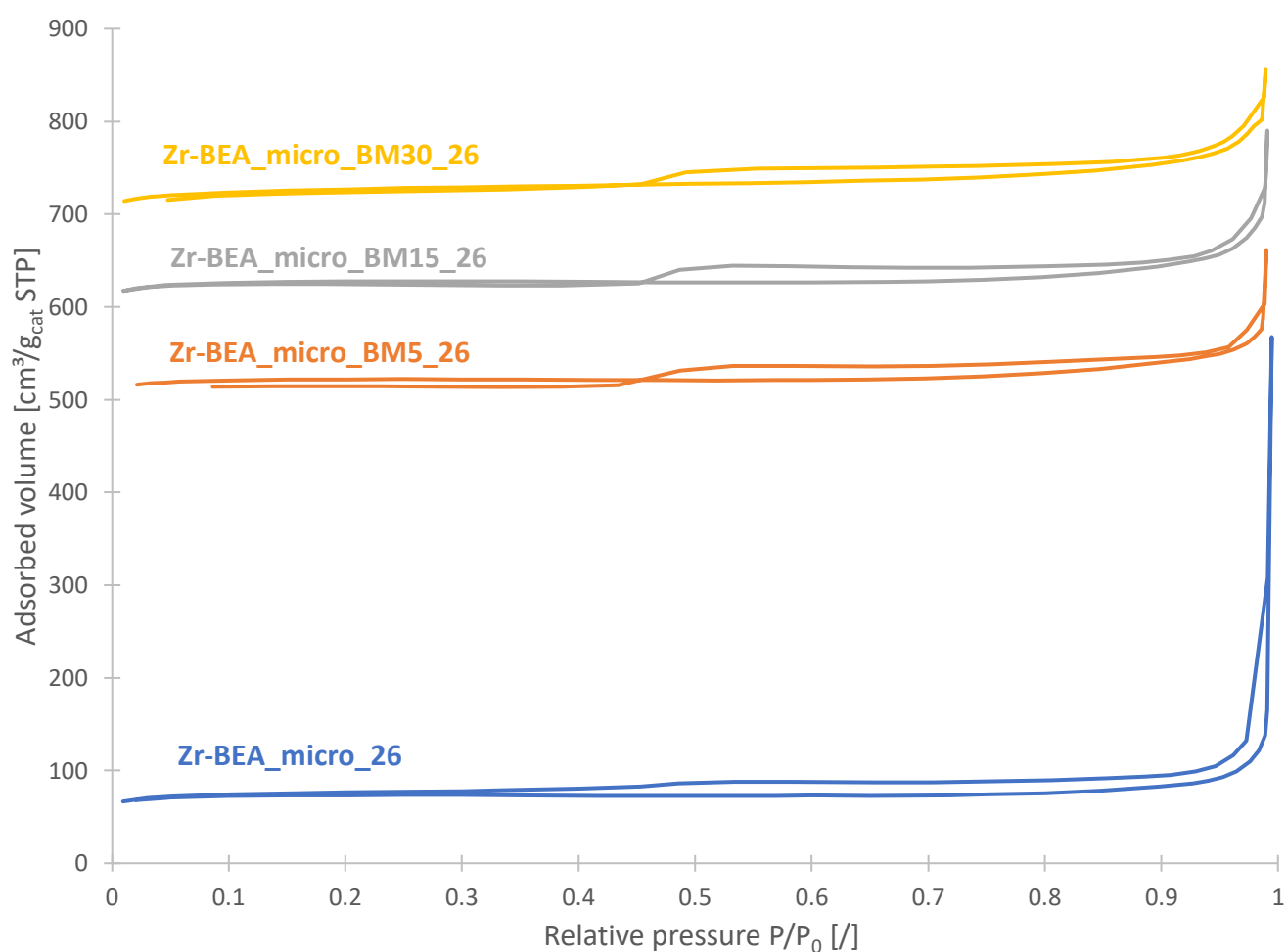


Figure 22. N_2 physisorption isotherms (adsorption and desorption) of Zr-BEA_micro_26 at different ball milling times (Zr-BEA_micro_BM5_26 (+ 450 cm^3/g), Zr-BEA_micro_BM15_26 (+ 550 cm^3/g), Zr-BEA_micro_BM30_26 (+ 650 cm^3/g)).

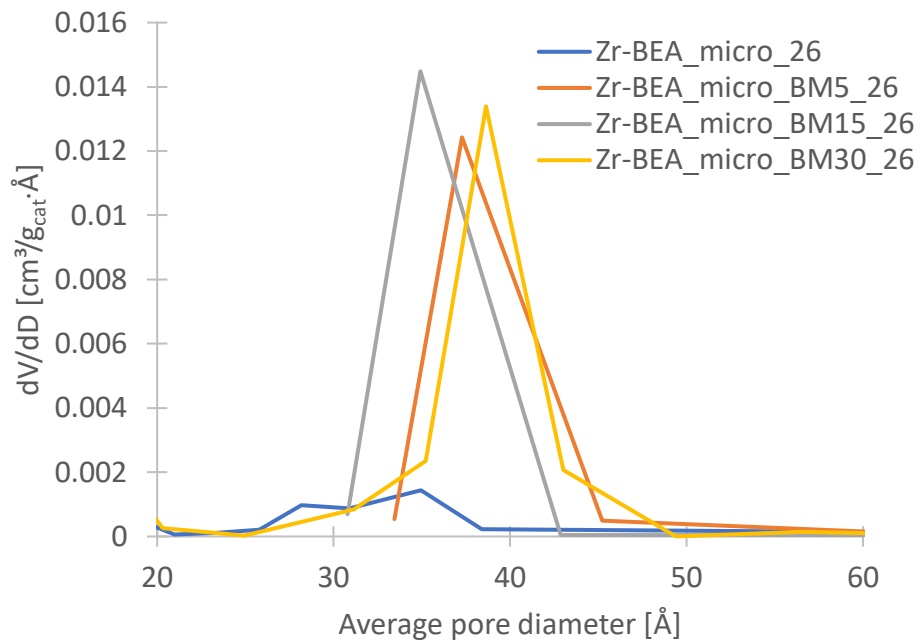


Figure 23. BJH desorption curves of Zr-BEA_micro_26 at different ball milling times (Zr-BEA_micro_BM5_26, Zr-BEA_micro_BM15_26, Zr-BEA_micro_BM30_26).

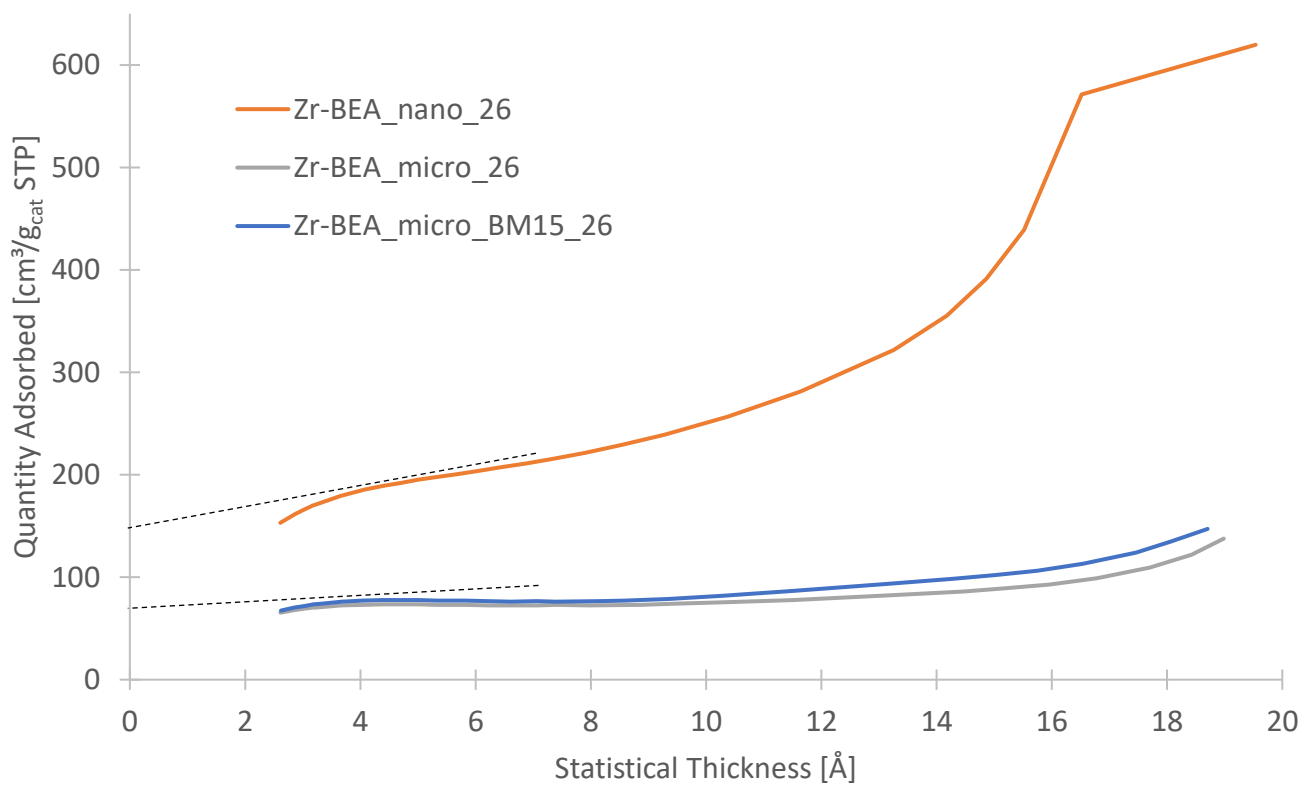


Figure 24. T-plot analyses of Zr-BEA_nano_26, Zr-BEA_micro_26 and Zr-BEA_micro_BM15_26. The dotted lines refer to the tangent taken in the statistical thickness range between 3.5 and 5 Å, which enables to calculate the micropore volume from the amount of adsorbed N_2 at the intercept of the slope.

Finally, a ball milled Zr-BEA_nano_26 sample was analyzed to check whether the ball milling procedure affected its textural properties. Dramatic drops of the mesoporosity (Figures 25 and 26), micropore volume and external surface area (Table 8) are observed in comparison to the parent material.

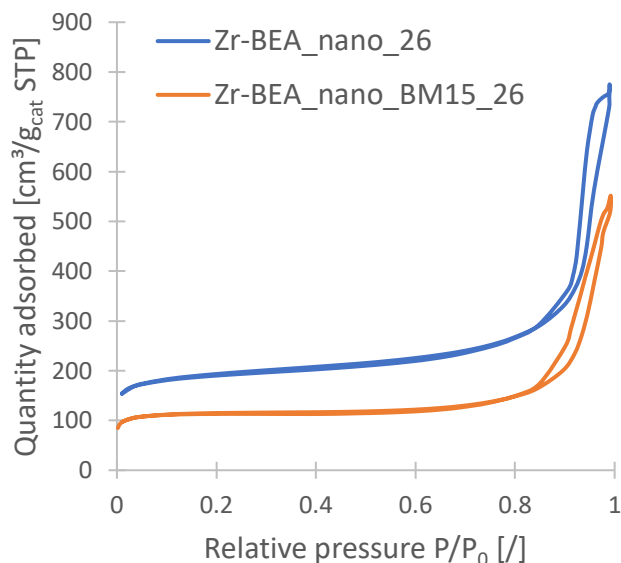


Figure 25. N_2 physisorption isotherms (adsorption and desorption) of Zr-BEA_nano_26 and Zr-BEA_nano_BM15_26.

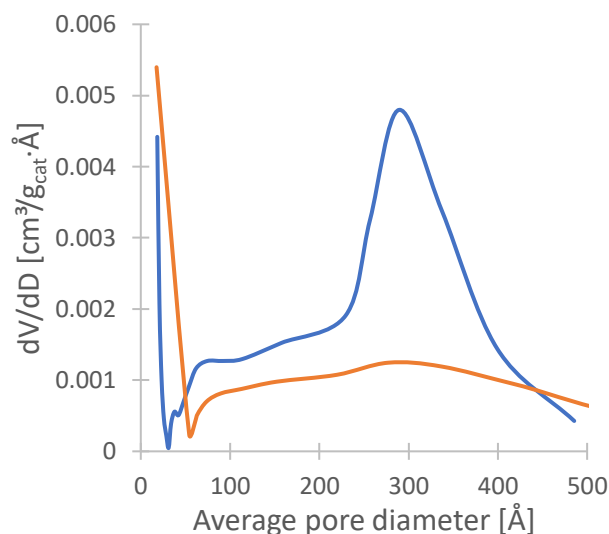


Figure 26. BJH desorption curves of Zr-BEA_nano_26 and Zr-BEA_nano_BM15_26.

3.1.3. NH_3 -TPD

NH_3 -TPD was performed to characterize changes in global acidity due to the dealumination and impregnation steps for Zr-BEA_nano (Figures 27 and 28).

The results suggest the dealumination step was successful as no acidity is observed for calci_deal_BEAnano (Table 9). Moreover, no acidity loss is observed between calci_non-deal_BEAnano (0.91 mmol/g) and Zr-BEA_nano_26 (0.93 mmol/g), which suggest no global loss in acidity between the Al-containing zeolite and the Zr-containing zeolite. However, a shift in acid sites strength is observed (Figure 27; see dotted lines). This suggests the presence of two types of acid sites of different strength in calci_non-deal_BEAnano (one desorption peak at 205 °C and another at 320 °C), which could be related to Lewis and Brønsted acid sites.

Samples with different Zr loadings share the same shape of desorption peak with a maximum at 250 °C (Figure 28), indicating they share the same relative strength in acid sites. A loss in number of acid sites is observed at increasing Si/Zr ratio (Table 9), which correlates with the decrease in Zr loading.

The increase in acidity observed after 320 °C for calci_non-deal_BEAnano, calci_deal_BEAnano and for Zr-BEA_nano_35 is due to a contamination of the NH_3 -TPD apparatus which resulted in a desorption peak at 500 °C.

Table 9. Summary of number of acid sites obtained via NH_3 -TPD for Zr-BEA_nano_26 at different synthesis steps (calci_non-deal-BEA_nano, calci_deal-BEA_nano, Zr-BEA_nano_26) and at different Zr loadings (Zr-BEA_nano_14, Zr-BEA_nano_26, Zr-BEA_nano_35). Values are rounded to two significant figures. bdl = below detection limit

Number of acid sites (mmol/g _{cata})	
calci_non-deal-BEA_nano	0.93
calci_deal-BEA_nano	bdl
Zr-BEA_nano_14	0.97
Zr-BEA_nano_26	0.91
Zr-BEA_nano_35	0.22

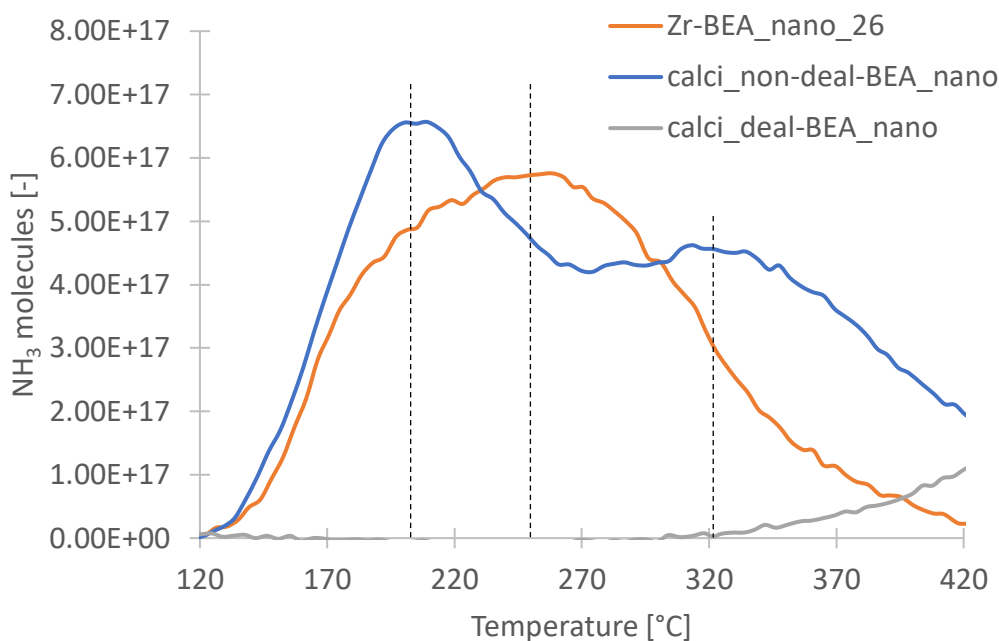


Figure 27. NH_3 -TPD profiles of Zr-BEA_nano_26 at different synthesis steps (calci_non-deal-BEA_nano, Zr-BEA_nano_26). The dotted lines refer to the maxima of the desorption peaks.

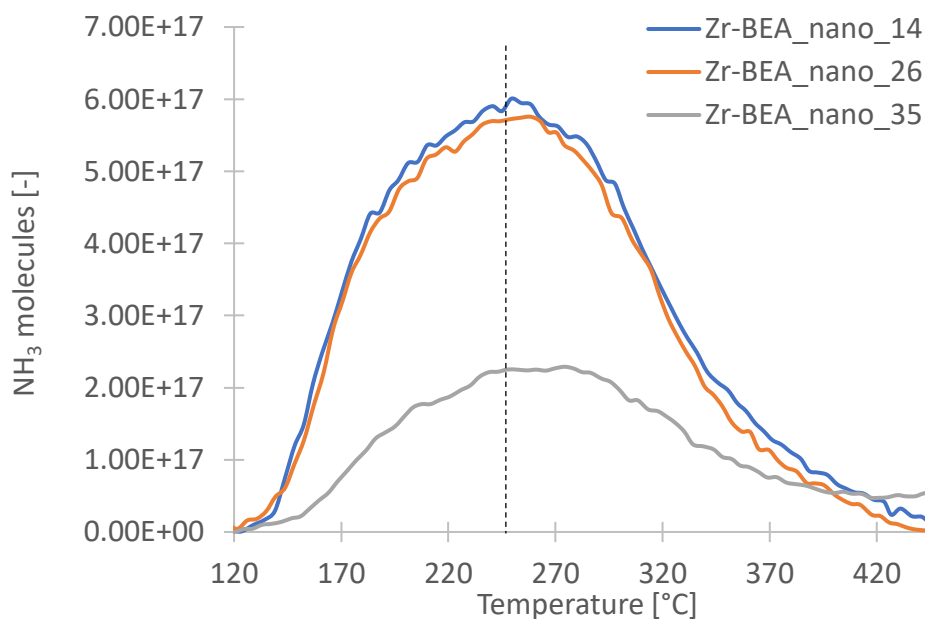


Figure 28. NH_3 -TPD profiles of Zr-BEA_nano with different Zr loadings (Zr-BEA_nano_14, Zr-BEA_nano_26, Zr-BEA_nano_35). The dotted line refers to the maxima of the desorption peaks.

NH₃-TPD was also performed to characterize potential changes in acidity due to the spray drying of Zr-BEA_nano_26. The results are compared to Zr-BEA_comm_26.

Figure 29 demonstrates a significant loss in acidity between Zr-BEA_nano_26 and Zr-BEA_SD_26 (Table 10), although the strength of the acid sites does not change. Hence, the spray-drying process reduces the amount of acid sites. In comparison to Zr-BEA_nano_26, fewer acid sites are quantified for Zr-BEA_comm_26.

Table 10. Summary of number of acid sites obtained via NH₃-TPD of Zr-BEA_nano_26, Zr-BEA_comm_26 and Zr-BEA_SD_26. Values are rounded to two significant figures.

Number of acid sites (mmol/g)	
Zr-BEA_nano_26	0.91
Zr-BEA_comm_26	0.46
Zr-BEA_SD_26	0.27

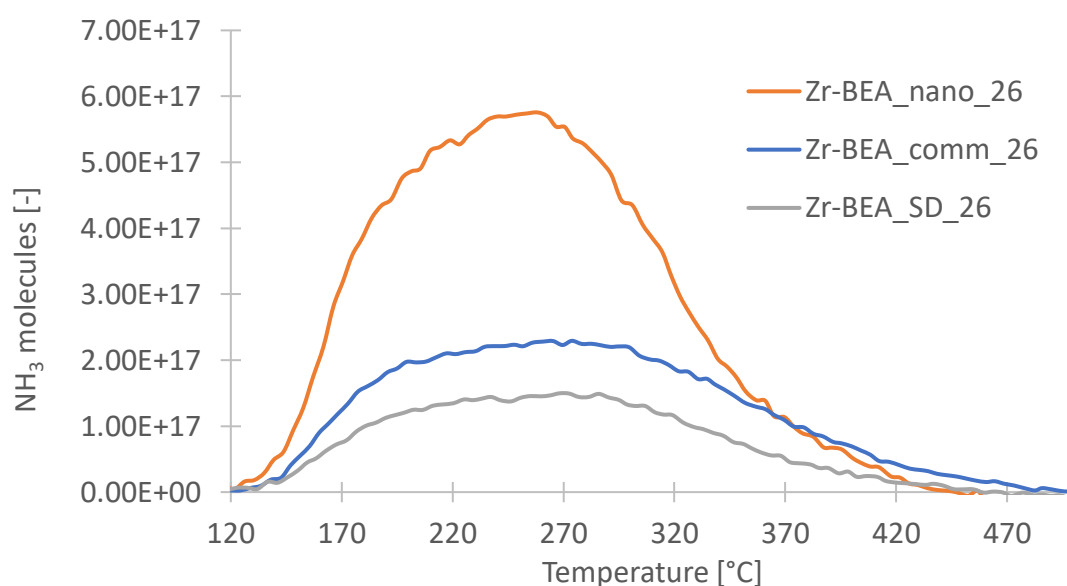


Figure 29. NH₃-TPD profiles of Zr-BEA_nano_26, Zr-BEA_comm_26 and Zr-BEA_SD_26.

Finally, NH₃-TPD was performed to characterize potential changes in acidity due to the ball milling of Zr-BEA_micro_26. Figure 30 shows the very low acidity of the parental Zr-BEA_micro_26. Although a small loss in acid strength is observed for Zr-BEA_micro_BM30_26, the ball milling does not seem to significantly change the acidity of the material (Table 11).

Table 11. Summary of number of acid sites obtained via NH₃-TPD of Zr-BEA_micro_26, Zr-BEA_micro_BM15_26 and Zr-BEA_micro_BM30_26. Values are rounded to two significant figures.

Number of acid sites (mmol/g)	
Zr-BEA_micro_26	0.22
Zr-BEA_micro_BM15_26	0.23
Zr-BEA_micro_BM30_26	0.18

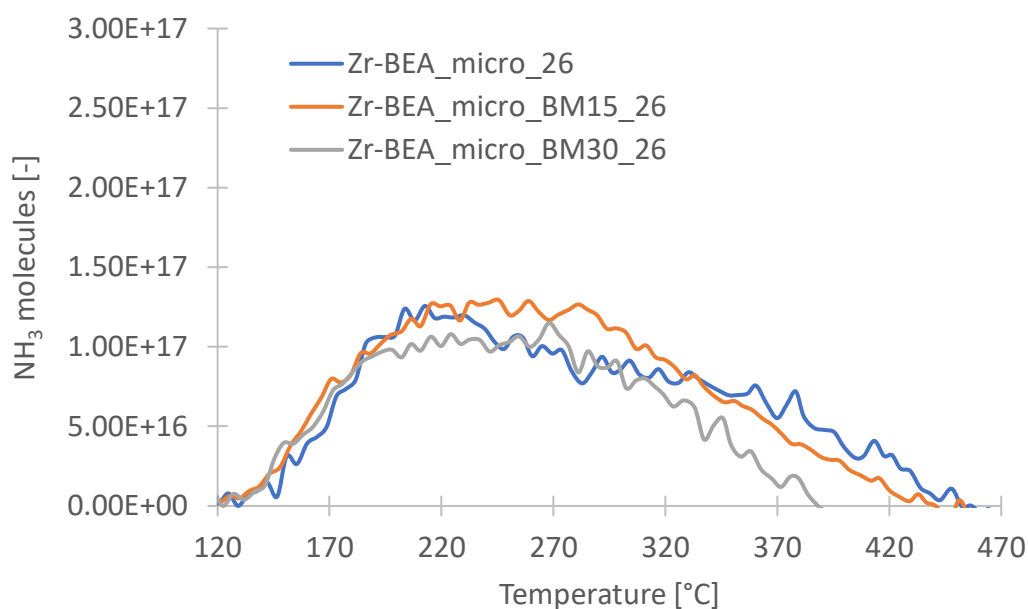


Figure 30. NH_3 -TPD profiles of Zr-BEA_micro_26, Zr-BEA_micro_BM15_26 and Zr-BEA_micro_BM30_26.

3.1.4. Pyridine-IR

Pyridine-IR measurements were performed to analyze the ratio in Lewis and Brønsted acid sites in Zr-BEA_nano_26. The IR profiles exhibited the 1551 cm^{-1} peak caused by vibrational modes of protonated pyridine on Brønsted acid sites of the material and the 1455 cm^{-1} peak caused by pyridine coordinated to Lewis acid sites (Figure 31).

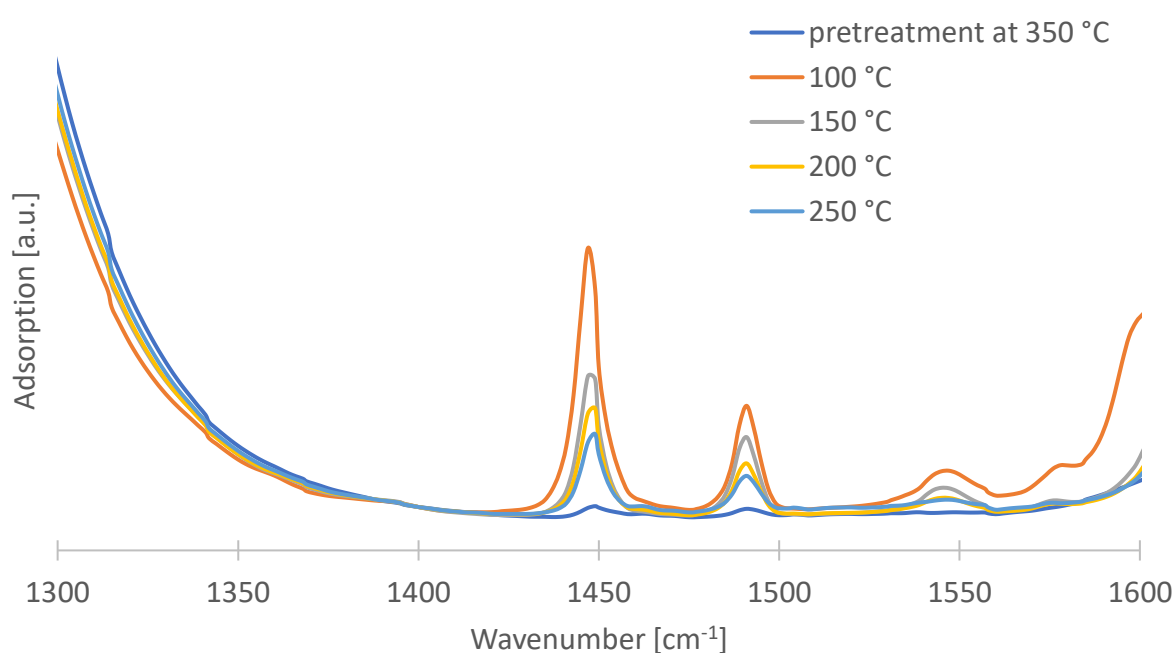


Figure 31. FT-IR spectra of Zr-BEA_nano_26 after degassing at 350 °C and after consecutive desorption of pyridine at 100 °C , 150 °C , 200 °C and 250 °C .

From the total area of each peak, it was possible to calculate the concentration in acid sites from equation (7), where A_L and A_B are the area of the peak corresponding to Lewis and Brønsted sites, ε_L and ε_B the molar extinction coefficient of pyridine bound to respectively a Lewis or a Brønsted site, S_{cat} and m_{cat} refer to the surface and the mass of the catalyst wafer.

$$n_T[\mu\text{mol}.g^{-1}] = n_L + n_B = \frac{A_L S_{cat}}{\varepsilon_L m_{cat}} + \frac{A_B S_{cat}}{\varepsilon_B m_{cat}} \quad (7)$$

A ratio of about 80 % of Lewis acid sites and 20 % of Brønsted acid sites is obtained for a total amount of 0.13 mmol_{acid sites}/g_{cata}. Acid strength distribution is obtained by desorbing the pyridine at different temperatures (100 °C, 150 °C, 200 °C and 250 °C) (Figure 32). Stronger sites are assumed to retain pyridine at higher temperatures. Figure 33 indicates the ratio in Brønsted and Lewis acid sites at different desorption temperatures, which is quite constant suggesting a similar strength of acid sites between Lewis and Brønsted acid sites.

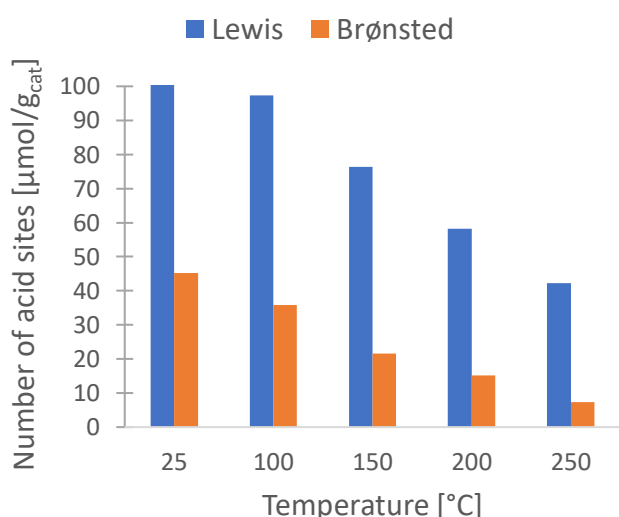


Figure 32. Number of Lewis and Brønsted acidic sites in Zr-BEA_nano_26 at different desorption temperatures.

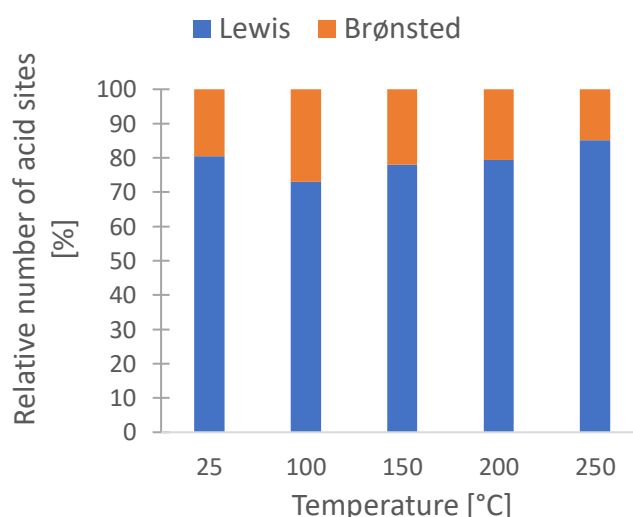


Figure 33. Relative amount of Lewis and Brønsted acidic sites in Zr-BEA_nano_26 at different desorption temperatures.

3.1.5. XPS and ICP-AES

Elemental analyses of the sample were performed through XPS and ICP-AES to verify whether the experimental Si/Al and Si/Zr ratios converged to the nominal ratios. Figure 34 demonstrates the XPS spectrum obtained for Zr-BEA_nano_26, from which the Si/Al and Si/Zr ratios were calculated (Table 12).

Regarding the Si/Al ratio, accurate ratios were obtained for calci_non-deal-BEA_nano through XPS and ICP-AES (Table 12, entry 1). Al surface content in Zr-BEA_nano, Zr-BEA_comm_26 and Zr-BEA_SD_26 is below the detection limit in XPS and very low in ICP-AES (Table 12, entries 3-9). It can thus be assumed the samples are almost Al free.

Regarding the Si/Zr ratio, a higher ratio is observed through XPS in comparison to the nominal Si/Zr ratio whereas highly accurate Si/Zr ratios are obtained by ICP-AES (Table 12, entries 2-9). This indicates a lower amount of Zr is impregnated on the surface in comparison to the bulk of the sample. In addition, experimental reproducibility issues are observed by XPS between three synthesis batches of Zr-BEA_nano_26 (Table 12, entries 4-6).

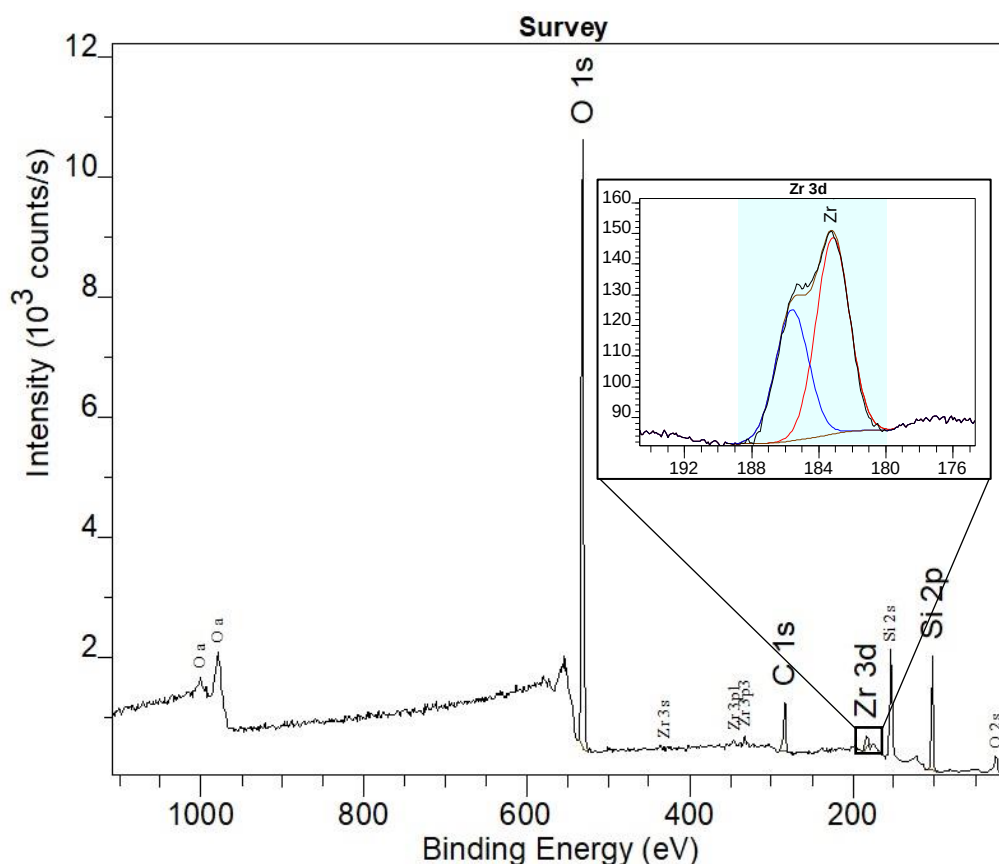


Figure 34. XPS spectrum of Zr-BEA_nano_26 (batch A) and zoom on the Zr 3d peak.

Table 12. Summary of Si/Al and Si/Zr ratios obtained via XPS and ICP-AES analyses of Zr-BEA_comm_26, calci_non-deal-BEA_nano, non-deal-Zr-BEA_nano_26 and Zr-BEA_nano with different Zr loadings (Zr-BEA_nano_14, Zr-BEA_nano_26, Zr-BEA_nano_35), including three Zr-BEA_nano_26 samples from different batches (A, B and C). Values are rounded to two significant figures. bdl = below detection limit

Entry	Sample	Nominal ratio		XPS		ICP-AES	
		Si/Al ratio	Si/Zr ratio	Si/Al ratio	Si/Zr ratio	Si/Al ratio	Si/Zr ratio
1	calci_non-deal-BEA_nano	12.5	0	12	bdl	11	bdl
2	non-deal-Zr-BEA_nano_18	12.5	18	11	36	9.2	20
3	Zr-BEA_nano_14 (batch A)	0	14	bdl	23	380	16
4	Zr-BEA_nano_26 (batch A)	0	26	bdl	32	430	29
5	Zr-BEA_nano_26 (batch B)	0	26	bdl	49	-	-
6	Zr-BEA_nano_26 (batch C)	0	26	bdl	52	-	-
7	Zr-BEA_nano_35 (batch A)	0	35	bdl	47	600	36
8	Zr-BEA_SD_26	0	26	-	-	180	26
9	Zr-BEA_comm_26	0	26	-	-	730	26

3.1.6. TEM and SEM

SEM analyses were performed to characterize the morphology of the spray dried zeolite microspheres. Figures 35a and 35b illustrate SEM images of spray dried H-beta zeolites and not Zr-BEA_SD_26. These zeolites are TEA-BEA_nano samples which have been ionically exchanged with NH_4NO_3 to obtain NH_4 -BEA zeolites. They were then spray dried and calcined to burn the ammonium to obtain H-BEA_SD. As the spray drying process is identical for H-BEA_SD as for Zr-BEA_SD_26, similar results are expected. The SEM images demonstrate spherical aggregated zeolites with a 1-10 μm diameter size range. A significant number of broken spheres are also present.

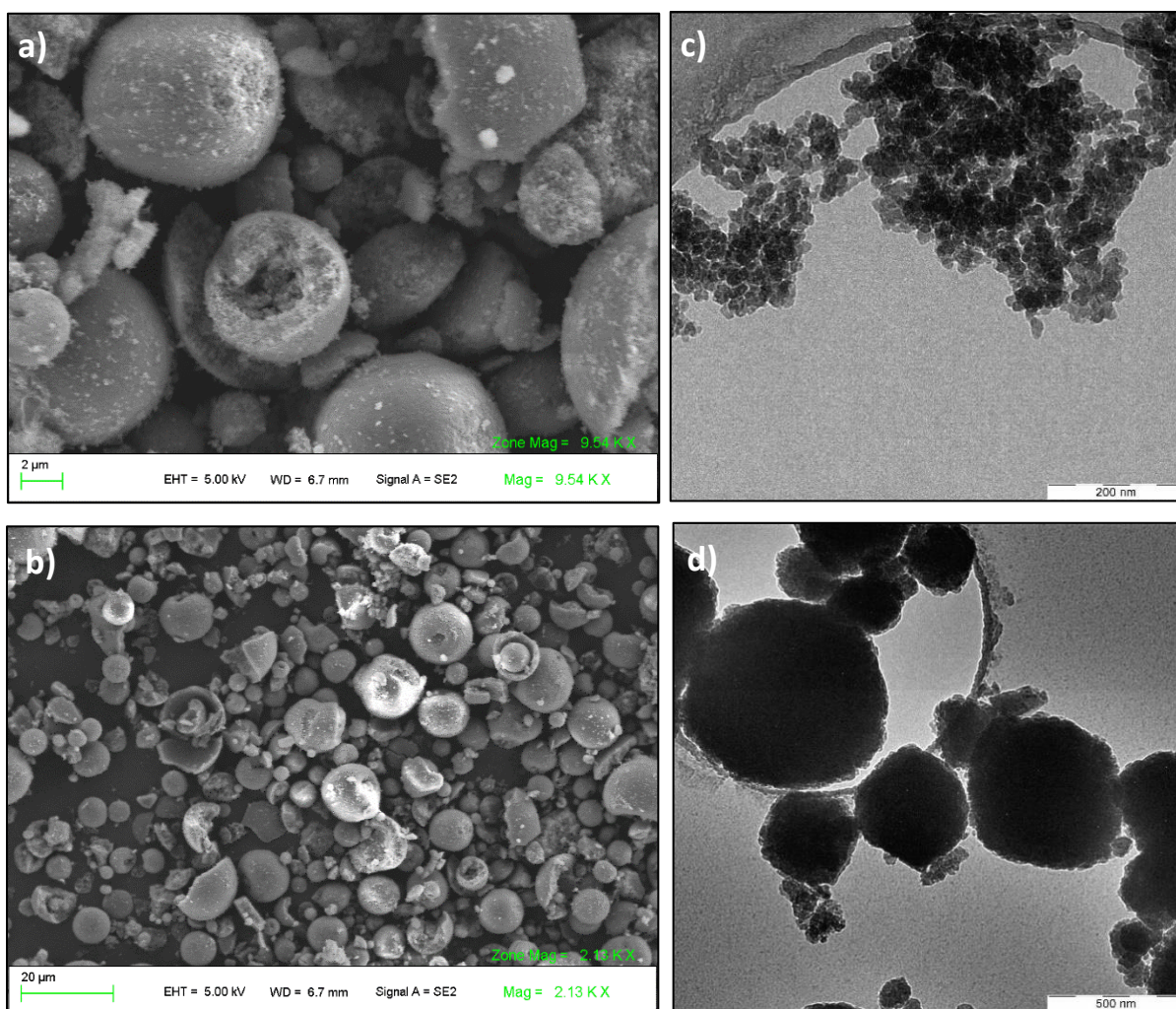


Figure 35. a) and b) SEM images of H-BEA_SD, c) TEM image of Zr-BEA_nano_26 and d) TEM image of Zr-BEA_comm_26.

In addition, TEM analyses were performed to characterize the morphology of Zr-BEA_nano_26 (Figure 35c). The obtained TEM images show the sample is made of approximately 10 nm nanocrystallites but with different packing densities. The clusters demonstrate inter-particle mesoporosity visible by the lighter regions inside them. In

comparison, a representative TEM image of Zr-BEA_comm_26 (Figure 35d) shows ball-like grains with a diameter size up to 0.7 μm . The interparticular porosity is so low that the catalyst nanoparticles are not distinguishable on the image, preventing crystal size quantification. These images confirm that Zr-BEA_comm samples are highly aggregated which prevents its use as parent material for spray drying.

Furthermore, Zr-BEA_micro_26 was analyzed to confirm its bigger crystal size in comparison to Zr-BEA_nano_26. TEM images were performed and enabled to show the presence of an amorphous phase in the sample (Figure 36a), but bigger and regular structures between 1 and 10 μm were also present (Figure 36b). It is however not clear whether these structures are agglomerates or indeed microcrystals. Additional SEM images were performed on a second batch of Zr-BEA_micro_26 (Figures 36c and d). This batch could not be further analyzed during this master thesis. The sample did not demonstrate any amorphization and regular structures of a 5-15 μm size range were observed, which could actually correspond to unique microcrystals due to their highly regular structure. This could suggest the bigger structures observed in TEM images on the first batch also correspond to zeolite microcrystals.

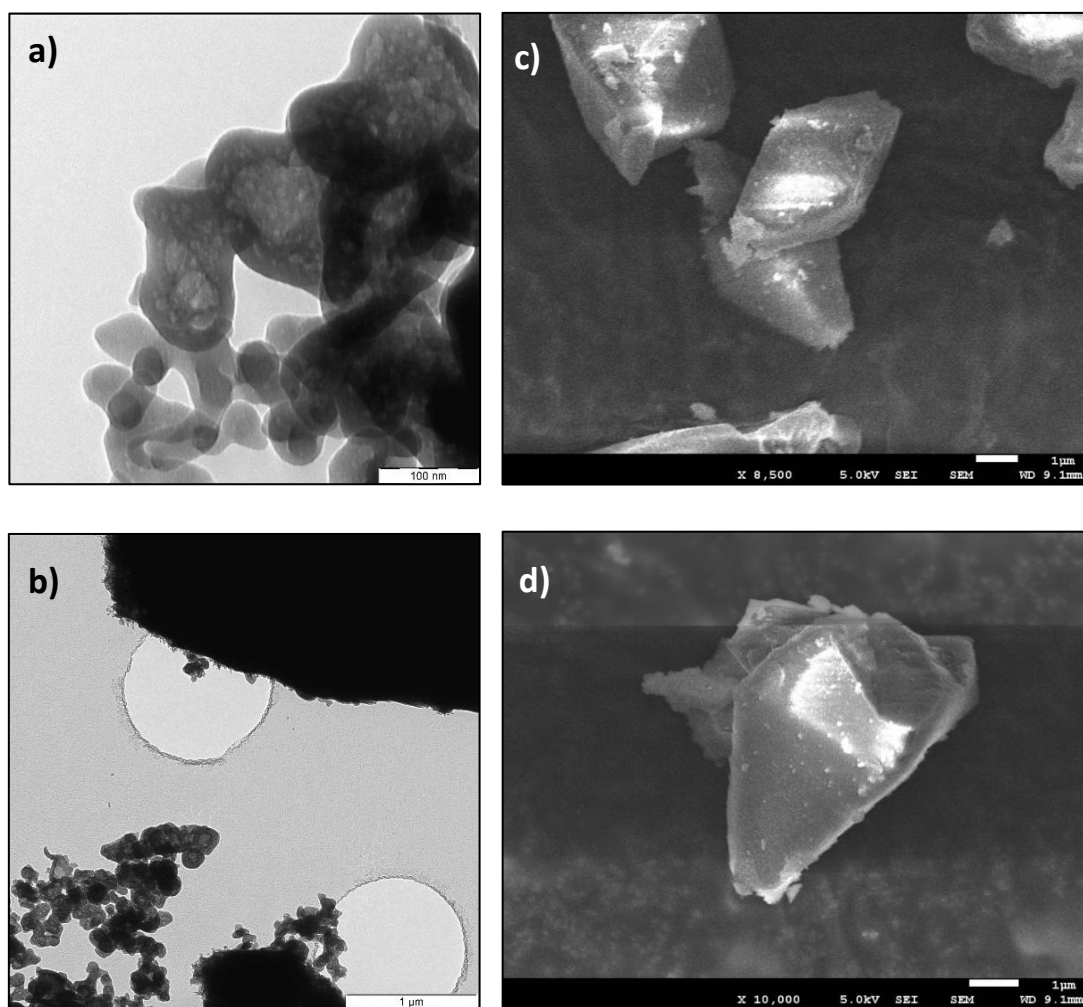


Figure 36. a) and b) TEM images of Zr-BEA_micro_26, c) and d) SEM images of Zr-BEA_micro_26 from another synthesis batch.

3.2. Catalytic testing of the synthesized catalysts

3.2.1. Screening of Zr-BEA_nano with variable Zr loading

3.2.1.2. Overview of screening

The synthesized Zr-BEA_nano catalysts with variable Zr loading (Si/Zr = 14, 18, 22, 26, 30 and 35) were tested on the MPV reduction of EL to GVL. The range in Zr loadings was chosen based on previous research during this ongoing PhD research. Back then, a broader screening was performed on Zr-BEA_comm (Si/Zr = 12, 15, 33, 50, 66 and 100) which led to the identification of an optimum Si/Zr ratio close to 15.

In this master thesis, the catalytic performances of Zr-BEA_nano were compared to the commercial benchmark Zr-BEA_comm. A total of 12 samples were tested. The specific productivities per mass of catalyst (after 30 min of reaction time to obtain initial reaction rates) were calculated and are presented in Figure 37. A maximum productivity is observed for Zr-BEA_nano_26 with 4.5 mmol_{GVL}/h.g_{cat}. The selectivity proved to be constant for the different catalysts, varying between 85.0 and 89.3 % at a 100 % conversion after 6 h. Regarding the benchmark, the highest specific productivity was obtained for Zr-BEA_comm_22 with 2.9 mmol_{GVL}/h.g_{cat}.

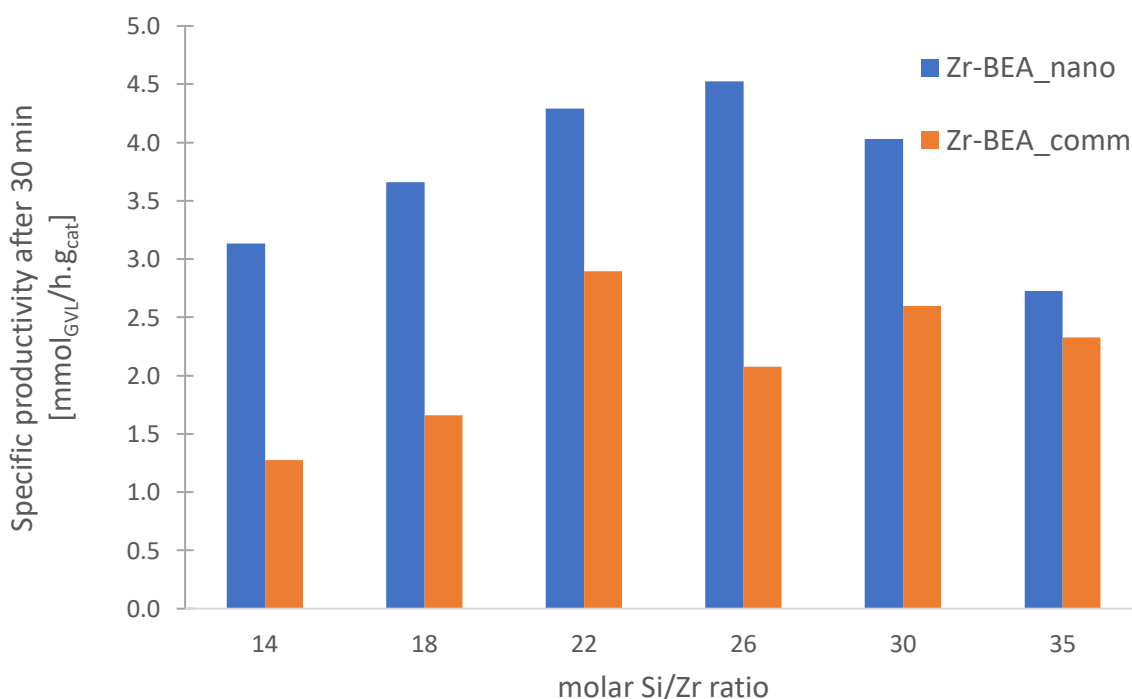


Figure 37. Summary of specific productivity (after 30 min reaction time) of Zr-BEA_nano and Zr-BEA_comm with variable Zr loadings (Si/Zr = 14, 18, 22, 26, 30 and 35) for the conversion of EL to GVL.

3.2.1.2. Repeatability and reproducibility

Repeatability and reproducibility tests were performed for Zr-BEA_nano_26 to assess the significance of the obtained catalytic performances. Three batches of Zr-BEA_nano_26 were synthesized and each batch was tested three times for the MPV reduction of EL to GVL.

The values were statistically analyzed using JMP® Pro 15 (Figure 38). Batch A, which is extensively discussed in this master thesis, obtained an average specific productivity of 4.05 ± 0.55 mmol_{GVL}/h.g_{cat}. A Fischer test of equality of variances was performed and demonstrated the standard deviation of the three batches can be considered equal (p-value < 0.05). This enables to calculate a mean standard deviation of 0.30 mmol_{GVL}/h.g_{cat} for the three batches. This mean standard deviation is further used in this master thesis to demonstrate the significance between two results (only for catalytic tests of Zr-BEA_nano in the same reaction conditions).

Moreover, an ANOVA test was performed to analyze the reproducibility between the three batches by comparing their mean specific productivities. The test demonstrated that at least one of the means is not equal to the others (p-value < 0.05). Therefore, a Tukey-Kramer HSD test was performed to compare all possible pair of means. It appeared that only batch A and batch C can be considered equal (p-value > 0.05).

Overall, these statistical analyses enabled to demonstrate a good repeatability of our catalytic tests for the same synthesis batch. However, all batches could not be considered equal for the threshold value of $\alpha = 0.05$. This indicates reproducibility issues between different synthesis batches. Therefore, only catalyst from the same synthesis batch are compared with each other in this master thesis.

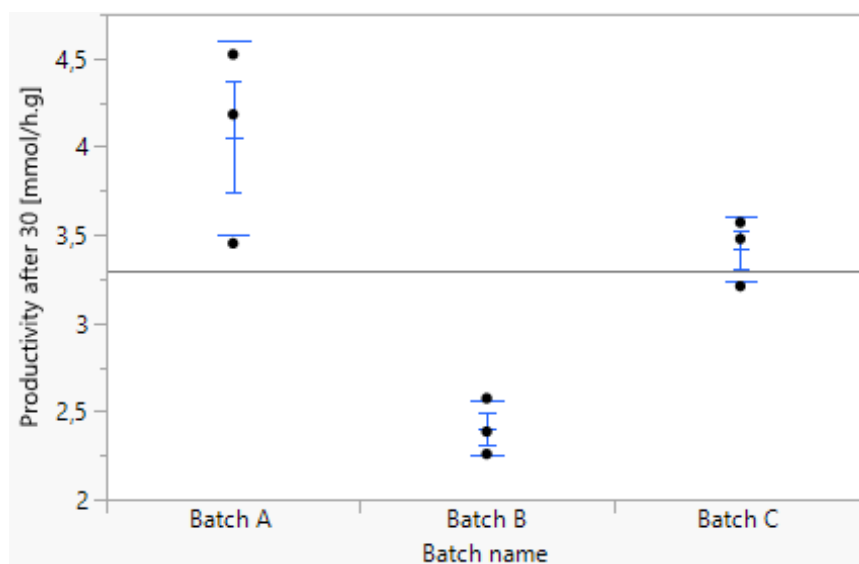


Figure 38. Statistical analysis of three Zr-BEA_nano_26 batches (A, B and C) with three repetitions of each batch. The error bars indicate the mean value, the standard error ($\alpha = 0.05$) and the standard error mean (standard error divided by two degrees of freedom).

3.2.1.3. Kinetics of Zr-BEA_nano_26

The detailed kinetics enable to observe a first order relationship for the consumption of EL (Figure 39), which is confirmed by linearization (Figure 40). Surprisingly, the apparition of the product GVL does not appear to follow a first order relationship, as it cannot be linearized. In the following, the reaction constant $k = 1.26 \text{ h}^{-1}$ was calculated relative to the consumption of EL.

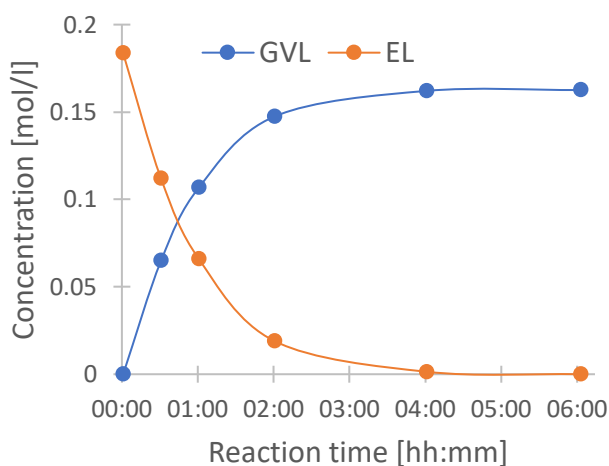


Figure 39. Evolution of the EL and GVL concentrations in function of time.

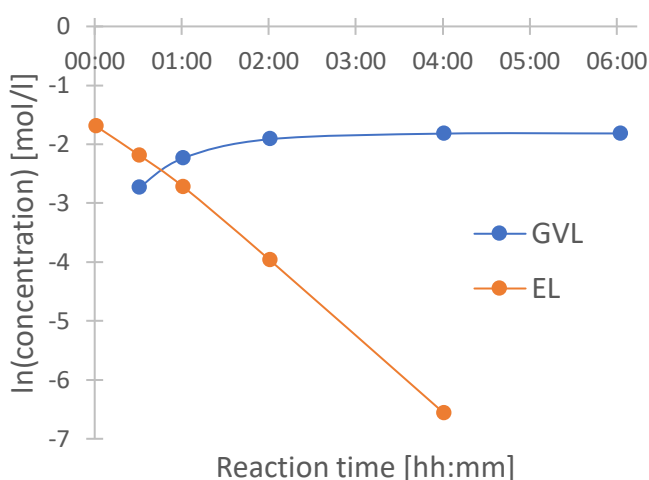


Figure 40. Linearization of the evolution of EL and GVL concentrations in function of time.

Figure 41 illustrates the internal standard (IST) equivalents of EL and the main products detected by GC analysis with the FID detector. Only EL and GVL were identified and quantified to obtain the corresponding concentrations using the appropriate FID response coefficient. Three by-products are observed which are indicated by BP1, BP2 and BP3.

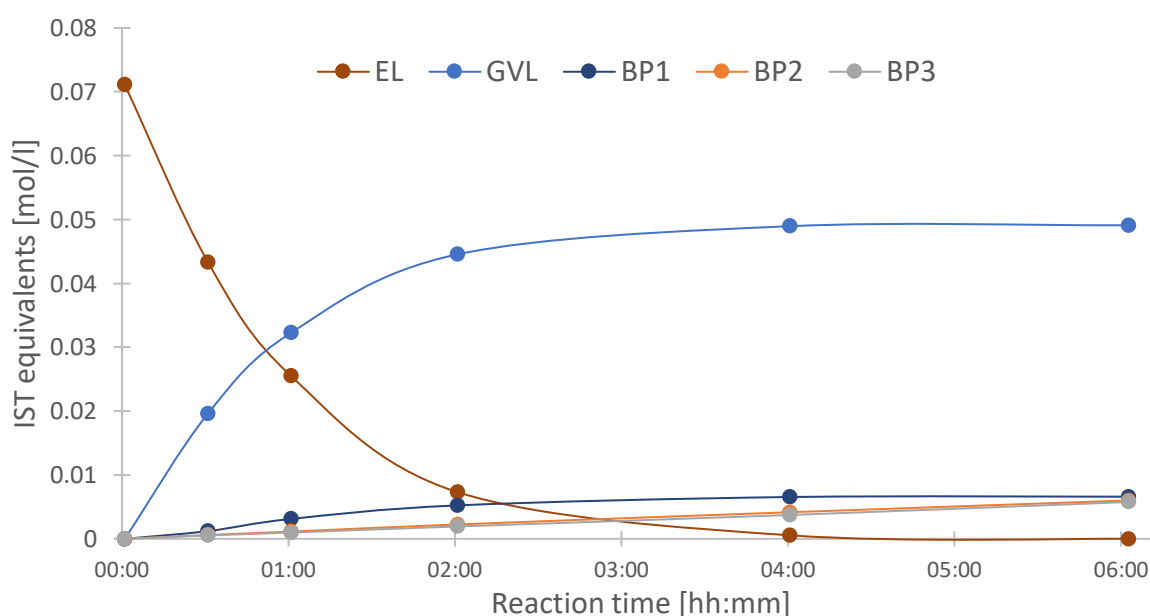


Figure 41. Detailed kinetics of EL, GVL and by-products (BP1, BP2, BP3) in function of time.

3.2.2. Evaluation of the potential of Zr-BEA_SD_26

To evaluate the potential of Zr-BEA_SD_26 for the MPV reduction of EL to GVL, catalytic performances were compared to Zr-BEA_nano_26 and Zr-BEA_comm_26 (Figure 42). A specific productivity after 30 min of 1.0 mmol_{GVL}/h.g_{cat} is obtained for Zr-BEA_SD_26 in contrast to the 4.5 mmol_{GVL}/h.g_{cat} obtained for Zr-BEA_nano_26, which indicates a significant loss in productivity due to the spray drying step. At a 70 % conversion, the selectivity is a bit lower for Zr-BEA_SD_26 with 84 % in comparison to 91 % for Zr-BEA_nano_26. After 6 h, a 60 % yield is obtained in comparison to 89 % for Zr-BEA_nano_26.

The impregnation step of Zr-BEA_SD_26 is performed after spray drying. Hence, it is possible the spray drying process prevents the formation of active Zr species. Therefore, an additional catalytic test was performed using non-deal-Zr-BEA_nano_18, which had been impregnated without prior dealumination. A similar 1.0 mmol_{GVL}/h.g_{cat} productivity is obtained after 30 minutes, but a lower 37 % yield is obtained after 6 h.

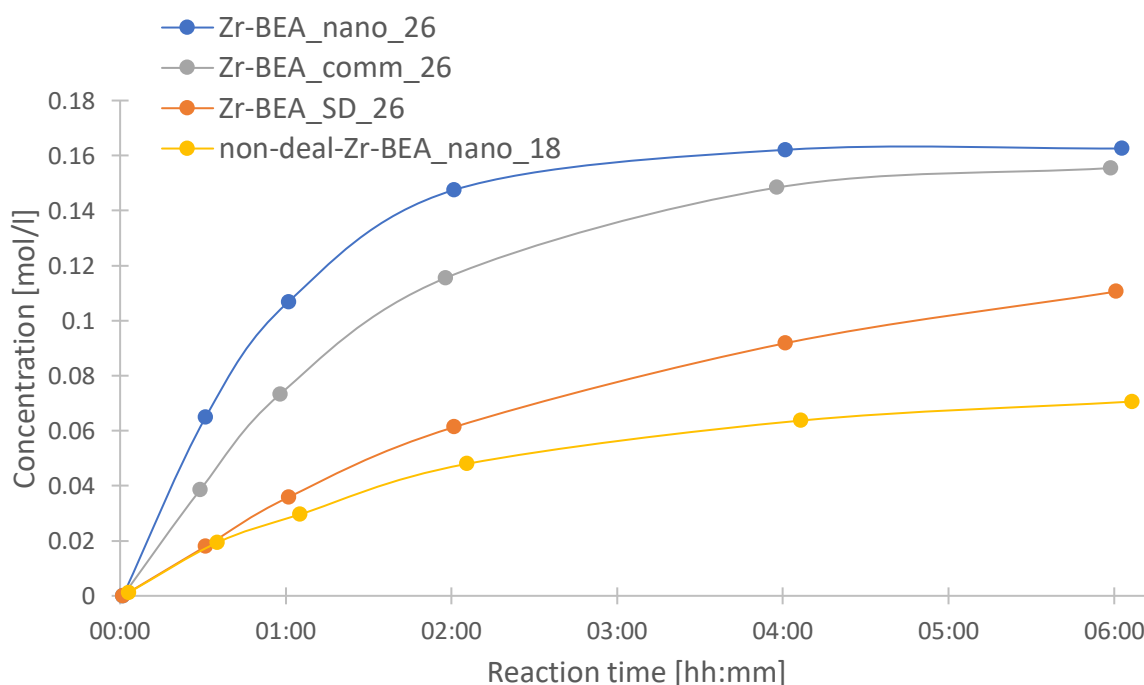


Figure 42. Detailed kinetics of the GVL production for Zr-BEA_nano_26, Zr-BEA_comm_26, Zr-BEA_SD_26 and non-deal-Zr-BEA_nano_18.

3.2.3. Investigation of the potential issue of diffusional limitations

3.2.3.1. Influence of the levulinate chain length

Catalytic tests were performed using levulinates with different chain lengths (methyl levulinate, ethyl levulinate and butyl levulinate) to investigate potential diffusional limitations due to the size the levulinate. The same amount of moles was used for the different tests.

Figure 43 demonstrates an increase in the levulinate chain length results in an increase in specific productivity. A specific productivity of 2.6 mmol_{GVL}/h.g_{cat} was obtained for methyl levulinate, 3.5 mmol_{GVL}/h.g_{cat} for ethyl levulinate and 4.0 mmol_{GVL}/h.g_{cat} for butyl levulinate. The selectivity is relatively constant and varied between 83 and 89 % for a >99 % conversion. These results are considered significant as the difference between the productivities is greater than the mean standard deviation (0.30 mmol_{GVL}/h.g_{cat}) obtained for Zr-BEA_nano_26 (see Chapter 3.2.1.2.).

Surprisingly, no significant difference in specific productivity is observed for Zr-BEA_SD_26 using different levulinates (Figure 44), which could be linked to the overall lower catalytic performances of the catalyst.

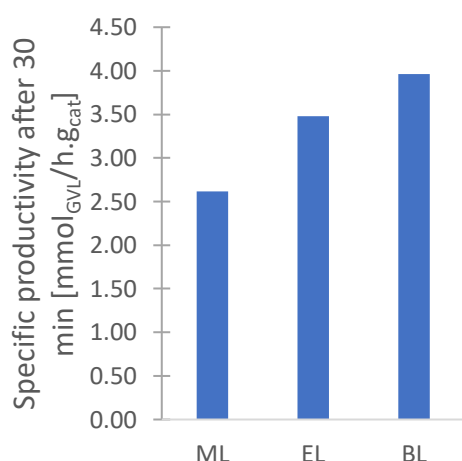


Figure 43. Summary of specific productivities (after 30 min reaction time) of Zr-BEA_nano_26 with different levulinates (ML: methyl levulinate, EL: ethyl levulinate, BL: butyl levulinate).

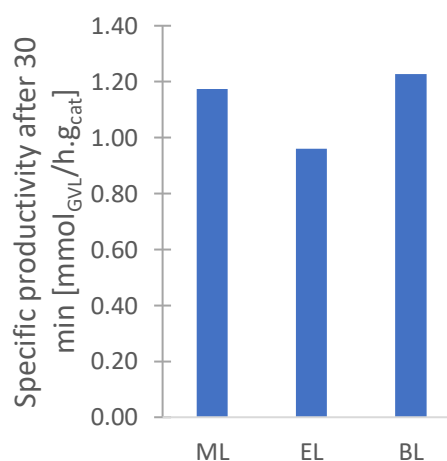


Figure 44. Summary of specific productivities (after 30 min reaction time) of Zr-BEA_SD_26 with different levulinates.

3.2.3.2. Influence of the alcohol chain length

Catalytic tests with different secondary alcohols (2-propanol, 2-butanol, 2-pentanol) were performed for the conversion of EL to GVL at 80 °C, in contrast to the 118 °C reaction temperature for standard catalytic tests. This lower temperature was used to work at equal temperature for each solvent as the boiling temperature of 2-propanol is equal to 82.3 °C.

Figures 45 and 46 demonstrate that a higher alcohol chain length results in a lower specific productivity for Zr-BEA_nano_26 and Zr-BEA_SD_26. Regarding Zr-BEA_nano_26, a 74 % conversion is obtained with 2-propanol after 6 h, 65 % with 2-butanol and 34 % with 2-pentanol. The selectivity is quite constant at different conversion rates, between the different tests (between 85 and 90 %) and does not correlate with the alcohol chain length.

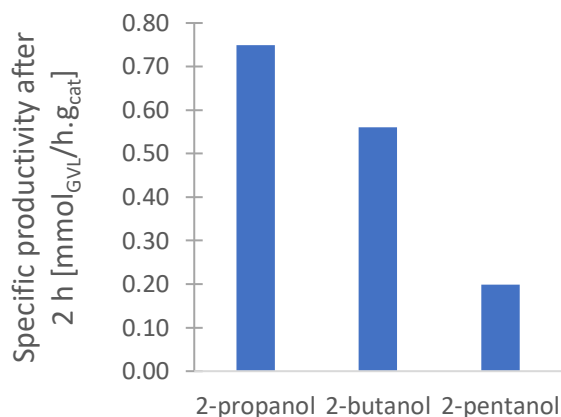


Figure 45. Summary of specific productivities (after 2 h reaction time) of Zr-BEA_nano_26 with different secondary alcohols (2-propanol, 2-butanol, 2-pentanol) for the conversion of EL to GVL at 80 °C.

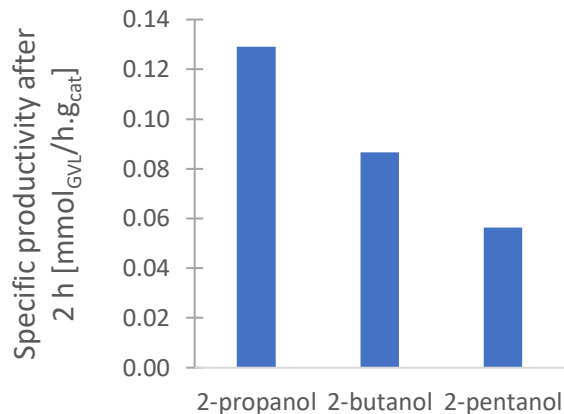


Figure 46. Summary of specific productivities (after 2 h reaction time) of Zr-BEA_SD_26 with different secondary alcohols for the conversion of EL to GVL at 80 °C.

3.2.3.3. Influence of the crystal size

Zr-BEA_micro and the ball milled samples (Zr-BEA_micro_BM5_26, Zr-BEA_micro_BM15_26, Zr-BEA_micro_BM30_26) were tested on the conversion of EL to GVL.

Figure 47 demonstrates an increase in ball milling time results in an increase in specific productivity calculated after 9 h. The specific productivities are extremely low in comparison to Zr-BEA_nano_26. For example, a 2 % conversion was obtained after 6 h in comparison to the 100 % conversion obtained for Zr-BEA_nano_26 in the same reaction time. This indicates the Zr-BEA_micro_26 is poorly active, but it did not prevent the ball milling to increase its activity.

To assess the effects of ball milling on the catalysts, a Zr-BEA_nano_26 sample was ball milled during 15 minutes. The sample lost significantly in catalytic activity, going from a 2.1 to a 0.3 mmol_{GVL}/h.g_{cat} specific productivity after 2 hours (Figure 48).

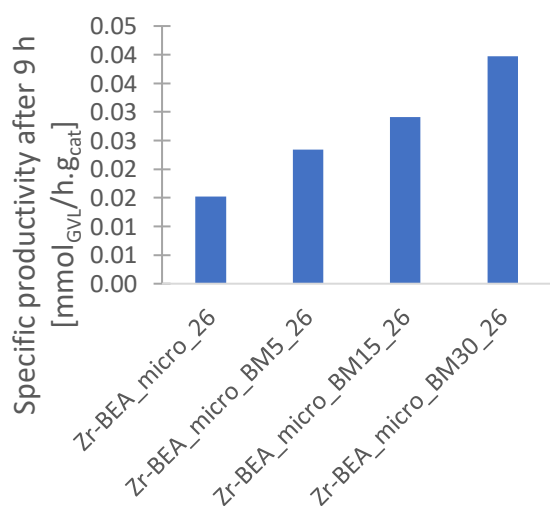


Figure 47. Summary of specific productivity (after 9 h reaction time) of Zr-BEA_micro_26 at different ball milling times (5, 15 and 30 minutes).

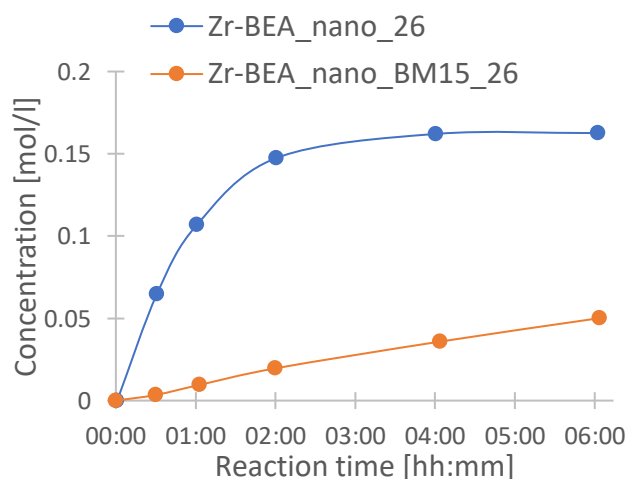


Figure 48. Catalytic performances of Zr-BEA_nano_26 and Zr-BEA_nano_BM15_26.

4. Discussion

4.1. Effect of the synthesis process and the Zr loading on Zr-beta nanocrystals

XPS and ICP-AES analyses demonstrated the dealumination and impregnation steps were successful for Zr-BEA_nano and Zr-BEA_comm. Moreover, the characterization results of the beta zeolite nanocrystals demonstrated the dealumination and the Zr impregnation steps could affect the crystallinity and the strength of the acid sites. The obtained results are further discussed below.

XRD patterns indicated that the crystallinity of the zeolite is preserved after dealumination as no amorphization of the sample could be demonstrated. The observed 0.11° increase in 2θ angle of the main diffraction peak is linked to the contraction of the beta matrix.⁶⁴ After Zr impregnation, a 0.14° increase in 2θ angle is observed, although a decrease is mentioned in the literature.⁶⁴ This observation could suggest the Zr is not incorporated in the zeolite matrix as expected. However, previous research in this ongoing PhD research demonstrated effective incorporation of Zr in the lattice by Fourier Transform Infrared spectroscopy – Attenuated Total Reflectance (FTIR-ATR).¹³

Textural properties obtained by N_2 physisorption indicated an increase in BET surface area from $600 \text{ m}^2/\text{g}$ before dealumination to $680 \text{ m}^2/\text{g}$ after dealumination, in line with previous findings.⁶⁴ However, no significant increase in micropore volume area ($0.20 \text{ cm}^3/\text{g}$) is observed although a $0.2 \text{ cm}^3/\text{g}$ increase had previously been reported in the literature. This result questions the significance of the increase in BET surface area observed after dealumination. After Zr impregnation, a decrease in BET surface area between 70 and $160 \text{ m}^2/\text{g}$ is observed depending on the amount of Zr impregnated. However, no correlation between Zr loading and BET surface area is observed. These results do not conform to previously obtained results, as researchers demonstrated that the BET surface area slightly decreases at increasing loading due to the blockage of micropores.⁶⁸ Hence, it is not confirmed that the dealumination or the impregnation significantly modifies textural properties of the catalyst.

NH_3 -TPD analyses before dealumination suggested the presence of two types of acid sites. The low temperature peak (around 215°C) is probably related to the Lewis acid sites whereas the high temperature peak (around 320°C) to the stronger Brønsted acid sites.⁶⁴ Subsequent dealumination caused an almost complete suppression of the acidity (Lewis and Brønsted) of the material. After Zr impregnation, only the Lewis peak is observed which could suggest a suppression of the strong Brønsted acid sites due to the suppression of the Al.

No global change in acidity is observed before dealumination and after impregnation, which is unexpected as dealumination has been reported to lower the overall acidity of the

catalyst, as it was also observed by Pyridine-IR during previous measurements conducted in the PhD research of Arnaud Detaillé.^{13 64}

Pyridine-IR measurements were performed on Zr-BEA_nano_26 and enabled to quantify an approximative ratio of 80 % Lewis acid sites and 20 % of Brønsted acid sites, comparable to the 8.4 Lewis/Brønsted ratio obtained by Wang and co-workers.³³ Lewis and Brønsted sites exhibited similar acid strengths as their ratio remained relatively constant at increasing desorption temperature. This similarity in acid strength could explain the absence of two distinct peaks in NH₃-TPD for Zr-BEA_nano_26 in contrast to calci_non_deal-BEA_nano. This suggests that although the dealumination and the Zr impregnation steps did not suppress all the Brønsted acid sites, it is still very effective in significantly reducing the amount of strong Brønsted acid sites.

The question that follows concerns the origin of this Brønsted acidity, as almost no Al should be present in the zeolite matrix, no Brønsted acidity (caused by the negatively charged Al atom which is compensated by a proton) should remain. Moreover, NH₃-TPD demonstrated a complete suppression of the acidity of the material after dealumination, which would suggest the remaining Brønsted acidity appears following the Zr impregnation step. The origin of this Brønsted acidity is in fact unknown, but could potentially be linked to negatively charged species which appear during the impregnation step (for example from the Zr precursor). The fact that weaker Brønsted acid sites remain on the catalyst is not an issue, considering the fact that Brønsted acidity catalyzes the conversion of the 4-hydroxypentanoic acid intermediate to GVL.¹⁴

Regarding the catalytic performances, an increase in productivity was attributed to an increase in Zr loading. An optimum Si/Zr ratio of 26 could be identified with a specific productivity of 4.05 ± 0.55 mmol_{GVL}/h.g_{cat}. At a higher Zr loading (lower Si/Zr ratio than 26), the Zr atoms did not seem to actively participate to the reaction and a decrease in productivity was observed. The obtained characterization and catalytic results do not enable to explain why a higher Zr loading results in a lower GVL productivity. Pore blocking by the increased Zr loading was not significant enough to be observed by N₂ physisorption, changes in Zr loading are not expected to change morphological characteristics (such as particle aggregation) and no correlation is observed between the Si/Zr ratio and the GVL selectivity.⁶⁸

Overall, the Zr-beta nanocrystals performed better than the commercial benchmarks and their productivity are among the highest reported in the literature (Table 13; entries 1-4).^{20 33 43} TOF and specific productivity per mass of Zr were calculated based on the Zr content measured by ICP-AES (Table 13; entries 5-7).

Table 13. Comparison of obtained catalytic performances for Zr-BEA_nano with reported performances of Zr-beta catalysts in the literature. The molar Si/Zr ratio obtained by ICP-AES is presented between brackets. (HT: hydrothermal, PS: postsynthetic, LA: levulinic acid, ML: methyl levulinate, EL: ethyl levulinate, 2-PrOH: 2-propanol, 2-BuOH: 2-butanol, 2-PeOH: 2-pentanol).

Entry	Synthesis	Si/Zr ratio	Substrate	Conversion [%]	GVL yield [%]	GVL selectivity [%]	TOF [s ⁻¹]	Productivity [mmol _{GVL} /g _{Zr} .h]	Solvent and H donor	Temp. Time
1	HT ³³	100	LA	100	96	96	-	30 (after 2 h)	2-PeOH	118 °C, 10 h
2	HT ²⁰	127	LA	98	-	>99	0.004 (-)	99 (-)	2-BuOH	120 °C, 11 h
3	HT ²⁰	127	ML	97	97	>99	0.026 (-)	213 (-)	2-BuOH	120 °C, 5 h
4	PS ⁴³	32	LA	99	84	85	0.008 (after 6 h)	60 (after 6 h)	2-PrOH	150 °C, 3 h
5	PS	14 (16)	EL	>99	89	89	0.002 (after 30 min)	78 (after 30 min)	2-PeOH	118 °C, 6h
6	PS	26 (29)	EL	100	88	88	0.006 (after 30 min)	203 (after 30 min)	2-PeOH	118 °C, 6h
7	PS	35 (36)	EL	100	89	89	0.001 (after 30 min)	150 (after 30 min)	2-PeOH	118 °C, 6h

Finally, though the repeatability tests of the catalytic performances were excellent, reproducibility issues were encountered during this master thesis and are discussed below.

A lack of reproducibility in catalytic performances was observed for Zr-BEA_nano_26 and confirmed by statistical analyses. This issue could be linked to the lack in reproducibility observed by XPS, because the lower Zr loadings (in comparison to the nominal Si/Zr = 26) obtained by XPS correlated with the lower productivity.

During this master thesis, the zeolites were recovered after impregnation by evaporation. Ideally, the Zr atoms should be incorporated in the sillanol nests produced by the removal of Al atoms, which had previously been demonstrated for commercial Zr-BEA zeolites by Arnaud Demaille using FTIR-ATR.¹³ However, when the zeolites are recovered by evaporation, all the non-coordinated Zr atoms are deposited on the surface or inside the pores of the catalyst and are recovered, which could potentially lead to reproducibility issues in the amount of loaded Zr as this depositing process is a bit unpredictable. The low Zr loading could explain why no significant changes in binding energy are observed in XPS for the detailed Zr spectrum, which makes it difficult to differentiate coordinated from non-coordinated Zr species. Recovering of the zeolites through filtration could possibly avoid the problem. Hence, spray drying of the nanocrystals into microparticles (if problems related to the use of a binder are solved) prior to the impregnation should make it easier to recover the catalyst by filtration.

4.2. Investigation of the potential of spray drying for the shaping of Zr-beta nanocrystals

The results demonstrated the initial GVL productivity is 78 % lower for Zr-BEA_SD_26 than for Zr-BEA_nano_26, which indicates the postsynthetic process of spray drying deactivates the parent material. Characterization of the catalyst enabled to give some insights to understand the loss in activity.

XRD patterns demonstrated Zr-BEA_nano_26 did not undergo phase changes or significant structural damages. Only minor changes in peak intensity and resolution for Zr-BEA_SD_26 compared Zr-BEA_nano_26 were observed, which is expected as spray drying processes should not change chemical composition and nature of the parent material.⁵⁹

Textural properties obtained by N₂ physisorption suggested that Zr-BEA_SD_26 is more aggregated than Zr-BEA_nano_26 due to the decrease in mesopore diameter size. A decrease in external surface area is also observed and could be caused by the aggregation of the particles or by the binder.^{53 70 71} Interestingly, no decrease in micropore volume is observed, although it is reported in the literature as the binder can block pores.⁵³ Hence, it is not clear whether the loss in external surface area is only due to the aggregation of the particles or due to the addition of the binder. Anyway, the loss in catalytic activity cannot solely be caused by the aggregation of the particles. Indeed, Zr-BEA_comm_26 is more aggregated than Zr-BEA_nano_26, but only demonstrated a 53 % lower productivity in comparison to a 78 % lower productivity regarding Zr-BEA_SD_26.

The lower catalytic performance of the spray dried sample could however be attributed to other factors than purely the aggregation of the nanocrystals. First, the use of the binder could dilute the active component of the sample, resulting in a reduction of the productivity per unit of mass. To demonstrate this effect, textural properties should be analyzed for Zr-BEA_SD with an increasing amount of binder used.⁷³ Second, the binder could cover the surface of the zeolite and could block the pores (although not observed in N₂ physisorption), which could lower the accessibility of the acid sites.^{72 73}

NH₃-TPD highlighted the lower amount of acid sites after spray drying. Ideally, the concentration in acid sites should remain constant although the use of a binder can change acidic properties of the material by creating or suppressing new acid sites, which might be the case here.^{53 72}

SEM analyses enabled to demonstrate the formation of spheres when the zeolites are spray dried, although the sample is rather heterogeneous as many spheres are broken. The use of more binder could potentially limit the attrition of the sample, but it is probably not desired as it could be the cause behind the acidity loss.⁷³

In fact, during the PhD research of Arnaud Detaille, H-BEA_SD were tested on the conversion of ethylene to ethanol and displayed enhanced catalytic performances in comparison to their nanoscale parent material. This suggests the spray drying is effective on the catalyst for other reactions. The limiting step is the impregnation step as the main difference between H-BEA_SD and Zr-BEA_SD is the impregnation of Zr. This impregnation step is performed after spray drying. As the binder may partially cover the surface of the catalyst, the impregnation of Zr is possibly not successful. This is also suggested by the detailed kinetics of non-deal-Zr-BEA_nano_18 (non-dealuminated and Zr impregnated sample), which demonstrated a similar profile as Zr-BEA_SD_26.

ICP-AES of both non-deal-Zr-BEA_nano_18 and Zr-BEA_SD_26 demonstrated Si/Zr ratios close to the nominal Si/Zr ratios. However, the low acidity observed through NH₃-TPD and the lower catalytic activities suggest these Zr sites are mostly non-active sites. To avoid that the binder hinders accurate impregnation of Zr in the beta matrix, the impregnation should be performed prior to the spray drying. The risk however is that the heating due to the impregnation could aggregate the particles, which would prevent spray drying. To further study the spray drying process, additional screening of critical parameters (inlet temperature, binder concentration, ...) should also be performed.

4.3. Investigation of the potential issue of diffusional limitations

The performed catalytic tests demonstrated the initial productivities of Zr-BEA_nano_26 and Zr-BEA_SD_26 varied according to the chain lengths of the levulinate ester and the secondary alcohol.

Catalytic performances are significantly increased when levulinates with a longer chain length are used. If diffusional limitations would exist due to the size of the levulinate, lower catalytic performances would be expected for longer levulinates. In addition, levulinates with a longer chain length have a greater viscosity which would expect to lead to lower catalytic performances as a higher viscosity would limit the mass transportation rate of the molecules.²

These above observations suggest other processes are involved in the increase of the specific productivity at an increasing chain length of the levulinate. Tabanelli *et al.* reported similar observations using ZrO₂ catalysts. They obtained better catalytic performances with EL than methyl levulinate and suggested the phenomenon could be attributed to the increase efficiency of ethanol as the leaving group (for the intramolecular cyclization of EL to α -angelica lactones) in comparison to methanol.⁷⁷

On the contrary, catalytic performances are decreased when longer secondary alcohols are used at 80 °C. This has been previously reported in the literature and would be caused by steric hindrance at low temperature (see Chapter 1.3.).²⁵ The activity is significantly

increased at 118 °C (from 0.2 to 2.1 mmol_{GVL}/h.g_{cat} for 2-pentanol) which suggests the steric hindrance is overcome at this temperature.

Regarding Zr-BEA_micro_26, an increase in ball milling time correlated with an increase in specific productivity. This increase can also be positively correlated with the external specific area obtained by N₂ physisorption (Figure 49). Together, this suggests an increase in external surface area increases the productivity, which would indicate diffusional limitations, at least to some extent, in the micropores.

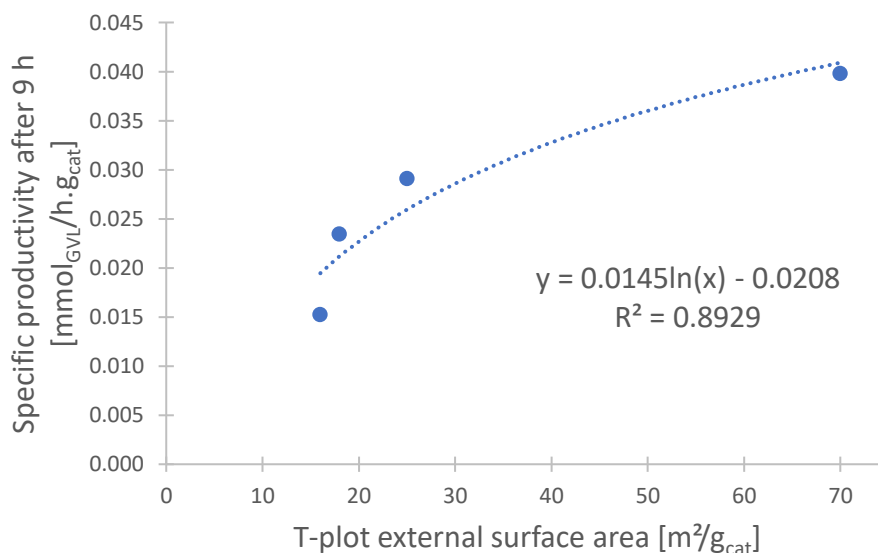


Figure 49. Positive correlation between specific productivity and external surface area for Zr-BEA_micro_26, Zr-BEA_micro_BM5_26, Zr-BEA_micro_BM15_26 and Zr-BEA_micro_BM30_26. The dotted line refers to the logarithmic relationship between productivity and external surface area.

These results are obtained for Zr-BEA_micro_26 which demonstrated extremely low activity (0.015 mmol_{GVL}/h.g_{cat} at a 3 % conversion after 9 hours). If it is assumed the reaction only occurs at the surface of the catalyst and not inside the micropores, it could be suspected the low activity is due to the extremely big crystal size of the catalyst which would lead to an extremely low external surface area, and consequently to an extremely low activity. However, the performed characterization, which are discussed below, demonstrated it was not the case.

XRD patterns demonstrated the beta framework was obtained for Zr-BEA_micro_26. However, crystal size calculations using the Scherrer equation yielded a lower crystal size than expected. 60 nm was obtained instead of the 1-2 μm expected from the performed synthesis protocol. However, caution is required for big crystal zeolites as the crystal size can be severely underestimated. Therefore, the Scherrer equation should not be applied to crystals bigger than 100 nm.⁷⁴ Moreover, the significant background observed on the XRD pattern would suggest the sample is partially amorphous.

Textural properties obtained by N₂ physisorption suggested the presence of micropores (type I isotherm) and possibly macropores (type II isotherms). After 30 minutes of ball milling, a possible decrease in micropore volume is suspected. A loss in micropore area and external surface area have been repeatedly reported in the literature when ball milling is used to reduce the size of zeolites.^{75 76} Moreover, the ball milled Zr-BEA_nano_BM15_26 demonstrated a significant loss in mesopore volume after only 15 minutes certainly due to a loss in crystallinity, whereas no effect on micropore volume was observed for Zr-BEA_micro_BM15_26. A possible explanation would be that the amorphous phase of Zr-BEA_micro_26 softens the shocks of the ball milling process.

NH₃-TPD demonstrated the ball milling did not change the acidity of Zr-BEA_micro_26. Only after 30 minutes of ball milling, a small acidity loss in amount and strength is observed, which correlates with the small loss in micropore area. It is not surprising as ball milling times have been reported to modify (and especially lower) the acidity of zeolites.^{75 76}

TEM images demonstrated a significant portion of Zr-BEA_micro_26 is amorphous, but bigger and regular structures (1-10 µm) were present. The additional SEM images suggested these structures are microcrystals rather than particulate aggregates. This observation could explain why lower crystal sizes were obtained by XRD than expected, as the Scherrer equation cannot be applied with accuracy to crystals bigger than 100 nm.

In summary, because DRX and TEM analyses suggested significant amorphization of the sample and NH₃-TPD demonstrated an overall low acidity of the catalyst, the low activity would probably more be related to issues in the crystallization process of the sample than to its low external surface. Hence, to confirm the results obtained at different ball milling time, it would be interesting to synthesize Zr-BEA_micro at a higher temperature (between 150 and 180 °C instead of 140 °C) to obtain a higher crystallization degree.

Finally, the fact that the consumption of EL follows first order reaction kinetics whereas the apparition of GVL does not, suggests diffusion limitations in regards to GVL and not the reactant. In addition, as it was previously discussed (see Chapter 1.6.3.4), molecules with longer chain length than EL did not demonstrate diffusional limitations. Steric hindrance in beta zeolites was mostly reported for cyclic molecules. However, the fact that at increasing external surface area of Zr-BEA_micro_26, a greater specific productivity is observed, is contradictory to the assumption that Zr-beta zeolite does not demonstrate diffusion limitations. These findings altogether suggest that diffusion limitations in Zr-beta zeolites could be caused by GVL, a cyclic molecule, rather than the levulinate.

5. Conclusion and perspectives

5.1. Conclusion

The overall aim of our ongoing research is to shape highly active Zr-beta zeolite nanocrystals through spray drying to obtain structured microparticles for the upgrading of ethyl levulinate to γ -valerolactone, using a secondary alcohol as hydrogen donor. In order to further our understanding of these nanocrystals, three features of the catalyst were investigated in this master thesis: the effect of the Zr loading, the effect of the spray drying process and the potential issue of diffusion limitations.

First, highly active Zr-beta nanocrystals were synthesized through a postsynthetic approach, by removing the aluminum of crystallized beta zeolites and subsequently incorporating zirconium. Overall, they performed better than commercial Zr-beta nanocrystals and their productivities are among the highest reported in the literature. An optimum molar Si/Zr ratio of 26 could be identified with a specific productivity of $4.05 \pm 0.55 \text{ mmol}_{\text{GVL}}/\text{h.g}_{\text{cat}}$.

In addition, the synthesis process was thoroughly investigated and the effects of dealumination and impregnation were analyzed by XRD, N_2 physisorption, NH_3 -TPD, XPS and ICP-AES. Dealumination and impregnation of the material both caused a slight crystallinity shift but neither of them significantly changed textural properties. NH_3 -TPD, XPS and ICP-AES analyses demonstrated a successful removal of Al atoms and impregnation of Zr atoms.

Second, the findings regarding the spray dried microparticles enabled to obtain a first impression on their potential for the upgrading of ethyl levulinate to γ -valerolactone. Ideally, the spray dried microparticles should have demonstrated similar activity to the optimized Zr-beta nanocrystals, but a 78 % decrease in specific productivity was observed. This indicates the spray drying process deactivates the Zr-beta nanocrystals, which could be linked to the use of a binder. As the binder could cover some parts of the surface of the catalyst and block pores, it could prevent the impregnation of active Zr species.

Third, the investigation of diffusion limitations suggested the cyclic structure of γ -valerolactone could cause steric hindrance in the micropores of the catalyst at 118 °C and atmospheric pressure. Regarding the reactants, the levulinate esters should not cause diffusion limitations (118 °C, p_{atm}) despite the small size difference between the micropores (5-6 Å) and ethyl levulinate (approximately 7 Å). Diffusion limitations related to the steric hindrance of the secondary alcohol were demonstrated at 80 °C, but were overcome at 118 °C.

5.2. Perspectives

This master thesis definitively confirmed the tremendous potential of Zr-beta zeolite nanocrystals for the upgrading of levulinates to γ -valerolactone. The next step would be to synthesize highly active spray dried zeolite microparticles for this particular reaction, based on the initial conclusions of this master thesis.

Further screening of the spray drying parameters (inlet temperature, binder concentration, ...) should certainly be performed. Spray drying should also be carried out after impregnation and additional characterization such as pyridine-IR should be performed to better understand the loss in acidity. XPS and diffuse reflectance UV-visible spectroscopy (DRUV) analyses could also enable to understand the impregnation of Zr and the problems related to the use of a binder.

Regarding the study of diffusion limitations, the experiment using the Zr-beta microcrystals should be replicated but with a higher crystallinity degree of the catalyst to confirm the obtained results. In addition, a screening at different reaction temperatures could be performed to investigate at which temperature the mass transport limitations are overcome.

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Shaping of Zr- β zeolite nanocrystals through spray drying for the upgrading of levulinates to γ -valerolactone

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This master thesis focusses on the upgrading of levulinate esters to γ -valerolactone, a green solvent and fuel additive, using Zr-beta zeolite *nanocrystals*. These *nanocrystals* were shaped into *microparticles* by spray drying to overcome practical issues related to the colloidal size of the nanocrystals (handling, recovery, reuse, ...). Three features of the catalyst were extensively studied during this master thesis.

First, screening of Zr loadings was performed to enhance the catalytic activity. Zr-beta *nanocrystals* with a molar Si/Zr ratio of 26 obtained the highest productivity with $4.05 \pm 0.55 \text{ mmol}_{\text{GVL}}/\text{h} \cdot \text{g}_{\text{cat}}$. Overall, the productivity of the catalyst is among the highest reported in the literature.

Second, the potential of Zr-beta *microparticles* obtained by spray drying of Zr-beta *nanocrystals* was investigated. A 78 % decrease in productivity was observed, which could be associated with the use of a binder covering the surface and blocking the pores of the catalyst, preventing subsequent impregnation of active Zr species.

Third, the potential issue of internal diffusional limitations was studied to demonstrate whether the levulinate esters mostly react on the *surface* of the catalyst or rather in the *micropores*. Based on the conducted experiments and on the literature, the levulinate ester should not cause diffusion limitations in the micropores. However, the catalytic results suggested potential mass transport limitations to some extent due to the diffusion of γ -valerolactone in the micropores.

In summary, this work enabled us to showcase the high catalytic activity of Zr-beta nanocrystals and to demonstrate potential issues regarding the spray drying process of nanocrystals and the diffusion of γ -valerolactone in micropores.