

Faculty of bioscience engineering

Preparation of nano-sized beta zeolites aggregated by spray drying for bioethanol conversion

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Abstract

In a context where finite fossil oil resources are depleting and environmental awareness is rising, it has become a priority to mitigate our dependence to petro-based chemicals. **Biomass upgrading** aims at developing bio-based platform chemicals, that can help reduce the consumption of fossil energy sources and lower our dependence to petroleum. Among these platform molecules, bio-alcohols are interesting alternatives to replace crude oil and coal as raw materials for olefins production. Particularly, the catalytic transformations of **bioethanol** into **ethylene and 1,3-butadiene** are one the most promising ways to produce such key building block compounds currently obtained from petrochemical industry. By aiming to develop heterogeneous catalysts active for bioethanol conversion by innovative methodology, this master thesis contributes therefore to sustainable development researches.

The materials developed herein are **beta zeolites (BEA)**. Their microporous nature implies the need of high surface-to-volume ratio and short diffusion path length, as the mass transfer is restricted inside these zeolite crystals. We therefore decided to synthesize nano-sized BEA particles. We were able to show that the synthesis method presented here allowed the obtention of the desired H-BEA structure, but in the form of well dispersed **nanocrystals** (in suspension) which are not available commercially.

In order to facilitate their recovery from the reaction media and further control their (potential) aggregation occurring upon thermal process, these nano-crystals were shaped into microspheres by **spray drying**, as such process allows fine control of the particle size and morphology.

On the one hand, the synthesized BEA were ionically exchanged to generate their H form (H-BEA), that was tested in ethylene production at low temperature (240 °C). It resulted that two of the three synthesized and tested H-BEA catalysts were significantly more active and selective to ethylene than a commercially available H-BEA. The highest ethylene productivity was obtained with H-BEA microspheres prepared by spray drying. By generating $4.89 [\text{g}_{\text{ethylene}} \cdot \text{g}_{\text{zeolite}}^{-1} \cdot \text{h}^{-1}]$, this catalyst stands among the most performant catalysts reported so far in terms of ethylene productivity.

On the other hand, to perform the ethanol to butadiene (ETB) reaction, the need of a bifunctional catalyst, capable of achieving simultaneously dehydrogenation and dehydration reactions, is highlighted in the litterature. Therefore, a fraction of the synthesized BEA was modified with Ta and Cu to generate **Cu-doped Ta(V)-single site BEA** catalysts. This was performed by applying postsynthetic method involving i) the dealumination of a pre-synthesized BEA ii) the subsequent Ta incorporation in the defect sites formed by the removal of Al and iii) a final copper (dry) impregnation. We managed to suggest that Cu-doped Ta(V)-single site BEA covered by Cu and additional Ta₂O₅ species were obtained using this method. Such catalyst, however, was not found efficient to produce butadiene from ethanol at 325 °C.

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1. Introduction

1.1. Biorefinery and biomass valorization

1.1.1. Definition and approaches of biorefining

In a context where finite fossil oil resources are depleting and environmental awareness is rising, it has become a priority to establish solutions which help to reduce the rapid consumption of the non-renewable fossil resources.(1) It is therefore important to mitigate our dependence to petro-based chemicals. For example, for the production of olefins, we have alternatives to hydrocarbon cracking. Among these alternatives, one of the most promising is the use of renewable bio-sourced compounds (such as bio-alcohols) that would replace crude oil or coal as raw materials.

A unifying concept, in this perspective, is that of the “biorefinery”, i.e. *an integrated concept aiming at full utilization of biomass, in which different fractions of biomass are converted in large-scale plants (economy of scale) or in small-scale units (economy of numbers) in an economically optimal product state.*(2) A biorefinery may produce several “low-volume, high-value” (fine) chemicals and a “low-value, high-volume” liquid transportation fuels. The high-value products enhance profitability while the high-volume fuels help to meet energy needs. This concept is illustrated in Figure 1.(3)

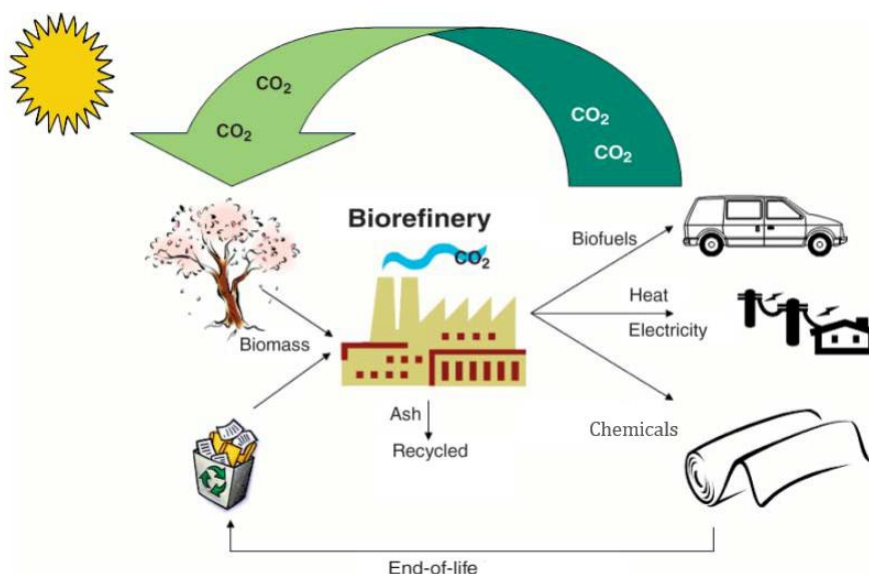


Figure 1 : representation of the proposed self-sustained integrated biomass zero-emission cycle, where the biorefinery uses biomass and waste, produces waste products (CO_2 and ash), both recycled for the production of biofuels, heat and electricity and chemicals. (3)

Such a biomass valorization targets biofuels as well as value-added chemicals via “platform chemicals”. These platform chemicals contain a high degree of chemical functionality (bear at least one functional group such as carboxyl, hydroxyl, carbonyl and aldehyde), which give them the capacity to be employed as building blocks in the synthesis of various chemicals and polymeric materials.(2)

However, in general these processes cannot yet compete economically with their fossil counterparts, because yields of target molecules are not maximized, or/and by-products often have a very low (or even negative) value. Biobased industrial products can thus only compete with petro-based products if the raw materials employed for their production are optimally exploited.(4)

In this context, heterogeneous catalysis plays a key role in development of biorefinery, as chemo-catalytic routes constitute one of the three approaches for exploiting biomass, along with the biocatalytic (enzymatic hydrolysis and fermentation) and thermal (pyrolysis) routes.(2,5) Catalysis allows a better utilization of primary resources as well as higher atomic efficiency, which is a key aspect of competitive chemical synthesis from biomass. To meet the challenge posed by the future increasing use of renewables, the catalytic conversion of platform molecules (produced by bioconversion of renewables) into bioproducts needs to be enhanced, by designing more active and selective catalysts.(2,5)

1.1.2. Biomass

The main biomass components are polysaccharides (such as cellulose, hemicellulose and starch), lignin, triglycerides, proteins, and various extractives.(5) Lignocellulosic biomass is the most promising renewable source of carbon, as it is widely available worldwide at a relatively low cost. It is typically composed of cellulose (40-50%), hemicellulose (25-35%), lignin (15-20%) and other compounds (such as proteins and fats).(2,4) A simplified structure of lignocellulosic biomass is presented in the Figure 2.(6)

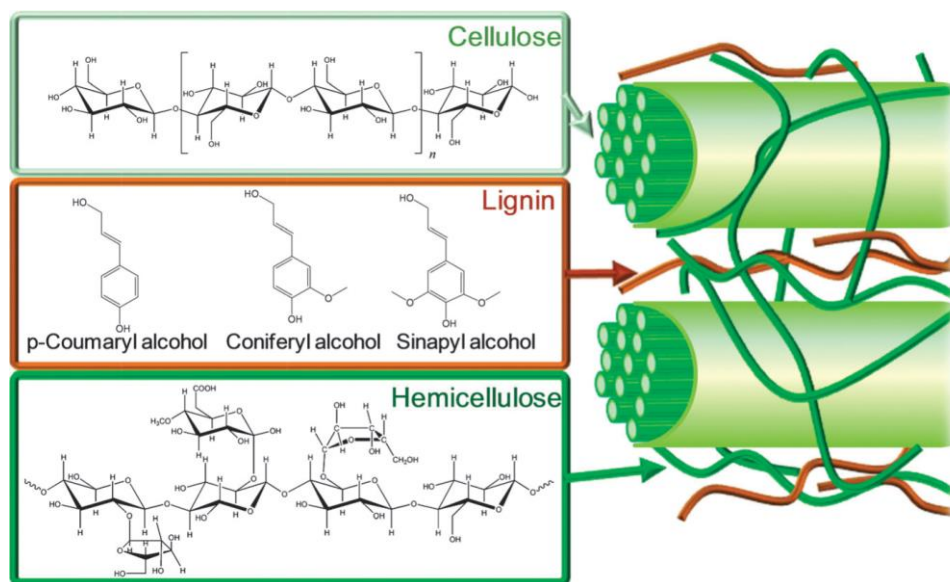


Figure 2 : Representation of the structure of lignocellulosic biomass and of its main components : Cellulose, hemicellulose and (the main building blocks of) lignin.(6)

As biomass components are highly functionalized and present an O/C ratio close to 0.8, biomass seems to be more suitable to produce oxygenated compounds like alcohols. Crude oil, on the other hand displays O/C ratios close to zero, as shown on Figure 3.(7) Therefore, it might

be more rational to produce unfunctionalized molecules from oil and functionalized molecules from biomass. Indeed, due to the oxygen-rich composition of carbohydrates, their conversion into renewable chemicals that preserve the functional groups is an advantage over the current petrochemical conversion routes.(5)

While oil has to be functionalized in a traditional refinery in order to produce oxygenated molecules, biomass has to be deoxygenated on the other hand.

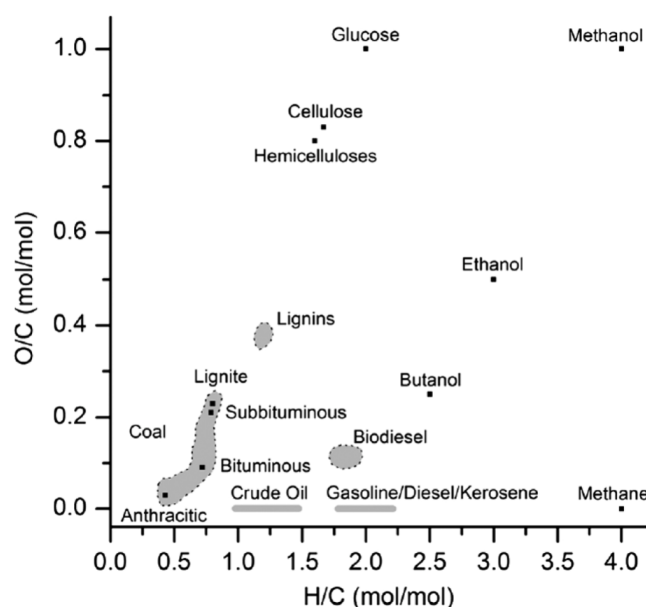


Figure 3: Inverted van Krevelen plot showing O/C versus H/C molar ratios of selected feedstocks and molecules.(7)

In fact, it has been shown that some oxygenated compounds such as ethanol and acetic acid can be produced at lower costs from biomass, as well as ethylene (that can be readily obtained by ethanol dehydration).(8) A comparison of relative prices for a range of some chemicals produced (in one or more steps) from either renewable or fossil resources is presented in Figure 4.(9)

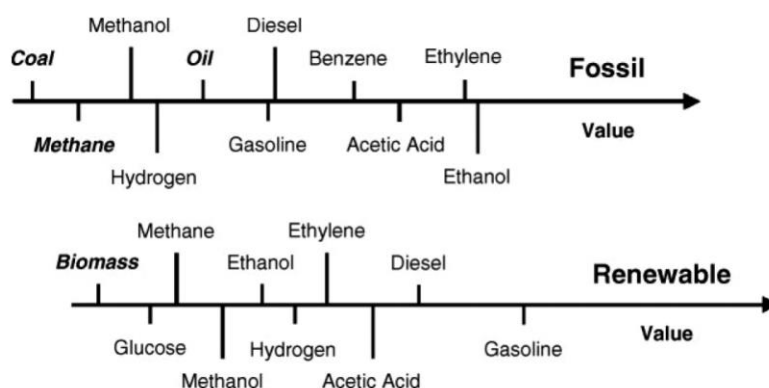


Figure 4 : Relative price scales for a range of selected chemicals produced from either renewable or fossil resources, with the raw materials shown in bold.(9)

Interestingly, Rass-Hansen et al. argued that the use of bioethanol to produce added-value chemicals might be more economically viable compared to its use in the transportation sector and could also generate higher CO₂ savings.(9)

1.2. Bioethanol

The catalytic reactions involving bio-alcohols are relevant regarding the development of a bio-based industry. Particularly, the transformations from ethanol are very attractive and widely studied. Indeed, bioethanol is a major bio-sourced chemical, listed among the revised top 10 of “most valuable biobased chemicals” from biorefinery carbohydrates by the US Department of Energy (DOE).(10) In fact, it meets all the criteria required in the screening which was performed to identify the most interesting platform chemicals. In other words, this study ensured that bioethanol displays (or is a):

- Extensive recent literature
- Multiple product applicability
- Direct substitute for petrochemicals
- High volume product
- Platform potential
- Industrial scaleup
- Existing commercial product
- Primary building block
- Commercial biobased product

1.2.1. Bioethanol production

Nowadays, 90 % of the ethanol on the market is derived from biomass.(11) The annual bioethanol worldwide production has significantly increased over the past years and reached more than 100 billion liters in 2013,(12) and it is expected to grow gradually (Figure 5).(13) In 2019, more than 128 billion liters of bioethanol were produced worldwide, of which more than 85% was dedicated as biofuel blending. The worldwide bioethanol production leaders are the United States, closely followed by Brazil.(14)

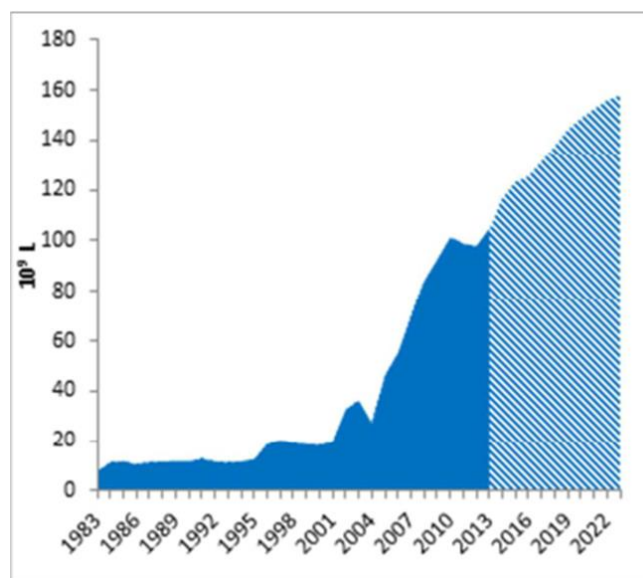


Figure 5 : Registred (until 2013) and projected (hatched area) worldwide bioethanol production over the years.(13)

Bioethanol can be obtained by fermentation from a wide range of biomass feedstocks, which can be classified according to the substrate they mainly contain. They can be divided into sugary (e.g.: sugar cane, sugar beets), starchy (e.g.: wheat, corn) and (ligno)cellulosic (e.g.: sugar cane bagass, wheat straw) feedstock.(15)

Ethanol from sugar and starch containing plants is readily available today. These feedstocks are also called 1st generation feedstocks, as they are characterized by the fact that only the edible parts of the plants (starch, sugar) are used for bioethanol production. Unfortunately, the number of candidate feedstocks is limited and their use competes with food supply.(16)

On the other side, 2nd generation feedstocks provide the opportunity to use other parts of the plants for bioethanol production: the ligno-cellulosic parts. The utilized ligno-cellulosic biomass comes from agricultural wastes (including those resulting from the 1st generation ethanol production), forest residues, municipal solid wastes (MSW), etc.(9,15) On the one hand, as this bioethanol production exploits nonedible biomass, it could be more interesting than the first generation bioethanol, on the economical, ecological and societal points of view. On the other hand, the cellulose and hemicellulose from these feedstocks have to be separated through a difficult process (either physical, chemical, physico-chemical or biological) called pretreatment,(4) and converted to sugar before the fermentation step. It makes the 2nd generation bioethanol production more challenging than the 1st one.(9,15)

Eventually, an emerging 3rd generation bioethanol technology allows the production from non-terrestrial plants or microorganisms like *algae* and seaweeds.(16)

It is expected that technologic and scientific progress will soon result in 2nd and 3rd generation processes being able to compete with actual processes and thus, provide more efficient and environmentally friendly ways to produce bioethanol from biomass.(16)

1.2.2. Applications of bioethanol – platform molecule

(Bio)Ethanol (EtOH) is already well-known as a biofuel and as additive to gasoline (ethanol blends) due to its interesting properties, such as i) its higher octane number than the one of conventional petrol (resulting in a fuel more resistant to uncontrolled combustions, called antiknocking fuel) and ii) its lower vapor pressure than gasoline (which limits risks of evaporative emissions).(15)

Apart from its biofuel applications, bioethanol is often defined as a platform chemical, as it serves as starting material to produce derivatives offering flexibility and potential to the biorefinery.(10) Furthermore, its production via fermentation is now well-established.(17) Bioethanol has the advantage compared to other biomass feedstocks, that it can be directly converted into “drop-in” chemicals,(7) as shown in Figure 6.(16) This means that bioethanol can be used to obtain some of the building block chemicals that are currently obtained from petroleum, such as ethylene, 1,3-butadiene and higher hydrocarbons and alcohols. Moreover, ethanol can also be oxidized to commodity and bulk chemicals such as acetic acid and ethyl acetate.(10)

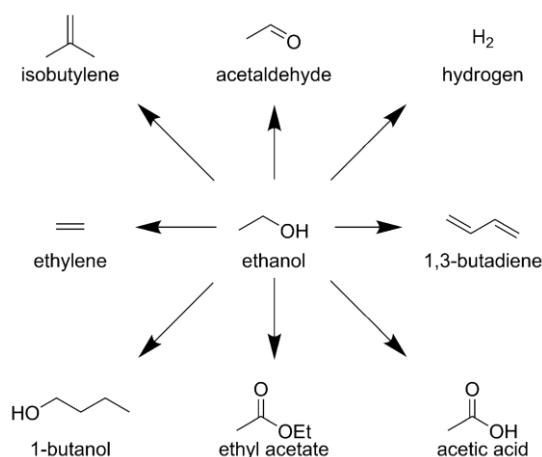


Figure 6 : Major bulk and drop-in chemicals obtained from ethanol.(16)

In the present master thesis, we will mainly focus on the conversion of ethanol to ethylene and butadiene, widely used chemicals in the polymer industry, from bioethanol.

1.3. Ethylene

1.3.1. Current global ethylene production

Ethylene is the most produced organic compound on Earth. Its worldwide production has been increasing over the years (Figure 7) and was reported to reach 150 million tons in 2017.(18) Moreover, it is expected that more than 200 million tons will be needed by 2025 to meet global demand.(19)

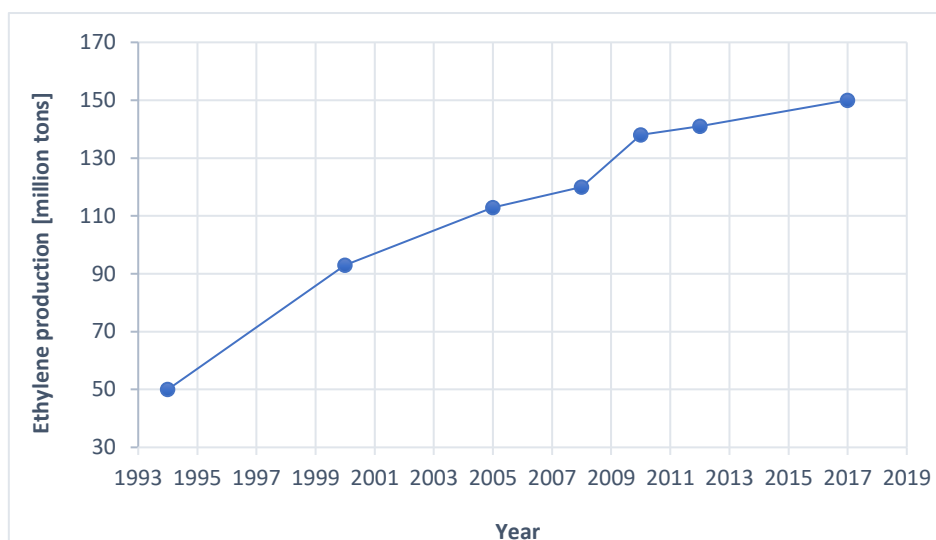


Figure 7 : Global ethylene production from 1994 to 2017.(19,20)

It is nowadays typically obtained from petroleum through thermal cracking of paraffinic hydrocarbons, mostly ethane and naphtha. This process is polluting and energy consuming as it is estimated that it is responsible for 8 % of the global energy consumption and the release of 180-200 million tons of CO₂ worldwide.(16,20) Indeed, in steam crackers, 1 – 1.6 t of CO₂ are produced per ton of ethylene, depending on the feedstock used for cracking. In addition, due to the high temperature pyrolysis, NO_x are produced when using conventional technology.(21) Ethylene production has been ranked as one of the most energy-intensive process in the chemical industry.(22)

Due to the significant CO₂ footprint and energy consumption of steam cracking processes, alternative technologies to produce ethylene have been re-evaluated. One of the most promising routes is the dehydration of bioethanol, as bioethanol offers production from renewable resources and as its production is increasing dramatically.(21)

However, it is noteworthy that it is currently not possible to produce all the required ethylene from renewable sources as the demand for ethylene worldwide is approximately three times the amount of ethanol produced nowadays.(9)

Demand for green ethylene could, nevertheless, be an important reason to further increase bioethanol production. Indeed, it has been estimated that the demand for bio-based olefins corresponds to 10% of the global polyethylene demand, while its supply presently (2013) represents less than 1%.(23) Table 1 compares bio-based and conventional petro-based ethylene production routes. It notably illustrates that ethylene can be produced at lower temperature and with higher selectivity from bioethanol than through steam cracking process, when using an appropriate catalyst, such as HZSM-5 zeolites (see section 1.3.3).

Table 1 : Comparison between bioethanol catalytic dehydration and steam cracking routes for ethylene production. The references are indicated in each case of the table.

	Bioethanol dehydration	Steam cracking
Feedstock origin	Renewable (21)	Non-renewable (21)
Feedstock price	Lower, Decreasing (24)	Higher, Increasing until 2014 (25)
Max. selectivity achieved at iso-conversion ($\geq 95\%$)	$\sim 99\%$ (26) *	$\sim 40\%$ (21) **
Process temperature range	200°C to 450°C (7,16,26)	[500-680]°C for inlet [775-850]°C for outlet (21)
Amount of generated biproducts	Low	High
Max. CO₂ emissions	~ 0.65 [t/t _{ethylene}] (21)	1.6 [t/t _{ethylene}] (21)
Max. energy requirements	$\leq 11 \times 10^9$ [J/t _{ethylene}] (21)	22×10^9 [J/t _{ethylene}] (21)

*: using HZMS-5 (300°C, Weight Hourly Space Velocity (WHSV) of 3 g_{EtOH}.g_{cata}⁻¹.h⁻¹), **: Taking butane as feedstock

The produced ethylene is exclusively used as a chemical building block, mostly in the production of polymers such as polyethylene (PE) (which represented more than 50% of ethylene demand in 2000), or polyvinylchloride (PVC), and to produce ethylene oxide and ethylene dichloride.(21)

As ethylene derived from biomass is identical to the petro-based one, it is easy to implement technically, as existing infrastructure and production chain can be used without being modified. This is the reason why it is often referred as a “drop-in” chemical.

1.3.2. Ethanol to ethylene (ETE)

Despite the simple chemistry one might expect for the catalytic dehydration of ethanol into ethylene, the careful tuning of catalysts properties as well as their time on stream stability are challenging requirements. As an example, a significant number of catalysts manage to achieve ethanol conversion and ethylene selectivity >90% but only a few of them are able to resist well to coke deactivation and perform stable performance.(7,17,23)

Two main reactions can occur in parallel during catalytic dehydration of ethanol: i) ethylene and ii) diethylether (DEE) (the main by-product) formation (Figure 8).(16,27)

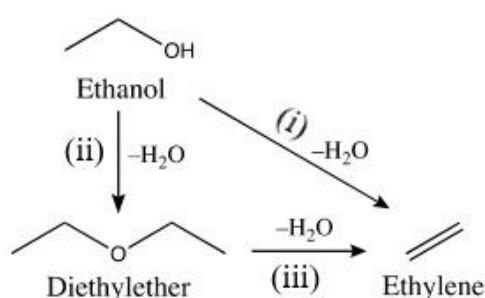


Figure 8 : Possible dehydration reactions from ethanol to ethylene.(12)

In the typical temperature range of the process ethylene formation is endothermic whereas diethylether formation is exothermic (Figure 9).

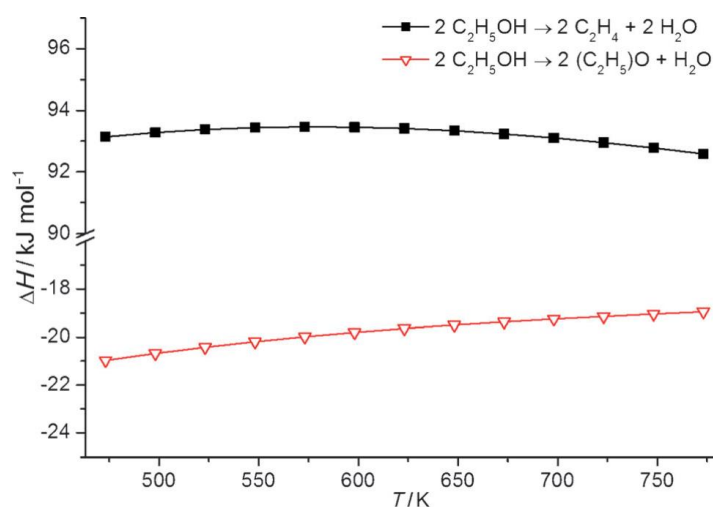


Figure 9 : Temperature profile of enthalpy of ethylene (black) and diethylether (red) formation from ethanol.(16)

The main challenge is therefore to design catalysts able to perform selectively the target reaction at low temperature. Indeed, when only taking Le Chatelier principle and enthalpy into account, one can expect that ethylene formation should be favored with increasing temperatures.

DEE may be subsequently converted to ethylene and could be therefore considered as a reaction intermediate. So that, in general, when the reaction is carried out at low temperatures (between 150 and 300 °C), DEE is observed as a product, but at higher temperatures, DEE is further dehydrated into ethylene (reaction iii on Figure 8)).(27–29)

1.3.3. Catalysts for ETE

Industrially, the gas-phase dehydration ethanol is carried out over solid acid catalysts, among which γ -alumina and HZSM-5 zeolite are the most widely used and thus considered as benchmark catalysts.(16,17)

On the one hand, γ -alumina features a moderate activity, low degree of coking and therefore a relatively good stability with time on stream (TOS). However, it is necessary to apply fairly high temperatures (300–500 °C) in order to achieve reasonable ethylene productivities and yields (~80%).(17,26)

On the other hand, H-ZSM-5 zeolite is a highly active catalyst in ethanol dehydration and features higher ethylene selectivity and yields ($\geq 98\%$ reported), at lower temperature (in the 250–400°C temperature range) than alumina.(17) However, the strong Brønsted acid sites (i.e. sites that are able to easily exchange protons) present on this catalyst also promote ethylene oligomerization and consequently, coke deposition. It results in poor stability, as its

deactivation occurs relatively fast.(26) Alumina remains therefore as the traditional catalyst for ethanol dehydration on an industrial scale.(16)

In addition to these two benchmarks, a large variety of catalysts has been tested for this reaction. Heteropolyacids and their salts,(30,31) amorphous silica-alumina (ASA),(17,32) transition metal oxides,(33) silicoaluminophosphates (SAPO),(26) other zeolites (29,34,35), and even hybrid metallosilicate catalyst can be pointed out as other frequently studied catalysts.

Zeolites are among the most promising catalysts for industrial ethylene synthesis from bioethanol, since they are more selective than alumina and catalyze the reaction at much lower temperatures. Moreover, zeolites are commercially available, widely used in laboratories and in numerous industrial processes, including the traditional refinery sector. Several studies reported on the high catalytic activities of different zeolites such as beta (BEA), faujasite (FAU), ferrierite (FER) and mordenite (MOR) for ethanol dehydration.(29,34,36) We therefore decided to employ zeolites as catalyst in the present master thesis. Yet, there are questions to be addressed related to the zeolite stability.(7) Further in this document, a section 1.5.) is specifically devoted to the presentation of these materials.

Table 2 summarizes the performances of selected catalysts, with a focus on zeolites, in the ETE route. It is noteworthy that catalytic stability performances were not considered in this table. The selection of the catalysts included in this table is based on the conditions in which the dehydration reactions were performed. Indeed we only selected catalytic performances obtained at medium temperatures (i.e. $T \leq 350\text{ }^{\circ}\text{C}$)¹ and using the same reactant as the one used in this master thesis (i.e. very concentrated (absolute) ethanol). We also wanted the authors to mention either concentration of ethanol in the gas feed (% mol. EtOH in N₂) or the WHSV [$\text{g}_{\text{EtOH}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$] in their study.

¹ Except for one of the two benchmarks ($\gamma\text{-Al}_2\text{O}_3$, 450 °C).

Table 2 : Performances of selected catalysts in ETE reaction. Note that X, S and Y represent respectively the conversion, the selectivity and the yield while Prod. is the productivity, expressed in $[g_{\text{ethylene}}.g_{\text{cat}}^{-1}.h^{-1}]$.

Catalyst		Temp. [°C]	% mol. EtOH (in N ₂)	WHSV [h ⁻¹]	EtOH X (%)	Ethylene S (%) Y (%) Prod.			Ref.
Zeolite	H-ZSM-5 (Si/Al=25)	300	/	3	95	98	94	1.71	(26)
Al ₂ O ₃	γ-Al ₂ O ₃	450	/	3	86	92	79	1.44	
Zeolite	SAPO-34	350	/	3	91	94	86	1.57	
Zeolite	Ni-SAPO-34	350	/	3	93	99	92	1.69	
Zeolite	H-ZSM-5 (Si/Al=15)	240	4,4	1.1 17.5	100 93	91 84	91 78	0.61 8.34	(17)
ASA	16Si-Al-Ac-T*	240 275	4.4	1.1 2.34	86 94	57 98	48 92	0.32 1.31	
ASA	SA Comm. (Si/Al=16)	240 275	4.4	1.1 1.1	65 81	12 44	8 35	0.05 0.24	
HMS **	Al-8SiPhSi- Et*	275	4.4	1.1	91	89	80	0.54	(37)
ASA	Al-16Si-Et*	275	4.4	1.1	84	95	80	0.54	
Zeolite	H-FAU (Si/Al=20)	350	25	15	97	82	80	7.27	(34)
Zeolite	H-BEA (Si/Al=11)	350	25	15	97	84	81	7.44	
Zeolite	H-MOR (Si/Al=10)	200	7.9	1.43	77	90	70	0.61	(29)
Zeolite	H-Y (Si/Al=2.5)	250	7.9	1.43	80	47	38	0.33	
Zeolite	H-BEA (Si/Al=12.5)	250	7.9	1.43	92	91	84	0.73	
Zeolite	H-USY (Si/Al=15)	250	7.9	1.43	80	40	51	0.44	

*: Samples prepared by non-hydrolytic sol-gel (NHSG), **: Hybrid Metallosilicate

As evidenced in Table 2, the highest ethylene productivities are obtained with zeolites, more precisely with H-ZSM-5 (low temperature) and H-BEA and H-FAU (higher temperature).

1.4. Butadiene

1.4.1. Current global butadiene production

1,3-butadiene (BD) is one of the most important bulk chemicals produced in the petrochemical industry.(13) It is typically used in the polymer industry (Figure 10 (38)), mostly as a building block for the production of styrene-butadiene rubber (SBR) and polybutadiene rubber (PBR), widely employed in the pneumatic tires and rubbers industries. Acrylonitrile-butadiene-styrene resins (ABS), styrene-butadiene latex (SBL) are also important products

obtained from butadiene. Among the other products mainly synthesized from BD, one can cite chloroprene rubber and adiponitrile, a precursor of nylon 6-6.(16)

Butadiene market share - 2016

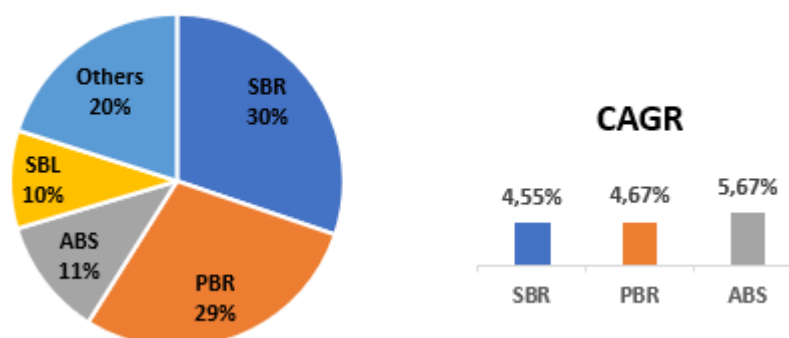


Figure 10 : Butadiene market share and Compound Annual Growth Rate (CAGR) of SBR, PBR, ABS in 2016.

The global butadiene production reached 12 million tons in 2015 and tends to grow gradually,(13) expecting to reach 16 million tons by 2021.(38)

Currently, ~95% BD is produced by the steam cracking of paraffinic hydrocarbons into light olefins, as a by-product of ethylene production (31.5% yield for ethylene, 4.5% for BD).(20,21) As mentioned earlier, this process is very polluting, environmentally stressful and requires huge amounts of energy.(16,20,21) From both environmental and economic perspectives, it is therefore of interest to develop more sustainable alternative than this greenhouse gas-emitting fossil fuel-based process to produce butadiene. One well-known pathway to produce BD from a renewable source uses (bio)ethanol and is commonly named ethanol-to-butadiene (ETB) reaction.

1.4.2. Ethanol to butadiene (ETB)

1.4.2.1. Lebedev and Ostromislensky processes

Historically, ETB was linked to two main industrial processes: the Lebedev process and the Ostromislensky process.(12,39,40) On the one hand, the Ostromislensky process uses a mixture of gaseous ethanol and acetaldehyde to produce butadiene. As acetaldehyde has first to be generated in a separate reactor by partial ethanol dehydrogenation, it is therefore denominated as the “two-step” process. On the other hand, the Lebedev process refers to the gas-phase conversion of ethanol into butadiene in one reactor, therefore called the “one-step” process.(39,40) Even though The Lebedev process leads generally to lower BD productivity than the two-step route, it is considered more attractive on an environmental and economic point of view.(12,13,41) Indeed, it requires only one reactor and a simpler feed (that contains only ethanol) compared to the Ostromislensky process, that requests two reactors (one for the acetaldehyde generation and one for the butadiene production) with two different catalysts.(16,41) For this reason, we will focus on the Lebedev process in this master thesis.

1.4.2.2. Mechanisms and generated by-products

Currently, mainly two reaction mechanisms, proposed by Kagan *et al.* and Cavani *et al.*, are generally proposed for butadiene formation from ethanol.

In the so-called “Kagan mechanism”, ethanol undergoes five main reactions (Figure 11) to obtain butadiene, following the global reaction (i): first, (ii) non-oxidative dehydrogenation of ethanol to generate acetaldehyde (AA); (iii) condensation of two AA molecules into 3-hydroxybutanal (acetaldo); (iv) acetaldo into crotonaldehyde (v) Meerwein-Ponndorf-Verley (MPV) reduction involving another ethanol molecule to produce crotyl alcohol and AA; Finally, (vi) crotyl alcohol dehydration to BD.(41)

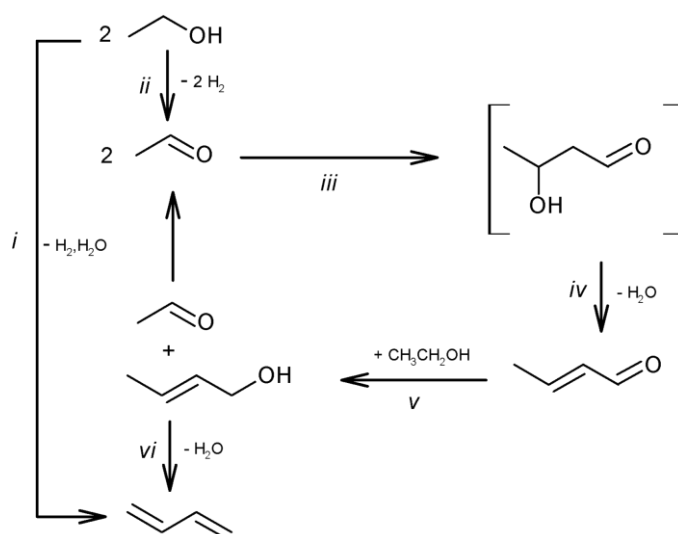


Figure 11 : Overall (i) reaction and (ii), (iii), (iv), (v), (vi) reaction pathway of ethanol conversion to BD, proposed by Kagan *et al.*(41)

This mechanism is generally reported as the most likely reaction pathway for ETB reaction involving acidic catalysts.(16,40)

However, some issues were pointed out by Cavani *et al.* (2016) when working with basic MgO-based catalysts.(23) As a result, it led them to propose a new reaction pathway, involving deprotonated ethanol (carbanionic) species.(40)

Nevertheless, both mechanisms involve dehydration and dehydrogenation steps and thus highlight the requirement of a bifunctional catalyst system, possessing well-balanced acid/base and redox properties in order to reach high butadiene yields. In other words, bifunctional catalysts featuring both acid sites for dehydration and metallic clusters/nanoparticles for dehydrogenation are needed to complete the direct conversion of ethanol into BD and limit the by-products formation.(12)

Figure 12 shows the complete network, including likely formed by-products, of the direct conversion of ethanol into BD according to the Kagan mechanism. It is noteworthy that an excessively acidic catalyst will mainly produce ethylene and DEE, and if the dehydrogenation function is too weak, the production of acetaldehyde will be low, resulting in poor butadiene

yield. On the other hand, catalysts with strong dehydrogenation activity and poor acidity will produce large amounts of acetaldehyde, but will not be able to catalyze the next steps of crotonaldehyde formation, also resulting in low butadiene yields.(39) In the ETB reaction, the challenge is therefore to design catalysts with well-balanced dehydration and dehydrogenation activities.

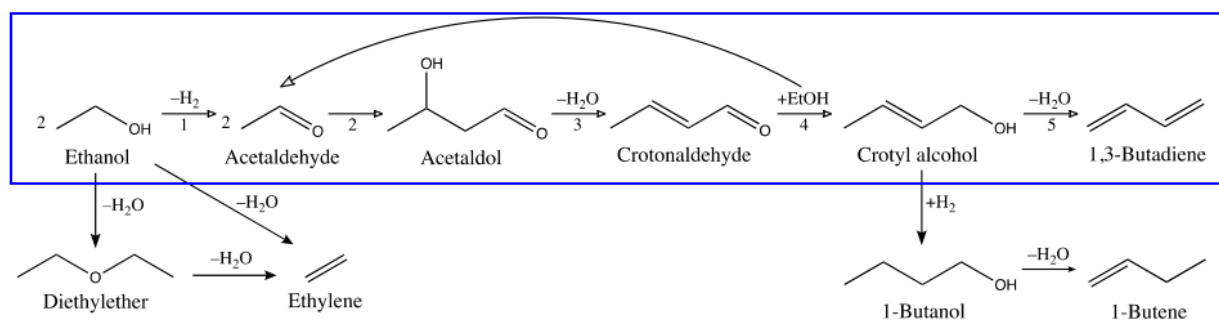


Figure 12 : Kagan mechanism showing the direct conversion of ethanol into butadiene (highlighted in blue) as well as the possible by-products generated.(12)

Finally, the feasibility of ETB reaction as well as its most favorable operational window have been assessed by Angelici et al.(16) by determining Gibbs free energy-temperature profile. It appeared the reaction becomes favorable at temperatures above 150°C and that the optimal temperature range for the different reported examples of this reaction didn't exceed 425 °C.(40)

1.4.3. Catalyst for ETB

As previously mentioned, the challenge for the design of optimal catalysts is the understanding of the optimal catalytic functions (acid/base/redox), the “structure-catalytic performance” relationship and the balance between them.(16,40)

Several catalytic systems have been proposed, which initially mostly featured i) mixed oxides with either acid, basic or redox properties (e.g., Al₂O₃-ZnO, MgO-SiO₂) (41) and ii) supported catalysts, mainly silica-supported Lewis acidic metal oxides (e.g., Ta₂O₅/SiO₂, ZrO₂/SiO₂), promoted with metals known for their redox properties, like Ag, Co, Cu, Zn or Fe.(12,40,42,43)

During the second World War, an extensive library of catalysts was compared, showing that mainly fourth and fifth-group elements active as were Lewis acid sites active when combined with silica. It resulted that, when supported on silica, tantalum oxide alone was the most active in the two-step process, while the binary catalyst Ta-Cu figured among the best catalysts in both routes.(16,40) The activity of tantalum compounds (tantalum oxide here) in ETB reaction was thus demonstrated. As it appears to be the most active of IV and V group elements when supported on silica, we decided to mainly focus on Ta-based catalysts.

Recently, microporous BEA zeolites and mesoporous MCM-41 were investigated as alternatives to a silica to support for Ta (doped with Ag or Zr).(43) At equal amounts of Ag and

Zr, the Ag-Zr-BEA was found to be most active catalyst, due to the higher dispersion of active sites (isolated Zr(IV) sites) in the Zr-BEA catalyst.(44) Subsequently, the nature of Zr-BEA active sites was further investigated (45) and BEA became the support of choice for ETB reaction.(40) Therefore, and as we planned to work with zeolites (see section 1.3.3), we pushed further our researches towards BEA-based catalyst.

Various BEA-based catalysts were therefore investigated for the ETB reaction, notably monofunctional ones including the Lewis acidic Nb(V) and Ta(V)-single site beta zeolites (named respectively Nb-BEA (44) and Ta-BEA (46)), Y-BEA but also redox clusters containing BEA (Cu-BEA and Zn-BEA),(47) all prepared by a two-step postsynthesis method. Nevertheless, the catalytic performances of these catalysts in the one-step process sat under average when compared to many of the recent reported systems, highlighting again the requirement of a bifunctional catalyst.(40) However, remarkable BD selectivity was achieved using the Ta-BEA in the two-step process. (46)

Consequently, further investigations on bifunctional BEA catalysts were performed, including Ta-based ones (Ta-BEA) promoted with Ag, Cu or Zn.(48) A summary of the performances of selected modified BEA (and one TUD-1) zeolites for the Lebedev route is presented in Table 3. The catalysts selected in this Table were all BEA-based catalysts (except the most productive one, that is a TUD-1 based catalyst) with either Ta, Zr or Y as Lewis acid site and with Zn, Cu or Ag as promoted redox metal.

Table 3 : Performances of selected BEA-based (and of one TUD-1-based) catalysts for ETB reaction in one-step. Note that X, S and Y represent respectively the conversion, the selectivity and the yield while Prod. is the productivity, expressed in $[g_{BD}.g_{cat}^{-1}.h^{-1}]$.

Catalyst (M1x)-M2y- Support (x, y in wt%)	EtOH	TOS [h]	WHSV [h ⁻¹]	Temp. [°C]	AA	Ethylene	BD			Ref.
	X (%)				S (%)	S (%)	S (%)	Y (%)	Prod.	
Monofunctional										
Ta1-BEA	13	4	0.5	325	33	28	16	2	0.01	(48)
Zn5-BEA	81	1	1.3	350	33	14	33	27	0.21	(47)
Cu5-BEA	93	1	1.3	350	44	44	1	1	0.01	(47)
Bifunctional										
Ag1-Ta1-BEA	83	4	0.5	325	23.9	8	63	52	0.15	(48)
Cu1-Ta1-BEA	88	4	0.5	325	15.0	3	73	64	0.19	(48)
Zn1-Ta1-BEA	52	4	0.5	325	22.7	17	43	22	0.06	(48)
Ag1-BEA+Ta-BEA *	58	4	0.5	325	16.0	12	46	27	0.08	(48)
Ag1-Zr1.5-BEA	30	3	0.64	320	/	4	64	19	0.07	(43)
Zn6.5-Ta10-TUD-1	94	3	5.3	400	18	10	73	69	2.13	(49)
Zn6.5-Ta10-BEA	95	3	5.3	400	25	8	59	56	1.74	(49)
Cu5-Y5-BEA	50	1	1.3	350	0	0	19	0.1	0.07	(47)
Zn2-Y8-BEA	90	1	0.3	330	0	12	81	73	0.12	(47)
	82		7.9	400	7	12	63	52	2	

*: mechanically mixed catalysts

It can be pointed out that, to date, the most productive catalytic system for BD production is obtained by combining Zn(II) species either with Ta(V) or Y(III) single-sites into a mesoporous TUD-1 or a microporous BEA zeolitic framework, at 400°C.(47,49) However, fairly high loadings (2 to 6.5 wt% for Zn, 8 wt% for Y and 10 wt% for Ta) of these metals seems to be required. Another interesting catalyst resulting from the doping of Ta-BEA zeolites with Cu(II) clusters displays high BD selectivity at lower temperature (325°C). Despite the lower BD productivity reported for this catalyst, the fact that only low metal loadings (1 wt%) have been tested yet make him promising. Moreover, at equal metal loadings and in the same experimental conditions, it displays higher BD yield and selectivity than the Zn and Ag doped Ta-BEA.

Therefore, we decided to focus, in the present master thesis, on BEA zeolites modified to i) contain Ta(V)-single sites and Cu(II) clusters for the ETB reaction but also to ii) obtain H-BEA for the ethylene synthesis.

1.5. Zeolites, BEA zeolites and nanosized BEA zeolites

Zeolites are crystalline microporous aluminosilicate materials displaying periodic one-to-three dimensional frameworks, well-defined porous structures (with pores diameters in the range of 0.3 to 2 nm), (50) as well as remarkable thermal and chemical stability.(51) The framework structure contains intracrystalline channels (interconnected voids).

These aluminosilicates are typically negatively charged, as they are made of both SiO_4 and AlO_4^- tetrahedra in given proportions (Si/Al ratios), linked to each other by common shared corner oxygen atoms.(50) Therefore, their intracrystalline porosity hosts a variety of charge-compensating (extra-framework) cations, such as Na^+ , K^+ , etc. These cations are mobile and can undergo ion exchange, (50,52,53) which can provide chemical functionalities for the interaction with appropriate guest molecules.(53) The acidity of zeolites can thus be tuned as it will tend to increase with increasing Si/Al ratios, if exchanged with protons.

Zeolites have found wide range of applications in many industrial fields, as they are ubiquitous in petrochemical processes, (52,54) and rising for the transformation of biomass-derived molecules. (55) Typically, they are used as efficient catalysts, adsorbent and ion exchangers.(51) Up to now, more than 200 types of zeolites, which differ from each other by their structure, pore size and composition have been identified and synthesized by hydrothermal routes. (55)

1.5.1. BEA zeolites

1.5.1.1. Structural features

Beta zeolites (BEA) are a family type of zeolites first described by Mobil Oil Corporation in 1967.⁽⁵⁵⁾ Their molecular structure was, however, only proposed later (1988) by Newsam et al. thanks to a combination of characterization technics including electron microscopy, electron diffraction and powder X-ray diffraction.⁽⁵¹⁾ It consists in “two sets of perpendicular channels, which intersect to form a three-dimensional array of cages that have three 12 membered-ring apertures”.⁽⁵⁴⁾ These apertures display diameters of 5.6 Å x 5.6 Å and 6.6 Å x 6.7 Å (Figure 13).^(29,56)

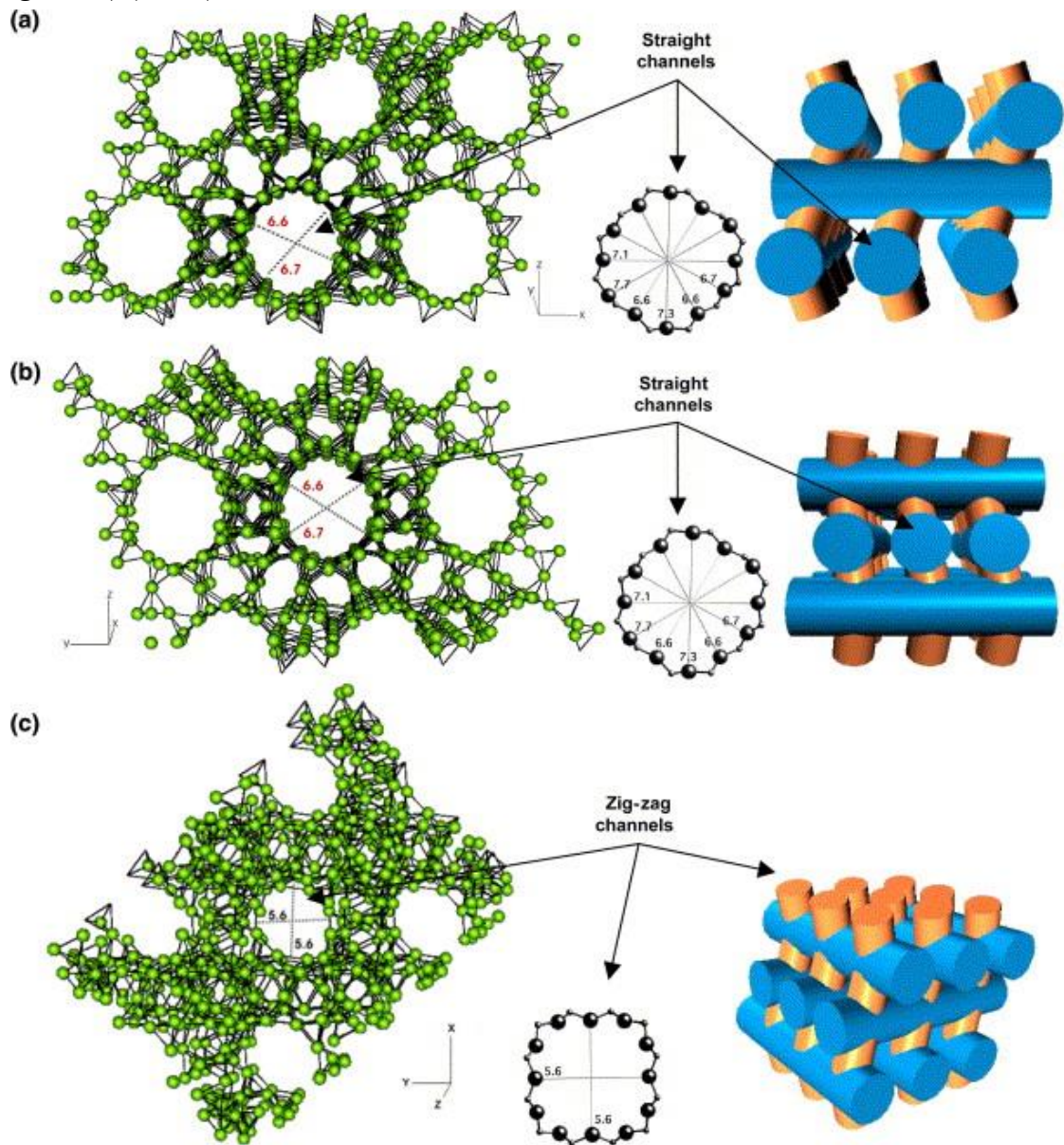


Figure 13: Stereographic drawings and perspective views of BEA zeolite viewed along axis (a) [010], (b) [100] and (c) [001]. Pore diameters are showed in Å. The spheres represent the oxygen atoms and the tetrahedron around which surround the Al or Si (T)-site. The cylinders on the right represent the channels of the BEA zeolite.

BEA can thus be classified as a medium (29) to large pore zeolite with a 12-ring structure.(51) This is similar to FAU, Y and MOR type zeolites, but in addition, BEA zeolite display a more intricate architecture due to the presence of two different types of channels.(56)

Typical BEA zeolites display high specific surface areas ranging from 400 m²/g to 750 m²/g. Micropore volume is consistently estimated around 0.15-0.20 cm³/g.(55,57,58)

1.5.1.2. Nano-sized zeolites,

Despite the fact that BEA zeolite are ranked among the medium-to-large pore zeolites, their texture is still characterized by micropores (5-7 Å of diameter). Therefore, mass transfer is restricted inside the zeolite crystals and only a small proportion of the materials (at the external surface) is effectively available for catalytic activity. Indeed, only a few reactant molecules are able to reach the active sites as diffusional constraints increase with decreasing pore radii ($R_{\text{pore}} \geq 7 \cdot R_{\text{molecule}}$ can be taken as general reference for a non-limited diffusion through a pore).(59) As a result, most of the zeolite's internal surface is rendered unavailable and so, useless.

Nevertheless, it is possible to increase the proportion of available (i.e. external) surface area by reducing the particle size (as decreasing particle sizes lead to higher (external/internal) surface area ratios). Therefore, it is interesting to develop nano-sized zeolites (Figure 14), in order to benefit from the large available (external) surface area and the shorter diffusion path length to active site offered by nanoparticles (<100 nm).(52,58) Note that another well-known way to overcome the mass transfer limitation mentioned below is to generate mesoporosity, i.e. pores displaying diameters larger than 2 nm.

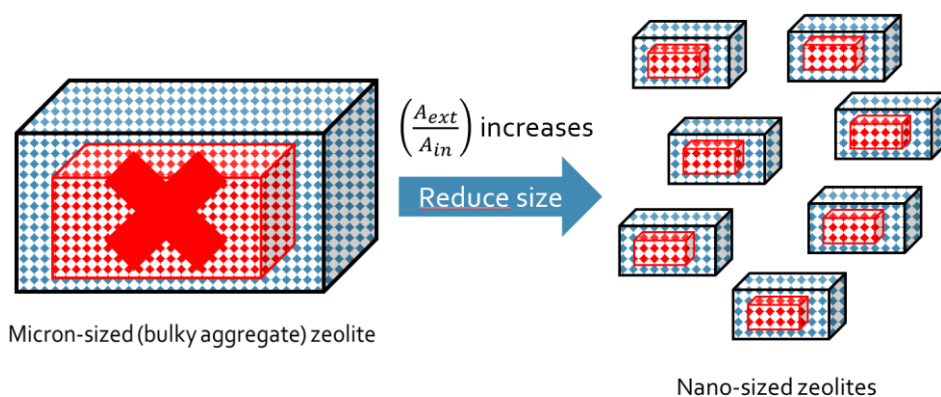


Figure 14 : Schematic representation of a bulky aggregate zeolite fragmented into nano-sized zeolites. The latter display higher external surface area over internal surface area (in red, unavailable for catalysis) ratios with respect to the former.

1.5.1.3. BEA and nano-sized BEA synthesis

Zeolites are usually obtained by hydrothermal crystallization of a gel. The reaction medium contains: (i) a source of framework elements $T = \text{Si}, \text{Al}$, (ii) mineralizing agents OH^- , F^- , (iii) inorganic cations and/or organic species, called structure-directing agent (SDA), (iv) a solvent (water). Generally, their synthesis occurs in a basic medium at temperatures below 200°C and

low pressures (in autoclaves, with autogenous pressure < 20 bar), for variable times ranging from few hours to several days.(60)

Alkali metal cations (hydroxide route) or fluoride media (fluoride route), along with tetraethylammonium hydroxide (TEAOH) as SDA, are generally employed for BEA and nanocrystalline BEA zeolites synthesis.(61–64) These two routes both impact the synthesis and have several different drawbacks. For example, the former decreases crystallization kinetics and influences the nature of phases obtained,(61) while the latter tends to generate bigger crystals and is hazardous both for human and environmental health.(62) Apart from these two (Na^+/Si and F^- presence in the medium), other important variables (i.e. the temperature, the Si/Al ratio and H_2O and TEAOH content) can influence key parameters of the crystallization, as shown in Table 4. We notably observe that higher Si/Al ratios tend to decrease the crystallization time and to generate bigger crystals. These same effects are also observed when operating at higher crystallization temperatures. Moreover, it is evidenced that the higher the TEAOH content, the lower the crystallinity. Eventually, higher water content in the medium often implies higher crystallization time and leads to bigger crystal.

Table 4 : Effect of an increase in selected experimental conditions variables on important crystallization parameters (crystallinity, obtained crystalline phase, time and crystal size).

	Crystallinity (%)	Crystalline phase	Crystallization time	Crystal size
+ Si/Al	+ (61)	To ZSM-12 if too high (64)	- - (61–63)	+ (61–63)
+ TEA⁺/Si	- (61)	Not reported	+ , - (61,65)	/ (65)
+ H₂O/Si	/ (61)	Not reported	+ (61,62)	+ (61)
+ Temperature	Optimal range ~[140-180°C] (61–63)	Amorphous if too low, to ZSM-5 if too high (61)	- (61)	+ (63)
+ Na⁺/Si	- (61)	To ZSM-5 if too high (61)	+ (61)	+ (64)
+ Presence of F⁻	+ (62)	Not reported	Not reported	+ + (62)

*: + + =Important increase, + =Increase, / =No effect, - =Decrease, - - =Important decrease of the crystallization parameter upon increasing the experimental variable.

Herein, we use a novel method to synthesize nanocrystalline BEA zeolites without adding either alkali metal cations or fluoride anions in the media (see Experimental part). This method was followed by Arnaud during his PhD in the lab.

1.5.1.4. Aggregates and spray drying

The use of nano zeolites particles may however cause some problems, (notably) as i) they develop high pressure drop and ii) their recovery from the reaction media is often difficult.

(66,67) Therefore, a “shape aggregation” process of these small catalytic particles is required, so that larger particles can be used in the catalytic process, allowing for an easier catalyst recovery.(68) The formation of too large and too dense aggregates should however be avoiding, as this would lead again to diffusion limitations.

A classical way to perform particles aggregation is by spray-drying. In such aerosol process, a mist of liquid droplets is formed from a suspension and dispersed in a drying gas phase (Figure 15).(68,69)

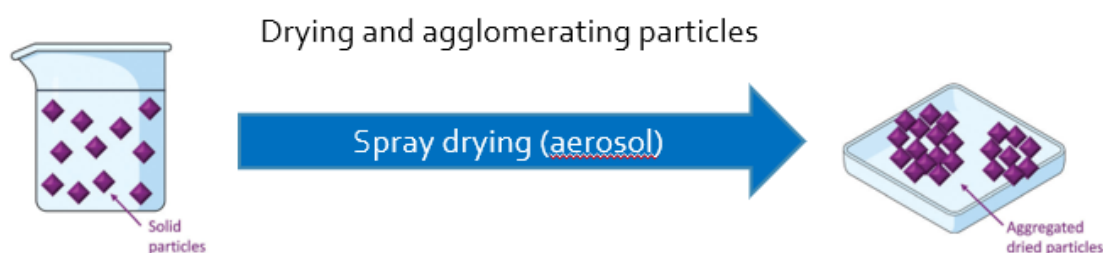


Figure 15 : Schematic representation of the spray drying process, a type of aerosol process in which pre-existing particles in suspension are atomized and dried, leading to (controlled) particles controlled aggregates.(68)

Such a process allows the control of the particle size and morphology, two key parameters closely related with catalytic performances. Notably, they will play crucial role in industrial catalytic applications using fixed bed or fluidized bed technologies, in which low pressure drop and resistance to attrition, respectively, are highly desired.(70,71) As particles formation results from the drying of liquid droplets – for which the spherical shape is the most stable – aerosol processes typically produce spherical particles. However, by changing several parameters related mass and heat transfer of the droplets, other particle morphologies such as hollow or toroid structures, can be obtained.(68,69,72)

Moreover, lab-scale catalysts preparation employing spray drying can be easily scaled up, and this technique has been widely used at the industrial scale for nearly a century.(68,69,71)

Accordingly, we decided to focus on nano-sized BEA zeolites shape agglomerated by using (notably) the spray drying method.

1.5.1.5. Tantalum incorporation into zeolitic framework

Only two different methods of incorporation of Ta into BEA zeolite framework have been reported so far : the “One-pot synthesis” and the “Two-step postsynthesis method” (Table 5). (53,73,74)

Table 5 : Features of the reported methods of incorporation of Ta(V) into BEA zeolite framework.

Zeolite type	Incorporation method (description)	Ta(V) precursor	Ta loading assumed (Si/Ta)	Real Ta loading (Si/Ta)	Ref.
BEA	One-pot (autoclave, 140°C, HF media)	Ta(OC ₂ H ₅) ₅	50	n.d.	(73)
			100	78	
BEA	Two-step (dealumination then impregnation)	Ta(OC ₂ H ₅) ₅	293	293	(74)
			150	150	

On the one hand, the one-pot synthesis of the metal-containing zeolite Beta materials were performed in fluoride media starting from gels composed of tantalum ethoxide, tetraethylorthosilicate as the silica source, TEAOH, HF and water. The crystallization was carried out in Teflon-lined stainless-steel autoclaves at 140 °C under rotation for a given time (not reported). After the desired time, the autoclaves were cooled down to room temperature and the zeolites were recovered by filtration, washed with water, and dried overnight.(73) The thermal treatment led to the formation of tetracoordinated Ta species in the zeolite framework. This synthesis is performed in fluoride media, since the probabilities for metal incorporation in the framework should be higher than those in OH⁻ media (where the precursor is often precipitated as metal oxide).(53)

On the other hand, the two-step postsynthetic method consists in adding tantalum precursor to a pre-made BEA zeolite that has been dealuminated by acid treatment. It first involves the creation of vacant T-atom (i.e. Si or Al atom) sites associated with silanol groups by dealumination of BEA zeolite with nitric acid and then the impregnation of the resulting BEA zeolite with tantalum ethoxide. This postsynthesis procedure allows to incorporate Ta into the framework of BEA zeolite as isolated mononuclear Ta(V) ions and to obtain Ta-single site BEA zeolite.(74)

As shown in Table 5, a greater amount of Ta was incorporated into the zeolite framework using the postsynthetic method.(53) Moreover, unlike the one-pot route, it does not require the use of hazardous chemicals (HF). Therefore, we chose the postsynthesis method to incorporate tantalum into the nano-BEA zeolites.

To summarize, in the present master thesis, we planned to perform the innovative preparation of Ta(V)-single site BEA microspheres. We therefore first synthesized nano-sized BEA zeolites, that we further shaped and aggregated by spray-drying process. A fraction of these agglomerated zeolites was then modified postsynthetically upon tantalum introduction in the BEA framework.

1.6. Objectives

This master thesis aims first at producing nano-sized beta zeolites (BEA) shaped by spray drying for the effective conversion of bioethanol into ethylene and 1,3-butadiene, in an innovative and green way compared to the conventional known methods.

Another focal point of this work is to investigate and to assess the impact of such a process on the activity and some properties of the obtained catalyst. In other words, our second objective consist in establishing a first screening of the effects of such shape-aggregation process on the resulting material, in order to optimize this important step of our preparation method.

1.7. Strategy

To reach our objectives, a general methodology based on three main steps will be followed.

The first main step consists in the synthesis of our heterogeneous BEA-based catalysts. It is noteworthy that different catalysts will be used for the ethanol-to-ethylene (ETE) and for the ethanol-to-butadiene (ETB) reactions. Indeed, non-impregnated H-BEA will be employed for the ETE reaction while bifunctional Cu-doped Ta(V)-BEA catalyst will be used to produce 1,3-butadiene. However, both catalysts will be prepared from the same nano-sized BEA suspensions obtained through our synthesis method.

The second step consists in the characterization of the prepared catalysts. Firstly, the synthesized BEA suspensions will be analyzed by Dynamic Light Scattering (DLS) to ensure that we obtained nano-sized particles. When their preparation is complete, the powder will be analyzed characterized via X-Ray Diffraction (XRD) to assess if the BEA structure is obtained and to estimate the crystal size. Afterwards, further characterized will be performed to probe the texture (N_2 physisorption) and the acidity (Ammonia Temperature Programmed Desorption (NH_3 -TPD)) of the samples. Eventually, X-ray Photoelectron Spectroscopy (XPS) will be performed to provide elemental analysis of the catalysts' surface.

Finally, the catalytic performance of our samples in either ETE or ETB reaction samples will be assessed through catalytic tests. Note that the same catalytic set-up is employed for both reactions, but the experimental conditions (Temperature, WHSV) differ.

2. Materials and Method

2.1. Materials

Ammonium nitrate (NH_4NO_3 ; $\geq 98\%$) and nitric acid (HNO_3 ; 60%) were purchased from Carl Roth. Aluminum isopropoxide ($\text{Al}(\text{OCH}(\text{CH}_3)_2)_3$; 98%) were purchased from Arcos Organics. Tantalum ethoxide ($\text{Ta}(\text{OC}_2\text{H}_5)_5$; 99.98 %), LUDOX® AS-40 (Colloidal silica; 40 wt.% in H_2O) and glass beads (diameter 0.75-1 mm) - from Sigma-Aldrich. Copper nitrate hemipentahydrated ($\text{Cu}(\text{NO}_3)_2 \times 2.5\text{H}_2\text{O}$; 98 %) and tetraethylammonium hydroxide (TEAOH) ($((\text{C}_2\text{H}_5)_4\text{N}(\text{OH}))$; 35 wt.% in H_2O) - from Alfa Aesar while ethanol ($\text{C}_2\text{H}_5\text{OH}$; absolute) comes from VWR Chemicals.

2.2. Method

2.2.1. Catalysts preparation

2.2.1.1. Nanocrystalline beta zeolite suspensions

For the synthesis of nanocrystalline beta zeolites (BEA), the procedure proposed by Arnaud Detaille in his PhD was adopted. A colloidal silica suspension (LUDOX) and aluminum isopropoxide (Al iso.) are used as silica and aluminum precursors respectively, while tetraethylammonium hydroxide (TEAOH) is employed as structure directing agent.

First, aluminum isopropoxide was dissolved in TEAOH under vigorous stirring (500 rpm) for one hour. Once the dissolution was complete, the appropriate amount of LUDOX AS-40 and deionized water were added to the solution, and the vigorous agitation was kept for two more hours. The resulting gel was then transferred in a stainless-steel autoclave with Teflon cup and set to crystallize at 140°C under autogenous pressure, for a given crystallization time.

The different Si/Al ratios were synthesized as shown in Table 6 (for a 50mL autoclave).

Table 6 : Materials quantities added and synthesis times used to synthesized the different BEA zeolite suspensions.

Si/Al ratio (Z)	TEAOH [mL]	LUDOX [mL]	Al iso. [g]	H ₂ O [mL]	Crystallization time [h]
12.5	29	14.5	2.0424	6	160
25	29	14.5	1.0212	6	96
50	29	14.5	0.5106	6	96

The resulting suspension is composed by a negatively charged zeolitic aluminosilicate framework compensated by tetraethylammonium cations (TEA^+). Therefore, it was denoted TEA-BEA_Z, where Z represents the Si/Al ratio. This suspension was washed four times with deionized water and recovered by centrifugation (14.000 rpm, 45 minutes). All the catalysts

used in this master thesis (i.e., H-BEA and impregnated BEA catalysts) were obtained from these TEA-BEA_Z suspensions.

2.2.1.2. H-BEA catalysts synthesis

The global synthesis scheme for H-BEA catalysts preparation is presented on Figure 16. It is noteworthy that only TEA-BEA_12.5 suspensions (i.e., displaying Si/Al ratio equal to 12.5) have been employed for their synthesis, in order to be compared to commercial H-BEA (calcined (6h at 550°C, 3 K.min⁻¹ ramp) NH₄-BEA purchased from Zeolyst International (CP814E, Si/Al=12.5), named H-BEA_comm.) in ethanol catalytic dehydration.

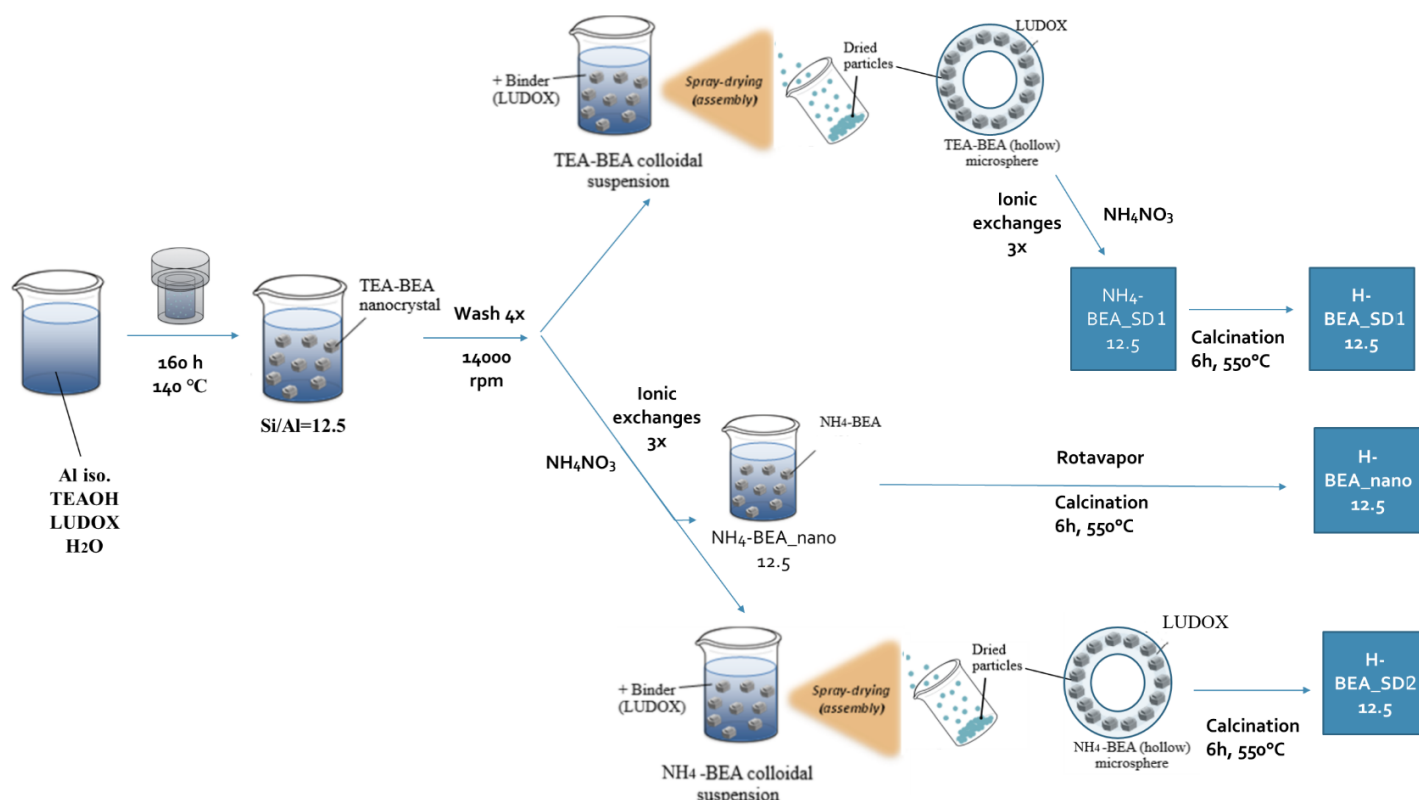


Figure 16 : Global synthesis scheme of the H-BEA nanocrystals (H-BEA_nano12.5) and of H-BEA microspheres (H-BEA_SD1_12.5 and H-BEA_SD2_12.5).

2.2.1.2.1. Preparation of H-BEA nanocrystals (H-BEA_nano_12.5)

The solid TEA-BEA_12.5 was then ionically exchanged by being re-suspended three times in a 1M NH₄NO₃ solution at 80°C for 3 hours (solid fractions were kept as close as possible to 5 wt%). After each ionic exchange, the resulting suspension was washed with deionized water by repeated suspension and centrifugation (14,000 rpm, 5 minutes) and was denoted NH₄-BEA_nano_12.5. This suspension was then dried overnight (120°C) and calcined (6h at 550°C, 3 K.min⁻¹ ramp) to generate H-BEA_nano12.5 (Figure 16 (middle scheme)).

2.2.1.2.2. Preparation of H-BEA microspheres by spray drying followed by ion exchange (H-BEA_SD1_12.5)

In order to synthesize H-BEA_SD1_12.5, a spray drying step was performed on TEA-BEA_12.5 suspension before the ionic exchange step (see Figure 16 (top scheme)).

In other words, the solid TEA-BEA_12.5 was re-suspended with distilled water and additional LUDOX (5 wt% of the resulting suspension) before being subsequently spray-dried by a Büchi Mini Spray Dryer B-290. Briefly, the suspension (5 wt % solid content) was pumped (8 mL/min pump rate) to a spray nozzle and was subsequently atomized through contact with gas flow (rotameter 45%). The aerosol was dried (applying inlet temperature of 175°C (the measured outlet temperature was ~75°C)) and the dried particles (TEA-BEA_SD1_12.5) were separated through a cyclone (with an aspirator at 80%).

TEA-BEA_SD1_12.5 were then ionically exchanged and washed with distilled water to generate NH₄-BEA_12.5_SD1 suspensions. H-BEA_12.5_SD1 was obtained after subsequent drying (overnight, 120°C) and calcination (6h at 550°C, 3 K.min⁻¹ ramp) of NH₄-BEA_SD1_12.5.

2.2.1.2.3. Preparation of H-BEA microspheres by ion exchange followed by spray drying (H-BEA_SD2_12.5)

To obtain H-BEA_SD2_12.5, the TEA-BEA_12.5 suspension underwent first ion exchange before being spray dried, as shown in Figure 16 (bottom scheme). Thus, the solid TEA-BEA_12.5 was ionically exchanged, washed and then re-suspended with distilled water and additional LUDOX (5 wt%). The resulting suspension was subsequently sprayed and dried (in the same condition as described for H-BEA_SD1_12.5) to generate NH₄-BEA dried microspheres (NH₄-BEA_SD2_12.5). Eventually, the further calcination (6h at 550°C, 3 K.min⁻¹ ramp) led to H-BEA_SD2_12.5 catalyst.

2.2.1.3. Tantalum and copper impregnated BEA synthesis

For the preparation of impregnated BEA catalysts, three different TEA-BEA suspensions were used: TEA-BEA_12.5, TEA-BEA_25 and TEA-BEA_50. The obtained impregnated catalysts were named **(Cu_x)-Ta_y-H-BEA_z** where X and Y represent the Cu and Ta loadings (in wt%) and Z, the Si/Al ratio. A general scheme summarizing the preparation of the different synthesized impregnated catalysts is shown in Figure 17. Note that X, Y and Z were not included in the scheme for convenience reasons.

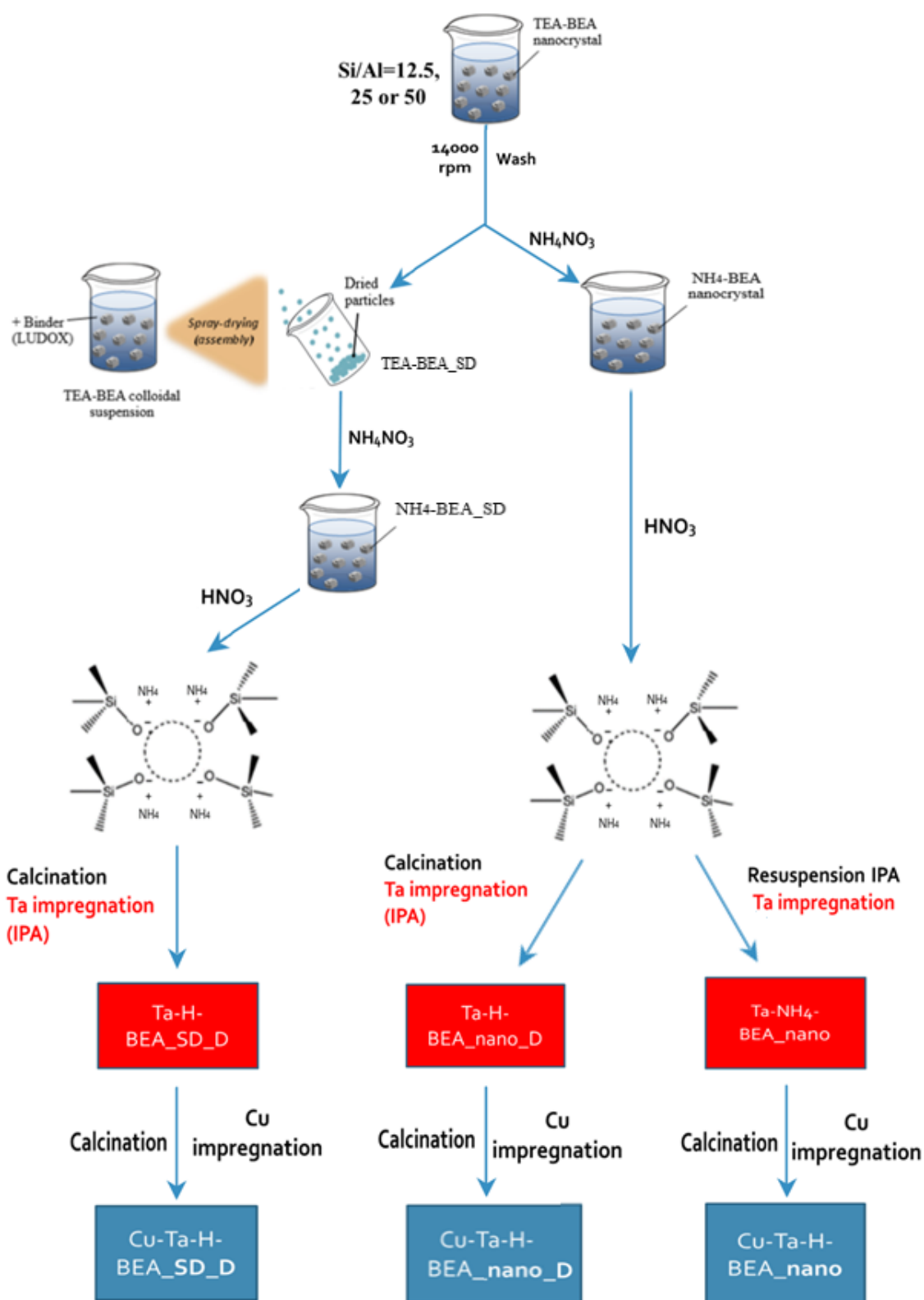


Figure 17 : Scheme of preparation of impregnated beta zeolites starting from TEA-BEA suspensions (the synthesis step of TEA-BEA_Z suspensions is not represented here).

2.2.1.3.1. Preparation of Ta(V)-single site BEA zeolites (Ta_Y-H-BEA_Z)

2.2.1.3.1.1. Preparation of tantalum BEA nanocrystals by wet impregnation (Ta_Y-H-BEA_nano_Z)

The solid TEA-BEA_Z was first ionically exchanged and washed to generate NH₄-BEA_nano_Z suspension (see Figure 17 (right scheme)).

The solid NH₄-BEA_nano_Z was subsequently dealuminated in order to generate silanol nests (i.e. vacant T-atom sites) in the beta zeolite framework, before the impregnation steps. The dealumination step was inspired from a standard procedure reported by Wang et al. in 2015.⁽⁷⁵⁾ Briefly, the solid NH₄-BEA_nano_Z were suspended in 60% nitric acid (20mL HNO₃/g_{cat}) for 20 hours at 80°C. The suspension was then cooled and washed by three successive centrifugations and resuspensions (14,000 rpm, 5 minutes).

Then, in order to introduce tantalum into vacant T-atom sites a change of solvent was required as tantalum compounds readily reacts with water to form their corresponding oxide. In other words one has to get rid of the water of the medium and inside the zeolite's porosity to avoid risks of tantalum oxide precipitation at the catalyst surface. Therefore, the resulting dealuminated solid fraction was recovered by centrifugation and washed four times by centrifugations and resuspensions into isopropanol (IPA).

The performed Ta impregnation was inspired from the procedure described by Dzwigaj and Millot in 2010.⁽⁷⁴⁾ The appropriate amount of tantalum precursor (Ta(OC₂H₅)₅) was added to the dealuminated H-BEA suspension in IPA. The obtained suspension (Ta_Y-NH₄-BEA_nano_Z) was then transferred into a rotary vacuum evaporator (rotavapor) at 20°C until complete evaporation of isopropanol. As preconized by Dzwigaj and Millot in 2010,⁽⁷⁴⁾ the resulting solid was washed three times in distilled water (through centrifugations and resuspensions) before being dried overnight at 120°C. The dried powder was eventually calcined at 550°C for 3 h (3 K.min⁻¹ ramp) to generate Ta_Y-H-BEA_nano_Z.

However, this method was suspected to be inefficient for the removal of water stuck inside zeolite's micropores (and therefore, to generate Ta₂O₅ species (see section 4.2.1.)). We decided thus to perform (and to focus) on dry impregnation method.

2.2.1.3.1.2. Preparation of tantalum BEA nanocrystals by dry impregnation (Ta_Y-H-BEA_nanoZ_D)

In order to obtain Ta_Y-H-BEA_nano_Z_D catalyst (Figure 17 (middle scheme)), the same procedure than for Ta_Y-H-BEA_nano_Z preparation was followed, until the Ta impregnation step. Thus, the solid TEA-BEA_Z was ionically exchanged and washed to generate NH₄-BEA_Z, which was subsequently dealuminated and washed (as explained previously).

A dry Ta impregnation was then carried out. Therefore the dealuminated suspension was first dried overnight at 120°C and calcined 3h at 500°C (3 K.min⁻¹ ramp). 1 g of solid dealuminated BEA was then stirred for 3 h at 80°C in an isopropanol solution containing the appropriate amount of tantalum precursor (Ta(OC₂H₅)₅) to obtain Ta_Y-H-BEA_nano_Z_D suspension (D being a reference to the dry impregnation method). After evaporation of IPA in

a rotavapor at 20°C, the obtained solid was washed with distilled water and dried overnight at 120°C. Its further calcination (3h at 550°C, 3 K.min⁻¹ ramp) led to Ta_Y-H-BEA_nano_Z_D catalyst.

2.2.1.3.1.3. Preparation of tantalum BEA microspheres by spray drying followed by ion exchange and dry impregnation (Ta_Y-H-BEA_Z_SD_D)

To prepare Ta_Y-H-BEA_SD_Z_D, a spray drying step was performed before ion exchange, dealumination and dry impregnation steps (Figure 17 (left scheme)). Thus, the solid TEA-BEA_Z was re-suspended with distilled water and additional LUDOX (5 wt% of the resulting suspension) before being subsequently spray-dried (in the same conditions as previously described). The dried particles (TEA-BEA_SD_Z) were then ionically exchanged and washed to generate NH₄-BEA_SD_Z, which was subsequently dealuminated and washed (as explained previously).

The dry Ta impregnation was then carried out in the same way as described for Ta_Y-H-BEA_nano_Z_D catalyst. After evaporation of IPA in a rotavapor at 20°C, the obtained solid was washed with distilled water and dried overnight at 120°C. Its further calcination (3h at 550°C, 3 K.min⁻¹ ramp) led to Ta_Y-H-BEA_SD_Z_D catalyst.

2.2.1.3.2. Preparation of bifunctional catalysts by copper impregnation (Cu_X-Ta_Y-H-BEA_Z)

In all Ta_Y-H-BEA_Z samples, the doping of zeolites with Cu(II) clusters was performed following the procedure used by Kyriienko et al. in 2017 (dry impregnation).(48) Briefly, a given mass of Ta_Y-H-BEA_Z was stirred under aerobic conditions for 2 h at 25°C in an aqueous solution of Cu(NO₃)₂×2.5H₂O to obtain Cu_X-Ta_Y-H-BEA_Z zeolites. Finally, the sample was dried in a rotavapor at 65°C and then calcined at 550°C for 3h (3 K.min⁻¹ ramp). The obtained solid had a pale blue to green aspect.

This method allowed us to perform the Cu(II)-doped Ta(V)-single site BEA nanocrystals obtained by wet (Cu_X-Ta_Y-H-BEA_nano_Z (Figure 17, right scheme)) and dry (Cu_X-Ta_Y-H-BEA_nanoZ_D (Figure 17, middle scheme)) tantalum impregnation, as well as Cu_X-Ta_Y-H-BEA_SD_Z_D microspheres (Figure 17 (left scheme)).

2.2.1.4. Prepared catalysts

Although three different synthesized BEA zeolites (i.e. displaying three different Si/Al ratios) were impregnated, we decided to focus on the synthesis of zeolites with the same Si/Al ratio (or a close one) of that commercial BEA zeolites (H-BEA_comm.) used in ETB reactions (Si/Al=12.5),(48,49,76) as their performances are therefore readily comparable.

Table 7 summarizes all the prepared catalysts during this master thesis.

Table 7 : Summary of the synthesized catalysts during this master thesis.

Catalyst name	Ta(OC ₂ H ₅) ₅ mass [g/gdeal zeolites]	Ta loading (wt%)	Cu(NO ₃) ₂ ×2.5H ₂ O mass [g/gdeal zeolites]	Cu loading (wt%)	Initial Si/Al ratios
H-BEA catalysts					
H-BEA_nano	/	/	/	/	12.5
H-BEA_SD1	/	/	/	/	12.5
H-BEA_SD2	/	/	/	/	12.5
Impregnated H-BEA catalysts					
Ta₁-H-BEA_nano_D*	0.0225	1	/	/	12.5
Ta₁-H-BEA_nano		1	/	/	25, 50
Ta₁-H-BEA-S.D_D*	0.0225	1	/	/	12.5
Cu₁-Ta₁-H-BEA_D*	0.0225	1	0.0366	1	12.5
Cu₁-Ta₁-H-BEA_nano		1		1	25, 50
Cu₁-Ta₁-H-BEA-SD*	0.0225	1	0.0366	1	12.5
Cu₁-Ta₁-BEA_nano**	0.0225	1	0.0366	1	12.5
Cu₅-Ta₁-H-BEA_nano_D	0.0225	1	0.183	5	12.5
Cu₅-Ta₁-H-BEA_SD_D*	0.0225	1	0.183	5	12.5

*: Unfortunately, we were not able to fully synthesize these catalysts (one impregnation step was missing for each of them) due to COVID-19 crisis. As a result they could not be either characterized or tested catalytically.

**: This samples represents a non-ionically exchanged Cu-Ta-BEA zeolite.

2.2.2. Characterization techniques

2.2.2.1. N₂ physisorption

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

The specific surface area (S_{BET}) was estimated by applying the Brunauer-Emmett-Teller (BET) model in the P/P_0 range values lower than 0.05, as preconized by Rouquerol et al. (2007) for microporous samples.(77) The microporous volume and external surface area were computed from the intercept and the slope of the linear regression of the t-plot, respectively. The fitted points to generate this regression were taken in a statistical thickness range of 3,5-5 Å.

2.2.2.2. X-Ray Diffraction (XRD)

X-Ray diffraction relies on the elastic diffusion of photons through the crystalline planes of the sample. Diffraction results in this case from a constructive interaction between matter and an X-ray. Constructive interferences occur when the waves reflected by two consecutive planes are in phase, which means that the phase difference between these 2 waves is a multiple of the X-ray wavelength λ . If this condition is satisfied, the difference in optical path traveled by the radiation between the crystal planes ($2.d.\sin\theta$) must be equal to an integer multiple of λ .(78)

Hence one can derive Bragg's equation [1], which allows the identification of crystalline phases.

$$2d\sin\theta = n\lambda \quad [1]$$

One can also estimate the crystal size (D) via Scherrer equation [2] knowing the wavelength of the X-rays sent by the source (λ), the peak full width at half maximum (FWHM) (β) and the diffraction angle (θ). (79) Indeed, it can be shown (for cubic crystals) that :

$$D = 0.89 \frac{\lambda}{\beta(\cos\theta)} \quad [2]$$

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

2.2.2.3. Dynamic light scattering (DLS)

In order to estimate the average particle size of the nano-sized beta zeolites in suspension, DLS analyses were performed. This technique allows the determination of the radius of particles in a nano-dispersed system through analysis of scattered light.

It consists in a LASER shot directed into the suspension (sample) which results in light scattering when light hits small particles compared to its wavelength (below 250 nm (Rayleigh scattering)). A detector measures the intensity of this scattered light which is the result of the interference of the light scattering produced on/from each particle (Figure 18). (80)

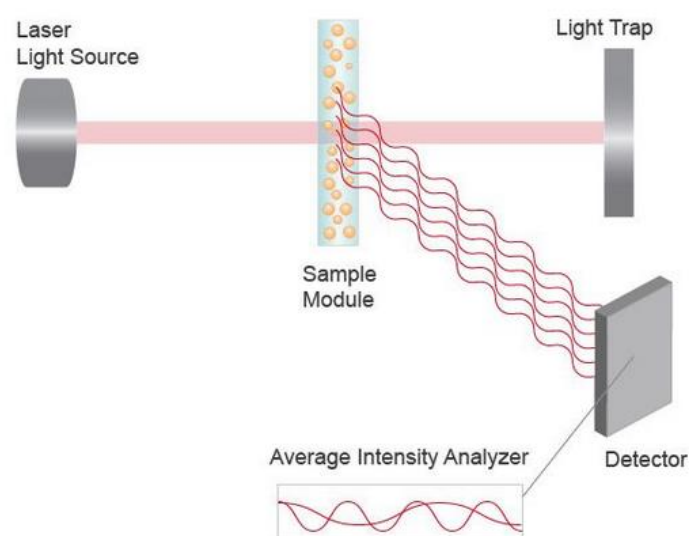


Figure 18 : Schematic representation of the setup for a typical DLS measurement (80)

Thus, even if the light source is monochromatic and coherent, the scattering intensity fluctuates over time due to these interferences. Such interferences result from small particles in the suspension undergoing Brownian motion, which make the distance between the scatterers constantly changing with time.(80)

Therefore, from the measured intensity fluctuations, one can determine (through complex mathematical models) the rate of diffusion and its corresponding diffusion coefficient D [m^2/s]. Consequently the average hydrodynamic particle radius R_p can be obtained using the Stokes-Einstein equation (with k_B , η and T representing the Boltzmann constant, the dynamic viscosity and the absolute temperature, respectively) [3].

$$r_p = \frac{k_B T}{6\pi\eta D} \quad [3]$$

2.2.2.4. Ammonia Temperature Programmed Desorption (NH_3 -TPD)

To investigate the acidic properties of a catalysts, the controlled desorption of a basic molecule can be exploited. In this work, the temperature programmed desorption of ammonia is used. Briefly, the sample is saturated with a flow of ammonia at a given temperature. Then it is flushed under inert. By subsequently increasing the temperature, the energy provided eventually leads to the desorption of chemisorbed NH_3 . By knowing the amount of ammonia desorbed and the temperature at which it desorbed, the number and the strength of acid sites can be determined. The TPD- NH_3 analysis is run on approximately 60 mg of catalyst in a Hiden CATLAB-PCS microreactor in line with a mass spectrometer equipped with a quadrupole separator. The temperature program used is represented in Figure 19. First, the sample is degassed at 500 °C to remove any adsorbed species like water. Then, ammonia adsorption takes place at 100 °C for 55 minutes followed by a purge of 30 minutes. Finally, the temperature increases to 700 °C at a rate of 10 °C/min to desorb ammonia.

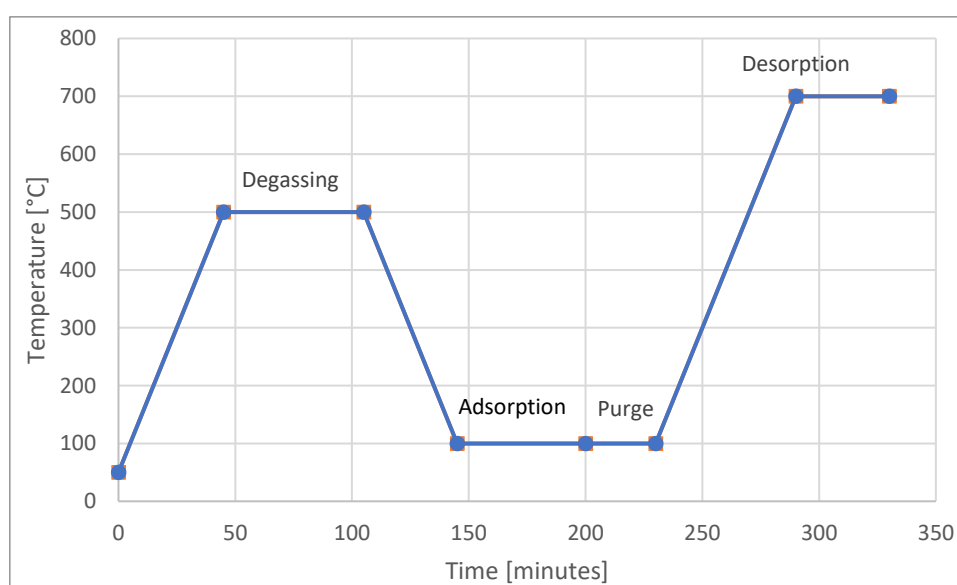


Figure 19 : NH_3 -TPD temperature program used in this work

2.2.2.5. X-ray Photoelectron Spectroscopy (XPS)

An incoming monochromatic X-ray beam induces the ejection of photoelectrons from the sample surface on a depth of around 10 nm. These emitted photoelectrons have a specific kinetic energy depending on their binding energy. They are filtered and analyzed to deduce this binding energy. The binding electron energy is specific for each orbital of a certain element. This technique therefore provides a quantitative elemental analysis of the catalyst's surface.

In this work, an SSX 100/206 Photoelectrons Spectrometer from Surface Science Instruments was used, equipped with an Al K α monochromatic and a micro-focused source. The pressure inside the analysis chamber is about 10^{-6} Pa, the analysis angle is 55 °C and the pass energy is fixed at 150 eV. Data was processed with CasaXPS from Casa Software Ltd, UK. To calibrate the binding energy scale, the Si 2p peak has been set at 103.5 eV. (81) Spectra are then decomposed, and molar fractions can be obtained based on the acquisition parameters and sensitivity factors provided by the manufacturer.

2.2.3. Catalytic testing: set-up and conditions

The experimental catalytic set-up used is the same as the one described by Denis Dochain during his Master Thesis (2019). (12,39)

2.2.3.1. General experimental setup

Briefly, each catalyst is first sieved to get particle size comprised between 0.2 and 0.4 mm. A constant mass (comprised between 0.048 and 0.192 g) of catalyst, diluted with glass beads in order to keep the volume of the catalyst bed constant, is then added in the reactor. Glass beads are finally added to fill completely the reactor, which is then fixed in a Minicor 42 Coreci furnace and heat insulated with glass wool.

Catalytic testing was carried out by injecting a given flow of liquid absolute ethanol by means of a NE-300 syringe pump, in a given gas flow (N₂) delivered by an E-flow mass controller from Bronkhorst into the reactor. At the outlet of the reactor, the flow is directed to a 6-path valve connected to a Varian 3800 Gas Chromatograph.

2.2.3.2. GC analysis

The analysis of the effluent reactor gases was carried out by this GC, which is equipped with a flame ionization detector (FID) and a Restek Rt-U-Bond (30 m x 0.32 mm x 10 μ m) column. The vector gas is helium, the pressure at the start of the column is 15 psi, the injector is kept at 150 °C and the detector is at 190 °C. The temperature program of the column starts at 110 °C for 5 minutes, increases to 150 °C at a rate of 10 °C/min and stays at 150 °C for 5 minutes.

In each experiment conditions (i.e. at each different Temperature or Weight Hourly Space Velocity (WHSV) tested), at least 5 injections were performed to ensure reproducibility of the signal.

2.2.3.3. Ethanol dehydration test conditions

The catalytic performance in the ethanol-to-ethylene reaction of the synthesized H-BEA zeolites was compared to those of a benchmark catalyst performance. The H-ZSM-5 zeolite was chosen as benchmark catalyst, as it is known to be the most productive catalyst in ethylene production. (17)

Therefore, ethanol dehydration tests were carried out in the conditions (described as Styskalik et al. in 2020) that maximized the ethylene productivity of HZSM-5.(17) Briefly, 0.048 g of catalyst were used, with a N₂ flow of ~150 mL.min⁻¹ and ethanol feed of ~0.84 g.h⁻¹ (WHSV = 17.5 g_{ethanol}.g_{cat}⁻¹.h⁻¹) at 240 °C. (17)

2.2.3.4. Ethanol to butadiene (ETB) test conditions

For the ETB reaction, one has to work with lower WHSV (0.5 to 2.2 h⁻¹ at 325°C) in order to effectively produce butadiene. (12,39,48) Moreover, copper has to be in its reduced state to ensure its redox activity. Therefore we proceeded as follow:

Before reaction, the catalyst was pretreated in situ by feeding hydrogen (30 vol.% H₂ in N₂) for 1 h at 355 °C (copper reduction). Then, catalytic testing was carried out by feeding of ~0.212 g h⁻¹ of ethanol absolute and a N₂ flow of ~40 mL.min⁻¹ into the reactor containing 0.192 g of calcined catalyst (WHSV=1.10 h⁻¹) at 325°C.

3. Results

Results that are presented below are those that could be obtained on the large series of catalysts prepared in the framework of this master thesis. Unfortunately, the COVID crisis has prevented us from completing some of the analysis campaigns. Therefore, in some instances, meaningful comparisons with reference samples are not feasible. In the discussion part, in addition to a general discussion of the presented results, we comment on the experiments that should be carried out in priority to complete this study.

3.1. H-BEA and NH₄-BEA catalysts characterization

3.1.1. Comparison of the synthesized BEA with commercial BEA zeolites

3.1.1.1. X-ray diffraction (XRD)

XRD analysis was performed to verify that the synthesized zeolites samples are effectively beta (BEA) zeolites. Only the non-spray-dried synthesized nano-zeolites (H-BEA_nano_12.5) and the commercial zeolites could be analyzed by this technique. The obtained XRD patterns (Figure 20) confirm that BEA zeolites were successfully synthesized by using the present synthesis method. Indeed, H-BEA_nano_12.5 sample displays the same diffraction lines as the reference zeolite H-BEA_comm. (Si/Al=12.5) which confirms no change of phase was evidenced.

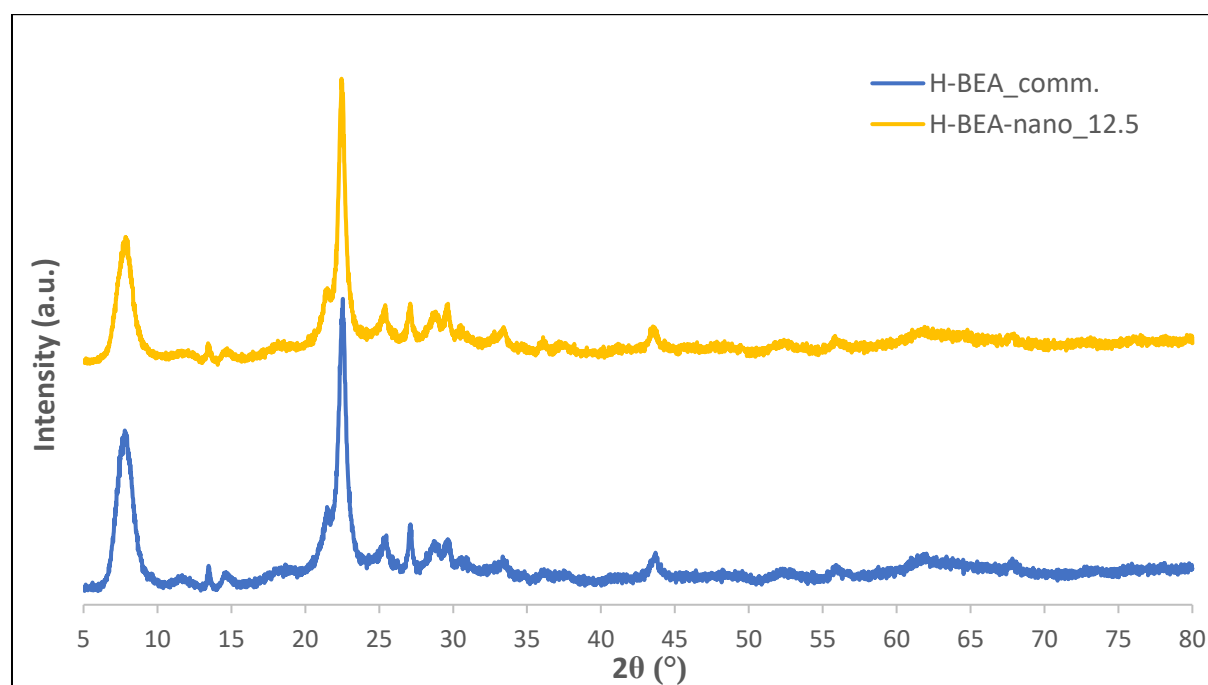


Figure 20 : XRD patterns of synthesized nano-zeolites (H-BEA_nano12.5) and of commercial BEA zeolites (H-BEA_comm.).

Additionally, the mean crystallites size of H-BEA_nano_12.5 and H-BEA_comm. was estimated by Scherrer equation (Table 8). It resulted that both samples display very similar

crystal size of nearly 30 nm. Such crystal size is consistent with what has been reported (10 to 30 nm) in the literature on this same H-BEA_comm..(66,82)

Table 8 : Estimated mean crystallites size of H-BEA_comm. et an H-BEA_nano_12.5.

Sample	Mean crystallites size [nm]
H-BEA_comm.	28.5
H-BEA_nano_12.5	27.2

3.1.1.2. Dynamic light scattering (DLS)

The average particle size (radius) of our BEA zeolites in suspension was estimated performing DLS analysis with the aim to investigate if our synthesis method led to significant particle size change (with respect to commercial sample). These analyses were thus performed on NH₄-BEA_nano_12.5 (Figure 21) and NH₄-BEA_comm. (Figure 22) samples. Note that each “Run” highlighted on the Figures corresponds to a repetition of the experiment (i.e. a new measure on the same cuvette to probe the sample’s particle size). The different results obtained for each run are therefore related to the variability of the experiment.

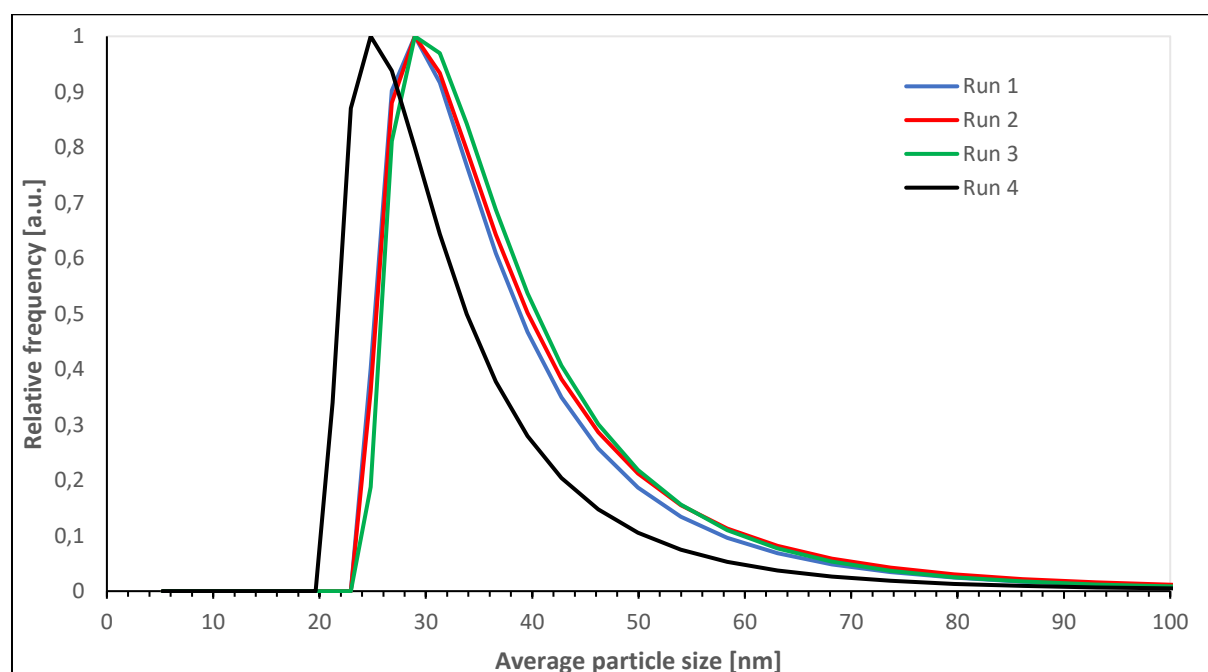


Figure 21 : DLS profile analysis (weighted particle number distribution) obtained for NH₄-BEA_nano_12.5 sample

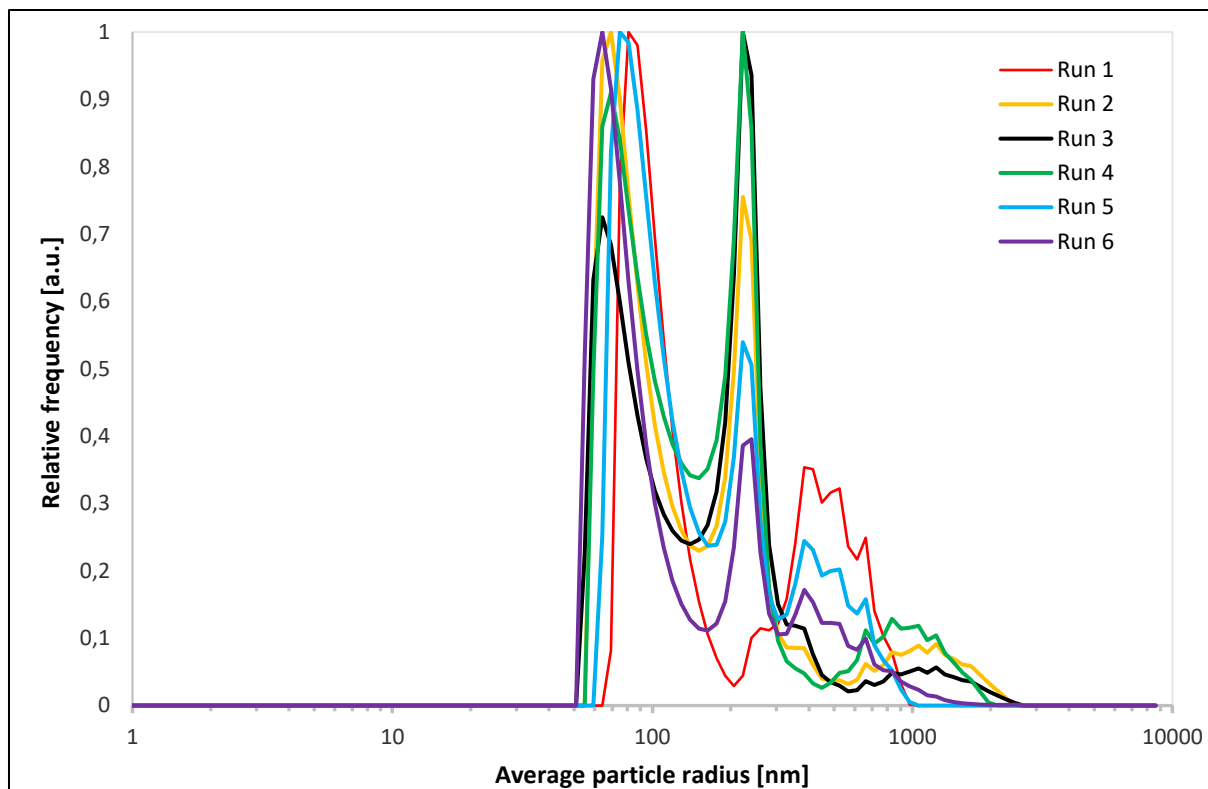


Figure 22 : DLS analysis profile (weighted particle number distribution) obtained for sonicated NH₄-BEA_comm. sample

One can observe a significant difference in the average particle size measured by DLS between NH₄-BEA_nano_12.5 and NH₄-BEA_comm. samples as the latter seems to be composed of bigger particle. However, as suggested by XRD analyses (Table 8), these big particles are in fact bulky aggregates composed of small crystals. (82) This information provided by DLS measurements are summarized in Table 9. They go along with our expectations and suggest that our synthesis method allows obtaining smaller zeolites particles.

Table 9 : Summary of DLS data obtained for sonicated H-BEA_comm. and H-BEA_nano_12.5 samples

	Particle size distribution	Average particle radius [nm]	
H-BEA_nano_12.5	Monomodal	25 to 30	
H-BEA_comm.	Bimodal	65 to 80	~223

3.1.1.3. Nitrogen physisorption

Nitrogen physisorption was performed to characterize and compare the textural properties of synthesized and commercial H-BEA samples. N₂ adsorption-desorption isotherms of H-BEA_SD1_12.5, H-BEA_nano_12.5 and H-BEA_comm. samples are shown in Figure 23.

As expected, all H-BEA samples display micropores and mesopores (interparticular voids generated by aggregation), which contribute to the total pore volume. This is evidenced by the shape of the type IV isotherm (hysteresis between adsorption and desorption curves)

additionally to the type I isotherm characteristic of zeolites (important uptake at P/P_0 values lower than 0.05, due to samples' micropores).

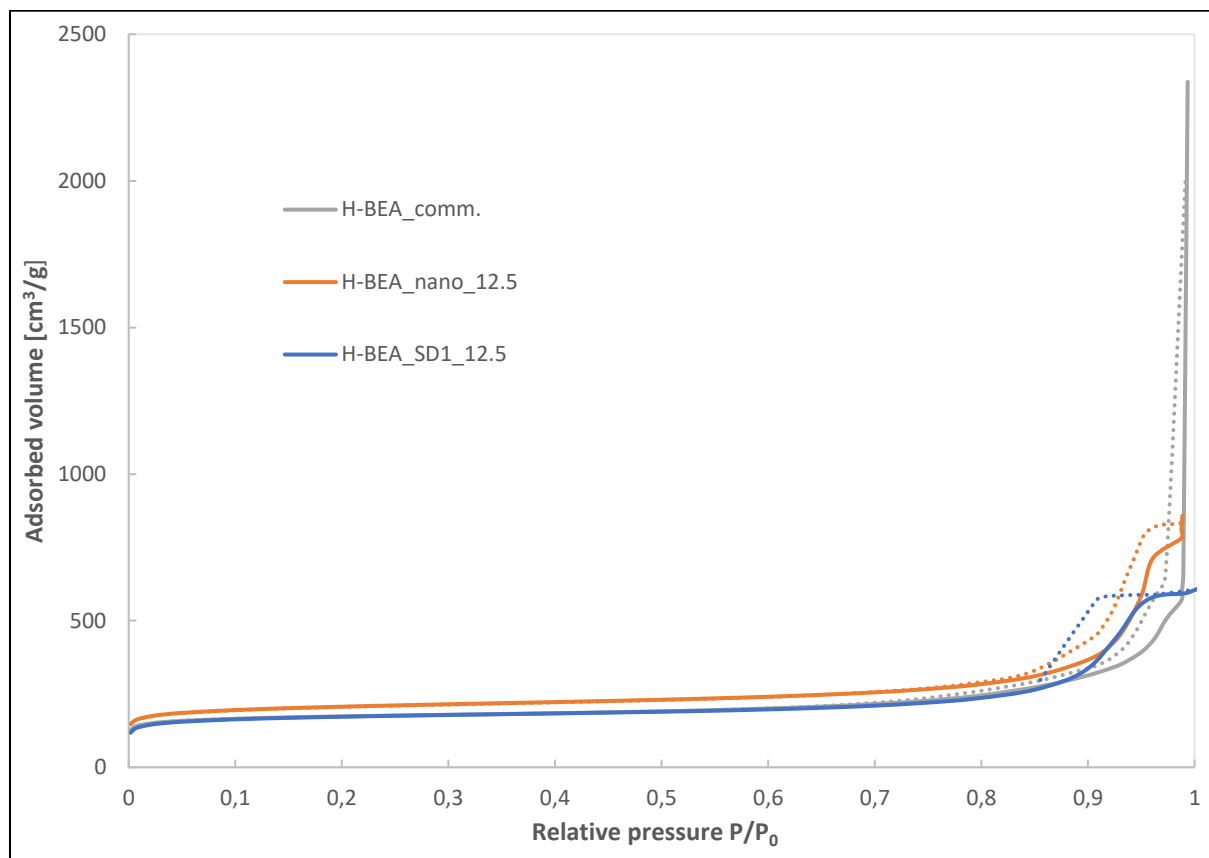


Figure 23 : N_2 physisorption (adsorption and desorption) isotherms of synthesized H-BEA zeolites (H-BEA_nano12.5 and Zr-H-BEA_SD112.5) and commercial H-BEA sample (H-BEA_comm.). The dotted lines represent the desorption curves.

This textural information obtained by N_2 physisorption analyses are presented in Table 10. The S_{BET} was estimated by applying Brunauer-Emmett-Teller (BET) model in the P/P_0 range of 0-0.05, as preconized by Rouquerol et al. (2007) for microporous samples. (77) Microporous volume and external surface area were computed from the intercept and the slope of the linear regression of the t-plot, respectively. The fitted points to generate this regression were taken in a statistical thickness range of 3,5-5 Å.

Table 10 : Summary of main textural properties obtained via N_2 physisorption analyses on synthesized (H-BEA_nano_12.5 and H-BEA_SD1_12.5) and commercial (H-BEA_comm.) BEA zeolites.

Sample	S_{BET} [$m^2 \cdot g_{cat}^{-1}$]	External surface area [$m^2 \cdot g_{cat}^{-1}$]	Micropore volume [$cm^3 \cdot g_{cat}^{-1}$]
H-BEA_comm.	660	170	0.19
H-BEA_nano_12.5	775	240	0.22
H-BEA_SD1_12.5	650	185	0.19

On the one hand, these data indicate that H-BEA_nano12.5 zeolites display higher (external) surface area than commercial ones (H-BEA_comm.). However it is important to take

into account that estimated error related to physisorption measurements is at least of 10% (83). On the other hand, no significant differences in terms of textural properties could be noticed between H-BEA_SD1_12.5 and H-BEA_comm.

Pore size distribution (PSD) obtained by Barrett, Joyner and Halenda (BJH) model during desorption is shown in Figure 24. On the one hand we notice that the PSD is quite heterodispersed (broad distribution) and suggests that interparticular voids with average diameters of c.a. 30 nm were generated in H-BEA_nano_12.5. On the other hand, a rather sharp (homodispersed) PSD with average mesopore diameters of c.a. 15 nm was obtained for the H-BEA_SD1_12.5, which could be the sign of a more regularly organized mesoporosity (e.g. associated with a closer packing of particles having similar size). Eventually, in H-BEA_comm, a more random distribution suggesting the presence of few mesopores with average diameter of c.a. 10 and 35 nm was observed.

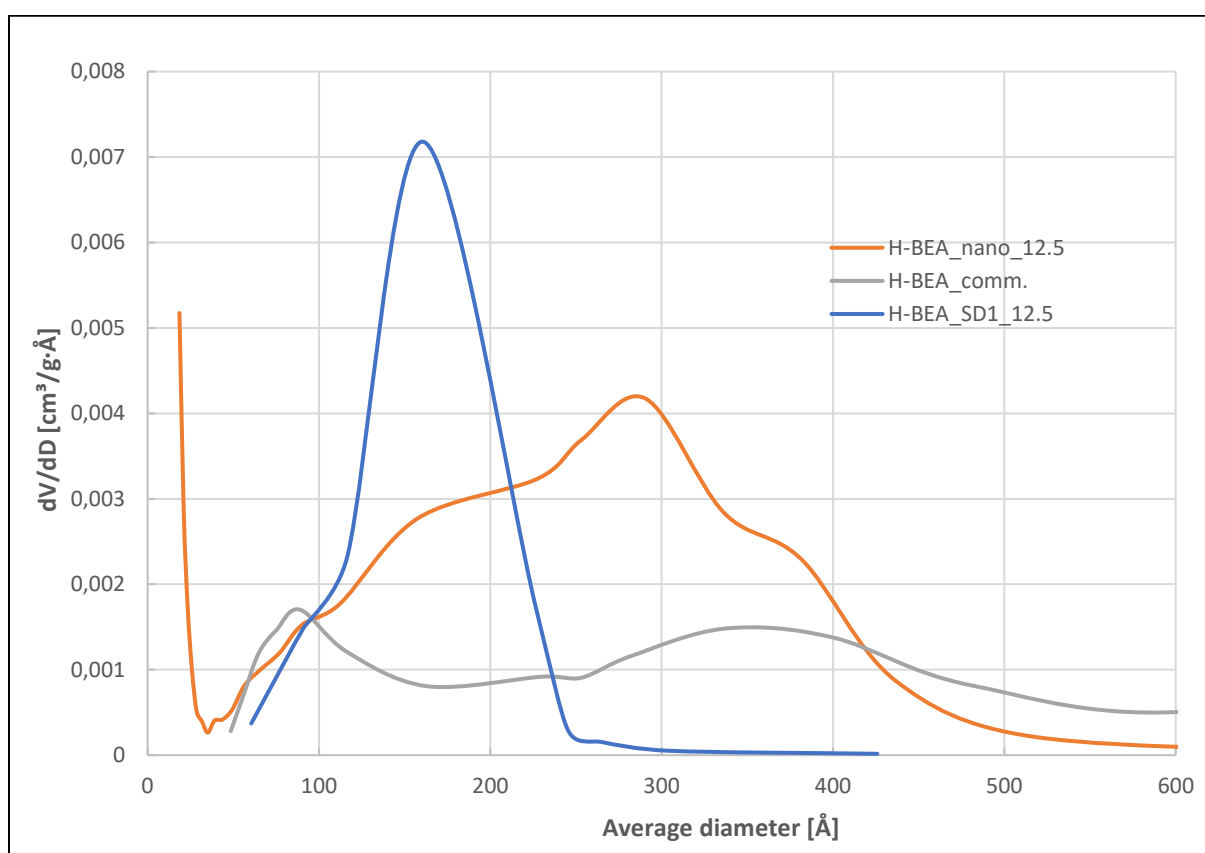


Figure 24 : Pore size distribution profiles obtained for synthesized (H-BEA_nano_12.5 and H-BEA_SD1_12.5) and commercial (H-BEA_comm.) BEA zeolites by BJH model

3.1.1.4. NH₃ - Temperature Programmed Desorption (TPD)

Ammonia thermodesorption analyses were performed on H-BEA zeolites samples in order to investigate the strength of their acid sites. The obtained NH₃-TPD profiles are shown in Figure 25.

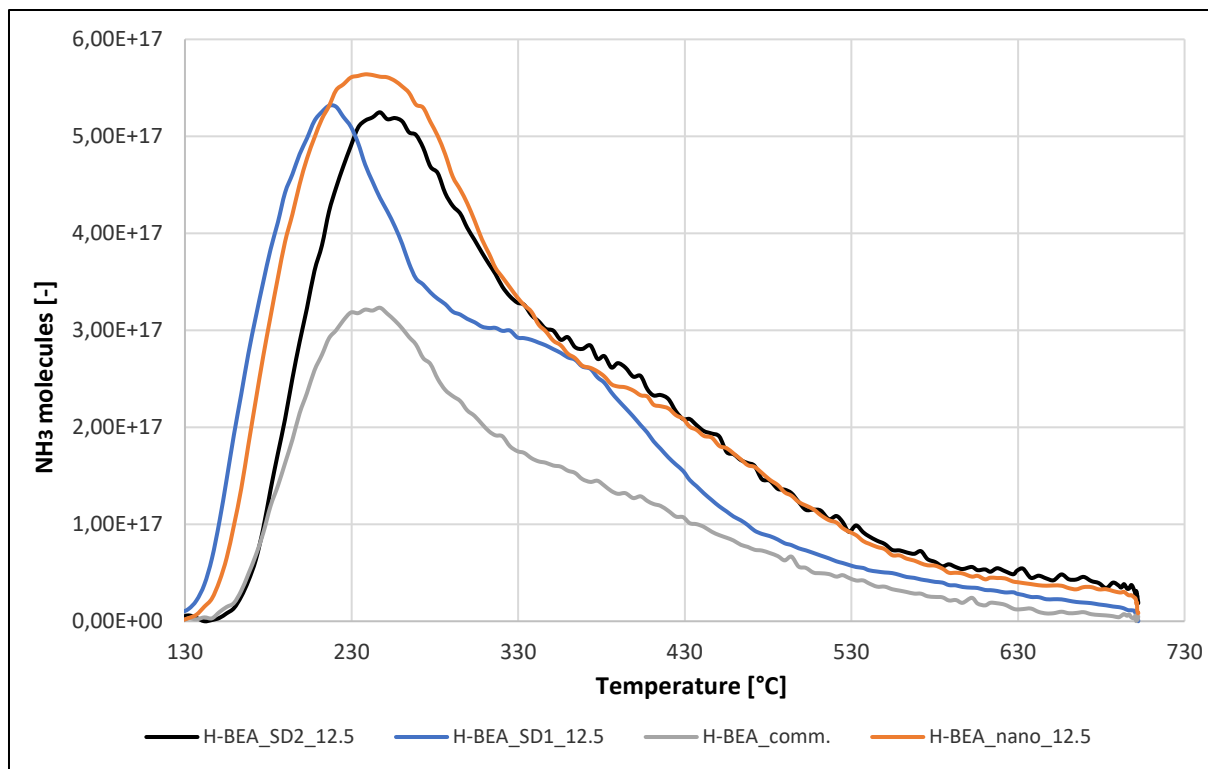


Figure 25 : NH_3 -TPD profiles obtained for synthesized (H-BEA_nano_12.5, H-BEA_SD1_12.5 and H-BEA_SD2_12.5) and commercial (H-BEA_comm.) catalysts.

One can observe that the overall shape of the desorption peak is very similar for all samples. Also, the maximum of the NH_3 desorption peak temperatures was $\sim 250^\circ\text{C}$ for both H-BEA_nano_12.5 and H-BEA_comm. samples, which suggests that these catalysts exhibit only slight (or no) difference in terms of acid site strength. However, it is not the case for the spray dried samples as H-BEA_SD1_12.5 shows slightly lower maximum desorption peak temperature ($\sim 220^\circ\text{C}$) compared to H-BEA_SD2_12.5 (and to the other samples) ($\sim 250^\circ\text{C}$). Such result suggests that H-BEA_SD1_12.5 displays slightly weaker acid sites compared to H-BEA_nano_12.5, H-BEA_SD2_12.5 and H-BEA_comm. catalysts (that exhibit very similar acid site strength).

On the second hand, we can notice that the area under TPD peaks does not significantly differ between the synthesized zeolites (H-BEA_nano_12.5, H-BEA_SD1_12.5 and H-BEA_SD2_12.5). However, it was found twice as lower for H-BEA_comm. with respect to the other tested samples. Such result can be expressed in terms of acid sites concentration, as the number of acid sites of the samples can be computed directly from their peak area (Table 11).

Table 11 : Acid sites concentrations (estimated from the peak area on NH_3 -TPD profiles) obtained for synthesized (H-BEA_nano_12.5) and commercial (H-BEA_comm.) BEA zeolites.

Sample	Acid sites concentration [mmol/g _{zeolite}]
H-BEA_comm.	0.54
H-BEA_nano_12.5	1.03
H-BEA_SD1_12.5	0.95
H-BEA_SD2_12.5	0.98

3.1.1.5. X-ray Photoelectron Spectroscopy (XPS)

An elemental analysis of our synthesized H-BEA zeolites is useful in order to confirm that these samples display Si/Al ratios close to the targeted value (i.e., 12.5 in this case). Therefore the surface elemental composition of H-BEA_nano12.5 and H-BEA_SD1_12.5 samples was probed through XPS.

The obtained Si/Al ratios (Table 12) were found very close to 12.5 in both sample, which suggests that we successfully synthesized BEA zeolites displaying similar Si/Al ratios to the benchmark catalyst (H-BEA_comm.). Additional ICP-AES analysis should be performed on these samples in order to confirm this hypothesis.

Table 12: Atomic Si/Al ratio obtained by XPS on H-BEA_nano12.5 and H-BEA_SD112.5 samples

Sample	Si/Al
H-BEA_nano_12.5	14.7
H-BEA_SD1_12.5	13.5

3.2. Modified and impregnated BEA catalysts characterization

3.2.1. Effect of dealumination of H-BEA zeolites

As all the impregnated samples synthesized were first dealuminated in nitric acid solutions, we studied the impact of such acid treatment on the resulting catalysts.

3.2.1.1. XRD

XRD analyses were performed to assess the effect of dealumination of the catalysts on the beta zeolite structure. By exploiting potential shifts present on the diffractograms, one can investigate the structural impact of this dealumination. The non-aggregated synthesized nano-zeolites, H-BEA_nano12.5 (Figure 26) and the commercial zeolites (Figure 27) could be analyzed by this technique.

When comparing the XRD patterns obtained for the dealuminated samples with those of the parent H-BEA catalysts, one can assume that beta zeolite structure was preserved upon dealumination as no significant change was evidenced. However one can observe a slight shift to higher angles for the peaks after 20° of the dealuminated sample, as seen with the two last dotted lines on the diffractogram. This shift indicates a decrease of the d spacing, which corresponds to a smaller average bond length in the lattice. As the Al—O bond being 0.1 Å longer than the Si—O bond, this could be the sign of the removal of aluminum from the zeolitic structure. Such result might thus indicate that our samples were successfully dealuminated.

Even though this shift is visible both on H-BEA_comm. and on H-BEA-nano_12.5 samples, it seems to be more pronounced on H-BEA-nano_12.5.

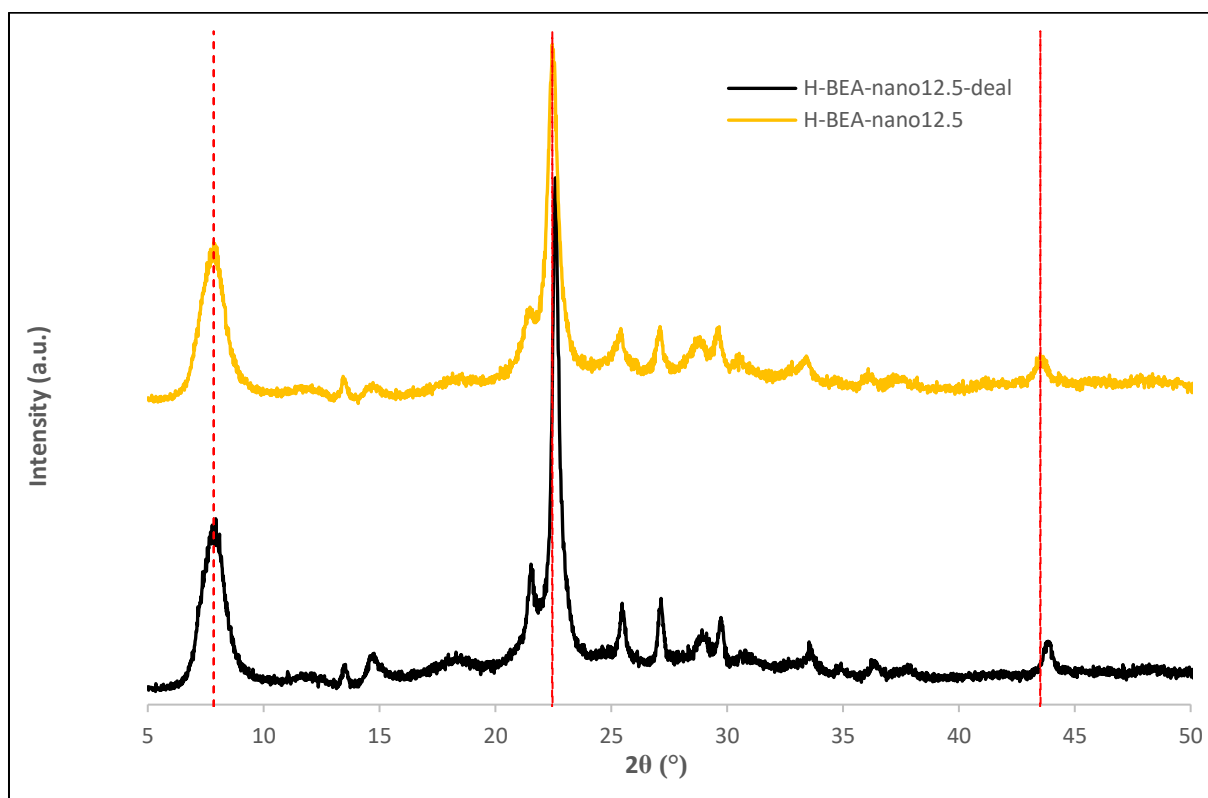


Figure 26: Comparison of XRD patterns of the dealuminated and original H-BEA-nano_12.5 samples. The red dotted lines represent the angle values of the three main peaks (taken at highest intensity) of the original H-BEA-nano_12.5.

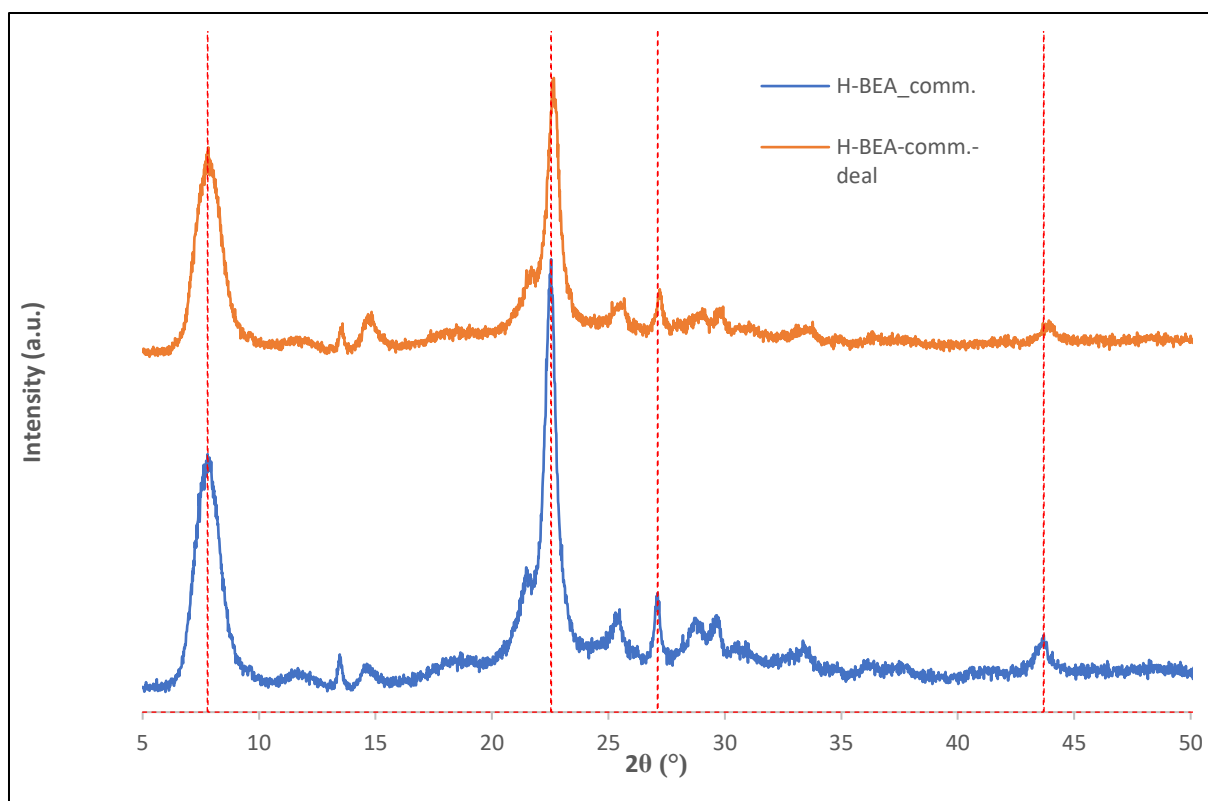


Figure 27 : Comparison of XRD patterns of the dealuminated and original H-BEA-comm. samples. The red dotted lines represent the angle values of the main peaks (taken at highest intensity) of the original H-BEA-comm.

We were only able to study the impact of dealumination on structural properties of our samples (by XRD). However, it has been suggested in a previous study that dealumination does not impact the textural properties of beta zeolites samples. (83)

3.2.2. Effect of the Si/Al ratio

The effect of the Si/Al ratio on the structure, texture and particle size was investigated.

3.2.2.1. XRD

To assess the effect of the Si/Al ratio on BEA crystalline structure, we compared the XRD patterns of the synthesized (dealuminated²) H-BEA_nano_12.5, H-BEA_nano_25 and H-BEA_nano_50 samples (Si/Al ratios of 12.5, 25 and 50, respectively) (Figure 28).

² Unfortunately, all the H-BEA_nano_25 and H-BEA_nano_50 samples were dealuminated before XRD analyses were performed. Otherwise it would have been more relevant to compare the parent (non-dealuminated) samples.

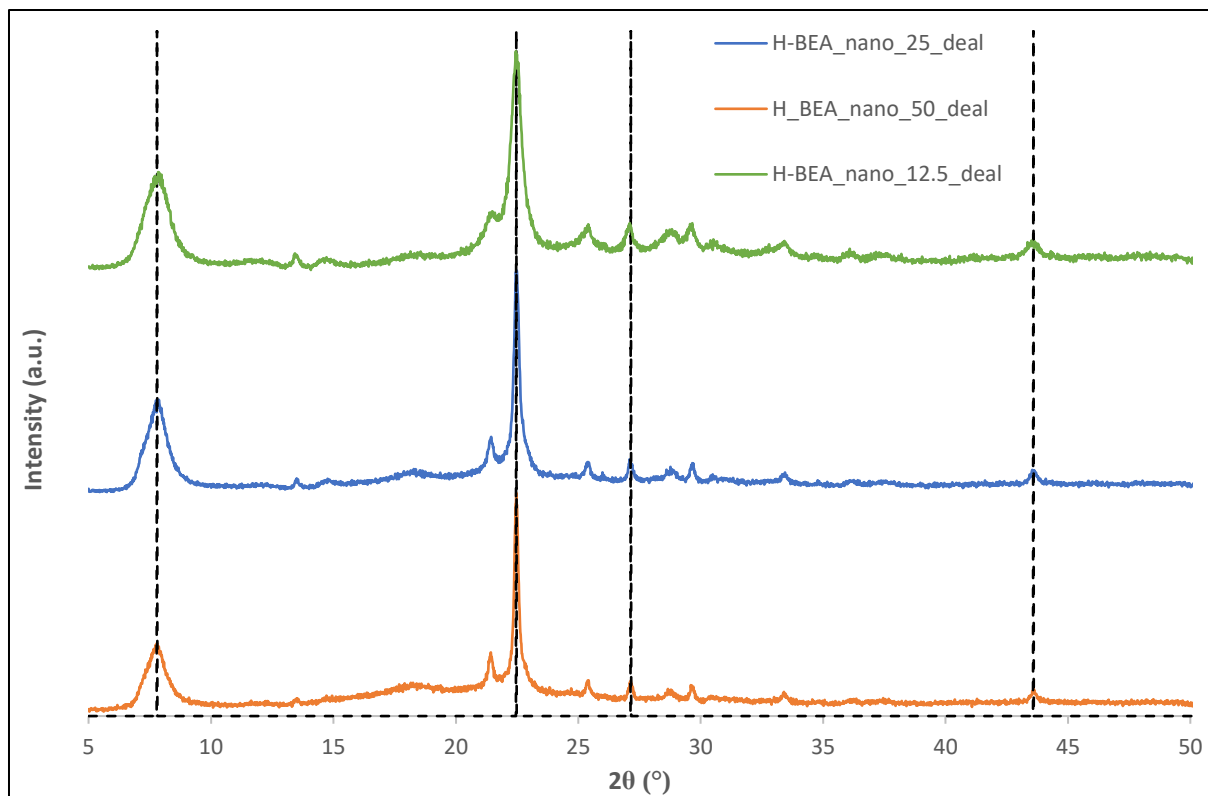


Figure 28 : XRD patterns of synthesized nano-zeolites dealuminated with targeted Si/Al ratios of 12.5 (H-BEA_nano_12.5_deal), 25 (H-BEA_nano_25_deal) and 50 (H-BEA_nano_50_deal). The dotted lines represent the angles values of the main peaks of H-BEA_nano_50_deal.

One can observe that the main peaks of the beta structure are found on both diffractograms. Moreover no significant phase change or shift can be evidenced by XRD between these two BEA catalysts, suggesting we obtained the same structure in both samples.

Such result is consistent with other studies reporting that Si/Al ratio does not significantly impact the XRD patterns in certain ranges, dependent of the synthesis conditions (Si/Al from 10 to 50 without Na^+ (64), Si/Al from 8 to 200 in fluoride media (62)).

3.2.2.2. N_2 physisorption

Adsorption and desorption N_2 isotherms related to H-BEA_nano_12.5 and H-BEA_nano_25 are shown in Figure 29.

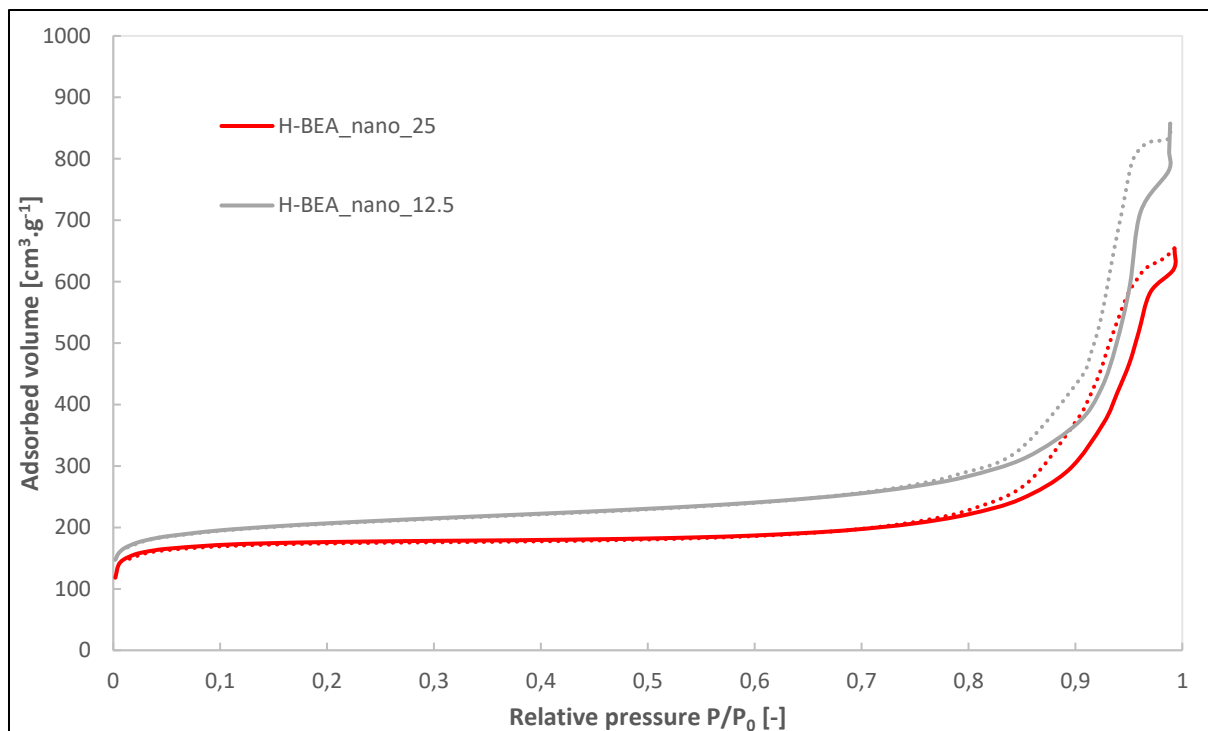


Figure 29 : N_2 physisorption (adsorption and desorption) isotherms of synthesized H-BEA zeolites with targeted Si/Al ratios of 12.5 (H-BEA_nano_12.5) and 25 (H-BEA_nano_25). Dotted lines represent the desorption curves.

As expected, the H-BEA_nano_25 sample displays very similar isotherm shape to H-BEA_nano_12.5 (type IV isotherm additionally to the type I isotherm, characteristic of zeolites (microporous samples)). Nevertheless we can observe that microporous area (proportional to the first uptake of N_2 , at P/P_0 values lower than 0.05) of the two samples are quite similar whereas the external surface area (related to the slope of the isotherm after the first uptake) seems higher in H-BEA_nano_12.5. This observation is confirmed in the main textural results obtained from these isotherms (Table 13).

Table 13 : Summary of main textural properties obtained via N_2 physisorption analyses on synthesized H-BEA zeolites with targeted Si/Al ratios of 12.5 (H-BEA_nano12.5) and 25 (H-BEA_nano25).

Sample	S_{BET} [$m^2.g_{cat}^{-1}$]	External surface area [$m^2.g_{cat}^{-1}$]	Micropore volume [$cm^3.g_{cat}^{-1}$]
H-BEA_nano_12.5	775	240	0.22
H-BEA_nano_25	690	90	0.23

These results suggest that both H-BEA_nano_25 and H-BEA_nano_12.5 display similar total specific surface areas whereas their external surface areas significantly differ. It is reported that the lower the Si/Al ratio the lower the crystal size, (61–63) and therefore, the lower the particle size. We might thus expect that H-BEA_nano_12.5 sample is made of even smaller crystallites (and thus possibly of smaller particles) than H-BEA_nano_25 sample, what could explain the difference in terms of external surface area between the samples.

3.2.2.3. DLS

In order to assess the impact of the Si/Al ratio of our beta zeolites suspensions on their average particle size, DLS analyses were performed on NH₄-BEA_nano_12.5 (Figure 21) and NH₄-BEA_nano_25 (Figure 30).

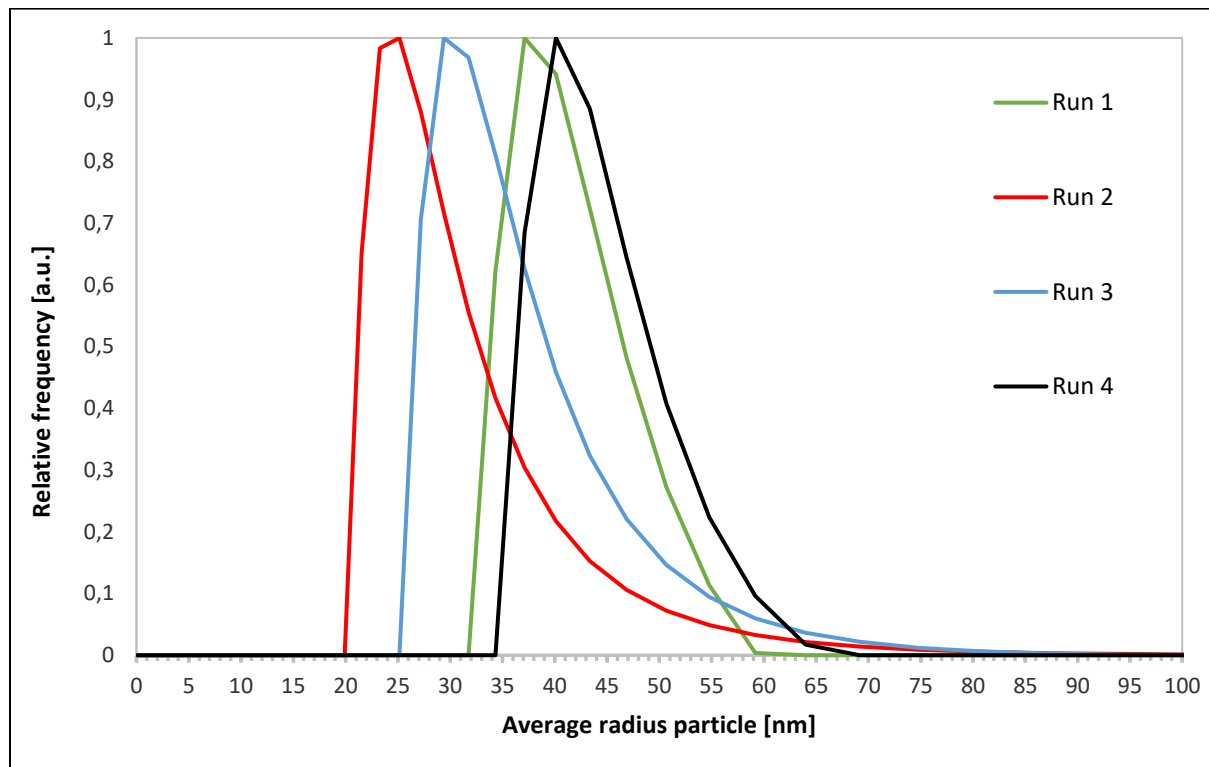


Figure 30 : DLS profile analysis (weighted particle number distribution) obtained for NH₄-BEA_nano_25 sample

This information provided by DLS measurements on NH₄-BEA_nano_12.5 (Figure 21) and NH₄-BEA_nano_25 samples are summarized in Table 14.

Table 14 : Summary of DLS data obtained for sonicated H-BEA_comm.and H-BEA_nano_12.5 samples

	Particle size distribution	Particle radius [nm]
H-BEA_nano_12.5	Monomodal	25 to 30
H-BEA_nano_25	Monomodal	25 to 40

One can observe that very similar average particle radius were obtained for both samples, even though the degree of variability seems higher in NH₄-BEA_nano_25 sample analysis. Therefore the average particle radius range is wider for this sample. Such result suggests that the Si/Al ratio of the suspension has little to no impact on particle size

3.2.3. Effect of tantalum incorporation in the framework and copper addition

The impregnated catalysts obtained through wet tantalum impregnation could be analyzed (characterized and catalytically tested). The samples were denominated **Cu_x-Ta_y-H-BEA_nano_z** where *x* and *y* represent the Cu and Ta loadings (in wt%) and *z*, the Si/Al ratio, respectively. We were only able to synthesize and fully characterize **Cu₁-Ta₁-H-BEA_nano_z** catalysts (*z* being equal to 25 and 50).

3.2.3.1. XRD

In order to investigate the incorporation of tantalum into zeolite's framework, we characterized the structure of the impregnated samples by XRD. Therefore, Ta-containing H-BEA zeolites (wet impregnation) could be analyzed by XRD. We observe on Figure 31 that Ta₁-H-BEA_nano(25,50) samples display characteristic BEA-type XRD patterns, which suggests that no significant crystalline phase change was detected.

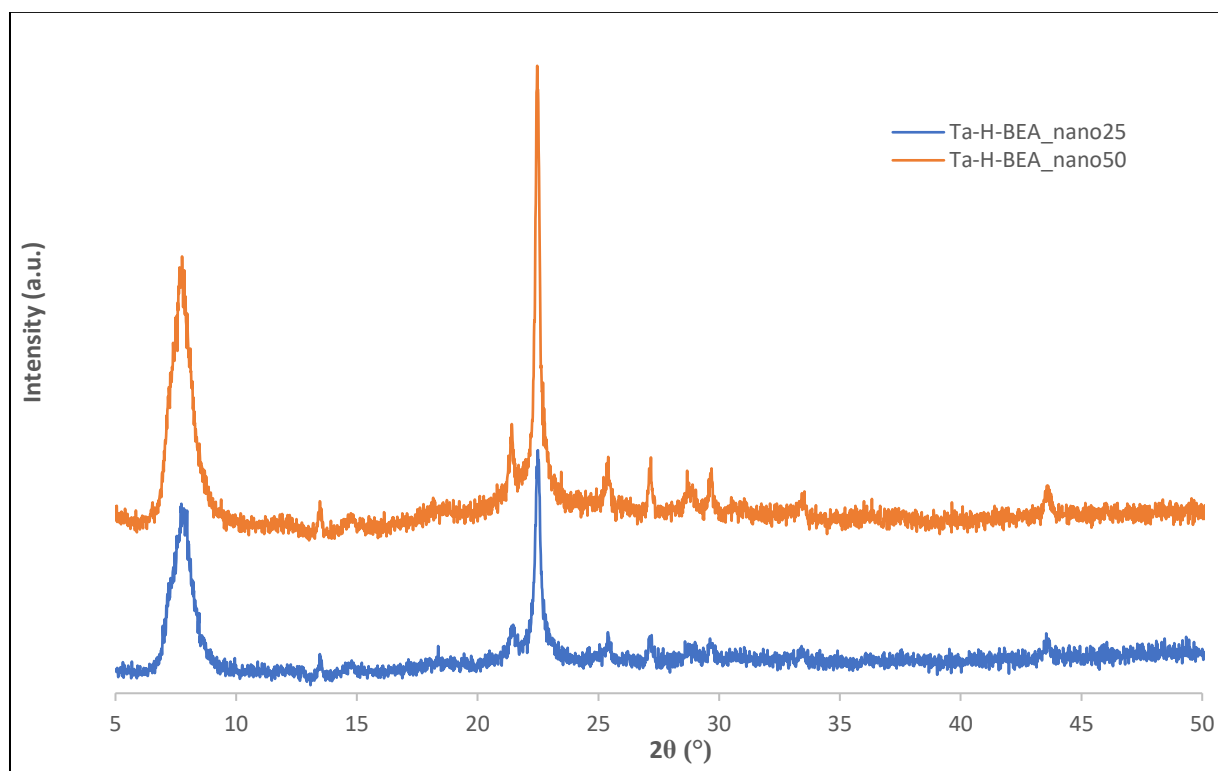


Figure 31 : XRD patterns of Ta impregnated nano H-BEA displaying Si/Al=25 (Ta₁-H-BEA_nano25) and 50 (Ta₁-H-BEA_nano50).

3.2.3.2. N₂ physisorption

To assess if the incorporation of tantalum and the impregnation of copper have impacted the textural properties of the catalyst, we used N₂ physisorption. Figure 32 shows N₂ isotherms of wet impregnated catalysts (Cu₁-Ta₁-H-BEA_nano_25, Cu₁-Ta₁-H-BEA_nano_50 and Ta₁-

H-BEA_nano_50) while those of a sample prepared by dry Ta impregnation (Cu₅-Ta₁-H-BEA_nano_12.5_D) are shown in Figure 33.

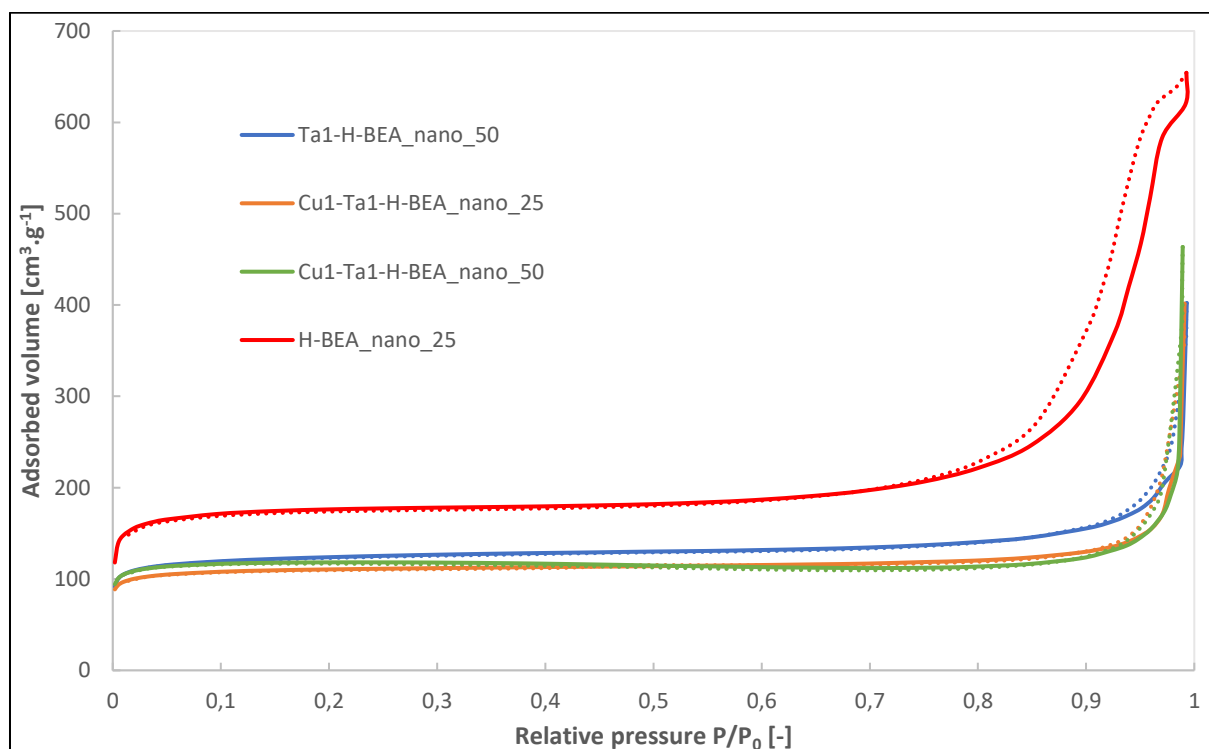


Figure 32 : N₂ physisorption (adsorption and desorption) isotherms of parent nano-zeolite (H-BEA_nano_25) and of resulting impregnated (Ta₁-H-BEA_nano_50 and Cu₁-Ta₁-H-BEA_nano_25 and Cu₁-Ta₁-H-BEA_nano_50) zeolites

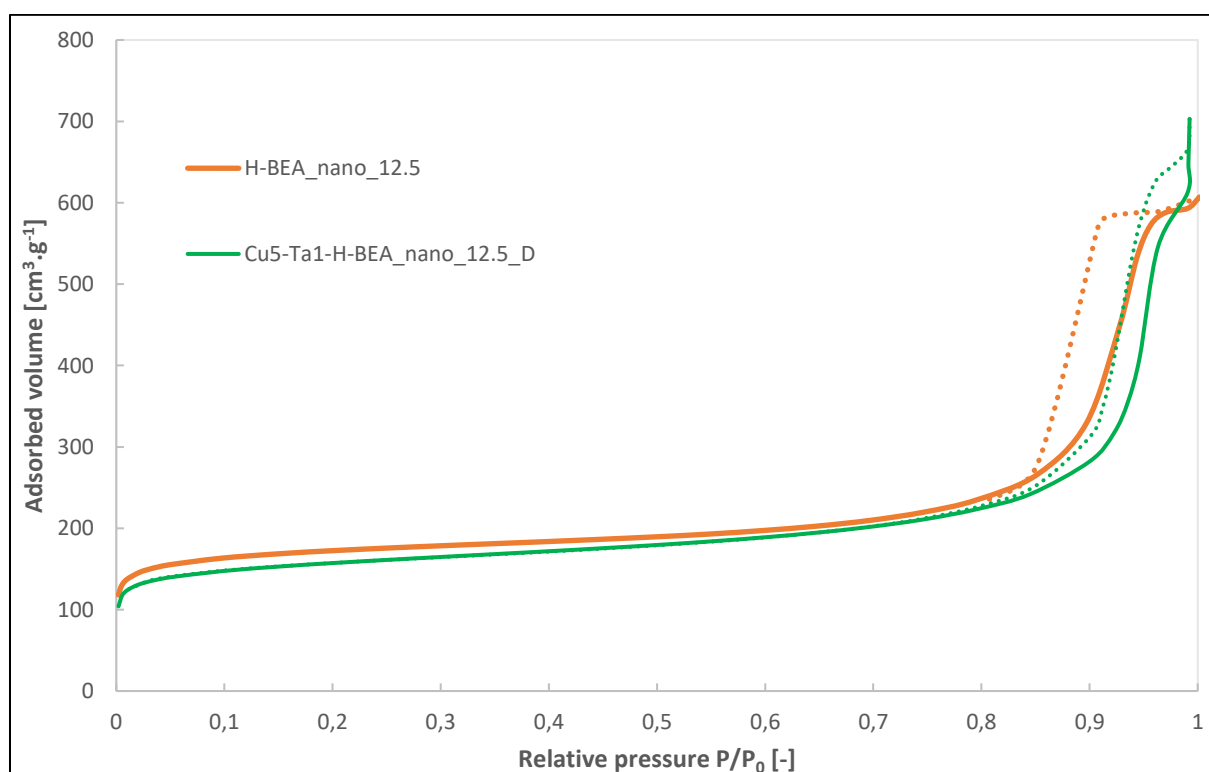


Figure 33 : N₂ physisorption (adsorption and desorption) isotherms of parent nano-zeolite (H-BEA_nano_12.5) and of resulting dry Ta impregnated (Cu₅-Ta₁-H-BEA_nano_12.5_D) zeolites

One can notice on Figure 32 that both Cu₁-Ta₁-H-BEA_nano_25 and Cu₁-Ta₁-H-BEA_nano_50 isotherms are very similar and look like the Ta₁-H-BEA one. The three impregnated samples feature the same type I and IV isotherms as the parent H-BEA_nano_25 zeolite. Unfortunately, we see that Cu₁-Ta₁-H-BEA_nano_50 adsorption isotherm decreases at intermediate values of P/P₀, which is non-sensed physically. Because of this artefact, the t-plot analysis could not be exploited for this sample.

The same trend is exhibited on Figure 33 as both Cu₅-Ta₁-H-BEA_nano_12.5_D and H-BEA_nano_12.5 samples show similar type I and IV isotherms.

Table 15 summarizes the principal textural information of the catalysts presented on Figures 32 and 33.

Table 15 : Summary of main textural properties obtained via N₂ physisorption analyses on parent (H-BEA_nano25) and impregnated (Ta-H-BEA_nano50 and Cu-Ta-H-BEA_nano25 and Cu-Ta-H-BEA_nano50) nano BEA zeolites

	Sample	S _{BET} [m ² .g _{cat} ⁻¹]	External surface area [m ² .g _{cat} ⁻¹]	Micropore volume [cm ³ .g _{cat} ⁻¹]
/	H-BEA_nano_25	690	90	0.23
Wet impregnation	Cu ₁ -Ta ₁ -H-BEA_nano_25	435	50	0.15
	Cu ₁ -Ta ₁ -H-BEA_nano_50	470	/	/
	Ta ₁ -H-BEA_nano_50	480	90	0.15
/	H-BEA_nano_12.5	775	240	0.22
Dry impregnation	Cu ₅ -Ta ₁ -H-BEA_nano_12.5_D	585	205	0.15

One can notice that the S_{BET} measured for all the impregnated catalysts ((Cu_x)-Ta_y-H-BEA_nano_Z) are significantly lower than those of the parent H-BEA_nano_Z. These differences in terms of total specific areas seems mainly due to lower microporous surface areas in both dry and wet Ta impregnated catalysts. Such observation might suggest a partial occlusion of these micropores by corresponding oxides of impregnated metals (Ta₂O₅ or CuO).

We also observe that the external surface area measured for Cu₅-Ta₁-H-BEA_nano_12.5_D sample is higher than those of the other impregnated catalysts (which display higher Si/Al ratios (25 or 50)). This observation goes along with what was reported for the non-impregnated H-BEA catalysts (i.e., that H-BEA_nano_12.5 shows higher external surface area than H-BEA_nano_25).

3.2.3.3. XPS

To investigate the presence of tantalum and copper on impregnated zeolites' surface (Ta₁-H-BEA_nano(25 and 50) and Cu₁-Ta₁-H-BEA_nano(25 and 50)), we performed XPS analyses. The surface atomic ratios obtained on these samples are presented in Table 16.

Table 16 : Atomic Si/Al, Si/Ta and Si /Cu ratios measured by XPS on wet-impregnated samples ((Cu₁)-Ta₁-H-BEA_nano_Z).

Sample	Si/Al	Si/Ta	Si/Cu
Ta ₁ -H-BEA_nano_25	>500	78	/
Ta ₁ -H-BEA_nano_50	>500	48	/
Cu ₁ -Ta ₁ -H-BEA_nano_25	n.m. ^a	80	96
Cu ₁ -Ta ₁ -H-BEA_nano_50	n.m. ^a	44	120

^a These ratios could not be calculated because of the overlap between the Al 2p, the Cu 3p and Cu 3s peaks.

On the one hand, these results allow us to conclude that the samples were successfully dealuminated before the impregnation steps, as the Si/Al ratios exhibited by Ta impregnated samples (Ta₁-H-BEA_nano_Z) are extremely high compared to the nominal ratio the parent zeolites (H-BEA_nano_Z, with Z equal to 25 and 50). However these ratios could not be computed in the Cu₁-Ta₁-H-BEA_nano_Z catalysts due to the superposition (in terms of binding energy (E_b)) of Al 2p_{3/2} (72.7 eV), (84) and of Cu 3p (~75 eV) and Cu 3s peaks.(85,86) Hence it is reported that, when copper is present in the sample, measuring aluminium using XPS spectra is an issue because of this overlapping of aluminium signal with copper species peak position.(86) Nevertheless, since Cu₁-Ta₁-H-BEA_nano_Z catalysts were directly generated from Ta₁-H-BEA_nano_Z, we can therefore reasonably assume that Cu₁-Ta₁-H-BEA_nano_Z displays the same Si/Al ratio as Ta₁-H-BEA_nano_Z samples. Such result implies thus that dealumination was complete in all impregnated samples.

On the other hand, the Si/Ta measured by XPS were fairly lower than the targeted ratios (i.e. 1 wt% of metal loading, which corresponds to a Si/Ta molar ratio of ~300). Such result indicates that Ta has a certain tendency to accumulate at the zeolite surface. However, the Ta content might have been misestimated due to an overlapping of the obtained Ta 4f_{7/2} with O 2s peak position (as shown in Supplementary Figure 1). The observed surface atomic Si/Cu ratio is however consistent with the targeted ratio (i.e. 1 wt% of metal loading, which corresponds to molar ratios of Si/Cu~100).

The obtained binding energies (E_b) for Ta in the impregnated samples are presented on Table 17. Such E_b values obtained for Ta 4f_{7/2} coincides with those reported for Ta in its +5 oxidation state.(87,88)

Table 17 : Binding energies (E_b) of Ta measured through XPS on the analyzed (wet) impregnated samples ((Cu₁)-Ta₁-H-BEA_nano_Z)

Sample	E _b Ta 4f _{7/2} [eV]
Ta ₁ -H-BEA_nano_25	27.4
Ta ₁ -H-BEA_nano_50	27.0
Cu ₁ -Ta ₁ -H-BEA_nano_25	27.4
Cu ₁ -Ta ₁ -H-BEA_nano_50	27.2

3.3. Catalytic results

3.3.1. Catalytic dehydration of ethanol into ethylene

3.3.1.1. H-BEA performances

The synthesized H-BEA catalysts were tested in the dehydration of ethanol and their performance was compared with that of commercial H-BEA and of a benchmark catalyst. The H-ZSM-5 zeolite was chosen as benchmark catalyst, as it is well-known to be highly active in ethanol dehydration, and highly selective to ethylene.(17)

Accordingly, conditions that maximize ethylene productivity of the benchmark (i.e. 240°C, 0.84 g_{EtOH}.h⁻¹ over 0.048 g_{cat} (WHSV=17.5 h⁻¹)) were selected first, which allowed us to measure the productivity of each catalyst (Table 18).

Table 18: Reported experimental conditions (catalyst mass, WHSV) at 240°C and catalytic performances in ethanol to ethylene reaction (ethylene yield and productivity) of tested zeolites.

Catalyst name	Catalyst mass [g _{zeo}]	WHSV [g _{EtOH} .g _{zeo} ⁻¹ .h ⁻¹]	Yield ethylene (%)	Ethylene productivity [g _{ethylene} .g _{zeo} ⁻¹ .h ⁻¹]
H-BEA_comm.	0.0498	17.97	21.2	2.32
H-BEA_nano_12.5	0.0496	18.04	30.2	3.32
H-BEA_SD1_12.5	0.0458**	19.55	41.1	4.89
H-ZSM-5*	0.048	17.5	78.3	8.34

*: The results related to this catalyst (Si/Al=15, from Alfa Aesar) were obtained on the same set-up by Dr. Ales Styskalik.(17)

The benchmark H-ZSM-5 proved to be the most productive. However, it is noteworthy that significant differences of productivities were obtained among the H-BEA samples as well. Indeed, the spray-dried catalyst, which displays the highest productivity among the H-BEA, appears to be more than twice as productive as the commercial one.

Consequently, a WHSV screening test (at constant temperature) was performed until reaching close to complete ethanol conversion. The obtained ethanol conversions and ethylene selectivities are presented in Figure 34 and Figure 35.

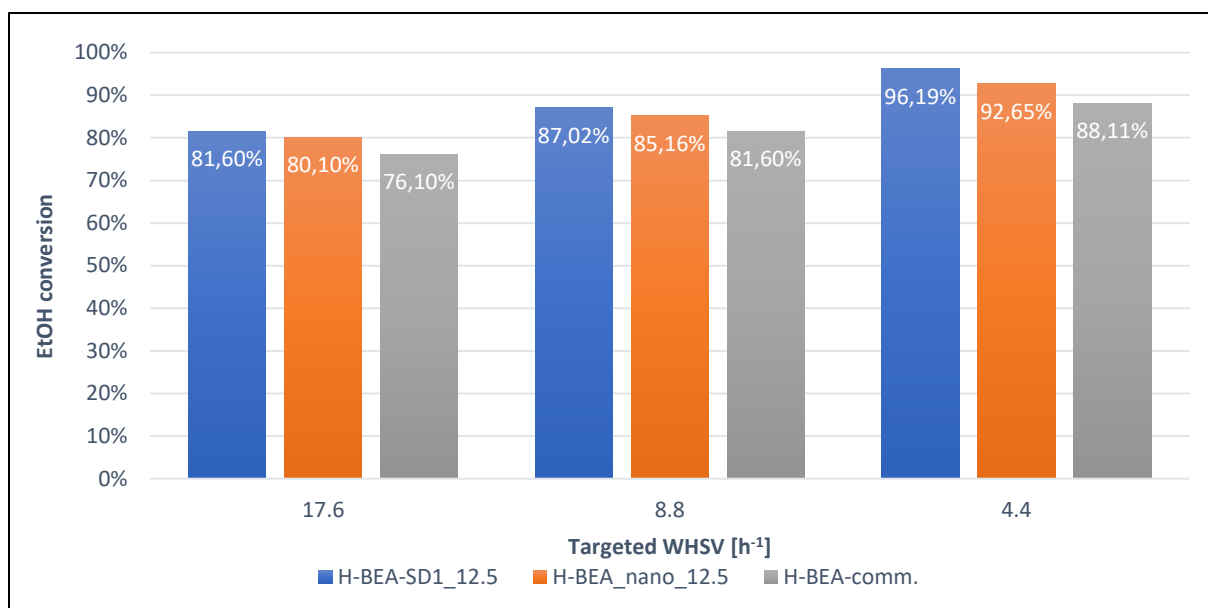


Figure 34 : Ethanol conversions of tested H-BEAs catalysts at different WHSV [h^{-1}] and at 240°C.

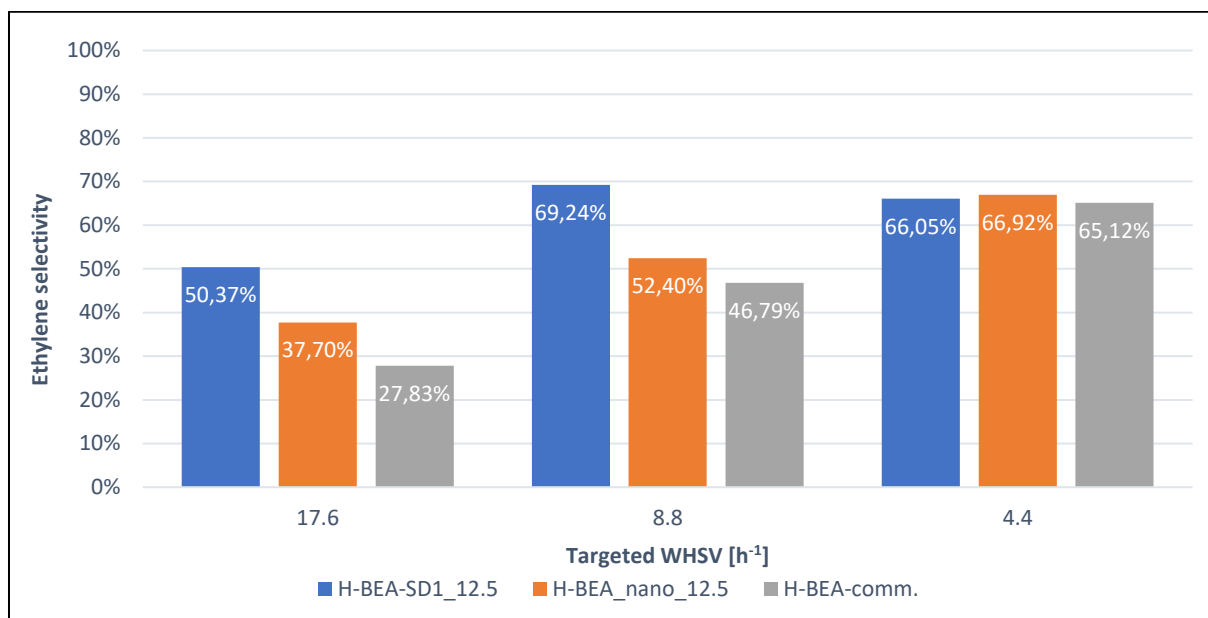


Figure 35 : Ethylene selectivities achieved over tested H-BEAs catalysts at different WHSV [h^{-1}] and at 240°C.

Generally speaking, both ethanol conversion and ethylene selectivity were found to increase along with decreasing space velocities. A marked tendency is also observed when looking at catalytic performances in ethylene production obtained with the different samples. At least at the two highest WHSV, either ethanol conversion and ethylene selectivity results followed the trend H-BEA_SD1_12.5 > H-BEA_nano_12.5 > H-BEA_comm,. When decreasing the space velocity from 8.8 to 4.4 h^{-1} we can however observe a decrease in terms of ethylene selectivity on the spray-dried sample. It results that at a WHSV around 4.4 h^{-1} , the three samples display very similar ethanol conversion and ethylene selectivity.

Eventually, stability tests were performed on fresh H-BEA catalysts by maintaining stable conditions for 9h in order to assess the effect of time on stream (TOS) on ethanol conversion

(Figure 36) and ethylene selectivity (Figure 37). The conditions that maximized ethylene selectivity of H-BEA_SD1_12.5 were chosen for this test (240°C , $\text{WHSV}=8.8\text{ h}^{-1}$). The stability with TOS of H-BEAs was compared to the one of H-ZSM-5 at its maximum productivity (240°C , $\text{WHSV}=17.5\text{ h}^{-1}$).⁽¹⁷⁾ It is noteworthy that an additional catalyst was tested here: H-BEA_SD2_12.5. We were not able to assess its catalytic performance in the previous tests.

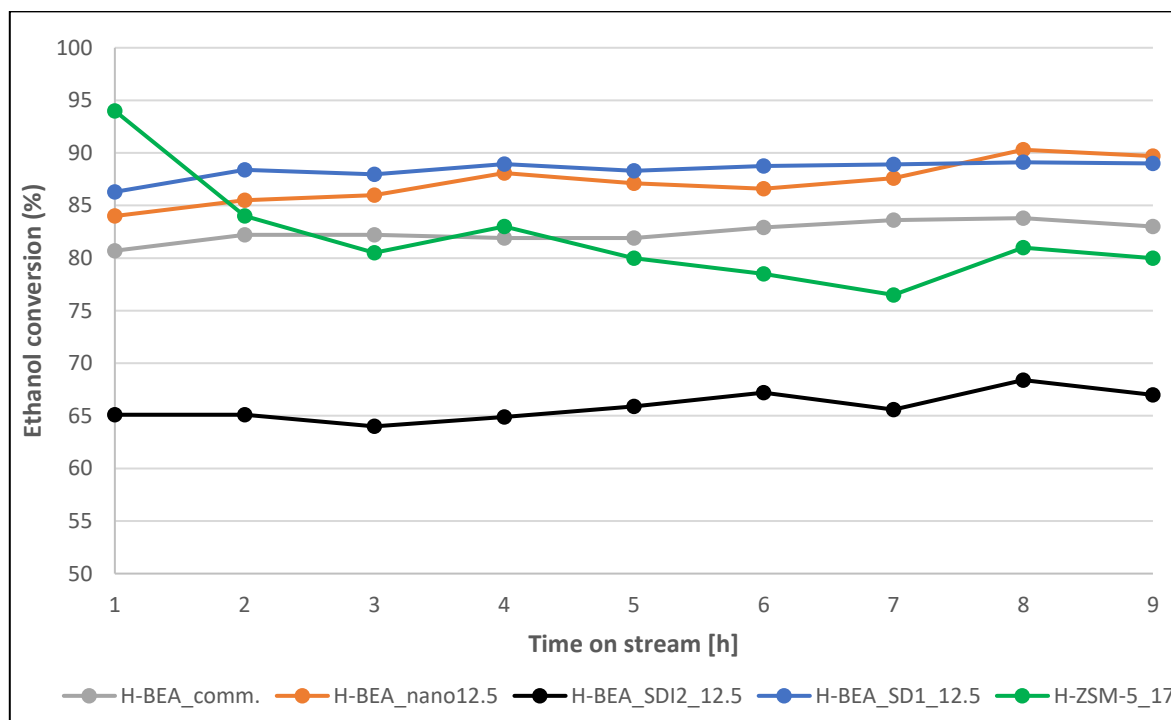


Figure 36 : Ethanol conversion of tested H-BEA catalysts at constant conditions (240°C , $\text{WHSV}=8.8\text{ h}^{-1}$) and of H-ZSM-5 at maximum productivity (240°C , $\text{WHSV}=17.5\text{ h}^{-1}$) during 9h TOS stability test.

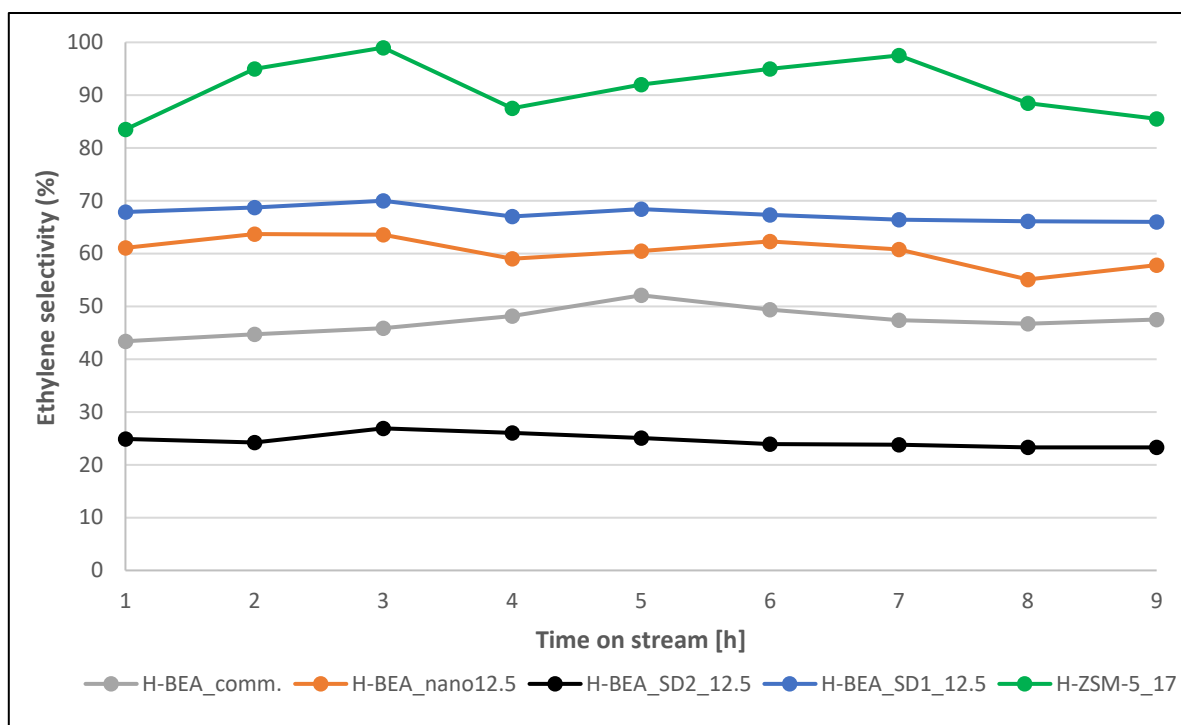


Figure 37 : Ethylene selectivity of tested H-BEA catalysts at constant conditions (240°C, WHSV=8.8 h⁻¹) and of H-ZSM-5 at maximum productivity (240°C, WHSV=17.5 h⁻¹) during 9h TOS stability test.

On the one hand we can observe that all H-BEA catalysts gave stable conversions (maximum 5% drops) whereas H-ZSM-5 exhibited a marked 15% drop during 9h. Moreover, ethylene selectivity remained very stable for all H-BEAs catalysts while it was found oscillating (between 82 and 99%) for H-ZSM-5. On the other hand we noticed that H-BEA_SD2_12.5 catalytic performances were much lower than those of the other H-BEAs whereas the other spray dried catalyst (H-BEA_SD1_12.5) is the most productive H-BEA tested here.

3.3.1.2. Ta₁-H-BEA_nano25 performances

In order to estimate its dehydration power and its acidity, we perform ethanol dehydration catalytic tests over a Ta-containing BEA zeolite: Ta₁-H-BEA_nano25. In such temperature screening test we proceeded by keeping the WHSV constant and increasing temperatures by 15°C (or 30°C) increments, until a ~95% ethanol conversion was reached. Two different WHSV were tested: a higher one for ethanol-to-ethylene reaction (8.8 h⁻¹) and a lower one, similar to ETB reaction conditions (1.1 h⁻¹). The ethanol conversion and ethylene-diethylether (DEE) selectivity profiles obtained are presented in Figure 38 and Figure 39.

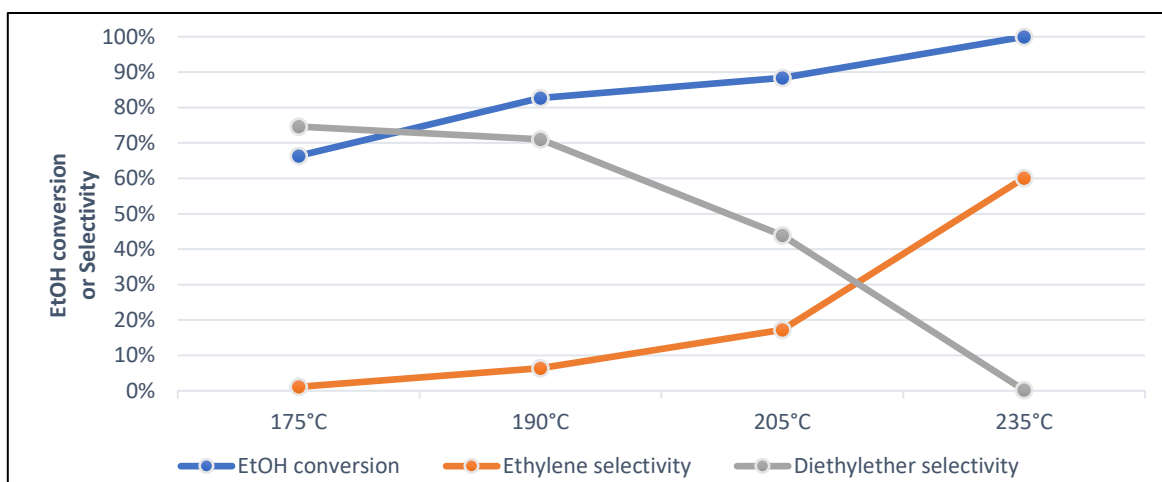


Figure 38 : Ethanol conversion, DEE and ethylene selectivities temperature profiles obtained over Ta₁-H-BEA_nano_25 catalyst at WHSV=1.1 h⁻¹.

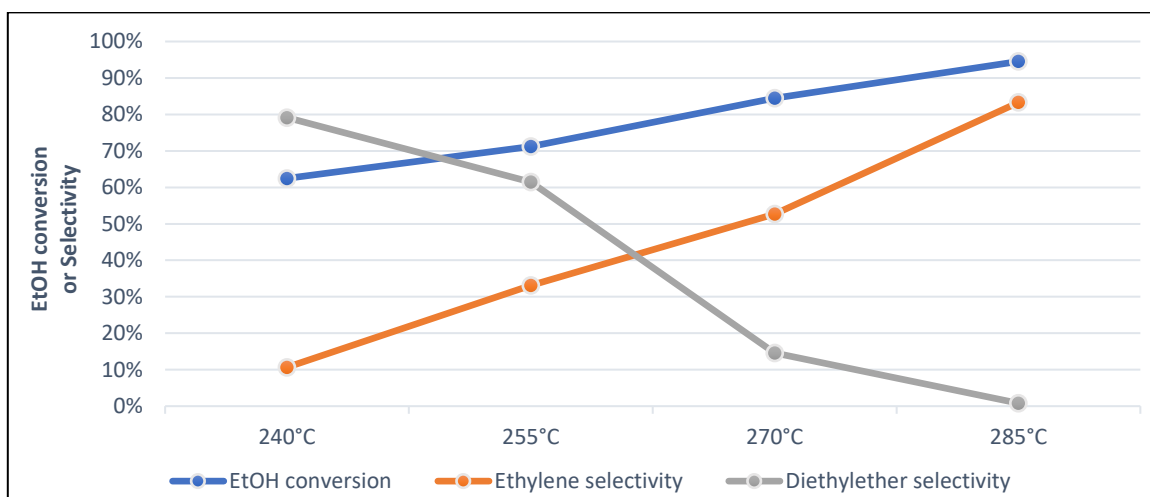


Figure 39 : Ethanol conversion, DEE and ethylene selectivities temperature profiles obtained over Ta₁-H-BEA_nano_25 catalyst at WHSV=8.8 h⁻¹.

We can observe two important tendencies, independent of the WHSV. An increase of the temperature leads to:

- i) an increase of ethanol conversion
- ii) a shift towards increasing ethylene selectivity (at the expense of DEE).

Moreover, as expected, the higher the WHSV, the lower the ethanol conversion and ethylene selectivity at a given temperature. At 240°C this Ta-based catalyst showed much lower performance than the parents H-BEAs catalysts in terms of ethylene production. This was expected because Ta has replaced Al in an attempt to modify the acidic properties of the catalyst, and thereby tempering its dehydration activity in the perspective of the complex cascade reaction that should lead to butadiene, when a metal is incorporated.

3.3.2. Catalytic conversion of ethanol into butadiene

The catalytic performances of Cu₁-Ta₁-BEA_nano50 were tested for the ethanol to butadiene reaction at 325°C. At the three tested different space velocities (1.1 h⁻¹, 2.2 h⁻¹ and 4.4 h⁻¹), ethanol conversion remained equal to 100%, and ethylene selectivities close to 100% were obtained as well. Thus, despite the addition of Cu, these catalysts did not exhibit sufficient dehydrogenation activity to trigger the reactions that lead to butadiene.

4. Discussion

4.1. Nano H-BEA: synthesis, shaping and performance in the ethanol to ethylene (ETE) reaction

4.1.1. Comparison of the synthesized nano-H-BEA with commercial H-BEA zeolites

XRD results (Figure 20) showed that the structure of the nano-sized H-BEA zeolite synthesized here is identical to a commercial H-BEA sample. In parallel, Figure 21 showed that the protocol implemented here led to small particles of about 30 nm. This particle size coincides with the crystal size estimated by XRD analyses through Scherrer equation (Table 8). Thus, the synthesis method presented here allowed obtaining the desired H-BEA structure, but in the form of well dispersed nanocrystals (in suspension) which are not available commercially. This is important, considering our strategy to build zeolite microspheres from small nanocrystals in order to benefit from a higher external surface-to volume ratio. This strategy relies on spray drying and requires a stable colloidal suspension (see below).

As far as N₂ physisorption experiments are concerned, we noticed that the nano-sized BEA zeolites (H-BEA_nano_12.5) display higher total surface area than the commercial zeolite (H-BEA_comm.) (Table 10). However, one should keep in mind that approximatively 10% of error is related to these textural measurements.⁽⁸³⁾ Indeed, even on commercial beta zeolites catalysts the results obtained from such experiment showed an important variability.

Taking these information into account, the total surface area only slightly differs between each sample of BEA zeolite.

Importantly, however, the external surface of H-BEA_nano_12.5 appears to be significantly higher than the one of H-BEA_comm., which is surprising considering the fact that these zeolites show the same crystal size. Indeed, as the elementary crystallites seem to have the same size in both samples, there should not be any difference in terms of S_{BET} measured by N₂ physisorption, unless if these crystals are partly fused together in H-BEA_comm..

Commercial BEA are typically described as bulky aggregates of nanocrystals displaying average diameter of ~100 nm to 200 nm.^(66,89) This was suggested by DLS measurements (Figure 22). Even though DLS measures performed on H-BEA_nano_12.5 (Figure 21) suggest the presence of dispersed nanoparticles of about 30 nm (nanocrystals), we might think that aggregation (or sintering) of such H-BEA_nano_12.5 nanocrystals probably occurred upon thermal processes (drying and calcination). Therefore we should perform SEM images on H-BEA_nano_12.5 sample to assess their morphology and estimate their final particle size.

From the NH₃-TPD profiles (Figure 25), we could observe that both commercial and nano H-BEAs display similar acid strengths. Such result suggesting that the synthesis method has no effect on the acid sites strength of zeolites (estimated by NH₃-TPD) seems to go along with what has been reported in studies working with nano-sized zeolites (H-ZSM-5 and SAPO-34).

(90,91) Indeed, acid strength is determined by the crystal structure, and hence is homogeneous on one zeolite, as long as the Al species are incorporated in the crystal structure. (92) Therefore, varying its composition (i.e., changing the Si/Al ratio of the hydrothermally synthesized sample, extent of ion exchange) affects the number of acid sites, but does not affect the acid strength (unless the aluminum loading is increased so much that extraframework species are formed). Hence, our result reporting no differences in terms of acid site strength between different H-BEA zeolites seems consistent with the literature. It is also consistent with the fact that the same BEA structure is obtained in the nano version of the zeolite, compared to the commercial sample.

According to the literature, NH_3 -TPD-curves of zeolites usually show two desorption peaks, indicating the existence of at least two types of acid sites. (93) Coupling TPD data with – for example – infrared spectroscopy coupled with pyridine allowed to decipher the different contributions. On the one hand, zeolitic Brønsted acid sites (BAS) (formed by aluminum atoms connected to silicon by a bridging hydroxyl (Si-OH-Al) where the negative charge generated is compensated for by a proton) leads to the main NH_3 desorption peak in temperature range of 150 to 450°C. These acid sites may bind basic molecules such as ammonia via hydrogen bonds.(94) These BAS can be described by two acid sites and thus decomposed in two peaks, corresponding to weak and strong sites, respectively.(93) On the other hand Lewis acid sites (LAS) are composed of aluminum with low coordination formed from dihydroxylation acting as an electron pair acceptor, are observed at $T > 450^\circ\text{C}$. Hence, three different adsorption sites for ammonia coexist in the zeolites (Figure 40).(93) According to this classification, the obtained NH_3 -TPD profiles suggest that H-BEA mainly contain BAS as no peak at $T > 450^\circ\text{C}$ could be evidenced in Figure 25.

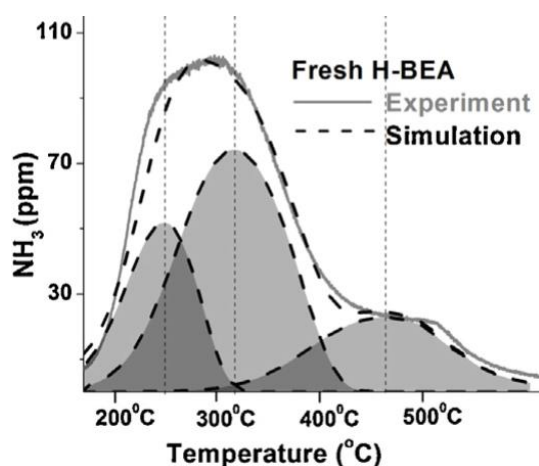


Figure 40 : Theoretical (simulation) and observed (experiment) NH_3 desorption peaks in function of temperature obtained by Shwan et al. (2015)(93) on H-BEA. Hatched areas represent the peak decomposition into weak (250°C) and strong BAS (300 °C) and LAS (450°C)

It was also evidenced (in Table 11) that H-BEA_comm. features a much lower amount of acid sites (per gram) than the synthesized H-BEA_nano_12.5 catalyst. It is noteworthy that for a zeolite with a “perfect” structure (meaning perfect crystallinity and suffering from no effects

due to a high aluminum concentration), each aluminum atom is supposed to be a Brønsted acid site.(94) Therefore the acid site concentration is expected to decrease with increasing Si/Al ratios. Here, the nominal Si/Al ratio is the same for both catalysts, Yet, as we could not perform ICP elemental analyses on the synthesized H-BEA samples, we cannot be sure that they actually feature the same Si/Al ratio. Hence these different acid concentrations obtained for both samples by NH₃-TPD might be the result of different Si/Al ratios (lower for the synthesized nano H-BEA than for H-BEA_comm.). However, XPS results obtained on H-BEA_nano_12.5 – though valid only for the surface – do not support this hypothesis as we observed that the synthesized H-BEAs display Si/Al ratios close to (slightly higher than) 12.5. Eventually, these different acid site concentrations could either be due to a difference in terms of particle (or crystal) shape which could generate different defects in the lattice. These differences could indeed have been generated as very different synthesis methods were (probably) employed to prepare H-BEA_nano_12.5 and H-BEA_comm.

4.1.2. Effect of the spray drying of nano H-BEA

Unfortunately, the spray-dried microspheres could not be analyzed by XRD. Yet, from previous experience in the group and from results published in the literature, we can put forward that the spray drying process will not have affected the structure of the sample.(95,96) In other words we do not expect any change in terms of framework topology in H-BEA_SD1_12.5 and H-BEA_SD2_12.5.

N₂ physisorption experiments performed (Table 10) showed that H-BEA_SD1_12.5 sample displays significantly lower total (and external) surface area than the non-spray dried (parent) H-BEA_nano_12.5 catalyst. Such result seems to be inconsistent with those reported by authors working with spray dried nano-sized TS-1 zeolites.(95) In that case, the authors obtained higher external surface area (as well as higher total pore volume) for nano zeolites aggregated using aerosol process than for same nano zeolites dried in air. However, the result that they obtained was logical as they used mesoporous silica as binder, which conferred additional texture to the material. Here, we add a non-porous binder (LUDOX®). Nevertheless, in another study focusing on the fabrication of microspheres made of nano TS-1 crystals via a spray drying process, a negative impact of the binder (a silica sol (non-mentioned product)) addition on the S_{BET} of the material was evidenced.(67) Total pore volume was yet increased as the binder has a bridging effect.

Taking these information into account, we could think that the added binder (LUDOX® AS-40 (135 m²/g according to the manufacturer, (97) before its further polycondensation) could play a role in the explanation of this lower external area value. It could indeed occupy a fraction of this external surface and thus “hide” the rugosity of the sample’s surface. However, the quantity of LUDOX® added (5 wt%) was reported to be an optimal value to limit the impact of such binder on textural properties (notably).(67) Moreover, previous N₂ physisorption analyses performed by Arnaud Detaille on the same spray dried catalyst (containing the same

LUDOX® content) indicated the opposite (i.e., that H-BEA_SD1_12.5 displays higher S_{BET} than H-BEA_nano_12.5).

To assess the presence of LUDOX® at the surface of the spray dried catalyst, additional bulk elemental analysis (ICP-AES) should be performed and compared with XPS results in order to investigate if the LUDOX® significantly covers the external surface. It could be correlated with a higher Si/Al ratio obtained in XPS than in ICP results.

Nevertheless a clear impact of the spray drying process on textural properties was noticed when looking at the PSD presented in Figure 24. Indeed while broad and random distributions were obtained for H-BEA_nano_12.5 and H-BEA_comm. respectively, H-BEA_SD1_12.5 showed a narrow distribution, which seems typical of hollow hierarchical (spray dried) zeolites.(95,96,98) Such result suggests the presence of well-defined mesoporosity composed of interparticular voids with average diameter of ~15 nm. This could have an impact on the catalytic activity of this catalyst, particularly on the diffusion of ethanol to the active sites. For this reason we should perform N_2 physisorption for the other spray dried catalyst (H-BEA_SD2_12.5) in order to completely assess the effect of spray drying on textural properties.

Eventually it would also be interesting to use SEM to have a better view on the morphology of H-BEA_SD samples, in particular in terms of microsphere size and structure (hollow vs. plain; intact vs. broken; etc).

As far as their acidity is concerned, H-BEA_SD1_12.5 and H-BEA_SD2_12.5 have been obtained from the same batch of H-BEA_nano_12.5 and display therefore exactly the same Si/Al ratio (not taking into account the added LUDOX® binder). Consistently, they displayed very similar NH_3 -TPD profiles and can be considered to develop the same acidic properties. This confirms that the spray drying process does not affect the acid site concentrations. However, a slight (but significant) difference in terms of acid strength was evidenced between both spray dried samples as H-BEA_SD2_12.5 seems to possess stronger acid sites than H-BEA_SD1_12.5. Such result goes against our expectations as both catalysts also come from the same batch of H-BEA_nano_12.5 and therefore present the same BEA structure and the same Si/Al ratio. These catalysts only differ from each other by the position of the spray drying step in their preparation. While the spray drying was only used to shape nano H-BEA particles as microspheres (that subsequently underwent ion exchanges) in H-BEA_SD1_12.5, it was performed as drying final step before calcination in H-BEA_SD2_12.5.

One could therefore think that a possible poisoning of acid sites could have occurred on H-BEA_SD1_12.5 due to the presence of some impurities (e.g. sodium) in the binder, for example. Indeed, Na is a severe catalyst poison that can cause significant activity loss even at low levels. For example, from ~0.05 wt% Na, the activity is equal to ~90% of the of the “non-poisoned” (fresh) catalyst (see Supplementary Figure 2).(99) Theoretically, however, we never exceeded 0.01 wt% of Na content in our catalyst as we added 5 wt% of LUDOX® AS-40 colloidal silica containing ~0.2 wt% of Na,(100) therefore no significant activity loss should be noticed. Moreover, many washings were applied on H-BEA_SD1_12.5 (as the ion exchanges were performed after the spray drying process), which further decreases the probability of this

catalyst to be contaminated by the binder. Eventually, such a contamination should also (mainly) lead to a decrease of acid site concentration measured by NH_3 -TPD, which is not evidenced here.

Hence, the origin of the enhanced acid strength of H-BEA_SD2_12.5 compared to H-BEA_SD1_12.5 remains thus unclear.

4.1.3. Further interpretation on the catalytic performance of H-BEA catalysts

4.1.3.1. Ethylene productivity trend

A clear tendency was observed regarding the catalytic performance in ethylene production obtained with the different samples. At all WHSV screened at 240°C , ethylene productivities followed the trend $\text{H-BEA_SD1_12.5} > \text{H-BEA_nano_12.5} > \text{H-BEA_comm}$, as shown in Figure 41 (containing the results presented in Table 18). In the additional tests (Figures 36 and 37) that consisted in time on stream stability (TOS) tests in constant conditions ($\text{WHSV} \sim 8.8 \text{ h}^{-1}$, 240°C), this activity trend was preserved.

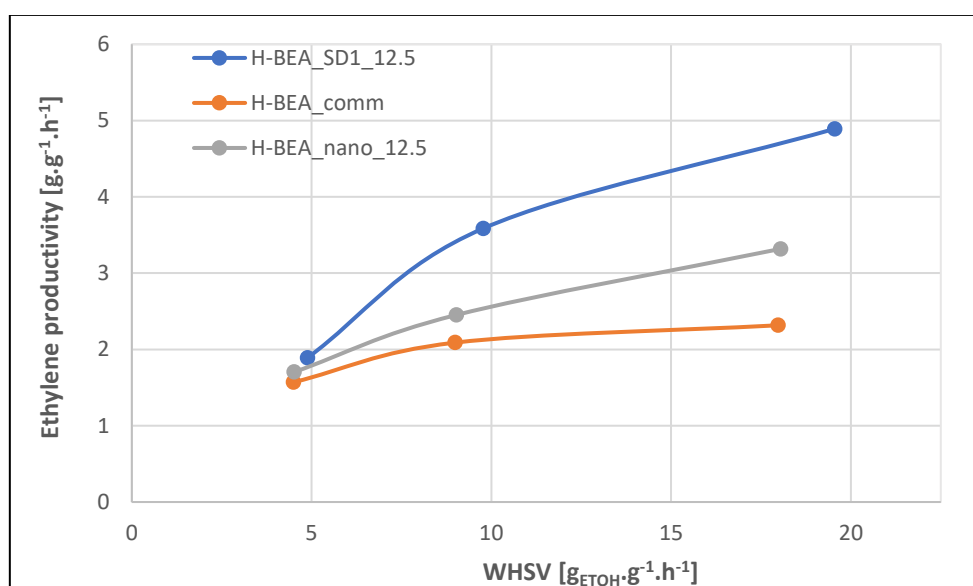


Figure 41 : Evolution of the computed ethylene productivities in function of WHSV for the three tested H-BEA catalysts at 240°C .

Interestingly, we notice that ethylene productivity of the three catalysts increases with the WHSV. It is due to the fact that at higher space velocity, the boundary layer thickness (at the surface of the catalyst) decreases and therefore the mass transfer across this boundary layer is increased.(101) Consequently ethylene productivity (which is proportional to the reaction rate) is found increasing as well. Such profile obtained in Figure 41 suggests thus that the reaction is mass transfer limited (i.e. that external diffusion limitations are significant and limit the reaction rate). If one keeps increasing the WHSV, at some point, the mass transfer across the boundary layer will no longer limit the rate of reaction. Hence, specific reaction rate is independent of the velocity and a plateau will be reached. (101)

However at the lowest tested WHSV ($\sim 4.5 \text{ h}^{-1}$) the three catalysts showed conversions close to 100%, which suggests that catalyst amount is in excess with respect to the feed of reactant. Hence we should not compare their productivities at such space velocity.

Nevertheless, at higher WHSV than 4.5 h^{-1} we observe that this ethylene productivity increases at a higher extent in the spray dried H-BEA_SD1_12.5 compared to the other tested catalysts (H-BEA_nano_12.5 and H-BEA_comm.). We might attribute these differences to the higher ethylene selectivities achieved for H-BEA_SD1_12.5 at these higher space velocities.

It is noteworthy that the conversion is always higher in the synthesized samples (H-BEA_nano_12.5 and H-BEA_SD1_12.5) than in the commercial sample, which has to be related to their significantly higher acid sites concentrations measured by NH_3 -TPD. Indeed, ethanol dehydration is effectively catalyzed by BAS.(17,29,102,103) However, such differences could also be generated by different levels of accessibilities (to ethanol) of these acid sites. Hence we should more in-depth investigate their acidic properties by characterizing them by Infrared spectroscopy (IR) coupled with a basic molecule (e.g. IR coupled with pyridine adsorption) and separately investigate diffusion limitations with dedicated experiments in which we would systematically vary the particle size, the space velocity, the contact time, etc.

4.1.3.2. Ethylene selectivity

In order to assess the ethylene selectivities of the different catalysts, we compared them at iso-conversion (80%) by adapting the space velocity (Table 19). At 240°C , H-BEA_SD1_12.5 is the most selective to ethylene and, surprisingly, H-BEA_comm. is more selective than H-BEA_nano_12.5. H-BEA_SD2_12.5 catalyst could not be included in this comparison since it never reached 80% of conversion. However, as it never showed ethylene selectivity over than 25% (at 65% conversion), we can reasonably think that this catalyst is (from far) the less selective to ethylene.

Table 19 : Ethylene selectivity of H-BEA_comm. (WHSV= 8.8 h^{-1}), H-BEA_SD1_12.5 (WHSV= 17.5 h^{-1}) and H-BEA_nano_12.5 (WHSV= 17.5 h^{-1}) at iso-ethanol conversion (80%) and at 240°C .

Samples	Ethylene selectivity (%)
H-BEA_comm.	46.8
H-BEA_nano_12.5	37.7
H-BEA_SD1_12.5	50.4

It is important to consider exactly the same conversion levels as we observed (Figures 34 and 35) that huge differences in terms of selectivity are generated by slight variations of conversion. It has been reported that ethylene formation can be correlated with the number of strong BAS in the catalyst.(29,34,102) However, NH_3 -TPD analyses did not reveal significant variation in terms of acid strength between H-BEA_nano12.5, H-BEA_SD2_12.5 and H-BEA_comm.. Even more surprisingly, these results suggested that H-BEA_SD1_12.5 sample exhibits weaker acid sites than the other catalysts. Therefore, we put forward that acidic

properties of the catalyst might not be the main determining factor of activities and selectivities in ETE reaction over the tested H-BEA catalysts here.

The other factors susceptible to affect these catalytic performances are the texture and the morphology. Hence, looking at the reaction mechanism of ethanol dehydration, we tried to focus on how these textural properties and mass transfer parameters could affect it. The accepted general mechanism on zeolites (Figure 42) includes the adsorption of ethanol on a BAS to form an ethanol monomer (Step 1) and its subsequent decomposition into a surface-bound ethoxide species and water (Step 2).⁽¹⁰⁴⁾ Desorption of the surface-bound ethoxide species then generates ethylene (Step 3). A parallel (concurrent) reaction involving co-adsorption of another ethanol molecule to form an ethanol dimer can occur (Step 4) and lead to the formation of DEE and water (Step 5). ⁽¹⁰⁴⁾

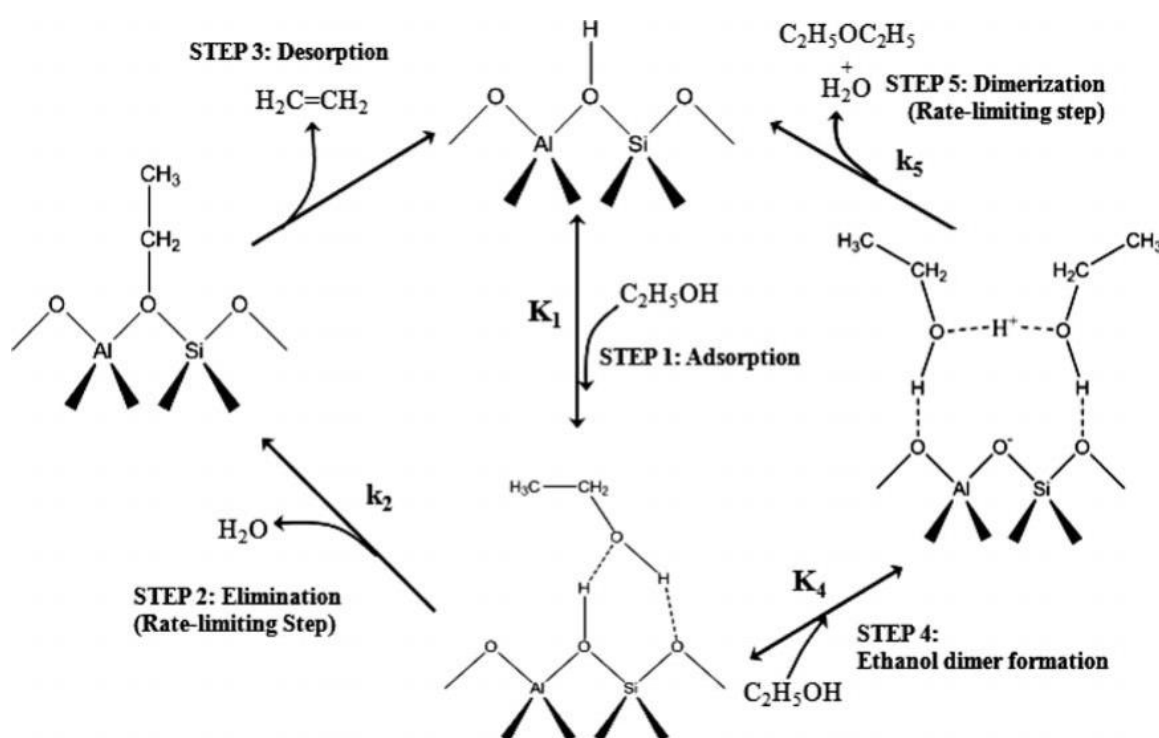


Figure 42 : Proposed mechanism for ethanol conversion into ethylene and diethylether on a 12-membered ring (MR) channels zeolites.⁽¹⁰⁴⁾

As it is reported that the concurrent (parallel) reaction to ETE (i.e. DEE formation from ethanol) includes a bulky molecule (an ethanol dimer). We might therefore think that the diameter of the interparticular voids (i.e. mesoporosity in which ethanol dehydration takes place) can impact the selectivity. Indeed in large enough mesopores to accommodate ethanol dimers, ethanol preferentially dehydrates via a bimolecular pathway to generate DEE. In contrast, the spatial constraints imposed by smaller mesopores favor unimolecular reaction pathway to generate ethylene. Taking these information into account, we could argue that H-BEA_SD1_12.5 is more selective to ethylene because of its well-ordered mesopores of 15 nm; it might be more suitable to produce ethylene than an ethanol dimer with maximum diameter of approximately 1.2 nm (considering C-C, C-H and C-O bond lengths equal ~ 0.12 nm, ⁽¹⁰⁵⁾ and H-bonds of ~ 0.25 nm ⁽¹⁰⁶⁾) compared to bigger (H-BEA_nano_12.5) or randomly

distributed ones (H-BEA_comm.). One should characterize the textural properties of H-BEA_SD2_12.5 and see if the obtained PSD goes along with this explanation. As a matter of fact, these mesopores still remain 1 order of magnitude larger than the molecules of reactants and products, which implies that, if such effect is present, it should have a minor contribution only.

Such reasoning suggesting that mass transfer issues impacts the distribution of products formed by ethanol dehydration in zeolites has already been discussed by some authors.^(29,104,107) However these authors consider that the reaction takes place in the zeolite micropores whereas we think that they suffer from diffusional limitations. We therefore consider another level of porosity (i.e. the inter-crystalline mesoporosity) as host for ETE reaction.

4.1.3.3. Stability with TOS

When performing the WHSV screening test (240 °C), we noticed a maximum value in terms of ethylene selectivity at a space velocity close to 8.8 h⁻¹ for the spray dried sample while it keeps increasing over all WHSV tested for the two other catalysts (see Figure 35). To assess the origin of this maximum value, we had a look at the carbon balance evolution during catalytic tests (Table 20). Note that in this test, for each tested catalyst, we proceeded by decreasing the space velocity. Therefore, the lowest WHSV (~4.4 h⁻¹) was applied after 3h on stream.

Table 20: Carbon balances (%) evolution related to ethanol dehydration tests performed on H-BEA catalysts at different WHSV.

Time on stream	1h	2h	3h
Targeted WHSV	17.5 h ⁻¹	8.8 h ⁻¹	4.4 h ⁻¹
H-BEA_comm.	81%	81%	81%
H-BEA_nano_12.5	80%	76%	75%
H-BEA_SD1_12.5	84%	86%	68%

We can observe that carbon balances are quite similar and around 80% for the three samples, except when the space velocity is decreased from 8.8 h⁻¹ to 4.4 h⁻¹ (after 2 and 3 hours on stream) for the spray dried sample. This significant decrease of carbon balance coincides with an increase in the yield for “others” for this catalyst (Table 21).

Table 21: Others yields evolution recorded over H-BEA_SD1_12.5 during ethanol dehydration tests carried out at different WHSV

Time on stream	1h	2h	3h
Targeted WHSV	17.5 h ⁻¹	8.8 h ⁻¹	4.4 h ⁻¹
“Others” yield	0%	7%	31%

The “others” yields represent the “unexplained” fraction of converted ethanol. In other words, it is the sum of other compounds that are detected (mainly propylene and butenes) and not detected (such as coke) by the GC. As propylene and butenes yields together account for

less than 4%, it mainly suggests coke deposition (or possibly, the presence of other products that are too strongly adsorbed) on this catalyst. This potential coke deposition occurring at decreasing WHSV is in line with what has been reported in the literature. Indeed higher WHSV generally leads to suppression of coke deposition,(108) probably due to the lower time allowed to ethylene oligomerization to occur and form bulky carbonaceous compounds (C_{3+}) on zeolites pores mouth. Such an increase in C_{3+} species, associated with a decrease in terms of ethylene was clearly evidenced when comparing H-ZSM-5 performances at high (17.5 h^{-1}) and low (1.1 h^{-1}) space velocities at 240°C .(17,107). The origin of this potential coke formation occurring on the spray dried catalyst only is however unknown.

In order to confirm this hypothesis, we performed stability test on these three catalysts at higher time on stream in constant conditions (240°C , $\text{WHSV} = 8.8\text{ h}^{-1}$ (Figures 36 and 37)).As all the tested H-BEAs showed stable conversion and ethylene selectivity, and as no carbon balance drop was evidenced (they remained oscillating around 80-85% during 9h), one can reasonably assume that no rapid coke accumulation occurred on these zeolites. Hence these catalysts proved their capacity to perform the ETE reaction during prolonged experiments, at 240°C and moderate space velocity ($\sim 8.8\text{ h}^{-1}$).

To assess the impact of such TOS test on their properties, we should perform additional characterization on these spent catalysts such as N_2 physisorption, thermogravimetric analyses (TGA) or even NH_3 -TPD measurements to investigate this potential coke deposition. We expect that the higher the differences measured by these techniques on fresh and spent catalysts, the higher the coke deposition.

4.1.3.4. Discussion on the spray dried catalysts performances

As previously discussed, the origin of the enhanced acid strength of H-BEA_SD2_12.5 compared to H-BEA_SD1_12.5 remains unclear. Furthermore the stronger acidity of H-BEA_SD2_12.5 is not corroborated by better performances in ETE reaction as this catalysts showed the lowest ethanol conversion and ethylene selectivity among the tested catalyst.

Nevertheless it is suggested that either the ion exchanges or the washing steps (performed on H-BEA_SD1_12.5 after the spray drying process) are involved in the explanation. A potential poisoning of the acid sites of this catalyst could normally be excluded as this sample exhibited nearly equal total amount acid sites as H-BEA_SD1_12.5 in NH_3 -TPD analysis. We might however think that a different acid sites distribution, leading to less accessible acid sites, could be generated in H-BEA_SD2_12.5. Such lower acid site accessibility could explain the lower conversion obtained for this catalyst with respect to H-BEA_SD1_12.5.

4.1.3.5. Discussion on H-ZSM-5 and H-BEA catalytic performances

Despite displaying a significantly lower S_{BET} ($380\text{ m}^2/\text{g}$) than H-BEA catalysts, H-ZSM-5 zeolite initially (after 1h of TOS) showed the highest conversion and ethylene selectivity at both high (17.5 h^{-1}) and low (1.1 h^{-1}) WHSV (at 240°C). It has to be related to the fact that, according to IR measurements performed on commercial zeolites, H-BEA contain a lower total amount

of strong acid sites (i.e. able to retain pyridine at 350 °C) and lower BAS/LAS ratios than H-ZSM-5.(29,34) However, it cannot be due to differences in terms of acid sites strength as the strongest acid sites observed (NH₃-TPD) for H-BEA (325 kJ/mol) were greater than those observed for H-ZSM-5 (250 kJ/mol).(109) It should be therefore interesting to perform N₂ physisorption in order to compare the PSD obtained for this commercial H-ZSM-5 zeolite with that of H-BEA_SD1_12.5.

Nevertheless, as evidenced in Figures 36 and 37, all tested H-BEA catalysts (at WHSV~8.8h⁻¹) exhibited more stable conversions and ethylene selectivity than H-ZSM-5 (at 17.5 h⁻¹) during 9h of TOS.

4.2. Impregnated nano H-BEA: identification of impregnated metals and performances in ETE and ETB reactions

4.2.1. Proof of Ta incorporation into zeolitic framework and evidence of Cu presence on zeolites' surface

When a metal is incorporated into the zeolite structure during the synthesis, three possibilities can be considered: (i) the metal is not able to occupy any positions in the zeolite structure, (ii) the metal is located in the zeolite skeleton and tetrahedrally coordinated with oxygens (like silicon and aluminium) and (iii) the metal occupies extra framework positions as cations or metal oxides.(88) Herein, we would like to prove that, on the one hand, Ta has been incorporated into zeolitic framework and that it is tetrahedrally coordinated with oxygens, in the form of single-site. On the other hand, we would like to show the presence of Cu at the zeolites' surface.

With this first aim, one can expect the zeolite matrix expansion occurring due to longer Ta–O bond length (1.90 Å for mononuclear Ta(V) species in BEA zeolite) than Si–O (1.60–1.65 Å in zeolites) to be detectable by XRD.(48) This would indeed lead to an increase of d₃₀₂ spacing (related to the peak located between 22 and 23°) and thus to a peak shift to lower values of 2θ. However, such shift was not observed between the Ta impregnated and dealuminated (parent) BEA zeolites, as shown in Table 22. Nevertheless, as the tantalum loading targeted for this catalyst is extremely low (1 wt %) and knowing that XRD starts to be sensitive from amount of crystalline phases of ca. 5 wt%,(88) it is not that surprising.

Table 22: Comparison of the maximum peak position in XRD (in terms of 2θ values) between impregnated (Ta-H-BEA_nano) and parent dealuminated (H-BEA_nano deal) samples.

Sample	Peak position (2θ)
Ta ₁ -H-BEA_nano_25	22.47°
H-BEA_nano_25_deal	22.48°
Ta ₁ -H-BEA_nano_50	22.47°
H-BEA_nano_50_deal	22.47°

To examine more deeply if tantalum is present in the form of an oxide layer on the material surface, the XRD patterns of Ta_2O_5 were added to these of the postsynthesized Ta-H-BEAs analyzed. As shown in Figure 43, crystalline Ta_2O_5 shows main XRD peaks at 2θ values of ca. 22.6, 28.3 and 36.6°. It is noteworthy that the 22.6° peak interferes with that of non-modified BEA zeolites. Therefore, it is not attributed to Ta_2O_5 , and no other peak related to the oxide form was detected. However, Ta_2O_5 could also be present in the form of an amorphous layer, therefore undetectable by DRX.

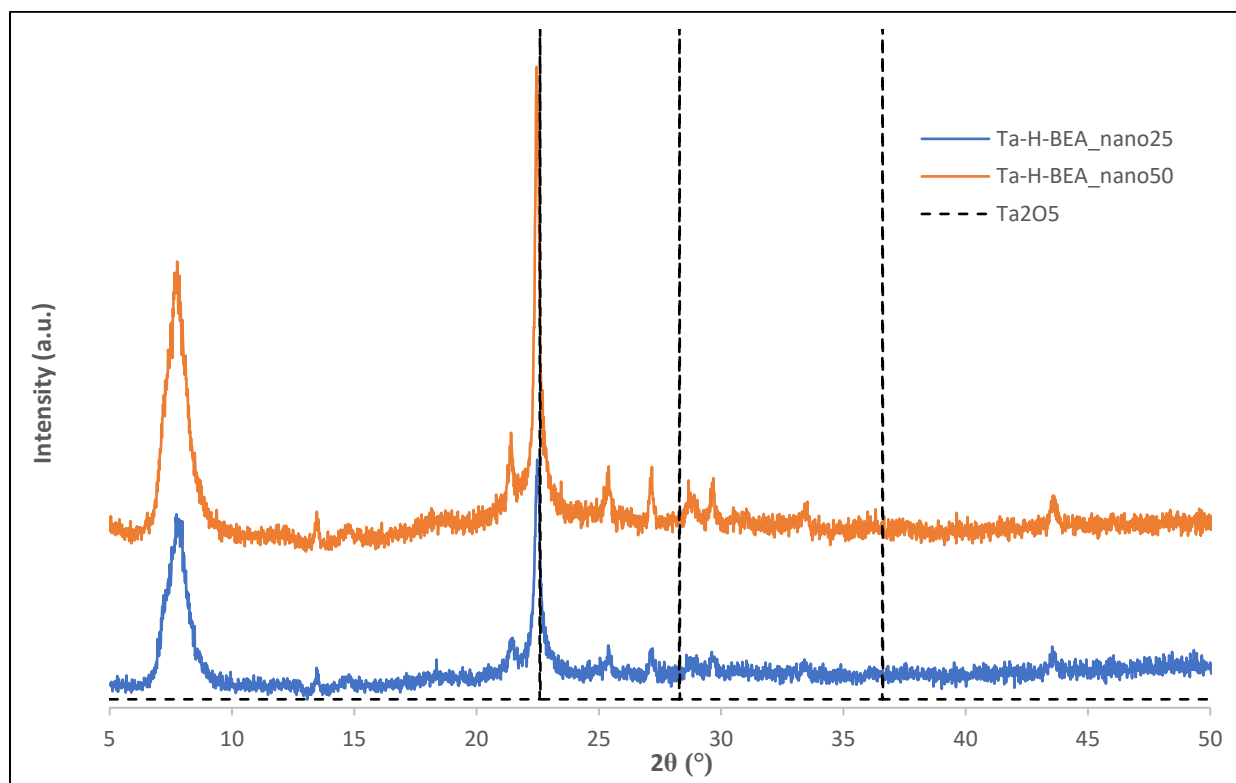


Figure 43: Comparison of XRD patterns of synthesized Ta-containing nano zeolites (Ta1-H-BEA_nano_25 and Ta1-H-BEA_nano_50) with those (main peaks) of crystalline Ta_2O_5 .

When looking at their textural properties (Figures 32 and 33, Table 15), all the impregnated samples displayed a significantly lower S_{BET} than the parent nano-zeolite, which seems to be due a decrease in their microporous surface areas. Moreover the bifunctional catalysts (obtained by wet Ta impregnation) showed significantly lower external surface area than Ta₁-H-BEA_nano_Z and H-BEA_nano_Z.

Such loss of microporous area could be explained by the possible precipitation of the impregnated Ta or Cu at the zeolite surface. Indeed as tantalum compounds readily reacts with water to form its corresponding oxide Ta_2O_5 . As only resuspension into isopropanol were made (and thus no calcination was performed) to obtain the wet impregnated Ta catalysts ((Cu₁)-Ta₁-H-BEA_nano) we might think that some water could still be present in the pores and therefore that Ta_2O_5 could be generated. For this reason we thought that in the samples obtained by dry Ta impregnation method ((Cu_x)-Ta_y-H-BEA_nano_D), tantalum would be less likely to

precipitate at the surface because of the absence of water in the medium. However it was actually not the case as a significant diminution of the microporous area was also noticed on Cu₅-Ta₁-H-BEA_nano-12.5_D.

Taking this last result into account, one could think that the impregnation of the metals (mostly Ta) did not occur in the way we wanted in (Cu_x)-Ta_y-H-BEA_nano(_D) samples. Indeed, we wanted to generate Ta-single site BEA zeolites, i.e. perform the isomorphous substitution of (some) zeolite lattice Al atoms by Ta. If such incorporation was achieved, Ta would be located in the zeolite framework and tetrahedrally coordinated with oxygen atoms. Thus, the textural properties might not be affected.

In order to confirm this hypothesis, we compared the S_{BET} obtained with our Cu-Ta impregnated catalysts to Ta-single sites BEA zeolites found in the literature. Unfortunately, Kyriienko et al. did not perform any textural measurements in their studies based on Ta-BEA and Cu-Ta-BEA. The only result we found on this purpose was that of Zn-Ta-H-BEA (with 6 and 10 wt% of Zn and Ta respectively, incorporated by dry impregnation in commercial BEA, Si/Al=19 (CP814C)).(49) This catalyst showed S_{BET} close to 500 m²/g whereas the parent BEA zeolite displays specific surface area around 700 m²/g according to the manufacturer (Zeolyst International). (110) This decrease in terms of specific surface area is consistent with what we obtained with our impregnated nano-zeolites catalysts (Cu_x)-Ta_y-H-BEA_nano(_D). Such result suggests that the authors also had problems with this impregnation, and that their material lost some texture through this step.

The obtained XPS results performed on the wet impregnated catalysts (Table 16) showed that tantalum seems effectively concentrated on the material surface. Indeed, the surface atomic Ta/Si are ~4 and ~7 times higher than the targeted ratios in Cu₁-Ta₁-H-BEA_nano_25 and 50, respectively. Therefore, we don't expect Ta to be uniformly dispersed in the zeolite framework as the Si/Ta observed in XPS should be then close to (or higher than) 300. Such result suggests the presence of Ta₂O₅ could also be present in the form of an amorphous layer at the surface, therefore undetectable by XRD However, it is noteworthy the Ta content might have been misestimated due to an overlapping of the obtained Ta 4f_{7/2} with O 2s peak position.

Cu was also evidenced at the (Cu₁)-Ta₁-H-BEA_nano surface and the observed surface atomic Si/Cu ratio seems consistent with the targeted ratio (i.e. 1 wt% of metal loading, which corresponds to molar ratios of Si/Cu~100), which suggest a homogeneous dispersion of Cu throughout the material.

In order to determine if the impregnated metals are in the form of their corresponding bulk oxides, we compared their respective binding energies (see Table 17) with that of bulk Ta₂O₅ (26.1 eV).(88) It can be found that the energies recorded for tantalum-containing zeolites were higher than those characteristic of bulk metal oxides. The increase in the binding energy can be attributed to different surroundings of tantalum species in zeolites than in bulk or tantalum(V) oxides.(88) Such surroundings are indeed generated when Si–O–Ta links are created. Therefore, the obtained XPS results go along with the fact that tantalum is present in the form of Ta(V)-single sites in the impregnated BEA zeolites.

Hence, taking into account the results obtained by XPS, XRD and N₂ physisorption analyses, we suggest the presence of Ta(V) (in the zeolite skeleton) and Ta₂O₅ (amorphous layer at the surface) as well as Cu species (at the surface). We should however corroborate this hypothesis with elemental bulk analysis (ICP-AES).

4.2.2. Catalytic activity in ETE of Ta₁-H-BEA_nano_25 catalyst

It resulted that Ta₁-H-BEA_nano_25 catalyst showed from far lower ethanol conversion and ethylene selectivity than all tested H-BEAs catalysts in comparable conditions (240°C, WHSV=8.8h⁻¹). Several reasons can explain its lower activity with respect to the tested H-BEAs:

- (i) the lower specific surface area (i.e. potentially lower number of active sites)
- (ii) the partial replacement of BAS by LAS occurring through the isomorphic substitution of Al atoms by Ta in the framework.

However, as we mainly target butadiene production when using the impregnated H-BEA zeolites, it is desired to have a catalyst that rather displays such “moderate” Brønsted acidity rather than a highly acidic one (that would only produce ethylene at higher temperature).

As far as the catalytic test at lower space velocity (1.1 h⁻¹) is concerned, we can reasonably say that this catalyst is acidic enough in order to perform the dehydration reactions required in the ETB reaction. It is indeed important that the catalyst displays acidic properties as it is proposed that Lewis acid sites (such as those brought by Ta (V)) catalyze every reaction steps subsequent to the initial ethanol dehydrogenation step (aldol condensation, MPV reaction and alcohol dehydration).(49) Accordingly a linear correlation between the amount of acid sites at the catalyst surface measured by NH₃-TPD [μmol/m²] and selectivity towards BD (after 3 h on stream, at 400°C, WHSV=5.3 h⁻¹ using Ta-Zn bifunctional catalysts) was observed.(49)

According to Kyriienko et al. (2017), a relatively low WHSV is needed (0.5 to 1.1 h⁻¹) in order to achieve high butadiene selectivity (>50%) with a Cu-Ta-BEA catalyst.

4.2.3. Catalytic activity in ETB of Cu₁-Ta₁-H-BEA_nano_50 catalyst

This catalytic test was performed at 325°C, i.e. the temperature at which Cu-Ta-BEA catalytic system showed its maximum butadiene selectivity.(48) At three different space velocities, ethanol conversion remained equal to 100% and high ethylene selectivities were obtained. Such result might indicate that dehydrations occurred much faster than dehydrogenation reaction. It highlights the need for higher copper loading into these bifunctional catalysts.

Indeed Dai et al. (2017) studied several catalytic systems based on commercial beta zeolites for the ETB reaction.(47) Notably, Cu₅-H-BEA (5 wt% Cu loading) showed 44% of both acetaldehyde and ethylene selectivity but no butadiene at 93% of ethanol conversion and in

similar experimental conditions ($\text{WHSV}=1.3 \text{ h}^{-1}$, 350°C). Such result suggests that that dehydrogenation can be achieved with higher copper loading. Indeed, a significant fraction of the transformed ethanol successfully underwent dehydrogenation but not the further dehydrations and MPV reaction steps. This might also be due to an unbalanced (too high) BAS/LAS ratio, which may be “corrected” by a better incorporation of Ta in the framework. In other words with additional Lewis acid sites (such as Ta-single sites) one could potentially convert the acetaldehyde produced into butadiene.

On the other hand, Kyriienko et al. (2017) obtained with a $\text{Cu}_1\text{-Ta}_1\text{-BEA}$ (non ionically-exchanged commercial beta zeolites) 73% and 16% of butadiene and acetaldehyde selectivity, respectively, at 87% ethanol conversion (at 325°C , $\text{WHSV}=0.5 \text{ h}^{-1}$). Furthermore, they also obtained in the same conditions with $\text{Ta}_1\text{-BEA}$ 33%, 16% and 28% of acetaldehyde, butadiene and ethylene selectivity, respectively.(48) These results lead us to think that the ionically exchanged H-BEA zeolites might display a too strong Brønsted acidity to effectively form acetaldehyde and butadiene (at least, at low metal loadings ($<5 \text{ wt}\%$)).

In all cases, we wanted to impregnate and test our nano H-BEA with different amounts of metal, particularly apply fairly higher copper loadings (such as 5 wt%). We also planned to synthesize a bifunctional catalyst based on nano non-ionically exchanged beta zeolites (Cu-Ta-BEA_nano) in order to compare its activity with those of Kyriienko et al. (based on commercial BEA).

5. Conclusion and outlook

5.1. Conclusion

This master thesis aimed first at producing nano-sized beta zeolites (BEA) for the effective conversion of bioethanol into ethylene and 1,3-butadiene, in an innovative, green and efficient way compared to the conventional known methods. Studying the effect of their aggregation by spray drying was another point of interest. Therefore some of the prepared nano BEA were further aggregated into microspheres by spray drying in order to assess the impact of such a process on the activity and some properties of the obtained material.

On the one hand, the synthesized BEA were ionically exchanged to generate their H form (H-BEA), that was tested in ethylene production. On the other hand, as the need of a bifunctional catalyst for the ethanol to butadiene (ETB) reaction is highlighted in the literature, (12,16,40,41) a fraction of these ion exchanged zeolites was impregnated with Ta and Cu. Indeed, the silanol nests (or vacant sites) generated upon dealumination of BEA zeolites were used as hosts for tantalum, that was notably incorporated in the framework as Ta(V)-single site. In a second step, the subsequent Cu dry impregnation of these catalysts led to the formation of copper clusters at their surface.

Characterizations performed on non-modified H-BEA samples indicate that nano-sized BEA suspensions with lower particle size than a commercial manufactured H-BEA (H-BEA-comm.) were successfully obtained. This particle size coincides with the crystal size estimated by XRD analyses. Thus, the synthesis method presented here allowed the obtention of the desired H-BEA structure, but in the form of well dispersed nanocrystals (in suspension) which are not available commercially. Moreover, both spray dried (H-BEA_SD_12.5) and non-spray dried (H-BEA_nano_12.5) catalysts exhibited enhanced acid site concentrations compared to H-BEA_comm. despite showing very similar (surface) Si/Al ratios (i.e., ~12.5 in this case).

It resulted that two (H-BEA_SD1_12.5, H-BEA_nano_12.5) of the three synthesized tested H-BEA catalysts were significantly more active and selective to ethylene at 240 °C than H-BEA_comm.. The highest ethylene productivity was obtained with H-BEA microspheres prepared by spray drying followed by ion exchange (H-BEA_SD1_12.5), at WHSV of 19.55 h⁻¹. By generating 4.89 [g_{ethylene}.g_{zeolite}⁻¹.h⁻¹], H-BEA_SD1_12.5 stands among the most performant catalysts reported so far in terms of ethylene productivity. Nevertheless, all the tested H-BEA catalysts yet showed lower ethylene selectivity and productivity compared to the benchmark zeolite (H-ZSM-5).

Among the tested H-BEA, the highest ethylene selectivity (70%) was also achieved with H-BEA_SD1_12.5, but at lower WHSV (~8.8 h⁻¹). The effect of spray drying on the textural properties of this sample was evidenced in N₂ physisorption (BJH model) by a sharp distribution of mesopore diameter, suggesting that monodispersed interparticular voids were generated during the aggregation process. Surprisingly, the less active and selective catalyst tested in ethanol to ethylene reaction was the other spray dried catalyst, H-BEA_SD2_12.5 (H-BEA microspheres obtained by ion exchange followed by spray drying). To assess the origin of these

different catalytic activities between H-BEA_SD1_12.5 and H-BEA_SD2_12.5, several hypotheses were advanced. Among these, we can cite the possible poisoning of active sites of H-BEA_SD2_12.5 (that could have occurred due to the addition of the binder (LUDOX) as final step before calcination), and a different acid site distribution, lowering their accessibility in this catalyst.

Impregnated catalysts characterization showed that BEA structure was retained upon Ta incorporation into zeolite framework but suggested that the texture was affected during metals impregnation. Furthermore, the presence of Cu and Ta could also be evidenced and quantified through XPS analyses performed on wet Ta impregnated catalysts (Cu₁-Ta₁-H-BEA_nano_Z, where Z equals to 25 and 50). On the one hand it resulted that Cu amount measured at the surface was close to its nominal loading, which suggest a homogeneous dispersion of Cu throughout the material surface. On the other hand, Ta amount was fairly higher than expected in the four analyzed impregnated samples. Such result suggests the presence of Ta₂O₅ could also be present in the form of an amorphous layer at the surface, therefore undetectable by XRD.

The location of this metal in the zeolite was also assessed from their respective binding energies. Therefore we suggested the presence of Ta(V) (in the zeolite skeleton) and amorphous Ta₂O₅ as well as Cu species (at the surface). Hence it seems that Cu-doped Ta(V)-single site BEA covered by Cu and Ta₂O₅ species were synthesized through our method.

Finally, the bifunctional catalyst tested in the ETB reaction (Cu₁-Ta₁-H-BEA_nano_50) only produced ethylene at 325 °C. Such result might indicate that dehydration occurred much faster than dehydrogenation reaction and therefore highlights the need of higher copper loading into such bifunctional catalyst.

To conclude, an innovative method followed by Arnaud Demaille allowed us to successfully produce nano-sized BEA, whose H-form features greater amount of acid sites and higher activity in ethanol conversion into ethylene than H-BEA_comm.. We also evidenced positive effects of spray drying on the catalytic activity and some properties of obtained catalysts. Eventually, we also effectively prepared Cu-Ta-H-BEA bifunctional catalysts from nano-sized BEA.

5.2. Outlook

To complete and further improve our investigations, it would be of interest to fully characterize our catalysts. Therefore in addition to the completion of structural and textural analyses, the assessment of the morphology of non-modified H-BEA through SEM images would be useful to better understand the impact of spray drying and of nano-sized BEA on the catalytic activity. Moreover, additional characterizations of their acidic properties through Nuclear Magnetic Resonance (NMR) and pyridine-adsorbed infrared spectroscopy could also implement our analyses.

Concerning the impregnated catalysts, additional elemental analyses (XPS, ICP-AES) and Diffuse reflectance (DR) UV–Vis spectroscopy should be performed on catalysts prepared by both dry and wet Ta impregnation methods. This might allow us to identify which of these methods allows the higher incorporation of Ta(V) species into the zeolite framework. Eventually, the dispersion of Cu species is also an interesting parameter to study.

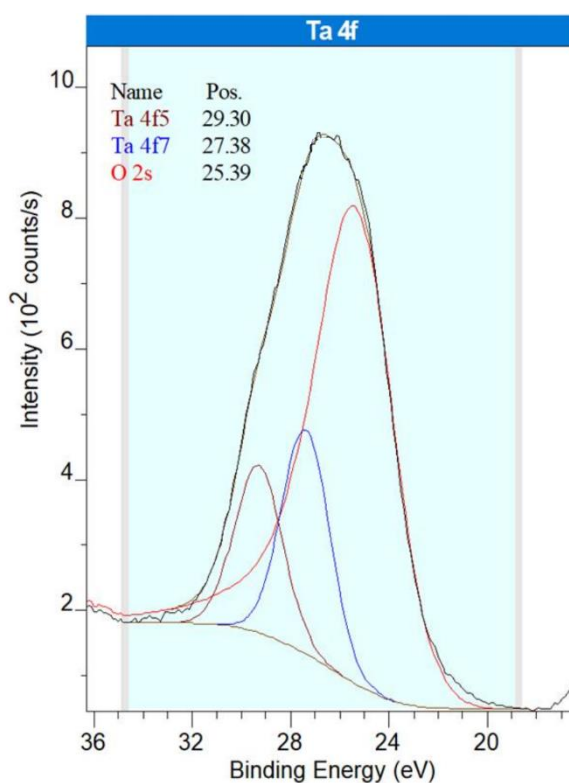
Another important point to focus on would be the optimization of the Ta and Cu loadings on bifunctional BEA-based catalysts for the ETB reaction. We also wanted to impregnate non-ionically exchanged BEA zeolites with Ta and Cu to investigate the potential impact it could have on catalysts performance in the ETB reaction.

Our method could also be further improved by implementing the spray drying step. Hence it would be of interest to keep studying the impact of spray drying on BEA-based catalysts, but also to screen the effect of different parameters (e.g. the solid and binder contents in the suspension, the inlet temperature) on the obtained properties (e.g. the particle size and shape or the catalytic activity). (67)

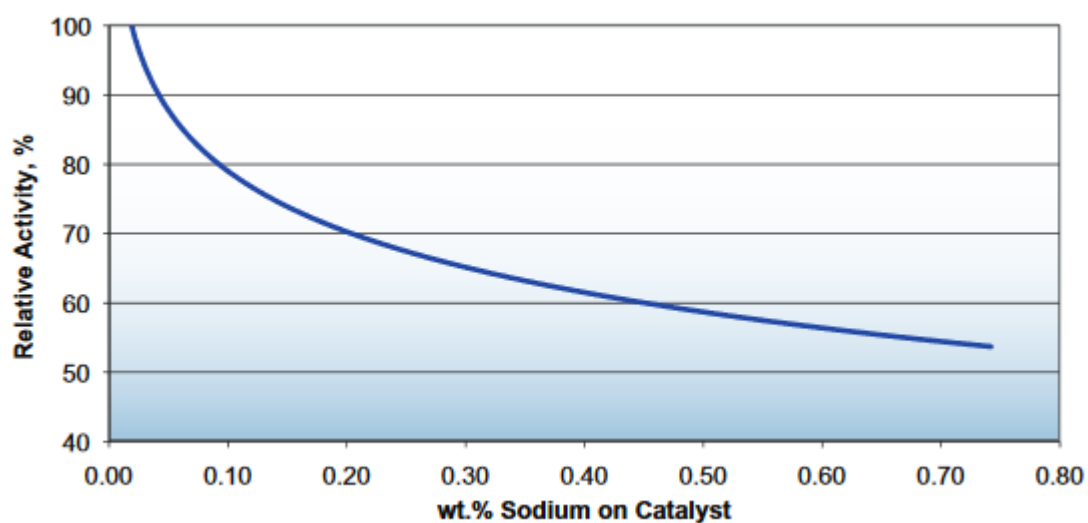
Finally, with industrial applications purpose, further studies focusing on the catalytic stability (with longer time on stream) and recyclability (e.g. effective recovery of the active sites) should be performed on our catalysts.

6. SUPPLEMENTARY INFORMATION

1. XPS peaks (in the E_b range of 16 to 36 eV) recorded on one impregnated ($\text{Cu}_1\text{-Ta}_1\text{-H-BEA_nano_25}$) catalyst.



2. Effect of Na content on the catalytic activity of a catalyst (99)



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Preparation of nano-sized beta zeolites aggregated by spray-drying for bioethanol conversion

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In a context where finite fossil oil resources are depleting and environmental awareness is rising, it has become a priority to mitigate our dependence to petro-based chemicals. Biomass upgrading aims at developing bio-based platform chemicals, that can help reduce the consumption of fossil energy sources and lower our dependence to petroleum. Among these platform molecules, bio-alcohols are interesting alternatives to replace crude oil and coal as raw materials for olefins production. Particularly, the catalytic transformations of bioethanol into ethylene and 1,3-butadiene are one the most promising ways to produce such key building block compounds currently obtained from petrochemical industry. By aiming to develop heterogeneous catalysts active for bioethanol conversion by innovative methodology, this master thesis contributes therefore to sustainable development researches.

The materials developed herein are beta zeolites (BEA). Their microporous nature implies the need of high surface-to-volume ratio and short diffusion path length, as the mass transfer is restricted inside these zeolite crystals. We therefore decided to synthesize nano-sized BEA particles. We were able to show that the synthesis method presented here allowed the obtention of the desired H-BEA structure, but in the form of well dispersed nanocrystals (in suspension) which are not available commercially.

In order to facilitate their recovery from the reaction media and further control their (potential) aggregation occurring upon thermal process, these nano-crystals were shaped into microspheres by spray drying, as such process allows fine control of the particle size and morphology.

On the one hand, the synthesized BEA were ionically exchanged to generate their H form (H-BEA), that was tested in ethylene production at low temperature (240 °C). It resulted that two of the three synthesized and tested H-BEA catalysts were significantly more active and selective to ethylene than a commercially available H-BEA. The highest ethylene productivity was obtained with H-BEA microspheres prepared by spray drying. By generating $4.89 \text{ [g}_{\text{ethylene}} \cdot \text{g}_{\text{zeolite}}^{-1} \cdot \text{h}^{-1}]$, this catalyst stands among the most performant catalysts reported so far in terms of ethylene productivity.

On the other hand, to perform the ethanol to butadiene (ETB) reaction, the need of a bifunctional catalyst, capable of achieving simultaneously dehydrogenation and dehydration reactions, is highlighted in the literature. Therefore, a fraction of the synthesized BEA was modified with Ta and Cu to generate Cu-doped Ta(V)-single site