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Shaping of Zeolite Pellets: Formulation and Procedures to Improve Material Properties as Catalytic Support

Modelatge de Pellets de Zeolita: Formulació i Procediments per Millorar les Propietats del Material com a Suport Catalític.

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June 2023

UNIVERSITAT DE BARCELONA

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REPORT

IDENTIFICATION AND REFLECTION ON THE SUSTAINABLE DEVELOPMENT GOALS (SDG)

The Sustainable Development Goals (SDGs) are a set of global targets aimed at achieving a just and sustainable future. They encompass a wide range of challenges, including poverty eradication, environmental protection, and promoting peace and prosperity for all. The SDGs require collaborative efforts from governments, businesses, and civil society to create a more inclusive and sustainable world.

Within the larger domains, this project is aligned with the Planet dimension, It focuses on the protection and conservation of the environment, including climate change mitigation, preservation of natural resources, promotion of clean energy, and safeguarding ecosystems.

The final purpose of the project, which this work is a part of, is to develop sustainable aviation fuel (SAF) from electrolyzed CO_2. Based on this objective, I believe this work can be related to the following SDGs:

SDG 7: Affordable and clean energy. By developing a sustainable aviation fuel, the project contributes to promoting clean energy sources and reducing greenhouse gas emissions in the aviation sector. By improving the process with hydrocracking, costs are reduced, making it more affordable.

SDG 9: Industry, innovation, and infrastructure. The project is a very innovative route to produce sustainable aviation fuel, contributing to the sustainable development of the industry and technological advances.

SDG 13: Climate Action. The project's aim to mitigate climate change aligns with this goal by reducing carbon emissions associated with aviation fuel, which is difficult to electrify.

CONTENTS

1. SUMMARY

This study focuses on the shaping of zeolites for their application as catalyst supports for nickel-based catalysts in hydrocracking reactions. Zeolites are porous materials with high surface areas and unique structures that offer excellent catalytic properties. The shaping process involves forming zeolite particles into desired shapes to enable their application in industrial reactors and enhance their performance and stability in catalytic reactions. The effects of shaping parameters, including binder and plasticizer selection, shaping conditions, and post-treatment techniques, are investigated to achieve improved mechanical strength, porosity, and catalytic performance.

A rheological study has been carried out which has shown to reduce the work of formulation. It was found that the use of a plasticizer, such as methylcellulose, is necessary to achieve good extrusion. An inorganic binder, specifically boehmite, accompanied by a peptizer like acetic acid, is used to achieve good mechanical strength. Additionally, the effects of the alkaline desilication technique and the dealumination caused by the use of acetic acid on the zeolite structure are investigated. These treatments aim to modify the zeolite framework by reducing the silica and alumina content, respectively, in order to improve diffusion properties by increasing the pore size. The resulting shaped zeolites exhibit improved mechanical strength and increased pore size.

Keywords: Zeolites, shaping, binder, plasticizer, hydrocracking, desilication, dealumination

2. RESUM

Aquest estudi es centra en el modelatge de zeolites per a la seva aplicació com a suports de catalitzadors de níquel en reaccions d'hidrocracking. Les zeolites són materials porosos amb àrees superficials elevades i estructures úniques que ofereixen excel·lents propietats catalítiques. El procés de modelatge implica donar forma a les partícules de zeolita per obtenir les formes desitjades i permetre la seva aplicació en reactors industrials, millorant així el seu rendiment i estabilitat en reaccions catalítiques. S'investiguen els efectes dels paràmetres de modelatge, incloent la selecció d'aglutinant i plastificant, les condicions de modelatge i les tècniques de post-tractament, per aconseguir una millora en la resistència mecànica, porositat i rendiment catalític.

S'ha realitzat un estudi reològic que ha demostrat reduir la tasca de formulació. Es va trobar que és necessari l'ús d'un plastificant, com la metilcel·lulosa, per aconseguir una bona extrusió. Un aglutinant inorgànic, en aquest cas boehmita, acompanyat d'un peptitzant com l'àcid acètic, ha sigut clau per obtenir bona resistència mecànica. A més, s'investiguen els efectes de la tècnica de desilicació alcalina i de desaluminació causada per l'ús de l'àcid acètic en l'estructura de la zeolita. Aquests tractaments tenen com a objectiu modificar l'estructura de la zeolita reduint el contingut de silici i alumini, respectivament, per millorar les propietats de difusió mitjançant l'augment de la grandària dels porus. Les zeolites modelades resultants exhibeixen una millora en la resistència mecànica i un augment de la grandària dels porus.

Paraules claus: Zeolites, modelatge, aglutinant, plastificant, hidrocracking, desilicació, desaluminació.

3. INTRODUCTION

3.1. ZEOLITES

Zeolites are inorganic solid materials with complex porous structures, widely used in science and industry, due to their excellent properties and physicochemical characteristics.[1] Among their most outstanding features are selective adsorption and high ion-exchange capacity, which are produced by the porous crystalline structure of the zeolite and the negatively charged tetrahedral AlO_4 units distributed throughout the aluminosilicate framework, and their charge compensating cations occupying the nearby pores. Another important characteristic of this material is its regular porous system at the micro-pore range, which provides them with a very high surface area, making them ideal as catalyst supports. These characteristics make zeolites very versatile and useful materials in many fields, such as petrochemistry, agriculture, fine chemistry, and water purification.[2] [3]

The porous structure of zeolites also makes them useful for molecular separation and removal of impurities in the chemical industry, allowing them to act as efficient molecular sieves. They are used for the separation and purification of gases such as nitrogen and oxygen.[4]

J.V. Smith proposed the following generic formula for zeolites:

$$M_{x/n}Al_xSi_yO_{2(x+y)} \cdot w\ H_2O$$
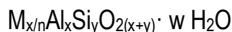
Where 'n' represents the valency of the cation present in the zeolite structure, 'x' and 'y' represent the number of aluminium and silicon atoms, respectively and 'w' represents the number of water molecules present in the zeolite structure.[5]

According to the Lowenstein's rule, the Si/Al ratio is always ≥ 1, since Al-O-Al bonds are forbidden in zeolites. However, there are currently known cases of some zeolites that do not follow this standard.[6]

3.1.1. Zeolite structure

Zeolites have a crystalline structure composed of SiO_4 and AlO_4 tetrahedra interconnected by oxygen bridges, with silicon and aluminium atoms occupying the central positions. The tetrahedra exhibit high regularity, but the angle of the oxygen bridge between central atoms can vary, leading to the formation of different structures [7].
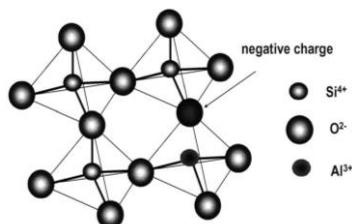
Figure 1. Idealized structure of zeolite framework of tetrahedral $[SiO_4]^{4-}$ with a Si/Al substitution ($[AlO_4]^{5-}$).[26]

The key characteristic of zeolites is that, despite being crystalline materials, they contain a significant number of pores within their structure, resulting from the diverse conformations of adjacent tetrahedra[8]. Depending on the complex structure formed by the union of these tetrahedra, different types of zeolites can be distinguished[9], more than 200 are currently known, listed in the International Zeolite Association Database.[27]
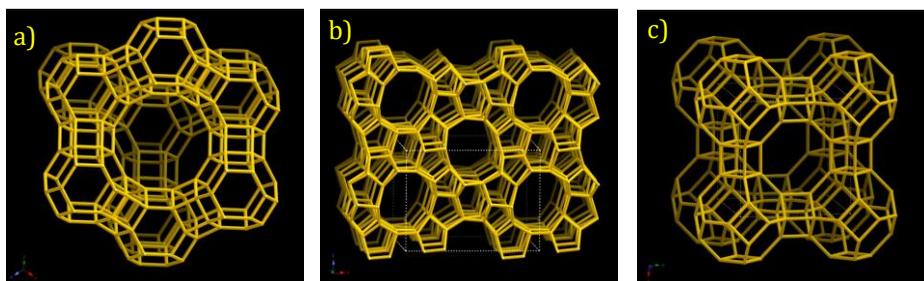
Figure 2. Example of different zeolites structures. a) Fau-type, Zeolite Y b)MFI-type, ZSM-5 c)LTA-type, Zeolite A[27]

Each structure forms distinct channels, which contain water molecules and cations that compensate for the negative charges left by the aluminium tetrahedra.[10] Zeolites can be classified based on their pore size, which is determined by the arrangement of oxygen atoms that form the micropore openings. [11]

According to IUPAC, porous materials can be classified based on their pore diameter as follows:

- Microporous: diameter <2 nm.
- Mesoporous: diameter ranging from 2-50 nm.
- Macroporous: diameter >50 nm.[12]

Zeolites belong to the group of microporous materials as their pores are typically smaller than 2 nm.

The structure of Faujasite, which is the type of zeolite used throughout this work, is among the "hollowest" zeolites structures. Approximately 50% of the volume of dehydrated crystals is empty space, which becomes filled with water when Faujasite is exposed to air. The pore size ranges between 0,7 and 1,2 nm. Several types of cavities, such as large cavity, sodalite cavity, and hexagonal prism, can be found within the structure of faujasite, accommodating the compensating cations.[5]
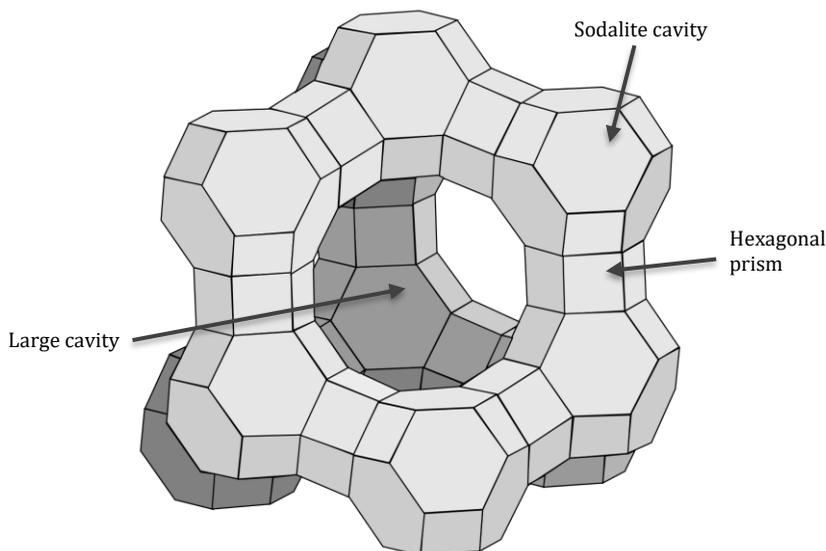
Figure 3. Structure of Faujasite zeolite[28]

3.1.2. Hierarchical Zeolites

The small pores of zeolites severely limit the diffusion of molecules in such small pores, for example, cyclohexane, which has a diameter of approximately 2,3nm while zeolites pores typically range between 0.7 and 1,2nm. Therefore, zeolites are often subjected to chemical processes to modify the pore size.[2] These processes can be either bottom-up, following modified synthetic approaches or top-down, which entails a modification of the pores after the zeolite synthesis.[13] The latter is currently the most commonly used, and two of the most common methods are the following:

Alkaline Desilication: Bases such as NaOH are employed for the generation of mesopores in zeolites through silicon extraction. In this process, silicon extraction occurs via basic hydrolysis, essentially preserving the aluminium environment and its associated acidic properties. The

formation of mesopores using this treatment predominantly takes place at the edges or defects of the crystalline structure.[14]

The Si/Al ratio significantly influences the creation of mesopores as aluminium hinders silicon extraction, see Figure 4. If the Si/Al ratio is excessively high, uncontrolled silicon extraction is observed, whereas if the Si/Al ratio is too low, the formation of mesopores is insignificant. The optimal Si/Al ratio for controlled desilication and induced enhancement of mesoporosity in zeolites lies between 25-50.[14]
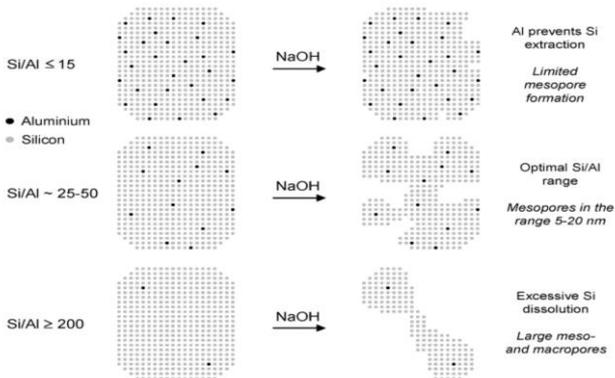
Figure 4. Effect of the Si/Al ratio on pore creation in the desilication process.[13]

<u>Acid dealumination:</u> It involves removing aluminium (Al) atoms from the framework through strong acid treatment in water. The process converts the natural zeolite to its acid form, creating Bronsted acid sites near the framework Al atoms. Extended treatment leads to the formation of silanol nests. This results in the formation of a polymeric gel of extra-framework alumina (EFAL) within the material channels, which can be removed by lixiviation with a very dilute acid. The removal of acid sites simultaneously obviates the need for cations, thereby expanding the void regions. Therefore, pores of sufficient size can be obtained to ensure effective diffusion of relatively large molecules throughout the zeolite matrix. [15]
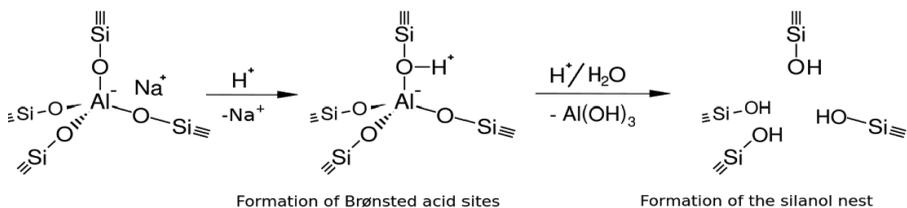
Figure 5. Zeolite reaction in acid medium[14]

3.2. ZEOLITES AS CATALYSTS

3.2.1 Outstanding properties

The **acidity** of zeolites plays a crucial role in catalysis, particularly in the formation of carbocations.[11] The presence of **Bronsted acid sites** in zeolites can be attributed to bridging hydroxyl (OH) groups between aluminium (Al) and silicon (Si) tetrahedra, while the **Lewis acid sites** have been associated to the presence of EFAL.[11] Adsorption of trace amounts of water facilitates the generation of surface hydroxyl (OH) groups, resulting in the creation of acid-base active sites.[16]

Zeolites exhibit ion **exchange capability**, facilitated by charge-balancing cations that are bonded to the lattice by Coulombic forces and, occupy the micropore space. This property allows for total or partial exchange with different cations and finds application in water softening, where zeolites remove Ca^{2+} ions from hard water through ion exchange with Na^+.[11]

Zeolites are utilized as molecular sieves due to their **well-defined porous crystal lattice**, enabling precise control over pore size. This characteristic allows selective diffusion of molecules through the zeolite pores, enabling separation based on molecular size. Smaller molecules can permeate the pores, while larger molecules are either trapped or unable to access the pore structure.[4] The extensive porous structure of zeolites, characterized by a significantly **high surface** area, endows them with exceptional capabilities as catalytic supports.

3.2.2. Application in hydrocracking reactions

A hydrocracking reaction is a reaction in which one or more carbon-carbon bonds in a reactant molecule, typically a hydrocarbon, are broken in presence of H_2, and the resulting free valences are saturated with hydrogen.[17]

Depending on the nature of the catalyst, hydrocracking can occur in different ways. In the particular case of bifunctional zeolite-based catalyst, where a metal active specie is supported over a zeolite support, the main function of the metal is to dehydrogenate saturated hydrocarbons into alkenes and hydrogenate olefinic intermediates desorbed from the Bronsted acid sites of the zeolite.[17]

Figure 6. Hydrocracking reaction mechanism on a bifunctional catalyst[17]

Alkenes desorbed from the metal site, diffuse to the Bronsted acid sites, where they undergo protonation, leading to the formation of n-alkylcarbenium ions. These highly reactive intermediates can undergo (i) chain structure rearrangements or (ii) carbon-carbon bond cleavage, which commonly occurs via β-scission, yielding an alkene and a smaller n-alkylcarbenium ion. Primary n-alkylcarbenium ions predominantly undergo rearrangement reactions, forming monobranched n-alkylcarbenium ions. However, secondary or tertiary n-alkylcarbenium ions tend to undergo β-scission reactions, which take place at acidic sites. The resulting alkenes and n-alkylcarbenium ions desorb and undergo hydrogenation at the metal sites.[17]

Figure 7. β-scission reaction mechanism[17]

3.3. SHAPING ZEOLITES

3.3.1. Zeolites as technical and research support

As previously mentioned, zeolites are widely employed in the realms of research and industry. In basic research, zeolites are often used in powdered form, whereas in industry, catalysts are implemented in reactors, where if zeolite powder were to be employed directly, clogging issues could arise due to agglomeration. To circumvent such complications and ensure smooth operation of the process, shaped catalyst bodies are employed. These specially designed catalyst bodies help mitigate agglomeration-related challenges, limiting pressure drop, enhancing mechanical stability and improving heat and mass transfer, thus optimizing the efficiency of the catalytic process.[18]

3.3.2. Components of shaped body zeolite catalyst

To shape zeolite-based catalyst supports by extrusion techniques, the use of a variety of additives, see Figure 4a, is necessary to enable extrusion and pelletizing, and improve the final properties of the shaped materials. In the process, some of the properties of the material, such as acidity or, porosity can be altered.[19]

One of the essential characteristics of that shaped bodies require is high mechanical strength, which can be enhanced by the use of inorganic binders, commonly ceramics such as boehmite, alumina, silicas or natural clays[20]. Peptizers such as acetic acid or nitric acid act by dispersing particles, aiding in the homogenization of the wet formulations[18]. In the case of boehmite, decreasing the pH of the mixture below the point of zero charge of boehmite ($AlO(OH)$), results in protonation of the boehmite surface and creates particle repulsion, see Figure 4b. Additionally, peptizers as acids, hydrolyse the oxygen bridges in the zeolite structure, leading to the loss of some acid sites and the formation of new pores through dealumination. Plasticisers and lubricants, such as methylcellulose, glycol or sugars are used to reduce friction between zeolite particles and decrease the viscosity of the mixture, and as they are removed by calcining the formed catalyst, they lead to the formation of new pores.[18] When using methyl cellulose as a plasticizer, it is important to consider that when combined with water, it also acts as a thickening agent, despite reducing the friction between zeolite particles.[21]
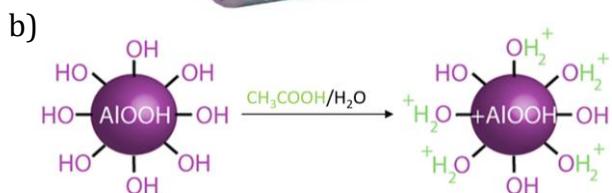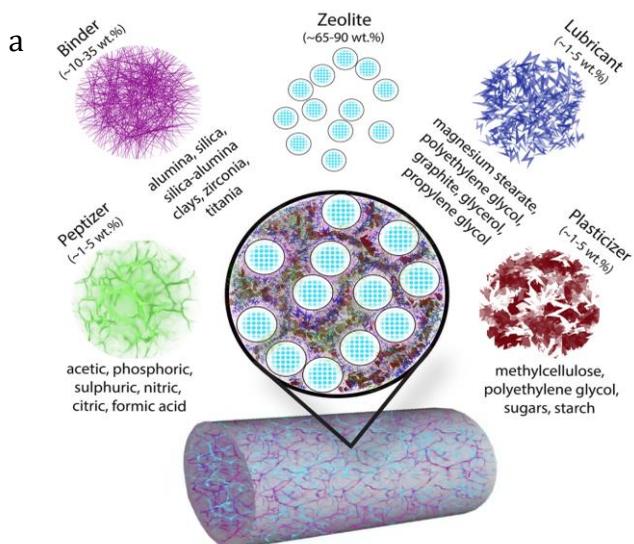
Figure 8. a) Representation of the components of a zeolite body shaped catalyst. b) Representation of the hydrogenation of boehmite by acetic acid.[18]

4. OBJECTIVES

This work is part of a project aimed at obtaining sustainable aviation fuel (SAF) from electrolyzed CO_2. In this process, syngas (CO + H_2) is obtained through CO_2 electrolysis. Subsequently, two sequential processes are conducted. First, the Fischer-Tropsch reaction, where hydrocarbons are formed. Second, the Hydrocracking of the Fischer-Tropsch products, to converts straight-chain or linear hydrocarbons, which are poor fuels, into branched-chain compounds, which are high-performance fuels [22].

The main goal is to manufacture zeolite-based pellets to use as a support of Ni species for hydrocracking reactions.

One of the other objectives of this work is to test whether a rheological study can facilitate the work of formulating for extrusion, obtaining the value of binder ratio at which the capillary state is reached.

The impact of different additives, such as methyl cellulose, boehmite, and acetic acid, on the shaping process of a zeolite catalyst will be studied. Additionally, we aim to investigate the effect of calcination conditions on the porosity and mechanical properties of the catalyst body.

In industrial applications, zeolites often face challenges related to pore size. To address this issue, we will explore the variation in pore size resulting from a desilication technique carried out in an alkaline medium. Furthermore, we will examine the influence of acetic acid on the formation of mesopores through dealumination.

5. EXPERIMENTAL SECTION

5.1. MATERIALS

A commercial faujasite zeolite (CBV760, Zeolist) with a SiO_2/Al_2O_3 ratio of 60 and protons as charge balancing cation was used in this study. This commercial sample had been previously steamed and acid-leached. Henceforth, we will refer to this product as zeolite Y. For the desilication process, sodium hydroxide (Panreac), sulphuric acid (Alfa, ≥98%) and ammonium nitrate (Sigma, ≥98%) were used as reactants.

For the fabrication of the zeolite-based supports, boehmite (Sasol) was employed as the inorganic binder, and methylcellulose (Sigma) as the plasticizer. Deionized water and an aqueous acetic acid solution (2% wt.), obtained through dilution from acetic acid (Sigma, ≥99%), were utilized as the liquid binders.

5.2. DESILICATION

For the desilication process, a synthetic procedure reported in the literature was followed[23]. 5,0 grams of Zeolite Y were weighed and stirred for half an hour in a 1M NaOH aqueous solution. After the allotted time, the mixture was centrifuged for 10 minutes at 10.000 rpm and neutralized with a 1M H_2SO_4 solution. Upon decanting the liquid phase, 40 mL of a 0,2M NH_4NO_3 solution were added, followed by another 10-minute centrifugation at 10.000 rpm repeating the process 3 times. Finally, the solid phase was washed with deionized water, undergoing 3 cycles of centrifugation for 10 minutes at 10.000 rpm each. After decanting the water from the last cycle, the desilicated zeolite was left to dry at 105°C overnight. Finally, it was calcined at 500ºC for 4h with a heating ramp of 2ºC/min.

5.3. SHAPING OF ZEOLITES INTO PELLETS

Figure 9. Scheme of the procedure to be followed in the shaping of the Body Shaped Catalyst.

5.3.1. Mixer torque rheometer

A rheological study of different support formulations was carried out using a Mixer Torque Rheometer (MTR3, Caleva, UK).

Six rheometric measurements of three different formulations were carried out. The following table displays the weights of zeolite Y, boehmite, and methyl cellulose employed in each formulation.

	Zeolite Y (g)	Boehmite(g)	Methyl cellulose (g)
1	15	-	-
2	15	-	0,30
3	13	2	0,30

Table 1. Components weight for the different formulations

Two measurements were conducted for each of the aforementioned formulations, one using water as the liquid binder and the other employing an aqueous acetic acid solution (2 wt%).

Figure 10. Caleva Mixer Torque Reometer

During the experiment, the torque measures the resistance that the mass opposes to the rotation of the rotors, which is related to the progress of the granulation process. The rheological data was obtained using a multiple addition method. First, mixing of the dry components was performed for 120 seconds. Then, additions of 1 mL were made while mixing for 45 seconds before the next addition, and the average reading obtained during the last 30 seconds of mixing was recorded. After ten additions of 1 mL, subsequent additions were made in increments of 0.5 mL with a mixing time of 30 seconds until the slurry state was reached.

5.3.2. Extrusion and pelletising

Based on the data obtained from the Mixer Torque Rheometer, extrusions with different formulations were essayed. A Caleva Multi Lab (CML) was used to perform the extrusions. To prepare the extrudable mass, the dry components for each formulation were weighed, and a known amount of liquid binder, either water or an acetic acid solution, was added. The mixture was then mixed using a Thinky ARE250 planetary mixer for three cycles of 5 minutes at 1400 rpm. After completing the mixing process, the mixture was gradually introduced into the extruder, and extruded at a rotation speed of 70-90 rpm.
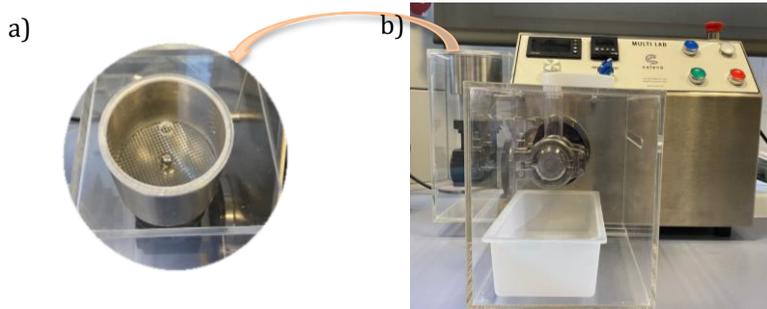
a)   b)

Figure 11. Caleva MultiLab picture. a) Spheronizer b) Extruder

For palletisation, the spheronizer unit was used, where the filaments obtained from the extruder were left for 10 minutes at a rotation speed of 900-1000 rpm. It was then observed that if the extrudates were transferred to the spheronizer right after the extrusion step, the mixture expels water that caused re-agglomeration of the paste. Therefore, once the extrudates were obtained, they were dried for 30 minutes at 105°C before they were processed in the spheroniser.

Some of the tested formulations can be seen in Table 2.

	Zeolite Y (g)	Boehmite (g)	Methyl cellulose (g)	Liquid binder(mL)
1	10,02	-	-	8,4
2	10,0	-	0,45	10,0
3	10,03	-	0,45	9,0
4	10,00	-	1,00	9,0
5	10,02	-	0,30	9,0
6	8,03	2,00	0,30	7,3
7	8,02	2,00	0,30	8,1
8	8,01	2,02	0,31	8,1

Table 2. Composition of the studied formulation. The values of liquid binder are represented in blue when water is used and orange when acetic acid is used.
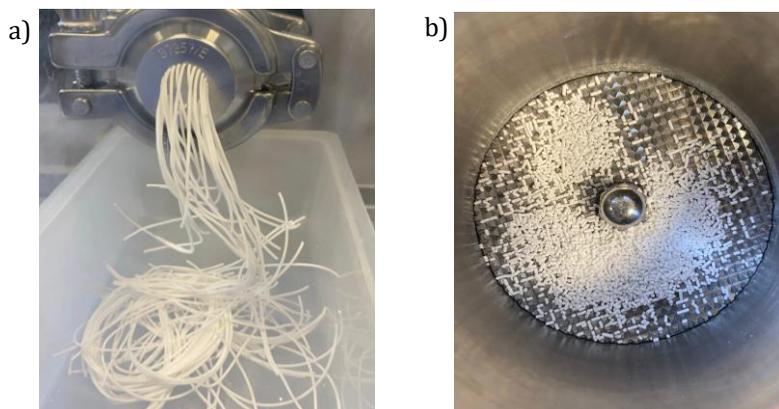

Figure 12. Extrusion (a) and palletisation (b) processes

5.3.3. Thermal treatment

Once the pellets were obtained, they were dried in the oven at 105ºC for 12h and then, calcined at different temperatures. The calcination conditions are specified in Table 3.

	Holding time	Temperature
Calcination 1	4h	500ºC
Calcination 2	8h	550ºC
Calcination 3	8h	600ºC

Table 3. Calcination conditions, all with a 1ºC/min heating ramp

5.4. CHARACTERISATION

5.4.1. Powder size distribution

A Mastersizer 2000 was used to carry out a particle size study. Prior the measurement, three system washes were performed to ensure no remnants of previous assay samples were left in the system. For the measurement, the cell was filled with distilled water, which acts as dispersant, and the background signal was measured. The sample was added and stirred and sonicated for 3 minutes to avoid particle agglomerations. Then, the particle size measure was carried out by a laser diffraction technique. Three measurements were performed and the results were reported as the average of the three.

5.4.2. Nitrogen physisorption

The surface area and the pore size distribution of the materials studied was performed by nitrogen physisorption. The instrument used was a Micromeritics FlowPrep 060 and a Micromeritics TriStar II, along with software that enabled temperature control and continuous monitoring of the gas volume and system pressure.

To perform this study, the sample first underwent degassing. The sample was initially heated at 90°C for 30 minutes, followed by a gradual temperature increase with 30-minute dwell times at each increment until reaching 120°C. Subsequently, the sample was heated at 250°C for 5 hours. This cautious approach was employed to prevent excessive water evaporation, which could create non-intrinsic cracks in our zeolitic materials, thus compromising the integrity of the sample. Once the sample was thoroughly degassed, vacuum was applied, and a precisely known volume of nitrogen was injected while recording the pressure values at each moment. Upon reaching the

maximum relative pressure, vacuum was again applied. Through various mathematical adjustments, the BET surface area (SA_{BET}), the pore volume and the pore size distribution were obtained.

This study was carried out on commercial zeolite Y before and after the desilication process and on pellets of different formulations calcined at various temperatures.

5.4.3. Compressive strength

To measure the ultimate compression strength of the obtained pellets, a Zwick-Roell universal testing machine was used. 15 measurements were taken for each sample. The test involved placing a pellet on the base and applying a gradually increasing force. The machine measures the deformation of the material and the force applied throughout the test, so from the graph obtained, the force (N) at which the first crack occurs was determined. The precision of these measurements wasn't very accurate due to the relatively small forces involved.

This test was performed for the pellets obtained in section 5.3.3 after calcination, providing data on the influence of the different additives and calcination conditions on the mechanical resistance of the final zeolite-based materials.

5.4.4. Energy dispersive X-ray spectroscopy

Scanning Electron Microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDX) was used to study the elemental composition of the pellets shaped. To prepare the sample, a resin was prepared by mixing EpoFix Resin and EpoFix Hardener in a ratio of 7:1. The mixture was then transferred to a mould with the sample and allowed to harden. Once hardened, the piece of resin with the sample was partially filed with a polishing machine until the cross-section of the pellets was obtained. Since the resin is non-conductive, it was gold-coated using the Emitech k575X Peltier cooled sputtering system. Energy dispersive X-ray spectroscopy was performed.

6. RESULTS AND DISCUSSIONS

6.1 CHARACTERISATION OF DESILICATION PROCESS

A preliminary study was carried out to determine the powder size and homogeneity of the zeolite used, as powder size may affect the rheological behaviour of the paste, so that if the particle size is very heterogeneous it can hinder extrusion.[24] The results indicate that it is a fairly homogeneous sample and the mean particle diameter (dv_{50}) is 4,2 µm, see Appendix 1.

Understanding the characteristics of the commercial zeolite used for the shaping is crucial in assessing the effects of the desilication process. By comparing the results of the N_2 physisorption technique applied to the untreated commercial zeolite and the zeolite subjected to desilication, see Figure 13, we can gain valuable insights into the impact of the process. It can be seen that the desilication process has successfully generated additional mesoporosity. Upon comparing the BET area values, non-treated sample exhibited a value of 888 m²/g, whereas post-desilication, the value decreased to 201 m²/g. This observation validates the occurrence of micropore loss, as these micropores are known to contribute significantly to the overall surface area.
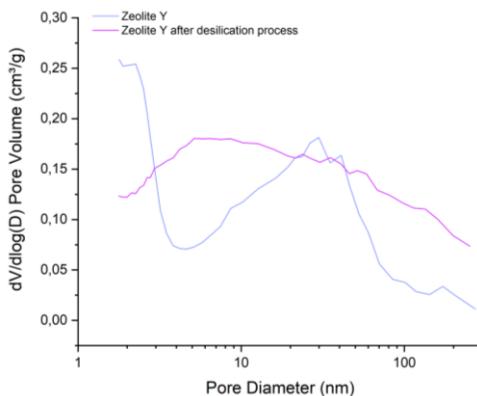

Figure 13. Pore size distribution of zeolite Y before and after the desilication process

6.2. PASTE FORMULATION

A rheological study was conducted to investigate the behaviour of zeolite-wet masses of different compositions, using methylcellulose as plasticiser, boehmite as inorganic binder, and water or an aqueous acetic acid solution (2%wt.) as liquid binders. The objective of this study is to determine the optimal liquid to powder ratio, which normally coincides with the binder ratio at which the capillary state is reached, facilitating the extrusion process and reducing the preformulating work.

When a liquid binder is added to a solid material it is slowly dispersed throughout the powder bed via mixing process[25], see Figure 14.
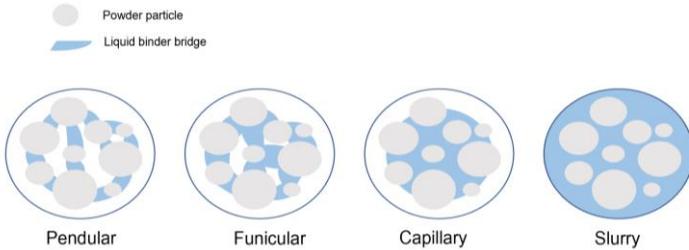

Figure 14. Stages of wet granulation.

The maximum value of mean line torque is achieved upon reaching the capillary state, where particle-particle binding forces are maximum and the mean line torque decreases back to zero at the slurry state.

In Figure 15 a), the process of liquid saturation of three different zeolite-based formulations using water as liquid binder is represented. With the obtained data, we can observe the effect that different components have on the mixture. When only the zeolite Y is used, we observe a lower maximum of mean line torque and more displaced to lower binder-to-powder ratios. Therefore, this mixture opposes less resistance and can absorb more water than the rest of the formulations before reaching the capillary state. When methylcellulose is added, we observe an increase in the maximum value of mean line torque. Because methylcellulose acts as a thickening agent in aqueous solutions, creating a gel-like structure that increases viscosity[21]. With the addition of boehmite to the formulation in a 8:2 zeolite-boehmite ratio, the relative zeolite content is
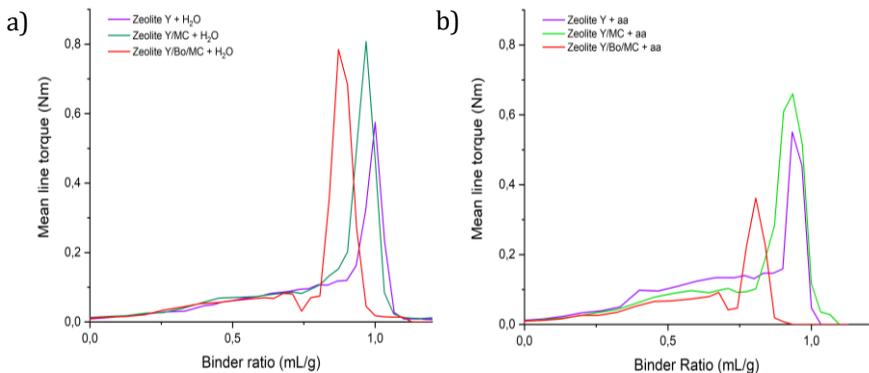

Figure 15. Rheological profiles of zeolite-based formulations using a) water and b) acetic acid solution as liquid binder.

decreased, which results in a lower water absorption capacity. Therefore the capillary state is reached with less binder additions.

Similar results were obtained when using an acetic acid solution as liquid binder, see figure 15 b). The most significant change is observed when boehmite is present, see Appendix 2. This is because the acid acts as a peptizing agent, lowering the pH below the point of zero charge (PZC) of boehmite (~9), causing hydrolysis of the oxo bridges between particles and protonation of the surface of the alumina binder, making them more hydrophilic and creating repulsion between particles, which improves their dispersion and homogenization[18].This effect results in a decrease in the resistance of the mixture to the rotational movement exerted by the rheometer, which is why the mean line torque is considerably lower when acetic acid is used instead of water.

The values at which the capillary state is reached for each of the studied formulations are gathered in table 4.

Liquid binder used	Zeolite Y	Zeolite Y/MC (10:0,3)	Zeolite Y/Boe/MC (8:2:0,3)
Water	1,00mL/g	0,97mL/g	0,87mL/g
Acetic acid	0,93mL/g	0,94mL/g	0,81mL/g

Table 4. Binder ratio values at which the mean line torque reaches its maximum value.

6.3. SHAPING

Extrusion and palletisation were performed with various formulations, varying the quantity of methylcellulose and adding or not boehmite, see Table 5. It has been observed that the rheometer data are useful to give us an idea of which binder ratio to start testing and then adjust according to the appearance of the mixture until we find the binder ratio that works best for extrusion. In this case, it has been observed that the liquid-powder ratios that have provided us with the best results are between 90-96% of the liquid binder needed to achieve the capillary state, according to the rheological profiles obtained. The amount of plasticizer used was varied and it was concluded that without it, the mixture could not be extruded (entry 1) and water was expelled out of the extruder holes, and that a too high ratio (entry 4) does not give good extrusion results either. A ratio of 0,3-0,45g methyl cellulose to 10g zeolite/boehmite is sufficient for good extrusion.

	Zeolite Y/Boe/MC	Liquid binder(mL)	Binder ratio(Br)	Capillary state (Br')	Br/Br' (%)	Extrusion	Pelletising
1	10:0:0	8,4	0,84 mL/g	1,0 mL/g	84%	🔴	-
2	10:0:0,45	10,0	0,95 mL/g	-	-	🟢	🔴
3	10:0:0,45	9,0	0,86 mL/g	-	-	🟠	🔴
4	10:0:1	9,0	0,81 mL/g	-	-	🔴	-
5	10:0:0,3	9,0	0,87 mL/g	0,97 mL/g	90%	🟢	🟢
6	8:2:0,3	7,3	0,71 mL/g	0,87 mL/g	81%	🟠	🔴
7	8:2:0,3	8,1	0,78 mL/g	0,87 mL/g	90%	🟢	🟢
8	8:2:0,31	8,1	0,78 mL/g	0,81 mL/g	96%	🟢	🟢

Table 5. Components of the formulations submitted to extrusion. Values in blue indicate the use of water as liquid binder and values in orange the use of acetic acid. The results of extrusion and pelletising are represented by colours: red indicates that the extrusion was not good, orange indicates that the extrusion was not good but some of the extrudate came out, and green represents that almost all the extrudate can be used for pelletising. Regarding pelletising, red shows the cases in which agglomerates have been formed and green shows the pelletised pellets that have come out well.

After conducting several palletisation tests, it was observed that between extrusion and palletisation, the extruded filaments must be dried. Failure to do so results in zeolites expelling part of their absorbed water during palletisation, leading to agglomeration. Considering the good results of these specific formulations, only 5, 7, and 8 will be used henceforth.

Figure 16. Pellets obtained from formulations a) 8, b) 7 and c) 5 after calcination at 500ºC.

6.4. PELLETS CHARACTERISATION

6.4.1. Pore size

One of the most important properties of zeolites is their porosity, and therefore, determining the pore size and surface area of your zeolite can provide valuable information on their eventual role as catalyst support. The N_2 physisorption technique was used to obtain this information.

This technique is based on the physisorption of nitrogen on the surface of the material under study, in this case, Zeolite Y pellets. By using the logarithmic isotherm (Appendix 3), applying different mathematical adjustments we can obtain, the BET surface area and pore size measurements.
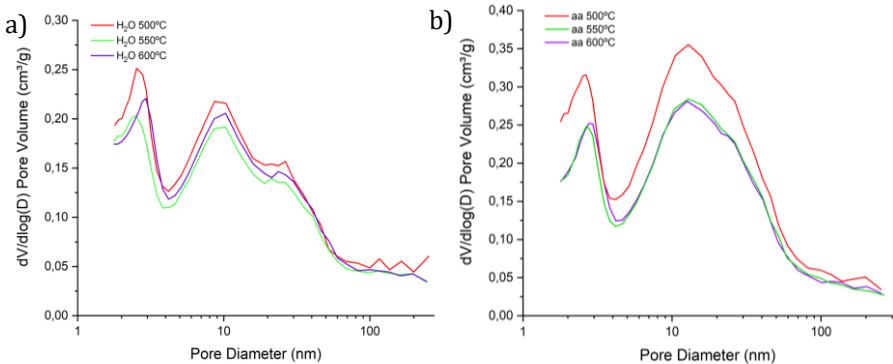

Figure 17. Changes in pore size with temperature and calcination time. Pellets from formulations a) 7 with water as liquid binder and b) 8 with acetic acid.

The effect of calcination time and temperature on the porosity of the zeolite pellets has been examined, see figure 17. The difference of pore size is minimal when comparing samples calcined for 8 hours at 550ºC and 600ºC. However, when comparing with samples calcined at 500ºC for 4 hours, an increase in pore size is observed. This is attributed to the lower temperature and shorter duration, which results in reduced diffusion between particles and, consequently, a higher quantity of pores maintaining their original size or experiencing a smaller decrease in size.

Additionally, the porosity of the zeolite-based pellets of three selected formulations was carried out. As observed in Figure 18, when acetic acid is used as a liquid binder, the graph shows a significantly higher amount of pores ranging from 5 to 70 nm compared to the cases where
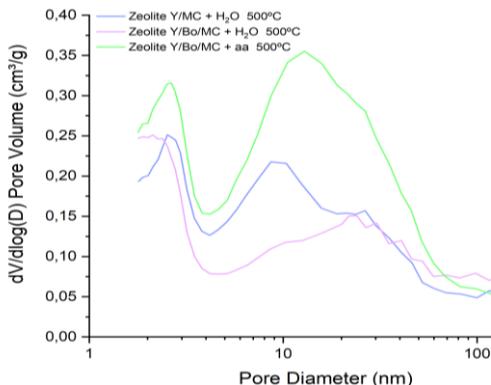

Figure 18. Pore size distribution of pellets with different formulation calcined at 500ºC.

water was used as the liquid binder. This can be attributed to the dealumination process induced by acetic acid, which affects the zeolite structure. When comparing the samples prepared with water as the liquid binder, slight differences in pore sizes can be observed. These variations may be attributed to the presence of boehmite which has pores of different sizes compared to those of the zeolite, the most noticeable differences are found in the range of 4 to 20 nm.

Comparing the same sample under different calcination conditions, the trend of BET surface area, as shown in Table 6, is observed to decrease with increasing time and temperature. When comparing the BET surface areas of three different samples calcined at 500ºC for 4 hours, it is evident that the Zeolite Y/Boe/MC sample with acetic acid as the liquid binder exhibits the highest surface area. On the other hand, comparing the other two samples that utilize water as the liquid binder, the sample containing only Methylcellulose in addition to Zeolite Y has a larger surface area than the sample with Boehmite. This difference can be attributed to the higher content of Zeolite in the former, which possesses a larger surface area compared to Boehmite.

	Holding time	*Temperature*	*BET surface*
Zeolite Y/MC + H_2O	4h	500ºC	881,3 ± 0,4 m²/g
Zeolite Y/Boe/MC + H_2O	4h	500ºC	754,5 ± 0,1 m²/g
Zeolite Y/Boe/MC + H_2O	8h	550ºC	685.64 ± 0.05 m²/g
Zeolite Y/Boe/MC + H_2O	8h	600ºC	714.07 ± 0.08 m²/g
Zeolite Y/Boe/MC + aa	8h	500ºC	978.69 ± 0.03 m²/g
Zeolite Y/Boe/MC + aa	8h	550ºC	777.70 ± 0.08 m²/g
Zeolite Y/Boe/MC + aa	8h	600ºC	753.07± 0.09 m²/g

Table 6. BET area obtained for each sample and their calcination conditions.

6.4.2 Effects of acetic acid use on pellet compressive strength

By observing the results of the compression strength test performed on the formed zeolites, we can see the effect of calcination temperature and time, and most importantly, the improvements in resistance that the use of acetic acid provides.

	Holding time	Temperature	Crush strength (N)
Zeolite Y/MC + H_2O	4h	500ºC	0,9 ± 0,3
Zeolite Y/Boe/MC + H_2O	4h	500ºC	0,9 ± 0,3
Zeolite Y/Boe/MC + H_2O	8h	550ºC	1,2 ± 0,4
Zeolite Y/Boe/MC + H_2O	8h	600ºC	1,5 ± 0,5
Zeolite Y/Boe/MC + aa	8h	500ºC	12 ± 3
Zeolite Y/Boe/MC + aa	8h	550ºC	12 ± 4
Zeolite Y/Boe/MC + aa	8h	600ºC	12 ± 3

Table 7. Compressive strength results obtained from different samples previously subjected to different calcination conditions.

As can be seen in Table 7, the influence temperatures and calcination times in the improvement of the mechanical resistance of the studied materials is minimal, although in the case where water is used as a binder ratio, a 60% increase in mechanical strength is observed in the calcination at 600°C compared to 500°C, the values are so small that they do not represent a significant change. However, a remarkable enhancement in compression strength is observed when acetic acid is used as the liquid binder instead of water, the compressive strength is 8 times higher than the best obtained in cases where water is used. This increase in breaking strength is due to the better dispersion of boehmite in the presence of acetic acid, which serves as an additive that enhances the strength of the formed zeolite. This fact has been proved by EDX mapping where the homogeneity dispersion of boehmite can be seen, see Figure 19. As can be observed, in the absence of acetic acid, the boehmite particles tend to agglomerate, whereas in the presence of acetic acid, a uniform distribution of boehmite is achieved, in the composition study at the different points this can also be corroborated, See Appendix 4. The sample with water as liquid binder displays lower values of Al content (8±2 % w.), because none of the points studied probably coincided with boehmite agglomerates in which the Al content would be much higher. In the case of the sample containing acetic acid, the boehmite has been homogeneously distributed

throughout the pellet leaving higher Al values (18±3 % w.) as they complement the Al in the crystal lattice.
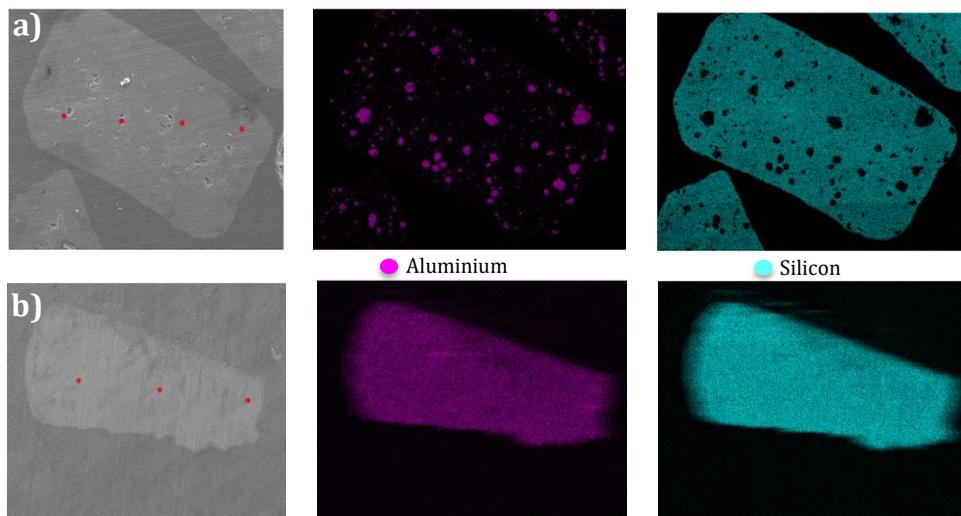

Figure 19. Energy dispersive X-Ray Al and Si mapping of formulation 7 (a) and 8 (b). The points where the compositional study has been carried out on each sample are shown in red.

Based on the results obtained with the Zeolite Y/Boe/MC 8:2:0.3 formulation using acetic acid as liquid binder, we can assert that we have successfully prepared well-designed zeolite-based catalyst supports that meet the desired characteristics and are ready for catalytic testing.

7. CONCLUSIONS

In conclusion, this study has yielded significant results regarding our objectives. Firstly, we have determined that the optimal powder-liquid ratio for extrusion of zeolite wet masses lies around 90-96% of the binder ratio at which the capillary state is achieved. This has facilitated the formulation work, reducing trial-error time and reducing the amount of wasted material.

Furthermore, the presence of methyl cellulose has been found to be essential for successful extrusion. Without the addition of this additive, satisfactory results in the extrusion step of catalyst body have not been achieved.

Regarding boehmite, we have confirmed that its utility lies in its homogeneous distribution within the mixture. To achieve this, we have employed acetic acid as a peptizer agent, which has proven effective in ensuring proper dispersion of boehmite. This process has significantly increased the strength of the zeolite-based catalyst.

Additionally, the use of acetic acid has demonstrated an increase in pore size, which benefits the diffusion properties of the catalyst supports. We have also successfully carried out alkaline desilication, resulting in significant changes in pore size.

In summary, the results obtained in this study underscore the importance of the powder-liquid ratio in the paste formulation, the addition of methyl cellulose, and the homogeneous distribution of boehmite in the zeolite extrusion process. Moreover, the positive impact of acetic acid on pore size and catalyst strength has been evidenced.

Once satisfactory zeolite-based catalytic bodies have been obtained, they should be impregnated with nickel and subjected to testing to assess their functionality in hydrocracking reactions. For future development in this project, the intention is to manufacture catalytic bodies using zeolite that has undergone a desilication process. However, due to time constraints, we were unable to pursue this aspect fully.

8. REFERENCES AND NOTES

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9. ACRONYMS

nm $\rightarrow$ nanometres

SAF $\rightarrow$ sustainable aviation fuel

EFAL $\rightarrow$ extra framework aluminium

Al $\rightarrow$ aluminium

Si $\rightarrow$ silicon

MC $\rightarrow$ methulcellulose

Boe $\rightarrow$ boehmite

aa $\rightarrow$ acetic acid

SA_{BET} $\rightarrow$ surface area Brunauer-Emmett-Teller

Br $\rightarrow$ binder ratio

Br' $\rightarrow$ experimental binder ratio obtained on the point where the mean line torque is maximum

BET $\rightarrow$ Brunauer-Emmett-Teller

EDX $\rightarrow$ energy dispersive X-ray

APPENDICES

APPENDIX 1: RESULTS OF THE PARTICLE SIZE STUDY
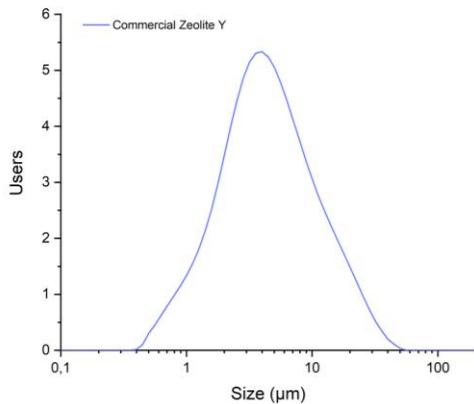
Figure A1. Commercial zeolita particle size distribution

APPENDIX 2: RHEOLOGICAL EFFECT OF USING ACETIC ACID AS LIQUID BINDER INSTEAD OF WATER
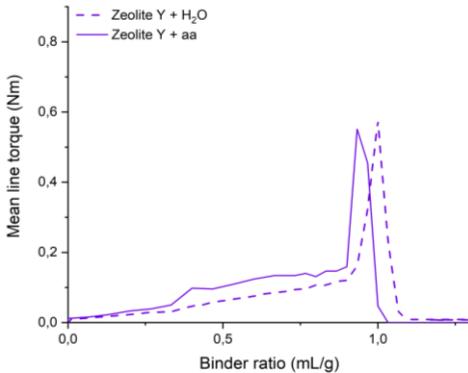
Figure A2. Comparison between the use of acetic acid or water as a liquid binder in a formulation containing only Zeolite Y.
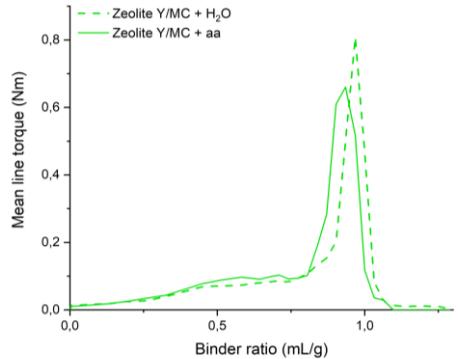
Figure A3. Comparison between the use of acetic acid or water as a liquid binder in a formulation containing Zeolite Y and methylcellulose.
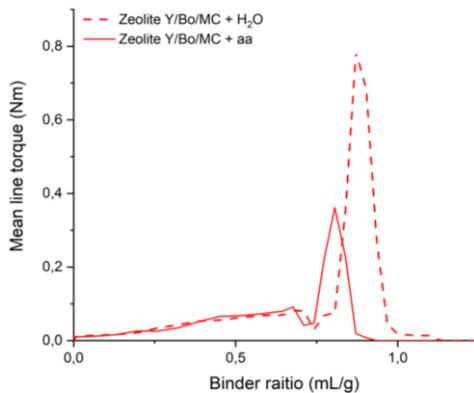
Figure A4. Comparison between the use of acetic acid or water as a liquid binder in a formulation containing Zeolite Y, boehmite and methylcellulose 8:2:0,3.

APPENDIX 3: ISOTHERM LINEAR PLOTS FROM NITROGEN PHYSISORPTION
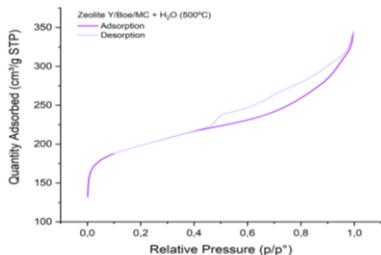
Figure A5. Isotherm results from pellets containing Zeolite Y/Boe/MC + H2O calcined at 500ºC.
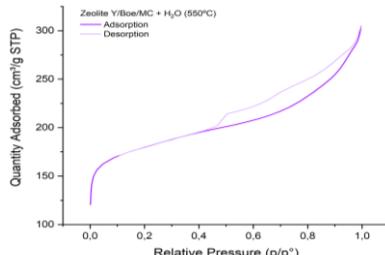
Figure A6. Isotherm results from pellets containing Zeolite Y/Boe/MC + H2O calcined at
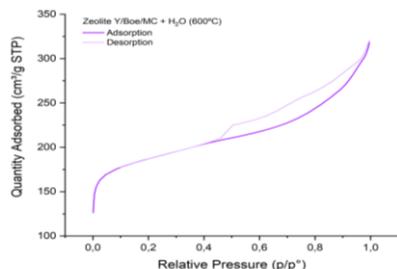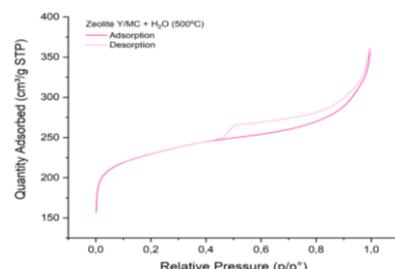

Figure A7. Isotherm results from pellets containing Zeolite YBoe//MC + H2O calcined at 600ºC.

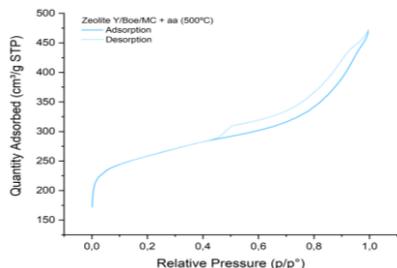Figure A8. Isotherm results from pellets containing Zeolite Y/MC + H2O calcined at 500ºC.

Figure A9. Isotherm results from pellets containing Zeolite Y/Boe/MC + aa calcined at 500ºC.
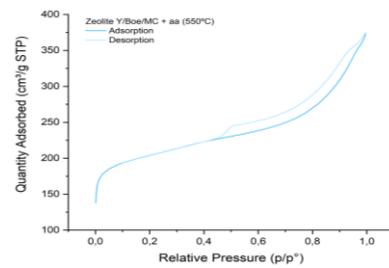

Figure A10. Isotherm results from pellets containing Zeolite Y/Boe/MC + aa calcined at
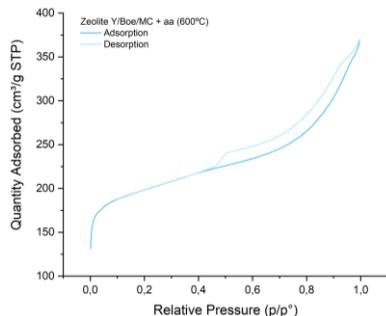

Figure A11. Isotherm results from pellets containing Zeolite Y/Boe/MC + aa calcined at 600ºC.
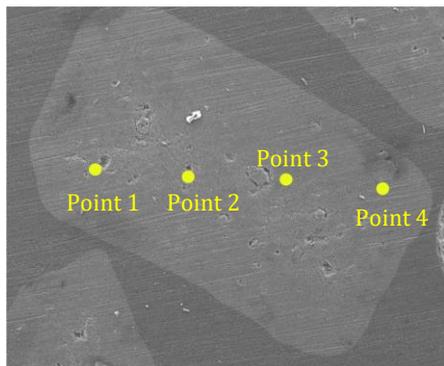
APPENDIX 4: ELEMENTAL COMPOSITION

Figure A12. Electron image of formulation 7.

	Weight %		Atomic %	
	Aluminium	**Silica**	**Aluminium**	**Silica**
Point 1	10,0	90,0	10,4	89,6
Point 2	5,1	94,9	5,3	94,7
Point 3	9,5	90,5	9,8	90,2
Point 4	7,5	92,5	7,8	92,2
Mean	8±2	92±2	8±2	92±2

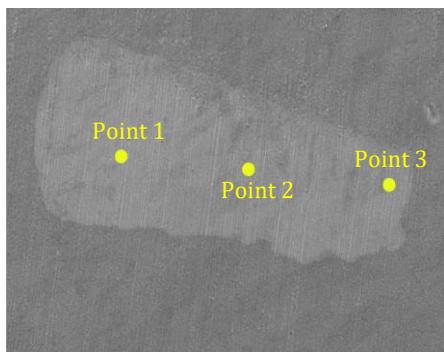*Table A1. Aluminium and silica composition at 4 points of the pellet composed by formulation 7.*

Figure A13. Electron image of formulation 8.

	Weight %		Atomic %	
	Aluminium	**Silica**	**Aluminium**	**Silica**
Point 1	20,0	80,0	20,7	79,3
Point 2	20,2	79,8	20,8	79,2
Point 3	14,9	85,1	15,4	84,6
Mean	18±3	82±3	19±3	81±3

Table A2. Aluminium and silica composition at 3 points of the pellet composed by formulation 8.