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# Dedication

## أهدي هذا العمل المتواضع إلى:

إلى من وضع المولى سبحانه وتعالى الجنة تحت قدميها ووقرها في كتابه العزيز... إلى من أفضلها على نفسي ولم لا فلقد ضحت من أجلي، ولم تدخر جهداً في سبيل إسعادي على الدوام (أمي الحبيبة) إلى صاحب السيرة العطرة والفكر المستنير، فلقد كان له الفضل في بلوغي التعليم العالي (والذي الحبيب) أطل الله في عمره.

إلى اخوتي الاعزاء (أسماء وسليم وإيمان) الذين كانوا دائماً معي في الأوقات السعيدة والصعبة لقد مشيتم إلى جانبي في كل خطوة من رحلتي العلمية، ولم تترددوا في دعمي وتشجيعي في الأوقات الصعبة ولا يمكنني نسيان أبناء إخوتي الرائعين (هارون . مسلم . عبدالحى . سفيان . غزلان . يسرى . يمى) الذين أصبحوا جزءاً لا يتجزأ من حياتي.

وإلى صغيرتي التي لم تراها عيني ولكن قلبي تعلق بها كثيراً ابنت اختي (حسنا صالحى) رحمك الله وإلى زوج اختي العزيز (صلاح الدين صالحى) حفظك الله وألهمك صبراً من عنده ولأصدقائي الأعزاء، كنتم رفقة لا تقدر بثمن خلال سنوات الدراسة. كنتم دعماً لا يضاهى ومصدراً للابتسامات . لقد قضينا سوياً أوقاتاً رائعة وأنشأنا ذكريات لا تنسى.

إلى أعلى أخت (حسنا) رحمك الله يا عزيزتي إلى من كانت روجى وبهجتي على الرغم من غيابك الجسدى، إلا أن ذكراك وحضورك يملأان حياتي بالسعادة ، أشعر بالحزن لأنك كنت تنتظرينى بفارغ الصبر ولكن شاءت الأقدار أن تكونى خارج هذا اليوم ، لكننى أعلم أنك تراقبينى من السماء وتشجعينى بكل فخر. إذا كان هناك شيء واحد تودين أن أحققه فى حياتى، فسيكون ذلك أن أفخر بك كأختى. أتمنى أن تكونى فخورة بي وبكل ما حققته حتى الآن.

أهديكم بحث تخرجى (الطالب صخر فارس).

## **Dedication**

**To my dear parents and the whole family. . .**

**To all those who have given me so much. . .**

**To all those who are dear to me...**

**To my teachers. . .**

**Thank you all. . .**

**Gifted by student Ghilani Abd Raouf. . .**

# Thanks

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Please accept my sincere thanks for all your support

# ABSTRACT

ملخص: تلعب المحفزات ثنائية الوظيفة ، التي تجمع بين المواقع الحمضية والأساسية ، دورًا حيويًا في تعزيز التفاعلات المعقدة التي تتضمن كيمياء قاعدية حمضية. وجدوا استخدامًا مكثفًا في تفاعلات التكسير الهيدروجيني ، والأزمنة ، والألكلة ، مما يعزز معدلات التفاعل ، والانتقائية ، ويمكن من تحويل الركائز الصعبة من ناحية أخرى ، تعتبر الزيوليت معادن ذات بنية بلورية مميزة تتميز بقنوات ومسام مترابطة ، مما ينتج عنه مساحة سطح عالية ومسامية. لديهم خصائص امتصاص وتبادل أيوني استثنائية ، مما يجعلها ذات قيمة عالية في مختلف التطبيقات. تعمل الزيوليت كمحفزات في تكرير البترول وإنتاج البتروكيماويات وفصل الغاز ومعالجة المياه والمعالجة البيئية. ركزت دراسة على تحضير محفزات Co-Mo / Zeolite Y باستخدام طريقة التشريب. تشمل هذه المحفزات على مكونات معدنية لتسهيل تفاعلات الهدرجة والمكونات الحمضية لتعزيز تفاعلات التكسير ، والتي تعتبر بالغة الأهمية في العديد من العمليات الصناعية. تم استخدام تقنيات التوصيف مثل حيود الأشعة السينية (XRD) وقياسات الأس الهيدروجيني الثقالي لتقييم وفهم خصائص المحفزات. تم استخدام أطياف XRD لتحليل التركيب البلوري للمحفزات. تعزز حموضة محفزات Co-Mo / Zeolite Y بشكل كبير من نشاطها التحفيزي ، خاصة في تفاعلات التكسير.

Abstract: Bifunctional catalysts, which combine acidic and basic sites, play a vital role in promoting complex reactions that involve acid-base chemistries. They find extensive use in hydrocracking, isomerization, and alkylation reactions, boosting reaction rates, selectivity, and enabling the conversion of challenging substrates. On the other hand, zeolites are minerals with a distinctive crystalline structure characterized by interconnected channels and pores, resulting in a high surface area and porosity. They possess exceptional absorption and ion exchange properties, making them highly valuable in various applications. Zeolites serve as catalysts in petroleum refining, petrochemical production, gas separation, water treatment, and environmental remediation. A study focused on preparing Co-Mo/Zeolite Y catalysts using the impregnation method. These catalysts incorporate metal components to facilitate hydrogenation reactions and acidic components to promote cracking reactions, which are crucial in numerous industrial processes. Characterization techniques like X-ray diffraction (XRD) test acidity measurements were employed to assess and understand the catalysts' properties. XRD spectra were used to analyze the catalysts' crystal structure. The acidity of Co-Mo/Zeolite Y catalysts significantly enhances their catalytic activity, particularly in cracking reactions.

Résumé : Les catalyseurs bifonctionnels, qui combinent des sites acides et basiques, jouent un rôle essentiel dans la promotion de réactions complexes impliquant des chimies acide-base. Ils trouvent une utilisation intensive dans les réactions d'hydrocraquage, d'isomérisation et d'alkylation, augmentant les taux de réaction, la sélectivité et permettant la conversion de substrats difficiles. D'autre part, les zéolithes sont des minéraux avec une structure cristalline distinctive caractérisée par des canaux et des pores interconnectés, ce qui donne un grande surface et porosité. Ils possèdent des propriétés d'absorption et

d'échange d'ions exceptionnelles, ce qui les rend très précieux dans diverses applications. Les zéolithes servent de catalyseurs dans le raffinage du pétrole, la production pétrochimique, la séparation des gaz, le traitement de l'eau et l'assainissement de l'environnement. Une étude s'est concentrée sur la préparation de catalyseurs Co-Mo/Zéolite Y en utilisant la méthode d'imprégnation. Ces catalyseurs intègrent des composants métalliques pour faciliter les réactions d'hydrogénation et des composants acides pour favoriser les réactions de craquage, cruciales dans de nombreux procédés industriels. Des techniques de caractérisation telles que la diffraction des rayons X (XRD) et le test l'acidité ont été utilisées pour évaluer et comprendre les propriétés des catalyseurs. Les spectres XRD ont été utilisés pour analyser la structure cristalline des catalyseurs. L'acidité des catalyseurs Co-Mo/Zéolite Y améliore significativement leur activité catalytique, en particulier dans les réactions de craquage.

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# **General Introduction**

## General Introduction

In chemistry, a catalyst is a substance that enhances the rate of a chemical reaction without being consumed in the process. It achieves this by providing an alternative pathway with lower activation energy, thereby accelerating the reaction without undergoing any permanent changes itself. Catalysts have significant importance in numerous industrial processes and find applications in diverse fields such as petroleum refining, chemical synthesis, and environmental control[1]. Bifunctional catalysts are often composed of two distinct active sites, such as an acidic site and a basic site. The acidic site facilitates acid-catalyzed reactions, while the basic site assists base-catalyzed reactions. By combining these two functions into a single catalyst, bifunctional catalysts can promote complex reactions involving both acid-base chemistry. These catalysts are widely employed in various chemical processes, including hydrocracking, isomerization, and alkylation reactions. The presence of multiple active sites in bifunctional catalysts improves reaction rates, enhances selectivity for desired products, and enables the conversion of challenging substrates.

Zeolites, on the other hand, are a group of naturally occurring or synthetically produced minerals that possess a unique crystal structure. They exhibit a three-dimensional network of interconnected channels and pores, which results in a high surface area and porosity. Zeolites offer exceptional adsorption and ion exchange properties, leading to their wide range of applications[2]

Zeolites are commonly utilized as catalysts in industrial processes such as petroleum refining and petrochemical production. They are also employed as adsorbents for gas separation and purification, water treatment, and environmental remediation. Additionally, zeolites find use in detergent production as molecular sieves and as catalysts in the conversion of biomass into biofuels. The distinct properties and versatile nature of zeolites make them valuable materials in various scientific, industrial, and environmental fields. The study involves the preparation of Co-Mo/Zeolite Y catalysts using the impregnation method. These catalysts contain metallic components to facilitate hydrogenation reactions and acidic components to promote cracking reactions, which are crucial in numerous industrial applications. Characterization techniques such as X-ray diffraction (XRD) and gravimetric test acidity

have been employed to evaluate and understand the catalysts' properties. XRD spectra are used to analyze the crystal structure of the catalysts.

The increased acidity of Co-Mo/Zeolite Y catalysts can significantly enhance their catalytic activity, particularly in cracking reactions. These findings contribute to a deeper understanding of the properties of Co-Mo/Zeolite Y catalysts and their potential in hydrogenation and cracking processes. The ability to manipulate the crystallinity and acidity of catalysts opens up possibilities for improving their performance in various industrial applications.

## **CHAPTER I :BIBLIOGRAPHIC STUDIES**

## **I.1. Introduction**

Heterogeneous catalysis plays a crucial role in the chemical industry, and the main challenge is to design catalysts with high activity, selectivity, and stability. Researchers are exploring new approaches to catalyst design, and the use of bifunctional catalysts has shown promise for multistage catalytic reactions. These catalysts contain both metallic sites over metal nanoparticles and acid sites from the support, such as metals combined with zeolite. However, designing efficient bifunctional catalysts remains a major challenge [3].

Zeolites are crystalline aluminosilicates with uniform micro pores smaller than 2 nm, which have been widely used in catalysis due to their ordered microporosity and presence of Brønsted and Lewis acid sites. Zeolites have high thermal stability, mechanical strength, high specific surface area, and high ion-exchange capacity. Their strong acid sites and thermal stability make them promising materials for catalysis, and they can be used as acid or bifunctional catalysts when a metal has been added to the structure. The location of the metal in the support is also important, as it can affect the catalytic performance of metal zeolite composite catalysts.

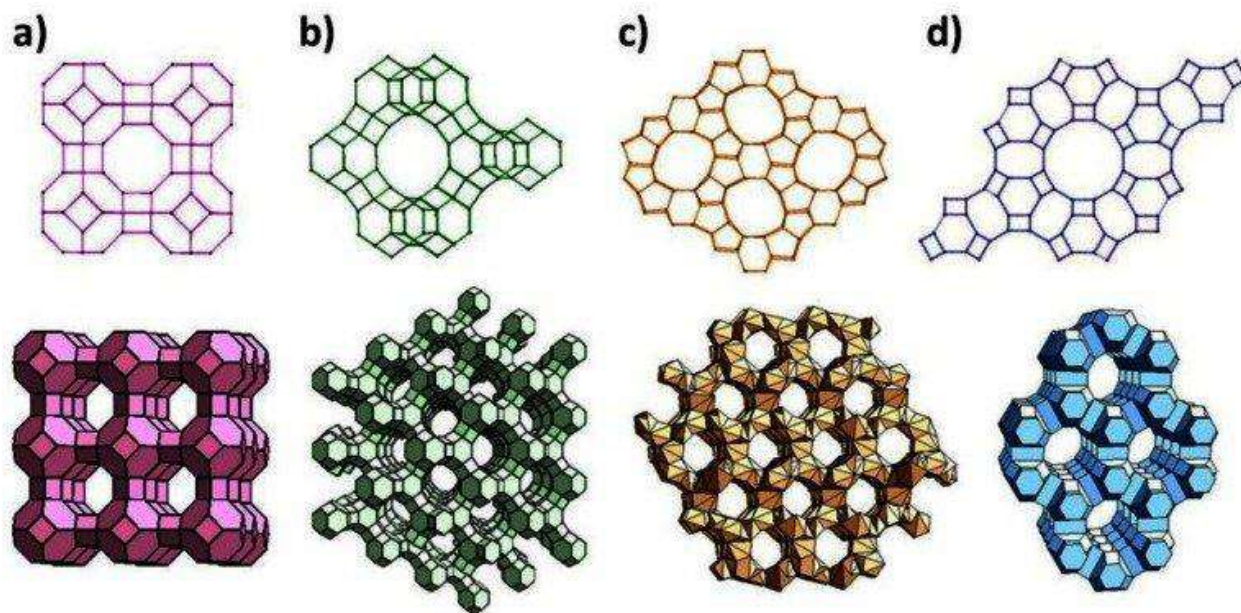
## **I.2. Challenges in the design of bifunctional catalysts**

Bifunctional metal-zeolite catalysts using innovative synthetic strategies to create hierarchical metal-zeolite nanocomposites. The two main challenges identified in the design of these catalysts are the pore size of the zeolite, which can lead to diffusion limitations, and the localization of metals and acids in the zeolite, which can impact the catalytic performance. The objectives are to optimize the impregnation sequence to introduce the cobalt ions into the zeolite, to create hierarchical zeolites using carbon nanotubes such as the sacrificial template to obtain bifunctional catalysts with cobalt particles uniformly distributed throughout the zeolite's mesoporous structure, and to extend the methodology to include other metals such as nickel and magnesium. The bifunctional catalysts designed are evaluated on reaction models such as the hydrogenation of aromatics and the acylation of anisole[4].

### I.3. Zeolites: structure, , acidity and catalysis

Zeolites are crystalline structures composed of microporous aluminosilicates, formed by the linkage of  $\text{AlO}_4$  and  $\text{SiO}_4$  tetrahedra through their edges. They are crucial as industrial catalysts in petroleum refining processes, such as catalytic cracking, hydrocracking, isomerization, alkylation, and fuels production, as well as in chemical processes, including the oxidation of olefins and fragrance synthesis. The primary synthetic zeolites used in these processes are Mordenite Framework Inverted (MFI), Faujasite (FAU), and Beta (BEA), which have been commercialized as catalysts[5].

Zeolite materials possess unique features, including a large surface area, high thermal stability, high ion-exchange capacity, strong acid sites, and shape-selectivity. However, the structural micropores of zeolites can also be a disadvantage for the mass transfer of bulky molecules, causing diffusion limitations for reagents, intermediates, and products. In recent years, extensive research has been conducted to develop zeolites with mesopores and to minimize the diffusional limitations[6].

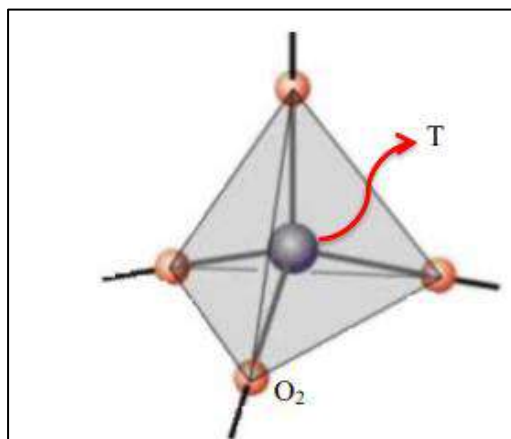


**Figure I.1** Representative Zeolite tires with porous holes (3D zeolite)



### I.3.1 Structure

Zeolites have a crystalline structure composed of tetrahedra of  $TO_4$ , where T represents either Si or Al in natural zeolites and can be other elements such as Ga, Ge, Fe, B, P, or Ti in synthetic materials. These tetrahedra are connected through oxygen atoms, forming a three-dimensional network of channels and cavities with sizes of approximately 1 nm, which are accessible to many molecules. The combination of silicon and oxygen in tetrahedra forms an uncharged solid ( $SiO_2$ ). When aluminum is incorporated into the silica structure, the structure becomes negatively charged. This occurs through the  $Al^{3+} \leftrightarrow Si^{4+}$  substitution and requires compensating cations to maintain an overall neutral framework[7].



**Figure.I.2:** Zeolite structure

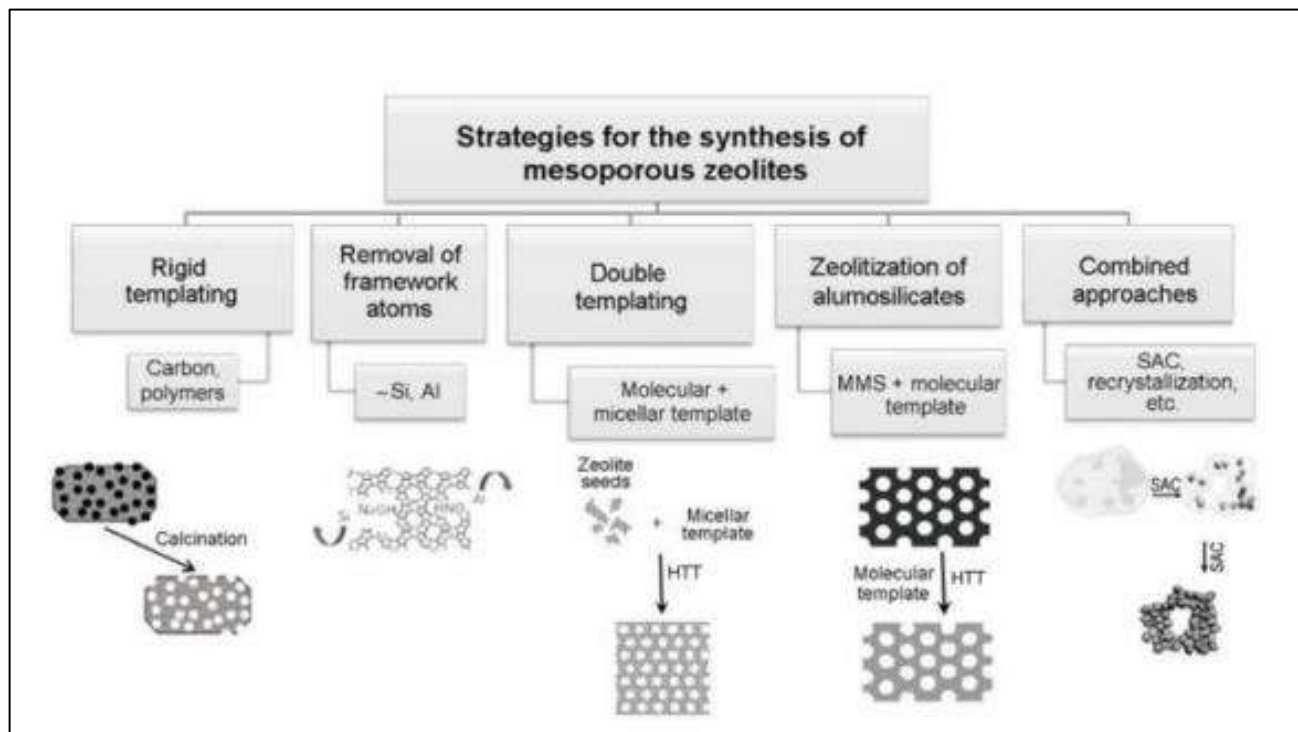
### I.4 Porosity and hierarchical zeolites

Zeolites are known for having small pores, which can limit the mass transport of chemical compounds of similar size, resulting in the production of undesired by-products and catalyst deactivation. However, the development of hierarchical zeolites with mesopores ranging from 2 to 50 nm has proven to be a promising approach to overcome these limitations. Mesopores are not inherent to the zeolite structure, but they can improve accessibility to active sites, delay catalyst deactivation, and reduce diffusion limitations.

There are two main approaches to creating hierarchical zeolites: "top-down" and "bottom-up." The "top-down" approach involves modifying already synthesized zeolites through dealumination and desilication techniques. Dealumination can be achieved using chemical agents or high-temperature steaming, while desilication involves extracting silicon from the zeolite framework using alkaline solutions. However, this approach may lead to the partial destruction of the zeolite structure and the creation of non-uniform mesopores.

On the other hand, the "bottom-up" approach involves the use of templates and specific synthesis conditions such as hard and soft templating. Hard templates can be made from carbon nanoparticles, nanotubes, and polymer beads, while soft templates include various cationic surfactants, organosilane, cationic polymer, and ionic liquids. Both types of templates can be removed by calcination. Several methodologies involving soft and rigid/hard templating for creating hierarchical zeolites are described, including double templating and rigid or hard templating using hollow or porous solids.[8]

Hierarchical zeolites with mesoporosity have been shown to improve molecular diffusion and reduce molecule residence time, resulting in higher catalyst lifetime and less deactivation. Large pore zeolites are useful in various reactions, including cracking, alkylation, isomerization, and oxidation. Encapsulation of metal nanoparticles in zeolite micro- and mesopores is a challenge for designing bifunctional catalysts. The confined metal is expected to enhance catalytic performance, activity, and stability in Fischer-Tropsch synthesis and other reactions.



**Figure. I. 3:** Approaches for creating a hierarchical zeolite.

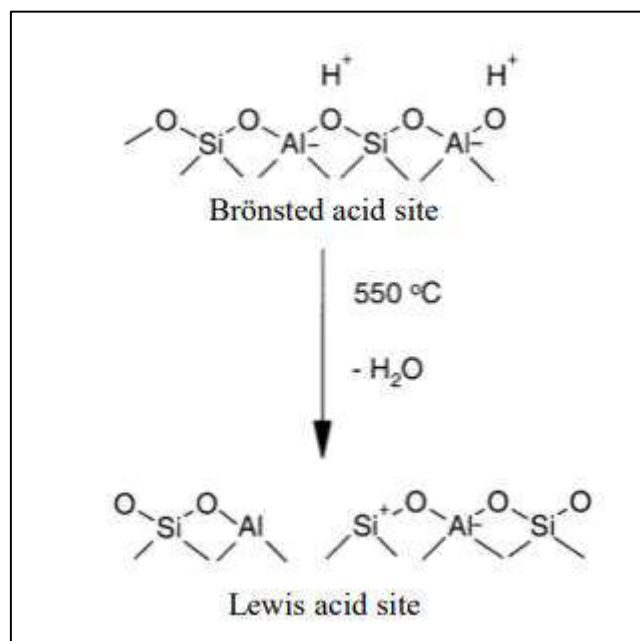
### I.5 Brönsted and Lewis acidities:

The acidity of zeolites is determined by their chemical composition and structural properties, with acid sites primarily located within their pores. Compared to highly corrosive liquids such as sulfuric acid, zeolites offer a safer alternative. The catalytic activity of zeolites is closely linked to the number and types of Brönsted and Lewis acid sites present within their solid structure. The strength and amount of these acid sites are influenced by the distribution and concentration of aluminum (Al) within the zeolite framework.[9]

Brönsted acidity is formed through the substitution of  $\text{Si}^{4+}$  atoms with  $\text{Al}^{3+}$  atoms, which results in a negatively charged structure requiring protonation to compensate. This leads to the formation of hydroxyl groups ( $\text{Si-O(H)-Al}$ ) that are responsible for Brönsted acidity. The concentration of acid sites is directly proportional to the concentration of Al in the lattice. The formation of Lewis acid sites typically occurs during calcination at temperatures above  $500^{\circ}\text{C}$ , where dehydroxylation of Brönsted acid sites takes place.

Lewis acid sites are characterized by their electron-receptor properties and are associated with Al atoms located outside the zeolite framework in octahedral coordination or with low coordinated T atoms within the framework.[9] These extra-framework aluminum species may exist in different forms, including  $\text{Al}^{3+}$ ,  $\text{Al}(\text{OH})^{2+}$ , and  $\text{AlO}^+$ , and exhibit weak Brönsted acidity. The nature of the acid sites can be determined using various techniques, such as  $\text{NH}_3$ -stepwise temperature-programed desorption ( $\text{NH}_3$ -STPD), infrared spectroscopy (IR) with molecular probes, nuclear magnetic resonance (NMR), and microcalorimetry.

Among these techniques, IR spectroscopy is the most commonly used for measuring acidity in porous solids, with pyridine frequently used as a probe molecule. The interaction of pyridine with Brönsted or Lewis acid sites results in adsorbed species with characteristic vibrational frequencies that correlate with the type and concentration of acid sites. The quantification of these species can be achieved using a variety of methods.



**Figure. I.4:**Formation of Lewis acid sites in zeolites.

## **I.6 Model reactions on acid sites**

To describe the active basic, acidic, or acid-basic solid supports, model reactions are utilized as tools. Examples of reactions using zeolite catalysts are listed in Table. A reaction known as isomerization creates isomers, which are molecules with the same type, quantity, and size of atoms but a different molecular structure. Due to the significant commercial value of these chemical compounds, branching isomers are produced by the hydrocarbon isomerization process. The branched hydrocarbons have a higher octane value than the linear counterparts.

Olefin isomerization is a quick reaction, whereas paraffin isomerization takes longer and calls for extremely high temperatures. On a bifunctional catalyst containing acid sites for isomerization by carbenium ions formed from olefins and metallic sites for dehydrogenation/hydrogenation from paraffins, the paraffin isomerization reaction takes place.

There are numerous processes that take place over bifunctional catalysts, such as Friedel-Crafts alkylation and acylation, cracking, and oligomerization. Amorphous oxides, combinations of oxides, zeolites, silicoaluminophosphates, and mesoporous materials can all be used as acid supports for bifunctional catalysts. The first step in the protonation of paraffins by a catalyst is protolytic cracking, which results in the production of carbenium ions and paraffins.

Acid catalysts support the exothermic reaction of oligomerization, which produces C-C bonds. For the production of alkyl and ketone aromatics for diverse industries, Friedel-Crafts alkylation and acylation processes are crucial. Due to their diverse ranges of acidity, Si/Al ratios, and crystalline structure, zeolites like BEA, ZSM-5, and Y have been employed for these reactions. Lewis and Brønsted acids, among other catalysts employed in these processes[10].

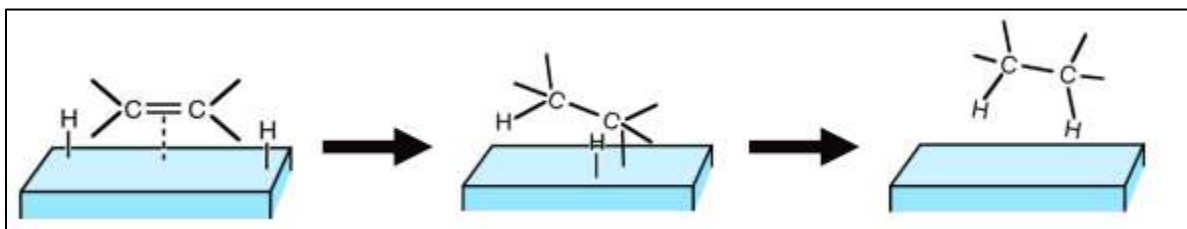
## **I.7 Model reactions on metal sites**

On catalysts with metallic properties (like Pt, Pd, or Rh), hydrogenation and dehydrogenation processes take place. Metal sites have the ability to hydrogenate olefin intermediates desorbed from acid sites and dehydrogenate saturated reactant molecules to alkenes.

According to thermodynamics, hydrogenation is highly exothermic, results in a decrease in the number of molecules, and is most likely to happen at low temperatures and high pressures.

The hydrogen-hydrogen bond is broken by the hydrogen activation, which is carried out by a metal catalyst. The hydrogenation reaction between the ethylene and toluene molecules serves as an illustration[11].

The increased demand for higher-quality diesel fuels with higher cetane numbers and stricter environmental laws has increased interest in toluene hydrogenation. For these reasons, toluene is less dangerous than benzene despite having similar characteristics.



**Figure I.5.** Ethylene hydrogenation reaction

## I.8 Bifunctional catalysis and catalysts

The concept of multi-functional catalysis was first introduced by Weiss in the 1960s. Bifunctional catalysts contain two types of active sites - metallic and acid. Typically, these catalysts consist of metallic sites, which function in dehydrogenation/hydrogenation, and acid sites, which catalyze acid-catalyzed reactions such as cracking, isomerization, and more. The components responsible for hydro-dehydrogenation can be transition or noble metals with good dispersion, such as platinum (Pt), palladium (Pd), metal sulphides, or metal oxide such as cobalt (Co), nickel (Ni), iron (Fe), copper (Cu) supported on zeolite.

Industrial bifunctional catalysts often contain Pt, which plays a critical role in hydrogenation-dehydrogenation. The presence of metallic sites is essential as they can catalyze various reactions such as hydrogenation-dehydrogenation, hydrogenolysis, aromatization, and hydrocarbon cyclization. Metallic sites mainly catalyze hydrogenation-dehydrogenation reactions, while acid sites catalyze carbocation rearrangements. The combination of acid and metallic sites in bifunctional catalysts enhances catalytic activity and product yield. The balance and synergy between acid and metallic sites are essential in determining the catalyst's activity, stability, and selectivity.[12]

In bifunctional catalysis, the strength of acid sites and the distribution of metal and acid sites are crucial parameters. The kinetic steps of the consecutive reactions are interdependent through the processes of diffusion of intermediates from one type of site to another. The two types of active sites in bifunctional catalysts should be as close as possible to achieve higher catalytic activity and selectivity. Various methods can be used to introduce metals into zeolite, with incipient wetness impregnation (IW or IWI), also known as capillary impregnation or dry impregnation, being the most common.

In incipient wetness impregnation, a solution containing a metal precursor is added to the catalytic support, filling the zeolite pores, followed by drying and calcination/reduction steps. This technique is called "incipient wetness impregnation" when the volume of the solution is equal to or smaller than the total pore volume of the support

**Table I.1.** Model reactions on zeolite acid sites.

Type of Reaction	Typical applications and catalysts
Isomerization	Bifunctional Pt/Fe-ZSM-5 catalyst for xylene isomerization
Cracking	SO <sub>4</sub> <sup>2-</sup> /TiO <sub>2</sub> promotion on HZSM-5 for catalytic cracking of paraffin
Oligomerization	Butene oligomerization reaction over the hemicellulose modified HZSM-5
	Benzene alkylation with methanol over ZSM-5 zeolite Friedel-Crafts acylation reactions over hierarchical MCM-22 zeolites .Acylation of anisole with long-chain carboxylic acids over wide pore zeolites

Friedel-Crafts	.Effects of acid-modified HBEA zeolites on thiophene acylation and the origin of deactivation of zeolites
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## I.9 Heterogeneous catalysis

Heterogeneous catalysis offers various advantages, including easy preparation of the catalyst through aqueous methods. It also enables form selectivity, such as in zeolites, resulting in different selectivity than expected from thermodynamics due to either constrained diffusion paths or optimal occupation of space by the channels and cavities. Furthermore, the temperature range for operation is typically wide, allowing for favorable thermodynamic conditions, activation energies, product desorption, and reduced effect of polar impurities. Separating the reaction products and catalyst is straightforward, and the catalyst's utilization is optimal, remaining in the reactor as long as it remains active. Finally, thermal regeneration of the catalyst is often feasible. Despite the absence of continuous rejection, using a heterogeneous catalyst still comes with certain drawbacks.

For instance, it is not possible to take advantage of the effects of ligands, leading to fixed selectivity. Additionally, achieving homogeneity of the active species proves difficult, and only a small fraction of the solid is accessible, typically only its surface. There are also mass and heat transfer issues to contend with, making implementation complex and costly and requiring expertise in chemical engineering [13]

Another challenge is that the amount of catalyst cannot be adjusted to match the flow of reactants, which can result in selectivity issues, particularly when they depend on the conversion. Moreover, the presence of impurities in the reactants can deactivate the entire catalyst. Table lists the primary processes and catalysts used



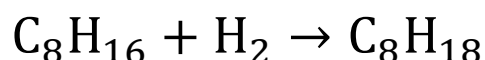
## I.10 Mechanism of heterogeneous catalysis

Heterogeneous catalysis involves the adsorption of reactants onto the catalyst surface before the reaction occurs. This is similar to the formation of intermediate complexes in homogeneous catalysis. Typically, the heat generated from adsorption activates the reactants and facilitates the reaction.

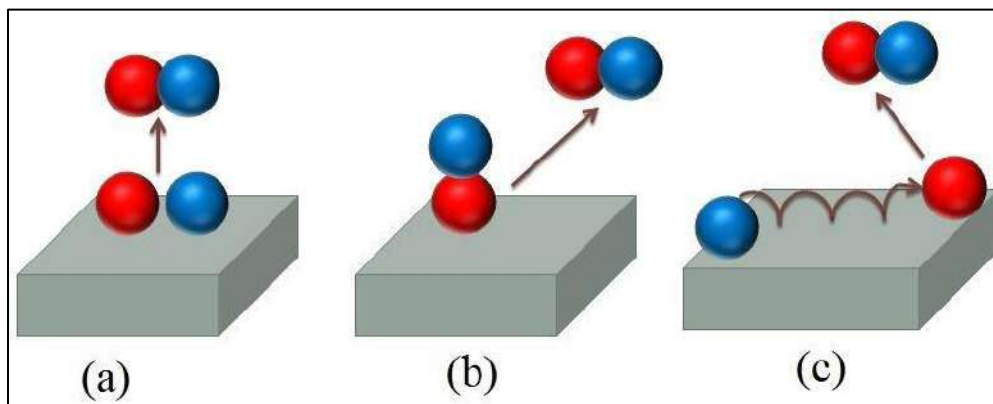
The reaction mechanism for heterogeneous catalysis involves four steps:

- diffusion of reactants on the catalyst surface,
- adsorption of reagents on the catalyst surface leading to chemical adsorption, where the reactive molecule dissociates and forms chemical bonds with the catalyst
- chemical reaction between the chemisorbed reactant molecules on the surface of the catalyst, which is the slowest step and kinetically determining
- desorption of the formed products from the catalyst surface and their diffusion away from the surface

For example, the catalytic hydrogenation of 3,4-dimethyl-3-hexene using a metal catalyst such as palladium (Pd), nickel (Ni), platinum (Pt), or rhodium (Rh) leads to the formation of 3,4-dimethylhexane[14]



The reaction occurs when dihydrogen is activated on the surface of the catalyst and adsorbed. The chemisorption of dihydrogen on the metal catalyst leads to the dissociation of the H<sub>2</sub> molecule into atoms and the formation of a metal hydride on the catalyst surface, which is a highly irreversible and exothermic step[15]



**Figure I.6.** The Mechanisms of heterogeneous catalysts surface reactions

The role of supports in heterogeneous catalysis can be summarized as follows:

- ✓ Dispersing the active phase (regardless of its nature) improves the density of active sites for the desired reaction.
- ✓ In the case of nanoparticle catalysts, enhancing the metal-support interaction improves their stability, which mitigates deactivation due to sintering.
- ✓ Supports facilitate the transfer of reactants to active sites and enable the separation of the catalyst from the reaction medium at the end of the reaction.
- ✓ In exothermic reactions, supports can reduce the formation of local hotspots in the catalyst, thereby minimizing selectivity loss and improving operational safe

## **I.11 Catalyst Preparation Methods**

### **I.11.1 The ceramic method**

The ceramic method is commonly utilized in industrial preparations and for creating phase diagrams, as well as for conducting crystallographic studies. The process involves crushing a precise amount of solid compounds, usually oxides or metal carbonates, into a fine powder. The resulting powder is then calcined at the crystallization temperature of the compound. The effectiveness of the preparation is dependent on the number of grinding and heat treatment cycles. Despite the potential benefits of this method, such as increased efficacy, the process is limited by its high energy costs, the heterogeneity of the resulting compounds, and their low specific surface area[16].

### **I.11.2 The impregnation method**

The impregnation method is one of the simplest ways to prepare catalysts. This method involves wetting a support material, typically a stable refractory oxide, with a solution containing a metal salt precursor for the active phase, based on the desired volume ratio. The next steps include drying and calcination of the support material[17].

### **I.11.3 Co-precipitation method**

The process involves dissolving various metallic salts in stoichiometric proportions, usually in water. Afterwards, metal cations are precipitated by the addition of a precipitating agent such as hydroxide (e.g. NaOH, KOH), oxalic acid, or ammonia. The resulting precipitate serves as the catalyst precursor, which is then filtered, washed, and calcined to produce a metal oxide[18].

### **I.11.4 Sol-gel method**

The sol-gel process is a chemical method used to create oxide-based materials such as ceramics and glasses. It begins by producing a stable suspension (sol) from chemical precursors in solution, which evolves during gelation to form a solid network in a liquid medium. Wet gels are then transformed into dry matter by evacuating solvents to create an aerogel or through

simple evaporation under atmospheric pressure to produce a xerogel. Thin film deposition can be achieved using dip-coating, spin-coating, or micro-droplet deposition. The resulting deposit or gel is then dried and annealed in an oxidizing atmosphere to create a crystallized material.

The sol-gel process offers several advantages over traditional methods, including low energy costs, simplified implementation, customized materials, and high purity and homogeneity. Depending on the molecular precursor used, the sol-gel process can be carried out through the mineral route, which involves reacting a metallic salt  $MX_n$  in an aqueous solution through a simple variation of pH, or the organic route, which involves an alkoxide ( $M(OR)_n$ ) and allows for further customization[19].

## **I.12 Physico-chemical characterization techniques for catalysts:**

### **I.12.1 Fluorescence X**

Fluorescence X (Fluorescence X-ray or XRF) is a non-destructive analytical technique used to determine the elemental composition of a material. It relies on the principle of fluorescence, where atoms or molecules absorb energy, typically in the form of X-rays or high-energy photons, and then re-emit lower-energy photons.

In XRF analysis, a sample is irradiated with X-rays, often generated by an X-ray tube or a radioactive source. When the X-rays interact with the atoms in the sample, inner-shell electrons are excited to higher energy levels. These excited electrons quickly return to their ground state, emitting secondary X-rays or characteristic X-rays in the process[20].

The characteristic X-rays emitted by the sample are specific to the elements present in the material. By detecting and analyzing the energy and intensity of these emitted X-rays, it is possible to identify and quantify the elements present in the sample. This information can be used to determine the chemical composition or elemental concentrations of the material.

### **I.12.2 X-ray diffraction**

x-ray diffraction is used to determine the atomic arrangement and distances between atoms in crystal lattices and to estimate the average size of the domains of coherent diffraction or crystallites. X-ray diffraction occurs when the Bragg condition (I.1) is fulfilled. For an incident X-radiation of wavelength  $\lambda$  this condition meets:

$$2d \cdot \sin\theta = n\lambda \quad (\text{I.1})$$

$\theta$ : incident angle between the ray and the sample plane.

$\lambda$ : wavelength of the radiation.

$n$ : network order (integer)

$d$ : inter-reticular distance between two crystallographic planes

The analysis of the diffraction diagram as a function of the angle makes it possible to determine the phase

crystallography of the material and to estimate the average size of the crystallites  $d$  by the calculation of

the half-height width  $H$  of the diffraction peaks by applying the Debye-Scherrer formula

(I.2)[21]

$$d = K \cdot \lambda / (H \cdot \cos.\theta) \quad (\text{I.2})$$

$d$ : taille moyenne des cristallites ( $\text{\AA}$ )

$k$ : constante de Scherrer, facteur correctif égal à 0,89 dans nos conditions expérimentales

$\lambda$ : longueur d'onde du faisceau incident

$H$ : largeur angulaire du pic de diffraction à mi-hauteur (rad)

$\theta$ : angle de diffraction de Bragg (rad)

### I.12.3 The BET method

The Brunauer-Emmett-Teller (BET) method is a technique used to identify a certain porous material's surface. She is based on how much gas is absorbed onto the material's surface.

The BET method is based on the BET isotherm of adsorption, which is a curve that depicts the amount of adsorbent (gas) adsorbed in relation to relative pressure. This isotherm

often measured by measuring the amount of a gas, such as azote, adsorption at various related pressures.

The foundation of the BET method is the notion that adsorption occurs both on the material's external surface and within its pores. Adsorption isotherm BET follows a theoretical model that considers both multimolecular adsorption inside of pores as well as monomolecular adsorption on external surfaces. By adjusting the data[22]

#### **I.12.4 Scanning Electron Microscopy (SEM)**

The electron microscopy technique known as scanning electron microscopy (SEM) is founded on the theories of electron-matter interactions. It entails moving an electron beam across the sample's surface for analysis; as a result, certain particles are released. Numerous detectors pick up these particles, allowing for the reconstruction of a three-dimensional image of the surface. SEMs frequently come with an X-ray spectrometer, which enables them to be used for chemical analysis and energy-dispersive X-ray spectroscopy.[23]

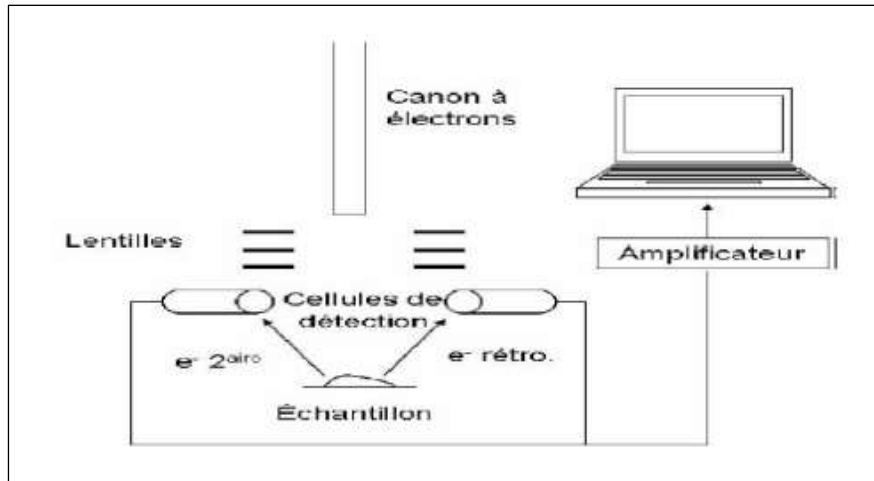
In comparison to optical microscopy, SEM offers a substantially larger depth of field for the examination of sample surface morphology. Several emissions happen when a substance is subjected to the electron beam, including:

( 0–30 eV) Secondary electrons

( eV0) Backscattered electrons

electrons with agers

X-ray photons (RX), ultraviolet (UV), infrared (IR), and visible photons



**Figure I .7.**Operating principle of a scanning electron microscope

### **I.12.5 Transmission electron microscopy (TEM)**

Without affecting the material, transmission electron microscopy enables viewing at nanometric and sub-nanometric scales. The idea is to bombard the sample with a stream of high-energy electrons, which should have a thickness that allows them to pass through it. With a high resolution processed point per dot up to 2 nm, the magnitude of the image TEM can be amplified by a factor higher than 106. The interaction of electron flow with samples also results in the emission of X-radiation, which has a characteristic wavelength for each element. By analyzing the photons produced and passing them through an EDX dispersive energy analyzer, the components of the sample can be chemically analyzed in detail[24]

## **CHAPTER II: CATALYST PREPARATION METHOD**



## **II.1 Introduction**

The impregnation method is a technique where chemical species are physically blended inside pores to modify the surface of the adsorbent. There are two types of impregnation methods, dry and wet, depending on the quantity of solvent added to the surface of the adsorbent. Anionic surfactants can be used to increase the active sites on the surface. Impregnation with metal salts can result in the formation of an oxide film on the surface, which can decrease regeneration temperature and increase the lifespan of the adsorbent. Mesoporous materials can be produced using the incipient-wetness impregnation technique, which is carried out in two steps to change the surface and texture of the adsorbent and deposit the material used for thermal activation[25].

The impregnation method can enhance pore volume and pore diameter by regulating the solid structure. Impregnated adsorbents are stable and have promising regeneration capacity compared to normal adsorbents

## **II.2 Operating mode**

### **II.2.1 Materials**

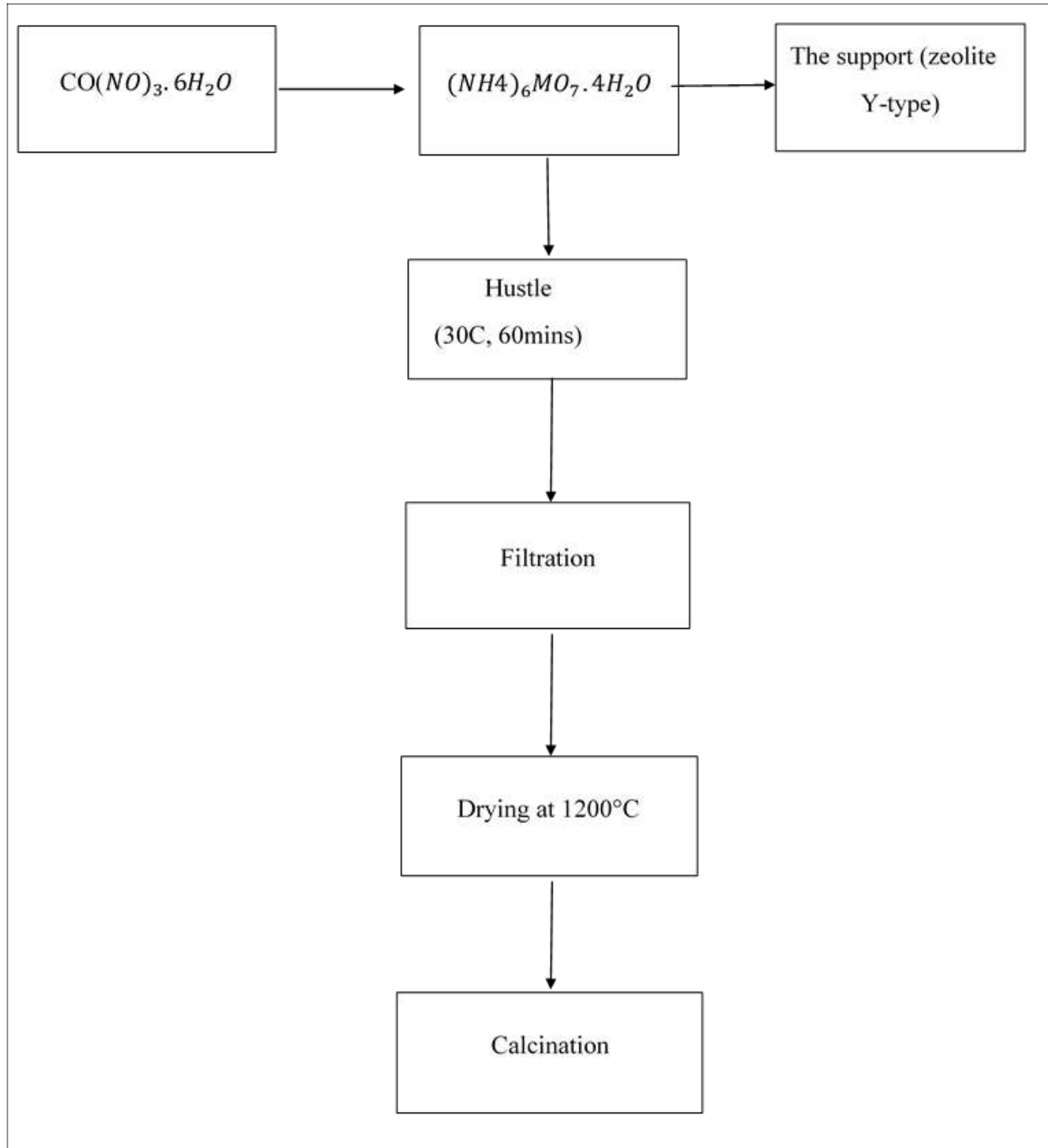
Balance, watch glass, Erlenmeyer flask, graduated cylinder, magnetic stirrer, filter paper, funnel, proofer, oven.

### **II.2.2 Experimental protocol**




- ✓ Put 25 mL of distilled water in a graduated cylinder
- ✓ We put a mass of cobalt (II)-nitrate hexahydrate in beaker 1 and add 25 ml of distilled water
- ✓ We put a mass of ammonium molybdate tetrahydrate, in beaker 2 and add 25 ml of distilled water
- ✓ A mass of 20g of type Y zeolite.
- ✓ place the three previous masses in an Erlenmeyer flask.
- ✓ The mixture should be stirred at 30°C for 60 minutes,

- ✓ The dried mass finally has to be calcined at 450°C for 2 hours preceded stages of 1 hour at 150°C, 250°C and 350°C.

**Diagram II.1:** The catalyst preparation process



### II.2.3 Products:

Support	Zeolite type Y			
Metal Precursors	Cobalt(II)-Nitrathexahydrate	291.03g/mol	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	
	Ammonium molybdate Tetrahydrate	1234.86g/mol	$\text{H}_{24}\text{M}_7\text{N}_6\text{O}_{24}\text{H}_2\text{O}$	

**Table .II.1** Composition and semi-developed structure of a catalyst based on zeolite, cobalt and Ammonium molybdate

## II.2.4 Preparation steps:



**Figure.II.1**The mixture should be stirred at 30°C for 60 minutes



**Figure.II.2** filtered with filter paper



**Figure .II.3** drying in the oven 120°C for 24 hours.



**Figure .II.4**The dried mass finally has to be calcined at 450°C for 2 hours precededstages of 1 hour at 150°C, 250°C and 350°C.

**Table.II 2.** Catalyst of Co-Mo/Zeolite Y prepared by ion exchange method

Run	Cobalt(gram)	Molybdenum(gram)	Zeolite Y(gram)	Catalyst Name
1	1.2	7	20	MO7 CO1.2 ZY
2	1.2	6	20	MO6 CO1.2 ZY
3	1.2	5	20	MO5 CO1.2 ZY
4	0.8	7	20	MO7 CO0.8 ZY
5	1	7	20	MO7 CO1 ZY

### **II.3 Role of drying in the preparation of catalyst**

The drying process that follows impregnation typically occurs in a temperature range of 50 to 250°C, which facilitates evaporation of the liquid solvent. During this process, the liquid solution is transported by capillary flow and diffusion towards the outer surface of the support, while the starting material may undergo redistribution via adsorption/desorption phenomena.

Drying consists of three distinct phases: a preheating period, a constant rate period, and a falling rate period. In the pre-heating period, the drying medium heats the support, causing the rate of evaporation and drying of the liquid to increase as the temperature rises. Then, during the constant rate period, steam is evaporated from the surface of the support through capillary action[26].

Drying is a critical step in catalyst preparation, in which catalysts are dried in gel or suspension form containing solvents and water to obtain a ready-to-use solid catalyst. The drying process is essential in increasing the surface area of the catalyst, which leads to improved reaction and efficiency due to the availability of more active sites for chemical reactions[27].

## **II.4 Role of calcination in the preparation of catalysts**

Calcination is an important step in the preparation of catalysts, in particular supported catalysts. It involves heating the starting material to high temperatures in a controlled environment, usually in a furnace or reactor.

Calcination is performed after the catalyst preparation step, which may include steps such as dispersing the catalytic metals on a solid support.

The main role of calcination is to cause physical and chemical changes in the starting material, which leads to the formation of an active and stable catalyst. Here are some important effects of calcination in the preparation of catalysts:

**Removal of impurities:** Calcination burns off and volatilizes unwanted impurities present in the starting material. This may include organic residues, stabilizers or inorganic salts. Removal of these impurities is essential to obtain a pure and reactive catalyst.

**Activation of the support:** In the case of supported catalysts, calcination activates the solid support by modifying its crystalline structure, increasing its specific surface and promoting the formation of active sites. This activation of the support creates a more reactive surface and promotes the interaction between the support and the catalytic species[28]

## II.5.measuring acidity

The acidity of zeolites was analyzed using the gravimetric method for pyridine adsorption. Glass plate were utilized for this purpose. Each catalyst sample weighing 0.5 g was placed in a glass plate. The glass plate, containing the catalyst, were then placed in a desiccator containing 50 mL of pyridine for a duration of 24 hours. After the 24-hour period, the catalyst with adsorbed pyridine was weighed, and its acidity was determined using the following equation.

$$\text{Acidity of catalyst} \left( \frac{\text{mmol}}{\text{g}} \right) = \frac{\text{Pyridine weight (g)}}{\text{MW of pyridine} \left( \frac{\text{g}}{\text{mol}} \right) \times \text{catalyst weight (g)}} \times \frac{1000 \text{ mmol}}{\text{mol}}$$



**Figure.II.5** Acidity analysis of zeolites using the gravimetric method for pyridine adsorption



## II.6.The BTX II Benchtop X-ray Diffraction/X-ray Fluorescence

The BTX II Benchtop X-ray Diffraction/X-ray Fluorescence is, simply put, the first combined XRD/XRF instrument designed with ease of use in mind. From educational settings, to the rigors of a QC application, BTX II is well suited. Based on the filled proven reliable design of TERRA, our field portable XRD/XRF instrument, BTX II features the same level of performance, but without the aspects of a portable instrument. The technology used in the portable rock and mineral analyzer received a prestigious R&D 100 award and was chosen to fly on the Mars Science Laboratory Rover scheduled for launch in 2011. Check out the NASA site for more.

The BTX II is a compact combination XRF/XRD system designed for powder analysis. Now XRD work can really be done in an easy to use, small footprint, low-cost configuration. With the BTX II patented sample handling system, not only is sample preparation time minimized, but accuracy in peak identification previously only available using large and expensive laboratory-based systems can now be achieved.



**Figure.II.6:** BTX™ III Benchtop XRD/XRF Analyzer

## **CHAPITRE III: RESULTS AND DISCUSSIONS**

### III.1. Acidity in zeolites

The zeolites' pore sizes line up with those of the molecules that have been adsorbed, is demonstrated by mesoscale zeolites. Because of the confinement, some orbitals become more energetic, activating the base molecules there. Both the local environment and the size of the cavity have an impact on the site's acidity. Stronger Acid sites are present in mesoscale zeolites with pores, and these sites are correlated with the amount of hydrocarbons found in the oil fractions[29]

Since these reactions include bond breaking and the creation of carbohydrates, acidity is crucial for the catalytic processes in the zeolites employed in refining. Although measures of supraacid behavior have been used to argue the acidity of zeolites, catalytic cracking occurs at higher temperatures and calls for stronger acid sites[30].

**Table.III.1.**Effect of Co and Mo on zeolite Acidity

Run	Catalyst Name	Acidity
1	MO6 CO1.2 ZY	0.457 g/mol
2	MO5 CO1.2 ZY	0.455 g/mol
3	MO7 CO0.8 ZY	0.869 g/mol
4	MO7 CO1 ZY	1.137 g/mol
5	MO7 CO1.2 ZY	0.498 g/mol
6	fresh Y Zeolite	0,505 g/mol

The results obtained showed that different metal concentration loading increases catalyst acidity, that observed with MO7 CO0.8 ZY for 0.869 g/mol and MO7 CO1 ZY for 1.137 g/mol compared with fresh zeolite it found 0,505 g/mol , that

demonstrating a rise in the number of Brønsted and Lewis acid sites in the zeolite. Therefore the activity of the metal impregnated catalyst increases.

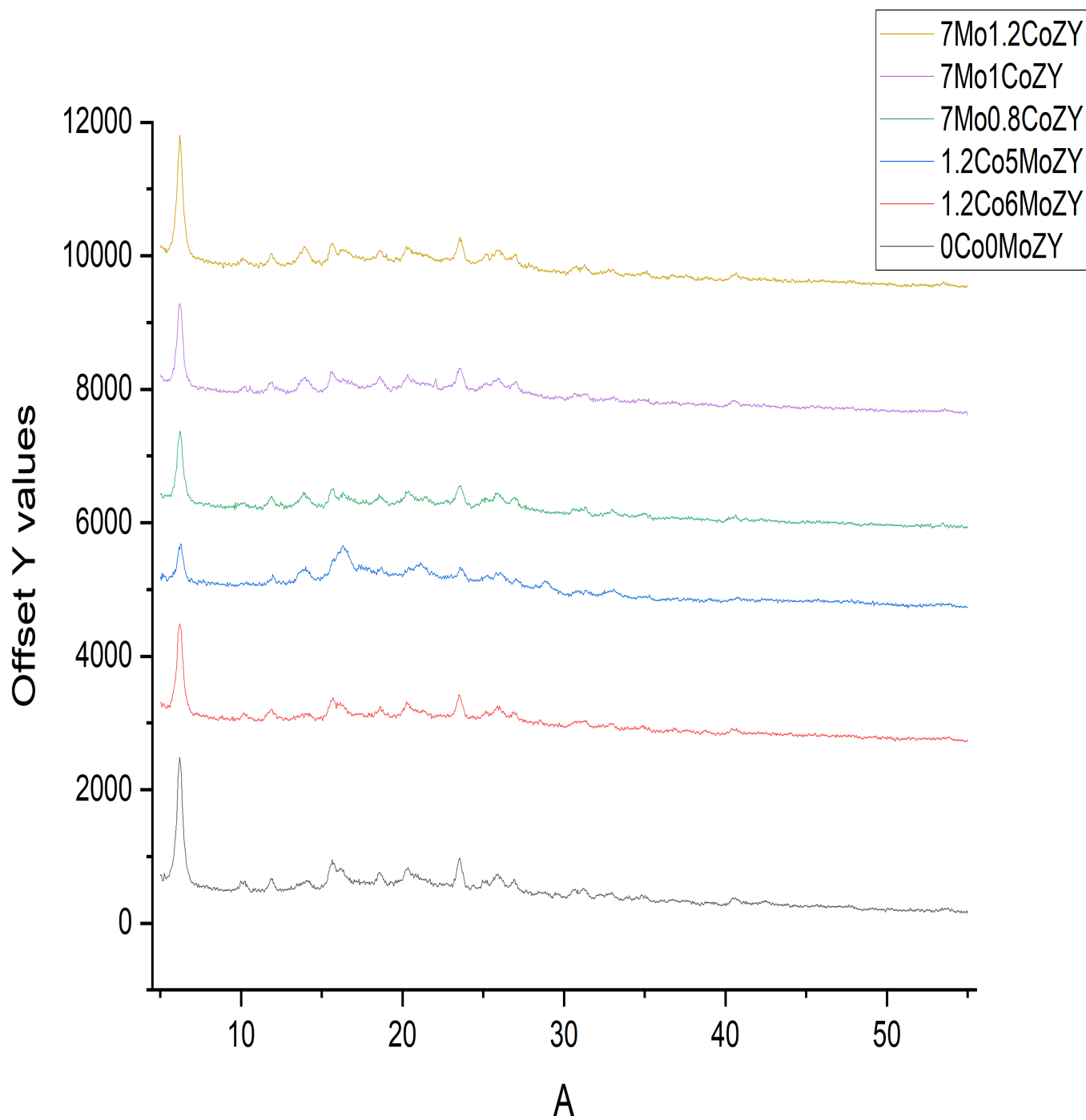
### **III.2 Stability of Crystallinity and Metal Composition**

XRD (X-ray diffraction) analysis was performed qualitatively and quantitatively to evaluate the structure and crystallinity of the zeolite. The purpose of this analysis was to ensure that the zeolite structure remains intact and that its composition remains constant throughout the catalyst preparation process. The crystallization stability of zeolite was determined by comparing the XRD results before and after the adhesion process.

The obtained Figure (1) clearly indicates that the stability of the zeolite structure has not changed. This observation is supported by the absence of any significant differences between pre-commitment and post-commitment XRD patterns. The diffraction data, presented in Figure. (1), show the XRD patterns of the different formulations of the Co-Mo/Y zeolite catalyst.

Upon closer examination of Figure (1), it is evident that the diffraction patterns of all samples are relatively similar to those of the Y-zeolite. This indicates that the catalyst preparation steps involved in the creation of the Co-Mo/Y-zeolite catalyst did not significantly alter the overall Y-zeolite structure. However, there is a discrepancy in the intensities of the Co and Mo peaks, which can be attributed to the incorporation of Co and Mo species into the zeolite pores.

These observations indicate that the structural integrity of the zeolite remains unaffected by the catalyst preparation process, ensuring that the desired properties of the zeolite and subsequent catalyst are maintained. Analysis of reflection patterns provides valuable insights into changes in peak intensities, reflecting the successful incorporation of Co and Mo into the zeolite framework while preserving its overall structure.



**Figure.III.1:** XRD Diffractogram of all catalyst samples obtained from impregnation method

### III.3 Catalyst characterization by X-Ray Diffraction (XRD)

$$\text{X R D Crystallinity} = \frac{\text{Sum of peak intensities of sample}}{\text{Sum of peak intensities of reference}} \times 100\%$$

**Table.III.2.**Effect of Co and Mo on zeolite crystallinity

Run	Catalyst Name	% Crystallinity
1	MO6 CO1.2 ZY	77.81348
2	MO5 CO1.2 ZY	77.4608
3	MO7 CO0.8 ZY	55.75017
4	MO7 CO1 ZY	83.10731
5	MO7 CO1.2 ZY	99.6413

The table presents the effect of cobalt loading on zeolite Y with respect to catalyst crystallinity. The table shows that increasing the amount of cobalt in the Y zeolite, while maintaining the same amount of 7 g Mo, results in a higher crystallization rate of the catalyst. Cobalt migrates within the pores of the zeolite, promoting crystallization of the catalyst.

In addition, when more Mo was added to the catalyst under the same constant cobalt amount of 1.2 g. a significant improvement in the crystallinity ratio could be observed. This improvement is likely due to the presence of many Mo metals adhering to the surface of the catalyst, thus promoting the formation of crystal structures and accelerating the crystallization rate.

## **General conclusion**

To evaluate and understand the properties of the catalysts, various characterization techniques have been used, including X-ray diffraction (XRD) and gravimetric pH measurements. XRD spectra were used to analyze the crystal structure of the catalysts. Interestingly, it was observed that the addition of Co and Mo metals did not significantly affect the overall structure of the catalysts. However, the presence of these metals did indeed affect the crystallinity ratio, indicating some influence on the microstructure of the catalyst.

Furthermore, this indicates that the impregnation method resulted in the formation of a Co-Mo/Zeolite Y catalyst with more defined crystal structures.

In addition to the structural aspects, the acidity of the catalysts was also investigated. The introduction of Co and Mo metals into the catalysts increased their acidity. This increased acidity can play an important role in enhancing the catalytic activity of Co-Mo/Zeolite Y catalysts, especially in cracking reaction.



## REFERENCES

- [1] B. Xie *et al.*, “Emerging material engineering strategies for amplifying photothermal heterogeneous CO<sub>2</sub> catalysis,” *Journal of Energy Chemistry*, vol. 59, pp. 108–125, Aug. 2021, doi: 10.1016/J.JECHEM.2020.11.005.
- [2] S. Mostafa Hosseini Asl, A. Ghadi, M. Sharifzadeh Baei, H. Javadian, M. Maghsudi, and H. Kazemian, “Porous catalysts fabricated from coal fly ash as cost-effective alternatives for industrial applications: A review,” *Fuel*, vol. 217, pp. 320–342, Apr. 2018, doi: 10.1016/J.FUEL.2017.12.111.
- [3] W. Lee, T. Lee, H. G. Jang, S. J. Cho, J. Choi, and K. S. Ha, “Effects of hierarchical zeolites on aromatization of acetylene,” *Catal Today*, vol. 303, pp. 177–184, Apr. 2018, doi: 10.1016/j.cattod.2017.09.014.
- [4] A. Corma and H. García, “Lewis acids: From conventional homogeneous to green homogeneous and heterogeneous catalysis,” *Chem Rev*, vol. 103, no. 11, pp. 4307–4365, Nov. 2003, doi: 10.1021/cr030680z.
- [5] Ruren Xu .Jihong Yu . Wenqin Pang .Jiesheng Chen. Qisheng Huo, “Chemistry of Zeolites and Related Porous Materials: Synthesis and Structure,” p. 616, May 2009.
- [6] C. S. Cundy and P. A. Cox, “The hydrothermal synthesis of zeolites: History and development from the earliest days to the present time,” *Chem Rev*, vol. 103, no. 3, pp. 663–701, Mar. 2003, doi: 10.1021/cr020060i.
- [7] Donald\_W.\_Breck, *Zeolite molecular sieves structure, chemistry*. R.E.\_Krieger, 1984.
- [8] C. G. Flores and A. Khodakov, “Thesis for obtaining a title of Doctor of Chemical Engineering of Federal University of Rio Grande do Sul a title of Doctor of Université de Lille Specialty: Organic, Mineral and Industrial Chemistry Molecules and Condensed Matter SYNTHESIS AND CATALYTIC PERFORMANCE OF METAL-ZEOLITE COMPOSITE CATALYSTS.”
- [9] E. M. F. J. C. J. H. van B. P.A. Jacobs, “Introduction to Zeolite Science and Practice,” Jun. 2001.
- [10] Jacob A. Moulijn Michiel Makkee Annelies E. van Diepen, “Chemical Process Technology,” p. 576, Mar. 2013.
- [11] J. Weitkamp, “Catalytic Hydrocracking-Mechanisms and Versatility of the Process,” *ChemCatChem*, vol. 4, no. 3, pp. 292–306, Mar. 2012, doi: 10.1002/cctc.201100315.
- [12] “chapter-11-catalytic-hydrogenation-and-dehydrogenation-1995”.
- [13] I. Fechete, Y. Wang, and J. C. Védrine, “The past, present and future of heterogeneous catalysis,” *Catal Today*, vol. 189, no. 1, pp. 2–27, Jul. 2012, doi: 10.1016/J.CATTOD.2012.04.003.
- [14] Bezzi.Nacer /Fatiha Barka, *Surfaces et catalyse :cours et exercices corrigés*. paris, 2022.
- [15] A. Ait Khouya, M. RITLENG Vincent, M. GIAMBASTIANI Giuliano, and M. PHAM HUU Cuong, “UNIVERSITÉ DE STRASBOURG ÉCOLE DOCTORALE DES

SCIENCES CHIMIQUES-ED222 Laboratoire d'Innovation Moléculaire et Applications-UMR CNRS 7042 THÈSE présentée par : Mousses de polyuréthane à cellules ouvertes : supports structurés pour catalyseurs hétérogènes à sites uniques et multiples THÈSE dirigée par : RAPPORTEURS : AUTRES MEMBRES DU JURY.”

- [16] A. Malfliet *et al.*, “Degradation mechanisms and use of refractory linings in copper production processes: A critical review,” *J Eur Ceram Soc*, vol. 34, no. 3, pp. 849–876, Mar. 2014, doi: 10.1016/J.JEURCERAMSOC.2013.10.005.
- [17] Société royale des sciences de Liège, “Mémoires de la Société royale des sciences de Liège,” pp. 500–554, Mar. 1967.
- [18] D. Levy and M. Zayat, “Part One Sol-Gel Chemistry and Methods.”
- [19] É. Doctorale Louis Pasteur *et al.*, “UNIVERSITÉ DE FRANCHE-COMTÉ THÈSE A. BENLHACHEMI Professeur,” 2013.
- [20] K. Janssens *et al.*, “Recent trends in quantitative aspects of microscopic X-ray fluorescence analysis,” *TrAC Trends in Analytical Chemistry*, vol. 29, no. 6, pp. 464–478, Jun. 2010, doi: 10.1016/J.TRAC.2010.03.003.
- [21] É. Doctorale Louis Pasteur *et al.*, “UNIVERSITÉ DE FRANCHE-COMTÉ THÈSE A. BENLHACHEMI Professeur,” 2013.
- [22] M. Naderi, “Surface Area: Brunauer-Emmett-Teller (BET),” in *Progress in Filtration and Separation*, Elsevier Ltd, 2015, pp. 585–608. doi: 10.1016/B978-0-12-384746-1.00014-8.
- [23] C. Sorgi and V. De Gennaro, “ESEM analysis of chalk microstructure submitted to hydromechanical loading,” *Comptes Rendus - Geoscience*, vol. 339, no. 7, pp. 468–481, 2007, doi: 10.1016/j.crte.2007.06.003.
- [24] F. Z. Fang, X. D. Zhang, W. Gao, Y. B. Guo, G. Byrne, and H. N. Hansen, “Nanomanufacturing—Perspective and applications,” *CIRP Annals*, vol. 66, no. 2, pp. 683–705, Jan. 2017, doi: 10.1016/J.CIRP.2017.05.004.
- [25] C. R. Girish, “Various Impregnation Methods Used for the Surface Modification of the Adsorbent: A Review,” 2018. [Online]. Available: [www.sciencepubco.com/index.php/IJET](http://www.sciencepubco.com/index.php/IJET)
- [26] J. R. (John R. Regalbuto, *Handbook of catalyst preparation*. Taylor & Francis, 2007.
- [27] M. Bellardita, A. Di Paola, S. Yurdakal, and L. Palmisano, “Preparation of Catalysts and Photocatalysts Used for Similar Processes,” *Heterogeneous Photocatalysis: Relationships with Heterogeneous Catalysis and Perspectives*, pp. 25–56, Jan. 2019, doi: 10.1016/B978-0-444-64015-4.00002-X.
- [28] A. A. Mirzaei, M. Faizi, and R. Habibpour, “Effect of preparation conditions on the catalytic performance of cobalt manganese oxide catalysts for conversion of synthesis gas to light olefins,” *Appl Catal A Gen*, vol. 306, pp. 98–107, Jun. 2006, doi: 10.1016/J.APCATA.2006.03.036.
- [29] E. G. Derouane *et al.*, “The acidity of zeolites: Concepts, measurements and relation to catalysis: A review on experimental and theoretical methods for the study of zeolite

acidity,” *Catal Rev Sci Eng*, vol. 55, no. 4, pp. 454–515, Sep. 2013, doi:  
10.1080/01614940.2013.822266.

- [30] A. Primo and H. Garcia, “Zeolites as catalysts in oil refining,” *Chemical Society Reviews*, vol. 43, no. 22. Royal Society of Chemistry, pp. 7548–7561, Nov. 21, 2014. doi:  
10.1039/c3cs60394f.