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Thème

Etude de l'activité d'un catalyseur hétérogène pour la réaction de synthèse des Dihydropyrimidinones.

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Dedications

this work is dedicated to

every person who accompanied me through this journey, to those who believed in me when i didn't believe in myself and my capacities.

my past and future self, this is your achievement.

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List of Abbreviations

Symbol	Description
al	Alginate
DHPM	Dihydropyrimidinone
Gul A	Acid guluronic
IR	Infrared
Man A	Mannuronic acid
MCR	Multicomponent reactoin
Mt	Montmorillonite
Mt-al	Montmorillonite and alginate beads
Mt-al(0,5M)	Montmorillonite and alginate beads treates with 0,5M of sulfuric acid
Mt-al(0,5M)	Montmorillonite and alginate beads treates with 1M of sulfuric acid
Mt-2m	Montmorillonite treated in an 2M of sulfuric acid
Mt-3M	Montmorillonite treated in an 3M of sulfuric acid
S_p	Specific surface
TLC	Thin Layer Chromatography
XRD	X-Ray Diffraction

GENERAL INTRODUCTION

Over the past few decades, organic chemistry has focused on the synthesis of biologically active molecules involved in various medical treatments. Among synthetic processes, multi-component reactions (MCR) are of particular interest because of their economic and ecological advantages.

Among the widely exploited multicomponent reactions, that of Biginelli which produces dihy-dropirimidinones (DHPM) from ethyl acetoacetate, an aromatic aldehyde that is benzaldehyde and urea in a single step, including the presence of a solid catalyst having the advantages of heterogeneous catalysis with adequate structural and economic characteristics.

The search for new materials in the field of applied catalysis is directed towards the preparation of high-performance solid catalysts which must meet certain criteria: long-term chemical and mechanical stability, high catalytic activity, ease of implementation, and a large specific surface area.

The present work aims to test the catalytic activity of montmorillonite treated with different concentrations of sulfuric acid for the Biginelli reaction. It follows the work started by Belmer-abet and Hanieche [1] who studied the effect of the temperature of the treatment solution on the structural and catalytic characteristics of montmorillonite, the concentration of the treatment sulfuric acid solution being the subject of their work was 1M.

In our work we will study the effect of 2M and 3M treatment concentrations as well as the montmorillonite formulation giving the best performance in the form of an alginate-montmorillonite composite to facilitate the separation of the catalyst.

Activated montmorillonite was characterized by X-Ray Diffraction (XRD) and BET, the reaction was followed by Thin Layer Chromatography (TLC) and the product of the DHPM reaction was analyzed by (IR) and by measuring its melting temperature.

This manuscript is divided into three main chapters:

The first chapter gives a theoretical idea on the subject treated evoking catalysis, its mech-anism and advantages, as well as clay generally and montmorillonite specifically, its structure and properties. We close this chapter with a look on multicomponent reaction such as Biginelli reaction, mentioning alginate the matrix of composite materials of catalyst beads.

The second chapter, presents the preparation methods of the catalysts clay, the operating modes of the Biginelli reaction, and the methods of characterization of both montmorillonite and DHPMs.

The third and final chapter includes the results and their analysis.

The work is closed with a general conclusion

Chapter 1

THEORETICAL PORTION

1.1   Catalysis

1.1.1   Definition

In industrial facilities, engineers prefer procedures that optimize yields and can be economically beneficial, along the same way, the field of chemical reaction engineering and through the introduction of the principle of catalysis tends to save time and resources while protecting the environment.

In the past, catalytic reactions were already used but without much insight of the workings of its principal.

The concept of catalysis was introduced in 1836 by Berzelius, who assumed that catalysts influence the affinity of chemical substances involved in decomposition and transformation reactions [2].

In 1895, Ostwald put on a definition that we still go by until today, stating that a catalyst accelerates a chemical reaction without affecting the position of the equilibrium [2].

Therefore, catalysis is the interactions of a substance called catalyst, considered as a chemical composition capable of influencing the evolution of a thermodynamically possible transformation, replacing a complicated step in a non-catalyzed reaction with a succession of simpler steps leading to a decrease in the global activation energy of the catalyzed reaction, the figure 1.1 represents the effect of catalysts on the activation energy. Without being consumed at the end of the reaction [3].
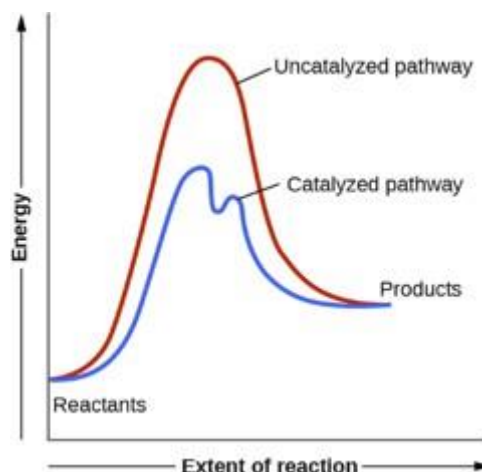
FIGURE 1.1: Catalysis effect on the activation energy [4]

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1.1.2   Classification of catalysts

Catalysts are classified according to several criteria:

- Structure.

- composition.

- Area of application.

- State of aggregation[2].

Based on the state of aggregation we can name:

1.1.2.1   Homogeneous catalysts

The catalytic reaction takes place in the same phase, which means that the reactants, the products as well as the catalyst are in the same phase.

1.1.2.2   Heterogeneous catalysts

The reaction combines several phases usually the catalyst is a solid and the reactants are in a gas or liquid phase.

1.1.2.3   Enzymatic catalysts

They are protein molecules of colloidal size, they are known for having a notable activities and selectivity.

1.1.3   Advantages of heterogeneous catalysis

- The catalyst is easily separates of the reactional environment

- The catalyst is thermally stable.

- The use of solvent is optional.

- The catalyst is easy to separate, recycle and regenerate [4]

1.1.4 Description of the catalytic cycle

The ensemble of both chemical and physical phenomenons contribute to the making of a catalytic cycle. The reaction takes place on the interface solid-liquid leading to a five steps catalytic reaction:

1. Diffusion of the reactants through the boundary layer to the catalyst surface.

2. Diffusion of the reactants into the pores (pore diffusion).

3. Adsorption of the reactants on the inner surface of the pores.

4. Chemical reaction on the catalyst surface.

5. Desorption of the products from the catalyst surface.

6. Diffusion of the products out of the pores.

7. Diffusion of the products away from the catalyst through the boundary layer and into the gas phase [5]

The figure 1.2 demonstrates the operational mode of a heterogeneous catalyst:
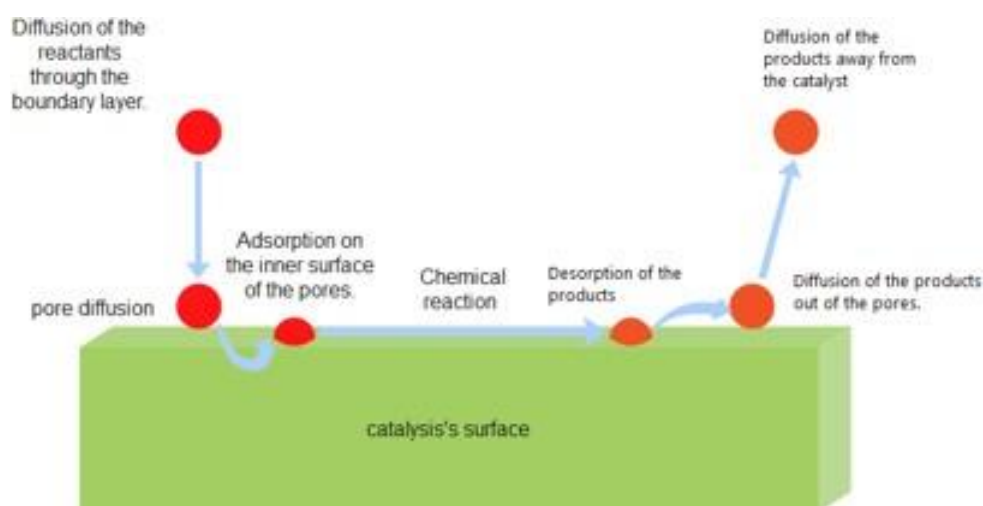
FIGURE 1.2: Catalytic cycle of a heterogeneous catalyst

1.1.5 Property of the catalysts

A catalyst is suitable for an industrial process if it has the following properties:

1.1.5.1 Activity

Activity measures the speed of one or more reactions proceed in the presence of the catalyst. Activity can be defined in terms of kinetics. There are three possibilities for expressing catalyst activity:

- The reaction rate r.

- rate constant k.

- Activation energy Ea [2].

1.1.5.2 Selectivity

The selectivity of a reaction is the fraction of the starting material that is converted to the desired product P giving information about the course of the desired reaction also as the sequential and parallel reactions [2]. The figure 1.3 demonstrates the difference between parallel and sequential reactions.
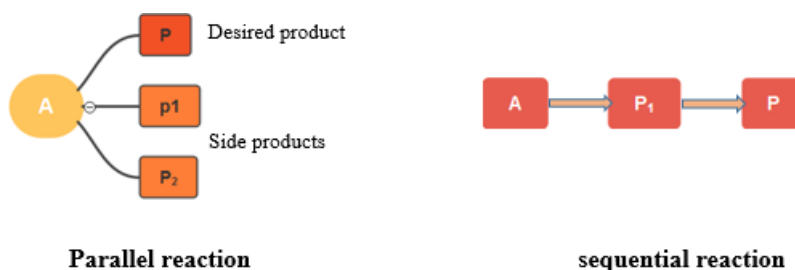
FIGURE 1.3: Parallel and sequential reactions

A same catalyst can support a targeted reaction, meaning completely different products can be obtained from a given starting material by using different catalyst systems [5].

1.1.5.3 Stability

Numerous factors determine the stability of a catalyst such as chemical, thermal and mechanical stability, which can be influenced by different factors including decomposition, coking and poisoning that causes a deactivation of the catalyst [2].

1.1.5.4 Catalyst regeneration

In theory, an ideal catalyst would not be consumed, but it is different on ground based practice, the catalyst undergoes chemical changes and its activity becomes lower known as

catalyst deactivation. Therefore, the catalyst must be regenerated Catalyst. Regeneration can take place batch wise or preferably continuously while the process is running [2], the figure1.4 shows the different ways to a catalyst deactivation.

The four most common causes of catalyst deactivation are:

- Poisoning by H_2S, Pb, Hg, S, P.

- Deposits blocking the active centers and change the pore structure (coking).

- Thermal processes and sintering of the catalyst cause a loss of active surface area.

- Catalyst losses by evaporation of components [6].
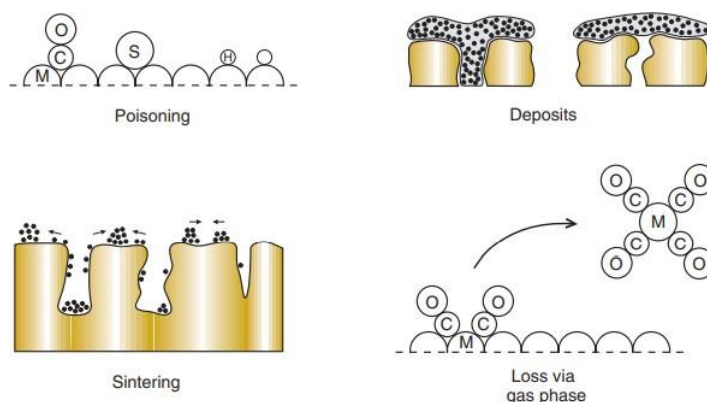
FIGURE 1.4: Deactivation mechanisms of catalysts (M = metal)[6]

1.2 Clay

1.2.1 Definition

Clay as a term comes from the old English clæg "stiff, sticky earth; clay," from Proto-Germanic. We consider clay as the most available starting materials on earth and known for the diversity of its uses in different areas as in construction and production such as: building materials, pharmaceuticals and catalysts in chemical reactions.

Clays are small-sized minerals with a dimension of 2 to 4 μm, they are aluminosilicates consisting of a stack of sheets, hence their names of phyllosilicates they countain mostly silica, aluminum, oxygen, magnesium, iron, sodium, potassium... [7]

1.2.2   Clay origin

Geologists came to the conclusion that clay comes from the degradation of volcanic rocks under the influence of atmospheric agents and by the alteration of erosion phenomena [8].

1.2.3   Clay structure

Clay has a sheet structure made out of the stacking of tetrahedral and octahedral layers, separated by a space called the interleaf space [9]. The alternation between sheets and interfoliar space form the crystals of clay, the interfoliar can hold alkaline or alkaline-earth and water molecules. These cations have the ability to leave the interfoliar space and be replaced with other alternative cations [10].

The tetrahedral layer consists of a set of tetrahedra whose center is occupied by Silicon Si^{4+} surrounded by $4O^{-2}$, the octahedral layer consists of a set of octahedra whose center is $Al3+$ and surrounded by $6O^{-2}$ or OH^-. The figures 1.5 and 1.6 [11] show the octahedral and tetrahedral structures and layer.
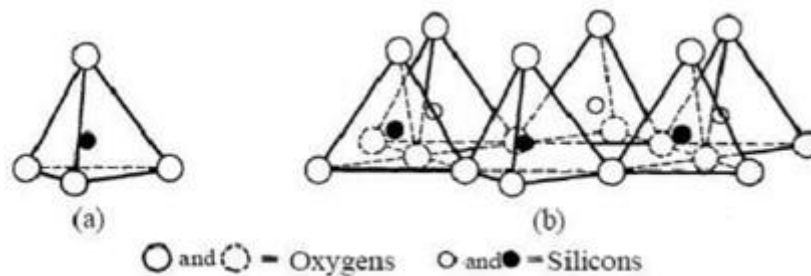
FIGURE 1.5: (a) Silica tetrahedral structure (b) a tetrahedral layer (Grim 1968)[[11]
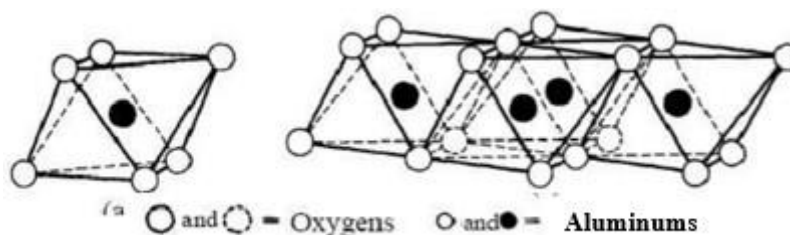
FIGURE 1.6: (a) Aluminum octahedral structure (b) an octahedral layer (Grim 1968)[11]

1.2.4   Criteria to classify clay

- Theet combination.

- Type of cations in the octahedral and tetrahedral layers.

- The charge of the sheet.

- The nature of the interleaf space.

- The nature of isomorph substitutions.

- Type of stacking[12].

1.2.5   Classification of mineral clays

1.2.5.1   Minerals type 1:1 (T-O)

They are constituted of a sheet holding an octahedral layer combined with a layer of tetrahedral, the characteristic equidistance is near 7Å with an empty interfoliar space between two sheets. Kaolinite belongs to this group[9] holding the structure shown in figure 1.7.
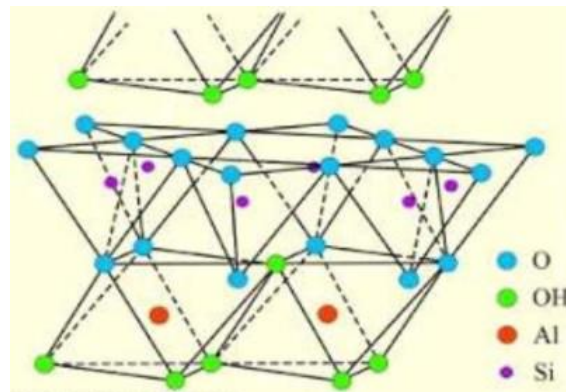
FIGURE 1.7: A representation of mineral type (T-O)[9]

1.2.5.2   Minerals type 2:1 (T-O-T)

This type of minerals has an octahedral layer sandwiched by two tetrahedral layer giving the mineral type T-O-T[9].

In this case, the unit cell contains six octahedral active sites and eight tetrahedral active sites, the characteristic distance varies between 9.4Å and 15Å depending of the interfoliar space. Smectite's structure corresponds to this group(montmorillonite,nontronitte)[8]. The T-O-T structure is represented in figure 1.8.

1.2.5.3   Minerals type 2:1:1 (T-O-T-O)

This type of minerals has an octahedral disposed between two tetrahedral, and the interfoliar space occupied by an octahedral layer having a distance of 14Å, chlorites belong to this type
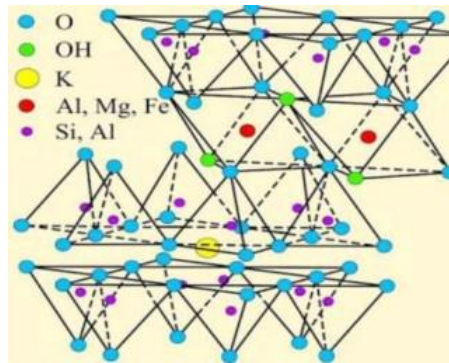
FIGURE 1.8: A representation of mineral type (T-O-T)[9]

of minerals [9], the figure 1.9 represents this type of structure.
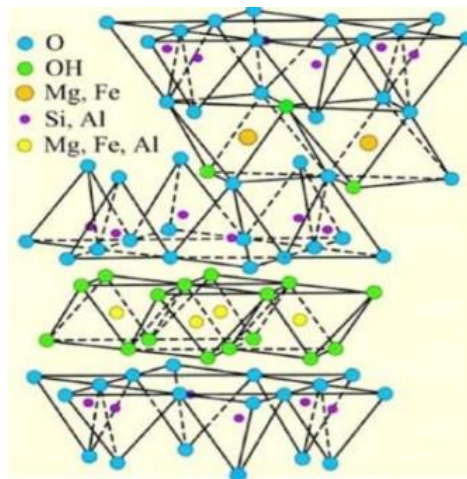
FIGURE 1.9: A representation of mineral type (T-O-T-O)[9]

1.2.5.4 Interstratified minerals

This type represents the association of multiple sheets that can alternate in different ways that can be regular and irregular[9].

1.2.6 Types pf stacking sheets

Sheets can have different types of primary particle stacking as presented in the figure 1.10.

1.2.6.1 Ordered stacking

The sheet has a perfect overlay where the interfoliar space is regular and stable [13].
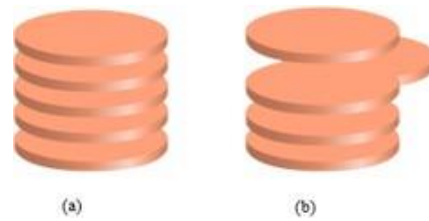
FIGURE 1.10: Type of stacking structure: (a) ordered stacking, (b) semi-ordered stacking

1.2.6.2 Semi-ordered stacking

Caused by random translations of the sheets that we call clutter. A shifted overlay of sheets caused by the translations and rotation giving a turbostatic clutter[14].

1.3 Montmorillonite

1.3.1 Definition

Montmorillonite is a clay also known by its commercialized name bentonite, that's considered a powder rich in minerals and montmorillonite as a main component.

We classify montmorillonite as a phyllosilicate type 2:1 containing essentially various elements of silica, aluminum under a base formula of: $4SiO_4, Al_2O_3, 2H_2O$ [14].

1.3.2 Structure of montmorillonite

Generally, montmorillonite has a crystal like structure, classified as a phyllosilicate of 2:1 structure having an octahedral structure sandwiched between two sheet of tetrahedral, and an interleaf space occupied by cations of compensation [14], the detailed structure of montmorillonite is represented in figure 1.11.

Montmorillonite has the particularity of presenting different stages of organization according to the observation echelon. The figure 1.12 represents the different characteristic objects of the multi echelon structure [14].

1.3.2.1 The sheet

Horizontal repetition of half-cell in the directions x and y under a diskette form, with lateral micron dimensions and near nanometers thickness, and considered being relatively flexible[15].
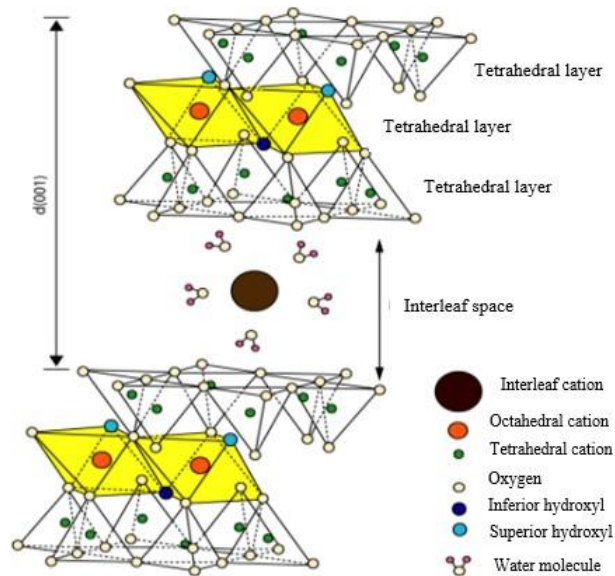
FIGURE 1.11: Representation of montmorillonite [8]
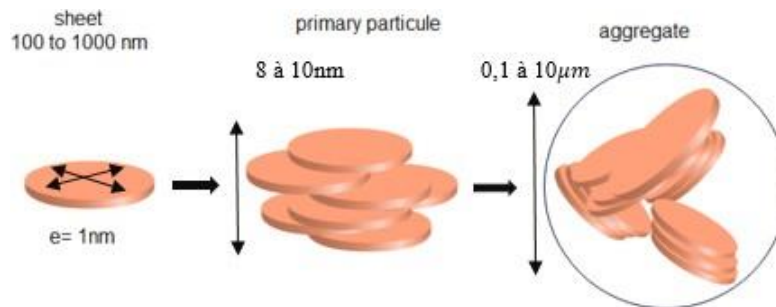
FIGURE 1.12: Multi echelon structure of montmorillonite

One of the most important proprieties is the anisotropy of the sheets. The charge of the sheet varies according to the localization of substitutions and the occupation rate of the octahedral layer[15].

Montmorillonite has 0,3 to 0,4 electron per cell. The compensatory cations at the surface of the sheets are generally ions of calcium and sodium[15].

1.3.2.2 Primary particle

The primary particle is established of five to ten stacked sheets maintained by attractive electrostatic forces between the compensatory ions and the sheets[15].

It has a thickness of eight to ten nanometers. The particle's size is constant that means when a montmorillonite swells the interleaf space increases and the particles in the sheets

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decreases[14].

The global arrangement of the sheets within a primary particle of montmorillonite is turbostatic, it presents a disturbance in the x and y directions while being perpendicular to the direction z[14].

1.3.2.3 Aggregate

It's an ensemble of primary particles oriented in all different directions. The aggregates has a stature that varies from 0,1 to 10 microns [16].

This multi echelon structure develops different levels of porosity that explain the aptitude of montmorillonite to swell[16].

The figure 1.13 help us understand the structure.

FIGURE 1.13: Association modes of montmorillonite sheets [14]

There are different ways of associations:

- Dispersion.

- Face to face aggregation.

- Edge to face aggregation.

- Edge to edge aggregation.

1.3.3 The chemical composition of montmorillonite

The ideal formula of a unit cell of montmorillonite is: $[(Si_{(8-x)}Al_x)(Al_{(4-y)}Mg_y)O_{20}.(OH)_4]^{-(x+y)}$ $CE_{(x+y)}.nH_2O[(Si_{(8-x)}Al_x)(Al_{(4-y)}Mg_y)O_{20}.(OH)_4]^{-(x+y)}$: Macro anion composing the sheet
.

- y/8: Proportion of Si substituted by Al tetrahedral.

- x/4: Proportion of Al in the octahedral layer substituted by Mg.

- CE(x+y): exchangeable cations in the interleaf space.

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Chemical formula of montmorillonite exchanged of Hammam Boughrara: - Montmorillonite Na: $(Si^{4+}3, 8368Al^{3+}0, 1632)(Al^{3+}1, 4612Fe^{3+}0, 1224Fe^{2+}0, 0025Mg^{2+}0, 4139)O_{10}.(OH)_2Na^+0, 58$ [9].

1.3.4 Property of montmorillonite

1.3.4.1 Capacity of cationic exchange CCE

A remarquable property of clay meaning its capacity of interacting with chemical ionic or molecular substances in an aqueous solution by adsorbing them into the internal surfaces[8].

CCE is determined by the calculation of the number of charges fixated on the surface of the clay, as the bond between sheets is considered weak by the presence of water molecules. The figure 1.14 represents the interleaf space[8].
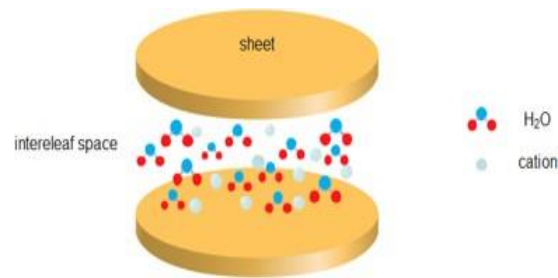
FIGURE 1.14: Representation of the interleaf space filled with hydrated cations

1.3.4.2 Swelling capacity

One of the important properties of bentonite, it determines its ability of swelling in water producing products under vacuous and gelatinous forms. The swelling of bentonite is mainly caused by the absorption of water by the molecule structure causing the distance between the sheets to grow [9], as it is represented in figure 1.15.
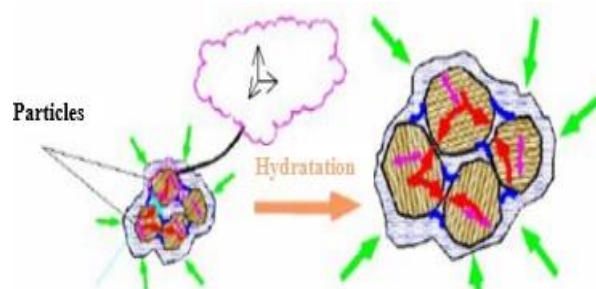
FIGURE 1.15: Swelling of clay[9]

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1.3.4.3 Colloidility

Propriety has a great importance, colloidility is directly related to the presence of negative load on the surface of every clay grain, by the disposition of a double layer of hydro soluble ions on the surface of the clay grains [10].

1.3.4.4 Specific surface

The table 1.1 classifies the specific surfaces of clay.

We can divide clay to two surfaces:

- Internal surface representing the interleaf space.

- External surface representing the space between the particles.

The augmentation of the specific surface influence the swelling capacity and causing consequentially a rise in the potential of swelling[8], table 1.1classifies the specific surfaces of clays.

Names	type	specific surface m^2/g
Kaolinite	1:1	10-20
illite	2:1	65-100
Montmorillonite	2:1	100-850
Chlorite	2:1:1	800

TABLE 1.1: Surfaces of clay [10]

1.3.5 Examples of montmorillonite uses

- Montmorillonite's adsorption capacities guarantees the clarification of soiled waters, degradation of polluting organic compounds or transform them into less harmful products [17].

- Used as a source of silica and alumina, montmorillonites form minerals basic building materials, refractories, insulation industry.

- In the pharmaceutical and medical industries, it forms the basis of dressings stomach and intestinal. These absorbent properties allow the manufacture of drugs with delayed effects. Smectites in particular are involved in the manufacture of many cosmetics [18].

- In chromatography as a stationary phase[19].

- In the chemical industry, they activate certain reactions (Alkylation of phenols, dimerization and oligomerization of alkenes, synthesis of aldehydes, and formation of esters)[20].

1.4   Composites

The idea of combining materials with complementary characteristics within a single solid called composite, with the aim of obtaining a performance better than those of each constituent [21].

The present study concerns composites made by dispersion of fillers (i.e. silica filled particles) in a soft polymer matrix, focusing on the link between structural and dynamical properties which are strongly influenced by the characteristics of the polymer matrix, the fillers and the interactions between them [21].

1.4.1   Definition of alginate

Alginate is one of the most versatile natural biopolymers. It is used in the agro-food sector and pharmaceutical industry because it has many properties: thickener, stabilizer, gelling agent, formation of biofilms [22].

1.4.2   Structure of alginate

Alginic acid is a natural, linear polymer of heterogeneous structure, consisting of two monosaccharide units: β-D-mannuronic acid and α-L-guluronic acid. He it is therefore a polyuronide. These acids are linked together by glycosidic bonds of the type β-(1-4). It is important to note that the proportion of mannuronic acid (Man A) and acid guluronic (Gul A) varies from species to species[22].

Alginic acid contains a fraction rich in ManA called block M, a GulA-rich fraction called G and a fraction or both units of uronic acids are alternately bound together, called MG or GM block[22].

The figure 1.16 is a representation of the structural characteristics of alginates:

1.4.3   Methods of gelling

There are three methods of gelling:

1.4.3.1   External gelling

This is the simplest technique. It is implemented at room temperature. The process consists of pouring a solution of alginate drop by drop into a solution containing free calcium. The
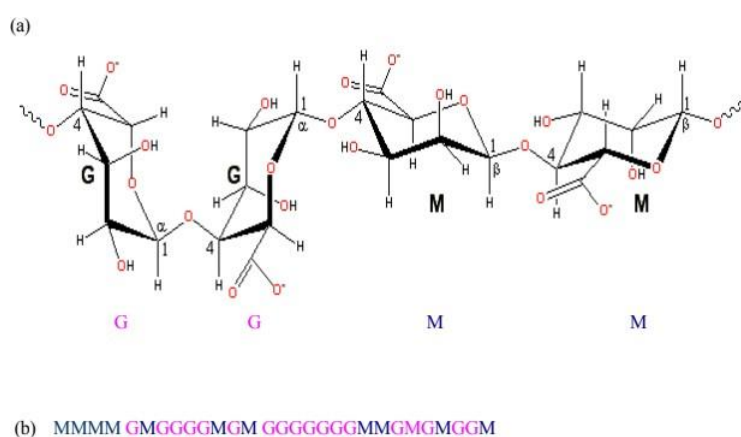
FIGURE 1.16: Structural characteristics of alginates: (a) conformity chain, (b) block distribution [22]

gelation of the alginate is immediate at the periphery of the drop. The exchanges can then occur between the inside and the outside of the droplet [23].

1.4.3.2 Internal gelling

In this technique, the calcium sulfate is present in the mass of the product and reacts with alginate following controlled kinetics. It takes place, just like for the previous method, at room temperature. To obtain a homogeneous alginate gel, it is necessary to trap the calcium middle. Once the calcium is trapped, the alginate can dissolve. Then, a calcium salt at slow dissolution gradually releases the calcium which can react with the alginate to give a freeze [24].

1.4.3.3 Gelling by cooling

All the constituents necessary for gelation (alginate, source of calcium, sequestrant) are mixed under heat. The organization of the gel takes place on cooling. Frost is not thermoreversible but it is less subject to syneresis than gels implemented cold[23].

1.4.4 Properties of alginate gels

1.4.4.1 Solubility

Alginates are soluble in the cold and thus make it easy to obtain viscous solutions. Thanks to its solubility in water, sodium alginate is the most used because it is insoluble in ethanol and organic solvents [24].

1.4.4.2 Viscosity

Essentially the viscosity measured is that of alginate solutions, it depends on the concentration of polymers and the molecular weight, the more it increases the more the solution is viscous[24].

The shape and stiffness of the macromolecule also determine the rheological behavior of the solution obtained.

1.4.4.3 Stability

A dry sodium alginate powder has a shelf life of several months if it is stored in a dry, cool and dark place. On the other hand, a dry alginic acid has a very limited stability at ordinary temperatures due to the existence of intramolecular catalytic degradations [24].

Thus, the viscosity of a solution of the same alginate can be greatly reduced in a short period due to the existence of degradation phenomena.

The stability of alginate is influenced by two important parameters:

- **influence of temperature**

  Alginate gels are thermo-irreversible. The viscosity of alginate solutions decreases with increasing temperature, but if the high temperature is not maintained for a long time, this phenomenon will be reversible. Partial depolymerization will be observed if the solutions are exposed to an excessive temperature or a more moderate temperature for a long time. The depolymerized alginates then have an almost Newtonian rheological behavior (shear stress proportional to shear rate; constant viscosity regardless of or shear)[24].

- **influence of pH**

  At very basic pH, sodium alginate forms a gel. Propylene glycol alginate is soluble and stable between pH 2 and 3, and non-soluble above pH 6.5 [24].

1.5 Multicomponent reaction

Classic chemical reaction known as sequential reactions are reactions that use several successive steps adding two reactants at a time and was proven being not practical, that's when the idea of multiple component reaction was introduced[25].

In general a multicomponent reaction is considered as a one pot reaction, where all the reactants are present in the same reactional environment interacting with one another resulting

in a one final product containing all the starting atoms[25].

The multi component reaction tend to give both simple and complexe molecules that contributes in modern organic reactions[25], as shown in figures 1.17 & 1.18 .
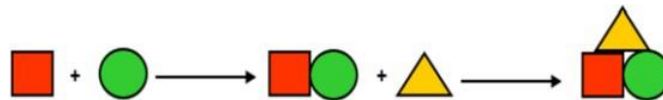
FIGURE 1.17: Classic reaction

FIGURE 1.18: Multicomponent reaction

1.5.1   Biginelli reaction

In 1891, the Biginelli reaction was developed by Pietro Biginelli who combined the work of both Behrend and Schiff that resulted in giving:

- Urea, acetoacetate of ethyl for Behrend [26].(see figure 1.19)

FIGURE 1.19: Reaction of Behrend producing DHPM [25]

- Urea, benzaldehyde for Schiff.(see figure 1.20)
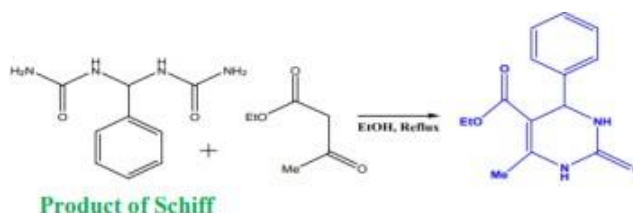
FIGURE 1.20: Reaction of Schiff producing DHPM [25]

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In 1893, Pietro Biginelli has studied the reaction of acetoacetate of ethyl and urea in the presence of benzaldehyde that resulted in the formation of DHPMS molecules, presented in figure 1.21.
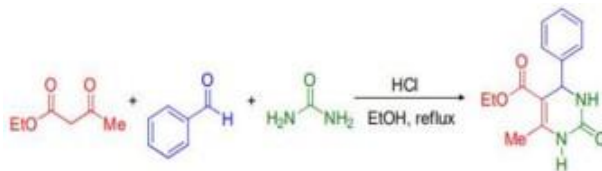
FIGURE 1.21: Reaction of Biginelli [25]

Thus, Biginelli was able to obtain DHPMS from the product of Behrend reaction and benzaldehyde. This observation was the bas of these hypothesis:

- The formation of Behrend product and Schiff component is reversible.

- The three reactants give a same product no matter the order of their combination.

- The DHPMS obtained by this reaction has a major importance in the pharmaceutical chemistry related to the diversity of its biological and pharmaceutical activity[25].

1.5.2 Methods of Biginelli reaction

1.5.2.1 Classic synthesis

The classic reaction is a simple reaction of cycloaddition of three components and in a single step by reacting benzaldehyde, acetoacetate of ethyl and urea under ethanol reflux and under the action of concentrated hydrochloric acid. The adduct of this new approach that precipitates after cooling the mixture reaction has been identified as known 3,4-dihydropyrimidin-2(1H)-one (DHPM) under the product name of Biginelli[27].

1.5.2.2 Improved synthesis

There are numerous of improves synthesis that got developed to accommodate the changes in the conditions of the reaction, we can name:

1. **Synthesis under microwave irradiation**

   Reactions under micro-radiation waves, without solvent and/or using a solid support such as clay, alumina, silica or graphite in short reaction times produce higher yields of DHPMs higher than those obtained by conventional heating.

They also offer low cost, simplicity of handling and treatment and reduction of pollution[26].

2. Use of Lewis acid

Among the variants of the Biginelli reaction the most common and the most effective remains the use of Lewis acids as catalysts.

Currently, more than 50 Lewis acids have been used successfully, among which we can mention: BF_3OEt_2, $LaCl_3$, and $FeCl_3$... [27]

3. Use of BrØnsted acids

The cyclocondensation of benzaldehyde derivatives with β-ketoesters and urea or thiourea can be efficiently catalyzed by a BrØnsted acid type $H_2SO_4 - SiO_2$. This reaction which proceeds simply by refluxing ethanol for 6 hours, a suallowingccessful one-pot synthesis[27]

4. Use of ionic liquids

During the Biginelli synthesis in the presence of ionic liquids type chloroaluminates as and Lewis acid catalysts influence the yield of DHPMs products[27].

5. Use of heteropolyacids

Among the heteropoly acids are the tungsten acids which are widely used because of their high acidity and thermal stability. Acid 12- tungstophosphoric was used as a catalyst recyclable from the Biginelli cyclocondensation reaction [27].

6. Use of solid support

The procedure followed involves heating to 80°C, an aldehyde, an ethyl acetoacetate and urea in the presence of a quantity of MoO_3/Al_2O_3 catalyst which can be recovered easily at the end of the reaction by simple filtration [27].

7. Use of polymers

The polyphosphate ester (PPE) is a promoter effective for the Biginelli reaction that leaves no metallic residues[27].

8. Use of composites

The composites are a mix of polymer matrixes and fillers containing the catalyst. The form of composites makes the separation of the product off the catalyst easier[27].

1.5.3 Reactional mechanism

The mechanism of the Biginelli reaction has been the subject of many discussions:

- **Folkers and Johnson (1933):**

  proposed a mechanism where they suggest that the first intermediate is the diamine from the condensation of the aldehyde with two molecules of urea [28].

- **Sweet and Fissekis (1973):**

  proposed another mechanism which begins with the aldol condensation of ethyl acetoacetate on the aldehyde whose intermediate reacts with urea[29].

- **Atwal (1987):**

  gave a proposal to overcome the problems related to the low yields of the Biginelli product, mainly in the case of aliphatic aldehydes and aldehydes substituted in the ortho position by carbonyl functions. This approach involves two steps: the first concerns the separate synthesis of the unsaturated carbonyl compound via Knoevenagel and the second is based on the catalyzed addition by a substituted urea[30].

- **Kappe (1997):**

  kappe He established that the key step is based on the addition of urea to the aldehyde which allows access to the formation of the intermediate ion N-acyliminium. This is followed by condensation of the intermediate with ethyl acetoacetate leading to the formation of a second intermediate. Cyclization of the resulting intermediate gives hexa hydropyrimidine, which undergoes dehydration to ultimately form the product DHPM[31].

- **Ivecea Cepanec (2007):**

  demonstrated that the Biginelli reaction passes through the intermediary. The ureidocrotonate formed by the bimolecular reaction of ethyl acetoacetate and urea[32].

The figure 1.22 shows the different mechanisms mentioned above:

1.5.4   Advantages of multicomponent reactions

We prioritize this method because of its numerous advantages, we can name in figure 1.23

- The formation of a single targeted molecule incorporating all the atoms of the Starting reactants is in accordance with the principle of economy of atoms and steps.

- MCRs are considered to be eco-compatible processes thanks to the reduction of waste and minimization of separation steps and treatments.

- The involving of a minimum of three functional groups reacting in a Well-defined order makes MCRs regio-selective reactions.
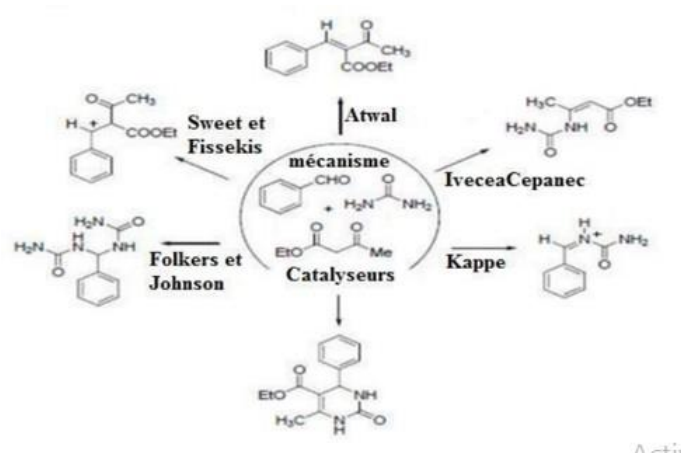
FIGURE 1.22: Mechanisms of biginelli reaction [25]
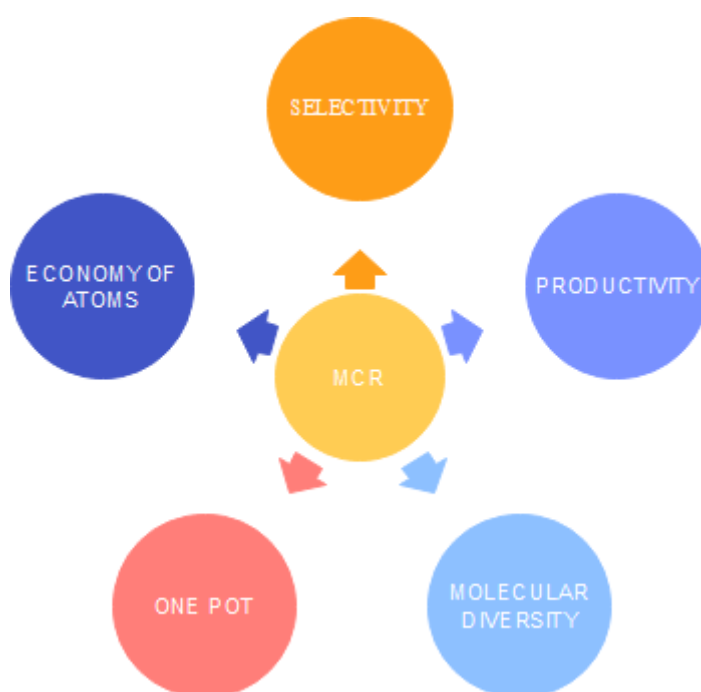
FIGURE 1.23: Advantages of MCR

- The great diversity and molecular complexity of molecules from MCR allows the creation of large molecular libraries [32].

Chapter 2

Experimental section

2.1   Introduction

In this chapter, the experimental protocol is presented starting with an acid treatment that undergoes a sodic montmorillonite, the preparation of polymer beads of alginate and composites beads of alginate/montmorillonite, as well as attacking them with sulfuric acid.

Thus, the Biginelli reaction will be highlighted by studying different parameter effects and determining the best condition based on the calculated efficiency.

2.2   The preparation of montmorillonite

2.2.1   Preparation of activated montmorillonite

The mineral used in this study is the Algerian montmorillonite coming from Hammam Boughrara in Maghnia (also known by Maghnite), produced by ENOF (National Firm Of Useful Substanced And Non-Ferrous Materials) under a specific composition: 5,37% NaO; 4,68 % MgO; 15,6% Al2O3; 62,1% SiO2; 4,82% K2O; 1,33% CaO; 0,34% TiO2; 5,76% Fe2O3.

Based on the previous studies of the activation conditions done by N. Belmerabet and M. Hanieche, the adequate temperature of activation has been set on 80℃ .

Clay is activated by a solution of sulfuric acid, which the concentration values are 2mol/l and 3mol/l, under the temperature of 80℃ and agitation of 3 hours. The proportions for this solution are: 10g of clay in 200ml of the acid sulfuric solution as represented in the figure 2.1.
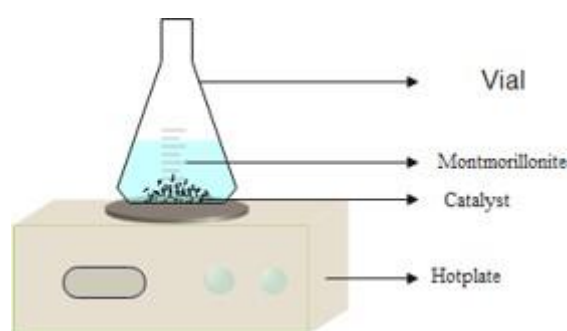
FIGURE 2.1: Montmorillonite activation by sulfuric acid

Afterwards, the mixture montmorillonite/ acid is separated by simple filtration the solid phase is washed using distilled water, then dried in a steam room under 80℃ heat for 24 hours. After that, the powder is grinded into an even finer granulation. The conservation of montmorillonite is done in a dry environment sheltered from humidity.

2.2.2   Preparation of beads

Collecting the reactional product and separating it from the catalyst is considered a difficult process, because of the fine nature of the catalyst powder.

To fix this problem, the catalyst powder is encapsulated in copolymers such as alginates. Alginates has an important feature that is forming a gel in presence of divalent cations, notably calcium ions.

This feature guarantees a combination of alginates and the catalyst by encapsulation resulting on obtaining an efficient composite materials.

2.2.2.1   Preparation of alginate beads

The alginate solution is prepared by stirring 1g of sodium alginate in 50ml of distilled water resulting in obtaining a homogeneous gel. The stirring is stopped so that the air bubbles scattered in the gel move to its surface and burst.

As for the beads, the alginate solution is introduced drop by drop in 100ml of calcium chloride solution (4%) using a syringe under a stirring motion. The method is represented in the figure 2.2.
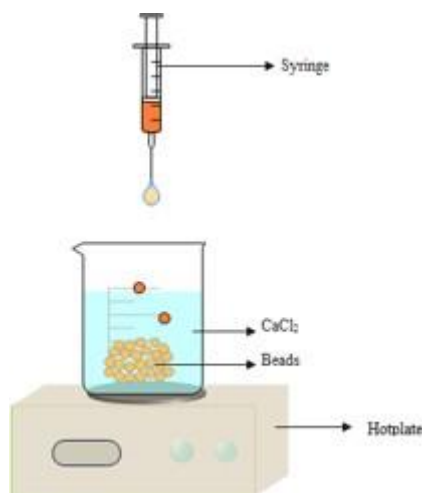
FIGURE 2.2: Formation of gel beads

The rapid reaction between alginate and divalent ions of calcium on the surface allows the formation of alginate gel beads the mixture (alginate beads and calcium chloride solution) is left to rest for 10 hours, a period that is deemed to be largely sufficient for a proper gelling.

After the 10 hours of reticulation, the beads are filtrated and washed several times using distilled water. The beads are dried in the open air.

2.2.2.2   Preparation of mixed beads alginate/montmorillonite

The preparation of mixed beads is based on the ratio 1/1, a 1g quantity of alginate is added to 50ml of water under stirring until the formation of a gelatinous solution. Then, we add 1g of montmorillonite treated with acid of 2mol/l we let stir until the obtaining of homogeneous solution. The mixture alginate/montmorillonite is introduced drop by drop using a syringe in a 100ml of calcium chloride (4%) under a normal rhythm of stirring. After a maturation time of 3 hours, the composite beads obtained are filtrated and washed.

The washing is repeated until the conductimetry of the filtrate is neutral. The beads are left in open air to dry down for 24hours we name them Mt-al. We introduce dried down beads in a 250ml solution of sulfuric acid of concentration values of 0.5mol/l and 1mol/l for 3 hours to obtain a more apparent pores on the surface to better the efficiency of the reaction the figure **2.3** shows this process. The beads are left to dry on open air, we name them Mt-al(0,5) and Mt-al(1).
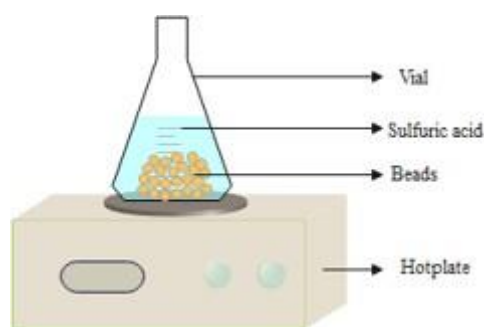
FIGURE 2.3: Activation of beads

The beads are dried in open air rather than the steam room to avoid any closure of the pore volume or the reduction of the alginate matrix pore's size.

2.3   The protocol of Biginelli reaction

In a double collar of 100 ml, we put benzaldehyde (5mmol), ethyl acetoacetate (12mmol), urea (6,25mml) and a quantity of catalyst taken based on the mass of the benzaldehyde (5% weight), the reaction mixture is stirred under reflux at the temperature of work. The assembly is shown in figure 2.4.

The assembly is shown. The progress of the reaction is monitored by Thin Layer Chromatography TLC after every 2h using an eluent consisting of a mixture of cyclohexane and ethyl acetate with a volume ratio of ¼ (1ml,of cyclohexane with 4ml of ethyl acetate) as presented   in   the   figure   2.5.

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Support

refrigerant

thermometer

support

double collar

Crystallizer

reactional product

silicone oil crystallizer

hotplate
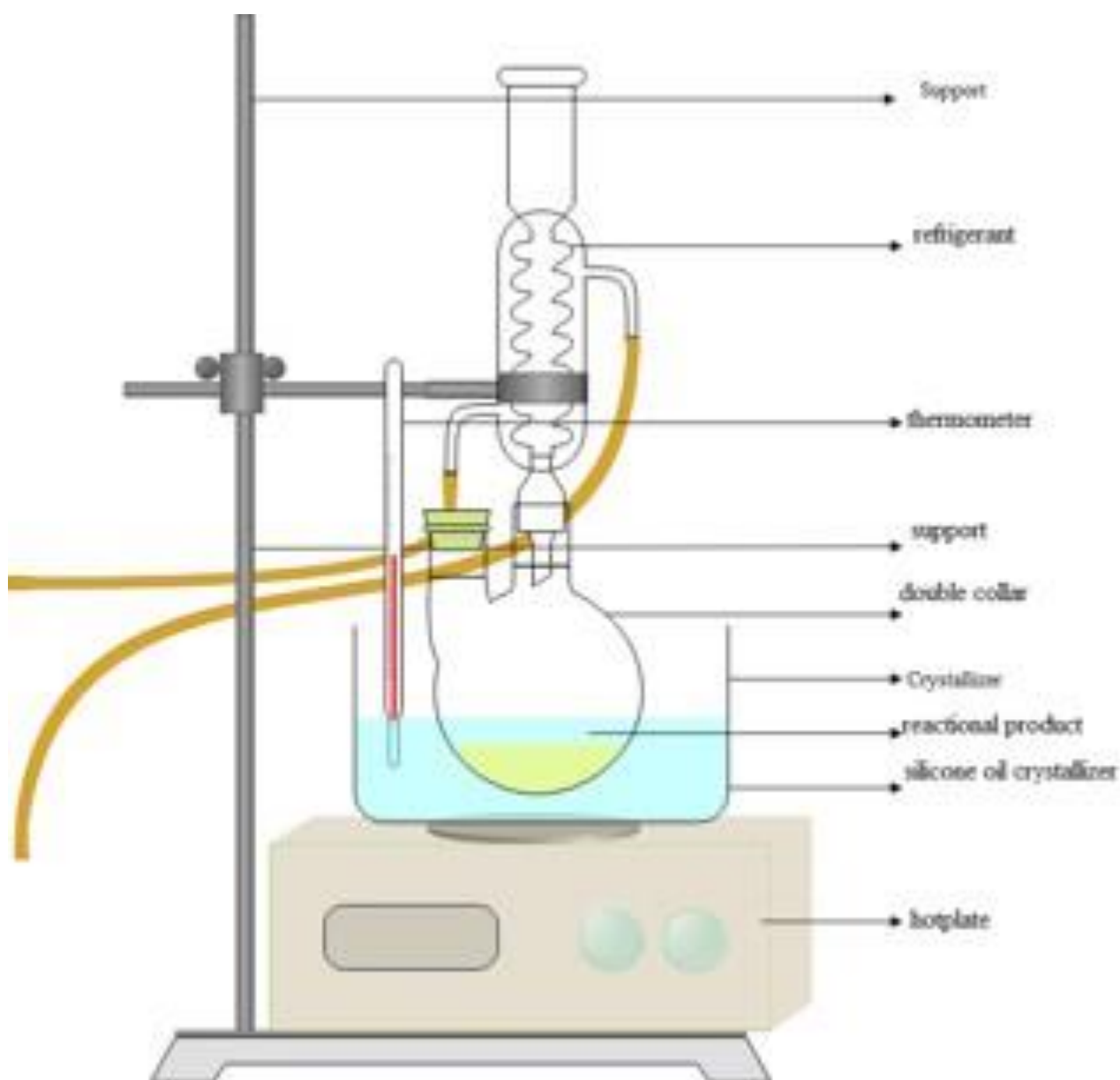
FIGURE 2.4: Assembly of biginelli reaction

To test the beads, the reaction with the better yields in weight have their powder catalyst changed by catalyst beads and put on under the same reactional path in addition to the control of the progress by the Thin Layer Chromatography TLC after every 2h, using a mixture of ethyl acetate and cyclohexane under a ¼ ration.

For the recovery of the Biginelli reaction product, the following steps were carried out:
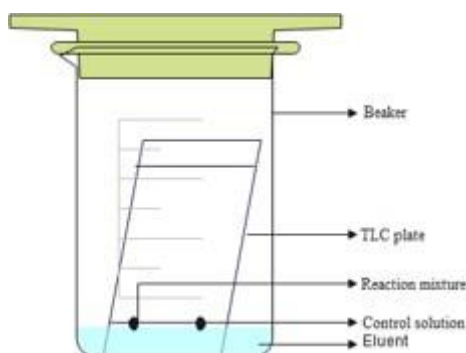
FIGURE 2.5: TLC of the reactional mixture

- The mixture is washed with methanol to recover the final product, we proceed to the filtration of the mixture.

- The product was collected by slow evaporation at room temperature.

- In order to obtain an analytically pure product, the product is recrystallized in hot ethanol.

- After the filtration presented in the figure 2.6, the product is dried for several hours then weighed, the yields were calculated using the method presented.
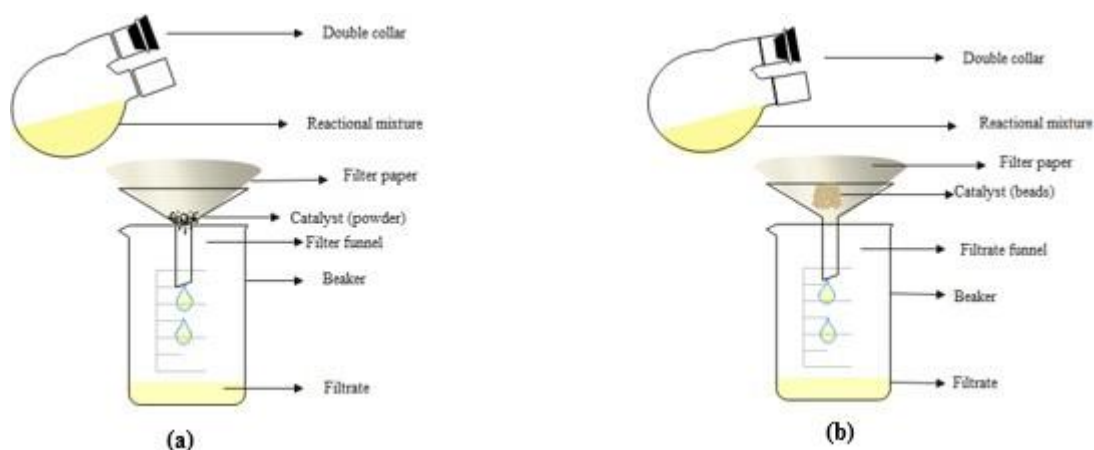
FIGURE 2.6: Filtration of DHPMS (a) powder catalyst, (b) bead catalyst

- The product obtained is identified by IR and determination of the melting point with a Fusiometer.

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2.4   Methods of characterization

2.4.1   Methods of characterization of montmorillonite beads

In order to know the different structural modifications of montmorillonite after its activation, and to confirm that the product synthesized is the product resulting from the Biginelli reaction. Different technics has been used to confirm the results of our work such as: x-ray diffraction (XRD), the measurement of the specific surface by the BET method, Infrared Spectroscopy IR, thin layer chromatography and measurement of melting points.

2.4.1.1   XRD:

X-ray diffraction is a characterization technic necessary for the identification of crystalline phases types of materials, in our case, it helps us know the structural modifications happening in the crystal lattice of the montmorillonite depending on the concentration of the activation solution by the distance d001 and an angel ranging between $5°<2\ \vartheta<80°$. The XRD spectra are realized at Boubnidar Saleh University in Constantine, Algeria.

2.4.1.2   BET:

Specific surface is one of the most important materials characteristics, it is determined by the adsorption of gas (N_2, He, CO_2) method on the surface of our sample.

Numerous parameters can be have an influence on the measured values of the specific surface for example the size, the form of the grains, the chemical composition, and the surface condition of the grain.

The specific surface is determined by the adsorption of azote under 77K, the measures are realized at Boubnidar Saleh University in Constantine, Algeria.

2.4.2   Methods of characterization of DHPMs

2.4.2.1   IR:

Infrared Spectroscopy makes it possible to detect the characteristic vibrations of the existing chemical bonds at the level of the montmorillonite, it can also confirm the results of X-ray diffraction.

IR spectroscopy made it possible to identify the different links of the chemical reaction

product (DHPMs) with 400< λ <4000cm-1. The spectra are carried out at the University of Bejaia, Algeria.

2.4.2.2 TLC

Is an analysis technic that is considered simple based on the difference in affinity of the chemical substances between a stationary phase (plate of silica gel) and a mobile phase (eluent).

The difference between the two phases helps us separate them on the plate. In our study, TLC is used to determine the necessary period to reach the end of the reaction.

Chapter 3

DISCUSSION OF THE RESULTS

3.1 Interpretation of the experimental results:

3.1.1 Montmorillonite characterization results:

3.1.1.1 XRD results:

The figure 3.1 represents XRD spectra corresponding to sodic montmorillonite and to activated montmorillonite with different concentrations of sulfuric acid
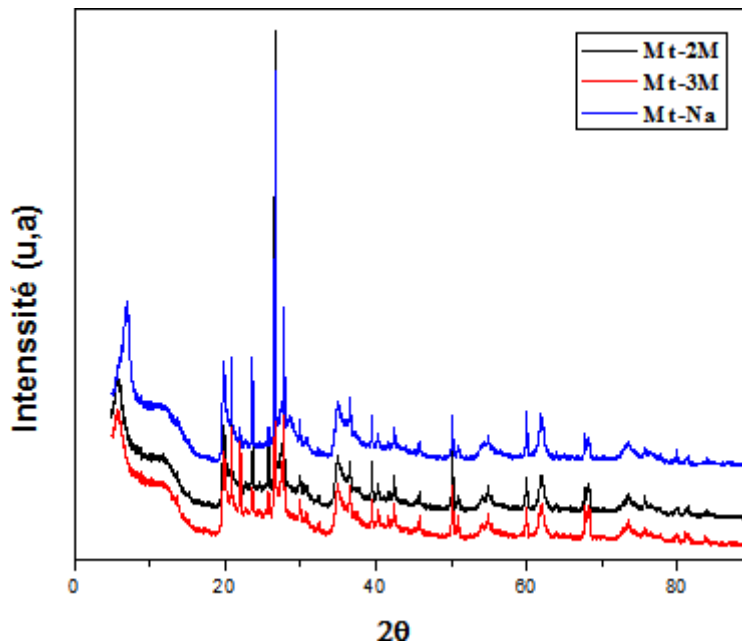
FIGURE 3.1: X-ray spectra of sodium montmorillonite and treated montmorillonite at different concentration

The characteristic rays of sodic montmorillonite are situated at $20°,21°,26°,28°,35°,50°,62°$,and $73°$[33], [32], [34].

The reflection observed at $2\vartheta= 6,84°$ is identified as the principal ray of montmorillonite corresponding to the basal spacing d001.

After the activation using the acid, the principal ray is largely moved at $2\vartheta= 5,49°$ with a lower intensity due to the effects from the acidification treatment; the cation exchange phenomenon of the compensating cations by H^+ protons of the acid solution.

The displacement of the basal space d001 to lower values of is accompanied with an augmentation of the space corresponding to 12,91Å to 16 Å.

Furthermore, the XRD spectra do not reveal any significe changes; in the structure of the studied samples, the presence of all the diffraction peaks in Mt-2M and Mt-3M strongly confirm

that the crystal structure of montmorillonite was not attacked and that the exchange process did not modify the structure of the montmorillonite layer.

3.1.1.2   BET results:

The values of the specific surfaces area measured for the samples (Mt-Na, Mt-2M, Mt-3M) are presented in the table 3.1.

Catalyst	Mt-Na	Mt-2M	Mt-3M
S_p m^2/g	145,517	374,364	742,583

TABLE 3.1: Specific surface of types montmorillonite

The values of the specific surface given by the BET method show that the acid treatment has a great influence on the textural properties of montmorillonite, and more the acid treatment concentration increases, more the value of the surface increases, this is due to the creation of pores by the acid treatment.

3.1.1.3   catalytic tests:

Montmorillonite treated with sulfuric acid at two different concentrations, 2mol/l and 3mol/l, is subsequently tested as a heterogeneous catalyst with respect to the Biginelli reaction for the synthesis of dihydropyrimidinone, the effect of different parameters on the yield of the reaction was studied, namely: mass of montmorillonite temperature, and introduction order of reagents.

Some catalytic tests were carried out by encapsulating the montmorillonite in alginate, these tests were carried out to have a better formulation which will allow easy separation of the catalyst from the reaction medium. The alginate beads were tested without the montmorillonite, then the beads in which the montmorillonite was encapsulated with a mass ratio of 1:1, and the beads containing the montmorillonite and treated with acid at two concentrations 0.5M and 1M.

To remain as much as possible within the framework of green chemistry, we have chosen to carry out all the reactions under solvent-free conditions.

1. **Effect of montmorillonite weight:** We chose 5 mass percentages for catalyst weight test (2,5%, 5%, 10%, 15%, 20% of benzaldehyde weight) to realize under 80℃ temperature for 6 hours.

   The catalysts used are montmorillonites treated with the two concentrations of sulfuric acid (Mt-2M and Mt-3M).

The results of the effect of montmorillonite weight on Biginelli reaction yield are presented on table 3.2.

Weight (Mt-2M)	2.5%	5%	10%	15%
Yield %	74%	81%	68%	61%
Weight (Mt-3M)	2.5%	5%	10%	15%
Yield %	63%	58%	50%	53%

TABLE 3.2: Yield of quantity of catalyst effect

We notice that montmorillonite Mt-2M gives better yields compared to montmorillonite Mt-3M. For montmorillonite Mt-2M, the yield increases when the mass of the catalyst increases from 2.5% to 5%, thereafter a reduction in the yield is observed with the increase in the quantity of the catalyst. For montmorillonite Mt-3M, the best yield is found with a mass of 2.5%. In both cases, the decrease in yield as a function of the increase in the mass of the catalyst is explained by the fact that more the mass increases, more a pasty appearance texture is obtained, and the reactional mixture become difficult to stir which slows down the diffusion of the reactants towards the surface of the catalyst

2. Effect of the reaction's temperature:

We change the temperature of the reaction to determine the suitable one, we chose (25℃ , 45℃ , 80℃ , and 100℃). The results of the effect of temperature on the reaction yield for Mt-2M and MT-3M are shown in Table 3.3.

Temperature (Mt-2M)	25℃	45℃	80℃	100℃
Yield %	46%	65%	81%	73%
Temperature (Mt-3m)	25℃	45℃	80℃	100℃
Yield %	23%	34%	63%	42%

TABLE 3.3: Yield of temperature effect

Based on the obtained results, it is noticed that the yield increases with the increase of the temperature, where it reaches a maximum at 80°C, then it decreases at the temperature of 100°C, this behavior, observed in the case of the two catalysts Mt-2M and Mt-3M, can be explained by the fact that the temperatures lower than 80°C are not sufficient for the diffusion and the adsorption of the reagents on the surface of the catalysts. Moreover, it was found during the course of the experiments that at low temperatures, the characteristic coloration of the reaction has not yet appeared.

The optimal temperature of 80°C is estimated as being the adequate temperature which facilitates the destruction of the bonds of the reagents and therefore their reactivity.

The decrease in the yield of the reaction under 100℃ is related to the sensitivity of the DHPM for high temperature, causing its degradation.

We notice, as in the case of the study of the mass effect o of the catalyst on the yield of the reaction in the presence of Mt-2M and Mt-3M, montmorillonite Mt-2M gives the best results, although it has a lower specific surface area, this shows that it is not the specific surface area which is responsible of the activity but rather the number of the active sites and their distribution on the surface. We can also affirm that their nature (acid of Lewis or Bronsted) may play a role. This can be confirmed by an infrared characterization of catalysts having adsorbed pyridine

3. **The order of reactant's introduction effects:** Knowing that in heterogeneous catalysis, one of the important and limiting steps of the reaction being the adsorption of the reactants on the surface of the catalyst, we have tried to see the effect of the order of introduction of the reactants into the reactional environment. Thus, we tried 7 different processes with different orders for a 2 hours duration to guarantee the action of the adsorption phenomenon.

- 1st **Process:** Stir the ethyl acetoacetate and the catalyst during 2 hours. After this time, the urea and the benzaldehyde are added.

- 2nd **Process:** Stir the benzaldehyde and the catalyst for 2 hours. After this time, urea and ethyl acetoacetate are added.

- 3rd **Process:** Stir the ethyl acetoacetate and the benzaldehyde with the catalyst for 2 hours. After this time, the urea is added.

- 4th **Process:** urea and catalyst are grinded together and introduced at the same time under stirring.

- 5th **Process:** Stir the ethyl acetoacetate and the urea with the catalyst for 2 hours. After this time, the benzaldehyde is added.

- 6th **Process:** Stir the benzaldehyde and the urea with the catalyst during 2 hours. After this time, ethyl acetoacetate is added.

- 7th **Process:** Biginelli process, the three reagents are introduced at the same time under stirring in the presence of the catalyst.

Procedure (Mt-2M)	1st	2nd	3rd	4th	5th	6th	7th
Yield%	73%	72%	56%	82%	45%	57%	81%
Procedure (Mt-3M)	1st	2nd	3rd	4th	5th	6th	7th
Yield%	45%	33%	49%	30%	44%	23%	63%

TABLE 3.4: Yield of order effect

According the obtained results, we can note that the process involving all the reactants at the same time (7th Process) is the one which gives the best yield in the case of the two catalysts Mt-2M and Mt-3M and the catalyst Mt-1M studied by Belmerabet and Hanieche [1].

It is very difficult to establish a single mechanism from the processes carried out, it is believed that each process has its own reaction mechanism which depends on the adsorption step of the reactants but also on the intermediates formed and the competition between these different species.

Finally, we can say that to better understand the mechanism with which the reaction takes place, it is necessary to follow the reaction by a more powerful characterization method such as NMR.

4. Beads:

We made two types of beads ones with alginate only (al) and the others as composites containing montmorillonite (2M) divided into three samples: non attacked composites (Mt-al), attacked with 0,5mol/l of H_2SO_4 (Mt-al (0,5M)), and attacked with 1mol/l of H_2SO_4 (Mt-al (1M)). We aim to define the suitable beads working as catalyst to have as a replacement of the powder catalyst: The observation of the reactions led us to note that

Types of beads	al	Mt-al	Mt-al (Mt-2M)	Mt-al (3M)
Yield%		54%	54%	64%	54%

TABLE 3.5: Yields of beads types

The beads suitable to replace the powder catalyst is the ones treated with sulfuric acid of 0,5mol/l concentration.

This part deserves further study.

3.1.2 results of DHPM characterization:

3.1.2.1 IR results:

The Biginelli reaction product (DHPM) IR spectrum is shown in the figure 3.2.

The DHPMs product spectrum is defined by the presence of two consecutive bands attributed to the two NH bonds of the DHPM core which occur respectively at approximately 3249 and 3123 cm-1. The band which appears around 1719 cm-1 is due to the C=O group of the ester function whereas the band of the C=O group of the amide function is located at 1645 cm-1. The spectrum also shows a band at 1470 cm-1, this band corresponds to the C=C bond. The
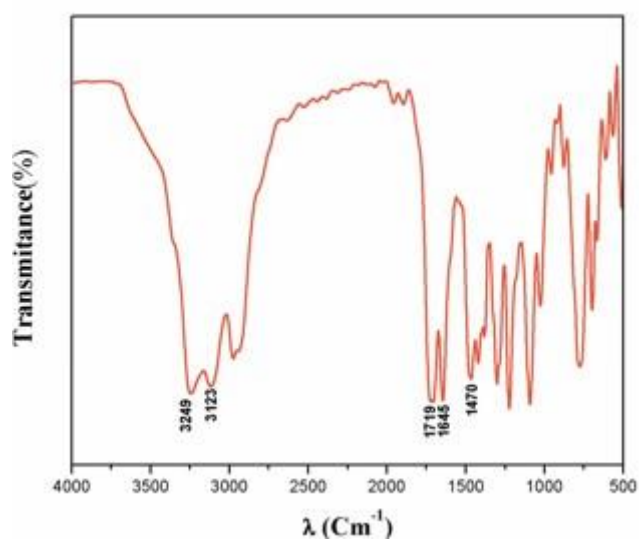
FIGURE 3.2: Infrared spectrum of organic product DHPMs

results found by IR are in good agreement with the literature so these results confirm the obtaining of the pure DHPM product.

3.1.2.2 melting point:

The melting point value of the product we obtained is 206℃ .The result obtained are in good agreement with supporting work on the melting point of DHPM [210-212°C] [35],[36]. This confirms that the product obtained is the same Biginelli product in all the reactions carried out.

3.2 Conclusion:

In conclusion of this part, it can be said that the acid-treated montmorillonite showed a very good catalytic activity towards the biginelli reaction under solvent-free conditions. This activity depends on the concentration of the treatment solution. The incorporation of montmorillonite in the alginate to form a composite that is easy to recover from the reaction medium is interesting and deserves further study

GENERAL CONCLUSION

The objective of this work is to study the effect of the activation solution concentration on the structural properties as well as on the catalytic activity of montmorillonite used as a heterogeneous catalyst for the Biginelli reaction. The main focus is on the work without solvent to enter into the frame work of green chemistry which aims to respect the environment through its use of synthetic methods that are respectful and less polluting.

The structure of activated montmorillonite was studied by X-ray diffraction (XRD) and its specific surface area was determined by the BET method. The reaction was followed by thin layer chromatography (TLC).

The product of Biginelli reaction DHPM has been analyzed by infra-red IR and by determining its melting point.

Montmorillonite was activated by sulfuric acid solutions at different concentrations (2mol/l and 3mol/l) under a temperature of 80℃ for 3 hours.

Regarding the study of the catalytic activity of montmorillonite activated on the Biginelli reaction under solvent-free conditions, we tested the effect of various parameters, namely the quantity of catalyst, the temperature of the reaction as well as the order of introduction of reagents.

The characterization by XRD has shown that the montmorillonite underwent an exchange of the compensating cations by H+ protons of the acid solution and an augmentation of the interlfoliar space.

The catalytic tests has shown that the yield of the reaction for different quantities of montmorillonite (2,5%, 5%, 10%, 15%) decreases for high quantities of catalyst, that is related to the pasty texture of the mixture effecting its stirring.

As for the temperature of the reaction varying from 25℃ to 100℃ passing by 45℃ and 80℃, it has been found that the adequate temperature for the reaction of Biginelli is 80℃ (81% for Mt-2M and 62% for Mt-3M).

To easily separate the DHPM and the catalyst, a test was carried out by transforming the montmorillonite powder into composite beads. The results showed that the separation was easier but the reaction yields decreased compared to using only montmorillonite. We can also conclude that alginate also has catalytic properties for Biginelli reaction.

The structure of the DHPM has been identified using IR alongside the determination of the melting point that matches the values found on papers. This work can be completed by an indepth study of the various conditions for the preparation of the composite beads as well as their regeneration.

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ANNEX

- **ANNEX 1:** The physicochemical properties of the reactants

Reactants	Physicochemical properties
Benzaldehyde	▪ The molecular formula: C7H6O ▪ Molar mass: 106.1219g / mol ▪ Melting T°: 26◦ C ▪ Boiling T°: 179◦ C ▪ Solubility: slightly soluble in water, ethanol, acetone. ▪ Density: liquid 1.046 g / cm3. ▪ Vapor pressure: 130 Pa.
Urea	▪ The molecular formula: CH4N2O ▪ Molar mass: 60.0553 g/mol ▪ Melting T°: 132,7◦ C to135℃. ▪ Solubility: 1080g/ 1 to 20℃. ▪ Density: solid 1.335 g/cm3.
Ethyl acetoacetate	▪ The molecular formula: C6H10O3 ▪ Molar mass: 130g / mol ▪ Melting T°: 45◦ C ▪ Boiling T°: 180.8◦ C ▪ Solubility: 111g/l. ▪ Density: liquid 1.03 g / cm3.

Table 3.6: The physicochemical properties of the reactants

- **ANNEX 2:** DHPMs pure product:

$m_{filterpaper} = 1,2635$ g.

$m_T - m_{filterpaper} = 2,3169 - 1,2635 = 1,0534g. = 1053,4mg.$

$n_{product} = 1053,4/260,3. = 4,0468$ mmol.

Yield% = nproduit/nbenzaldehyde.100 = 4,0468/5.100 = 81%.

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الملخص

تهدف هذه الدراسة الى معرفة مدى فعالية المنتموريلونيت الجزائري المعالج بحمض الكبريت في تحسين مردود تفاعل بيجينللي الذي يسمح بتخليق نواة ثنائي هيدروبيرميدنون. كما تناولت هذه الدراسة طريقة معالجة جديدة تمثلت في دمج المنتموريلونيت المنشط مسبقا بحمض الكبريت مع الجينات الصوديوم بغرض انتاج المركب مونتموريلونيت-الجينات الذي يكون على شكل حبات صغيرة.

من اجل معرفة مختلف التغيرات التي طرأت على البنية الهيكلية للمونتموريلونيت بعد معالجته تم توصيفه عن طريق توصيفه الاشعة السينية و قياس مساحة السطح المحددةBET .

هده الدراسة اثبتت ان مردود التفاعل متعلق ببعض المتغيرات ككمية المحفز، درجة حرارة التفاعل وبترتيب ادخال المتفاعلات في وسط التفاعل ومن اجل اظهار ان المركب الناتج عن التفاعل هو نفسه المركب المتواجد في المراجع تم توصيفه عن طريق التحليل الطيفي بالأشعة تحت الحمراء وقياس درجة انصهاره.

النتائج المتحصل عليها مثيرة للاهتمام وأظهرت ان المنموربلونيت الجزائري المعالج منافس للعوامل المحفزة الأخرى المتجانسة والغير متجانسة باهظة الثمن.

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Résumé

Ce travail vise à étudier l'efficacité de la montmorillonite algérienne traitée par l'acide sulfurique dans l'amélioration de rendement de la réaction de Biginelli qui permet de synthétiser les noyaux de dihydropyrimidinones.

On y trouve également la preparation de billes composites montmorillonite activée à l'acide sulfurique avec l'alginate de sodium et leur activité catalytique pour la réaction de Biginelli.

Pour connaitre les différents changements provoqués à la montmorillonite après leur traitement, elle est caractérisée par diffraction des rayons x et la determination de sa surface spécifique par la méthode BET.

Cette étude a confirmé que le rendement de la réaction est lié à certains paramètres comme la quantité de catalyseur, la température de réaction et l'ordre d'introduction des réactifs dans le mélange réactionnelle.

Les résultats obtenus sont intéressants et montrent que la montmorillonite traitée est compétitive avec les autres catalyseurs hétérogènes et homogènes couteux.

Abstract

This study aims to investigate the effectiveness of Algerian montmorillonite treated with sulfuric acid in improving the yield of the Biginelli reaction which allows the synthesis of dihydropyrimidinone.

To know the different changes caused to the montmorillonite after their treatment, it is characterized by x-ray diffraction and measurements of its specific surface by the BET method.

This study confirmed that the yield of the reaction is related to certain parameters such as the amount of catalyst, the reaction temperature and the order of introduction of the reagents in the reaction mixture.

The obtained results are interesting and show that the treated montmorillonite is competitive with other expensive heterogeneous and homogeneous catalysts.