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A green approach to the mechanochemical preparation of transition metal based catalysts and to their application in oxidation reactions

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Abstract

Green chemistry is a recent branch of chemistry that refers to the invention, design, and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances. Green Chemistry's popularity is in continuously increasing because it is recognized as a fundamental tool for design and attainment of sustainable development. The objective of this thesis is to synthesize different types of disperse materials, such as bimetallic structures with high surface-to-volume ratio, to be applied as catalysts in cyclohexane and 1-phenylethanol oxidation reactions which are of great industrial interest. Moreover, a core-shell (CS) structure and a metal-organic framework (MOF) were synthesize and applied as catalysts in the mentioned reactions. In addition, biomass derived catalysts supports, deriving from coffee wastes, will be applied in the heterogeneous 1-phenylethanol oxidation.

The general process scheme of the developed research consists in two main phases.

The first phase involve the synthetic routes applied, based on the Green Chemistry principles, to the preparation of the catalysts and their subsequent characterization. The catalytic systems prepared were either bi-metallic catalysts, metal organic frameworks or core-shell structures (CS). Besides the mechanochemical methods (planetary ball milling), wet impregnation was also applied to produce the supported catalyst. The characterization of all the synthesized catalysts was performed by SEM-EDS, FTIR-ATR and Elemental analysis.

In the second phase, all the catalysts have been tested in the oxidation of cyclohexane and 1-phenylethanol as model reactions, by using ball milling (BM) and microwave irradiation (MW) as an alternative reactional method or heating source, respectively. The reactions were operated under mild and environmentally acceptable conditions, namely involving solvent free reactions, and using $K_2S_2O_8$, TBHP or even O_2 as oxidants.

Riassunto

La Chimica Verde è una recente ramo della chimica che fa riferimento all'invenzione, alla progettazione e all'applicazione di prodotti e processi chimici per ridurre o eliminare l'uso e la generazione di sostanze pericolose. La popolarità di tale materia è in continua crescita perché viene sempre più riconosciuta come uno strumento fondamentale per la progettazione e il raggiungimento di uno sviluppo sostenibile. A tale proposito, l'obiettivo di questa tesi è quello di sintetizzare diversi tipi di materiali (strutture bimetalliche con elevato rapporto superficie-volume o strutture metallorganiche) aventi micro o nano dimensioni ed applicarli come catalizzatori nelle reazioni di ossidazione del cicloesano e del 1-feniletanolo, essendo reazioni chimiche molto importanti a livello industriale.

La tesi è articolata in un'introduzione, tre capitoli, le conclusioni e tre appendici.

Nel Capitolo 1 vengono descritti i metodi industriali che sono utilizzati attualmente per le reazioni di ossidazione del cicloesano e del 1-feniletanolo. Allo stesso tempo, vengono messe in luce le applicazioni dei prodotti derivanti da tali reazioni, i quali spaziano dall'uso nella produzione dei precursori per le polimerizzazioni di Nylon 6 e Nylon 6,6 ad essere impiegati nella preparazione di fragranze nei profumi. Successivamente, viene spiegata la distribuzione mondiale di produzione di sostanze chimiche, evidenziando la visione che l'Europa, a partire dal XXI secolo, ha intrapreso a tale riguardo, ovvero, quella di promuovere la produzione/utilizzo di sostanze chimiche in modo più eco-sostenibilmente possibile. Infine, il capitolo termina con una spiegazione delle tecniche *green* utilizzate in questo elaborato per sintetizzare i catalizzatori e come forme alternative di energia durante le reazioni catalizzate, collegandole ai 12 principi della Chimica Verde.

Il Capitolo 2 illustra la preparazione di materiali dispersi in condizioni *green* attraverso un trattamento meccanochimico, sviluppato con il mulino a biglie. Le strutture sintetizzate, contengono diversi tipi di ossidi metallici o sali metallici. La scelta dei materiali si basa principalmente su due ragioni: la loro riconosciuta attività catalitica e le proprietà specifiche che possono essere attivate durante la preparazione meccanochimica (cioè magnetismo o cambiamento nello stato di ossidazione). I metalli testati sono: rame (Cu), vanadio (V), ferro (Fe) e renio (Re). In secondo luogo, una struttura *core-shell* viene preparata dalla riduzione dei

sali metallici secondo un metodo di impregnazione ad umido. Le nanoparticelle *core-shell* (CSNPs) hanno ricevuto maggiore attenzione per le loro proprietà catalitiche e la loro ampia gamma di applicazioni. Inoltre, per quanto riguarda l'approccio meccanochimico, si propone un metodo alternativo per la sintesi di strutture metallorganiche (MOFs), seguendo la procedura descritta da Maria Klimakow *et al* ([1]).

Il Capitolo 3 illustra il lavoro sperimentale riguardante l'ossidazione catalitica del cicloesano (cicloalcano) e del 1-feniletanolo (alcool secondario). Gli ossidanti impiegati sono perossidisolfato di potassio ($K_2S_2O_8$), ter-butile idroperossido (soluzione 70% in acqua) o O_2. Le reazioni sono condotte in condizioni miti ed ecologicamente accettabili, sottoponendole a due diverse forme alternative di energia: radiazione a microonde oppure mescolamento meccanochimico. Viene studiata l'influenza dei parametri di reazione come il tipo di catalizzatori e le quantità, gli additivi e le condizioni operative (temperatura e tempo di reazione). L'ultima parte del Capitolo è focalizzata sull'ossidazione del 1-feniletanolo nel reattore a microonde, utilizzando come catalizzatori sali metallici supportati da biomassa derivante da residui del caffè. Questi catalizzatori sono sintetizzati mediante un metodo di impregnazione ad umido o mediante mescolamento meccanochimico.

Le Appendici contengono le caratterizzazioni spettroscopiche della maggiore parte dei catalizzatori sintetizzati (Appendice A), l'elenco dettagliato delle reazioni di ossidazione del cicloesano (Appendice B) e l'elenco dettagliato delle reazioni di ossidazione del 1-feniletanolo con i catalizzatori metallici supportati da biomassa (Appendice C).

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Introduction

In our days, one of the most important challenges that Chemistry and Technology are facing is the preparation, characterization, and application of dispersed materials with high surface-to-volume ratio, since most of the new developments in these fields require an extensive knowledge of the behaviour of the materials and their reactivity. Also, factors as engineering simplification and cost efficiency must be taken in account during the preparation ([2]).

In this view, mechanochemical and similar dry synthetic methods can be pursed since they do not require the use of VOC solvents, which can influence the preparation and characterization of this new dispersed materials. Furthermore, such methods can lead to micro- or nano-compounds in one step thus, saving energy, time and money. For this reason, the ball milling technique will be used as a fast, simple and eco-friendly method of preparation of dispersed catalyst ([2-3]). At the same time, wet synthetic methods will be tested to produce core-shell structures and biomass catalysts.

Besides the Introduction and Conclusion, the thesis is structured in three Chapters and starts with an introductory chapter concerning the industrial methods and applications of the reaction of interest and a brief introduction to Green Chemistry principles to highlight the positive aspects that can be achieved by using ball milling and microwave irradiation.

Chapter 2 illustrates the preparation of dispersed materials under nontoxic green conditions that are of vital importance to address growing concerns on the overall toxicity of these compounds for technological applications. The composites that will be synthesized, contain different types of metal oxides or metal salts. The choice of the starting materials is mainly based on two reasons: their specific properties that can be activated during the mechanochemical preparation (i.e. magnetism, changing in the oxidation state) and for their recognized catalytic activity in alkanes and alcohols oxidation. Independently on the chosen metal oxide or metal salt, the metals that are going to be tested are: Copper (Cu), Vanadium (V), Iron (Fe), and Rhenium (Re). Secondly, a core-shell structure will be prepared by the reduction of metal salts, according to the wet impregnation method. Core-shell nanoparticles (CSNPs) received increased attention due to their interesting properties and broad range of applications in catalysis. Regarding the mechanochemical approach is proposed as an alternative synthetic green route for metal Organic frameworks (MOFs), following the procedure described by Maria Klimakow *et al* ([1]).

Moreover, the MOF compounds will be supported with other transition metals (core-shell, core and titanium isopropoxide) and tested in oxidation reaction.

In chapter 3, the catalytic activity and selectivity of the synthesized particles will be screened for the oxidative functionalization of organic substrates such as cyclohexane (alkane) and 1-phenylethanol (alcohol). Oxidants will be $K_2S_2O_8$, TBHP or even O_2 and the reactions will operate under mild and environmentally acceptable conditions, namely involving green solvent such as water or solvents free reactions using microwave and mechanochemistry. The influence of reaction parameters such as catalysts type and loadings, additives, and operating conditions (temperature and reaction time) will be described and studied. The end of the chapter deals with the optimization of the operating conditions of 1-phenylethanol oxidation using metal salts supported in biomass as catalysts. These latter catalysts are synthesized by a wet impregnation method or by mechanochemical technique.

Finally, the results will be compared with the aim of finding out the best possible solution in terms efficiency and catalytic activity in green conditions.

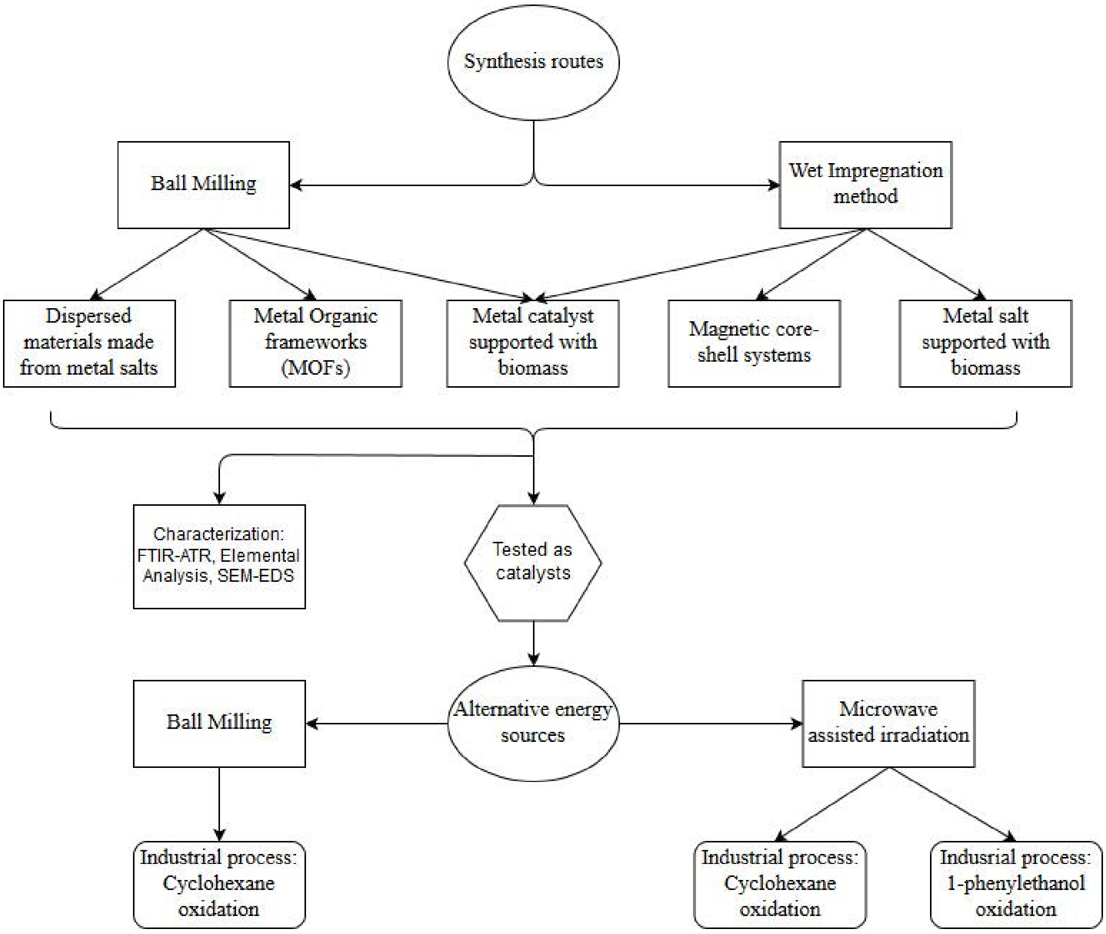


Figure 1.1. Scheme of the procedure followed in this work.

Figure 1.1 shows the general procedure followed in this work. The objective is to propose greener routes to carry out cyclohexane and 1-phenylethanol oxidations, which are the model reactions in this work due to their importance in the global market.

CHAPTER 1

From industrial cyclohexane and 1-phenylethanol oxidation to a green chemistry alternative

Chapter 1 deals with an explanation of the importance that acetophenone and cyclohexanol/cyclohexanone have from an industrial point of view and the industrial methods that are commonly used to produce them. Finally, a brief explanation of Green Chemistry principles is presented, mainly focusing on green approaches that are applied in this work such as the ball milling and the microwave irradiation as synthetic route and heating source, respectively.

1.1 Cyclohexanol and cyclohexanone production and applications

In the past years, cyclohexanol and cyclohexanone have attracted the attention of numerous industries, as well as researches, in order to improve its oxidation process and to investigate new possible routes to produce them. The reason why these compounds are important is linked to their various applications, in particular in the production of plastics. The main plastics that are produced by these compounds are Nylon 6 which is made starting from caprolactam while Nylon 6,6 requires adipic acid and hexamethylenediamine. World adipic acid production is around 2 million tons/year and the 93% of this capacity comes from the oxidation of cyclohexane. More precisely, Figure 1.1 presents worldwide consumption of cyclohexane and this figure states the importance of cyclohexanone and cyclohexanol ([4]).

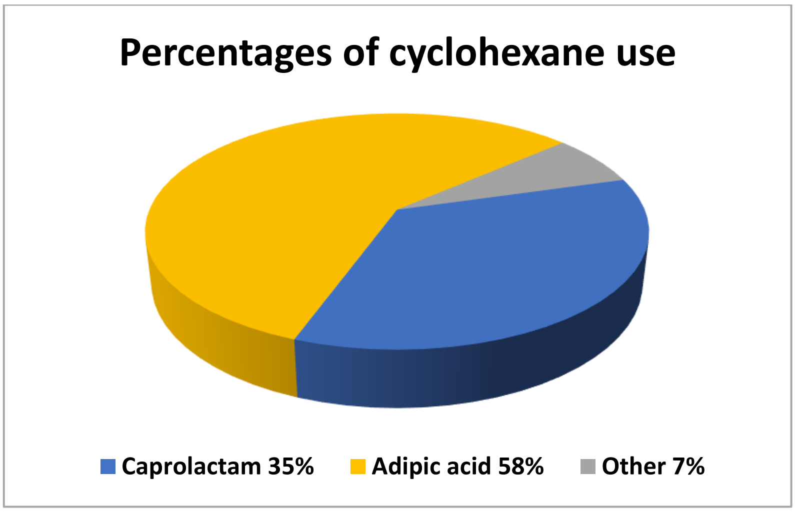


Figure 1.1. Chart of cyclohexane world use ([4]).

In this view cyclohexanone and cyclohexanol mixture, known as KA oil, are mainly used as precursors for the production of adipic acid and caprolactam, respectively. More precisely, most cyclohexanol and cyclohexanone (over 95%) is consumed captively on site for the production of adipic acid and caprolactam, so only a small amount (4%) enters the world's trade markets which is used as solvents for paints and dyes, in pesticides, and as an intermediate for pharmaceuticals, films, soaps, and coatings. Indeed, cyclohexanone is an excellent solvent for DDT and organic phosphorous pesticides and insecticides. Cyclohexanone is also used for the synthesis of cycloamines, pharmaceuticals, rubber chemicals, dyes, plasticizers, herbicides, and plant growth regulators, among others. Instead, cyclohexanol undergoes all expected normal reactions for a secondary alcohol. By oxidation it gives cyclohexanone, which in turn is converted into the corresponding oxime, intermediate in caprolactam production. By esterification, it will be transferred into dicyclohexyladipate and dicyclohexylphthalate, two plasticizers and finally, by heating in the presence of acidic catalysts, cyclohexanol undergoes dehydration and is converted to cyclohexene.

1.1.1 Cyclohexane oxidation to KA oil

The industrial cyclohexane oxidation usually occurs in liquid phase reactors which are placed in series, with temperatures that range between 140°C and 180°C and pressure between 0.8 and 2 MPa. Since the oxidation occurs in the liquid phase, the residence time can vary until one hour due the mass transfer of oxygen that has to be solubilized in the organic phase. In our days, the most applied catalysts are cobalt naphthenates which are soluble in the reaction mixture.

Nevertheless, there are other methods that employ boric acid or vanadium-, molybdenum- and chromium-based catalysts.

In Figure 1.2, the DuPont process scheme is shown. The first reactor is fed with recycled cyclohexane together with some fresh one and air while the following reactors receive the output of the first reactor and fresh air. In the second step, the product exits from the last reactor and is washed with water, creating a biphasic system and left in a decantation vessel. The aim is to remove the aqueous phase in this way the water produced during the reaction is separated from the organic phase. Subsequently, the solution is washed with a caustic solution in order to remove the acid by-products and to decompose the unreacted hydroperoxides (hydroperoxide cyclohexyl). Cyclohexane is recovered from the top of this column and recycled to the first reactor. Instead, the bottom product feeds another column, from which the KA oil exits on the top ([5]).

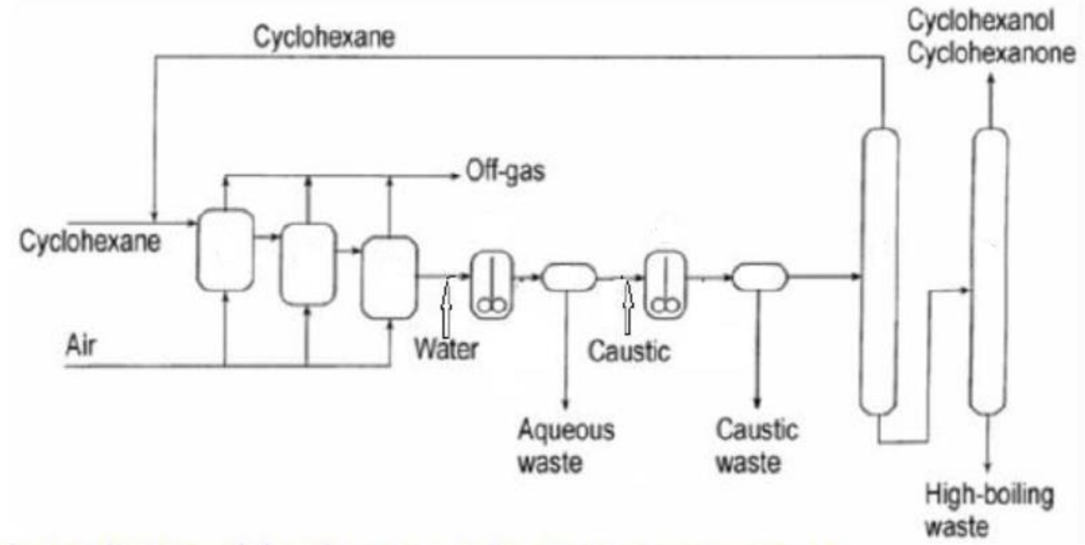


Figure 1.2. DuPont process scheme for cyclohexane oxidation to KA oil ([5]).

The reaction, as all oxidation reactions, is exothermic, with an enthalpy of -70 Kcal/mol, and it is composed by two steps: first, the formation of an intermediate, the cyclohexyl hydroperoxide (2.1), then, the KA oil formation, with other by-products (carboxylic acids, esters, aldehydes, oxidized compounds). The catalyst is responsible for the peroxide decomposition (2.2).

$$C_6H_{12} + O_2 \rightarrow C_6H_{11}OOH \qquad (1.1)$$

$$3C_6H_{11}OOH \rightarrow 2C_6H_{11}OH + C6H_{10}O + H_2O + O_2 \qquad (1.2)$$

1.2 Acetophenone production and applications

Acetophenone (also known as phenyl methyl ketone, acetlylbenzene and hypnone) is the simplest form of the ketones containing both an aromatic and aliphatic group. Acetophenone is present in the heavy oil fraction of coal tar boiling at 180°C and it is also found in nature. The worldwide production of acetophenone has been increasing in the last years. America and China are the world top suppliers of acetophenone while Italy is one of the European top suppliers. Regarding Europe, the countries that import major quantitates of acetophenone are Belgium (3 thousand tons/year), Germany (1.7 thousand tons/year) and the Netherlands (759 tons/year), stating the importance of acetophenone in the market. In Figure 1.3 the total value of imports shows that America and China are the countries that import the highest amounts of acetophenone.

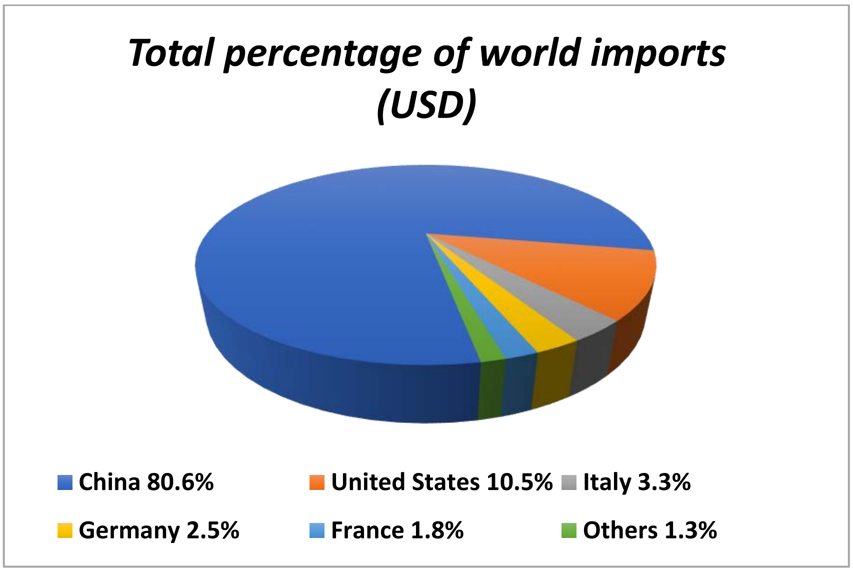


Figure 1.3. Chart of total percentage of world imports.

The major use of acetophenone is as a catalyst for the polymerization of olefins; in organic synthesis, especially as a photosensitizer and as a specialty solvent for plastics and resins. It is also approved as a synthetic flavouring substance and adjuvant in food. It is used as a flavouring agent in non-alcoholic beverages, ice cream, candy, baked goods, gelatines, puddings, tobacco, and chewing gum. It is used to impart an orange-blossom fragrance in soaps, detergents, creams, lotions, and perfumes. Moreover, acetophenone market is set to witness notable gains from pharmaceutical industry because of the rising demand for hypnotic and anticonvulsant.

Since the first synthesis of acetophenone that was carried out in 1857, a number of alternative routes for its synthesis have been developed. However, because of thigh cost, low yield and other factors, only a few of these syntheses have attained commercial status (^{6}). Among the most known reactions are:

- Catalytic dehydrogenation of ethylbenzene to styrene (acetophenone found as a by-product)
- Benzene and acetyl chloride in presence of aluminium chloride
- Benzene and acetic anhydride in the presence of aluminium chloride
- Benzoyl chloride and dimethyl zinc

As a new development, acetophenone may be made available as a by-product from the phenol to cumene process.

1.3 Chemical Industry in our days

Since the 1980s, the global chemical industry has grown by 7% annually, reaching €2.4 trillion in 2010. Starting from the 1990s the growth has been driven by Asia, which now owns almost half of the global chemical sales (^{7}). Meanwhile, in Europe the growth is expected to be less than 1% causing by 2030 a 30% loss of workforce in this sector, as Figure 1.4 shows.

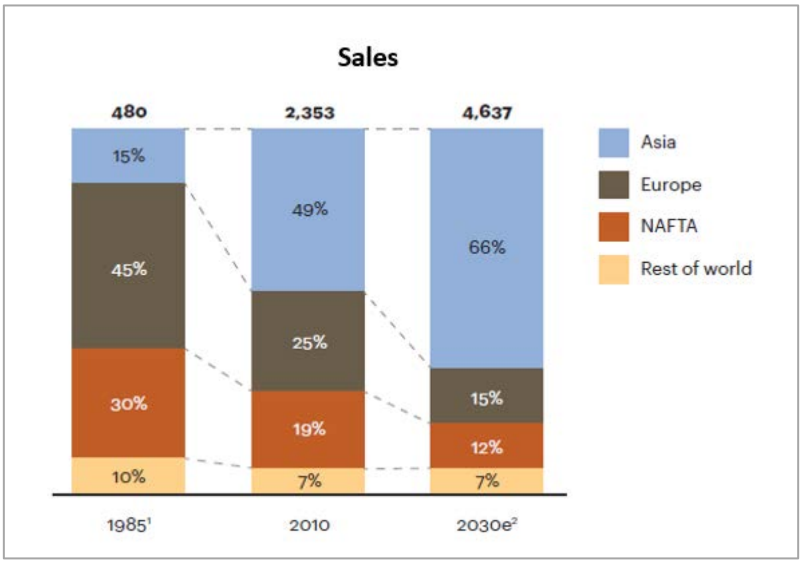


Figure 1.4. Sales in € billion; 2030 is calculated at 2010 prices and exchange rates (^{7}).

The competitive advantage of the European chemicals industry appears to decline, as the US and Asia develop low-cost production for chemicals. In addition, stringent regulations in the European chemicals industry, heavy green taxes and slow take up of alternate feedstock technology (shale, etc.) contribute to the slow growth of the industry. Indeed, the regulatory cost in Europe has doubled during 2004-2014 as well as labour cost per employee that is increased during 2002-2014, as it is shown in Figure 1.5. Furthermore, the emission and industrial process legislation costs index quadrupled between 2004 and 2014. Additionally, rigid labour laws in the European manufacturing industry make layoffs difficult for companies experiencing an economic down cycle, forcing them to absorb the cost burden. This burden is worsened for the major European producers (Germany, the Netherlands and Italy) that have a high cost of laying off tenured employees (^{8}).

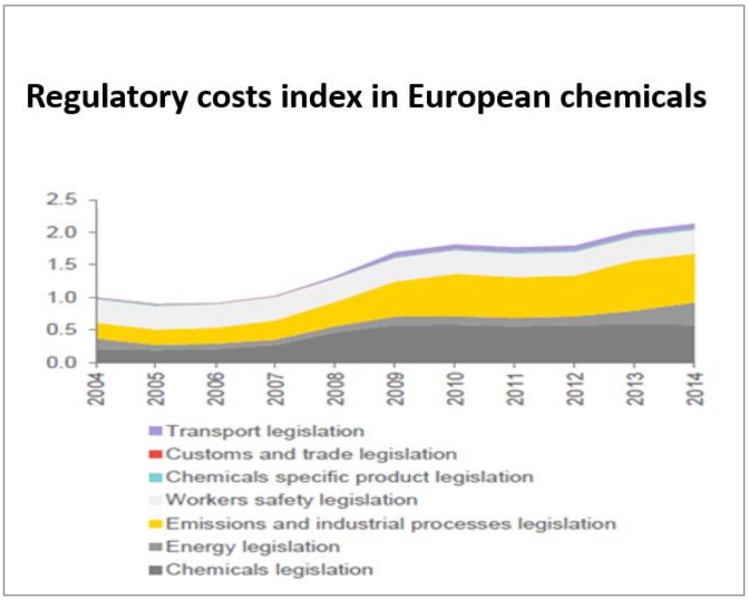


Figure 1.5. Regulatory costs index in European chemicals industry (^{8}).

Even tough strict regulations are placed in the European continent, investments in chemical industry have not been weighted down. What paves the way to future chemicals, which facilitate safety of employees and consumers, is the sustainable view of the industry. Sustainable chemistry has already reduced greenhouse gas emissions by approximately 60% in the 20 years. Sustainable chemicals and processes are the way for chemicals tomorrow, and European chemicals have taken that direction such as alternative feedstock (bio and renewable feedstocks, energy sources (shale gas, solar thermal and wind energy), intelligent materials (nano materials and functional textiles) and improved energy storage (fuel cells).

These green alternatives, together with other eco-friendly approaches, are part of a new branch of chemistry, known as Green Chemistry which provides a unique approach of innovative research on the development of alternative sustainable technologies.

In this view Green Chemistry is becoming every year a more known and respected discipline because it is recognized as a fundamental tool for design and attainment of sustainable development. With multi-disciplinary scientific know-how, such a field produces benefits in all areas concerning sustainable development: environment, economy and society. The term ''Green Chemistry'' has been validated in the beginning of the 21st century by the IUPAC Working Party on Synthetic Pathways and Processes in Green Chemistry that agreed to adopt the following definition: *"The invention, design, and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances."*

1.4 Green Chemistry Principles

Every year more severe regulations are placed on chemical industries due to the long-term negative effects of the processes used in factories and laboratories, promoting pollution which is threatening the survival of fauna and flora and subsequently of human health (where cancer and diseases are becoming every day more common). This awareness inspired scientist, by the mid-20th century, to explore eco-friendly methods to carry out reactions and improving the quality of life in general.

These environmental issues are now addressed by a new branch of chemistry known as Green chemistry. Green chemistry is a vast and multifield area of chemistry and chemical engineering focused on the designing of products and processes that minimize the use and generation of hazardous substances. In the 1990s, Paul Anastas and John Warner postulated the 12 principles of Green chemistry ([9]), still in use today, that rely on the minimization of raw materials and secondary products waste, use of safe and environmental benign solvents and design of energy efficient processes. The principles are reported in Table 1.1 together with a brief description of each of them.

Table 1.1. Green Chemistry principles by Paul Anastas and John Warner (⁹).

N°	Principles	Description of the Principles
1	Prevention	It concerns the prevention of waste generation. It is better to avoid generating waste than to treat it after its generation.
2	Atom Economy	The final product of a reaction should be planned in order to incorporate as much of the reagents used during the process to minimize secondary products.
3	Safer chemical synthesis	The final product should be achieved by a chemical synthesis that avoids reagents or by-products harmful for human life.
4	Safer chemical design	Attention should be given to the toxicity of the designed chemicals. They should obviously fulfil their functions, but should also present the lowest possible toxicity.
5	Use of safer solvents	Avoid the use of solvent or other reagents. If not possible then innocuous substances are demanded.
6	Design of energy efficiency	Try to conduce the reaction at standard temperature and pressure. If not possible optimize the energy requirement.
7	Use of renewable feedstocks	Whenever it is economically and technically feasible, renewable raw materials should be used instead of non-renewable.
8	Reduce derivatives	Unnecessary derivatization steps require the use of reagents and so waste is produce.
9	Catalysis	Use of catalysts is highly recommended if it allows to carry out reactions in a more selective way and at lower operating conditions.
10	Design for degradation	Chemicals should be designed so that at the end of their function they decompose into harmless degradation products and do not persist in the environment.
11	Real-time analysis for pollution prevention	Analytical methods should be analysed in rea-time thus avoiding the creation of substances that may pollute.
12	Inherently safer chemistry for accident prevention	Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

These principles propose eco-friendly actions to minimize the environmental and human hazards in industrial activities. Moreover, in Table 1.1 it is stated that the main concept of sustainable chemistry is to promote the use of chemical skills in order to reduce or eventually eliminate the use of hazardous substances during the planning, manufacturing and application of chemicals in order to minimize threats to the health of operators and the environment ([10]). In this view, the 12 principles are clearly linked to each other. Also, it demonstrates that the atomic, catalytic and energy economies occupy prominent places due to the fact that by optimizing them, most of the green principles are, at least in part, achieved.

Although major efforts have been done in the last 20 years, there is still several fields in chemistry that need continuous ameliorations, in order to improve the life quality without sacrificing the environment and putting at risk the resources available for future generations.

1.4.1 Ball milling as an alternative energy system

Green chemistry deals with several principles such as minimize raw materials and secondary products waste, use of safe and environmental benign solvents, design of energy efficient processes and use of renewable materials feedstocks.

The thrust for finding alternative energy sources for enhanced chemical transformations under mild reaction conditions led to the discovery during the years of the following alternative energy systems:

- Light induced-photochemistry
- Microwave-assisted irradiation
- Sonochemistry—ultrasonic irradiation
- Mechanochemical mixing

One of the possible ways to promote chemical reactions is by applying mechanochemical energy, as in this case. The most obvious advantage is that reactions can be performed under solvent-free conditions indeed, many catalysts and reagents can be very sensitive towards water or other types of solvents and reactions that require hazardous solvents could be made safer by using solvent-free conditions, in line with Green Chemistry principles.

By applying the ball milling technique, the crystalline structure order is braked several times during the grinding treatment, causing the production of new surfaces and cracks. Indeed, the total area available for the oxidation increases and this enhances conversion. Moreover, at the points where nanoparticles collide, an increase in temperature appears, forming hot dots where molecules may rich higher energy states leading to bond breakage ([11]). These random processes occur in without thermal equilibrium between the phases and in a period between micro – and nanoseconds. This range time is defined as plasma phase and it is followed by a post plasma phase that lasts the more or less as the previous phase, in which relaxation processes dissipate the accumulated energy following the Maxwell-Boltzmann distribution. These high energy release, are responsible of the products formed during ball milling treatment. Nevertheless, the energy accumulation may lead to slow down rate of reactions and therefore chemical transformations. Hence, ball milling reactions can significantly differ from those performed by microwave reactor ([12]).

1.4.2 Microwave-assisted irradiation as an alternative energy system

The application of a second type of alternative energy system such as microwave is one of the ways, according the Green chemistry principles, to perform chemical transformations under mild reaction conditions. In this view, reactions are performed in solvent-free ambient.

The combination of solvent-free reaction conditions and microwave irradiation (wavelengths of 1 mm to 1 m) may lead to reducing reactions time and enhance conversions as well as yields. The origins of the microwave effects results from a material-wave interaction leading to thermal effects and specific effects. The first effects are related to dipolar polarization as a consequence of dipole-dipole interactions between polar molecules and the electromagnetic field. This interaction will induce energy dissipation as heat due to friction and agitation between molecules. Therefore, the dissipation of heat energy, from the core to the outside, brings a more homogeneous distribution of heat in the sample ([13]).

In the same frequency range, the charge space polarization can intervene and may be of extreme importance in chemical reactions because it concerns solid materials which contain free conductive electrons, as catalysts. This induces a second thermal effect, known as hot spots, that is the creation of localized microscopic high temperatures spots.

However, the utilization of microwave is not always advantageous due to its complicated relation to the composition mixture, reaction mechanism, reactions rate and other factors. Regarding the reaction rate connection with the microwave effects, the relationship is rather complicated since thermal and specific effects have an active part in rate of reactions values. For instance, the velocity rate constant (k) is determined by the Arrhenius Equation:

$$\mathrm{k} = \mathrm{A}e^{\frac{-E_a}{\mathrm{RT}}} \tag{1.3}$$

First of all, the pre-exponential factor (A) which is representative of the probability of the molecular impacts can be effectively influenced by the orientation of the polar molecules involved in the reaction, E_a ($J \cdot mol^{-1}$) is the activation energy required for the reaction, R is the universal gas constant ($J \cdot mol^{-1} \cdot K^{-1}$) and T (K) the temperature. At the same time, the activation energy term can also be effectively influenced because of the entropy contribution due to dipolar polarization. Temperature can change during the experiment undergoing hot spots that could increase it in localized areas.

CHAPTER 2

Synthesis details

The main objective of Chapter 2 is to illustrate the preparation procedure of composites by ball milling, using greener evolutions. Two different types of ball billing equipment, which are described in this chapter, are used to produce dispersed materials. Before the description of the experimental synthesis, a brief explanation of different methods that are used to synthesize core-shell composites is added. The synthetized catalyst will be then characterized by performing conventional techniques such as FTIR, elemental analysis, SEM-EDS and the magnetic properties were determined using a Gouy balance.

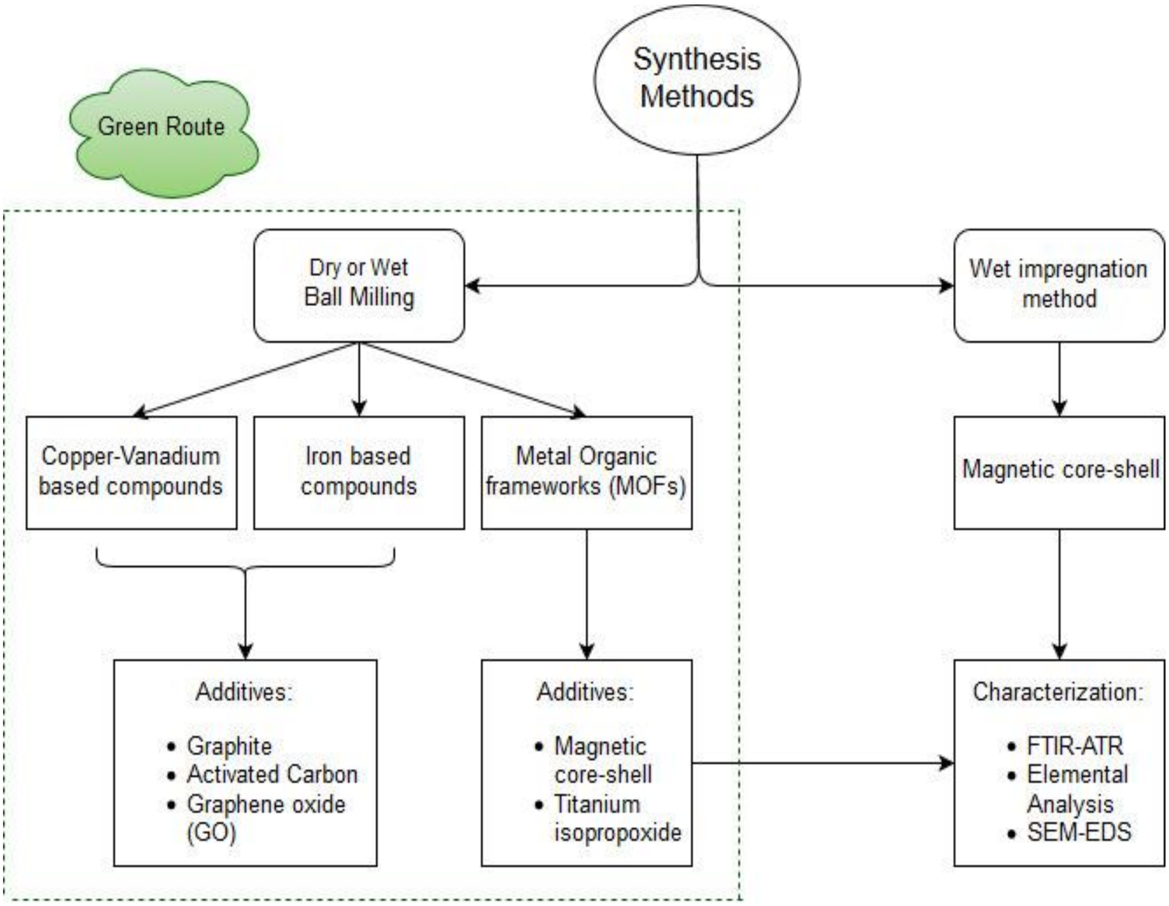


Figure 2.1. Synthesis scheme that is followed in this work.

In Figure 2.1 the experimental synthesis carried out in this work are shown. The image remarks that not all compounds have been fully characterized with FTIR, elemental analysis, SEM-EDS.

2.1 The ball milling unit PM 100

During the milling treatment, the commercial salts or oxides are mixed mechanically in a PM 100, Retsch GmbH, planetary ball mill reactor which is shown in Figure 2.2.

Figure 2.2. PM 100 by Retsch GmbH website.

The grinding jar is fixed eccentrically on the sun wheel of the planetary ball mill and the grinding jars direction is exactly opposite to the one of the sun wheel, as Figure 2.3 shows. Furthermore, the number of grinding balls can be chosen depending on the purpose of the experiment thus changing the total energy in the system, since they are made to rotate within the jars and their movements are linked to Coriolis forces. Indeed, the balls are subjected to different speed with respect to the grinding jar causing the release of high dynamic energies produced by interactions between impact and fractional forces.

Figure 2.3. PM 100 by Retsch GmbH website.

The interplay between these forces produces the high and very effective degree of size reduction of the planetary ball mill. Since it is a planetary mill with a single grinding station a counterweight for balancing purposes is need. In the Ball Mill PM 100 this counterweight can be adjusted on an inclined guide rail. In this way, the different heights of the grinding jars can be compensated in order to avoid disturbing oscillations of the machine.

2.1.1 The ball milling unit Emax 2000

During the milling treatment, the commercial salts or oxides are mixed mechanically in an Emax 2000, Retsch GmbH, ball mill equipment (Figure 2.4).

Figure 2.4. Emax 2000 by Retsch GmbH website.

Thanks to the high energy input, the oval shape of the jars and their movement, the Emax allows a novel size distribution of the particles reducing their size. Indeed, the interplay of jar geometry and movement causes strong friction between grinding balls, sample material and jar walls as well as a rapid acceleration which lets the balls impact with great force on the sample at the rounded ends of the jars. This significantly improves the mixing of the particles resulting in smaller grind sizes and a narrower particle size distribution.

Nanogrinding is favoured thanks to the high rotational speed that the machine can reach (2000 RPM) and the cooling system, integrated in the machine, making the control of temperature possible and therefore improving of the reaction parameters.

2.2 Core-shell synthesis for oxidation purposes

Core-shell nanoparticles are composite nanostructures that are made of an internal core coated with a shell and can be composed of different particles. Both the core and the shell can be made of inorganic (metal oxides or silica) or organic materials. Core-shell nanoparticles (CSNs) received increasing attention due to their interesting properties and broad range of applications in catalysis, biology, materials chemistry and sensors. By rationally tuning the core as well as the shell of such materials, a range of core-shell nanoparticles can be produced and can play important roles in various catalytic processes and offer sustainable solutions to current energy problems ([13]).

Typical preparation techniques of metallic core-shell structures are: microwave synthesis, micelle-controlled growth, spray pyrolysis, reduction of metal salts, Stober method, sol-gel method and solvothermal precipitation. Due to nanoparticles properties (metallic properties and the high surface area-to-volume ratios), there are a countless number of articles that employ classical methods and modifications of them in order to synthesize this type of composites.

2.2.1 Reduction of metal salts

There are two types of classical reduction processes known as one-step or two-step processes that require a suitable reducing agent. The reduction mechanism involves electrons transfer process by means of a reduction reaction and a complementary oxidation one. In the one-step or simultaneous reduction process, nanoparticles are simultaneously reduced together with the precursor. In this case, it is not possible to control the shell growth and it is suitable for core-shell structures based on zirconium, silver or titanium. Meanwhile, the two-step or successive reduction process, the core is prepared at first and then the shell is coated onto the core through successive reduction using a suitable agent for both steps. Dung Chinh Trinh *et al* (2015) propose a one-pot method to create Cu-Ag core-shells using Polyvinyl pyrrolidone (PVP) as capping agent, and ascorbic acid ($C_6H_8O_6$) and sodium borohydride ($NaBH_4$) as reducing agents. The article describes how it is possible to optimize the molar ratio between Cu and Ag in order to obtain stable composites and more important it suggests a promising strategy to improve Cu oxidation resistance since several strategies have been already but none of them seems to have solved this issue.

Another interesting publication that illustrates an alternative and greener method to synthesize CSNPs was published in 2014 by Zhenyang Wang ([14]). The technique described by the author employs an irreversible solid-gas reaction cycle that promotes the metal salt reduction and oxidation in a one-pot mechanism. In this view, the process does not require specific coatings but the use of a gas-solid reaction therefore avoiding issues regarding the treatment of waste water solutions that is instead used in the conventional techniques (cost reduction). By applying the briefly described method, the author compares Al_2O_3-Fe_2O_3 core-shell and TiO_2- Fe_2O_3 powder which are subjected to the same cyclic reactions (reduction with H_2 and oxidation with O_2). In the following image, taken from the article, the cyclic process is represented in which 50 cycles of reduction and oxidation are repeated at 900°C.

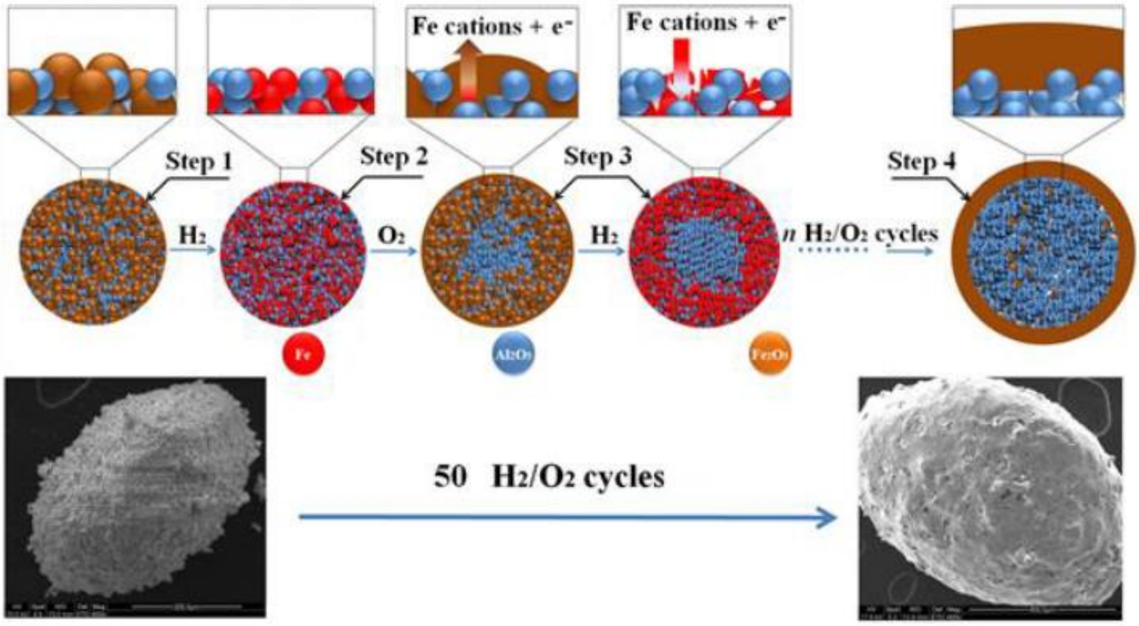


Figure 2.5. Synthesis procedure of an Al_2O_3-Fe_2O_3 or TiO_2- Fe_2O_3 catalyst ([14]).

The processed mixtures were analysed by SEM and EDX and in the case of the titanium oxide no core-shell structure was formed by mixing TiO_2 and Fe_2O_3, where O^{2-} becomes the main oxidation specie in the cycles, which causes sintering ([15]).

2.2.2 Solvothermal method

In the case of solvothermal to synthesis of CSNPs, an article published in 2011 by Fei Mi *et al* that describes a novel core-shell structure, which is then used in the 1-phenylethanol oxidation to acetophenone ([16]). The authors report a facile method to support gold nanoparticles on the MgAl-LDH surface of Fe_3O_4-MgAl-LDH core-shell composite whereas, the previous articles employed synthesis routes that needed multi-step and sophisticated procedures ([16,17]). The procedure, shown in Figure 2.6, is mainly divided in two steps which involve the deposition of a carbonate–MgAl–LDH layer on top of the Fe_3O_4 negatively charged spheres that are previously synthesized using a surfactant-free solvothermal method. The layer that coats the magnetic nanoparticles is obtained via electrostatic attraction followed by nucleation and crystal growth under addition of salts and alkaline solutions ([16]). The second main step is the addition of gold nanoparticles in the shell structure by a deposition-precipitation method.

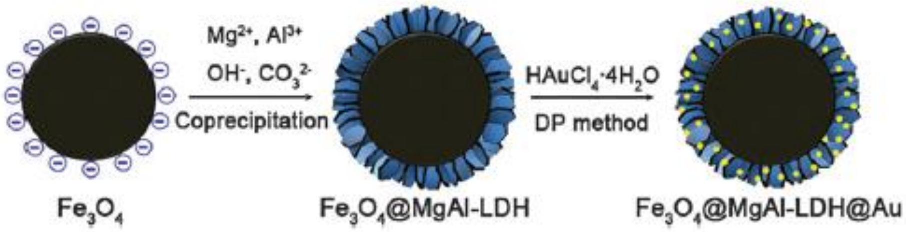


Figure 2.6. Synthetic procedure of an Fe_3O_4@ MgAl-LDH@Au catalyst ([16]).

Finally, oxidation results demonstrate that the Au nanoparticles supported on the shell layer enhances the conversion (99%) of the substrate under O_2 atmosphere without additives. In addition, the magnetic properties of the catalyst allow a simple separation and then recycling (5 cycles are reported) without decreasing the yield.

2.2.3 Stober method

The Stober method (1968) is a chemical process used to prepare silica particles of controllable and uniform size and remains to our days the most widely used wet chemistry synthetic approach for the production silica particles. There are two types of Stober classical processes known as one-step or two-step processes. In the classical one-step process, silica precursor tetraethyl orthosilicate (TEOS) is hydrolysed in alcohol (typically methanol or ethanol) in the presence of ammonia as a catalyst and condensation occurs in the same vessel. On the other hand, hydrolysis is completed in acid solution (pH 1-4) before the condensation reaction is initiated by the addition of sodium fluoride. The two-step procedure includes the addition of a anionic surfactant template thanks to which the diameter and shape of the product particles as well as the pore size are determined solely by the reaction kinetics. In this view, a modified Stober method is applied in Ali Maleki and Tooraj Kari article (2107), as a synthetization method to create a core-shell super magnetic catalyst in this form: $Fe_3O_4@SiO_2@mTiO_2$–$HN(CH_2CH_2NH_2)_2/Pd$.

Selective oxidation of alcohols is known to still be a challenge in organic chemistry due to the lack of efficient methods that operate in green conditions. Different articles have been recently published regarding alcohols catalytic oxidation by means of core-shell composites ([18]). Palladium-based nanomaterials are known to be, in presence of an oxidant, efficient catalysts in terms of selectivity for the oxidation of alcohols to their corresponding carbonyl compounds ([19]).

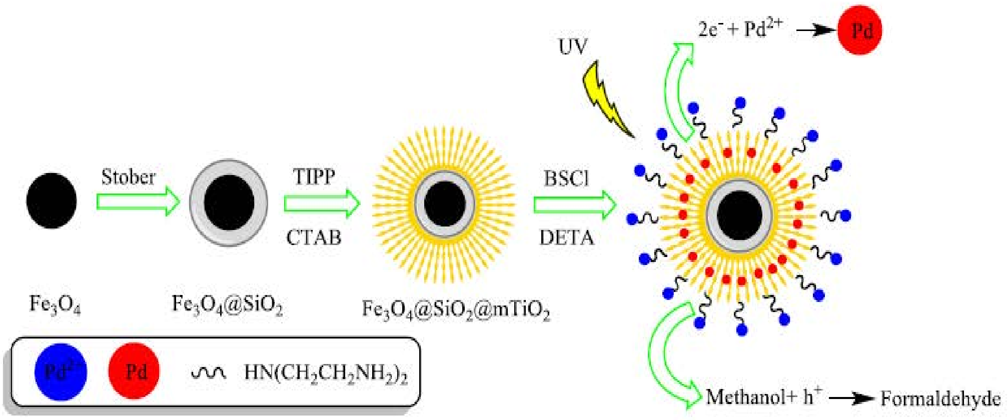
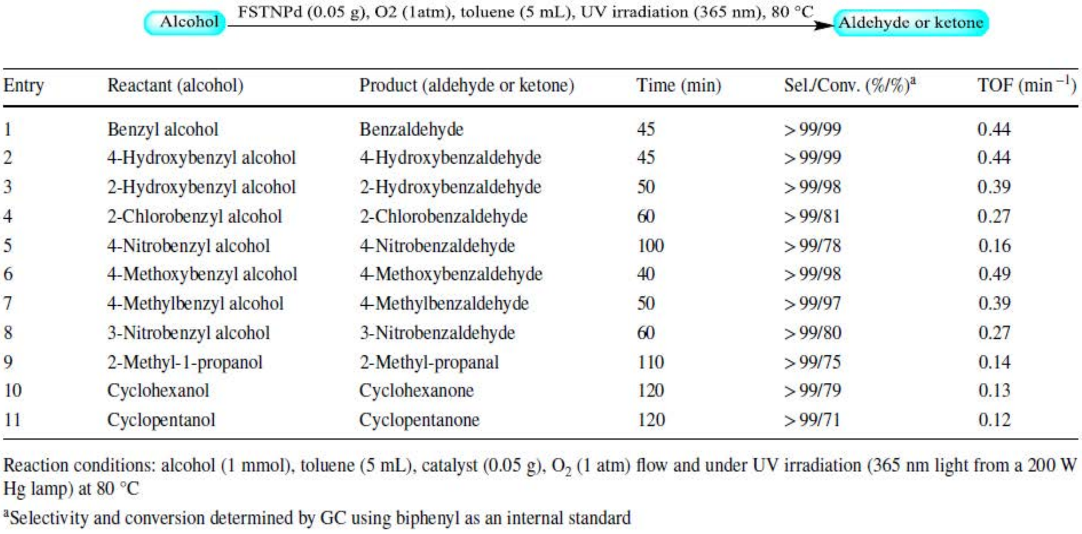


Figure 2.7. Synthetic procedure of $Fe_3O_4@SiO_2@mTiO_2$–$HN(CH_2CH_2NH_2)_2/Pd$ catalyst ([19]).

In Figure 2.7, synthetic steps are shown in the preparation of a novel nanocatalyst containing Fe_3O_4 as a core, coated by a thin layer of SiO_2, a mesoporous TiO_2 shell, functionalized with diethylenetriamine substituents and palladium nanoparticles dispersed on the surface and coordinated to organic groups.



Alcohol $\xrightarrow{\text{FSTNPd (0.05 g), O2 (1atm), toluene (5 mL), UV irradiation (365 nm), 80 °C}}$ Aldehyde or ketone

Entry	Reactant (alcohol)	Product (aldehyde or ketone)	Time (min)	Sel./Conv. (%/%)[a]	TOF (min^{-1})
1	Benzyl alcohol	Benzaldehyde	45	>99/99	0.44
2	4-Hydroxybenzyl alcohol	4-Hydroxybenzaldehyde	45	>99/99	0.44
3	2-Hydroxybenzyl alcohol	2-Hydroxybenzaldehyde	50	>99/98	0.39
4	2-Chlorobenzyl alcohol	2-Chlorobenzaldehyde	60	>99/81	0.27
5	4-Nitrobenzyl alcohol	4-Nitrobenzaldehyde	100	>99/78	0.16
6	4-Methoxybenzyl alcohol	4-Methoxybenzaldehyde	40	>99/98	0.49
7	4-Methylbenzyl alcohol	4-Methylbenzaldehyde	50	>99/97	0.39
8	3-Nitrobenzyl alcohol	3-Nitrobenzaldehyde	60	>99/80	0.27
9	2-Methyl-1-propanol	2-Methyl-propanal	110	>99/75	0.14
10	Cyclohexanol	Cyclohexanone	120	>99/79	0.13
11	Cyclopentanol	Cyclopentanone	120	>99/71	0.12

Reaction conditions: alcohol (1 mmol), toluene (5 mL), catalyst (0.05 g), O_2 (1 atm) flow and under UV irradiation (365 nm light from a 200 W Hg lamp) at 80 °C

[a] Selectivity and conversion determined by GC using biphenyl as an internal standard

Figure 2.8. Alcohols oxidation results ([19]).

In Figure 2.8 the results of different alcohols oxidation in a quartz vessel and stirred under O_2 flow (1 atm, purity >99%) at 80 °C under UV irradiation (365 nm light from a 200 W Hg lamp) are shown. The results are interesting due to their high selectivity in all cases and conversion which his higher for alcohols with electro donating groups rather than electro-withdrawing groups. Thanks to the catalyst magnetic properties, the authors points out that the catalyst can be reused for 10 consecutive times without any significant reduction in selectivity and conversion.

2.2.4 Microwave synthesis

Regarding the microwave as a method to synthesize core-shell composites, Alexander G. R. Howe *et al* published in 2018 in which the microwave is used to prepare core-sell Au/Pd composites ([20]). The authors synthesize a series of 1 wt% supported Au, Pd and Au/Pd nanoalloy catalysts via microwave assisted reduction of $PdCl_2$ and $HAuCl_4$. Moreover, the CSNPs show excellent stability during the hydroperoxide synthesis from H_2 and O_2 and non-catalytic deactivation is mentioned after 4 cycles of the recovered CSNP sample. Regarding the core-shell preparation, 1 wt% Pd, 1 wt% Au and bimetallic Au/Pd catalysts are prepared using a CEM Discover SP reactor. Moreover, TiO_2 is used as the support an aqueous stock solution of $PdCl_2$ and $HAuCl_4$ are prepared in 0.2 M HCl. The mixture undergoes to microwave treatment for 15 min at 150°C and stirred at 1200 RPM using a magnetic stirrer ([20]).

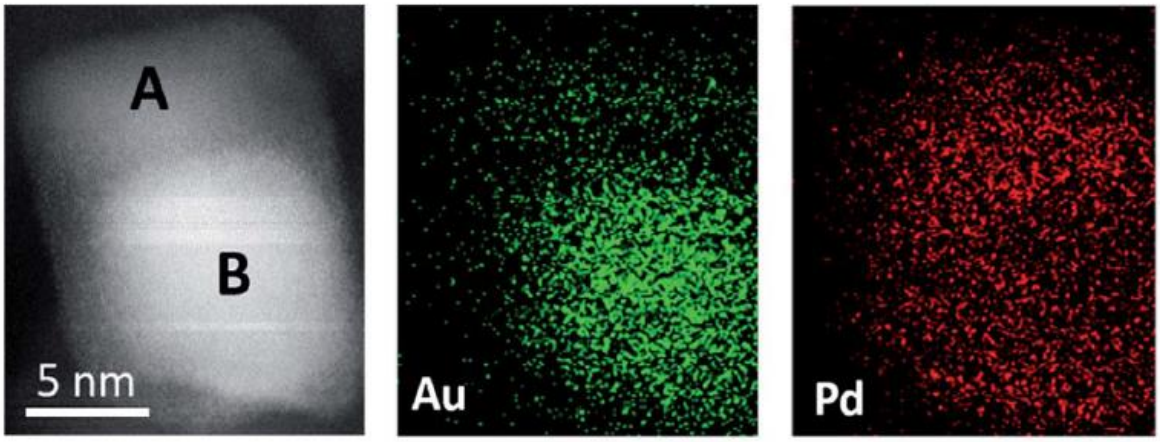


Figure 2.10. Representative STEM-HAADF image of 0.5Au–0.5Pd/TiO2 (20).

In Figure 2.10 it is shown the 0.5Au–0.5Pd/TiO_2 catalyst morphology thanks to STEM X-ray energy dispersive spectroscopy (X-EDS) in which it is clearly distinguished the gold core (B) and the palladium rich shell (A).

2.2.5 *Sol-gel Method*

The sol-gel method is one of the most used techniques to produce nanomaterials. In general, this method can be divided into two main steps. In the first step the metal salt or oxide are hydrolysed in solution to produce a colloidal suspension and in the second step, and that involves condensation and gelation, a 3d network is produced with an increased viscosity becoming a gel. Afterwards, the gel is processed by various drying methods to produce nanoparticles. By modifying the sol-gel method a serious of core-shell structures can be created. In this view, Hyun Sik Chae *et al* (2016), describe a sol-gel method based on a two-step process to synthetize iron oxide-silica in a core-shell structure. The structure and properties of this CSNP are fully characterized showing that the composite is a soft magnetic material. Furthermore, a magnetorheological (MR) suspension was prepared based on the synthesized Fe_3O_4@SiO_2 nanoparticles dispersed in silicone oil and mechanical properties were studied (21). The magnetic core is synthesized by means of a solvothermal method in which hydrated iron chloride and sodium acetate are dissolved in ethylene glycol and then transferred in a stainless-steel autoclave which is heated at 200°C for 12 h.

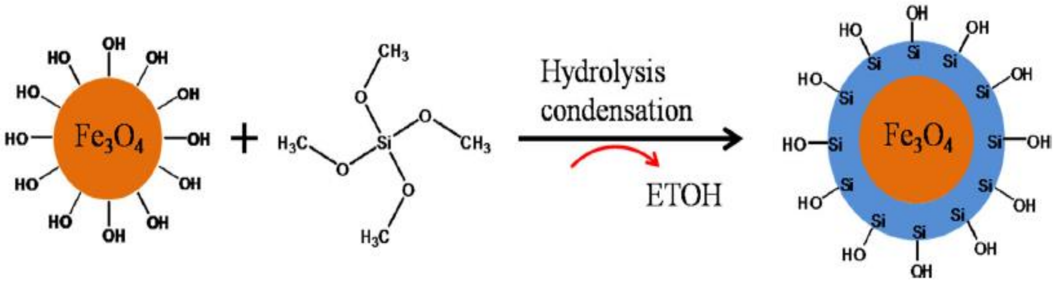


Figure 2.11. Synthetic procedure of $Fe_3O_4@SiO_2$ catalyst ([21]).

Once the particles were washed and dried, the sol-gel method is applied to coat the core with silica. More precisely, 4 g of Fe_3O_4 particles and 4 mL tetraethyl orthosilicate are added into 40 mL of deionized water and mixed using ultrasonication until it became a stable emulsion. Afterwards, the emulsion was added into a mixture of ethanol and ammonium hydroxide solution. The reaction solution was stirred at 400 RPM at room temperature for 4 h ([21]). TEM images are reported in Figure 2.12 where it is clearly visible that the $Fe_3O_4@SiO_2$ nanoparticles are of core-shell structure, in which the Fe_3O_4 nanoparticles have a mean diameter of roughly 200 nm and the average thickness of SiO_2 shell is approximately 40 nm.

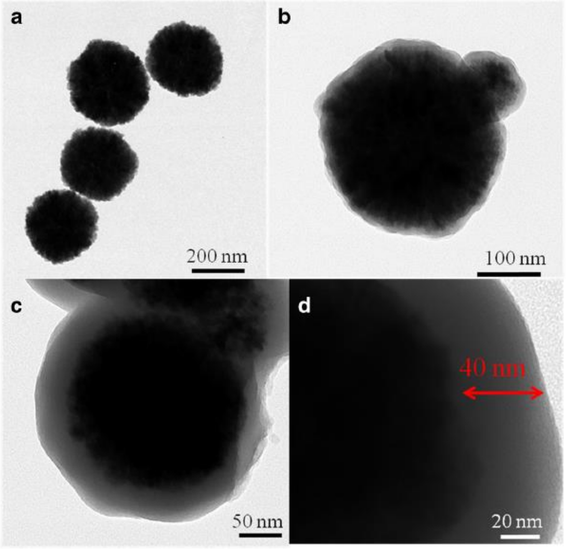


Figure 2.12. TEM image of $Fe_3O_4@SiO_2$ ([21]).

Regarding the sol-gel method to produce core-shell structures, a recent article reports a surface treatment process to synthesize, in situ, $Fe_3O_4@SiO_2$ ([22]). As in the previous article, the core is made with the same solvothermal method in which starting reagents are iron chloride and sodium acetate. Afterwards, the iron oxide nanoparticles are treated with an acid or a base causing changes in the shape of the spherical particles. More precisely, nanoparticles are dispersed in 500 mL of distilled water. This dispersion was sonicated for 30 min and once separated from the solution is stirred in various amounts of 2 N aqueous ammonia solution or a hydrochloric acid solution. In Figure 2.13 the FE-SEM images are shown to put in evidence that the morphological changes in the nanoparticles depend upon the acid or base concentration. Due to the described treatment, magnetic properties also change depending on the acid/base concentration.

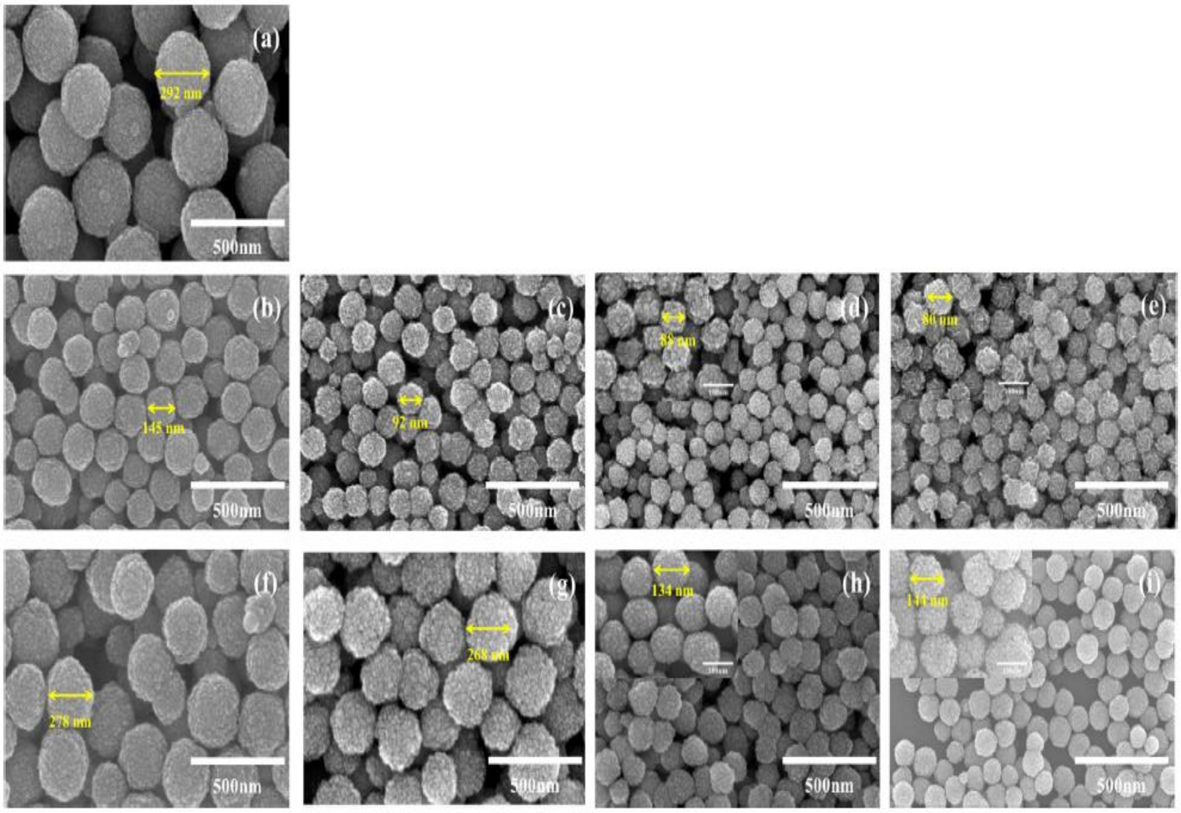


Figure 2.13. FE-SEM images of (a) as-prepared Fe_3O_4 nanoparticles, (b) 0.5 M acid, (c) 1 M acid, (d) 3 M acid, (e) 5 M acid, (f) 0.5 M base, (g) 1 M base, (h) 3 M base and (i) 5 M based-treated Fe_3O_4 nanoparticles ([22]).

Furthermore, the authors established the optimum surface treatment conditions for silica deposition on nanoparticles using a sol-gel reaction without undergoing a washing procedure in order to remove the organic residuals. Finally, to coat the nanoparticles 3 mL of tetraethyl orthosilicate are dissolved in 100 mL of ethanol. This precursor solution was charged into a suspension containing the surface treated nanoparticles and in Figure 2.14 the core-shell structure is shown.

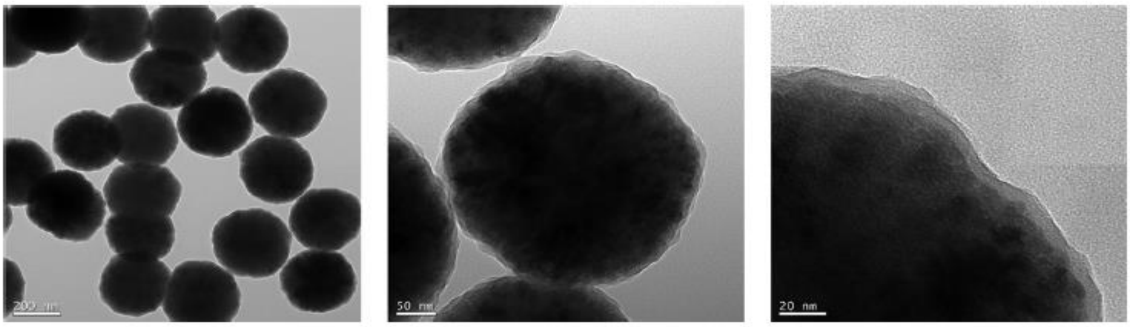


Figure 2.14. HR-TEM images of $Fe_3O_4@SiO_2$ (22).

About 8 nm of a single coating layer was homogeneously formed due to excellent initial dispersibility of Fe_3O_4 nanoparticles according to the modified surface characteristics.

2.3 Experimental synthesis of copper based catalysts

The materials that are used as reagents to produce different types of catalyst are commercial salts and oxides. None of the reagents are significantly sensitive to air or moisture and therefore they were handled in normal ambient/lab conditions without any previous purification steps. Table 2.1 reports the reagents that were used. Reagents were weighted and directly added to the grinding jars.

Table 2.1. Main characteristics of the reagents used in this work.

Compound	Colour	Purity	Molecular Weight [g/mol]	STATE	Firm
Pentahydrate copper (II) sulphate $CuSO_4·5H_2O$	Blue	99.5%	249.69	Solid	Carlo Erba
Vanadium oxide V_2O_5	Grey with metallic lustre	100%	181.88	Solid	Sigma Aldrich
Hexahydrate iron (III) chloride $FeCL_3·6H_20$	Yellow	97%	270.3	Solid	Alfa Aesar
Activated carbon	Black	100%	12.01	Solid	Panreac
Graphite	Black	100%	12.01	Solid	Sigma Aldrich

The catalysts that have been synthetized are divided in the following subchapters, depending on the composition or on the type of green solvent used.

2.3.1 Copper sulphate and additive in solvent free conditions

The first catalysts to be prepared are made of copper sulphate and an additive (total mass 200 mg) in solvent free systems. Initially, the tested additive is graphite, a crystalline allotrope of carbon and the most stable form of carbon under standard conditions. Secondly, activated carbon is used as additive due to its small volume pores that increase the surface area available for adsorption or chemical reactions.

During the dry milling treatment, the reagents are mixed mechanically for 1 hour in the planetary ball mill reactor, equipped with a 50 mL grinding bowl and 10 stainless steel balls of 5 mm radius. Moreover, the grinding jars rotational speed is 500 RPM and every 5 minutes the direction is changed from clockwise to anticlockwise.

Finally, the produced catalysts are tested in order to verify magnetic properties that may arise during mixing, because of possible changes in the oxidation state of the metal, especially for iron. The followed procedure is the Gouy balance which is extremely fast but at the same time makes it easy to detect magnetic properties. Each eppendorf is passed close to a very strong magnet that will induce catalysts powder movements if affected by the magnetic field. In the case of magnetic properties, the catalyst could be easily recovered and recycled, but studies in the catalytic activity should be carried out to understand if recycling is a convenient strategy. In this view, each catalyst is tested but no magnetic properties are detected. Finally, Table 2.2 shows in detail the composition of each test. The molecular weight showed in the all the Tables is a result of the fractional contribution of each reagent that were used in the mixtures. At the same time, in all Tables the reported ratio refers to anhydrite reagents.

Table 2.2. Composition details of pentahydrate copper *sulphate and carbon.*

N°	Reagent 1	Mass 1 [mg]	Reagent 2	Mass 2 [mg]	Molecular Weight [g/mol]
1	$CuSO_4 \cdot 5H_2O$	180.2	graphite	20.4	82.8
2	$CuSO_4 \cdot 5H_2O$	189.5	graphite	10.1	124.7
3	$CuSO_4 \cdot 5H_2O$	198	graphite	2.2	205.1
4	$CuSO_4 \cdot 5H_2O$	180	activated carbon	19.5	85.1
5	$CuSO_4 \cdot 5H_2O$	189.4	activated carbon	10.6	125.6
6	$CuSO_4 \cdot 5H_2O$	197.6	activated carbon	2.4	201.7

2.3.2 Copper sulphate and vanadium oxide in solvent free conditions

Bi-metallic particles are prepared in the ball milling reactor. Catalysts composition is related to a precise mass and molar ratio, more precisely it is considered a 2:1 and 1:2 ratio. Moreover, the total mass is close to 200 mg, to avoid reagents waste.

During the dry milling treatment, the reagents are mixed mechanically for 1 hour in the planetary ball mill reactor, equipped with a 50 mL grinding bowl and 10 stainless steel balls of 5 mm radius. Moreover, the grinding jars rotational speed is 500 RPM and every 5 minutes the direction is changed from clockwise to anticlockwise.

Finally, each bi-metallic catalyst is tested in order to detect magnetic properties that may pop up during ball milling. Nevertheless, the produced catalysts are completely non-magnetic and in Table 2.3 reagents weights are shown for every synthesized sample.

Table 2.3. Composition details of pentahydrate copper sulphate and vanadium oxide. Entry 7 and 8 are calculated in mass ratio (2:1 and 1:2) while entry 9 and 10 in molar ratio (2:1 and 1:2).

N°	Reagent 1	Mass 1 [mg]	Reagent 2	Mass 2 [mg]	Molecular Weight [g/mol]
7	$CuSO_4{\cdot}5H_2O$	133.7	V_2O_5	66.8	221.8
8	$CuSO_4{\cdot}5H_2O$	66.6	V_2O_5	133.4	199.5
9	$CuSO_4{\cdot}5H_2O$	149.6	V_2O_5	54.5	227.8
10	$CuSO_4{\cdot}5H_2O$	74.7	V_2O_5	109.3	204.4

2.3.3 Synthesis of copper sulphate and vanadium oxide in a green solvent

Also, in this case, bi-metallic catalysts are prepared from copper sulphate and vanadium oxide. Nevertheless, 0.5 mL of water is added once the reagents are weighted and directly added to the grinding jars. The green solvent is used to promote the formation of chemical bonds during mixing in order to improve the mechanochemical method. In this view, solvent may enhance bonds formation because it increases the probability of continuous contacts between copper sulphate and vanadium oxide (Solid-Solid reaction) that may induce chemical bonds. Nevertheless, solvent pollutes the catalysts even if water is used since it is necessary to remove it after the ball milling procedure. Indeed, each solid-liquid solution are peaked up, put in an Eppendorf, and left with the cap open, so water evaporates spontaneously. Otherwise, samples are placed in an oven (60°C) to increase drying speed.

During this wet milling treatment, the reagents are mixed mechanically for 1 hour in the planetary ball mill reactor, equipped with a 50 mL grinding bowl and 10 stainless steel balls of 5 mm radius. Moreover, the grinding jars rotational speed is 500 RPM and every 5 minutes the direction is changed.

Finally, each bi-metallic catalyst is tested in order to detect magnetic properties that may appear during ball milling. Nevertheless, the produced catalysts are completely non-magnetic and the experiments are reported in Table 2.4.

Table 2.4. Composition details of pentahydrate copper sulphate and vanadium oxide. Entry 11 and 12 are calculated in mass ratio (2:1 and 1:2) while entry 13 and 14 in molar ratio (2:1 and 1:2).

N°	**Reagent 1**	**Mass 1 [mg]**	**Reagent 2**	**Mass 2 [mg]**	**Molecular Weight [g/mol]**
11	$CuSO_4{\cdot}5H_2O$	133.3	V_2O_5	66.2	221.9
12	$CuSO_4{\cdot}5H_2O$	66.2	V_2O_5	133.1	199.5
13	$CuSO_4{\cdot}5H_2O$	149.4	V_2O_5	54.5	227.3
14	$CuSO_4{\cdot}5H_2O$	74.5	V_2O_5	108.7	204.25

2.3.4 Copper sulphate, vanadium oxide and additive in solvent free conditions

In this case copper sulphate/vanadium-based catalyst are mixed together with an additive. The two additives that are used are graphite and activated carbon. The additive concentration with respect the total mass is 1% w/w only.

During the dry milling treatment, the reagents are mixed mechanically for 1 hour in the planetary ball mill reactor, equipped with a 50 mL grinding bowl and 10 stainless steel balls of 5 mm radius. Moreover, the grinding jars rotational speed is 500 RPM and every 5 minutes the direction was changed from clockwise to anticlockwise. Finally, magnetic property has been verified but none of the samples are magnetic. The experiments are reported in Table 2.5.

Table 2.5. Composition details of pentahydrate copper sulphate, vanadium oxide and additive. Entry 15 and 17 are with a 2:1 molar ratio while entry 16 and 18 with a 1:2.

N°	Reagent 1	Mass 1 [mg]	Reagent 2	Mass 2 [mg]	Additive	Mass 3 [mg]	Molecular Weight [g/mol]
15	$CuSO_4{\cdot}5H_2O$	187.7	V_2O_5	68.5	graphite	2.6	221.9
16	$CuSO_4{\cdot}5H_2O$	93.9	V_2O_5	136.6	graphite	2.3	199.5
17	$CuSO_4{\cdot}5H_2O$	187.7	V_2O_5	68.3	activated carbon	2.5	227.3
18	$CuSO_4{\cdot}5H_2O$	93.8	V_2O_5	136.6	activated carbon	2.3	204.25

2.3.5 Copper sulphate, vanadium oxide and additive in a green solvent

The last copper sulphate-based catalysts are prepared together with vanadium oxide, water and an additive. As usual, two different carbon-based additives are mixed with the reagents: graphite and activated carbon. Moreover, each additive has been tested at 1/5/10 % in weight with respect the total mass.

During the wet milling treatment, the reagents are mixed mechanically for 1 hour in the planetary ball mill reactor, equipped with a 50 mL grinding bowl and 10 stainless steel balls of 5 mm radius. Moreover, the grinding jars rotational speed is 500 RPM and every 5 minutes the direction is changed.

Finally, each bi-metallic catalyst is tested in order to detect magnetic properties that may appear during ball milling. Nevertheless, the produced catalysts are completely non-magnetic. The experiments are reported in Table 2.6.

Table 2.6. Composition details of pentahydrate copper sulphate, vanadium oxide and additive. Entry 19,21,23,25, 27 and 29 are with a 2:1 molar ratio while entry 20,22,24,26,28 and 308 with a 1:2.

N°	Reagent 1	Mass 1 [mg]	Reagent 2	Mass 2 [mg]	Additive	Mass 3 [mg]	Molecular Weight [g/mol]
19	$CuSO_4 \cdot 5H_2O$	187.5	V_2O_5	68.1	activated carbon	2.6	192.67
20	$CuSO_4 \cdot 5H_2O$	93.7	V_2O_5	136.7	activated carbon	2.4	175.4
21	$CuSO_4 \cdot 5H_2O$	187.9	V_2O_5	68	graphite	2.5	192.6
22	$CuSO_4 \cdot 5H_2O$	93.9	V_2O_5	136.4	graphite	2.4	175.5
23	$CuSO_4 \cdot 5H_2O$	188	V_2O_5	68.3	graphite	12.4	124.1
24	$CuSO_4 \cdot 5H_2O$	93.5	V_2O_5	136.9	graphite	11.5	115.9
25	$CuSO_4 \cdot 5H_2O$	187.5	V_2O_5	68.5	graphite	25.4	85.4
26	$CuSO_4 \cdot 5H_2O$	93.56	V_2O_5	136.4	activated carbon	23.3	81.3
27	$CuSO_4 \cdot 5H_2O$	187.6	V_2O_5	68.3	activated carbon	12.7	121.7
28	$CuSO_4 \cdot 5H_2O$	93.8	V_2O_5	136.5	activated carbon	11.5	115.9
29	$CuSO_4 \cdot 5H_2O$	187.7	V_2O_5	68.2	activated carbon	26.7	83
30	$CuSO_4 \cdot 5H_2O$	93.6	V_2O_5	136.5	activated carbon	22.9	82.9

2.4 Experimental synthesis of iron based catalysts

New catalysts are made by mixing hexahydrate iron chloride and graphite/activated carbon (total mass 200 mg). Also, for this type of composites, additives concentration is 1/5/10% with respect the total mass.

Even if, the metal salt is changed, ball milling conditions are not changed. Thus, during the dry milling treatment, the reagents are mixed mechanically for 1 hour in the planetary ball mill reactor, equipped with a 50 mL grinding bowl and 10 stainless steel balls of 5 mm radius. Moreover, the grinding jars rotational speed is 500 RPM and every 5 minutes the direction was changed. Finally, each metallic catalyst is tested in order to detect magnetic properties that may appear during ball milling. Nevertheless, the produced catalysts are completely non-magnetic. The experiments are reported in Table 2.7.

Table 2.7. Composition details of hexahydrate iron chloride and additive.

N°	Reagent 1	Mass 1 [mg]	Reagent 2	Mass 2 [mg]	Molecular Weight [g/mol]
31	$FeCl_3 \cdot 6H_2O$	198.1	graphite	2.5	216.06
32	$FeCl_3 \cdot 6H_2O$	190.7	graphite	10.2	128.2
33	$FeCl_3 \cdot 6H_2O$	180.2	graphite	20.3	84.33
34	$FeCl_3 \cdot 6H_2O$	198.2	activated carbon	1.9	223.8
35	$FeCl_3 \cdot 6H_2O$	190.4	activated carbon	10.4	125.6
36	$FeCl_3 \cdot 6H_2O$	179.4	activated carbon	20.3	84.8

2.4.1 Iron chloride and vanadium oxide in solvent free conditions

Bi-metallic catalysts are prepared by mixing iron chloride and vanadium oxide. Metal salt and metal oxide are added to the grinding jars considering 2:1 and 1:2 molar ratio.

During the dry milling treatment, the reagents are mixed mechanically for 1 hour in the planetary ball mill reactor, equipped with a 50 mL grinding bowl and 10 stainless steel balls of 5 mm radius. Moreover, the grinding jars rotational speed is 500 RPM and every 5 minutes the direction was changed. Finally, no magnetic properties appeared after mechanochemical mixing. The experiments are reported in Table 2.8.

Table 2.8. Composition details of hexahydrate iron chloride and vanadium oxide.
Entry 37 is with a 2:1 molar ratio while entry 38 with a 1:2.

N°	Reagent 1	Mass 1 [mg]	Reagent 2	Mass 2 [mg]	Molecular Weight [g/mol]
37	$FeCl_3 \cdot 6H_2O$	200.7	V_2O_5	67.5	240.8
38	$FeCl_3 \cdot 6H_2O$	100.8	V_2O_5	134.6	211.5

2.4.2 Iron chloride and copper sulphate in solvent free conditions

Finally, bi-metallic catalysts are made from two metal salts and have been added to the grinding jars considering 2:1 and 1:2 molar ratio. Also, in this case, the molar ratio refers to anhydrous reagents even if the used reagents are hydrate.

During the dry milling treatment, the reagents are mixed mechanically for 1 hour in the planetary ball mill reactor, equipped with a 50 mL grinding bowl and 10 stainless steel balls of 5 mm radius. Moreover, the grinding jars rotational speed is 500 RPM and every 5 minutes the direction was changed. Finally, no magnetic properties appeared after mechano-chemical mixing but changes in the oxidation state occur. The experiments are reported in Table 2.9.

Table 2.9. Composition details of hexahydrate iron chloride and pentahydrate copper sulphate.
Entry 39 is with a 2:1 molar ratio while entry 40 with a 1:2.

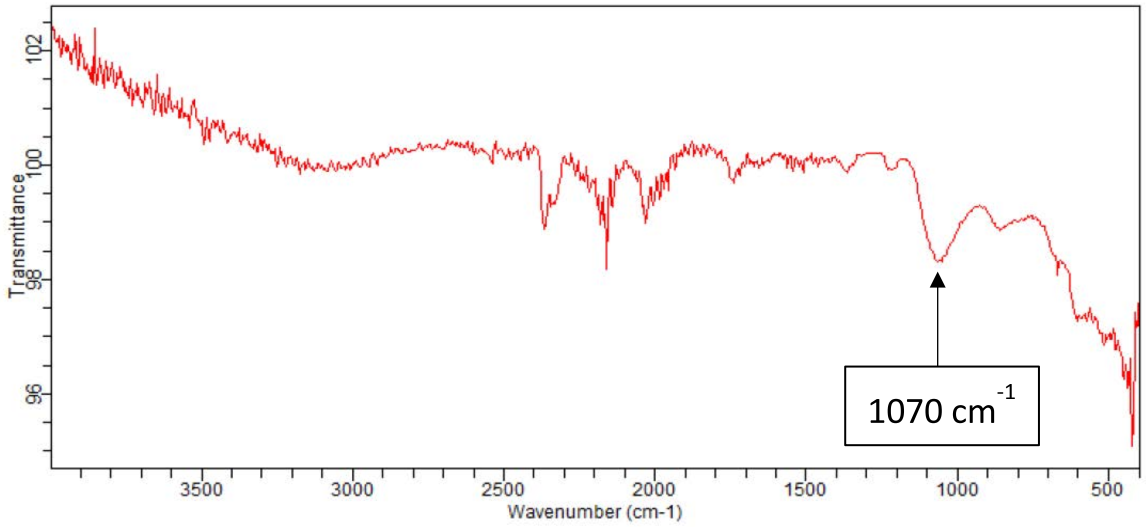
N°	Reagent 1	Mass 1 [mg]	Reagent 2	Mass 2 [mg]	Molecular Weight [g/mol]
39	$FeCl_3 \cdot 6H_2O$	200.7	$CuSO_4*5H_2O$	92.4	263.4
40	$FeCl_3 \cdot 6H_2O$	100.7	$CuSO_4*5H_2O$	184.7	256.5

2.5 FTIR-ATR analysis

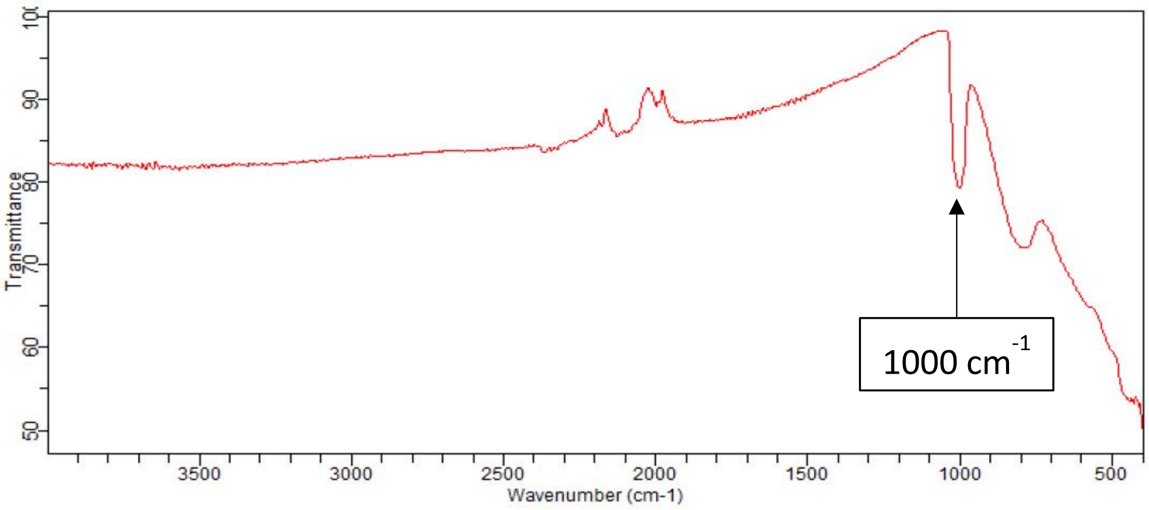
The dispersed catalytic materials are then characterized by infrared spectroscopy (FTIR) that provides specific information about the chemical composition throughout signal analysis concerning the transitional vibrations of chemical bonds. Such analysis is carried out with a Cary 630 FTIR Spectrometer from Agilent.

Each sample are analysed by FTIR in order to detect the chemical bonds resonance frequency in the mid-infrared region (4000 and 400 cm^{-1}). Most of the samples spectra are reported in Annex A. The catalyst spectrum is then compared with the one of the reagents. The comparison between them will allow to reveal the presence of new chemical bonds. The aim of this analysis is to verify if the ball milling procedure induces chemical reactions and therefore new bonds between reagents due to kinetic and heat energy that are provided by the mechanical treatment. Moreover, it is expected to easier detect new bonds in solid-liquid mixing thanks to the green solvent (H_2O) that enhances solids contact, so the probability of new bonds increases. Nevertheless, solvent pollutes the catalyst since it must be extracted from the solid. Indeed, new bonds formation from solid-solid mixing would turn to be the best solution.

From the comparison between the pure reagents spectroscopy and each catalyst spectra, no difference is detected. Figure 2.15 reports the spectroscopy of catalysts n°22 which is mixture of copper sulphate, vanadium oxide and graphite. Comparing Figure 2.15 with the pure reagents spectra, it is confirmed that peaks represent already existing bonds thus, no new structures appear. In other words, the dispersed materials are a mixture of reagents powder.



(a)



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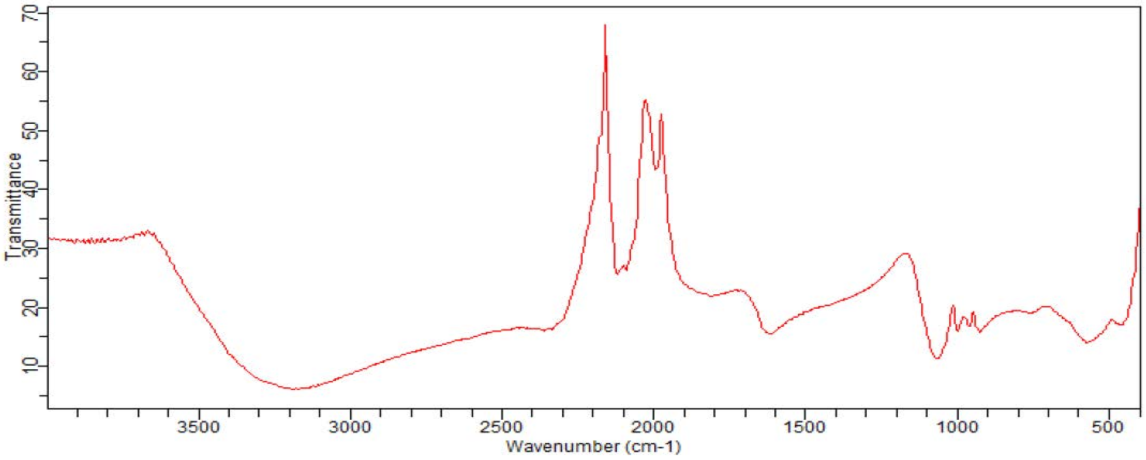


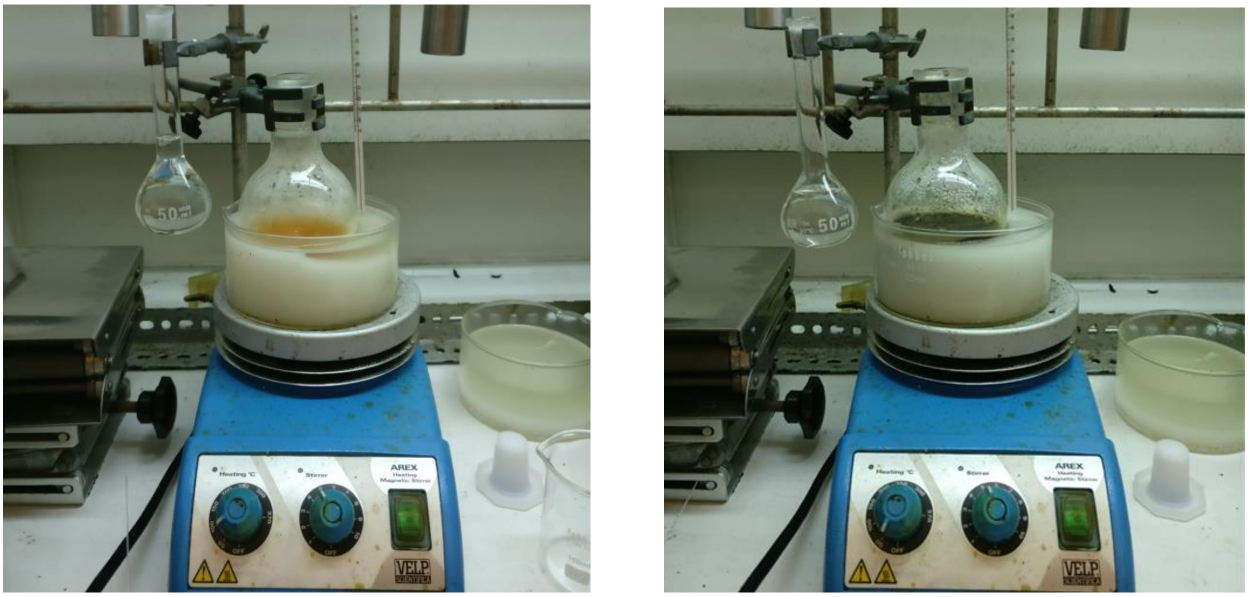
(c)

Figure 2.15. Comparison between the spectra of pentahydrate copper sulphate (a), vanadium oxide (b), and the synthesized compound n°22.

Characterizing the spectroscopy from right to left, it is stated that the catalyst spectra is an overlap of the reagents one the first peak that appears in the catalyst spectroscopy is of 1000 cm^{-1}, which also appears in vanadium oxide spectrum. Then, a second peak appears close to 1000 cm^{-1}, more precisely 1070 cm^{-1}, which also characterizes copper sulphate spectrum. Instead, peaks placed between 2000 and 2500 cm^{-1} concern to triple bond stretching, more precisely carbon monoxide stretching present in the air. Moreover, the air moisture also causes a second peak, at 3200 cm^{-1} because of the presence of water.

2.6 Preparation of Fe_3O_4@TiO_2 by reduction of metal salts

The objective is to create a core-shell system in order to coat metallic nanoparticles with TiO_2. This procedure was chosen because it does not use harsh chemicals and it is carried out below 100°C. For this procedure, a round bottom flask (250mL) is filled with 80 mL of distilled water, 1 mmol of iron(II) sulfate hexahydrate and 2 mmol of iron(III) chloride, and then, stirred at 50°C. In order to heat and stir at the same time, the round bottom flask is immersed in an oil bath and placed on a magnetic stirrer. At the same time, a 1 M sodium hydroxide solution is prepared.



(a) (b)

Figure 2.16. Acid solution with pH=3 (a), basic solution with pH=10 (b).

The aim was to add dropwise the basic solution in the metal one until it reached a pH of 10 (dark solution), as in Figure 2.16. The reason for the pH to be is adjusted is to convert the dissolved (ionic) metals into insoluble nanoparticles of Fe_3O_4. During the sodium hydroxide injections, the pH is measured every 15/20 droplets until the solution started to become black which meant that nanoparticles were created, and the solution approached basicity. Once the solution reaches pH 10, it is removed from the magnetic stirrer to cool down to room temperature and from Figure 2.17 it is possible to detect nanoparticles depositing in the flask bottom

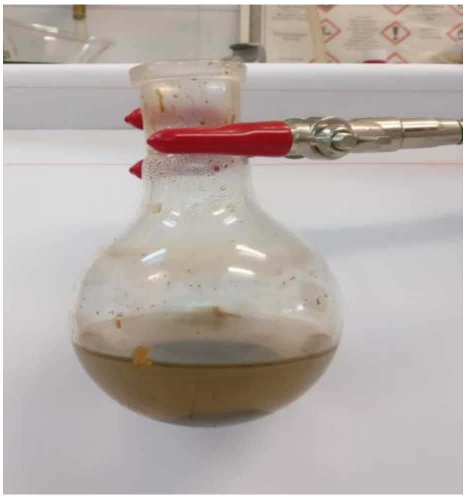


Figure 2.17. Nanoparticles depositing in the flask bottom once the solution is cooled.

Finally, the dispersed particles must be separated from the solution, washed with distilled water, and completely dried. Thanks to the magnetic property of the nanoparticles, the washing procedure is simplified. A strong magnet is placed in the flask bottom so, magnetic particles did not follow the solution while pouring it. Secondly, distilled water is added until the pH became neutral in order to stabilize the nanoparticles, which are separated, and finally placed in an oven at 60°C to dry completely. Once the magnetic nanoparticles were completely dry, a mortar and pestle were used to prepare a powder by crushing and grinding them.

Once the magnetic nanoparticles are pulverized, the objective is to coat them with TiO_2. The core-shell system is created adding 100 mg of magnetic nanoparticles in 250 mL of dry ethanol and 1 mL of titanium isopropoxide solution. The round-bottom flask that contains the mixture is magnetically stirred at 600 RPM and heated at 75°C.

Figure 2.18. Reflux system to avoid the loss of ethanol during core-shell synthesis.

Moreover, a reflux system, as shown in Figure 2.18, is placed on the flask neck to avoid losing ethanol due to evaporation. During mixing 7 mL of dry ethanol and 1 mL of distilled water are added. The solution is mixed for 18 h and afterwards it is removed from the magnetic-heating system to cool down to room temperature. The core-shell particles are removed from the solution by filtration, dried in the oven at 60°C overnight and stored.

2.7 Experimental synthesis of Metal Organic Frameworks

Microporous and mesoporous metal-organic frameworks (MOFs) are a recent class of crystalline materials, which are currently of great interest for different types of applications such as sorption, separation, catalysis and sensor technology. Besides the important results obtained in the area of high surface materials, many groups are focused on the synthesis of new materials for catalysis applications. By following the procedure described by Klimakow *et al*, a mechanochemical approach is proposed as an alternative synthetic green route for MOFs preparation (1).

Mechanochemical synthesis is carried out in an Emax 2000, Retsch GmbH, ball mill reactor via the liquid assisting grinding of fine particles of copper acetate monohydrate and 1,3,5-benzenetricarbocylic acid (H_3BTC), respectively in a 3:2 molar ratio, as shown in Figure 2.19. The synthesis is carried out using a 50 ml stainless steel grinding jar and 5 stainless steel balls of 10 mm diameter. The objective is to reproduce the metal-organic framework, named HKUST-1 which was synthesized by Hong Kong University of Science and Technology.

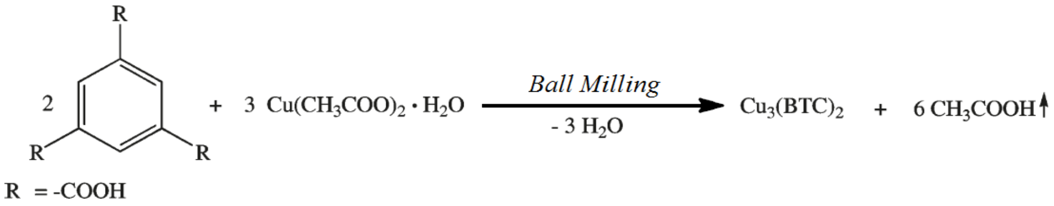


Figure 2.19. HKUST-1 reaction mechanism (1).

For the synthesis of this type of MOF copper acetate monohydrate (0.57 g) and H_3BTC (0.4 g) are placed in the grinding jar together with 5 stainless steel balls at 1500 RPM for 10 min. As shown in Figure 2.20, the colour of the powder turned into turquoise accompanied by a release of acetic acid (by-product).

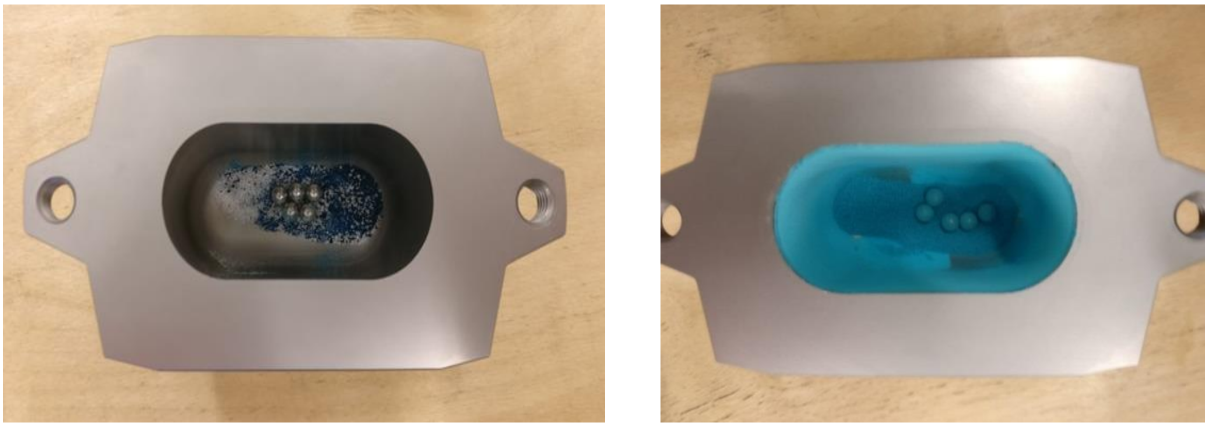

(a) (b)

Figure 2.20. Copper acetate monohydrate and H_3BTC before the mechanochemical mixing (a), and after the treatment (b).

Afterwards, a small amount of pure ethanol (1 mL) is added in order to assist the reaction and the mixture was further grinded for 15 min at 1500 RPM. The sample is then dried in oven at 60°C. The synthesized MOF is then characterized with FTIR, elemental analysis and SEM-EDS. The MOF spectroscopy is reported in Annex A. Comparing both characterization techniques with the ones published by, it is stated that the synthesized MOF corresponds to HKUST-1. The elemental analysis of the synthesized MOF and the HKUST-1 are reported in Table 2.10.

Table 2.10. Elemental analysis (mass %) and comparison between the synthesized MOF and HKUST-1

Element	Synthesized MOF	HKUST-1 (**)
Copper (*)	18.8%	-
Carbon	32.7%	29.63%
Hydrogen	3.15%	3.112%

(*) is not included in the scope of the LAIST accreditation.
(**) composition reported from Klimakow *et al [14].*

Klimakow *et al* article does not provide the copper percentage. The external surface is characterized by SEM analysis, as shown in Figure 2.21.

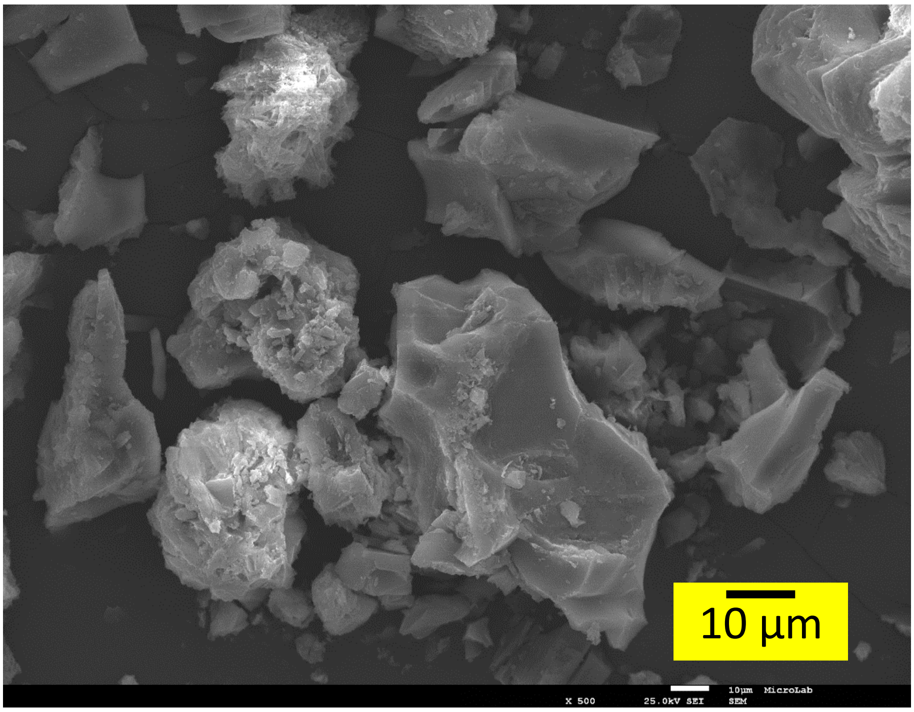


Figure 2.21 SEM image of HKUST-1.

Figure 2.21 shows an inhomogeneous size distribution of the particles and distinct crystal habitus and it is possible to state that the grinding process created microscopic composites with size that ranges from bulk to 10 µm while the corresponding EDS shows the presence of the metal with a mass composition that is almost equal to the theoretical quantities (Table 2.11).

Table 2.11. EDS analysis (mass %) and comparison between the synthesized MOF and HKUST-1 theoretical composition.

Element	**EDS analysis**	**HKUST-1 Theoretical composition**
Copper	32.87%	28%
Carbon	30.37%	32.81%
Oxygen	36.75%	37.36%

Finally, it is possible to state that the synthesized MOF corresponds to HKUST-1. Another proof is shown in Table 2.11, in which the composition determined by EDS analysis is almost equal to the theoretical composition of HKUST-1 which states that the elements are well dispersed.

2.7.1 Preparation of supported Metal Organic Frameworks

A serious of catalysts are synthesized by mechanochemical treatment in an Emax 2000, Retsch GmbH, ball mill reactor via the liquid assisting grinding fine particles of HKUST-1. The procedure was repeated for each type of catalysts and consists in grinding HKUST-1 for 1 min at 1500 RPM. Afterwards, a precise amount of another compound is added and the mixture is grinded for 5 min at 1500 RPM. Each synthesis required 5 stainless steel balls of 10 mm of diameter that are placed in 50 mL stainless steel jars. The supported MOFs are reported in the Table 2.12.

Table 2.12. Composition of HKUST-1 supported with core, core-shell and titanium isopropoxide.

Name	Reagent 1	Mass 1 [mg]	Reagent 2	Mass 2 [mg] or [mL]
HKUST-1/ Fe_3O_4@TiO_2	HKUST-1	150 mg	Fe_3O_4@TiO_2	150 mg
HKUST-1/ $C_{12}H_{28}O_4Ti$	HKUST-1	350 mg	Titanium isopropoxide	1 mL
HKUST-1/ Fe_3O_4	HKUST-1	50 mg	Fe_3O_4	50 mg

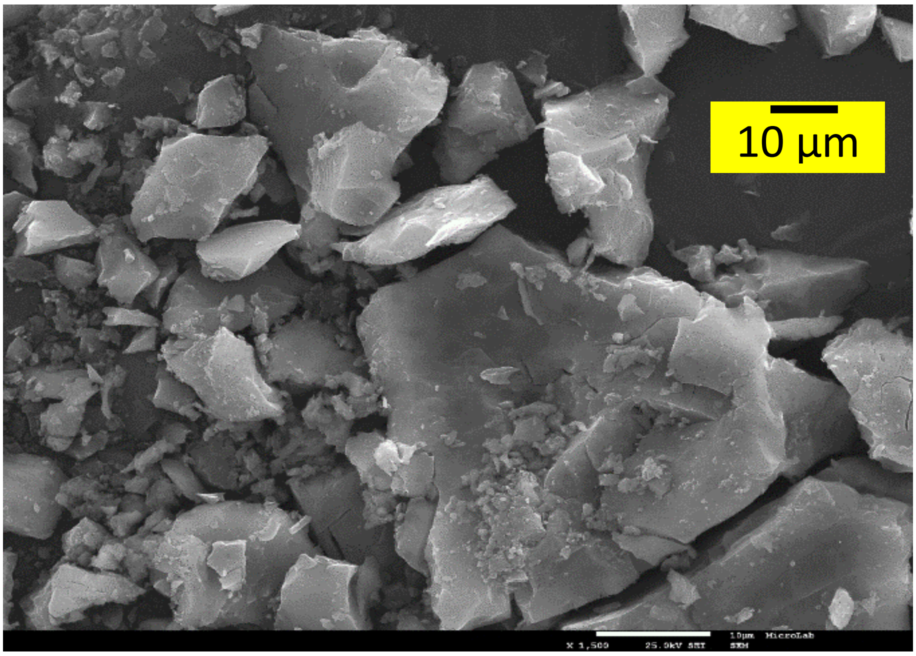
The supported MOFs have been characterized by elemental analysis and SEM-EDS. Regarding the elemental analysis of the 3 compounds, Table 2.13 shows the mass quantity of each element (oxygen is not detected by the equipment).

Table 2.13. Elemental analysis (mass %) of supported HKUST-1 compounds.

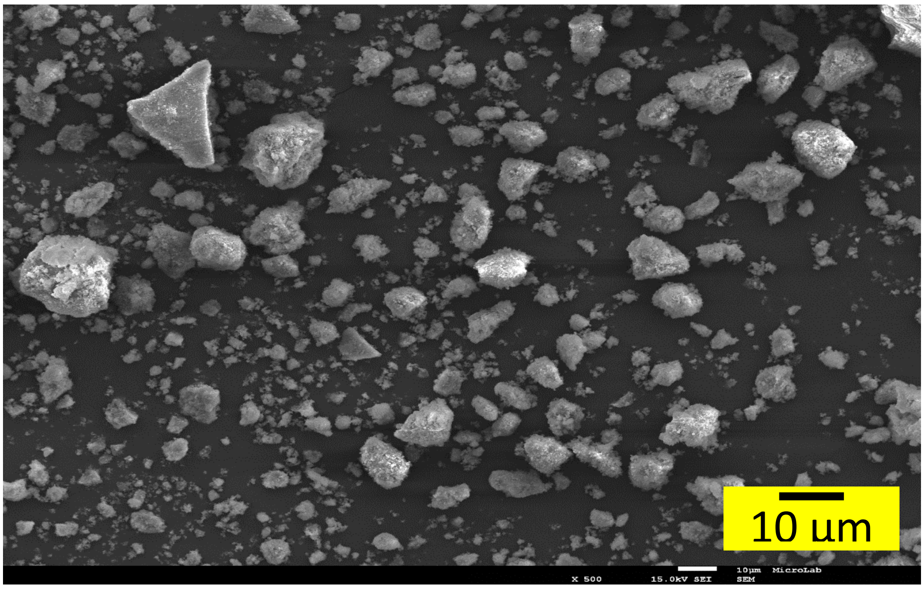
Element	**HKUST-1/ $Fe_3O_4@TiO_2$**	**HKUST-1/ $C_{12}H_{28}O_4Ti$**	**HKUST-1/ Fe_3O_4**
Copper (*)	11.4%	9.6%	14.1%
Carbon	17.82%	21.48%	21.41%
Hydrogen	2.3%	2.84%	2.30%
Iron (*)	4.9%	-	21%
Titanium (*)	14.8%	18.3%	-

(*) is not included in the scope of the LAIST accreditation

Furthermore, the surface of the synthesized supports is characterized by SEM. Figure 2.22 states that from the grinding process microscopic compounds are obtained with sizes that reach a minimum of 10 µm.



(a)



(b)

Figure 2.22. SEM image of HKUST-1 supported with titanium isopropoxide (a) and HKUST-1 supported with $Fe_3O_4@TiO_2$ (b).

Comparing the images reported in Figure it is possible to affirm that the HKUST-1 supported with $Fe_3O_4@TiO_2$ creates a more homogeneous composite than the HKUST-1 supported with titanium isopropoxide even tough clear bulk agglomerations are visible. Finally, the samples are characterized by EDS analysis. The elements mass percentages are reported in Table 2.14.

Table 2.14. EDS analysis (mass %) of supported HKUST-1.

Element	**HKUST-1/ $Fe_3O_4@TiO_2$**	**HKUST-1/ $C_{12}H_{28}O_4Ti$**
Copper	11.67%	6.18%
Carbon	25.6%	17.34%
Oxygen	42.69%	50.87%
Iron	3.98%	-
Titanium	16.06%	25.61%

Analysing Table 2.14 it is stated that for both composites the elements are well dispersed on the surface but this characterization cannot be extended to the samples internal composition because of the agglomerations that for both compounds are formed.

CHAPTER 3

Oxidation of cyclohexane and 1-phenylethanol

Chapter 3 is dedicated to the application of compounds which are synthesized in Chapter 2 and some not directly synthesized in this work, as catalysts for the oxidation of organic substrates such as alkanes and alcohols with green oxidants (*tert*-Butyl hydroperoxide solution 70% in H_2O, $K_2S_2O_8$ or even O_2). Reactions take place in the ball milling equipment or in the microwave reactor. In this view, the influence of reaction parameters (catalyst type and loadings, operating conditions and additives) will be studied for the most promising systems and results will be compared. The procedure that has been followed in this Chapter is shown in Figure 3.1.

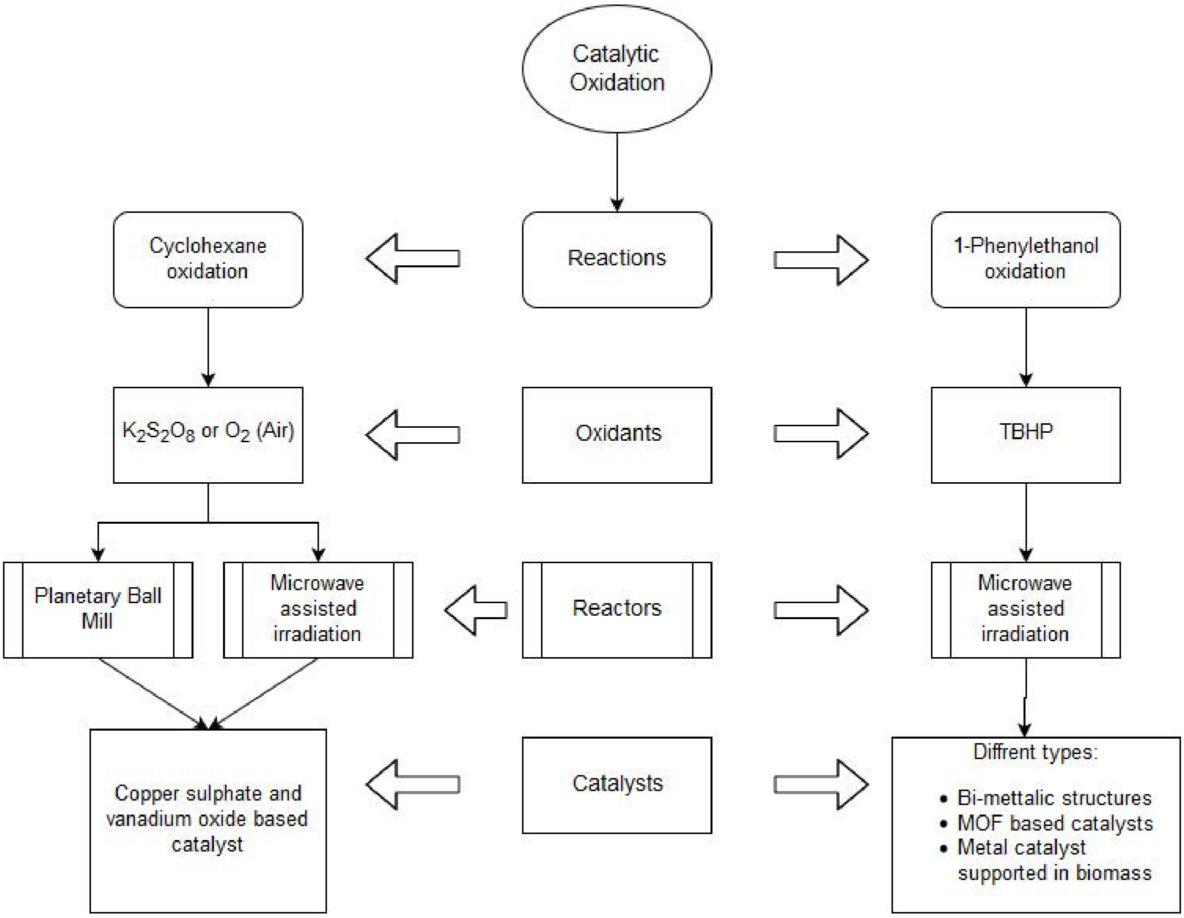


Figure 3.1. Schematic view of the procedure followed in this chapter.

3.1 Reactors

The studied reactions occur in two types of reactors that differ for the energy input and stirring conditions. Both can be considered as batch reactors therefore, reagents and products composition change in time and they do not deliver the products continuously but it in discrete amounts. The first type of reactor unit is the PM 100, Retsch GmbH, planetary ball mill, that is used to synthesize the metal-based composites obtained by mechanochemical treatment (Figure 2.1).

The second type of reactor is a Monowave 300 by Anton Paar GmbH (Figure 3.2), a high-performance microwave reactor specially designed for small scale microwave synthetic applications. The two main differences with respect the ball milling equipment are the stirring and microwave heating techniques. Indeed, an adjustable high-performance magnetic stirring device provides agitation at any time, enhancing the quality of chemical transformations. The magnetic stirring mechanism consists on a magnetic bean placed inside the pyrex tube (G10) that mixes the solution thanks to an invertible magnetic field.

Figure 3.2. Monowave 300 by Anton Paar GmbH.

Microwave is a form of electromagnetic radiation with wavelengths ranging from about one meter to one millimeter; with frequencies between 300 MHz (1 m) and 300 GHz (1 mm). Microwave chemistry is based on the efficient heating of materials by “microwave dielectric heating” effects. This phenomenon is dependent on the ability of a specific material (solvent or reagent) to absorb microwave energy and convert it into heat. MW heating occurs from the inside to the outside, so, from the bulk of the sample towards the flask walls. On the other hand, conventional heating involves the exact opposite heat transfer mechanism and this difference causes a decrease in the heating homogeneity.

3.2 Reactants and catalysts

None of the reagents are significantly sensitive to air or moisture and therefore were handled in normal ambient conditions without any previous purification step. Table 3.1 reports the regents used and some other specifications. In this work, reagents are weighted and directly added to the grinding jars or to the vial, always remembering to add the oxidant in the last place.

Table 3.1. *Main characteristics of the reagents used in Chapter 3.*

Compound	**Chemical formula**	**Colour**	**Purity**	**Molecular Weight [g/mol]**	**State**	**Suppliers**
Cyclohexane	C_6H_6	transparent	99.50%	84.16	liquid	Acros Organics
Tert-Butyl hydroperoxide	$(CH_3)_3COOH$	transparent	70% in H_20	90.12	liquid	Acros Organics
1-Phenylethanol	$C8H_{10}O$	transparent	100%	122.16	liquid	TCI
Potassium peroxodisulphate	$K_2S_2O_8$	white	100%	100	solid	Sigma-Aldrich

The catalysts that are tested in this work are, in part, the ones whose synthetic process are described in Chapter 2 as well as the bi-metallic compounds that have not been synthesized during this work, but will be studied, and the specifications are reported in Table 3.2.

Table 3.2. *Bi-metallic compounds not synthesized in this work.*

Catalyst number	Metal 1	Metal 2	Molar ratio	Additive	Test conditions
41	CuO	$KReO_4$	1:1	-	Ball milling; 1 h at 500 RPM
42	CuO	$KReO_4$	2:1	-	Ball milling; 1 h at 500 RPM
43	CuO	$KReO_4$	1:2	-	Ball milling; 1 h at 500 RPM
44	Fe_2O_3	$KReO_4$	1:1	-	Ball milling; 1 h at 500 RPM
45	Fe_2O_3	$KReO_4$	2:1	-	Ball milling; 1 h at 500 RPM
46	Fe_2O_3	$KReO_4$	1:2	-	Ball milling; 1 h at 500 RPM
47	V_2O_5	$KReO_4$	1:2	1% GO	Ball milling; 1 h at 500 RPM

3.3 Peroxidative oxidation of cyclohexane

The first reaction of interest concerns the catalytic oxidation of cyclohexane in order to produce cyclohexanone and cyclohexanol mixture, as shown in Figure 3.3. The significant industrial applications for these latter products brought about an enormous demand (more than 10^6 ton/year of cyclohexanone alone) and therefore stimulated studies aiming to find milder, energy-saving and possibly green conditions.

Nearly all cyclohexane is used to make cyclohexanol and cyclohexanone, which, in turn, are used mainly as precursors for the production of adipic acid and caprolactam, respectively. Other uses for cyclohexane include various solvent applications. Indeed, most cyclohexanol/cyclohexanone (over 95%) is consumed captively on site for the production of adipic acid and caprolactam, so only a small amount (4%) enters the world's trade markets which is used as solvents for paints and dyes, in pesticides, and as an intermediate for pharmaceuticals, films, soaps, and coatings.

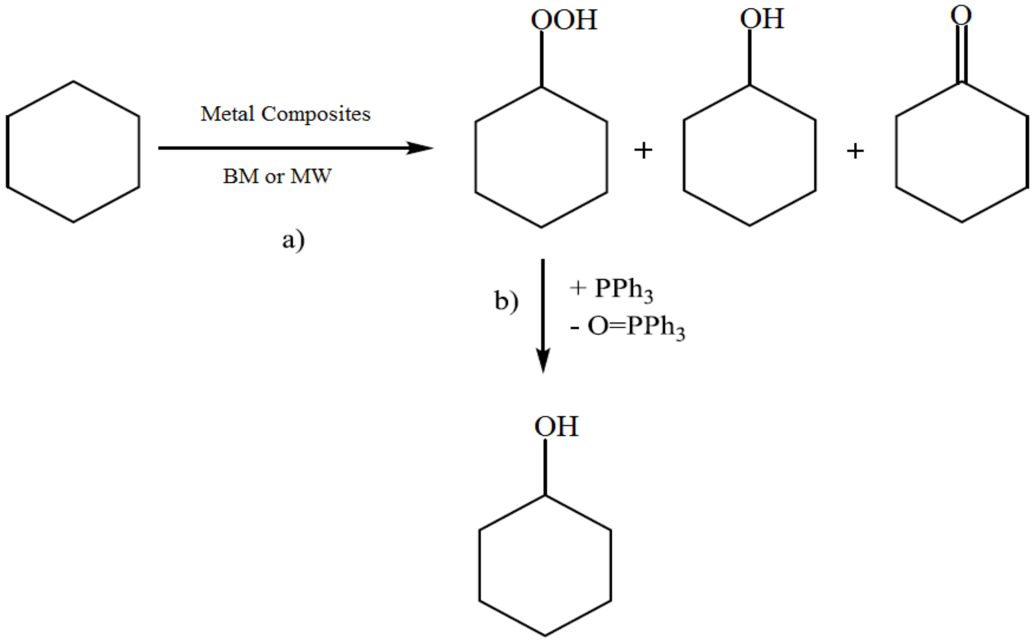


Figure 3.3. *Cyclohexane oxidation (path a) and PPh_3 treatment for the alkyl hydroperoxide (path b).*

Path a) in Figure 3.3 describes cyclohexane catalytic oxidation under mild conditions and an oxidant thanks to which is produced the corresponding alkyl hydroperoxide that leads to the formation of cyclohexanone/cyclohexanol. Once the reaction is ended, by adding an excess of solid triphenylphosphine (PPh_3) to the solution to transform the remaining hydroperoxide in the corresponding alcohol. Path b) was published in 2001 by Georgiy B. Shul'pin thanks to which the alcohol yield remarkably increases. Indeed, cyclohexyl hydroperoxide is known to be readily and quantitatively reduced by PPh_3 to yield the corresponding alcohol:

$$C_6H_{11}OOH + PPh_3 \rightarrow C_6H_{11}OH + OPPh_3 \qquad (3.1)$$

In this work the cyclohexane catalytic oxidation is tested using different types of green oxidants such as O_2 or potassium peroxodisulphate ($K_2S_2O_8$) rather than hydrogen peroxide. Shul'pin method is followed, before gas chromatographic (GC) analysis, in order to convert, if peroxidation occurs, cyclohexyl hydroperoxide to cyclohexanol. Operating conditions such as temperature, composition and mixing parameters have been changed during the experiments as well as the reactional media (BM or MW).

In general, once the reaction was ended, each sample was analysed by gas chromatography (GC). Gas chromatographic measurements were carried out using a FISONS GC 8000 series gas chromatograph with a capillary column (DB-WAX, column length: 30 m; internal diameter:

0.32 mm) and an FID detector. The initial temperature of the column was 100°C (for 1 min) and the final one was 180°C (for 1 min) with a total time of 10 min since temperature increasement was 10 K/min. Before injecting in the column, 90 μL of cycloheptanone (internal standard), 5 mL of diethyl ether (solvent used to extract the substrate and products from the reaction mixture) and the sample are put inside a round-bottom flask with a magnetic bean. The obtained mixture was magnetically stirred for 5 minutes and then, 1 mL of sample is extract from the organic phase and placed in an Eppendorf, thus centrifuged for 30 min particles that would damage the column were not injected. Finally, an excess of triphenylphosphine was added in order to eventually stop the cyclohexane oxidation and convert cyclohexyl hydroperoxide to cyclohexanol.

3.3.1 Ball milling cyclohexane oxidation with copper and vanadium based catalysts

Copper sulphate and vanadium oxide based catalysts, synthesized in Chapter 2 by mechanochemical mixing, are tested in the PM 100 by Retsch GmbH, planetary ball milling unit. The reaction takes place at normal conditions (25°C and 1 atm). The tested catalysts are n° 9 to 16, therefore including Cu-V composites synthesized with/without solvent and supported or not supported.

During the one-pot reactions, the system is mixed mechanically for 2 hours in the planetary ball mill reactor, equipped with a 50 mL grinding bowl and 10 stainless steel balls of 5 mm radius. Grinding jars rotational speed is 500 RPM and every 5 minutes the direction is changed. Detailed descriptions of the experiments are reported in Annex B.1.

The results show low conversions, mainly due to the high stability of cyclohexane. The higher conversion obtained with catalyst n°12 was 8.5%, which is an average value for cyclohexane oxidation. Indeed, the results are similar to the ones obtained by industrial methods.

3.3.2 Microwave-assisted cyclohexane oxidation with copper and vanadium based catalysts

In this case the Cu-V based materials are tested as catalysts in the microwave reactor. The tested catalysts have been synthesized in this work and correspond to n° 9 to 16. In this case, 3 mL of acetonitrile (ACN) are added to favour the reaction. 110 μl (1 mmol) of substrate (cyclohexane) is added to the vial together with 10 mg of catalyst and 400 mg of $K_2S_2O_8$. Detailed descriptions of the experiments are reported in Annex B.2. Reaction is carried out at 50°C, microwave irritated (10 W) and mixed at 650 RPM. Results showed lower conversions and the higher one (5%) is obtained with catalyst n°12, as in the ball milling tests. This is due to the fact that that n°12 is a Cu-V catalyst with a 1:2 mass ratio which evidences the fact that for cyclohexane oxidation vanadium is more active than copper.

3.4 Peroxidative oxidation of 1-phenylethanol

The oxidation of primary and secondary alcohols to carbonyl compounds is one of the most important reactions is synthetic organic chemistry. In this view, the peroxidative oxidation of 1-phenylethanol to acetophenone is particular important due to the high market request of the product of interest. Acetophenone is an organic compound and the simplest form of ketone which is used in various applications such as ingredients of fragrances in food and beverages, precursor as solvent soap in plastics and resins and as catalyst in olefins reactions. Its increasing demand is also due to the end industries request that use it in the production of cigarettes, chewing gum and tobacco. Nevertheless, the growth of acetophenone in the global market is restrained because of numerous constraints that regulates its use since it may arise skin irritation and corneal injury. For this reason, together with the fact that traditional oxidation reactions often involve the use of harmful oxidants, such as CrO_3 or $KMnO_4$, and/or halogenated solvents, with the generation of large amounts of wastes, the development of new green routes is a matter of current interest. One of the possible routes that can be followed to produce acetophenone in a greener way is by oxidation of 1-phenylethnol, as shown if Figure 3.4, in the microwave reactor. Moreover, it is known that microwave irradiation provides a more efficient heating than conventional ones thanks to which similar yields and higher selectivity can be attained ([23,24,25]).

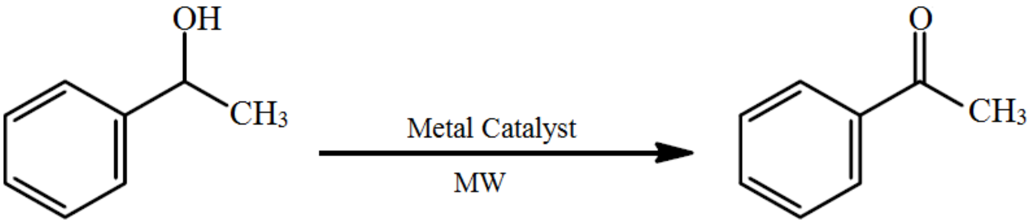


Figure 3.4. Reaction mechanism of 1-phenylethanol oxidation to acetophenone.

In this work the peroxidative oxidation of 1-phenylethnol is tested in the microwave reactor with the different types of catalysts produced in this work in order to analyse has the best efficiency comparing the yield, turn over number (TON) and turn over frequency (TOF). Moreover, catalysts are tested at different temperatures and additive loadings and results are characterized by gas chromatography.

In general, once the reaction was completed, the mixture is allowed to cool down to room temperature and each reaction is analysed by gas chromatography. Gas chromatographic measurements are carried out using a FISONS GC 8000 series gas chromatograph with an FID detector and a capillary column (DB-WAX, column length: 30 m; internal diameter: 0.32 mm). The initial temperature of the column was 120°C (for 1 min) and the final one was 200°C (for 1 min) with a total time of 10 min since temperature was increasing by 10 K/min. Before injecting in the column, a short procedure was followed in order to analyse correctly the samples. First of all, 90 µL of benzaldehyde (internal standard), 3 mL of acrylonitrile (solvent used to extract the substrate and products from the reaction mixture) and the sample are put inside a round-bottom flask with a magnetic bean inside. The obtained mixture is magnetically stirred for 10 minutes and then, 1 mL of sample was extract from the organic phase, placed in an Eppendorf and centrifuged for 30 min, to avoid injecting solid particles in the column. Finally, 0.4 µL were injected in the column.

In order to quantify GC results a calibration step is needed. Calibration is carried out by injecting four samples of known quantities of solvent, internal standard, product and substrate. After injecting these solutions, it is possible to find out the linear relation between the substrate or product concentration and the ratio between their area and the internal standard one. Both calibrations are reported in Table 3.5.

Table 3.5. *Measurements of the 4 samples injected in GC for calibration purposes.*

N°	ACN [mL]	Internal Standard [mL]	Acetophenone [mL]	Substrate [mL]	Total Volume [mL]
1	3	0.09	0.2	0.2	3.49
2	3	0.09	0.4	0.4	3.89
3	3	0.09	0.6	0.6	4.29
4	3	0.09	0.8	0.8	4.69

The GC software calculates each chromatographic peak area automatically. Figure 3.5 shows the linear regression concerning acetophenone calibration with a slope equal to 6.6291.

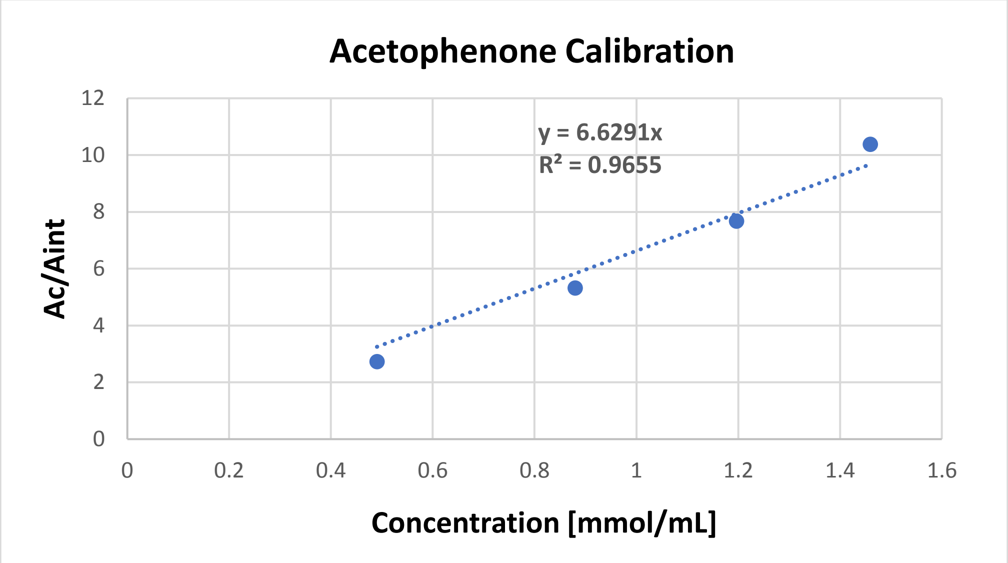


Figure 3.5. Acetophenone calibration curve by linear regression, (Ac= acetophenone area, Aint=internal standard area).

Figure 3.6 shows the linear regression concerning the 1-phenylethanol calibration with a slope equal to 6.6845.

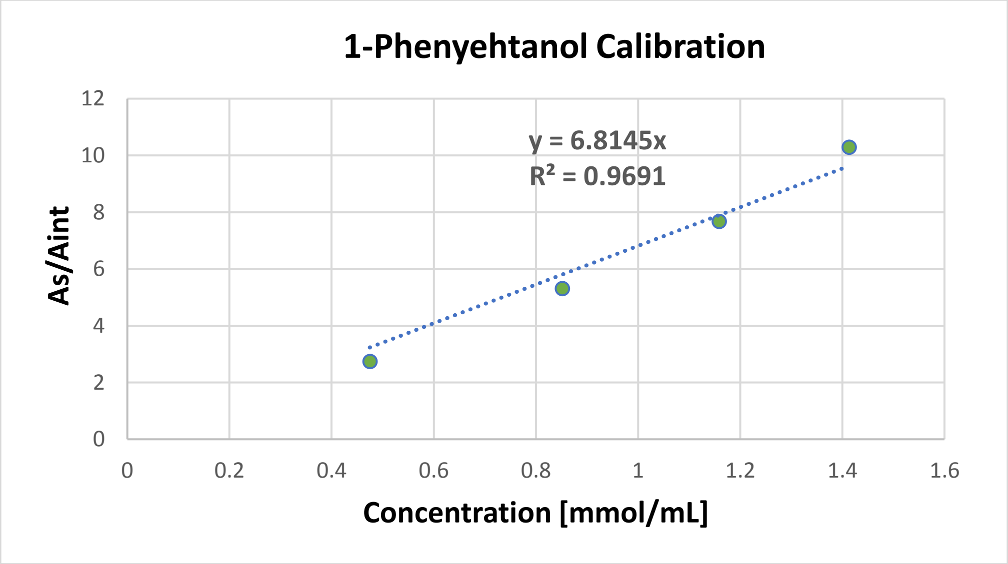


Figure 3.6. 1-phenylethanol calibration curve by linear regression, (As= substrate area, Aint=internal standard area).

As expected, the slope of both calibrations is almost equal since the amounts of substrate and product are used in each calibration sample. Calibration curves are used to calculate substrate and acetophenone concentrations of each reaction once the ratio between their area and the internal standard one is known, therefore with this calibration, all of the performed reactions can be quantified.

3.4.1 Copper oxide and potassium perrhenate based catalyst

1-Phenylehtanol peroxidation is tested with the copper- and rhenium-based catalysts at different molar ratios (1:1, 1:2 and 2:1). For each experiment, 5 mmol of substrate together with 10 mmol of tert-butyl hydroperoxide (70% aqueous solution) and 10 ± 0.2 mg of catalyst are introduced in a cylindrical Pyrex tube, which has then been placed in the focused microwave reactor. The system is magnetically stirred (650 RPM) and irradiated (10 W) for 30 min at 80°C. Details are reported in Table 3.6.

Table 3.6. MW-assisted 1-phenylethanol oxidation, over ball milled Cuo-$KReO_4$ with different molar ratios as catalysts. (*)

N° Catalyst	Catalyst [µmol]	Time [h]	Yield [%]	TON	TOF [h^{-1}]
41	54.22	0.5	2.84	3	5
42	67.58	0.5	3.21	2	5
43	46.04	0.5	2.94	3	6

(*) Reactions conditions: 1-phenylethanol (5.0 mmol), 10 mg of catalyst, TBHP 70% aq. solution (10 mmol), 0.5 h, 80°C, microwave (MW) irradiation 10 W, mixing at 650 RPM.

Analysing Table 3.6 it is evident that the catalyst with a highest yield, at the chosen operating conditions, is the 2:1 molar ratio one. Nevertheless, the turnover number (TON) and, as a consequence the turnover frequency (TOF), are higher for the 1:2 molar ratio due to catalyst amount. Indeed, the 1:2 ratio shows best performances with respect the other compositions.

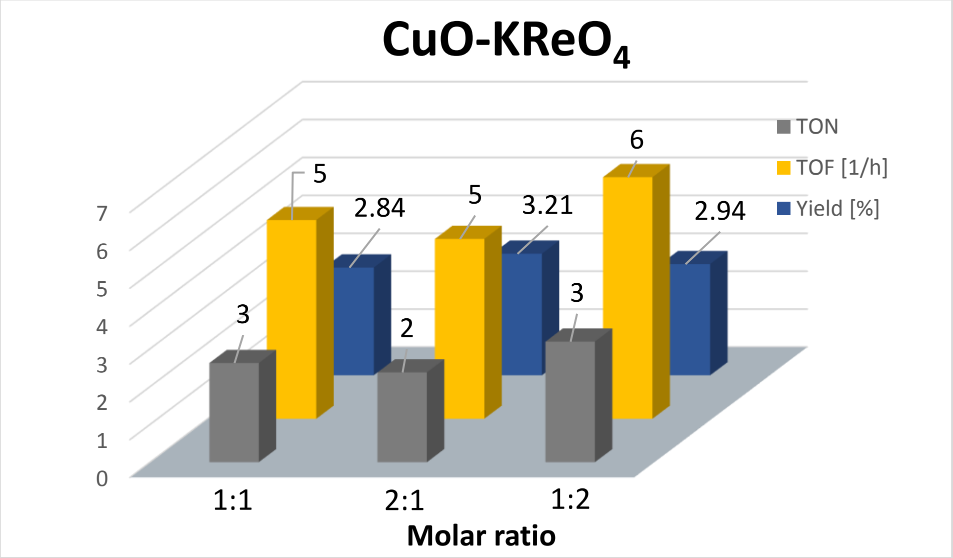


Figure 3.7. 3D bar chart with the results for CuO-KReO$_4$ in terms of TON, TOF and yield.

As it is shown in Figure 3.7, it is possible to state that the rhenium enhances the substrate conversion more than copper, consequently the rhenium molar fraction should show an acetophenone increase. The more performant catalysts Cu-Re 1:1 and 1:2 molar ratio were supported with 1% w/w of graphene oxide (GO) in order to analyse if the additive brings improvements in the 1-phenylehtanol oxidation at the same operating conditions. Graphene oxide is an oxidized form of graphene, laced with oxygen-containing groups. Results are shown in Table 3.7.

Table 3.7. MW-assisted 1-phenylethanol oxidation, over ball milled Cuo-KReO$_4$ Supported with 1% GO, as catalysts. (*)

N° Catalyst	Catalyst [μmol]	Time [h]	Yield [%]	TON	TOF [h^{-1}]
41	54.22	0.5	3.85	4	7
43	46.50	0.5	4.22	5	9

(*) Reactions conditions: 1-phenylethanol (5.0 mmol), 10 mg of catalyst, TBHP 70% aq. solution (10 mmol), 0.5 h, 80°C, microwave (MW) irradiation 10 W, mixing at 650 RPM.

It is possible to state that performances of Cu-Re based catalysts with 1:1 and 1:2 and supported with 1% GO are enhancing the production of acetophenone.

3.4.2 1 Iron oxide and potassium perrhenate based catalyst

1-Phenylehtanol peroxidation is tested with iron- and rhenium-based catalysts at different molar ratios (1:1, 1:2 and 1:3). For each experiment, 5 mmol of substrate together with 10 mmol of tert-butyl hydroperoxide (70% aqueous solution) and 10 ± 0.2 mg of catalyst are introduced in a cylindrical Pyrex tube, which is then placed in the focused microwave reactor. The system is (magnetically) stirred and irradiated (10 W) for 30 min at 80°C. Details are reported in Table 3.8.

Table 3.8. MW-assisted 1-phenylethanol oxidation, over ball milled Fe_2O_3-$KReO_4$ with different molar ratios as catalysts. (*)

N° Catalyst	Catalyst [µmol]	Time [h]	Yield [%]	TON	TOF [h^{-1}]
44	44.55	0.5	2.56	3	6
45	49.79	0.5	1.65	2	3
46	41.05	0.5	2.11	3	5

(*) Reactions conditions: 1-phenylethanol (5.0 mmol), 10 mg of catalyst, TBHP 70% aq. solution (10 mmol), 0.5 h, 80°C, microwave (MW) irradiation 10 W, mixing at 650 RPM.

Analysing Table 3.8 it is clear that these bi-metallic catalysts have lower performances than copper- and rhenium-based catalysts. Indeed, yield ranges between 1.6% and 2.5% while TON and TOF are relatively low for all 3 samples.

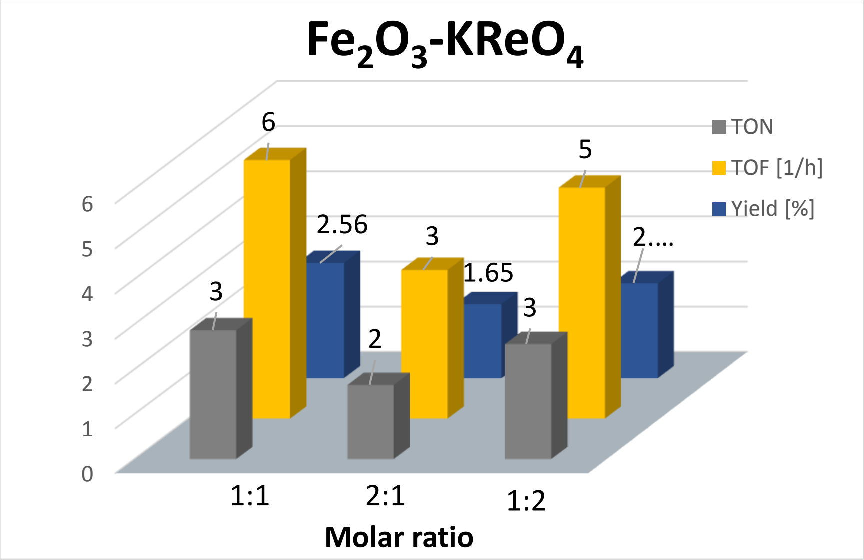


Figure 3.7. 3D bar chart with the results for Fe_2O_3-$KReO_4$ in terms of TON, TOF and yield.

Figure 3.8 sums up the results by representing them in a bar chart plot and it is highlighted that the best performance concerns the catalyst with a 1:1 molar ratio. As a result, it is possible to state that the rhenium enhances the substrate conversion more than iron. Even though, catalysts are not as performant as Cu-Re ones their magnetic properties can be used easily recover them from the reaction pot and recycled but studies in the catalytic activity should be carried out to understand if recycling is a convenient strategy.

3.4.3 Vanadium oxide and potassium perrhenate based catalyst

1-phenylethanol oxidation is tested with vanadium oxide and potassium perrhenate catalysts with a 1:2 molar ratio and 1% w/w of graphene oxide (GO) as additive. As usual, 5 mmol of substrate together with 10 mmol of tert-butyl hydroperoxide and 10± 0.2 mg of catalyst are added to the cylindrical Pyrex tube. Table 3.9 sums up the reaction details.

Table 3.9. MW-assisted 1-phenylethanol oxidation, over ball milled V_2O_5-$KReO_4$ as catalysts. (*)

N° Catalyst	Catalyst [µmol]	Time [h]	Yield [%]	TON	TOF [h^{-1}]
47	39.85	0.5	11.56	15	29

(*) Reactions conditions: 1-phenylethanol (5.0 mmol), 10 mg of catalyst, TBHP 70% aq. solution (10 mmol), 0.5 h, 80°C, microwave (MW) irradiation 10 W, mixing at 650 RPM.

Analysing Table 3.9 it is noticed that more acetophenone is produced than with the other tested catalysts. Yield reaches 11.5% even considering that the moles of catalyst are the lowest tested comparing them with Cu-Re and Fe-Re ones.

Due to the obtained results, the catalyst was tested at different operating conditions in order to understand which is the more efficient in terms of performance. The catalyst was tested at different reaction times, more precisely 1 h, 1.5 h and 2 h while temperature remained constant (80°C) as well as stirring conditions (650 RPM). In Table 3.10 the experiments are reported in details.

Table 3.10. MW-assisted 1-phenylethanol oxidation, over ball milled V_2O_5-$KReO_4$ as catalysts. (*)

N° Catalyst	Catalyst [µmol]	Time [h]	Yield [%]	TON	TOF [h^{-1}]
47	39.85	1	12.32	15	15
47	39.85	1.5	17.02	21	14
47	39.85	2	19.51	24	12

(*) Reactions conditions: 1-phenylethanol (5.0 mmol), 10 mg of catalyst, TBHP 70% aq. solution (10 mmol), 80°C, microwave (MW) irradiation 10 W, mixing at 650 RPM.

As it is expected, conversion is enhanced by increasing the reaction time but its increase is more or less of 5% every 0.5 h as shown in Figure 3.8. It is shown that yield reaches almost its maximum value after 0.5 h.

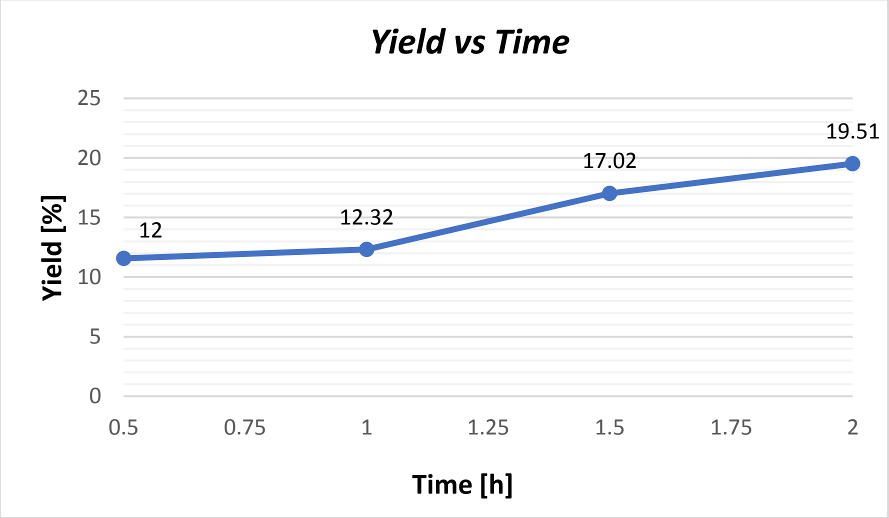


Figure 3.8. Yield vs Time plot for the 1-phenylethanol oxidation with V_2O_5-$KReO_4$ as catalyst.

In this view, the catalyst was tested at different temperatures in order to understand if temperature could allow to increase the yield. 1-phenylethanol oxidation was tested at 100°C and 120°C and results were then compared with the reaction at 80°C. The reason why the temperature was not raised above 120°C is due to TBHP boiling temperature (96.2°C) that may cause an excess of concentration in the vapor phase (flammable substance). Table 3.11 sums up the reaction details.

Table 3.11. MW-assisted 1-phenylethanol oxidation, over ball milled V_2O_5-$KReO_4$ as catalysts. (*)

N° Catalyst	Catalyst [μmol]	Temperature [°C]	Yield [%]	TON	TOF [h^{-1}]
47	39.85	80	12.32	15	15
47	39.45	100	17.06	22	43
47	40.64	120	43.75	54	108

(*) Reactions conditions: 1-phenylethanol (5.0 mmol), 10 mg of catalyst, TBHP 70% aq. solution (10 mmol), 0.5 h, microwave (MW) irradiation 10 W, mixing at 650 RPM.

As expected, the yield increases with temperature and the highest yield is obtained to the at 120°C therefore, the optimal temperature is 120°C, as shown if Figure 3.9.

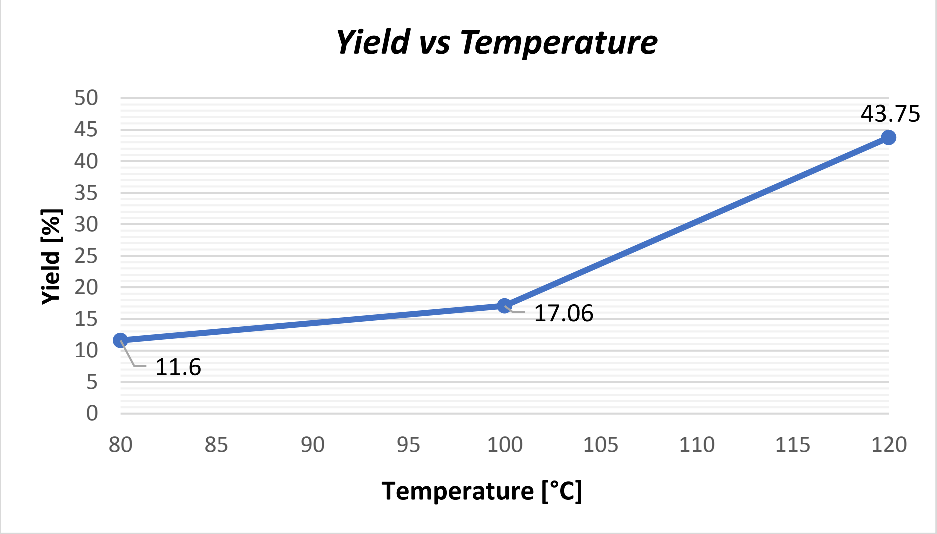


Figure 3.9. Yield vs Temperature plot for the 1-phenylethanol oxidation with V_2O_5-$KReO_4$ as catalyst.

In conclusion, the parameter that most influences the reaction is temperature. Knowing the optimal temperature at which the reaction should be run, another test was carried out in order to verify if the reaction is affected by time, considering 3 h. Another parameter that affects the reaction is the catalyst loading so, the reaction is tested with 20 mg of catalyst while temperature and reaction are set at the optimal values determined previously.

Table 3.12. MW-assisted 1-phenylethanol oxidation, over ball milled V_2O_5-$KReO_4$ as catalysts. (*)

N° Catalyst	Time [h]	Catalyst [µmol]	Yield [%]	TON	TOF [h^{-1}]
47	0.5	80.09	41.11	30	60
47	3	39.85	63.42	79	26

(*) Reactions conditions: 1-phenylethanol (5.0 mmol), 10 mg of catalyst, TBHP 70% aq. solution (10 mmol), 120°C, microwave (MW) irradiation 10 W, mixing at 650 RPM.

The results are quite interesting because thy show that doubling the catalyst loading, does not bring any advantage (yield still 41%). Instead, different results are obtained with 3 h reaction indeed, yield reaches 63.5%. This is an important observation that can lead to understand the catalyst activation is greatly depended on temperature.

To conclude, it can be observed that the most important operating parameter that affects the catalytic oxidation of 1-phenylethanol is temperature while the catalyst loading is not that relevant. Moreover, time has a positive effect on the alcohol oxidation but enhancements are not as positive. In this view, temperature can be coupled in order to optimize the process.

3.4.4 Copper sulphate and vanadium oxide based catalyst

The alcohol oxidation is tested with $CuSO_4$-V_2O_5 catalyst. The dispersed materials that are used as catalysts, have been synthesized in this work and more precisely are n° 9, 10, 15, 16, 17 and 18. As usual, to test the goodness of the mentioned catalyst the reactions are carried out with 5 mmol of substrate together with 10 mmol of tert-butyl hydroperoxide and 10± 0.2 mg of catalyst that are added to the cylindrical Pyrex tube. Results are shown in Table 3.13.

Table 3.13. MW-assisted 1-phenylethanol oxidation, over ball milled $CuSO_4$-V_2O_5 with different molar ratios as catalysts. (*)

N° Catalyst	Catalyst [µmol]	Yield [%]	TON	TOF [h^{-1}]
9	45.37	11.48	13	25
10	49.40	13.03	13	26
15	44.48	13.08	15	29
16	50.39	12.19	12	24
17	44.93	11.24	13	25
18	49.89	13.63	14	27

(*) Reactions conditions: 1-phenylethanol (5.0 mmol), 10 mg of catalyst, TBHP 70% aq. solution (10 mmol), 0.5 h, 80°C, microwave (MW) irradiation 10 W, mixing at 650 RPM.

By analysing the results in Table 3.13, it is possible to state that supporting Cu-V dispersed materials supported with graphite or activated carbon does not bring about improvements in the yield.

3.4.5 Metal Organic Framework based catalyst

MOFs derivatives are tested as catalysts in the 1-phenylethanol oxidation. As usual, to test the activity of the mentioned catalyst the reactions are carried out with 5 mmol of substrate together with 10 mmol of tert-butyl hydroperoxide and 10± 0.2 mg of catalyst that are added to the cylindrical Pyrex tube. Results are shown in Table 3.14 and highlights that the best result are obtained for the HKUST-1 itself. Moreover, the mixture of this MOF with core-shell system or core, creates a more active catalyst than the supports themselves, mainly thanks to the presence of HKUST-1.

Table 3.14. MW-assisted 1-phenylethanol oxidation, with HKUST-1 based structures as catalyst. (*)

Catalyst type	Catalyst [µmol]	Yield [%]	TON	TOF [h^{-1}]
HKUST-1	16.70	9.72	29	58
HKUST-1/ Fe_3O_4@TiO_2	51.42	3.59	3	7
HKUST-1/ $C_{12}H_{28}O_4Ti$	-	3.11	-	-
HKUST-1/ Fe_3O_4	30.09	6.31	10	21
Fe_3O_4@TiO_2	84.94	3.00	2	4
Fe_3O_4	43.63	2.70	3	6

(*) Reactions conditions: 1-phenylethanol (5.0 mmol), 10 mg of catalyst, TBHP 70% aq. solution (10 mmol), 0.5 h, 80°C, microwave (MW) irradiation 10 W, mixing at 650 RPM.

To conclude it can be then affirmed that HKUST-1 derivatives have a positive effect on the catalyst activity. On the other hand, it can be stated that the core-shell or core systems are its selves are an unappropriated catalyst for 1-phenylethanol oxidation. Figure 3.10 shows, after the reaction, that the MOF and MOF/Core-Shell catalysts are suspended in the liquid environment and the MOF/Core-Shell catalyst is still magnetic once the reaction is ended.

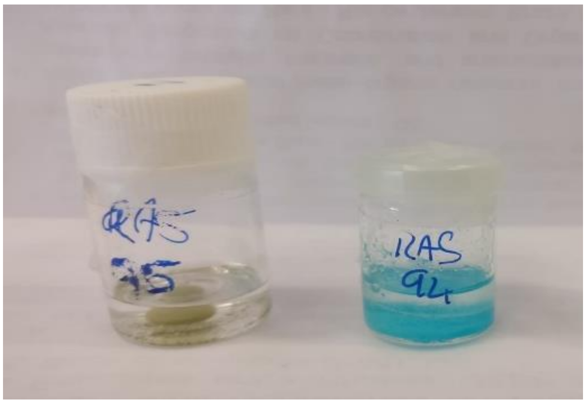


Figure 3.10. Caption of MOF/Core-Shell (left) and MOF (right) after 1-phenylethanol reaction.

Table 3.14 shows that the best results, in term of conversion, are achieved with the HKUST-1, so operating conditions are then changed in order to optimize the operating conditions. First of all, the catalyst is tested at different temperatures in order to understand if temperature could be the parameter that decisively affects the reaction. 1-phenylethanol oxidation is tested at 100°C and 120°C and results are then compared with the reaction at 80°C. The reason why the temperature is not raised above 120°C is due to TBHP boiling temperature (96.2°C) that will cause an excess of concentration in the vapor phase (flammable substance). Table 3.15 sums up the reaction details.

Table 3.15. MW-assisted 1-phenylethanol oxidation, with HKUST-1 as catalyst. (*)

Temperature [°C]	Catalyst [µmol]	Yield [%]	TON	TOF [h^{-1}]
100	16.86	23.60	70	140
120	17.03	52.00	153	305

(*) Reactions conditions: 1-phenylethanol (5.0 mmol), 10 mg of catalyst, TBHP 70% aq. solution (10 mmol), 0.5 h, microwave (MW) irradiation 10 W, mixing at 650 RPM.

As it is expected, the yield increases directly with temperature and the highest slope, shown in Figure 3.11 is related to the interval between 100°C and 120°C which states that the optimal temperature is close to 120°C whereas with 100°C the yield is below 20%.

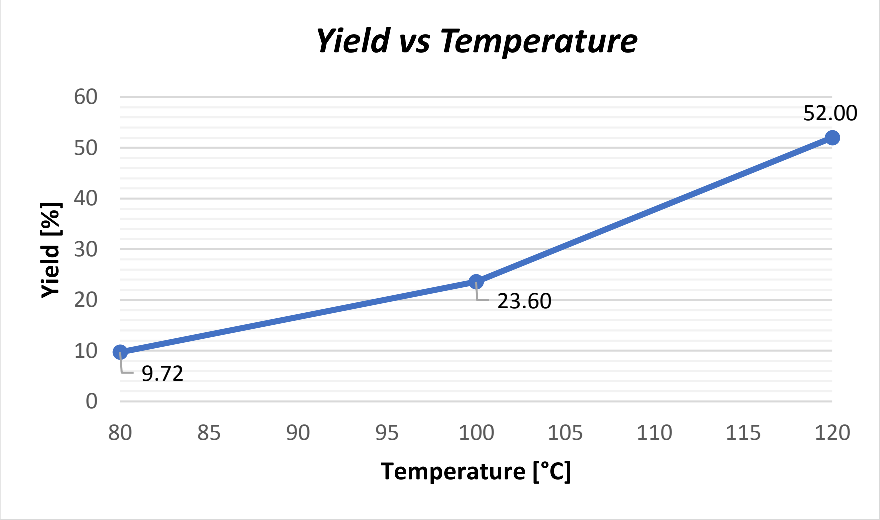


Figure 3.11. Yield vs Temperature plot for the 1-phenylethanol oxidation with HKUST-1 as catalyst.

Another operating parameter that is analysed is the reaction time while temperature was held constant at 120°C. The results are reported in the Table 3.16.

Table 3.16. MW-assisted 1-phenylethanol oxidation, with HKUST- as catalyst. (*)

Time [h]	Catalyst [µmol]	Yield [%]	TON	TOF [h^{-1}]
0.5	17.03	52.00	153	305
1	17.03	61.07	117	117
1.5	16.86	72.25	214	143
2	17.03	99.07	291	145

(*) Reactions conditions: 1-phenylethanol (5.0 mmol), 10 mg of catalyst, TBHP 70% aq. solution (10 mmol), 120°C, microwave (MW) irradiation 10 W, mixing at 650 RPM.

Results are quite interesting in comparison with the Re-V (2:1) catalyst since the latter one is more active than this MOF at 80°C but more expensive due to rhenium. This is not true if the temperature is increased, indeed it is analysed that the MOF reaches higher conversion at 120°C. Moreover, the catalyst is tested at increasing reaction times and with 2 h of reaction 100% of conversion is almost reached whereas the Re-V catalyst, after 3h reaction, it allows to reach 64%, as reported in the previous reports. It is possible to state that the with the HKUST-

1 it is possible to reach 50% of conversion in 1/4 of the time with respect the mentioned bi-metallic catalyst.

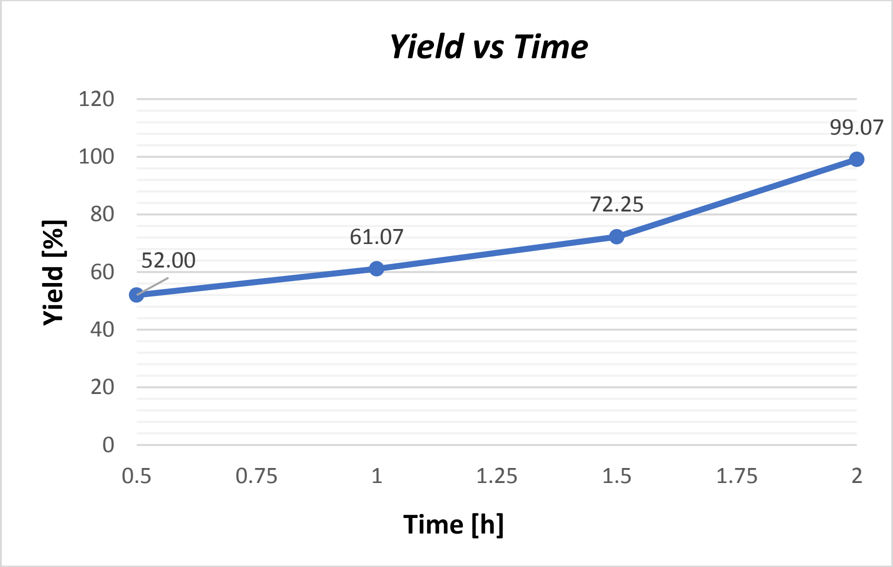


Figure 3.12. Yield vs Time plot for the 1-phenylethanol oxidation with HKUST-1 as catalyst.

Finally, from the last reaction it is demonstrated that doubling the catalyst amount has an extremely positive response on the oxidation results whereas with the Re-V catalyst it has been shown that there are no remarkable improvements.

3.4.6 Metal catalyst supported with biomass

According to Green Chemistry principles number 1 and 5 which deal with preventing the generation of waste and using renewable resources in reacting systems, the 1-phenylethanol oxidation is tested with metal catalysts supported with coffee waste. In this view, this type of support allows to use waste that is generated in everyday life and at the same type substitutes natural resources role, thus improving waste management.

The aim is to optimize the operating conditions for the 1-penyethanol catalytic oxidation with three different bio-supported metal catalysts. The attention is focused on temperature, catalyst loading and reaction time as operating parameters that can be tuned in order to achieve high conversion/yield by lowering temperature as much as possible, thus, taking in account Green Chemistry principles concerning safety design and energy optimization.

It must be specified that these catalysts have been not synthesized in this work, nevertheless the synthetization procedure is briefly explained before illustrating the oxidation results.

The starting material is coffee waste which is pyrolyzed and then treated with a wet impregnation or mechanochemical method. There are two different impregnation methods used to synthesize the biomass catalyst which are briefly described.

In the first case, 90 mg of the pyrolyzed coffee are placed in a round bottom flask (250 mL) together with 10 drops of acid chloride and stirred overnight until a good suspension is achieved. Afterwards, 140 mg of copper(II) chloride dihydrate are added to the suspension and stirred for several hours. Finally, the solution is neutralised (pH=7) by adding drop after drop a 1M sodium hydroxide solution and then the solvent is removed and the powder completely dried out. In the second case, 90 mg of the pyrolyzed coffee are placed in a round bottom flask (250 mL) together with 80 mL of ethanol and stirred overnight until a good suspension is achieved. Afterwards, 140 mg of copper(II) chloride dihydrate are added to the suspension and stirred for several hours and then the solvent is removed and the powder completely dried out.

In contrast with classical methods that are applied in the synthetization process of catalysts, such as the wet impregnation method, the latter type of coffee-based catalyst is synthesized by pursuing the ball milling technique. This greener route allows to synthesize the catalyst in a dry ambient and it grinds particles to nanoscale order. Indeed, 90 mg of the pyrolyzed coffee and 140 mg of copper(II) chloride dihydrate are placed for 1 hour in the PM 100, Retsch GmbH, planetary ball mill reactor, equipped with a 50 mL grinding bowl and 10 stainless steel balls of 5 mm radius. Moreover, the grinding jars rotational speed is 500 RPM and every 5 minutes the direction is changed from clockwise to anticlockwise.

Multiple testes are carried out by always adding in Monowave 300, a Pyrex tube with 5 mmol of 1-phenylethanol (600µL), 10 mmol of tert-butyl hydroperoxide (955µL) and the studied catalysts. Afterwards, once each reaction is completed, it is allowed to cool down to room temperature and then is analysed by gas chromatography. Gas chromatographic measurements are carried out using a FISONS GC 8000 series gas chromatograph with an FID detector and a capillary column (DB-WAX, column length: 30 m; internal diameter: 0.32 mm). The initial temperature of the column is 120°C (for 1 min) and the final one is 200°C (for 1 min) with a total time of 10 min since temperature is increasing 10 K/min. Before injecting in the column, a short procedure is followed in order to analyse correctly the samples. First of all, 90 µL of benzaldehyde (internal standard), 3 mL of acrylonitrile (solvent used to extract the substrate and products from the reaction mixture) and the sample are put inside a round-bottom flask within a magnetic bean inside of it. The obtained mixture is magnetically stirred for 10 minutes and then, 1 mL of sample is extract from the organic phase and placed in an Eppendorf thus centrifuged for 30 min, to avoid injecting solid particles in the column.

3.4.6.1 1 Synthesized by wet impregnation method

Operating conditions are optimized for the coffee catalyst synthesized in acid solution by wet impregnation method. Multiple testes are carried out by always adding in the microwave reactor, a Pyrex tube with 5 mmol of 1-phenylethanol (600µL), 10 mmol of tert-butyl hydroperoxide (955µL).

First of all, the influence of the reaction time is analysed by carrying out the reaction at 0.5 h, 1 h and 2 h while temperature is held constant at 80°C as well as the catalyst amount. Detailed information regarding the reactions is reported in Annex C.1. In Figure 3.13 the results are reported in terms of yield and it is observed that yield increases with time.

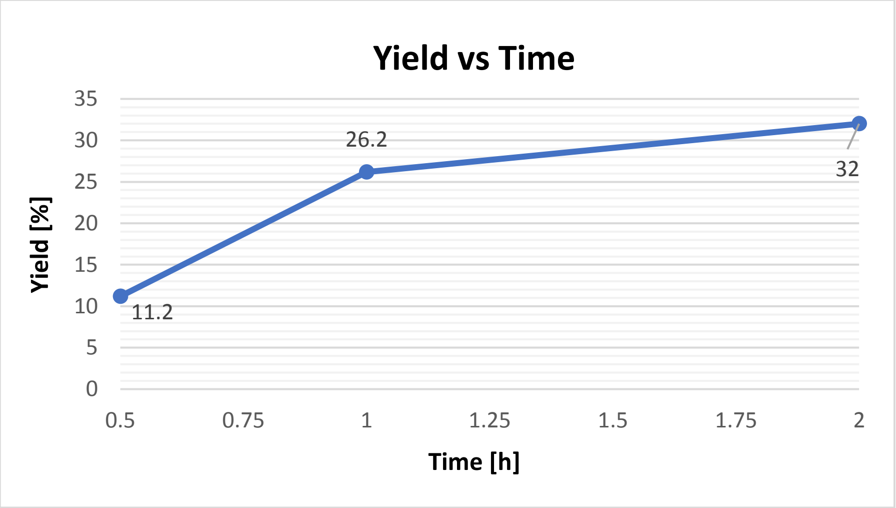


Figure 3.13. Yield vs Time plot for the 1-phenylethanol oxidation with metal catalyst supported with biomass and synthesized in acid solution.

It is also stated, in Figure 3.13, that the yield is more affected by reaction time in between 0.5 h and 1 h reaction but also increases between 1 h and 2 h reaction. Secondly, the same catalyst is tested holding constant the reaction time (0.5 h) while temperature is increased from 80°C to 120°C. Temperature is not increased above 120°C for safety reasons and to comply with green chemistry principles. Yield as a function of temperature is shown if figure 3.14.

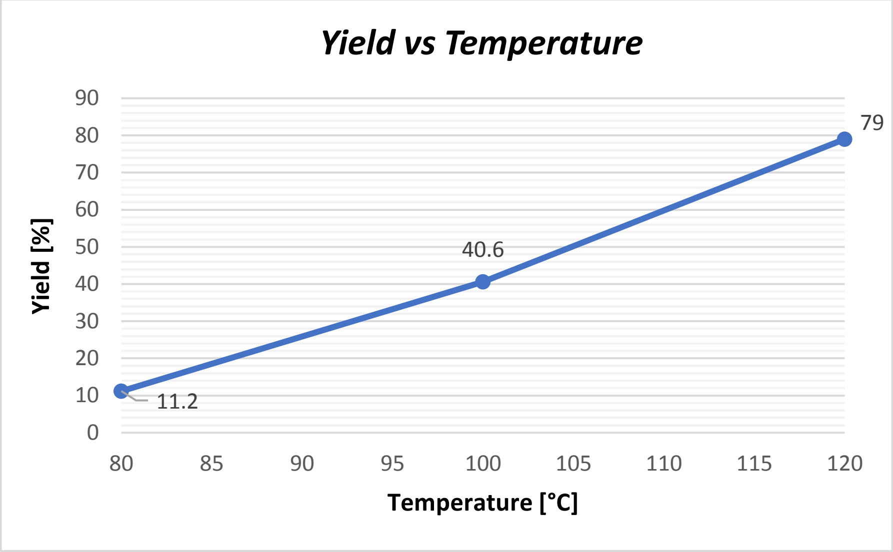


Figure 3.14. Yield vs Temperature plot for the 1-phenylethanol oxidation with metal catalyst supported with biomass and synthesized in acid solution.

Relying on the above figure, it is stated that temperature has a dominant effect on the catalyst activity thus, on the product formation. Moreover, it is stated that increasing the temperature of 20°C with respect the 80°C reaction, the yield is enhanced of 30% whereas at 120°C it increases of 40%.

In line with the optimization study, the catalyst loading effect is analysed while temperature is held constant at 100°C as well as reaction time (1 h). The tests are carried out with 5 mg and 20 mg of catalyst and it is found out that yield is slightly improving by increasing the catalyst amount (Figure 3.15).

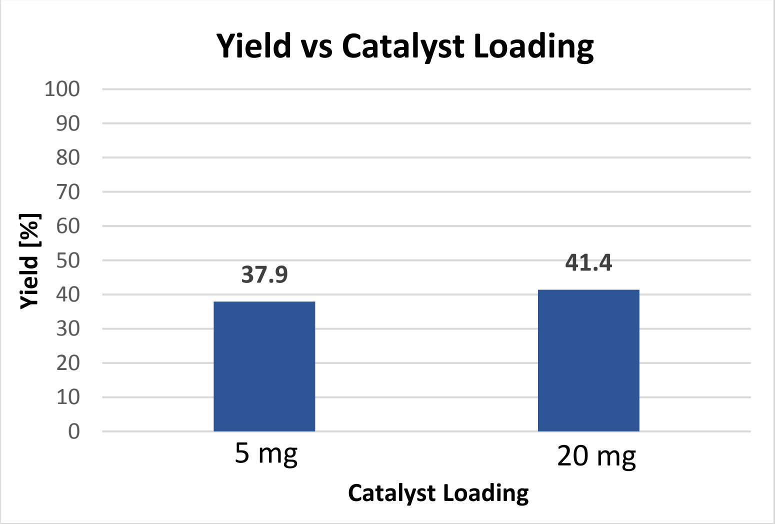


Figure 3.15. Yield vs Catalyst loading plot for the 1-phenylethanol oxidation with metal catalyst supported with biomass and synthesized in acid solution.

Relying on the above figure, it is stated that no improvement is observed when the reactions are carried out with catalyst loading that exceeds 5 mg.

Operating conditions are optimized for the coffee catalyst synthesized in ethanol by wet impregnation method. Multiple testes are carried out by always adding in the microwave reactor, a Pyrex tube with 5 mmol of 1-phenylethanol (600μL), 10 mmol of tert-butyl hydroperoxide (955μL) while the catalyst loading is changed. Detailed descriptions of all the are reported in Appendix C.2.

Temperature is hold constant at 80°C as well as the catalyst amount while reaction time is changed in order to analyse the catalytic activity behaviour. This understanding is done by analysing the conversion/yield as it is reported in Figure 3.16.

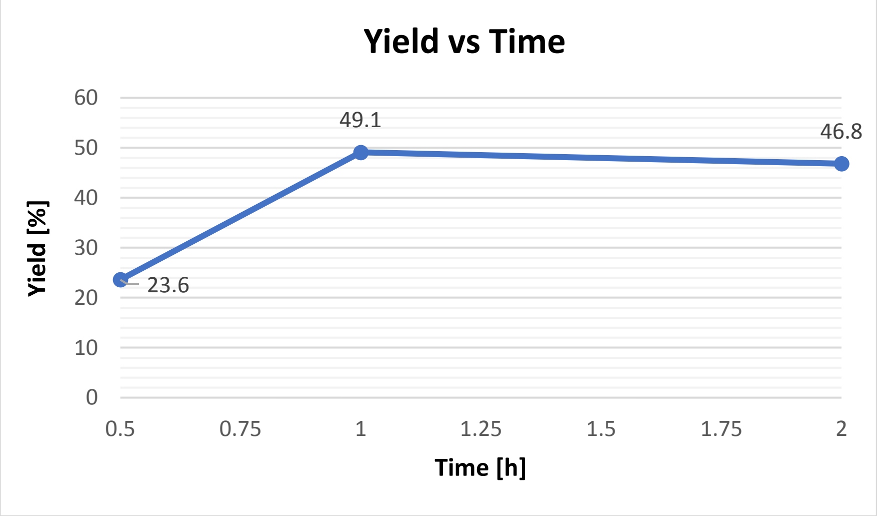


Figure 3.16. Yield vs Time plot for the 1-phenylethanol oxidation with metal catalyst supported with biomass and synthesized in ethanol.

Relying on the above figure, it is stated that time has an opposite effect towards conversion depending on the reaction time. It is clearly stated that the best option is 1 h of reaction. Furthermore, comparing the reaction time effect for both catalysts made through out wet impregnation, it is possible to state that the latter one is more suitable for 1-phenyehtnol oxidation since yield is quite higher. Secondly, temperature effect is analysed while reaction time (0.5 h) and catalyst amount are held constant as shown in Figure 3.17.

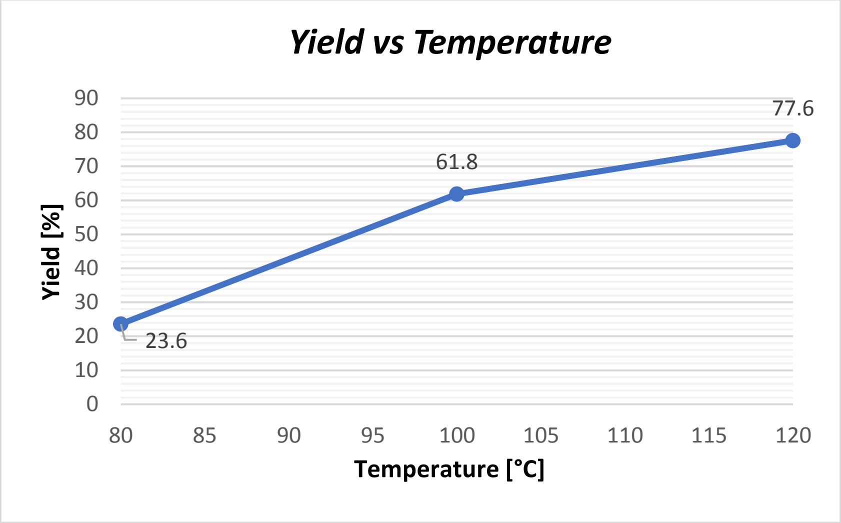


Figure 3.17. Yield vs Temperature plot for the 1-phenylethanol oxidation with metal catalyst supported with biomass and synthesized in ethanol.

In line with the reaction time optimization, this catalyst is more active than the previous one in particular for lower temperatures. Finally, the catalyst loading effect is analysed while temperature is held constant at 100°C as well as reaction time (1 h). The tests are carried out with 5 mg and 20 mg of catalyst and it is found out that yield is slightly improving by increasing the catalyst amount.

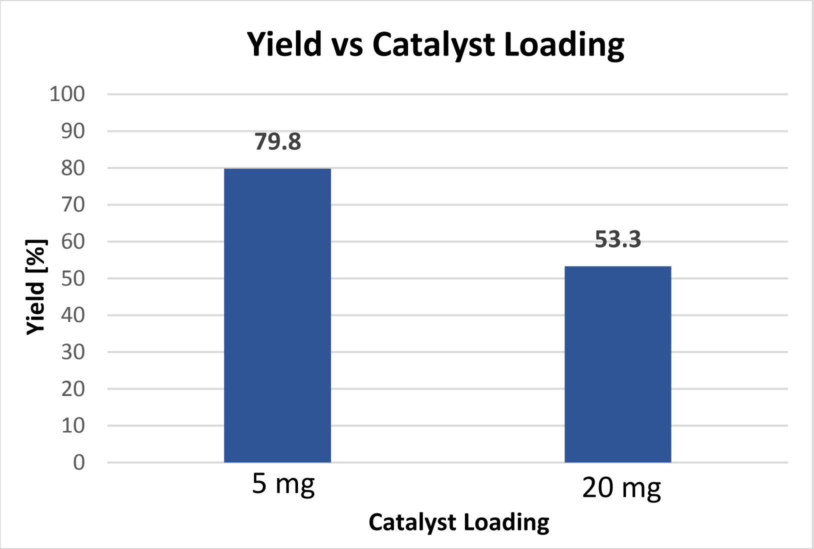


Figure 3.18. Yield vs Catalyst loading plot for the 1-phenylethanol oxidation with metal catalyst supported with biomass and synthesized in ethanol.

By having a look at the Figure 3.18, it is clearly visible that it is convenient to carry out reactions with 5 mg of catalyst.

3.4.6.2 Synthesized by mechanochemical treatment

Operating conditions are optimized for the coffee catalyst synthesized by ball milling. Multiple testes are carried out by always adding in the microwave reactor, a Pyrex tube with 5 mmol of 1-phenylethanol (600μL), 10 mmol of tert-butyl hydroperoxide (955μL) while the catalyst loading is changed. Detailed descriptions of all the experiment are reported in Appendix C.3. Temperature is maintained constant at 80°C as well as the catalyst amount while reaction time is changed in order to analyse the catalytic activity behaviour. This understanding is done by analysing the yield as it is reported in Figure 3.19.

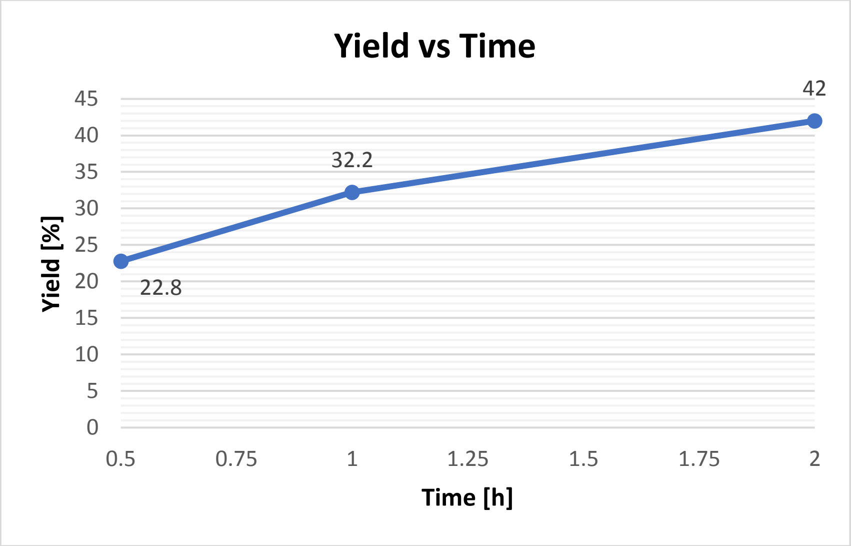


Figure 3.19. Yield vs Time plot for the 1-phenylethanol oxidation with metal catalyst supported with biomass and synthesized by mechanochemical treatment.

Analysing figure 3.19, it is possible to evidence that increasing the reaction time up to 2 h has a positive effect on the catalytic activity. Indeed, yield in enhance of 10% for 1 h reaction with respect 0.5 h and increases of the same amount for 2 h reaction. On the other hand, if temperature is changed from 80°C to 120°C while the other operating parameters are held constant (0.5 h and 10 mg of catalyst), yield reaches promising results as it is shown in Figure 3.20.

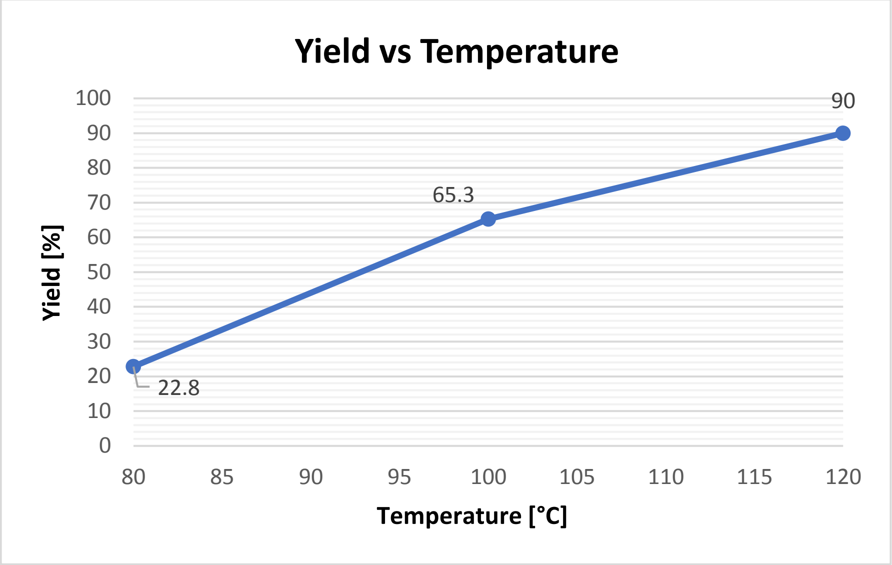


Figure 3.20. Yield vs Temperature plot for the 1-phenylethanol oxidation with metal catalyst supported with biomass and synthesized by mechanochemical treatment.

Analysing the figure above, the catalyst effect on the alcohol oxidation until 100°C is similar to the previous ones. Instead, when temperature is raised towards 120°C the catalyst becomes extremely more active and the substrate is almost fully converted. Finally, the catalyst loading effect is analysed.

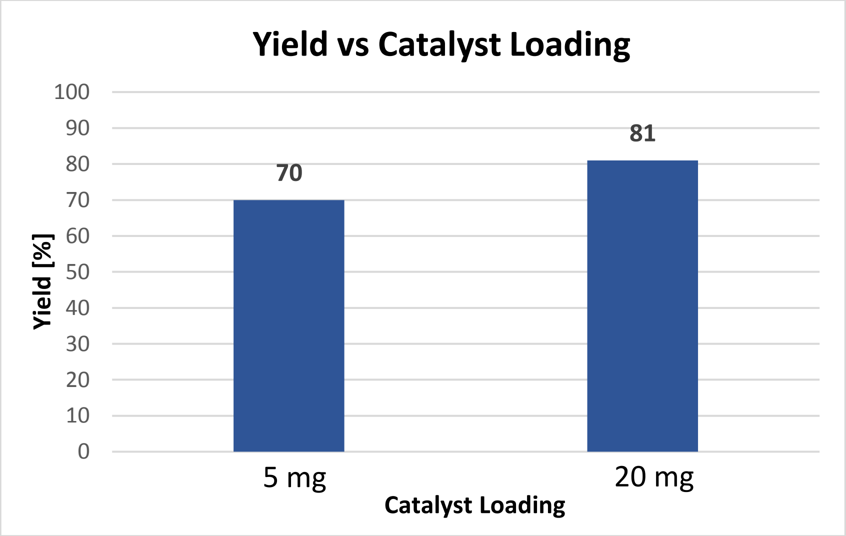


Figure 3.21. Yield vs Temperature plot for the 1-phenylethanol oxidation with metal catalyst supported with biomass and synthesized by mechanochemical treatment.

By having a look at Figure 3.21, it is understood that the loading must not be lower than 10 mg since it favours yield

Conclusions

The main objective of this work was the screening of potential new catalysts for the well-known reactions with industrial relevance of cyclohexane and 1-phenylethanol oxidation. The tested catalysts are abundant and cheap transition metals (namely copper and iron) and are appealing to the industry because these types of reactions are a multibillion market since the commodities that are produced from these reactions are the base of thousands of products used nowadays in our society.

The synthetic methods were chosen and applied based in their availability in the industry (namely ball milling, which is quite economic in factories and laboratories) and according to Green Chemistry principles. Almost all of the catalysts were characterized by FTIR-ATR and part of them by SEM and EDS. Overall, 40 composites were synthesized by ball milling whereas a wet impregnation method was applied to create some with a core-shell structure. The latter one has then been used as a support for HKUST-1, a copper-based Metal Organic Framework which has been synthesized by mechanochemical treatment.

In terms of application, this work focused on the oxidation of cyclohexane and 1-phenylethanol under mild conditions. First of all, application Cu-V catalyst on cyclohexane oxidation was studied by comparing the influence of two different types of energy input, namely mechanochemical (ball milling) and microwave irradiation. The highest conversion was obtained by ball milling, in solvent free procedure, with Cu-V catalyst (1:2 mass ratio). This is a good indication that improvements are still possible, since the reactor conditions used in industry are over dated (they have more than 30 years) and this green procedure, performed for the first time in this work, is a promising result in order to implement a change in the industrial process. With this new procedure it is possible to diminish the amount of waste because is solvent free and the cost of the catalyst preparation is low.

Secondly, the different composites were tested as catalysts in 1-phenylethanol oxidation. As reported, several conditions were studied, namely the effect of time, temperature and quantity. At first, the substrate was reacted in the presence of different types of bi-metallic composites that were synthesized by ball milling. Results show that the addition of additives enhances the catalyst activity and that temperature is the clue operating parameter. The best results are obtained with a rhenium-based catalyst supported wit 1% of graphene oxide.

The 1-phenylehtanol oxidation was also tried with copper-based MOF (HKUST-1) and results (yield, TON, TOF) show improvement with respect the bi-metallic composites since 90% yield is reached with 2 h reaction at 120°C. Finally, 1-phenylethanol oxidation with biomass supported metal catalyst was also performed. In general, the catalyst shows higher activity, with respect the HKUST-1 and the bi-metallic compounds. The best performance concerns the biomass supported metal catalyst that was synthesized by mechanochemical mixing and results are quite promising since a 90% yield is achieved with half an hour reaction at 120°C.

In terms of societal improvement, the work described in this thesis shows that the application of biomass from waste is a promising filed for changing the paradigm in industry and consequently improving the management of waste produced, obtaining a more efficient and eco-friendly process that leads to a better quality of life. Moreover, this promising application is in agreement with The European Chemical Industry Council (CEFIC), which commits the chemical industry to improve its management of chemicals and chemical processes, which are central to its commitment to Sustainable Development.

As future work, characterization by X-ray Photoelectron Spectroscopy (XPS) should be performed for all composites to evaluate if the grinding only mixed the salts or created new compounds in different oxidation states. Nonetheless, further work in optimizing the operational parameters for the synthesis of the catalysts should be done to decrease the size of the composites. The operational parameters that can be improved are the number of spheres, reactional time and grinding velocity.

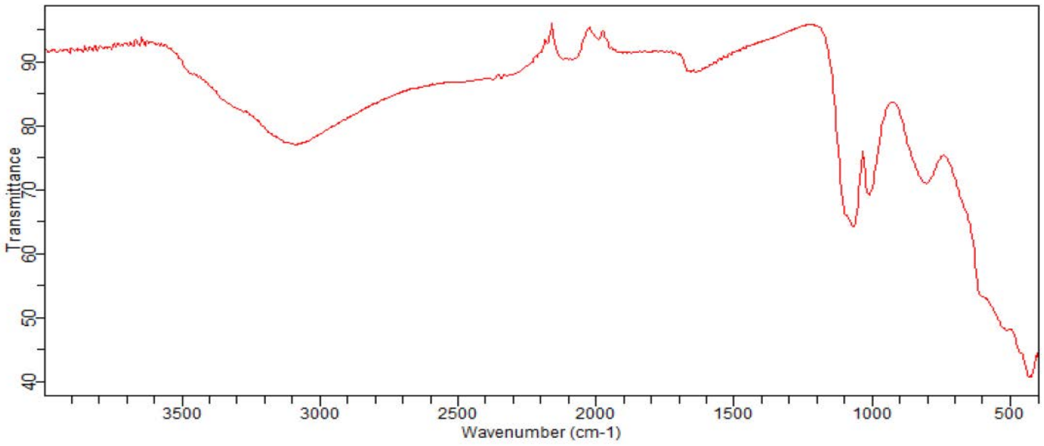
Regarding the MOF, supporting it for improving dispersion is a possible solution. Also synthesizing new MOFs with higher content of metal can be a possibility to improve the yield of the studied reactions.

For biomass, the best results observed were obtained using the ball milling procedure which means that the size of the composite is an important parameter and grinding at higher velocities or with different number of spheres should be studied. Another task that should be done as future work is a systematic analysis of the operational cost for industry to compare the final cost of the product obtained.

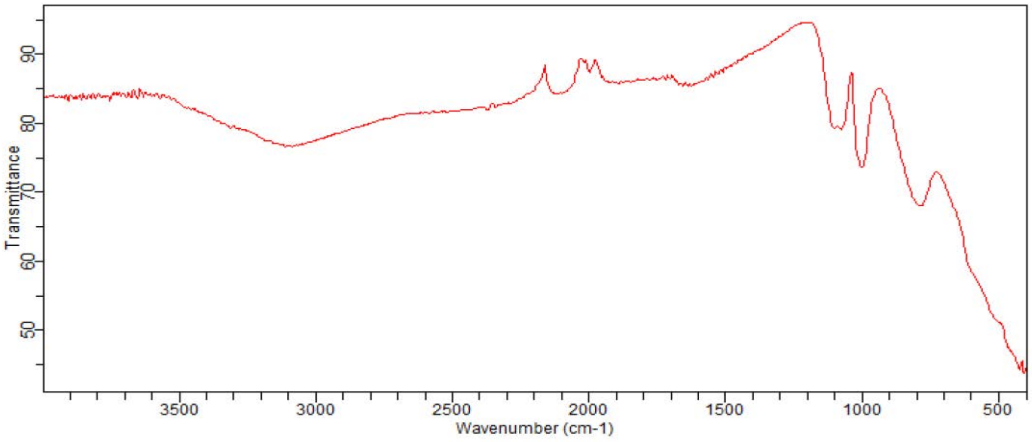
Annex A

FTIR-ATR spectroscopy

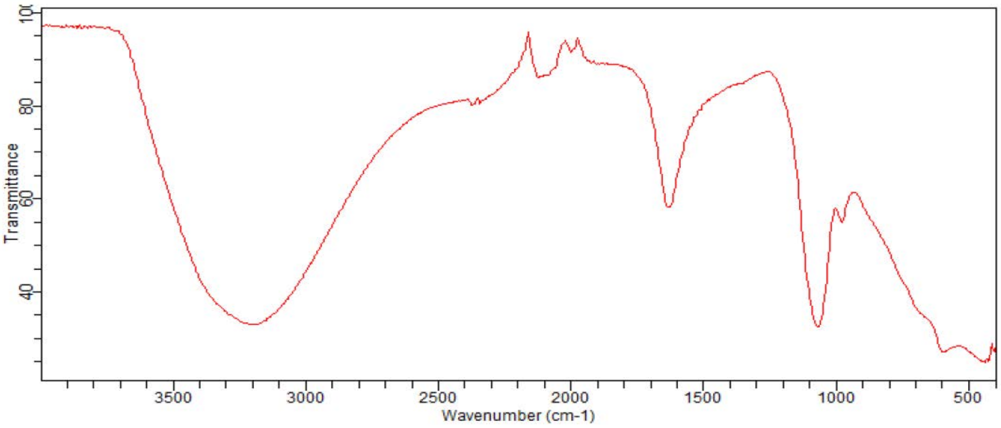
The reported spectroscopies concern catalysts n°9 to 16, 33, 37 and 39. Also the HKUST-1 spectroscopy is reported.



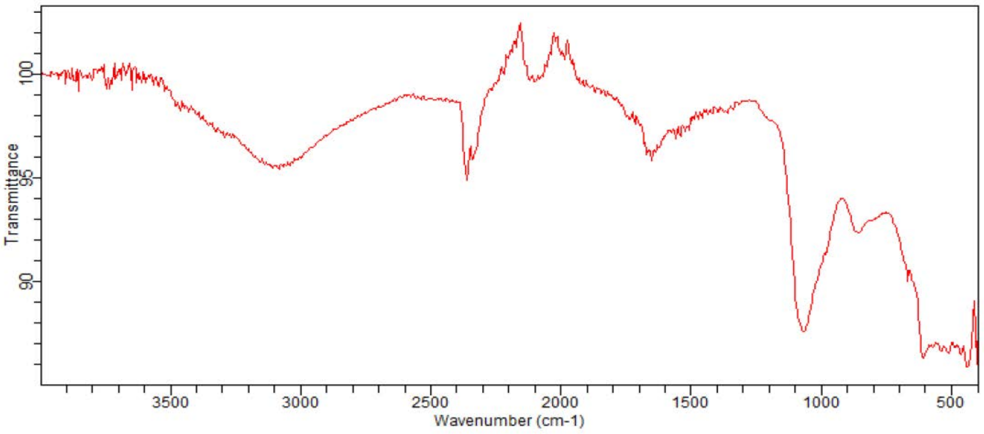
Catalyst n°9



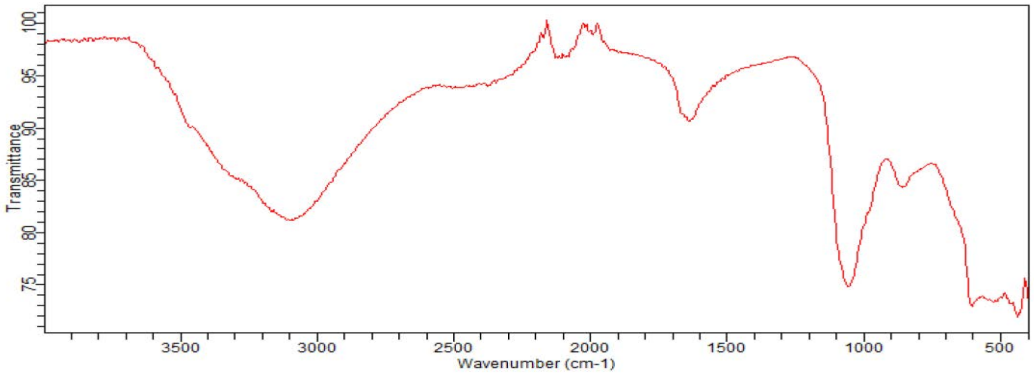
Catalyst n°10



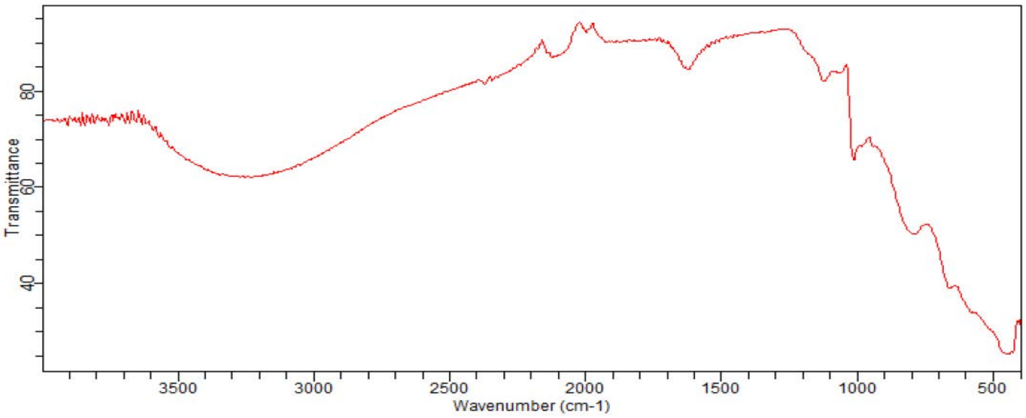
Catalyst n°11



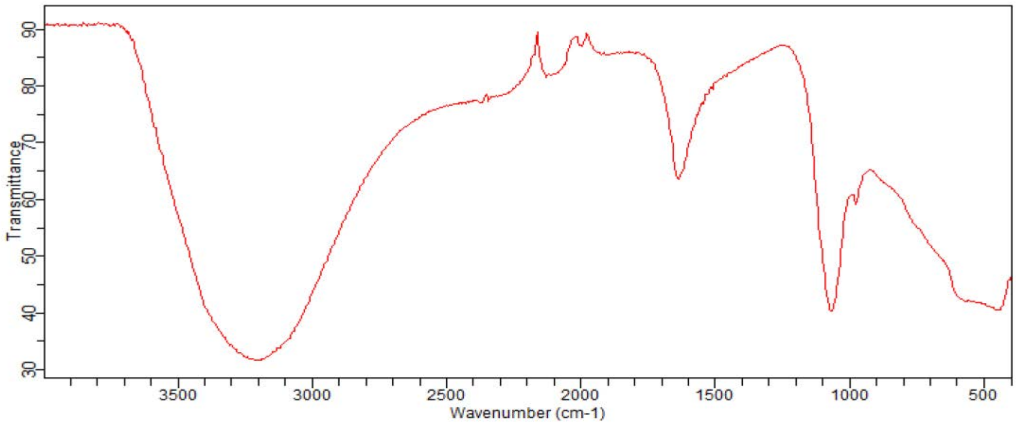
Catalyst n°12



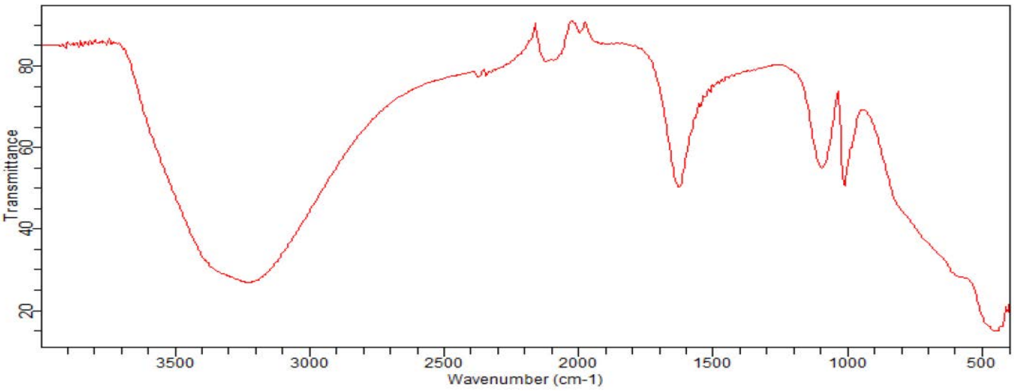
Catalyst n°13



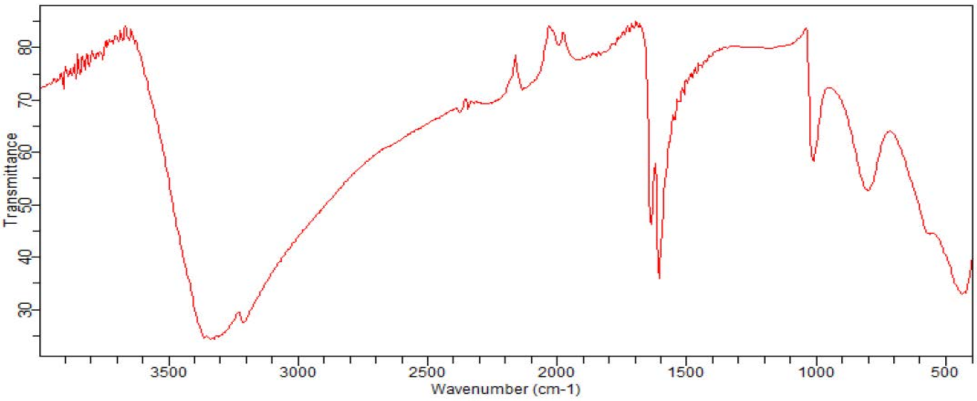
Catalyst n°14



Catalyst n°15



Catalyst n°16



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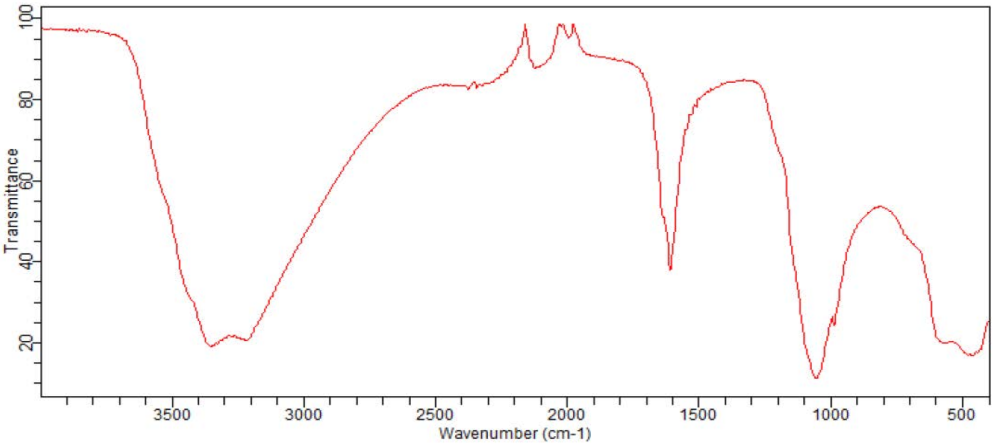
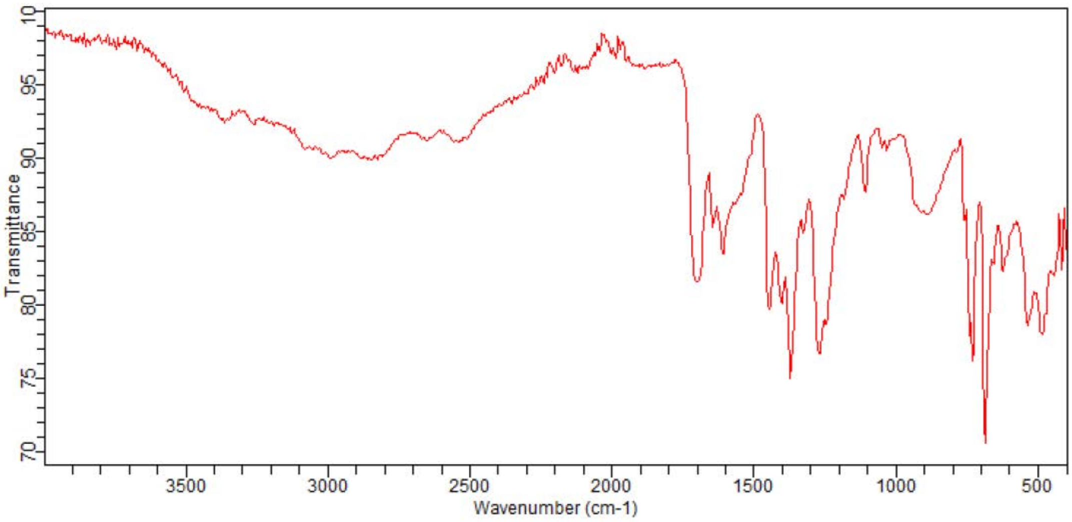


Catalyst n°16


Transmittance
10
95
90
85
80
75
70
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

HKUST-1

Annex B

Cyclohexane reactions list

B.1 Ball milling reactor

N° Catalyst	Catalyst [µmol]	Reactant	Qt [µL]	Oxidant	Operating Parameters
9	44.04	Cyclohexane	540	O_2	2 h; 10 spheres; 500 RPM
10	48.43	Cyclohexane	540	O_2	2 h; 10 spheres; 500 RPM
11	44.55	Cyclohexane	540	O_2	2 h; 10 spheres; 500 RPM
12	50.52	Cyclohexane	540	O_2	2 h; 10 spheres; 500 RPM
13	43.60	Cyclohexane	540	O_2	2 h; 10 spheres; 500 RPM
14	49.40	Cyclohexane	540	O_2	2 h; 10 spheres; 500 RPM
15	52.49	Cyclohexane	540	O_2	2 h; 10 spheres; 500 RPM
16	57.00	Cyclohexane	540	O_2	2 h; 10 spheres; 500 RPM

B.2 Microwave reactor

N° Catalyst	**Catalyst [µmol]**	**Reactant**	**Qt [µL]**	**Oxidant**	**Qt [mg]**	**Operating Parameters**
9	44.04	Cyclohexane	110	$K_2S_2O_8$	400.1	1 h; 50°C; 650 RPM
10	48.92	Cyclohexane	110	$K_2S_2O_8$	400.2	1 h; 50°C; 650 RPM
11	45.00	Cyclohexane	110	$K_2S_2O_8$	400.1	1 h; 50°C; 650 RPM
12	49.52	Cyclohexane	110	$K_2S_2O_8$	399.9	1 h; 50°C; 650 RPM
13	44.04	Cyclohexane	110	$K_2S_2O_8$	399.8	1 h; 50°C; 650 RPM
14	48.42	Cyclohexane	110	$K_2S_2O_8$	399.8	1 h; 50°C; 650 RPM
15	51.46	Cyclohexane	110	$K_2S_2O_8$	400.1	1 h; 50°C; 650 RPM
16	57.57	Cyclohexane	110	$K_2S_2O_8$	400.1	1 h; 50°C; 650 RPM

Annex C

1-Phenylethanol reactions list for biomass supported catalyst

C.1 Biomass supported catalyst synthesized in acid solution

Entry	**Reactant**	**Qt [µL]**	**Oxidant**	**Qt [µL]**	**Catalyst Qt [mg]**	**Operating Parameters**
1	1-Phenylethanol	600 µL	TBHP	955 µL	9.9	0.5 h; 80°C; 650 RPM
2	1-Phenylethanol	600 µL	TBHP	955 µL	10	1 h; 80°C; 650 RPM
3	1-Phenylethanol	600 µL	TBHP	955 µL	10.2	2 h; 80°C; 650 RPM
4	1-Phenylethanol	600 µL	TBHP	955 µL	10.2	0.5 h; 100°C; 650 RPM
5	1-Phenylethanol	600 µL	TBHP	955 µL	10	0.5 h; 120°C; 650 RPM
6	1-Phenylethanol	600 µL	TBHP	955 µL	5.2	1 h; 100°C; 650 RPM
7	1-Phenylethanol	600 µL	TBHP	955 µL	20.1	1 h; 100°C; 650 RPM

C.2 Biomass supported catalyst synthesized in ethanol

Entry	**Reactant**	**Qt [µL]**	**Oxidant**	**Qt [µL]**	**Catalyst Qt [mg]**	**Operating Parameters**
1	1-Phenylethanol	600 µL	TBHP	955 µL	9.9	0.5 h; 80°C; 650 RPM
2	1-Phenylethanol	600 µL	TBHP	955 µL	10	1 h; 80°C; 650 RPM
3	1-Phenylethanol	600 µL	TBHP	955 µL	10.3	2 h; 80°C; 650 RPM
4	1-Phenylethanol	600 µL	TBHP	955 µL	10	0.5 h; 100°C; 650 RPM
5	1-Phenylethanol	600 µL	TBHP	955 µL	10	0.5 h; 120°C; 650 RPM
6	1-Phenylethanol	600 µL	TBHP	955 µL	5.4	1 h; 100°C; 650 RPM
7	1-Phenylethanol	600 µL	TBHP	955 µL	20.1	1 h; 100°C; 650 RPM

C.3 Biomass supported catalyst synthesized by mechanochemical treatment

Entry	**Reactant**	**Qt [µL]**	**Oxidant**	**Qt [µL]**	**Catalyst Qt [mg]**	**Operating Parameters**
1	1-Phenylethanol	600 µL	TBHP	955 µL	10	0.5 h; 80°C; 650 RPM
2	1-Phenylethanol	600 µL	TBHP	955 µL	9.9	1 h; 80°C; 650 RPM
3	1-Phenylethanol	600 µL	TBHP	955 µL	10.2	2 h; 80°C; 650 RPM
4	1-Phenylethanol	600 µL	TBHP	955 µL	10.2	0.5 h; 100°C; 650 RPM
5	1-Phenylethanol	600 µL	TBHP	955 µL	10.3	0.5 h; 120°C; 650 RPM
6	1-Phenylethanol	600 µL	TBHP	955 µL	5.3	1 h; 100°C; 650 RPM
7	1-Phenylethanol	600 µL	TBHP	955 µL	20.6	1 h; 100°C; 650 RPM

Nomenclature

Aint = Internal standard area (μV·s)

Ac = Acetophenone area (μV·s)

As = Substrate area (μV·s)

TON = $\frac{\text{Moles of product}}{\text{Moles of catalyst}}$

TOF = $\frac{\text{TON}}{\text{Time } [h]}$

RPM = Revolutions per Minute (rounds/min)

A = Pre-exponential factor

E_a = Activation energy ($J \cdot mol^{-1}$)

R = Universal gas constant ($J \cdot mol^{-1} \cdot K^{-1}$)

T = Temperature (°C or K)

Acronyms

BM = Ball Milling

CS = Core-Shell

CSNPs = Core-shell nanoparticles

GC = Gas Chromatography

TON = Turn Over Number

TOF = Turn Over Frequency

Qt = Quantity

EDS = Energy Dispersive X-RAY Spectroscopy

SEM = Scanning Electron Microscopy

FID = Flame Ionization Detector

MW = Microwave

MOFs = Metal Organic Frameworks

GO = Graphene Oxide

KA oil = Ketone-alcohol oil

ACN =Acetonitrile

FE = Field Emission

TEM = Transmission Electron Microscopy

UV = Ultraviolet

FTIR-ATR = Fourier Transform Infrared Spectroscopy-Attenuated Total reflection

USD = United States Dollar

TBHP = Tert-butyl hydroperoxide

XPS = X-ray Photoelectron Spectroscopy

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