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Mechanochemical solvent-free synthesis of Sn-β Zeolite and Ag_2O/TiO2 catalysts

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KEY WORDS

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Ag_2O/TiO_2

Acronim List

MPV reaction: Meerwein-Ponndorf-Verley Reaction

DMGA: 2,2 Dimethyl-Glucaric Acid

HMF: Hydroxymethylfurfural4

HPLC: High Performance Liquid Chromatography

GC: Gas Chromatography

XRD: X-Ray Diffraction

TPR: Temperature Programmed Reduction

TCD: Thermal Conductivity Detector

XPS: X-ray Photoelectron Spectroscopy

MP-AES: Microwave Plasma Atomic Emission Spectroscopy

UV-vis: Ultraviolet-Visible

IR: Infrared

MAS-NMR: Magic Angle Spin Nuclear Magnetic Resonance

SSI: Solid State Incorporation

Abstract:

Preparations of heterogeneous catalysts are usually complex processes that involve several procedures as precipitation, crystallization and hydrothermal treatments. These processes are tightly dependent by the operative conditions such as temperature, pH and concentration. Hence, the resulting product is extremely affected by any possible variations in these parameters making these syntheses really difficult to carry out with reproducible results. With the aim to improve these operations has been decided to exploit a new possible strong environment-respectful process by mechanochemical treatment, which permits to carry out solvent free-solvent synthesis exploiting the Mixer Mill MM400 (Retsch) in order to have reproducible results.

Two different systems have been studied in this kind of synthesis: a tin β -zeolite tested in the H-transfer reaction of cyclohexanone and a silver on titania catalyst used in the fluorination of 2,2 dimethyl glucaric acid. Each catalyst has been characterized by different techniques in order to understand the transformations involved in the mechanochemical treatment.

The training period for the production of this work was done at the University of Cardiff with Dr. C. Hammond

Summary

1.Objective

This project has been developed my period of thesis at Cardiff Catalysis Institute (CCI) (Wales) in the Hammond group.

This group is spending a lot of effort in order to produce catalyst by solvent-free synthesis, respectful for the environment and more convenient from an economic point of view than the normal routes of synthesis[4].

However, optimize this kind of synthesis is not easy at all. In fact, the research until now has found many issues related to the reproducibility of the catalyst properties, this kind of operation in fact are usually carried out manually by operators with pestle and mortar. This implies that many variables can interfere in the process every time that it is performed.

Hence, until now, it has been difficult to synthesize a catalyst with reproducible performances every time, and this has influenced a lot the trustworthiness of the data making impossible an accurate scientific work on this catalyst.

The aim of this project is to find a strong and reproducible method to carry out this synthesis by a mechanochemical process with the same results every time that the synthesis takes place. Indeed, it has been decided to study this new route of catalyst synthesis for two systems that are characterized by completely different properties to understand which kind of effects this treatment produce on different materials:

- Synthesis of *10% (w/w) Sn-β Zeolite* for Meerwin-Ponndorf-Verley (MPV) reaction for Cyclohexanone to Cyclohexanol[1]
- Synthesis of *1% (w/w) silver on titania catalyst* exploited in the fluorination reaction of 2,2 dimethyl glucaric acid with SelectFluor®[24].

It is important to remember that even if mechanochemistry is a powerful technique is not possible (at least nowadays) to perform the synthesis of a whole catalyst with it, in fact we are suppose just to perform some steps of the their synthesis as the incorporation of tin the β zeolite framework and the deposition of silver(I) oxide on titania.

1.1 Syntheis of Silver on Titania catalyst for fluorination reactions

The target reaction for this part of the project is the fluorination reaction for 2,2 dimethyl glucaric acid with selectfluor® as fluorinating agent (figure 1.1):

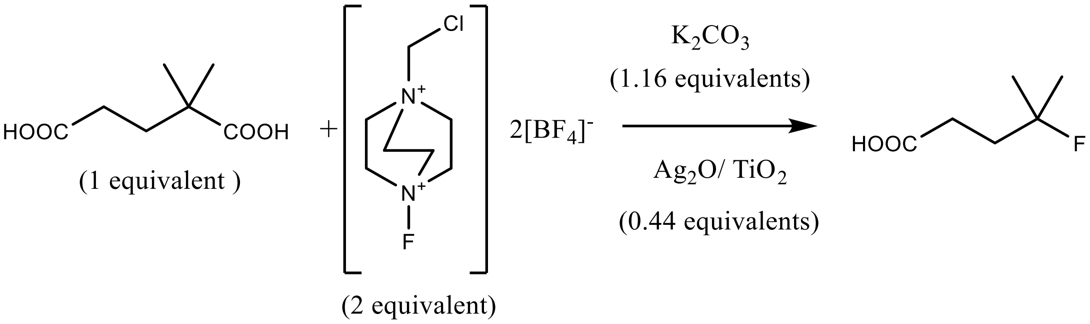


Figure 1.1: scheme of target fluorination reaction

Several problems have been met in the synthesis of this catalyst in Hammond group, in fact, the catalyst made by physical mixture performed with pestle and mortar has never showed the same catalytic performance, this probably is caused by the kind of treatment sensitive to the strength that the operator applies to perform the synthesis.

Indeed this catalyst showed another important issue: the leaching value was high, some silver was brought in aqueous solution during the reaction, and this silver was able to keep on catalyzing the reaction on its own.

This obviously has to be improved because the main scope of this part of the project is carry out this reaction in heterogeneous conditions, instead of the already known homogeneous reaction catalyzed by silver (I) nitrate[23].

Hence, the necessary development to achieve for this part of the project is essentially:

- Find out a mechanochemical route of synthesis for this catalyst that permits to obtain reproducible data every time that the catalyst is produced. This probably means that the exploitation of a machine is necessary to have a constant strength applied on the powder in the grinding.
- Explore these possible routes also in order to find a way to support strongly the silver (I) oxide on titania in order to have low value of silver leaching.
- Explore the possibilities to recycle this catalyst and, if necessary, develop a method to regenerate it after the fluorination reaction.

1.2 Synthesis of 10% tin β-Zeolite for H-transfer reaction

The reaction performed in order to test this catalyst is Meerwin-Ponndorf-Verley (MPV) reaction for transforming cyclohexanone in cyclohexanol with 2-butanol (figure 1.2):

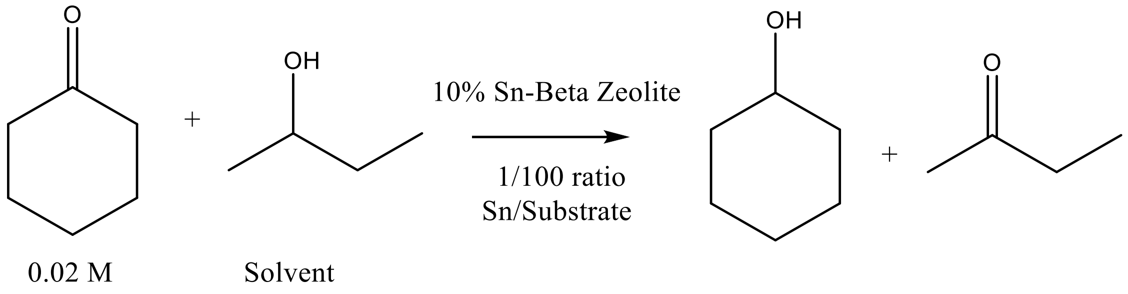


Figure 1.2: scheme of MVP reactions

This is a standard reaction that has not a great importance from an Industrial point of view, but it is largely used in order to check if a catalyst is able to perform H-transfer reactions. Hence, this is the starting point to develop catalyst able to perform the glucose-fructose isomerisation that instead has a great importance nowadays in order to exploit renewable sources.

The main issues that Hammond group has found in development of this material are two:

- the reproducibility is not high, in fact sometimes changing the operator the catalysts have different performances, this probably is caused by the a different application of strength that could disperse the source of tin differently, and so different loadings of tin are incorporated in the silanol holes
- Has been noticed that increasing the loading of tin above 8% the incorporation is difficult because the tin tends to aggregate as SnO_2 during the calcinations, so it could be a good achievement to find a synthesis route that disperse better the source of tin preventing the agglomeration during the calcinations, allowing higher value of incorporate tin[5].

2. Introduction

2.1 Heterogeneous catalysis

One of the most important fields of chemistry from an industrial point of view is Catalysis; this subject is interested in the development of catalytic materials that allow to carry out reactions with higher constant rate or with a better selectivity. It is so easy to understand why catalysis is really important for environment issues, in fact improving the performances of a reaction is possible to get better the whole Industrial process and so for example have less waste from by-products that could be harmful for the nature and can be eliminated with a new catalytic material. Indeed development in catalyst are also important because they can permit to change the raw material of a reaction: in the last 20 years a lot of efforts have been done to change the substrate for a huge number of productions, that were used to be done from petroleum. Nowadays instead, renewable sources of energy as biomass are exploited in order to have Green Processes respectful for the environment. These are only a few example of what catalysis represent for improving the efficiency of chemical processes in the world, but are already useful to understand the extreme importance of the research in this field of chemistry.

Exploring deeper catalysis is important to explain that we have basically two kind of catalysis: the homogeneous catalysis (where the catalyst and the substrate are dispersed in the same phase) and heterogeneous catalysis (where the catalyst and substrate are in two or three different phases). It is difficult to say which is the best in terms of costs and performances, it might be correct to say that this two kind of catalysis are used depending at the process requests and issues. Anyway it is easy to say which are their advantages: homogeneous catalysis permits a great interaction with the particles of the substrate and the catalyst and so it is possible to have mild reaction conditions, the main problems of this catalysis are about the separations of the catalyst and its recycle, in facts being the two components in the same phase it is much more expensive to separate them; otherwise if they were in different phases, as in heterogeneous catalysis, downstream processes would be much easier. However, heterogeneous catalytic materials have problems about mass transfers from the substrate phase to the catalyst and because of this; the conditions of reaction have to be harsher.

This simplicity in the downstream processes of heterogeneous catalysis is its strong point, in fact the 80% of catalysts in the world are heterogeneous, but it is important also to study the synthesis processes for this catalysts, because it is important have new catalytic material that permit to carry out new environment respectful processes but it doesn't make sense if in order to do that catalyst harmful and dirty synthesis are used. A multitude of technique are exploited to synthesize catalysts and sometimes the mechanisms that take place in them are not well understood and so it is important to improve the knowledge about them considering how huge is their production.[2].

2.2 Standard preparations of the catalysts

Solid catalysts are highly sophisticated products derived from chemicals by several different procedures.

The catalytic properties of heterogeneous catalysts are strongly affected by every step of the preparation and from the quality of the raw material, but different method can be applied even for the same catalyst, thus gives an idea of how much is complicate and sometimes unknown what is happening during the preparations at these kind of materials. Anyway despite the complexity and the multitude of the methods it is possible to indentify some unit operations that present some analogies from one catalyst to another one and can be described in a general way[2]:

- Chemical and physical transformations taking place in the synthesis
- The scientific laws that rule this kind of transformation (most of the case from inorganic chemistry)
- Variables operations such as Temperature, pressure, pH, concentration etc
- Characteristic of the product after the synthesis
- Type of required apparatus

Al the methods that will be discuss later present almost all this kind of operations, that are a good general guide of what implies the synthesis of a catalyst. However if the methods change as function of the material that we want to build up it is also important to figure out and classify the kind of heterogeneous catalyst with respect to the preparations procedure[3,4]:

1) *Bulk Catalyst and Supports:* bulk catalysts are mainly composed of all active phase, such as the Pt/Re net used for the oxidation of NH_3 to NO. Supports, prepared by

similar procedures, are usually oxides on which active phase is deposed in order to perform the reaction. Often these materials have some activity on their own (Al2O3, TiO2, SiO2...)

2) *Impregnated catalyst:* are usually obtained from preformed support by impregnation with active phase.
3) *Mixed-Agglomerated Catalyst*: they are obtained by mixing the active substance with a powdered support or a support precursor and then agglomerating the mixture[3].

2.2.1Precipitation and Co-precipitation

This way of synthesis is based on the precipitation of a solid from a liquid phase; this could happen for physical ways (such as increasing the temperature or for solvent evaporation) or could be due to a chemical process (addition of acids and bases or using complexes agents).

This method consists basically of three moments.

The first is *Supersaturation:* in this while the concentration of the precursors of the catalyst have an higher concentration then their maximum solubility, this metastable phase precedes the precipitation and can be caused by a changing of pH, a decreasing of temperature or the with the adding of an anti-solvent . This moment is really important in order to decide the particle size that will be precipitated; in fact increasing the supersaturation a faster *Nucleation* will take place. This is the second crucial moment of the precipitation process, in this moment nuclei of precipitate are formed in solution and their number depends on how much is high the supersaturation value. With a high supersaturation rate, more nuclei are formed in solution and so smaller particles are formed; this could not be spontaneous and so sometimes seeds of precipitations are added to the solution. The last moment is the *Growth* of the nuclei: in this moment the size of the nuclei growths, and so it is possible to have the dimension control.

It is possible to build some graphs in temperature vs concentration for each system, where can be identified some the condition of solubility of the system (figure 2.1)[4].

The difficult task of this process is obtaining high supersaturation values because the natural evolution of the system toward a decrease of supersaturation by nucleation of solid particle and consumption of the reagent, indeed high supersaturation value gives some problem about the mass and heat transport rate that bring to non-homogeneous precipitate respect to the size and structure.

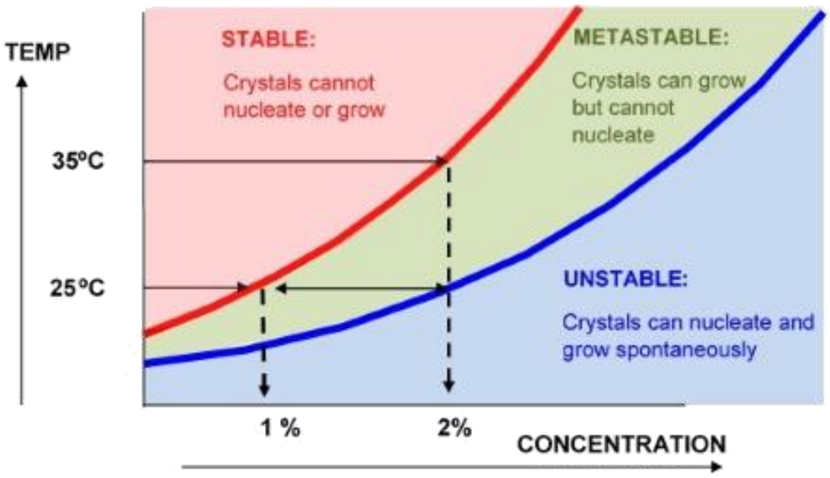


Figure 2.1: The solubility and supersaturation curves of precipitating component material[4]

In the synthesis of multicomponent system the mechanism is even more complex. In coprecipitation in fact is really difficult to have a good macroscopic homogeneity, thus is caused from the differences in solubility of the different species to precipitate. Generally after the formation of the precipitate hydrothermal treatment are necessary in order to transform the structure from amorphous to crystalline with improved thermal stability and surface area acidity[4].

These kinds of catalysts are the most diffused because this method is relatively simple, it is possible to control the size of the precipitate and the costs are not so high for industrial application. The most used catalysts are the hydroxides and carbonates that have a really low solubility but high solubility of the precursors, known structure and usually the doesn't give environmental problem during the calcinations[3].

2.2.2 Impregnation

The impregnation method is widely used in order to prepare catalyst composed of noble metal on supports, and it consists in the mixing of a solution of precursor of the metal and the support as solid; this method is divided in three steps[3]:

1) Contacting of the support with the impregnating solution for a certain period of time
2) Drying the support to remove the imbibed liquid
3) Activating the catalyst by calcinations, reduction or other appropriate treatment

These are the topic moments of the synthesis but we have two kind of impregnations in which this phases can be recognized. The first is the *wet impregnation,* here an excess of solution is used; after a certain time the solid is separated from the solution, and the excess solvent is removed by drying. The amount of the active precursor mounted onto the porous carrier, its concentration profile within the carrier grains, and its chemical environment on the support surface depend significantly on the conditions during these first two steps in catalyst preparation. Then the laws and parameters that rule the loading of active phase on the support are basically the mass transfer that is possible in the pores of the support, the concentration of the precursor in the solution and the adsorption isotherm which describes the binding energy of the precursor on the support surface. In figure 2.2 is possible to see how this process is carried out in an industrial implant[3].

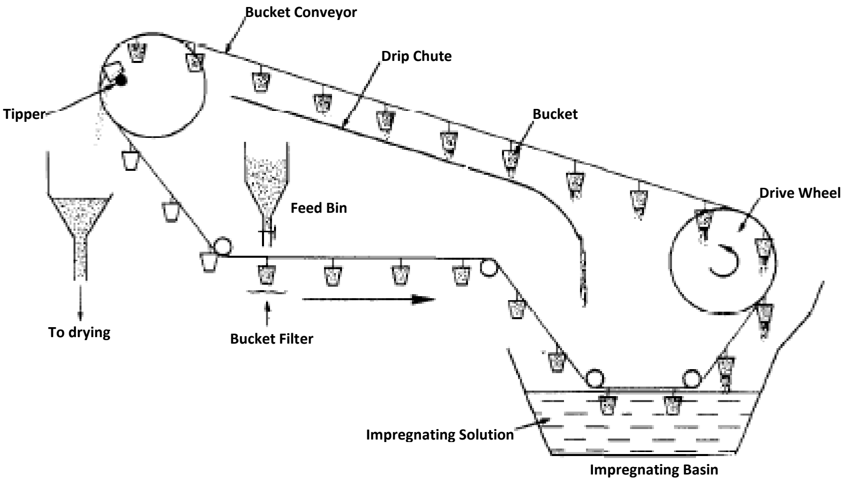


Figure 2.2: wet impregnation process[3]

The second way to carry the impregnation out is through *incipient wetness impregnation*, in this way repeated applications of solution are used. A more precise control is achieved with this technique. The support is contacted with a solution of appropriate concentration, corresponding in quantity to the total known pore volume or slightly less. This operation can be performed continuously as in figure 2.3. The catalyst is kept in motion in a rotating cylinder or drum, and is sprinkled as required with a solution of salt by sprayers. The disadvantage is the poorer distribution of the precursors that bring to an inhomogeneous deposition of the active phase on the support.

The limit of this method is obviously the solubility of the precursor in the solvent, in order to avoid that it is possible to use two strategies: the easier way is drying the catalyst and then repeat the process of impregnation, but this obviously brings to higher costs and longer time of production. The other possibility is to increase the solubility of the precursor increasing the acidity or others parameters, the problem of this route are the damages that the support could undergo for the extreme conditions of the treatment[4].

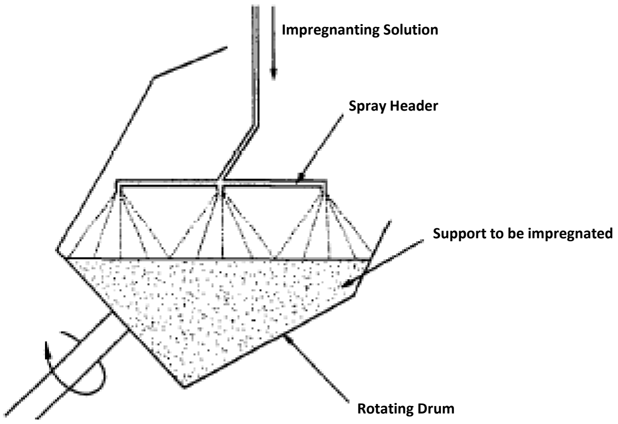


Figure 2.3: incipient wetness process[3]

2.2.3 Gelation and Floculation

Gelation and flocculation are two catalyst way of synthesis that can be carried out by hydrophilic colloidal solution of the catalyst precursors; these are formed of micelles that remain separated because of electrical charges on their surface and in surrounding solutions. This kind of solutions can be obtained via chemical reactions of polymerization and polycondensation. The reticulation of these micelles forms the hydrogel, a three dimensional network that imprisons molecules of water. This point of the process is called gelation and it depends from many features as pH, temperature, concentration and ionic strength (Figure 2.4 is possible to see the mechanism of gelation and flocculation).

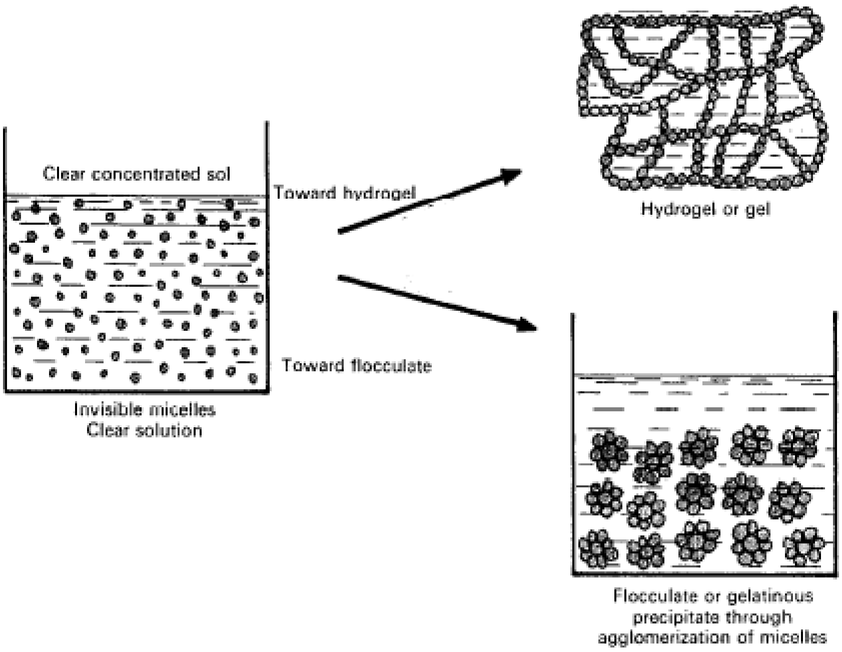


Figure 2.4: schematic mechanism of flocculation and gelation[3]

These gels can be dried by simple evaporation of the solvent, but evaporating the solvent in the pores of the material it is possible to provoke at the pores shrinkage with a concomitant reduction of surface area. The mechanical forces due to the retreating water menisci in the pores cause this; the easiest way to avoid that is try to replace water (the most used solvent) with another one that is characterized by a lower surface tension. This should prevent the shrinkage of the pores during the drying or of evaporation of the solvent.

Other two ways are possible in order to prevent the breaking of the structure in the evaporation phase: the first is by formation of an *Areogel*, this method carries out the drying of the solvent by supercritical extraction. For this reason, this method needs for high temperature and pressure in order to transform the liquid into the pores of the material in a supercritical fluid that does not present a so high surface tension to break the material's structure.

The second method to perform this synthesis by the formation of a *Cryogel*, that way exploits the freezing and the sublimation of the solvent in which is dissolved the gel[4].

The flocculation of a sol can be obtained through the neutralization of the micelles charges (Figure 2.4). The final surface area of the solid depends on the original micelle size and also on the drying conditions.

2.2.4 Crystallization and Hydrothermal treatment

Crystallization is widely exploited in the preparations of homogeneous microporous solids; a class of monophase crystalline solids in which the active phase is distributed uniformly. When these kind of operation are carried out in water at 375 K the conditions are designed as ''hydrothermal''; this has proven to be the most efficient way to produce these microporous materials.

Hence for hydrothermal transformations are considered all the modifications of precipitates, gel or flocculates induced by temperature, under aging or ripening in the presence of mother liquor and they usually involves textural or structural modification of the solid that can be summarized in:

1) Small crystals → Big crystals
2) Small amorphous particles → large amorphous particles
3) Amorphous solid → crystalline solid
4) Crystal type ''A'' → Crystal type ''B''
5) High porous gel → low porous gel

All this transformations follow the laws of thermodynamic and thus proceed in a direction corresponding to a decrease in free energy of the system[4].

This method of catalysts synthesis is exploited also to produce the Zeolite: this is a crystalline porous material made up by Silicates (SiO_4) and alluminates ions (AlO_4^-) polymerized together in a uniform structure. The synthesis of this material usually passes through sol-gel dissolution of the ions that under hydrothermal treatment crystallize in the wanted kind of

Zeolite. Nowadays several zeolite structures are known and they are exploited in a lot o chemistry field for their great activity, selectivity and resistance at the reactions conditions.

For example zeolite are widely exploited in the fluid catalytic cracking of petroleum, It is widely used to convert the high-boiling, high-molecular weight hydrocarbon fractions of petroleum crude oils to more valuable gasoline, olefinicgases, and other products. This process is carried out at very high temperature and the raw material is not clean, for that are used zeolites as a catalyst; in fact, they are suitable materials to resist and be regenerated easily in this conditions.

2.3 Mecchanomechanical synthesis of catalysts

Previously the most exploited ways to produce heterogeneous catalysts have been described; it is possible to understand how complicated and fragile methods they are.

In facts, they depend strongly from a huge number of conditions as pH, temperature, concentration, stirring etc...

These features have a great effect on the final products and a changing in one of them could compromise the result of the synthesis, these problems obviously generate high cost and the need of sophisticated apparatuses. Indeed high amounts of solvent are usually required in these kind of synthesis, that is obviously a problem as a process point of view because it is necessary to have an efficient downstream separation, but it is also a problem for the environment because the solvent will be polluted by all the chemicals involved in the process, and so it has to be treated before to be disposed[5].

Considering that this synthesis last usually days, the researchers working in this field of chemistry are looking for developing new kind of synthesis that can improve the preparations of catalysts reducing the costs and simplifying all the processes.

It is so easy to understand why many groups are recently working on the developing of *mechanomechanical synthesis of heterogeneous catalyst.*

2.3.1 Mechanochemistry: general features

‘’ Mechanochemistry is a branch of chemistry dealing with the chemical and physicochemical changes of substances in all states of aggregation due to the influence of mechanical energy’’; this is the first definition of mechanochemistry given in 1887 by Ostwald[8].

When energy is added to a solid substance by mechanical treatment such as crushing, grinding, rolling or impacting, the deformation and subvision of the solid occur simultaneously with rapid increase of the surface energy due to the increase of surface area. The mechanical energy added to crystal particles during grinding has a great effect of the crystal structure of the particles and the changing of the physicochemical property of the solid due to the mechanical action is thus call "mechanochemical effect"[6]. Different kind of devices are used to transmit this mechanical energy, one of the most used machine industrially exploited is the Ball Mill (Figure 2.5)

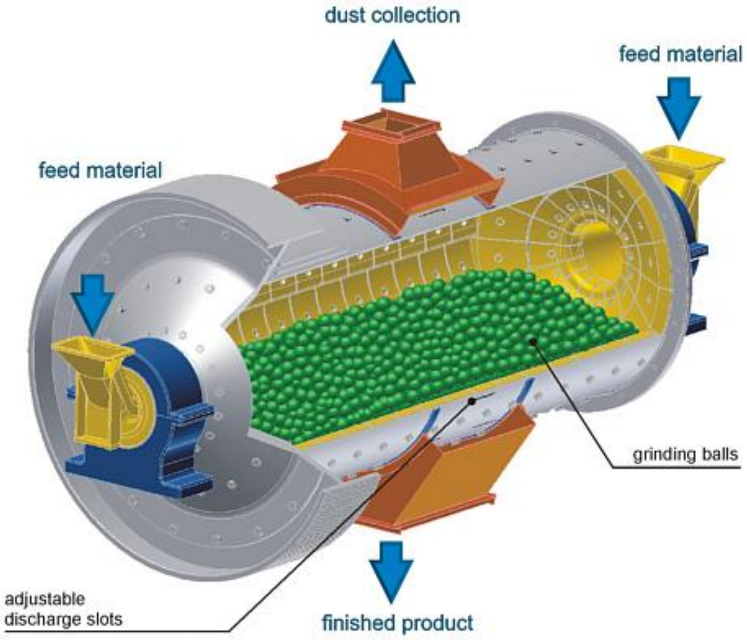


Figure 2.5: Example of Industrial Ball[7]

Nowadays it is increasing the interest for this field of chemistry for different kind of applications, since inorganic chemistry to the most sophisticated organic synthesis.

This technique in fact, even if it works by complicated mechanisms, permits to carry out processes in solvent-free conditions that have a great gain in terms of implant, costs but especially for developing green-sustainable processes. From an industrial point of view, this kind of operations are not properly solvent-free, in fact they are use to be carried out in wet conditions in order to control the emission of the fine dust and improve the mixing, but in any case they allow to reduce substantially the volumes and amount of solvent.

For this incredible potentialities researchers are trying to understand what is happening in this complicated mechanichal treatment and in particular applying this concept to all kind of chemistry: organic chemistry in facts employs mechanochemical treatment on cellulosic materials, whose molecular chain can be degraded by mechanical comminution; but also in organic synthesis this kind of technique is becoming really important because has been studied that some organic reactions present a different activity and selectivity if carried out with a solvent-free mechanical synthesis, instead of a normal reaction in solvent[8].

On the other hand, what is more important for the aim of this work is the applicability of these techniques in Inorganic Chemistry; in fact, many mechanochemical operations are actually exploited to synthesize or modify some inorganic materials[8].

2.3.2 Mechanochemistry and Inorganic Materials

Resuming the effect of this treatment on inorganic materials is possible to identify these four generic ones[8]:

- Generations of new large surfaces
- Formation of point defects
- Phase transformation in polymorphic materials
- Chemical reactions

In most of the works, the cause for the mechanocemical effects is not qualitatively discussed in terms of the energetic conditions of collision. However these phenomena have been explained in terms of near surface dislocations and slip, and highly localized transient ‘’hot spots’’. For example in the high speed rolling of aluminium, temperatures close to the melting point of the metal are generated in the vicinity of the line of contact in the rolling operation, at these temperatures the higher mobility of atoms in the near-surface regions, near-surface dislocation, and oxidation are realities.

This explains why some reactions that take place usually in solution can be carried out also with this method in fact in inorganic synthesis such solid state reaction are possible only under three conditions[9]:

1) The reaction should be thermodynamically feasible from the consideration of Gibbs free energy changes
2) The two reacting species should be in intimate contact
3) The temperatures should be typically above the 40% of the melting point of the inorganic solid.

These temperatures are empirically defined to be between 0.4T_m and 0.5 T_m (T_m is the fusion temperature), usually after 0.3 T_m the mobility of surface defects becomes significant and increasing over this point the mobility of the species on the surface is possibly to carry out reactions on the solid material[7].

Then changing point of view on the physical properties of the material treated in the communiting device, it is possible to imagine many types of forces occurring when solids are ground but the most common forces that particles undergo are compression, impact and shear (Figure 2.6). Finely ground particles with a narrow size distribution are produced when the applied stresses are mainly due to *shear*. It is difficult instead to produce fine particle when only compressive stresses are used, and the width of the size distribution obtained tends to be broadened. Impact forces instead give intermediate results between shear and compressive forces; obviously is not possible to apply selectively one kind of stress or another one, but it is possible to have a predominant stress as function of the device exploited[6].

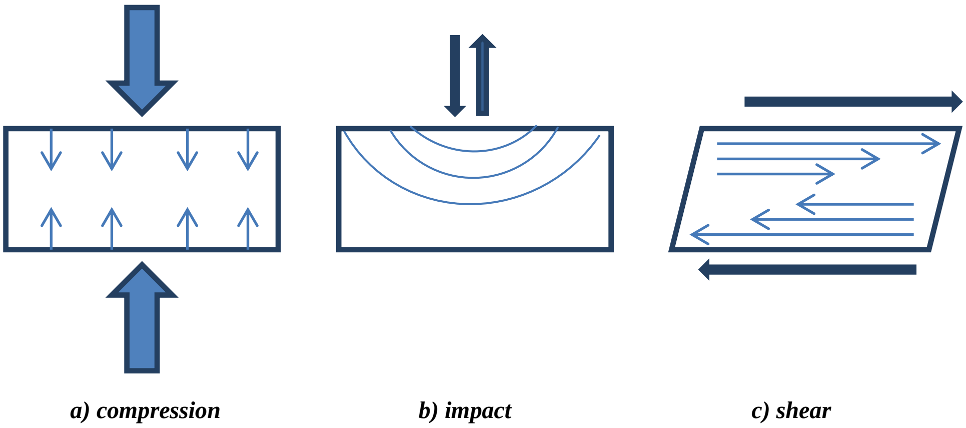


Figure 2.6: The most common forces applied on the materials by mechanical treatment[5]

2.3.3 Ball mill as grinding device

Of particular interest in this field is the exploitation of the ball mills as device to treat the materials, this device is composed of a capsule in which is located the solid and the balls, that will grind the powder during the movement of the capsule. A multitude of different type of ball mills are available but all of them have general points in common, in fact this kind of device is generally use to apply impact stress that, as explained before, is a middle way between the shear and the compressive stress, making so really interesting its effects on materials[5].

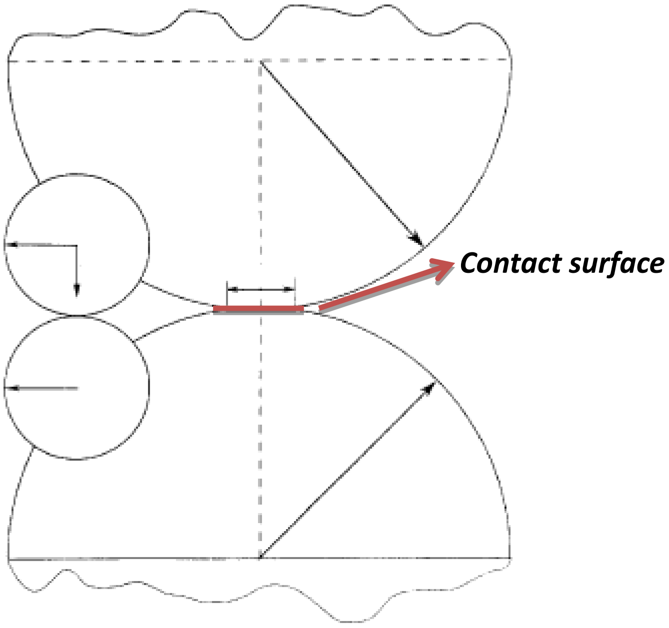


Figure 2.7: schematic illustration of ball mill spheres[7]

In this apparatus the particles caught between the colliding balls (or between the ball and the capsule) experience high stress; further, most of the collision energy is applied over a small contact area, represented by the surface contact between the spheres, that makes the applied energy per area extremely high (Figure 2.7). Indeed considering the high velocity of the balls in the capsules this strength is applied for a short time, and the time of relaxing is short as well leading to very high stress gradient. All the factors are conductive to giving highly localized and transient hot spots, where the temperatures are high enough to cause thermally induced atom mobility in the near surface region in and around the contact area between the colliding balls, leading to mechanochemical effects on the material[9]

2.4 Introduction to the Reaction involved in the work

In order to apply the mechanochemical synthesis we chose different material to study the answers of different supports to this kind of preparation, but it has been decided to apply this technique also for catalysts that were intended to work in two different field of chemistry.

In fact, we chose to study the fluorination reaction to employ this catalyst mainly in production of fine chemical with high added value. Instead, the Meervein Ponndorf Verley (MVP) H-transfer reaction was chosen as test reaction of the more industrially important glucose-fructose isomerisation. This reaction is studied to convert glucose in fructose from which is possible to synthesize a huge number of molecules; hence, this catalyst is intended to work in bigger market, near to the bulk chemicals[10].

2.4.1 Glucose-fructose isomerisation and Sn-β Zeolite

Nowadays is of great interest the exploitation of renewable sources of raw material, especially if they are second generation sources (that means they are not in competition with food resources), hence biomass are playing an important role in this revolution of chemistry, but their utilization is not so easy to execute[11].

Biomass is a complex material made up different parts as lignin, cellulose, and hemicelluloses; between them, the easiest material that can be used as source of raw molecules is the cellulose that is a polymer made up by β-glucose monomers that in this way can be easily obtained.

Glucose is an important raw material to obtain a huge number of molecules of great interest for Industrial chemistry as Adipic Acid (use in the synthesis of nylon), Lactic acid (exploited in the synthesis of biocompatible polymers), Methacrylic acid (used as well in polymers synthesis) and Furanic cycles[11] (figure 2.8).

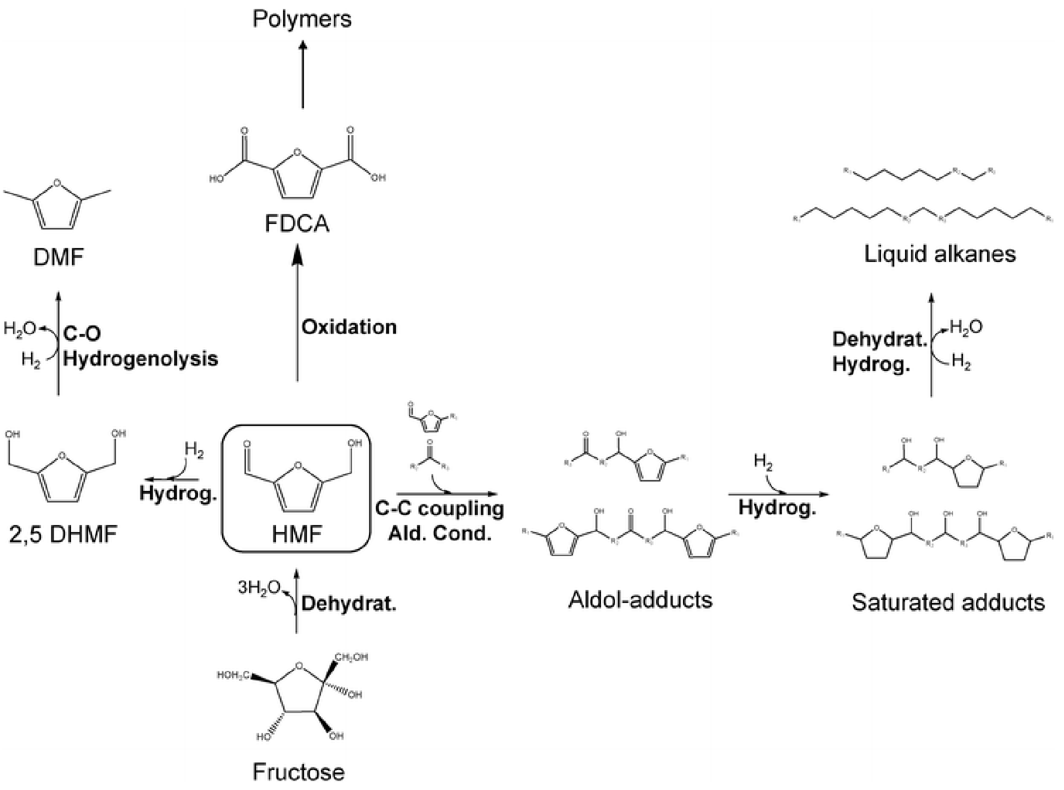
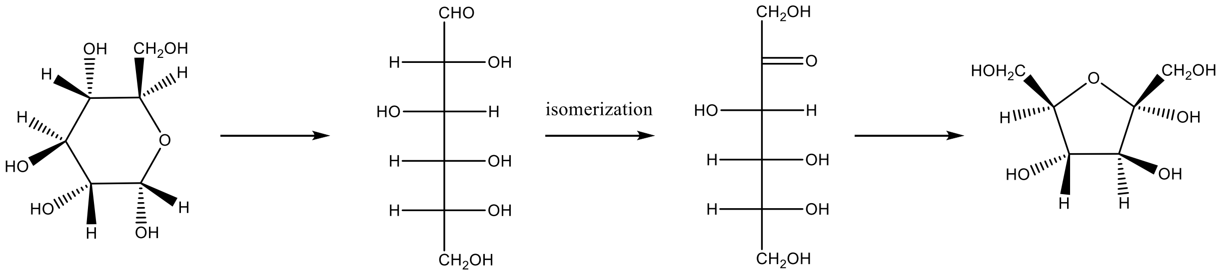


Figure 2.8: examples of fructose exploitation as platform molecule[11]

A lot of other molecules can be synthesized by glucose but furanic cycles, for example Hydroxy-methyl Furfural (HMF), are having a great success as platform molecules.

Hence their synthesis is deeply studied and all of this kind of cycles come from Fructose, that is obtained by glucose via isomerisation (Fig 2.9), this is not a banal reaction in fact was used to be carried out with enzymes that have great efficiency and selectivity for this reaction. On the other hand, their problem is that enzymes are complex systems that have to work in restricted conditions of temperature, pH and pressures[10].



ring form Glucose
open form glucose
open form fructose
ring form fructose

Figure 2.9: glucose-fructose isomerisation

These issues added to the high costs of enzymes made difficult their exploitation in processing huge amounts of glucose: so many efforts have been spent in order to find an inorganic catalyst that can perform this reaction in larger range of conditions but also with fewer problems from a separation point of view.

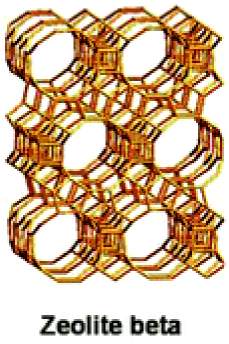


Figure 2.10: typical structure of β-Zeolite[12]

Tin-containing silicates have recently emerged as a new class of inorganic solids with Lewis acid character capable of activating carbonyl functional groups in the presence of water. The pioneering work of Moliner at al[13] showed that Sn-β Zeolite (Figure 2.10) is highly active in Meerwin-Ponndorf-Verley (MPV) reaction; this is a family of H-transfer reactions that can be used to test the effectiveness of this catalysts. The same, but intramolecular, H-transfer reaction in fact can be exploited to perform the isomerisation glucose-fructose. The mechanism of action of this catalyst is shown in Figure 2.11

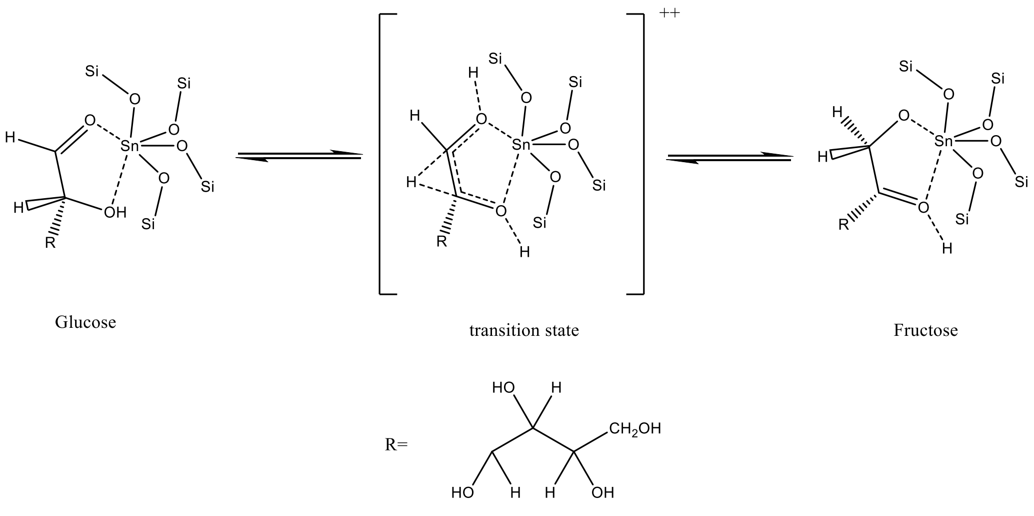


Figure 2.11: mechanism for intramolecular H-transfer reaction in glucose-fructose isomerizatio

2.4.2 Synthesis of Sn-β Zeolite

Tin-β Zeolite is actually produced by hydrothermal crystallization process in which is used a reaction mixture prepared by combining sources of tin, silicon, a templating agent a fluoride source and water. In this preparation method are used as reactive tin tretrachloride and fluoric acid as source of tin and fluoride respectively, obviously these are not the best reagent as green chemicals, in fact fluoric acid is extremely toxic and has to be avoided in all the processes and tetrachloride releases chloridric acid that is highly corrosive, harmful for the workers and its acidity ruins the implants apparatus. Indeed 40-50 days are necessary to crystallize the material that is a very long time that enhances the costs of production (Figure 2.12)[14].

For this reasons many efforts are being spent to discover new way of synthesis for the Sn-β zeolite that can decrease the costs and safety of the process.

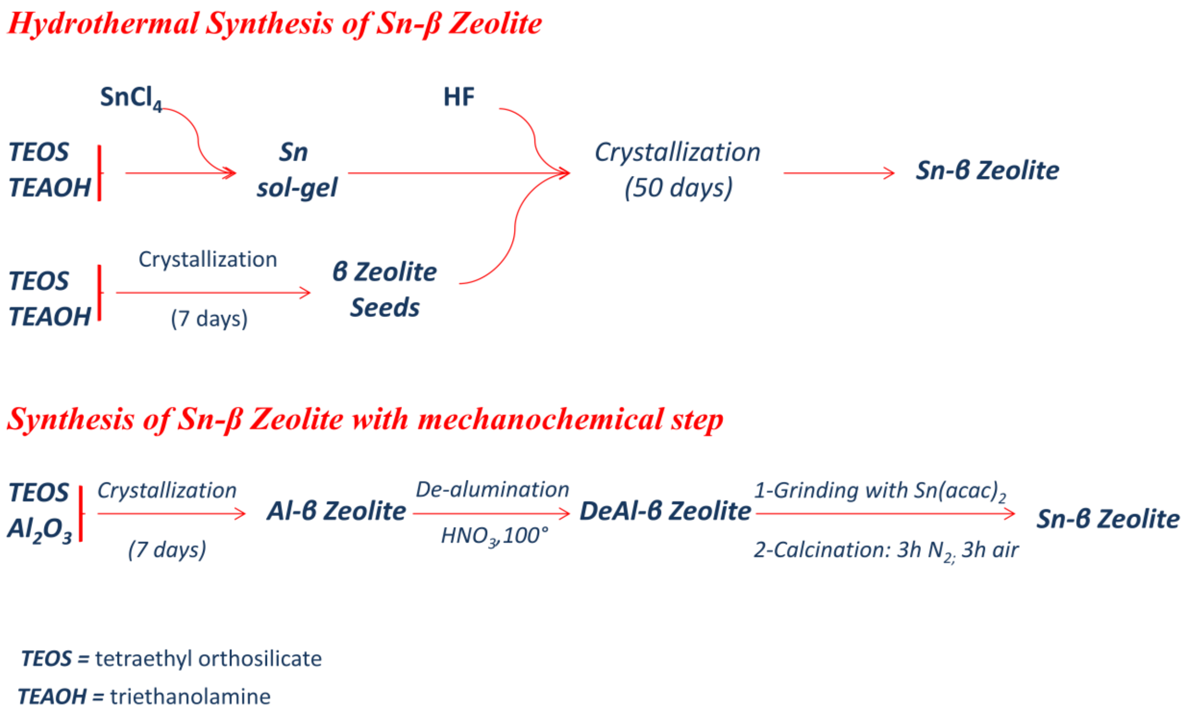


Figure 2.12: comparison between hydrothermal and mechanochemical synthesis

Actually Hammond group has developed a new way of synthesis for this catalyst by mechanochemical treatment, this method consist in a solid state incorporation (SSI) of the Tin exploiting as source of tin the tin (II) acetate. The SSI method is divided in two fundamental steps[4]:

- De-Alumination of β-zeolite by acid treatment with a solution of HNO_3
- Grinding of De-Aluminated zeolite with the source of tin and calcination of the mixture

In the first step, the aluminium is removed from the structure leaving so some vacations between the silanols group (silanol holes). Then during the grinding the tin(II) acetate is dispersed in the solid and then is incorporated in this holes during the process of calcinations in air that permits to burn the acetate anion of the salts (figure 2.13). If the tin is well incorporated it will full the silanol holes instead of aluminium, otherwise it will form some tin (IV) oxide agglomerates that are not useful for carrying out the H-transfer reaction.

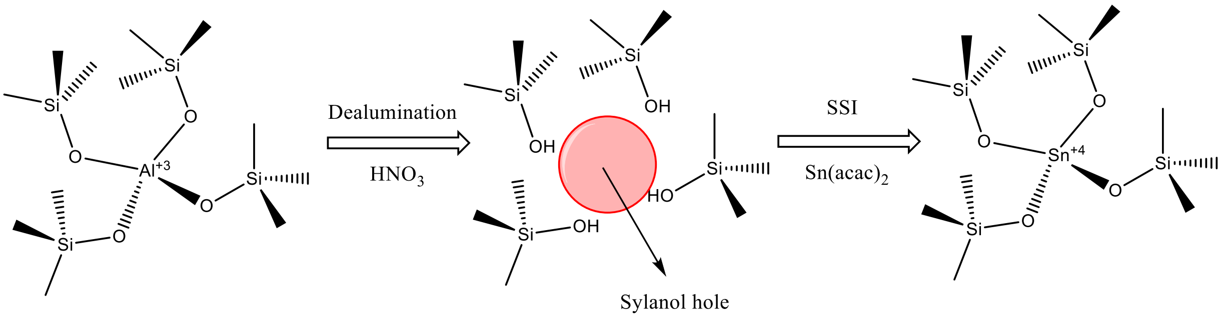


Figure 2.13: Solid-state incorporation mechanism

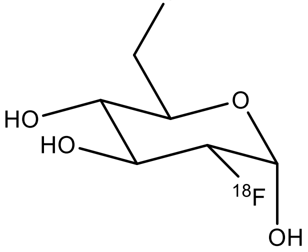
2.4.3 Fluorination: industrial importance

Carbon-fluorine bond formation is playing an ever-growing role in the synthesis of chemicals and pharmaceuticals, because the introduction of fluorine atoms alters markedly the physical, chemical, and biological properties of the organic molecules. Hence, a lot of groups and researchers are committed to developing new way to construct C-F bond[15].

The main applications for this fluorination reactions compounds are in the synthesis of drugs where fluorine atoms can alter the lipophilicity and metabolic stability, which can enhance the bioavailability and efficacy of a drug compound. In 2006 in fact the percentage of the drugs containing fluorinated structures reached approximately 20% of the total market, and in agrochemical market up to 30% of the compound in general use contain fluorine atoms in the main structure[16].

Indeed fluorine it is widely exploited in the polymer industries where it is used to functionalize monomers to synthesize chemicals-resistant polymers such as Teflon (polytetrafluorethylene). Then it is used also for the synthesis of compounds for molecular emission tomography (PET) imaging that is a technique exploited for cancer diagnosis. The most produced compound for this scope is Fluorodeoxyglucose (Figure 2.14), that is a modified glucose molecule with the –OH group on the second atom of carbon that is substituted by an ^{18}F atoms[17-18]. This modification does not allow the metabolisation of this molecule that is accumulated in the tissues, and will be absorbed only by cells that have a fast metabolism and therefore need a large need of glucose to be operative, such as the brain, kidneys and rapidly multiplying tumours.

Despite fluorine is abundant in nature there only a small number of organic compounds occurring naturally, also for this reason the development of facile and versatile fluorination method are essential.



ùFigure 2.14: Fluorodeoxyglucose (^{18}F)

2.4.4 Reactants and Processes

Reactants for carrying out fluorination reaction can be divided in two main categories: nucleophilic and electrophilic fluorinating agents**,** several examples of this kind of reactants are reported in table 2.1[19].

Nucleophilic fluorinating agent	**Electrophilic fluorinating agent**
Alkali metal fluoride	N-fluoropyridinium salts
Tetraalkylammonium fluoride	Selectfluor® and derivates

Table 2.1: Reagent exploited as fluorinating reactants

Nucleophilic reactants are exploited in the fluorination of hydrocarbons having a leaving group that can be easily substituted with the fluoride ions supplied by the fluorinating agent.

In industries, this kind of reaction often exploits ion exchange of halogen (Halex process) to replace one halogen atom in the molecule (typically chlorine) with another one that in this case is fluorine[20].

In order to perform this process are required electron-withdrawing groups (EWGs), that are able to activate the halogen atom in the molecule, that so can be substituted by halide ion supplied by the metal halide (usually employed as source of new halogens in this reactions) .

Unfortunately this reaction has several drawbacks that makes this synthesis really costly, in facts in order to activate the halogen atom the EWGs groups required are really strong and the temperature are usually up to 200°C, high temperatures are not only a problem for the energetic costs and implants materials, but usually they cause side reactions that decrease the hypothetic performances of the process.

For this reasons it is also of great importance the study of electrophilic reactants as fluorinating agents, but with them, it is not simple to get reactions to occur producing the specific hilarity required. In order to improve the regioselectivity and enantioselectivity for this reaction has been exploited the use of nucleophilic organometallic reagent to react with the electrphilic fluorinating agents[21]. Otherwise is also studied the exploitation of transition metals as catalyst to improve the performances of this fluorinating agents[22].

2.4.5 *SelectFluor® and Silver catalyst*

Selectfluor® is an electrophilic fluorine source firstly described in 1992 and since then become one of the most widely available and often used commercial sources of fluorine for fluorination reactions. SelectFluor® is a trademark of the company ''Air products and Chemicals'' it has been projected to be a safe electrophilic fluorinating agent but at the same time with a strong fluorination effect. This reactant has been studied for different reactions and with many catalysts, of great interest is the reaction of decarboxylative fluorination promoted by $AgNO_3$ (20% mol) in homogeneous solution and carried out in mild condition, this reaction is performed in a mixture water-acetone in order to dissolve catalyst and the SelectFluor® (two equivalents)[23].

The proposed mechanism for this reaction on 2,2 dimethyl glucaric acid is shown in figure 2.15.This is a radicalic reaction, that is highly selective for the substitution of the carboxylic group linked to the tertiary carbon, that thanks to the influence of the vicinal methyl-group stabilize better the incipient radical formed in the intermediate of reaction.

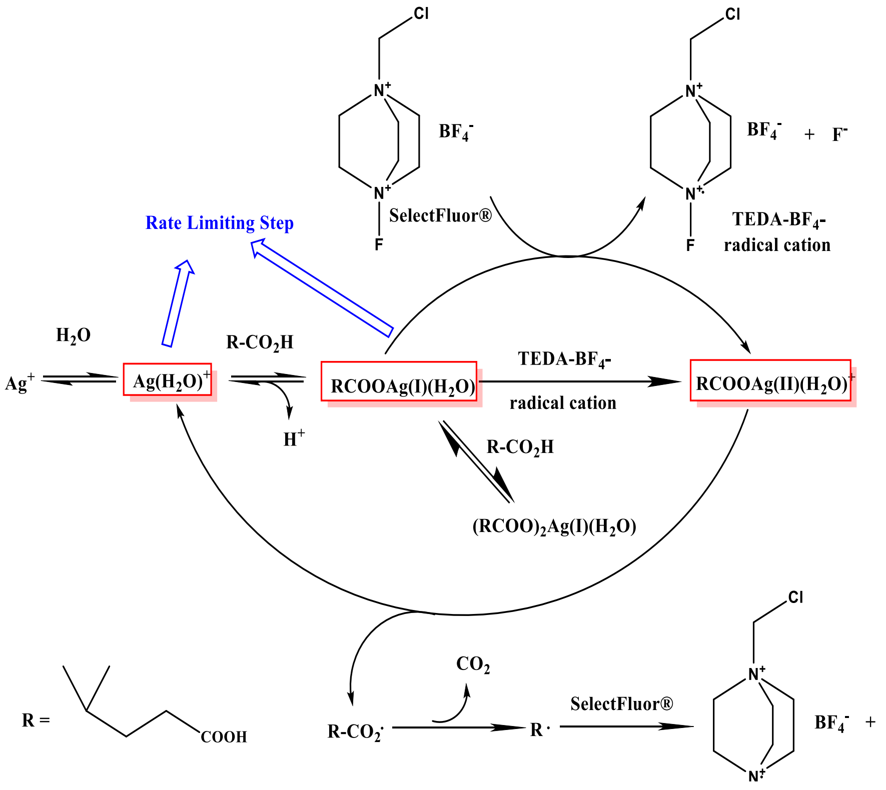


Figure 2.15: mechanism of Fluorination Reaction for 2,2 Dimethyl glutaric acid by computational work of X.Zhan[24]

Recently Hammond group has developed a new heterogeneous route for this kind of fluorination, in fact reactions performed with SelectFluor® have been usually carried out in homogeneous solution, this kind of condition brings to high cost for the product purification from the metal dissolved in solution as catalyst, instead with the heterogeneous conditions the separation is much easier and the recycling of the catalyst could be much more convenient.

Firstly the heterogeneous catalyst was synthesized by sol-gel immobilisation where silver-nanoparticles were deposited on titania; then ,thanks to the mechanistic study in Figure n.11 has been demonstrated how the reaction doesn't need for the presence of metallic silver to carry out the reaction, but Ag (I) and Ag(II) are the only active species[24]. Hence, from this achievement a solvent-free synthesis has been developed to produce a catalyst of silver (I) oxide deposited on Titania, simply by grinding the support with the oxide powder.

3. Experimental Part

3.1 Chemicals

In Table 3.1 is possible to find the chemicals exploited for the synthesis of the titania and silver catalysts, and their subsequent catalytic reactions.

Chemical	Brand	Purity
TiO_2 aeroxide P25	Aerosil®	>99%
AgO_2	Sigma Aldrich®	>99%
2,2 Dimethyl Glutaric Acid	Sigma Aldrich®	98%
Succinic Acid	Sigma Aldrich®	>99%
K_2CO_3	Sigma Aldrich®	>99%

Table 3.1: Chemicals used in fluorination reaction

In table 3.2, the chemicals used in the synthesis and catalytic reactions of Sn β-zeolite are reported.

Chemical	Brand	Purity
Zeolite β (Si/Al=38)	Zeolyst®	>99%
Sn(II) $(acac)_2$	Sigma Aldrich®	>99%
Nitric Acid	Sigma Aldrich®	70%
Cyclohexanone	Sigma Aldrich®	99%
Cyclohexanol	Sigma Aldrich®	99%
Biphenyl	Sigma Aldrich®	>99%
2-Buthanol	Sigma Aldrich®	>99%

Table 3.2: chemicals used in MPV Reaction

3.2 Catalyst synthesis

3.2.1 Synthesis of 10% Tin β-Zeolite

Commercial zeolite Al-β (Zeolyst, NH_4- for, SiO_2/Al_2O_3) was dealuminated by treatment in HNO_3 solution (13 M HNO_3, 100°C, 20h, 20 mLg^{-1} zeolite). The reaction mixture was washed extensively with water (around 500 mL per g of catalyst), and dried overnight at 110°C in an oven. The solid obtained was later grinded with pestle and mortar to get a homogeneous powder, after which period Solid State Incorporation was performed by a modified procedure of ref[5] using a mixer mill (mixer mill M400, Retsch). The appropriate amount of tin (II) acetate was added at the zeolite and the sample was grinded in the mixer mill for 20 minutes at various frequencies (3 – 30 Hz). The amount of metal to use in the catalyst synthesis was calculated with the equation n.1.

$$\frac{\boldsymbol{w}}{\boldsymbol{w}}\% = \frac{\boldsymbol{mass\ of\ metal\ (g)}}{\boldsymbol{mass\ of\ support\ (g)}} * \mathbf{100}$$

Equation n.1: calculation to find out the metallic loading in a supported catalyst

Following this procedure, the sample was heated in a combustion furnace (Carbolite MF12/38/400) to 550°C (10°C min^{-1} ramp rate) first in a flow of N_2 (3h) and subsequently air (3h) for a total of 6h. Gas flow rates of 60 mL^{-1} were employed at all the times. The sample was held horizontally in an alumina combustion boat (10 mL capacity), and a quartz tube was used to seal the sample environment and permit gas flow.

The catalysts synthesised by this protocol are reported in Table 3.3.

Name	***Catalyst***	***Preparation***	***Note***
FM016	10% Sn β-Zeolite (w/w)	mechanochemical+calcinations	3 s^{-1}, 3h air + 3h N_2
FM017	10% Sn β-Zeolite (w/w)	mechanochemical+calcination	7.5 s-1, 3h air + 3h N_2
FM018	10% Sn β-Zeolite (w/w)	mechanochemical+calcination	11 s-1, 3h air + 3h N_2
FM019	10% Sn β-Zeolite (w/w)	mechanochemical+calcination	15 s-1, 3h air + 3h N_2
FM020	10% Sn β-Zeolite (w/w)	mechanochemical+calcination	22.5 s-1, 3h air + 3h N_2

Table 3.3 : catalysts synthesized in to explore 10% Sn β-Zeolite activity

3.2.2 Synthesis of silver (I) on Titania catalyst

The silver(I) supported on titania catalysts were synthesized with the Mixer Mill (mixer mill M400, Retsch^{TM}) according to the following procedure. Silver (I) oxide (>99%, Sigma Aldrich) was added to the Titania Aeroxide P25 (Acros Organics) in order to have a catalyst with a metal loading of 1wt.%, as calculated by equation n.1. The mixture was grinded for 20 minutes at different frequencies (3 – 30 Hz). Then samples were subsequently heated in a combustion furnace (Carbolite MTF 10/25/150) at different temperatures. The synthesized catalysts are reported in table 3.4.

Name	Catalyst	Preparation	Note
FM001	1% Ag/Titania (w/w)	physical mixture	10 minutes high intensity
FM002	1% Ag/Titania (w/w)	physical mixture	20 minutes high intensity
FM003	1% Ag/Titania (w/w)	physical mixture	40 minutes high intensity
FM004	1% Ag/Titania (w/w)	physical mixture	20 minutes low intensity
FM005	1% Ag/Titania (w/w)	FM001+calcination	150°C, 3h air atmosphere
FM006	1% Ag/Titania (w/w)	FM001+calcination	200°C, 3h air atmosphere
FM007	1% Ag/Titania (w/w)	FM001+calcination	250°C, 3h air atmosphere
FM008	1% Ag/Titania (w/w)	FM001+calcination	300°C, 3h air atmosphere
FM009	1% Ag/Titania (w/w)	FM001+calcination	350°C, 3h air atmosphere
FM010	1% Ag/Titania (w/w)	FM001+calcination	400°C, 3h air atmosphere
FM011	1% Ag/Titania (w/w)	mechanochemical	3 s^{-1} of frequency
FM012	1% Ag/Titania (w/w)	Mechanochemical	7.5 s^{-1} of frequency
FM013	1% Ag/Titania (w/w)	mechanochemical	15 s^{-1} of frequency
FM014	1% Ag/Titania (w/w)	mechanochemical	22.5 s^{-1} of frequency
FM015	1% Ag/Titania (w/w)	Mechanochemical	30 s^{-1} of frequency

Table 3.4: synthesized catalyst for the fluorination reaction

3.2.3 Mixer Mill MM400 (Retsch^{TM})

In order to perform the target work of this project, a milling machine was employed, in order to allow all the catalysts preparation to be performed with a high degree of reproducibility and under a wide range of experimental conditions. The machine employed was a Mixer Mill MM400 from Retch (Figure 3.1).

Figure 3.1: Mixer Mill MM400 (Retsch^{TM})

This machine is composed by two arms that are each attached to one steel jar (25mL). The sample is located within this capsule, along with a steel ball of 0.7 cm diameter.

In this machine, the grinding jars of the MM 400 perform radial oscillations in a horizontal position. The inertia of the grinding balls causes them to impact with high energy on the sample material at the rounded ends of the grinding jars and pulverizes it. Also, the movement of the grinding jars combined with the movement of the balls result in the intensive mixing of the sample; and the important thing is that is possible to regulate accurately the oscillation of the jars in order to have a reproducible energy in the grinding. The Mixer Mill MM400 can cover from 3s^{-1} to 30 s^{-1} of oscillation frequency with steps of 0.1 s^{-1}, so a huge number of frequencies can be explored reproducibly.

3.3 Catalytic Tests

3.3.1 Fluorination Reaction

The fluorination of 2,2-dimethyl glucaric acid (figure 3.2) was performed with a 10 mL round bottom flask at room temperature under stirring (700 rpm), every reaction has been performed with these reaction parameters:

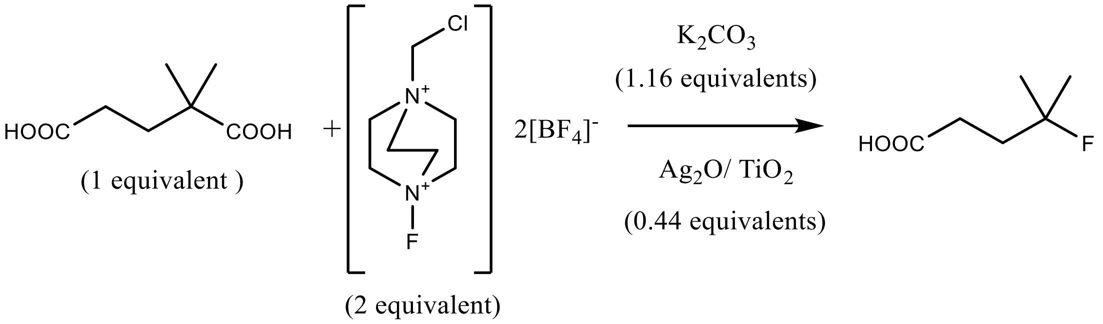


Figure 3.2: Fluorination reaction scheme

SelectFluor®: 0.1417 g (0.4 mmol)
K_2CO_3: 0.032 g (0.231 mmol)
Silver (I) oxide on titania (1wt.% loading of Ag) : 0.100 g
2,2-Dimethyl glucaric acid solution (2.5 mM) : 4 mL
Atmosphere : N_2
Temperature : Room temperature
Stirring : 700 rpm
Time : 2 hours

The reaction was started by adding a solution of 2,2-Dimethyl glucaric acid (2.5 mM) by syringe. During the reaction, samples of 0.1 g were withdrawn periodically for analysis. Prior to injection into the HPLC, samples were centrifuged and diluted to 0.5 mL by addition of a solution of 1,4-succinic acid (3 mM) taking note of the exact mass of sample that was diluted. Since the standard is not internal (it was used to react instead of the 2,2 Dimethyl Glucaric acid) all aliquots of the reaction solution and external standard were weighed in order to produce trustworthy data. These sample were analysed by high-performance liquid chromatography (HPLC, Agilent 1220 Infinity LC) using a column for acid separation (MetaCarb 87H 250 x 4.6 mm, Varian, at 60°C) and a UV-Vis detector. The eluent was an aqueous solution of phosphoric acid (0.1 wt %) and the flow rate was 0.4 mL min^{-1}.

During the recycle tests, reactions were performed at 30 °C in order to have reproducible data given that the room temperature during the summer months was unstable. Moreover, the time of reaction was kept shorter (30 minutes) to avoid as much as possible to leave the catalyst in contact with the pollutant chemicals in the reaction mixture.

Photoreactor reaction: The fluorination reaction was also performed in a photoreactor **(**PV cell testing solar simulator 16S-300-002, Solar light **).** The reaction conditions were identical to the non-photocatalytic tests (2.3.1) except the atmosphere was air (not N_2) and the reaction time was just ten minutes long). This experiment was exploited to test the 30 s^{-1} frequency of grinding in a photocatalysed reaction. Additionally, the blank reaction without catalyst was also performed under identical conditions, to check if SelctFluor® alone was active under the light source in the absence of a catalyst.

All the calibrations were done by the commercial reactants by Sigma Aldrich, only the product of the reaction (5-fluoro-4,4-dimethyl-5-oxopentanoic acid) was isolated by chromatography on silica and then calibrated with succinic acid as external standard.

Experiments to explore the homogeneous rate of the reactions: this reaction has been performed in heterogeneous condition for the first time, so it is necessary to check if the catalyst has some leaching of Silver, and if this silver that will be homogeneously dissolved can carry out on its own the reaction. Two methods have been employed to measure that:

- *Leaching Analysis:* in this analysis the normal reaction is performed and stopped after 10 minutes, the solution is filtered from the catalyst and then analyzed by MP-AES (Chapter 2.4.5) in order to measure the amount of silver leached from the catalyst.
- *Hot Filtration:* In this analysis, the fluorination reaction has performed as previously explained, but the catalyst was filtered from the solution after 5 minutes (for catalyst FM012) and after 10 minutes (for catalyst FM013. It is important in this case not to mix the reaction mixture with air but maintain it under a N_2 atmosphere, because the reaction in air is much slower. Changes in conversion following removal of the solid catalysts were monitored in order to check if the reaction mixture is active after the

filtration or if it is stopped. This result gives an indication of how much the homogeneous silver leached from the catalyst can catalyse the reaction on its own.

3*.3.2 Meerwein Ponndorf Verley transfer Hydrogenation-C6 Reaction*

The MPV transfer hydrogenation of cycloheaxanone (figure 3.3) was performed in a 50 mL two necked round bottomed flask equipped with a reflux condenser, which was thermostatically controlled by immersion in a silicon oil bath. The vessel was charged with a 10 mL solution of cyclohexanone in 2-butanol (0.2 M), which also contained an internal standard (biphenyl 0.01 M). The reaction was performed at 100°C[13].

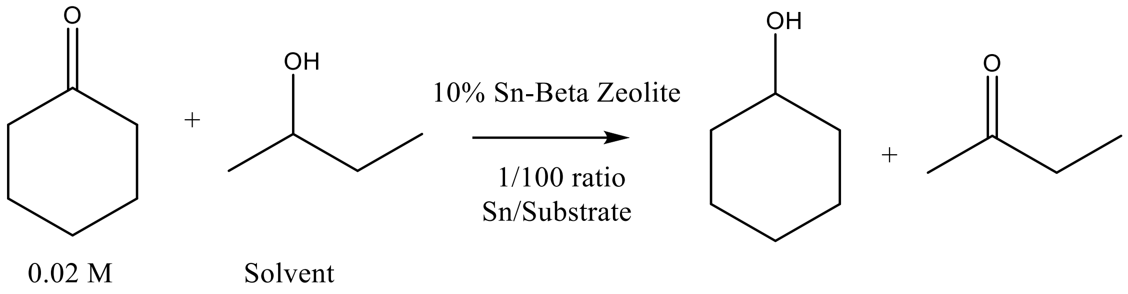


Figure 3.3: MVP-C6 Reaction scheme

The reaction was initiated by addition of an appropriate amount of catalyst, corresponding to 1 mol % of Sn relative to cyclohexanone. The solution was stirred at 800 rpm with an oval magnetic stirrer bar. Aliquots of reaction solution were taken periodically for GC-analysis and were centrifuged prior to injection into the GC (Agilent 7820, 25 m CP-Wax 52 CB). Reactants were quantified against a biphenyl (>99%, Sigma Aldrich) internal standard. These tests were used to analyze the catalysts synthesized with the Mixer Mill MM400 in order to find out if there was a maximum of catalytic performance corresponding to a frequency of grinding. This is a standard H-transfer reaction usually performed to check if the catalyst is effective in H-transfer reaction, hence it is usually the starting point in order to study the isomerisation of glucose to fructose.

The calibrations were carried out by commercial chemical by Sigma Aldrich with an internal standard (Biphenyl).

3.3.3 HPLC-analysis of Fluorination Reaction

In order to analyze the reaction mixture HPLC (High Performance Liquid Chromatography) was exploited; a specific column (MetaCarb 87H 250 x 4.6 mm) was necessary because in fluorination reaction is involved 2,2-dimethyl-glucaric acid and this column is specifically designed for organic acids, which are typically harmful to standard HPLC columns. The HPLC employed was an Agilent 1220 Infinity HPLC equipped with an autosampler, an oven to maintained at 60°C the columns located inside and with a variable wavelength UV-VIS (VWD) detector set at 210 nm and the flow has been set at 0.400 mL/min. The liquid-carrier was phosphoric acid (0.1 % wt) in ultrapure HPLC-water.

The calibration for the 2,2-Dimethyl-glucaric acid was carried out with the commercial chemical from Sigma Aldrich and the results are shown in Table 3.5 and figure 3.4

Chemicals	***Retention Time** [min]*	***Equation***	***R^2***
• 2,2 –Dimethyl-glucaric acid	6.61	y = 0,5284x	0.9987
• 5-fluoro-4,4-dimethyl-5-oxopentanoic acid	9.01	y = 4,7378x	0.9983
• Succinic Acid	5.02	internal	standard

Table 3.5 :calibration results for the reactants involved in the reaction

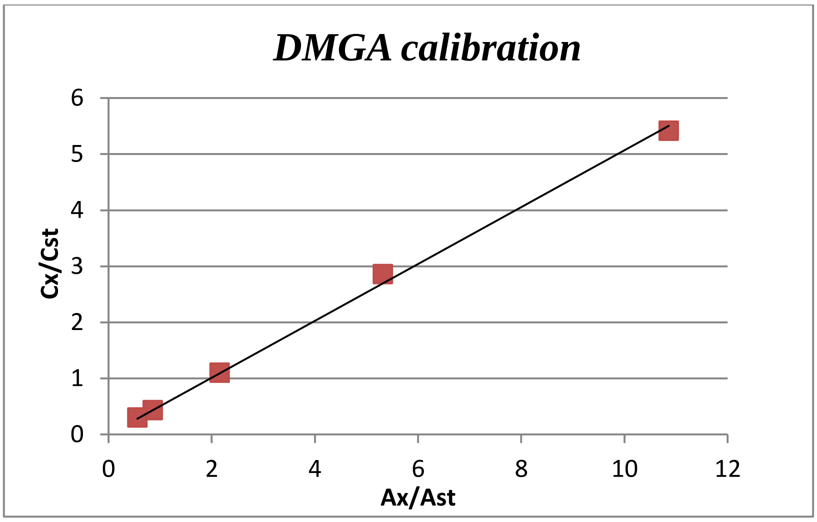


Figure 3.4: calibration of reactants performed with the HPLC

The analysis of the product of reaction (5-fluoro-4,4-dimethyl-5-oxopentanoic acid) was much more complicated: the chemical was not available as commercial so it was necessary to isolate it via Silica-gel chromatography, but as we can see in the chromatogram (figure 3.5) the peak was not so easy to calibrate because it is quite broad (retention time: 9.307 m).

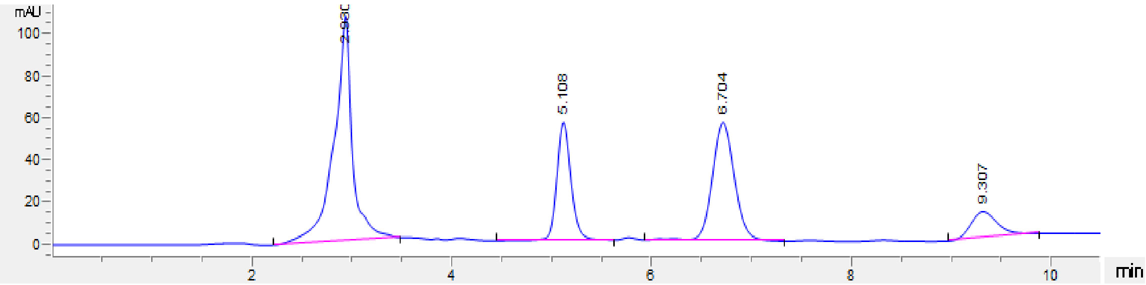


Figure 3.5: chromatogram for the fluorination reaction from HPLC analysis

Verification that there were no other byproducts was achieved by F-NMR experiments that clearly shown as the fluorine atoms in solutions are due to the Select Fluor® peaks and to the product. Selectivity was calculated with the calibrations in Figure n.4 in order to check if there were important changes that could suggest the presence of a by-product.

Preparation of the sample: the withdrawn sample was centrifuged in order to separate the solid catalyst from the liquid reaction mixture, 0.1 g of liquid were withdrawn and add in a

GC-vial containing 0.5 mL of Succinic Acid solution (3 mM). The vial is waved strongly and then injected in the HPLC.

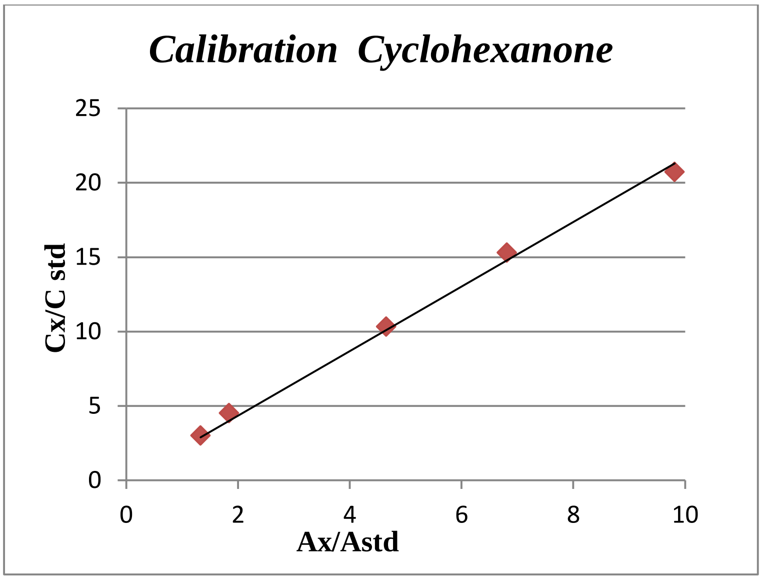
3.3.4 GC-analysis of MVP-C6 Reaction

The MVP-C6 reaction has been analyzed by gas chromatography (GC), and a polar column was employed in order to separate all the required compounds (25 m CP-Wax 52 CB that is filled with a polyethylene glycol phase). The machine used was an Agilent 7820 equipped with an autosampler and a FID (Flame Ionization Detector). The gas carrier was Helium and it was maintained with a flow of 3mL/min.

The analysis is performed checking the concentration of cyclohexanone and cyclohexanol, their calibration was performed with an internal standard (biphenyl) and all the chemicals were available from Sigma Aldrich. In table 3.6 and figure 3.6 are reported the calibration lines equations for the cyclohexanone and for cyclohexanol.

Chemicals	***Retention Time*** *[min]*	***Equation***	***R^2***
• Cycloheanone	14.2	y = 2,1716x	0.9957
• Cyclohexanol	15.4	y =2,1907x	0.9955

Table 3.6: Results of Calibrations of the Reactants



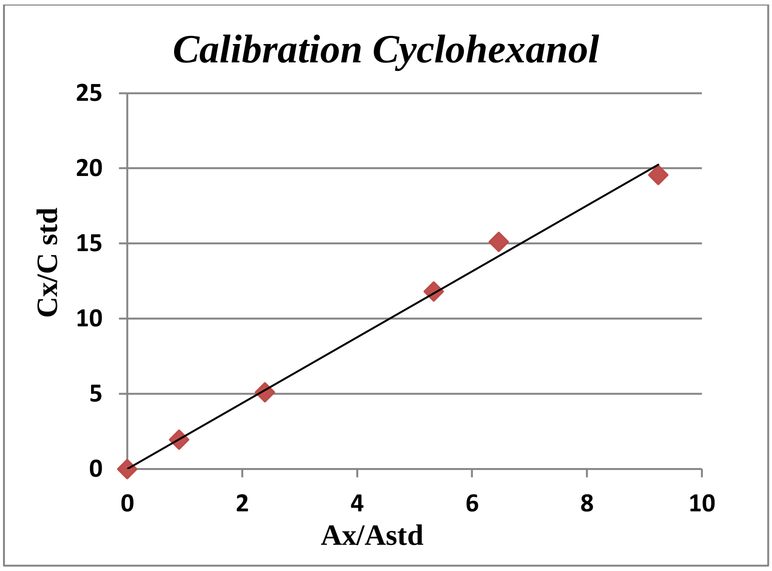


Figure 3.6: Calibration line for Cyclohexanone and Cyclohexanol

Preparation of the sample: a sample of 0.100-0.150 mL is withdrawn from the reaction misture and centrifuged to deposit all the catalyst at the bottom of the capsule, then about 0.1 mL of the liquid phase of the sample is added in a GC vial containing 0.300 mL of 2-butanol.

3.4 Characterization of the catalysts

3.4.1 Diffraction Ray-X analysis (XRD)

X-ray diffractometry (XRD) is a powerful technique widely exploited to study the properties of a solid sample.

This technique is useful to study:

- The crystallinity rate of a particular solid or of its component
- Size of crystals
- The kind of allotropic shape in the sample
- Cell's size and the kind of atoms of which is composed

The analysis is performed directing a collimated X-ray beam on the sample; this beam will be diffracted only in some particulars directions, depending on the crystal phase that is present in the sample. This diffraction is ruled by the Bragg rule:

$$n\lambda \ = 2d\ sin\theta$$

In this equation n is a whole number, λ is the wavelength of the incidence X-ray, d is the distance between the atomics layers in a crystal, and θ is the angle of incidence. The intensity of the diffracted angle is measured as a function of the diffraction angle. Indeed is possible to estimate the size of the crystals of the sample thanks to this equation:

$$d = K\lambda\ /bcos\theta$$

In this equation $b = \sqrt{B^2 - \beta^2}$ (B = the width of the peak at the half of its total height), θ is angle of incidence, λ is the wavelength of the incidence X-ray and K is a constant with a value about 0.9-1[25].

Every diffraction peak is linked with the Bragg law to an exact distance d between the layers of the crystal lattice, these distances are typical of every crystal cell, and so it is possible to identify the phases that are in the analyzed sample.

Powder X-ray diffraction analysis was performed on PANalytical X'PertPRO X-ray diffractometer, with a CuKα radiation source (40kV and 40mA). Diffraction Patterns are recorded between 6-55° at step size of 0.0167° (time/step = 150s). The scheme of the instrument is shown in Figure 3.7.

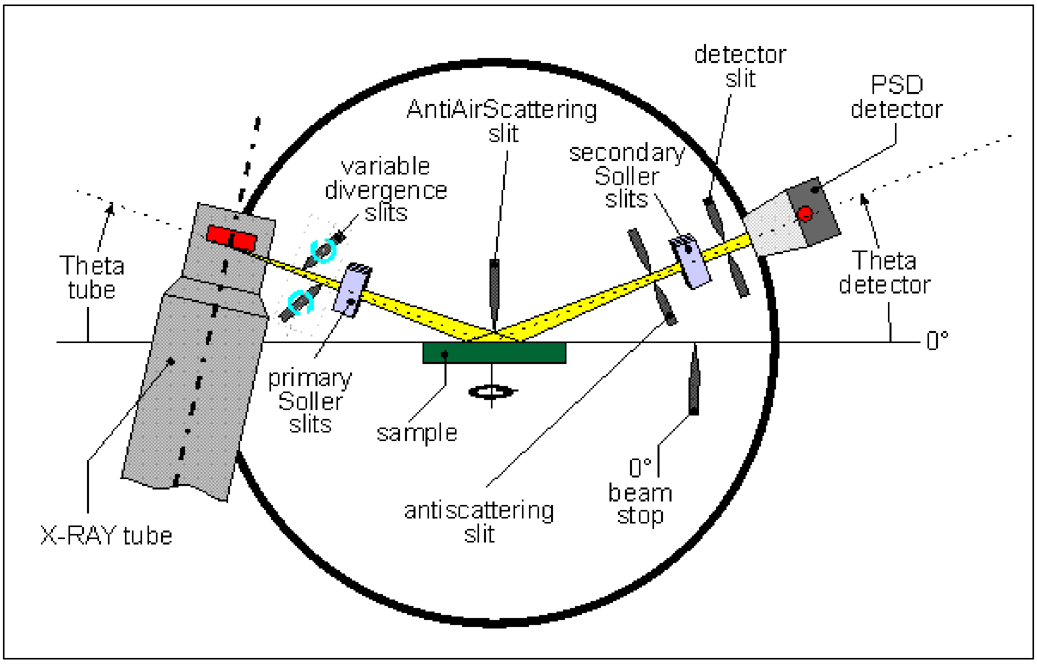


Figure 3.7 : Scheme of the XRD diffractometer exploited in the analysis

3.4.2 Surface area analysis

The surface area of a catalyst represent the ratio between the whole surface of the sample and its weight, it is usually expressed as m^2/g.

This parameter is important because it is one of the main features that can describe a catalyst from a catalytic point of view. In order to measure this property of the sample a Quantachrome Autosorb has been employed. The surface area is recorded thanks to the amount of gas (usually N_2 at 77K) that is physically adsorbed as molecular monolayer, this is possible knowing the diameter of the N_2 molecule (0.162 mm^2) because:

- It is a spontaneous process
- It has a really low rate of specificity and so all the surface is recovered and not only on specific sites
- It is fast
- It is reversible

After a degassing phase, to push the gases and adsorbed component off from the catalyst surface, the sample is depressurized under vacuum and then N_2 adsorption begins.

The gas volume physically adsorbed is measured from the difference of thermal conductivity before and after the adsorption. This difference is given from the decreasing of nitrogen (that is adsorbed on the sample surface). Considering that the most suitable condition for N_2 adsorption on the catalyst surface is near to the condensation temperature of nitrogen (77 K), the measure of the surface area takes place just after the cooling of the solid with liquid nitrogen.

This technique exploits the BET theory (developed form Brunauer, Emmett and Teller), which is explained from this equation[26]:

$$\frac{P}{V(P° - P)} = \frac{1}{VmC} + \frac{P(C-1)}{VmCP°}$$

This is the equation line in which:

V = total adsorbed volume

Vm= saturation volume with molecule monolayer

P= adsorbed gas pressure

$P°$= saturation pressure gas

C = BET constant, is linked to the strength of the bond between the first layer and the surface of the sample

From this equation knowing this parameters it is possible to find out the value of the gas monolayer's volume; this feature than can be used to discover the surface area of the sample from this equation:

$$S_{BET} = \frac{\frac{Vm}{V°} * Na * A\mathrm{N2}}{g}$$

$V°$ = molar volume of the gas

Na = Avogadro number

AN2 =Diameter of nitrogen molecule

g = mass of analyzed sample

Preparation of the sample: A mass close to 0.1 g of the sample in powder is located in a sample holder and dried at 120°C and for three hours (Ag2O Catalyst) or 275 °C for five hours (Sn-β zeolite). This difference is due to the properties of the zeolite, which hold adsorbed water and adsorbed gas more strongly than other materials.

3.4.3 Porosimetric analysis

This analysis has been carried out with the same machine already used in the surface area analysis, and so also this kind of analysis exploits the physical adsorption of N_2 at 77 K after the degassing of the sample to analyze.

First of all the N_2 molecules are adsorbed on the catalyst surface and in the pores as a monolayer, than increasing the pressure a multilayer is formed and finally the nitrogen liquefies; the second part of the analysis consist in the desorption of the gas.

At the end, it is possible to have an isotherm like the one shown in Figure 3.8, where it is possible to notice two lines: the isothermal line of adsorption and desorption of nitrogen, these can be studied with specific models that are able to give information about the morphology and the structural properties of the solid sample.

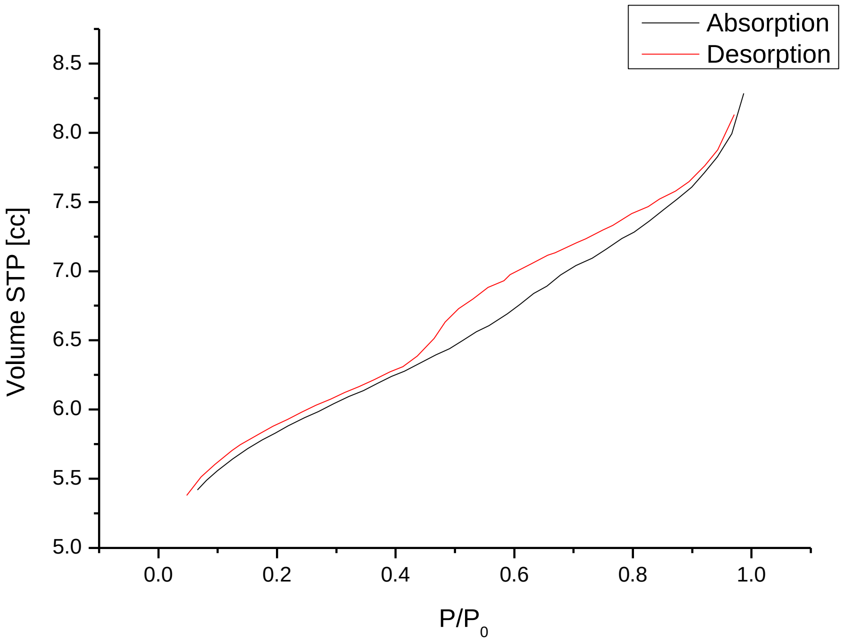


Figure 3.8: Absorption and Desorption lines of 10%Sn-β Zeolite(15s^{-1}frequency of grinding)

In particular, the pores dimension and their distribution have been found out applying a mathematic model BJH (Barrett-Joyner-Halenda), this model is based on Kelvin equation modified for multilayer adsorption and for the t-plot model.

3.4.4 Temperature Programmed Reduction analysis (TPR)

The Temperature programmed Reduction analysis (TPR) is extremely is useful in order to determine the reducible species in the sample and their reduction temperature. Indeed TPR is particularly exploited when we want to evaluate:

- The reduction temperature of oxidised species in the sample
- The number of the reducible component in the sample.
- Temperature of reduction changes as function of the metallic species on the support material.

With this technique we register the reduction in programmed temperature of the sample, this is exposed to a reducing gas stream that is usually hydrogen diluted in an inert gas (in this particular case 5% H_2 in argon was employed), and the temperature is linearly increased.

The sample is located in a fixed bed reactor, this reactor is located in an oven that can be heated in different rate on temperature, during the heating the flow of H_2 goes through the sample and then through a moisture trap before to reach the TCD (Thermal Conductivity Detector). This detector has two lines, that go through two small space where is located a heated filament, the gas going through this spaces is able to remove heat from the filament and obviously different kind of gases have a different thermal conductivity for removing the heat from the filament.

This difference of conductivity what the instrument detects, in fact in one of this space we have the carrier gas that has not gone through the sample, instead the other one is crossed from the gas come out from the reactor, these two gasses have a different proportion of H_2 that remove heat in different way from the filaments that come to have different temperatures. This difference of temperature is read as a difference of electric potential between the filaments. (Figure 3.9).

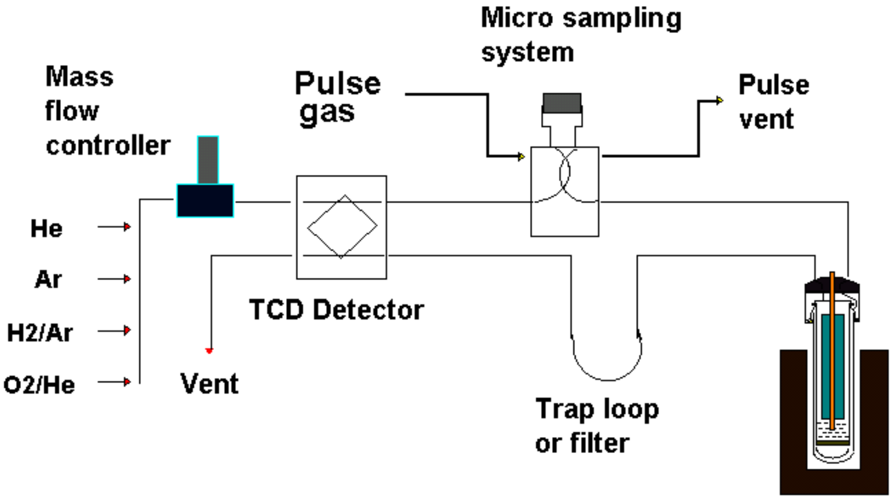


Figure 3.9: Scheme of TPR exploited in the experiment

In our case the use of this instrument has been used easily in order to confirm the presence of different speciations of Silver in the catalyst, in fact there is the possibility to have three species of silver due to mechanochemical reactions: Ag^0,$Ag^{(I)}$ and $Ag^{(II)}$.
Metallic silver obviously is not visible with this technique because it can't be reduced, instead the cationic species can be easily reduced and in particular they are used to be reduced at really low temperature (below 250°C).[27]

3.4.5 X-ray Photoelectron Spectroscopy (XPS)

The X-ray photoelectron Spectroscopy (XPS) is a surface sensitive quantitative spectroscopic technique that measures the elemental composition of the sample surface at the parts per thousands range and the chemical state of the elements in the sample. In this machine, a X-ray is emitted from the source and goes on the sample surface and here it hits the electrons in the atoms elements of the sample. Hence some electrons are removed from the nucleus and acquire energy thanks to the X-ray beam; this electrons are picked up from the detector that can measure their energy, from this measurement knowing the energy of the source we can easily identify the Binding Energy of the Electrons, and this is the key in order to understand which kind of species has emitted the them.

$$E_{binding} = E_{photon} - (E_{kinetic} + \varphi)$$

This is the equation that allow to measure the binding energy from the X-ray energy, it is basically a conservation of Energy equation where:

$E_{binding}$: is the binding energy of the detected electron

E_{photon}: is the energy of the emitted X-ray

$E_{kinetic}$: is the kinetic energy of the electron measure by the instrument

Φ: is the work function, dependent both on the sample material and the spectrometer.

The signal is registered in number of electron as function of the binding energy, so we have different peaks at different binding energies that allow to understand the kind of element that are in the sample and the peaks correspond to the electron configuration of the electrons within the atoms[28].

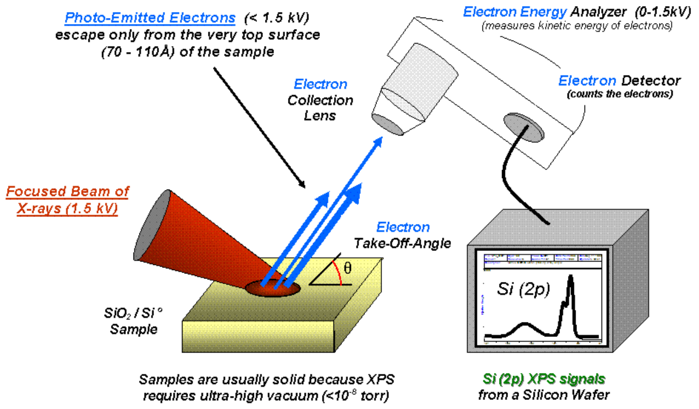


Figure 3.10: typical scheme of the XPS spectrometer

In this project a Kratos Axis Ultra DLD spectrometer was employed in order to understand which kind of oxidation state of silver are present in the sample (scheme in figure 3.10). All data was acquired using a monochromatic Al source, operating at 120 W. All spectra were acquired using the Kratos immersion lens system for charge compensation, and the hybrid spectroscopy mode at pass energies of 40 and 160 eV for high resolution and survey scans respectively. Data were calibrated to the C 1s line at 284.8 eV, attributable to adventitious carbon and quantified using CasaXPSTM v2.3.15, using sensitivity factors supplied by the manufacturer.

3.4.6 Microwave Plasma Atomic Emission Spectroscopy (MP-AES)

Atomic emission spectroscopy is a spectroscopic method exploited in chemical analysis, it employs the administration of high energy to an analyte, this energy brings to the atoms dissociation and to their excitement. After the excitement the atoms will emit light coming back to the ground electronic state, this light is dispersed by a grating and then detected by a spectrometer.

It is possible to perform quantitative and qualitative analysis with this kind of instrument; in fact each element emits a characteristic wavelength, and so it is possible to recognize the kind of atoms that are present in our sample. Indeed the intensity of the signal depends on the number of atom that has been excited to a higher energetic state and from the probability of the transition. Thanks to this, it is possible to perform a quantitative analysis in order to find out the amount of the analysed atom in the sample.

$$I = K\, N_i P_I$$

This equation links the intensity of the signal I to the number of the population N_i derived from Boltzmann equation thanks to the constant K and to the probability P_I of the electron promotion to an excited state.

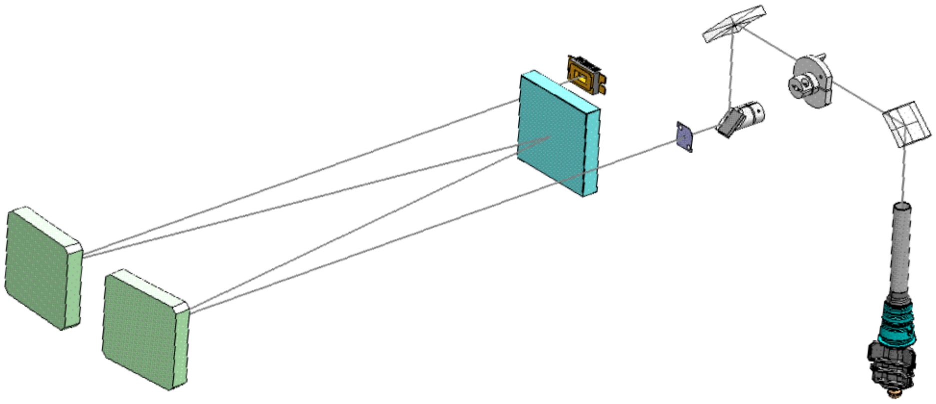


Figure 3.11: Scheme of the MP-AES exploited in the analysis

The source of energy was microwave plasma, this kind of energy to atomize the sample requires high temperature (6500-10000 K), but it allows atomizing almost all the atoms in the sample. Thus permits to have low detection limit and so really stable and reproducible analysis[29].

In this study, a 4100 MP-AES (Agilent Technologies) was employed in order to detect Ag traces in the solution, which may arise from Ag leached from the catalyst (figure 3.11). Silver was detected at 338 nm and 328 nm and then the value of silver concentration was calculated with an average between both the results. Calibration of the instrument has been performed for every analysis with four different solutions: 2,5,10 and 15 pap.

Preparation of the sample: After ten minutes of reaction, the solution is filtered from the heterogeneous catalyst and it is diluted three times with HPLC-water. The resulting solution is then analyzed to the MP-AES taking care in the calculation of the dilution.

3.4.7 Ultraviolet -Visible spectroscopy in reflectance analysis

Ultraviolet-Visible spectroscopy is a powerful technique that exploits the light from near UV (200 nm-380nm) to near IR (up to 1000 nm) in this region of the electromagnetic spectrum the analyzed chemicals could undergo electronic transitions, due to this transitions the materials absorb or reflect some wavelengths of the light and this affect the perceived colour of the chemicals involved.

It is possible to measure the value of absorption, transmission and reflection, hence this technique is widely used to carry out qualitative and quantitative analysis (usually liquid are used in this kind of analysis, but also gasses and solid could be studies).

It is common to analyze with this analytic technique solution of transition metal that are coloured thanks to the d-electrons that can be excited from an electronic state to another one, but also organic compounds with an high degree of conjugation. Charge transfer complexes can also be easily analyzed with this kind of technique. This quantitative analysis is possible thanks to the Lambert-Beer law that links the absorbance to the concentration of the analyte:

$$A = \varepsilon c L$$

Where ε is the molar absorptivity, L is the path length through the sample and c is the concentration of the analyte in the studied sample, indeed is possible to correlate easily the absorbance to the transmittance in order to have more possibilities to read the data[30]:

$A = \log_{10}(I_0/I) = -\log_{10}(T)$

Where I_0 is the incident light, I is the transmitted light and T is the transmittance that can be linked to the absorbance and so to the concentration of the sample. However in this work this technique has been exploited to analyze the presence of Ag $^{(0)}$ in the Ag/Ti_2O catalyst and to understand if the sample was photosensitive; this has been possible for the plasmonic peak of metallic silver that can strongly interact with light and so shows off an intense peak around 400nm; the broadness of the peak depends closely to the distribution size of the metallic particles.

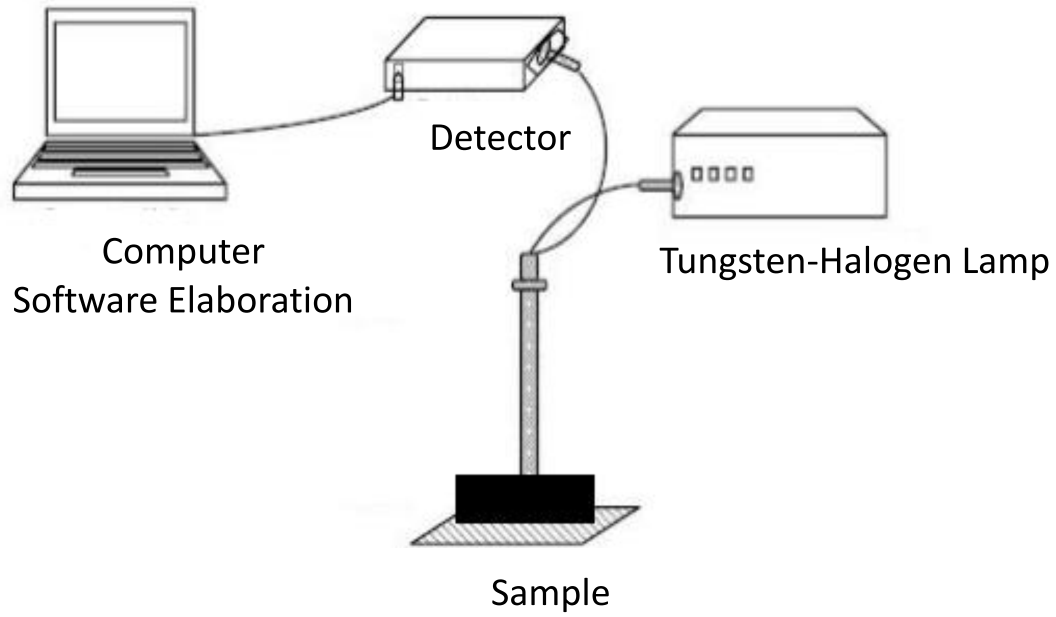


Image 3.12: system used in the UV-vis analysis

In order to do it was necessary to use a specific instrumentation: the analysis has been performed with an AvaLight-DH-S-BAL (Avantes) that covers effectively from 200 to 1000 nm with a power of 90W; the sample was a solid powder of titania and silver for this reason it was necessary to exploit a probe in order to carry the beam on the surface of the sample and record the spectra in reflectance.

Indeed a black block was necessary to fix the probe on the sample and to stop the widespread light that could give some noise and interference in the analysis; the block was leant on the sample that was located on an aluminium paper (figure 3.12).

The analysis needs for a blank before to carry out the measurements that was performed with a sample of polytetrafluoroethylene (PTFE) and for a dark light reference data that was performed just stopping the beam coming from the source lamp.

In the detector (AvaSpec-2048, Avantes) is located a photodiode, it is a semiconductor device that turns light in to current and so an electric signal, this device made of silicon doped with traces of metal allows to record signals on all the UV-vis range of wavelengths at the same time and send them to the computer where all the data are analyzed.

Then thanks to the software *''Avantes''* it was possible to record the data in reflectance and to convert them in absorbance and so have some graphs in Absorbance as function of the wavelength. For the photosensitivity analysis of the sample, the same procedure was applied but recording the date in step of 10 s and checking if the peak around 400 nm was getting higher.

All the results have been treated and modified with the software *‘’Origin Pro 8.5’’*.

3.4.8 Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR)

The magic angle spinning NMR, is a widespread technique that allows to perform some NMR experiments on solid sample, this technique is based on the same theory of the classic NMR analysis but with some precautions that extend this technique also to the solid phase.

NMR analysis is based on the magnetic properties of the nuclei in the sample, and it basically gain information on this actives nuclei; this method exploits the magnetic moment μ caused by their rotation. Only the nuclei with a odd mass number or/and atomic number are active in this kind of analysis, and their quantic number of spin is +/- ½.

Now if a magnetic field B_0 is applied to the sample, the magnetic moment of the nuclei will be aligned with the magnetic field, and so two level are created for the nuclei (figure 3.13): one in which the nuclei is oriented against to the magnetic field (higher in energy) and another one that is aligned with it (lower in energy). The extent of splitting is directly proportional to the applied field:

$$\Delta E = h\gamma\ B_0/2\pi$$

γ = giromagnetic ratio

h = Planck costant

B_0 = magnetic field

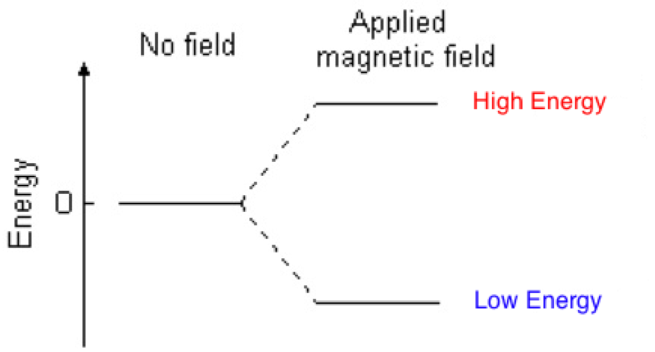


Image 3.13: splitting of the energy level in a proton

Looking this equation could seem that all the nuclei have the same energy width, but is important to consider that every proton is surrounded from electrons, this electronic cloud depends on all the structure surrounding the nuclei, and for this reason there is a specific energy for each nucleus, that permits do differentiate every species in the sample and also the near structure/atoms around.

In order to perform the measure an electromagnetic wave is exploited to promote every nuclei to the higher state and a detector capture the energy that the proton release to come back at the ground state, with this data is possible to plot a graph where on the x axis is locate a parameter that gives an idea of the nucleus energy and on the y axis a parameter that is linearly proportional to the amount of nuclei of the same energy.

That is the basic theory for a NMR-analysis, what has been done in this project is quite different, in fact bring this concepts to the solid analysis need for some cares, in fact in the solid phase the nuclear spin experiences a great number of interaction that affect the analysis.

The main interaction are: magnetic dipolar-dipolar interaction, chemical shift anisotropy and quadropular interaction. In the liquid phase these interactions are averaged due to rapid molecular movements that occur, but in the solid phase the atoms are fixed in place and thus movements and molecular vibrations are not averaged, leading to substantial line broadening. In order to avoid this noise in the results is employed the *Magic Angle Spinning*, whereby the sample is spun around an axis with an angle $\theta = 54.7°$ respect to the magnetic field all the interactions are getting really low, thanks to this is possible to minimise line broadening substantially and have a great resolution in this analysis[31]. A schematic illustration of the sample position is shown in figure 3.14.

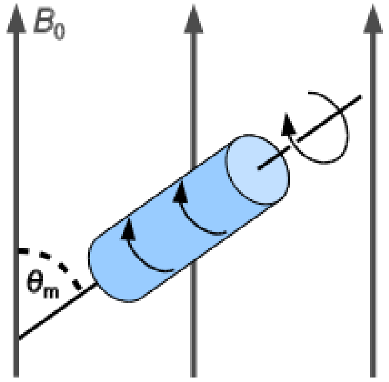


Image 3.14 : in this image is possible to see the sample position compared to the magnetic field

In this project this technique has been employed to understand the speciation of tin in the 10%Sn-β Zeolite. Tin as tin oxide (SnO_2) has a peak around -602 ppm, whereas the hydrated form of tin in the zeolite framework has a typical peak around -602 ppm. Important is to notice that is quite hard to compare this peak between them as in the common ^{1}H-NMR, because the relaxation times are significantly different; anyway very useful is the comparison between different samples in order to see in which one is present more hydrated tin.

All the analysis have been performed in collaboration Durham Univeristy (GB) through the EPSRC UK National Solid-State NMR Service. Sample were measured on both a Varian VNMRS spectrometer, and a Bruker Avance III HD spectrometer with comparable performances. Both spectrometers possess operating frequencies of 149 MHz, approximately 60-100 mg of sample was packed into a 4 mm rotor. Measurements were performed in direct excitation mode (spin-echo 90x-t-180y), with a recycle delay of 2s. Samples were spun at 12000 Hz, and approximately 50000 repetitions were typically employed for each sample.

4. Results and Discussion

4.1-Introduction

The aim of this thesis was to explore the application of mechanochemistry in the synthesis of two kinds of catalysts, composed by two systems very different between them:

- Silver oxide on titania catalysts, exploited in the fluorinaton reaction of 2,2-dimethyl glucaric acid[23]
- 10% tin-β zeolite, tested for the Meerwein-Pondorf-Verley[13] (MPV) of cyclohexanone with iso-butanol

Solvent-free synthesis on laboratory scale is usually carried out with physical mixtures performed with pestle and mortar. Although it is very simple and easily accessible, this kind of procedure has a one very important drawback: reproducibility. Reproducibility issues typically arise due to the strength used by the operator during the grinding of the sample. In order to avoid this kind of inconvenience, it was decided to replace the manual operation with a mechanical one, involving a mixer mill machine: the Mixer Mill MM400 (Retsch^{TM}). This machine allowed us to perform the catalysts' grinding with an exact frequency, every single time we want to carry out a synthesis, thus leading to substantial improvements in the control of the synthesis parameters.

4.2 Silver (I) oxide/ Titania Catalyst

4.2.1 Introduction

The aim of this part of the thesis was focused upon developing a novel, heterogeneous catalyst for the decarboxylative fluorination reaction with SelectFluor®. This homogeneous reaction has previously been catalysed by $AgNO_3$.

In order not carry out the reaction in a homogeneous solution, the silver has been deposited on the titania support as silver(I) oxide. The Catalysts have been prepared firstly with the manual physical mixture performed with pestle and mortar with a different strength and time, then in order to explore the activity of these catalysts and understand their behaviour we have calcined them at different temperatures. The last step of the synthesis study of this catalyst involved the mixer mill MM400 that allowed us to choose the exact strength (in term of frequency) to apply to the samples.

Every catalyst has been tested in the fluorination reaction of 2,2 dimethyl glucaric acid performed in water with Selectfluor® and K_2CO_3. The characterization has been carried out with different techniques: XRD and TPR were used in order to check how the crystallinity of Titania is changed and to analyse if there are some changes in the Silver Speciation. Then BET has been employed to understand if the crystals of Titania undergo some modifications due to the meccanomechanical treatment. Finally the UV-VIS analysis was exploited to check the presence of some $Ag^{(0)}$ in the catalysts and to the test their photosensitivity.

In order to study all the effects as completely as possible we synthesized different kind of catalyst shown in the table 4.1.

Name	Catalyst	Preparation	Note
FM001	1% Ag/TiO_2(w/w)	physical mixture	10 minutes high intensity
FM002	1% Ag/ TiO_2 (w/w)	physical mixture	20 minutes high intensity
FM003	1% Ag/ TiO_2 (w/w)	physical mixture	40 minutes high intensity
FM004	1% Ag/ TiO_2 (w/w)	physical mixture	20 minutes low intensity
FM005	1% Ag/ TiO_2 (w/w)	FM001+calcination	150°C, 3h air atmosphere
FM006	1% Ag/ TiO_2 (w/w)	FM001+calcination	200°C, 3h air atmosphere
FM007	1% Ag/ TiO_2 (w/w)	FM001+calcination	250°C, 3h air atmosphere
FM008	1% Ag/ TiO_2 (w/w)	FM001+calcination	300°C, 3h air atmosphere
FM009	1% Ag/ TiO_2 (w/w)	FM001+calcination	350°C, 3h air atmosphere
FM010	1% Ag/ TiO_2 (w/w)	FM001+calcination	400°C, 3h air atmosphere
FM011	1% Ag/ TiO_2 (w/w)	mechanochemical	3 s^{-1} of frequency
FM012	1% Ag/ TiO_2 (w/w)	mechanochemical	7.5 s^{-1} of frequency
FM013	1% Ag/ TiO_2 (w/w)	mechanochemical	15 s^{-1} of frequency
FM014	1% Ag/ TiO_2 (w/w)	mechanochemical	22.5 s^{-1} of frequency
FM015	1% Ag/ TiO_2 (w/w)	mechanochemical	30 s^{-1} of frequency

Table 4.1 : synthesized catalyst for the fluorination reaction

4.2.2 Results and Discussion

Firstly, we decided to synthesize the manually grinded catalysts to test the reproducibility of this method, and to obtain a benchmark for the mechanochemical study. Every catalyst has been grinded for 10, 20 and 40 minutes trying to apply the same strength by the operator who was performing the synthesis. Later, another catalyst was synthesized applying lower energy for 20 minutes (FM004).

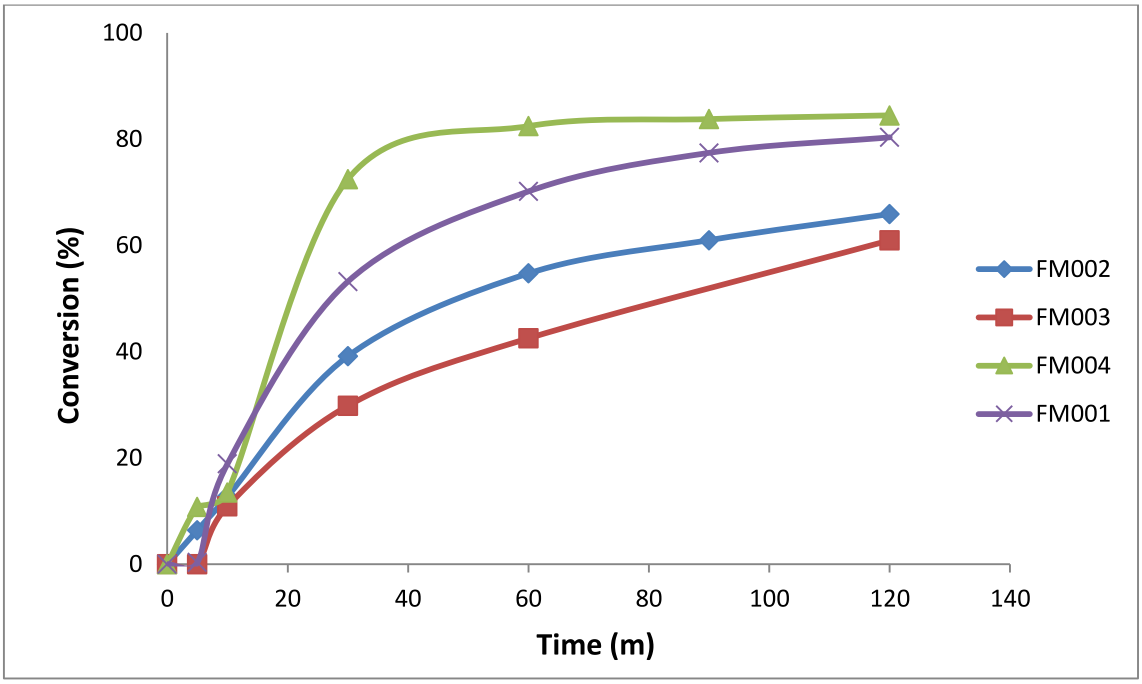


Figure 4.1: Reactivity of physical mixture catalysts

As can be seen in figure 4.1**,** clear differences in the activity for each catalyst prepared by physical grinding are observed. By changing the strength of grinding, activity is found to vary from a minimum conversion of 30 %, to a maximum of 72 %. Although this method cannot be considered scientific because the input of energy from the operator carrying out the synthesis is not reproducible, it clearly demonstrates that reproducibility by typical pestle-and-mortar grinding is not guaranteed. In general, it is observed that by grinding the catalyst with lower energy, the conversion and the rate constant are definitely increased. However, since it has been demonstrated that it is not possible to perform a reproducible synthesis just with the physical mixture method, it is necessary to exploit a kind of machine that can permit to us to keep constant the parameters of grinding during the synthesis.

Before to move to another kind of preparation we tried to see if calcining the catalysts we could notice some drastic changes in their behaviour, to understand if it was possible to increase the performance with a thermal treatment. This catalyst in order to work at the best in this reaction needs to be loaded with oxidised silver[32], hence carrying out a calcinations in air we wanted to oxidize all the silver if it wasn't already all cationic, so we calcined the sample grinded for ''10 minutes at high intensity'' (FM001) at 150°C,250°C, 300°C, 350°C, 400°C and 450°C in air for three hours.

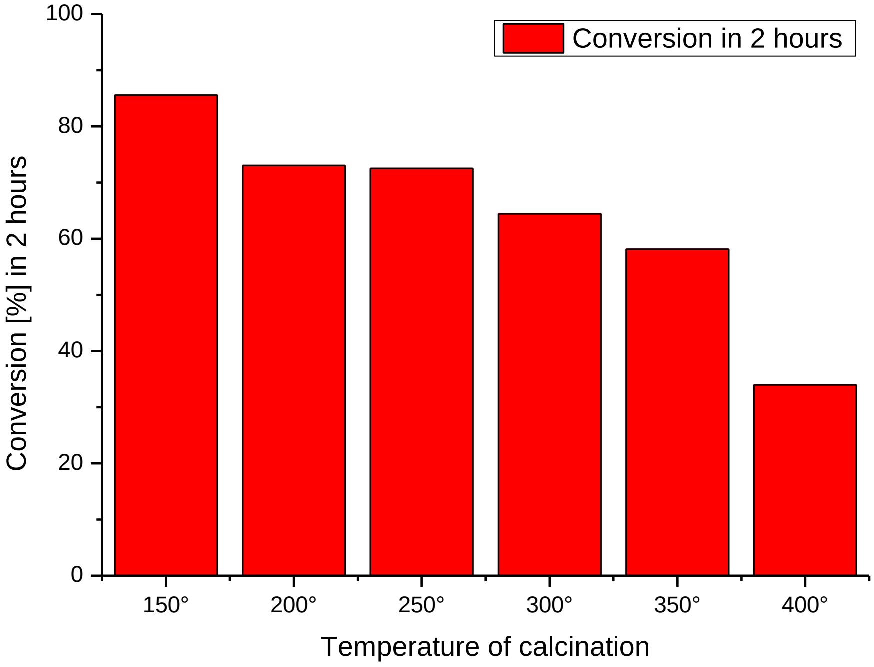


Figure 4.2 : catalytic performance of calcined catalysts

What we noticed from the results in figure 4.2 was that the activity of the catalyst is dropped down increasing the temperature of calcination. In order to try to understand the reason of this behaviour of the catalysts, silver (I) oxide was calcined alone. During this process, we noticed that in the inner of the powder metallic silver was formed, so we supposed that the same reaction probably takes place in the calcined catalyst as well. Considering that information it is logical how the catalytic performance is decreased, in fact .as previously seen in the introductive part in the mechanicistic study of X. Zhang[24], metallic silver is not active in the reaction, but only the cationic species of silver are involved. Hence if increasing the temperature of calcination we increase also the loading of metallic Silver in the catalyst, then it is normal that the catalytic performance is affected.

In order to have a more accurate and reproducible synthesis method, we subsequently explored the utilisation of a mechanical mixer (MM400,Retsch^{TM}), which provides greater control over the synthesis parameters (time, frequency, mass of catalyst).

We explored different frequencies in order to understand how the catalyst's properties change due to this preparation. We therefore prepared five catalysts with five different frequencies:

- 3 s^{-1} frequencies (FM011)
- 7.5 s^{-1} frequencies (FM012)
- 15 s^{-1} frequencies (FM013)
- 22.5 s^{-1} frequencies (FM014)
- 30 s^{-1} frequencies (FM015)

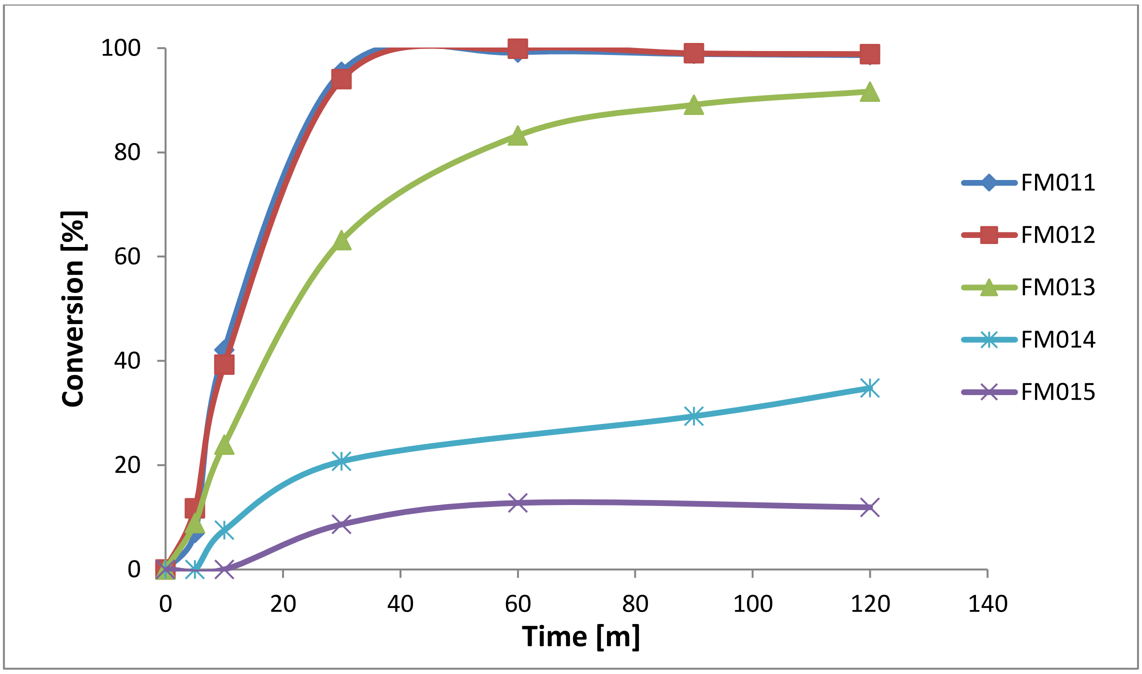


Figure 4.3: catalytic performance of Mixer Mill MM400 catalysts at different frequencies f grinding

As can be seen in Figure 4.3 increasing the energy of the grinding (in terms of frequency) there is a loss in catalytic activity. In fact with the catalysts grinded at lower energy of grinding (FM011 and FM012) the conversion is almost 100% in 40 minutes, instead analyzing the catalyst synthesized with the highest frequency 2 hours are not enough to reach 20% of conversion.

However it is important to note that this set of reactions are not enough to predict what is the best catalyst, because we had to analyse also the leaching of silver for each preparation and how much is the homogeneous contribution to the reaction rate. In order to do that we have involved the MP-EAS to analyse the leaching of Silver from the catalyst during the reaction. (Figure 4.4)

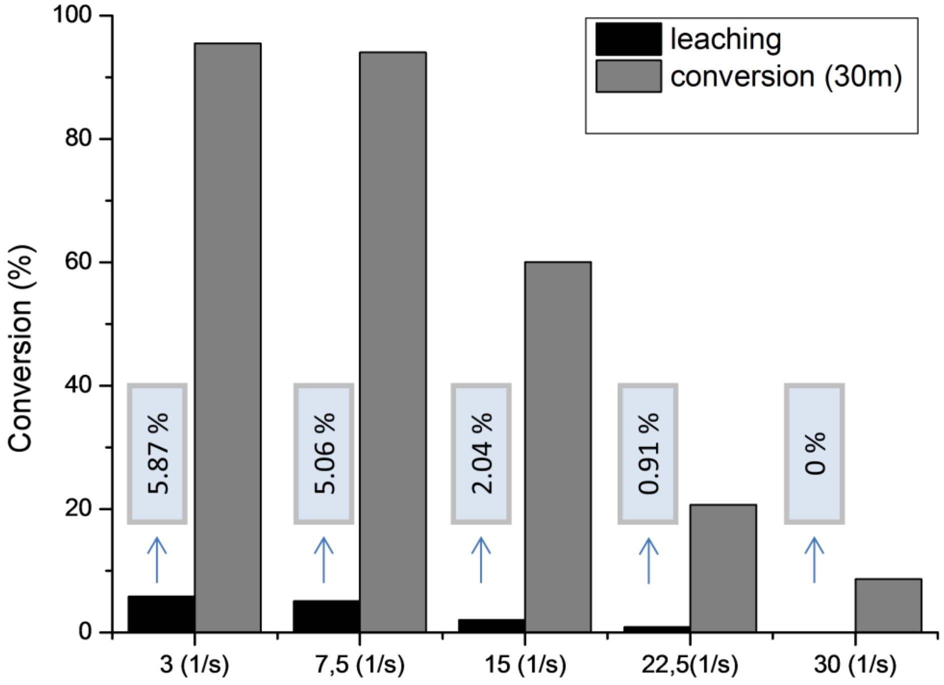


Figure 4.4: Leaching in the different catalysts synthesized in comparison with the conversion in 30 m

Here is evident how increasing the frequency of grinding the leaching is dropping down, in fact at 3 s^{-1} of frequency the leaching of the system is about 5.87% and it is reduced to 0% going to 30 s^{-1}. On the other hand increasing the grinding energy it is remarkable also a drop in activity: we have a conversion of almost 100% in 30 minutes with the catalyst grinded at 3 s^{-1}, then the conversion decreases to 10% carrying out the synthesis with highest frequency (30 s^{-1}). In order to understand which catalyst is the best for our aim it is necessary to carry out some other catalytic experiments, hence we have decide to perform some hot filtrations. In these experiments the catalyst has been removed from the reaction mixture after 5-10 minutes of reaction and the conversion has been monitored in order to see how much leached silver could be able to perform the reaction on its own. Then based on these results it was possible to choose the best catalyst. (Figure 4.5-4.6).

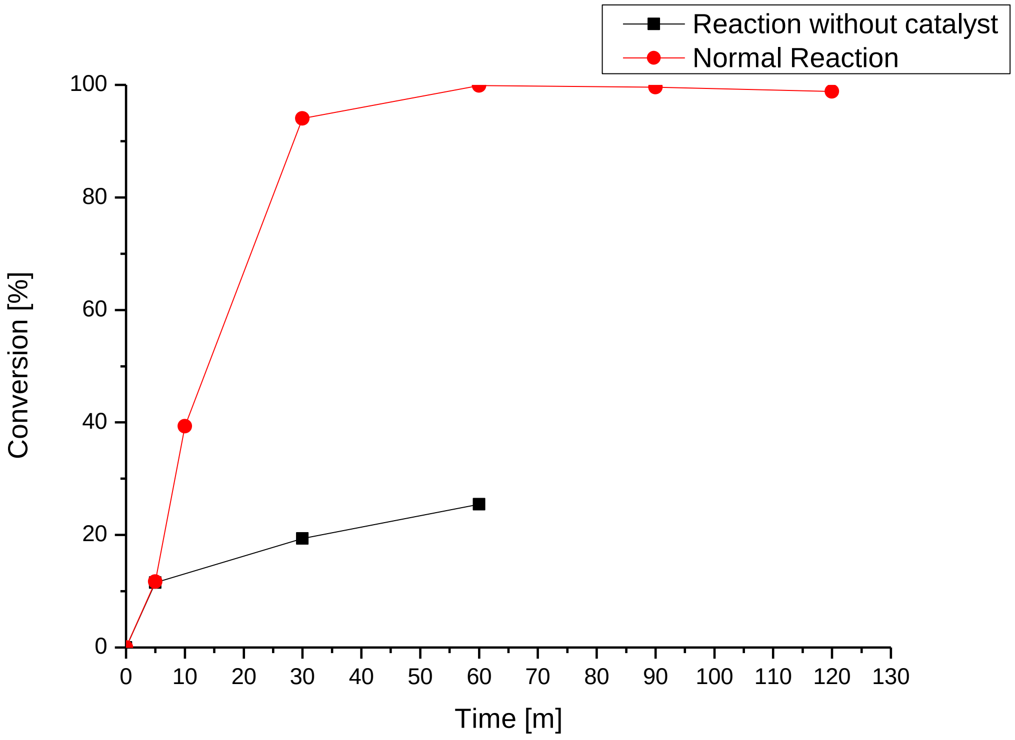


Figure 4.5 : hot filtration for catalyst FM012(7.5 s^{-1})

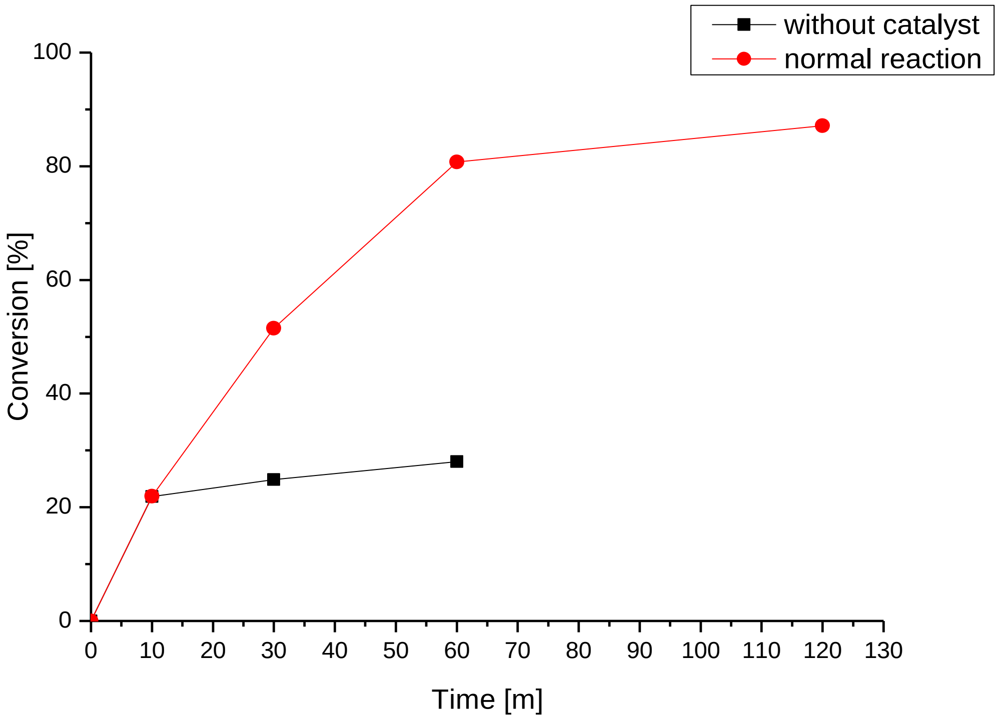


Figure 4.6: hot filtration for catalyst FM013 (15 s^{-1})

Looking the data in figure 4.5 and 4.6 is remarkable how the homogeneous rate in these catalysts is very different: the catalyst FM012 has a higher homogeneous rate of reaction. In fact, the conversion level observed after the catalysts filtration increases from 12% to 20% (an increase of about 70%). Conversely, filtering FM013 we can see how the increasing of the conversion is much lower: in fact, it increases from 21% to 24%, with an increasing of only 15% after an hour. These results remark how the catalyst FM013 is better from this point of view.

Considering all this data, we finally concluded that the best catalyst for our reaction is the one prepared using 15 s^{-1} frequency (FM013) with the Mixer Mill.

In order to go deeper in the reactivity's analysis of these catalysts we tried to find how was the performance recycling the catalyst several times. We started doing a normal recycle just filtering the heterogeneous catalyst from the reaction's solution, washing it on the filter just with water and let it dry in the oven at 100°C for one hour, then the catalyst has been re-used in the same reaction. All the recycles have been performed at 30°C in order to have a stable temperature and the reaction has been carried out in 30 minutes in order not to leave the catalyst in contact for long time with the poisoning reactant.

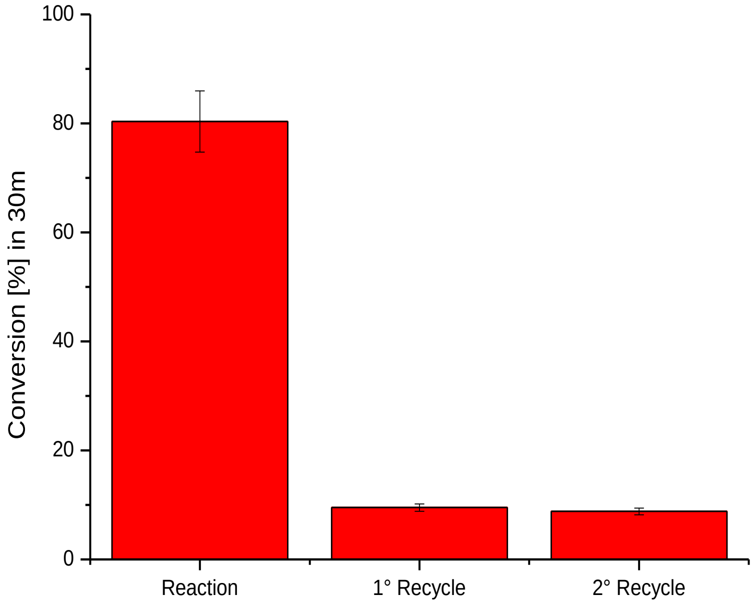


Figure 4.7: recycling tests of FM013 catalyst just for filtration and drying of the catalyst

It is possible to notice in figure 4.7 that in this kind of recycle the catalyst is highly deactivated and in the second reaction is already almost not active, this huge drop in the activity could not be caused by the low Silver's leaching that is really small if compared to the drop in activity. Hence, the possible causes of this deactivation of the catalyst could be related mainly to two phenomena that can take place during the catalytic tests:

- Poisoning of the active site: in fact the silver particles could be poisoned by some chemical in the reactions mixture and so it is maybe necessary a regenerating step to reactivate the catalyst
- Modifications of particles size: during the reaction the silver particles could undergo some changes, for example could become bigger for a sintering process and so they could have a loss in active surface that can compromise the activity

Hence, in order to understand if some chemicals could have a poisoning effect on these catalysts a pre-treatment has been performed on all of them with the chemicals involved in the reactions.

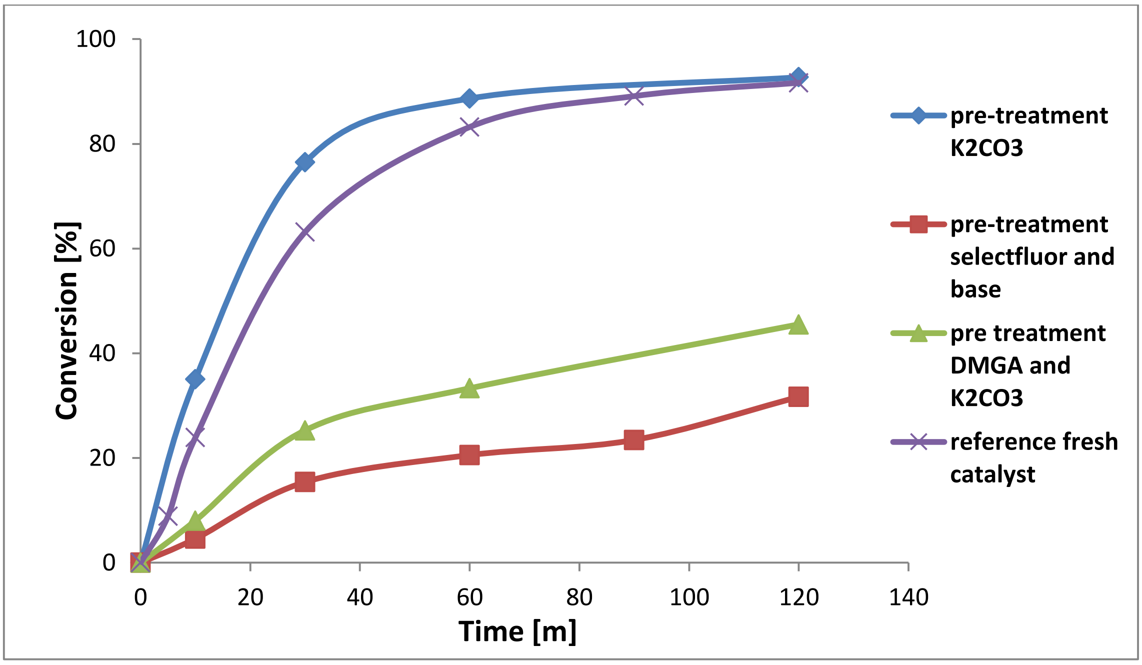


Figure 4.8: pre-treatment of catalyst FM013 to explore its deactivation

It’s remarkable in figure 4.8 how a pre-treatment with Selectfluor® decreases a lot the activity of the catalyst: the conversion in two hours in fact drops from about 90% to 25%, then the catalyst is really sensitive also to the 2,2-dymethyl glucaric acid (after this treatment the conversion is dropped to 45%), but what is more surprising is that the K_2CO_3 seems to increase, even if only a little, the activity of the catalyst. Indeed we have checked, with the HPLC-analysis, if during the treatment with 2,2-dymethyl glucaric acid the substrate was absorbed on the catalyst, but the conversion was at 0% so it meant that the organic acid is not absorbed on the surface.

After the base treatment it was possible to notice that the catalyst was dark grey, this because some silver is reduced in a basic in environment and gives this metallic colour. It seemed weird because the metallic silver is not supposed to be active in this reaction, but on the other hand, it might be that this low reduction could clean the active phase from some pollutant. This is just a hypothesis so we decided to perform a recycle with K_2CO_3 -regeneration steps in order to see if this treatment before of every reaction could prevent the huge drop of activity. (Figure 4.9).

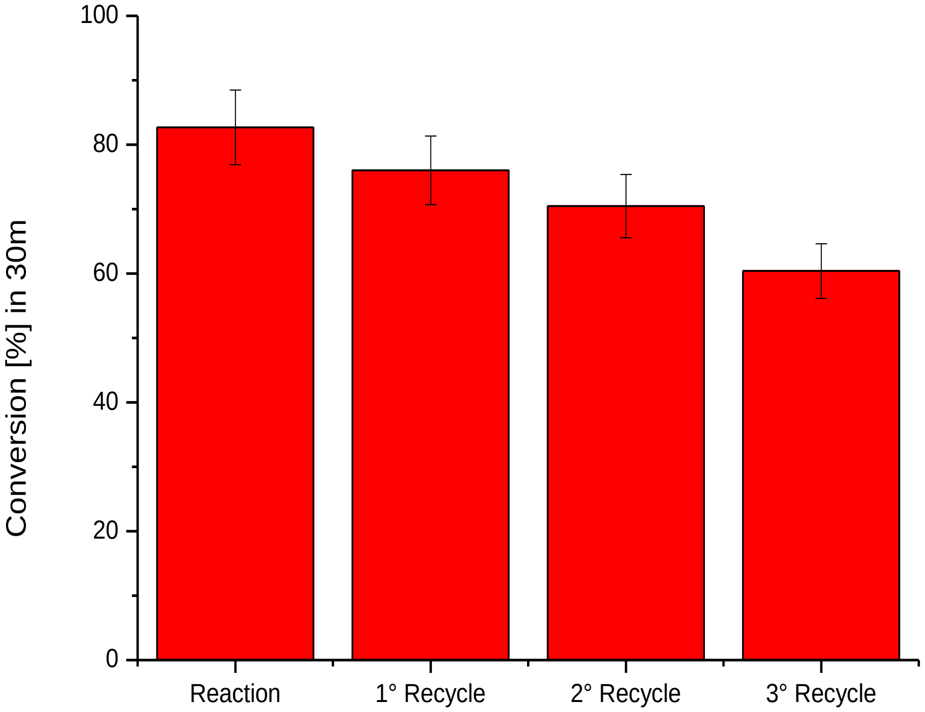


Figure 4.9: recycle of the catalyst with K_2CO_3- regeneration

As it possible to notice the recycle is definitely better with this regenerating treatment (Figure 4.9), this was a great development of the work because now a good recycle is possible and this process of regeneration could help to formulate some hypothesis about the deactivation of the catalyst. In fact is possible that the normal activity drop of the catalyst is due to a poisoning by some chemicals, such as the SelectFluor®, in facts the fluorine atoms could be absorbed on the catalyst surface and then the regeneration of with base could wash them. Also is not to exclude that this reduction could affect also the size of the active phase particles. Hence, further studies are necessary to fully understand the reactivation mechanism and the causes of the catalyst deactivation.

4.2.3 Characterization

Characterization for this kind of catalyst (supported silver nanoparticles) is not straightforward because the several speciations of silver are not easily recognizable in several methodologies. Despite this, we have acquired some evidence about the kind of transformations that the catalyst undergoes during the different kinds of preparation.

The first technique that has been used was the XRD of the solid powder, this techniques permits to us to gain important information about the crystal structure of the material that we are analyzing and we can also gain a qualitative analysis about the kind of materials that we have in our sample (as long as these materials have a crystal structure). We started to analyse the Mixer Mill catalysts at the different frequencies of grinding in order to see which kind of modification is possible to see:

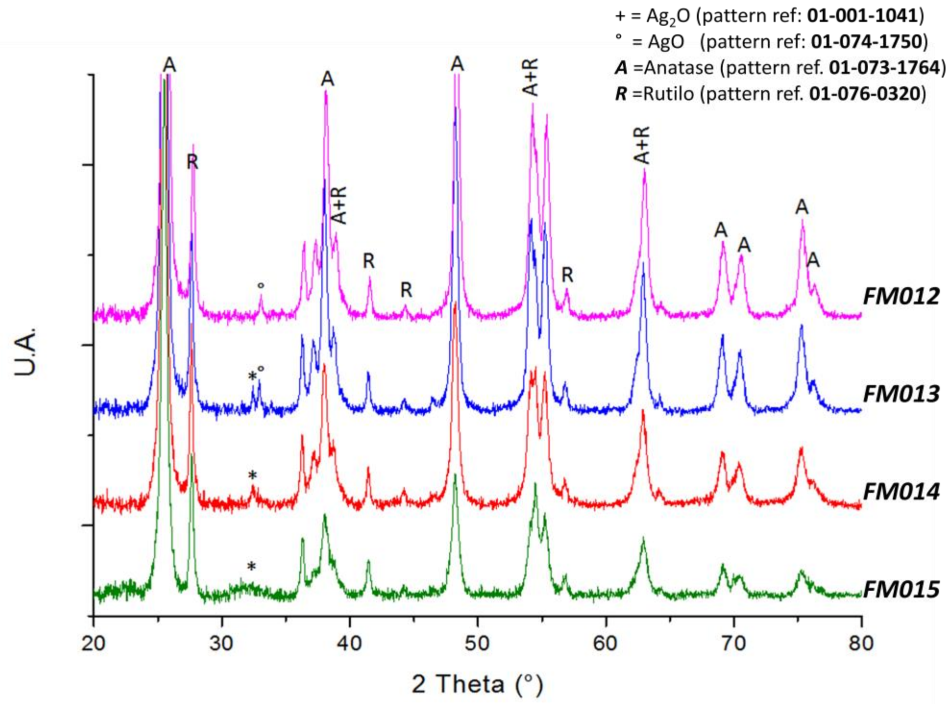


Figure 4.10: Mixer Mill prepared catalysts XRD

In figure 4.10, we can see the diffraction patterns of all the catalysts prepared with different frequencies in comparison with those observed in a standard sample of silver oxide. As can be seen all the samples possess the characteristics peaks of anatase and rutile (the two allotropic phases of titania that are present in Titania P25), but what is more interesting is about the silvers diffraction patterns in figure 4.11:

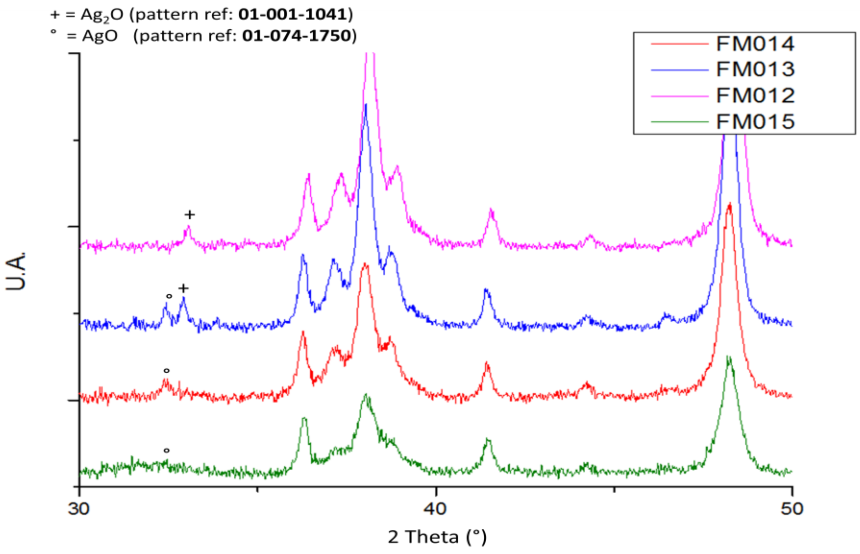


Figure 4.11: magnification of spectra in image n.10 between 30° and 50°

Due to the low loading of silver in the catalyst, the only visible reflection of silver (I) oxide is that found at 32.9°. This single reflection is sufficient to track the change of silver throughout the grinding. Indeed, as the frequency of grinding is increased, this reflection disappears. In its place, a new peak at 32.5° is observed. This new reflection has been attributed to the silver (II) oxide. Subsequently we have clearly seen how increasing the frequency of grinding the peaks become broader and shorter, this means that the crystalline of the material is dropped down, and/or that the particles are getting smaller during the treatment.

In order to understand the behaviour of Silver and Titania during this preparation we tried to find out more information performing others kind of characterization, first of all we proceeded with an XPS analysis; this experiment has been performed on all the samples and the following shown spectra is the one of the catalyst prepared with 15 s^{-1} of frequency. (Figure 4.12).

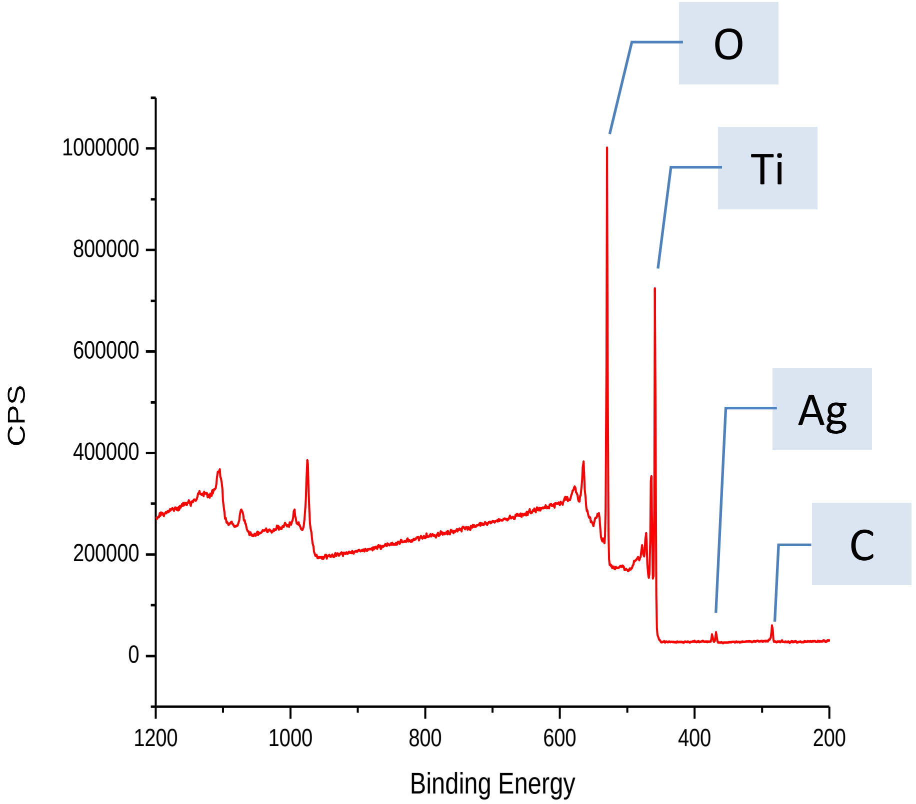


Figure 4.12: XPS of FM013 (15 s^{-1} of frequency)

This technique usually is powerful but the peaks of the different speciations of Silver are really near each other:

Ag (0): 368.2 mV
Ag (I) as Ag_2O: 367.67 mV
Ag (II) as AgO: 367.06 mV

Because of this behaviour of Silver, we couldn't easily recognize the different kind of ions present in our sample, probably the resolution of our instrument was not sufficiently high in order to find out the exact energy of the emitted photons, so we moved to other kinds of technique to explore the catalyst's composition.

The technique was exploited to detect how many speciations of silver are present in the sample was the TPR, with this technique is possible to have a peak for each oxidized species present in the catalyst, so it is a suitable technique to verify that Ag(II) is formed during the grinding.

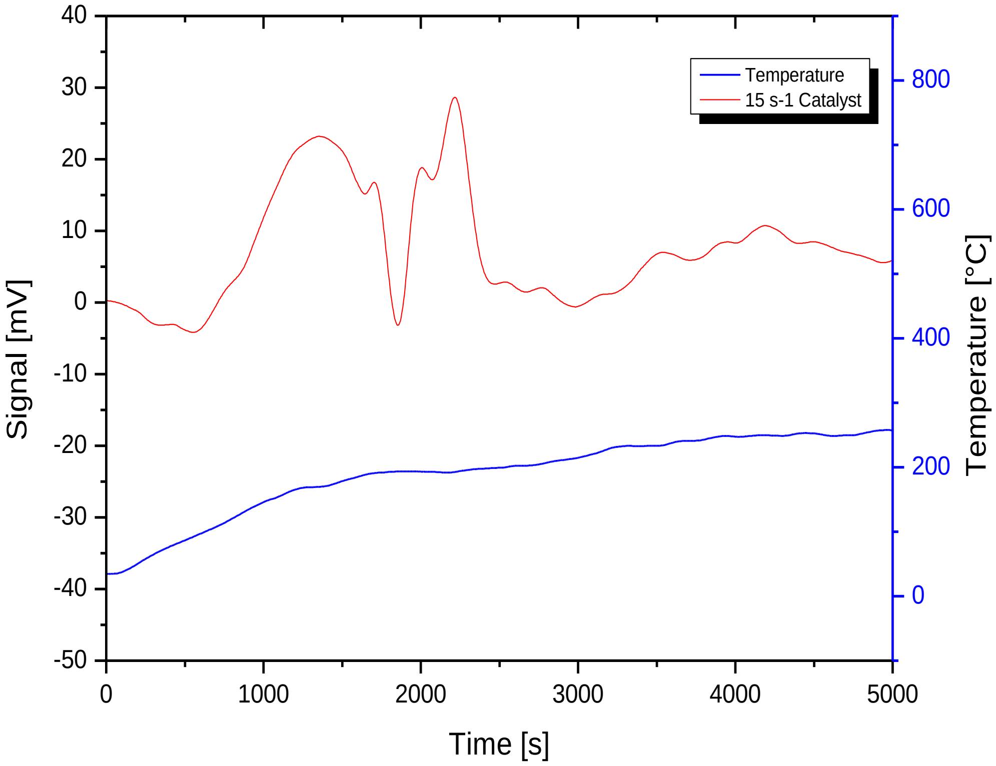


Figure 4.13: TPR of FM013 with H_2 (5% in Argon)

In the graph in figure 4.13 we can clearly see two peaks at 200°C and 220°C, these peaks probably belong to silver speciations that is used to be reduced at low temperatures, so with this analysis we can see that we have surely two species of Silver in our catalyst (in fact the support is reduced at much higher temperatures than the Silver's one) and matching this data with XRD ones it is possible to conclude that they probably belong to AgO and Ag_2O.

Once ascertained the behaviour of Silver we wanted to understand if the broader peaks in Titania XRD spectra are due to the particles that are getting smaller with the mechanical treatment or to the crystalline framework that is broken and is becoming amorphous during the synthesis of the catalyst. In order to confirm one of these two theories we exploited the BET analysis for gaining some data about its surface area (Table 4.2):

Ag on Titania (1% loading of Silver)	Specific Surface Area m^2/g	Pores Area m^2/g	Total Volume cc/g	Micropores Volume cc/g	Mesopores Volume cc/g
FM011	56.690	4.214	7.947×10^{-2}	2.000×10^{-3}	7.747×10^{-2}
FM012	58.822	0	8.800×10^{-2}	0	8.800×10^{-2}
FM013	65.160	2.605	9.805×10^{-2}	2.000×10^{-3}	9.605×10^{-2}
FM015	55.226	0	1.065×10^{-1}	0	1.065×10^{-1}

Table 4.2: BET and porosimetry results of Fluorination Reaction catalysts synthesized in the Mixer Mill

Looking the shown results it is hard to predict if the particles are getting smaller because the changing of the surface area is quite small if compared to the instrumental error (that is about +/- 10 m^2/g). What it could be possible to conjecture is that the support's particle are getting smaller until 15 s^{-1} of grinding (FM013) and then it seems the the particles are getting bigger again. Maybe this behaviour could be explained by the particles that are getting smaller increasing the frequency until 15 s^{-1} of grinding and then increasing the energy it is possible to have the presence of more hotspots that could aggregate and melt together the particle of Titania with the local high temperature but with a less crystallinity rate. This is just a hypothesis, what it sure is that the difference in surface area is not so high to say something sure about particle sizes.

Hence, what surely happens during the grinding is the loss of crystallinity that makes thee XRD peaks shorter and larger than in the not treated catalyst. Anyway, the group is planning to carry out some more accurate experiments with TEM to calculate the diameters of particles support and understand if there is a particular trend compared to the frequency of grinding.

With most of the techniques used until this point, only the oxidized species of silver have been detected. However, the co-presence of metallic silver could be possible in the catalyst, due to the nature of the mechanochemical synthesis.

To investigate the possible presence of metallic silver, we performed UV-vis experiments in reflectance for solids, with this technique we are able to see the plasmonic peak of Silver nanoparticles (if they are in the sample) and so to confirm their formation during the preparation[33]. We tried to carry out this experiment on the most used catalyst FM013 (15 s^{-1} frequency) but the results were not clear and was not easy to understand if the peak was just instrumental noise or a proper peak of $Ag^{(0)}$. So we carried out the same experiment but on the 30 s^{-1} frequency catalyst (FM015) because if the preparation produce metallic Silver this sample should contain the hugest amount.

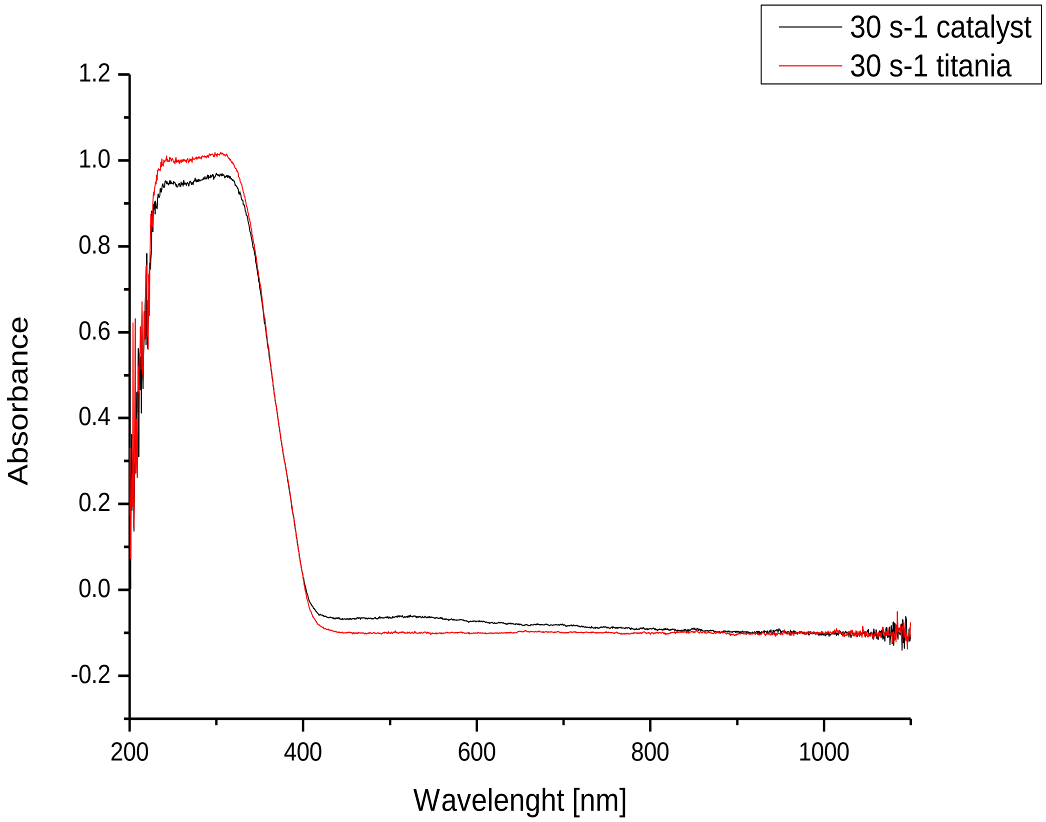


Figure 4.14 : UV-VIS analysis in reflection of FM015

In this figure 4.14 is possible to notice a kind of peak between 400-500 nm, this is probably related to Ag$^{(0)}$. It is difficult to recognize because the intensity is quite low probably due to the low loading of silver (1%) and to the broadness of the peak that is usually a symptom of a large size distribution of the particles. Obviously this is only a hypothesis that has to be verified with further experiments. Anyway it is possible to remark this peak with the a subtracted graph showed in figure 4.15, in which the line of 30 s^{-1} Titania has been subtracted to the line of the catalyst.

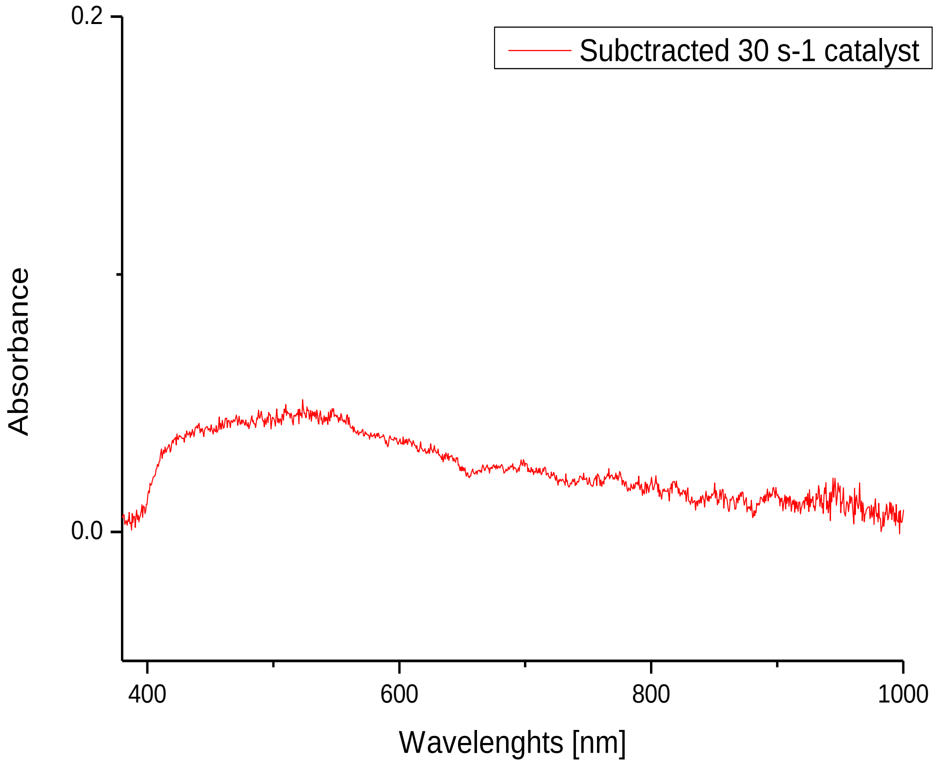


Figure 4.15: subtraction of the graphs in UV-VIS analysis in reflection of FM015

As we can see in this graph in figure 4.15 is clear that there is a peak between 400 and 600 nm. This is a clear sign that the metallic silver is present in our sample, although the very broad peaks makes it hard to say if silver (0) is in nanoparticluate form, or if there is a broad distribution size of the diameters particles. In the absence of TEM analysis, confirmation of the nature and size of the nanoparticles is not yet possible. However, future work in the group will focus on both TEM and EXAFS experiments at the Harwell Synchrotron. With these experiments we will be able to see which kind of bond are doing the silver atoms and to establish their oxidation state; but unfortunately the instrument has a lot of queue so we couldn't perform the analysis during this period.

4.2.4 Conclusion and future works

Thanks to this set of experiment we have shown how it is possible to prepare an heterogeneous catalyst for this reaction exploiting a mechanochemical way of preparation using the Mixer Mill M400. Exploring the catalytic performances of all the catalysts we realized how the 15 s^{-1} frequency of preparation (FM013) was the best compromise between a very performing catalyst but with an high value of metal's leaching (that imply an high rate of homogeneous catalyst in the reaction mixture), and a catalyst with basically no leaching but with a really poor catalytic performance.

In fact, this catalyst shows a conversion of 60% in 30 minutes and a value of leaching around 2%, and the most important thing is that this kind of preparation leads to a catalyst that is reproducible every time we want to prepare it; this was impossible with the normal physical mixture method. In this kind of preparation, the performance of the catalyst was unpredictable and highly dependent from the operator who was carrying out the analysis.

Then we tried to understand what was going on during the grinding procedure in the ball mill, this was the most challenging part of this work. Thanks to the TPR, UV-vis and XRD analysis we could see that during the preparation different species of Silver appear in the sample; in particular we clearly saw AgO and probably some metallic silver. Two main hypotheses have been formulated about the silver behaviour:

- Disproportion: $Ag_2O \rightarrow AgO + Ag(0)$
- Consecutive reaction $Ag_2O \rightarrow AgO \rightarrow Ag(0)$

Should be important to extend the knowledge about the transformation undergone by silver in order to predict the Silver behaviour in these kinds of mechanochemical treatments and so find new kind of applications for this catalyst.

Indeed working on the catalyst prepared with the 30 s^{-1} frequency something of really interesting has been found out: in fact leaving the sample under the UV-vis lamp we notice that this catalyst (as solid) shows a high degree of photosensitivity. (Figure 4.16).

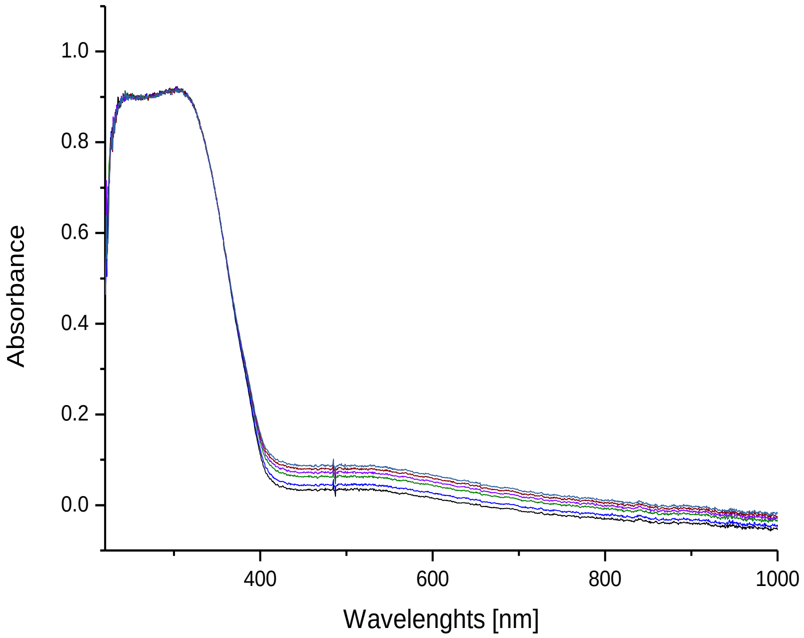


Figure 4.16 : photoactivation of catalyst FM015 under UV-VIS light

Studying this behaviour of the material we have supposed that the Titania used as support is the reducing agent for the Silver, and the role of the light is promote the electrons from the valence band to the conduction band in the support. Once seen this kind of activity we wanted to see if there were some possibilities to use this application in photochemistry with the same fluorination reaction used previously: we performed the reaction under a sunlight simulator with great effect:

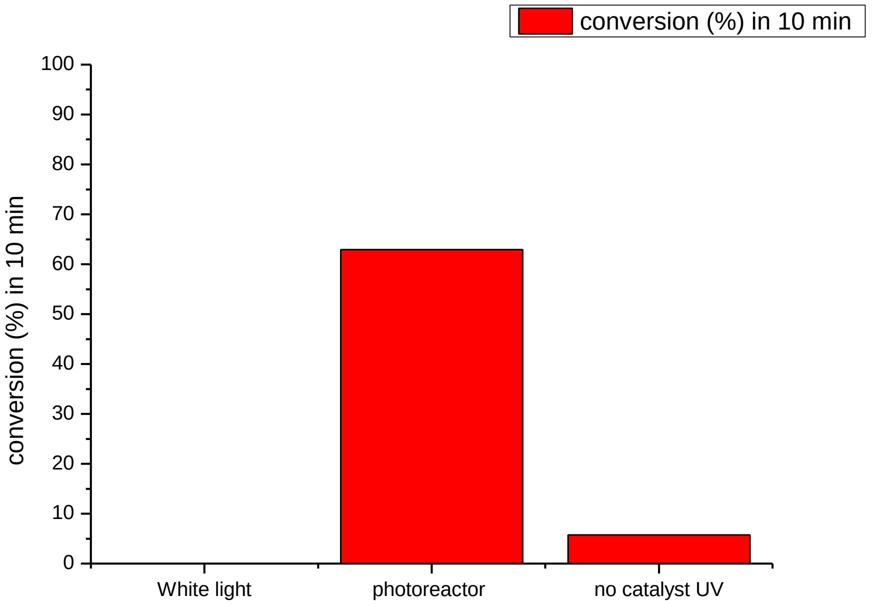


Figure 4.17: Fluorination reaction carried out with FM015 catalyst in a photoreactor, in normal condition and without catalyst.

Looking figure 4.17 we notice that they are absolutely the best results achieved with this kind of catalyst, and it is different from the same reaction but without the sun simulator, for this reason has been supposed that the reaction's mechanism should be very different in this case. Finally with this project the group has achieved the target to find a new heterogeneous catalyst for this reaction synthesized by mecchanochemical preparation, but not only in fact new research ways have been open and will be important to carry on some future works on this material to achieve other important goals that could be the starting point for new projects:

- Study the transformation that Silver undergoes during the Mixer Mill's grinding thanks to the EXAFS experiments performed in Harwell
- Explore the performance of this reaction also with other substrates different from 2,2-Dimethyl Glutaric acid
- Study the photocatalytic activity of Silver for this reaction under the sun-light simulator
- Extend the knowledge about the photosensitivity of this material in order to have a new method to produce easily metallic silver on titania.

- Improve the knowledge about the recycle mechanism performing some TEM experiments in order to measure the particles size after the recycle and some experiments in order to find out which kind of poisoning the catalyst undergoes.

4.3 10%Sn- Zeolite: mechanomeccanical incorporation of Tin β

4.3.1Introduction

This project has been developed in order to analyse the same synthesis method but on a completely different system, in fact in this case what has been performed is the incorporation of 10% of tin into dealuminated β-Zeolite. In our group, the incorporation of tin in this material via solvent-free incorporation has been already used several times but it has never been carried out with a Mixer Mill, but only with pestle and mortar via physical mixture. With this method on this catalyst, the group has found some problems:

- With this high load of Tin in the previous work has been noticed that the Tin is not well incorporated but a lot of Tin oxide is present in the sample, in particular if higher load of tin (above 8% are used)[5].
- The reproducibility is not great because sometimes the incorporation of Tin goes better and the activity of the catalyst is much higher.

The catalysts prepared in this section have been tested in a MPV-reaction of Cyclohexanone and isobutanol (used as solvent), this reaction is an H-transfer reaction promoted by Lewis acid sites in the zeolites as Tin (figure 4.18). This reaction is important as first step to test the effectiveness of this catalyst in other kind of reactions more important from an industrial point of view, such as the isomerisation of glucose to fructose.

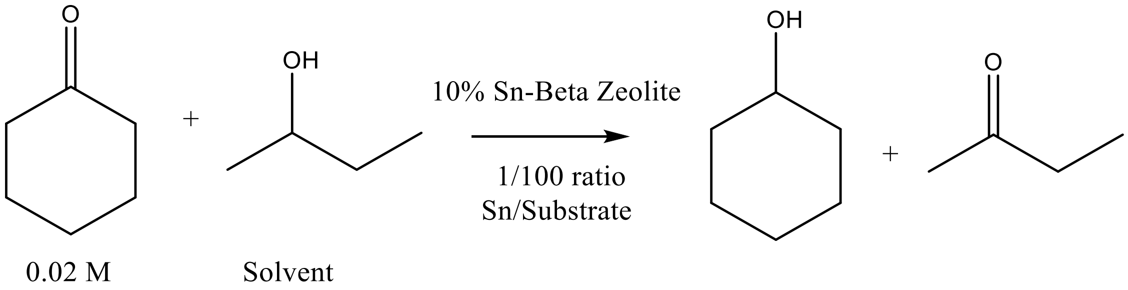


Figure 4.18: C6-MVP scheme reaction

Then all the catalysts have been characterized with different techniques to see the effect of the treatment on them; XRD and BET have been exploited in order to check the if the crystal framework has undergone some modifications during the synthesis, then the Solid-Mass NMR has been used to check the relative incorporation of Tin.

The catalysts synthesized in order to carry out this project are shown in table 4.3:

Name	***Catalyst***	***Preparation***	***Note***
FM016	10% Sn β-Zeolite (w/w)	mechanochemical + calcination	3 s^{-1}, 3h air + 3h N_2
FM017	10% Sn β-Zeolite (w/w)	mechanochemical + calcination	7.5 s-1, 3h air + 3h N_2
FM018	10% Sn β-Zeolite (w/w)	mechanochemical + calcination	11 s-1, 3h air + 3h N_2
FM019	10% Sn β-Zeolite (w/w)	mechanochemical + calcination	15 s-1, 3h air + 3h N_2
FM020	10% Sn β-Zeolite (w/w)	mechanochemical + calcination	22.5 s-1, 3h air + 3h N_2

Table 4.3 : catalysts synthesized in to explore 10% Sn β-Zeolite activity

4.3.2 Results and Discussion

First of all it has been necessary to de-aluminate the Al-β-Zeolite with an acid treatment, then the Solid Incorporation of Tin has been performed in the Mixer Mill MM400 (Retsch) for 10 minutes with Tin (II) acetate as source of Tin at different frequencies:

- 3 s^{-1} of grinding frequency (FM016)
- 7.5 s^{-1} of grinding frequency (FM017)
- 11 s^{-1} of grinding frequency (FM018)
- 15 s^{-1} of grinding frequency (FM019)
- 22.5 s^{-1} of grinding frequency (FM020)

Then all these catalysts have been tested in the MVP reaction of Cyclohexanone at 100°C for 30 minutes with these results:

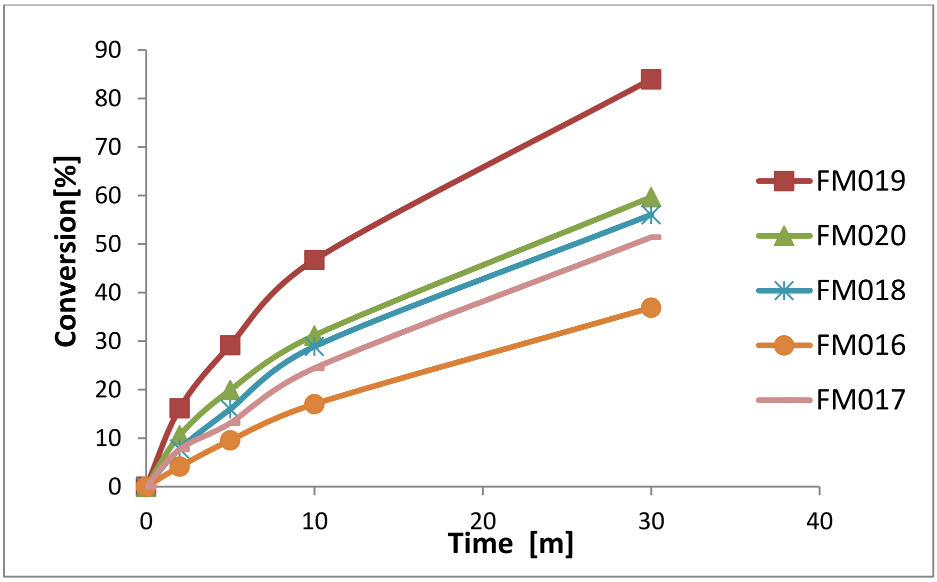


Figure 4.19 : catalytic performance of Mixer Mill synthesized catalysts

These results are really interesting (Figure 4.19) because as we can see from the final conversion there is a specific trend with the frequency used in the grinding treatment:

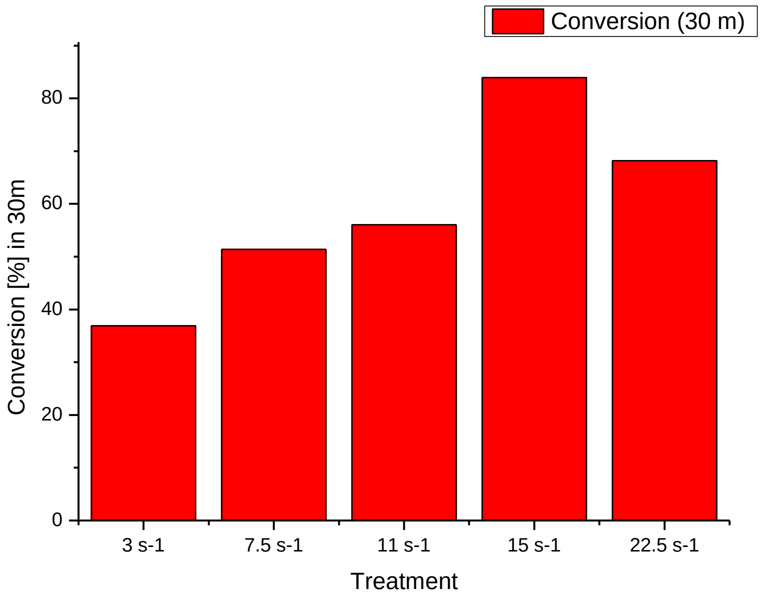


Figure 4.20: trend of catalytic performance compared to the grinding frequency

In figure 4.20, it is easier to see that we have a maximum at 15 s^{-1} of frequency then the activity is decreasing. This phenomenon was important to study in order to understand the real effect of this synthesis on a zeolite as a material support so we thought to start our study on this catalyst carrying out some XRD analysis:

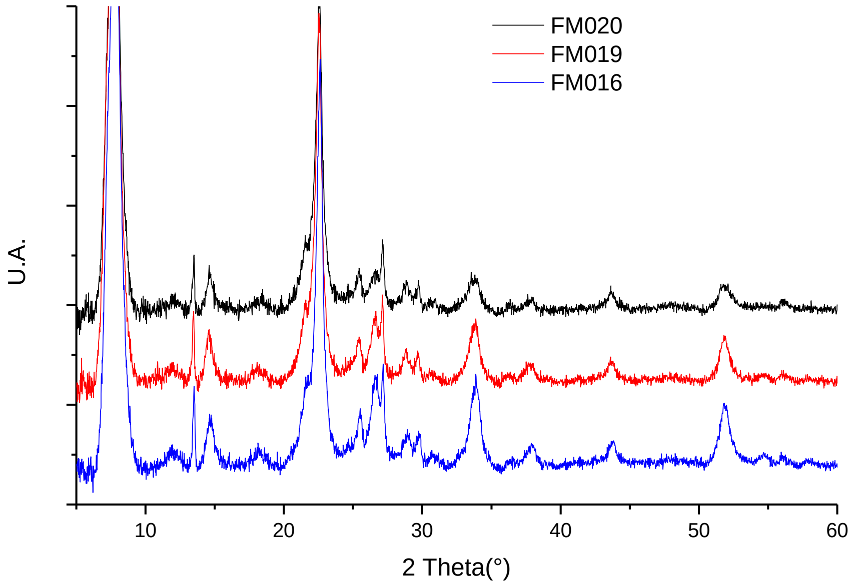


Figure 4.20: XRD of 10% Sn β-Zeolite catalysts

In this graph in figure 4.20, we can clearly see one effect of the mechanical treatment. The peaks intensity is getting smaller increasing the grinding energy, this probably means that the crystal framework of the zeolite is broken by the high energy used in the treatment. However to be sure of this data we have performed a BET analysis on the samples. This is the what we can see from the Support point of view, but the XRD analysis could be exploited also to gain some clues about the behaviour of Tin: if we consider the not incorporated Tin, it is not going to be inserted in the silanol holes left free by the Deallumination procedure and will be present in the Catalyst as SnO_2 after the calcinations. We know that the characteristic peak of SnO_2 is around 26.7°[5] so we can try to gain some information about Tin from a magnification of the previous spectra (figure 4.22):

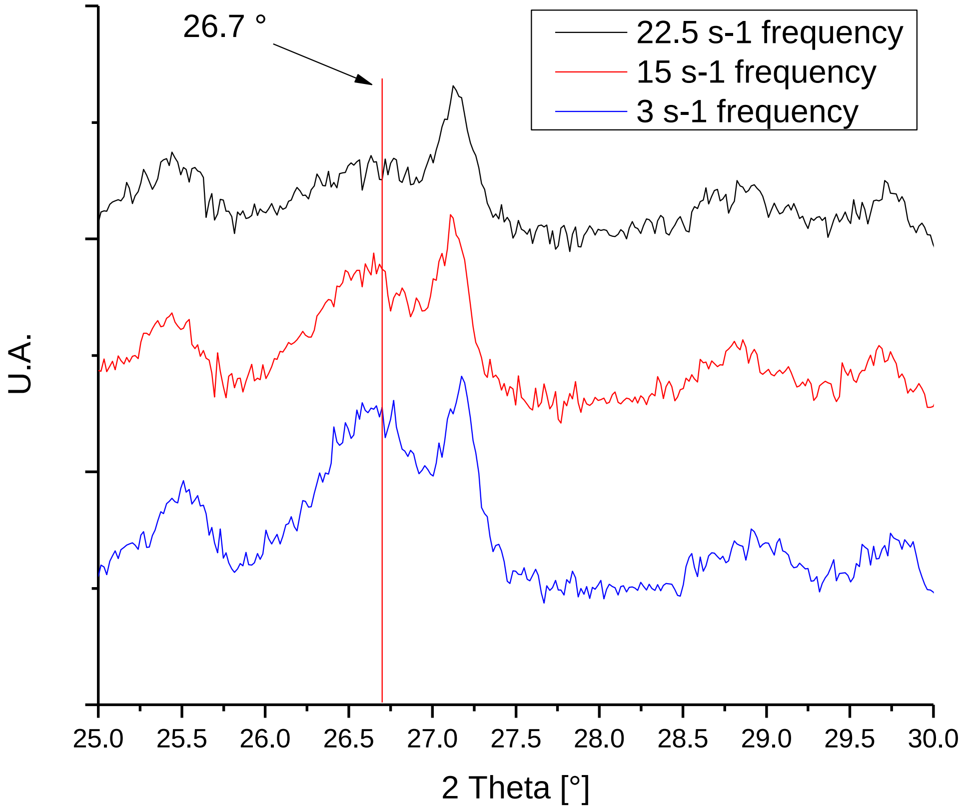


Figure 4.22: magnification of XRD analysis

It is remarkable that this peak is getting smaller with the higher energy treatment, it means that we have less SnO_2 in the sample increasing the frequency of grinding; but considering that the ratio of Son in all the samples is the same, it means that increasing the energy increase also the load of Tin incorporated in silanol holes. However, it is better to verify with a finer technique this results because the noise of the support could influence the intensity of the peaks and so our prediction about the behaviour of the catalyst.

Resuming these results seems that we have two contrasting effects due to the Mixer Mill treatment:

1. The destroying of the crystal framework of the zeolite increasing the energy of the treatment.
2. The better dispersion of the Tin thank to higher frequency in the catalyst's synthesis.

In order to verify the first hypothesis the surface area and porosimetry analysis has been exploited on the catalysts to see if the framework undergoes some modifications during the treatment.

Catalyst Zeolite	Specific surface area m^2/g	Pores area m^2/g	Total Volume cm^3/g	Micropores volume cm^3/g	Mesopores volume cm^3/g
FM016	454.631	380.559	0.2927	0.191	0.1017
FM019	431.646	372.661	0.2679	0.187	0.0809
FM020	373.453	311.090	0.2433	0.156	0.0873

Table 4.4 : BET and porosimetry results about 10% Sn β-Zeolite catalysts

As we can see in table 4.4, we have a decrease of surface area, the destroying of the crystal framework causes this drop, and in fact, it is possible to read in the upper table how the micropore volume is decreasing increasing the treatment energy.

The breaking of the crystal framework probably is the cause of the low activity of this catalyst, this experiment so permitted us to understand that we have a limit of energy treatment that has to be respected in order to not brake the structure of this particular zeolite.

The last experiment that we performed on this material was the Solid State NMR; these experiments are useful because they permit to register two different signals for each kind of Tin in our sample[5]:

- SnO_2 signal is $\delta = -602$ ppm that represent the not incorporated Tin in the zeolite, that during the calcinations forms the $Sn^{(IV)}$ oxide.

- $Sn^{(IV)}$ hydrated at δ = -688 ppm that instead represent the Sn incorporated in the silanol holes.

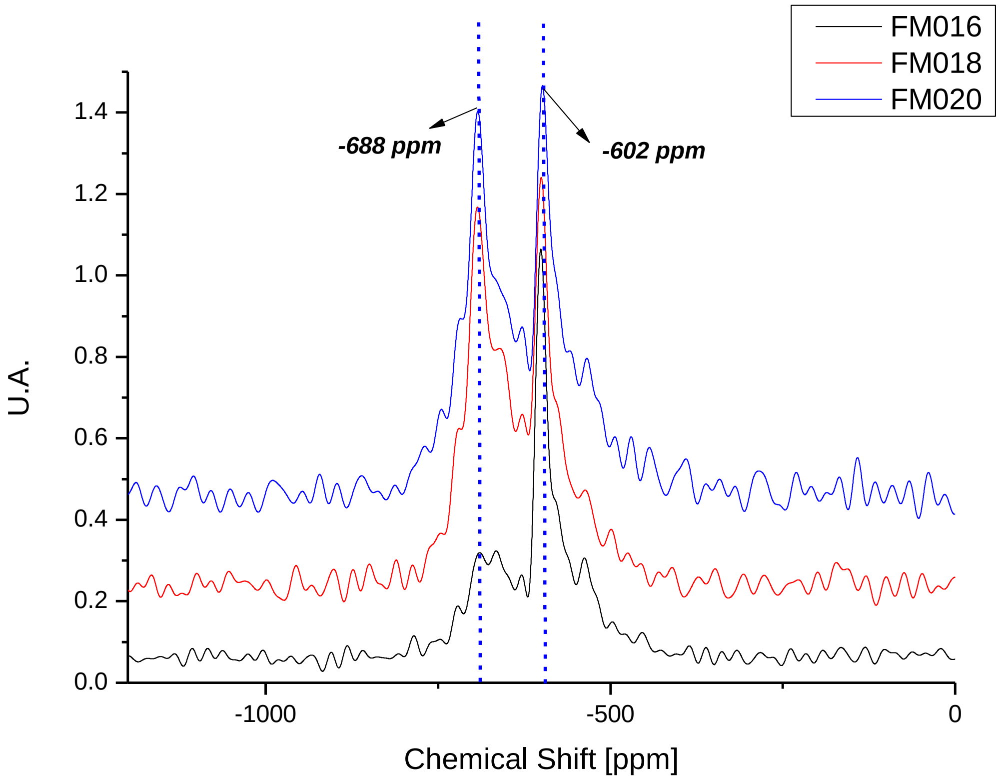


Figure 4.23 : Mass NMR analysis on 10% Sn β-Zeolite catalysts

As we can see in figure 4.23 using low frequencies as 3 s^{-1} the Tin is not well incorporated in the structure and we see basically only a huge peak for SnO_2 at -602 ppm and a lower peak at higher ppm that represent the peak of incorporated tin. Looking the others graphs we see that at 15 s^{-1} frequency of preparation the peak at -688 ppm has basically the same intensity of the other one a -602 ppm. It does not mean that the two species are present in the same amount in the sample, in fact is not easy to have a comparison between them because the nuclei relaxation times are different. For this reason, we have usually preferred a qualitative analysis in order to analyze this material.

Then we have analysed the material at 22.5 s^{-1} of frequency, as we can see the graph seems the same of the one catalyst at 15 s^{-1} of frequency, this interesting because it means that in these case the loss of activity should be due to something else. We have supposed that probably the intensity of this peak is the limit of active phase that can be incorporated, what differs is the crystallinity. This braking in the crystal framework is probably the cause of the loss of activity in this case, in fact some problem of reagent mass transfer could affect the catalytic event. Anyway these are just hypothesis, it necessary to improve the knowledge through in situ experiment on the material to find out some more information about its behaviour

4.3.3 Conclusion

At the end of this work we did not get the expected results, in fact we hoped that the structure was strong enough to withstand more energy before to be broken. Anyway, we achieved a good result because we have synthesized a good catalyst with the 15 s^{-1} frequency of preparation that has a similar activity of the ones synthesized in the previous works[5], but with a higher reproducibility.

Indeed was really interesting to understand the behaviour of this kind of support in order to have a good idea of the different materials behaviour during a mechanochemical treatment. In particular we have seen that this Dealuminated β-zeolite undergoes a breaking in the structure just with a 15 s^{-1} of frequency that compromise the structure and so the crystallinity of the material.

This is very interesting because could be also really useful study different kind of zeolite in order to explore them resistance to mechanical strength and maybe find a new zeolite that can incorporate better Tin than β-Zeolite and so maybe have an higher performance in this MVP reaction.

5. Conclusion

Considering both the projects together, we gathered very good results about the mechanchemical way of synthesis employed. In fact, the two catalytic systems exploited in this work were completely different and so it was possible to see the macchanochemical synthesis from two different chemical points of view.

With the Ag_2O/TiO_2 catalyst we have seen how increasing the energy of the treatment the conversion for the reaction of interest was decreased (Figure 4.24).

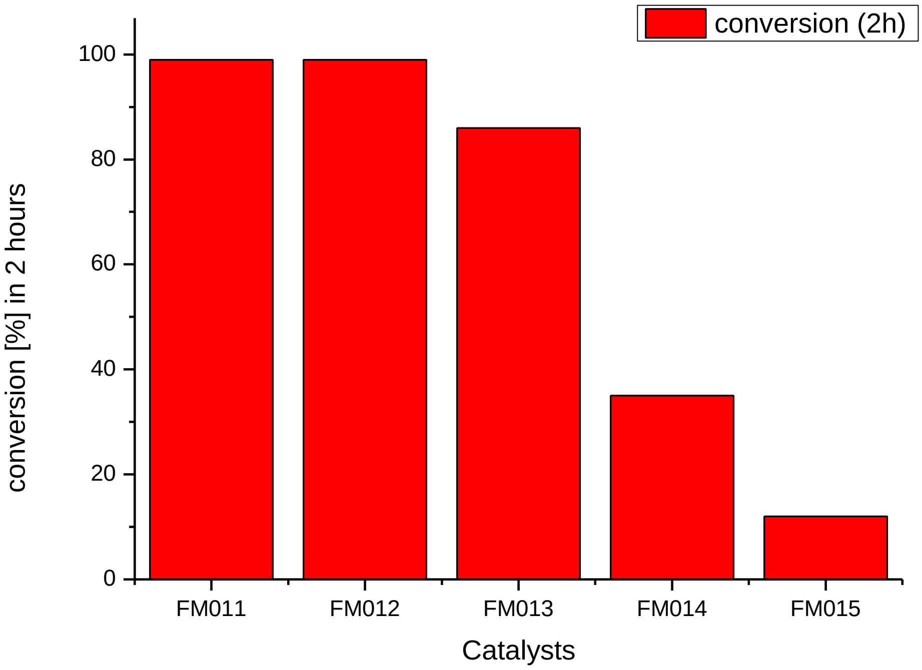


Figure 4.24: trend of catalytic performance in Fluorination reaction

This drop in activity in the fluorination reaction is probably causes by the modifications that Ag (I) undergoes during the mechanical treatments; in facts the energy transmitted to the materials is enough to permit an oxidation of Ag(I) to Ag (II) or a disproportion to Ag(II) and Ag (0) (which option is taking place is actually studied). These reactions that take place during the synthesis decrease the amount of silver(I) in the catalyst and, since it is the active phase in the catalytic event (as explained previously at page n.23)[24] a loss of performance of the catalyst is observed. Indeed titania is losing some crystallinity for the invasive treatment and the particles are not undergoing substantial modifications in sizes.

This is what has been understood about the general behaviour of this material under a mechanochemical treatment, then considering the aim of the project, we could achieve three important targets:

- The catalysts synthesized have been produced with a high reproducibility thanks to the exploitation of the mechanic mixer mill.
- The leached Silver has been reduced significantly; in fact in the main catalyst (FM013) has been found a value of leaching low that was not enough to promote the reaction on its own.
- The recycle of the catalyst is possible thanks to a regenerating step with K_2CO_3 that has probably cleaned the active site by pollutants.

Instead, for the 10 % Tin β-Zeolite the behaviour was very different: the trend of activity increases with higher frequencies until 15 s^{-1}. After this point it is remarkable a drop in activity that is caused probably by the braking of the crystal framework in the zeolite. In fact, the zeolite used as support that has a framework too fragile to stand the energy of the Mixer Mill MM400 and at high frequencies it is clear that the zeolite crystallinity is compromised.

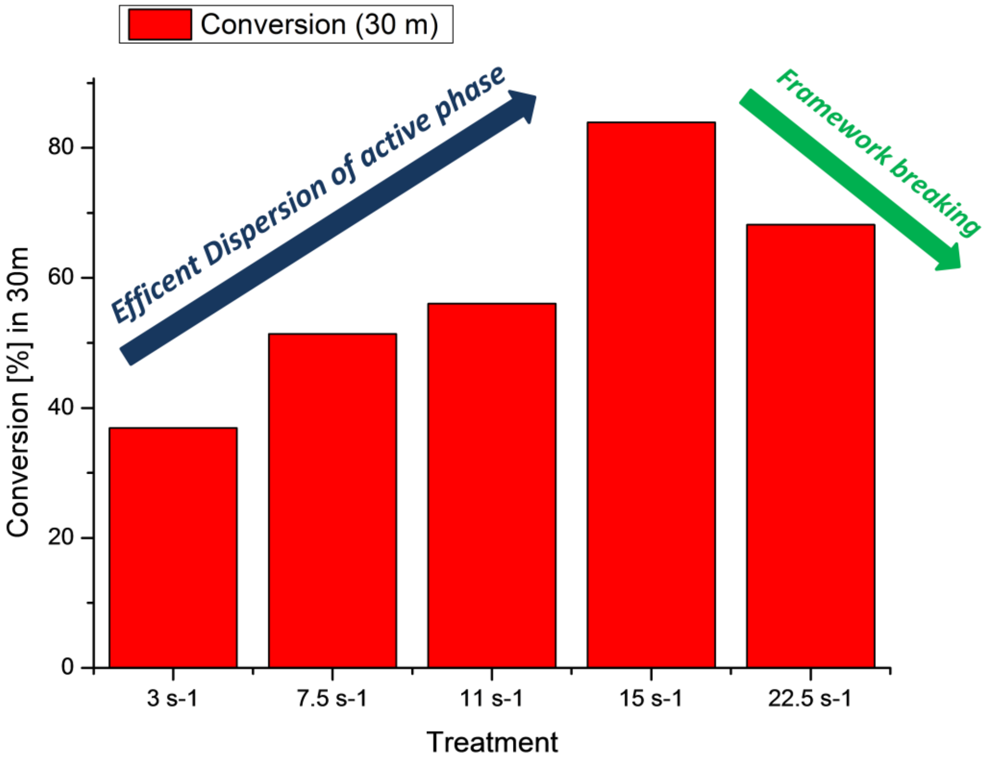


Figure 4.25: trend of catalytic performance in C6-MPV reaction

Looking at the catalytic performance in C6-MPV reaction (figure 4.25), it is easy to understand why we have a maximum of conversion around 15 s^{-1} of treatment. This is the best compromise between a good dispersion of Tin acetate and an energy of grinding not so high to brake to zeolite structure. Considering this achievement, finally we have gained two important targets:

- The synthesis of the catalyst was reproducible every time that was performed thanks to the Mixer Mill employed in the mechanochemical step that allowed to use the same energy of grinding every time.
- a general idea of what is happening at the material during the treatment has been achieved and will be useful in order to start new research routes on this materials

The results obtained in this work are a good starting point in order to study this way of synthesis of catalysts. We could understand some aspects about the behaviour of these systems, but considering the complexity of the phenomena taking place in the mechanochemical synthesis is important to keep on studying these mechanical routes of synthesis. Experiments in situ in particular can help to understand the transformations that are taking place during the grinding of the chemicals, because micro-hotspots at high temperature are created for few seconds during the grinding. This spots are responsible of several modifications in the chemicals that are unpredictable otherwise looking only to the macroscopic phenomena.

Indeed important is also to study new kind catalysts and understand if it is possible their synthesis in this way. In facts supporting other kind of metals on Titania we might have more stable catalysts than with the silver that is use to change oxidation state during the grinding. Looking at the zeolite catalyst it should be important to find a new zeolite strong enough to resist to the strength used in the grinding, in order to get the maximum rate of Tin incorporated in it.

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