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Brief Review on the Evolution of Catalysis in Chemistry

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Abstract This review focuses on the different modes of catalysis that have long been considered a considerable asset in chemistry. Since its appearance to the present day, catalysis has undergone considerable evolution and has contributed greatly to the selective development of molecules of very great importance. It is involved in several reactions, in particular those that allow the formation of carbon-carbon, carbon-heteroatom bonds, etc. It characterizes the acceleration or reorientation of the kinetics of chemical reactions by means of a catalyst. In some cases, it promotes selectivity to direct the reaction in a preferred direction to obtain one product rather than another. The classification of such catalysts is based on several criteria, in particular their behavior in the reaction medium, their structures and often the type of reactions catalyzed. There are several types of catalysis: homogeneous, heterogeneous, enzymatic, phase transfer and organocatalysis. The last one, since its advent in 2000, has attracted growing interest among chemists. Organocatalysts are classified into two categories according to their activation mode: those that activate by covalent bonds and those that activate by non-covalent bonds. A brief presentation of biomimetic catalysis, photocatalysis and electrocatalysis was made on the section of history. Catalysis has made possible reactions that were previously considered impossible and has allowed a gain in time for slow reactions. Catalysis has long played and continues to play a very important role in organic synthesis.

Keywords Review, Catalysis, Evolution, Chemistry

1. Introduction

The synthesis of a chemical molecule is based on several parameters including reagents, reaction conditions, reaction time, etc. Thus, to prepare a specific organic compound, efficiently and in high purity, organic chemists often use catalysts to guide the reaction in the desired direction. A large number of chemical processes involve at least one catalyzed step, whether for the manufacture of synthetic fibers, drugs or food additives, not to mention all the biological reactions catalyzed by enzymes. In addition, the synthesis of low-polluting molecules by environmentally friendly processes is a requirement for modern society, thus organocatalysis, a third branch of catalysis after organometallic catalysis and enzymatic catalysis, is one of the pillars of green chemistry. More than 80% of industrial chemical reactions are carried out using catalytic processes. A catalyst is considered to be any chemical species (metal, organometallic complex, acid, base, enzyme, organic molecule, etc.) capable of exerting an accelerating effect and/or an orienting effect on the evolution of a thermodynamically possible transformation. It must, moreover, be unaltered at the end of the reaction, the thermodynamic equilibrium of which it cannot, consequently, modify [1]. The catalyst is used in much smaller quantities than the reactants. However, the catalyst molecules contribute to the reaction in a specific phase, which justifies their impact on the speed of the reaction. Subsequently, they remain in a following phase. In this review we will present catalysis in its historical and evolutionary framework before detailing the different types of catalysis illustrated by examples, without forgetting to highlight the advantages and limitations.

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2. Historical Framework of Catalysis

The idea of catalysis can be considered to have begun in 1814, when Gustav Kirchoff published his work on the hydrolysis of starch to glucose by acids [2]. A number of people had investigated hydrolysis, but Kirchoff was the first to understand what was happening. The second development in catalysis was in 1817, when Humphrey Davy, assistant to Michael Faraday, discovered that introducing a hot platinum wire into a mixture of air and coal gas caused the platinum to become hot and white. Davy considered that there was oxidation but no flame and that the platinum was unchanged [3]. Technologies based on heterogeneous catalysis were introduced at the end of the 19th century and at the turn of the 20th century, such as: the oxidation of sulfur dioxide (SO_2) to sulfur trioxide or sulfuric anhydride (SO_3) [4], [3], the oxidation of methane by water vapor catalyzed by nickel [5] and later catalyzed by molybdenum in 1971 by

Blanchard and Yim [6], then the synthesis of ammonia (NH_3) catalyzed by iron [7] and its oxidation catalyzed by platinum [8], the reduction of ethylene to ethane by H_2 catalyzed by nickel [9], the use of clay to catalyze dehydrogenation, hydrogenation and polymerization [10]. There are also organometallic catalysts that have developed very rapidly over the years. Fischer and Wilkinson were awarded the Nobel Prize in chemistry in 1973 [11], "for their pioneering work carried out independently on the chemistry of organometallic compounds, called sandwich compounds". One of the very important applications of organometallic catalysis is the Ziegler-Natta process which is an industrial process for the production of polyolefins with controlled tacticity. This discovery earned them a Nobel Prize in Chemistry.

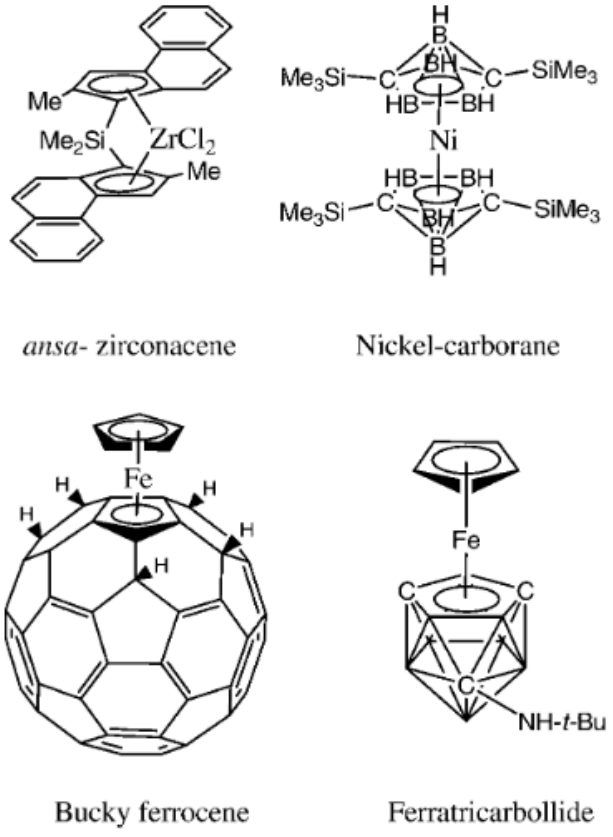


Figure 1. Some examples of organometallic compounds (sandwich)

We can also note the Fischer-Tropsch process developed in 1923 and the 2nd quarter of the 20th century saw the development of gasoline production for engines [12], and since then, catalysis has continued to make significant progress in providing effective solutions to the challenges of synthesizing molecules of interest. Since 1932, there has been organocatalysis introduced by Langenbeck in these terms "the acceleration of a chemical transformation by the addition of a small amount of an organic compound that does not contain metal atoms". The term organocatalysis was used for the first time in 2000 by MacMillan [13]. The first enantioselective organocatalyzed Diels-Alders reaction was carried out by Riant and Kagan in 1989 [14]. The latter demonstrated the effectiveness of prolinol and quinidine as the best catalyst for the reaction between anthrone and a maleimide with a moderate selectivity of (43ee) and an excellent yield of 100% [15].

Subsequently, MacMillan et al. [13] demonstrated the efficiency of a new catalyst, imidazolidinone, in the cycloaddition reaction between cyclohexa-1,3-diene and an α,β-unsaturated aldehyde such as propenal which leads to bicyclo[2.2.2]oct-5-ene-2-carbaldehyde derived from norbornene with a good yield (82%) and excellent diastereo (endo:exo 94:6) and enantioselectivity (ee=94%).

These results provided the basis for two new modes of organocatalytic activation of carbonyl compounds: enamine catalysis and iminium ion catalysis. These two activation modes are based on an intermediate covalence generated by the condensation of the chiral amine on the carbonyl group. Subsequently, other types of organocatalytic activation of carbonyl compounds were developed, respectively dienamine catalysis and SOMO (Singly Occupied Molecular Orbital) catalysis. Since MacMillan's remarkable work in 2000, organocatalysis has experienced real development caused by its proven efficiency and especially by its appropriate response to the standards of green chemistry. For this work in organocatalysis MacMillan was awarded the 2021 Nobel Prize in Chemistry [16].

However, one of the disadvantages of organocatalysis is that many organocatalytic reactions require a high catalyst load (20 – 30 mol %) and a long reaction time (day) [17].

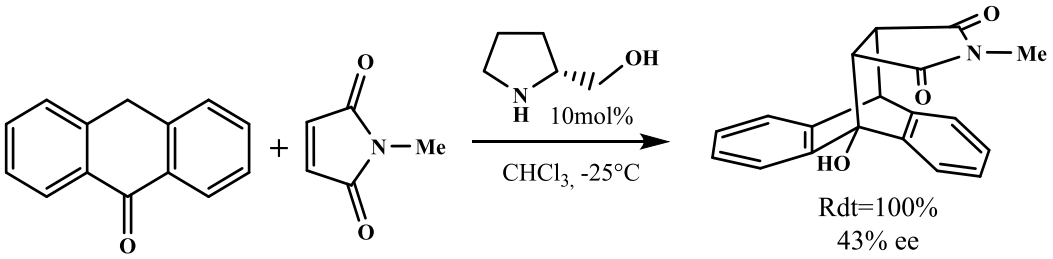
Catalysis is important both academically and industrially. It plays a vital role in the manufacture of a wide range of products such as high octane gasoline, plastics, fertilizers, herbicides, pharmaceutical drugs that would otherwise be unobtainable or prohibitively expensive [18]. There are few chemical or petroleum-based products in modern society that do not depend in some way on a catalytic step in their manufacture. In addition to manufacturing processes, catalysis has other important and ever-increasing uses; for example, the successful applications of catalysis in pollution control and its use in environmental control have multiplied considerably in recent years. Additionally, there is electrocatalysis [19], [20], photocatalysis [21], and biomimetic catalysis [22]. Biomimetic catalysis is an important field of biomimetic chemistry that involves chemical catalysis that mimics certain key characteristics of enzymes found in bacteria and some mammals. This process is carried out in water, with no oxidant other than ambient air, and is self-regenerating [23], [24]. For example, C–H functionalizations of alkanes used as key steps in the synthesis of bioactive molecules [23].

Photocatalysis is an ecofriendly technique that emerged as a promising alternative for the degradation of many organic pollutants. The weaknesses of the present photocatalytic system which limit their industrial applications include low-usage of visible light, fast charge recombination, and low migration ability of the photo-generated electrons and holes. Therefore, various elements such as noble metals and transition metals as well as non-metals and metalloids (i.e.,

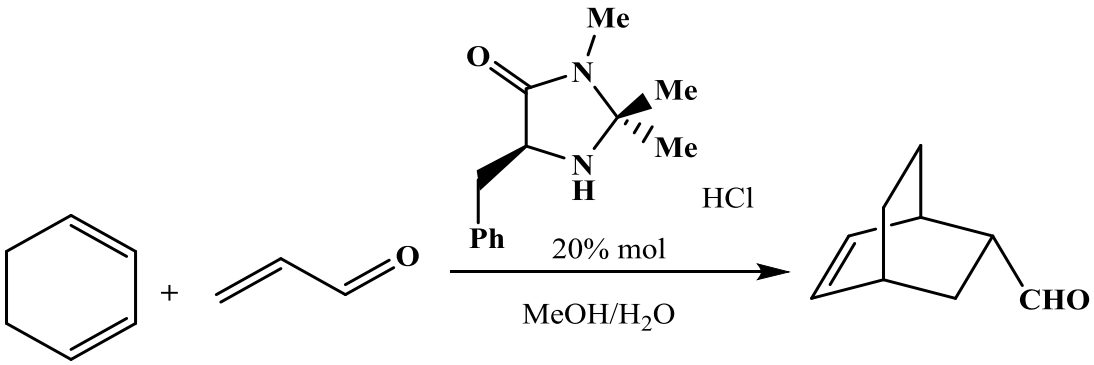
graphene, carbon nanotube, and carbon quantum dots) are doped into the photocatalyst as co-catalysts to enhance the photodegradation performance [25]. The principle of photocatalysis is based on the activation of a semiconductor by light.

Electrocatalysis studies the physico-chemical properties of electrode materials, as well as the mechanism and rate of electrode reactions. Electrocatalysis aims to minimize electrode overpotential, which in turn depends on the electrode material, reactants, products, and intermediates at the electrode-electrolyte interface [26]. This catalysis can be heterogeneous (e.g., a platinum surface or nanoparticles) or homogeneous (e.g., a coordination complex or an enzyme) [27].

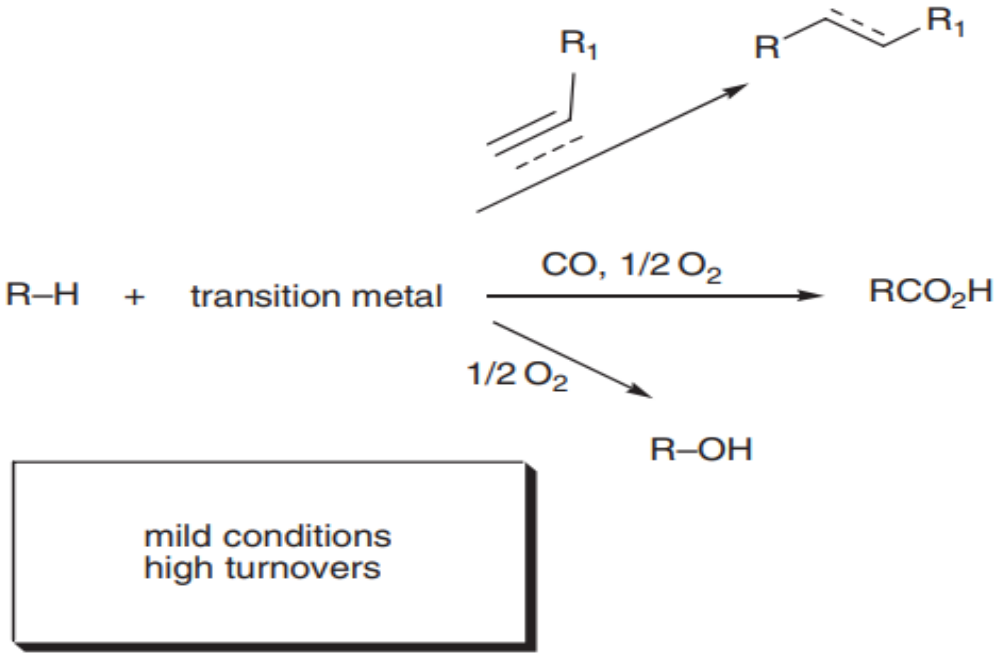
Catalysis is a central science that will have a key contribution to the development of more sustainable processes, in connection with the current emerging and yet urgent societal challenges related to climate change and environmental concerns [28].



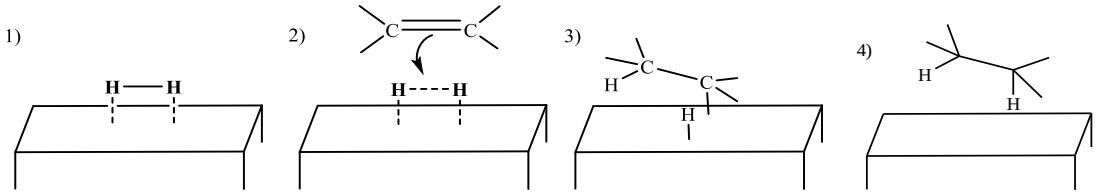
Scheme 1. Kagan's prolinol-catalyzed Diels-Alder reaction



Scheme 2. First enantioselective Diels-Alder reaction catalyzed by imidazolidinone



Scheme 3. Fonctionalization of alkene for the synthesis of bioactives molecules



Scheme 4. Mechanism of nickel- and platinum-catalyzed hydrogenation of alkenes

3. Types of Catalysis

3.1. Classification According to the Nature of the Catalyst or Its Structure

Catalysts can be classified according to their nature or according to their physical state during their action or according to the environment in which the reaction takes place. They can interact differently with the reactants to form reaction intermediates and therefore accelerate and/or direct the reaction.

3.1.1. Heterogeneous Catalysis

Catalysis is heterogeneous when the catalyst and the reactant(s) are not in the same phase. The vast majority of cases of heterogeneous catalysis involve a catalyst in solid form, the reactants being gaseous and/or liquid [29]. Adsorption occurs when the reactants stick to the surface of the catalyst so that the reaction can take place. The place on the surface of the catalyst where the reactants adhere is called the active site. Indeed, the greater the contact surface between the catalyst and the reactants, the faster the reaction. A powder or foam catalyst is generally used rather than a wire or blade. The main steps in the mechanism of heterogeneous catalysis (example of the hydrogenation of an alkene) are described in the figure below. In heterogeneous catalysis, at least one of the reactants is adsorbed on active sites on the surface of the catalyst.

At first glance, heterogeneous catalysis seems very far from organometallic chemistry and homogeneous catalysis. However, it is essential to introduce these concepts because they are complementary to those of homogeneous catalysis and the majority of industrial processes are driven by heterogeneous catalysis. In addition, the molecular approach has become increasingly common in heterogeneous catalysis, and a continuity of disciplines is currently being established between molecular activation and that involving the solid state. The species establishing this link are aggregates ("clusters"), and this from organometallic aggregates to nanoparticles of various sizes stabilized by ligands. Catalytic converters in cars are an example of heterogeneous catalysts at work. In a catalytic converter, a gaseous reactant passes over a solid catalyst usually [30]. The Haber and Contact processes use transition metal catalysts to increase the reaction rate. Heterogeneous catalysis plays a key role in the manufacture of essential products in key areas of agriculture and pharmaceuticals, but also in the production of polymers and numerous essential materials [31], [32].

3.1.2. Homogeneous Catalysis

The catalyst and reactants are present in the same phase, which is often liquid or gaseous, in homogeneous catalysis. In organic chemistry, where several reactions occur with reactants in solution, in the presence of H^+ ions, Lewis acids, complexes, etc., all of which are equally soluble, this kind of catalysis is frequently observed.

$$\text{R-CH=CH-R} + \text{CO} + \text{H}_2 \xrightarrow{\text{Co}} \text{R-CH}_2\text{-CH(R)-CHO}$$

Scheme 5. Hydroformylation of alkenes

However, homogeneous catalysis has consistently been able to make its presence known in the industrial sector without hiding. Among the major steps that marked its development, noteworthy are hydroformylation (Scheme 5) [33], the trimerization of butadiene by Hüls in 1955, the metathesis of olefins [34], the oxidation of ethylene to acetaldehyde (scheme 6) [35], the carbonylation of methanol to acetic acid [36], the hydrocyanation of butadiene to adiponitrile by DuPont in 1971 and the asymmetric isomerization of allylamines for the synthesis of menthol [37]. This final example is significant since the majority of industrial uses of homogeneous catalysis in recent years have unquestionably arisen in the field of fine chemistry.

$$C_2H_4 + H_2O + PdCl_4^{2-} \xrightarrow{H_2O} CH_3CHO + Pd(0) + 2HCl + 2Cl^-$$

Scheme 6. Oxidation of ethylene to acetaldehyde

Academic and industry advancements in homogeneous catalysis have been greatly aided by the boom of the tastes and perfumes industries, particularly in the pharmaceutical and agrochemical sectors, with the emergence of chiral active components. It is true that catalysis by coordination complexes can best demonstrate its qualities in these highly demanding domains in terms of selectivity and high added value. The main intermediates, commodities and specialties are not excluded, though, and novel catalysts with noticeably better performances as well as new homogenous catalytic reactions have been established in recent years. To our knowledge, the manufacture of polyethylene by titanium catalysts known as constrained geometry catalysts (CGC) constitutes the only purely homogeneous process exploited industrially. In a continuous homogeneous catalysis process, the reactants and the catalyst enter simultaneously, in solution, into a stirred reactor. The products, the catalyst and possibly the solvent, exit forming a single liquid phase.

The advantages of this technology are no longer to be demonstrated. One of them, particularly appreciated by users, is its great operating flexibility. For example, the addition of the catalyst could be adjusted according to the feed rate to maintain a continuous conversion of the reactants. Consequently, accidental deactivations, caused by contamination due to impurities present in the industrial feeds, only concern the section of the catalyst located at the exact moment in the reactor and are therefore quickly overcome.

3.1.3. Enzymatic Catalysis

Enzymes are catalysts that can be used for most reactions known in organic chemistry. In biology, enzymes are catalysts for metabolic reactions. They have structures based on polypeptide. Biological catalysts are called enzymes and biological catalysis is called enzymatic. Enzymes are proteins made up of chains of amino acids $RCH(NH_2)CO_2H$. There are more than 20 different natural occurring amino acids. More than half of enzymes are metalloenzymes in which the metal plays the very important role of active site. These metals, present in biological systems in trace amounts since they have a catalytic action, are Mg, V, Cr, Mn, Fe, Co, Ni, Cu, Zn and Mo. The other elements present in trace amounts, but also essential, are B, Si, Se, F, I and Br. With the elements present in large quantities: Na, K, Ca, P, S and Cl, they constitute the field of bioinorganic chemistry, a discipline currently in full swing [38]. Soluble enzymes can be considered as intermediates between homogeneous and heterogeneous catalysts; they are homogeneous at the macroscopic level but at the molecular level the catalyzed reactions take place on the surface of the enzyme as for heterogeneous catalysis. Enzymes bound to biological membranes on the other hand are heterogeneous. Generally, an enzyme catalyzes only one chemical reaction. Enzymes are proteins present in all cells of living beings whose role is to catalyze (accelerate) biochemical reactions. Some enzymes contain a non-protein part essential to the activity, the cofactor. This cofactor can be a mineral ion such as Mg^{2+} or Fe^{3+}. A cofactor of organic nature is called a coenzyme. Adenosine triphosphate (ATP) and nicotinamide adenine dinucleotic (NAD) are very common examples figure 2 [39].

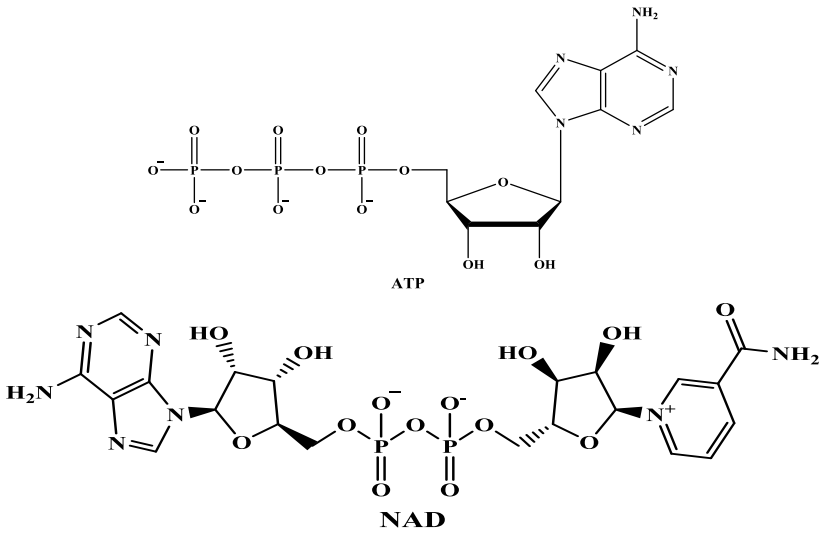


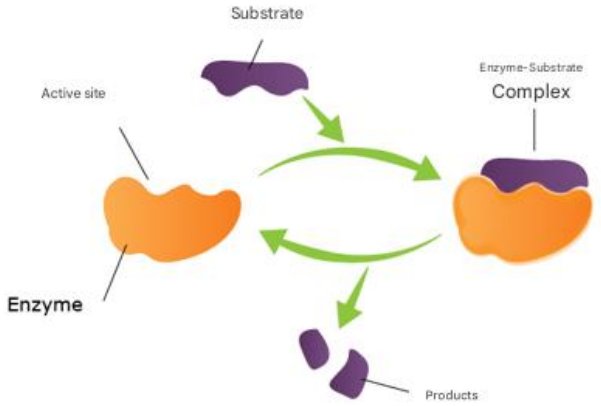
Figure 2. Representation of adenosine triphosphate (ATP) and nicotinamide adenine dinucleotide (NAD)

The main biological ligands and the metals with which they complex most strongly are shown below.

Table 1. Amino acids of proteins forming the most stable complexes in biological media

aspartate	glutamate	histidine	tyrosine	cysteine	methionine
Zn^{II}, Mg^{II}, Ca^{II} Mn^{III}, Fe^{II}, Fe^{III}		Zn^{II}, Cu^{II} Cu^{I}, Fe^{II}	Fe^{III}	Zn^{II}, $Cu^{I/II,}$ $Ni^{I/III}$, $Fe^{II/III}$, $Cu^{I/II}$ $Mo^{IV/VI}$, $Fe^{II/III}$	

Bioinorganic chemistry also requires the development and analysis of low molecular weight models to comprehend and understand systems. Enzymes are proteins that participate in metabolic reactions within living organisms. The enzyme combines with the substrate to form a complex [enzyme-substrate] that evolves to give the product.



Scheme 7. Example of the mode of action of an enzyme

Indeed, enzymes are used in the field of biotechnology: manufacturing detergents, fructose syrup from corn starch, fermentation of barley into amino acids and sugars, etc.

Enzymes generally exhibit very low in toxicity, they can even be reusable and act in mild conditions. *In vivo*, enzymes are very effective catalysts and their reaction speed can be multiplied by a factor of 10^8-10^{12}. They comply with environmental standards. Despite their various advantages, enzymes have disadvantages, including their high cost caused by the fact that they only exist in the form of a single isomer, their sensitivity to inhibition phenomena, i.e. their actions can be blocked by certain products. They have complex and flexible molecular structures, which complicates the predictability of the products [40].

The International Union of Biochemistry and Molecular Biology (IUBMB) has classified enzymes according to the type of reaction they catalyze. Each enzyme class is identified by the letters EC (Enzyme Commission), followed by a decimal notation, all in the following form: EC a.b.c.d [41]. There are six classes of enzymes: oxidoreductases, transferases, hydrolases, lyases, isomerases, and ligases.

3.1.4. Organometallic Catalysis

The discovery of sandwich compounds (such as ferrocene) has been a growing interest in the history of inorganic and organic chemistry with the launch of a new era of organometallic chemistry. Such a breakthrough in the development of this field is partly explained by the enormous applications of sandwich molecules such as ferrocenylphosphines [11], [42], [43] and metallocenes based on Ti, Zr and Hf [44], [45], in homogeneous catalysis. Examples include carbon–carbon and carbon–heteroatom coupling, asymmetric synthesis, carbonylation, hydroformylation and single-site catalysis for the polymerization of olefins. Catalysis using metal compounds, often transition metals, has long been the main form of asymmetric catalysis used in chemistry. Organometallic complexes have many advantages, particularly due to their diversity of structure and their reactivity. They have several disadvantages, such as their high cost and their toxicity, which complicates waste treatment and they often contaminate the final product [46]. These catalysts are metal complexes (often transition metals). However, organometallic catalysis poses a major problem: that of separating the catalyst (and possibly the solvent) and the products resulting from the reaction. In practice, one of three techniques is used: destruction and simple rejection of the catalyst, decomposition and recycling after reactivation, or recycling in its active form. The products are separated either by distillation or by chemical extraction; but even if it is recycled in its active form, the catalyst suffers and the treatment costs are often high. This is why it is often necessary to immobilize the organometallic catalyst, either by grafting onto a support (mineral or organic), or by dissolution in a medium that is poorly or not at all miscible with the reaction products. This last approach is called liquid-liquid biphasic catalysis [47].

3.1.5. Biphasic Catalysis or Phase Transfer Catalysis (PTC)

It combines the benefits of homogeneous catalysis (uniqueness of active centers, operating capacity, etc.) with ease of product separation (by simple decantation). The reactions are rapid and are carried out at moderate temperature, with an increase in nucleophilicity (poorly solvated nucleophile), and quantitative recycling of the catalyst in its active form. The reactions are carried out at a lower cost with the elimination of the catalyst by washing with water or by column chromatography (scheme 8). For reasons of economy and environment, homogeneous catalysis methods often favor the use of a solvent, although the latter can contribute favorably to the reaction speed or to the different selectivities (chemo-, regio- or enantio-). Biphasic catalysis makes it possible to simultaneously solve two problems: the purification and recycling of the catalyst, and the use of a solvent. However, only a few organic solvents meet the physical and chemical requirements necessary for such an application.

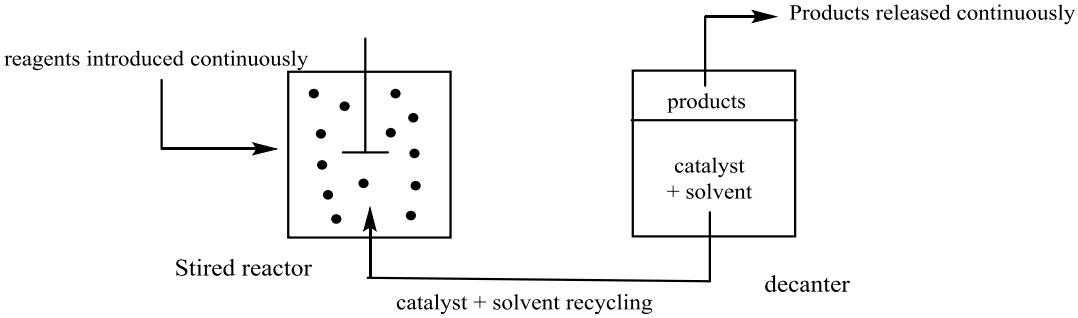
The reactants enter continuously into a perfectly stirred reactor. The polar phase in which the catalyst is dissolved is introduced at the beginning of the reaction. The catalyst operates in this phase (or at its interface if the solubility of the reactants in the polar phase is very low). The reaction products, which are very poorly miscible, are separated at the outlet of the reactor in a decanter. The catalyst and the solvent are recycled to the reactor and reused. Phase transfer catalysis is a synthesis method allowing, in a two-phase medium (liquid-liquid or liquid-solid), nucleophilic substitution, oxidation [48], and cyclization [49], [50], [37], [38] reactions, which are impossible or difficult to carry out in a single-phase medium. The principle of this method is based on the fact that an anionic nucleophilic reagent, formed in an aqueous medium by the action of a strong base on an acid or pseudo-

acid, is concentrated in this medium where the organic substrate is not or is poorly miscible and has a reactivity very attenuated by the specific solvation due to the protic solvent. The reaction of substitution of a chlorine by a cyano group was attempted without success in 1950 by Hennis and then in 1960 by Makosza Brändström in the presence of NaCN in water.

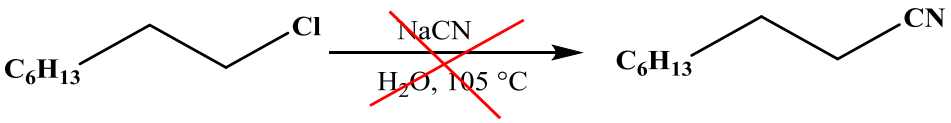
This reaction was successfully resumed later in 1971 by Starks in the presence of a biphasic catalyst [51] (Schema 9).

Since the reactions occur at the interface, stirring the two-phase mixture (lipophilic organic substrate-hydrophilic anionic reagent) only slightly improves the reaction rate. If, on the other hand, a catalytic amount of a lipophilic cation halide (a quaternary ammonium or phosphonium with 12 or more carbon atoms) is added to the reaction medium, the nucleophilic anion will form a pair of lipophilic ions with the onium cation which penetrates into the organic substrate with which it reacts rapidly, releasing an onium salt which returns to the aqueous phase and renews its transfer action between the two phases of the nucleophilic reagent. Martin and co-workers [48] studied the oxidation reaction of primary and secondary alcohols without organic solvent using hydrogen peroxide in the presence of tungsten and a phase transfer catalyst. This provided a general, safe, simple and inexpensive solution of the effective means to carry out this functional group transformation. The work is exceptionally simple, and the yields are high.

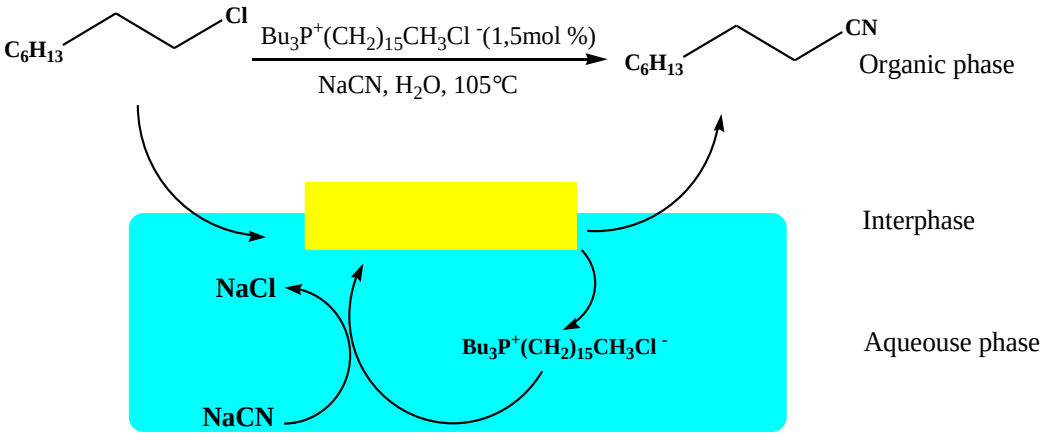
Six representative alcohols, 1-phenylethanol, 1-phenylpropanol, benzhydrol, 4-methylbenzhydrol, *cis*-, *trans*-4-tert-butylcyclohexanol, and benzyl alcohol are oxidized to the corresponding aldehyde or ketone in 1 to 3 hours in yields of 81 to 99%. Purities are very high, with only small amounts of starting alcohol. *In situ* preparation of the catalyst *N*-methyl-*N*,*N*-dioctyloctan-1-aminium hydrogen sulfate $[CH_3(C_8H_{17})_3N]HSO_4$ is performed by mixing *N*-methyl-*N*,*N*-dioctyloctan-1-aminium chloride $[CH_3(C_8H_{17})_3N]Cl$ and sodium hydrogen sulfate monohydrate $NaHSO_4.H_2O$. Ionic liquids are widely used in phase transfer catalysis [52]. Zhao and co-workers successfully used an ionic liquids based on pyridinium cations as phase-transfer catalysts (PTCs) for phase-transfer catalytic oxidation of dibenzothiophene (DBT) dissolved in n-octane [53]. Another example of using ionic liquids as catalysts was achieved by Cheng and Yen during deep oxygenative desulfurization [54].



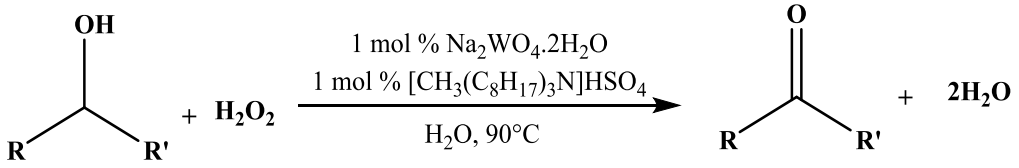
Scheme 8. A schematic representation of biphasic catalysis



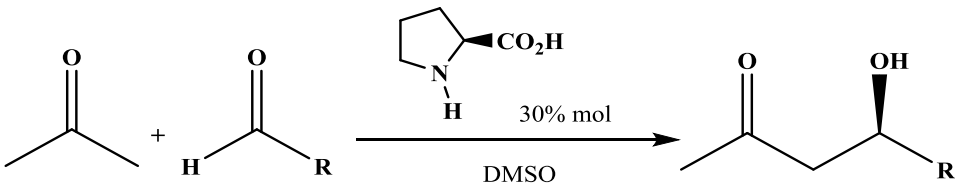
Scheme 9. Substitution reaction of chlorine by a cyano group without catalyst



Scheme 10. Mechanism of the substitution reaction of chlorine by cyano catalyzed by a phosphonium salt



Scheme 11. Oxidation of alcohols by phase transfer catalysis



Scheme 12. Condensation between a ketone and an aldehyde catalyzed by L-proline

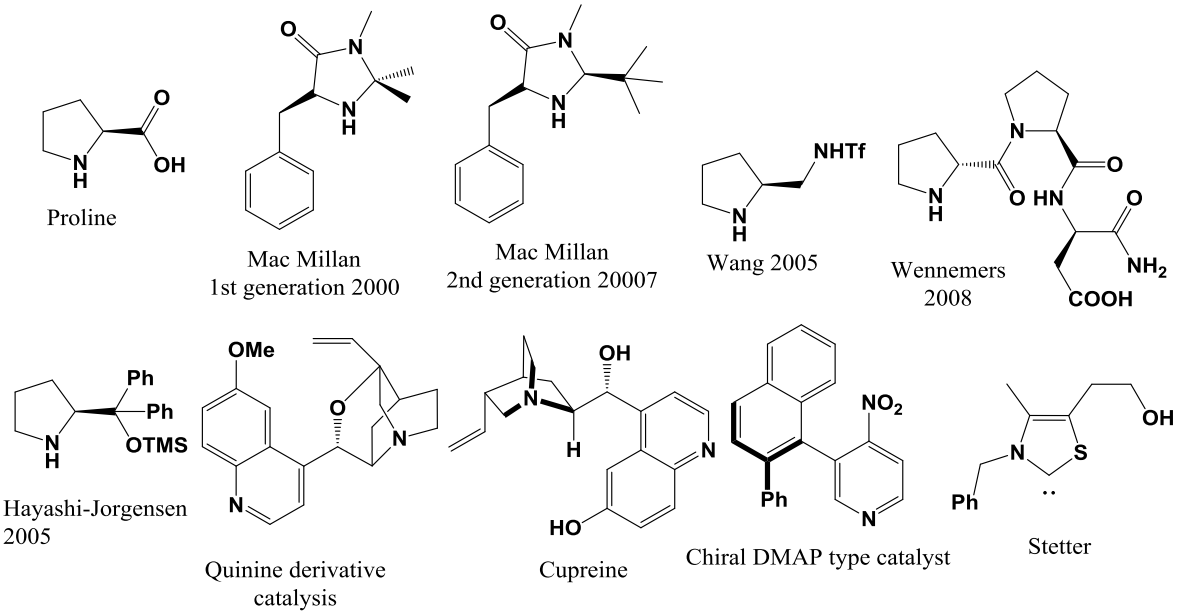


Figure 3. Some examples of organocatalysts activating by covalent bonding

3.1.6. Organocatalysis

Asymmetric catalysis has long been reserved for transition metals via chiral ligands and enzymes (biocatalysis) [55]. The concept of organocatalysis is not new since the first example of addition of hydrogen cyanide HCN to benzaldehyde catalyzed by alkaloids, with a low enantiomeric excess, was described in 1912 by Bredig and Fiske and this reaction is often cited as the first non-enzymatic asymmetric catalysis reaction [56]. The term organocatalysis was proposed and conceptualized by David MacMillan in the year 2000 [13]. It designates all the synthesis processes using purely organic molecules as catalysts containing elements such as oxygen, nitrogen, sulfur or phosphorus without metal [55]. The majority of organic catalysts explored are based on chiral amines (amino acids, peptides, alkaloids such as cinchona quinine, chiral imidazolidinones) [57]. In 2005, Benjamin List introduced a classification system, based on the nature of the catalyst, allowing to obtain four categories: Lewis acid, Lewis base, Brönsted base and Brönsted acid [58]. Another classification can also be made according to the mechanism because organocatalysts are often bifunctional such as proline which is both a Brönsted acid and a Brönsted base. Indeed, during the 2000s, List, Lerner and Barbas [59] showed that it was possible to achieve a highly enantioselective aldol reaction (ee > 96%) catalyzed by a natural amino acid: *(S)*-proline with a yield greater than 97%.

Chiral organocatalysts usually have more than one active center. They are bifunctional catalysts having a Bronsted acid and a Lewis base. These catalysts are able to activate both the donor and the acceptor, which not only results in a considerable acceleration of the reaction, but also an increased selectivity due to the highly organized transition state [60]. Organocatalysts can be classified according to their modes of activation of the reactants, i.e. their reaction mechanism, we distinguish activation by covalent bond and activation by non-covalent bonds.

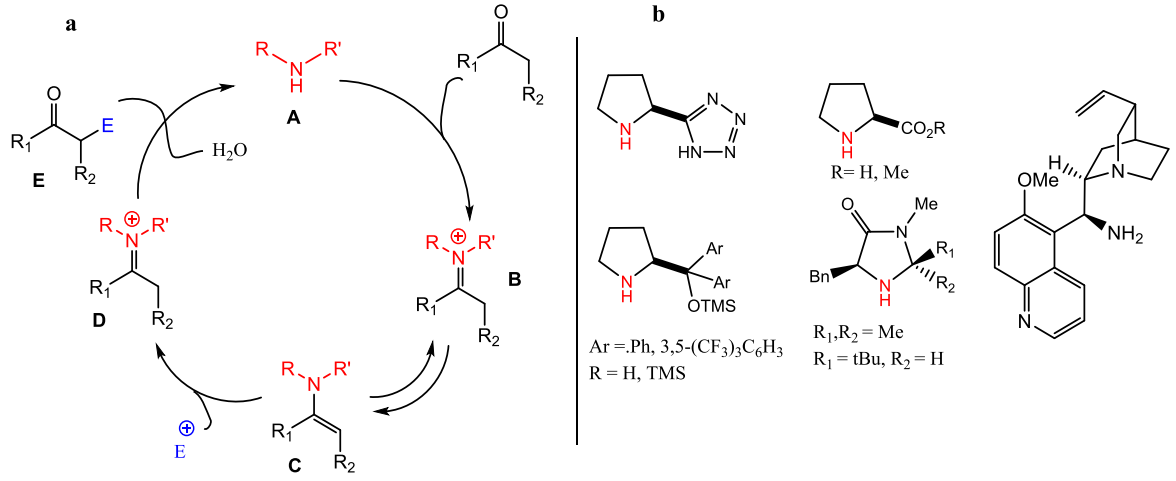
3.1.6.1. Activation by Covalent Bond

The vast majority of organocatalytic reactions proceed via the covalent formation of a catalyst-substrate adduct to form

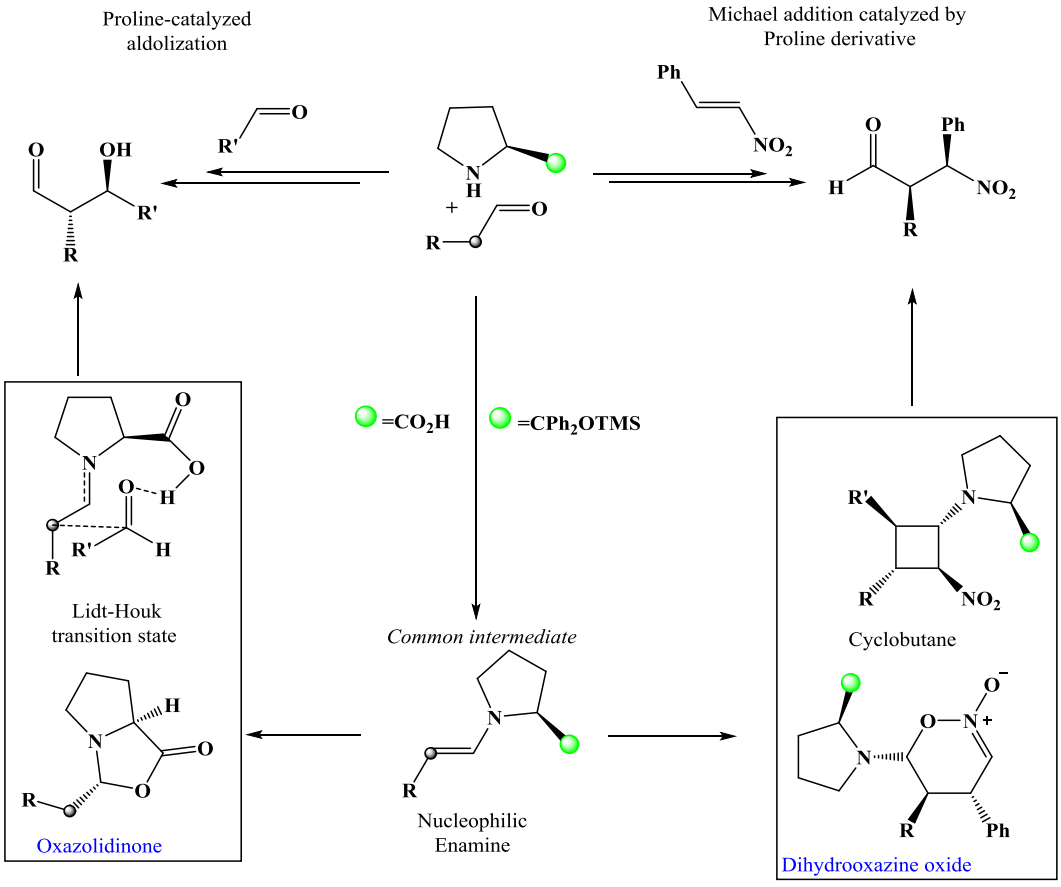
an activated complex [61], [62], [63], [64]. Amine-based reactions are typical examples in which amino acids, peptides, alkaloids and synthetic molecules containing nitrogen are used as chiral catalysts. This activation method is generally ensured by Lewis acid and Lewis base catalysts. By definition, a Lewis acid is any chemical species (molecules or ions) capable of accepting an electron pair, and a Lewis base is any chemical species capable of sharing its electron pairs.

In this type of catalysis, the nucleophilic catalysts used are often nitrogenous, but also sulfurous or carbonaceous compounds, some examples of which are shown in Figure 3 [65].

On this list of catalysts some are capable of activating by hydrogen bonding and or by combination of the two activation modes namely by covalent bonds and by non-covalent bonding. These latter are often called multifunctional catalysts. Among the types of activation by covalent bonding we have: HOMO, LUMO, SOMO and NHCs activation.



Scheme 13. a) Enamine-mediated activation mechanism, b) Some catalysts activating by covalent bonding



Scheme 14. Transformation of proline enamine to Oxazolidinone and a proline derivative to dihydrooxazine oxide

3.1.6.1.1. Catalysis via Enamine (HOMO Activation)

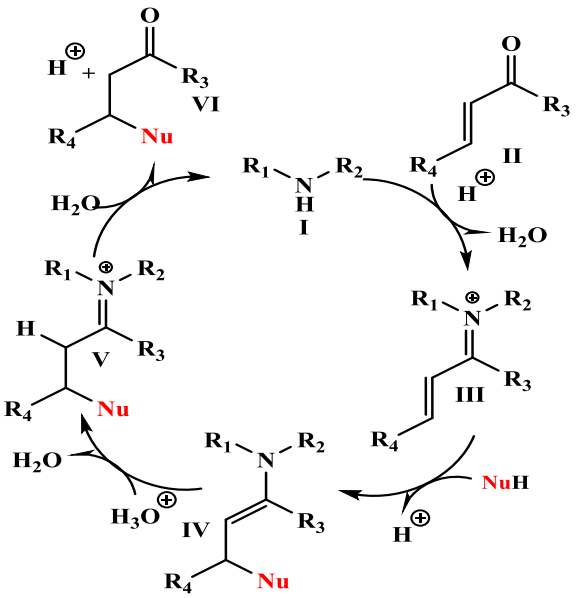
Covalent activation by reversible enamine formation is based on the ability of a primary or secondary amine to shift the equilibrium of a carbonyl compound toward the more reactive enamine. The highest occupied molecular orbital (HOMO) of the enamine formed then has a higher energy than the HOMO orbital of the enol form of the carbonyl derivative, thereby increasing the nucleophilicity of the substrate, which facilitates its addition to a suitable electrophile [65]. Stork was the first to describe the general utility of enamines as intermediates in a wide range of transformations in classical organic synthesis [66]. This type of catalysis is involved in an α-functionalization reaction of a carbonyl compound.

In the proposed mechanism (Scheme 13 a), catalyst A, a primary or secondary amine, reacts with the carbonyl compound to form an iminium ion B, which tautomerizes to enamine C. After reaction with an electrophile, a new iminium ion D is formed. Hydrolysis of the latter allows the recovery of the product and regeneration of the catalyst. The driving force of this reaction is the formation of a strongly nucleophilic enamine intermediate. Various chemical transformations use enamine as a nucleophile, such as Michael reactions, Mannich reactions or aldol reactions. It can also act as a dienophile in Diels-Alder cycloaddition reactions. Thus, many chiral catalysts have been developed to study and improve the efficiency and selectivity of these transformations (Scheme 13 b) [67]. However, it is important to note that these primary catalytic species can also be transformed into secondary intermediates, where their role in catalysis is less obvious. Relevant examples in the field of proline catalysis include parasitic oxazolidinones [68] and dihydrooxazine oxides (Scheme 14) in organocatalytic additions of enamines to aldehydes or nitroalkenes, respectively. Clarifying the role of these intermediates in catalysis remains an active area of research and a topic of ongoing debate [69].

3.1.6.1.2. Catalysis via Iminium ion (LUMO Activation)

Reversible reactions between α, β-unsaturated carbonyl compounds and chiral amines lead to the formation of iminium ions, characterized by a lower level of vacant lowest molecular orbital (LUMO) energy than in the initial compounds. This leads to an increase in the electrophilic character of the generated iminium ions, which can then react in cycloaddition and conjugate addition reactions [70]. Catalyst **I** reacts with the α, β-unsaturated substrate **II**, thus leading to the formation of an iminium ion **III**; due to the presence of unsaturation, the iminium will this time activate the terminal β position allowing the addition of a nucleophilic species in this position 4 (intermediate **IV**). The β-substituted product (**VI**) will then be released, and catalyst **I** regenerated, by the acid hydrolysis of intermediate **V**.

The use of optically pure secondary amine catalysis allows a number of highly chemo- and stereo-selective functionalizations of carbonyl compounds, giving access to complex molecules of great interest and possessing several chiral centers. In general, aldehydes and ketones are activated in the presence of optically pure amines via the formation of enamines, while unsaturated carbonyl compounds are activated via the formation of iminium. These two chiral intermediates are likely to react with electrophiles or nucleophiles in order to carry out a variety of reactions in a very selective manner.



Scheme 15. Activation via imminium ion

3.1.6.1.2.1. SOMO Activation Mode (Singly Occupied Molecular Orbital)

SOMO activation, an acronym from the English term "Single Occupied Molecular Orbital", introduced mainly by the MacMillan group in 2007 [71], is based on the activation of the enamine by a single-electron transfer which leads to an iminium radical intermediate thus facilitating the addition of a nucleophile in the α position of the carbonyl [72]. This type of activation often leads to selective α-allylation, α-enolation and α-arylation of aldehydes.

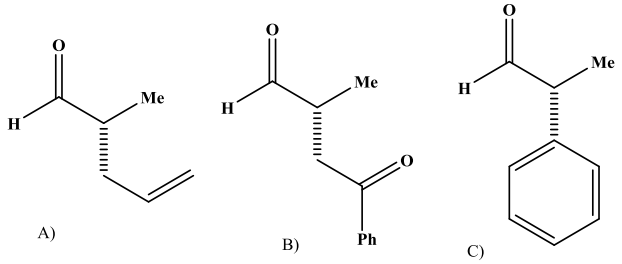
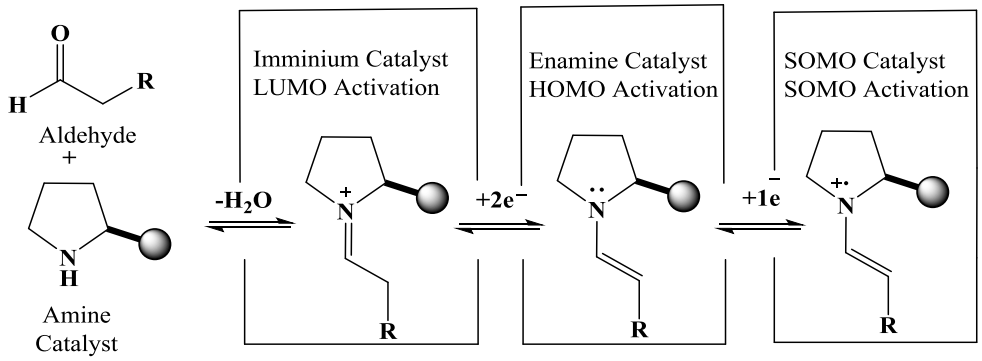
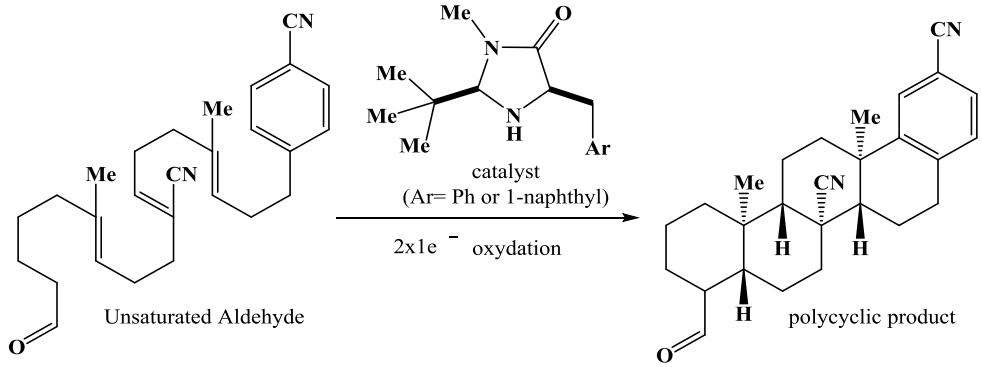


Figure 4. Aldehyde functionalized by a **A)** α-allylation ; **B)** α-enolation ; **C)** α-arylation

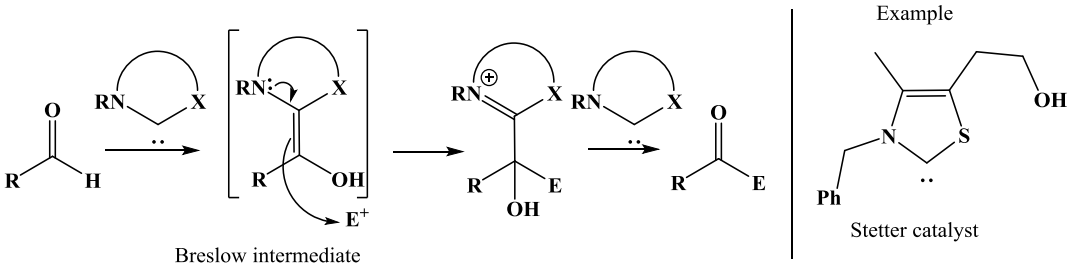
SOMO catalysis has also been used by Muriel and her collaborators, during an α-chlorination of aldehydes and an epoxidation of the latter [73]. A polycyclization of polyenes has been successfully achieved via Organo-SOMO catalysis [74]. The enantiomeric excesses vary from 85 to 93% and with good yields ranging from 54 to 77% scheme 14.



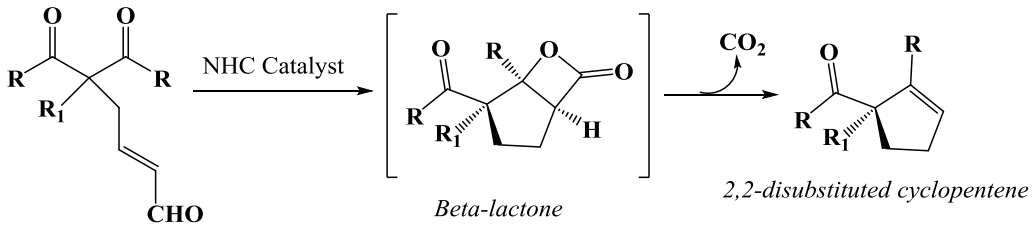
Scheme 16. SOMO catalysis via single-electron oxidation of a transiently formed enamine



Scheme 17. Enantioselective polycyclization via SOMO catalysis



Scheme 18. Mechanism of activation by NHCs of a carbonyl



Scheme 19. Synthesis of *2,2*-disubstituted cyclopentene from *β*-diketones catalyzed by *N*-heterocyclic carbenes

3.1.6.1.2.2. NHC activation Mode (N-HeteroCyclic)

For about twenty years, *N*-heterocyclic carbenes (NHCs) have proven their effectiveness in organocatalysis and as ligands in organometallic catalysis [75]. The use of *N*-heterocyclic carbenes (NHCs, Nucleophilic Heterocyclic Carbenes = Nucleophilic heterocyclic carbenes) as organocatalysts has the particular advantage of being able to reverse the polarity of aldehydes. Indeed, the NHC is capable of adding to an aldehyde, thus forming the Breslow intermediate [71] which can then perform a nucleophilic addition to a suitable electrophile [76].

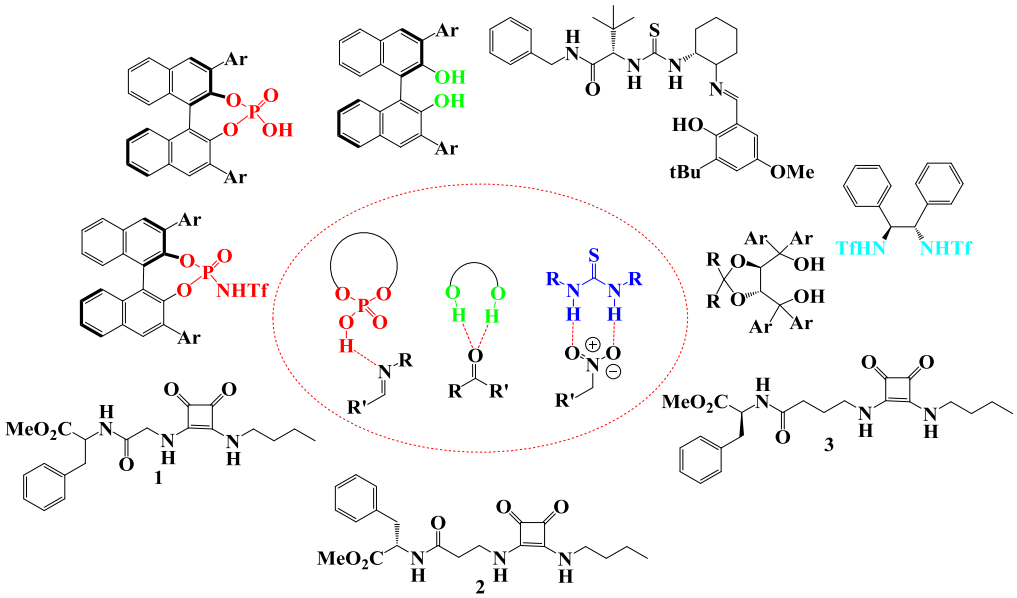
N-heterocyclic carbenes (NHC)s have been used as organic catalysts for the stepwise polymerization of terephthalaldehyde. This constitutes an application in polymer chemistry of the NHC-catalyzed “benzoin condensation” reaction involving an analogous monoaldehyde. Poly(1,4-phenylene-1-oxo-2-hydroxyethylene)s or “polybenzoins” have thus been obtained by solution polymerization in DMSO or THF as solvent at a temperature below 40°C. The presence of cyclic polybenzoin

chains has been demonstrated. The proportion of these cycles depends on the nature of the carbenic catalyst and the polarity of the reaction medium. To avoid the premature degradation of NHCs, simple solutions have been proposed by developing polymer supports carrying carbenic sites, i.e. "poly(NHC)s", used for organocatalysis purposes. Although recyclable, these "poly(NHC)s" remain quite sensitive to traces of impurities. One way to protect them is to react them with CO_2. The adducts thus formed, «poly(NHC-CO_2)s», can then be used as precursors to generate the "poly(NHC)s" in situ, by simple thermal activation, the return to the "poly (NHC-CO_2)s" being able to be carried out by carboxylation of the "poly(NHC)s" [77]. Wadamoto et al. developed a method for the enantioselective synthesis of *α,α*-disubstituted cyclopentenes starting from symmetrical *β*-diketones [78] possessing an aldehyde function.

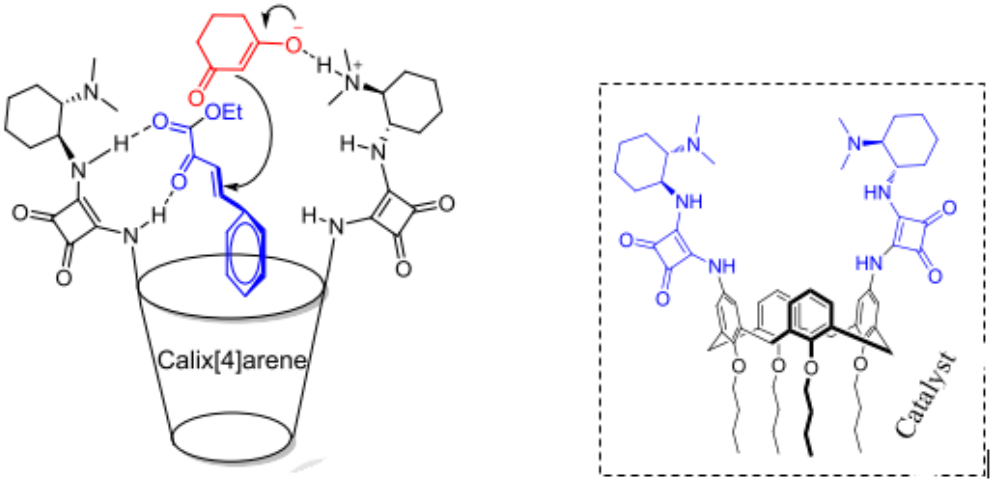
This reaction is catalyzed by N-heterocyclic carbenes. The reaction proceeds through a beta-lactone which undergoes decarboxylation to yield the corresponding cyclopentene.

3.1.6.2. Activation by Non-Covalent Bond

There are a growing number of asymmetric organocatalytic reactions that are accelerated by weak interactions. This type of catalysis involves neutral complexation or acid/base associations between the catalyst and substrate. The former is very reminiscent of the way many enzymes carry out reactions, by bringing together reactants in an active site without forming covalent bonds [64]. The formation of a weak acid–base chiral complex represents hydrogen bond catalysis and deprotonation followed by cation–anion association under homogeneous conditions and also under phase transfer conditions [79], [80], [81], [82], [83]. Activation by noncovalent bonding is a method used by Bronsted acids and bases. It is often achieved by hydrogen bonding between the substrate and the catalyst to increase the rate and/or direct the selectivity of the reaction. It can also occur by interaction between depleted π-systems.



Scheme 20. Hydrogen bond activation mode and example of developed chiral catalysts



Scheme 21. Transition state of the Michael reaction catalyzed by calix[4]arene squaramide

Scheme 22. Different non-covalent interactions with an aromatic π-system

3.1.6.2.1. Hydrogen Bond Catalysis

Hydrogen bonding is an attractive interaction between the lone pair of a strongly electronegative atom (N, S, O, etc.) and a hydrogen atom covalently bonded to an electron donor atom (also strongly electronegative). It occurs at short distances. From an energetic point of view, hydrogen bonding is between covalent bonds and Van Der Waals interactions (10-65 KJ/mol) [84]. It plays a central role in biological processes and determines the structure and properties of many biological molecules, such as the DNA double helix where the two strands are linked together by hydrogen bonding [85].

In enamine-mediated catalysis, some catalysts (e.g. proline) use a hydrogen bond to direct the electrophile. Other catalysts such as diols, phosphorus or thioureas are able to activate a carbonyl function and thus increase its electrophilicity (Scheme 20). In the case of using a chiral catalyst, a chiral environment will be provided near the activated function, thus allowing an induction of asymmetry during the chemical reaction. Organocatalysts have several important advantages over the use of transition metal complexes. They are generally stable, less expensive, less toxic and not sensitive to atmospheric oxygen and humidity. In other words, they are less sensitive compared to experimental conditions, which allows highly selective reactions to be carried out under simple, ecological, economical conditions and compatible with industrial processes [55] giving very satisfactory results. However, during a reaction, organocatalysis also has disadvantages such as the increase in the catalytic charge in the case of covalent catalysis and to this is also added a problem of predictability [86]. In 2020, Ke Yang and his collaborators studied a Michael reaction between a 1,3-diketone and aromatic nitroolefins or with a β-unsaturated α-ketoester catalyzed by a supramolecule resulting from an association between two squaramide units and a calix[4] arene diamine unit [87]. They obtained very good results in terms of selectivity (ee: 55 to 99) and yield ranging from 80 to 99 % [88]. It should be noted that in these reactions, the reactants are activated by hydrogen bonding.

A selectivity due to a highly organized transition state (Scheme 21) caused by a coordinated action between the calixarene cavity and the squaramide motifs thus increasing the stereoselectivity of the reaction.

3.1.6.2.2. Non-Covalent Interactions with Depleted π-Systems

Non-covalent interactions involving a π-system include fairly classical interactions such as π-π or π-stacking interactions, as well as π-H, π-cation and π-anion interactions (Scheme 22) [89]. Less conventional interactions observed more recently and which are beginning to be better developed by chemists are π-anion type interactions or π-non-bonding doublet type interactions.

3.1.6.2.2.1. π-Anionic Interaction

The term π-anionic interaction refers to a non-covalent bond between an anion and the π-acid surface of an aromatic system. Unlike π-cationic interactions, which have been known since the second half of the 20th century, the term π-anionic interaction only appeared in 2002 following computational studies carried out by the team of Frontera and Deyà [90]. The reason is that this concept is based on the counter-intuitive idea that an aromatic ring can interact with a negatively charged anion. However, these theoretical calculations have shown that the electronic depletion of the aromatic ring allows this type of interaction to be observed (Scheme 23).

Scheme 23. Representation of π-anion interactions

3.1.6.2.2.2. Non-Bonding π-Doublet Interaction

Like π-anionic interactions, π-lone pair-π interactions are the stabilizing forces that result from the association of an electronically depleted receptor, but this time of a neutral but electron-rich entity. Currently, there are relatively few concrete examples reported in the literature. It is generally accepted that the intensity of such an interaction is less than 5 kJ/mol [91], [92]. This is why, in the majority of systems analyzed, it is often essential that they be reinforced by other supramolecular interactions such as hydrogen bonds [89], [93].

3.2. Classification of Catalysts According to the Type of Reactions Activated

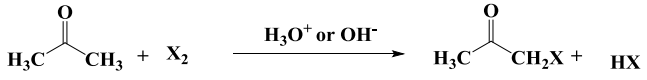
Organic catalysts can be classified according to the type of reactions catalyzed, that is, according to whether the reaction is specifically catalyzed by a well-defined catalyst or by a general catalyst.

3.2.1. Acid-Base Catalysis

Acid-base catalysis is common in chemistry and biochemistry. In these reactions, the catalyst acts as an acid or base. These acids or bases are generally H^+, HO^- ions, Lewis acids or bases, or metal oxides (Al_2O_3, V_2O_5, etc.). There are two cases, depending on whether the reaction is accelerated by all acids (respectively all bases), which is called general catalysis, or whether a particular acid (or base) is required, which is called specific catalysis. If the acid-base catalysis takes place at the same time, we speak of concerted catalysis.

3.2.2. Specific Catalysis

In some cases, a particular acid serves as a catalyst. The mechanism then goes through a mechanism specific to it, which would be different for another acid. This is the case of the halogenation reaction of propanone [94].



Scheme 24. Halogenation reaction of propanone (X = I or Br)

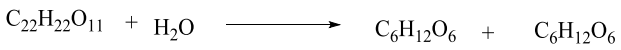
This reaction is accelerated by H_3O^+ (or by HO^-). The rate constant is of the form

$$k = k_0 + k_1[H_3O^+] + k_2[HO^-].$$

With k_0, the rate constant of the uncatalyzed reaction. The value of k_0 is very low compared to k1 and k_2 (hence the notable effect of the increase in rate by the catalysts H_3O^+ and HO^-). The addition of a weak acid only modifies the rate by the variation of the $[H_3O^+]$ concentration that it allows, and not by the variation of its own concentration [95]. This indicates that it is specifically H_3O^+ the catalyst, and not just any acid.

The inversion of sucrose is also of specific catalysis type. Its equation is:

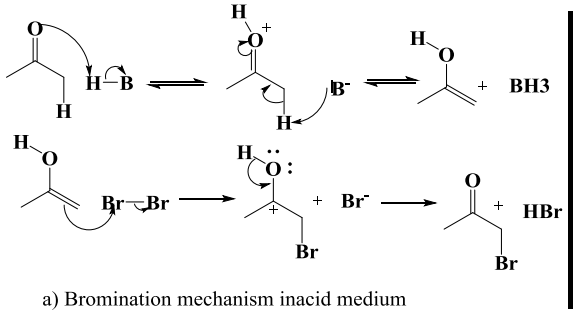
Sucrose + water → glucose + fructose



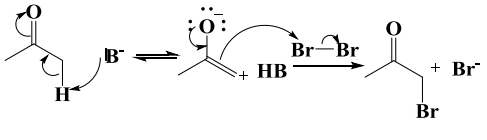
Scheme 25. Sucrose inversion

The halogenation of nitroalkanes is an example of specific base catalysis. Another example of specific acid-base catalysis is the monobromination of ketones, carried out in an acidic medium (BH) or in a basic medium (B^-).

In this case the speed of the reaction depends only on the pH of the reaction medium.



a) Bromination mechanism inacid medium



b) Bromination mechanism in basic medium

Scheme 26. Mechanism of the catalyzed acid-base reaction

3.2.3. General Catalysis

For a catalysis to be general acid-base, weak acids (or bases) must also catalyze the reaction. This catalysis must depend on the concentration of weak acid, and not only on the fact that this acid can release H^+ ions.

The rate constant, in specific acid catalysis, is therefore of the form:

$$k = k_0 + k_1[H_3O^+] + k_2[AH].$$

Where [AH] is the weak acid concentration.

To demonstrate this property of general acid catalysis, it is necessary, for example, to determine the dependence of the rate (and therefore of k) on the amount of AH added, but this in a buffered medium, so that the term $k_1[H_3O^+]$ is kept constant. An example of general acid catalysis was studied by Barber et al. during a hydrolysis of *tert*-butyl ethers (1) and 1-arylethyl ethers (2) of salicylic acid [96]. This reaction is carried out with an efficient general acid catalysis by the -COOH group in ortho. The carboxylic group which catalyzes the reaction is intramolecular, so the hydrolysis is carried out by intramolecular hydrogen transfer. The mechanism is very different from classical general acid–base catalysis. Proton transfer occurs very rapidly in the strong hydrogen bond that develops and, although it is an integral part of the C-O bond cleavage process, there is virtually no coupling.

4. Conclusions

Catalysis has long been considered an asset for chemists, especially organic chemists, around the world. This is why it has undergone several major advances since its advent to the present day. Its contribution in terms of efficiency and flexibility is no longer in dispute. In this chapter, we have recalled the history of catalysis and its progress over time. We have also classified catalysts according to several criteria. The modes of action of several types of catalysts have been illustrated by examples. Organocatalysis remains the current champion of catalysis due to its remarkable advantages, in particular respect for the environment and the principles of green chemistry. It should be noted that organocatalysis is subdivided into several categories according to well-established criteria. Among the types of catalysts developed in this manuscript, organocatalysis has a guaranteed future with full hope based on its advantages including its flexibility and low toxicity.

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