

Green Chemistry and Catalysis united: The emergence of nanocatalysis

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Glossary

Sustainability: Ability to implement and perpetuate industrial and social practices with the protection of the environment as a focus.

Green Chemistry: Philosophy focused on the design, development and implementation of environmentally friendly, harmless, and economical chemical processes.

Catalysis: Increase of the reaction rate by means of an additional organic/inorganic/hybrid substance called catalyst, which remains unaltered during the course of the reaction.

Nanocatalysis: Enhancement of the reaction rate by means of a solid substance of nanometer dimensions.

Nanoparticle: Organic/inorganic/hybrid material of nanoscale dimensions.

Definition of the Subject

Nanocatalysis is a new *Green Chemistry era*. The continuous increase of recalcitrant pollutants in the environment calls for the sustainable development of the chemical industry. Nanocatalysis has the potential to improve substantially a variety of chemical processes by minimizing energy and feedstock requirements. Most of all, nanocatalysis fulfills all the Green Chemistry principles, allowing the development of truly sustainable processes.

Introduction

The current environmental and organizational global challenges comprising

- climate change mitigation,
- depletion of traditional feedstocks (i.e. petroleum),
- intensification of the world-wide population density (hence, continuous increase of energy and food demands)

call for the development of new technologies and materials, as well as the evolution towards a new *mental age* where sustainability, durability, recycling, cost-effectiveness, and conservation of limited resources are part of a person's daily life.

Anthropological development in the past centuries has seen an incredible technology *boom*, improving the quality of life of a substantial part of the world population. The particular development of coal-fired steam engines marked the first Industrial Revolution of the 18th century. At that time, the world saw a shift from less efficient renewable resources (e.g. wood for heat and energy, water wheels/wind mills as early turbines) to fossil fuels, opening incommensurable possibilities in the chemical, energy, and transportation industries. Later in mid-19th century, the first rock oil well was drilled, and the petroleum era begun. Kerosene was the first commercial oil-based product, substituting whale oil and wood for illumination and heating, respectively. The rapid technological improvement in oil wells exploration made petroleum the major source of commodity chemicals, materials, and fuels. For instance, synthetic petroleum-based plastics promptly flourished in the early 1900s, first with the advent of Bakelite (1907), followed by polystyrene (1929), polyester (1930), polyvinylchloride (1933), and nylon (1935) [1]. Plastics became integrative part of the ordinary life of the average person, starting the concept of disposable objects and the deleterious throwaway-culture. The petroleum industries at that time seemed self-perpetuating, and impacts on the environment were overlooked.

The exceptional broad success of plastics has not gone unnoticed. Nowadays, microplastic pollution is ubiquitous. Micro-sized plastic materials were found in freshwaters, seas, and even fish [2]. As a curious fact, the average European shellfish eater would consume 11,000 microplastics per year [3]. Additionally,

the recent break of record of continuously increasing atmospheric CO₂ [4] level calls for the development of truly sustainable processes and the full embrace of the *Green Chemistry* concept.

Sustainability is a joint global effort, where science covers a special role. Thanks to talented scientists, renewable, harmless, non-toxic processes can be achieved. In particular, catalytic processes can improve greatly the sustainability of a process, as well as reduce the amount of energy and feedstock needed for an industrial manufacture. As a result, this chapter aims to contribute on the role of catalysis in green chemistry. An overview on the main principles and concepts of green chemistry and catalysis will be given. In particular, the bridge between homogeneous and heterogeneous catalysis, *nanocatalysis*, will be discussed. A particular focus to sustainable catalytic nanomaterials will be given in honor of the 12 Principles of Green Chemistry.

Green Chemistry

In 1962, American marine biologist Rachel Carson published *Silent Spring*, a book that would change the general view on chemicals and their detrimental effect on humans and the environment. With her groundbreaking book, Carson was able to trigger people's awareness on the harmful effect of pesticides on local ecosystems (in particular, persistent organic pollutant, DDT), affecting different environmental compartments (i.e. water, sediments, and biota). *Silent Spring* became the first hallmark of the modern environmental movement for both the public and scientific community. Chemicals started to be under scrutiny in terms of unwanted effects on human and animal health, soil, ground water, and atmosphere.

The increase of awareness in the beginning of the 60s on the anthropological effect on Earth's ecosystems has moved political agendas to the implementation of new legislations protecting the environment, such as the 1969 US National Environmental Policy Act (NEPA). This act was aimed to enforce the Environmental Assessments (EAs) and Environmental Impact Statements (EISs) prior to undertaking any major federal action (e.g. airports, military complexes) that would affect negatively the environment. Shortly after, former US president Richard Nixon instituted the Environmental Protection Agency (EPA)

whose regulations have played a significant role in the prevention of anthropological pollution. For instance, EPA's first action was to ban the use of DDT, along other chemical pesticides. Finally the dangers of chemicals were understood, and the scientific community had the role of finding the solutions to irreversible human-induced changes to the environment. International treaties started to be implemented, such as the Montreal Protocol (1987), which aimed to ban ozone-depleting substances based on the work of talented researchers of the time (a few names: Mario Molina, Frank Sherwood Rowland, Paul J. Crutzen–Nobel Prize for Chemistry 1995), reducing dramatically the number of emitted atmospheric pollutants [5]. The Montreal Protocol proves that sustainability is only achieved as a joint global effort: the ozone layer hole over the South Pole is predicted to close permanently by 2050 [6].

Although bans and remediation of contaminated areas were the original priority of the environmental agencies of the time, the idea of pollution prevention consequently started to develop among environmentalists, culminating in the establishment of the Office of Pollution Prevention and Toxics within the EPA in 1988, and of the Pollution Prevention Act of 1990. Concepts such as benign-by-designs [7], green chemistry [8], E-factor [9], and atom economy [10] began to be developed, marking the beginning of a new philosophy among the researches. In the interim, the scientific journal *Green Chemistry* was brought forth by Prof. James Clark (University of York), giving a tangible platform to motivated academic and industrial scientists.

With the revolutionary book *Green Chemistry: Theory and Practice* written by Anastas and Warner [11], a new doctrine was born in the scientific community based on the reduction and/or elimination of hazardous substances (i.e. risk and hazards) in each step of a chemical synthesis, as well as minimization of wasteful practices, reducing costs, energy, and materials employed. In particular, the book proposed the now famous 12 principles of Green Chemistry, being:

- 1. Prevention:** Waste is unnecessary. Prevention of waste shall be preferred to its subsequent disposal/treatment.

2. **Atom Economy:** Chemical processes shall be designed to be as efficient as possible: all the atoms used as reagents should be incorporated in the final product.
3. **Less Hazardous Chemical Syntheses:** A chemical process shall be designed to incorporate and/or produce the least or zero substances that might have a harmful impact on humans, animals, and the environment.
4. **Designing Safer Chemicals:** The product of a new chemical process shall be designed to have the best properties for their application, but most importantly should not possess any toxic/noxious/deadly properties.
5. **Safer Solvents and Auxiliaries:** A chemical process shall involve the least amount of “spectator substances”: solvents, separating/drying agents, surfactants, stabilizers, viscosifiers, etc. that are not strictly necessary for the function of the product. If inevitable, the substance shall be harmless.
6. **Design for Energy Efficiency:** The absolutely energy efficient process is when conducted at room temperature and atmospheric pressure. Not only this has positive economic impacts, but also the environment greatly benefits from reducing the energy requirements (mainly fossil-based).
7. **Use of Renewable Feedstocks:** When a non-renewable feedstock/raw material is used, a future where that chemical process is unfeasible shall be imagined. Renewable feedstocks will allow the ever endurance of the process.
8. **Reduce Derivatives:** Every added step in a chemical process generates waste. The transformation of a chemical product into its derivative by the use of blocking groups for protection/deprotection and/or temporary modification of physical/chemical processes applications should be avoided or minimized if necessary.
9. **Catalysis:** If a chemical process can be carried out with a catalyst instead of a reagent, thus it shall be implemented.

10. Design for (Bio)Degradation: Chemical products shall be designed to degrade in the safest way for human, animal and environment. End-of-life products should preferably be biodegradable, if not, be degraded into harmless compounds.

11. Real-time analysis for Pollution Prevention: Only with the understanding of each chemical step a process can be designed to be as safe as possible. In-situ/real-time analytical methods need to be developed to control in advance the possible formation of hazardous substances.

12. Inherently Safer Chemistry for Accident Prevention: Leakages of dangerous chemicals to the environment, explosions, and fires must be null. Careful design of the process and substances used can prevent hazards, casualties, and environmental imbalances.

Conceptually, the whole list of principles of Green Chemistry can be summarized in one word: *design*. In fact, prevention and minimization of risks and hazards for the environment, production costs (in terms of operating conditions, atom economy, auxiliary substances), and waste generation (reagents in excess, non-selective processes) can be achieved through careful process/product design (and *re-design*, if unsuccessful or with a margin of improvement). Being a Green Chemist is to consider in advance the environmental issues of a particular process, and dedicate the efforts into carrying out the chemical steps with the 12 principles in mind, where one does not exclude the other. In fact, the list of principles is meant to be a *cohesive system of design* [12], as a truly sustainable process is achieved when all the green chemistry requirements are implemented.

Peculiarly, catalysis (9th principle) fulfill most of the Green Chemistry requirements, as the use of a catalyst has been proven more selective (minimization of waste and improvement of atom economy) and safer (prevention of risks). Furthermore, catalysis is able to reduce overall production costs by reducing energy requirements for a given reaction. Also, catalysis has the potential of allowing (unfavorable) reactions to take place with greener solvents and conditions.

Catalysis

One of the pillars of Green Chemistry, catalysis, demonstrated to be the optimum ally for many chemical syntheses, as well as *making the impossible possible*.

The term catalysis was first coined by Jacob Berzelius (1835) [13] in the attempt to describe the acceleration phenomena given by certain substances that remain unchanged after a reaction, exercising an “*action very different from chemical affinity*”. De facto, a catalyst is a material or substance with the *action* (ability) of lowering the activation energy of a given reaction without being consumed, resulting in faster and/or more energy efficient (lower operating conditions) processes. The key steps of a catalytic process are:

1. **Diffusion** of the reactant towards the catalytic active site;
2. **Adsorption/Coordination** of the reactant with the catalytic active site;
3. **Reaction** on the catalytic active site;
4. **Desorption/Elimination** of the product from the catalytic active site;
5. **Diffusion** of the product to its collection point.

In particular, the adsorption or coordination of a compound on a catalytic surface or metal centre can drastically lower the required energy for the reaction completion. In fact, a catalytic process in kinetic regime may allow overcoming thermodynamic limitations of unfavorable reactions by increasing the reaction rate. For instance, olefin metathesis would have been unfeasible without the development of transition-metal based catalysis which awarded Chauvin, Grubbs, and Schrock the Nobel Prize in Chemistry in 2005 [14].

A catalytic system is classified as *homogeneous* if in the same phase as the reactants (e.g. soluble metal complexes), and *heterogeneous* if immiscible with the reactants (e.g. metal oxides) (**Figure 1**). Homogeneous catalysis often allows the same reaction to be carried out with higher selectivities at lower operating conditions compared to heterogeneous systems, however presenting drawbacks in terms of catalyst separation and reuse. Common industrial practices include at least one catalytic step with either a

homogeneous or heterogeneous catalyst, accounting for *ca.* 90% of all chemical production [15] thanks to its energy, feedstocks and waste-related benefits.

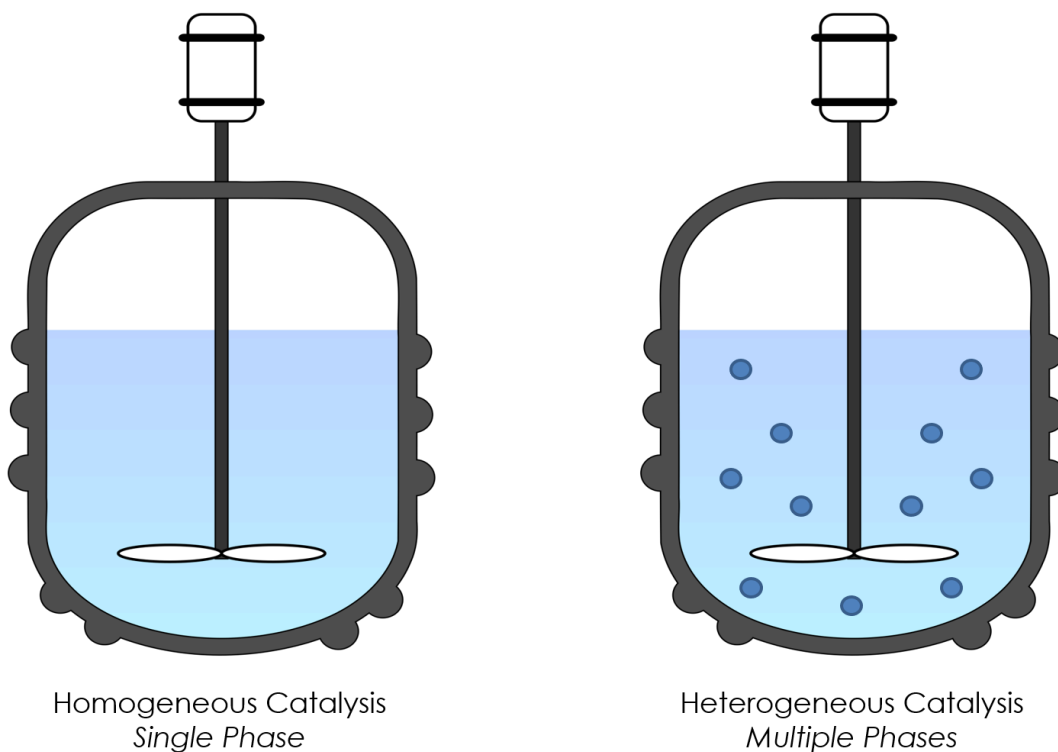


Figure 1. Schematic difference between homogeneous and heterogeneous catalysis in a batch reactor.

Importantly, catalysis has covered a key role in the advancement of green chemistry practices. For instance, challenging selective oxidations or reductions were traditionally carried out with hazardous stoichiometric reagents (e.g. permanganates, chromates, and metal hydrides), producing copious amounts of waste (i.e. inorganic salts) [16]. The use of recyclable solid acids and bases in juxtaposition with *green* reagents (e.g. molecular oxygen, hydrogen peroxide, and hydrogen) can substitute efficiently classical stoichiometric methodologies with atom-efficient catalytic alternatives. Examples of process improvement via catalysis include *i*) the asymmetric hydrogenation of ketones, and *ii*) the production of hydroquinone, in particular:

- i)* **Asymmetric hydrogenation of ketones:** traditionally carried out with DIBAL-H as hydride donor, the process would culminate with stoichiometric amounts of aluminum salts to be disposed [17]. The Noyori process was instead able to hydrogenate different ketones with a Ru-based homogeneous catalyst (Noble Prize in Chemistry, 2001) [18].
- ii)* **Hydroquinone production:** originally produced via aniline oxidation with manganese dioxide and Béchamp reduction with iron and hydrochloridric acid, inorganic salts generated in the process would add up to ten times the amount of product generated. Solid ion exchange resins were found to catalyze the aerobic oxidation to isopropylbenzene with acetone as a by-product [19].

The above examples clearly show how catalysis is able to minimize waste production and improve atom economy, thus following the principles of green chemistry.

Catalysis is also able to improve the energy efficiency of a process. A relevant industrial example is given by the Dow Chemical pharmaceutical-grade propylene glycol production from bio-derived glycerin (by-product of biodiesel synthesis) via subsequent dehydration to the ketol, and hydrogenation to the final product [20]. Non-catalytic routes to propylene glycol employed high temperatures and pressures (typically, >250 °C and >100 bar) [21], while the use of a catalytic material such as copper chromite allows to drastically reduce the required hydrogen pressure (<20 bar) at moderate temperatures (<200 °C) [22]. Additionally, the combination of catalysis with lower pressures was also found to suppress by-product formation, thus improving atom economy [23]. In this sense, many researchers have put their effort in energy minimization through catalysis, with the final aim of running reactions at room temperature and atmospheric pressure, with plenty of examples found in literature [24].

From an engineering point of view, catalysis can also be a tool for inherently safer chemical processes. In fact, mass and heat transfer limitations in a given reaction carried out in a batch reactor can cause the formation of hot spots and pressures build-ups which could in turn induce runaway reactions. When using

a (micro-) continuous flow reactor, mass and heat diffusivity are largely improved, enabling a better control over the reaction parameters and confining the problem in the apparatus [25] (**Figure 2**). For this reason, reactions involving explosive/toxic/hazardous intermediates see an incredible benefit in being run in continuous flow.

Batch Reactor	Continuous-Flow Reactor
Fixed residence times	Variable contact times
Required catalyst/product separation	Fixed catalytic bed eases product separation
High reactor volumes	Scalable reactor volumes
Thermal and mass gradients difficult to control (mixing-rate dependent)	Thermal and mass gradients easy to control (flow-rate dependent)
Runaway reactions difficult to control	Runaway reactions easy to control

Figure 2. Main differences between batch and continuous-flow reactor with schematic drawing of the two types of reactors.

Furthermore, in this type of reactors, temperatures can be raised above the solvent's boiling point resulting in a gas phase reaction, or liquid phase if pressure applied according to the simplified Clausius-Clapeyron equation (Equation 1), allowing different chemistries with a straightforward scale up. For instance, renewable future possibility for the production of chemicals and fuels relies on liquid processing of biomass. Thus, continuous flow conversion of biomass will require higher pressures in the system as opposed to traditional gas-phase processing.

Equation 1. Clausius-Clapeyron logarithmic equation. Legend: T (K) operating temperature, T₀ (K) boiling point at pressure p₀, p (atm) vapor pressure at T, p₀ (atm) vapor pressure at T₀, ΔH_{vap} (J · mol⁻¹) vaporization enthalpy, and R (J · K⁻¹ · mol⁻¹) universal gas constant.

$$\ln \frac{p}{p_0} = -\frac{\Delta H_{vap}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)$$

In this way, catalysis in continuous flow allows the development of safe and scalable processes. A recent publication from Kappe's research group on Pd-catalyzed olefin cleavage shows the possibility of working safely within the oxygen explosive regime in continuous flow [27]. Other examples of *forbidden chemistry* made safe can be found within the same research group [28].

Although a catalyst is defined as a substance that remains unaltered during the course of a reaction, deactivation phenomena often occur making the material itself a source of waste. Heterogeneous catalysts generally have longer lifetimes as opposed to homogeneous catalysts; however, they can become waste themselves. In-situ and ex-situ catalyst regeneration can extend the solid catalyst lifetime, reducing the amount of metal waste going to landfills [29]. On the other hand, homogeneous catalysis suffers from enormous drawbacks in catalyst recovery and recycling, generating auxiliary liquid waste in the catalyst quenching step and removal from product mixture (if possible). In fact, implementation of homogeneous catalysis is severely hindered by inefficient separation processes. Supercritical carbon dioxide would be an easy-to-separate solvent if not its low compatibility with common polar organometallic catalysts. Polarity and density of supercritical CO₂ can be improved by the addition of an organic solvent which undergoes volume expansions (i.e. *expanded liquid phases*) [30]. Industrially, common practice to recover homogeneous catalysts is by the aid of biphasic systems, producing copious amount of liquid waste. Water-soluble metal complexes catalyze the reaction at the interface with the organic-soluble reactant, decreasing the overall efficiency of the process. Scavenging and organic solvent nanofiltration of molecular weight enlarged catalysts are also contemplated at an industrial level; however, highly efficient and stable resins and membranes (respectively) need to be developed [31]. Green chemistry advances in the homogeneous catalyst recovery involve supercritical CO₂ and/or ionic liquids [32]. However, trace

amounts of catalysts often leach to the organic phase and/or remain in the end product, widely limiting its applications due to high purity products demand and regulations.

Immobilization of homogeneous catalysts is one of the areas of research attempting to create a system with the activity and selectivity of homogeneous catalysis, and the stability and recyclability of heterogeneous catalysis. Anchoring of the homogeneous catalyst onto a solid support can occur via covalent bonding or by simple adsorption, achieved through grafting or in situ sol-gel [33]. This particular approach enables the dispersion of well-defined catalytic systems (e.g. organometallics), which, contrary to heterogeneous catalysts (irregular surface, defective sites), would possess the same activity and selectivity in any point of the catalyst surface. The excellent thermal and chemical stability of silica has made this support the main choice for heterogenization of organometallics [34], however other supports are being investigated. Costly triazolium carbene, also known as Rovis catalyst, was successfully supported onto silica and polystyrene and tested in a model stereoselective reaction [35]. Only poor results were obtained with silica as support, while high yields and fair enantioselectivity were obtained with the polymeric support. Comparably, solid single-site catalysts have been designed similar to organometallics grafting, allowing a dispersion of active metal sites with consistent activity and selectivity. Crystalline supports were found to enhance the stability of grafted catalytic sites, such as for isolated Fe^{3+} . In particular, crystalline delaminated zeolite was found to better stabilize the grafted iron species due to a chelating effect of the support hydroxyl groups [36]. Good performances can be achieved in silica-supported single-site catalysts for polymerizations, alkanes hydrogenolysis, and alkanes and olefins metathesis [37]. Nevertheless, heterogenization by immobilization has yet to be proven cost, stability, and activity competitive with the heterogeneous catalysis market at an industrial level [38].

The advancement of the so-called *nanoscience* has allowed the development of catalytically active nanoparticles at the interface of heterogeneous and homogeneous catalysis [39]. The nano-size of various metals allows the catalytic system to have activity comparable to homogeneous catalysts and stability/separability of heterogeneous catalysts. In fact, *nanocatalysts* possess extensive accessible (solid)

surface area which gives a more *intimate* contact between reactant and active site. In particular, the new trends in catalytic processes call for the development of hydrothermally stable catalytic materials, as for the conversion of biomass. The next paragraph is thus dedicated to promising advances in nanocatalysis, with particular distinction between metal and sustainable catalytic nanomaterials.

Nanocatalysis

Perhaps the most known catalytic process is the Haber-Bosch ammonia production developed at the beginning of the 20th century, revolutionizing the world's food production thanks to the development of an efficient route for fertilizers manufacture [40]. Thanks to Bosch's laboratory experiments and Haber's scale up, fertilizers were synthesized with abundant atmospheric nitrogen gas and steam-reforming hydrogen, making obsolete the previous and inefficient processes based on nitrogen fixation to nitric acid (Birkeland-Eyde process) or cyanamide (Frank-Caro process) [41]. The industrial process would have likely been unfeasible without the development of a nanocatalyst based on magnetite/wüstite ($\text{Fe}_3\text{O}_4/\text{FeO}$) and promoted against sintering by K, Ca, Si and Al oxides (BASF S6-10) [42]. At that time, the concept of *nano* was only under development [43]. The correlation between size and catalytic activity was first questioned by Boudart later in the 60s, who supposed an intermediate ideal size between atoms and bulk that would maximize the crystallite's catalytic activity [44]. Later in the 80s, Haruta *et al.* discovered that catalytically inert metal, gold, would possess exceptional oxidation activity on an iron oxide support if smaller than 5 nm. In fact, traditionally, (bulk) noble-metal gold was considered as one of the least reactive transition elements with little-to-no application in heterogeneous catalysis, although with potential in oxygen transfer catalysis or as a dopant [45]. With the discovery of the remarkable oxidation activity at low temperatures of finely dispersed gold nanoparticles, Haruta *et al.* enlightened the importance of the size effect on the catalytic activity of materials [46]. A new *gold rush* had started, and the power of nanoparticles was beginning to take shape.

The particular advantages of catalysis in the *nano size* lie in the higher efficiency, activity and selectivity typical of homogeneous catalysts, and the higher stability of the heterogeneous counterpart. A particle is considered *nano* if of nanometers dimensions, being bigger of an atom and smaller than bulk materials (Figure 3).

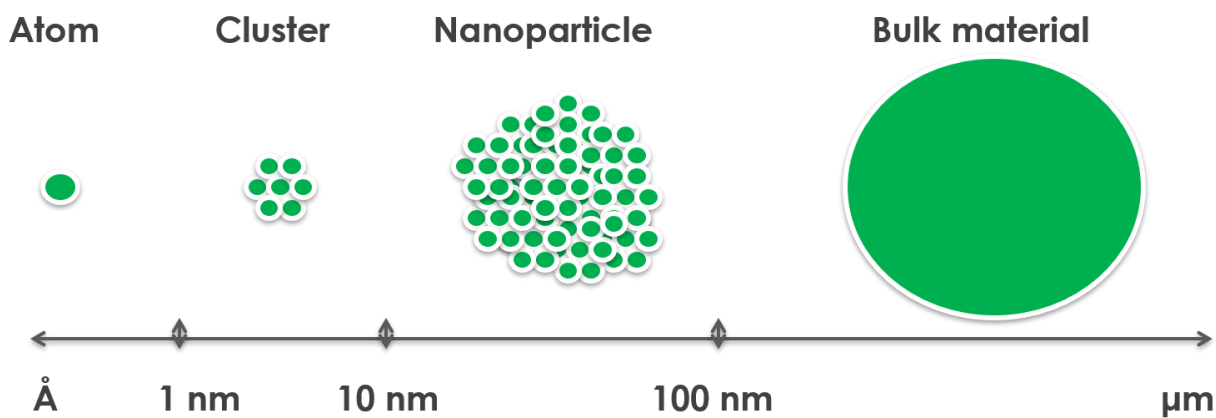


Figure 3. Schematic representation of a *not-to-scale* conventional classification of atom, cluster, nanoparticle and bulk material.

The nanoparticles often have large surface-to-volume ratio and sizes comparable to the reactants, thus increasing the contact feed/catalyst, and overall accessible surface area. This particular feature enhances the catalytic activity and selectivity of the nanoparticles, mimicking the transition metal complexes employed in homogeneous catalysis. On the other hand, their typical insolubility in common solvents allow the easy recovery and reuse of the materials. The *green chemistry* energy, material, and waste minimization requirements are thus fulfilled in the *nano regime* with the possibility of carrying out reactions at milder operating conditions, for longer process times, and with a better atom economy thanks to the formation of less side stream products. These materials possess exceptionally high surface areas and specific reactivity given by the nano-dimension, as new properties appear when the functional sites distribution narrows due to the smaller dimension.

The nanoscale state of these systems offers a strong chemical bonding with an extensive delocalization of the electrons. Besides, the structural changes given by the confined space can induce different chemical and physical properties [47]. In fact, nanoparticles catalysts are often forced into nonequilibrium shapes (e.g. platelet, rod, cubic) which confer different catalytic properties, as activity, selectivity, and accessible surface area to the reactants. For instance, the internalization of drug-releasing nanocarriers by the cell membrane of a living organism is strictly dependent on the size and shape of the nanoparticles [48]. Thus, the synthesis of specific size and shape nanoparticles is crucial to obtain highly active and selective catalytic systems with the advantage of easy separation and reusability.

Advances in syntheses of materials through physical, chemical, or biological methods and surface characterization allow the design of highly functional nanoparticles with different surface energies and morphologies [49]. In general, nanoparticles syntheses follow either a top-down or a bottom-up approach, where:

- **Top-down approach:** the nanoparticles are produced from a larger material by physical or chemical deconstruction. Ball milling of biomass is an example of a top-down approach to carbon nanoparticles.
- **Bottom-up approach:** nanoparticles are arranged from smaller components (e.g. molecules, quantum dots, other nanoparticles) using chemical or physical means. Carbon nanotubes (CNT), for instance, are produced by a bottom-up approach (**Figure 4**).

Various well-defined morphologies nanocatalysts based on different precursors (organic, inorganic) have been synthesized. In the next paragraphs the most notorious and recent examples in literature of different categories of nanocatalyst for green chemistry will be given.

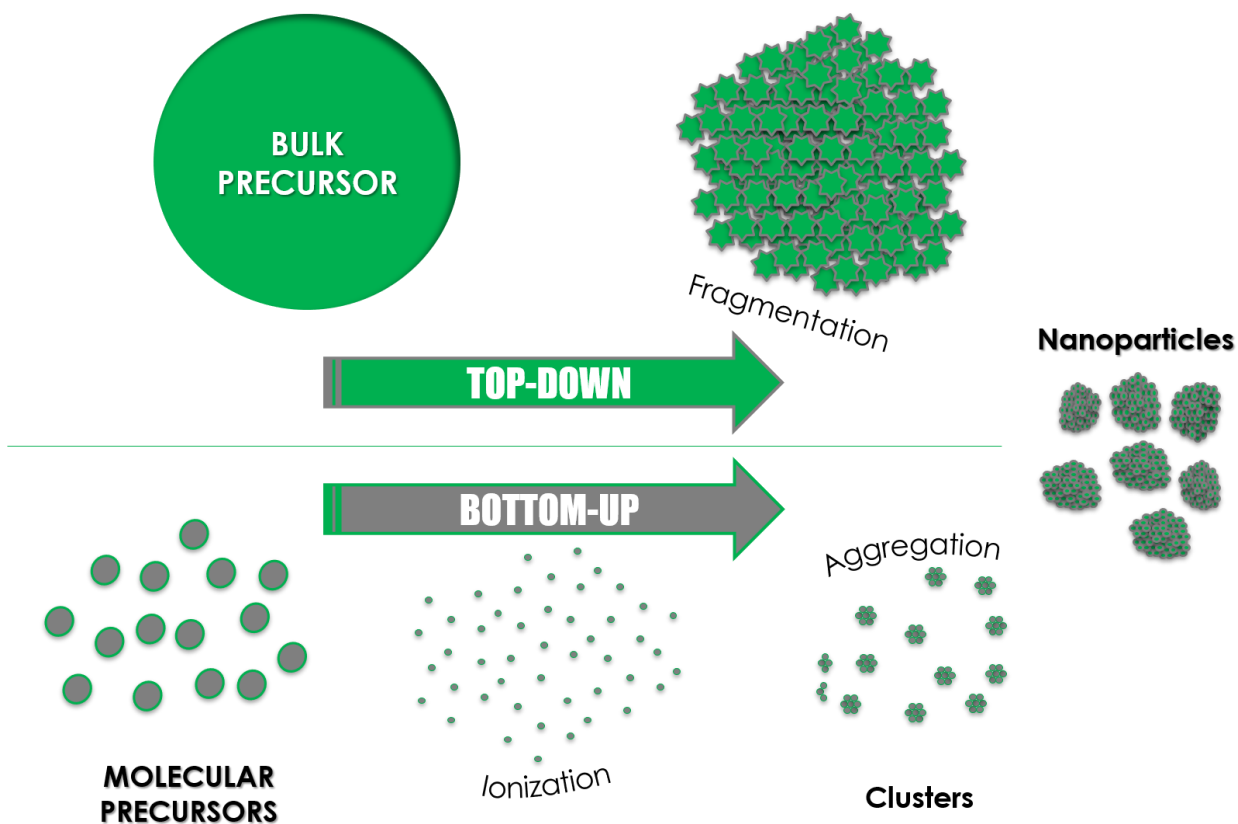


Figure 4. Schematic representation of a Top-Down (above) and Bottom-up (below) approach to nanoparticles synthesis.

Noble Metal Nanoparticles: Gold and Palladium

Metallic nanoparticles are elemental nanoclusters of a metal that can be amorphous, crystalline, or single crystallites (nanocrystal). The contiguous electron energy levels of the nanoparticles confer to the system peculiar electronic properties intermediate between molecules and bulk metals. In general, metallic nanoparticles are more active with decreasing particle size, in particular:

1. Exposed surface atoms increase with decreasing particle size.
2. Defective atoms (at the edges, in the corners) also increase with decreasing particle size.

Thus, small nanoparticles with a high number of defects will possess high catalytic activity [50]. In general, shape and size will influence greatly the activity of a nanoparticle. In fact, these two parameters

influence the surface free energy of a nanoparticle, which in turn influence the reactivity of the system. The higher the surface free energy is the higher the catalytic activity, but the lower the stability [51]. As metallic nanoparticles possess high surface energy, the dispersion on a metal oxide or carbon support is the most common strategy to stabilize the metal against sintering (**Figure 5**).

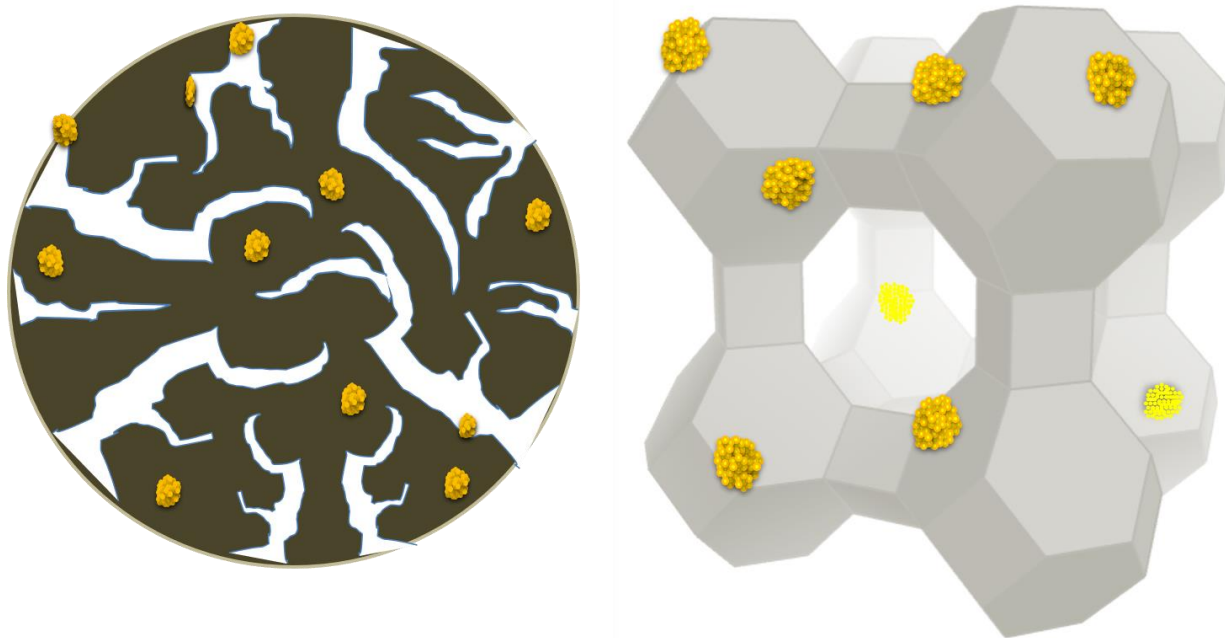


Figure 5. Representation of dispersed nanoparticles (in gold) over a *i*) disordered porous support (e.g. carbon black), and *ii*) ordered porous support (e.g. zeolite).

Furthermore, the nanosize of the particles limits their isolation and recovery from the reaction mixture by conventional techniques such as filtration, making deposition of metal nanoparticles on an inert/synergistic support the most used stabilization technique for their dispersion and stabilization. The nature of the support will control both the reactivity and stability of the nanoparticles, due to different metal-support interactions and anchoring properties. For instance, tunable reactivity of Au nanoparticles on carbon in the selective oxidation of styrene is achieved by variation of solvent polarity [52]. Noble metal nanoparticles have been extensively studied due to their remarkable catalytic activities in a plethora of reactions [53].

Haruta's discovery on the particular low temperature CO oxidation activity of finely dispersed gold nanoparticles has made this metal perhaps the most explored of the past few decades, marking the era of the "Au rush" [54]. Due to the environmental and health harmful effects of carbon monoxide, its oxidation increased the scientific interests in the past decades. The common Pt/Pd catalytic converter (also known as three way catalyst) in the car exhaust system is activated at temperatures as high as 200 °C, reached only after a few minutes of starting an engine. Thus, within a few minutes of driving a car, a breakthrough of carbon monoxide will occur. Carbon monoxide oxidation is also an important model reaction for probing the carbon oxidation properties of a catalytic material [55]. The use of (noble) metallic nanoparticles is often limited by sintering and fast deactivation of the catalyst. Thus, metallic nanoparticles are commonly dispersed on metal oxides systems, such as silica, titania, alumina, to name a few. For instance, the low temperature oxidation properties of Au nanoparticles supported on different metal oxides found by Haruta and coworkers could be applied to minimize the formation of polluting carbon monoxide [56]. In particular, density functional theory (DFT) calculations and kinetic modeling data attribute the strong interaction between Au nanoparticles and CO to the high density of potent under-coordinated sites in a nanoparticle of a determined size which provides optimal binding to carbon monoxide and oxygen [57]. However, sintering of size-sensitive Au nanoparticles causes fast deactivation of the catalytic activity, thus with inefficient lifetimes [58]. To further prevent sintering, Somorjai and coworkers coated Pt metallic nanoparticles with mesoporous silica nanomaterials. The silica conferred exceptionally high thermal stability to the nanoparticles (up to 750 °C in air), without compromising in Pt active site accessibility of the reactants thanks to the mesoporous system. [59]. High activity of these systems has allowed their employment in various catalytic reactions such as ethylene hydrogenation and CO oxidation [60]. Nanoparticles coating is thus proven as an efficient sintering preventing system, however a compromise on activity might be necessary.

Gold-catalyzed oxidation reactions were also investigated by Hutchings' research group, such as carbon monoxide oxidation [61]. The oxidation activities of gold nanoparticles were also tested for primary

alcohols and hydrocarbons for important applications in the agrochemical and pharmaceutical industries [62]. Gold nanoparticles were extensively studied also by Corma and coworkers, with a particular focus to green and sustainable chemistry. For instance, a safer process was advanced by the research group by using gold nanoparticles in the chemo-selective oxidation of nitro compounds without the accumulation of explosive intermediates [63]. A one-pot process for the synthesis of aromatic azo compounds was developed by the same research group where gold nanoparticles supported on titania are found to possess dual functionality: activity in the reduction of nitroaromatic compounds, and in the oxidation of the so-formed aromatic amine [64].

Another green chemistry relevant reaction is the direct synthesis of hydrogen peroxide. In fact, hydrogen peroxide is a powerful oxidant with water as solely by-product [65].

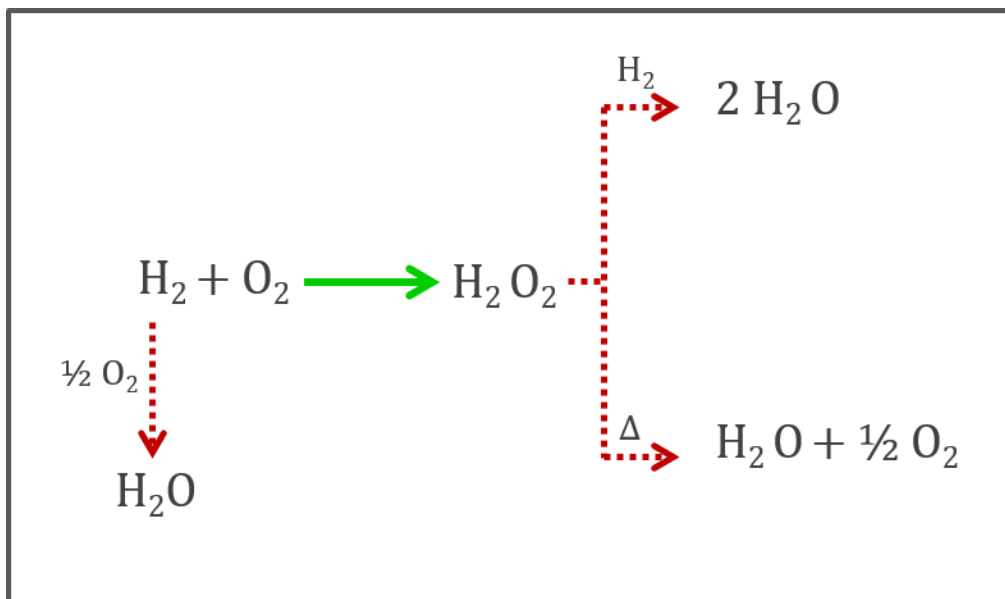


Figure 6. Schematic representation of the direct synthesis of hydrogen peroxide (green arrow), and the undesired side reactions to water (red dotted arrows).

However, hydrogen peroxide production could be environmentally sustainable if produced from hydrogen and water. The main issue is the non-selective formation of water through side reactions due to incomplete oxidations of the reactants or hydrogenation of the product [66] (**Figure 6**). Traditionally,

metallic Pd is considered the best catalysts for the direct synthesis of hydrogen peroxide, thanks to its well-known remarkable selectivity [67]. However, the presence of acids and suitable anions (e.g. Cl⁻, Br⁻) is often required to increase the hydrogen peroxide production, increasing the waste of the system [68]. For instance, NaBr and sulfuric acid improve the activity of mesoporous carbon Pd-supported catalysts. The addition of heteropolyacid to the carbon support was found to give the optimum acidity to the catalytic system, circumventing the addition of H₂SO₄ [69]. As agglomeration of nanoparticles is the main source of deactivation of the catalysts, different preventing approaches are being brought forth. Pd-supported silica nanoparticles were coated by a mesoporous silica shell, finding higher catalytic activities as opposed to microporous shells [70]. Hybrid ligand-modified Pd nanoparticles supported on carbon were recently found active in hydrogen peroxide direct synthesis. Furthermore, although long term stability has to be further explored, a higher leaching resistance was observed [71]. The use of coatings and ligands might be a necessary solution to improve the stability of dispersed nanoparticles, however the overall cost of synthesis is increased.

Direct synthesis of hydrogen peroxide was found possible also with gold nanoparticles, as pioneered by Hutchings research [72], and also observed by Haruta and coworkers [73]. In particular, gold nanoparticles were found to have a higher hydrogen peroxide formation rate as opposed to Pd nanoparticles [75]. The use of gold nanoparticles allows running the process at lower temperatures and with shorter reaction times, improving selectivity, thus the overall *greenness*. In particular, Pd-Au alloys were found exceptionally active even in the absence of acid and/or halides. Choudhary *et al.* screened various metal promoters finding Au and Pt as optimum for bimetallic Pd-based catalysts [75]. Thus, alloying Pd and Au catalysts can enhance H₂O₂ production, becoming an efficient strategy for industrial applications. A recent work found that addition of organic functional groups such as -SO₃H and -NH₂ to the Au-Pd support (e.g. SBA-15) was found to improve the system by enhancing hydrogen peroxide formation rate (acid groups), and suppressing the hydrogenation/decomposition side-reactions thanks to the amine groups [76]. Mesoporous carbon was found more convenient compared to microporous

systems, thanks to the enhanced diffusivity of hydrogen peroxide with wider pores [77]. However, variation of the oxidation state of the superficial species and sintering after the first run of reactions still limits the applications of these catalytic systems.

Gold nanoparticles in general can find applications in a plethora of catalytic reactions, such as additions to multiple C-C bonds, benzannulations, and molecular oxygen oxidations of alcohols [78]. A commercial application of a gold-nickel catalyst is given by a Japanese methyl methacrylate production [79]. Nevertheless, current applications are still limited by cost and stability. Further improvements in the synthesis of gold nanoparticles with specific shape and sizes might improve their reactivity; however, sintering has to be stabilized [80].

Growing concerns about the scarcity, toxicity, and cost of precious metal catalysts however is pushing the scientific community to the development of cheaper, more abundant, and less harmful catalytic materials. In this sense, non-noble metal, transition metal oxides and carbon-based nanoparticles have been investigated.

Non-noble metal: Iron/Iron Oxide nanoparticles

As one of the 4th most abundant (hence, inexpensive) and environmentally friendly elements on Earth, iron is advancing as a valid catalyst substitute to noble metals. The magnetic properties of iron further increase the scientific interest as catalyst. In fact, as mentioned earlier, the small size of the nanoparticles limits their separation and reuse by conventional methods (e.g. filtration). Separation of the nanoparticles by applying a magnetic field appears to be highly promising.

The high oxidation tendency of metallic iron (zero oxidation state), thus possessing (dangerous) pyrophoric properties, has limited its applicability as bare catalyst [81]. Stabilization of iron nanoparticles by the use of a protective layer or the control of the reaction environment allows the use of metallic iron as catalyst, as hydrogenations under inert conditions. Nonetheless, the oxidative reactivity of iron oxides

nanoparticles has also been explored. In fact, the different oxidation states of iron oxide nanoparticles confer a potential of reactions, including aerobic conditions and hydrogen peroxide decompositions. In this sense, iron nanoparticles have been employed in a large variety of reactions, including: unsaturated hydrocarbon and alcohol oxidations, oxidative coupling reactions, olefin and carbonyls hydrogenations and transfer hydrogenations, as well as hydrogen evolution from ammonia borane compounds [82].

The pioneering work by de Vries and coworkers disclosed the reductive properties of Fe(0) nanoparticles [83]. Prepared by an inexpensive iron precursor, Fe(III) chloride, with three equivalents of a Grignard metal reagent (e.g. EtMgCl), iron (0) nanoparticles (1-5 nm size) were proven active in the hydrogenation of alkenes and alkynes under moderate conditions (1 bar of H₂, 25-100 °C temperature range, up to 15 hours). In particular, strained alkenes were found with a higher hydrogenation propensity as opposed to linear alkenes, whereas alkynes transformation could be tuned towards the alkene or alkane depending on the catalytic residence time. As often happens for the first works in an innovative field, a few aspects of the catalytic system had to be improved. The bare iron nanoparticles were found highly susceptible to oxidation and consequent deactivation. The absolute absence of oxidants or moisture is required for the stability of the system. Furthermore, the use of Grignard reagents in excess copiously reduces the sustainability of the synthesis. Finally, the minute size of the nanoparticles hinders the magnetic properties of iron, thus their recoverability and reuse. In an improvement attempt, Stein *et al.* synthesized magnetic Fe nanoparticles supported on chemically derived graphene sheets by ultrasound degradation of Fe(CO)₅ [84]. The work used an environmentally friendly method in the nanoparticles synthesis, plus widely improved the recoverability of the catalyst by magnetic decantation. Bulk magnetization on small iron(0) nanoparticles (*ca.* 2 nm) was also obtained by Chaudret *et al.* by the hydrogen-assisted reduction of an iron bis(trimethylsilyl)amide complex, found active in the alkene/alkynes hydrogenation under higher hydrogen pressure (10 bar), at longer reaction times (20 hours), and room temperature [85]. However, deactivation by oxidation is still a cause of concern. Coating of the Fe(0) nanoparticles appears to be a promising strategy in increasing the stability of the system. Polyethylene glycol was used to

protect the iron nanoparticles in the ammonia-borane dehydrogenation [86]. The polymeric shell allowed the reuse of the catalyst for up to 10 cycles, however strongly reductive reaction conditions are required. Amphiphilic polymers were also employed by Moores *et al.* to stabilize metallic iron in the alkenes/alkynes hydrogenation in flow. Protection by the polystyrene-polyethylene glycol block copolymer allowed the use of the catalyst in water-rich media up to 90% [87]. The same research group also investigated Fe(0) nanoparticles stabilization with an iron oxide shell. The relatively big sized nanoparticles (*ca.* 50 nm) granted the magnetic properties to the nanoparticles, making them recoverable, as well as stabilized the metallic iron core allowing to carry out olefins hydrogenation in 1:1 water/ethanol mixtures [88]. The substitution of traditional hydrogenation catalysts based on noble metals (e.g. Pt, Pd) can be indeed achieved, upon protection of the metallic core.

Iron oxides, on the other hand, have shown promising activities in oxidation reactions, as well as stabilities. In particular, the iron oxidized states have been proven catalytically active in the industrially challenging selective oxidative cleavage of hydrocarbons [89]. In particular, the ability of iron of activating *green* reactants such as molecular oxygen and hydrogen peroxide has made iron oxide particularly relevant in the selective oxidation of alkenyl aromatics, olefins, and alcohols [90]. A wide variety of substrates were tested by Shi *et al.* [91] and Rajabi *et al.* [92], proving the activity of iron oxide nanoparticles. By focusing their attention on styrene oxidation, Rak *et al.* [93] emphasized the importance of a porous system. In fact, etched hollow Fe₃O₄ nanoshells were found more active as opposed to commercial Fe₂O₃ and Fe₃O₄ nanoparticles, and core-shell iron/iron oxide.

The different polyforms of iron oxide: *i*) magnetite, Fe₃O₄ (Fe(II,III) oxide) *ii*) hematite, α -Fe₂O₃ (iron (III) oxide) and *iii*) maghemite, γ -Fe₂O₃ (iron (III) oxide) confer different chemical and physical properties. Magnetite and maghemite bestow magnetic properties to the final properties, while hematite is debated to be the *real* catalytically active specie, in particular in H₂O₂-assisted selective oxidations. In fact, hydrogen peroxide decomposition rates were largely enhanced by the presence of hematite, as elucidated by the work of Hermanek and coworkers [94]. Interestingly, higher hematite content improved

the catalytic activity even if with lower surface area. Hematite was also found as the active specie in the oxidative cleavage of lignin-model compound, isoeugenol, towards high-end flavoring product, vanillin [95]. In particular, various carbon/iron oxide nanocomposites were prepared *via* environmentally friendly syntheses, namely ball milling and solvent-free thermal decomposition, employing inexpensive iron precursors and a relevant chemical biorefineries by-product: humins [96]. The hematite- and hematite/maghemite-based catalytic materials (with or without magnetic properties, depending on precursor) showed promising activities and selectivities in the microwave-assisted oxidation within 3 minutes of reaction. In particular, the hematite-carbon nanocomposite was found the most active. On another note, the particular use of a carbon material, namely humin by-products, appeared to further reduce the Fe oxidation state towards metallic iron content as elucidated by SEM-EDX analyses. This is a sign that carbonaceous materials have the potential of reducing metal centers. This particular property could be applicable for the reduction of other metals. Nonetheless, further research on the catalytic activity of the various iron oxides species is indispensable to further elucidate the activity of Fe-based catalytic systems.

Transition metal oxide nanoparticles

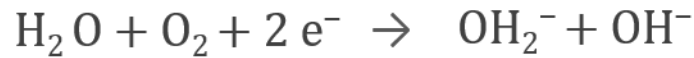
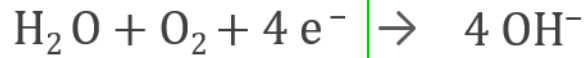
Metal oxide nanoparticles have also attracted a fair deal of attention for their catalytic properties. For instance, palladium oxide was found to be more active and selective in the direct synthesis of hydrogen peroxide as opposed to its metallic counterpart [75], attributed to a suppression of the side reaction involving H_2O_2 decomposition [97]. Although catalytic activities comparable (or superior) to noble metal nanoparticles can be achieved with metal oxides, the main attractiveness of oxide nanoparticles relies on their mechanical or structural stabilities. In fact, nanostructured metal oxides possess a lower surface energy, hence higher stability, compared to their bulk counterparts, as found for Al_2O_3 , TiO_2 , and VO_x , to name a few [98]. For instance, micro-sized alumina is most stable in its α form, while nanostructured aluminum oxide appears to be more stable as γ phase [99]. Also, a defined shape of the nanoparticles may play a highly influential role in the catalytic activity of a material. The importance of a defined

morphology of metal oxide nanoparticles was shed by Xie and coworkers, achieving moist-insensitive low temperature CO oxidation (temperatures as low as $-77\text{ }^{\circ}\text{C}$) employing Co_3O_4 nanorods. The shape of the nanoparticle would preferentially expose active Co^{3+} species on the surface, increasing its activity and stability [100]. To a degree, the catalyst could find applications in aqueous environments (such as the ones used in biomass conversion), thanks to stability of the catalyst in the presence of water.

Peculiarly, inexpensive metal oxides can find a variety of applications in green chemistry. Arena and coworkers have studied low loaded iron oxides/silica catalysts for the methane partial oxidation to formaldehyde prepared via an advantageous adsorption-precipitation route, although finding sintering and surface reconstructing phenomena [101]. Higher stability of the catalytic nano-system can be achieved with a different preparation method. In fact, the same research group has also investigated the catalytic properties of nanostructured manganese oxide with cerium or iron as additives in a number of environmentally benign reactions, e.g. CO oxidation, prepared via a novel *redox-precipitation* route from inexpensive precursors [102]. In particular, the redox-precipitation synthesis of the catalytic systems would enable a monolayer dispersion of the active phase, conferring a higher density of superficial active species with homogeneous morphologies (spherical, *ca.* 10 nm) [103]. The manganese-ceria mixed oxide catalytic systems were found with optimum activities and stabilities in CO oxidation, catalytic wet air oxidation, and benzyl alcohol oxidation to benzaldehyde with molecular oxygen [104].

The biggest advancement of metal oxide nanoparticles for green chemistry applications lays in electrocatalysis, in particular for oxygen reduction (storage of electrons, ORR) and evolution (release of electrons, OER) reactions for energy storage and conversion (**Figure 7**).

Oxygen Reduction



Oxygen Evolution



Figure 7. Schematic representation of the oxygen reduction (above) and oxygen evolution (below).

In fact, efficient energy storage systems (e.g. batteries) could be used to store renewable energies (e.g. wind, solar) that are highly affected by seasonal and daily changes. Generally, noble metal bimetallic systems are used for ORR/OER cycling reactions, where Pt is active as a oxygen reduction catalysts, while Ir or Ru are active as oxygen evolution catalysts [105]. Often the reactivity of one of the metals in the cycle can be hindered by the presence of the other metal nanoparticles (antagonist reactivity) [106]. Limitations in the reactivity, as well as cost and limited resources of noble metal nanoparticles have pushed the scientific community towards transition metal oxides. In this sense, manganese oxide has attracted a fair deal of attention due to its remarkable redox properties, as well as abundance and price. A highly nanostructured manganese oxide inspired by nature was found exceptionally active for both oxygen reduction and water oxidation, with activities comparable (or higher) than the typical noble-metal catalysts [107]. The importance of morphology of the active phase is also stressed in this field. In particular, α - MnO_2 was found the most active compared to β -, δ - and amorphous manganese oxides. The phase of manganese oxide consisted of tunneled structures (nanofibers) with small tetragonal structures, and the highest pore volume, as opposed to the other manganese phases. These features, alongside a higher presence of superficial Mn^{3+} species, attributed high activity and stability to the catalytic system [108]. Nonetheless, manganese oxides often suffer from poor conductivity which limits their applications

as electrocatalysts. To circumvent this problem, combination of metal oxides with more conductive materials (e.g. carbon, stainless steel, titanium) is currently explored, with promising results in activity and stability [109]. Yet, further understanding of the mechanism of action of transition metal oxides, as well as the effect of dopants and additives is a due in order to industrially implement cheap and abundant oxides as metal catalysts.

Organic nanoparticles: Carbon

Carbon is the 6th most abundant element in the universe, and the most abundant in natural systems after oxygen [110]. The number and variety of allotropes make carbon materials highly versatile for different applications. In fact, the different polymorphs possess different physical properties to the carbon material, including density, surface area, and porosities [111]. In particular, nanostructured carbon materials have attracted the attention of the scientific community thanks to:

- Abundance, thus inexpensive
- Exceptionally high surface areas attainable (>1000 m²/g)
- Tunable pore size distribution ranging from micro to macro
- Resistance to acids and bases
- Stability at high temperatures under inert atmospheres (>1000 K)
- Tunable functional groups and surface (from hydrophobic to hydrophilic, oxidized, etc)

Thanks to these properties, carbon has been extensively studied as a catalyst support, owing to also the easy recovery of the active phase by complete gasification of the carbon. Carbon materials allow a high dispersion of the metal nanoparticles in the porous system, with the surface functionalities acting as anchors and stabilizing the metal. Furthermore, the use of carbon as a support grants an easy reduction of the metal species at the most economical cost [112]. Nonetheless, the functional groups on the carbon surface have been found catalytically reactive, with activities comparable to metal catalysts [113]. In general, carbon materials catalyze the following reactions: *i*) oxidations/reductions (e.g. deNO_x), *ii*)

hydrogenations/dehydrogenations (e.g. formic acid decomposition), *iii*) decompositions (e.g. of hydrogen peroxide), *iv*) dehydrations/polymerizations (e.g. poly- α -olefins production), *v*) isomerizations (e.g. α - to β -oximes), among others [112].

Carbon catalysis would represent the *ne plus ultra* in sustainable processes, if:

- **Resistance** to gasification in high temperature hydrogenation and oxidation reactions would increase
- **Reproducibility** of the reaction activities would improve
- **Heterogeneity** of the carbon product is minimized, as impurities (mineral matter) are often present depending on starting materials
- **Synthesis from renewable sources** (e.g. biomass) can be standardized in terms of quality of product (random reconstruction, different ash contents)

In fact, the new trends in green chemistry catalytic reactions, such as biomass transformations, see the employment of hydrothermal conditions where a variety of metal oxides (e.g. TiO₂, Al₂O₃, mesoporous SiO₂, zeolites) are unstable. For instance, zeolites may cover a pivotal role in biomass conversion; however, the hot aqueous media of biomass upgrade strategies severely impact the stability of the aluminosilicates. Additionally, polar solvents deeply affect the nature of the active sites, their deactivation, thus long term activities [114]. The typical hydrophobicity of carbon, instead, allows its use in certain conditions, becoming extremely advantageous. These findings suggest that the typical petrochemical catalysts will be inefficient in the conversion of biomass. Thus, the design of new catalytic materials via the green chemistry principles can find an answer in biomass-derived nanostructured catalysts.

Nanocarbons exist with different carbon atom hybridizations (e.g. sp² for graphene, sp³ for diamond, *quasi* sp² for carbon nanotubes), giving different electronic properties to the materials, including conductivity and electron transfer (**Figure 8**).

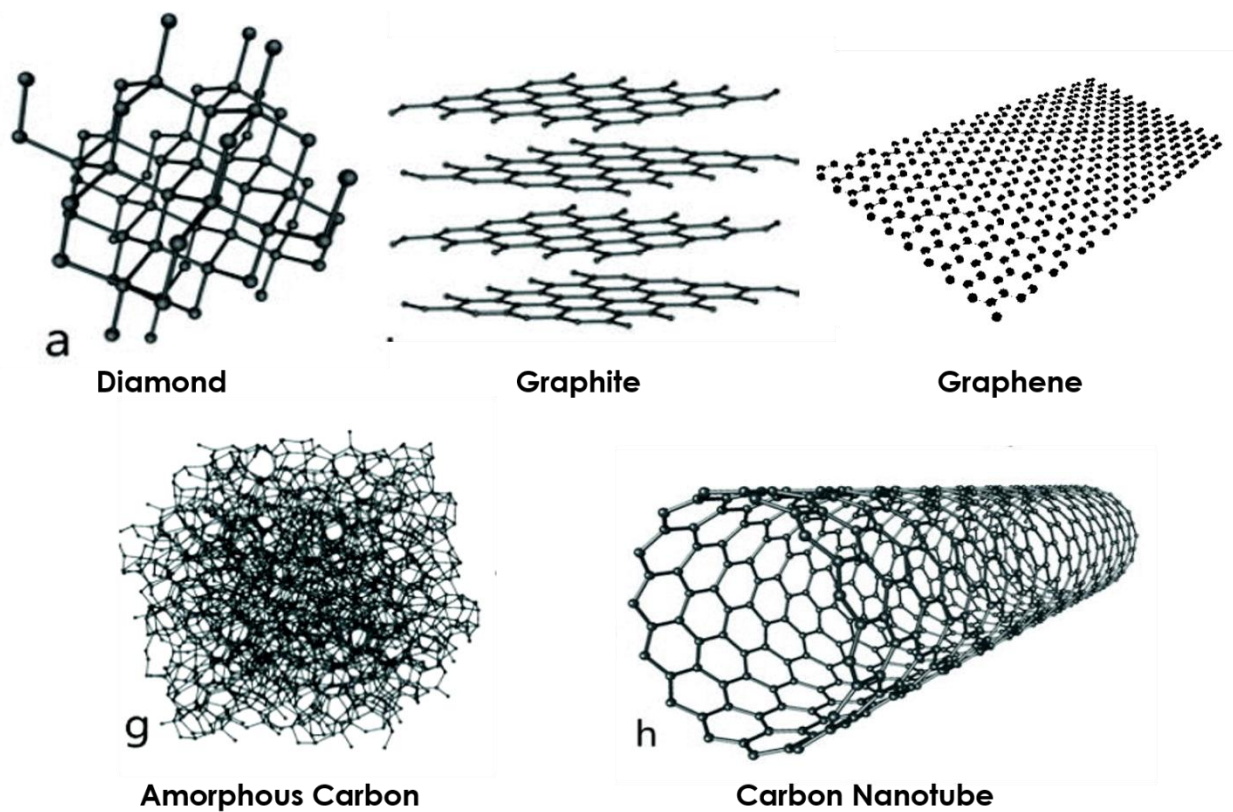


Figure 8. Structural representation of the different allotropes of carbon.

In fact, carbon can form linear (sp), planar (sp^2), and tetrahedral (sp^3) bonds, however intermediate hybridizations exist (e.g, fullerene) [115]. Based on pore size, carbons can be classified as microporous (<2 nm), mesoporous (2-50 nm), and macroporous (> 50 nm). Plus, porous carbon can be distinguished into *disordered* and *ordered* (**Figure 9**). Activity and selectivities of nanocarbons are often dictated by: *i*) surface energy density in the case of microporous systems, or *ii*) surface functional groups for mesoporous systems [116]. Macroporous carbons do not allow the necessary molecule confinement for catalysis; microporous carbons often possess diffusion limitations, being used mostly as adsorbents; mesoporous carbons, instead, are regarded as the best compromise between heat/mass diffusion and catalytic activity.

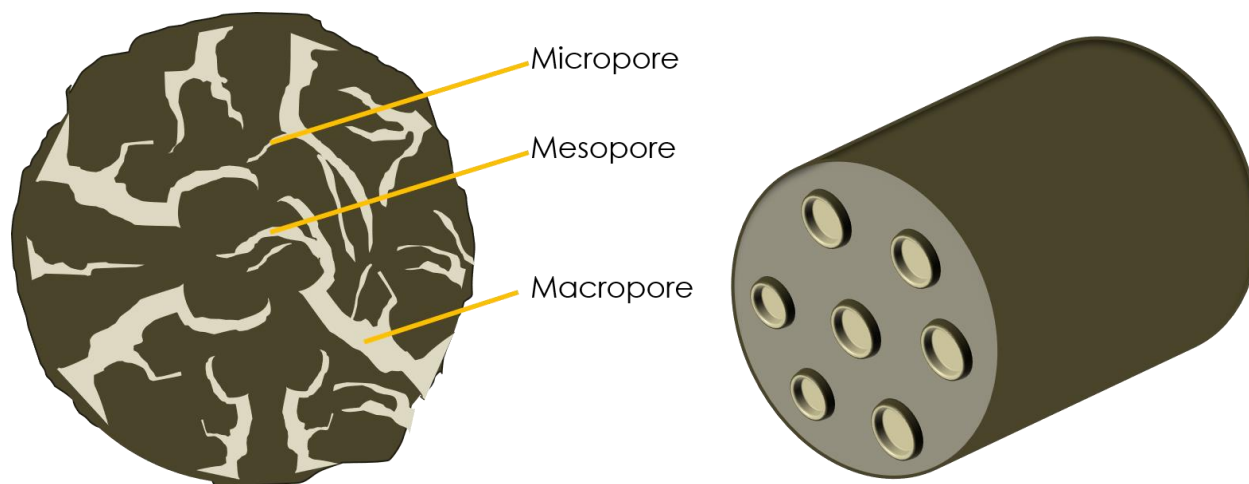


Figure 9. Drawing of a disordered porous carbon (left) and *ideal* ordered mesoporous carbon (right).

Different conformations and crystalline orders of carbon nanomaterials can be achieved by tuning the various synthesis parameters. For instance, synthetic method (catalytic) chemical vapor deposition can yield different carbon nanostructures by varying the operating conditions, obtaining: *i*) multiwalled carbon nanotubes, *ii*) fishbone carbon nanofibers, or *iii*) platelet carbon nanofibers [117]. The formation through synthesis of different functional groups, defects, edges, sheets orientations, faces exposure will influence the catalytic activity and selectivity of the final carbon material.

Inorganic and organic carbon nanotubes (CNT) have attracted an enormous scientific interest thanks to their large surface areas, good electrical and thermal conductivity, and excellent mechanical strength [118]. These nanomaterials are composed of highly condensed curved graphitic layers with well-defined and nanosized inner hollow cavities [119]. Praised for their inertness, pristine carbon nanotubes have been extensively studied as support for metal (especially noble) nanoparticles [120]. The functionalization of these materials via acid or bases treatments allow the attainment of reactive surface groups (e.g. lactone, ketone, carboxylic, hydroxyl), thus higher catalytic activity [121]. Traditionally, these materials are synthesized from high-energy methods (chemical vapor deposition, arc discharge, laser ablation, and spray pyrolysis) of petroleum-derived precursors obtaining extensive sp^2 hybridization (graphene-like) [122]. Often, the preparation of these materials involves the decomposition of the fossil compound by metal catalysts, making the process cost-ineffective. Although efforts are currently ongoing in the

efficiency improvements of the synthesis process, the use of non-renewable feedstocks and metal catalysts make their synthesis wasteful and unendurable. Attempts of making the synthesis of carbon nanotubes *greener* involve the use of vegetable oils as carbon feedstock (e.g. coconut, turpentine, palm oil). For instance, CNT with diameters <2 nm were synthesized via spray pyrolysis with an iron-cobalt catalyst from eucalyptus oil [123]. The study of different natural precursors (e.g. rocky sediments, clay, natural fibers) and/or catalysts based on volcanic residues (e.g. lava) has been also carried out, however impurities in the starting materials lead to inhomogeneous carbon materials [124]. Although CNT from natural resources can be achieved, other sustainable routes may be more advantageous in the synthesis of (catalytically active) carbon nanomaterials.

Graphene oxide, a by-product from graphite oxidation, has been researched as a cheaper alternative for graphene-like carbon materials [125]. The reduction of graphene oxide yields to a material structurally similar to pristine graphene, reduced graphene oxide (rGO), that possess high electron transfer abilities thanks to the sp^2 hybridization. Full graphitization of the materials is often difficult to achieve, resulting in residual oxygen functionalities. Nonetheless, these oxygen functional groups, alongside defective edges, frustrated Lewis pairs, and carbon vacancies, have been recognized as catalytically active sites. In fact, carbon-mediated catalytic activities have been attributed to different oxygen-containing functionalities, in particular:

- **(Hydro)quinone groups** for hydrazine/hydrogen peroxide/potassium peroxydisulfate/persulfate decompositions, selective reductions, (photo-)Fenton mineralizations, and other advanced oxidation processes;
- **Epoxy groups** in SO_x/NO_x removal and aerobic oxidations;
- **Benzyl alcohol-type groups** in coupling reactions such as Suzuki-Miyaura C-H arylation of benzene;
- **Acidic O-H groups** in alkylations, $NaBH_4$ -mediated reduction of nitrophenols, or cyclocondensations to quinazolinone derivatives [126].

Even so, rGO has been used as a support to numerous metallic species, improving the catalytic activities for electrocatalytic oxygen reduction reaction (ORR), photoelectrochemical hydrogen evolution, and catalytic oxidation to name a few [127]. However, the reducing agents and surfactants used in the reduction of graphene oxide are often toxic and harmful, as well as increasing the overall waste of the system. A sustainable reduction of graphene oxide with bio-based molecules can be achieved by employing proteins, polysaccharides (e.g. dextran), or glycine [128]. Nonetheless, the green chemistry production of carbon nanomaterials can be further improved by using renewable compounds as opposed to graphite.

The active sites of graphene-based materials include N- and P- dopants, defects, vacancies, edges, sulfur groups, and especially oxygen functionalities. A DFT study on carbon materials illuminates the high activity of oxygen-containing superficial groups on carbon materials, with quinone and lactone groups being the most active [129]. In this sense, biomass is an oxygen-rich carbon material, making it reasonable to produce C-based catalytically active materials. Peculiarly, untreated soil, peat, and humic/fulvic substances were found active in a number of condensation reactions [130]. These premises, completed with the knowledge gained on fossil-based carbon materials, allow the development of sustainable carbon catalysts (or, support).

Chemical and/or physical activation of bio-based precursors generally yields microporous carbons known as activated carbon. The simplicity of the activation method (e.g. NaOH impregnation-chemical; steam gasification-physical) allows the application to various carbon based materials. Inexpensive resources, such as lignocellulosic biomass, coconuts residues, and fruit stones, are typical substrates in the preparation of activated carbons. These materials have been extensively used as carbon supports for many heterogeneous catalysts, but most importantly find more interesting applications as supercapacitors for gas and energy storage for their microporous range of pores [131].

Mesoporous carbons are a relatively new class of materials which can be used as catalysts and prepared from natural resources. Tailoring and design of the preparation method can yield homogeneous porous systems in the range between 2 and 50 nm. In particular, hydrothermal carbonization and template-directed synthesis are taking a hold of the scientific community in the synthesis of truly sustainable carbon materials with regular porosity and functional sites tenability. In this context, many isolated carbohydrates, whole lignocelluloses, and urban/agricultural wastes have been employed for the synthesis of nanocarbons. In particular, detailed ^{13}C -NMR studies show little-to-no difference in the final chemical structure of the material obtained via hydrothermal carbonization of either isolated sugars or whole biomass [132]. This suggests that mesoporous carbons can be produced from complex biomass residues, without the need of hydrolyzing in order to obtain the isolated carbohydrate.

The simplicity of hydrothermal carbonization (HTC) makes it an advantageous synthetic procedure for carbon nanomaterials. HTC is a thermo-chemical process for the conversion of C-rich materials at elevated temperatures and pressures (often autogenous) in the presence of water. In particular, high- and low-temperature HTC processes can be identified, where the former is usually carried in the 300-800 °C range, while the latter reaches only 250 °C. Low-temperature HTC is applicable to bio-based materials within the temperature stability range of the organic molecules. Dehydration, condensation, polymerization and aromatization are the reactions governing the HTC process. In fact, HTC of biomass is believed to go *via* decomposition/dehydration to soluble products (e.g. furanics, organic acids, phenols), and subsequent polymerization to the final carbon nanomaterial [133]. Activation temperature and time are important variables in the HTC of biomass. Nonetheless, the textural and morphological properties of the starting materials will influence greatly the final properties of the HTC carbon. In fact, compact textured biomass materials will result in small surface areas, while high porosity and surface area can be obtained from loose textured bio-materials [134]. Retention of the morphology of some types of biomass (e.g. pine sawdust) is achieved through microwave-assisted hydrothermal carbonization, whereas α -cellulose would yield spherical particles in the same HTC conditions [135]. Hybrid carbon-polymer

latex materials can be obtained by carrying out the HTC process of biomass in the presence of organic monomers. For instance, a carboxylate-rich (i.e. acid) carbon material was obtained in a one-step HTC process of glucose and acrylic acid [136]. Similarly to activated carbons, HTC materials have been investigated as sorbents by chemisorption for e.g. Uranium and tetracycline removal [137], suggesting their possible use as catalytic materials being adsorption one of the crucial steps in a (heterogeneous) catalytic process (*vide supra*). In fact, hydrothermal post-modification of carbon nanotubes in the presence of glucose, urea and/or glucosamine improved the oxygen reduction reaction activity for fuel cell applications by increasing the electron density at the Fermi level [138]. Also, acid HTC obtained by sulfonation or in the presence of acrylic acid (*vide supra*) were found active in biomass-relevant reactions such as cellulose hydrolysis to glucose or fructose dehydration to HMF [139]. In general, HTC materials show lower-to-comparable activities to metal-containing catalysts. This slight drawback in activity could find justification in the low synthetic cost of the potential material, even though further investigations are due in terms of long-term stability (for instance, in continuous flow), and preserved selectivities with longer reaction times.

Although HTC is a simple and inexpensive procedure only involving a heated closed system and water, thus advantageous and green, wide size distribution of the pores is often obtained. In order to narrow the distribution, template-direct syntheses are advancing in the production of carbon nanomaterials. Generally two classes of template are distinguished:

- **Hard-template synthesis:** the carbon nanoparticles are deposited onto a sacrificial porous inorganic template;
- **Soft-template synthesis:** sacrificial molecular or polymeric species stabilize the carbon nanoparticles into ordered mesophases.

An example of hard-template synthesis is given by the work of Titirici *et al.* who used a variety of nanostructured silicas with different surface polarities as templates. By modifying the functional groups

on the silica and the carbon precursor loading, the research group was able to obtain different morphologies of hierarchical carbon: macroporous casts (very hydrophobic silica), hollow spheres (moderately hydrophobic silica), mesoporous microspheres (60wt% carbon precursor to silica), and simple carbon nanoparticles (60wt% carbon precursor to silica). In particular, a product of the acid conversion of a fraction of lignocellulosic biomass (in detail, hemicelluloses, i.e. pentoses), furfural [96], was used as carbon precursor [140]. By using a starch/gelatin ink in the presence of silica spheres in 3D printing, a metal-free catalyst active in the selective oxidation of benzyl alcohol was synthesized via hard templating [141]. In particular, the use of a 3D printer allows the easy and rapid synthesis of different open structures with fewer limitations in mass and heat diffusion. In fact, large open porosities (> 60%) gave systematically higher conversions over the studied reactions times with slight improvements in selectivity.

An example of a soft-template synthesis procedure is given by the surface coating technique on a sugarcane bagasse scaffold. A phenol-formaldehyde resin was employed as carbon precursor with a triblock polymer (F127) as mesostructuring agent. A high surface area (*ca.* 500 m²/g) was obtained upon removal of the polymer by carbonization, with the micropore contributing at 66%. In this way, micro-meso hierarchically porous materials have been obtained with superior thermal stability [142]. In this sense, hierarchical porous carbons for supercapacitor applications were synthesized in the presence of dioxane as both solvent and mesopore-directing agent, acetic acid as catalyst, and polymeric organic frameworks (namely phloroglucinol, terephthaldehyde) as ultra/super-micropore-directing agent [143]. The particular synthesis yielded to excellent electrochemical properties, alongside a high specific surface area.

Thus, in general both soft- and hard-template syntheses can be seen as multi step processes:

1. Synthesis of the template with predefined porosity, or purchase
2. Deposition of the carbon precursor on the template surface
3. Cross-linking of the precursor on the template surface

4. Dissolution in acidic or basic media of the hard template, or carbonization of the soft template.

Although defined structures can be induced on carbon nanomaterials, it is clear how this particular synthesis does not follow the principles of green chemistry. In fact, the utilization of a *sacrificial* template represents readily a waste, even if removed by heat and not inorganic acid or bases.

A more sustainable approach along these lines was taken by the group of Clark *et al.*, with the development of the Starbon® materials. Starting from starch, the research group was able to develop mesoporous carbons *via* controlled carbonization. In particular the following steps were followed:

1. Expansion of the starch macromolecules by thermal treatment in water
2. Cooling at 5 °C to produce a retrograded starch gel
3. Solvent exchange step with lower surface tension solvents (ethanol, acetone)
4. Carbonization/Pyrolysis of the mesoporous starch

The obtained mesoporous carbons were found to possess intermediate chemical properties between polysaccharides and activated carbons, finding a variety of possible applications including catalysis and/or catalyst support [144]. Nonetheless, recently Starbon® were found to be exceptional sustainable sorbents for bioactive phenolic compounds [145]. The degree of carbonization (proven tunable for temperatures between 200-1000 °C) influences the surface properties of the highly mesoporous carbon, with tunable hydrophobicity/hydrophilicity and functional groups.

The specific hydrophobic/hydrophilic environments of sulfonated Starbon® materials were in fact found advantageous over commercial microporous carbons in the esterification of succinic acid, giving quantitative conversions and selectivities within 5 hours of reaction time [146]. Not only the higher hydrophobicity favored the synthesis of mono/di-esters in an aqueous environment, but their mesoporosity positively influenced the mass diffusion of reagents and products.

As opposed to hydrothermal carbonization, the synthetic procedure for Starbon® materials calls for two extra pure solvents, and it might be debated that the process is not sustainable. However, high purity acetone and ethanol can be produced by ABE (Acetone, Butanol, Ethanol) microorganisms fermentations of biomass [147]. Thus, with the collaboration of each field of science, sustainability can be achieved.

Overall, carbon materials show potential as metal-free catalysts. In fact, depending on their superficial properties different reactions can be carried, such as oxidative dehydrogenations [148], esterifications/etherifications/alkylations/dehydrations/hydrolysis [149], as well as photocatalysis [150]. Nonetheless, their research is still limited to traditionally inert inorganic carbons, thus requiring the doping with a metal or metal oxide. Further investigations of bare biomass-derived carbon materials might pave the future towards truly sustainable and renewable processes.

Future Directions

The future can be *green*. The emergence of new technologies with renewability as a focus requires further research in terms of chemical process. The environmental impact of industrial chemical processes can be copiously reduced by the employment of catalysis, in particular nanocatalysis. In fact, nanocatalysis bridges the activity and selectivity of homogeneous catalysts and the stability of heterogeneous catalysts. These properties imply energy and feedstocks savings in a chemical process, thus improving the environmental and economic impact of the production. Nonetheless, nanocatalysis is a continuously emerging field, where new applications and reactivities are progressively discovered. The options are still boundless: the concept of nanocatalysis is merely *ca.* 30 years old. Metal, metal oxide, organic are the main categories of nanocatalysts, and all of these fields have large margins of improvements.

Noble metal nanoparticles, the most studied so far, suffer mainly of deactivation by sintering, thus there is a fair deal of research into their stabilization. Commonly, dispersion on a support is the popular method of preventing agglomeration of the metal nanoparticles. Nonetheless, recent development on the field looks for the addition of ligands, stabilizers, and organic/inorganic coatings. However, this particular

approach is against the 8th principle of Green Chemistry. In this sense, a different approach could be thought of: using of stabilized strong reducing supports (e.g. coffee/tea extracts on a hierarchically porous carbon). In fact, if a reducing material is present on the surface, oxidized/deactivated metal particles would be in turn reduced. Nonetheless, noble metal nanoparticles are non-renewable resources, and their use should be limited until complete substitution.

Transition metals are generally more abundant than their noble counterpart. Nonetheless, their use as metallic nanoparticles is hindered as for noble metals mentioned above. The employment of a more stable form, oxides, should be thus favored. Elucidation on the metal oxides activity mechanism is essential for their implementation, in particular for the new emerging reactions, such as biomass processing. Nonetheless, as noble metals, transition metal oxides would also deplete.

Carbon nanoparticles are the future. As one of the most abundant elements, the most inexpensive, the most equally distributed source of the planet, carbon shall cover a key role in the future sustainable and green processes. A carbon-based catalyst would be easily recovered, reused and/or disposed. Nonetheless, understanding of its reactivity, as well as improve its usually inhomogeneous porosity and stability is still required. Synthetic methods will cover a key role in improving these properties, where methods involving solvent-free thermal decompositions, mechanochemical activations (e.g. ball milling), benign-solvent expansion and pyrolysis should be preferred. Combination of different nature-derived compounds to create carbon nanocomposites can largely improve the mechanical properties (e.g. brittleness), without impacting the environment and society.

Research should always advance by keeping the 12 Principles of Green Chemistry in mind. Only like this, true sustainability can be achieved.

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