

Strategies to Immobilized Catalysts: A Key Tool for Modern Chemistry

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1.1 Introduction

In all the different cultural and scientific areas, modern era is characterized by the high attention dedicated to the concept of sustainable development and sustainability. In what is nowadays indicated as “circular economy,” chemistry plays a pivotal role to steer modern production toward safety, environmental efficiency, reduction of waste, and minimization of CO₂ emissions. Both academic and industrial researches are focused in this direction and are, often in collaboration, effectively working at the definition and implementation of innovative solutions [1, 2].

In chemistry, sustainability has become synonymous with *green chemistry*, a term that appeared in the 1980s in the United States and associated to a multidisciplinary area of research aimed at developing innovative approaches to fundamental and applied research that could eventually lead to industrial competitiveness and minimal environmental impact.

The definitions of green chemistry are several, and often they vary according to the most critical chemistry-related issues for specific region of the world. Anyway, Paul T. Anastas recognized the merit of the definition of the 12 Principles of Green Chemistry (Figure 1.1), which simply and in exhaustive manner indicate the most important topics toward which modern research and society need to focus to attain a sustainable development [3]. These principles represent not only a sort of guidelines to the perfect chemical process but also a very useful vademecum to identify the key issues and the key research areas that need to be developed in order to actually achieve sustainability.

An ideal green modern chemical process does not feature one of the different principles. It is instead the combination of all of the principles and the result of a careful process design where strategic political solutions are combined with the development of key strategies and technologies. Therefore, a modern process needs to be based on safer solvents and chemicals, possibly coming from the valorization of waste and renewable resources. Energy-efficient technologies must

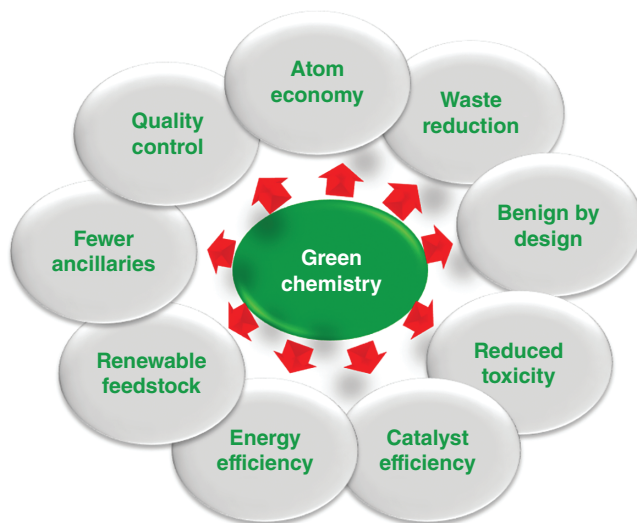


Figure 1.1 Principles of green chemistry.

be developed and used to maximize safety and quality of a chemical process while minimizing the waste and the cost associated to its implementation.

A central role is played by catalysis [4]. By aiming at the use of safer chemicals and at the same time at the reduction of steps in a chemical process, it is necessary to develop innovative catalytic technologies not only to resolve the use of dangerous highly reactive chemicals but also to minimize the energy consumption and the production of the waste associated [5, 6].

The use of effective catalytic systems mainly based on metals has been always crucial in the chemical industry, and homogeneous catalysis has been generally preferred over the use of heterogeneous/solid catalytic systems, especially in the production of fine chemicals and complex active pharmaceutical ingredients (APIs) [7, 8].

The design of a modern chemical process should carefully evaluate the actual need for using toxic and exhaustive metal catalysts, and inevitably, it should consider all the available possibilities for their recovery and reuse to consequently minimizing pollution.

Different solutions for the recovery and reuse of a catalytic system are available and all of them need to be implemented in the future. These comprise the phase-transfer/separation techniques, largely already used in industry, and above all, the use heterogeneous/immobilized catalytic systems [9, 10].

Heterogeneous catalysts should be effectively recovered and reused at the end of a process simplifying the work-up procedures for the isolation of the desired final target material.

It is also kind of reasonable that current industrial production looks at heterogeneous catalysis skeptically, as homogeneous catalysis is often more effective and the cost of production more easily predictable. In fact, definition of a heterogeneous system featuring a perfectly repetitive catalytic efficiency is truly challenging. Accordingly, the reproducibility of the results for the sufficient

number of cycles that justify the use of a heterogeneous catalyst remains a critical point in real industrial cases. Nevertheless, although the difficulty of the challenge, the definition of heterogeneous recoverable catalytic systems is of major importance, and a successful research in this direction is the only manner to pave the route for the ideal chemical processes endowed with the highest innovation and efficiency features.

To completely access the ideal overallly efficient green chemical process, heterogeneous catalysts should be developed considering the need for use of novel safer chemicals and solvents deriving from renewable resources and the use of innovative stirring and heating technologies such as flow reactors, microwave, or ultrasounds, which could optimize its reuse and its reproducible catalytic efficiency at the most convenient energy cost [11].

1.2 Catalysis

The word catalysis was first coined by Berzelius in 1836 [12]. It has now grown into a multidisciplinary research field playing a central role in many scientific and industrial activities including chemical, biological, nanotechnology, polymer, energy, pharmaceutical, and agriculture fields. The catalyst alters the reaction course via accelerating the reaction process by decreasing the activation energy without affecting the thermodynamics of the overall reaction. More often, high yields of the desired product are obtained in shorter period of time while consuming less energy compared with the corresponding stoichiometric reactions [13].

Plethora of novel catalysts have been developed over the years and actively employed both in the industrial and academic research communities. Broadly, catalysts are classified into two categories, homogeneous and heterogeneous. In homogeneous catalysis, both the reactants and catalysts are present in the same phase, and active catalytic sites are easily accessible to reactants and generally result in higher activity and reaction selectivity of catalysts. It is possible to fine-tune the regio-, chemo-, and enantioselectivity of reactions through appropriate selection of metals, ligands, and organocatalysts [14].

Despite the impressive achievements in the field of homogeneous catalysis, the recovery and recyclability of the catalysts is a major issue. Substantial production costs and time-consuming purification techniques are employed for the isolation of the catalytic species from the reaction mixture. Recovery and reuse of the catalysts are a vital issue for ecological and economical demands [1]. In heterogeneous catalysis, the catalysts are heterogeneously dispersed in the reactant phase. In the past decades, wide range of methods has been investigated for the development of heterogeneous catalytic systems with inherent ability of being easily separated from the reaction [15–17].

1.3 Heterogenization of Homogeneous Catalysts

Typically, the motive behind the immobilization of compounds onto solid supports is to facilitate their handling and separation. The latter is an especially

challenging problem faced when dealing with homogeneous catalysts. Upon heterogenization, the immobilized compounds can be easily separated from the reaction media by simple techniques such as filtration, decantation, and centrifugation, thus enabling multiple reuse and recycling of the immobilized compounds. This is particularly beneficial when working with expensive materials [18–20]. In addition, studies have shown that heterogenization can enhance the stability of embedded compounds and in some cases boost the reactivity and selectivity of catalytic reactions [21].

Nature of the catalyst support and the heterogenization process influence the performance of the heterogenized catalysts. To date, numerous catalytic supports both organic and inorganic, with different methodologies for the immobilization of homogeneous catalysts have been designed and applied in catalysis [22]. The resulting properties and potential application of an immobilized catalyst strongly depend not only on the (i) physicochemical nature, (ii) porosity, and (iii) dimensions of support, but also on the (iv) nature and length of the spacer between the catalytic sites and the surface of matrix, and (v) the density of catalytic sites on the surface of support.

Catalysts immobilization is typically based on the intermolecular interactions between the support and the catalytically active species. These interactions are classified into three types, covalent bonding, non-covalent interactions, and encapsulation. In the covalent bonding the catalysts are covalently tethered to the support; in non-covalent interactions, which are also called physisorption, the catalysts are adsorbed on the surface of the support via weak intermolecular interactions such as hydrogen bonding and electrostatic or van der Waals interactions; while encapsulation implies the physical entrapment of catalyst inside of the pores or cavities of support. More recently metal–organic coordination polymers have been designed through coordination assembly of multitopic ligands and metal ions without using any supports (self-supporting approach) (Figure 1.2).

Several approaches have been explored for heterogenization of catalysts while using the aforementioned interactions; for example, immobilization on inorganic bulk supports [23, 24], organic polymers [9, 25, 26], organic–inorganic materials [27], nanomaterials, and magnetic nanoparticles (MNPs) [24, 28]. The catalyst supports, in addition to enabling facile isolation of the catalysts from the reaction medium, should be chemically inert and environmentally benign. Because of that, biowaste valorization approach for the catalyst development is highly desirable [29, 30].

In the Section 1.3.1, we select to discuss the immobilization of catalysts on silica-based materials, polymeric supports, and supports with high surface areas.

1.3.1 Immobilization on Silica

Silicate materials exhibit numerous interesting properties that render them ideal for immobilizing different materials. In addition to their biofriendly nature, inertness, and impressive thermal stability, silica matrices are porous compounds that can be designed to have different shapes and sizes of pores. Hence, they enable

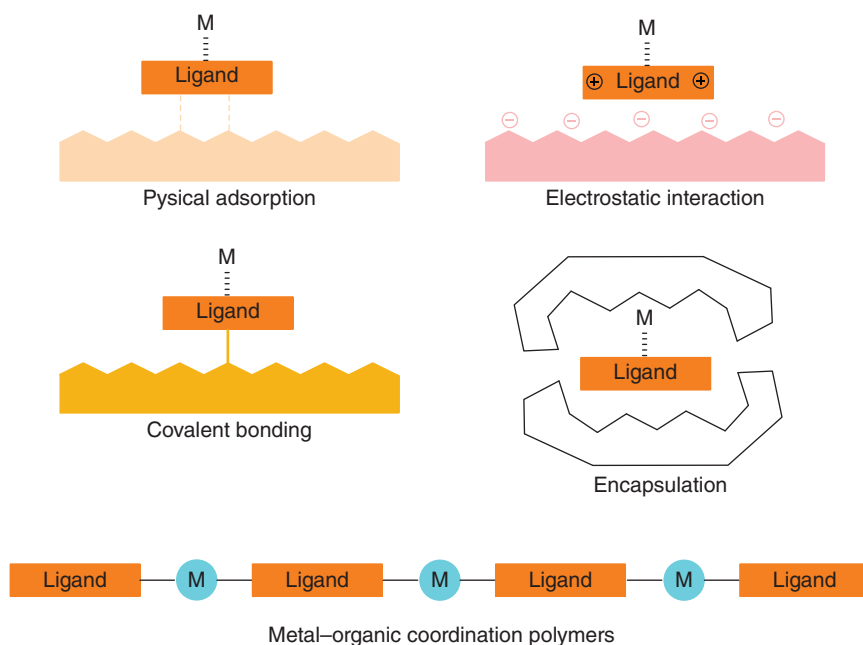
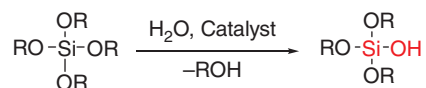


Figure 1.2 Methods for the immobilization of catalyst onto solid supports.

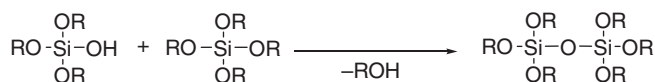
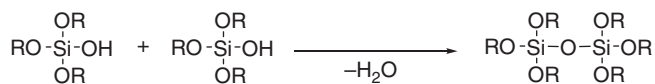
the diffusion of various materials within their ceramic structure, depending on their size [31, 32]. Silica supports are commonly prepared via sol–gel process. It is a technique that transforms precursors such as silicon alkoxides into inorganic ceramic polymers under mild conditions. This process involves hydrolysis and condensation of silicon alkoxide in liquid medium under basic or acidic conditions to form metal oxide network with Si—O—Si bonds (Scheme 1.1) [33].

The versatility of these supports offers a high degree of control over the properties of the final products and enables accurate engineering of complicated systems

(1) Hydrolysis



(2) Condensation

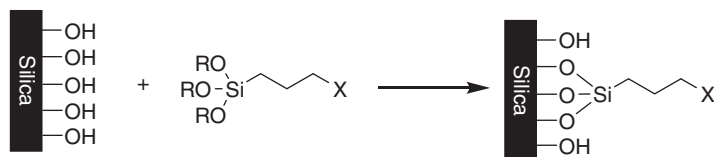


Scheme 1.1 The hydrolysis and condensation of alkoxy silane monomers in aqueous medium.

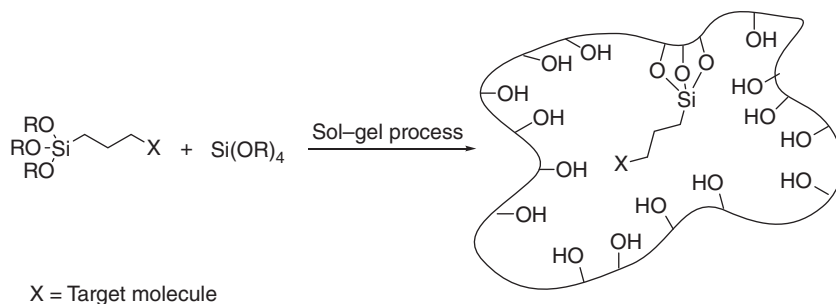
that address the needs of specific problems. Currently, the field of heterogeneous compounds comprises a diverse archive of silica-based supports, ranging from traditional xerogels and aerogels to mesoporous silica [34, 35], periodic mesoporous organosilica (PMO) [36], silica nanoparticles (NPs) [37], microcapsules [38], and nanospheres [39, 40]. These supports have proved useful for immobilizing various compounds and have been applied for heterogenizing different organo- and organometallic catalysts. The immobilization of compounds on silica falls into four categories: (i) covalent binding, (ii) physical entrapment, (iii) electrostatic interactions, and (iv) silica microencapsulation.

1.3.1.1 Covalent Binding

Covalent binding of targeted compounds onto functionalized silica matrices is by far the most popular method of immobilization. The grafting can be performed using post-synthetic methods by attaching the desired compound onto the surface of pre-prepared silica supports (Scheme 1.2) [41–45]. Otherwise, the modification proceeds by binding the compound of interest to a suitable silane precursor prior to synthesizing the inorganic matrices. The modified silane then co-condensates with other silane monomers during the sol–gel process to produce matrices with a homogeneous distribution of the heterogenized material (Scheme 1.3) [46–48]. Either way, the covalent binding provides strong tethering of the desired compounds on the silica support, thereby maximizing their stability and minimizing any chances of leaching. The grafting, however, changes the chemical composition of the immobilized materials. Hence, it affects their chemical and physical properties. Furthermore, these processes require additional synthetic steps for binding the targeted materials, which reduce the overall greenness of the methods and complicate their adoption in industrial applications. In 2004, Sánchez and coworkers presented a relatively short procedure for attaching chiral



Scheme 1.2 Immobilization of molecules and catalysts on silica.



Scheme 1.3 Immobilization of molecules and catalysts by sol–gel process.

Pd and Ni Schiff bases onto different silica-based supports. The heterogenized complexes provided impressive turnover frequencies (TOFs) in the catalytic hydrogenation of olefins, reaching, in some cases, up to $1\,000\,000\text{ h}^{-1}$ [42].

1.3.1.2 Physical Entrapment

Physical entrapment remains among the simplest methods for immobilizations on silica. The compounds adsorb to the silica support through weak interactions such as van der Waals interactions and hydrogen bonds [49–51]. Therefore, no prominent changes occur to the structure and to the intrinsic properties of the immobilized materials. However, these systems are extremely prone to leaching due to the weak interactions between the entrapped compounds and the ceramic support. Physical entrapment is accomplished by (i) the introduction of the targeted compound to the reaction mixture during the preparation of the support, which usually relies on sol–gel methods or coprecipitation techniques [52, 53], and (ii) incorporating the compounds within pre-synthesized systems via deposition precipitation and impregnation methods [54–56]. The first contributions involving the physical entrapment of catalysts within a sol–gel matrix were introduced in 1993 by Rosenfeld et al. Different metal chlorides such as cobalt, rhodium, and platinum chlorides were introduced to sol–gel solutions containing cetyltrimethylammonium bromide (CTAB) prior to gelation [50]. The metal chlorides formed salts with the quaternary ammonium surfactant and were physically entrapped once the sol–gel process was complete. The metal-containing supports were then employed in a wide variety of chemical transformations, which included the hydrogenation of olefins, the isomerization of allylbenzene, the disproportionation of 1,3-cyclohexadiene, and the hydroformylation of cyclohexene. Moreover, the catalytic supports exhibited negligible leaching of the metallic species and were successfully recycled several times.

1.3.1.3 Electrostatic Interactions

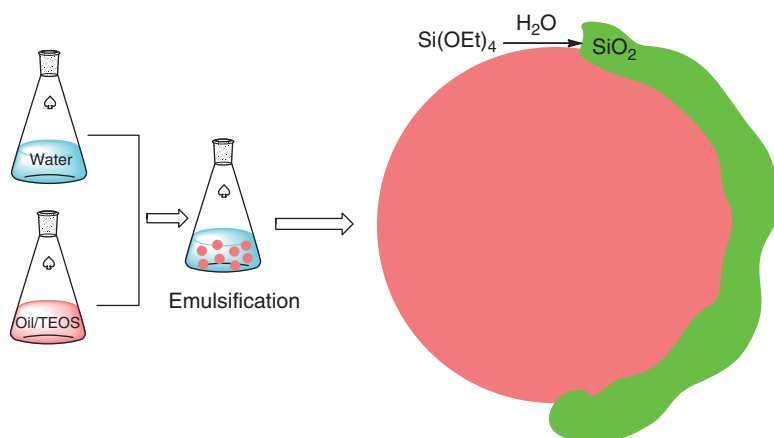
This method is suitable for ionic compounds that are capable of interacting with charged supports. Examples include ionic liquids, enzymes, and organometallic catalysts [57]. Most of the silica supports comprise surfaces that are filled with silanol groups, apart from silica matrices prepared from non-hydroxyl-based non-hydrolytic sol–gel procedures. Therefore, depending on the pH of the solution, the surface of the silica can acquire either a positive or a negative charge. As a result, it is possible to attach ionic compounds with the opposite charge to the surface of the silica through electrostatic interactions. Other approaches rely on modifying the silica with charged functional groups in order to attain optimal electrostatic binding [58]. Fortunately, the electrostatic interactions between the immobilized substance and the support are sufficiently strong and, hence, keep the materials from leaching.

1.3.1.4 Silica Microencapsulation

Microencapsulation is a process in which micrometer-sized particles of solids, liquid droplets, or gases are enclosed with an inert shell [59]. The goal is (i) to protect compounds from undesired reactions such as hydrolysis or oxidation by separating them from the outer environment, (ii) to target and control the release

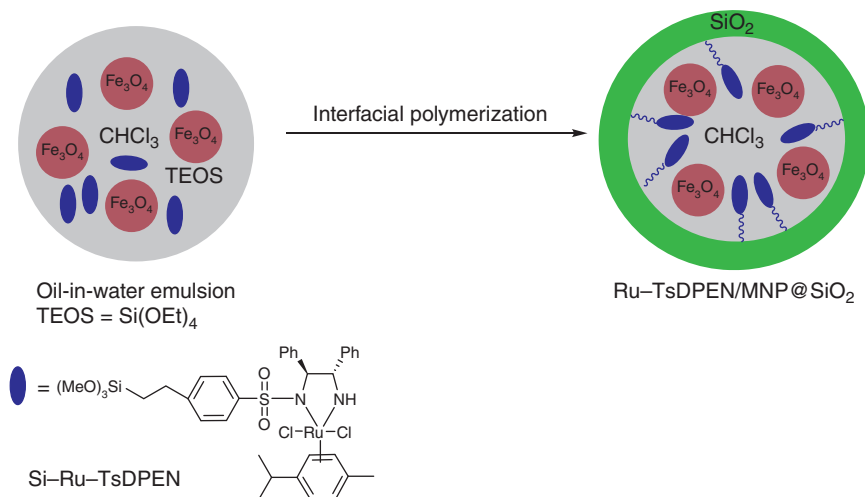
of drugs, (iii) to facilitate the handling of certain materials, or (iv) to mask the color, taste, and smell of a substance. In contrast to other immobilization techniques, microencapsulation does not require any type of interaction between the immobilized material and the support. Therefore, virtually any compound can be microencapsulated. However, the shell material should be inert toward the confined compounds and, in addition, be cheap and abundant and provide sufficient stability. Consequently, the use of silica as a shell material has significantly increased in the last decade [60, 61]. Compared with polymeric materials, silica exhibits higher stability when exposed to different temperatures, pHs, and reaction conditions. The silica materials do not swell and maintain their structure. Furthermore, they are nontoxic, mechanically robust, and highly versatile materials that can be easily modified with different moieties. Another important aspect of microencapsulation in which silica excels lies in the high control over the porosity, shell thickness, and surface properties of the ceramic material.

Silica-based microcapsules are usually prepared using chemical methods that bridge between emulsions and the sol-gel technique [62]. During the microencapsulation process, emulsions act as soft templates for fabricating the silica shell. Normally, the targeted compounds are dissolved inside the dispersed droplets, which represent the core material, prior to emulsification (Scheme 1.4). Then, the silane monomers meet and react with the oxygen donors either at the interface of the emulsion droplets or inside the core to produce microcapsules (Scheme 1.5).



Scheme 1.4 Preparation of silica microcapsules by emulsification and sol-gel process.

According to the literature, silica microcapsules are commonly produced from oil-in-water (O/W) or water-in-oil (W/O) emulsions [62]. Recently, O/W emulsions were used to prepare microcapsules bearing catalytic moieties. Thus, Zoabi et al. synthesized magnetically separable silica microcapsules that contained Noyori's Ru-TsDPEN (TsDPEN = (1*R*,2*R*)-*N*-(*p*-tolylsulfonyl)-1,2-diphenylethylenediamine) catalyst anchored to the interior part of the shell [63]. The catalyst was installed by attaching the Ru complex to a silane monomer, which was condensed with tetraethyl orthosilicate (TEOS)



Scheme 1.5 Immobilization of chiral ruthenium-based catalyst within magnetically separable silica microcapsules.

during the interfacial polycondensation process under basic conditions. The microcapsules were then applied in the asymmetric transfer hydrogenation of aromatic ketones using sodium formate as a hydrogen donor. The hydrogenation reactions were conducted in water in the presence of the surfactant CTAB to enhance the solubility of the hydrophobic substrates. Hence, they mimic the emulsion–solid transfer (EST) approach previously reported by Abu-Reziq et al. that combined emulsion systems and xerogels [64]. Fortunately, the microreactors delivered the corresponding alcohols products with excellent yields and enantioselectivities. Moreover, the microreactors maintained their high catalytic activity even after being employed in four consecutive cycles. To cite another example, Natour et al. described the preparation of catalytic solid lipid particles by combining O/W emulsions and the sol–gel mediated interfacial polymerization of TEOS. The lipid was composed of polyethyleneimine modified with oleic acid [65]. Here, the authors aimed to synthesize microcapsules that comprised solid cores. Therefore, they decided to mix the amine-modified lipid with paraffin oil and TEOS. The whole microencapsulation procedure was then performed at 80 °C in order to melt the core mixture and maintain it in liquid form until the process was completed. Afterwards, the obtained solid particles were successfully applied in the Knoevenagel condensation of various aromatic aldehydes with malononitrile and other active hydrogen compounds in triple distilled water (TDW).

1.3.2 Polymeric Supports

Several organic polymers such as insoluble and soluble polymers have been investigated as catalyst supports due to their easy synthesis and facile separation by filtration [9, 25, 26].

1.3.2.1 Insoluble Polymers

Insoluble polymers, also known as cross-linked polymers, have been used as catalyst support since they are easy to synthesize, chemically inert, inexpensive, and easily separated from the reaction medium by filtration. Such polymers can be prepared using suspension polymerization technique [66, 67]. In this process, organic medium comprised of monomer(s), radical initiator, and stabilizing (surfactants) and cross-linking agents are dispersed and stirred in aqueous medium. Using different types and concentrations of these parameters will afford resins in different sizes and degree of cross-linking.

In 1963, Merrifield reported the synthesis of the first insoluble chloromethylated cross-linked resin from copolymers styrene and divinylbenzene and utilized it for supporting peptides [68]. Since this study, myriad of polystyrene-based cross-linked resins (macroporous or microporous) have been developed, commercialized, and utilized in organic synthesis and catalysis as supports for various metal complexes and organocatalysts [69–72].

Additional group of polymers used as catalyst supports is ion-exchange resins (cationic and anionic), which are mostly comprised of functionalized cross-linked polystyrene-divinylbenzene copolymer [73–75]. Ion-exchange resins are employed for supporting metal NPs such as Pt, Rh, Pd, Au, and Ru within the pores of the framework through non-covalent interactions. The metal NPs are electrostatically and sterically stabilized via the charged functional groups and matrix porosity [76].

Despite the advantages of the insoluble polymer supported catalysts such as easy separation and catalyst recovery, enhanced catalytic stability and sometimes improved selectivity encounter certain drawbacks such as low loading capacity and brittleness. Moreover, diminished catalyst activity compared with the homogeneous counterpart is obtained since reagents' and solvents' diffusivity and accessibility into the catalytic sites are hindered as a result of the high degree of cross-linking; hence they are unfeasible for large-scale production [26].

1.3.2.2 Soluble Polymers

In the early 1970s, viable alternative supports based on soluble polymers have been proposed in order to overcome the limitations associated with the insoluble polymers [77, 78]. Soluble polymers gained much attention in catalysis since they provide homogeneous environment, mimicking the activity of non-supported catalyst, and can be recovered by filtration/membrane filtration, solvent precipitation, and liquid–liquid extraction [26, 79–82]. These polymers are generally classified into two main groups: linear polymers and branched polymers.

Among the existing soluble linear polymers, polyethylene glycol (PEG), monomethylated PEG, and non-cross-linked polystyrene are mostly employed for immobilization of a wide variety of metal complexes and organocatalysts [72, 83]. These polymers are soluble in some solvents and can be precipitated and isolated by adding anti-solvent. For example, PEGs are soluble in polar solvents such as water and dimethyl sulfoxide (DMSO), while insoluble in nonpolar solvents such as diethyl ether and hexane [84, 85]. Therefore, supported catalysts on PEGs behave as homogeneous catalysts in polar solvents and can be readily

precipitated and recovered with decreasing the polarity of the reaction medium via addition of nonpolar solvent.

Different organometallic complexes and organocatalysts either have been immobilized on soluble linear polymers by anchoring them on the terminal sites of the polymer forming end group functionalized polymeric support or have been introduced along the polymer chain [86–90].

Linear polymers have limited solubility in organic solvents, high melting points and T_g , and relatively low loading capacity. Overcoming these disadvantages can be achieved by using branched polymers such as dendrimers.

Dendrimers are nanostructured materials with a discrete well-defined and organized tree-like structure constructed of a central core, branching units, and peripheral groups [91–93]. They proved to be applicable in various fields such as in biomedicine and biotechnology, electrical field, and catalysis, as their symmetrical architecture provides great degree of surface functionalities, which allows versatile chemical modifications. In addition, it is defined with unique features such as uniform size, multivalency, and defined molecular weight [94–96].

Dendrimers are used in catalysis since they combine the merits of homogeneous and heterogeneous catalysis. They are soluble in different organic and can be recovered by precipitation and nanofiltration methods [97]. As opposed to the linear polymers, dendrimers are synthesized in a controlled step-by-step process and, therefore, have more defined molecular structure. Two main approaches are used for the synthesis of dendrimers: divergent and convergent approaches [98–100]. In divergent approach, the dendrimer is synthesized in a stepwise manner starting from the core on which the next generations are built in a sequential process via coupling reactions (core to periphery). While in convergent approach, initially introduced by Hawker and Fréchet in 1990 [101], the dendrimer is synthesized starting from preparation of dendrons, which later are coupled to a multifunctional core (periphery to core).

Varieties of dendritic catalysts with tunable catalytic activity and selectivity have been prepared by introducing catalysts in the core, on the branches, or on the peripheral sites [102, 103]. For example, in 1995, Brunner reported the synthesis of catalytic dendritic system comprised of chiral rhodium–diphosphine complex as catalytic core functionalized with menthyl containing dendrimer for the hydrogenation reaction acetamidocinnamic acid. This system afforded the desired product however with very low enantioselectivities [102]. Confined catalysts at the core of the dendrimers generally suffer from reduced reaction rate and catalytic activity due to low catalyst loading. Additionally, the steric crowding that aroused from the dendritic branches leads to the isolation of the catalyst from the reaction medium, and therefore substrates' accessibility to the active site is decreased. Overcoming this obstacle could be achieved by encapsulating or attaching the catalyst within the dendritic backbone (branches), which provide a localized environment for binding catalytic species [93]. Additionally, the dendrimer branches serve as templates for controlling the size and stability of the catalytic metal NPs and prevent their agglomeration. Also it acts as a selective gate to control the access and diffusivity of substrates to the catalytic sites and out [103].

1.3.2.3 Polymeric Microcapsules

In 1998, Kobayashi was the first to apply the microencapsulation technique for immobilizing metal catalysts onto polymers. In this study, Lewis acid scandium trifluoromethanesulfonate (scandium triflate, $\text{Sc}(\text{OTf})_3$) was microencapsulated in polystyrene using coacervation process and employed in Lewis acid catalyzed carbon–carbon bond-forming reactions. The catalyst was recovered by simple filtration and recycled several times without exhibiting decrease in the catalytic activity [104].

Since this study, myriad of heterogeneous catalytic systems based on microencapsulation process using physical techniques have been reported [105–108]. For example, palladium, platinum, and ruthenium catalysts were encapsulated in cross-linked polymer based on styrene, 4-vinylbenzyl glycidyl ether, and methacrylic acid or alcohol using polymer incarcerated method, and applied in various catalytic reactions [59, 109–111]. However, in these processes the polymer needs to be dissolved in organic solvents, therefore in certain cases swelling and leaching of catalysts occur. Furthermore, they are time- and energy-consuming processes. Overcoming such drawbacks can be achieved by employing chemical encapsulation technique such as *in situ* interfacial polymerization and polycondensation [112–114].

Interfacial polymerization is a straightforward and simple method for the synthesis of condensation polymers affording high yields of product. Also it is relatively cheap, moderate to fast synthetic process allowing control over capsules mean size and shell thickness and does not require reactant stoichiometric balance. Interfacial polymerization approach involves emulsification process and reaction between complementary monomers or pre-polymer at the interface of two immiscible phases (emulsion). In general there are three types of emulsion systems used in this technique as templates: O/W, W/O, and oil-in-oil (O/O) emulsions [113, 115–119].

Mostly, polyurea (PU) was found to be suitable for encapsulation of catalysts due to its chemical and mechanical stability and facile and fast synthesis and because it is relatively cheap and environmentally friendly [120, 121]. PU capsules can be fabricated using O/W, W/O, and O/O emulsions, in the presence of suitable surfactant, followed by interfacial polymerization between amines and diisocyanates monomers dissolved in aqueous (or polar organic solvent) and non-polar organic phase [122–125].

In 2002, Ramarao and Ley et al. were one of the first to report the encapsulation of catalyst within PU microcapsules. They encapsulated palladium acetate and palladium NPs within PU matrix ($\text{PdEnCat}^{\text{TM}}$) using interfacial polymerization approach. These catalytic microcapsules showed good catalytic activity and recyclability in different cross-coupling reactions such as Suzuki, Heck, Stille, and carbonylation and in hydrogenation reactions [126, 127]. The catalyst was recovered from the reaction medium by filtration and reused four times without exhibiting any significant loss in catalytic activity. However, the active catalytic system required high catalyst loading (up to 5 mol%) and hydrogen pressure (~50 bar) for activating the catalyst over the period of 48 hours. In 2003, they prepared PU encapsulated palladium NPs (Pd^0EnCat) by reducing encapsulated palladium acetate with formic acid and applied it in transfer hydrogenation

and reductive ring-opening hydrogenolysis of epoxides [128]. Inspired by this work, McQuade and coworkers demonstrated the microencapsulation of 4-(*N,N*-dimethylamino)-pyridine (DMAP)-modified linear polystyrene within PU capsules [129]. They demonstrated that their catalyst has better catalytic activity compared with DMAP supported on cross-linked polystyrene and is readily tunable. Additionally, they exhibited the effect of the shell thickness on the reaction rate and activity and showed that the encapsulated catalyst has better activity compared to the attached catalyst on insoluble support.

1.3.3 Other Supports

All the aforementioned heterogeneous catalytic systems are highly efficient due to the limited usage of natural resources and can be easily recovered and recycled from the reaction medium by utilizing simple physical separation techniques such as filtration, extraction, decantation, and centrifugation. However, their catalytic activity in general lacks behind their homogeneous counterparts due to lower surface area to volume ratio, which leads to reduced contact between the substrate and the catalytic active sites. To circumvent this problem, numerous studies have led to the development of alternative catalytic systems especially those with high surface areas. Materials with high surface areas that have attracted much attention in the last two decades because of their potential in a wide range of applications, particularly in catalysis, are presented in the Sections 1.3.3.1–1.3.3.4.

1.3.3.1 Metal–Organic Frameworks (MOFs)

Metal–organic frameworks (MOFs) and their derivatives consist of metal ions or clusters coordinated to bridging organic ligands [130]. They require a minimum amount of metal ions and organic ligands to form predictable porous solid structures with high surface areas and pore volumes [120]. These materials have been found to be very promising for applications in the heterogeneous catalysis owing to their unique properties such as high porosity and crystallinity and to the possibility to easily tune their pore size, shape, and chemical environment [131, 132]. There are different approaches for using MOFs as catalysts. The first approach is based on utilizing as-synthesized active MOFs in catalytic transformations. These MOFs contain coordinatively unsaturated sites that can facilitate the coordination of substrates with the metallic sites [133]. Anchoring catalytic active species to the metal ions in MOFs containing coordination vacancies is another possibility for preparing heterogeneous catalysts. Another approach is based on using organic linkers containing functional groups that can be used for immobilization of organometallic complexes or organocatalysts [123]. Encapsulation of catalytic species inside MOFs is mostly used as strategy for preparing solid catalysts [134–137]. Although MOFs seem to be highly efficient as a catalyst support, there are still some drawbacks that can limit practical applications related to their low thermal stability and the possibility for degradation of the framework in certain media. In addition, the leaching of metal ions or organic components can be detected under catalysis conditions.

1.3.3.2 Periodic Mesoporous Organosilicas (PMOs)

A significant breakthrough in porous materials came in the year 1999 by three research groups who independently discovered the PMOs [138–140]. PMOs materials have soon took their special position in the field of organic–inorganic hybrid materials [141–146] and were investigated intensively because of their highly promising potential in a wide range of applications as optical materials, adsorbents, trapping agents, drug delivery agents, and catalyst supports [147–152]. The success in this term is mainly attributed to the convenient preparation of these PMOs. Within few years, PMOs with myriad bridging organic groups, narrow distribution pore sizes, and well-defined pore geometries have been synthesized and characterized [153–156]. Generally, PMOs are synthesized by sol–gel process under mild conditions, and their preparation is based on the hydrolysis and condensation of bridged organo-alkoxysilane precursor compounds, $(\text{OR})_3\text{Si}-\text{R}-\text{Si}(\text{OR})_3$, in the presence of surfactants or block copolymers, which assist to create uniform pores in the size of 2–30 nm [157–160]. The organic moieties of the PMOs are implemented directly and distributed homogeneously within the inorganic walls. This organic hybridization of the silicate network permits precise control over the surface properties, modification of the hydrophilic/hydrophobic character of the surface, alteration of the surface reactivity, protection of the surface from attack, and modification of the bulk properties of these materials [161, 162]. The surface area of PMOs can reach up to 1800 m²/g, which makes these materials particularly attractive for the various applications especially catalysis. Mostly, immobilization of catalysts within the pores of PMOs is performed by co-condensation the bridging silane monomers and the catalysts functionalized with silane groups [36, 149, 150, 162].

1.3.3.3 Magnetic Nanoparticles

Magnetic nanomaterials have attracted significant interest as support for catalytic systems as metal complexes, organocatalysts, enzymes, or metal NPs. Among their unique properties, most functional to heterogeneous catalysis is the superparamagnetism, which can be instrumental for their efficient separation and recovery of catalyst. Magnetic separation complies with green chemistry principles, as the simplified work-up procedure may lead to the elimination of tedious separation techniques and minimizes or avoid the usage of additional organic solvents. Magnetite (Fe_3O_4) is the most exploited iron oxide nanomaterial used for magnetic separation. The surface of MNPs can be modified simple by non-covalent adsorption of surfactants, polymers, or bifunctional molecules or by coating the magnetic core with protective layers like silica, carbon, metal, and polymer shell that can be easily functionalized for binding various catalytic species [24, 28, 163–170].

1.3.3.4 Membranes

Monolithic inorganic materials (ceramics membranes) or organic polymeric membranes can be also efficaciously used as support for catalysts. Membranes are also regarded as multifunctional reactors due to the unique possibility they

offer to combine a chemical reaction, promoted by the immobilized catalyst, with the membrane-based separation. With the catalyst immobilized inside the membrane, no separation of the catalyst from the reaction medium is necessary for its reuse. Furthermore, membrane catalysts are very stable, have a high surface area, and can be adopted to construct flow reactors for a best contact between the reactant mixture and the catalyst for continuous reactions [171–175].

1.4 Characterization of Heterogeneous Catalysts

The characterization of a heterogeneous material used as catalyst is a fundamental aspect for the heterogeneous catalysis. In fact, the accessibility of the catalytic sites of a heterogeneous system, the preservation of the catalytic efficiency once immobilized, its adequacy to the reaction conditions, and its stability and durability over the time and over the quantity of material converted are all key features that to be evaluated or determined require trustworthy characterization technologies. Characterization of the fresh as well as the recovered heterogeneous catalytic systems is crucial to assess the quality and the efficiency of a catalytic system and to direct the proper design of the support for the optimization of the catalytic efficiency of a selected system.

To establish if the homogeneous catalyst is successfully immobilized on the support, if the support and the catalyst are affected by the immobilization process and also to evaluate the stability of supported catalyst under the reaction conditions, a full characterization of the catalytic materials by analytical and spectroscopic techniques is required.

The surface structures can be physically explored by advanced surface characterization spectroscopic techniques: e.g. IR and UV–Vis are used to monitor the modification of support and the catalytic sites after chemical treatment; solid-state NMR spectroscopy can provide information on the chemical structure especially in the close environment of the catalytic center; X-ray diffraction is also often used to investigate the crystalline structure of the support after its immobilization and after each catalytic cycle; X-ray photoelectronic spectroscopy (XPS) is a key tool to determine the chemical and electronic state of surface atoms, which is generally extremely useful and fundamental in the cases where a metal catalyst varies its oxidation state under the reaction conditions; electron paramagnetic resonance (EPR) is used for the characterization of unpaired electrons species; transmission electron microscopy (TEM) is of general utility to obtain images of the surface of the materials at nanoscale and get information about leaching or aggregation of the catalytic species immobilized; and N_2 adsorption–desorption isotherm provide information about the specific surface area, pore size distribution, and pore volume of porous materials.

While thermogravimetric analysis (TGA) measures the weight loss of a materials as a function of temperature and it is generally used to confirm the incorporation of catalyst in the hosting support, elemental analysis is a unique fundamental

technique that allows to obtain the elemental composition of the catalytic materials, and often it represents the only tool for assessing the catalyst loading with precision. Associated with the loading and leaching of metal catalytic species from the support, inductively coupled plasma-atomic emission spectroscopy (ICP-AES) is used to determine the metal species both on the support and in solution; when the leached concentration is very low, ICP combined with mass spectrometry (ICP-MS) is preferred allowing to reach ppb levels.

1.5 Conclusions

In conclusion, heterogeneous catalysis is certainly a fascinating multidisciplinary arena where different joining efforts from different areas of expertise are needed to set a credible strategy for the preparation, characterization, and use of stable, highly active, and durable catalytic systems.

The type of chemically relevant and interesting catalytic systems is wide as it is variable and the efficiency of all the possible strategies can be used for the effective preparation of a solid catalyst. From the simplest purely inorganic or organic catalysts to complex enzymatic catalytic systems, the common goal is to create a stable yet highly effective material able to show durable catalytic performances over the time and over the mass of material converted. At this aim the challenge for modern chemists is to develop tailor-made synthetic technologies for the preparation and/or the immobilization of heterogeneous catalysts and to define characterization tools for the correct evaluation of their chemical efficiency.

As witnessed by the different contributions present in this book, recent developments confirm that there already exist several promising routes to make heterogeneous catalysis a generally competitive and sustainable strategy to replace classic homogeneous catalysis in the modern chemical production.

List of Abbreviations

CTAB	cetyltrimethylammonium bromide
DMAP	4-(<i>N,N</i> -dimethylamino)-pyridine
DMSO	dimethyl sulfoxide
EST	emulsion–solid transfer
MOFs	metal–organic frameworks
NPs	nanoparticles
O/O	oil-in-oil
O/W	oil-in-water
PEG	polyethylene glycol
PMOs	periodic mesoporous organosilicas
PU	polyurea
Ru–TsDPEN	(1 <i>R</i> ,2 <i>R</i>)- <i>N</i> -(<i>p</i> -tolylsulfonyl)-1,2-diphenylethylenediamine
TDW	triple distilled water
TEOS	tetraethyl orthosilicate
W/O	water-in-oil

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