

Introduction to Room-Temperature Catalysis

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1.1 Introduction

The world's energy demand is expected to increase significantly in the coming years as a result of the exponential economic growth of emerging countries, BRIC (Brazil, Russia, India, and China). Such an increased energy request is closely associated with environmental concerns and deficiency in water supply. These key challenges should be addressed by creating and maintaining conditions that allow humans and nature to exist in productive harmony. Only such a sustainable direction will permit fulfilling the social, environmental, and economic requirements of present and future generations and avoid the world passing the point of no return [1].

Chemistry has always played a pivotal role in development of societies by improving the quality of life, the lifespan, and so on. However, despite its many important progresses, chemistry is often recognized more as a problem than as the solution to our daily needs. Indeed, the task of changing the persisting vision that society and governments uphold about chemistry is one of the biggest challenges of chemists for the 21st century; this challenge should start from the design and development of benign and efficient manufacture protocols. To improve chemical production efficiency and fulfill international legislation, a multidisciplinary approach aimed at reducing by-products/waste, optimizing energy utilization, controlling emissions (climatic change), and using renewable materials to avoid hazardous or toxic substances is mandatory. In this connection, the "Green Chemistry" concept, being a list of 12 principles, is one of the most exciting, innovative, and realistic approaches that has emerged in order to minimize the drawbacks of chemical processing and contribute to the protection of the environment [2]. "Green Chemistry" advocates increasing research on new renewable feedstocks, environmentally benign solvents (preferably water), catalysis, and greener technologies, processes, and products. Among the "Green Chemistry" principles, the ninth, focused on catalysis, plays

a key role in certifying the world's sustainability by improving processes in the chemical industry, making them more efficient and benign. The development of greener catalytic protocols through the rational design of new catalysts, both homogeneous and heterogeneous, as well as solvent choice is important as it will increase valuation and understanding at the government level and in society.

A “catalyst” is a substance that increases the rate at which a chemical reaction proceeds without itself becoming permanently involved. There are many fundamental parameters in a chemical reaction that can be controlled by selecting the appropriate catalyst, including, for example, energy consumption, selectivity, productivity, and atom economy. Accordingly, the development of new catalysts or catalytic systems can be considered as an important step toward establishing a more green and sustainable chemical industry. In this regard, the design of more effective catalysts and catalytic protocols that allow a chemical process to be carried out at room temperature is a highly beneficial way to minimize both the energy demand and the risk (minimizing safety issues) for employees of a chemical plant. Furthermore, by decreasing the reaction temperature, the selectivity toward the desired product normally increases, thereby minimizing undesired side reactions and by-products. On the other hand, the reaction kinetics can be significantly hampered at room temperature and the catalyst should therefore be selected carefully to provide a system having a sufficiently low activation energy that allows the reaction to proceed at an acceptable rate without auxiliary energy input. Such selected catalysts for room-temperature reaction protocols can be both homogeneous (e.g., organometallic complexes, ionic liquids) and heterogeneous (e.g., metal nanoparticles, supported nanoparticles). Recently, excellent reviews by Lam and Luque have covered this topic in detail [3].

The aim of this chapter is to provide an overview and point out some of the most relevant catalytic systems that allow carrying out catalytic reactions at room temperature. The catalytic systems will be divided in two main groups depending on the nature of the catalyst involved, namely, (i) ionic liquids and (ii) homogeneous and heterogeneous catalyst-containing transition metals from groups 9 to 11 of the periodic table.

1.2 Room-Temperature Homogeneous Catalysts

Homogeneous catalysts are often superior to heterogeneous ones in terms of activity and, in particular, selectivity. In addition, the reaction conditions (temperature, pressure, etc.) are usually milder. However, homogeneous catalysis is hampered by other important issues from an industrial or applicability point of view, such as catalyst recovery and recyclability.

1.2.1 Ionic-Liquid-Based Catalytic Systems at Room Temperature

Ionic liquids are defined as salts only composed of ions, which melt without being decomposed. A special group of ionic liquids are the so-called room-temperature ionic liquids, which are liquid below 100 °C. The first known ionic liquid (ethanolammonium nitrate) was reported in 1888 by Gabriel and Weiner [4]. Later in 1914, Walden reported the synthesis of other ionic liquids

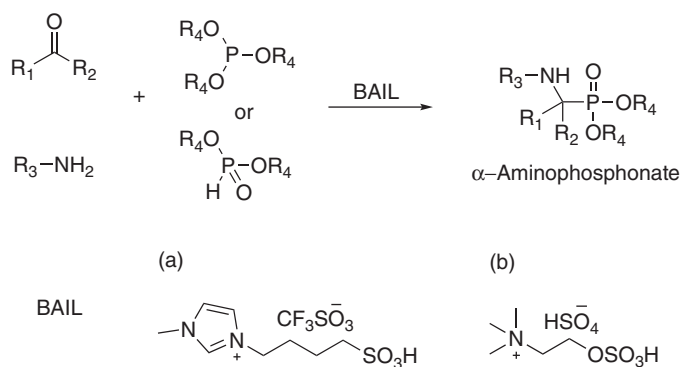


Figure 1.1 Brønsted acidic ionic liquids (BAILs) used as catalyst in the synthesis of α -aminophosphonates in a one-pot, three-component reaction. (Adapted with permission from Ref. [8]. Copyright (2014) Wiley.)

such as, for example, ethylammonium nitrate [5], but it was only in 1943 that the term “ionic liquid” was coined by Barrer [6]. In the 1970s to the 1990s, novel ionic liquids were developed and studied by US military researchers to be applied mainly as electrolytes in batteries [7]. In the past 15 years, ionic liquids have become of great importance for scientists due to their unique properties, mainly their low vapor pressure, solubility, easy functionalization (task-specific ionic liquids), and their successful applications in catalysis, nanoparticle stabilization, electrochemistry, medicine, analytical methods, benign reaction media, and so on. One main advantage of ionic liquids is the huge pool available. In principle, this allows the possibility of selecting just the right ionic liquid for a specific application. In catalysis, the selection of the ionic liquid is determined mainly by solubility characteristics (providing often biphasic systems that allow the recovery of the employed catalyst), intrinsic catalytic properties, as well as their thermal and chemical stability. Here, we overview some reactions that are conducted at room temperature in the presence of ionic liquids as catalyst and/or reaction media.

An important subgroup of ionic liquids are the so-called acidic ionic liquids, where a Brønsted or Lewis acid functionality is part of the ionic liquid ions. They have been used to replace traditional mineral acids ($MeSO_3H$, H_2SO_4 , HF) or traditional Lewis acids ($AlCl_3$, $FeCl_3$) successfully and, often, with superior performance. In organic synthesis, the acidic ionic liquids have been extensively used and numerous reports have come out in the past years concerning their use as solvents or catalysts at room temperature. Since it is not possible to survey all these applications, representative examples will be pointed out to show the potential of the acidic ionic liquids in organic synthesis.

α -Aminophosphonates are compounds of great interest due to their biological and chemical applications (antibacterial, antitumor, antiviral, enzyme inhibitors). The synthesis of these compounds is normally carried out through the so-called Kabachnik–Fields reaction in the presence of a dehydrating agent and a Lewis acid. In 2009, Akbari and Heydari used a Brønsted acidic ionic liquid (BAIL) (Figure 1.1a) as catalyst instead of the Lewis acid for the synthesis of α -aminophosphonates through a one-pot, three-component (phosphite,

aldehyde or ketone, and amine) reaction [9]. They got excellent results in terms of yield (up to 98%) in short reaction times at room temperature. Furthermore, the employed BAIL catalyst could be recovered and reused up to six times without any deactivation. In 2010, Fang *et al.* prepared a series of “halogen-free” BAILS to be tested as catalysts in the same reaction and obtained good results at room temperature in aqueous media [10]. In 2014, Peng *et al.* prepared a different BAIL based on the choline cation (Figure 1.1b), also to be used as catalyst in the same one-pot, three-component reaction. They claimed that their synthesized choline-based BAIL was cheaper and less toxic than the one previously reported by Akbari and Heydari [9]. Excellent results were obtained under solvent-free conditions at room temperature in short time reactions with isolated yields up to 95%. The recyclability of the catalyst was also tested up to six times without any decrease in activity or degradation of the BAIL [8].

In a recent work, Ying *et al.* [11] showed the effectiveness in terms of activity and recyclability of using multiple-acidic ionic liquids as catalysts for the synthesis of α -aminophosphonates at room temperature under solvent-free conditions. The same authors used the multiple-acidic ionic liquids in the synthesis of bis-indolylmethanes (Figure 1.2), compounds with biological activity and of great interest in the medical chemistry, under solvent-free conditions and at room temperature. Among the applied multiple-acidic ionic liquids, [TEOA][HSO₄] (triethanolammonium hydrogensulfate) showed the best performance, giving the products in excellent yield (up to 90%) after a few minutes of reaction. In addition, the catalytic system was reused up to five times without showing any sign of deactivation [12].

The protection of hydroxyl groups is an essential task in organic synthesis to avoid unwanted reactions where, for example, Grignard or alkyllithium reagents are involved. In this connection, acidic ionic liquids have shown to be alternatives to commonly used volatile organic solvents in the protection of alcohols at room temperature with excellent yields in less than 5 min reaction, making the overall process safer and greener [13]. The esterification of carboxylic acids with alcohols is a reaction of great interest because it yields esters that are valuable intermediates in the chemical industry. Chloroaluminate-based acidic ionic liquids, as substitutes of inorganic acids, were first tested in the esterification reaction by Deng *et al.* [14]. The authors highlight two main advantages of using

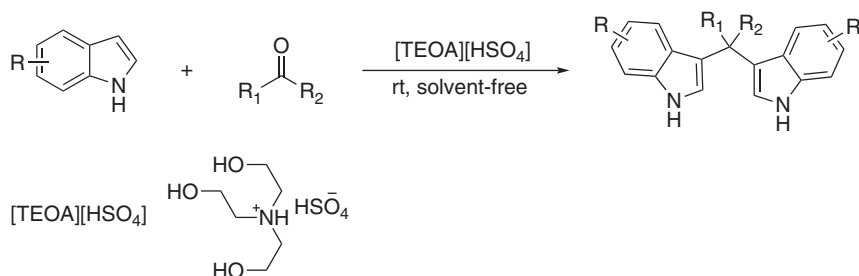


Figure 1.2 Multiple-acidic ionic liquids in the synthesis of bis-indolylmethanes. (Adapted with permission from Ref. [12]. Copyright (2014) Elsevier.)

chloroaluminate-based acidic ionic liquids instead of, for example, sulfuric acid: (i) The insolubility of the produced esters facilitate easy separation from the reaction media and (ii) the recovery and reuse of the employed ionic liquid after removing the water formed during the reaction. Despite these advantages, the well-known high sensitivity of this kind of acidic ionic liquids to moisture or organic acids make them nonideal candidates for the esterification reaction since one of the by-products is water. Esterification of alcohols with acetic acid anhydride was probed to proceed in the presence of BAILs at room temperature, achieving good conversion without detecting any side reactions. Furthermore, due to the insolubility of most of the esters into the ionic liquids, the catalytic system allowed to be recycled and reused up to five times with only a small decrease in activity due to the loss of ionic liquid during the recycling procedure [15]. Upgrading of bio-oil in order to extend the range of its application could be achieved through a Fischer esterification with alcohols in the presence of dicationic ionic liquids with Brønsted acidity at room temperature, overcoming moisture and acidity problems related to bio-oil (Table 1.1) [16].

The Diels–Alder reaction is an important organic reaction for the synthesis of natural products and physiologically active molecules, and any improvement in the reaction rate and/or the selectivity is of special interest. In 1999, chloroaluminate-based ionic liquids were tested in the room-temperature Diels–Alder reaction between cyclopentadiene and methylacrylate as a test reaction. The employed ionic liquid showed to be superior to the traditional organic solvents employed so far, yielding high conversion and higher endo/exo selectivity [17]. In the Diels–Alder reaction between cyclopentene and methylacrylate, the selectivity toward the endo product was attributed by Welton and coworkers to the ability of the employed ionic liquid to form H-bonds with the dienophile. The use of ionic liquids offers the potential to be used as solvents for Diels–Alder reactions, substituting even the traditional Lewis acids and extending the application to other reagents that can be sensitive to moisture, oxygen, or to strong Lewis acids [18]. Chiral ionic liquids are an interesting kind of ionic liquids that theoretically could transfer their chirality to the final

Table 1.1 Properties of crude and upgraded oil.

Properties	Crude oil	Upgraded oil
Moisture (wt%)	32.8	8.2
pH	2.9	5.1
Kinematic viscosity ($\text{mm}^2 \text{s}^{-1}$)	13.03	4.90
High heating value (MJ kg^{-1})	17.3	24.6
C (%)	41.82	50.64
H (%)	8.75	10.77
O (%)	48.73	38.03
N (%)	0.64	0.39

Source: Xiong *et al.* 2009 [16]. Adapted with permission of American Chemical Society.

product when applied as solvent, making them highly attractive for asymmetric synthesis. In this sense, the asymmetric aza-Diels–Alder reaction between asymmetric amines and the Danishefsky's diene was carried out successfully with moderate to high diastereoselectivity at room temperature using a chiral ionic liquid catalyst/reaction media without the presence of Lewis acids or organic solvents [19]. Many other ionic liquids – with or without special modifications – have also been used successfully at room temperature in other organic asymmetric and nonasymmetric reactions, such as Knoevenagel condensation [20–22], asymmetric aldol condensation [23], and so on. In general, the use of ionic liquids has demonstrated their potential to make chemical reactions safer, greener, and energetically more efficient; and, in many cases, the use of the ionic liquids allows the formation of biphasic systems that make product separation and reutilization of the catalysts easy. However, their application at the industrial level is still hampered by their relatively high viscosity and price level compared to common reaction media, which give rise to concerns about mass transfer limitations and process economy due to the large amounts required. Hence, to overcome these problems, development of improved ionic liquids and associated technology is needed in the future.

1.2.2 Transition Metal Homogeneous Catalysts

Transition metals, and mainly their organometallic complexes, represent a benchmark in homogeneous catalysis. The complexes are special because their electronic and steric properties – which normally rule the catalytic reaction – can be modified and fine-tuned by choosing the appropriate metal and rational design of the ligand. Transition-metal-based homogeneous catalysts are well known to catalyze many reactions of industrial interest, such as polymerization, carbonylation, hydrogenation, oxidation, cross-coupling, epoxidation, and so on, and have historically contributed to develop systems that work under mild conditions. However, the use of such homogeneous catalysts is hampered by their recovery and separation from the reaction media, which normally is energy intensive. Only a limited number of examples of transition-metal-based catalysts operating at room temperature are reported. Here, a few late transition catalysts – mainly with metals from the groups 9 to 11 – and their performance in reactions at room temperature are discussed.

1.2.2.1 Group 9-Based Homogeneous Catalysts (Co, Rh, Ir)

Homogeneous hydrogenation of arenes at room temperature was performed in 1977 by Muettterties and coworkers with a cobalt complex catalyst, $\eta^3\text{-C}_3\text{H}_5\text{Co}[\text{P}(\text{OCH}_3)_3]_3$ [24]. Such reactions were earlier dominated by heterogeneous metallic systems based mainly on Ni, Pd, Pt and Rh, but these systems were hampered by lack of stereo- and chemoselectivity. The use of homogeneous catalysts enabled the possibility of getting systems where good stereoselectivity as well as chemoselectivity could be achieved.

A rhodium-based catalyst, $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$, was tested in the homogeneous carbonylation of liquefied propane at room temperature yielding butanal with high selectivity [25]. This catalytic system was shown to be a promising

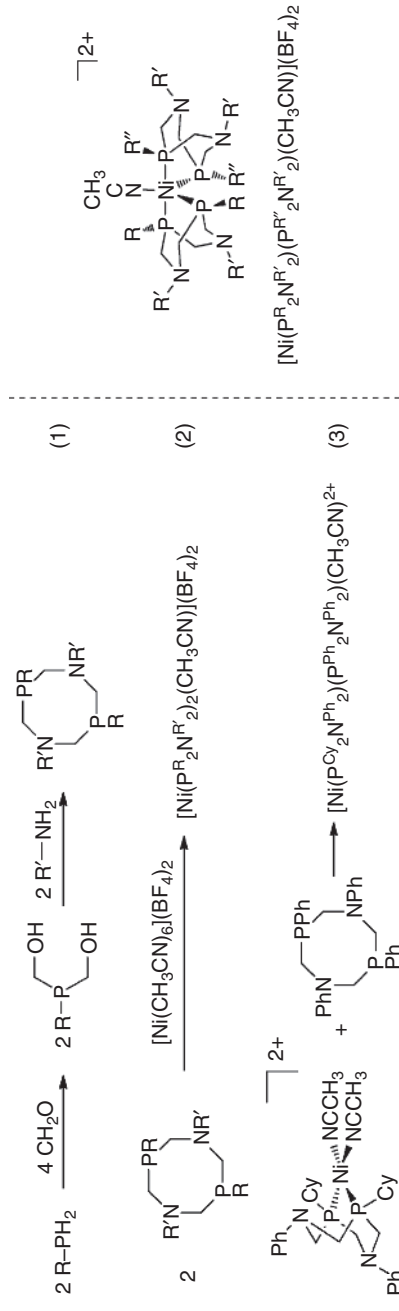
alternative for the selective functionalization of gaseous alkanes. A series of water-soluble rhodium complexes obtained by reaction of rhodium precursors with 1,3,5-triaza-7-phosphaadamantane (PTA) were used as catalysts in the isomerization and condensation of allylic alcohol at room temperature in aqueous media, showing advantages over commercial methods [26]. The selectivity of the reaction was easily controlled by the amount of base added, obtaining one of the products in quantitative yield. In addition, these water-soluble catalysts allowed also catalyst recovery and reutilization, making the overall process greener and energetically efficient. Another water-soluble Rh(I)-complex, $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ ($\text{TPPTS} = m\text{-P}(\text{C}_6\text{H}_4\text{SO}_3\text{Na})_3$), was used successfully in the polymerization of terminal alkynes at room temperature under mild reaction conditions. The reactions were carried out under biphasic conditions, which allowed the recovery and reutilization of the catalytic system [27]. The polymerization of these alkynes yielded conjugated systems that are interesting due to their photosensitivity and optical nonlinear susceptibility. The first polymerization of terminal alkynes was performed by Natta using Ziegler catalysts in 1958 [28]. The homogeneous hydrogenation of olefins and acetylenes was carried out efficiently at room temperature and atmospheric pressure of hydrogen with an iridium-based catalyst, $[\text{Ir}(\sigma\text{-carb})(\text{CO})(\text{PhCN})(\text{PPh}_3)]$ ($\sigma\text{-carb} = 7\text{-C}_6\text{H}_5\text{-1,2-C}_2\text{B}_{10}\text{H}_{10}$) [29].

1.2.2.2 Group 10-Based Homogeneous Catalysts (Ni, Pd, Pt)

Among group 10 metals, Ni is more attractive and preferable as catalyst since it is cheaper than Pd and Pt. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was used as a homogeneous catalyst at room temperature for the production of 2-((1*H*-benzo[*d*]imidazol-2-ylamino)(aryl)methylthio)acetates in a multicomponent reaction (MCR) [30].

$[\text{Ni}(\text{P}_2\text{N}^{\text{R}'}_2)_2(\text{CH}_3\text{CN})]^{2+}$ complexes (Scheme 1.1) are the first example of homogeneous catalysts employed successfully in the electrocatalytic oxidation of formate to be used in fuel cells [31]. Mechanistic studies showed that the pendant amine plays the main role in the rate-determining step that involves the transfer of a proton from the formate to the amine. The turnover frequencies (TOFs) for the catalyst employed were comparable to any other reported formate/formic acid oxidation catalysts. Asymmetric α -arylation of ketones with chloro- and bromoarenes has been catalyzed by a homogeneous Ni(0)-complex, $[(R)\text{-BINAP}]\text{Ni}(\eta^2\text{-NC-Ph})$ ($(R)\text{-BINAP} = (R)\text{-}(+)\text{-}(1,1'\text{-Binaphthalene-2,2'\text{-diyl)bis(diphenylphosphine)}$), in toluene at room temperature at high reaction rates with excellent yield (up to 91% and above 98% of enantiomeric excess, ee) [32]. The advantage of running the reaction at room temperature is the attenuation of the decomposition of the Ni(0) complex to form the less active Ni(I) species.

Water extract of rice straw ash (WERSA) was employed as reaction media together with $\text{Pd}(\text{OAc})_2$ without the presence of any ligand, base, or promoter in the Suzuki–Miyaura cross-coupling reaction at room temperature of different bromoaryl compounds and arylboronic acids, yielding good to excellent conversions [33]. WERSA was prepared by burning the rice straw to ashes that were further suspended in water and filtered off (Figure 1.3). Since WERSA is composed of different cations and anions and due to its basic nature (Na^+ ,



Scheme 1.1 Synthetic procedure for $[\text{Ni}(\text{P}^{\text{R}}_2\text{N}^{\text{R}'})_2(\text{CH}_3\text{CN})]^{2+}$ complexes. (Galan *et al.* 2012 [31]. Reproduced with permission of American Chemical Society.)

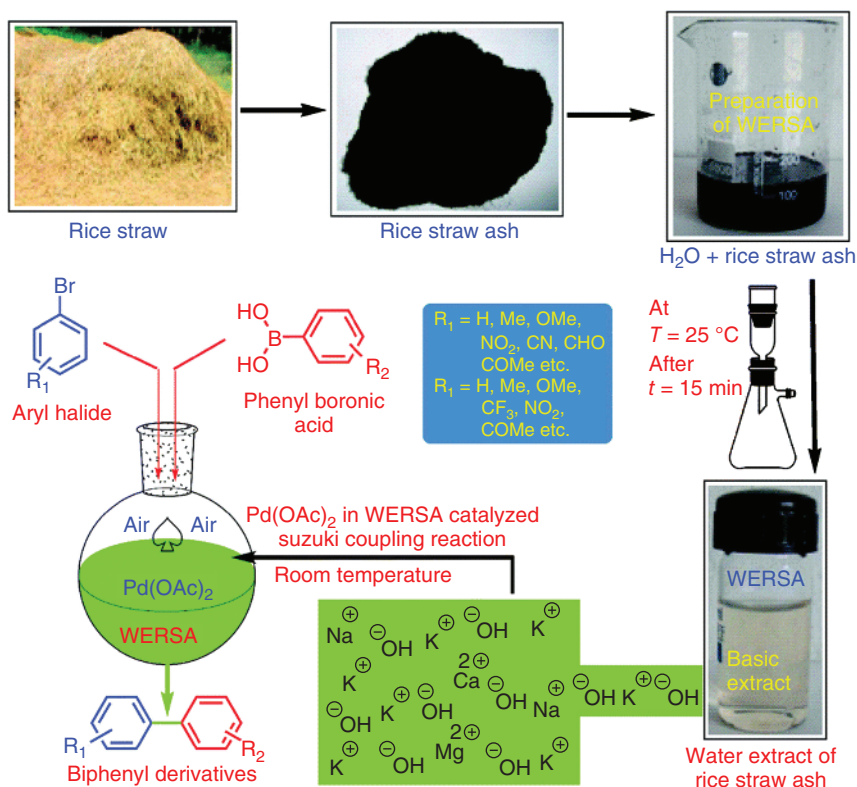
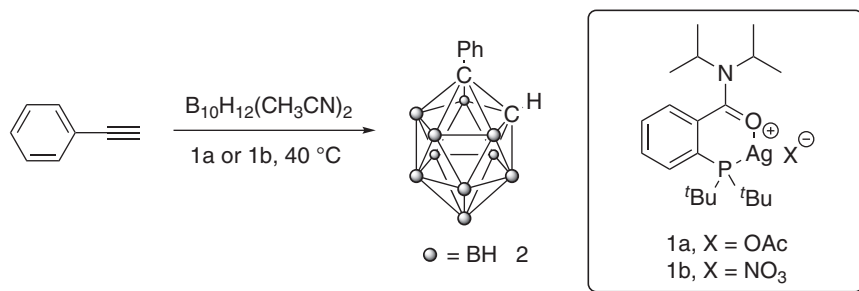


Figure 1.3 WERSA isolation procedure from rice straw. (Boruah *et al.* 2015 [33]. Reproduced with permission of Royal Society of Chemistry.)

K⁺, Mg²⁺, Ca²⁺ and OH⁻), the addition of a base—essential for the Suzuki reaction—was not needed. WERSA is an aqueous-based reaction medium where the palladium can be immobilized and after extraction of the reaction products with a nonpolar organic solvent, such as diethylether, the WERSA-Pd system can be recovered and reused. In this manner, the system could be reused up to six times without significant loss of activity after the fourth run, probably due to metal leaching into the organic phase.

Catalytic oxidation of secondary alcohols to ketones have been carried out efficiently at room temperature or slightly higher temperature (38 °C) in 1977 with a catalytic system formed by PdCl–NaOAc using molecular oxygen as oxidant [34]. This catalytic system substituted the previous PdCl–Cu(II)-salt catalytic system, where higher temperatures (70–120 °C) were required. A series of five-membered P,C-orthopalladate complexes with different monodentate ligands were synthesized and tested in the Suzuki–Miyaura cross-coupling at room temperature [35]. The palladium-based catalyst, [Pd(PPh₃)(Cl){P(OPh)₂(OC₆H₄)}], showed good to excellent activity for all the substrates tested including the cheaper, more available, less reactive, and challenging arylchlorides.

A homogeneous diplatinum complex, [Pt₂(μ-dppm)] (dppm = Ph₂PCH₂PPh₂) showed to be effective in the catalytic synthesis of dimethylformamide through



Scheme 1.2 Synthesis of carboranes with homogeneous silver catalysts. (El-Zaria *et al.* 2014 [37]. Reproduced with permission of Wiley.)

the hydrogenation of CO₂ at room temperature under mild reaction conditions. This catalyst substituted previous ones where the required reaction conditions were more harsh [36].

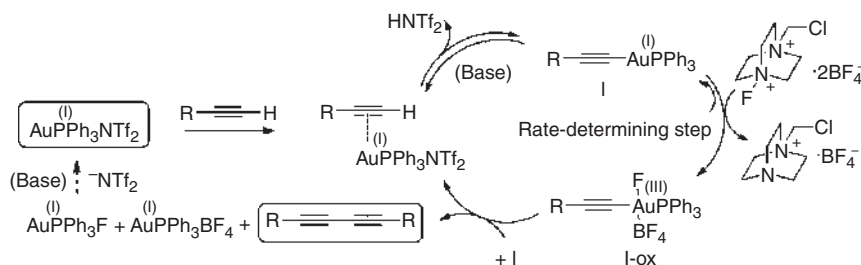
1.2.2.3 Group 11-Based Homogeneous Catalysts (Ag, Au)

A homogeneous silver catalyst was used for the synthesis of carboranes in temperatures ranging from room temperature to 40 °C [37]. Carboranes are boron clusters with unique structural and electronic properties with potential use in creating new diagnostics, therapeutics, and electronically tunable materials. The preparation of these compounds usually required high temperatures (80–120 °C) [38–40], but the tested homogeneous silver catalysts (Scheme 1.2) facilitated preparation of functionalized carboranes in good to excellent yield at reduced reaction temperatures in the range from room temperature to 40 °C. The lower reaction temperature opens up the possibility of preparing carboranes from thermally sensitive alkynes that otherwise undergo degradation or side reactions at higher temperatures. McNulty *et al.* described the first examples of homogeneous intramolecular hydroamination of 2-alkynylanilines using a homogeneous silver catalyst leading to substituted indoles. The reactions were performed with low catalyst loading (1.0 mol%) and at room temperature. Normally the cyclization takes place under harsh reaction conditions and high temperatures.

Gold-based homogeneous catalysts were reported for the first time in the epoxidation of aromatic alkenes at room temperature using sodium chlorite as stoichiometric oxidant [41]. More recently, in 2012, Corma and coworkers showed the first application of a homogeneous gold-based catalyst in the oxidative homocoupling of terminal alkynes in excellent yields at room temperature. Their mechanistic studies demonstrated that at least two different Au–alkyne complexes are needed for the homocoupling reaction (Scheme 1.3) [42].

1.3 Room-Temperature Heterogeneous Catalysts

Heterogeneous catalysis overcomes some of the main drawbacks in homogeneous catalysis, such as the recovery and recycling of the catalysts. In traditional



Scheme 1.3 Plausible mechanism for the gold-catalyzed oxidative homocoupling of terminal alkynes. (Leyva-Perez *et al.* 2012 [42]. Reproduced with permission of American Chemical Society.)

heterogeneous catalysis, the catalytic system comprises a porous solid material in which the metals are immobilized. The high surface areas of the solid materials allow the catalytic metal to be deposited on the surface, becoming available for the substrates.

1.3.1 Group 9-Based Heterogeneous Catalysts (Co, Rh, Ir)

From an economic point of view, cobalt is the preferred group 9 metal since it is the cheapest, but it is a challenge to develop an efficient and robust Co-based catalyst that could replace the precious metals-based catalysts in industrial applications. A heterogeneous Co-based catalyst was prepared by immobilization of a Co(II) complex on mesoporous SBA-15 silica and successfully applied in the synthesis of α -aminonitriles, which are compounds with useful biological activities and important building blocks for peptides and proteins preparation, through the three-component Strecker reaction at room temperature under solvent-free conditions [43]. The Co-based catalyst was tested in the reaction with different aldehydes and amines obtaining the corresponding products in excellent yields, typically in the range of 90–97%. For practical viability, the recyclability of the catalyst was also studied. The catalyst could be recycled up to 10 times with unchanged catalytic activity and no detectable metal leaching by inductively coupled plasma (ICP) spectrometry.

Another Co-based catalyst consisting of a Co(II) complex supported on ethylenediamine-functionalized nanocellulose (EDANC), which is a biodegradable solid support, was prepared and tested in the aerobic oxidation of various benzyl alcohols at room temperature [44]. The Co(II) complex was immobilized through coordination of the metal to the amine-functionalized cellulose, achieving a good distribution of cobalt on the cellulose surface. The Co(II)–EDANC catalyst was effective in the oxidation of different benzyl alcohols with good conversions in the range of 81–97% using both air and molecular oxygen as oxidants. The recyclability of the catalyst was also shown to be good, resulting in only a minor decrease in activity after the fifth reaction cycle. In comparison with homogeneous Co(II) catalyst and Co(II)-impregnated on nonmodified cellulose, the Co(II)–EDANC catalyst was also demonstrated to be superior. The better performance compared to the other catalysts was due to the presence of

ethylenediamine in the support, which could act as a ligand activating the Co(II) toward the alcohol's oxidation.

Rhodium nanoparticles prepared by chemical reduction of a $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ precursor in the presence of a surfactant (*N,N*-dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl) ammonium chloride, HEA16Cl) were immobilized by simple impregnation on silica in a very easy way without any further hydrogenation or calcination step [45]. The obtained catalyst was tested in the hydrogenation of aromatic compounds at room temperature. The hydrogenation of aromatic compounds is of great importance and an industrially challenging reaction applied in refineries to reduce the volatile organic matter (VOM) emissions, normally under harsh conditions. The authors suggested that the Rh(0) nanoparticles were anchored to the silica via oxygen bonding through the silanol groups. The Rh/SiO₂ catalyst was tested in the hydrogenation of a series of aromatic compounds such as, for example, benzene, toluene, styrene, xylene, and methylanisole, in a triphasic system composed of water/hydrocarbon/silica, at room temperature under ambient hydrogen pressure. All the tested substrates were fully converted into products with TOFs ranging from 93 to 129 h⁻¹. Notably, cumene – which is quite difficult to hydrogenate – was reduced with a TOF of 93 h⁻¹ under the mild reaction conditions. Increasing the hydrogen pressure in the reaction to 30 bars, TOF as high as 6429 h⁻¹ was achieved using anisole substrate. The Rh/SiO₂ catalyst was found to be around four times more active than other traditional Rh-based heterogeneous catalysts. In addition, good recyclability of the catalyst was achieved, allowing it to be used up to five times with only a slight decrease in activity (TOF decrease from 129 to 120 h⁻¹) in the hydrogenation of anisol.

The aerobic oxidative homocoupling of aryl amines was carried out for the first time using heterogeneous rhodium catalysts at room temperature in the presence of acids [46]. The reaction protocol offered an efficient methodology for the preparation of biaryl diamines via oxidative C–H activation. The studied reaction is very sensitive to the $\text{p}K_{\text{a}}$ and the choice of acid is essential. The role of the acid is to protonate the aryl amine resulting in an ammonium salt that prevents its oxidation as well as side reactions, which typically makes the reaction difficult to control. The best acid for the reaction was trifluoroacetic acid with a $\text{p}K_{\text{a}}$ of -0.2 . The Rh/C heterogeneous catalyst was superior to other heterogeneous metal-based catalysts or homogeneous Rh catalysts investigated in the study. No recycling tests were done but a greener and more energetically efficient route than previously reported was developed.

Iridium(0) nanoparticles dispersed in a zeolite (FAU) framework (IrNPs@FAU) were employed as heterogeneous catalyst in the hydrogenation of aromatic molecules under mild conditions at room temperature [47]. The hydrogenation of aromatic molecules is a key reaction in synthetic and petroleum chemistry. The catalyst was prepared by cation exchange of Na⁺ with Ir³⁺ in the zeolite, followed by reduction with NaBH₄ at room temperature. The sodium cation sites were completely restored after reduction by sodium cations from the NaBH₄ used as reducing agent. The micropore area and pore volume of the zeolite was decreased after incorporation of the rhodium nanoparticles due to the formation of the nanoparticles in the cavities and the external surface of the zeolite-Y. Benzene is challenging to hydrogenate due to the resonance stabilization from

the π -conjugation in the aromatic ring and, in consequence, its hydrogenation requires normally high temperature and pressure. Thus, it remains a challenge to find new heterogeneous catalysts capable of hydrogenating neat aromatics at room temperature. The IrNPs@FAU showed to be highly active and selective in the hydrogenation of aromatics with TOF as high as 3215 h^{-1} in the hydrogenation of benzene to cyclohexane. Also, a high resistance to agglomeration and metal leaching was obtained achieving a cumulative turnover number (TON) of 197 000 before complete deactivation was observed after 92 h. Despite the activity and selectivity for the prepared catalyst being lower than that previously reported for the best catalyst (Ru–Ni/C; TOF = 7905 h^{-1}), it was higher than most catalysts used for hydrogenation of benzene under these mild conditions. The major drawback of this catalyst was that reactivity was low toward bulky substrates such as, for example, mesitylene due to size restrictions of the zeolite-Y cages, making it impossible for the substrate to reach the active Rh sites inside the pores. Accordingly, only the Rh on the zeolite surface contributed to the catalytic activity.

1.3.2 Group 10-Based Heterogeneous Catalysts (Ni, Pd, Pt)

In 1998, a novel supported nickel complex was employed as heterogeneous catalyst in Baeyer–Villiger oxidation of cyclic and linear ketones to lactones and esters, respectively, using molecular oxygen as oxidant at room temperature [48]. The catalyst was prepared in an elegant way at room temperature, where mesoporous silica in a first step was functionalized by reacting with trimethoxy-3-aminopropylsilane yielding aminopropyl silica (AMPS) and thereafter successively treated with terephthaldialdehyde and *p*-aminobenzoic acid. To an ethanoic suspension of the resulting solid a Ni complex was subsequently added, yielding the desired heterogeneous catalyst. The catalyst proved to be efficient in the tested reaction, yielding good conversions and high selectivities. For example, cyclopentanone was selectively oxidized to valerolactone with 91% conversion and TON of 31 h^{-1} per catalytic site. Unfortunately, no recyclability test of the catalysts was performed.

A macroporous polystyrene–divinylbenzene cross-linked Merrifield resin was used as support for the covalent anchoring of a homogeneous unsymmetrical Salen-type nickel(II) catalyst [49]. The heterogeneous catalyst was effective in the Tamao–Kumada–Corriu cross-coupling reaction between a Grignard reagent and an organobromide compound at room temperature. In addition, the catalyst was able to be recycled several times and did not leach metal into solution. The catalyst stability was attributed to a combination of hard and soft donor atoms around the nickel metal centers, the oxidation state of which varies between 0 and 2. The same Ni(II) catalyst was immobilized onto silicon-hydride-functionalized silica in a two-step procedure [50]. The first step was an etherification and the second a hydrosilylation reaction catalyzed by a platinum catalyst. The prepared catalyst showed high activity in the Tamao–Kumada–Corriu reaction between 4-bromoanisole (organobromide) and phenylmagnesium chloride (Grignard reagent) at room temperature without addition of phosphine ligands. The catalyst could be recovered by simple filtration and reused several times. ICP

analysis revealed that very low amount of Ni was leached into the solution. Catalytic tests were performed in a mini-flow reactor system where conversion could be achieved after a few minutes, while in batch conditions hours were required.

A room-temperature Suzuki–Miyaura cross-coupling reaction was performed in the presence of a heterogeneous palladium catalyst [51]. The catalyst consisted of palladium nanoparticles immobilized in multiwalled carbon nanotubes (MWCNTs) using the layer-by-layer approach [51, 52] (Figure 1.4).

The catalyst showed to be efficient in the coupling of different halogenated aromatics with boronic acids under sustainable conditions. The more challenging arylchlorides were also tested, showing unprecedented results using heterogeneous catalysts at room temperature with yields up to 89%. The catalyst was easily recovered from the reaction media and reused up to five times with no decrease in catalytic activity. Furthermore, transmission electron microscopy (TEM) analysis of the catalyst recovered after five cycles did not show major changes in its morphology.

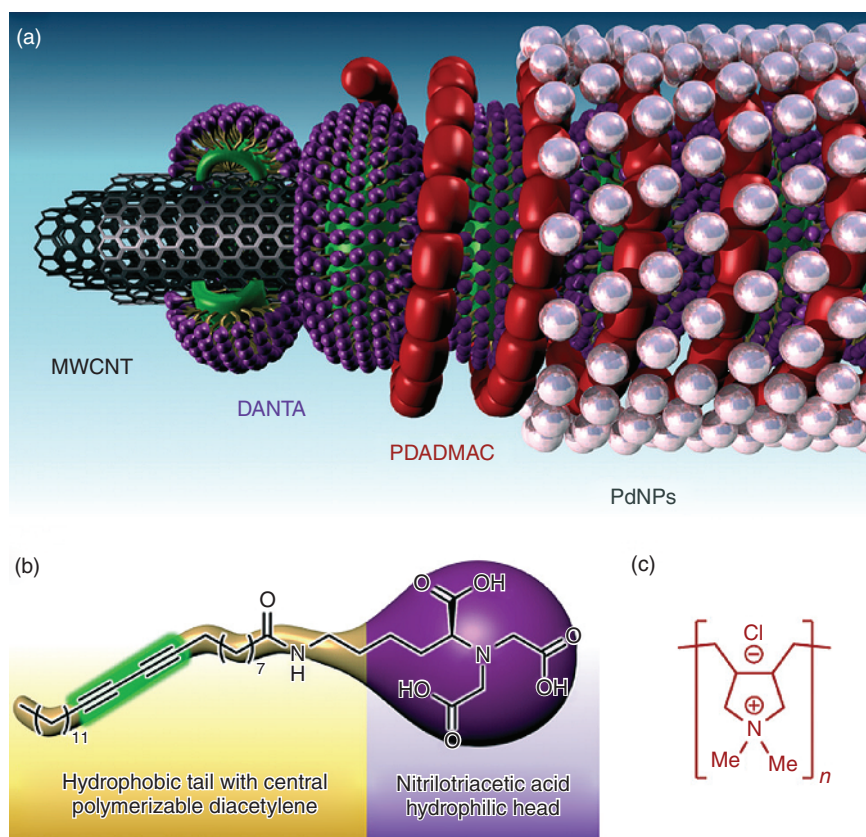


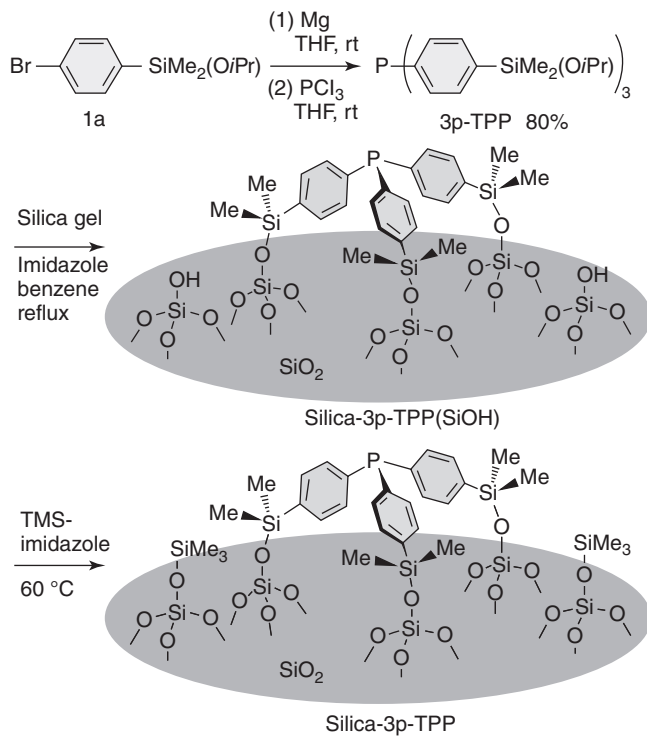
Figure 1.4 (a) Overview of the PdCNT catalyst assembly; (b) structure of DANTA; (c) structure of PDADMAC. (Jawale *et al.* 2015 [51] <http://pubs.rsc.org/-/content/articlehtml/2015/cy/c4cy01680g>. Used under CC BY 3.0.)

A montmorillonite K-10 clay was used as support for immobilizing a $\text{Pd}(\text{TPP})_2\text{Cl}_2$ complex [53]. The immobilization was performed by addition of the clay to a solution containing PdCl_2 and the triphenylphosphine (TPP) after stirring the mixture for 6 days. The incorporation of the complex in the clay was confirmed by a decrease in the surface area of the clay by Brunauer–Emmett–Teller (BET) analysis, and the presence of the complex was confirmed by infrared (IR) spectroscopy with the appearance of signals at 426 and 337 cm^{-1} for Pd–P and Pd–Cl vibrations, respectively. The catalyst was tested in the coupling of different functionalized arylbromides and boronic acids at room temperature, achieving conversions between 90 and 99% in a variable reaction time from 0.5 to 18 h depending on the functionalization of the substrates. The recyclability of the catalysts was not successful, which was attributed to deactivation of the catalyst during the course of the reaction and recovery process.

Heterogeneous palladium catalysts were also prepared and applied in the room temperature Suzuki–Miyaura coupling of various activated and deactivated chloroarenes, achieving excellent yields after 16 h of reaction [54]. The heterogeneous catalysts were prepared in an original way. First, the silica-supported tripod phosphine (silica-3p-TPP) was prepared containing a disiloxane linkage at the para position on each phenyl ring of TPP, as shown in Scheme 1.4. Next, the bromobenzene derivative **1a**, with a $(i\text{PrO})\text{Me}_2\text{Si}$ substituent in the para position, was converted into the corresponding Grignard reagent. Subsequently, the Grignard reagent was treated with PCl_3 , yielding the soluble silyl-functionalized Ph_3P species 3p-TPP in 80% yield. The obtained specie was then grafted onto silica gel by refluxing in benzene in the presence of imidazole, yielding the silica-supported tripod phosphane Silica-3p-TPP(SiOH). The latter was treated with Me_3Si –imidazole in order to end cap the silanol groups with Me_3Si , giving the desired Silica-3p-TPP. Once the TPP grafted on silica was obtained, the palladium catalyst was immobilized by reaction of the prepared silica-3p-TPP with a palladium(II) complex ($\text{PdCl}_2(\text{PhCN})_2$), and the coordination of Pd(II) was confirmed by solid-state nuclear magnetic resonance (NMR) spectroscopy. The catalyst was recovered from the reaction media by simple filtration and reused up to four times with conversion ranging between 95 and 99% in the coupling of *p*-chloroanisole and phenylboronic acid. However, the fifth run showed a decrease in activity, yielding only 74%.

A composite PVP/KIT-5 (PVP = Poly(*N*-vinyl-2-pyrrolidone); KIT-5 = cage-type mesoporous silica) was prepared by *in situ* polymerization method and used as solid support for the immobilization of palladium nanoparticles (Figure 1.5). The resulting heterogeneous catalyst was used in the Suzuki–Miyaura coupling between arylhalides and phenylboronic acid at room temperature in water as solvent and under aerobic conditions [55]. The catalyst was recovered by filtration and reused up to eight times with good yield. The excellent performance in recyclability was attributed to the interconnected large-pore, cage-type mesoporous KIT-5 with three-dimensional (3D) porous networks.

Selective and sequential reduction of nitroaromatics to nitroanilines and to adiamines was performed for the first time in quantitative yield at room temperature and ambient pressure in ethanol in 1989 using a Pd-based heterogeneous



Scheme 1.4 Preparation of Silica-3p-TPP. (Iwai *et al.* 2014 [54]. Reproduced with permission of Wiley.)

catalyst. The catalyst was prepared by complexation of H-Montmorillonite, previously synthesized, with $\text{PdCl}_2(\text{PhCN})_2$. The catalyst showed to be active for aromatic systems but inert for aliphatic ones [56].

Encapsulated silica nanosphere decorated with palladium nanoparticles in a nanoporous silica shell was reported and tested in the hydrogenation of various olefins at room temperature. The heterogeneous palladium catalyst was prepared in a smart way in various steps (Scheme 1.5). In the first step, the silica nanospheres were prepared through the Stöber method [58]. In the second step, the surface of the silica nanospheres were modified with 3-aminopropyltrimethoxysilane. Then, previously prepared Pd nanoparticles were chemisorbed on the silica nanospheres, whereafter the $\text{SiO}_2/\text{Pd-NP}$ core-shell nanospheres were coated with a silica shell through a sol-gel process. In the final step, the controlled etching of the silica shell with NaOH generated the desired Pd-based heterogeneous catalyst $\text{SiO}_2/\text{Pd-Np}/\text{porous-SiO}_2$ core-shell-shell nanospheres, as shown in the TEM images (Figure 1.6) [57]. The catalyst was tested at room temperature in the hydrogenation of various olefins, reaching styrene hydrogenation in 25 min with a TOF h^{-1} of 5000. The reached TOF was found to be three times higher than the one found for the most efficient polymer-supported Pd heterogeneous catalyst at 35°C . The recyclability of the catalyst, through centrifugation, proved to be efficient, showing only a small

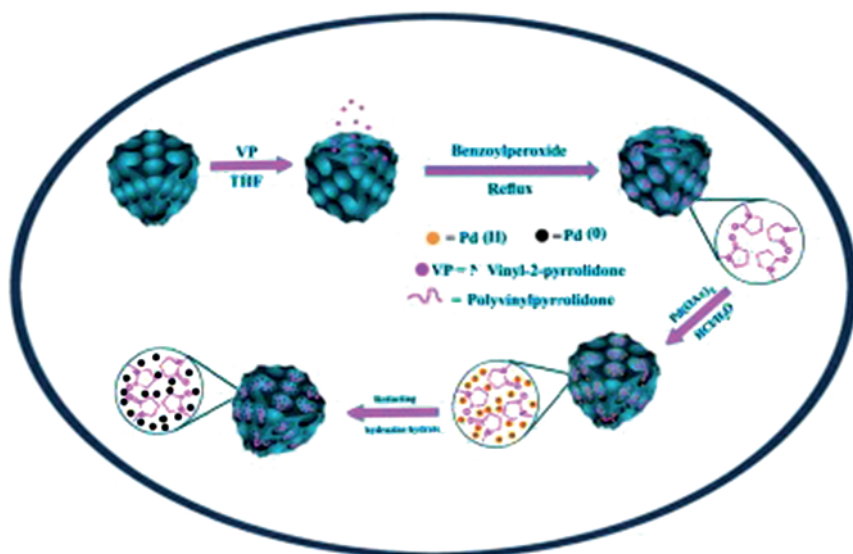
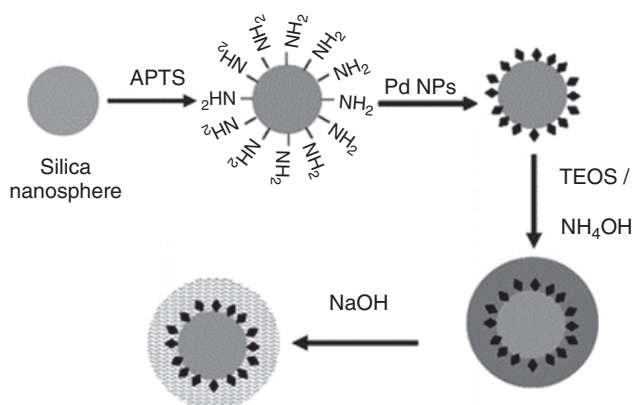


Figure 1.5 Encapsulation of PVP and Pd in the 3D interconnected pore channels of KIT-5. (Kalbasi and Mosaddegh 2011 [55]. Reproduced with permission of Elsevier.)



Scheme 1.5 Schematic representation of the synthesis of $\text{SiO}_2/\text{Pd-NP}/\text{porous-SiO}_2$ core-shell-shell nanospheres. (Wang *et al.* 2010 [57]. Reproduced with permission of Royal Society of Chemistry.)

decrease in catalytic activity attributed to loss of the catalyst during the recycling tests.

Encapsulated palladium nanoparticles in silica MCM-48 were used as a novel and recyclable heterogeneous catalyst for chemo- and regioselective hydrogenation of olefins at room temperature [59]. Silica MCM-48 is more attractive as support than the MCM-41 due to the presence of an interpenetrating network of 3D pores that are expected to facilitate molecular transport of reactants and products more efficiently than in the case of the 1D network found in

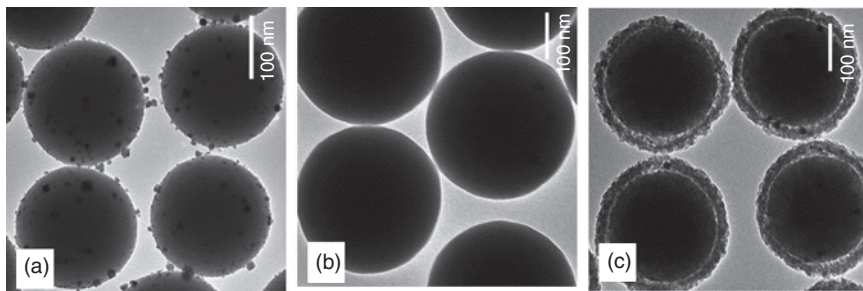


Figure 1.6 TEM images of (a) $\text{SiO}_2/\text{Pd-NP}$ core-shell nanoparticles with 20 nm Pd-NP chemisorbed on aminopropyl-modified silica nanoparticles and the corresponding (b) $\text{SiO}_2/\text{Pd-NP}/\text{SiO}_2$ core-shell-shell nanoparticles, and (c) $\text{SiO}_2/\text{Pd-NP}/\text{porous-SiO}_2$ core-shell-shell nanoparticles etched for 120 min. (Wang *et al.* 2010 [57]. Reproduced with permission of Royal Society of Chemistry.)

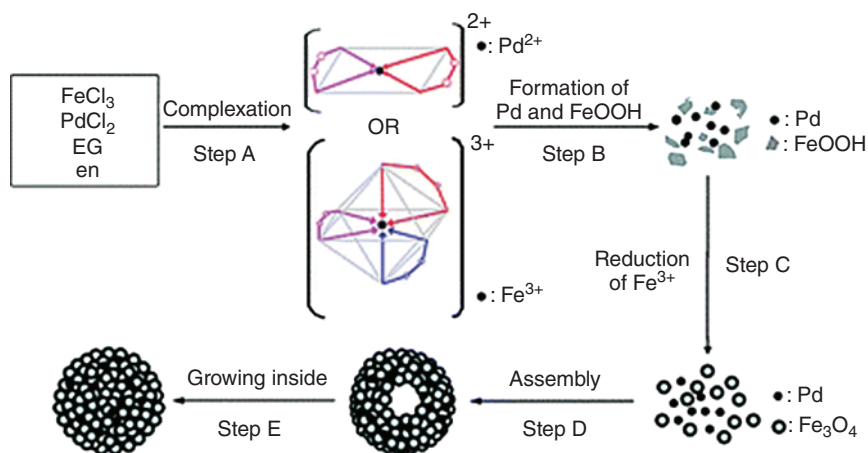
MCM-41. The heterogeneous Pd catalyst was prepared by encapsulating the preformed PdNPs into the cubic phase of MCM-48 following the Stöber method [58]. The obtained material was calcined, followed by reduction under H_2 , and characterized by means of powder X-ray diffraction (XRD), TEM, and BET. The surface area was found to be approximately $1800 \text{ m}^2 \text{ g}^{-1}$ with a metal dispersion of around 22%. The catalyst was tested in the hydrogenation of various olefins at room temperature, yielding good to excellent conversions with TOF as high as 4400 h^{-1} . The good performance was attributed to the high metal surface area (approximately $95 \text{ m}^2 \text{ g}^{-1}$) and the high dispersion of the nanoparticles. High chemoselectivity toward the reduction of double bonds was observed with the prepared catalyst in the presence of carbonyl, acetate, and ketone groups. Furthermore, the prepared catalyst exhibited good regioselectivity, hydrogenating selectively terminal alkenes. This selectivity behavior was completely opposite to the previously reported Pd-MCM-48 catalyst, where the Pd nanoparticles were deposited on preprepared MCM-48. Analysis of this catalyst revealed that the surface area was around $637 \text{ m}^2 \text{ g}^{-1}$ (three times less than the one prepared by the authors) and the nanoparticle dispersion was 12% (half of the one prepared by the authors). After testing different ways of incorporating the Pd nanoparticles onto the silica MCM-48 and evaluating the performance of the catalyst in the hydrogenation of different olefins, it was established that the selectivity was significantly influenced by the preparation method of the catalysts.

A heterogeneous Pd catalyst consisting of $\text{Pd}(\text{OAc})_2$ dissolved in ionic liquid and immobilized in the pores of an amorphous mercaptopropyl silica gel (Pd-SH-SILC) was employed successfully for the hydrogenation of olefins under very mild conditions (atmospheric pressure and room temperature) with excellent results in terms of activity and selectivity [60]. The catalyst was reused, by means of simple decantation, up to 10 times without observation of any decrease in conversion and/or selectivity. The catalyst was prepared by stirring a suspension of the modified mercaptopropyl silica gel in a solution of $\text{Pd}(\text{OAc})_2$ and the ionic liquid in tetrahydrofuran (THF) followed by the removal of the solvent under vacuum. The high content of $\text{Pd}(\text{OAc})_2$ in the mercaptopropyl silica compared with other silica supports was attributed to the presence of the

-SH and the affinity of Pd for them. The Pd-SH-SILC catalysts were applied in the hydrogenation of cyclohexene as a test reaction. Before use the catalyst was pretreated with hydrogen with the aim of reducing the Pd(II) to Pd(0). Among the tested Pd-SH-SILC catalysts, the one immobilized with [BMIm]BF₄ showed the best catalytic activity with TON and TOF of 40 000 and 555 h⁻¹, respectively, at room temperature, due to high solubility of H₂ into the IL in comparison to other employed ILs in the study, for example, [BMIm]PF₆. The Pd-SH-SILC with [BMIm]BF₄ was recycled up to 10 times by simple decantation maintaining a 100% conversion. Palladium leaching was evaluated by means of inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis being below the detection limit of the technique. Due to the excellent catalytic performance of the catalyst, its application was extended to a variety of olefinic substrates, yielding moderate to excellent conversions.

A heterogeneous catalysts consisting of palladium nanoparticles immobilized on a highly acidic metal-organic framework (MOF), known as MIL-101 (MIL, Material Institute Lavoisier) Cr₃F(H₂O)₂O[(O₂C)C₆H₄(CO₂)₃]₃.nH₂O (with n ~ 25), was used as catalyst in an industrially relevant process such as the selective hydrogenation of phenol and other related alcohols at atmospheric pressure, at room temperature, and in water as solvent [61, 62]. Traditionally, this reaction is carried out in the range of 150–300 °C and in non-environmental-friendly solvents. These high temperatures allow coke formation during the reaction and consequently catalyst deactivation. The tested catalyst (Pd/MIL-101) gave 100% conversion of phenol with more than 99.9% selectivity toward cyclohexanone. The results were remarkably superior in terms of both conversion and selectivity to those obtained with a Pd/C catalyst employed for comparative purposes in the work. Pd/MIL-101 was recovered from the reaction media by simple centrifugation and washed before being reused under identical reaction conditions. The catalyst was tested up to five consecutive runs without observing any decrease in conversion or selectivity. Furthermore, AAS (atomic absorption spectroscopy) experiments measured after the reaction did not show any Pd traces (<0.5 ppm) and TEM analysis after the fifth run showed only minimum aggregation of Pd nanoparticles. The findings from these two measurements are in complete agreement with the obtained results. In addition, mechanistic studies showed the important role of the supported Lewis acid sites (Cr(III)) on the catalytic activity, leading their partial or total suppression to low activity or no activity, respectively.

Solid and hollow spheres of Pd/Fe₃O₄ with magnetic properties were prepared as illustrated in Scheme 1.6 through a solvothermal reaction route, and used as catalysts in the hydrogenation of *p*-nitrophenol at room temperature [63]. Besides the intrinsic easy recovery of the catalysts from the reaction mixture due to their magnetic properties, the hollow sphere catalysts showed to be superior in activity to the solid spheres (85.2 vs 58.9%). The high conversion obtained with the hollow spheres was attributed to the fact that more active Pd sites can be reached than in the solid spheres. Concerning the selectivity, both catalysts lead to 100% toward *p*-aminophenol. Even if the catalysts were easily recoverable due to their magnetic nature, the recycling experiments were unsuccessful. The authors claimed this was due to poisoning of the Pd-active sites by coordination of the N atom in *p*-aminophenol.



Scheme 1.6 A schematic illustration of the formation and shape evolution of the Pd/Fe₃O₄ spheres in the whole synthetic process. (Wang *et al.* 2012 [63]. Reproduced with permission of Royal Society of Chemistry.)

Well-dispersed Pd nanoparticles (4.0–6.0 nm) were encapsulated within an organosilica matrix (SilicaCat Pd⁰) via an alcohol-free sol–gel process that is often used for enzyme sol–gel encapsulation [64]. The prepared SilicaCat Pd⁰ catalyst was tested in the selective hydrogenation of various alkenes under mild conditions (atmospheric pressure and room temperature) with palladium loadings of 0.1 mol% in MeOH as solvent [65]. Leaching of metal during the catalytic reactions was measured by inductively coupled plasma-optical emission spectrometry (ICP-OES), showing in most of the cases values for leached Pd less than 5 ppm. However, the amount of leached Pd was found to be around three to four times higher for those substrates containing nitrogen atoms, such as 1-vinyl-2-pyrrolidinone, with a lone pair of electrons that could coordinate to Pd and consequently facilitate leaching into the solution. Catalytic recycling tests of SilicaCat Pd⁰ were performed using *trans*-cinnamic acid as substrate under the investigated optimal reaction conditions. Consequently, the heterogeneous catalyst could be reused in up to five consecutive cycles without any loss of activity or selectivity (Table 1.2). The catalyst showed to be much better than other conventional heterogeneous Pd catalysts such as, for example, Pd/C, for most of the studied substrates. The excellent performance of the investigated catalyst was attributed to the small size of the Pd(0) nanoparticles (4.0–6.0 nm) and to their sol–gel entrapment in the organosilica matrix that gives physical and chemical stabilization to the nanoparticles and ensures optimal diffusion of the reactants.

The first example of chemoselective hydrogenation of unsaturated compounds in water at room temperature was carried out with a heterogeneous catalyst composed of Pd metal nanoparticles and carbon nitride (Pd/CN) prepared by the wet impregnation method. The catalyst was employed in the hydrogenation of alkenes and unsaturated biomass-derived compounds using formic acid as H₂ source, yielding excellent conversion and selectivity after short reaction

Table 1.2 Reusability of the SiliaCat Pd(0) hydrogel in the selective catalytic hydrogenation of *trans*-cinnamic acid under mild conditions.

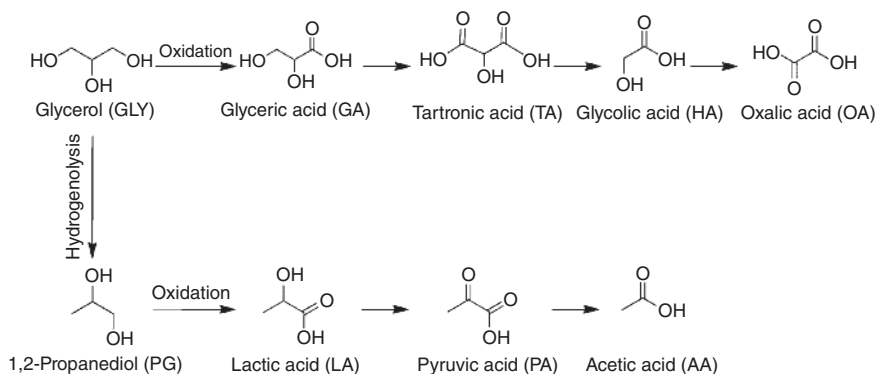
Run	Time (h)	Conversion (yield) ^{a)} (%)	Selectivity (%)	Leaching ^{b)} (ppm)	
				Pd	Si
1	2	100 (99.4)	100	0.09 (1.8)	0.06 (1.2)
2	2	100 (99.8)	100	0.09 (1.8)	0.03 (0.6)
3	2	100 (99.3)	100	0.12 (2.3)	0.02 (0.4)
4	2	100	99	0.09 (1.6)	0.03 (0.5)
5	2	100	99	0.08 (1.5)	0.02 (0.3)

- a) Conversion in final product determined by GC/MS analysis. Isolated yield of the crude product.
- b) Leaching in Pd and Si determined by ICP-OES analysis in solution (DMF solvent 50 mg ml⁻¹, with respect to the crude product) and in the solid crude product.

Source: Pandarus *et al.* 2012 [65]. Adapted with permission of American Chemical Society.

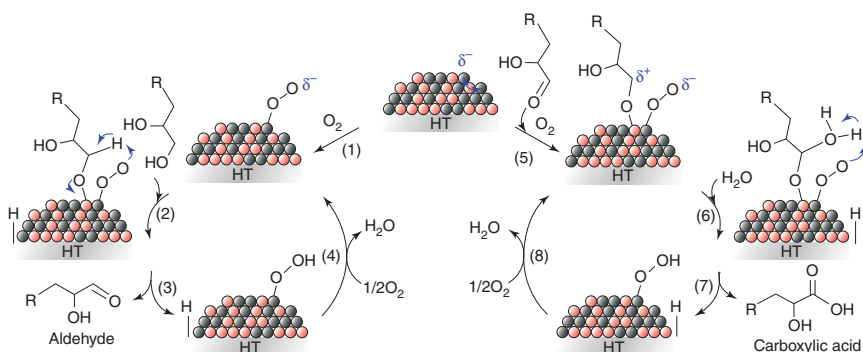
times [66]. The use of water as a reaction medium allowed facile separation of the products, due to the generation of a biphasic product media. Furthermore, the strong Mott–Schottky effect between the metal nanoparticles and the carbon nitride support allowed a high degree of reusability and stability of the prepared catalyst. Indeed, the Pd/CN catalyst could be reused up to 26 consecutive runs in the hydrogenation of 2-methylfuran to 2-methyltetrahydrofuran at room temperature without any loss of catalytic activity, and the leached palladium was below 0.1 ppm. After five more recycling experiments, the conversion was gradually decreasing, and in the 31st run the yield dropped to 60%. Since the chemical structure and morphology of both the palladium nanoparticles and the CN support remained unchanged after 31 cycles, the effect of the structural variation in the catalytic activity was ruled out. Instead, the drop in activity could be attributed to changes in the Pd and CN interface, due to protonation by the formic acid (used as hydrogen source) of the terminal amino groups and bridging nitrogen present on the surface of the CN support. If fact, when the interfacial area between the Pd nanoparticles and the CN support was deprotonated, the catalyst recovered its initial activity for two more additional runs.

Bimetallic Pt–Au alloy nanoparticles incorporated into the channel pores of hydrotalcite (HT) were prepared and tested as catalyst in the selective aerobic oxidation of polyols in base-free aqueous solution at room temperature [67]. The catalyst was prepared by impregnation of HT with previously synthesized Pt–Au nanoparticles by chemical reduction using starch as reducing agent (Scheme 1.7). In these reactions, a base is normally required to enhance the abstraction step involved in the reaction mechanism, and for neutralization or acidification of generated by-products. In the prepared catalyst, the HT support is alkaline enough to function as the base in the reaction mechanism. The results obtained with the catalyst in the oxidation of glycerol (GLY) and 1,2-propanediol (PG) toward the formation of glyceric acid (GA) and lactic



Scheme 1.7 General reaction pathways for the oxidation of GLY and PG. (Tongsakul *et al.* 2013 [67]. Reproduced with permission of American Chemical Society.)

acid (LA), respectively, were excellent in terms of both activity and selectivity. The improvement found in activity and selectivity with this Pt–Au/hydroxalcite catalyst was attributed to both geometric (d-spacing) and electronic changes (by electron transfer from the adjacent Au atoms) of the catalytic active Pt sites by the neighbor Au atoms and the starch used as stabilizer and reducing agent in the nanoparticles' preparation. Evidence of the changes was confirmed by X-ray photoelectron spectroscopy (XPS) and X-ray absorption near-edge structure (XANES) analyses. Based on these findings, a mechanism for the oxidation of polyols with Pt–Au/hydroxalcite catalyst under ambient and aqueous base-free conditions was proposed (Scheme 1.8). In a first step, O_2 is adsorbed onto the negatively charged (due to the presence of the Au atoms) Pt atoms. O_2 is activated by donation of electrons from the Pt atoms to the antibonding orbital generating anionic O_2^- (superoxo or peroxy oxygen). Afterwards, the hydroxalcite support abstracts a proton from the polyol yielding an alkoxide, enhancing the interaction of the polyol with the Pt atom. Then the proton is transferred to the adsorbed oxygen, yielding aldehyde and water regenerating the peroxy oxygen form. The formed aldehyde is attracted by the Au atoms, creating a



Scheme 1.8 Proposed reaction mechanism for polyols oxidation catalyzed by PtAu–starch/HT. (Tongsakul *et al.* 2013 [67]. Reproduced with permission of American Chemical Society.)

partial positive charge on the carbonyl carbon followed by nucleophilic attack of water on the electron-deficient carbonyl carbon. Finally, the adsorbed oxygen abstracts the proton to give the carboxylic acid re-forming the peroxy form to complete the catalytic cycle.

The use of CO_2 as the C1 building block in the chemical industry is of special interest despite its high thermodynamic stability. In fact, it is usually employed as a precursor for C1-type chemicals at high temperature and pressure, but the development of catalysts able to achieve the reduction of CO_2 under ambient conditions and resistant to solvent, air, moisture, and so on is highly demanded and it is still a challenge. In this sense, Pt nanoparticles immobilized on a polymeric monolithic support were used in the reduction of CO_2 at room temperature and atmospheric pressure as a ligand-free heterogeneous catalytic system using dihydrosilanes as the hydrogen source [68]. The employed cross-linked polymeric support was prepared by ring-opening metathesis polymerization (ROMP) of *cis*-cyclooctene-based monomer and cross-linker using a third-generation Grubb's catalyst [69]. Afterwards, the polymeric support was modified by introducing *vic*-diol sites in order to enhance the stabilization, given by the double bonds present in the polymeric support, of the Pt nanoparticles obtained by chemical reduction of PtCl_4 with NaBH_4 . Scanning electron microscopy (SEM) analysis showed the globular morphology of the monolith with globule diameters in the range of 1–2 μm (Figure 1.7) [70]. The catalyst was tested in the reduction of CO_2 using methylphenylsilane (MPS) as hydrogen source, and the system showed high activity in the reduction of CO_2 for the synthesis of C1-type products such as MeOH, formic acid (after hydrolysis with water), formamides (after addition of amine), and other derived compounds. The proposed catalytic system was not only maintenance free and easy to handle compared with the organometallic and organocatalyst systems but it also revealed 3–11 times higher catalytic activity reaching TONs up to 21 900.

1.3.3 Group 11-Based Heterogeneous Catalysts (Cu, Pt, Au)

A supported ionic liquid catalyst with CuBr dissolved in the pores of an amorphous mercaptopropyl silica gel (Cu-SILC) was applied successfully in the regioselective catalysis of Huisgen [3+2] cycloadditions at room temperature in aqueous solution (Scheme 1.9) [71, 72]. This was the first example of a

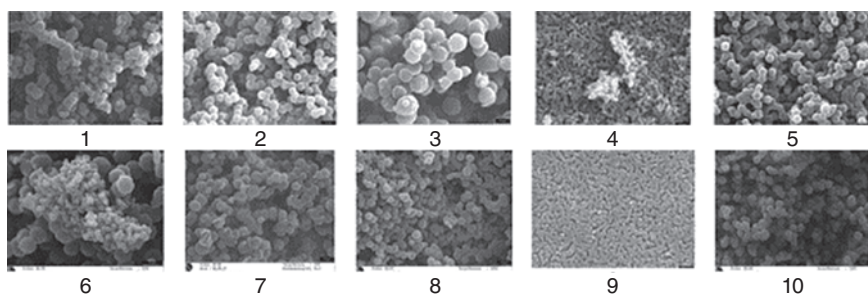
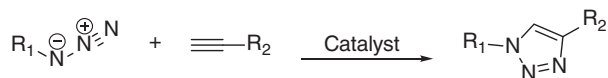


Figure 1.7 Structure of monoliths 1–10. (Bandari *et al.* 2006 [70]. Reproduced with permission of American Chemical Society.)



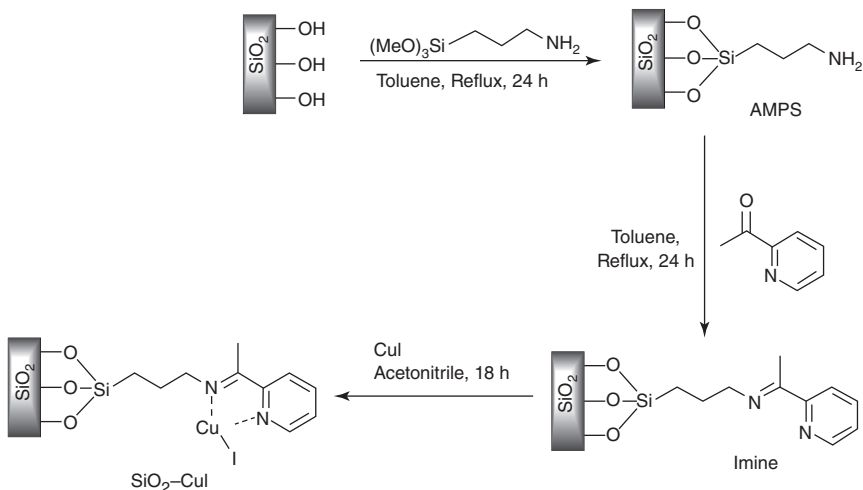
Scheme 1.9 Huisgen [3+2] cycloaddition.

heterogeneous Cu-based catalyst applied in the Huisgen [3+2] cycloaddition, making, at that time, the overall process more efficient and greener from an environmental point of view.

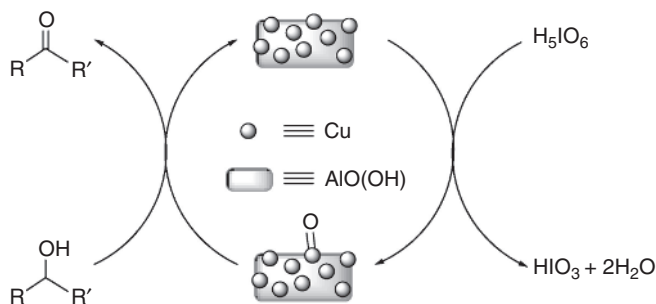
The catalyst was tested with a variety of substrates at room temperature, exhibiting high activities and regioselectivities. In addition, the catalyst was recycled up to six times with relatively good activity. An interesting finding was that the same catalyst was less active when tested without the ionic liquid ([BMIM][PF₆]), thus showing that the presence of the ionic liquid played a key role in maintaining the catalytic activity of the Cu(I) species. The leaching of Cu into the solution was around 0.13%, which was less than required for pharmaceutical standards.

A silica-functionalized Cu(I) catalyst was later employed as a green and recyclable catalyst for the same Huisgen [3+2] cycloaddition reaction at room temperature [73]. The catalyst was prepared by anchoring, as showed in Scheme 1.10, and tested in the preparation of 1,4-disubstituted-1,2,3-triazoles in water and at room temperature, obtaining excellent yields in a short reaction time (≤ 20 min). The recycling experiments were successful and the catalyst could be reused up to seven times without any significant loss of activity, and no leaching of Cu was detected by AAS.

A heterogeneous catalyst comprising copper supported on boehmite [Cu/AlO(OH)] was prepared from CuCl₂·2H₂O, pluronic 123 and Al(O-*sec*-Bu)₃ and tested in the selective oxidation of various alcohols using periodic acid



Scheme 1.10 Synthesis of silica-functionalized Cu(I) iodide [SiO₂-Cu]. (Shamim and Paul 2010 [73]. Reproduced with permission of Springer.)



Scheme 1.11 Suggested mechanism for the Cu/AlO(OH)-H₅IO₆ catalytic system. (Babu *et al.* 2011 [74]. Reproduced with permission of Elsevier.)

(H₅IO₆) as oxidant [74]. The oxidation of alcohols to aldehydes or acids is of particular interest in organic synthesis, since the derived products are important intermediates or products that are in high demand in the perfumery industry [75]. The reusability of the catalyst was tested in the oxidation of α -methyl-2-naphthalene methanol with 3.2 wt% of Cu; the catalyst was reused up to four times with a slight decrease in yield from 88 to 82%. Based on the study, the authors proposed a mechanism for Cu/AlO(OH)-catalyzed alcohol oxidation (Scheme 1.11). In the first step, the H₅IO₆ releases O₂ to form the Cu oxo species; and in the second step, the Cu oxo species convert the alcohols to the corresponding carbonyl compounds regenerating the catalyst.

Cu(0) nanoparticles supported on a magnetic silica support (SiO₂/CoFe₂O₄) were employed as catalyst in the hydrolysis of ammonia-borane (NH₃BH₃; AB), which is one of the most promising solid hydrogen carriers due to its high gravimetric hydrogen storage capacity (19.6 wt%), high stability, and low toxicity [76]. The catalyst was prepared by wet impregnation of Cu(II) precursor on previously prepared silica-coated cobalt ferrite nanoparticles (SCF) followed by *in situ* reduction of Cu(II) to Cu(0) under the H₂ produced during the hydrolysis of the AB compound. The prepared catalyst was fully characterized by means of XPS, high-resolution transmission electron microscopy (HRTEM) and N₂ physisorption. The catalyst (CuNPs@SCF) showed unprecedented activity in the hydrolysis of AB at room temperature with an initial TOF of 2400 h⁻¹, being the most effective catalyst within the non-noble metals and higher than the majority of the noble metal catalyst used for AB hydrolysis. Furthermore, due to the magnetic properties of the catalyst, its recovery and separation were facilitated from the reaction mixture by an external magnet, thus allowing its reuse, after water washing, up to 10 times without significant loss in catalytic activity (Figure 1.8). In addition, no copper was detected in the filtrate by ICP analysis, and the TEM analysis after reaction did not show any agglomeration or bulk copper formation. However, an increase in the size of the Cu(0) nanoparticles was observed (0.7–1.1 nm), which could be responsible for the slight decrease in activity observed after the 10th cycle.

A homogeneous copper catalyst (copper-tetrasulfonate phthalocyanine) was heterogenized by grafting on nanocrystalline cellulose (NCC) and employed in the selectivity oxidation of alcohols and alkyl arenes in aqueous solvents at room

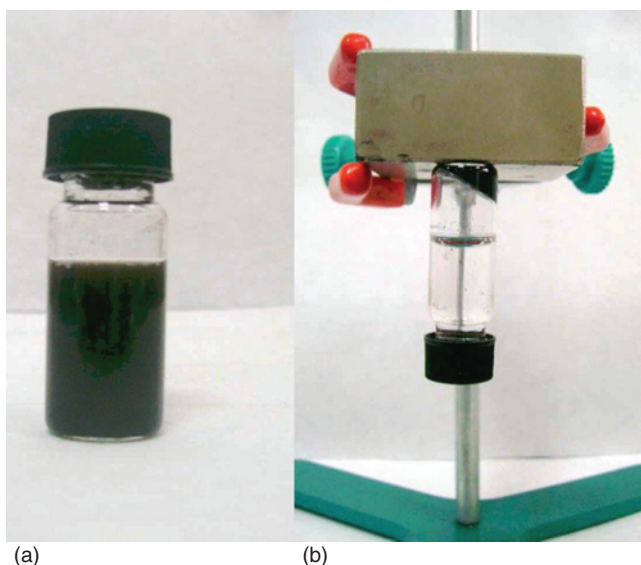
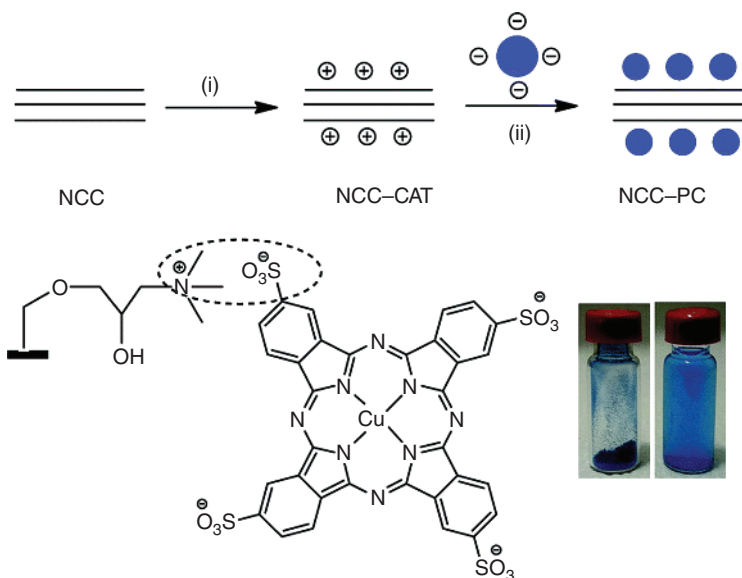


Figure 1.8 The pictures of (a) CuNPs@SCF dispersed in the reaction solution, (b) the reaction solution at the end of the reaction after the application of lab magnet. (Kaya *et al.* 2012 [76]. Reproduced with permission of American Chemical Society.)

temperature [77]. Scheme 1.12 shows the two-step procedure for grafting the copper compound on the NCC. In the first step, the NCC was converted to a cationic form by treatment with NaOH (NCC-CAT). In the second step, the grafting of the copper compound (Cu-PC) was achieved by strong electrostatic interaction and hydrogen bonding between the NCC-CAT and the anionic Cu-PC.

The grafted Cu-PC was characterized by various spectroscopic techniques such as, for example, XRD and XPS, and the copper loading was determined by ICP-AES analysis. The prepared catalyst was tested successfully in the oxidation of alcohols at room temperature using water as solvent and air as oxidant in the presence of 0.004 mol% of Cu. The catalyst could be recovered by centrifugation and used further in the same reaction, as demonstrated for the oxidation of benzyl alcohol where the catalyst was reused up to seven times with only a slight decrease in yield and no leaching of the metal detected after reaction by ICP-AES analysis.

Another heterogeneous copper catalyst, prepared by incorporation of Cu into a mesoporous silica in order to enhance the surface acidity of the silica, was employed in a one-pot MCR between dimedone, formaldehyde, and amines to yield 3,5-dispirosubstituted piperidines at room temperature using ultrasound [78]. Such piperidine products are important compounds due to their activities as pharmacophores in several biologically active compounds. High activity for the studied catalyst under conventional heating can be explained on the basis of the enhanced surface activity in the silica due to the combination of Cu(II) and the silanol groups, while higher activity of the catalyst observed in the studied



Scheme 1.12 Grafting of phthalocyanine on crystalline nanocellulose: (i) EPTMAC, NaOH; (ii) Cu-tetrasulfonate phthalocyanine. Inset: Digital photos of NCC-PC (solid) and NCC-PC (aqueous suspension). (Kaya *et al.* 2012 [76]. Reproduced with permission of Royal Society of Chemistry.)

reaction under sonochemical conditions was explained on the basis of higher adsorption and mass transfer of the organic molecules on the catalyst surface caused by the shockwave and microjets formed. The prepared catalyst could be reused up to six times without observing significant decrease in activity and leaching of the metal.

Examples of heterogeneous silver catalysis reported in the literature at room temperature are scarce. In fact, only one example of Ag nanoparticles supported on tungsten oxide used in the selective oxidation of aniline to azoxybenzene at room temperature has been reported, to the best of our knowledge [79]. The catalyst was prepared in a simple way at room temperature – avoiding the use of hydrazine – by mixing the silver precursor (AgNO_3), ammonium metatungstate hydrate, and cetyltrimethylammonium bromide (CTAB) as reducing agent in a molar ratio $\text{Ag}:\text{CTAB}:\text{H}_2\text{O} = 1:0.7:800$. The catalyst was fully characterized by means of XRD, ICP-AES, SEM, TEM, BET, extended X-ray absorption fine structure (EXAFS), XPS, and thermogravimetric analysis (TGA). The size of the obtained silver nanoparticles was found to be between 2 and 5 nm on the WO_3 support. The catalytic activity of the prepared catalyst was tested in the oxidative coupling of aniline to azoxybenzene in acetonitrile at room temperature in the presence of hydrogen peroxide as oxidizing agent. A major challenge in this reaction is to be able to control the selectivity to the desired product. The prepared catalyst showed high activity (87%) together with a remarkable 91% selectivity to the azoxybenzene after 24 h reaction with an aniline: H_2O_2 ratio of 1:3. A molar ratio of 1:1 yielded very low conversion (23%) of aniline with

poor selectivity (63%), while a molar ratio of 1:5 improved conversion (93%) but maintained a low selectivity to the azoxybenzene (70%). The scope of the catalyst use was extended to other substituted anilines in the optimal reaction conditions found for aniline with good to excellent results in terms of conversion and selectivity. The enhanced activity of the Ag/WO₃ catalyst in the studied reaction was proposed to result from two factors; (i) the small size and high dispersion of the silver nanoparticles and (ii) the synergistic interaction between the silver nanoparticles and the crystalline WO₃ support. Reusability of the Ag/WO₃ catalyst up to four times without any loss of activity and selectivity was demonstrated in the oxidative coupling of aniline. Furthermore, filtration test did not show any catalytic activity, indicating no leaching of the metal species into the solution. Analysis of the catalyst after the fourth use by TEM, ICP-AES, and XPS did not show any change compared to the freshly prepared catalyst.

Laser-driven heterogeneous catalysis using gold nanoparticles in SiO₂ systems was employed efficiently for amide formation at room temperature. This work relies on excitation of the surface plasmon resonance in the gold nanoparticles at a particular wavelength (532 nm) by a laser, which allows the reaction to take place at room temperature [80]. The gold catalyst was prepared by a previously described method, where the gold nanoparticles are bound to amino-functionalized silica [81]. TEM images of the catalyst showed gold nanoparticles of 1.85 nm that were well distributed on the surface of the functionalized silica (Figure 1.9). The catalyst and the new concept (excitation of the surface plasmon of the gold nanoparticles by laser at the required wavelength and the use of the generated energy to perform catalytic reaction at room temperature) were tested successfully in the synthesis of 4-benzoylmorpholine from benzaldehyde and morpholine. Furthermore, the reaction time was reduced significantly by 8 h compared to previous literature reports, highlighting the economic impact of this new energy-saving approach. The concept was also applied for tandem oxidation/amination for amide synthesis from benzyl alcohol and morpholine giving poor conversion (38%), but excellent selectivity to the target product (>99%). The stability of the gold nanoparticles after laser exposure was investigated in great detail, indicating incipient sintering and gold nanoparticles agglomeration after 15 h and a large sintering after 24 h of laser exposure. Therefore, recycling experiments were not carried out.

Ionic liquids grafted on graphene were employed to support gold nanoparticles (AuNP@SIL-*g*-G) and the resulting heterogeneous catalyst was employed in the selective aqueous, aerobic oxidation of alcohols to carbonyl compounds at room temperature [82]. The supported gold nanoparticles were prepared by impregnation using an ultrasound bath of an aqueous solution of the gold precursor (HAuCl₄) in the ionic-liquid-grafted graphene support followed by reduction with NaBH₄. TEM analysis of the prepared catalyst showed gold nanoparticles in the size range of 2–3 nm. The reaction conditions were optimized using benzyl alcohol as model compound with water and O₂ as the most suitable solvent and oxidizing agent, respectively. The optimum amount of catalyst was found to be 0.2 mol% without addition of any inorganic base, which otherwise typically are required in the oxidation of alcohols mediated by gold catalysts due to the presence of support OH groups that can act as internal base.

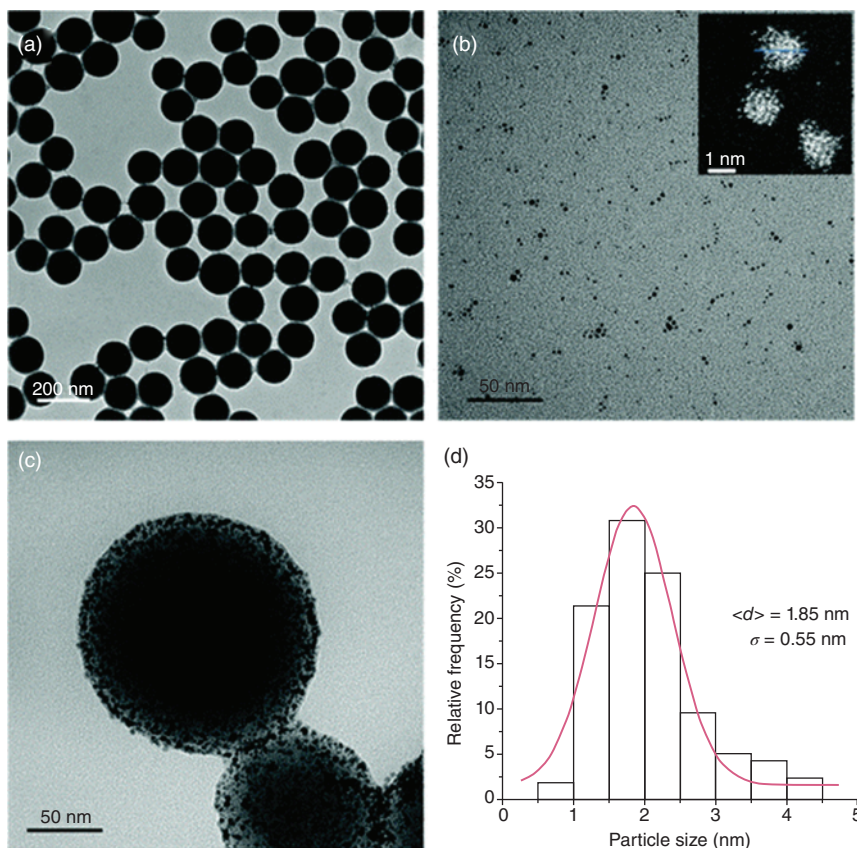


Figure 1.9 TEM photographs describing the morphology of the catalyst: (a) silica nanoparticles used as a support, (b) Au seeds, and (c) Au nanoparticles decorating the surface of the silica after amino–silane coupling. (d) Histogram ($N = 220$) showing the particle-size distribution of the Au nanoparticles. (Pineda *et al.* 2013 [80]. Reproduced with permission of Royal Society of Chemistry.)

The prepared catalyst was effective in the aerobic oxidation at room temperature of a pool of alcohols with excellent conversions (>95%) and selectivities (>97%). The AuNP@SIL-*g*-G catalyst was, in comparison with other supported Au catalysts, superior in performance in terms of reaction temperature and time or the use of toxic organic solvents (Table 1.3). The catalyst showed also a good stability and recyclability (up to four cycles), with no observed metal leaching.

1.4 Conclusions and Perspectives

Catalysis plays an essential role in driving the chemical industry toward more sustainable production. Accordingly, the development of more efficient catalytic processes through the rational design of new homogeneous and heterogeneous catalysts and catalyst–solvent systems continuous to constitute a highly

Table 1.3 Comparison of the results obtained from Au NP@SIL-*g*-G with other supported Au catalysts for the oxidation of benzyl alcohol.

Entry	Catalyst	Solvent	Temperature (°C)	Time (h)	Base	Yield (%)	Selectivity (%)
1	AuNP-SIL- <i>g</i> -G	H ₂ O	25	1	—	>99	>99
2	PS-PAMAM-Au NPs ^{a)}	DCM/H ₂ O	25	16	K ₂ CO ₃	99	—
3	Fe ₃ O ₄ /Au	Toluene	100	6	K ₂ CO ₃	100	100
4	Fe ₃ O ₄ :PVP ^{b)} /Au	H ₂ O	25	6	K ₂ CO ₃	94	5
5	Au/MgCr-HT ^{c)}	Toluene	100	1	—	96	99

a) Polystyrene-polyamidoamine-supported gold nanoparticles.

b) Poly(*N*-vinyl-2-pyrrolidone).

c) Layered double hydroxide hydrotalcite.

Source: Mahyari *et al.* 2013 [82]. Adapted with permission of Royal Society of Chemistry.

important research field, both in academics and in industry. Implementation of effective and benign catalytic protocols that enable chemical reactions to be performed under ambient conditions – most preferentially at room temperature – is especially desirable, as it facilitates energy intensification and minimizes hazards and risk in production plants. Furthermore, production selectivity toward the desired product is normally increased by lowering the reaction temperature, thus circumventing undesired side reactions and by-products constituting to waste production. In contrast to the reaction selectivity, the reaction rate can, however, be significantly hampered at room temperature, thus limiting the process productivity. Therefore, only selected catalyst systems with sufficiently low activation energy are applicable to such reactions, since only such systems will ensure that the production process proceeds at an acceptable rate without additional energy input.

This chapter surveys some of the most relevant homogeneous and heterogeneous catalytic reaction systems reported in literature, allowing reactions to be carried out at room temperature. Focus is especially on application of catalytically active transition metals from groups 9 to 11 of the periodic table, while fewer studies apply the more accessible and – often cheaper – base metals. Application of catalytic systems relying on ionic liquid catalysts and/or reaction media is a rather new direction in room temperature catalysis that may offer added advantages, as highlighted in selected examples. Such advantages include, for example, tunable reactant/product solubility profiles enabling formation of biphasic systems where catalyst recovery and reuse is facilitated, stabilization of metal nanoparticles through charge separation, as well as incorporation of intrinsic catalytic properties into the reaction media via function group derivatization. These characteristics are either difficult or impossible to obtain with traditional homogeneous and heterogeneous catalytic systems, thus making the novel IL systems interesting alternatives to already established catalyst systems and for possible future industrial validation.

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