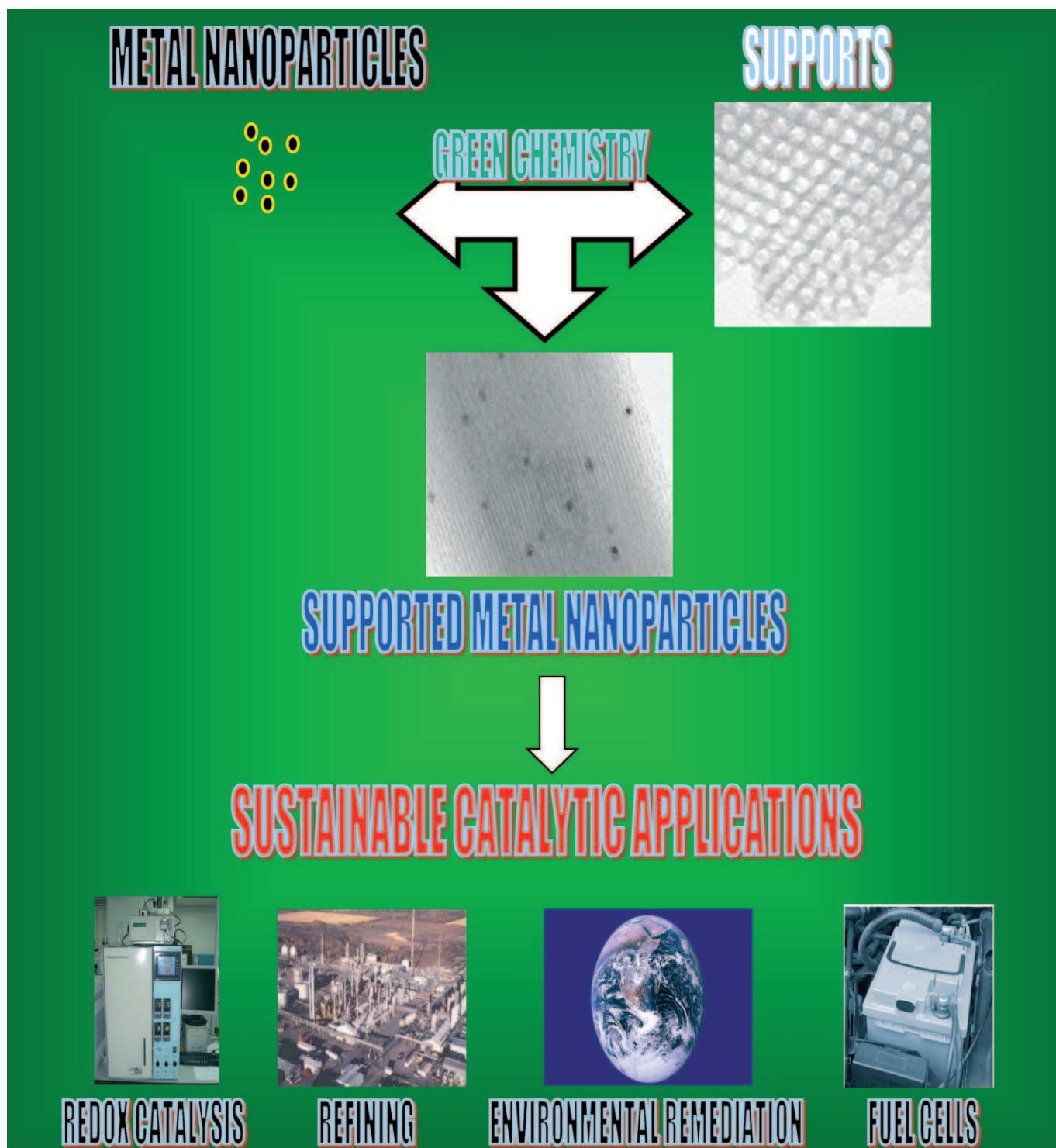# Sustainable Preparation of Supported Metal Nanoparticles and Their Applications in Catalysis

Juan M. Campelo, Diego Luna, Rafael Luque,* José M. Marinas, and Antonio A. Romero[a]

Metal nanoparticles have attracted much attention over the last decade owing to their unique properties as compared to their bulk metal equivalents, including a large surface-to-volume ratio and tunable shapes. To control the properties of nanoparticles with particular respect to shape, size and dispersity is imperative, as these will determine the activity in the desired application. Supported metal nanoparticles are widely employed in catalysis. Recent advances in controlling the shape and size of nanoparti- *cles have opened the possibility to optimise the particle geometry for enhanced catalytic activity, providing the optimum size and surface properties for specific applications. This Review describes the state of the art with respect to the preparation and use of supported metal nanoparticles in catalysis. The main groups of such nanoparticles (noble and transition metal nanoparticles) are highlighted and future prospects are discussed.*

1. Introduction

The scientific community has witnessed an explosion of interest and investment in the field of nanoscience and nanotechnology over the last few years. The nanoscience revolution (in terms of sheer interest and investment) is one of the biggest things to happen since the beginning of modern science,[1] and it is nowadays at the core of future technological progress owing to the increasing ability to manipulate matter on the nanometer scale. The ability to directly work and control systems at the same scale as nature (e.g. mitochondria, DNA, cells) can potentially provide a very efficient approach to the production of chemicals, energy and materials. Over a billion years, natural systems have evolved nanoscale biological entities for the efficient production of materials (i.e. enzymes) and energy (i.e. chlorophyll). By mimicking these systems, scientists may be able to reach the aims of a future sustainable society. Nanomaterials have therefore been regarded as a major step forward to miniaturisation and nanoscaling with various sub-fields that have been developed to study such materials. Every different subdiscipline plays its hand in modern nanoscience and technology (Figure 1). The nanotechnology field is highly multidisciplinary; inputs from physicists, biologists, chemists and engineers are required for the advancement of the understanding in the preparation, application and impact of new nanotechnologies.
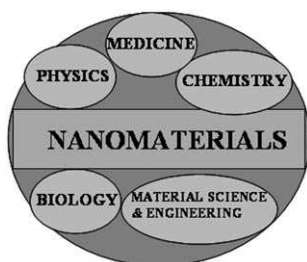

Figure 1. Nanomaterials encompass all fields, from materials science and engineering to (bio)medical applications.

A nanomaterial can be defined as a material that has a structure in which at least one of its phases has one or more dimensions in the nanometer size range (1–100 nm). Such materials include polycrystalline materials with nanometer-sized crystallites, materials with surface protrusions spatially separated by distances on the order of nanometers, porous materials with particle sizes in the nanometer range or nanometer-sized metallic clusters dispersed within a porous matrix (supported metal nanoparticles).

Among them, metal nanoparticles have attracted much attention over the last decade owing to their relatively high chemical activity and specificity of interaction. Furthermore, the properties of metal nanoparticles are very different to those of their bulk equivalents, such as a large surface-to-volume ratio.[2] Bearing in mind the briefly mentioned advantages and many outstanding features of metal nanoparticles, it is not surprising that the number of publications dealing with metal nanoparticles has increased almost exponentially over the last few years (Figure 2), with over 5000 publications so far
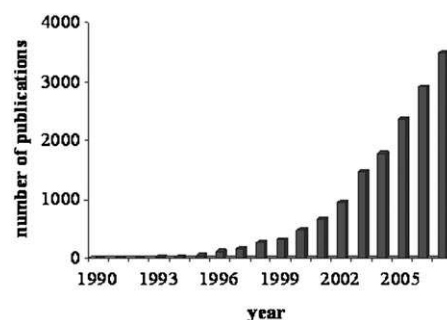

Figure 2. The growth in the number of publications dealing with metal nanoparticles (1990–2007). Source: SciFinder Scholar.

in 2008 alone. Research efforts are expected to continue increasing as the benefits of the chemical properties achieved at the nano level become increasingly apparent for applications.

One of the key driving forces for the rapidly developing field of nanoparticle synthesis is the already mentioned distinctly differing physicochemical properties presented by metal nanoparticles as compared to their bulk counterparts. Nanoparticles typically provide highly active centers, but they are very small and not in a thermodynamically stable state. Structures at this size regime are indeed unstable as a result of their high surface

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energies and large surfaces.[1,2] To produce stable particles, it is necessary to terminate the particle growth reaction and there are a number of methods by which this has been achieved. The addition of organic ligands or inorganic capping materials, or other metal salts, creating core–shell-type particle morphology as well as colloids and soluble polymers has been utilized to achieve this aim.[3–5] These materials can be grouped in the so-called "unsupported" metal nanoparticles. However, a problem arises with regard to the activity and reuse of these materials: the nanoparticles may undergo aggregation and suffer from poisoning under the reactions conditions resulting in deactivation and loss of catalytic activity.

A significant amount of research with the expressed aim of inhibiting aggregation and producing highly active nanoparticles with homogeneous size dispersity has been published.[3,5,6] The control of size, shape and dispersity of nanoparticles is key to selective and enhanced activity. A mechanism to achieve this control is to utilise another nanotechnology, that of (nano-porous) supports. These materials can be grouped as the so-called supported metal nanoparticles. The unique properties of supported metal nanoparticles are directly related to the specific particle morphology (size and shape), metal dispersion, concentration and the electronic properties of the metal within their host environment (Figure 3).[1,7]

Immobilisation and stabilisation of the nanoparticle form allows exploitation of the special properties that occur at this size regime. The fusion between porous materials and nanoparticle technology is potentially one of the most interesting and fruitful areas of this interdisciplinary research. The potential for increased efficiency from nanoparticle catalysts, in combination with the advantages of such heterogeneous supports, increases the "green" credentials of the process, with higher selectivity, conversion, yield and catalyst recovery being proposed advantages and targets. This provides the opportunity to develop specific devices for specific applications in various fields including medicine,[8] sensors[9] and catalysis.[5,10] Support-

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Prof. Diego Luna obtained his PhD in chemistry from the Universidad de Córdoba (Spain) and later began his teaching career there. His research activities have focused on heterogeneous catalysis and heterogenized homogeneous catalysis. He has (co-)authored over 140 publications and seven patents. From 2006, he has been involved in the technology-based SME, Seneca Green Catalyst, SL.

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Prof. José María Marinas has been a professor at the Departamento de Química Orgánica at the Universidad de Córdoba since 1976. He has published over 450 manuscripts related to his main research interests: applied heterogeneous catalysis and photocatalysis for the preparation of fine chemicals, sustainable and green chemistry and environmental remediation.
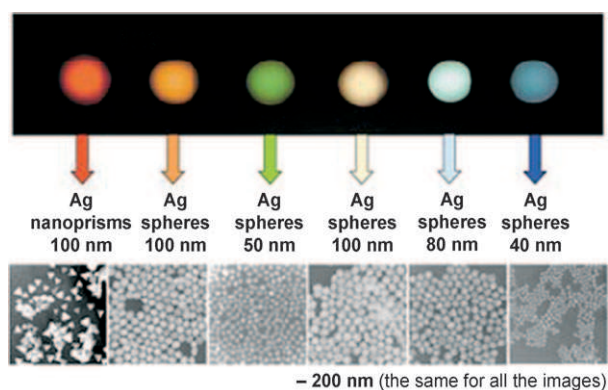
Figure 3. Nanoparticles: size, shape and composition (the quoted nanoparticle sizes are all approximate).[1] Reproduced with permission.

ed metal nanoparticles play an important role in catalysis, which is the most widely studied application of these materials, as they have been extensively employed in many industrial processes.[11]

Far from providing a comprehensive revision of all the reported protocols and catalytic applications of supported metal nanoparticles, this Review describes the state of the art with respect to the preparation of supported metal nanoparticles and provides an overview of the recently reported key preparation protocols and applications of such materials in catalysis. Owing to the rapidly expanding nature of this field, we hope that this Review provides a helpful overview and introduction to readers in this exciting research area.

2. Supported Metal Nanoparticles

2.1. What Is a Metal Nanoparticle?

The term metal nanoparticle is normally used to described nanosized metals with dimensions (length, width or thickness) within the nanometer size range (1–100 nm). Bulk metals are typically ductile and possess high thermal and electrical conductivity; properties resulting from electron delocalisation within the bulk matrix. In contrast, such physical properties are not typical amongst metal nanoparticles, as the delocalisation observed in the bulk is typically absent, thus giving rise to properties that are completely different to those of the bulk equivalent.

Metal nanoparticles have a large surface-area-to-volume ratio as compared to the bulk equivalents, making them partic-

ularly attractive candidates for catalytic applications. Their main features also include a unique transition between molecular and metallic states (providing a local density of states (LDOS)), a short-range ordering and increasing number of kinks, corners and edges.[1,2,7] Futhermore, recent advances in controlling the particle size and shape have opened the possibility to optimise the geometry of the particles for enhanced activity, providing the optimum size and surface properties for specific reactions. Decreasing metal cluster or nanoparticle size also results in an increase in the available surface of the system. The relationship between this surface, intraparticle metal–metal bonding, the particle shape and atom-packing geometry ultimately determines the efficacy of these nanoparticles in their catalytic applications.

2.2. Density of States and Surface Plasmon Resonance

Quantisation of the electronic states of nanoparticles, and manipulation of these states through size and shape control, is one of the main factors driving research in this field. Changes in properties at the nano level occur by different mechanisms for different materials. As a general rule, as we progress from the bulk metal to ever decreasingly smaller metal nanoparticles the energy continuum of the bulk metal changes to produce increasingly more discrete energy levels; that is, the density of the electronic states decreases (Figure 4). This phenemon is important as, for example, the lowering of the density of states within Ag nanoparticles in medical applications facilitates the existence of migratory Ag^+ ions, which have a high affinity for sulfur and phosphorus.

One of the primary reasons that nanoparticles have received such attention in the field of analytical science and sensors is that the adsorption of an analyte onto the nanoparticle surface will disrupt this resonance oscillation and generate a change in
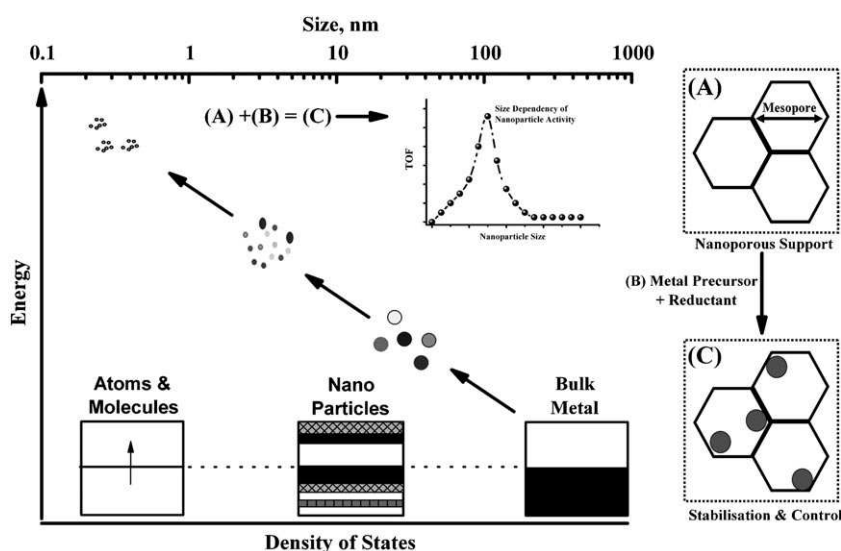

Figure 4. Relationship between nanoparticle size, energy and the principle of energy of states. Stabilisation and control of nanoparticle size can be achieved by selecting a nanoporous support potentially leading to enhanced catalytic activity and selectivity and ultimately designer catalysts.[7] Reproduced with permission from the Royal Society of Chemistry.

the electric field which can then be detected. This resonance behaviour is a phenomenon described as the surface plasmon adsorption (also termed the localised surface plasmon resonance (LSPR); Figure 5), and typically occurs as the nanoparticles decrease in size below the 100 nm threshold and commonly generates a strong colour in the visible region, the result of specific scattering interactions.
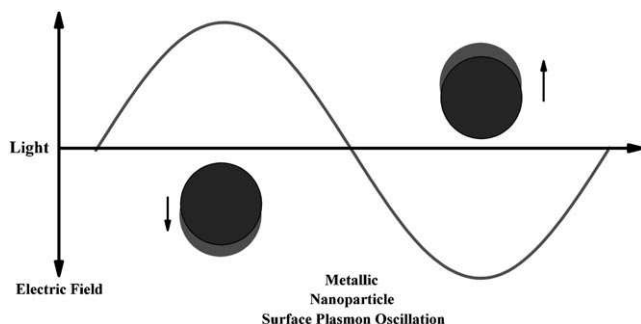

Figure 5. Oscillation of a metal nanoparticle's electron cloud (background) relative to the metal core (foreground), in response to the electromagnetic field—the basis for the surface plasmon resonance effect observed in nanoparticles.[7] Reproduced with permission from the Royal Society of Chemistry.

The electric-field component of the incident light induces oscillation of the nanoparticle's electron cloud.[13] Therefore, the size and shape of the metal nanoparticles will have a direct impact on this oscillation as this will affect the electron cloud density. Contributions from effective metal nuclei charge and polarisation within the electron cloud (affected by the dielectric constant of the metal) are also expected, as is influence from the support material surrounding the nanoparticle.

2.3. Porosity of the Support

2.3.1. Porous Materials

A porous material is normally a solid that comprises an interconnected network of pores (voids). Many natural substances such as rocks, clays, biological tissues (e.g. bones) and synthetic materials including ceramics, metal oxides, carbonaceous materials and membranes can be considered as porous materials. A porous material is characterised by its porosity (e.g. macro, meso-, microporosity or combinations thereof) as well its textural and physical properties which are dependent on its constituents.

The use of porous materials with defined pore sizes and characteristics as supports for nanoparticles allows the generation of specific adsorption sites, creating a partition between the exterior and the interior pore structure.[5, 14] It also has the added advantage of inhibiting particle growth to a particular size regime as well as reducing particle aggregation.[5–7, 10, 14] Furthermore, by selecting and manipulating the textural properties of the porous support (sometimes in unison with a reduction step), it should be possible to control the size and shape of the resulting nanoparticles. For example, Au has been

shown to demonstrate strong size selectivity, with the metal–oxygen interaction, which is important in oxidation reactions, altering as a result of the particle size. This behaviour leads to the possibility of size-selective and reusable heterogeneous catalysts based on the size of the nanoparticle rather than the pore size.

A variety of porous materials have been utilised as the support media for the controlled preparation of metal nanoparticles. Each support offers its own advantage, with specific thermally stable materials such as carbons receiving greater interest in high-temperature and high-pressure catalytic transformations (i.e. hydrogenations).[5, 10, 15] Some of the most commonly used supports and features associated with these materials regarding the preparation of supported metal nanoparticles will now be discussed. Among the wide range of solid supports employed for the deposition of metal nanoparticles, carbonaceous materials, metal oxides and polymers are the three main families of widely reported solid supports.

2.3.1.1. Carbonaceous Materials

Carbon-related materials offer great advantages as supports. First, recent advances in the field have allowed the preparation of carbon nanostructures with well-defined porosities and high surface areas. Second, the carbonaceous surface can be conveniently modified through different approaches (e.g. ozonolysis, plasma, doping with heteroatoms, acid or basic treatment) to stabilise catalyst–support interactions.[16] Despite the conventional use of microporous carbons as supports for metal nanoparticles,[17] there have been recent advances in the preparation of a range of carbonaceous materials as flexible supports. Budarin et al. have recently reported the preparation of a wide range of supported metal nanoparticles[18] on a novel family of mesoporous carbonaceous materials called Starbon[19] prepared from controlled carbonisation (under nitrogen atmosphere) of mesoporous starch.[20]

Endo et al. have also described the preparation of Pt nanoparticles (<3 nm) using carbon-fiber-type materials and, interestingly, a carbon cup-stack motif to effectively trap the growing nanoparticles between the cups.[21] Pt nanoparticles were observed inside and outside of the carbon-fiber structure.

Carbon nanotubes have also been investigated as supports for metal nanoparticles.[10, 22–24] Their intrinsic properties include high surface areas, unique physical properties and morphologies, high electrical conductivity and inherent size and hollow geometry that makes them extremely attractive as supports for heterogeneous catalysts (Figure 6).[24]

2.3.1.2. (Bio)Polymers

Polymers are another group of extensively employed supports for metal nanoparticles (Figure 7).[3–5, 25] They have been widely employed as a result of their availability, enhanced stabilisation properties of metal nanoparticles and resistance to particle sintering/agglomeration. Recently, the use of novel engineered polymers such as polyorganophosphazenes with an inorganic
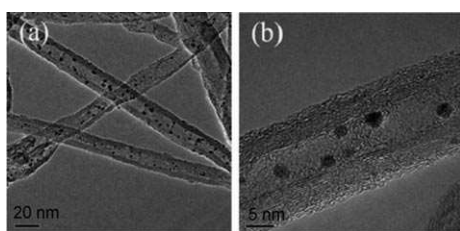
Figure 6. Transmission electron microscopy (TEM) images at different magnifications of Ru nanoparticles homogeneously dispersed inside the channels of carbon nanotubes.[24] Reproduced with permission from the Royal Society of Chemistry.
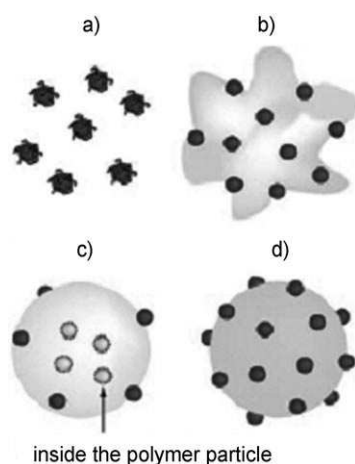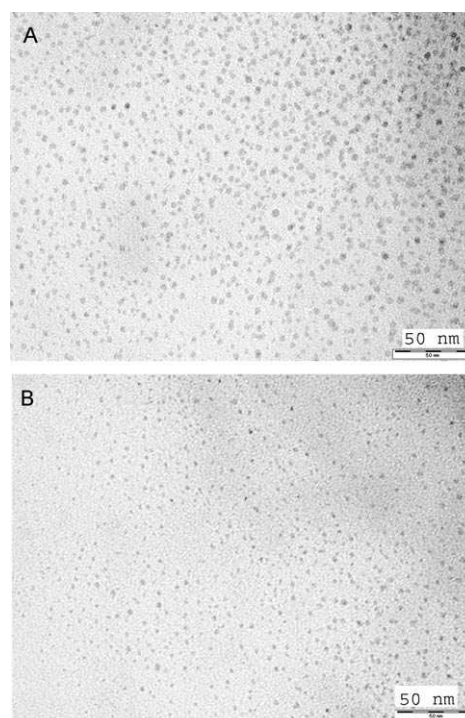

Figure 8. TEM images of 5 wt% Pd supported on mesoporous starch prepared in A) ethanol and B) acetone.[30] Reproduced with permission from the Royal Society of Chemistry.

Figure 7. Four examples of polymer-stabilised gold nanoparticles and clusters: a) gold clusters stabilised by water-soluble polymers; b) gold nanoparticles immobilised in the pores of a functionalised resin; c) gold clusters supported inside a polymer particle; and d) gold nanoparticles deposited on polymer surfaces.[41] Reproduced with permission.

backbone,[26] polyvinylpyridine,[5,27] fibers[5] and dendrimers[5,28] as supports has become increasingly popular.

Alternative supports including biopolymers and biomass-related polymers have been recently employed for the preparation of supported metal nanoparticles. Biopolymers are indeed attractive candidates for use as supports for catalytic applications.[29] They offer several advantages compared to traditional supports including low toxicity and cost as well as high biocompatibility, availability and abundance. Much work has been devoted to the preparation of different metal nanoparticles on various biopolymers including our own work on mesoporous starch[30] that afforded highly dispersed Pd metal nanoparticles with a narrow particle size distribution (Figure 8), and natural porous materials (e.g. diatomite).[31]

2.3.1.3. Metal Oxides

In general, metal oxides offer high thermal and chemical stabilities combined with a well-developed porous structure and high surface areas (> 100 m^{2}g^{-1}), meeting the requirements for most applications. They can also be easily prepared and further functionalised, adding value to their use as support or catalyst. Depending on the chemical reactivity of the support, metal oxides can be classified as inert (e.g. SiO$_2$) and reactive (e.g. CeO$_2$) metal oxides. Among the metal oxides, silica,[32–35] alumina,[32,34,36–38], titania,[34,35,39–42] ceria[32,34,36,43] and zirconia[36,37,44] are the most commonly employed supports.

Superparamagnetic oxides (e.g. Fe$_3$O$_4$) have recently emerged as new materials for the immobilisation of metal nanoparticles with improved separation capabilities.[45] Well-distributed and stabilised supported Pd[45a] and Rh[45b] MNPs in the magnetisable support surface (particle size in the 2–3 nm range) were found to be very active in the hydrogenation of cyclohexene[45] and benzene.[45a] The most attractive feature of the protocol is that the materials can be easily recovered using a permanent magnet in the reactor and can be reused in up to 20 runs without a significant loss in catalytic activity.

Mesoporous aluminosilicates from the SBA and M41S families have been also reported to be good supports for metal nanoparticles. We recently reported the preparation of Pt nanoparticles on the mesoporous aluminosilicate MCM-48.[46] The Pt metal nanoparticles were highly dispersed on the support with a very narrow (4–6 nm) particle size. Materials with low Pt loading (typically 0.5%; Figure 9A) were found to be highly active in the hydroisomerisation of *n*-octane. More recently, metal phosphates have also been reported as a novel family of efficient supports for Au metal nanoparticles.[47]
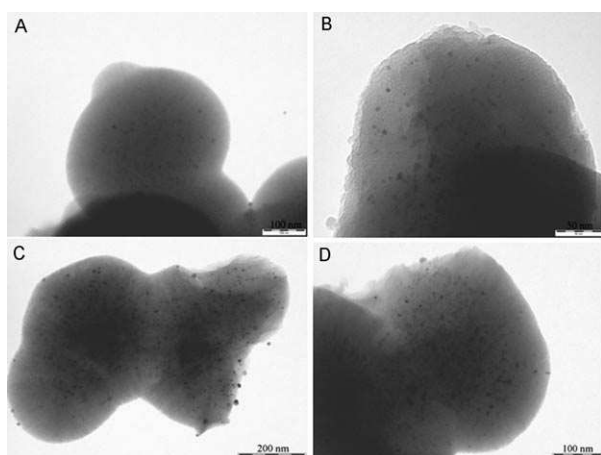
Figure 9. TEM images of Pt/Al-MCM-48 materials with different Pt loadings prepared by the traditional impregnation/reduction method: A) 0.5 wt% Pt; B) 1 wt% Pt; C) 3 wt% Pt; D) 5 wt% Pt.[46] Reproduced with permission.

2.3.2. Nonporous Materials

Nonporous materials can be defined as materials that do not have any voids or pores in their structure. These include metals, foils, glass, hard plastic and some polymers including polyethylene, polypropylene and other engineered polymers not included in the porous polymer section (e.g. poly(*N,N*-di-alkylcarbodiimide)).[48]

Despite the use of these common supports for the preparation of supported metal nanoparticles, other biomaterials and biomass have recently been reported as supports for metal nanoparticles. Following the initial reports by Raveendran et al.,[49] and He and Zhao,[50] much work has been devoted to the preparation of different metal nanoparticles on various biopolymers including cellulose,[51,52] chitosan[53–55] and poly(allyl-amine) gels.[56]

3. Preparation Routes

The preparation of supported metal nanoparticles for a wide range of catalytic applications has been well developed over the last few years. However, with sustainability emerging as a design criterion in nanoparticle synthesis and applications since the mid-1990s, there is still room for improvement in the methodologies employed for this purpose.[3,57]

In the context of nanomaterials, the sustainability concept is reflected in many of the green chemistry principles.[58] Ideally, the metal nanoparticle should be prepared with less toxic precursors, in water or more environmentally benign solvents (e.g. ethanol) using the least number of reagents and a reaction temperature close to room temperature and as few synthetic steps as possible (one-pot reaction) as well as minimising the quantities of generated by-products and waste.[3,58] Also, the nanoparticles should be well dispersed on the support surface and highly active in their catalytic applications. The use of less toxic precursors in benign solvents (e.g. metal acetate or nitrate solutions in water and/or ethanol) using more environmentally friendly supports (e.g. biopolymers and biomaterials)

and less energy-intensive protocols have been the subject of many recent reports. In this section, we briefly discuss the main sustainable approaches for the preparation of supported metal nanoparticles. These can be subdivided into physical (e.g. sonication, microwaves, UV), chemical (e.g. electrochemical, impregnation) and physicochemical (i.e. sonoelectrochemical) routes.

3.1. Physical Routes

The development of a range of green technologies including sonication, microwaves, UV, laser, plasma and supercritical fluids in the preparation of supported metal nanoparticles is evident in the literature. Some examples of reported protocols are examined herein.

3.1.1. Sonochemistry

Sonochemistry deals with the understanding of the effect of sonic waves and wave properties on chemical systems. Ultrasounds remarkably enhance mass transport, reducing the thickness of the diffusion layer, and also affect the surface morphology of the treated materials, normally enhancing the surface contact area.[59] Deposition and reduction of the particles (favoured by ultrasonic radiation) takes place almost consecutively so that the heating step normally employed in other protocols can be avoided,[39] making the preparation of supported metal nanoparticles more energy-efficient and environmentally friendly. Another interesting feature of the methodology is the controllable nanoparticle size distribution that can be achieved. These advantages are related to the acoustic cavitation phenomena, that is, the formation, growth and collapse of the generated bubbles in a liquid medium. The extremely high temperatures ($>5000\,°C$), pressure (>20 MPa) and cooling rates ($>10^{10}\,°C\,s^{-1}$) lead to many unique properties in the irradiated solution.[60] The preparation of metal nanoparticles is usually performed using a conventional ultrasonic cleaning bath or a high-power probe (Figure 10).[61] However, these ultrasonic-assisted protocols sometimes require the additional

Figure 10. Traditional ultrasonic bath (left) and ultrasonic probe (right) employed for the preparation of supported metal nanoparticles.

use of a reductant including sodium borohydride,[62] hydrogen[39] and hydrogen/polyalcohols,[60–63] to further ensure the reduction of the nanoparticle on the support.

3.1.2. Microwave Irradiation

It has been recently demonstrated that microwaves are a very effective technology in applied chemistry. Several examples of microwave-assisted deposition of metal nanoparticles on supports have been reported, mainly employing solutions of metal salts as precursors. Microwave irradiation has several advantages over conventional methods, including short reaction times, small particle sizes, narrow size distributions and high purity.[18,64] El-Shall and co-workers have extensively investigated the use of microwaves for the preparation of a range of supported metal nanoparticles including Au and Pd.[32,65] They have also prepared capped Au and Pd nanoparticles on metal oxides using polyethylene glycol and poly(N-vinyl-2-pyrrolidone) as protective polymers prior to microwave-heating to further stabilise the nanoparticles from agglomeration. In this way, the obtained metal nanoparticles were better dispersed and had a narrower particle size distribution, which in turn increased their activity for the investigated application (e.g. oxidation of CO). They claimed that fast and uniform heating (due to high dielectric constants of PEG and PVP) achieved under microwave irradiation allows a quicker reduction of the metal precursor on the support.[32,65]

We recently reported the preparation of a range of metallic nanoparticles on an ordered mesoporous silica SBA-12 structure.[66] The metallic Au, Ag and Pd nanoparticles were prepared in a very short time (<2 min) under microwave irradiation of a solution of the metal salt precursor in ethanol/water or ethanol/acetone mixtures without the need of additional reductant.[66] Both the ethanol and the hydroxy-rich silica surface facilitate the reduction of the metal nanoparticle on the support as previously reported.[30,67] The microwave protocol afforded dispersed and relatively small metal nanoparticles (2, 3.8 and 11.3 nm average particle size for Au, Ag and Pd, respectively; Figure 11), which were highly active catalysts for oxidation reactions.

The time of microwave irradiation is a critical parameter in the preparation of these materials as longer reaction times lead to substantial particle agglomeration (Figure 12). Our recent studies were in good agreement with findings by El-Shall and co-workers.[65] This methodology has, in general, difficulties with respect to controlling the particle size and distribution of the metal nanoparticle on the support. However, the polyalcohols added as stabilisers/capping agents have been shown to help to achieve a more homogeneous and narrow particle size distribution.[68]

3.1.3. Pulsed Laser Ablation

The laser approach involves the vaporisation of metals employing a pulsed laser (e.g. Nd-YAG) and subsequent controlled deposition on the surface of the support under well-defined conditions of temperature and pressure.[32,69] Savastenko et al.
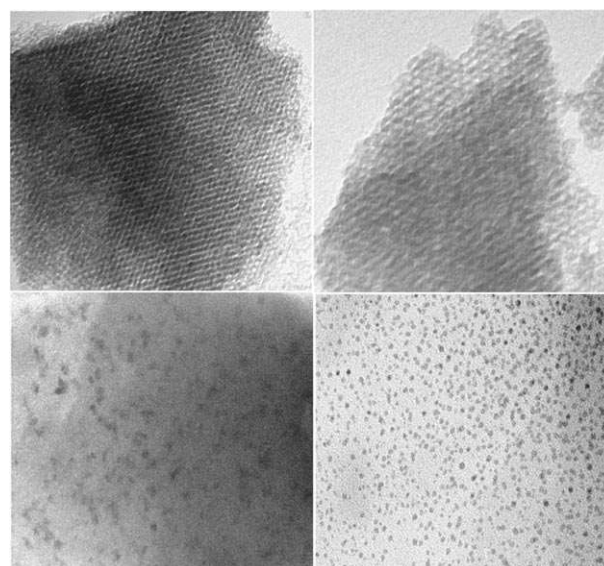

Figure 11. Top: TEM images of "bare" SBA-12 ($\times$160000, left; $\times$300000, right). Bottom: TEM images of Ag metal nanoparticles (left) and Au metal nanoparticles (right) supported on SBA-12 ($\times$300000, 50 nm) prepared in a domestic microwave oven.[66] Reproduced with permission from the Royal Society of Chemistry.
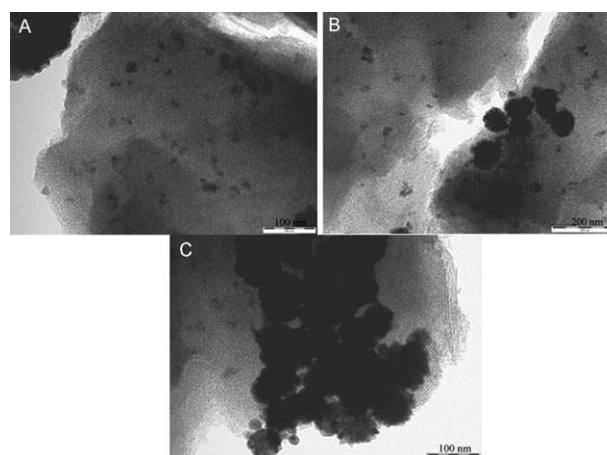

Figure 12. TEM micrographs of Pd/SBA-12 prepared in a domestic microwave oven at different times: A) 2 min; B) 10 min; and C) 20 min.[66] Reproduced with permission from the Royal Society of Chemistry.

recently reported the preparation of monometallic Pt and Rh nanoparticles (1 wt% loading) by the direct deposition on different SiO$_2$ supports by means of pulsed ultraviolet (248 nm) excimer laser ablation of Pt and Rh bulk metals.[70] The supported metal nanoparticles had a narrow particle size distribution (centered at ca. 2.5 nm) and exhibited high activities in the reduction of NO$_x$ compounds. The method has several advantages for the synthesis of supported metal nanoparticles. First, it does not usually involve the use of chemical precursors or solvents and therefore it provides a simple, environmentally friendly and effective synthetic route for supported contamination-free crystalline metal nanoparticles.[32] Second, almost any metal or mixtures in any composition and form (e.g. sheets,

films and powders) can be turned into metal nanoparticles. Third, metal nanoparticles can directly be supported on catalysts as they are created with a significant number of dangling bonds and they are strongly adsorbed and anchored onto supports. Last, and most importantly, no side products are created and the technique can be scaled up for industrial applications.[36] The sizes and compositions of the generated metal nanoparticles can be adjusted to generate materials for specific catalytic applications.[36,70]

Figure 13. A) TEM and B) HRTEM images of multiwalled carbon nanotubes decorated with Rh metal nanoparticles, prepared using supercritical CO_2.[76] Reproduced with permission from the Royal Society of Chemistry.

3.1.4. Supercritical Fluids

Another efficient and green alternative to prepare a wide range of supported metal nanoparticles has been the use of supercritical fluids. A very good revision on the subject was recently reported by Zhang and Erkey.[71] The conventional procedure involves the dissolution of a metal precursor in a supercritical (sc) fluid (e.g. $scCO_2$) and its subsequent incorporation on a substrate/support under various conditions.[71,72] The impregnated metal precursor can be reduced to its elemental form by three different approaches: 1) chemical reduction in the supercritical fluid (using a reducing agent such as H_2 or ethanol);[71,73] 2) thermal reduction in the supercritical fluid;[71,74] and 3) thermal decomposition (in an inert gas) or chemical reduction with hydrogen or air after depressurisation.[71,72,75]

Supercritical fluids offer several advantages as compared to traditional methods. First, they can provide enhanced mass-transfer properties owing to their higher diffusivities compared to liquids and lower viscosities. Second, the lower surface tension allows better penetration and wetting, avoiding problems related to partial structure shrinkage or pore collapse on certain materials (e.g. silica aerogels) that are present in conventional chemical methodologies. Third, it is possible to control the particle dispersion and morphology on various supports by employing different metal precursors and by varying the metal content and reduction temperatures and chemistry.[71] Supercritical CO_2 has been widely employed for the preparation of supported metal nanoparticles as it is abundant, inexpensive, non-flammable and non-toxic.[71–76]

Wai and co-workers have shown that it is possible to decorate multiwalled carbon nanotubes with ruthenium and rhodium nanoparticles through hydrogen reduction of the respective metal precursors and by using $scCO_2$ as the delivery medium for the deposition of the metal nanoparticles.[76] Supported particles with good dispersity along the external surface of the tube structure were produced in the 5–10 nm range (Figure 13). The resultant materials were shown to be active in the hydrogenation of a range of arenes.[76]

However, more studies are needed in terms of the solubility of the organic precursors in the supercritical fluid and the reduction step in order to further develop this technique. Another major issue in the widespread use of supercritical fluid is the cost of the equipment.
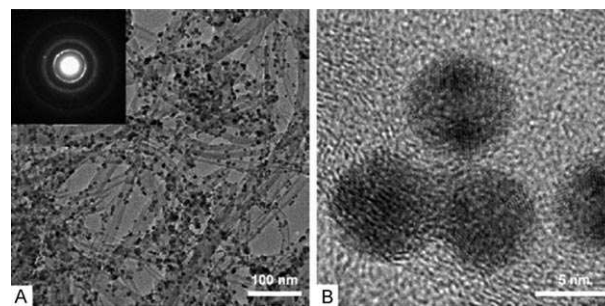
3.1.5. Plasma

A novel plasma reduction method at room temperature has been used to prepare supported metal nanoparticles. Legrand et al. employed a dihydrogen microwave plasma to reduce various metal solutions (Au, Pt and Pt-Au) on zeolites.[77] The afterglow of such microwave plasma (2.45 GHz) was found to contain hydrogen atoms at a sufficiently low temperature to effectively reduce the metal ions in solution to small metal nanoparticles (< 5 nm) on NaY and HY zeolites. The supported metal nanoparticles were found to be very stable to thermal treatment.

An Ar-glow discharged plasma has also been employed to support Pt, Pd, Ag and Au nanoparticles on a range of supports including nonporous TiO_2, γ-alumina and H-ZSM-5.[78] The metal nanoparticles were found to be homogeneously distributed on the surface of the support. Oxygen-glow discharge plasma allowed the preparation of supported metal nanoparticles, but small quantities of metal oxides were also found in their preparation. This technique is a very promising and straightforward way to prepare metal nanoparticles as it is an environmentally friendly, fast and simple methodology and also a promising alternative to hydrogen reduction at high temperatures. However, the specialised equipment needed makes difficult its widespread use.

3.1.6. Other Physical Routes

A range of other physical routes to prepare supported metal nanoparticles have also been reported, including the use of gamma radiation[79] and Au–Ag exchange.[80]

3.2. Chemical Routes

The classical chemical synthesis methods are co-precipitation, impregnation and deposition-precipitation. Some other novel greener routes include precipitation from reverse-micelle (water-in-oil) emulsions, photochemistry, chemical vapour deposition and electrochemical reduction.

3.2.1. Traditional Methods

3.2.1.1. Impregnation

This methodology entails the "wetting" of the solid support with a solution containing the metal precursor. The common method of chemical impregnation is the so-called wetness impregnation. In this method, the metal nanoparticle precursor, which is normally a salt (e.g. metal nitrate, chloride), is dissolved in the minimum quantity of solvent. The resulting metal salt solution is then added to the porous support, filling its pores so that a thick paste is formed. The solvent is then removed in a rotary evaporator and the final solid is oven-dried and subsequently calcined and reduced (if needed) before being tested as a catalyst (Figure 9 and Figure 14).[33,46,81] The metal nanoparticles obtained by this methodology are dispersed depending on the metal, support and loading of the final solid.[33,46,81,82]
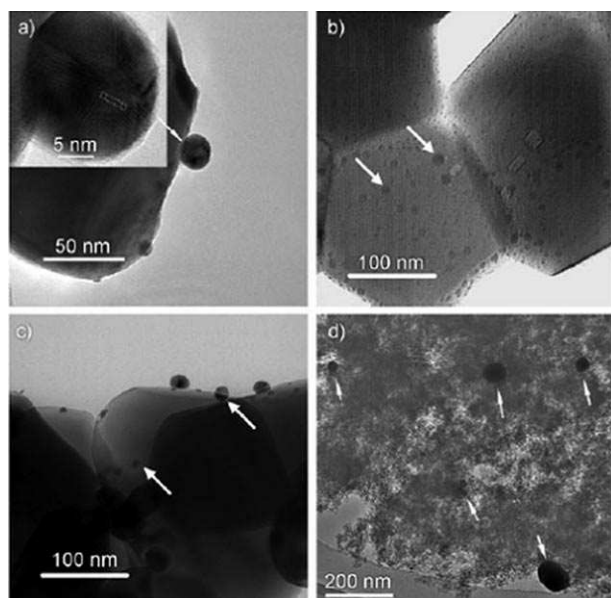

Figure 14. TEM images of gold metal nanoparticles on different oxide supports prepared by the impregnation method using citrate as reducing agent. a) Au/ZrO$_2$; b) Au/CeO$_2$; c) Au/Fe$_2$O$_3$; d) Au/SiO$_2$. Arrows indicate gold nanoparticles.[81] Reproduced with permission.

3.2.1.2. Co-precipitation

The co-precipitation method involves the simultaneous precipitation of the metal and the support.[83] In this way, the metal nanoparticles can be incorporated into the structure of various mesoporous materials.[33,84] Barau et al.[33] recently prepared supported Pd metal nanoparticles on hexagonal mesoporous silicas (HMS) using a sol-gel approach previously reported.[85] Such metallic Pd nanoparticles, with particle sizes around 4–5 nm, were found to be relatively well dispersed on the silica surface. However, the presence of the metal precursors in solution interfere with the polymerisation chemistry of the material, often resulting in samples with undesirable properties. Also,

the sol-gel technology cannot be easily applied to polymeric substrates.[71]

Bao and co-workers recently reported a modified one-pot co-precipitation approach to the preparation of supported Ag metal nanoparticles on silica.[86] The template-directed route comprises the capping of Ag$^+$ cations in solution with dodecylamine, subsequent reduction to Ag metal using formaldehyde (CH$_2$O) and eventual self-assembly of the material after addition of the silica source (e.g. tetraethyl orthosilicate (TEOS); Figure 15). Compared to conventionally impregnated materials that were found to have large particles (15–18 nm) unevenly dispersed on the support (Figure 16), the uniformly supported metallic silver nanoparticles prepared using this novel methodology had an average size of 3.5 nm and were found to be well dispersed and embedded in the silica matrix (Figure 16).
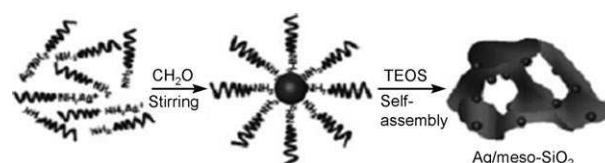

Figure 15. Schematic depiction of the preparation of Ag metal nanoparticles on silica using a modified co-condensation protocol.[86] Reproduced with permission from the Royal Society of Chemistry.
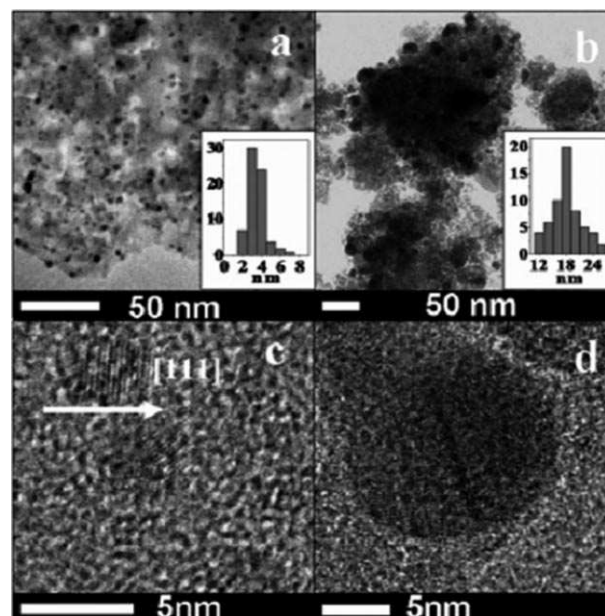

Figure 16. TEM and HRTEM images of a,c) Ag metal nanoparticles supported on SiO$_2$ prepared by a modified co-condensation protocol; b,d) Ag metal nanoparticles supported on SiO$_2$ prepared by conventional impregnation. The insets show the particle size distributions of silver nanoparticles.[86] Reproduced with permission from the Royal Society of Chemistry.

3.2.1.3. Precipitation-Deposition

This method was initially reported by Haruta et al.[87] and involves the dissolution of the metal precursor followed by ad-

justment of the pH (i.e. 5–10) to achieve a complete precipitation of the metal hydroxide (e.g. Au(OH)$_3$), which is deposited on the surface of the support. The hydroxide formed is subsequently calcined and reduced to the elemental metal (Figure 17).[84,88,89]
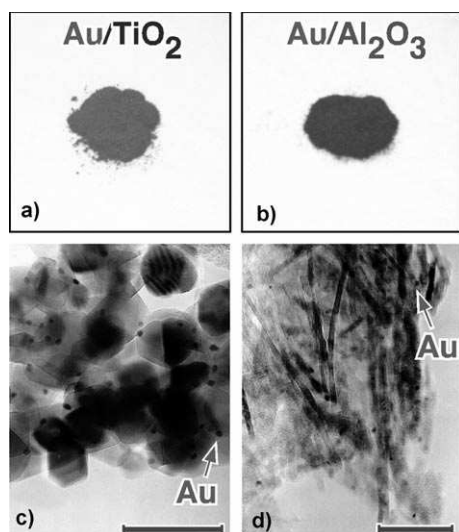

Figure 17. TEM micrographs of a) Au/TiO$_2$ (violet powder) and b) Au/Al$_2$O$_3$ (grey-blue powder) prepared by the deposition/precipitation method. Scale bars: 50 nm.[89] Reproduced with permission.

In general, these methodologies often provide a broad nanoparticle size distribution and it is difficult to tune the particle size for a particular application owing to a poor control of the nanoparticle size (Figures 9, 14 and 17), that also affects the dispersion and size of the metal nanoparticle with increasing metal loadings (Figure 9). Particle agglomeration is quite a common phenomena, and the use of liquid solutions has been reported to create a collapse of fragile supports (e.g. organic or silica aerogels) as a result of the high surface tension of the liquid solution.[90] Furthermore, many of the reported protocols require the use an excess of external reductant (e.g. NaBH$_4$, H$_2$, hydrazine) to ensure the complete formation of the supported metal nanoparticle, that has to be removed after the reaction.

3.2.2. Microemulsions

Microemulsions can be described as homogeneous-like combinations of water, oils and/or surfactants (often in the presence of alcohol- or amine-based compounds).[91] The formation of reverse micelles was confirmed to be an interesting and environmentally friendly alternative to the preparation of metal nanoparticles. Thus, a solid support is impregnated with a microemulsion containing a dissolved metal salt precursor,[90,92,93] in a similar way to that of the previously described traditional chemical impregnation. Metal nanoparticles obtained using this methodology have a more controllable, narrow crystallite distribution as compared to those obtained through the traditional impregnation, co-precipitation and precipitation-deposition methods.[92–94] This has been attributed to the confined location of a limited amount of metal salt in the micelles that

are subsequently taken up upon interaction with the support.[38,90,92–94] The microemulsion–support interaction can be enhanced by increasing the hydrophobicity of the support (e.g. silylation of hydroxy-rich surfaces), making it more chemically compatible with the microemulsion during the deposition step.[95] Wang et al. have also recently reported another interesting approach of this methodology employing a water–liquid CO$_2$ (as oil phase) microemulsion stabilised by sodium bis(2-ethylhexyl)sulfosuccinate as surfactant and hexane.[96] In this way, Pd, Rh and Pd-Rh nanoparticles with sizes ranging from 2 to 10 nm could be homogeneously deposited on the surface of multiwalled carbon nanotubes.

3.2.3. Photochemistry

Only a few reports can be found on photochemical protocols to prepare supported metal nanoparticles. Kohsuke et al. reported a photoassisted deposition method that allows the formation of Pt and Pd nanoparticles on the photoexcited tetrahedrally coordinated titanium species within the framework.[97] Similarly, He et al. demonstrated that metallic Au nanoparticles could be supported on a TiO$_2$ support by decomposition and photochemical deposition of a gold precursor (HAuCl$_4$) employing a 125 W high-pressure mercury lamp.[98] Yu et al. recently prepared bimodal metallic Pt nanoparticles (1–3 nm) supported on titania nanotubes through photochemical deposition of hexachloroplatinic acid (H$_2$PtCl$_6$·6H$_2$O) as the metal precursor on the titania nanotube.[99] These materials were found to be highly active in the hydrogenation of CO$_2$ to methane under mild reaction conditions (100 °C).

In general, the photochemical deposition of metal nanoparticles minimises the use of chemicals and solvents and is therefore more environmentally friendly than many of the reported chemical routes. However, it is still not clear how well the size and distribution of metal nanoparticles on a solid support can be controlled.

3.2.4. Chemical Vapour Deposition

Chemical vapour deposition is another promising route for the preparation of supported metal nanoparticles. It has been regarded as a powerful method to generate highly dispersed metal catalysts in a controlled and reproducible manner.[100] This procedure involves the vaporisation (sublimation) of metals and growth of the metal nanoparticles under high vacuum in the presence of an excess of stabilising organic solvents (e.g. aromatic hydrocarbons, alkenes and tetrahydrofuran) and/or reducing agents (e.g. H$_2$).[26,101,102] The metal nanoparticles have a relatively narrow particle size distribution (2–8 nm, Figure 18). Chemical vapour deposition is claimed to allow the preparation of metal nanoparticles on a wide range of organic and inorganic supports under very mild conditions (< 50 °C) to afford highly active heterogeneous catalysts,[102,103] thereby avoiding the formation of large agglomerated nanoparticles from other protocols. Nevertheless, the method is often limited by the vapour pressure of the precursor and mass-transfer-limited kinetics.[73]
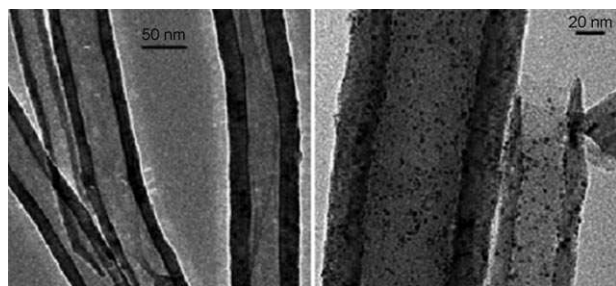
Figure 18. TEM images of untreated (left; scale bar: 50 nm) and functionalised carbon nanofibers (right, 2.04 wt % Pd; scale bar: 20 nm) with Pd metal nanoparticles through chemical vapour deposition.[103] Reproduced with permission from the Royal Society of Chemistry.

3.2.5. Electrochemical Reduction

The electrochemical deposition of metal nanoparticles, although not widely employed, has also been mainly reported for carbon-based supports.[104] The electrodeposition of Pt nanoparticles under potentiostatic conditions takes places from acidic aqueous solutions of H_2PtCl_6. The use of stabilisers (e.g. tetraalkylammonium salts) is needed to prevent the deposition of particles at the surface of the cathode.[90]

3.2.6. Other Chemical Methods

Alternative chemical protocols have been reported to prepare supported metal nanoparticles. Sunagawa et al. prepared a range of supported metal nanoparticles (Au, Ru, Rh, Pd, Ir and Pt) using an ion-exchange/reduction approach that involves the adsorption of metal ions or complexes on the surface of the support which are subsequently reduced to the metallic state by heating the solution.[105] In this way, metal loadings up to 20 wt % were achieved, allowing a substantial control of the particle size (below 2 nm).

Metallic Pd nanoparticles have also been prepared by confination/reduction of palladium acetate onto a urea cross-linked imidazolium-functionalised silica material.[106] These supported Pd metal nanoparticles were highly active, stable and reusable in Suzuki–Miyaura couplings (Figure 19) as compared to conventionally prepared silica-supported Pd metal nanoparticles, which suffered Pd leaching after one reaction cycle.[106] These
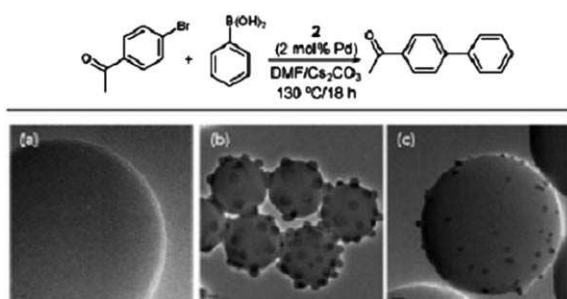

Figure 19. TEM images of Pd metal nanoparticles supported on functionalised silica: a) before (scale bar: 20 nm); b) after first reuse (scale bar: 100 nm); and c) after fifth reuse (scale bar: 20 nm) in the Suzuki reaction.[106] Reproduced with permission from the Royal Society of Chemistry.

methodologies offer a better control of the growth and distribution of nanoparticles. However, some of them involve the use of an excess of additional reductant (e.g. hydrazine, $NaBH_4$) to ensure the complete reduction of the metal nanoparticles and must be removed prior to the use of the supported nanoparticles in the catalytic reaction.

3.3. Physicochemical Routes

A few examples of greener combined physicochemical routes have been reported, the most common ones being sonoelectrochemistry and flame spray pyrolysis.

3.3.1. Sonoelectrochemistry

This approach involves a combination of ultrasound waves and electrochemistry. Comprehensive reviews about the use of sonoelectrochemistry have been recently reported.[107, 108] Ultrasounds have beneficial effects on electrochemistry. They enhance mass transport, therefore altering the rate and sometimes the mechanism of the electrochemical reaction.[59] They also affect surface morphology through cavitation jets at the electrode–electrolyte interface, increasing the surface area. Furthermore, ultrasounds reduce the diffusion layer thickness and therefore ion depletion. Silver-coated TiO_2 nanoparticles have been prepared in this way.[109]

3.3.2. Flame Spray Pyrolysis

This alternative method of preparation was initially reported by Madler et al.,[110] and further reports on the technique appeared recently.[111] The liquid precursor mixture was fed in the centre of a methane/oxygen flame by a syringe pump and dispersed by oxygen, forming a fine spray (Figure 20). The spray flame was surrounded and ignited by a small flame ring issuing from an annular gap (0.15 mm spacing at a radius of 6 mm). Product particles were then collected on a glass fibre filter (Whatmann GF/D, diameter 25.7 cm) with the aid of a vacuum pump. The technique afforded highly stable supported metallic Pd nanoparticles with small particle size (< 5 nm) that were suitable for various applications.[110, 111]

3.3.3. Other Physicochemical Routes

Ishida et al. recently reported the deposition of metallic Au nanoparticles on porous coordination polymers using the so-called solid grinding approach.[102] This methodology entails the grinding of volatile organogold complexes (e.g. [Me$_2$Au-(acac)]) with porous coordination polymers in an agate mortar in air for 20 min at room temperature and subsequent reduction of the resulting material in a stream of 10 vol % H_2 in N_2 at 120 °C for 2 h. The so-prepared materials exhibited small and well-distributed metallic Au nanoparticles with an average size of 2 nm compared to larger and less evenly distributed supported Au metal nanoparticles prepared by chemical vapour deposition (Figure 21). The reported materials were also highly active in the aerobic oxidation of alcohols.[102]
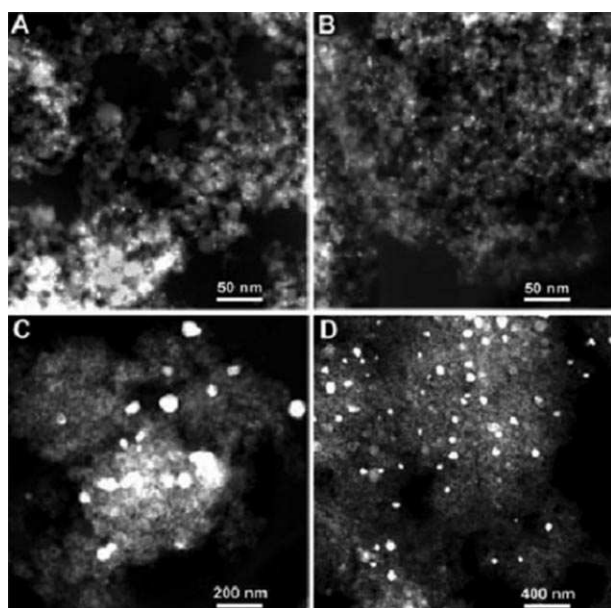
Figure 20. Scanning transmission electron microscopy images of Pd metal nanoparticles on a La$_2$O$_3$/Al$_2$O$_3$ support: A) as-made material; B) annealed at 800 °C; C) after reaction (five cycles from 200 to 1000 °C); d) annealed at 1000 °C.[111] Reproduced with permission from the Royal Society of Chemistry.
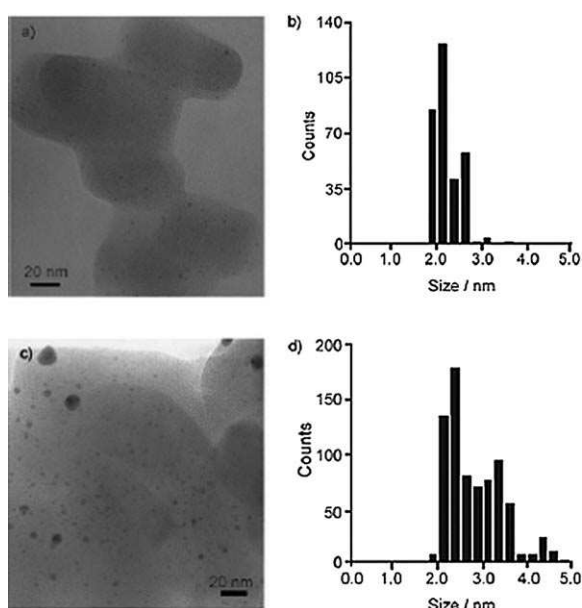

Figure 21. TEM images and the respective size distributions of Au metal nanoparticles supported on a porous coordination polymer ([Cu$_2$(pzdc)$_2$-(bpy)]$_n$; pzdc = pyrazine-2,3-dicarboxylate; bpy = 4,4'-bipyridine) prepared by a,b) solid grinding (1 wt% Au) and c,d) chemical vapour deposition (0.5 wt% Au).[102] Reproduced with permission.

4. Catalytic Applications

Herein, we aim to highlight some of the most commonly reported supported metal nanoparticles stemming from the number of publications and applications in catalysis from the last few decades. An elaborated monography about nanoparti-

cles and catalysis was recently edited by Astruc.[112] Here, we initially divide them into two main groups: supported noble-metal nanoparticles (i.e. Au, Ag, Pt and Pd) and transition-metal nanoparticles (i.e. Fe, Ni and Cu). This section, far from providing a comprehensive revision of all the reported catalytic applications of supported metal nanoparticles, gives an overview of the key applications of such materials in catalysis. Thus, each metal will be briefly introduced and some of the different reported methodologies/applications will be described.

4.1. Noble-Metal Nanoparticles

4.1.1. Gold

Gold nanoparticles have become increasingly popular in catalysis. Au was originally considered to be chemically inert and regarded as a poor catalyst. However, when gold is prepared as very small (less than 10 nm) and dispersed particles on a suitable support, it can be a highly active catalyst in a wide range of reactions including oxidations, hydrogenations and related reactions.[112] The most interesting methodologies and applications of Au nanoparticles has been recently reviewed by Daniel and Astruc.[113] Metallic Au nanoparticles have been reported to be well dispersed on different supports with nanoparticle sizes ranging from 1 to 10 nm.[40,41,113,114] They have been widely employed in the oxidation of CO.[40,41,113] The optimum size of metallic Au nanoparticles is highly dependent on their potential applications. Haruta and co-workers prepared supported metallic Au nanoparticles by a precipitation-deposition method using a basic solution of the gold precursor (HAuCl$_4$) which is gelated after adjusting the pH (6–10) to the corresponding deposition of the Au(OH)$_3$ hydroxide on the support (Figure 17). The catalyst is then washed and dried to give the supported metallic Au nanoparticles after calcinations at 300–400 °C.[89]

Stable spherical metal nanoparticles are formed and their size can be controlled by the calcination temperature. Haruta and co-workers showed that the optimum particle size for the oxidation of CO is 3 nm. This size can be obtained by calcining the material at 297 °C.[5,114] TiO$_2$ is the dominant support for

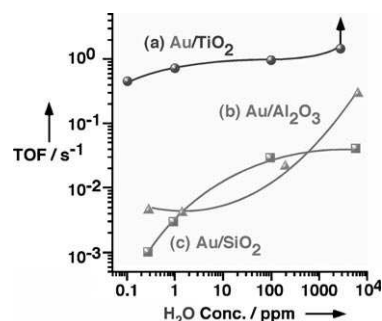**Figure 22.** Turnover frequencies per surface gold atom at 273 K for CO oxidation using a) Au/TiO$_2$ (●); b) Au/Al$_2$O$_3$ (▲), and c) Au/SiO$_2$ (■) as a function of moisture concentration. The superior performance of Au/TiO$_2$ in the CO oxidation is shown (arrow).[89] Reproduced with permission.

metallic Au nanoparticles employed for the catalytic oxidation of CO,[5,89,114] regardless of the reaction conditions (Figure 22).

Numerous supported metallic Au nanoparticles have been prepared and utilised in a wide range of catalytic applications, indicating the potential in utilising such supported metal nanoparticles in catalysis. Most of the work carried out with Au in the last few years has been carried out by the groups of Corma, Haruta and Hutchings. Some of these are briefly summarised in Table 1.
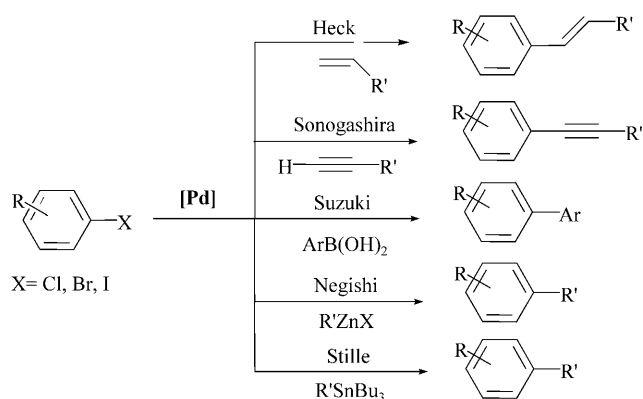
4.1.2. Palladium

Palladium is probably the most versatile metal in promoting or catalysing reactions, particularly those involving C—C bond formation (e.g. Suzuki, Heck and Sonogashira), many of which are not easily achieved with other transition-metal catalysts.[126] Thus, the preparation of supported metallic Pd nanoparticles on different supports has been extensively investigated. Several supported metallic Pd nanoparticles have been employed in

**Table 1.** Applications of various supported Au metal nanoparticles in catalysis

Application	Substrate	Support, method, nanoparticle size	Ref.
Hydrogenations of alkenes, alcohols and aldehydes		Various supports Various methods NP size: variable	[115]
Oxidations	alcohols	Metal oxides (e.g. Fe_2O_3, Al_2O_3, TiO_2), carbon Co-precipitation, impregnation/reduction NP size: 2–10 nm	[116, 117]
	aldehydes	Al_2O_3, SiO_2, activated carbon Impregnation (from metal sols)/reduction NP size: 2–13 nm	[116d]
	aromatic amines	Polymers Impregnation NP size: 5–10 nm	[118]
	alkenes	Metal oxides (e.g. Al_2O_3, SiO_2), activated carbon, polymers Various methods NP size: variable	[117, 119, 120]
	nitroarenes	TiO_2, Fe_2O_3, activated carbon Deposition/precipitation, impregnation NP size: 3–5 nm	[121]
Oxidative decomposition of alkylamines and dioxins		Fe_2O_3/La_2O_3 Deposition/precipitation NP size:1–10 nm	[114]
Direct epoxidation of propylene		TiO_2 (MCM-48) Deposition/precipitation NP size: 1–10 nm	[114]
C—C coupling reactions		Oxides (Ce, Ti, Zr, SiO_2) Deposition/precipitation NP size: 10 nm	[122]
Hydroamination of terminal alkynes		Chitosan, chitosan/SiO_2 Impregnation NP size: 2–6 nm	[53]
Benzannulation of 2-(phenylethynyl)benzaldehyde and phenylacetylene		CeO_2, TiO_2 and C Impregnation/reduction, precipitation NP size: 3–17 nm	[123]
Synthesis of methanol/dimethyl ether from syngas		ZnO, ZnO/Al_2O_3 H-Y zeolite Impregnation	[124]
Hydrochlorination of ethyne		Activated carbon Impregnation	[117]
Water gas shift reaction		Mesoporous TiO_2, CeO_2 Deposition/precipitation, coprecipitation and gelation NP size: 2–5 nm	[125]

C–C bond reactions including the Suzuki, Heck, Sonogashira and related C–C couplings (Scheme 1).[127]

Figure 23. Top: TEM images of Pd metal nanoparticles supported on polyaniline (PANI) fibers: A) before reaction; C) halfway through reaction; D) after two reuses.[133] Reproduced with permission.

Scheme 1. Selected C–C coupling reactions catalysed by supported Pd metal nanoparticles.

The Suzuki–Miyaura reaction involves the coupling of aryl halides (reactivity: iodides > bromides > chlorides) with aryl boronic acids (Scheme 1). Metallic Pd nanoparticles supported on alumina- and silica-based oxides,[35a, 37, 128] commercial magnetic nanoparticles,[129, 130] carbonaceous materials,[18, 131] siliceous mesocellular foams (MCF),[132] mesoporous biopolymers,[30] natural porous materials,[31] and other polymers including polyaniline nanofibers,[133] polysilane,[134] and related polymers[25e, 48] have been reported as highly active and reusable catalysts in the coupling of various aryl bromides and chlorides with aryl boronic acids. Budarin et al. prepared highly dispersed, active and reusable metallic Pd nanoparticles on biopolymers (Figure 8) that afforded quantitative conversion of bromobenzene (starting material) into the cross-coupled product (biphenyl) within a few minutes of reaction (Scheme 2).[18, 30]
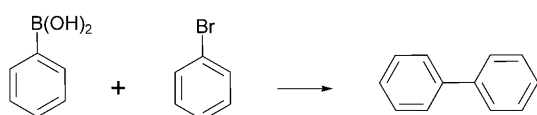
Scheme 2. Suzuki coupling of bromobenzene and phenylboronic acid using Pd metal nanoparticles on expanded starch.[18, 30]

Gallon et al. prepared supported metallic Pd nanoparticles on polyaniline nanofibers as semi-heterogeneous catalysts for C–C couplings in water.[133] The highly dispersed low-loaded metal nanoparticles were very effective in the Suzuki coupling of aryl chlorides and phenylboronic acids (Figure 23) as well as in the formation of phenols from aryl halides.[133] The catalysts were also highly stable and reusable up to 10 times in the Suzuki reaction.

The Heck reaction is another key C–C bond-forming reaction. It predates the Suzuki methodology and is one of the most useful derivations of palladium chemistry, giving access to new extended alkenes through the addition of halides and
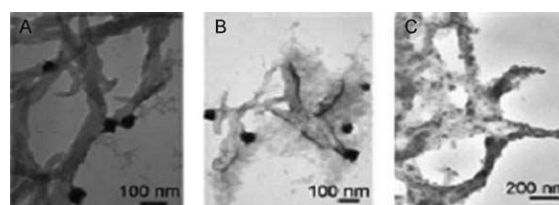
triflates to alkenes (Scheme 1). Several examples of catalytically active metallic Pd nanoparticles for Heck reactions supported on similar supports to those reported for the Suzuki reaction can also be found.[18, 30, 31, 33, 51, 101, 129, 130a, 131, 132, 135]

Budarin et al. recently reported the preparation of catalytically active Pd nanoparticles on silica and starch (Figure 8) for the Heck reaction under microwave irradiation.[18, 30, 33] This protocol afforded very good conversions and selectivities to the C–C coupled products using iodobenzene and methyl acrylate (Scheme 3 and Table 2) and styrene in a few minutes of reaction, in a similar way to those of related protocols of Cejka and co-workers using Pd/MCM-41 materials (Scheme 4).[136]
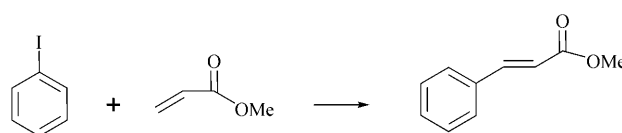
Scheme 3. Heck coupling of iodobenzene and methyl acrylate using Pd metal nanoparticles on expanded starch[18, 30] and silica.[33]
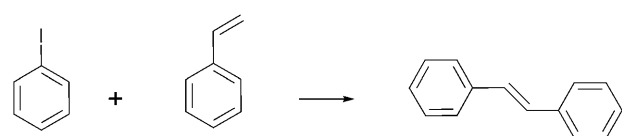
Scheme 4. Heck coupling of iodobenzene and styrene using Pd metal nanoparticles on expanded starch.[30]

Table 2. Heck reaction of iodobenzene and methyl acrylate using Pd/starch supported catalysts (adapted from ref. [30]; reproduced with permission from the Royal Society of Chemistry).[a]

Entry	Conv. [mol%]	Select. [mol%][b]
0.5% Pd/starch-1	50	> 99
2.5% Pd/starch-2	> 90	> 90
5% Pd/starch-3	> 99	85
0.5% Pd/starch-4	70	> 99
2.5% Pd/starch-5	> 95	> 95
5% Pd/starch-6	> 95	85

[a] Reaction conditions 8 mmol iodobenzene, 8 mmol methyl acrylate, 5 mmol triethylamine, 0.1 g catalyst, microwave irradiation, 300 W, 90 °C, 5 min. [b] Selectivity for methyl acrylate.

Another key C—C bond-forming reaction is the Sonogashira coupling of terminal alkynes (Scheme 1). It involves the alkynylation of aryl or alkenyl halides with alkynes to afford cross-coupled alkynes together with homocoupled dialkynes as by-products. Chinchilla and Najera recently reported the use of supported Pd nanoparticles in the Sonogashira reaction.[137] Many other protocols for the synthesis of various organic com-pounds of pharmaceutical interest can be found else-where.[18,30,51,130,134]

Supported Pd nanoparticles have also been used in a wide range of other catalytic applications including hydrogenations, oxidations, hydrodechlorinations and C—H activation. The list of applications is enormous. Some of them are summarised in Table 3.

Table 3. Selected applications of supported Pd metal nanoparticles.

Application	Substrate	Support, method, nanoparticle size	Ref.
Hydrogenations	alkynes, cinnamaldehyde	Polyaniline Deposition/reduction NP size: 200–500 nm (13 nm agglomerates)	[138]
	hydroxyaromatic derivatives	Hydrophilic carbon Co-precipitation/reduction NP size: 20–80 nm	[139]
	nitroarenes	Carbon nanofibers Impregnation/reduction NP size: 3–7 nm	[140]
C—H activation and C—C coupling		Alumina nanoparticles Impregnation, precipitation	[141]
Decomposition of H_2O_2		Polymer resin beads Impregnation/reduction NP size: 30–146 nm	[142]
Synthesis of H_2O_2		Metal oxides (e.g. Al_2O_3) Impregnation, sol-gel method	[143, 144]
Oxidations	alcohols	Metal oxides, mesoporous materials (e.g. SBA-15) Impregnation, microwaves NP size: 1–20 nm	[66, 144–146]
	glycerol	Metal oxides, mesoporous materials, polymers All methods NP size: 1–200 nm	[147]
	CO/NO oxidation	–	[148]
	benzene oxidation	SBA-15 Impregnation, grafting NP size: 5–20 nm	[149]
	alkenes	SBA-12 Microwave irradiation NP size: 2 nm	[66]
Conversion of $CHClF_2$ (gas-phase dismutation, hydrodehalogenation and pyrolysis)		Metal fluorides (e.g. CaF_2) Sol-gel synthesis/reduction NP size: 3–8 nm	[150]
Hydrodechlorination		Polymers, carbons, Al_2O_3, TiO_2, ZrO_2 Various procedures NP size: 2–50 nm	[44a, 151]
Hydrogen sorption		carbon nanotubes, activated carbon, yttrium oxides Various procedures NP size: variable	[152]
Synthesis of vitamin intermediates		Polymers Impregnation/reduction NP size: 1–2 nm	[153]

4.1.3. Platinum

The majority of supported Pt nanoparticles have been employed in hydrogenations[70, 140, 154, 155] or in electrocatalytic oxidations for fuel cell applications.[156, 157] Recently, Campelo et al. reported the preparation of metallic platinum nanoparticles supported on acidic Al-MCM-48 for the hydroisomerisation of *n*-alkanes.[46] Metallic Pt nanoparticles were found to be highly dispersed on the support (Figure 9), and their activities were comparable to those of silicoaluminophosphates and zeolites.[158, 159]

Metallic Pt nanoparticles have also been supported on magnetic nanoparticles through modification of Fe_3O_4 with ionic liquid groups and subsequent ion-exchange of platinum salts (e.g. K_2PtCl_4) with the linked groups and reduction of the Pt ions with hydrazine (Figure 24) to give highly stable and active
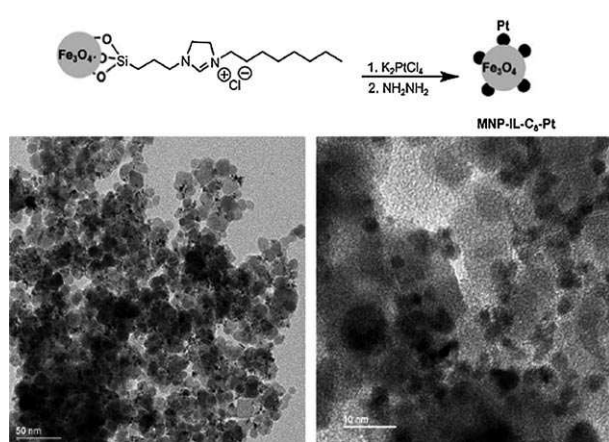

Figure 24. Top: Preparation of Pt metal nanoparticles supported on magnetic nanoparticles (top scheme). Bottom: TEM images of Pt metal nanoparticles supported on ionic liquid modified magnetic nanoparticles (MNP-IL-C_8-Pt); scale bars: 50 nm (left) and 10 nm (right), respectively.[154d] Reproduced with permission.

materials for the hydrogenation of alkynes and α,β-unsaturated aldehydes (Table 4).[154d]

Supported metallic Pt nanoparticles were also very active and selective in the oxidation of CO,[160] alcohols,[161, 162] alkenes[163] and other compounds[164] including the oxidation of vitamin precursors such as L-sorbose to 2-keto-L-gulonic

acid,[152] and the dehydrogenation of methylcyclohexane.[165] Layered double hydroxide supported nanoplatinum catalysts were also reported to be good catalysts for the allylation of aldehydes, giving moderate to good yields of homoallylic alcohols.[166]

4.1.4. Silver

Silver and silver-based compounds are highly antimicrobial by virtue of their antiseptic properties to several bacterial strains including *Escherichia coli* and *Staphylococcus aureus*. As a result, most of the recent applications of metallic Ag nanoparticles have been related to biological/medical areas.[167] Nevertheless, supported metallic Ag nanoparticles have been reported for a variety of catalytic applications.

Supported metallic Ag nanoparticles have become increasingly important in the selective oxidation of alkanes and alkenes for the synthesis of industrially interesting products including epoxides and aldehydes.[66, 168] Metallic Ag nanoparticles supported on alumina[168c] and calcium carbonate[168b] are very active and selective in the heterogeneous epoxidation of ethylene. More recently, Chimentao et al. prepared highly active and dispersed supported Ag metal nanoparticles on alumina and MgO for the selective gas-phase oxidation of styrene.[169] Loadings ranging from 11 to 40% Ag were obtained as well as different particle sizes and morphologies (from nanowires to nanopolyhedra). The activity and selectivity of the supported metallic Ag nanoparticles was found to be very strongly dependent on the morphology of the nanoparticles.

Mitsodume et al. recently reported the activity and reusability of low-loaded supported metal nanoparticles on hydrotalcites (prepared by conventional impregnation-reduction with hydrogen) in the oxidant-free dehydrogenation of alcohols.[170] Materials with less than 0.01 wt% metal and an average silver particle diameter of 3.3 nm provided extremely good conversions and selectivities to the ketones with exceedingly higher turnover numbers (TON = 600–22000) than previously reported values for the dehydrogenation of alcohols, and also were reusable four times with no decrease in reaction rates. Supported metallic Ag nanoparticles exhibited a superior performance as well as improved selectivities to dehydrogenation in the reaction compared to its Ru and Pd analogues (Figure 25).[170]

Supported Ag metal nanoparticles have also been employed in hydrogenations of dyes including methylene blue, eosin,

Table 4. Hydrogenation of various alkynes and α,β-unsaturated aldehydes[a] using platinum metal nanoparticles supported on functionalised magnetite nanoparticles.[154d] Reproduced with permission.

Entry	Substrate	*t* [h]	Products (yield [%])
1	diphenylacetylene	16	*cis*-stilbene (95), *trans*-stilbene (5)
2	1-ethynyl-4-methylbenzene	4.5	1-methyl-4-vinylbenzene (88), 1-ethyl-4-methylbenzene (12)
3	2-ethynyl-6-methoxynaphtalene	4.5	2-methoxy-6-vinylnaphtalene (67), 2-ethyl-6-methoxynaphtalene (33)
4	3-phenylprop-2-yn-1-ol	4.5	(*Z*)-methylprop-2-en-1-ol (78), (*E*)-methylprop-2-en-1-ol (11), 3-phenylpropanol (11)
5	methyl 3-phenylpropiolate	4.5	(*Z*)-methyl 3-phenylacrylate (67), (*E*)-methyl 3-phenylacrylate (15), methyl 3-phenylpropanoate (18)
6	cinnamaldehyde	12	3-phenylprop-2-en-1-ol (99)
7	2-methyl-3-phenylacrylaldehyde	12	2-methyl-3-phenylprop-2-en-1-ol (90)

[a] Reaction conditions: 0.5 mmol substrate, 5 mL methanol, 90 °C, 200 psi H_2, 22 mg catalyst.
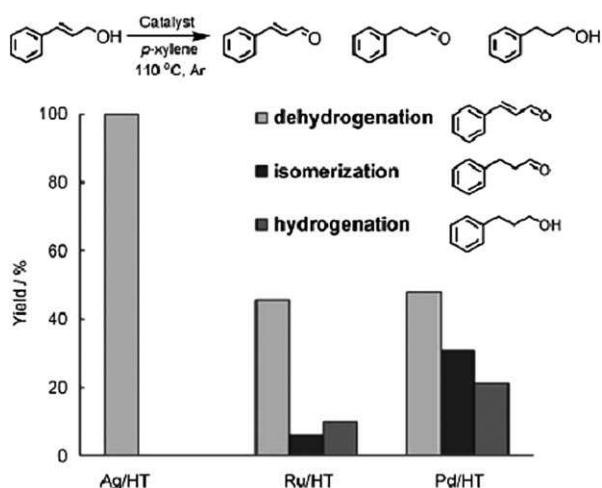
Figure 25. Oxidation of cinnamyl alcohol using supported metal nanoparticles on hydrotalcites (HT).[170] Reproduced with permission.

rose Bengal[171] and Rhodamine 6G[172] as well as in the hydrogenation of acrolein.[173]

4.1.5. Rhodium

Catalytically active supported metallic Rh nanoparticles have mostly been employed in hydrogenations including the reduction of 1-alkenes,[174] arenes,[45b, 175] and ketones[175] (Figure 26), CO hydrogenation,[176] and in the reduction of various α,β-unsaturated compounds.[177, 178]

Savastenko et al. reported the lean NO_x reduction using supported metallic Rh nanoparticles on SiO_2 in the 100–400 °C temperature range and employing a representative test gas
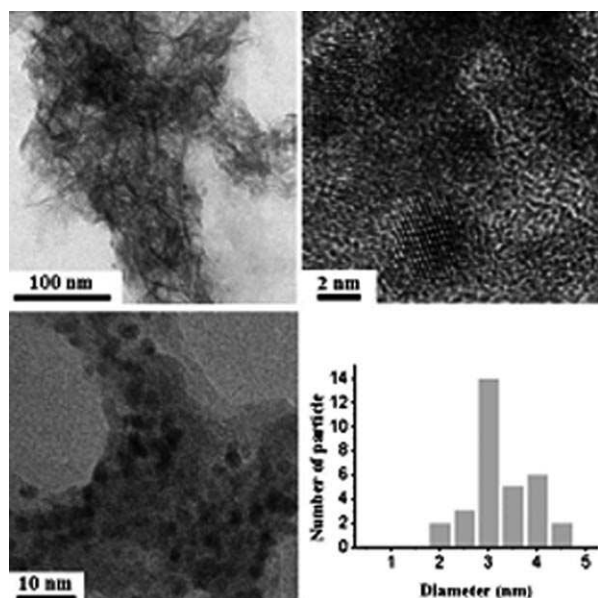

Figure 26. TEM images and particle size distribution of Rh metal nanoparticles on aluminum oxyhydroxide nanofibers, used in the hydrogenation of arenes at room temperature with a hydrogen balloon.[175] Reproduced with permission.

mixture of oxygen-rich diesel engine exhaust gas.[70] The results demonstrated that under cyclic lean/rich operating conditions, a laser synthesized $PtRh/SiO_2$ bimetallic catalyst showed the highest activity for NO_x reduction in the low temperature range 100–300 °C. At 150 °C, the activity of this catalyst was found to be around three times higher than that of a monometallic Rh/SiO_2 reference catalyst prepared by wet impregnation. The low-temperature NO_x reduction activity and the selectivity to N_2 of the conventional Rh catalyst could also be enhanced by additional laser deposition of Pt nanoparticles.[70] Bao and co-workers prepared catalytically active Rh metal nanoparticles confined inside carbon nanotubes for the conversion of CO and H_2 into ethanol.[179] The overall formation rate of ethanol (30 $mol\,mol_{Rh}^{-1}\,h^{-1}$) was found, for the first time, to be an order of magnitude superior for metallic Rh nanoparticles supported inside the carbon nanotubes than for metallic Rh nanoparticles supported on the surface of the nanotubes, despite the latter supported metal nanoparticles being more accessible.

Alumina-supported metallic Rh nanoparticles (particle size 4.4 nm) have been investigated in the ring opening of cyclohexane giving *n*-hexane, *n*-pentane and benzene as major products with minor quantities of methylcyclopentane and light alkenes (C_1–C_4).[180] Rh/TiO_2 materials with extremely low Rh loadings (0.004% Rh) were also found to be active in the partial oxidation of propylene, giving yields of about 13% at 275 °C.[36]

4.1.6. Ruthenium

Supported metallic Ru nanoparticles are highly active and selective in various catalytic processes. Alumina- or silica-supported ruthenium selectively reduces nitrogen oxide to nitrogen.[181] The hydrogenation of aromatic compounds including tetralin,[182] methyl benzoate,[182] 2-methoxycarbonylphenyl-1,3-dioxane[183] and CO[184] using Ru/HY and Ru/Al_2O_3 catalysts has also been reported. Miyazaki et al. prepared uniformly supported metallic Ru nanoparticles on γ-Al_2O_3 with an average diameter of 5 nm and a maximum loading of 6.3 wt% for ammonia synthesis.[185] The materials were prepared through reduction of a ruthenium colloid using ethylene glycol and subsequent deposition of the Ru metal nanoparticles on alumina. The rate of ammonia formation with these supported Ru nanoparticles was found to be 10 times higher than the rate obtained with non-promoted Ru/Al_2O_3 catalysts prepared by conventional impregnation methods.

Li et al. successfully prepared metallic Ru nanoparticles on SBA-15 using a simple ultrasound-assisted polyol method, where the ultrasounds were claimed to provide both the energy for the reduction of the Ru^{III} ions (by ethylene glycol) and the driving force for the loading of the Ru^0 nanoparticles into the pores of the SBA-15.[60] A loading of 14% Ru ensured highly active and selective materials ($>60\%$ conversion, $>80\%$ selectivity to CO) in the partial oxidation of methane by oxygen to give a mixture of CO and H_2 (syngas).

More recently, Pan et al. reported the use of Ru multiwalled carbon nanotubes for the hydrogenation of glucose to sorbi-

tol.[186] The nanotubes were impregnated with a solution of RuCl$_3$ in ethanol for 24 h and then treated at 300 °C for 2 h under He flow. Prior to the hydrogenation reaction, the catalyst was reduced under H$_2$ flow at 400 °C for 2 h. The supported Ru catalyst showed higher activity in the hydrogenation of glucose than Raney Ni and metallic ruthenium nanoparticles supported on Al$_2$O$_3$ and SiO$_2$.

The activity of Ru/γ-Al$_2$O$_3$ materials was also investigated in the Fischer–Tropsch synthesis at 170 °C and 4 bar (space velocity 7.2 mL min^{-1} g, H$_2$/CO 1:2 molar ratio).[38] The obtained CO conversion under the reaction conditions was less than 1 %, and the turnover frequency (TOF) of the catalyst was found to be strongly dependent on the nanoparticle size. The optimum activity was found for the catalysts with an average particle size of 10 nm.[38] Che and co-workes reported Ru nanoparticles supported on hydroxyapatite as an efficient and reusable catalyst for *cis*-dihydroxylation and oxidative cleavage of alkenes.[187] The catalyst showed excellent activities and selectivities in these oxidations.

4.2. Transition-Metal Nanoparticles

A wide range of supported transition-metal nanoparticles have been reported.[112] The most common metal nanoparticles reported to date include Fe, Ni and Cu. These supported metal nanoparticles have been extensively employed in industrial processes including hydrogenations, reforming and Fischer–Tropsch synthesis.[112, 188]

4.2.1. Iron

Iron is a well-known example of supported transition-metal nanoparticles. However, most of the reported protocols deal with the preparation of iron oxide nanoparticles as the complete reduction of Fe^{2+}/Fe^{3+} to metallic iron is highly challenging as compared to related transition/noble metals owing to its high electropositive standard reduction potential (Fe^{2+}/Fe = −0.44 V; Fe^{3+}/Fe = −0.037 V). Thus, only a few reports can be found on the preparation, characterisation and activity of supported metallic Fe nanoparticles. Fe on activated carbon and on Al$_2$O$_3$ materials are highly dispersed, with different particle size distributions (from 3 to 16 nm) depending on the method of preparation employed.[38] The materials were found to be differently active in the Fischer–Tropsch process, with the smaller Fe particles (< 9 nm) being remarkably less active than larger crystallites. Of note was also the influence of the support in the stability and activity of the supported Fe nanoparticles, with activated carbon being a better stabiliser and promoter of the Fe nanoparticle activity compared to alumina.[38]

Gonzalez-Arellano et al. recently reported a facile and environmentally friendly methodology to prepare supported metallic Fe nanoparticles on a range of supports including MCM-41, silica, starch and cellulose (Figure 27).[189] Fe/MCM-41 materials were found to be extremely active and selective in the oxidation of a variety of alcohols under microwave irradiation using hydrogen peroxide as green oxidant, with turnover numbers between 50 and 300 (Table 5). The oxidation was carried out
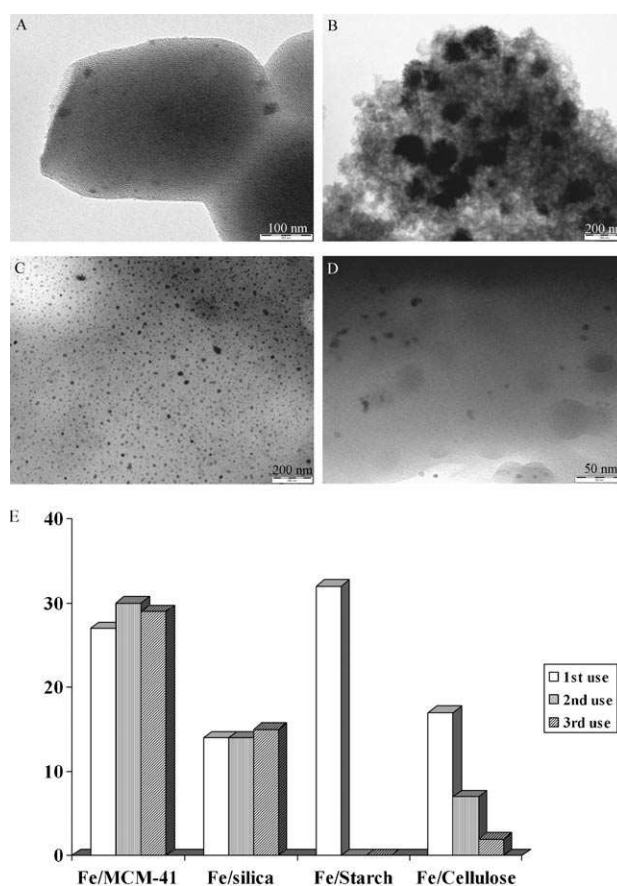

Figure 27. TEM images of Fe metal nanoparticles supported on A) MCM-41; B) DARCO; C) starch and D) cellulose. The bottom plot shows the TON value for the supported Fe nanoparticle after the oxidation of benzyl alcohol.[189] Reproduced with permission.

under mild reaction conditions (200 W, 70–90 °C, 1 h), and the Fe/MCM-41 catalyst was recyclable, preserving its activity and structure after three reuses (Figure 27, bottom).

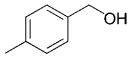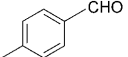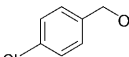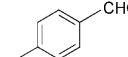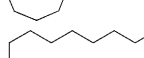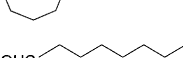These significant results were a clear improvement on reported protocols for the oxidation of alcohols,[14, 190] and provided exceedingly higher TON values as well as an important reduction in reaction times (from 8–24 h to a maximum of 1 h).

There are other interesting applications of supported Fe metal nanoparticles, including environmental remediation[191]. Metallic Fe nanoparticles on anionic hydrophilic carbon (Fe/C) and polyacrylic acid (Fe/PAA), with a particle size ranging between 20–100 nm, were employed in the remediation of soil and groundwater through the dehalogenation of chlorinated hydrocarbons,[192] and the remediation of metal ions such as Cr^{IV} and As^V.[191, 193] Both trichloroethylene and metal ions (Cr^{VI} and As^V) were effectively and rapidly reduced under the reaction conditions.

4.2.2. Nickel

Nickel metal nanoparticles have unusual properties and exhibit excellent catalytic activities.[194] Carbon- and silica-supported Ni metal nanoparticles have been widely investigated in the gas-phase hydrogenation of aromatic compounds.[195] Although

Table 5. Efficient and selective oxidation of alcohols using Fe/MCM-41[a] as catalyst.[189]

Entry	Substrate	Product	TON[b]	Conv. [mol %]	Select. [mol %][c]
1	(p-methylbenzyl alcohol)	(p-methylbenzaldehyde, CHO)	170	31	> 90
2	(4-chlorobenzyl alcohol, Cl)	(4-chlorobenzaldehyde, CHO, Cl)	294	60	> 95
3	(cyclohexanol, OH)	(cyclohexanone, O)	162	38	> 99
4	(cycloheptanol, OH)	(cycloheptanone, O)	290	54	> 99
5	(octanol, OH)	(octanal, OHC)	46	< 10	> 99

[a] 0.2 g substrate, 4 mmol H_2O_2 (0.4 mL, 30 wt % in water), 2 mL acetonitrile, 0.050 g catalyst, microwave irradiation, 200 W, 70–90 °C, 1 h. [b] Number of moles of product produced per mole of catalyst. [c] Selectivity based on alcohol conversion.

fectively dissociate hydrogen molecules in the gas phase to provide atomic hydrogen that can be bonded to the carbonaceous surface.[201] Hydrogen desorption spectra showed that around 3 wt % hydrogen was released in the range of 67–247 °C. The hydrogen chemisorption process facilitated by Ni metal nanoparticles was suggested as an effective reversible hydrogen-storage method.[201]

4.2.3. Copper

Supported Cu metal nanoparticles have been prepared on a range of supports and shown activity in various catalytic processes. Although some preliminary

the porous silica investigated had a low surface area (15 $m^2 g^{-1}$), the supported Ni metal nanoparticles were found to be relatively small (< 10 nm) and well dispersed, providing interesting activities that were dependent on the thermal pre-treatment step in such a way that the presence of NiO particles has some influence in the hydrogenation process. Ni and Ni-Cu metal nanoparticles supported on inorganic materials (e.g. sepiolite, $AlPO_4$) were also investigated in the liquid-phase hydrogenation of fatty acid ethyl esters[196] and propargyl alcohols.[197]

Ni/ZrO_2 and Ni/Al_2O_3 materials have been investigated in the steam reforming of methane and combined steam and CO_2 reforming of methane.[198] The two supported Ni catalysts (Ni/ZrO_2-CP and Ni/Al_2O_3-C) exhibited fairly stable catalysis under low gas hourly space velocities (GHSVs) of CH_4, but they are easily deactivated under high CH_4 GHSVs. Results of the combined steam and CO_2 reforming reaction of methane pointed out that the Ni/ZrO_2-AN catalyst may be a promising catalyst for the production of syngas with flexible H_2/CO ratios (H_2/CO = 1.0–3.0) to meet the requirements of various downstream chemical syntheses.

Supported nanosized nickel on carbon nanotubes can also catalyse the thermal decomposition of ammonium perchlorate, which is the most common oxidizer in composite solid propellants.[199] The addition of the supported Ni nanoparticles decreased the high decomposition temperature of ammonium perchlorate from 447 °C to 346 °C, increasing the total heat release (differential thermal analysis) by 1.21 $kJ g^{-1}$. Further burning-rate experiments revealed that the addition of Ni nanoparticle/carbon nanotube as catalyst increased the burning rate as well as lowered the pressure exponent of ammonium perchlorate based solid-state propellants.[200] Hydrogen storage is another interesting application of Ni metal nanoparticles supported on carbonaceous materials including (multiwalled) carbon nanotubes and mesoporous carbons. Kim et al. recently prepared 6 wt % Ni on multiwalled carbon nanotubes that can ef-

investigations on the preparation of supported Cu metal nanoparticles appeared in the late 1970s and 1980s,[202] most of the reported protocols have been published only recently.

Driessen and Grassien prepared Cu metal nanoparticles on silica and found that their activities in reactions of methyl fragments from methyl iodide dissociation on the catalyst surface were highly dependent on the oxidation state of the copper, the hydroxy group coverage on the silica support and the surface roughness of the Cu particles.[203] They obtained methane, ethane (and ethylene only on samples with a low content of hydroxy groups) as the main reaction products on a reduced Cu/SiO_2 surface containing only Cu metal nanoparticles.

Cu nanoclusters (typically 2–4 nm size, 0.8 nm height) supported on Al_2O_3 films were employed in the reduction of NO.[204] Also, Cu metal nanoparticles on metal oxides have been reported as highly active and selective catalysts in the selective dehydrogenation of methanol. The materials, prepared by reduction under hydrothermal synthesis conditions (promoted by the surfactant cetyltrimethylammonium bromide) without the use of additional reductant, were found to selectively yield formaldehyde and H_2 with almost 100 % selectivity.[205] Aziridination and cyclopropanation reactions are other interesting catalytic applications of Cu metal nanoparticles.[206] Cu-Al_2O_3 materials were found to be active and selective in the aziridination and cyclopropanation of a range of alkenes including styrene, cyclohexene and related aromatics, and 1-hexene in typically 3–4 h, with the cyclopropanation providing a 30:70 *cis/trans* ratio. Similarly, the same metal nanoparticles were employed in the synthesis of 1,2,3-triazoles, affording the products in moderate to high yields after 3–8 h reaction.[207] The catalysts were easily recovered by centrifugation and reused several times without a significant loss in activity.

More recently, supported Cu metal nanoparticles were reported to be active in the water gas shift reaction (Scheme 5). The reaction involves water splitting after reacting with carbon monoxide to give carbon dioxide and hydrogen. It is part of

$$CO + H_2O \longrightarrow H_2 + CO_2$$

**Scheme 5.** Water gas shift reaction catalysed by supported Cu metal nanoparticles.[208]

steam reforming of hydrocarbons and has been considered an interesting research avenue to produce hydrogen, although it is limited by the high temperatures used in the process. Cu/molybdena materials are five to eight times more active than Cu(100), with activities that are comparable to those of Cu/CeO$_2$ (111) and superior to those of Cu/ZnO (0001) surfaces.[208]

5. Future Prospects and Outlook

5.1. Sustainable Preparation

The preparation of supported metal nanoparticles for a wide range of catalytic applications has been well developed over the last few years. Thus section aims to provide an overview of the future prospects of supported metal nanoparticles in view of their methods of preparation and applications in catalysis. As it has been highlighted through this Review, the sustainable preparation of supported metal nanoparticles (e.g. the use of less toxic precursors in benign solvents,[30, 66, 189] environmentally friendly supports,[30, 31, 51, 53, 54] less energy-intensive protocols[30, 66]) has been the subject of many recent reports and reviews.[3, 7, 57, 112] Bioreducing agents including sugars, glutathione, starch and a range of plant and algal extracts have also been employed in the preparation of Au, Ag and Ni metal nanoparticles with reasonably good control over particle size and, in some cases, shape.[57]

Recently, there has been a significant growing interest in the development of bio-inspired approaches to achieve designer hybrid nanomaterials.[3, 57, 209] For example, Bale et al. reported the protein-directed preparation of supported Ag metal nanoparticles on carbon nanotubes.[210] A range of proteins were investigated, including poly-L-lysine, bovine serum albumin, soybean peroxidase and α1-acid glycoprotein. An aqueous dispersion of multiwalled carbon nanotubes and protein/polypeptide were stirred with a solution of silver nitrate for 24 h, and the conjugates were reduced using sodium borohydride
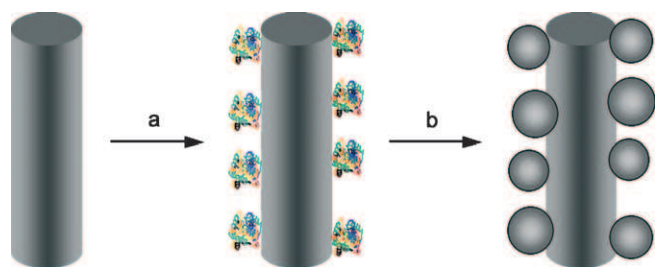
Scheme 6. Schematic depiction of the protein-mediated formation of Ag/multiwalled carbon nanotube materials: a) generation of multiwalled carbon nanotube-protein conjugates by incubating the nanotubes with an aqueous solution of protein; b) formation of Ag metal nanoparticles by exposing the nanotube-protein conjugates to a solution of silver nitrate, washing and subsequent reducing with sodium borohydride.[210] Reproduced with permission.
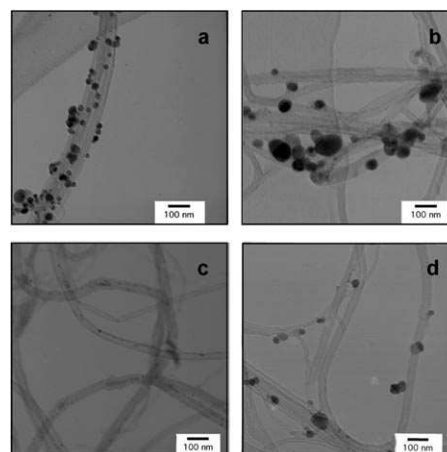
Figure 28. TEM images of Ag metal nanoparticle formation on a) multiwalled carbon nanotubes-poly-L-lysine; b) multiwalled carbon nanotubes-bovine serum albumin; c) multiwalled carbon nanotubes-α1-acid glycoprotein, and d) pristine multiwalled carbon nanotubes.[210] Reproduced with permission.

(Scheme 6). The dispersion of the Ag metal nanoparticles on the support was dependent on the protein employed for the synthesis (Figure 28).

Table 6. Top twelve sugar-derived platform molecules.[213]	
Platform molecule	Structure
1,4-diacids (succinic, fumaric and malic acids)	
2,5-furandicarboxylic acid	
3-hydroxypropionic acid	
aspartic acid	
glucaric acid	
glutamic acid	
itaconic acid	
levulinic acid	
3-hydroxybutyrolactone	
glycerol	
sorbitol	
xylitol/arabinitol	

5.2. Sustainable and Future Catalytic Applications

Some of the most interesting catalytic trends and future prospects for supported metal nanoparticles include applications in fuel cells, the transformation of platform molecules, environmental remediation and more recently NMR imaging.

Pd/Pt nanoparticles supported on carbonaceous materials have been reported as promising materials for hydrogen sorption, to be employed as fuel cells in cars.[151] However, there is still quite a way to go until we see the full implementation of such systems. Recent studies from Shao-Horn et al. demonstrated that the stabilities of supported Pt metal nanoparticles in low-temperature fuel cells were compromised by the degradation of the electrochemically active surface area in the material through

Scheme 7. Plan for the development of glycerol-based products from specialty to commodity chemicals.

loss of Pt from fuel cell electrodes and coarsening of Pt particles.[156] Manipulation of the surface structure[211] and chemistry (through deposition of Au clusters on Pt nanoparticles)[212] of the supported metal nanoparticles can improve the durability.

Transformations of platform molecules (e.g. 1,4-diacids, glycerol) is another interesting research avenue for supported metal nanoparticles. Platform molecules are generally compounds with various functionalities that can be turned into a plethora of chemicals and value-added products through different catalytic transformations including oxidations, hydrogenations, amidations and esterifications.[213] The US Department of Energy has generated a list of the so-called 12 top sugar-derived main platform molecules (or building blocks) that should receive attention in the next few years (Table 6). Glycerol and succinic acid are two examples of such platform molecules.

Glycerol is a well-known compound that has recently attracted a great deal of attention as it is produced in large quantities as by-product in the preparation of biodiesel. The glycerol surplus has challenged both industrial and organic chemists to come up with potential routes to obtain high-value-added products from glycerol (Scheme 7).[147] The oxidation and hydrogenolysis of glycerol have been extensively investigated with a wide range of Pt, Pd and Au metal nanoparticles supported on carbonaceous materials.[18b, 116a, 147, 214]

Succinic acid (1,4-dibutanoic acid) is another important platform molecule. Clark and co-workers recently reported the preparation of high-value-added products from succinic acid through different transformations,[18a, 215, 216] and further investigations are ongoing using supported noble-metal nanoparticles (Pt, Pd, Rh, Ru) in the hydrogenation of succinic acid.[217]
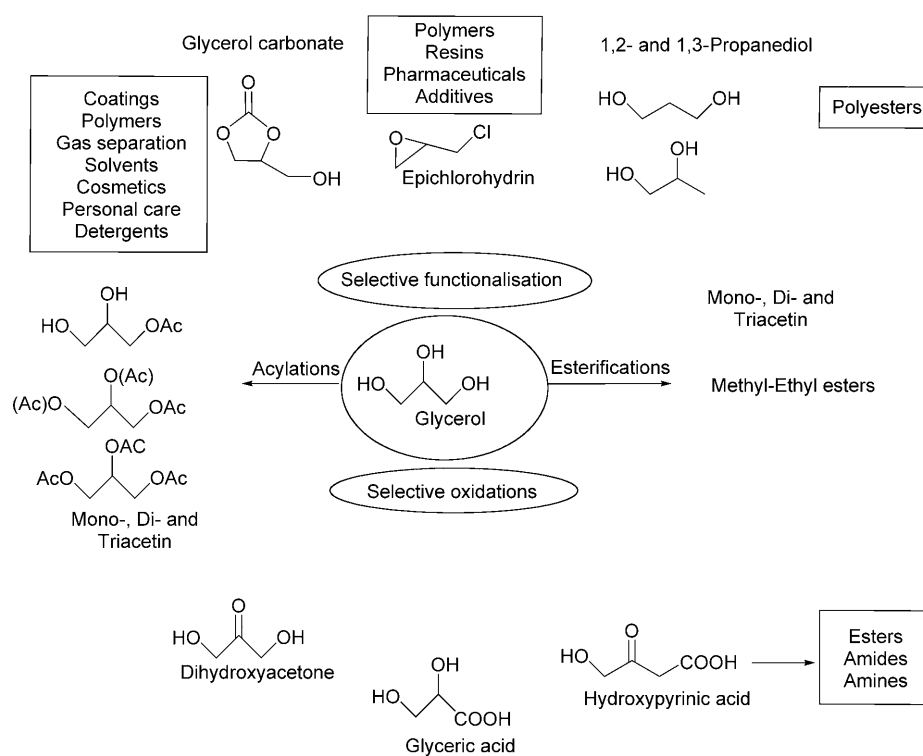
Supported metal nanoparticles have also been recently employed in a truly sustainable application: environmental remediation. Fe nanoparticles supported on chitosan and silica,[54] and Fe and Ni-cellulose acetate materials[218] were employed in the removal of chlorinated compounds in water. Chen et al. devised their oxide-supported Au metal nanoparticles (Figure 14) to work, for the first time, in the light-driven room-temperature oxidation of volatile organic compounds such as formaldehyde.[81] Upon irradiation with six light tubes of blue light (wavelength 400–500 nm, 0.17 W cm^{-2} irradiation energy), the initial CH_2O concentration decreased by 64% in 2 h and a parallel increase in CO_2 concentration was observed, confirming the oxidation of CH_2O (Figure 29). The activity of the materials was found to be highly dependent on the support, with ZrO_2 being the most effective support regardless of the type of light employed in the reaction (Figure 30). This effect is associated with the oxygen adsorbed on the more active supports (Zr and Ce oxides) that can migrate to the gold nanoparticles, thus accelerating the oxidation.[81]

Supported Pt and Pd nanoparticles on Al_2O_3 were recently reported to provide para-hydrogen induced polarisation (PHIP) signals in heterogeneous catalysed gas-phase hydrogenations (Figure 31).[219] PHIP can improve the NMR signals of reaction intermediates and products by several orders of magnitude, providing a high sensitivity which is ideal to follow reaction mechanisms.[220] Furthermore, the combination of para-hydrogen with supported metal nanoparticles in hydrogenations will aid the development of new research tools for fundamental and practical applications including kinetic and mechanistic studies and the production of polarized fluids for advanced
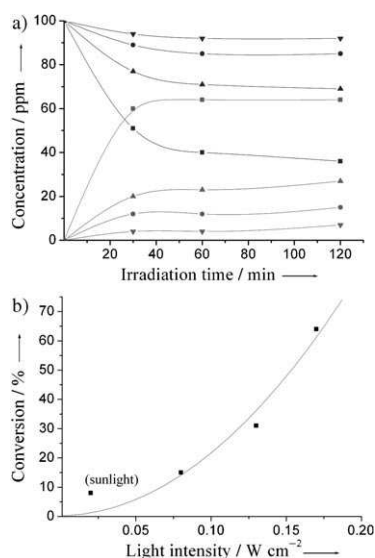
Figure 29. Oxidation of 100 ppm CH_2O on Au metal nanoparticles supported on ZrO_2 under blue light or sunlight at 25 °C. a) Changes in reactant concentration (CH_2O, four upper lines) and product (CO_2, four lower lines) under different light intensities as a function of irradiation time. b) Relationship between CH_2O conversion and light intensity.[81] Reproduced with permission.
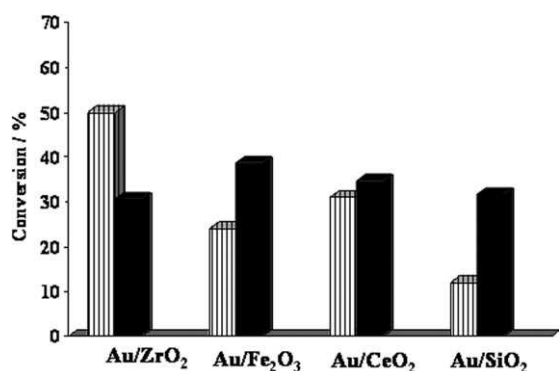

Figure 30. Influence of the support on the activity of the HCHO oxidation reaction. Black bars: CH_2O conversion (%) under illumination of blue light. Striped bars: conversion under red light.[81] Reproduced with permission.

Figure 31. Left: ^{1}H NMR spectra recorded in PASADENA[220] experiments during the in situ hydrogenation of propylene using Pt/Al$_2$O$_3$ catalysts with a) 1.1 nm Pt metal nanoparticles and b) 0.6 nm Pt metal nanoparticles. The two hydrogen atoms in the product from the para-hydrogen molecule are labeled A and B, and the residual NMR signals of the reactant (propylene) are labeled 1–3. Right: ALTADENA[220] experiments during propylene hydrogenation in the Earth's magnetic field using Pt/Al$_2$O$_3$ catalysts with a) 8.5, b) 3.5, c) 1.1 and d) 0.6 nm Pt particle size. The two hydrogen atoms in the product from the para-hydrogen molecule are labeled A and B. A broad band in the low-field part of the spectrum corresponds to H$_2$.[219] Reproduced with permission.

magnetic resonance imaging (MRI).[221] MRI techniques suffer from a low intrinsic sensitivity, and many efforts have been devoted to the use of homogeneous hydrogenations with para-hydrogen to produce hyperpolarised contrast agents for biomedical and related applications.[221–223] In this context, the use of active and reusable heterogeneous catalysts will produce catalyst-free polarised fluids (after separation of the catalyst from the reaction products) that can be used to prepare polarised gases. MRI has also been employed to study the morphology of catalysts and synthesis techniques.[224, 225]

5.3. Implications of Supported Metal Nanoparticles

Despite the development of more sustainable routes to their preparation as well as their high activities and selectivities in catalysi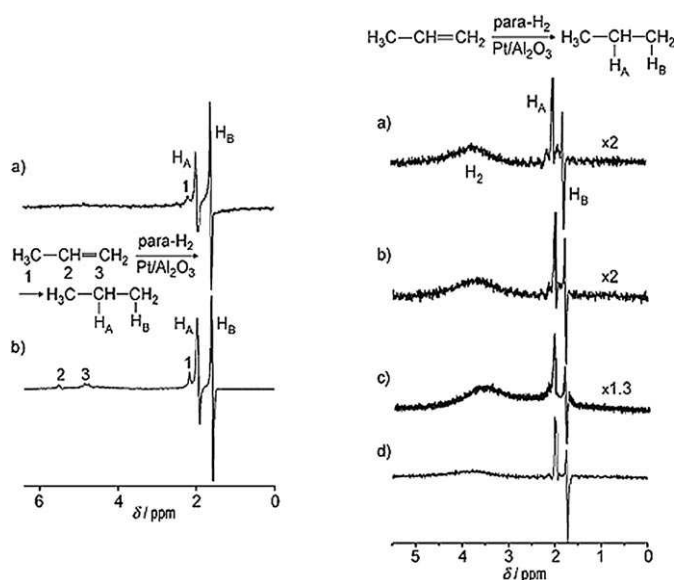s, the toxicity issue associated with engineered metal nanoparticles also needs to be addressed. It is not clear whether the highly active and dispersed supported metal nanoparticles desired for catalytic applications are hazardous in contact with human tissues (specially as a result of prolonged exposure) as a consequence of their unique physicochemical properties or the chemical nature of the metal nanoparticles and/or support surfaces.[226] Results from unsupported metal nanoparticles point to the absence of cytotoxicity and cellular oxidative stress, although there is in vitro uptake as well as retention in cells and tissues of metal nanoparticles (Table 7). Thus, the approach of covering potentially toxic surface groups with more innocuous ones to improve the biocompatibility of nanomaterials has recently been explored.[3, 57, 227, 228]

6. Conclusions

The 21st century has brought a great interest and expansion of the nanomaterials field. The timeliness of being "green and nano" for nanomaterials synthesis has become evident from the latest developments and publications in the field. Among them, supported metal nanoparticles are important owing to their unique properties and various methods of preparation. Recent advances in the design and preparation of supported metal nanoparticles confirmed that a numerous variety of metal nanoparticles can nowadays be synthesized through different preparation routes and supports to give tailored sizes, shapes and distributions, overcoming the main drawbacks of

Table 7. Summary of acellular, in vitro, and in vivo findings with Pt nanoparticles.[226] Reproduced with permission.

Property	Technique	Result
NP singlet size	TEM	11–35 nm
BET surface area	N$_2$ isotherm adsorption	1–27 m^2 g^{-1}
Agglomerate size in cell culture medium	Dynamic light scattering	92 (flowers) and 67 nm (multipods)
Cell-free oxidant capacity	2′,7′-dichlorofluorescin oxidation	low
Cytotoxicity	Release of lactate dehydrogenase	no
Cellular oxidative stress or inflammatory mediator release	Luciferase reporter activity; release of IL-6	no
in vitro uptake	TEM	flowers > multipods
in vivo acute inflammation	Intratracheal instillation	low; flowers and multipods
Retention of Pt nanoparticles in lung tissue	Atomic emission spectroscopy	flowers > multipods
Retention of Pt nanoparticles in lavage cells	Atomic emission spectroscopy	flowers > multipods

traditional synthetic methodologies. Such designer materials will have a significant impact in many areas including increasing applications in industrial catalytic processes.

However, we must not forget that the preparation of supported metal nanoparticles should be promoted in a more sustainable way, reducing waste generation and the use of toxic compounds with room-temperature aqueous solution protocols, improving manufacturing safety as well as decreasing the production costs. In addition to that, the implementation of such catalysts may not come without a price and the environmental impact associated with the preparation of supported metal nanoparticles must be assessed from many different points of view (transport, waste, biomagnification in the food chain) as well as their potential toxicity when released in ecosystems and humans.

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Keywords: heterogeneous catalysis · nanostructures · supported catalysts · sustainable chemistry

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