Review

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Magnetic nanocatalysts: supported metal nanoparticles for catalytic applications

Abstract: This review is focused on metal nanoparticles (NPs) supported on magnetic responsive solids and their recent applications as magnetically recoverable nanocatalysts. Magnetic separation is a powerful tool for the fast separation of catalysts from reaction medium and an alternative to time-, solvent-, and energy-consuming separation procedures. Metal NPs attached to a magnetic solid can be easily carried and recovered by magnetic separation. Some examples of magnetically recoverable metal NPs used in hydrogenation, oxidation, C-C coupling reactions, photocatalysis, and other organic reactions will be given.

Keywords: catalysis; magnetic separation; metal nanoparticles; photocatalysis.

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1 Introduction

The application of metal nanoparticles (NPs) in catalysis has received great attention in recent decades, thanks to the improvement made in the synthesis methodologies, especially by the introduction of bottom-up approaches. Reproducible syntheses and high control of particle size and size distribution are properties not found in traditional metal colloids synthesis, which are typically larger, polydisperse, and poorly reproducible [1]. The synthesis and stabilization of metal NPs require the presence of capping ligands, such as organic ligands, surfactants, and polymers, to stop the particle growth process and to control the size of NPs, otherwise bulk metal is favored [2–4]. These organic components play a key role in the synthesis of NPs but are also indispensable to keep the NPs stable in solution by steric or electrostatic interactions between them and with the solvent. High stabilization of the metal NPs in solution facilitates their characterization and is useful for many applications, for example, to explore their optical properties and to perform catalytic studies in the absence of interfering supports. Thus, they can be considered model systems for their heterogeneous catalyst analogous; however, if they are in the same phase as the reactants in a catalytic reaction system, separation is difficult. Filtration and centrifugation are not effective techniques to separate NPs from stable solutions unless they are precipitated by adding a counter solvent or other precipitating agent. For practical applications in catalysis, the immobilization of metal NPs on inorganic supports is advantageous for many reasons: the metal NPs can be handled as heterogeneous catalysts, which means they can be washed, separated by filtration or centrifugation, redispersed, and reused. As a consequence of the immobilization process, the excess capping ligands can be washed off and partially removed [5] or thermally decomposed in posttreatment steps [6] to recover catalytic activities. The role of capping ligands on the catalytic activity and selectivity of metal NPs has been discussed in the recent literature [7–9].

Methods to prepare well-defined supported metal NP catalysts are highly desired as well as innovative methods for catalyst separation and recycling. In this respect, strategies for supporting metal NPs on magnetic materials have received considerable attention and magnetic separation has been applied for many kinds of reactions catalyzed by metal NPs. The application of magnetic separation in nanocatalysis will be the subject of this review article. By definition, in nanocatalysis, the prefix “nano” refers to the catalyst itself (that are in the nano-size domain, mainly <10 nm) and do not refer to the support, which may or may not be in the nanoscale. Taking this into account, we will not include homogeneous catalysts supported on nanostructured magnetic supports in this review.

Superparamagnetic NPs have received a great deal of attention recently because of their unique properties
and potential technological applications [10]. This kind of material is susceptible to an external magnetic field, and in this regard, they behave like a paramagnetic material, but removing the applied magnetic field immediately reduces the overall net magnetic moment back to zero. Thus, the superparamagnetic NPs have no “magnetic memory” and they (or any other entity firmly attached to them) can be recovered by applying a remote magnetic field and redispersed immediately after the magnetic field is interrupted (Figure 1).

The first reports on the application of magnetic separation in the field of catalysis were regarding the use of intrinsic magnetic properties of metal catalysts, such as Fe, Ni, and Co [11–16], although examples of such materials as magnetically recoverable catalysts can still be found in the recent literature [17, 18]. However, the scope of application of magnetic separation in catalysis was broadened by the introduction of magnetic nanomaterials and nanocomposites, especially those based on iron oxides and cobalt, as solid supports for the immobilization of catalytically active metals, metal complexes, biocatalysts, and even organocatalysts [19–23].

A variety of methodologies were developed for the immobilization of catalysts on such kinds of supports with superparamagnetic properties, which include chemical modification of magnetic NP surfaces or coating the magnetic NPs with inorganic or organic polymer materials. Magnetic separation is a powerful tool for easy and fast separation of catalysts from the final product while improving their recycling and reuse in successive batch reactions. In contrast to conventional procedures such as filtration, centrifugation, or extraction (liquid-liquid or chromatographic), the magnetic separation avoids the use of auxiliary substances (solvents, filters, etc.) and makes the process cleaner, environmentally safer, and faster while using less energy in the catalyst separation process.

The whole separation process can be performed without removing the catalyst from inside the reactors, which greatly simplifies procedures such as repeated washing steps and isolation and recycling of moisture-sensitive components. The performance of a magnetic separation system depends on a strong catalyst-support interaction allowing repeated cycles of separation and redispersion. Coating the magnetic NP surface is a strategy to give extra protection to the magnetic material, because naked iron oxides (e.g., magnetite) and zero-valence metals (e.g., cobalt) easily oxidize in air atmosphere, which is reflected in changes of the magnetic properties and compromises the catalyst stability. Besides that, coating the magnetic particles with other oxides (e.g., SiO₂) helps the immobilization of catalysts through a covalent approach [19] and makes increasing the surface area by adding mesoporous silica layers possible [24]. In this review, we will focus our discussion on metal NPs immobilized on magnetic NPs and their application in various organic catalyzed transformations.

2 Hydrogenation reactions

Hydrogenation reactions are very important transformations in organic synthesis and are typically carried out in the presence of heterogeneous catalysts, which are composed of small metallic particles, as has been known for a long time. However, there is still room for the development of hydrogenation catalysts obtained with metal NPs prepared by modern colloidal synthesis approaches. The possibility of preparing controlled-size metal NPs opens the opportunity for the design of more active and selective catalysts than the traditional heterogeneous catalysts. The best-known metal catalysts for hydrogenations...
in liquid-phase reactions have been prepared as magnetically recoverable catalysts, as shown in Table 1.

The hydrogenation of cyclohexene is a standard reduction process and as such is often selected as a reference example for testing newly developed hydrogenation catalysts. The catalytic activity is usually expressed as the turnover frequency (TOF) that refers to the number of moles of substrate converted per mole of metal (or metal surface sites) per hour. In the literature, this value has been obtained using the time required for the complete substrate conversion or using the initial rates. It is worth noting that one should select one of these methods to compare distinct catalysts and also pay attention to the reaction conditions.

2.1 Palladium NPs

Palladium NPs have been supported directly on the surface of magnetite NPs [25, 34] or on silica-coated magnetic NPs [26, 35] to produce easily recoverable catalysts for hydrogenations under mild conditions. The strategies to immobilize Pd NPs on magnetic NPs involve chemical modification of their surfaces to provide anchoring groups to the metal atoms. Examples of surface modifiers include mercaptopropyl acid (MPA) [25] and dopamine molecules [34] (Figure 2). These ligands were considered as stabilizers for the Pd NPs that could be easily recycled via magnetic separation with no deterioration in the catalytic efficiency after five and 10 reuses.

The utilization of bare magnetic NPs is possible, but it has been shown that the coating of the magnetic material with a layer of dense silica improves the chemical stability (protects the magnetic NPs) and provides surface silanol groups that are reactive for further functionalization with alkoxyorganosilanes. Rossi et al. [26] and Yi et al. [36] prepared magnetically recoverable Pd NPs immobilized on the surface of silica-coated iron oxide NPs functionalized with organosilanes (Figure 3).

The influence of these functional groups grafted on the support surfaces on the catalytic properties of metal NPs is still not well elucidated, but it is true that there

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**Table 1** Selected examples of magnetically recoverable metal NP catalysts and their application in the hydrogenation of cyclohexene.

<table>
<thead>
<tr>
<th>Metal NPs</th>
<th>Support</th>
<th>Precursor/reductor</th>
<th>TOF (h⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>Fe₃O₄-MPA</td>
<td>PdCl⁴⁻/H₂</td>
<td>244</td>
<td>[25]</td>
</tr>
<tr>
<td></td>
<td>Fe₃O₄@SiO₂</td>
<td>Pd(OAc)₂/H₂</td>
<td>12,500</td>
<td>[26]</td>
</tr>
<tr>
<td></td>
<td>Fe₃O₄@SiO₂-NH₂</td>
<td>Pd(OAc)₂/H₂</td>
<td>5500</td>
<td>[26]</td>
</tr>
<tr>
<td></td>
<td>Fe₃O₄@SiO₂-en</td>
<td>Pd(OAc)₂/H₂</td>
<td>800</td>
<td>[26]</td>
</tr>
<tr>
<td></td>
<td>Fe₃O₄@SiO₂-NH₂</td>
<td>Pd(dba)₂/H₂</td>
<td>55,000</td>
<td>[27]</td>
</tr>
<tr>
<td></td>
<td>Fe₃O₄@SiO₂-terpy</td>
<td>Pd(dba)₂/H₂</td>
<td>12,300</td>
<td>[27]</td>
</tr>
<tr>
<td>Rh</td>
<td>Fe₃O₄@SiO₂-NH₂</td>
<td>RhCl/H₂</td>
<td>21,500</td>
<td>[28]</td>
</tr>
<tr>
<td></td>
<td>Fe₃O₄@SiO₂-NH₂</td>
<td>RhCl/NaBH₄</td>
<td>39,600</td>
<td>[28]</td>
</tr>
<tr>
<td></td>
<td>Fe₃O₄@SiO₂</td>
<td>RhPVA</td>
<td>21,800</td>
<td>[28]</td>
</tr>
<tr>
<td></td>
<td>Fe₃O₄@SiO₂</td>
<td>RhTOAB</td>
<td>56,000</td>
<td>[28]</td>
</tr>
<tr>
<td></td>
<td>Fe₃O₄@SiO₂</td>
<td>Rh⁺⁺⁺⁺⁺⁺(HEA16Cl)</td>
<td>143,000</td>
<td>[29]</td>
</tr>
<tr>
<td>Pt</td>
<td>Fe₃O₄@SiO₂-NH₂</td>
<td>PtCl⁴⁻/H₂</td>
<td>4000</td>
<td>[30]</td>
</tr>
<tr>
<td>Ir</td>
<td>Fe₃O₄@SiO₂-NH₂</td>
<td>IrCl/H₂</td>
<td>6000</td>
<td>[31]</td>
</tr>
<tr>
<td>Ni</td>
<td>Fe₃O₄@SiO₂</td>
<td>Ni(COD)₄/H₂</td>
<td>1500</td>
<td>[32]</td>
</tr>
<tr>
<td>Ru</td>
<td>Fe₃O₄@SiO₂-NH₂</td>
<td>RuCl₆/H₂</td>
<td>420</td>
<td>[33]</td>
</tr>
</tbody>
</table>

Reaction conditions: 75°C, 6 bar H₂. COD, 1,5-cyclooctadiene; dba, dibenzylideneacetone; en, ethylenediamine; HEA16Cl, N-N-dimethyl-N-cetyl-N-(2-hydroxyethyl) ammonium chloride; MPA, mercaptopropionic acid; PVA, polyvinyl alcohol; terpy, terpyridine; TOAB, tetraoctylammonium bromide; TOF, turnover frequency is expressed as moles of the substrate transformed per mole of catalyst per hour (at complete conversion).
are changes in the metal loading, reactivity, selectivity, and morphology of NPs prepared by salt impregnation and reduction. Rossi et al. [26] reported that the amine and ethylenediamine groups grafted on the surface of the silica support assisted the preparation of magnetically recoverable Pd NPs of different size by H₂ reduction of Pd²⁺ ions impregnated on modified silica surfaces. The ethylenediamine-supported catalyst is composed of small Pd NPs (~1 nm), which are less active in the hydrogenation of cyclohexene and deactivates faster (fourth recycle) than the amine-supported catalyst. The amino groups assisted the formation of highly active ~5 nm Pd NPs, which were reused for up to 20 successive runs corresponding to 50,000 mol mol⁻¹ Pd (cyclohexene, 75°C, 6 atm H₂) (Figure 4).

Yi et al. [36] prepared magnetically recoverable Pd NPs supported on silica-coated maghemite NPs functionalized with mercaptopropyl and aminoethyl groups and then loaded with palladium acetate and heated under microwave to produce Pd NPs of 2 to 3 nm. The catalysts were examined for the hydrogenation of nitrobenzene to aniline and resulted in reaction rates higher than a commercially available Pd/C catalyst. The catalysts could be reused but gradually deactivated after the sixth reaction cycle.

Ligands with more complex chemical structures were designed to be anchored on the surfaces of silica. Guerrero et al. [27] synthesized a modified terpyridine ligand and this ligand provided the stabilization of approximately 2.5 nm Pd NPs, which resulted in active and recyclable catalysts for hydrogenation of cyclohexene (Figure 5). In this example, the organometallic Pd₂(dba)₃ was used as the palladium precursor and the catalytic activity was superior to a catalyst prepared with palladium(II) acetate (same support). Even more important was the selectivity obtained in the hydrogenation of polyunsaturated substrates. The terpyridine-stabilized Pd NPs are much less effective in the activation of nonconjugated double bonds, which allows for the selective synthesis of monohydrogenated products. This catalytic behavior is very interesting because such a kind of selectivity was not obtained with Pd/C under similar conditions.
Magnetic support materials other than silica have been prepared and are equally effective in the magnetic separation from the reaction mixtures. Lu et al. [37] reported the stabilization of Pd NPs on ordered mesoporous carbons (OMC) with surface-grafted magnetic particles. Such magnetic nanocomposites have a very high surface area, a large pore volume, and uniform pore size, which are very interesting properties for the application of this Co-OMC as magnetically separable catalyst support. Amali and Rana [38] reported the coating of the surface of Fe₃O₄ NPs with highly branched polyethylenimine (PEI). The amine groups of branched PEI on the magnetite surface stabilize Pd NPs and prevent metal leaching during the reaction. The versatility of the catalyst was demonstrated for hydrogenation reactions involving reduction of various unsaturated compounds with excellent effectiveness.

### 2.2 Rhodium, platinum, and iridium NPs

Magnetically recoverable rhodium [39], platinum [30], and iridium [31] NPs were prepared by H₂ reduction of metal ion precursors loaded on the silica-coated magnetic support previously modified with amine groups. The magnetically separable catalytic system, composed of Rh NPs of approximately 3 to 5 nm immobilized on Fe₃O₄@SiO₂, is very active and could be reused for up to 20 times for hydrogenation of cyclohexene (180,000 mol mol⁻¹ Rh) and benzene (11,550 mol mol⁻¹ Rh) under mild conditions (Figure 6). This same catalyst has shown very interesting catalytic activities in the liquid hydrogenation of polycyclic aromatic hydrocarbons [40]. The magnetically recoverable Pt(0) NP catalyst exhibited high catalytic activities in the hydrogenation of ketones, olefins, and arenes in liquid-phase solventless reactions. The substrates were converted to the fully hydrogenated forms, but partially hydrogenated products were also isolated by stopping the reaction at the time indicated by the H₂ consumption profile of hydrogenation curve (e.g., ethylbenzene was isolated with 98.9% selectivity during hydrogenation of styrene). The catalyst could be reused for up to 14 successive reductions of ketones (15,600 mol mol⁻¹ Pt) without deactivation. The NH₂ groups present on the silica surface guarantee an enhanced metal uptake (65 times higher compared with nonfunctionalized particles) and most probably contributed to metal retention, which is confirmed by the negligible metal leaching into the liquid products and the high reusability of Rh, Pt, and Ir NP catalysts [31].

Very active Rh NP catalysts were prepared by the deposition of preformed colloidal NPs on the surface of silica-coated magnetite NPs. Examples of capping ligands...
used in the preparation of colloidal Rh NPs include Rh-HEA16Cl \([\text{HEA16Cl} = N,N\text{-dimethyl-N-cetyl-N-(2-hydroxyethyl) ammonium chloride}]\) \([29]\), Rh-PVA (PVA=polylevinyl alcohol) \([27]\), and Rh-TOAB (TOAB=tetraoctylammonium bromide) \([27]\). Rh-HEA16Cl and Rh-PVA have their catalytic activity improved after immobilization on the solid support in comparison with the activities obtained when using them soluble in water for biphasic catalysis. In all cases, the Rh NPs are more stable, and recyclable catalysts after immobilization and the preformed metal NPs displayed higher catalytic activities than the catalysts prepared by salt impregnation and reduction. Rh-TOAB NPs exhibited similar activities in solution and after immobilization, which is a good opportunity for the preparation of highly active Rh NP catalysts to be studied and characterized in solution and then used as a heterogeneous catalyst.

Jun et al. \([41]\) prepared a core-shell-type cobalt-platinum magnetic catalyst for the hydrogenation of various unsaturated organic molecules under mild conditions and also demonstrated the magnetic separation and recycling capabilities.

Abu-Reziq et al. \([42]\) prepared magnetically recoverable Pt NPs supported on ionic liquid-modified magnetite NPs (Figure 7). The NPs were applied by the selective hydrogenation of alkynes and \(\alpha,\beta\)-unsaturated aldehydes. Cinnamaldehyde was chemoselectively hydrogenated to 3-phenylprop-2-en-1-ol in 99% yield.

### 2.3 Ruthenium NPs

Magnetically recoverable ruthenium NPs were prepared by \(\text{NaBH}_4\) reduction of \(\text{Ru}^{3+}\) loaded into different magnetic supports. Jacinto et al. \([33]\) prepared a Ru NP catalyst using a silica-coated magnetic support previously modified with amine groups. The Ru NPs were active for hydrogenation of cyclohexene under mild conditions, but the reaction rate was not comparable with other platinum group metals. Baruwati et al. \([43]\) prepared a Ru NP catalyst supported on dopamine-modified magnetic NPs. The magnetically recoverable Ru NP catalyst was active for the hydrogenation of alkynes to their respective alkanes at room temperature as well as the transfer hydrogenation of a variety of carbonyl compounds under microwave conditions. Magnetically recoverable ruthenium hydroxide catalysts were also reported \([44, 45]\). Those catalysts are active for the hydration of nitriles with high yield and excellent selectivity and for aerobic oxidations and reductions with 2-propanol. A wide variety of substrates including aromatic, aliphatic, and heterocyclic could be converted into the desired products in high to excellent yields without any additives such as bases and electron transfer mediators.

### 2.4 Nickel NPs

Nickel NPs, in addition to their intrinsic magnetic properties, have been immobilized on the surface of magnetic supports based on iron oxides to improve the magnetic separation in catalytic reactions (magnetic separation of 1–2 wt.% of nickel on silica is not efficient). Costa et al. \([32]\) prepared a robust, oxidation-resistant, and very active nickel catalyst by the controlled decomposition of the organometallic complex \([\text{bis}(1,5\text{-cyclooctadiene})\text{ni}ckel(0)]\), \(\text{Ni(COD)}_2\), on a magnetic support. The Ni NP catalyst was characterized by the presence of Ni(0) and only partial surface oxidation could be detected after storage in air [X-ray absorption near-edge spectroscopy (XANES) and X-ray photoelectron spectroscopy results]. Moreover, the catalytic results indicate that these oxidized nickel species can be reduced back to the Ni(0) active catalyst under mild hydrogenation reaction conditions (1 bar \(\text{H}_2\) and 75°C), in contrast with NiO bulk that is nonreactive under these conditions. The catalyst exhibited high activity in the hydrogenation of cyclohexene and was recycled.

![Figure 7](image-url)  
*Figure 7* Preparation of magnetite NP functionalized with ionic liquid.
15 times without deactivation (TOF up to 1500 h⁻¹, 75°C, and 6 atm H₂). For comparison, the widely used Raney nickel catalyst was tested in the hydrogenation of cyclohexene under similar conditions (0.33 mol% Ni, 75°C, and 6 bar H₂), but only 29% conversion was reached after 48 h of reaction, which means that Raney Ni was not activated in the reaction conditions. An important feature of the Ni catalyst prepared from the organometallic precursor is that it can be activated in situ in the hydrogenation reaction under very mild condition.

Polshettiwar et al. [44] prepared a Ni NP catalyst by reduction of nickel chloride with hydrazine/NaBH₄ into dopamine-modified iron oxide NPs. The catalyst was not as well characterized as Ni(0), but the catalytic results are interesting. The catalyst was selective for the reduction of alkynes to alkenes or alkanes depending on the reaction conditions. The reduction of carbonyl compounds to the corresponding alcohols was also explored via catalytic transfer hydrogenation in isopropanol.

All the NP-supported catalysts reviewed here could be isolated and recycled with the assistance of an external magnet, which greatly simplifies the workup procedure and purification of products, minimizing the use of solvents, costly consumables, energy, and time.

### 3 Oxidation reactions

Oxidations are one of the most important reactions in chemical industry; in particular, epoxidation and allylic oxidation of olefins and selective oxidation of alcohols are of great interest for the synthesis of important chemical intermediates. Catalytic oxidations using molecular oxygen or hydrogen peroxide are preferable from both an ecologic and economic point of view, as these reactions traditionally are performed using chromium and manganese oxides and produce equimolar amounts of toxic waste. However, unlike the traditional oxidants, molecular oxygen is not a selective and active oxidant without a catalyst. Thus, the search for efficient metal-containing catalysts (e.g., metal NPs) has become the key to most of the aerobic oxidations and the possibility of using magnetic separation minimizes the problem of expensive and wasteful workup procedures.

#### 3.1 Iron oxide NPs

Iron catalysts are among the most used to promote aerobic oxidations due to the efficiency of Fe as an active site for the oxygen transfer to organic substrates. In the last decade, since the discovery of Fe-containing enzymes, many studies have focused on biomimetic catalysis, such as Fe-containing porphyrin and Schiff’s base. However, the difficult separation and the high cost of these catalysts make commercialization impracticable. The immobilization of this kind of catalyst became attractive, although both activity and selectivity can decrease after immobilization. Therefore, there is a need for more simple, efficient, safe, and cheap catalysts containing iron. Shi et al. [17] reported the catalytic activity and selectivity of free nano-Fe₂O₃ in oxidation of alcohols and olefins using hydrogen peroxide as an oxidizing agent. The Fe₂O₃ bulk displayed very low activity; however, the nano-γ-Fe₂O₃, with particle sizes of 20 to 50 nm rendered 33% conversion and 97% selectivity to benzaldehyde. Higher activities could be reached when using nano-γ-Fe₂O₃ with sizes of 3 to 5 nm. The conversion reached 85%, but the benzaldehyde selectivity dropped to 35%. Besides, the intrinsic magnetic properties of the maghemite NPs allowed the catalyst to be easily separated from the reaction media simply by using a permanent magnet. Gao et al. [46] reported the peroxidase-like activity of magnetite NPs. The authors reported that all sizes of magnetite catalyzes the reaction of the substrate 3,3,5,5-tetramethylbenzidine using H₂O₂ as the oxidant just like the enzymatic peroxidase activity. The catalyst was also active for the oxidation of other typical peroxidase substrates, and unlike the proteins, magnetite does not have the problems associated with degradation and cost of production and purification. Importantly, Fe₂O₄ NPs have the additional property of being magnetic, which allows them to be recovered for recycling. The use of iron oxide as catalysts for oxidation of different substrates was reported in the literature. El-Sheikh et al. [47] reported the catalytic performance of nanostructured iron oxides synthesized by a thermal decomposition technique. The catalytic process was essentially affected by the presence of the maghemite phase, crystal size, and surface area of the nanostructured iron oxide. The results showed that CO is completely oxidized to CO₂ at 200°C. Xue et al. [48] reported the oxidation of pentachlorophenol on the surface of magnetite used as a heterogeneous catalyst. The magnetite catalyst exhibited low iron leaching, good structural stability, and recyclability.

#### 3.2 Cobalt oxide NPs

Zhang et al. [49] reported a magnetically recoverable heterogeneous catalyst based on cobalt oxide NPs supported on hydroxyapatite encapsulated with maghemite NPs. The mixed Co₃O₄ and CoFe₂O₄ oxides were present on the surface...
of CoHAP-$\gamma$-Fe$_2$O$_3$, which exhibited good catalytic activity for the oxidation of various alkenes based on a cooperation effect between these two oxides. The magnetic properties of the CoHAP-$\gamma$-Fe$_2$O$_3$ provided a convenient route for separation of the catalyst from the reaction mixture by application of an external permanent magnet (Figure 8). The spent catalyst could be recycled without loss of catalytic activity.

Tong et al. [50] reported a heterogeneous catalyst consisting of magnetic CoFe$_2$O$_4$ nanocrystals used for the aerobic oxidation of cyclohexane in the presence of neither solvents nor reducing agents. The catalyst showed high activity for the oxidation of cyclohexane, especially when pure CoFe$_2$O$_4$ was used. The catalyst showed excellent selectivity for the formation of cyclohexanone and cyclohexanol (92.4% of selectivity) and could be easily separated by an external magnet and no obvious loss of activity was observed when reused in five consecutive runs. CoFe$_2$O$_4$ was also efficient for oxidation of linear alkanes. Silva et al. [51] reported a magnetically recoverable cobalt oxide NP catalyst. The catalyst was based on the immobilization of cobalt(II) ions on the surface of core-shell silica-coated magnetite NPs. In the next step, the cobalt(II) ions are precipitated using an aqueous solution of NaOH leading to the formation in a first step of cobalt hydroxide that are transformed in cobalt oxide by air oxidation, and the mean particle size of the supported CoO NPs was 2 to 3 nm. The catalyst was used in the oxidation of cyclohexene and exhibits selectivity for the allylic oxidation of the substrate and gains selectivity as the catalyst loss activity. The allylic oxidation occurs when the olefin undergoes oxidation on the double-bound adjacent carbon, and it is of great interest for the pharmaceutical and fragrances industries as a route for the formation of product precursors.

### 3.3 Ruthenium NPs

Ruthenium is a versatile catalyst and can be used in different reactions, including hydrogenation, metathesis, and oxidation. As an oxidation catalyst, Ru exhibits activity for oxidation of CO [52] and oxidation of alcohols with high selectivity. Mori et al. [53] reported a heterogeneous catalyst consisting of Ru NPs encapsulated in a hydroxyapatite matrix containing nanocrystallites of $\gamma$-Fe$_2$O$_3$ (Figure 9). The catalyst was used as an efficient catalyst for the oxidation of various alcohols to the corresponding carbonyl compound using molecular oxygen as a primary oxidant. The catalyst showed high selectivity for the formation of the carbonyl compound, even when the alcohol had a different functional group, such as -C=C-, and the catalyst was selective for the oxidation of the alcohol group, leaving the double bond intact. Costa et al. [54] reported the synthesis of heterogeneous ruthenium hydroxide supported on silica-coated magnetite NPs. The catalyst was used for the liquid-phase oxidation of a wide range of alcohols with molecular oxygen as a solo oxidant and in the absence of cocatalysts or additives. The material was prepared through the loading of the amino-modified support with ruthenium(III) ions followed by treatment with sodium hydroxide. Transmission electron microscopy (TEM) images showed that the ruthenium hydroxide is highly dispersed on the support surface. The catalyst was used in the oxidation of monoterpenic alcohols and
was active and selective for the formation of corresponding carbonyl groups with good yields.

### 3.4 Palladium NPs

Pd is also known for its high activity in oxidation reactions. Polshettiwar et al. [55] reported a magnetically recoverable Pd catalyst that showed high turnover numbers and selectivity in the oxidation of alcohols and olefins to carbonyl compounds. The catalyst was prepared by the functionalization of nanoferrites with dopamine followed by addition of palladium chloride at basic pH. The dopamine acts as a robust anchor and avoids Pd leaching. Excellent turnover numbers were observed for various aromatic alcohols as well as aliphatic alcohols within 6 h. A turnover number of 720 were achieved in the oxidation of benzyl alcohol.

### 3.5 Gold NPs

Au has received attention as a selective catalyst for oxidation of alcohols to the corresponding ketones and aldehydes. Oliveira et al. [56] reported a magnetically recoverable gold NP catalyst. The catalyst was based on the immobilization of gold(III) ions on the surface of amino-functionalized core-shell silica-coated magnetite NPs followed by metal reduction using two different methods. The gold NPs were prepared by thermal reduction in air and by hydrogen reduction at mild temperature. Interestingly, the mean particle size of the supported gold NPs was similar (~5.9 nm), but the polydispersity of the samples was quite different and the catalysts showed a distinct selectivity for benzyl alcohol oxidation. Another important feature in the preparation of supported gold catalysts is that gold(III) ions have shown very low affinity with silica surfaces of silica-coated magnetite, but an enhanced interaction was obtained by functionalization of silica surfaces with amino groups. Nonfunctionalized and amino-functionalized silica supports were loaded with Au³⁺ precursor and the intermediate species were characterized by XANES. The nonfunctionalized solid was prepared by wetness impregnation in such a way that both solids were loaded with the same amount of gold. The XANES spectra obtained from the material with and without functionalization, and the standards Au⁰ and Au³⁺ indicated a strong interaction between the amino groups and the gold ion, thus causing a change in coordination environment and oxidation state of the metal. The nonfunctionalized support suggested a weak interaction with the oxygenated species on silica surfaces.

After reduction of gold, the nonfunctionalized support contained NPs that were not attached to the support, indicating the weak interaction with the silanol groups. In the amino-functionalized support, the NPs formed were exclusively deposited on the support (Figure 10) [57]. The magnetically recoverable Au NP catalyst was able to discriminate oxygen-sensitive functionalities such as carbon-carbon double-bond functional groups and hydroxyl groups, for example, the oxidation of allyl alcohols to α,β-unsaturated carbonyl compounds [57], as known for other gold catalysts [58].

In summary, despite the enormous amount of work currently found in the literature on oxidations by metal NPs, much remains to be explored on the subject, in particular, the mechanism that drives some of these particles to lose activity during successive cycles of reaction or even the mechanism of oxidation itself.

### 4 Carbon-carbon coupling reactions

An important reaction for organic synthesis is the formation of C-C bonds, especially Heck and Suzuki reactions. Usually, these reactions are catalyzed with great performance by Pd complexes, although Ni, Ru, and Rh also presented catalytic activity [59–61]. The major problem related to the use of soluble complexes in C-C coupling
reactions is the catalyst separation, product contamination, and the very low possibility of reusing the catalyst. An alternative to these problems is the use of supported metal complexes, but in many cases this is followed by a decrease of activity [60, 62, 63]. NPs have demonstrated catalytic performance in C-C coupling reactions, although if the metal particles are the true catalysts or if they deliver active species to the solution is still under debate [64–66]. The use of magnetic separation for this kind of reaction is highly desired because it avoids the exposure of the catalyst to air. Most of the studies involve Pd NPs on a magnetic-responsive support as a catalyst for Heck and Suzuki cross-coupling reactions. Wang et al. [67] prepared a Pd/Fe\textsubscript{3}O\textsubscript{4} magnetic catalyst based on Fe\textsubscript{3}O\textsubscript{4} NPs functionalized with amino groups using 3-aminopropyltriethoxysilane for the Heck reaction. To achieve the maximum loading of Pd, the metal was deposited in successive steps using ethanol as the reducing agent; thus, the deposition of Pd(0) atoms on the magnetic support was gentle. The catalytic behavior of Pd/Fe\textsubscript{3}O\textsubscript{4} NPs in the coupling of acrylic acid with iodobenzene yielded 81% conversion, and when the catalyst was reused, a decrease of activity was observed. The reduction in the activity was explained by the fact that the catalyst agglomerated upon recycling. To improve the stability of the catalyst in both aqueous and nonaqueous solvent, Wang et al. [68] coated the magnetic NPs with a silica shell before functionalizing the solid with amino groups. A colloidal Pd NP solution (particle size of 3 nm) was previously synthesized and impregnated on the magnetic solid. This catalyst was also tested in the C-C coupling of acrylic acid or styrene with iodobenzene with a maximum yield of 58% and 71%, respectively. During the reuse, an amount of metal leached into the solution and some Pd NPs grew up, thus decreasing the catalytic activity. In both studies reported by Wang et al., the catalyst was separated from the reaction medium using a magnet while keeping the solid in the flask for the next reaction cycle.

Zhu et al. [69] enriched commercially available magnetic NPs with phosphate functional groups for use as catalyst support. The enriched suspension was submitted to a solution containing Pd(acac)\textsubscript{2} for impregnation of metal. The Pd was reduced using glycol under argon atmosphere to prepare ultra-small supported Pd NPs. This catalyst was studied in the Suzuki reaction of bromobenzene and phenylboronic acid yielding 83% conversion. For the Heck reaction, they have used the coupling of bromobenzene and styrene obtaining trans-stilbene as the major product in 56% yield. In both C-C coupling reactions, the catalyst did not lose activity in the reuses. The differences of the catalytic behavior of Pd(0) particles and Pd(II) complexes on magnetic solids were investigated by Laska et al. [70]. In the Heck reaction, the catalysts showed similar conversion (>99%), whereas in the Suzuki reaction the catalysts with Pd(II) complexes on a magnetic solid surface presented better performance than the Pd(0) catalyst.

Amali and Rana [39] reported a magnetic support based on magnetite NPs functionalized with PEI. Pd(0) deposited on the magnetic particles was tested in the Suzuki reaction with 75% to 95% yield for aryl chlorides bearing a variety of substituents. The authors compared the activity of their catalyst with the commercial Pd/C, and the latter showed low activity. The explanation for the high activity of the magnetic catalyst was the small size of the Pd NPs. An important feature of this catalytic system was the absence of drastic change in the shape and size on Pd NPs after the reaction and negligible metal leaching. Moreover, no reaction was observed with the filtrate, which is strong evidence of the heterogeneous nature of the catalyst.

Costa et al. [71] reported the preparation of magnetically recoverable Pd NPs stabilized by pendant phosphine groups on the support, by reacting a palladium complex containing the ligand 2-(diphenylphosphino) benzaldehyde with an amino-functionalized silica surface (Figure 11). The Pd(0) NPs prepared after reflux are active for a Suzuki cross-coupling reaction (>99% conversion and 100% selectivity to the biaryl coupling product), avoiding any addition of other sources of phosphine ligands. The catalyst could be reused for up to 10 recycles. The Pd catalyst prepared on the phosphine-functionalized support was more active and selective than a similar Pd catalyst prepared on an amino-functionalized support. Pd

Figure 11 Core-shell silica-coated magnetite functionalized with iminophosphine groups as support for palladium NPs.
NPs in the presence of phosphine-containing ligands presented high activity for C-C coupling reactions.

The search for different ligands and the development of greener processes are still necessary, because phosphine ligands are often expensive, air sensitive, and toxic. Zhang et al. [72] explored the functionalization of silica-coated magnetite NPs with iminopyridine by the “click” system to be used as a support for Pd(0) (Figure 12). The catalyst could be used successfully for several representative Suzuki-Miyaura coupling reactions in ethanol/water media. The functionalization of the surface of silica-coated NPs with ionic liquid was also explored for the preparation of Pd(0) NPs as a C-C coupling catalyst. Wang et al. [73] used an amine-functionalized ionic liquid that acts as a good stabilizer for the Pd NPs and improves the catalytic activity while making the catalyst more accessible to organic substrates. The resulting catalyst showed excellent activity for aryl iodides and bromides in the Suzuki coupling reactions at room temperature, and once again, the catalyst was reused seven times with yields higher than 90%.

Although silica-coated magnetite NPs are the most explored magnetic supports mainly due to the facility of surface modification, other coatings were explored (e.g., carbon). The catalytic activity of Pd(0) supported on Fe$_3$O$_4$@C was investigated in the model Suzuki coupling reaction of bromobenzene and phenylboronic acid and demonstrated superior catalytic activity to several catalytic systems reported in the literature [74]. The speculation of the high conversion rate in Suzuki-Miyaura C-C coupling reaction resulted from the ease with which the reactants accessed the active sites of noble metal particles due to the interaction between graphene and aromatic compounds encouraged Hu et al. [75] to explore magnetic graphene as support for Pd NPs. The magnetic graphene was obtained by coprecipitation of FeSO$_4$·7H$_2$O and FeCl$_3$·6H$_2$O with ammonia solution in the presence of graphene solution, resulting in magnetite NPs immersed in graphene. The next step was the reduction of Pd(OAc)$_2$ on the magnetic solid under reflux, resulting in Pd(0) NPs. With a magnetic graphene, the problems of dramatic loss of activity of Pd/graphene catalysts occasioned by filtration or centrifugation methods could be avoided and the catalyst could be successfully reused in 10 reaction cycles maintaining good conversion. However, the catalysts were unstable and aggregation of Pd(0) and Fe$_3$O$_4$ NPs was observed. The same catalyst was further investigated by Zong et al. [76] in a one-pot diazotation cross-coupling.
reaction of anilines and arylboronic acids. The interest in this reaction emerged from the search for suitable electrophilic reactants for enlarging the applied range of C-C coupling reaction that initially used aryl halides as electrophiles. The Pd(0) NPs supported on magnetic graphene demonstrated high activity but deactivated after the fourth cycle.

It is not only magnetite NPs that have been explored as a support for catalysts in C-C coupling reactions, because other ferrites also have superparamagnetic behavior. NPs of NiFe$_2$O$_4$ were used as a support for a Pd catalyst by Baruwiati et al. [77]. The magnetic NPs were synthesized by a hydrothermal route and their surfaces were modified with dopamine molecules. The catalyst was prepared by reducing Na$_2$PdCl$_4$ with hydrazine in the presence of the magnetic support. The catalyst was tested in Heck and Suzuki reactions with good conversion (>80%) for a variety of substrates and only 0.19% of metal leaching. An increase of the catalyst size after the reaction was also observed.

Ni(0) NPs were also explored for C-C bond formation reaction. The Ni NPs have intrinsic magnetic properties, and in principle, they can be used as catalysts for C-C coupling without the need for a magnetic support to provide the advantages of magnetic separation. Although some researchers have investigated the catalytic performance of Ni NPs in C-C bond formation, none of them explored the magnetic separation of Ni(0) colloidal NPs [78–80].

5 Photocatalytic reactions

Photocatalytic reactions using semiconductor NPs have received considerable attention over the past three decades because of their imminent potential for large-scale application in water purification, air treatment, and solar hydrogen production [81–84]. Among the various transition metal oxides, titanium dioxide (TiO$_2$) has been the most commonly applied photocatalyst due to its use in solar-hydrogen production from water in the early 1970s [85]. Many research papers and review articles have pointed to three important factors (among others) that involve the basic principles of photocatalysis using semiconductor materials under UV and visible light irradiation: (i) The semiconductor photocatalyst should have suitable solar UV or visible light absorption capacity, and appropriate band-edge potentials [86, 87].

(ii) Formation of electron-hole pairs (e$^-$, h$^+$) and migration to surface reaction sites [88, 89].

(iii) Photocatalyst with high crystallinity and large surface area [90, 91].

Figure 13 illustrates the basic mechanism of photogeneration of electron and hole pairs in a semiconductor photocatalyst. Under irradiation with an energy equivalent to or greater than the band gap of the semiconductor photocatalyst, an electron in the valence band (VB) is excited into the conduction band (CB), leaving a positive hole in the VB [88, 92]. After photoexcitation, electron-hole pairs (e$^-$, h$^+$) formed can migrate to the surface of the photocatalyst and induce a series of reductive and oxidative reactions in the presence of electron donors or acceptors adsorbed on the surface of the photocatalyst or recombine in a defect dissipating the input energy as heat [93]. The defects operate as trapping and recombination centers between photogenerated electrons and holes, resulting in a decrease in the photocatalytic activity. A strategy for decreasing the recombination of photogenerated electrons is the use of cocatalyst NPs loaded on the semiconductor photocatalysts. Cocatalysts such as Pt, Au, and NiO NPs are usually loaded to promote the separation of photoexcited electrons and holes [92, 94–96].

Recently, different compounds such as phenols, organic dyes, carboxylic acid, drugs, herbicides, and insecticides have been photodegraded (mineralized) by using magnetic NP photocatalysts. The great advantage in the use of magnetic photocatalysts is the possibility of separating the catalyst by applying a magnetic field, whereas their photocatalytic activity remains after repeated uses. Fe$_3$O$_4$/SiO$_2$/TiO$_2$ photocatalyst with controlled shape and magnetization properties were recently reported to exhibit excellent photocatalytic activity for organic dyes photodegradation [97, 98]. The presence of a thin layer of SiO$_2$ between Fe$_3$O$_4$ NPs and TiO$_2$ shell serves as an electron-hole trap center, which decreases the recombination of photogenerated electron-hole pairs leading to the enhancement of photocatalytic performance [98]. Ye et al. [99]
synthesized a core-shell \( \text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2 \) nanostructured via two steps of a sol-gel process. The core-shell structure is composed of a central magnetite core with an interlayer of \( \text{SiO}_2 \) and an outer layer of \( \text{TiO}_2 \) nanocrystals with a tunable average size. The core-shell structure samples exhibit high photocatalytic activity for degradation of rhodamine B (RhB) and good magnetic separation without significant mass loss [99]. The high photocatalytic activity of the \( \text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2 \) composites is attributed to the small size of the anatase nanocrystals and the presence of the \( \text{SiO}_2 \) interlayer. In addition, the authors studied the effect of the thickness of the \( \text{TiO}_2 \) layer on the photodegradation of RhB. The sample with a 12.6-nm-thick titania shell exhibited the highest photocatalytic efficiency compared with the samples with 13.08 and 14.7 nm thickness. Most significantly, \( \text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2 \) was stable during 18 cycles of reaction of photodegradation of RhB. Furthermore, the concentration of \( \text{Fe}^{3+} \) in the solution after recycles (40.6 mg L\(^{-1}\)) was only 0.0083% of total \( \text{Fe}_3\text{O}_4 \) in the system [99].

Wang et al. [100] reported the preparation of \((\gamma-\text{Fe}_2\text{O}_3@\text{SiO}_2)_n@\text{TiO}_2\) functional hybrid NPs. The synthesis involved three steps: (i) preparation of \( \text{Fe}_3\text{O}_4@\text{SiO}_2 \) composite NPs [101], (ii) resuspension of \( \text{Fe}_3\text{O}_4@\text{SiO}_2 \) particles in the hexane followed by the addition of tetrabutyl titanate and a few water drops (hydrolization), and (iii) the mixture was transferred to a Teflon-lined autoclave and kept at 100°C for 2 h [100]. The mean sizes of hybrid NPs with titania matrix and magnetic \( \gamma-\text{Fe}_2\text{O}_3 \) core particles are about 100 and 15 nm, respectively. The photocatalytic performance of \((\gamma-\text{Fe}_2\text{O}_3@\text{SiO}_2)_n@\text{TiO}_2\) NPs was evaluated in the degradation of methylene blue under UV light. A photodegradation of about 80% of methylene blue was obtained in only 80 min of irradiation [100].

Belessi et al. [102] obtained a novel kind of \( \gamma-\text{Fe}_2\text{O}_3/\text{TiO}_2 \) photocatalyst (without silica coating on the \( \text{Fe}_3\text{O}_4 \) cores) using \( \text{TiO}_2 \) NPs (Degussa P25) and \( \gamma-\text{Fe}_2\text{O}_3 \) NPs (3, 8, 13, 20, and 30 wt.%) through a protective lining made up of two oppositely charged polyelectrolytes. The developed nanocomposites with 20 wt.% \( \gamma-\text{Fe}_2\text{O}_3 \) (Fe(20)Ti) exhibit similarly catalytic activity to the commercial photocatalyst Degussa P25 for the degradation of a chloroacetanilide herbicide (propachlor) in water. The main advantage of \( \gamma-\text{Fe}_2\text{O}_3/\text{TiO}_2 \) core-shell NP over \( \text{TiO}_2 \) NPs (Degussa P25) is the magnetic separation, which facilitates the catalyst reuse without any change in photocatalytic activity or mass loss. Figure 14 shows that the magnetically separable photocatalyst is stable and effective for the decomposition of pesticide propachlor after four successive cycles.

Very recently, a novel magnetic photocatalyst with a hybrid nanostructure consisting of multiwalled carbon nanotubes (MWCNTs), \( \text{Fe}_3\text{O}_4 \) NPs, and a \( \text{TiO}_2 \) layer was reported by Zhou et al. [103]. The photocatalytic activity of the MWCNT/\( \text{Fe}_3\text{O}_4/\text{TiO}_2 \) hybrids was validated for phenol degradation under irradiation of UV-visible light. The MWCNT/\( \text{Fe}_3\text{O}_4/\text{TiO}_2 \) hybrids exhibited higher photocatalytic activity than the neat \( \text{TiO}_2 \) powder. This behavior was attributed to the positive effect of MWCNTs acting as a dispersing agent (the MWCNTs prevent \( \text{TiO}_2 \) from agglomeration) and as an adsorbent (the adsorption efficiency of \( \text{TiO}_2-\text{Fe}_3\text{O}_4-\text{MWCNTs} \) is higher than that of neat \( \text{TiO}_2 \) [103].

Another potentially promising strategy is the application of magnetic NPs in photodynamic therapy. He et al. [104] have reported the photokilling ability of \( \text{Fe}_3\text{O}_4/\text{TiO}_2 \) core-shell NP on HeLa cells in malignant tumor therapy. They have demonstrated that \( \text{Fe}_3\text{O}_4/\text{TiO}_2 \) core-shell NP is nontoxic and much more efficient than traditional \( \text{TiO}_2 \) NP for killing tumor cells. The external magnetic field makes \( \text{Fe}_3\text{O}_4/\text{TiO}_2 \) core-shell NPs cover the surface of HeLa cells well, which increases the efficiency of the photocatalysis of \( \text{Fe}_3\text{O}_4/\text{TiO}_2 \) core-shell NPs and further increases their killing efficiency. Furthermore, \( \text{Fe}_3\text{O}_4/\text{TiO}_2 \) core-shell magnetic NP photocatalysts are promising candidates in the field of malignant tumor therapy in the future [104].

### 6 Other reactions

Polshettiwar and Varma [105] reported a magnetically recyclable ruthenium hydroxide Ru(OH)x catalyst and its application in the hydration of nitriles in a benign aqueous medium.
Abu-Reziq et al. [106] combined the features of magnetic NPs and dendrimers to prepare a magnetically recoverable catalyst for hydroformylation reactions. After phosphination of the heterogenized dendron with various generations, it was complexed with rhodium and used as the catalyst for hydroformylation reactions. The reactivity and selectivity of the catalyst were very high.

As observed previously in this text, Pd is a very active metal for various different kinds of reaction, so it is common to find in the literature studies with Pd/magnetic support in unusual or emergent reactions explored in green chemistry [107, 108]. Pd(0) NPs supported on Fe₃O₄ were active for the carbonylation of aryl halides using atmospheric pressure of carbon monoxide and could be reused five times without losing activity (proposed mechanism in Figure 15). Carbonylation reactions by Pd usually occur via homogeneous catalysis; however, the association of Pd(0) with magnetite surface can result in a synergic effect that allows the alkoxy carbonylation of aryl iodides with different alcohols at mild reaction conditions. Therefore, not only the possibility of magnetic separation but also the presence of synergic effects makes metal NPs supported on superparamagnetic magnetite an interesting system to be explored for complex reactions [109].

A similar system containing Pd(0) NPs on Fe₃O₄ was also active for one-pot reductive amination of aldehydes with nitroarenes under mild conditions. Wei et al. [110] demonstrated that the catalyst Pd/Fe₃O₄ yielded 92% in 6 h of reaction for reductive amination of benzaldehyde with nitrobenzene, whereas the commercial Pd/C yielded only 16% for the same reaction conditions. The magnetically recoverable catalysts explored by Wei could be reused for eight cycles without a significant loss of yield and Pd leaching was negligible. However, the role of magnetite support for this reaction was not investigated.

7 Concluding remarks

Magnetically responsive solid supports that can be easily separated due to the magnetic interaction between the magnetic NPs and an external applied magnetic field have been used for the immobilization of various kind of catalysts, such as metal NPs, metal complexes, organocatalysts, and even enzymes for biocatalysis. In this review, we have selected examples of metal NPs supported on magnetic solid carriers and their application in catalysis and photocatalysis. This separation technique has received a great deal of attention lately, as it is an alternative to traditional time-, energy-, and solvent-consuming steps during catalysis purification processes. Magnetic separation is clean, fast, and easy to scale-up and avoids the use of chemical supplies and solvents that present considerable environmental hazards. Moreover, it allows the complete recovery of the catalyst inside the reactor wall with minimal mass loss and without over exposition to air. Therefore, it can be regarded as a new separation technology with great possibilities for applications in the field of catalysis.

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