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Bare Magnetic Nanoparticles: Sustainable Synthesis and Applications in Catalytic Organic Transformations

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Magnetic nanoparticles have become increasingly attractive in the field of catalysis over the last decade as they combine interesting reactivity with an easy, economical and environmentally benign mode of recovery. Early strategies focused on the use of such nanoparticles as a vehicle for supporting other catalytic nanomaterials or molecules to facilitate recovery. More recently, research has shown that bare magnetic nanoparticles may serve the dual role of a catalyst and a magnetically recoverable entity. At the same time, emerging sustainability concepts emphasize the utility of earth abundant and less toxic resources, especially iron. Herein, we review the recent progress made in the assembly of such systems and their direct application in catalysis. Examples of such bare nanoparticles include iron oxide (Fe₂O₃ and Fe₃O₄), metal ferrites (MFe₂O₄, M=Cu, Co and Ni), Fe(0), Co(0), Ni(0), and multi-component nanoparticles. Features such as reactivity, recoverability and leaching are discussed in a critical fashion.
Introduction

Catalysis is an essential tool of Green Chemistry as it enables the development of less polluting chemical processes and opens up synthetic pathways to desired products using sustainable resources. An essential property of catalysts, by definition, is their ability to be recovered: it is in fact a sine qua non condition of their applicability at the industrial scale. While homogeneous catalysts, including metal complexes of rhodium, palladium, iron, and heteroelement-containing molecules, have demonstrated superiority in terms of activity and selectivity, the majority of industrial catalysts remain heterogeneous because of the simplicity of the latter in terms of recovery. In this context, metal-containing nanoparticles (NPs) are attractive catalyst candidates because they combine high activity, selectivity and tunability, with improved recyclability possibilities. Among various properties of NPs, size, crystallinity, the nature of exposed facets, monodispersity and composition have a high impact on catalysis process.

During the past decade, the concept of magnetic NPs (MNs) has quickly evolved to further simplify the recovery process in catalysis, as well as in the fields of biology and medicine. In this approach, the catalytically active NPs can be directly separated from the reaction mixture using an external supermagnet or by magnetically-assisted cross-flow filtration and centrifugation. In early examples, MNPs are simply used as a supporting vehicle for recovery purposes via the post-synthetic anchorage of a ligand-bound metal center. This strategy is appealing notably for asymmetric catalysis but may suffer from a relative synthetic cost associated with the ligand design, potential leaching by ligand or metal detachment and loss of activity inherent to homogeneous catalysts immobilization. Several reviews have appeared on the use of MNPs in catalysis with an emphasis on synthetic methods and anchoring of non-magnetic catalysts. The focus of this review is on a simpler and rapidly developing strategy that uses bare magnetic NPs for catalysis. In these cases, the catalytic activity relies on the surface of the magnetic particle itself in a heterogeneous fashion. The active species is either the magnetic material itself, or another metal that is embedded in or attached to the MNPs. Many design features that include size, crystallinity, morphology, and composition of MNPs and the use of ligands or additives, have contributed to the development of the rich chemistry of MNPs over the past few years. In this review, the emphasis is on sustainable approaches relying earth-abundant elements such as iron and copper, and organic reactions conducted under mild conditions.

The various classes of MNPs described herein are divided according to the nature of the magnetic core, which can be made of either oxides or reduced species. Among oxides, iron oxide NPs (Fe₃O₄ and Fe₂O₃) have found applications in several oxidative and coupling reactions. The use of metal ferrites (MFe₂O₄, M=Cu, Co, Ni, Zn, Mn), generated by the partial substitution of iron by a second metal inside the crystal lattice of Fe₂O₃, allows the expansion of their catalytic scope, while the iron component continues to enable magnetic recovery.

The in situ reduction of a metal at the surface of oxide-based MNPs opens up the catalytic avenues for the metal used. Turning to the reduced species, Fe(0) NPs offer their own distinct reactivity, which has been exploited by several groups to catalyze reduction and coupling reactions. Here the protection against the oxidative catalyst deactivation is a major challenge that has been partly addressed. These highly reductive iron NPs also constitute a powerful platform to permit easy access to hybrid structures incorporating another catalytically active metals, either in decorated or core shell type entities (Scheme 1).

A distinct feature of naked MNPs is their magnetic properties, which are often stronger when compared to functionalized ones enabling easy recover with a supermagnet or simply with a stir bar; only a handful articles focusing on catalysis have reported extensive magnetic measurements. In the review, we have highlighted such examples and readers seeking in-depth information on magnetic properties of NPs are referred to reviews on this topic.

1 Iron oxide nanoparticles as catalysts

The iron oxide NP represents one of the simplest types of magnetically recoverable catalysts. These NPs are robust, stable in air, amenable to functionalization, suspendable in many solvents including water or other protic benign solvents; their size, shape and crystallinity can be finely tuned.

1.1 Synthesis

Bottom-up approaches for iron oxide NP synthesis include co-precipitation, microemulsion techniques and thermal decomposition. Iron (II) and (III) salts can be co-precipitated out of an aqueous solution by addition of base for the formation of Fe₃O₄ NPs. A microwave-assisted protocol was also developed. To gain more control over NPs size and morphology, techniques relying on oil-water microemulsions containing various salts were adopted. Given their dynamic nature, the micelles continually coalesce and break apart, ultimately forming microreactors containing homogeneous mixtures of the two metal salts. Micelle size can be tuned by controlling oil-water ratios, providing more

Scheme 1. Strategies for the design of catalytic bare magnetic NPs
control over the NP synthesis environment. Rather than forming NPs by chemically separating iron cations from their counteranions, the same can be achieved by thermal decomposition.\textsuperscript{50, 51} Essentially, the decomposition of metal acetoacetonates or other organometallic precursors in high boiling solvents effectively affords the desired oxides. Inclusion of appropriate surfactants or stabilizers restricts the growth of these solids to the nanometer size regime.

![Fig. 1. Synthesis of iron oxide NPs](image)

Top-down approaches for iron oxide NP syntheses have been reported and consist of transforming the existing bulk phase. Grinding of bulk iron oxide affords particles in the nanometer regime;\textsuperscript{52} such processes often yield irregular and polydisperse NPs. Another strategy uses nano-materials as starting materials and is referred to as lateral process. For a finer control of NP morphology, pre-existing, well-defined, and reduced iron NPs can be oxidized in a controlled environment to provide the desired iron oxide NPs with a high degree of precision (Figure 1).\textsuperscript{53}

### 1.2 Catalytic applications

The oxidized state of Fe in Fe\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{3}O\textsubscript{4} NPs provides a potential for oxidative reactions (scheme 2). Beller’s group exploited this property by catalyzing oxidation of olefins and alcohols with Fe\textsubscript{3}O\textsubscript{4} NPs using O\textsubscript{2} or hydrogen peroxide,\textsuperscript{54} the reactivity towards the oxidation of styrene was later probed to greater depths.\textsuperscript{55} Oxidative coupling reactions have been successful, as exemplified by the direct borylation of arenes with bis(pinacolato) diboron using Fe\textsubscript{3}O\textsubscript{4} NPs and mild oxidants (air and tert-butyl peroxide).\textsuperscript{56} Fe\textsubscript{3}O\textsubscript{4} NPs also catalyze the formation of 2-phenylquinazoline derivatives via the condensation of benzyl amine with 2-aminoketones.\textsuperscript{57} C-H activation is yet another appealing feature of oxidative chemistry and is typically achieved using Fe(II)/Fe(III) mixed oxides; the catalytic oxidative cross dehydrogenative coupling of two sp\textsuperscript{3} hybridized C-H bonds with Fe\textsubscript{3}O\textsubscript{4} and Fe\textsubscript{2}O\textsubscript{3} nanoparticles has been reported.\textsuperscript{58} In the same spirit, Csp-Csp\textsuperscript{2} coupling was performed with the Sonogashira-Hagihara reaction using Fe\textsubscript{3}O\textsubscript{4} NPs as catalysts.\textsuperscript{59} Of these examples, early reports focused more on demonstrating catalytic efficiency\textsuperscript{54, 56} and less on recycling and reuse, which has gained more attention recently. Later works investigated such recyclability, with styrene oxidation.\textsuperscript{55} 2-phenylquinazoline synthesis\textsuperscript{57} and cross dehydrogenative coupling examples\textsuperscript{58} all capable of at least 4 consecutive rounds of catalysis. Besides, the potential leaching of iron species in the solution is yet another important aspect to monitor. Iron oxide NPs are typically very robust under the conditions described and, for instance, the concentration of iron species in solution was below ICP-MS detection limit for oxidative cross dehydrogenative coupling.\textsuperscript{58}

The ease of recovery, coupled with the lack of particle degradation (even under oxidizing conditions) showcases the durability of these particles.

![Scheme 2. Selected oxidation and coupling reactions catalyzed by iron oxide NPs](image)

C-H activation has also been successfully harnessed in one-pot three-component coupling reactions. Fe\textsubscript{3}O\textsubscript{4} was shown to catalyze the coupling of aldehyde, trimethylsilyl cyanide and amine for the synthesis of \(\alpha\)-aminonitriles.\textsuperscript{60} Later, two other groups reported, independently, that Fe\textsubscript{3}O\textsubscript{4} and Fe\textsubscript{2}O\textsubscript{3} are active catalysts for the coupling of aldehyde, alkyn, and amine (\(\alpha\)-coupling, scheme 3) providing easy access to propargylamines.\textsuperscript{60, 61} Interestingly in this example, NPs displayed high catalytic efficiency both, in THF and in the absence of solvent. With THF, magnetic recovery proceeds very well and enables reuse up to 12 times; in the latter case, the neat medium is too viscous to enable magnetic recovery of iron oxide NPs. As a variant of the \(\alpha\)-coupling, the alkyn could be replaced with isatoic anhydride for the synthesis of 2,3-dihydroquinazolin-4-(1H)-ones,\textsuperscript{62} or with a phosphonate for the synthesis of \(\alpha\)-aminophosphonates.\textsuperscript{63} In a similar substitution, alkyn was replaced with dimedone for the synthesis of 1,8-dioxodecahydroacridines,\textsuperscript{64} all these methodologies shorten the circuitous pathways to useful synthons (scheme 3).

Finally, \textit{in situ} generated Fe\textsubscript{3}O\textsubscript{4} NPs were also demonstrated to be efficient catalysts for the reduction of nitrobenzene to afford industrially relevant anilines.\textsuperscript{65} In this example, a flow method is used and small magnetite NPs (6 nm) are used as homogeneous suspended catalysts to activate hydrazine as a reducer. At the end of the reaction, the catalysts could be recovered magnetically. ICP-MS measurements revealed that 95% of the catalysts could be recovered in this fashion.
2 Iron/transition metal mixed oxide NPs as catalysts

While iron oxide NPs could catalyze several oxidation and coupling reactions, the catalytic scope of magnetic NPs could be expanded by incorporation of a second metal in the spinel structures of Fe₂O₃. Stable bi-metallic spinels include Co, Ni, Zn, Cr, Mn, Cu, Ce, In and Mg ferrite, where the corresponding dications replaces Fe²⁺ in the lattice. Often, the second metal opens up new catalytic avenues, while the residual iron component improves the magnetic properties, Zhang et al. measured the saturation magnetization of CuFe₂O₄ nanoparticles to be 33.8 emu/g; CuFe₂O₄ nanoparticles for cross coupling reactions were recycled at least 3 times, with a limited drop in yield. Additionally, some groups reported catalyst loss and found that they could recycle up at least 85% of their catalysts after the 3rd run. Copper leaching was measured by Atomic Absorption Spectroscopy (AAS) in some cases and was found to be typically in the high ppb range, making this highly acceptable system for this application.

In addition to the aforementioned Csp-H coupling to aryl halides, the ability of copper to activate alkyne species assists with the azide-alkyne Huisgen condensation, cross dehydrogenative coupling and A³ coupling (scheme 5).

Typically, the traditional homogeneous version of the Huisgen condensation using Cu(I) species proceeds at room temperature. With copper ferrite NPs, however, the reaction requires elevated temperatures. Addition of an electron donating ligand such as 2,2-bipyridine can overcome the limitation of having Cu(II) species in the crystal lattice.

Although A³ coupling and cross dehydrogenative coupling can be catalyzed by Fe₂O₃ copper ferrite NPs offer distinct improvements. The use of CuFe₂O₄ instead of Fe₂O₃ for A³ coupling enables the use of milder conditions, while their use for cross-dehydrogenative coupling opens up new catalytic avenues. Additionally, CuFe₂O₄ enables Csp²-Csp² coupling, whereas Fe₂O₃ activity is limited to Csp²-Csp⁴ and Csp-Csp⁴ couplings.

2.1 Synthesis

In general, the synthesis of mixed metal ferrite NPs mirrors that of monometallic iron ferrite NPs (vide infra). Common methods again include co-precipitation, thermal decomposition, microemulsion techniques and mechanochemical milling.

2.2 Catalytic applications of mixed metal ferrite NPs

The incorporation of copper into the ferrite lattice constitutes a well-developed category of the mixed metal ferrites for catalysis of organic reactions; copper ferrite NPs can catalyze the coupling of aryl halides with C-H, N-H, O-H, S-H or Se-Se functionalities under basic conditions to activate the nucleophilic coupling partner (scheme 4). Although most papers in the field focus more on the catalytic applications than the magnetic properties, Zhang et al. measured the saturation magnetization of CuFe₂O₄ NPs under mild conditions (scheme 6). From run to run,
CuFe\(_2\)O\(_4\) NPs are powerful yet simple catalysts, where the reactivity originates from their bare surface. In some cases, catalytic activity can be boosted by the addition of a ligand interacting with the NP surface. For instance, addition of bipyridine allows CuFe\(_2\)O\(_4\) NPs to become catalytically active for the Huisgen condensation at room temperature.\(^{77}\) In other cases, the use of a chiral ligand confers access to asymmetric catalysis;\(^{78}\) BINAP ligands impart chiral information to the CuFe\(_2\)O\(_4\) NPs surface to generate the chiral alcohols via hydroisolation of ketones (scheme 8).\(^{84}\) AAS measurements on the MNPs before and after catalysis confirmed that the leaching of copper was minimal, and a heterogeneous mechanism is proposed. Copper content in solution, however, was not reported.

Substituting cobalt into the ferrite lattice imparts one advantage over the use of iron alone, as it offers a higher degree of thermal and chemical stability, enabling the use of more extreme conditions; oxidation reactions (scheme 9) demonstrate this increased stability. Fe\(_2\)O\(_4\) NPs can catalyze mild oxidation reactions, but cobalt ferrite NPs can withstand harsher conditions. For example, CoFe\(_2\)O\(_4\) NPs can catalyze the aerobic oxidation at 140°C and at 15 bar O\(_2\) for conversion of cyclohexane to cyclohexanol and cyclohexanone with improved selectivity for the alcohol and ketone over the alkene and ring-opened products.\(^{85}\) Similarly, CoFe\(_2\)O\(_4\) NPs can catalyze the oxidation of alkenes to ketones or epoxides with tert-butyl hydroperoxide at 70 °C.\(^{86}\)

The tuning of catalytic properties with other metals in the ferrite lattice is not limited to stoichiometric constructions. Menini et al.\(^{87}\) have doped ferrite structures with substoichiometric Co and Mn (approximate structure: \(M_xFe_2_x\Theta_1_3\)O\(_4\), where \(M = \text{Co or Mn and } \Theta = \text{cation vacancy}\)) to serve as catalysts for the aerobic oxidation of various monoterpenic alkenes; the catalysts operated under mild conditions: neat, 1 atm O\(_2\), 60 °C and provided a 40 % conversion with 75-95 % selectivity.\(^{88}\)

The wealth of reactions catalyzed by copper, cobalt and manganese ferrite NPs abundantly demonstrates the power of this approach. The less used NiFe\(_2\)O\(_4\) or ZnFe\(_2\)O\(_4\) are expected to show interesting reactivity in the near future as the explorations continue in this area. These catalysts are recoverable magnetically, although their stability and durability in the catalytic process was only limited again and renders these catalysts practical.

### 3 Reduced catalytic metals deposited onto oxide MNPs

Incorporation of another metal inside the crystal lattice of the oxide is not the only method to expand the catalytic scope of MNPs. An alternative strategy consists of depositing metals at the surface of oxide nanoparticles. This can be achieved by the use of a
ligand such as dopamine to attach the incoming metal at the surface of magnetite or silica covered magnetite nanoparticles. Following this route, Ni(II) species have been immobilized and reduced in situ to Ni(0) NPs to serve as hydrogenation catalysts for alkylene and ketone.

A system comprising magnetite NPs covered with silica and Ru island was exploited for the transfer hydrogenation of carboxyl compounds.

The magnetic oxide MNPs, especially Fe$_3$O$_4$ NPs, can be also directly decorated by rare catalytic metal nanoclusters like palladium and ruthenium to catalyze C-C coupling reaction and C-N bond formation, respectively. The two components of this type of NPs can catalyze the reaction in a cooperative manner. The easy recovery and reusability of this category of catalysts showed that they are robust catalytic species to conduct specific reactions.

4 Reduced iron NPs as catalysts

The NPs based on oxide species displayed great catalytic promise, especially towards oxidative processes. Reduced metal NPs have been exploited in catalysis as well. The case of iron is of particular interest because of the abundance of this metal. For a long time, the vigorous reactivity of Fe(0) towards oxidation has limited its applicability. Recently, several studies have featured Fe(0) NP in catalysis and for environmental remediation, where this reactive property has been either tamed by controlling the reaction environment (inert conditions) or by limiting oxidation using a protective layer. The following section discusses the synthesis and reactivity of pure Fe(0) NPs, as well as mixed structures containing both reduced and oxidized Fe.

Reactions catalyzed by Fe(0) NPs include: hydrogenation and transfer hydrogenation of unsaturated hydrocarbons and carbonyls for fine chemical synthesis, dehydrogenation of ammonia borane for release of stored hydrogen fuel, and coupling reactions. They also serve as active stoichiometric reducing agents for a variety of pollutants in environmental remediation namely phosphate, nitrate and trichloroethylene (scheme 12).

4.1 Synthesis

Reduced iron NPs can be synthesized by either a top-down or bottom-up approach. Industry usually prefers top-down options because they are often simpler, less expensive and easily scalable. Mechanical grinding of bulk iron represents one such industrially relevant process currently used on a large scale. The resultant NPs, though inexpensive, are typically polydispersed with regards to size and shape.

Bottom-up approaches, on the other hand, offer more control over particle size and shape. Reduction of Fe(II) or Fe(III) salts by various Grignard reagents, for example, generates highly monodispersed, oxidized NPs in the 1-5 nanometer regime; this synthesis is limited to inert conditions in apotic solvents because of the sensitivity of both the Grignard reagent and the ensuing reductants, one can also take advantage of the natural anti-oxidants (polyphenols) in tea or coffee extract to reduce Fe(NO$_3$)$_3$ or Fe(NO$_3$)$_2$. Alternatively, sodium borohydride is a common reducing agent for iron salts to generate NPs in protic media, including alcohols and water. The presence of water or alcohol via this route leads to the formation of an oxide layer surrounding the Fe(0) core; the size regime for these core-shell NPs is in the range of 50 to 150 nm. In search of more environmentally benign reductants, one can also take advantage of the natural anti-oxidants (polyphenols) in tea or coffee extract to reduce Fe(NO$_3$)$_3$.

Although recent accounts indicate these species are Fe(II) and Fe(III) polymeric structures. Similar to the sodium borohydride reduction, this synthesis could be conducted in water and afforded particles in the 40-50 nm range.

Bottom-up approaches are not limited to reductive strategies from iron salt precursors. Indeed, several methods have been developed for the decomposition of Fe(0) precursors, affording well defined, monodispersed NPs. Fe(CO)$_5$ can be effectively decomposed into NPs in the presence of appropriate ligands or stabilizing agents at high temperature (150-200°C) by ultrasound or UV. NPs generated by this method are extremely monodispersed with tunable sizes between 5 and 20 nm.
depending on the temperature and reaction conditions.

Figure 2 Synthesis of Reduced Iron NPs.

4.2 Catalytic Applications

4.2.1 Hydrogenation

Precious yet toxic transition metals such as Pt, Pd, Ru, Rh and Ni, on endangered periodic list of elements, dominate the field of hydrogenation catalysis. Although iron represents a cheaper and less hazardous alternative, it is generally considered a catalyst with inferior activity. In the homogeneous version, Fe complexes have been shown to catalyze the hydrogenation of alkenes, and carbonyls, in addition to the selective hydrogenation of alkenes to alkynes. However, the high hydrogen content (19.6 % by weight) of Fe(0) NPs makes them a desirable candidate for this process and Fe(0)NPs have demonstrated activity for this reaction. Additionally, under these conditions, Fe(0) NPs were demonstrated to be selective against chloro and nitro arenes. Besides the reactivity for hydrogenation, Fe(0)NPs are active as transfer hydrogenation catalysts.

4.2.2 Ammonia-Borane Dehydrogenation

Ammonia-borane and amine-borane have been intensely investigated in view of their potential to become commercially viable hydrogen carrier for the hydrogen energy economy, given their high hydrogen content (19.6 % by weight). A key reaction in this scheme is the ammonia-borane dehydrogenation, which must occur on the site of energy production, typically in a vehicle, and thus needs to meet a series of constraints including operation at ambient temperature and pressure, and inexpensive catalysts. Fe is a desirable candidate for this process and Fe(0)NPs have demonstrated activity for this reaction. Traditionally, NaBH₄ reduction of FeSO₄ has been used to generate Fe(0)NPs and ensuing NPs could catalyze the hydrolytic dehydrogenation of ammonia borane. The NPs were used up to 20 times with no appreciable decrease in yield. In an effort to further impart robustness to the catalyst system, Dinc et al. have wrapped the particles in polyethylene glycol and used them up to 10 times for catalysis. Despite the fact that these reactions occur in water, the oxidation of the Fe(0)NPs is limited by the strongly reductive reaction conditions. Morris and his group have used Fe(0)NPs generated in situ to perform the same reaction in THF. Recently, it has been demonstrated that several Fe complexes could be used for this reaction wherein [CpFe(CO)₂] proceeded via a purely homogenous mechanism, while CpFe(CO)₂I generated Fe(0)NPs which are responsible for the activity.

4.2.3 Coupling reactions

Fe(0) NPs have been active catalysts for coupling reactions, provided they were placed in highly reducing conditions to prevent their oxidation; Fe(0)NPs are produced in situ from molecular Fe(II) complexes during the coupling reaction of halides with Grignard reagents. Strictly inert conditions are required, as both Fe(0) NPs and Grignard reagents are air- and moisture-sensitive. This example, however, demonstrated the ability of Fe(0) to activate aryl halides. The Suzuki-Miyaura reaction of alkyl halides was reported with Fe(II) complexes by Nakamura et al. and...
proceeded well under dry and degassed conditions, using an activated lithium boronate.\textsuperscript{156} One could therefore, safely envisage that NP(0)NPs may be produced under such conditions and participate actively in catalysis.

### 4.2.4 Degradation of Environmental Contaminants

Besides common catalysis, Fe(0)NPs, commonly referred to as “zero-valent iron” (ZVI), have been intensely studied for their activity as environmental remediation agents;\textsuperscript{35, 106, 108} they can dechlorinate organic solvents (by reductive elimination, hydrolysis or hydrogenation), detoxify pesticides, transform fertilizers and immobilize heavy metals. ZVI are typically produced on industrial scale via a top-down grinding approaches, in water thus featuring a core of Fe(0) and a shell of oxides.\textsuperscript{113} In this context, ZVI serves as a source of electrons to stoichiometrically reduce environmental contaminants. The degradation of dye such as bromothymol blue was showcased by tea-derived Fe(0)NPs\textsuperscript{114} and methyl orange by NaBH\textsubscript{4}-reduced Fe(0)NPs.\textsuperscript{137} Chlorinated organics are a major class of environmental pollutants, with trichloroethylene being a popular solvent used in large volumes as a degreasing agent. ZVI are active for this reaction and the addition of small amounts of Pd to ZVI generates \textit{in situ} bimetallic NPs with much improved reaction rates.\textsuperscript{116} Since this vast field of environmental research is beyond the scope of this review, more extensive overviews are available.\textsuperscript{35, 106, 108}

### 4.2.5 Retrieval of Naturally-occurring NPs

Since metal NPs can be readily generated from reducing polyphenols and sugars present in tea, coffee, wine,\textsuperscript{138} there are distinct possibilities of naturally occurring or man-made NPs present in the aqueous streams or sediments. Although a general mechanism for the formation of naturally occurring NP was proposed by the Hutchison group,\textsuperscript{139} the recovery of such NPs is a challenge. A novel, simple and reliable method for the separation/pre-concentration of trace amounts of silver NPs has been developed which can enable their quantitation using inductively-coupled plasma mass spectrometry (ICP-MS). The synthesis of these NPs relies on galvanic reduction of an introduced metal salt by the Fe(0) core. Veinot\textsuperscript{36} et al. have postulated that hydroxyl groups on the iron oxide shell first chelate the metal centers, which can undergo reduction and finally seed the growth of a new particle (scheme 13). This synthetic strategy, which affords magnetically separable catalysts, is very atom-economical compared to conventional NP synthesis as the Fe(0) NPs serves as support, seed and reducer, thus avoiding the need to add additional reducing and stabilizing agents culminating in waste reduction. Examples of metal particles successfully plated to iron-iron oxide core-shell NPs include Pd,\textsuperscript{36} Cu\textsuperscript{77} and Ru.\textsuperscript{148}

**Scheme 13. Coordination, seeding and growth in the M@FeNPs synthesis**

### 6 Reduced iron NPs as seeds for other transition metal nanocatalysts

Besides the direct application of Fe(0)NPs as simple and recoverable catalysts, they can be used as seeds to deposit other metals on their surfaces to create bi-metallic reduced particles (M@FeNP); such NPs will expand the scope of MNP-based catalysts.\textsuperscript{36, 37}

#### 6.1 Synthesis

The synthesis of these NPs relies on galvanic reduction of an introduced metal salt by the Fe(0) core. Veinot\textsuperscript{36} et al. have postulated that hydroxyl groups on the iron oxide shell first chelate the metal centers, which can undergo reduction and finally seed the growth of a new particle (scheme 13). This synthetic strategy, which affords magnetically separable catalysts, is very atom-economical compared to conventional NP synthesis as the Fe(0) NPs serves as support, seed and reducer, thus avoiding the need to add additional reducing and stabilizing agents culminating in waste reduction. Examples of metal particles successfully plated to iron-iron oxide core-shell NPs include Pd,\textsuperscript{36} Cu\textsuperscript{77} and Ru.\textsuperscript{148}

### 6.2 Catalytic applications

The synthesis of Pd@FeNPs has served as catalysts for the Suzuki-Miyaura cross-coupling reaction in water at room temperature.\textsuperscript{36} Our group expanded the scope of these studies and synthesized Cu@FeNP using CuSO\textsubscript{4} as precursor; they are active for the heterogeneous “Click” Huisgen 1,3-dipolar cycladdition,\textsuperscript{37} and the cyclopropanation of diazoesters with styrene derivatives.\textsuperscript{149} Similarly, Ru@FeNP could be produced and used effectively for the selective transfer hydrogenation of ketones over nitro compounds.\textsuperscript{148} (scheme 14).
It is important to mention here that the successful future endeavors into this type of bi-metallic NP catalysis must be mindful of the second metals' compatibility with iron on several fronts. First, the redox potential of the second metal salt must be high enough to be reduced by Fe\(^{0}\). Second, the lattice of the second metal must be similar enough to the iron oxide shell in order for the second particle to remain attached for long-term use. In an analogous manner as MFe\(_2\)O\(_4\) NPs expanded the scope of reactions that could be catalyzed by simple Fe\(_2\)O\(_4\) NPs, these M@FeNPs could successfully expand the catalytic scope of reduced iron particles. However, this field is relatively less developed and requires further exploration to identify suitable metals, gain insight into the catalysts morphology and involved active species.

7 Conclusions

Magnetic NPs have been extensively studied as the catalyst supports essentially facilitating magnetic separation and recyclability. Recently, however, they have been used in a simplified manner, where the magnetic material acts as the catalyst, or as a reducer of another metal. This emerging and sustainable strategy avoids the use of organic ligands as stabilizers. Iron oxide particles provide open access to oxidation reactions and oxidative couplings, while Fe\(^{0}\)NPs are featured for hydrogenation, dehydrogenation, couplings and reductive processes. In either case, the incorporation of a second metal serves to expand the catalytic abilities of Fe. In the past 5 years, this field has expanded rapidly and future research in this area will presumably focus on the major issues faced by chemistry, including energy (through iron-based ammonia-borane dehydrogenation) and catalysis (replacement of noble metals with earth-abundant base metals, Fe and Cu). Another direction for investigation can be the use of magnetically recoverable catalysts for the synthesis of macromolecules and biomolecules, for which conventional separation techniques are limited or complicated. In all cases, leaching studies and deactivation mechanisms, as well as the important oxidation pathways for Fe\(^{0}\), at the nanoscale, need to be understood to fully unleash the potential of iron as the catalysts of the future.

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Notes and references


Naked magnetic nanoparticles are successfully used as magnetically recoverable catalysts for organic transformations; this review highlights recent progress in this rapidly growing field.