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ARTICLE TYPE

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 (Fe_2O_3 and Fe_3O_4), metal ferrites (MFe_2O_4, 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.

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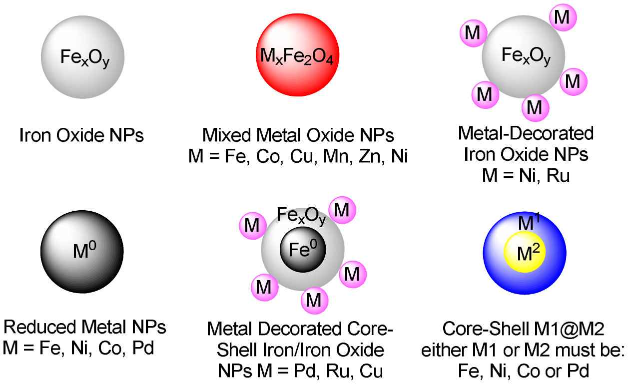
Introduction

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.[1-4] 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.[5] While homogenous catalysts, including metal complexes of rhodium, palladium, iron, and heteroelement-containing molecules,[6-12] 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.[5] In this context, metal-containing nanoparticles (NPs) are attractive catalyst candidates because they combine high activity, selectivity and tunability, with improved recyclability possibilities.[10-16] Among various properties of NPs, size, crystallinity, the nature of exposed facets, monodispersity and composition have a high impact on catalysis process. [14, 17-19]

During the past decade, the concept of magnetic NPs (MNPs) has quickly evolved to further simplify the recovery process in catalysis,[10-12, 20-23] as well as in the fields of biology and medicine.[24, 25] 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.[21] 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.[26, 27] This strategy is appealing notably for asymmetric catalysis[26] 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 is catalysis with an emphasis on synthetic methods,[21, 28-30] and anchoring of non-magnetic catalysts.[10, 13, 20] 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 MNP. 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.[10-12] 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 (Fe_2O_3 and Fe_3O_4) has found applications in several oxidative and coupling reactions.[31, 32] The use of metal ferrites (MFe_2O_4, M=Cu, Co, Ni, Zn, Mn), generated by the partial substitution of iron by a second metal inside the crystal lattice of Fe_3O_4, allows the expansion of their catalytic scope, while the iron component continues to enable magnetic recovery.[33] The *in situ* reduction of a metal at the surface of oxide-based MNP opens up the catalytic avenues for the metal used.[34] 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.[35] 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[36, 37] or core shell type entities,[38, 39] (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;[40] 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. [41-43]



Scheme 1. Strategies for the design of catalytic bare magnetic NPs

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.[44]

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 Fe_3O_4 NPs;[45, 46] a microwave-assisted protocol was also developed.[47] To gain more control over NPs size and morphology, techniques relying on oil-water microemulsions containing various salts were adopted.[48] Given their dynamic nature, the micelles continually coalesce and break apart,[49] ultimately forming microreactors containing homogeneous mixtures of the two metal salts.[21] Micelle size can be tuned by controlling oil-water ratios, providing more

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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.[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.

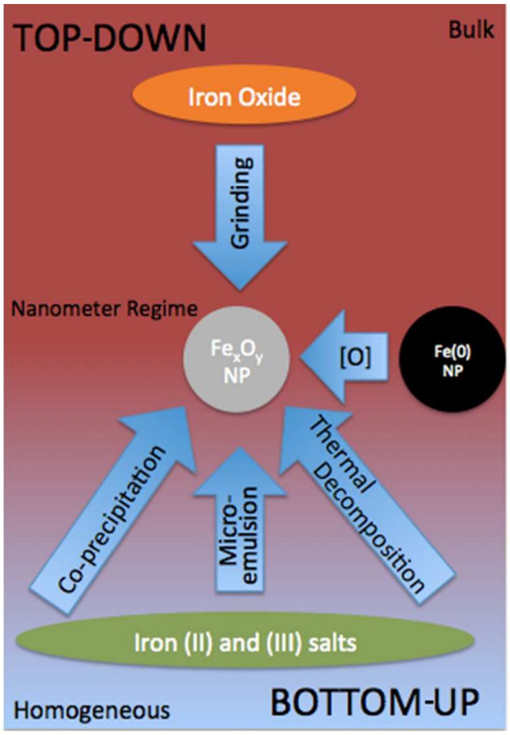
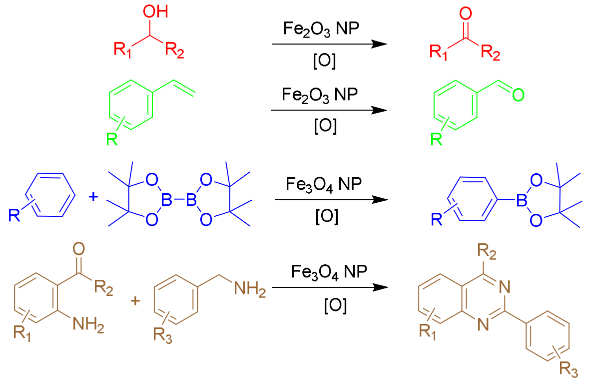


Fig. 1. Synthesis of iron oxide NPs

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;[52] such processes often yield irregular and polydispersed 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).[53]

1.2 Catalytic applications

The oxidized state of Fe in Fe_3O_4 and Fe_2O_3 NPs provides a potential for oxidative reactions (scheme 2). Beller's group exploited this property by catalyzing oxidation of olefins and alcohols with Fe_2O_3 NPs using O_2 or hydrogen peroxide;[54] the reactivity towards the oxidation of styrene was later probed to greater depths.[55] Oxidative coupling reactions have been successful, as exemplified by the direct borylation of arenes with bis(pinacolato)diboron using Fe_2O_3 NPs and mild oxidants (air and *tert*-butyl peroxide).[56] Fe_2O_3 NPs also catalyze the formation of 2-phenylquinazoline derivatives *via* the condensation of benzyl amine with 2-aminoaryl ketones.[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^3 hybridized C-H bonds with Fe_3O_4 and Fe_2O_3 nanoparticles has been reported.[58] In the same spirit, Csp-Csp^2 coupling was performed with the Sonogashira-Hagihara reaction using Fe_3O_4 NPs as catalysts.[59] Of these examples, early reports focused more on demonstrating catalytic efficiency[54, 56] and less on recycling and reuse, which has gained more attention recently. Later works investigated such recyclability, with styrene oxidation,[55] 2-phenylquinazoline synthesis[57] and cross dehydrogenative coupling examples[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. [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 [54-57]

C-H activation has also been successfully harnessed in one-pot three-component coupling reactions. Fe_3O_4 was shown to catalyze the coupling of aldehyde, trimethylsilyl cyanide and amine for the synthesis of α-aminonitriles.[60] Later, two other groups reported, independently, that Fe_3O_4 and Fe_2O_3 are active catalysts for the coupling of aldehyde, alkyne, and amine (A^3 coupling, scheme 3) providing easy access to propargylamines.[40, 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 A^3 coupling, the alkyne could be replaced with isatoic anhydride for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones,[62] or with a phosphonate for the synthesis of α-aminophosphonates.[63] In a similar substitution, alkyne was replaced with dimedone for the synthesis of 1,8-dioxo-decahydroacridines;[64] all these methodologies shorten the circuitous pathways to useful synthons (scheme 3).

Finally, *in situ* generated Fe_3O_4 NPs were also demonstrated to be efficient catalysts for the reduction of nitrobenzene to afford industrially relevant anilines. [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.

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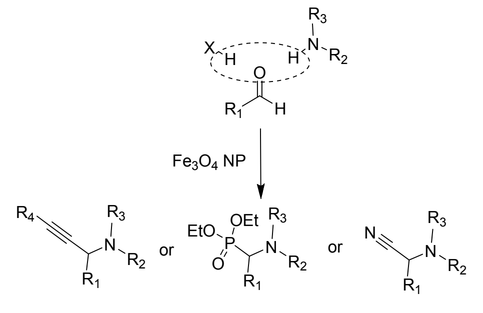


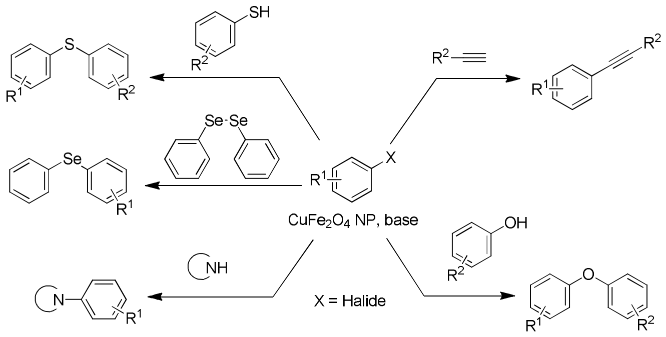
Scheme 3. A^3-type reactions catalyzed by iron oxide NPs

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 Fe_3O_4. Stable bi-metallic spinels include Co, Ni, Zn, Cr, Mn, Cu, Ce, In and Mg ferrite, where the corresponding dications replaces Fe^{2+} in the lattice. Often, the second metal opens up new catalytic avenues, while the residual iron component continues to provide an effective means for easy magnetic recovery. Mixed spinel, doped spinels and three component spinels have been intensely studied and their catalytic activity have been evaluated for CO_2 reduction,[66, 67] water splitting,[68] water-gas shift,[69] methane steam reforming,[70] and methanol decomposition.[71] In the examples below, we concentrate on applications to organic synthesis.

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.[21]



Scheme 4. $CuFe_2O_4$ NP catalyzed Cross-coupling reactions

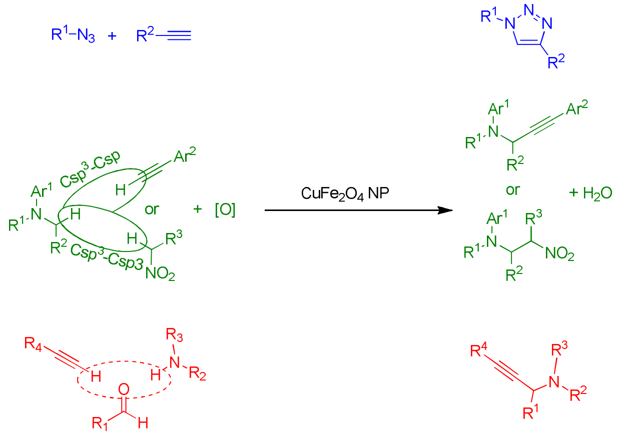
2.2 Catalytic applications of mixed metal ferrite NPs

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,[72] N-H,[73] O-H,[74] S-H,[75] or Se-Se[76] 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. [74] measured the saturation magnetization of their $CuFe_2O_4$ nanoparticles to be 33.8 emu/g; $CuFe_2O_4$ nanoparticles for cross coupling reactions were recycled at least 3 times,[72-76] with a limited drop in yield. Additionally, some groups[72, 73, 75] 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.[72, 73, 75]

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,[77, 78] cross dehydrogenative coupling[79] and A^3 coupling[80] (scheme 5).

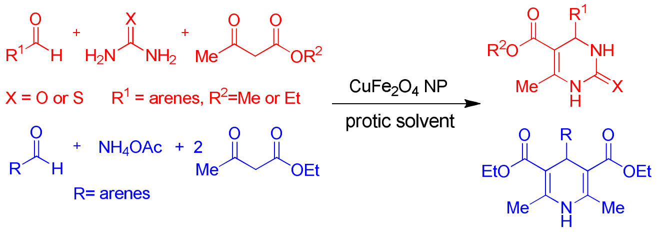
Typically, the traditional homogeneous version of the Huisgen condensation using Cu(I) species proceeds at room temperature. With copper ferrite NPs, however, the reaction requires elevated temperatures.[78] Addition of an electron donating ligand such as 2,2-bipyridine can overcome the limitation of having Cu(II) species in the crystal lattice.[77]

Although A^3 coupling[40] and cross dehydrogenative coupling[58] can be catalyzed by Fe_3O_4, copper ferrite NPs offer distinct improvements. The use of $CuFe_2O_4$ instead of Fe_3O_4 for A^3 coupling enables the use of milder conditions,[80] while their use for cross-dehydrogenative coupling opens up new catalytic avenues. Additionally, $CuFe_2O_4$ enables Csp^3-Csp coupling, whereas Fe_3O_4 activity is limited to Csp^3-Csp^3 and Csp-Csp^2 couplings.[79]



Scheme 5. $CuFe_2O_4$ NP catalyzed reactions with alkynes: the azide-alkyne Huisgen condensation (top), cross dehydrogenative coupling (middle) and A^3 coupling (bottom)

$CuFe_2O_4$ NPs are also active for the catalysis of the Biginelli[81] and related condensation reactions,[82] typically requiring elevated temperatures (scheme 6).



Scheme 6. $CuFe_2O_4$ NP catalyzed condensation reactions

Deprotection of acylated sugars has been achieved with $CuFe_2O_4$ NPs under mild conditions (scheme 7).[83] From run to run,

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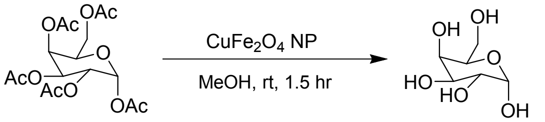
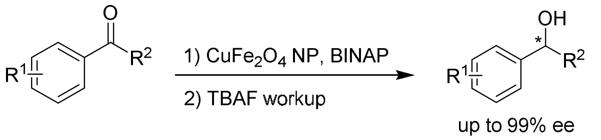
95% of the catalyst could be recovered and recycled for reuse. This reaction is highly appealing because magnetic separation offers a viable means to ease the purification of complex saccharide products.



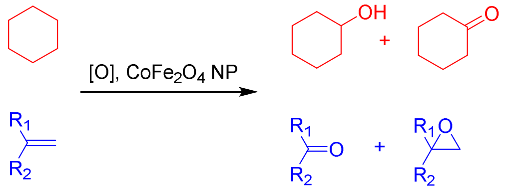
Scheme 7. $CuFe_2O_4$ NPs catalyzed sugar deacylation[83]

$CuFe_2O_4$ 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 $CuFe_2O_4$ 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;[30] BINAP ligands impart chiral information to the $CuFe_2O_4$ NPs surface to generate the chiral alcohols *via* hydrosilation 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.



Scheme 8. $CuFe_2O_4$ NP catalyzed asymmetric hydrosilation[84]

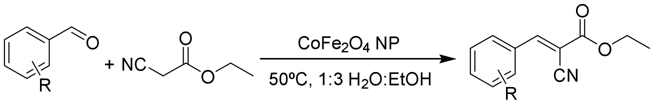
Substituting cobalt into the ferrite lattice imparts one advantage over the use of iron alone, as it offers a higher degree of thermal and chemical stability, enabling the use of more extreme conditions; oxidation reactions (scheme 9) demonstrate this increased stability. Fe_3O_4 NPs can catalyze mild oxidation reactions, but cobalt ferrite NPs can withstand harsher conditions. For example, $CoFe_2O_4$ 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, $CoFe_2O_4$ NPs can catalyze the oxidation of alkenes to ketones or epoxides with *tert*-butyl hydroperoxide at 70 °C.[86]



Scheme 9. $CoFe_2O_4$ NP catalyzed oxidation reactions

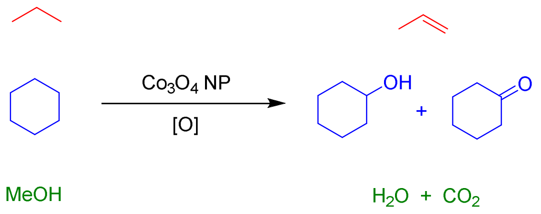
Senapati *et al.*[87] used $CoFe_2O_4$ NPs to catalyze the Knoevenagel reaction (scheme 10) between various aldehydes and ethyl cyanoacetate; the reaction proceeded under mild conditions (50 °C for 25 minutes), with a mixture of water and ethanol as an environmentally benign solvent (water:ethanol=1:3). This showcases the unique catalytic contribution of cobalt even under milder conditions.

The tuning of catalytic properties with other metals in the ferrite lattice is not limited to stoichiometric constructions. Menini *et al.* have doped ferrite structures with substoichiometric Co and Mn (approximate structure: $M_{0.5}Fe_{2.4}\otimes_{0.1}O_4$, where M = Co or Mn and ⊗ = 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]



Scheme 10. $CoFe_2O_4$ NP catalyzed Knoevenagel reaction[87]

On the other end of the doping spectrum, cobalt can entirely replace iron within the ferrite lattice, providing Co_3O_4 NPs. Although iron is absent, cobalt is still magnetic, which enables the same ease of catalyst recovery. Such particles have been used to catalyze ammonium perchlorate decomposition.[89] Similar to iron oxide NPs, these Co_3O_4 NPs provide an oxidizing potential, which has been exploited for methanol oxidation,[90] cyclohexane oxidation[91] to cyclohexanol or cyclohexanone and alkane to alkene conversion (scheme 11).[92]



Scheme 11. Co_3O_4 NP catalyzed oxidation reactions

The wealth of reactions catalyzed by copper, cobalt and manganese ferrite NPs abundantly demonstrates the power of this approach. The less used $NiFe_2O_4$ or $ZnFe_2O_4$ 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 evaluated by microscopy techniques;[74, 80, 93] metal leaching is 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 NMPs. An alternative strategy consists of depositing metals at the surface of oxide nanoparticles. This can be achieved by the use of a

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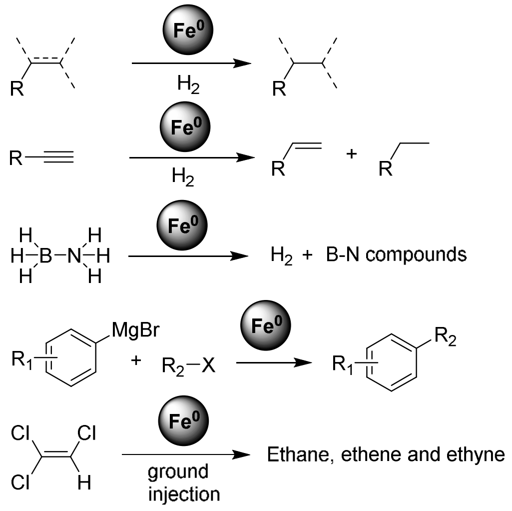
ligand such as dopamine to attach the incoming metal at the surface of magnetite or silica covered magnetite nanoparticles. Following this route, Ni(II) species have been immobilized and reduced *in situ* to Ni(0) NPs to serve as hydrogenation catalysts for alkyne and ketone.[34] A system comprising magnetite NPs covered with silica and Ru island was exploited for the transfer hydrogenation of carbonyl compounds.[94]

The magnetic oxide MNPs, especially Fe_3O_4 NPs, can be also directly decorated by rare catalytic metal nanoclusters like palladium[95] and ruthenium [96] 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. [96] The easy recovery and reusability of this category of catalysts showed that they are robust catalytic species to conduct specific reactions. [95, 96]

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.[97] 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. [41] 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[98-101] and transfer hydrogenation of unsaturated hydrocarbons and carbonyls for fine chemical synthesis,[102] dehydrogenation of ammonia borane for release of stored hydrogen fuel,[103-105] and coupling reactions. They also serve as active stoichiometric reducing agents[106, 107] for a variety of pollutants in environmental remediation namely phosphate,[108] nitrate[109] and trichloroethylene[110, 111] (scheme 12).



Scheme 12. Fe(0) NP catalyzed reactions

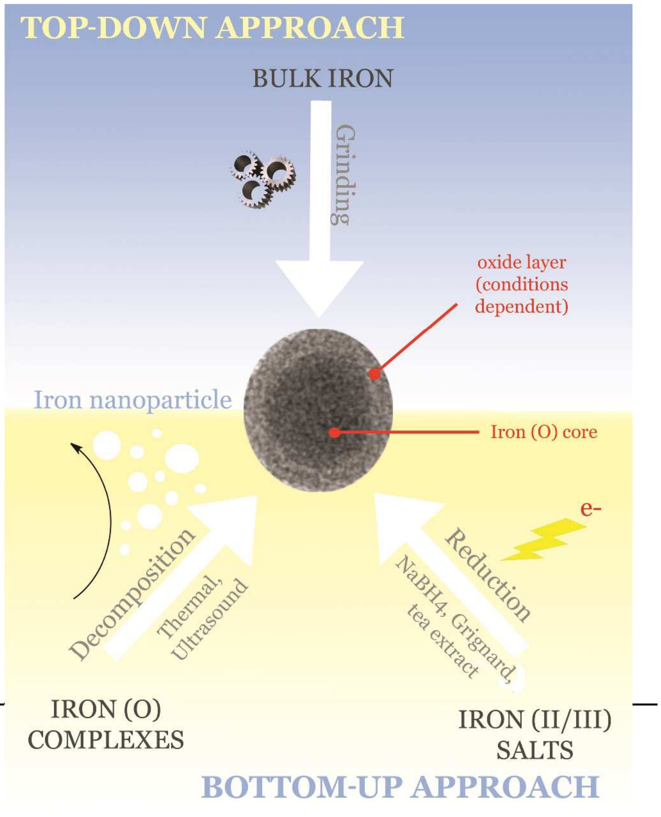
The synthesis and the catalytic applications in organic transformations has been described by Welther and Jacobi von Wangelin.[112]

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.[100]

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, unoxidized NPs in the 1-5 nanometer regime; this synthesis is limited to inert conditions in aprotic solvents because of the sensitivity of both the Grignard reagent and the ensuing NPs.[98, 99] Alternatively, sodium borohydride is a common reducing agent for iron salts to generate NPs in protic media, including alcohols and water.[100] The presence of water or alcohol *via* this route leads to the formation of an oxide layer surrounding the Fe(0) core;[113] the size regime for these core-shell NPs is in the range of 50 to 150 nm.[111] 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 $Fe(NO_3)_3$,[114-116] although recent accounts indicate these species are Fe(II) and Fe(III) polymeric strutures. [117] 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),[118] by ultrasound,[119] or UV;[120] NPs generated by this method are extremely monodispersed with tunable sizes between 5 and 20 nm,



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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.[121, 122] 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,[123, 124] carbonyls,[6, 125, 126] imines,[125] and carbonates[127] in addition to the selective hydrogenation of alkynes to alkenes,[128, 129] but such systems offer limited recoverability options.

De Vries and coworkers unlocked the hidden reductive potential of Fe(0) at the nanoscale.[98] Iron NPs (1-5 nm), generated by the reduction of Fe(II) or Fe(III) salts with an excess of Grignard reagent (EtMgCl, PhMgBr, MeMgCl, *etc*.), were used for the hydrogenation of alkenes and alkynes under hydrogen pressure in THF. Quantitative hydrogenation of norbornene, a strained, cyclic olefin was observed after half an hour at room temperature and 1 bar of H_2 pressure. Less strained, linear olefins, however, required 15 hours for completion. Alkynes could be hydrogenated under similar conditions, with selectivity for alkene or alkane product depending on reaction time.[98, 99] An *in situ* spectroscopic study was performed to demonstrate the heterogeneous nature of the catalysis.[130] This pioneering system suffered from two drawbacks: (i) the small size of NPs renders them non-magnetic and (ii) the particles are readily oxidized. Indeed, the reaction requires strict oxygen-free conditions, and even the presence of only 1 % water in the solvent completely deactivates the catalyst.[98] The first challenge, namely magnetic recoverability was circumvented by seeding Fe(0) on chemically derived graphene sheets, where particles then grew by ultrasound-induced degradation of $Fe(CO)_5$.[119] Recently, after fine characterization of the ultrasmall Fe(0) NPs at around 1.5 nm *via* thermal decomposition of the complex $\{Fe(N[Si(CH_3)_3]_2)_2\}_2$, Chaudret group showed that in the absence of oxidation on the surface, compared to De Vries' experiments,[98] their ultrasmall Fe(0) NPs are efficient in hydrogenation of C-C unsaturated bonds and C=X bonds under milder conditions. The reactions were conducted under 10 bar H_2 pressure at room temperature, and were completed in 20 hours for simple substrates. However, the steric hindrance of the substrates could hamper the catalytic efficiency.[131]

With the implicit aim of improving recoverability, while concurrently addressing the challenge of oxidative deactivation, we have studied the catalytic activity of larger core-shell iron-iron oxide NPs.[100] Their 30-50 nm size rendered them magnetically recoverable, while the oxide shell apparently slowed down further oxidation of the Fe(0) core. Indeed, the catalyst survived the exposure to air and demonstrated activity even in water: ethanol (1:1) mixtures for the hydrogenation of a series of alkenes and alkynes. Further improvements were sought to the system by using amphiphilic polymers to protect the activity of Fe(0) NPs. In this case, $Fe(CO)_5$ decomposition and Fe(II) reduction occurred inside a polystyrene-polyethylene glycol block co-polymer resin. The resulting catalyst demonstrated high activity for the hydrogenation of alkenes and alkynes in flow systems and in aqueous mixtures up to 90 % water.[101] Hydrogenation of cyclohexenone (100 % conversion) in this case afforded 100% selectivity for cyclohexanone, i.e. 0% conversion of the carbonyl. Similar results were obtained by Andanson *et al.*[132] when Fe(0) NPs were in ionic liquid to hydrogenate cyclohexenone with 82% selectivity for cyclohexanone over cyclohexanol (18%). The selective hydrogenation of alkynes to alkenes by Fe(0)NPs in the same medium was reported by the Jacobi von Wangelin group. {Gieshoff, 2014 #280} We further delineated that aromatic imines were active substrates for hydrogenation, as were aromatic aldehydes, whereas carboxylic acids, nitriles, aliphatic imines and aliphatic aldehydes remained inert.[101] Additionally, under these conditions, Fe(0) NPs were demonstrated to be selective against chloro and nitro arenes. [101] Besides the reactivity for hydrogenation, Fe(0)NPs are active as transfer hydrogenation catalysts.[102] Interestingly, in this example, the selectivity was reversed, with ketones being the substrates of choice; enantioselectivity was demonstrated which originated from the chiral NP-stabilizing agents.

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).[133] 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, $NaBH_4$ reduction of $FeSO_4$ has been used to generate Fe(0)NPs[103] 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.*[104] 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.[105] Recently, it has been demonstrated that several Fe complexes could be used for this reaction wherein $[CpFe(CO)_2]_2$ proceeded *via* a purely homogenous mechanism, while $CpFe(CO)_2I$ generated Fe(0)NPs which are responsible for the activity. [134]

4.2.3 Coupling reactions

Fe(0) NPs have been active catalysts for coupling reactions,[135] 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

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proceeded well under dry and degassed conditions, using an activated lithium boronate.[136] 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;[35, 106, 108.] they can dechlorinate organic solvents (by reductive elimination, hydrogenolysis 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.[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[114] and methyl orange by $NaBH_4$-reduced Fe(0)NPs. [137] Chlorinated organics are a major class of environmental pollutants, with tricholorethylene 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 *in situ* bimetallic NPs with much improved reaction rates .[116] Since this vast field of environmental research is beyond the scope of this review, more extensive overviews are available.[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 waste,[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,[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 structurally modified magnetic particles could successfully capture trace amounts of silver NPs (~2 ppb) and concentrate (up to 250 times) the particles for analysis with ICP-MS.[140] This is especially useful for silver NPs (AgNPs) as they are gaining popularity in various consumer products such as detergents, clothing, dishwashers, water filters, medical appliances and food packaging materials due to silver's antibacterial properties. [141]

5 Ni and Co NPs as magnetically recoverable catalysts

Apart from iron, there are several other metals that can be used as magnetically recoverable NP catalysts. For example, Co(0)[142] or Ni(0)[143, 144] NPs can be used for room temperature ammonia borane-dehydrogenation and for hydrogenation reactions;[39, 145] Ni and NPs were shown to be active Suzuki coupling catalysts.[146]

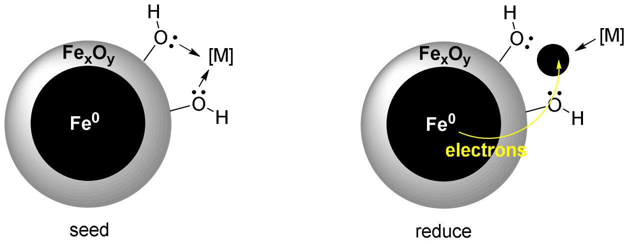
These examples encompass reactions that can already be performed by iron, so the most impactful future endeavors in this field may see reduced cobalt, nickel or gadolinium NPs for catalyzing reactions that are outside the known scope of iron. In this context, Shen et al. effectively used Ni NPs to catalyze the thermal decomposition of ammonium perchlorate.[147]

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. [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[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,[36] Cu[37] and Ru.[148]



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

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.[36] Our group expanded the scope of these studies and synthesized Cu@FeNP using $CuSO_4$ as precursor; they are active for the heterogeneous "Click" Huisgen 1,3-dipolar cycloaddition,[37] and the cyclopropanation of diazoesters with styrene derivatives.[149] Similarly, Ru@FeNP could be produced and used effectively for the selective transfer hydrogenation of ketones over nitro compounds[148] (scheme 14).

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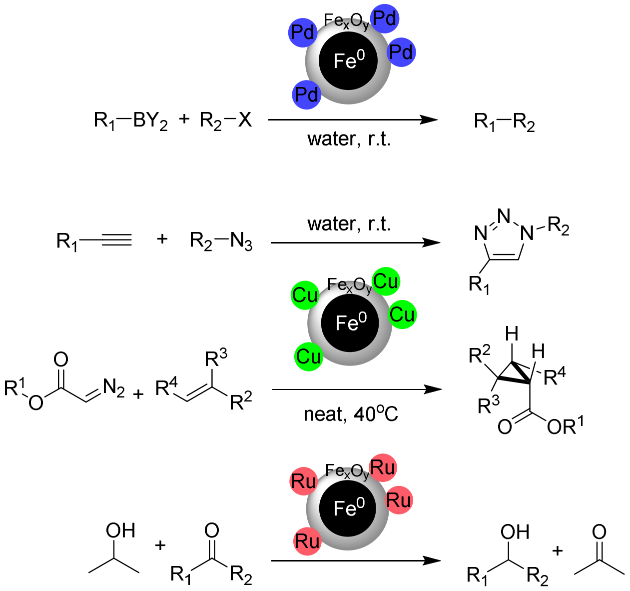

Scheme 14. Catalytic application of M@FeNPs

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_2O_4 NPs expanded the scope of reactions that could be catalyzed by simple Fe_3O_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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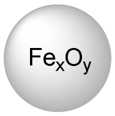
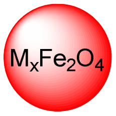
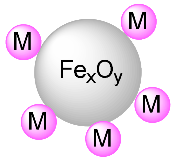
Naked magnetic nanoparticles are successfully used as magnetically recoverable catalysts for organic transformations; this review highlights recent progress in this rapidly growing field.



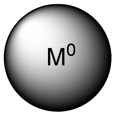
Iron Oxide NPs



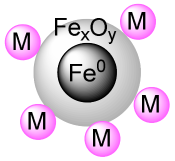
Mixed Metal Oxide NPs
M = Fe, Co, Cu, Mn, Zn, Ni



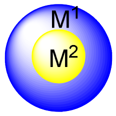
Metal-Decorated
Iron Oxide NPs
M = Ni, Ru



Reduced Metal NPs
M = Fe, Ni, Co, Pd



Metal Decorated Core-Shell Iron/Iron Oxide NPs
M = Pd, Ru, Cu



Core-Shell M1@M2
either M1 or M2 must be:
Fe, Ni, Co or Pd

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