CHEMICAL REVIEWS

Review

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# Fast-Growing Field of Magnetically Recyclable Nanocatalysts

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## 1. INTRODUCTION

Catalysis is a key component of "green chemistry", and one of the urgently needed challenges facing chemists now is the design and use of environmentally benign catalysts.[1−10] A sustainable and "green" catalyst must therefore possess specific features[11] including low preparation cost, high activity, great selectivity, high stability, efficient recovery, and good recyclability.

Conventional catalysts can be divided into homogeneous and heterogeneous, the former holding advantages such as good activity and selectivity and accessible mechanistic studies leading to catalyst optimization. However, the difficulty of separating homogeneous catalysts from reaction medium consumedly restricts their applications in industry, especially in the drug and pharmaceutical industry owing to the issue of metal contamination in the case of metal-catalyzed synthesis. Heterogenization of active molecules with a solid support fabricating insoluble heterogeneous catalytic systems is an efficient strategy in order to achieve the isolation and separation of catalysts. However, the activities of heterogeneous catalysts are generally lower than those of their homogeneous counterparts, due to the lower dimensionality of the interaction between the components and the catalyst surface.

As semiheterogeneous catalysts, nanocatalysts with a large surface-to-volume ratio, are attractive alternatives to conventional catalysts, substantial enhancements in catalytic activity, selectivity, and stability are realized by tailoring their size, shape, composition, and electronic structure.[12−22] Nanocatalysts are isolated and recovered through filtration or centrifugation methods, whereas the inconvenience and inefficiency of these tedious methods caused by the nano size of the catalyst particles hamper the sustainability and economics of the nanocatalytic strategy.

To overcome these issues, use of magnetic nanoparticles (MNPs) appears to be the most logical solution. Magnetic nanocatalysts are simply and efficiently removed from reaction mixtures with an external magnetic field, and MNPs have emerged as ideal catalysts or supports. This field has indeed been the subject of excellent reviews.[23−28]

Due to this explosive development, new reactions, nanocatalysts, systems, and trends are appearing at a fast rate, and about 400 publications have appeared in the last 2 years. Therefore, in this review, we briefly summarize the basic concepts and seminal studies of magnetically recoverable catalysts; then we highlight the new breakthroughs and trends in the area that have most recently appeared until 2014.

### 1.1. Synthesis and Modification of Magnetic Nanoparticles

The methods of preparation of MNPs play a key role in determining the particle morphology (size, shape, agglomeration, and size distribution), composition, magnetic property, surface chemistry, and catalytic applications. There are several protocols reported in the literature for synthesizing MNPs, such as the coprecipitation method, the micromulsion technique, the sol−gel method, spray and laser pyrolysis, the

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hydrothermal reaction method, sonolysis, microwave irradiation, biological synthesis, etc.[23,24,29−35] According to particular requirements for MNPs, these methods were operated under optimized conditions (mainly regarding reaction temperature, pH value, concentration, and proportion of starting materials) to synthesize MNPs in the forms of metals (Fe, Co, Ni), alloys (FePt, CoPt), iron oxides (FeO, $Fe_2O_3$, $Fe_3O_4$), or ferrites $MFe_2O_4$ (M = Co, Mn, Cu, Zn). These MNPs are directly used as catalysts or as supports for further modification or functionalization with the catalytic species.

Among these MNPs, magnetite ($Fe_3O_4$) has been identified as the ideal and most widely used support in catalysis[36,37] because of its low cost and easy preparation. Magnetite is inert and possesses a very active surface for immobilization or adsorption of catalytic fragments including metal catalysts (Au, Pd, Pt, Cu, Ni, Co, Ir), organocatalysts, and enzymes resulting in formation of remarkably sustainable catalysts. Magnetite has been used in recent years as a versatile catalyst support in a wide range of reactions, such as Suzuki, Heck, Sonogashira, Hiyama, hydrogenation, reduction, oxidation, cycloaddition reactions, asymmetric synthesis, etc. Magnetite has also been directly applied as catalyst in organic transformations. For example, $Fe_3O_4$ nanoparticles (NPs) exhibited high catalytic performance for the practical and atom-economic one-pot synthesis of propargylamines via three-component coupling of aliphatic aldehyde, alkyne, and amine. In addition, after completion of the first reaction cycle, $Fe_3O_4$ is magnetically separated from the reaction medium with an external magnetic field and reused at least five times without a significant decrease of activity.[38] Other forms of iron oxide, maghemite ($\gamma$-$Fe_2O_3$), and spinel ferrites ($MFe_2O_4$) have also received a lot of attention in the field of MNPs catalysis owing to their ferrimagnetism, environmental stability, and other properties.

Aggregation of the naked MNPs is virtually unavoidable because of their small interparticle distances, high surface energy, and the existence of van der Waals forces. To solve this problem, modification of MNPs using suitable stabilizing ligands or coating materials (including small molecules, silica, polymers, carbon, ionic liquids, metal or metal oxide NPs, and their layer-by-layer combinations) has been proved to be the best solution to date. Meanwhile, the modification procedures provide reaction sites or active groups for covalently or noncovalently grafting the active catalytic units onto the coated MNPs to construct magnetically recoverable catalysts.

Dopamine derivatives,[39−41] triethoxysilyl-[42−44] phosphonic acids-functionalized molecules,[45,46] and glutathione[47,48] were frequently applied to stabilize and functionalize MNPs. This process produces grafting sites or reaction sites to bind catalytic species. Dopamine, a natural neurotransmitter that is present in various animals, contains catechol and amine groups. It exhibits an outstanding capacity of coordination to Fe ions of MNPs, the coordination usually being promoted by sonicating the mixture in suspension. The amine groups of dopamine derivatives are versatile chelating reagents (or reactive fragment) to directly coordinate metal catalyst or react with other organic molecules. Triethoxysilyl-functionalized molecules such as commercially available $NH_2$-, SH-, and Cl-terminated compounds and their further functionalized derivatives are another type of popular reagents for surface modification of MNPs. The connection of MNPs with these silane reagents is achieved by coupling between the hydroxyl group of MNPs and silane reagents. For instance, the Sato group[44] reported the first example of phase-transfer catalyst (quaternary ammonium and phosphonium salts)-modified MNPs. In the synthetic process, (3-iodopropyl) trimethoxysilane successively reacted with quaternary ammonium and phosphonium salts, and the homogeneous triethoxysilyl-functionalized phase-transfer catalyst that was obtained was then anchored using MNPs. This semiheterogeneous catalyst showed high performance in terms of activity and stability in the O-alkylation reaction of PhONa with *n*-BuBr in the solvent mixture of toluene and water. Phosphonic acids and glutathione are also bifunctionalized linkers between MNPs and catalytic species.

Silica is the most popular inorganic coating material for MNPs, because it is very easily connected to MNPs. Most MNPs are synthesized in organic solvent using hydrophobic capping reagents, resulting in dispersibility in organic solvents but poor dispersion properties in environmentally benign aqueous media. Silica as coating shell improves the water solubility and biocompatibility of MNPs. The dense silica shell has plenty of Si−OH groups for potential derivatization with various functional units allowing introduction of catalytic molecules to MNPs. Silica shells prevent metal leaching from the core of MNPs under harsh shaking conditions. Coating silica is generally performed through the sol−gel method, microemulsion technique, and deposition of silica deposition from a silicic acid solution. Since the pioneering work on the application of silica-coated MNPs as a recyclable catalyst support was reported by Ying and co-workers,[49] a great variety of catalysts based on silica-coated MNPs have been developed. For example, Jin's group demonstrated that a triethoxysilyl-functionalized Pd complex was easily immobilized on the surface of $SiO_2@Fe_3O_4$ that was prepared by coating $Fe_3O_4$ NPs (20 nm in core) with a layer of silica through a sol−gel process. This Pd catalyst was highly active and magnetically recyclable in the Suzuki, Sonogashira, and Stille reactions of unreactive aryl chlorides in aqueous conditions.[50]

Recently, introducing a shell of polymers (or dendrimers) with functional groups to the surface of MNPs has been the subject of increasing attention.[28,35] In catalysis, the catalytic performance of MNPs can be flexibly tuned and considerably affected by the inherent properties of the polymers (or dendrimers), such as solubility, functional groups, molecular weight, degree of cross-linking, hydrophilicity, and hydrophobicity. In general, there are two protocols for the immobilization of MNPs with polymers: in situ polymerization on the surface of MNPs[51,52] and grafting of polymers onto MNPs via coordination, or hydrophobic, or electrostatic interations.[53,54] For instance, $Fe_3O_4$@PANI NPs with well-defined core−shell nanostructure were fabricated through polymerization of aniline on the surface of the $Fe_3O_4$ NPs. After treating $Fe_3O_4$@PANI under acidic or neutral pH conditions, its surface was covered by positive charge, which allowed negatively charged citrate-stabilized AuNPs to be attached to $Fe_3O_4$@PANI through electrostatic attractions.[55] Various commercially available polymers including Pluronic polymer,[56] poly(acrylic acid) (PAA), and polyethylenimine (PEI)[57] have been used as coating materials on the surface of MNPs. Dendrimers, exhibiting well-defined structure and a monodisperse nature, have been identified as ideal capping materials to MNPs for embedding molecular and nanocatalysts. The step-by-step divergent synthesis of dendrimers on the surface,[58] and the grafting of presynthesized dendrimers on the surface are two common protocols to form dendrimer shell of MNPs.[53,59] Alper's group[58] reported for the first time the growth of polyaminoamido (PAMAM) dendrons on silica-coated MNPs. The stability and solubility (in organic solvents) of $SiO_2@Fe_3O_4$ NPs were significantly improved after decorating with up to three generations PAMAM dendrons. The successive phosphination and complexation with rhodium toward PAMAM-coated MNPs produced a rhodium complex that was supported on dendronized MNPs. This nanocatalyst displayed excellent activity and selectivity in hydroformylation reactions.

Ionic liquids (ILs) have attracted growing interest owing to their safety, negligible vapor pressure with various polarities, good solubility, capacity as reaction media, and catalytic applications. In the recent reports, ILs-coated MNPs were widely used as catalysts for oxidation, hydrogenation, and condensation reactions.[60−62] They were also used as stabilizers for further immobilization of metal NPs.[63]

Encapsulation of MNPs in various solid supports such as mesoporous materials,[64,65] graphene,[66] carbon nanotubes,[67] and polymers was also efficient for stabilizing MNPs and therefore fabricating magnetic supports. Magnetic mesoporous materials, combining the advantages of mesoporous materials (uniform pore distribution and large surface area) and MNPs, have been used for a variety of applications, especially as supports in catalysis over the past few years. MCM-41 and SBA-15 are the most used mesoporous materials for the support of MNPs. Graphene is a remarkable support for encapsulation of metal NPs, because of its two-dimensional plate-like structure and large specific surface area. Use of graphene not only avoids the aggregation of metal NPs but also enhances their catalytic activity owing to the strong synergistic interaction between the two components. However, in the case of MNPs, the problem of site competition on the surface of graphene between MNPs and the further deposited catalytic species hampers the catalytic application of magnetic graphene as support. In a recent report, Cai's group[66] demonstrated that introducion of a polydopamine shell between MNPs and graphene perfectly solves this problem. Carbon nanotubes (CNTs) exhibit intriguing properties, such as nanoscale dimensions, high specific surface area, mechanical strength, and chemical stability. Implantation of MNPs in CNTs prevents agglomeration and brings the property of magnetic recovery to the support. Among various MNPs, $Fe_3O_4$ is the one most commonly used nanomaterial used in the preparation of magnetic CNTs.[68] Magnetic CNTs are assembled via high-temperature decomposition,[69] polymer wrapping and layer-by-layer assembly,[70] hydrothermal or solvothermal process,[71] and wet chemistry.[72] The in situ hydrothermal or solvothermal process is a fascinating method due to its capacity to easily control the properties of MNPs.

## 1.2. Synthesis and Seminal Studies of Magnetic Catalysts

Grafting transition metal catalysts (including metal complexes and metal NPs), organocatalysts, and enzymes to these MNPs that contain stabilizers, modifying reagents, or supports was achieved through covalent or noncovalent binding processes, providing various magnetic catalysts that have been used in a wide range of reactions.

MNPs-immobilized transition metal catalysts are divided into metal complex catalysts and metal NP catalysts. Metal complex catalysts supported on MNPs have generally been prepared through two procedures: (1) direct reaction of metal complexes with site-surrounded MNPs; (2) coordination of precursors of metal complexes with chelating ligand-modified MNPs. Taking Pd complexes as examples (Figure 1), the presynthesized triethoxysilyl-functionalized ($\beta$-oxoiminato)(phosphanyl) palladium complex was directly immobilized on the surface of $SiO_2@Fe_3O_4$ NPs via heterogenization with the Si−OH binding sites of the $SiO_2$ shell to give magnetic catalyst **A**.[50] MNP-supported di(2-pyridyl) methanol was obtained via click reaction between acetylene-terminated di(2-pyridyl) and azide-functionalized MNPs followed by complexation with palladium dichloride with the ligand providing magnetic catalyst **B**. This catalyst showed excellent catalytic performance in terms of activity and recyclability for Suzuki reactions.[73]

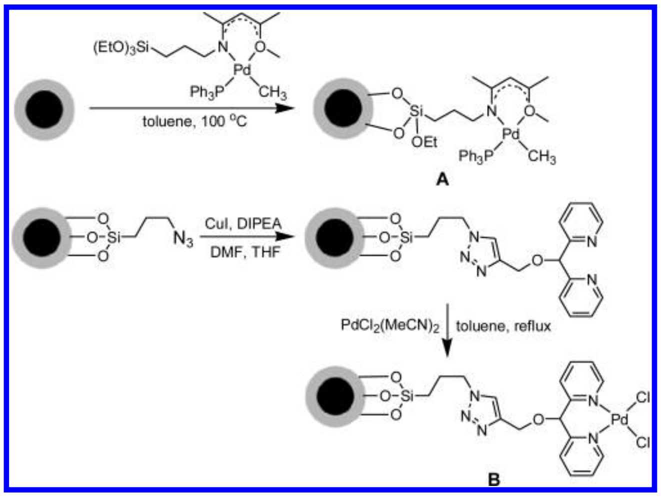


**Figure 1.** Synthesis of MNPs-immobilized Pd complexes.

Metal NPs anchored to MNPs have been extensively studied. Immobilization of metal NPs was essentially carried out using a process in which soluble metal precursors first coordinated to surface stabilizers or capping compounds of MNPs. Reduction was then performed, resulting in assembly of metal NPs on MNPs. The size, shape, morphology, and distribution of metal NPs are well tuned by various surface stabilizers or capping compounds under various conditions. Moreover, stabilizer-functionalized MNPs prevent aggregation and leaching of metal NPs. In the vast majority of examples the stabilizers appear to be amine ligands in the form of dopamine, triethoxysilyl amine, amine-containing polymers, or dendrimers (PAMAM). This is due to their excellent nanoparticle (NP) stabilizing properties against aggregation without disturbing their desirable properties. These stabilizers were also recognized to increase the catalytic activity. Pd and Au were the most widely used metals in NPs for MNP catalysis. MNP-immobilized PdNPs and AuNPs played a key role in a variety of catalytic processes including C−C coupling, hydrogenation, oxidation, reduction, and organic synthesis.[26,74,75] Use of MNPs as supports for these noble metals provided great progress regarding the cost, agglomeration, leaching issue, and catalytic efficiency and lifetime.

The catalytic efficiency, selectivity, and recyclability of MNP-immobilized metal NP catalysts are dramatically influenced by the catalytic NP size and shape as well as the MNP support. In general, smaller NPs possess higher catalytic efficiency and selectivity, due to their larger percentage of surface atoms, higher activation energy, and higher sensing response as compared to these of larger particles.[76,77] It has been verified that the shape of NPs, determined by the exposed crystal planes, considerably affects the catalytic performance.[78] The shapes of nanocatalysts are used to favor catalytic sites in specific surface planes. However, it is still a challenge to construct NPs shapes at will. The catalytic behavior also strongly depends on the choice of MNP support that does not only influence the size and shape of catalytic NPs through varied decorations and components in the synthetic processes of catalytic NPs but also determines the catalytic performance via the interaction with NPs during the catalytic processes.[79] These phenomena enhance the appeal of well-defined MNP-supported metal NP catalysts in a wide variety of organic transformations.

Organocatalysis dates back to more than 150 years ago. Organocatalysts offer several advantages such as high robustness, low toxicity, and straightforward accessibility compared with metallic catalysts.[80] Recently, immobilization of organocatalysts on MNPs was shown to be a highly efficient and environmentally benign approach in organic synthesis. MNPs-anchored organocatalysts were generally prepared by formation of robust chemical bonds between modified MNPs and organocatalyst units. In 2009, the Polshettiwar group[47,48] described the first magnetically recoverable organocatalyst. In this report, glutathione was covalently linked to $Fe_3O_4$ NPs via coupling the thiol group with the free hydroxyl groups of the surface of $Fe_3O_4$ NPs (Figure 2). The magnetic nano-organocatalyst **C** based on glutathione was highly active in the Paal–Knorr synthesis of a series of pyrrole heterocycles, aza-Michael reactions, and pyrazole synthesis in aqueous media under microwave conditions. The catalyst can be simply and efficiently collected using a magnetic field and reused at least three reaction cycles without any loss of activity. Afterward, the magnetic glutathione-based organocatalyst was successfully extended to the catalytic homocoupling of arylboronic acids.[81] A number of reports then followed in organic synthesis, particularly in asymmetric synthesis with magnetic organocatalysts.[41,82]

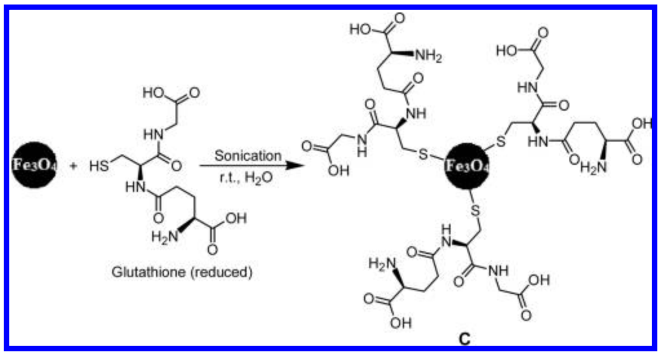


**Figure 2.** Synthesis of a magnetic organocatalyst based on glutathione.

Enzymes have provided a widespread application in the food, textile, chemical, and pharmaceutical industries, due to their crucial properties such as remarkably high activity, regio- and enantioselectivity, specificity, use of mild reaction conditions, and reduced energy consumption. However, complicated and inefficient recovery and purification stages of enzymes restricted their application. Immobilization of enzymes on MNPs (especially on $Fe_3O_4$ and $\gamma$-$Fe_2O_3$ NPs) was a logical solution to overcome these issues.[83,84] The existing immobilization protocols are classified into four categories: (1) adsorption–cross-linking methods; (2) entrapping methods; (3) ionic or covalent coupling methods; (4) other specific biorecognition methods.[85,86] Among them, covalent coupling is the best candidate to achieve this protocol. Several covalent linking chemistries including carbodiimide and maleimide coupling, disulfide bridges, click chemistry, and thiol–ene chemistry have been widely employed. Silica has been mostly explored as a coating material of MNPs for anchoring biocatalysts, because it is biocompatible, highly stable, and dispersible in aqueous solutions. Since Lilly et al. prepared iron oxide-supported cellulose in 1973,[87] more than 30 kinds of enzymes and biomolecules have been successfully immobilized on MNPs.[88]

Water purification has been studied for decades because of the serious concern of contaminated water (especially those contained organic pollutants) resulting from industrialization and fast development of economy. With the rapid development of photocatalysts,[89,90] magnetically recoverable photocatalysts have been recently extensively used in the field of degradation of pollutants including dyes, herbicides, and related pollutants,[91,92] due to their low toxicity, perfect biocompatibility, and excellent separation properties of MNPs.[93,94] MNP-supported nano-$TiO_2$ is one of the main and most widely investigated catalysts in the photodegradation of pollutants in water, because nano-$TiO_2$ is a highly efficient, low-cost, long-term stable, and perfectly biocompatible photocatalyst.[95−100] Moreover, MNPs-supported nano-$TiO_2$ is easily separated using an external magnetic field and repeatedly used. However, the energy requirement for effective photoexcitation (higher than 3.2 eV) lead to $TiO_2$-promoted photodegradation occurring only under UV irradiation. Renewable sunlight irradiation-involved photodegradation of pollutants over $TiO_2$ is a challenge.[101] Among several strategies to improve the catalytic properties of $TiO_2$ such as other elements doping, decorating with Lewis acids, dye sensitizing, and coupling with other semiconductors, doping $TiO_2$ with other elements is a promising strategy to increase its photocatalytic activity. Ao's group[102] synthesized a novel magnetic photocatalyst nitrogen-doped $TiO_2$-coated $\gamma$-$Fe_2O_3$ magnetic activated carbon that showed high photocatalytic activity in degradation of Reactive Brilliant Red X-3B in an aqueous solution under sunlight irradiation. The catalyst also exhibited excellent recyclability; it is magnetically separated using a magnet, and the catalytic activity was preserved for six runs. Magnetic multifunctional metal oxide/graphene composites were recently proved to be promising photocatalysts for degradation of water pollutants including organic dyes, water-borne pathogens, and heavy metal ions.[103,104]

Research on magnetically recyclable nanocatalysts is a fast-growing field. Many seminal studies recently appeared, such as catalytic applications of bimetallic NPs (excluding spinel ferrites), efforts to achieve completely sustainable, "green" and practical organic transformations based on MNPs catalysts, uses of new magnetic multifunctional materials with varied architectures including core-double shell, yolk–shell, hollow and bowl-like structures, and so on.

Bimetallic NPs have a bright future in catalysis due to their enhanced stability, activity, selectivity, and other properties compared to their monometallic counterparts.[105,106] The recently reported magnetically recyclable bimetallic NPs catalysts are divided into two categories: MNPs-immobilized bimetallic NPs (for instance, $Fe_3O_4$@AuPd NPs),[107] and bimetallic NPs containing a magnetic metal (for instance, Ni@Ru, Fe@Au and Ni@Ag).[108−110] These bimetallic NPs display higher activity and selectivity in various organic transformations than those of each monometallic counterpart and physical mixture of monometallic counterparts. Furthermore, these magnetic bimetallic NPs catalysts generally show good recyclability with magnetic separation.

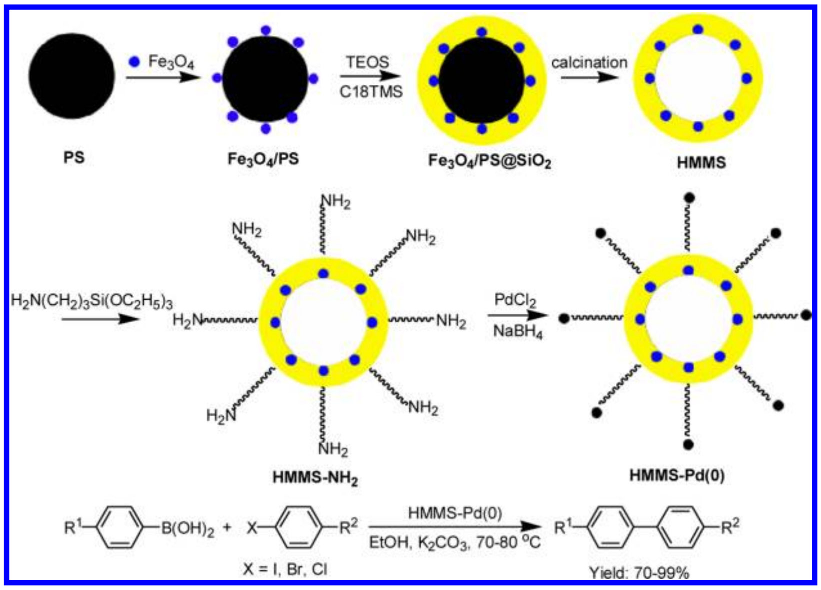


**Figure 3.** Preparation and catalytic applications of HMMS−Pd(0).

Development of sustainable and practical chemistry is a long-term subject. Using MNPs catalysts as platforms, chemists recently made tremendous efforts to achieve rapid and easy immobilization at room temperature in solvent-free conditions at low cost for preparation of highly efficient MNPs with high densities of functional groups, including use of flow reactors. Relevant advancements and progresses have been illustrated in the Recent Advances and Trends section.

Materials with multiple functionalities are presently of great scientific and technological interest. In the field of MNPs catalysis, a series of new multifunctional materials with various structures has been recently designed and used. These materials combine different properties into one particle such as magnetism, high surface area, mechanical strength, thermal stability, and various functional groups. For example, magnetic materials with signal or double-shelled yolk-like structure were constructed as ideal supports of noble metals.[111,112] These yolk−shell composites with a movable core have higher surface area, larger void space, and lower density, which promises higher catalytic efficiency and application as nanoreactors compared to common core−shell composites. Hollow magnetic mesoporous spheres (HMMS) also attracted extensive attention as catalyst carriers, due to their superparamagnetic property, uniform size, large surface area, high catalyst loading, and homogeneous spherical morphologies.[113] Exploration of novel magnetic multifunctional materials in catalysis will never stop.

### 1.3. Characterization of Magnetic Catalysts

After their preparation, the magnetic catalysts have been characterized using a great variety of methods to gain a comprehensive amount of data in order to properly analyze their properties.

The size, shape, and morphologies of magnetic catalysts are determined by transmission electron microscopy (TEM) and/or scanning electron microscopy (SEM). The structure of magnetic catalysts is usually determined by X-ray diffraction (XRD) and/or X-ray photoelectron spectra (XPS). The catalytic amount of magnetic catalysts is measured by elemental analysis (EA) or inductively coupled plasma analysis (ICP). Gas adsorption is a technique that is used for investigation of the surface area of magnetic catalysts. Fourier transform infrared spectroscopy (FT-IR) is used to monitor and confirm the functionalization of magnetic catalysts. The magnetic property is investigated utilizing the magnetic properties measurement system superconducting quantum interference device (SQUID) or vibrating sample magnetometer (VSM). Thermogravimetric analysis or thermal gravimetric analysis (TGA) is a suitable method to investigate the thermal stability of magnetic catalysts. Photoluminescence (PL) spectroscopy is used for detecting fluorescence property of magnetic catalysts.

## 2. RECENT ADVANCES AND TRENDS

### 2.1. Magnetically Recyclable Nanocatalysts Based on Transition Metals

**2.1.1. C−C Coupling: Miyaura−Suzuki, Heck, Sonogashira, and Hiyama Reactions.** Cross-coupling reactions to construct C−C bonds are of significant importance in modern chemical transformations. Various catalytic systems based on transition metals as catalysts have emerged. Utilization of MNP-supported transition metal catalysts for construction of C−C bonds via Suzuki, Heck, Sonogashira, and Hiyama reactions has received considerable attention during the past few years.

The Pd-catalyzed Suzuki coupling reaction has been recognized as the most powerful strategy for constructing carbon−carbon bonds. It has been extensively utilized in the synthesis of functional materials, pharmaceuticals, and natural compounds due to its wide substrate scope, mild conditions, high yields, and readily available starting materials.[114−116] The Suzuki reaction probably is the most classic reaction to evaluate the catalytic activities of nanocatalysts consisting in Pd species.

Magnetic mesoporous silica spheres (MMS) currently are very popular supports, among which MCM-41 and SBA-15 are frequently used mesoporous silica materials. $Fe_3O_4@SiO_2@mSiO_2$ with core-double-shell structure has been prepared by two-step silica-coated processes, two layers of silica shell playing the role of protection (inner shell) and offering large specific surface area (outer shell), respectively.[117] $Fe_3O_4@SiO_2@mSiO_2$-immobilized PdNPs have exhibited unprecedented catalytic activity in Suzuki reaction of phenylboronic acid

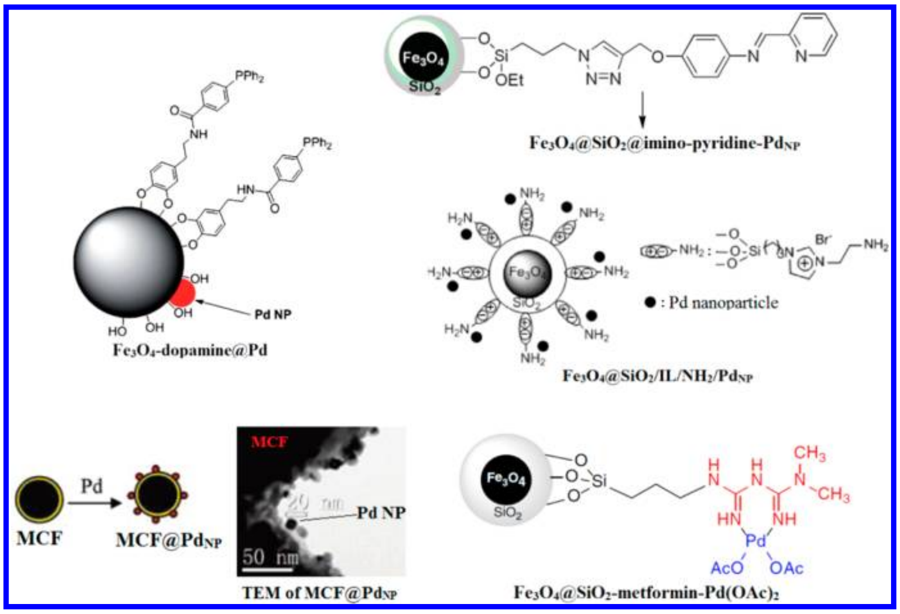


**Figure 4.** Examples for MNPs-supported Pd catalysts. Reprinted with permission from ref 125. Copyright 2012 Elsevier Ltd. Reprinted with permission from ref 127. Copyright 2011 American Chemical Society. Reprinted with permission from ref 130. Copyright 2013 Wiley-VCH Verlag GmbH & Co. Reprinted with permission from ref 137. Copyright 2012 Elsevier B.V.

with aryl halides, even aryl chloride with up to 93.77% conversion. This success is attributed to productive implantation of PdNPs on/in both of the surface and mesopore channels of attractive silica double shell. Moreover, the catalyst was conveniently recovered upon applying an external magnetic field, and it was recycled six times without any significant loss of catalytic activity.[117] Hollow mesoporous silica spheres (HMS) were not only useful drug carriers but also efficient catalyst carriers, owing to their low density, well-defined structures, and homogeneous spherical morphologies.[113] Compositions of hollow magnetic mesoporous silica spheres (HMMS)-embedded PdNPs were assembled using carboxylic polystyrene (PS) latex[118] or the colloidal carbon spheres of glucose[119] as the precursor of hollow space. PdNPs were implanted in the magnetic heteroaggregates of $Fe_3O_4$ and mesoporous shell, and the implantation step could be carried out either before or after formation of the hollow space (Figure 3). Suzuki reactions were conducted in ethanol in the presence of $K_2CO_3$ with 0.6−0.75 mol % HMMS−Pd as catalyst at 70−80 °C. This catalytic system was broad in substrate scope, efficient even for aryl chlorides,[118] and highly recyclable. The HMMS−Pd catalyst was also a competitive candidate in the hydrogenation of alkene and nitro compounds.

Recently, other magnetic nanocomposites including polymer-coated MNPs,[120−124] ionic liquid-modified MNPs,[125] sulfonated graphene(s-G)-decorated MNPs,[126] and magnetic $Fe_3O_4$@C (MFC)[127] were also used for stabilization of PdNPs aiming to catalyze Suzuki reactions. Song and coworkers[125] enriched ionic liquid-modified MNPs with amine functional groups and used this nanomatyerial as support for the synthesis of $Fe_3O_4$@$SiO_2$/IL/$NH_2$/$Pd_{NP}$ catalyst (Figure 4). The catalyst exhibited excellent activity in the Suzuki reaction of phenylbornic acid with iodobenzene or bromobenzene containing a wide range of substituents using NaOH as base in mixed solvent of ethanol and water at rt. The well-dispersed magnetic nanocatalyst was magnetically separated from the reaction mixture, and its catalytic activity did not deteriorate even after several repeated applications. Sun and his group[126] assembled $Fe_3O_4$ NPs and PdNPs on s-G and successfully used this semiheterogeneous catalyst in Suzuki reaction. TEM analysis revealed that the PdNPs with a size of 4−5 nm were homogeneously distributed on the $Fe_3O_4$/s-G pattern. The homogeneously water or water/ethanol-dispersed catalyst was very efficient and maintained similar catalytic performance during several cycles. Diao et al.[127] reported the construction of a magnetically retrievable Pd nanocatalyst that was anchored on magnetic MFC nanocomposites via a precipitation−deposition method. The diameters of MCF and PdNPs were about 360 and 15 nm, respectively (Figure 4). The Suzuki reaction was initially chosen as the model reaction for evaluating the catalytic ability. The MCF@$Pd_{NP}$ provided yields in the range 52−100% within 1−3 h when aromatic iodides and bromides were employed in refluxed ethanol. As for challenging chlorobenzene, 95% yield was obtaied within 3 h of reaction time in refluxed DMF using 0.308 mol % Pd with the assistance of a small amount of KI. The catalyst was easily handled and removed from the reaction mixture by magnetic separation owing to its good stability and the presence of $Fe_3O_4$. In addition, MCF@$Pd_{NP}$ was also efficient in Heck reactions. Comparing with other magnetic Pd nanocatalysts without phosphine ligands, MCF@$Pd_{NP}$ was outstanding.[127]

Synthesis of $MFe_2O_4$ (M = Zn, Co) NPs-supported Pd(0) NPs through ultrasound-assisted coprecipitation in the absence of surface stabilizer or capping agent was reported.[128,129] The solid catalyst $ZnFe_2O_4$−Pd(0) displayed good performance for the Suzuki reaction; both electron-deficient and electron-rich aromatic iodides and bromides substrates provided high yields of coupling products. The magnetic property allowed one to recover the catalysts magnetically with an external magnet, and no significant loss of activity of $ZnFe_2O_4$−Pd(0) was detected during five successive cycles.

Phosphine-based ligands proved useful to stabilize PdNPs onto magnetic supports. With the assistance of dopamine−$PPh_2$ stabilizer that was synthesized by coupling between dopamine and (diphenylphosphino)benzoic acid, PdNPs were successfully loaded on the surface of $Fe_3O_4$ NPs. In the process, besides phosphine ligands, hydroxyl groups of $Fe_3O_4$ also coordinated to Pd ion, which was depicted by the ratio Pd/dopamine−$PPh_2$ obtained from analytical data.[130] As suggested by the literature,[131] the formed PdNPs would stay neither on phosphine ligands nor hydroxyl groups but be positioned on the surface of $Fe_3O_4$ (Figure 4), which was further confirmed by analytical data. TEM images of $Fe_3O_4$−dopamine@Pd showed that the average size of the heteroparticle is around 12 nm. PdNPs with a mean diameter of 2 nm were embedded in the heteroparticles. PdNPs with larger sizes were provided when naked $Fe_3O_4$ was employed. The catalytic behavior of the $Fe_3O_4$−dopamine@PdNPs was demonstrated in the Suzuki reaction between phenylboronic acid and 4-substituted bromoarenes. When bromoarenes bearing electron-withdrawing groups were employed, high reactivity in terms of selectivity and conversion was found, but for the substrates bearing electron-rich groups the yields significantly decreased. Unfortunately, only 5% yield was obtained in the presence of the challenging chloride derivatives. Investigation of the recyclability of $Fe_3O_4$−dopamine@PdNPs was conducted by treating 4-bromoanisole with phenylboronic acid. The results showed that the catalyst kept similar catalytic performance after 10 cycles. In addition, $Fe_3O_4$−dopamine NPs decorated with AuNPs or RhNPs were also assembled, and their catalytic properties were evidenced in the reduction of 4-nitrophenol and hydrogenation of styrene, respectively.

Linkers containing nitrogen were the most frequently used and powerful chelating agents and stabilizers in the synthesis of MNP-supported Pd nanocatalysts.[132] Luo et al.[133] reported the preparation of new imino−pyridine-functionalized MNPs via click chemistry and the corresponding MNP-supported PdNPs $Fe_3O_4$@$SiO_2$@imino−pyridine−$Pd_{NP}$ (Figure 4). This catalyst was then initially evaluated in the Suzuki reaction of 4-bromoacetophenone with phenylboronic acid. Optimized results were obtained with 0.2 mol % catalyst and use of $K_2CO_3$ as a base in aqueous ethanol at 60 °C under air. Under these conditions, electron-withdrawing and electron-donating groups on aryl bromides were tolerated in the reaction, resulting in fairly good to excellent yields and selectivity. However, the catalytic system showed much less activity for the challenging aryl chlorides, even upon extending reaction times and increasing the catalytic amount to 1 mol %. Following the efficiency of $Fe_3O_4$@$SiO_2$@imino−pyridine−$Pd_{NP}$, the recyclability of the catalyst was investigated in several volume ratios of ethanol/water (1:1, 2:1, 19:1). The amount of water in the reaction medium significantly influenced the catalyst reusability; more water caused the gradual loss of catalytic activity. The best recyclability result was that the reaction could be maintained at 95% yield after six cycles, when 19:1 of ethanol/water was employed as solvent.

MNP-supported Pd complexes provide high performance in the Suzuki reaction, as expected. The chelating fragments mentioned in the literature include triarylphosphine,[134,135] (*β*-oxoiminato)-phosphine,[50] *N*-heterocyclic carbyne,[43,136] biguanide,[137] polymer,[138] etc. As described in the literature,[139] the real catalytic species of Pd complexes for Suzuki coupling reactions are Pd(0) NPs that are formed via fast reduction of $Pd^{2+}$ ions by the solvent. Complexation of metformin-modified MNPs with $Pd(OAc)_2$ was readily achieved, and $Fe_3O_4$@$SiO_2$−metformin−$Pd(OAc)_2$ (Figure 4) was further tested as a catalyst in aqueous ethanol.[137] Several aryl bromides containing substituent groups in broad scope were proved suitable partners for the Suzuki reaction reacting with phenylboronic acid. Upon completion of the reaction, the catalyst was easily collected using an external magnet that was further washed and dried and then subsequently reused in another run with fresh reactants. No significant degradation in catalytic performance was observed in eight successive runs. When inactive chlorobenzene was employed, the reaction proceeded moderately with a 45% yield. In addition, atomic absorption spectroscopy did not detect Pd ions after each reaction. The existence of Pd(0) NPs was confirmed by TEM, and the authors indicated that exposure of $Fe_3O_4$/$SiO_2$−Met−$Pd(OAc)_2$ to EtOH as cosolvent led to the reduction of $Pd^{2+}$ ions to Pd(0) species.

Among these magnetic nanomaterials, NiNPs have attracted great interest in organic synthesis due to their magnetically recoverable property and catalytic activity. NiNPs with a mean diameter of 100 nm and ferromagnetic property were prepared from $NiCl_2 \cdot 6H_2O$ with the assistance of hydroxypropylmethylcellulose (HPMC). The semiheterogeneous polymer-stabilized NiNPs showed good performance in Suzuki reaction relative to the traditional Ni catalyst, but the recyclability in terms of the number of times and yields was not detailed.[140]

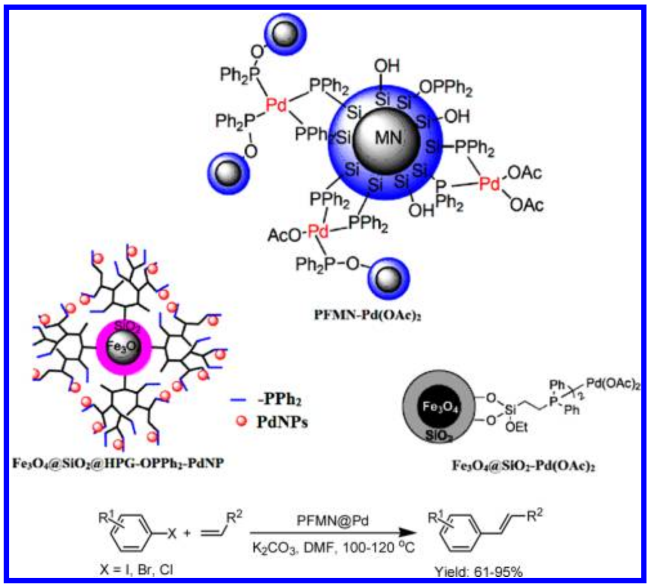


**Figure 5.** Examples for PFMN@Pd used in the Heck reaction. Reprinted with permission from ref 142. Copyright 2013 Elsevier B.V. Reprinted with permission from ref 144. Copyright 2012 Elsevier Ltd.

The Heck coupling reaction has been highlighted due to its high efficacy in the synthesis of arylated olefins that are widely utilized in pharmaceuticals, agrochemicals, and cosmetics production. Phosphine-functionalized magnetic nanoparticles (PFMN) have been suggested to be most efficient supports for stabilization of catalytic Pd species in the field of magnetic nanocatalysts in the Heck reactions, because phosphine ligands promote well the immobilization of Pd onto MNPs and control their size, modality, and distribution.[141] Starting from PFMN, the MNPs-anchored palladium(II) complex PFMN−Pd-$(OAc)_2$[142] (Figure 5) with a diameter of 10 nm was readily synthesized and tested initially in the Heck reaction of chlorobenzene with ethyl acrylate using 1 mol % Pd in the presence of $K_2CO_3$ in DMF at 120 °C. The corresponding *trans*-arylated olefin was produced in 93% yield. Investigation of the substrate scope showed that both electron-deficient and electron-rich aryl chlorides proceeded smoothly to furnish the desired products in 88−95% yields.[142] This catalytic system was remarkably efficient, even by comparison with classic homogeneous catalysts. The leaching of Pd species from the initial catalyst to the reaction medium is a very key issue for evaluation of heterogeneous catalysts. The catalyst PFMN–$Pd(OAc)_2$ was reused at least four times with sustained selectivity and activity, and ICP analysis revealed that less than 1% of Pd was released from the initial catalyst. In addition, comparative experiments were conducted in the absence of Pd-anchoring phosphine group for synthesis of PFMN–$Pd(OAc)_2$, and the phosphine-free catalysts provided much lower yields and recyclability.[142] X-ray photoelectron spectroscopy (XPS) determination indicated that only Pd(II) was found in freshly prepared PFMN-supported Pd catalysts;[142,143] however, the actual catalytic species was zerovalent Pd.[143] Li et al.[144] synthesized hyperbranched polyglycidol (HPG) phosphine-modified MNP that was further employed as support for immobilization of PdNPs. The catalyst $Fe_3O_4$@$SiO_2$@HPG–$OPPh_2$–PdNP (Figure 5) showed excellent activities in the Heck reaction of a range of aryl iodides and bromides with olefins with yields up to 95%. After almost complete recovery of the catalyst using an external magnetic field, it was used for five additional cycles without loss in catalytic performance. Moreover, the satisfactory catalytic behavior of $Fe_3O_4$@$SiO_2$@HPG–$OPPh_2$–PdNP was also verified in the Suzuki reaction.

Apart from phosphine-based ligands, other chelating fragments were aso efficiently used in Pd-catalyzed Heck reaction. The oleic acid (OA) functionalized $Fe_3O_4$ NPs exhibited good immobilization capability for PdNPs; the catalytic property of the assembled nanocatalyst $Fe_3O_4$@OA–PdNPs (Figure 6) was evaluated in Heck reaction.[145] The cross-coupled product was produced with 98% yield using 10 mg (0.2 mol % [Pd]) $Fe_3O_4$@OA–PdNPs in DMAc at 120 °C in the presence of $N(Butyl)_3$ and TBAB in the case of bromobenzene and styrene as model substrates. This catalyst showed extraordinary functional group tolerance to aryl halide (Ar–Br, Ar–Cl); a variety of arylated olefins compounds were isolated mostly in good to excellent yields. Investigation of its recyclability indicated that $Fe_3O_4$@OA–PdNPs could be easily collected by an external magnetic attraction. Repeated use for at least four runs retained almost the same activity, with only trace amounts of leaching Pd. Khosropour et al.[146] demonstrated that $Fe_3O_4$@$SiO_2$ MNPs-anchored dicationic ionic liquid with a 1,3,5-triazine core can be readily constructed and further coordinate with palladium–EDTA, offering a novel MNPs-supported Pd complex (named as $Fe_3O_4$@$SiO_2$–A–Pd-(EDTA)) (Figure 6). Its catalytic performance was tested by Heck coupling reaction of various aryl halides (Ar–I, Ar–Br) with styrene derivatives bearing a wide range of substituent groups. The corresponding products were synthesized with 80–97% yields and $1.9 \times 10^3$–$1.4 \times 10^4$ $h^{-1}$ TOFs using 0.003 mol % Pd at 90 °C under silent conditions. When these reactions proceeded under ultrasound irradiation (170 W, 50 °C) instead of silent conditions the yields and TOFs were increased to 88–97% and $5.1 \times 10^4$–$2.5 \times 10^5$ $h^{-1}$, respectively. Evaluation of recyclability and stability of $Fe_3O_4$@$SiO_2$–A–Pd(EDTA) was conducted under ultrasound irradiation. The catalyst was magnetically removed from the reaction medium and reused for six reaction cycles without obvious decrease in catalytic activity.

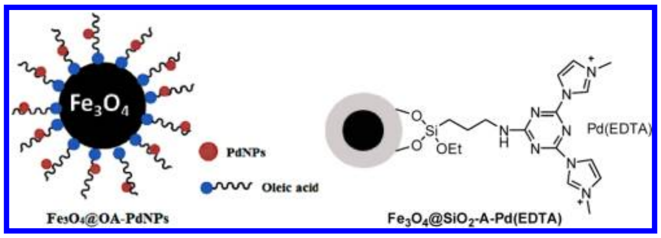


**Figure 6.** Magnetic catalysts $Fe_3O_4$@OA–PdNPs and $Fe_3O_4$@$SiO_2$–A–Pd(EDTA) for Heck reactions.[145,146] Reprinted with permissions from ref 145. Copyright 2013 Elsevier.

Safari et al.[147] prepared magnetic $Fe_3O_4$ NPs-supported $Ni^{2+}$ containing 1-methyl-3-(3-trimethoxysilylpropyl) imidazolium chloride ionic liquid (IL) catalyst by immobilizing a IL–Ni complex on the surface of MNPs and demonstrated their use as heterogeneous catalysts for the Heck reaction (Figure 7). Excellent yields of coupling products were provided from iodobenzene with olefins at 100 °C in 4 h. However, the coupling of aryl bromide or chloride gave significantly lower yields compared with those obtained with aryl iodides. The catalyst was simply recovered using an external magnetic yield and reused at least five times without loss of catalytic activity in the coupling of iodobenzene with ethyl acrylate. The most prominent advantage of the IL–Ni(II)-functionalized magnetic $Fe_3O_4$ NPs catalyst was to avoid the use of expensive Pd.

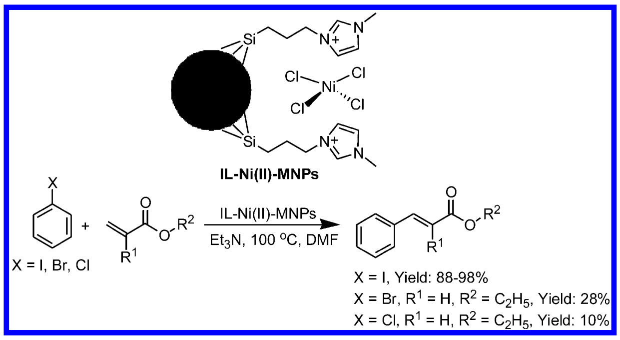


**Figure 7.** Heck reaction with IL–Ni(II)–MNPs.

Sonogashira coupling, a common strategy for construction of a C–C bond, has been frequently reported in organic chemistry, especially for synthesis of conjugated compounds. MNPs functionalized with Schiff base ligands have potential application in catalysis due to their excellent complexation ability with metal ions. Recently, MNPs-immobilized Schiff base–Pd (II) catalysts (Figure 8) were synthesized by easy-to-operate methods.[148,149] Their application as efficient catalysts for Sonogashira reactions under heterogeneous phosphine-free and copper-free conditions has been described. Using $Fe_3O_4$@$SiO_2$/Schiff base/Pd(II) catalysts, symmetric or asymmetric internal alkynes were produced from the reaction of aryl iodides, bromides, or chlorides with terminal alkynes. These catalysts were magnetically separated from the reaction mixture and recycled for several consecutive runs without appreciable loss of catalytic activity.[148,149]

The literature on catalytic applications of MNPs-supported catalysts is relatively underrepresented in the Hiyama reaction, which is known as a very important cross-coupling transformation of aryltrialkoxysilanes with aryl halides.The latest example of such a process was provided by Wang and coworkers,[150] who reported that the PFMN-immobilized Pd complex $Fe_3O_4$@$SiO_2$–$Pd(OAc)_2$ not only worked well in the Heck reaction[143] but also displayed high activity in the Hiyama

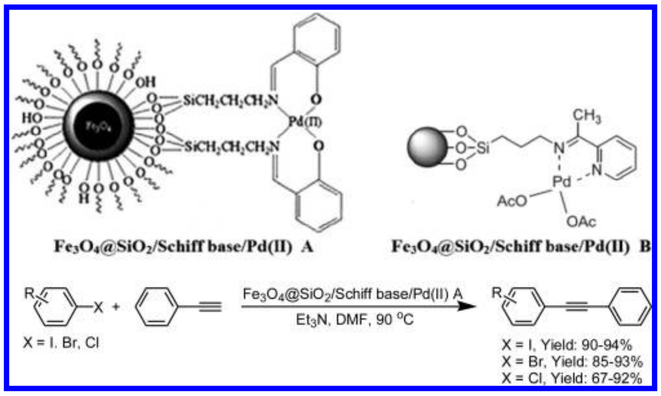


**Figure 8.** Sonogashira reactions with $Fe_3O_4@SiO_2$/Schiff base/Pd(II) catalysts.[148,149] Reprinted with permission from ref 148. Copyright 2013 Elsevier B.V. Reprinted with permission from ref 149. Copyright 2010 Elsevier B.V.

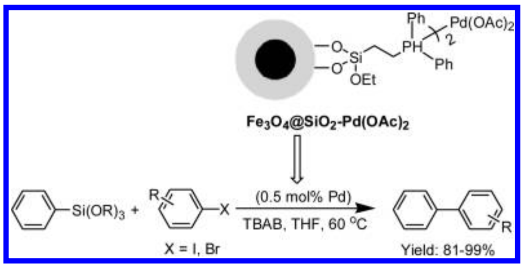


**Figure 9.** Hiyama reaction with PFMN@Pd catalyst.

reaction (Figure 9). The results of optimized investigations showed that a biaryl compound was isolated in 91% yield when the Hiyama reaction was carried out between 4-iodoanisole and phenyltrimethoxysilane using TBAF as base in the presence of 0.5 mol % Pd in THF at 60 °C. A variety of organic halides reacted with phenyltrimethoxysilane to give the cross-coupling products in good to excellent yields. The authors did not describe the substrate scope of aryltrimethoxysilanes. The recyclability of $Fe_3O_4@SiO_2-Pd(OAc)_2$ was also explored in the coupling of 4-iodoanisole and phenyltrimethoxysilane; the nanocatalyst was recycled at least 10 times with no detectable deactivation. MNPs-supported PdNPs consisting of $Fe_3O_4$ NPs of 25−50 nm in diameter and PdNPs of 5 nm encaged in $Fe_3O_4$ were easily prepared and evaluated in Hiyama reactions of a wide range of aryl bromides and aryl siloxanes.[151] A variety of biaryl subunits were constructed in good to excellent yields with 0.2 mol % of $Fe_3O_4$@PdNP at 90 °C in aqueous solution. In addition, the nanocatalyst exhibited quite the same morphology and catalytic activity even after five cycles.

### 2.1.2. Alkyne−Azide Cycloaddition.

1,2,3-Triazoles, five-membered nitrogen heterocyclic compounds, have tremendous applications in various research fields including synthetic organic, medicinal, materials, and biological chemistry. Therefore, synthesis of 1,2,3-triazoles has been one of the hottest subjects during the past few decades. Among numerous synthetic methods, catalyzed Huisgen cycloaddition of organic azides and alkynes by Cu and Ru catalysts are the most efficient ones and have been widely used to construct the 1,2,3-triazole heterocycles selectively, forming, respectively, 1,4- and 1,5-disubstituted 1,2,3-trizoles.

Copper-catalyzed cycloaddition of alkynes and azides (CuAAC)[152,153] is the most efficient means to incorporate two functional fragments, and it is undoubtedly to date the most representative example of "click" reaction.[154] Indeed, CuAAC holds several advantages over the thermal Huisgens version including mild reaction conditions, 100% atom economy, exclusive regioselectivity, and broad substrate scope. However, contamination with cytotoxic Cu ion is a long-standing problem that restricts the applications of CuAAC in electronics and biomedicine. To solve this problem, the use of heterogeneous CuAAC catalysts appears to be the most logical solution instead of the other methods including performing CuAAC under continuous flow conditions, chromatographic purification of crude product, or washing crude product with amine (or ammonia). For the heterogenization of CuAAC catalysts, functionalized MNPs have emerged as viable supports.

MNPs-supported Cu catalysts are divided into two sorts that are MNPs-supported Cu complexes and Cu(0) or Cu(I) NPs. MNPs-immobilized binuclear Cu(II)−*β*-cyclodextrin was easily prepared by addition of copper sulfate to a the sodium hydroxide solution of *β*-cyclodextrin.[155,156] This magnetic catalyst of 10−20 nm in diameter showed high activity in the facile one-pot synthesis of 1,4-disubstituted 1,2,3-triazole through azido reaction/cycloaddition of arylboronic acid, sodium azide, and alkyne in water at rt in air without any additives (Figure 10). The results of investigations of substrate scope indicated that both different substituted arylboronic acids and alkynes were successfully employed in the catalytic system providing excellent yields. $Fe_3O_4$−*β*-CD−$Cu_2$ was collected by a magnet and successively reused for four reaction cycles without considerable loss in activity.

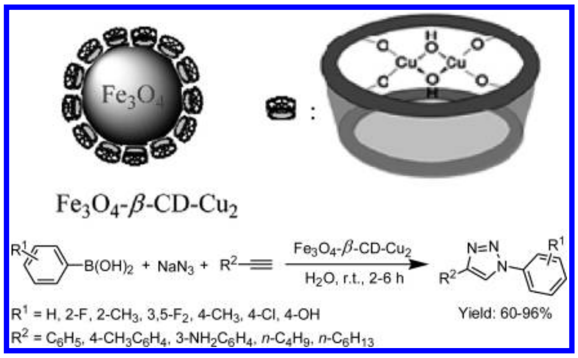


**Figure 10.** One-pot synthesis of 1,2,3-triazoles using $Fe_3O_4$−*β*-CD−$Cu_2$.[155] Reprinted with permission from ref 155. Copyright 2013 Royal Society of Chemistry.

Díez-González and co-workers[157] prepared nonmagnetic silica flakes and silica NPs- and magnetite/silica NPs-supported copper(I)-*N*-heterocyclic carbene (NHC) catalysts. All three silica materials were used as catalysts in the CuAAC reaction of benzyl azide with phenylacetylene using 1 mol % [Cu] on water at rt and gave quantitative formation of corresponding 1,4-disubstituted 1,2,3-triazoles. The catalysts were then separated from the reaction medium by filtration or using an external magnet, and after washing and drying they were reused for a new reaction cycle. In the fifth cycle, the catalyst supported on silica NPs almost completely lost its activity; the copper-functionalized silica flakes led to moderate yields. On the other hand, the magnetite/silica NPs-supported catalyst retained high activity and selectivity even after a minimum of nine consecutive cycles. Moreover, various 1,4-disubstituted 1,2,3-

triazoles were isolated in good to excellent yields, regardless of the substituent groups on either the alkyne or the azide.

Pincer-type ligands containing two chelating positions are another valuable template for complexation of Cu cation in the synthesis of magnetically separated catalysts for CuAAC.[158,159] Xiong et al. synthesized 3-aminopropyltrimethoxysilane (APTS) and [3-(2-aminoethylamino)propyl]trimethoxysilane (AAPTS)-modified MNPs that were further treated with CuBr to generate MNPs−CuBr **1** or MNPs−CuBr **2** (Figure 11).[160]

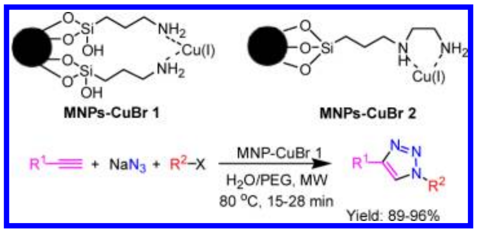


**Figure 11.** MNP−CuBr-catalyzed one-pot synthesis of 1,4-disubstituted 1,2,3-triazoles.

Catalytic applications of these two catalysts were evaluated in the one-pot CuAAC reaction of benzyl chloride and sodium azide with phenylacetylene in mixed reaction medium of water and PEG400 under microwave irradiation conditions. Initial results of the experiment showed that the reactions were performed smoothly using either MNPs−CuBr **1** or MNPs−CuBr **2**, and the former exhibited higher activity than the later. MNPs−CuBr **1** was then applied in the investigation of substrate scope using sodium azide and different alkyl halide and alkynes as starting materials, with 1.46 mol % of [Cu]. Most of the 1,4-disubstituted 1,2,3-triazoles were isolated in good to excellent yields with 100% selectivity. The reactivity of 4-bromobutane was lower than that of either benzyl chloride or bromide. The longer chain of the aliphatic halides significantly decelerates the reaction, and disubstituted aliphatic halides such as 1,6-dibromohexane and 1,10-dibromodecane gave very low yields upon reaction with phenylacetylene. The authors indicated that the poor results of aliphatic halides with long chains and disubstituted aliphatic halides were reasonably attributed to their low dielectric constants, poor microwave absorbing properties, and generation of undesired 1,3-diynes. Benzyl bromide showed higher reactivity than benzyl chloride; various functional groups on alkynes were highly tolerated for this catalytic system. In addition, the magnetically collected catalyst MNPs−CuBr **1** was easily recovered and reused for at least seven cycles with a slight decrease of catalytic activity.[160]

Iron oxide NP-supported tris(triazolyl) CuBr with a diameter of about 25 nm was readily prepared, and its catalytic activity was evaluated in the CuAAC reaction (Figure 12).[161] In initial experiments this catalyst with 0.5 mol % loading perfectly promoted the CuAAC reaction of benzyl azide and phenylacetylene in water at rt. After completion of the first run, the catalyst was simply collected and separated using an external magnet from the reaction medium and used for another five catalytic cycles without significant loss of catalytic activity. The amount of leaching copper from the initial catalyst to the reaction media after the first cycle measured by ICP analysis was almost negligible. The scope of the substrates was further examined, and the CuAAC reaction procedure was successfully extended to various organic azides and alkynes and also applied to the one-pot synthesis of triazoles through the cascade reaction of benzyl bromides, alkyne, and sodium azide. Remarkably, for each substrate, $\gamma$-$Fe_2O_3$@$SiO_2$−tris(triazolyl) CuBr was smoothly used for three catalytic cycles with similar catalytic efficiency or slightly decreased yields. In addition, the catalyst was used in the synthesis of allyl- and TEG-ended 27-branch dendrimers.[161]

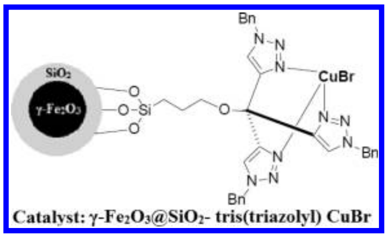


**Figure 12.** Click reactions catalyzed by $\gamma$-$Fe_2O_3$@$SiO_2$−tris(triazolyl) CuBr.[161] Reprinted with permission from ref 161. Copyright 2014 Wiley-VCH Verlag GmbH & Co.

MNPs-supported CuNPs have been proved to be useful to catalyze the cycloaddition of azides with alkynes.[162−164] Radivoy and co-workers[165] prepared silica-coated MNPs-supported CuNPs (CuNPs/MagSilica) by fast reduction of $CuCl_2$ using lithium sand in the presence of 4,4′-di-*tert*-butylbiphenyl. These CuNPs with a narrow size distribution and about 3.0 nm of mean diameter were found to be well dispersed on the magnetic support. CuNPs/MagSilica was used as nanocatalyst in the three-component synthesis of 1,4-disubstituted 1,2,3-triazloes using sodium azide, alkyne, and alkyl halide as reagents (Figure 13). A TOF of 0.012 $s^{-1}$ was provided when sodium azide, phenylacetylene, and benzyl bromide were employed in water at 70 °C with 4.3% [Cu]. The same methodology was successfully extended to the reactions of benzyl bromide with various aryl alkynes bearing both electron-rich or electron-poor groups and aliphatic alkynes and yielded the corresponding 1,2,3-triazoles in 85−98% yields. Other alkyl azides including 4-methylbenzyl bromide, 2-nitrobenzyl bromide, 4-vinylbenzyl chloride, and *n*-nonyl iodide showed lower reactivities compared with benzyl bromide. The authors did not report the recyclability of CuNPs/MagSilica in these CuAAC reactions.

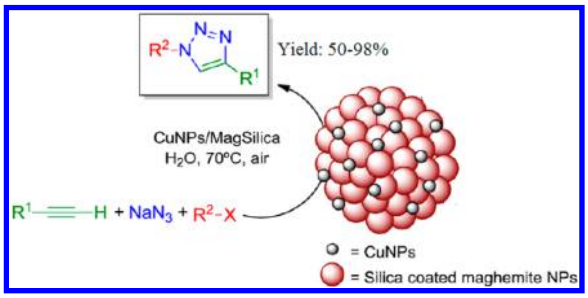


**Figure 13.** CuAAC reaction with CuNPs/MagSilica.[165] Reprinted with permission from ref 165. Copyright 2013 Elsevier B.V.

Magnetic $CuFe_2O_4$ NPs consisting of catalytically active copper centers were active for the CuAAC reaction.[162,166] $CuFe_2O_4$ was applied as catalyst in the formation of aryl azides from boronic acids under mild conditions. Then on this basis a one-pot approach was developed for the synthesis of 1,4-disubstituted 1,2,3-triazoles using alkyne, sodium azide, and boronic acids as reagents.[167] $CuFe_2O_4$ with particle sizes in the range 10−30 nm performed well toward the cascade reaction in terms of yield, selectivity, substrate scope, and recyclability. The strategy of multicomponent cascade reactions was repeatedly carried out the in synthesis of 1,4-disubstituted 1,2,3-triazoles in the field of MNPs-supported CuAAC reaction. This protocol made the CuAAC reaction consistent with the principles of click chemistry and green chemistry.

MNPs cores have been used as catalysts in some important reactions. A presynthesized graphene-capped $\gamma$-$Fe_2O_3$ composites was evaluated in one-pot synthesis of 1,4-disubstituted-1,2,3-triazoles through CuAAC reactions of benzyl halide, sodium azide, aryl alkyne in distilled water.[168] A series of 1,4-disubstituted-1,2,3-triazoles was smoothly isolated with 70−93% yields. The comparison test showed that graphene-capped $\gamma$-$Fe_2O_3$ composite exhibited better catalytic activity than pure $\gamma$-$Fe_2O_3$. The enhanced activity caused by the use of graphene was taken into account by its conducting properties and high migration efficiency of electrons[169,170] as well as the avoidance of aggregation of MNPs. In addition, the catalyst was simply collected from the final product by an external magnetic field and reused at least five times without significant loss of catalytic activity.

The [Cp*Ru(II)] complex-catalyzed cycloaddition of alkynes and azides (RuAAC)[171] is the most remarkable method for synthesis of 1,5-disubstituted 1,2,3-triazoles. $\gamma$-$Fe_2O_3$@$SiO_2$−Cp*$(PPh_3)_2$Ru was the first magnetically recyclable catalyst for RuAAC reactions (Figure 14).[172] The relatively uniform core−shell NPs with an average size of approximately 30 nm were prepared by immobilization of $Si(OMe)_3$-functionalized Cp*-$(PPh_3)_2$Ru complex on the surface of $\gamma$-$Fe_2O_3$@$SiO_2$ NPs. This catalyst was initially evaluated in the cycloaddition of phenylacetylene and benzyl azide with 2 mol % [Ru] in THF at 65 °C. After 3 h, the desired 1,5-disubstituted 1,2,3-triazole was isolated in 91% yield with over 99.9% selectivity, which was revealed by both NMR and GC. After completion of the reaction, the catalyst was magnetically separated from the reaction medium and reused for the next four runs with only a slight decrease in activity and selectivity. Investigation of substrate scope showed that all involved aryl, aliphatic, and ferrocenylacetylene exhibited good reactivities under the above-mentioned conditions. Reactions of aliphatic azides containing a linear chain and benzyl azides bearing different groups proceeded smoothly; aryl azides were also suitable cycloaddition partners. However, the yield of produced 1,5-disubstituted 1,2,3-triazole was somewhat lower.

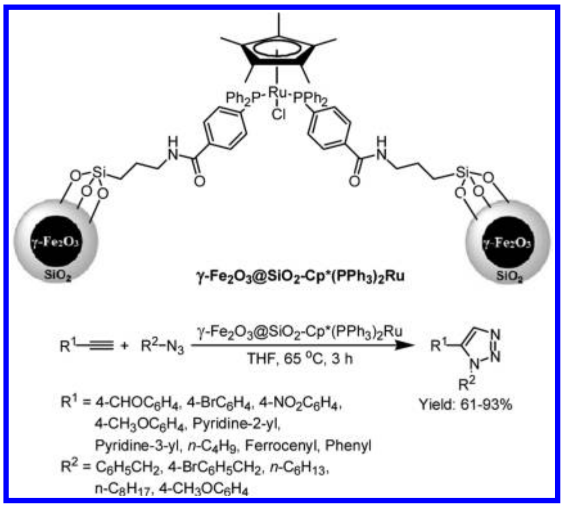


**Figure 14.** RuAAC reaction with $\gamma$-$Fe_2O_3$@$SiO_2$−Cp*$(PPh_3)_2$Ru.[172] Reprinted with permission from ref 172. Copyright 2013 Royal Society of Chemistry.

### 2.1.3. Hydrogenation of Unsaturated Compounds.

Hydrogenation of organic substrates is considered to be one of the most versatile reactions in chemistry, from pharmaceutical science to petrochemistry. Recently, in an effort to develop a more sustainable approach, magnetically retrievable nanocatalysts based on a transition metal were frequently used in the hydrogenation of various unsaturated compounds (including carbonyl compounds) and nitroaromatics. In this section, we focus on demonstrating the recent advance toward unsaturated compounds, and hydrogenation of nitroaromatics will be involved in the next section.

Pd is the most powerful catalyst for hydrogenation of olefins to saturated compounds. Li et al.[173,174] successfully assembled a chitosan magnetite NP-supported Pd catalyst through a facile metal adsorption−reduction procedure in one pot. This catalyst with a Pd content of 0.7 mol % was tested in the hydrogenation of olefins under 1 atm $H_2$ in ethanol at rt. Hydrogenation reached completion within 30−60 min. Moreover, the catalyst showed a good recyclability due to strong stabilization of Pd species by the amine groups of chitosan.

Reiser et al. deposited a series of PdNPs with diameters ranging from 2.7 to 30.4 nm onto the surface of Co@C NPs using $Pd_2(dba)_3 \cdot CHCl_3$ as precursor under microwave irradiation.[175] A trend to smaller PdNPs as well as an increased dispersion by decreasing the Pd content in the nanocomposite was observed. The catalytic test for hydrogenation of *trans*-stilbene showed an obvious trend of increasing activity with decreasing Pd NPs sizes, and the smallest PdNPs (2.7 nm) provided the highest TOF value (11 095 $h^{-1}$), which was at

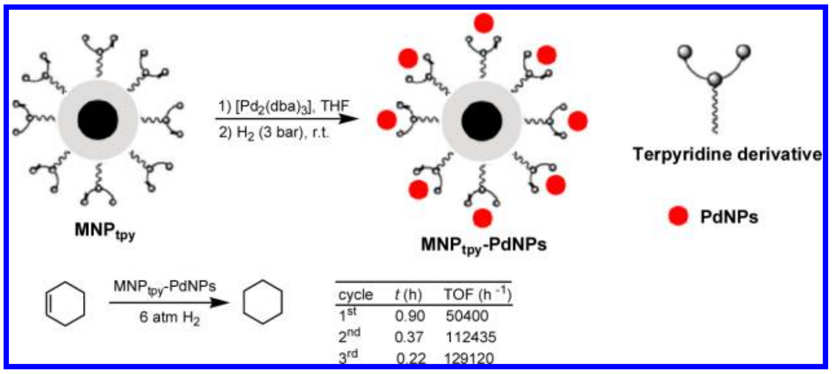


**Figure 15.** Hydrogenation of cyclohexene with $MNP_{tpy}$−PdNPs.

least 5 times more than other PdNPs prepared in this report.[175] However, obvious loss of activity was detected upon the recycling process. In addition, in order to achieve high catalytic activity, a larger amount of Co@C NPs support is needed because of the necessity of low palladium loading onto the support. Introduction of stabilizing imidazolium ILs on the surface of Co@C NPs brought a high loading of PdNPs and remarkable recyclability.[176] Magnetic Co@C-IL-immobilized PdNPs with a diameter of 5−15 nm and 34 wt % of Pd content provided a TOF of 50 $h^{-1}$ in the hydrogenation of *trans*-stilbene. In this case, 100% conversion was measured in each reaction cycle of the first 12 runs, and simple magnetic separation of catalyst was successfully carried out in the recycling test. It is apparent that the size of catalytic NPs and stabilizers significantly influences the catalytic activity and recyclability of MNP-supported NPs, respectively.

Terpyridine-functionalized $Fe_3O_4$@$SiO_2$ MNPs (named as $MNP_{tpy}$−PdNPs) were readily prepared and applied as efficient stabilizers to anchor PdNPs that were formed by direct decomposition of $[Pd_2(dba)_3]$ on the surface of MNPs (Figure 15).[177] In the preliminary experiments, well-dispersed and uniform PdNPs of about 2.5 nm average size with 180 or 90 ppm Pd content were employed in the hydrogenation of cyclohexene at 75 °C under 6 atm of $H_2$. An initial TOF of 50 400 $h^{-1}$, expressed as moles of the substrate transformed per mole of surface Pd atoms per hour, was observed in the first cycle. The TOF obtained in the second cycle was twice that of the first reaction, and an increase was also found from the second run to the third one.[177] This suggests that with the remaining Pd(II) species of the initial catalyst more and more Pd(0) species, the actual catalytic species were gradually formed during the reaction. In order to obtain a significantly high TOF, preactivation of the catalyst was needed in the first cycle; otherwise, the value of TOF decreased to 26 890 $h^{-1}$. Amine-functionalized MNPs-supported PdNPs (named $MNP_{amine}$−PdNPs) were similarly synthesized and compared with $MNP_{tpy}$−PdNPs. $MNP_{amine}$−PdNPs afforded a TOF value of 153 770 $h^{-1}$ in the first cycle, and this higher TOF could be attributed to the small mean size (1.8 ± 0.4 nm) of PdNPs.[177] However, a slight decrease in catalytic activity was detected in the second and third reaction cycles; therefore, it appears that the terpyridine ligand is a better stabilizer than the amine ligand; agglomeration of nanoparticles caused decreased activity in the case of $MNP_{amine}$−PdNPs. The morphology and size of the $MNP_{tpy}$−PdNPs did not change in the successive reaction cycles, and ICP analysis revealed that the amount of leaching Pd was negligible (<0.01 ppm). Furthermore, the behavior of the PdNPs as a heterogeneous catalyst was confirmed by a poisoning test with an excess of Hg.[177]

Selective hydrogenation of alkynes to alkenes is delicate because of the further hydrogenation of alkenes to saturated compounds occurring at the same time as a side reaction. Hur et al. reported that $CuFe_2O_4$ and PdNPs were sequentially encapsulated in mesoporous silica microsphere to produce magnetic $SiO_2$@$CuFe_2O_4$−Pd.[178] For the sake of comparison, other PdNPs such as $SiO_2$@Pd, $SiO_2$@$CoFe_2O_4$−Pd, and $SiO_2$@$Fe_3O_4$−Pd were assembled in the same method as $SiO_2$@$CuFe_2O_4$−Pd. Their efficacies for selective hydrogenation of phenylacetylene were tested under balloon pressure of $H_2$. The results showed that the nature of solvent deeply affected the reaction rate instead of selectivity. A 0.43 mol% of $SiO_2$@$CuFe_2O_4$−Pd achieved high conversion of over 98% in 2.5 h without any additives, with over 98% selectivity toward styrene (Figure 16). Under the same conditions, $SiO_2$@$CoFe_2O_4$−Pd and $SiO_2$@$Fe_3O_4$−Pd provided 18% and 60% conversion with 99% and 87% selectivity, respectively. $SiO_2$@Pd was almost inactive for hydrogenation. Use of the commercial Lindlar catalyst led to ordinary conversion (82%) and selectivity (92%), indicating that $SiO_2$@$CuFe_2O_4$−Pd was more selective than the commercial alternative. $SiO_2$@$CuFe_2O_4$−Pd also afforded excellent performance for phenylacetylene in terms of conversion and selectivity. The enhanced activity and selectivity of $SiO_2$@$CuFe_2O_4$−Pd were attributed to the existence of Pd and $CuFe_2O_4$ NPs and the facile coordination between Cu ions and the triple bond.[178]

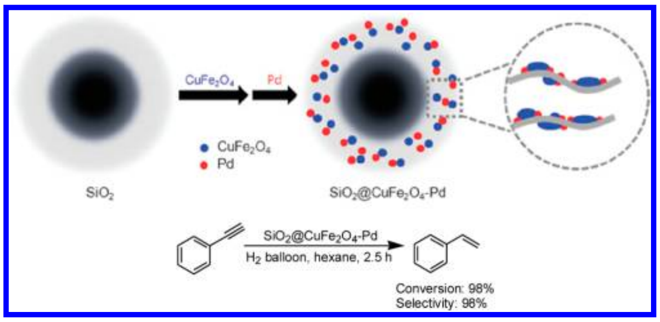


**Figure 16.** Selective hydrogenation of alkynes to alkenes.[178] Reprinted with permission from ref 178. Copyright 2012 Royal Society of Chemistry.

Reduction of alkynol to enol was a popular model reaction of selective hydrogenation.[179] The divergent synthesis of polyphenylenepyridyl dendrons (PPPDs) with anhydride, *o*-dicarboxyl, and *o*-dicarboxylate focal groups was developed by the groups of Brondtein and Shifrina.[180] PdNPs embedded in the second-generation PPPDs-coated magnetic nanocomposites showed high performance in selective hydrogenation of dimethylethynylcarbinol (DMEC) to dimethylvinylcarbinol (DMVC) (Figure 17). DMVC was produced in 98% yield, with over 98% selectivity, even in the third cycle. The comparison with commercial Lindlar catalysts demonstrated that the reported catalyst MNP@PPPDs−Pd displayed a more attractive activity, selectivity, and recyclability in the selective hydrogenation of DMEC. Bronstein et al.[181] modified original $Fe_3O_4$ with a series of acids bearing double bonds or pyridine

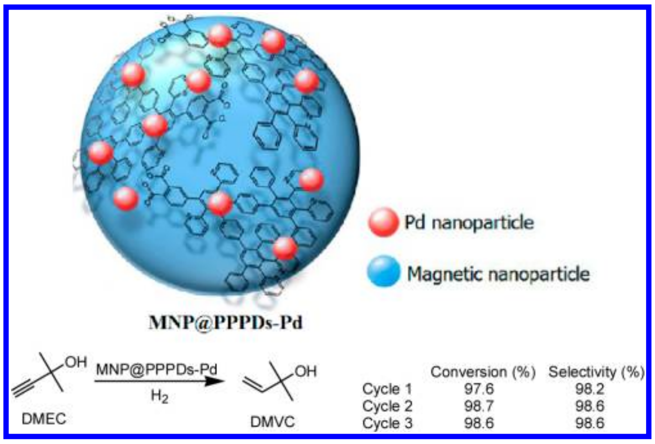


**Figure 17.** Selective hydrogenation of DMEC to DMVC catalyzed by MNP@PPPDs−Pd.[180] Reprinted with permission from ref 180. Copyright 2013 American Chemical Society.

fragments. These NPs were further used as a platform to immobilize Pd complexes and to produce magnetically separable Pd catalysts. These catalysts were evaluated in selective hydrogenation of DMEC to DMVC. The best performance in terms of TOFs (7.9 $s^{-1}$) and selectivity toward DMVC (92.5%) was achieved upon using $PdCl_2$ supported on linolenic (LLA)-coated $Fe_3O_4$ nanoparticles (named $Fe_3O_4$−LLA−Pd). In the recyclability test, $Fe_3O_4$−LLA−Pd showed an excellent capability to be magnetically collected, a slightly increased selectivity, and only a marginally decreased TOF value in the second reaction cycle. The authors believed that the real catalytic species for the hydrogenation were Pd(II) complexes rather than Pd(0) NPs (Figure 18).

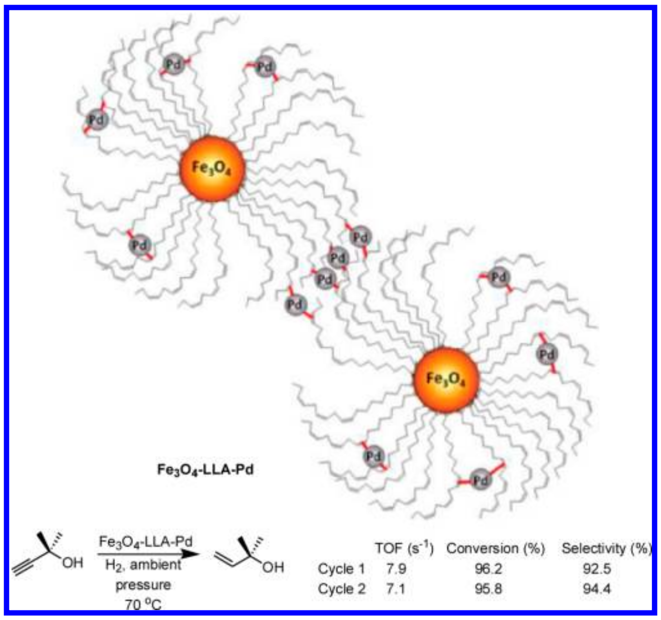


**Figure 18.** Selective hydrogenation of DMEC to DMVC catalyzed by $Fe_3O_4$−LLA−Pd.[181] Reprinted with permission from ref 181. Copyright 2012 American Chemical Society.

Besides Pd, other noble transition metal catalysts including Pt,[182] Ru,[183] bimetallic Ag/Ni,[110] Ir,[184] and Rh[185,186] were shown to have a wide range of catalytic applications in the hydrogenation of unsaturated compounds. MNPs-supported RuNPs were readily prepared through tandem generation of $Fe_3O_4$@$SiO_2$ and immobilization of RuNPs in one pot. Hydrogenation of acetophenone was successfully achieved with over 99% yield using KOH as base in the presence of a catalytic amount of $Fe_3O_4$@$SiO_2$−RuNPs at 100 °C in isopropanol under MW irradiation within 30 min. The scope of carbonyl compounds was then investigated under optimal conditions (Figure 19).[183] Acetophenones containing a wide range of substituents were transformed to the corresponding alcohols with high conversion and selectivity within 30−45 min. $Fe_3O_4$@$SiO_2$−RuNPs was magnetically collected and reused at least three times without a decrease of activity. Moreover, only 0.08% of Ru leached from initial catalyst after three reaction cycles. Peng's group[110] found that magnetic core−shell Ag@Ni NPs with a diameter of 14.9 nm were outstanding catalysts for hydrogenation of carbonyl compounds and nitroaromatics under relatively mild conditions. This nanocatalyst allowed easy magnetic separation and excellent recyclability.

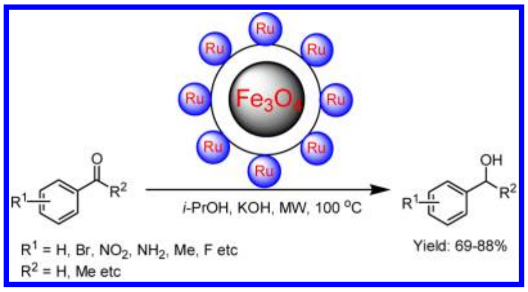


**Figure 19.** Hydrogenation of acetophenone and its derivatives with $Fe_3O_4$@$SiO_2$−RuNPs.

In practical applications, the cost, toxicity, and potential depletion of noble metals have restricted their utilization as catalysts. Thus, in this context FeNPs have emerged as viable alternatives.[187] Breit et al.[188] demonstrated that chemically derived graphene (CDG)-supported FeNPs were a highly efficient catalyst for hydrogenation of various olefins and alkynes. This catalyst was easily recovered using an external magnetic field and reused without any loss in activity. Moores et al.[189] synthesized stabilizer-free iron@iron oxide core−shell NPs (Fe CSNPs) and pioneered their catalytic application in the hydrogenation of alkynes and olefins. The robust nanocatalyst with an average core diameter of 44 ± 8.3 nm and a shell thickness of 6 ± 2 nm catalyzed the hydrogenation of various substrates in ethanol under 40 bar $H_2$ at 80 °C in the presence of 5 mol % Pd. Within 24 h, styrene was quantitatively converted to ethylbenzene, and 1-decene and 2-norbornene afforded 91% and 96% of hydrogenation yields, respectively. When 1-decyne was employed, decane was produced in 82% yield, meanwhile the incomplete hydrogenation compound 1-decene was isolated in 6% yield.[189] However, Fe CSNPs did not exhibit catalytic activity for carbonyl derivatives. The proposed alkene hydrogenation mechanism involved zerovalent FeNPs core as the real catalytic species. The iron oxide shell provided a substrate access to the surface of the core; the magnetic property was provided by both the shell and the core. Investigation of the recyclability proved that the Fe CSNPs maintained the capability of promoting quantitative transformation of styrene to ethylbenzene in eight successive cycles.[189]

Asymmetric transfer hydrogenation is an important branch of hydrogenation. Recent advances of asymmetric hydrogenation in the field of magnetic catalysis mainly focused on asymmetric hydrogenation of aromatic ketones,[190,191] 2-methylquinoline,[192] and *o*-methylanisole.[193]

$CuFe_2O_4$ NPs embedded in mesoporous silica KIT-6 were designed and used as catalyst in the asymmetric hydrogenation of aryl ketone.[191] In the synthetic process, the aggregation problem was solved by an ingenious predrying treatment between the impregnation and the calcination procedures. The desired alcohol product (*S*)-1-phenylethanol was synthesized with 93% ee and 93% yield when the reaction was carried out with 2 mol % KIT-6-supported $CuFe_2O_4$ using 0.5 mol % (*S*)-Xyl-Phos as the chiral modifier and PMHS as the reductant in the presence of *t*-BuONa and *t*-BuOH. This catalyst also showed easy recoverability and was utilized in the next reaction cycle after renewing activation under a nitrogen flow overnight at 120 °C.

Transfer hydrogenation reaction, a subsection of hydrogenation, is presently receiving increasing attention. Organorhodium-functionalized MNPs consisting of chiral 4-

((trimethoxysilyl)ethyl)phenylsulfonyl-1,2-diphenylethylene-diamine, 1,4-bis(triethyoxysilyl)benzene, Cp*Rh fragment, and $Fe_3O_4$ NPs were designed and synthesized.[194] The catalytic behavior of the presented catalyst $Fe_3O_4$@Cp*RhArDPEN−PMO was measured by asymmetric transfer hydrogenation of aromatic ketones (Figure 20). Reactions were conducted over 1 mol % [Rh] in the presence of 50 equiv of HCOONa in aqueous medium, providing the corresponding (*S*) ethanol with quantitative conversion and high enantioselectivity (up to 96% ee). Taking acetophenone as an example, a compared investigation showed that $Fe_3O_4$@Cp*RhArDPEN-PMO provided a higher conversion than its homogeneous counterpart and comparable enantioselectivity.[194] The authors indicated that the high efficiency was attributed to the high hydrophobicity and the confined nature of the catalyst. In addition, after completion of the reaction, $Fe_3O_4$@Cp*RhArDPEN-PMO was easily separable using an external magnetic field and recycled for at least 10 runs without significant loss in activity toward conversion and enantioselectivity.[194]

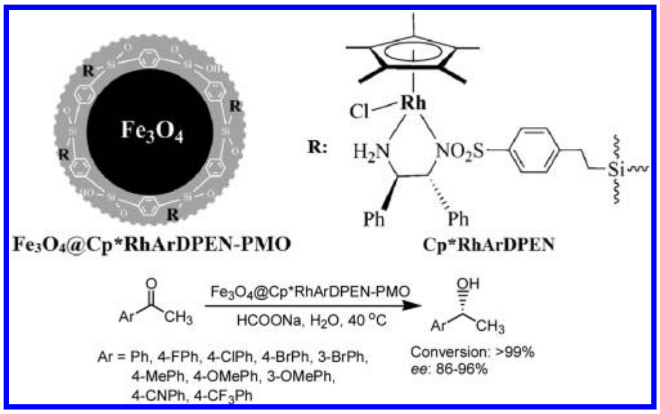


**Figure 20.** Asymmetric transfer hydrogenation reactions catalyzed by $Fe_3O_4$@Cp*RhArDPEN-PMO.[194] Reprinted with permission from ref 194. Copyright 2014 Wiley-VCH Verlag GmbH & Co.

### 2.1.4. Reduction of Nitroaromatics.

Functionalized anilines are key intermediates that are frequently used in the synthesis of pharmaceuticals, dyes, pigments, and pesticides, and reduction of nitroaromatics is the most general strategy yielding anilines. In order to achieve this transformation, various nanomaterials consisting of transition metals were recently designed and applied as catalysts. Reduction of nitroaromatics (especially for 4-nitrophenol that is the most refractory pollutants) probably is the most popular model reaction for evaluation of the catalytic application of magnetically recoverable catalysts.[195,196] During 2013 only, a variety of MNPs-supported Au, Pd, Ag, Pt, Ni, Fe, and Co catalysts for reduction of aromatic nitro were reported.

UV−vis spectroscopy is usually utilized to monitor the kinetics of nitroaromatic reduction. The reaction time of completed conversion is easily observed, and the linear relationships between $\ln(C_t/C_0)$ and reaction time (the rate constant $k$) are further calculated.

Cai's group synthesized AuNPs supported on graphene-encapsulated magnetic microspheres (named $Fe_3O_4$@PDA@RGO@Au),[66] magnetic yolk−shell microspheres-immobilized AuNPs (SiO2@$Fe_3O_4$/C@Au),[111] and AuNPs embedded in polydopamine-coated magnetic mecrospheres ($Fe_3O_4$@PDA−Au).[197] All three kinds of AuNPs were applied to catalyze nitroaromatic reduction. Synthesis of $Fe_3O_4$@PDA@RGO@Au is shown in Figure 21a.[66] As-prepared polydopamine (PDA)-coated $Fe_3O_4$ was treated with graphene oxide (GO), generating graphene oxide (RGO)-encapsulated $Fe_3O_4$@PDA that was further used as a platform to embed AuNPs. The catalytic performance of $Fe_3O_4$@PDA@RGO@Au was tested in *o*-nitroaniline reduction using a fresh $NaBH_4$ aqueous solution as reductant (Figure 21). Monitoring data of the reaction progress by UV−vis spectroscopy showed that quantitative transformation was achieved within 4 min. The catalyst was simply collected using an external magnet and reused for 10 runs, maintaining excellent conversion with increasing reaction time, which was related to the leaching of Au in each cycle. Unfortunately, about 30% of Au leached from the initial catalyst after 10 reaction runs. The Au content on $Fe_3O_4$@PDA−Au without RGO was about 4.3 wt %, which was much lower than that on $Fe_3O_4$@PDA@RGO@Au (13.58 wt %).[197] $Fe_3O_4$@PDA−Au led to complete transformation of *o*-nitroaniline to diaminobenzene in 7 min, and catalysis was extended to the reduction of other nitroaromatic analogues with excellent conversion within 5−120 min. A vibrating sample magnetometer experiment revealed that $Fe_3O_4$@PDA−Au showed a magnetization of 39.6 emu $g^{-1}$, which allowed easy removal by an external magnetic field. $Fe_3O_4$@PDA−Au

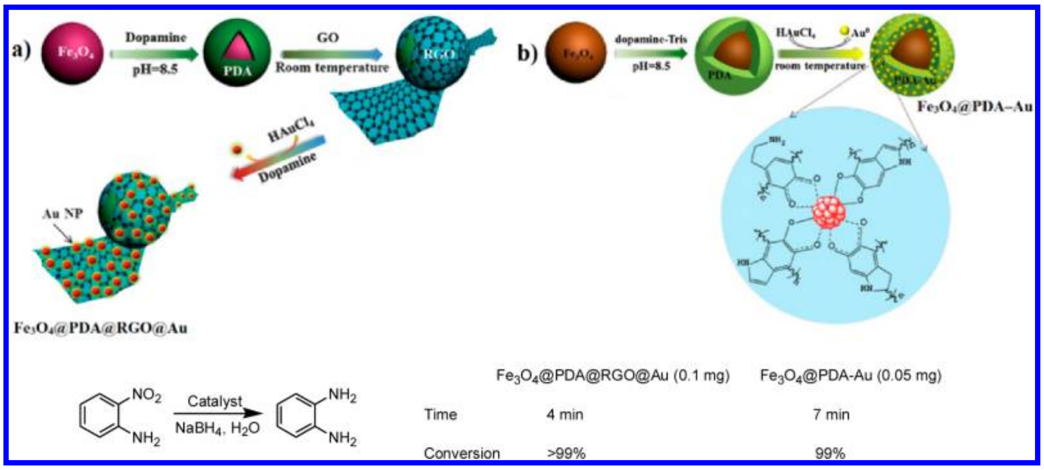


**Figure 21.** Reduction of *o*-nitroaniline catalyzed by $Fe_3O_4$@PDA@RGO@Au[66] or $Fe_3O_4$@PDA−Au.[197] Reprinted with permission from ref 66. Copyright 2012 Royal Society of Chemistry. Reprinted with permission from ref 197. Copyright 2013 Elsevier B.V.

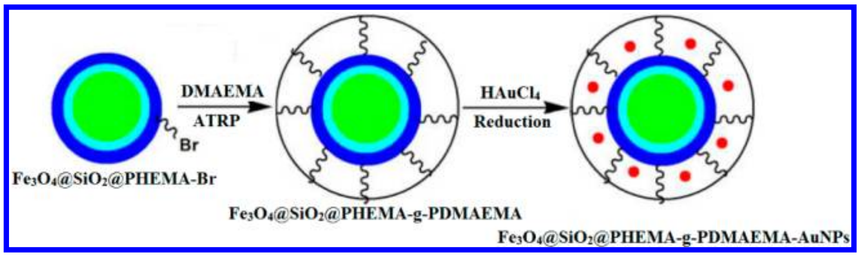


**Figure 22.** Synthetic route to $Fe_3O_4$@$SiO_2$@PHEMA-*g*-PDMAEMA−AuNPs.[202] Reprinted with permission from ref 202. Copyright 2013 American Chemical Society.

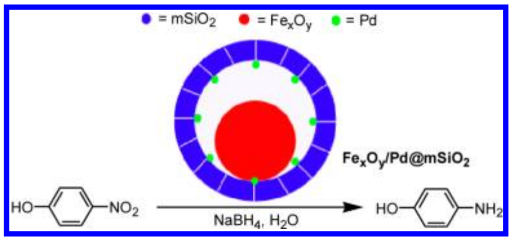


**Figure 23.** Reduction of 4-nitrophenol catalyzed by $Fe_xO_y$/Pd@$mSiO_2$.

was repeatedly used for at least 8 cycles, affording similar conversion. The leaching amount of Au was 17% after 8 runs.

Polymer-coated MNPs were also popular supports in the fabrication of magnetically separated nanocatalysts consisting of AuNPs for nitroaromatic reduction. These polymers included polypeptide,[198] polyethylenimine,[199] polydopamine,[197,200] cellulose,[201] and copolymers.[202−204] Bromide-functionalized poly(*N*,*N*′-methylenebis(acrylamide)-*co*-2-hydroxyethyl methacrylate)-coated $Fe_3O_4$@$SiO_2$ microspheres (named $Fe_3O_4$@$SiO_2$@PHEMA−Br) reacted with poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) brush to generate a copolymer-modified nanomaterial. AuNPs were then readily encapsulated in the PDMAEMA brush of the nanomaterial through in situ reduction (Figure 22). This hybrid consisting of AuNPs of 3.7 nm size with a narrow polydispersity promoted reduction of 4-nitrophenol to 4-aminophenol quantitatively within 15 min at rt with a rate contrast $k$ of $4.5 \times 10^{-3}$ $s^{-1}$. The magnetic character of this system allowed recovery and six times use without significant loss of catalytic activity.[202]

Reduction of nitroaromatics such as 4-nitroaniline and 1,3-dinitrobenzene has been highly efficiently catalyzed by PdNPs supported on various materials including $NiFe_2O_4$,[205] $Fe_3O_4$,[206,207] $BaFe_{12}O_{19}$, and $SrFe_{12}O_{19}$.[208] Pd−$CoFe_2O_4$−graphene composite nanosheets[209] and $CoFe_2O_4$−polypyrrole−Pd nanofibers[210] with diameters of PdNPs in range of 2−10 and 2−6 nm, respectively, prepared by Wang's group, catalyzed the quantitative reduction of 4-nitrophenol to 4-aminophenol within 7 min. The rate constants $k$ were $11.0 \times 10^{-3}$ and $13.2 \times 10^{-3}$ $s^{-1}$ for the first reaction cycles, respectively. The high catalytic activities were attributed to a synergistic effect between PdNPs and $CoFe_2O_4$−graphene (or $CoFe_2O_4$−polypyrrole). Unfortunately, a decrease of catalytic activity was observed in the successive reaction cycles due to Pd leaching and catalyst poisoning.

A strategy was proposed to assemble yolk−shell microspheres consisting of a movable silica core, a mesoporous $SiO_2$ shell, and PdNPs embedded on the surface of the core.[112] In this material (named $Fe_xO_y$/Pd@$mSiO_2$) the $Fe_xO_y$ core endowed the nature of superparamagnetism; the outer mesoporous $SiO_2$ shell not only protected the core from aggregation and outside harsh conditions but also afforded access for the starting materials toward catalytic applications (Figure 23). For comparison, $Fe_3O_4$@C/Pd composites were also prepared. Both $Fe_xO_y$/Pd@$mSiO_2$ and $Fe_3O_4$@C/Pd were evaluated in the reduction of 4-nitrophenol using $NaBH_4$ as reducing agent. With the same Pd loading, $Fe_3O_4$@C/Pd led to a higher $k$ value than that of $Fe_xO_y$/Pd@$mSiO_2$. The result was reasonably attributed to direct exposure of the $Fe_3O_4$@C surface to the reaction medium and smaller size of PdNPs of $Fe_3O_4$@C/Pd (10.2 versus 15.6 nm). In addition both catalysts were magnetically separated and reused for at least 10 cycles and maintained 100% conversion. However, $Fe_xO_y$/Pd@$mSiO_2$ showed a much higher stability than $Fe_3O_4$@C/Pd upon ultrasonic treatment in aqueous solution. Thus, loading NPs on the inner surface of capsules significantly prevented their leaching from the support. In this case, the high stability of $Fe_xO_y$/Pd@$mSiO_2$ also benefited from the larger size of PdNPs compared to the mesopores of $mSiO_2$ (15.6 versus 2.6 nm).[112]

The layer-by-layer synthesis of double-shell $Fe_3O_4$@$TiO_2$/Au@Pd@$TiO_2$ microsphere toward the reduction nitroaromatic involved 5 nm size AuNPs and PdNPs.[211,212] This nanomaterial catalyzed quantitative reduction of 4-nitrophenol to 4-aminophenol by $NaBH_4$ at rt in 4 min with a TOF value of 891 $h^{-1}$. The calculated rate constant $k$ value was $17.7 \times 10^{-3}$ $s^{-1}$, which indicated that $Fe_3O_4$@$TiO_2$/Au@Pd@$TiO_2$ was a better catalyst than most other $TiO_2$-supported catalysts. This catalyst exhibited remarkable recyclability that could keep with a similar catalytic performance for more than 20 runs.[211,212]

Almost all common stabilizers have been employed in the synthesis of magnetic AgNPs that were competitive candidates in the reduction of nitroaromatics. These magnetically recoverable Ag nanocatalysts included $Fe_3O_4$@$SiO_2$−Ag,[213] AgNPs-decorated copolymer-coated MNPs,[214] AgNPs supported on $Fe_2O_3$−carbons,[215,216] and iron oxide MNPs-supported AgNPs without stabilizer.[217] For instance, Wang et al.[214] reported the preparation of AgNPs loaded on a low-cost magnetic attapulgite nanocomposite grafted cross-linked copolymer (CPSA@MATP) through the adsorption of $Ag^+$ with CPSA@MATP and reduction. This CPSA@MATP/AgNPs catalyst system bearing AgNPs with a mean diameter of 20−30 nm was successfully employed in the reduction of 4-nitrophenol, and the reaction was completed within 6 min with a constant $k$ value of $17.7 \times 10^{-3}$ $s^{-1}$. The catalyst was simply collected with an external magnet and reused for at least three reaction cycles without a decrease in catalytic performance.

In situ-produced $Fe_3O_4$ NPs from a Fe precursor using hydrazine hydrate as the reducing agent catalyzed the reduction of nitroarenes.[218] The optimized investigation revealed that quantitative transformation was achieved using 20% excess hydrazine hydrate as reducing agent in the presence of 0.25 mol % of $Fe(acac)_3$ in 2 min under microwave conditions. Other Fe precursor such as $FeCl_2·4H_2O$, $FeCl_3·6H_2O$, and $Fe(OAc)_2$ also provided full conversion in 2 min, but neither commercially available $Fe_3O_4$ nor zerovalent Fe power promoted the reduction under the above-mentioned conditions. After the reaction cycle, the collected $Fe_3O_4$ was repeatedly used for several runs without loss of activity. Reactions of 20 nitroarenes containing a broad scope of substituent groups proceeded smoothly, and the corresponding anilines were obtained with >95% yields within a few minutes under optimized conditions (Figure 24). This attractive catalytic system was successfully extended to the reduction of aliphatic nitro compounds and azides.[219] As-prepared $Fe_3O_4$ deposited on graphene oxide (GO) sheets was shown to be a highly efficient catalyst for the reduction of nitroarenes with 3.6 equiv of hydrazine hydrate as reducing agent in refluxed ethanol.[220]

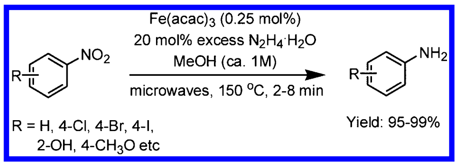


**Figure 24.** Catalytic reduction of nitroarenes to anilines with hydrazine hydrate using $Fe_3O_4$ NPs generated in situ.

In the synthesis of magnetically recoverable catalysts for the reduction of nitroaromatics, a two-dimensional carbon nanostructure RGO was found to be a versatile support.[109] $Fe_xCo_{100-x}$ NPs loaded on the surface of RGO sheets was prepared through a coreduction process.[221] Three kinds of RGO/$Fe_xCo_{100-x}$ hybrid with different Fe/Co molar ratio were tested as catalysts in the reduction of 4-nitrophenol using $NaBH_4$ as reductant, and RGO/$Fe_{25}Co_{75}$ afforded the highest catalytic rate (full conversion was achieved within 8 min), the largest constant $k$ value ($9.6 \times 10^{-3}$ $s^{-1}$), and the largest TOF value ($2.9 \times 10^{16}$ molecules $g^{-1}$ $s^{-1}$) compared to RGO/$Fe_{75}Co_{25}$ and RGO/$Fe_{50}Co_{50}$. In addition, RGO/$Fe_{25}Co_{75}$ was reused at least six times with only a slight decrease of activity. The authors indicated that the high efficiency of RGO in the reduction of 4-nitrophenol was attributable to the high adsorption capability of RGO toward 4-nitrophenol via $\pi-\pi$ stacking interactions, and electron transfer from RGO to catalytic species that resulted in a high concentration of 4-nitrophenol around catalytic species facilitating uptake of electrons by 4-nitrophenol molecules.[221,222]

The spinel-structured ferrites $CuFe_2O_4$ have been used in many applications including efficient catalysis of 4-nitrophenol reduction by excess $NaBH_4$ at rt with a constant $k$ up to $1.2 \times 10^{-1}$ $s^{-1}$.[223]

MNPs-immobilized NiNPs have been intensively used as catalysts in organic reduction reactions.[224,225] The presence of single poly(ethylene glycol)-10000 (PEG-10000), cetyltrimethylammonium bromide (CTAB), gelatin, and their composites controls the size and morphology of NiNPs, and the catalytic properties in the reduction of 4-nitrophenol were excellent.[226] The obtained NiNPs using composites of CTAB and PEG-10000 as modifier displayed the best catalytic performance with a constant $k$ value of $2.7 \times 10^{-3}$ $s^{-1}$. These magnetic NiNPs were magnetically separated with a hand-held magnet and repeatedly used for at least three reaction cycles without loss of activity. In another report, a magnetically separable nanocatalyst consisting of NiNPs 30 nm in size anchored on RGO has been artificially constructed. The catalyst exhibited good catalytic activity in the reduction of 4-nitrophenol to 4-aminophenol using sodium borohydride as reducing agent. An obvious enhancement of activity was achieved with near-infrared (NIR) irradiation because of the generation of hot spots on the catalyst surface caused by excellent NIR photothermal conversion property of RGO.[227]

$\gamma$-$Fe_2O_3$-supported PtNPs were fabricated through the metal vapor synthesis (MVS) procedure and applied to the reduction of halonitroaromatics using $H_2$ as reductant in the presence of 20 mg of Pt catalyst (containing 1 wt % Pt) at rt.[228] The nanocatalyst showed the best catalytic behavior compared with other Pt–iron oxide systems in the literature in terms of conversion and selectivity to haloaniline derivatives in the reduction reactions of *m*-chloro-, *o*- and *p*-bromo-, and *o*- and *p*-iodonitrobenzenes. In the case of the reduction of *p*-chloronitrobenzene, the catalyst was magnetically recycled and reused five times without significant loss of activity. In another report, Ma and co-workers[229] designed the synthesis of PtNPs decorated on carbon-coated MNPs. This $Fe_3O_4$@C@Pt catalyst consisting of PtNPs with a size around 5 nm was used in the reduction of nitroaromatic under $H_2$ atmosphere at rt (Figure 25) and showed high efficiency and reusability.

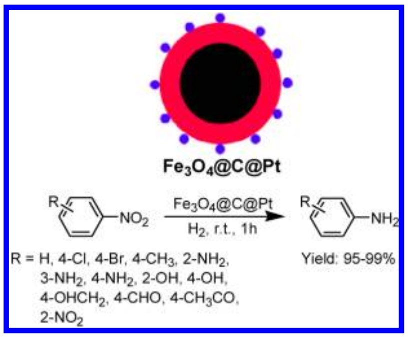


**Figure 25.** Reduction of aromatics catalyzed by $Fe_3O_4$@C@Pt.

### 2.1.5. Oxidation Reactions.

Oxidation reactions are fundamental organic transformation in both academic and industrial synthetic chemistry, but use of traditional stoichiometric or an excess amount of oxidants has caused serious environmental problems. Therefore, transition metal catalysts that are immobilized on modified MNPs have received considerable attention in catalyzing oxidation reactions of organic catalysts by themselves or with cocatalysts due to their high efficiency and recyclability.

Selective oxidation of alcohol is a primary example of oxidation reactions, because the carbonyl products are valuable chemicals both as active intermediates in organic synthesis and as high-value components for fine chemistry.[230] Thus, selective oxidation of alcohols over magnetically retrievable noble-metal-based catalysts is one of the hottest subjects in this research field.

Amino acids (L-cysteine, $\beta$-alanine, serine, or glycine) modified $Fe_3O_4$ NPs-trapped PdNPs were produced via a simple in situ method.[231] The average diameter sizes of the obtained magnetic hybrid and PdNPs were about 20 and 3 nm, respectively. In the catalytic application of these nanomaterials, oxidation of benzyl alcohol was chosen as model reaction. The reaction was initially carried out at 50 °C in the presence of 30 mg of catalysts under an $O_2$ atmosphere and under solvent-free conditions in 1.5 h with 2 mmol of benzyl alcohol. Among the four different nanocatalysts, $Fe_3O_4$/L-cysteine (Cys)−Pd provided the best catalytic results, and benzaldehyde was synthesized with 48% yield and >99% selectivity. The yield was raised to 85% upon increasing the catalytic amount from 30 to 60 mg (containing 6.27 wt % Pd) with the same selectivity. In addition, the catalytic performance was maintained in eight successive reaction cycles. When 80 mg of $Fe_3O_4$/Cys-Pd was employed, the yield did not change but the selectivity decreased to 94%. The strategy was extended to oxidation of other aromatic and aliphatic alcohols, yielding aldehydes with 58−85% yields with excellent selectivities.[231]

Starting from the functionalized MNPs, the proline moieties were covalently anchored providing proline-modified MNPs, and the magnetic catalyst based on Pd was synthesized via complexation with $Pd(OAc)_2$. This catalyst system catalyzed the aerobic oxidation of alcohols to aldehydes and ketones (Figure 26).[232] Benzyl alcohols bearing both electron-donating and electron-withdrawing groups were smoothly oxidized over 0.5 mol % of [Pd], producing the corresponding aldehydes in good to excellent yields. When aliphatic alcohols were employed, the yields of isolated products were somewhat lower. In addition, secondary benzylic alcohols were also suitable participants for the oxidation reaction, the desired ketone compounds being obtained in 71−81%. Importantly, catalyst separation was easily achieved using an external magnet with negligible Pd leaching, and the recovered catalyst was recycled for at least eight runs without loss in catalytic performance.

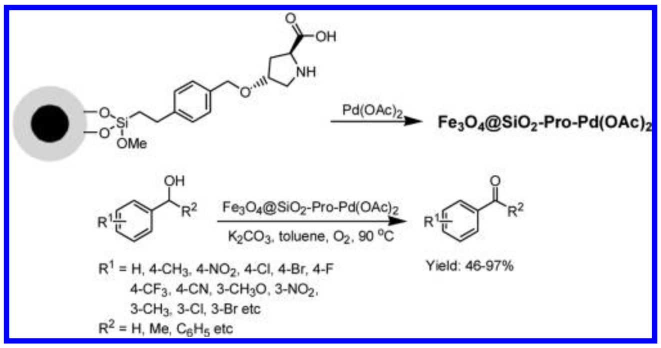


**Figure 26.** Oxidation of alcohols catalyzed by $Fe_3O_4@SiO_2$−Pro−$Pd(OAc)_2$.

Chen et al. reported the preparation of Pd@Ni bimetallic NPs on multiwalled carbon nanotubes (Pd@Ni/MWCNT) that was shown to be an efficient heterogeneous catalyst for oxidation of benzyl alcohol in $H_2O$ at 80 °C in 6 h using $H_2O_2$ as oxidant in the presence of $K_2CO_3$ (Figure 27).[233] Benzaldehyde was produced with 99% conversion and 98% selectivity, and under the same conditions both Pd/MWCNT and Ni/MWCNT afforded lower conversion and selectivity than Pd@Ni/MWCNT. Pd@Ni/MWCNT was magnetically collected and reused four times with steady decline in both conversion and selectivity.[233]

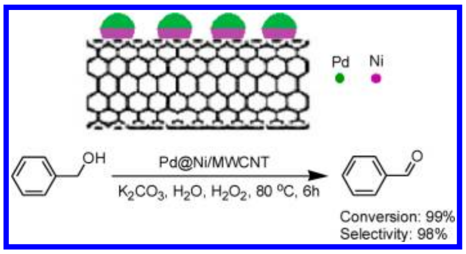


**Figure 27.** Oxidation of benzyl alcohol catalyzed by Pd@Ni/MWCNT.

Colloidal AuPd bimetallic NPs were loaded on amino- or thiol-functionalized or bare $Fe_3O_4@SiO_2$.[107] These nanocatalysts exhibited some deficiencies in the oxidation of benzyl alcohol with $O_2$ as oxidant, such as low catalytic activity, bad stability, and uneasy reusability. To overcome these drawbacks these AuPd NPs were calcined, and the hybrids $Fe_3O_4@SiO_2$−$NH_2$−AuPd(C) and $Fe_3O_4@SiO_2$−SH−AuPd(C) showed much better activities, selectivity, and reusability than their precursors.[107]

$Fe_3O_4$−Co MNPs were explored for oxidation of 1-phenylethanol using excess *tert*-butyl hydroperoxide (TBHP) as the oxidant at 80 °C, and a 92% yield of acetophenone was obtained in 6 h.[234] After completion of the reaction, the highly stable $Fe_3O_4$−Co MNPs were collected using an external magnet and reused for 7 runs without obvious loss of catalytic activity. ICP analysis revealed that only 0.09% Co was leached off the initial catalyst after seven reaction cycles. Other alcohol substrates were also successfully oxidized using this catalytic system, providing 18 ketones with 79−94% yields (Figure 28).

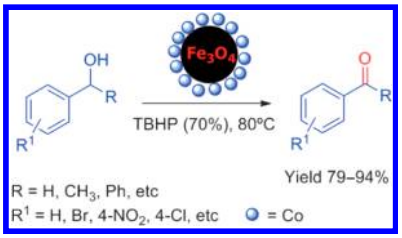


**Figure 28.** Oxidation of alcohols catalyzed by $Fe_3O_4$−Co MNPs and TBHP.[234] Reprinted with permission from ref 234. Copyright 2012 Wiley-VCH Verlag GmbH & Co.

Flow chemistry is an emerging area,[235] and combination of continuous flow technology with MNPs is especially attractive, because the use of MNP catalysts overcomes some limitations of continuous flow systems, such as uncontrollable fluid dynamics, limited accessibility of catalytic sites, and uncontrollable swelling.[236] Kappe et al.[237] used mesoporous aluminosilicate-supported iron oxide NPs as catalysts in a flow reactor for catalyzing selective aerobic oxidation of a primary alcohol with TEMPO as a cocatalyst. The model substrate benzyl alcohol was converted into the desired benzaldehyde with up to 42% conversion in a single pass, and continuous recirculation offered full conversion. In addition, the MNPs catalyst showed high stability in the flow process, and no leaching was observed.

Oxidation of sulfides to sulfoxides is a common reaction in the synthesis of pharmaceuticals, fine chemicals, and bioactive molecules. Recently, several magnetically recoverable nanocatalysts were designed and used in the oxidation of sulfides.[238]

The complex [Mn($Br_2$TPP)OAc] anchored on $Fe_3O_4@SiO_2$ NPs has been synthesized via amine functionality.[239] This thermostable nanocatalyst has a diameter of less than 10 nm and was investigated for oxidation of sulfides. Sulfoxides were efficiently formed in 60−96% yields in 1 h at rt with excellent selectivity when the oxidation reactions proceeded in air in a mixed solvent of water and ethanol with a molar ratio of sulfide/tetra-*n*-butylammonium peroxomonosulfate (TBAOX)/catalyst of 200:200:1 (Figure 29).[239] If the reactions were carried out in pure water with a molar ratio of sulfide/TBAOX/

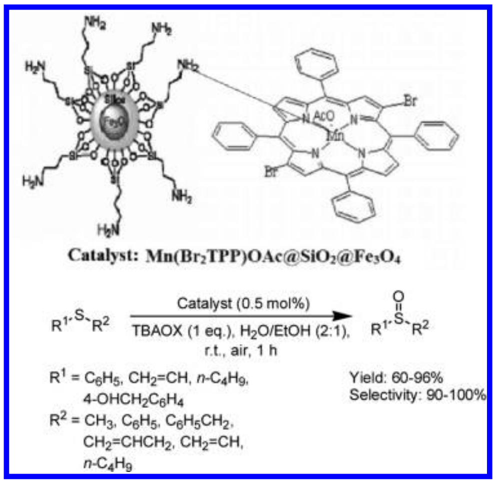


**Figure 29.** Oxidation of sulfides to sulfoxides catalyzed by Mn($Br_2$TPP)OAc@$SiO_2$@$Fe_3O_4$.[239] Reprinted with permission from ref 239. Copyright 2012 Wiley-VCH Verlag GmbH & Co.

catalyst of 200:600:1, the products were sulfone compounds instead of sulfoxides. In addition, the Mn($Br_2$TPP)OAc@$SiO_2$@$Fe_3O_4$ catalyst also showed good activity in the oxidation of saturated hydrocarbons to ketones.

$\gamma$-$Fe_2O_3$ was immobilized on graphene through a simple chemical route.[168] The resulting graphene-$\gamma$-$Fe_2O_3$ MNPs were used as recyclable catalysts for selective oxidation of sulfides to sulfoxides using hydrogen peroxide as the oxidant. Good to excellent yields and selectivity were recorded at 60 °C within a few hours, but meanwhile sulfone compounds were also observed as side products.[168] In the case of the oxidation of methyl phenyl sulfide almost complete conversion (98%) was obtained in the first cycle, and the recyclability of the nanocatalyst was further checked. It was found that the graphene-$\gamma$-$Fe_2O_3$ MNPs was recovered, recycled, and reused for more than five runs without loss of catalytic activity. The reused catalyst was found unchanged from TEM images and Raman spectra compared with those of the fresh catalyst.

A complex $[Mn(phox)_2(CH_3OH)_2]ClO_4$ (phox = 2-(2′-hydroxyphenyl)oxazoline)-based composite material with $Fe_3O_4$@$SiO_2$ was synthesized through aminopropyl linkage, and its catalytic activity was investigated for oxidation of thiols to disulfides using urea−hydrogen peroxide as the oxidant. This heterogeneous magnetic catalyst afforded moderate to good yields, higher selectivity toward disulfides compared with the homogeneous manganese complex, and excellent recyclability.[240]

Oxidative transformations of amines yielding useful nitrone building blocks were intermediate steps in the synthesis of heterocyclic compounds. $\gamma$-$Fe_2O_3$@$SiO_2$ NPs-encapsulated tungstophosphoric acid ($\gamma$-$Fe_2O_3$@$SiO_2$−$H_3PW_{12}O_{40}$) was synthesized and tested as catalyst for oxidation of secondary amines to nitrones with hydrogen peroxide as the oxidant.[241] Following optimization, oxidation of dibenzylamine at 23 °C in MeOH with 1.1 mol % of catalyst within 2 h afforded the corresponding nitrone in 85% yield, and extension to a variety of secondary amines led to nitrones in moderate to good yields. Moreover, $\gamma$-$Fe_2O_3$@$SiO_2$−$H_3PW_{12}O_{40}$ was magnetically removed and reused at least four times without loss of activity.

Sharma et al. reported the use of 2-acetylpyridine Zn(II) complex-grafted silica@magnetite NPs as catalyst for oxidation of aromatic amines yielding azoxyarenes.[242] In the optimized investigation using aniline as the test substrate the effects of reaction time and catalytic amount were involved at 80 °C in acetonitrile with $H_2O_2$ as oxidant. Encouraged by full conversion and 99% selectivity toward the corresponding azoxyarene, the reaction scope was further studied. The substrates with electron-withdrawing groups provided less conversion and selectivity than electron-rich anilines. The relative steric effect was shown to be negative in terms of conversion and selectivity. The TON values for azoxyarenes in all cases were high; when some substrates were employed, the obtained TOF values were much higher than with the previously reported catalysts. The catalyst was reused up to six consecutive cycles with a steady decline in yield and negligible Zn leaching.[242]

Oxidative amidation of aldehydes with amine salts is a practical and direct method for synthesis of carboxamides. Heydari et al. developed a heterogeneous CuI catalyst supported on silica-coated magnetic carbon nanotubes (MagCNTs@$SiO_2$) for oxidative amidation processes (Figure 30).[243] Various carboxamides compounds were effectively produced in the presence of 0.2 mol % of MagCNTs@$SiO_2$-linker-CuI in one pot with moderate to good yields. The stable catalyst was magnetically recovered from the reaction medium, and repeated use in five reaction cycles maintained similar activity. Another report demonstrated that magnetic $CuFe_2O_4$ NPs were also an efficient and “green” catalyst for oxidative amidation of aldehydes with amine salts.[244]

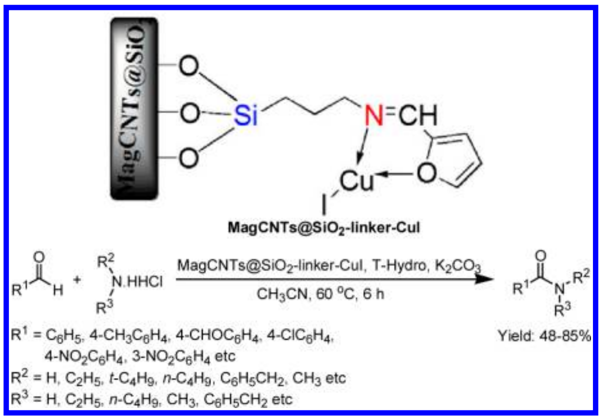


**Figure 30.** Oxidative amidation of aromatic aldehydes with amine hydrochloride salts catalyzed by MagCNTs@$SiO_2$−linker−CuI.[243] Reprinted with permission from ref 243. Copyright 2013 John Wiley & Sons, Ltd.

Oxidations of cyclohexane[245] and ethylbenzene[246] catalyzed by magnetic nanocatalysts are still challenging subjects, because in general the conversions and selectivities used to be very low. Oxidative degradation of organic pollutants in wastewater through Fenton-like reactions will be discussed in the section Fenton-Like Reactions.

**2.1.6. Arylation and Alkylation Reactions.** *S*-Arylation reactions for construction of carbon−sulfur bonds are a key step in the synthesis of biological molecules and functional materials. Recently, Cu-containing magnetic nanomaterials have emerged as catalysts in *S*-arylation reactions.[247] Uniformly spherical nanocrystalline (from XRD) superparamagnetic $CuFe_2O_4$ NPs with a size of 55 ± 5 nm were initially tested as catalysts in the *S*-arylation reaction betweern thiophenol and 4-iodoacetophenone. The desired 1-(4-(phenylthio)phenyl)-ethanone was isolated in 95% yield with 10 mol % of catalyst, 2 equiv of *t*-BuOK as base, 5 mL of 1,4-dioxane as solvent, 24 h reflux, and under a $N_2$ atmosphere. Extension to various aryl iodides afforded the corresponding organosulfur compounds in excellent yields, and no undesired disulfides were detected. Aryl bromides and chlorides were shown to be less reactive for the *S*-arylation with thiophenol than aryl iodides, and disulfides were produced in some cases. A range of aryl and alkyl thiols were subsequently employed in reactions with iodobenzene giving a series of organosulfur compounds in moderate to good yields, and the recyclability of $CuFe_2O_4$ was verified.[247]

$CuCl_2$ immobilized on $Fe_3O_4$ NPs modified with dopamine hydrochloride (DOPA) was a very efficient and reusable catalyst for the *S*-arylation of thiophenol with aryl halides. Immobilization of $CuCl_2$ with DOPA-functionalized MNPs was achieved by a one-pot multicomponent reaction under MW irradiation.[248] In the case of the *S*-arylation reaction between thiophenol and 1-bromo-4-nitrobenzene the product was obtained in quantitative yield under MW irradiation at 120 °C for 25 min. The scope of the reaction was subsequently extended to a range of thiophenols and aryl iodides and bromides, providing 12 organosulfur compounds in 85−98% yields within 25−30 min. The recovery test of $Fe_3O_4$−DOPA−$CuCl_2$ revealed that the catalytic behavior was unaltered in three consecutive cycles with only 0.01% leaching.

Sharma's group[249] developed a copper acetate-based magnetic nanocatalyst that was evaluated in the aerobic *N*-alkylation of amines (Figure 31). Starting from 3-aminopropyl triethoxysilane (APTES)-functionalized $SiO_2@Fe_3O_4$ NPs (Am−Si−$Fe_3O_4$), acetylthiophene (AcTp) was introduced yielding AcTp@Am−Si−$Fe_3O_4$, and the final magnetically separated catalyst Cu−AcTp@Am−Si−$Fe_3O_4$ was obtained through metallization of AcTp@Am−Si−$Fe_3O_4$ with copper acetate. This organic−inorganic hybrid nanomaterial was utilized as catalyst in the alkylation of aniline with benzyl alcohol under aerobic conditions. Almost quantitative conversion was obtained when the reaction was conducted at 100 °C for 10 h. Investigation of the reaction scope showed that the *N*-alkylation of anilines and benzyl amine with aliphatic alcohols proceeded smoothly under optimized conditions, and series of amines were synthesized in excellent yields with 95−100% selectivity. AcTp@Am−Si−$Fe_3O_4$ was magnetically collected after completion of the reactions and repeatedly used at least 10 times, maintaining >96.5% conversion in each cycle. $CuFe_2O_4$ NPs proved to be another cheap, efficient, recyclable catalyst in the *N*-arylation of imidazole upon building the C−N bond under ligand-free conditions.[250]

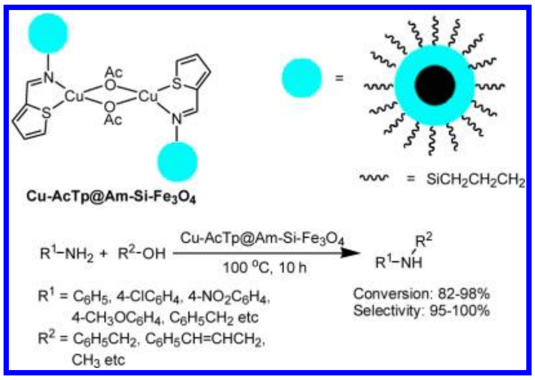


**Figure 31.** *N*-Alkylation of amines catalyzed by Cu−AcTp@Am−Si−$Fe_3O_4$.

Ring opening of epoxides was an efficient strategy for alkylation, and the $CuFe_2O_4$ MNPs exhibited high performance in the alkylation of substituted indoles or pyrroles with achiral or chiral epoxides under solvent-free conditions, resulting in regio- and stereoselective synthesis of C-alkylated indoles or pyrroles.[251]

Magnetically recyclable Pd−$Fe_3O_4$ NPs promoted direct arylation of imidazo[1,2-*a*]pyridine with 4-bromonitrobenzene and NaOAc in DMA at 166 °C with 1 mol % Pd in 88% yield.[252] Reactions of aryl bromides bearing electron-donating and electron-withdrawing substituents proceeded smoothly in moderate to good yields, and the Pd−$Fe_3O_4$ catalyst also showed excellent recoverability and recyclability.

### 2.1.7. Epoxidation of Alkenes.

Epoxidation of alkenes is attractive because of the wide applications of epoxides in the synthesis of many fine chemicals and pharmaceuticals.[253] Magnetically removable catalysts containing Ag, W, Mn,[254] Co, and Ru have been employed to achieve efficient epoxidation of alkenes.

Ag-catalyzed epoxidation of alkenes is a very important and powerful methodology for formation of epoxides in academic studies and toward industrial applications.[255−258] Pioneering work on the application of magnetically recyclable Ag-based catalysts for epoxidation of alkenes was reported by Chen's group.[259] A AgNPs−$Fe_3O_4$ nanocomposite with a size of 230 nm was readily produced in one pot with the assistance of PVP

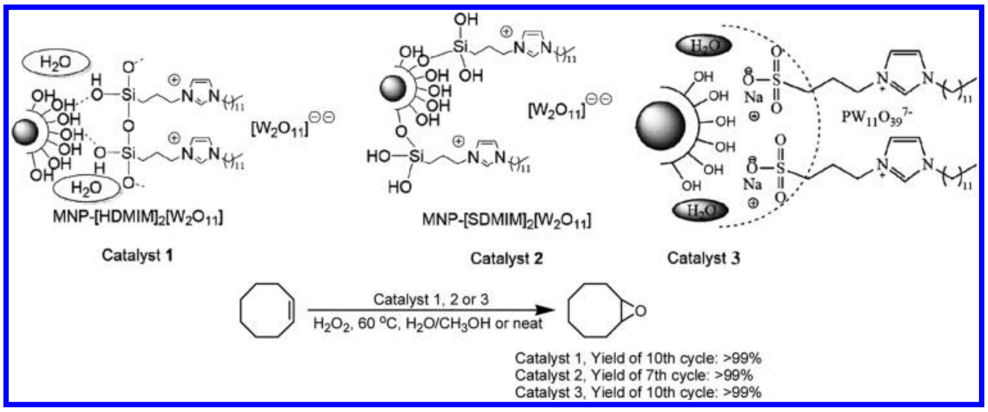


**Figure 32.** Epoxidation of cyclooctene catalyzed by MNP−$[HDMIM]_2[W_2O_{11}]$, MNP−$[SDMIM]_2[W_2O_{11}]$, or MNP−(DSPIM-$PW_{11}$).[260] Reprinted with permission from ref 260. Copyright 2012 Wiley-VCH Verlag GmbH & Co.

and ethylene glycol using $AgNO_3$ and $FeCl_3$ precursors and provided excellent catalytic activity and selectivity in epoxidation of styrene with TBHP as oxidant. Both the catalytic activity and the selectivity were much higher than those of unsupported Ag catalyst. Furthermore, the AgNP−$Fe_3O_4$ nanocatalyst was magnetically removed and reused at least five times keeping the same catalytic performance.[259] In order to demonstrate the effects of MNPs supports on the catalytic performance for epoxidation of alkenes, a series of AgNPs positioned on different ferrites ($M_{1-x}Fe_{2+x}O_4$; M = Co, Ni, Mn, Zn) was prepared via a similar procedure to that for AgNP−$Fe_3O_4$ nanocomposite.[79] The catalytic investigation showed that all AgNP−$M_{1-x}Fe_{2+x}O_4$ nanocatalysts were highly efficient and remarkably recyclable in the epoxidation of styrene; their catalytic activities were influenced by the variation of restriction behavior of ferrite supports for growth of AgNPs, resulting in different relative amounts of crystal planes of AgNPs as well as by the efficiency of ferrite supports in capturing reactive oxygen species.

Inspired by the high activity of tungstic peroxometalates for epoxidation, magnetic material-anchored tungstic peroxometalates catalysts have been designed and developed. Hou's group[260] immobilized an ionic liquid-type peroxotungstate on core−shell $Fe_{3}o_{4}$-$SiO_2$ NPs by hydrogen bonding or covalent Si−O linkage, assembling MNP−$[HDMIM]_2[W_2O_{11}]$ or MNP−$[SDMIM]_2[W_2O_{11}]$, respectively. Both nanocatalysts were shown to be efficient heterogeneous catalysts for epoxidation of a variety of alkenes using $H_2O_2$ as oxidant at 60 °C in $H_2O/CH_3OH$. In cyclooctene epoxidation, the catalysts were readily recovered by simple magnetic decantation and recycled 10 times without significant loss of catalytic activities and selectivities toward epoxide. Another MNPs-supported peroxometalate catalyst MNP−(DSPIM-$PW_{11}$) prepared through the hydrogen-bonding method exhibited excellent activity and recyclability in cyclooctene epoxidation with $H_2O_2$ under solvent-free conditions (Figure 32). The principles of immobilization by hydrogen bonding should open facile catalyst formation with excellent activities and superior recycling performance.

Using this principle, phosphotungstic acid was immobilized on imidazole-functionalized $CoFe_2O_4$ NPs, and the catalytic potential was evaluated in the epoxidation of various alkenes.[261] When the epoxidations were conducted with 0.1 g of this catalyst (0.98 mmol/g of tungsten content) and 2 equiv of *t*-BuOOH as oxidant in 1,2-dichloroethane at 70 °C within 6 h in 1 mmol-scale reactions the corresponding epoxides were obtained in good to excellent yields and excellent selectivity, and the catalyst displayed constant activity after several consecutive cycles.

Metalloporphyrin complexes are very active catalysts for epoxidation of alkenes; therefore, the MNPs-supported version has logically emerged.[262] Immobilization of tetra(4-*N*-pyridyl)-porphyrinatomanganese(III) acetate [Mn(TPyP)OAc] on $SiO_2@Fe_3O_4$ MNPs was reported by Tangestaninejad et al.[263] The narrowly distributed Mn(TPyP)/$SiO_2$−$Fe_3O_4$ with an average diameter of around 48 nm provided good catalytic performance, relatively good tolerance, and satisfactory recyclability using $NaIO_4$ as oxidant at rt (Figure 33). With regard to catalyst leaching, 0.33%, 0.18%, 0.12% of Mn leached off the initial catalyst in the first three cycles, respectively, and no leaching was detected in the fourth to sixth cycles. In addition, this catalytic system showed activity in alkane hydroxylation.

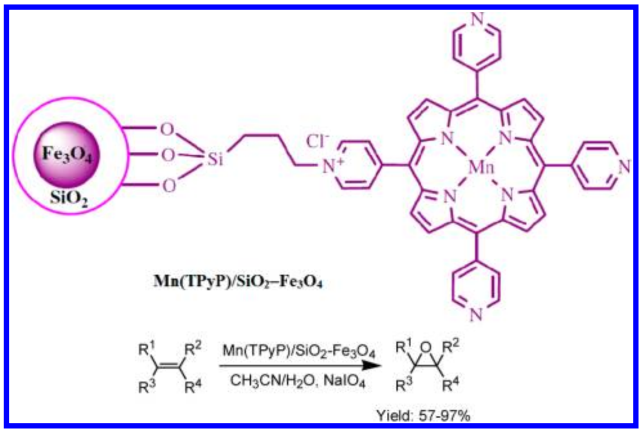


**Figure 33.** Epoxidation of alkenes catalyzed by Mn(TPyP)/$SiO_2$−$Fe_3O_4$.[263] Reprinted with permission from ref 263. Copyright 2012 Elsevier Ltd.

Li et al. reported the assembly of magnetic CoNPs within carbon nanotubes (CNTs) by a wet chemical method, and the existence of CoNPs in the interior of CNTs was confirmed by TEM.[264] The catalytic activity of the Co/CNTs in the liquid-phase epoxidation of styrene was studied under an atmospheric pressure of molecular oxygen, epoxidation being complete with 93% of epoxide selectivity within 1 h at 100 °C in DMF. The catalyst was recycled three times without loss of activity,[264] and it was indicated that Co/CNTs were a superior catalyst compared to previously reported catalysts.

Pericàs' group reported the preparation of a magnetically separable molecular ruthenium complex catalyst containing a phosphonated trpy ligand (Figure 34).[265] This nanosystem $Fe_3O_4$−Ru aqua proved to be an excellent catalyst for epoxidation of alkenes. In particular, this nanocatalyst promoted stereoselective synthesis of *cis*-epoxides from reactions of *cis*-olefins, and the $Fe_3O_4$ support in $Fe_3O_4$−Ru aqua did not cause any decrease in activity compared to the homogeneous counterpart. In the case of epoxidation of *cis*-*β*-methylstyrene, investigation of the recyclability showed that $Fe_3O_4$−Ru aqua was collected using magnetic decantation and exhibited constant activity and slightly decreased selectivity after at least five consecutive cycles.

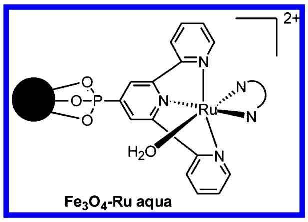


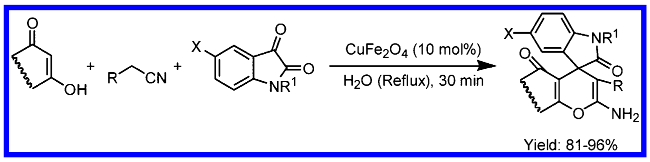
**Figure 34.** $Fe_3O_4$-supported $[Ru(trpy\text{-}P)(B)(H_2O)]^{2+}$ ($Fe_3O_4$−Ru aqua).

### 2.1.8. Multicomponent "One-Pot" Synthesis.

The multicomponent reaction (MCR) strategy[266,267] displays significant advantages over classical stepwise methods and has been proved to be a powerful method to build diverse and complex molecules, in particular, for the synthesis of biologically active and heterocyclic compounds. MCR offers rapid and convergent construction of molecules from commercially available starting materials without the need of isolation and purification of intermediates, and therefore, it requires less manipulation time, cost, and energy than classic methods. The combination of MCR with magnetic separation should thus significantly expand green procedures.

In the past two years, magnetically recoverable catalysts have been widely used in multicomponent "one-pot" synthesis of 4*H*-chromene derivatives,[268,269] spirooxindoles,[270] hydantoin derivatives,[271] xanthene derivatives,[272] hexahydroquinoline carboxylates,[273] pyrido[2,3-*d*]pyrimidines,[274] diazepine derivatives,[275] spirohexahydropyrimidines,[276] 1,2,3,5-tetrahydropyrazolo[1,2-*a*][1,2,4]triazole,[277] polysubstituted pyrroles,[278] 4*H*-pyrano[2,3-*c*]pyrazoles,[279] 1,4-dihydropyridine derivatives,[280,281] 4*H*-benzo[*b*]pyrans,[282] 1-amidoalkyl-2-naphthols,[283] spiro-furo-pyridopyrimidine- indulines,[284] and so on.

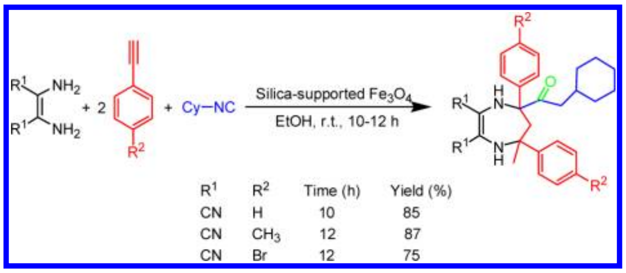
Ghahremanzadeh's group[270] reported that $CuFe_2O_4$ MNPs displayed high catalytic performance in the synthesis of spirooxindole fused heterocycles using isatins, cyanomethanes, and cyclic 1,3-dicarbonyl derivatives as starting materials in one pot in $H_2O$ (Figure 35). In the initial investigation, reaction of 3-hydroxy-1*H*-phenalen-1-one, malononitrile with isatin was carried out in refluxing water in the presence of 10 mol % $CuFe_2O_4$ for 30 min, and the desired spirooxindole was isolated in 90% yield. Investigation of the reaction scope using various cyclic 1,3-dicarbonyl compounds, cyanomethanes, and isatins revealed that the $CuFe_2O_4$-catalyzed tandem three-component reactions method tolerated a range of substrates, affording various spirooxindole fused heterocycles in 81−97% yields. The catalytic activity remained unaltered throughout four runs, showing the efficiency and "green" character of this catalyst.



Yield: 81-96%

**Figure 35.** Synthesis of spirooxindole-fused heterocycles from isatins, active cyanomethanes, and cyclic 1,3-dicarbonyl derivatives catalyzed by $CuFe_2O_4$.

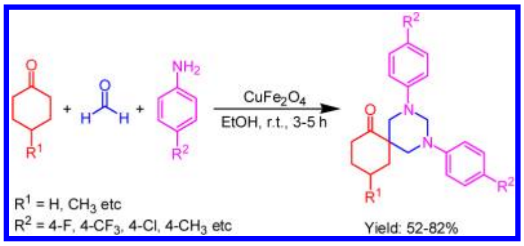
Silica-supported $Fe_3O_4$ NPs were applied to promote the reaction of 1,2-diamines, two components of terminal alkynes, and isocyanide in EtOH at rt, yielding diazepines (Figure 36).[275] This two-step procedure was achieved in one pot; first, reaction of 1,2-diamines with terminal alkynes proceeded in the presence of silica-supported $Fe_3O_4$ for a few hours; then isocyanide was added into the same pot. Three diazepine derivatives containing different substituents were synthesized with 83−92% yields. The magnetically recycled catalyst could be used for at least five times, and isolated yields were similar and remained with no detectable loss.



| $R^1$ | $R^2$ | Time (h) | Yield (%) |
|---|---|---|---|
| CN | H | 10 | 85 |
| CN | $CH_3$ | 12 | 87 |
| CN | Br | 12 | 75 |

**Figure 36.** One-pot multicomponent synthesis of diazepines using 1,2-diamines, terminal alkynes, and isocyanide catalyzed by silica-supported $Fe_3O_4$.

Dandia's group demonstrated that $CuFe_2O_4$ was as a highly efficient and magnetically recoverable catalyst for the one-pot synthesis of spirohexahydropyrimidines from ketones, aromatic amines, and formaldehyde (Figure 37).[276] Reaction of cyclohexanone, formaldehyde, and 4-fluoroaniline was chosen as the model reaction to optimize the reaction conditions of solvent, reaction times, and catalyst amount, and optimized results (82% yield) were obtained using ethanol and 10 mol % $CuFe_2O_4$ within 3 h. The reaction was extended to various aromatic amines, and $CuFe_2O_4$ was recovered and reused 5 times with 82%, 81%, 80%, 79%, and 79% yield.

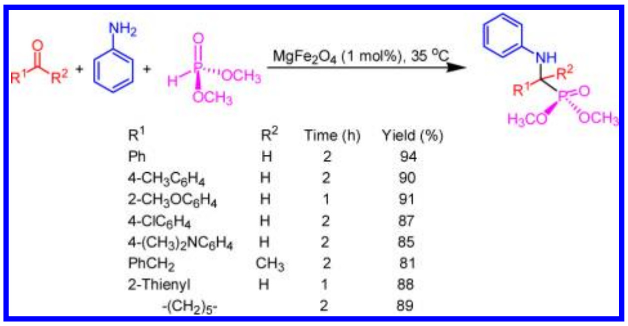


$R^1$ = H, $CH_3$ etc
$R^2$ = 4-F, 4-$CF_3$, 4-Cl, 4-$CH_3$ etc
Yield: 52-82%

**Figure 37.** Synthesis of spirohexahydropyrimidines from ketones, aromatic amines, and formaldehyde catalyzed by $CuFe_2O_4$.

A three-component coupling reaction of aldehyde, alkyne, and amine ($A^3$-coupling) catalyzed by graphene−$Fe_3O_4$ composite provided a wide range of propargylamines in 65−92% yields. This catalyst exhibited excellent magnetically recoverability, but decreases of 11% in yield were found from the first to the second cycle and from the second to the third cycle.[285]

*α*-Aminophosphonates are essential biologically active compounds. They were synthesized through a three-component coupling reaction involving carbonyl compounds, amines, and dialkyl phosphate using $MgFe_2O_4$ as Lewis acid catalyst in good to good to excellent yields in a short time (Figure 38). After completion of the first cycle, $MgFe_2O_4$ was removed with an external magnet from the reaction medium and reused for successive 5 runs with the same catalytic activity.[286]



| $R^1$ | $R^2$ | Time (h) | Yield (%) |
|---|---|---|---|
| Ph | H | 2 | 94 |
| 4-$CH_3C_6H_4$ | H | 2 | 90 |
| 2-$CH_3OC_6H_4$ | H | 1 | 91 |
| 4-$ClC_6H_4$ | H | 2 | 87 |
| 4-$(CH_3)_2NC_6H_4$ | H | 2 | 85 |
| $PhCH_2$ | $CH_3$ | 2 | 81 |
| 2-Thienyl | H | 1 | 88 |
| -$(CH_2)_5$- | | 2 | 89 |

**Figure 38.** One-pot multicomponent synthesis *α*-aminophosphonates catalyzed by $MgFe_2O_4$.

### 2.1.9. Fenton-Like Reactions.

Among various techniques of water treatment, the Fenton technique ($H_2O_2$ + $Fe^{2+}$/$Fe^{3+}$)[287] has proved to be one of the most effective methods for degrading organic pollutants in wastewater. It is an advanced oxidation process (AOP), where the "HO•" radicals (that might be coordinated to iron) usually are the main highly reactive oxidizing species generated from decomposition of hydrogen peroxide in the presence of iron cation. The homogeneous Fenton process has many drawbacks: it requires further treatment for toxic sludges and other waste products, neutralization of treated solutions before discharge, incomplete pollutant removal, and high-energy requirement. In order to overcome these drawbacks, heterogeneous Fenton-like systems using pure form or dispersed iron oxide particles on a support have been recently developed. Voelker and Kwan[288] provided a reasonable mechanism for production of $HO^{\bullet}$ via iron oxide particles as follows

$$Fe^{2+} + H_2O_2 \rightarrow HO^{\bullet} + Fe^{3+} \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{3+}(H_2O_2) \quad (2)$$

$$Fe^{3+}(H_2O_2) \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+} \quad (3)$$

Iron oxide NPs without support displayed good catalytic performance in the Fenton-like reactions for oxidative degradation of contaminants;[289,290] however, a severe Fe leaching problem restricted their applications. Therefore, various supports or stabilizers including MWCNTs,[68] rGO,[291] citrate,[292] $CeO_2$,[293] mesoporous $SiO_2$,[294] and hydrogel[295] were widely used for anchoring iron oxide NPs; moreover, the supports enhanced the activity of iron oxide through strong adsorption of pollutants to catalytic sites. In addition, several other strategies have recently been developed to improve the catalytic efficiency of iron oxide NPs, such as microwave assistance,[296] light assistance (photo-Fenton process),[297] and other metal doping processes.[298,299]

The catalytic property of a magnetic nanoscaled $Fe_3O_4/CeO_2$ composite in the Fenton oxidation of 4-CP was investigated by Wang's group.[293] The $Fe_3O_4/CeO_2$ composite with a size of 5−10 nm was prepared through the impregnation method with $CeO_2$ NPs and iron precursors and utilized for catalyzing degradation of 4-CP at different pH values, catalytic amounts, 4-CP concentrations, and reaction temperatures in the presence of various $H_2O_2$ dosages. When the reaction was conducted at 30 °C and pH 3.0 with 30 mM $H_2O_2$, 2.0 g $L^{-1}$ $Fe_3O_4/CeO_2$, and 0.78 mM 4-CP, a high pseudo-first-order kinetic constant of 0.11 $min^{-1}$ was provided. The catalyst was reused in six successive catalytic cycles, and partial dissolution of the NPs on the surface was observed from HRTEM analysis.

$SiO_2$ microspheres-supported and free $\gamma$-$Fe_2O_3$ NPs were applied as catalyst in a series of Fenton-like reactions for degradation of methylene blue (MB), methyl orange (MO), or paranitrophenol (PNP).[294] Investigation of the MO decomposition revealed that the free $\gamma$-$Fe_2O_3$ NPs showed higher activity than the supported version, which could be attributed to the facility for the reactants to access to the catalytic sites of free $\gamma$-$Fe_2O_3$. However, $SiO_2$ microspheres-supported $\gamma$-$Fe_2O_3$ NPs provided a better catalytic performance than the free version for degradation of MB in terms of the initial rates of decolorization ($v_0$) and the decolorization yield (DY), which was explained by the very strong adsorption of MB on the silica surface. Both catalysts afforded moderate mineralization yields (MY) for MO and PNP.[294]

#### 2.1.10. Other Reactions.

Other recent advances in magnetically recoverable transition metal catalysis focused on Cu-catalyzed oxidative polymerization,[300] Ru-catalyzed succinic acid synthesis from levulinic acid,[301] degradation of contaminants in water,[302−310] esterification,[311] synthesis of $\beta$-hydroxy hydroperoxides,[312] synthesis of bis(indolyl)methanes,[313] synthesis of spirooxindoles,[314] Cu-catalyzed oxidative homocoupling of terminal alkynes,[315] dehydrogenation,[316−319] Friedel−Crafts reaction,[320] synthesis of *N*-substituted pyrroles,[321] alkoxycarbonylation,[322] Pd-catalyzed reductive amination of aldehydes,[323,324] synthesis of diverse *N*-heterocycles,[325,326] oxidative cross-dehydrogenative coupling,[327] Cr-catalyzed hydroxylation of benzene,[328] glycolysis of poly(ethylene terephthalate),[329] synthesis of coumarins via Pechmann reaction,[330] and so on.

Cu(II)−PAMAM dendrimer complexes showed excellent catalytic activity in the aerobic oxidative polymerization of 2,6-dimethylphenol (DMP) to poly(2,6-dimethyl-1,4-phenylene oxide) (PPO).[331] To achieve the recovery of the Cu catalyst, Cu(II) complexes supported on G0−G3 PAMAM-coated $Fe_3O_4$ NPs (named Mag-PAMAM-Cu) were prepared and employed as catalysts in the polymerization that was carried out with an aqueous solution of DMP, sodium *n*-dodecyl sulfate, and sodium hydroxide under an oxygen atmosphere at 50 °C. The catalytic activity of the Cu complexes was influenced by the generation number of the PAMAM dendrimer, and Mag-PAMAMG3-Cu gave a superior performance (80.85% PPO yield and 99.8% selectivity toward PPO) than Mag-PAMAMG1-Cu and Mag-PAMAMG2-Cu in the first reaction cycle. Unfortunately, EA and TGA depicted that 25−30% Cu was lost during the reaction or recovery process, which caused an obvious decrease in yields and molecular weight of PPO in the second and third runs. The authors indicated that the main reason for low recovery ratios was the dissociation of Cu(II) with amine groups of PAMAM dendrimers occurring during the recovery after polymerization (Figure 39).[332]

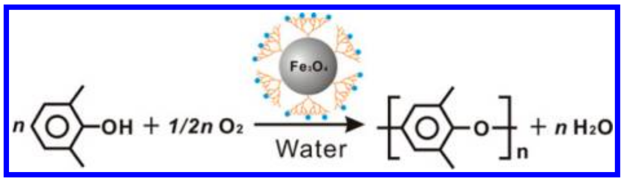


**Figure 39.** Oxidative polymerization of DMP with/Mag−PAMAM−Cu catalyst.[332] Reprinted with permission from ref 332. Copyright 2012 Elsevier Ltd.

MNPs catalysis is one of the most popular techniques in water treatment. Various contaminations including diclofenac, *p*-chlorophenol, organic dyes, tetrabromobisphenol A (TBBPA), rhodamine B, and acetylsalicylic acid were efficiently degraded in water by MNPs-supported catalysts.

Reduction of pollutants to nontoxic compounds is an effective strategy in water treatment. Zhou et al. demonstrated the preparation of AgNPs embedded in the $Fe_3O_4$@C template NPs with porous carbon shell and their catalytic application in the reduction of organic dye rhodamine B in water. The $Fe_3O_4$@C−Ag hybrid catalyst exhibited highly efficient property and was easily collected and reused without loss of activity.[333] $Fe_3O_4$-immobilized PdNPs provided a remarkable catalytic behavior in bromate reduction to bromide.[334] One hundred percent conversion was achieved within less than 2 h over a range of pH values. The quasi-monodisperse $Pd/Fe_3O_4$ catalyst showed good recoverability using an external magnetic field and stability.

A core−satellite structured $Au/Pdop/SiO_2/Fe_3O_4$ composite was synthesized via a simple method and provided high catalytic performance in the catalysis of MB reduction with $NaBH_4$ as a reducing agent at rt.[335] Full conversion of MB was observed within 30 s over 10 mg of $Au/Pdop/SiO_2/Fe_3O_4$ with a MB concentration of 0.02 mM. MB was completely degraded in 20 min when the concentration was increased to 0.2 mM.

The authors indicated that the high catalytic performance of Au/Pdop/$SiO_2$/$Fe_3O_4$ is partly attributed to the effective contact between Pdop (polydopamine) and the Au nanocatalysts. The catalyst was magnetically removed from the reaction medium, and a gradual decrease in catalytic efficiency was found in the first 5 runs. Zhang and co-workers[336] applied rGO-supported $Fe_3O_4$ (4.8 nm in size) PtNPs (5 nm in size) as a catalyst with high performance in the reduction of MB. The versatile rGO-supported $Fe_3O_4$−Pt composite also efficiently promotes aqueous-phase aerobic oxidation of benzyl alcohol. This kind of rGO-supported $Fe_3O_4$−metal composite is simply synthesized through the solvothermal method and possesses great potential applications in catalysis and other fields.

The Salen Cu(II) complex was connected to the surface of $SiO_2$-coated $Fe_3O_4$ nanoparticles, and this nanocatalyst was used in the synthesis of 1- and 5-substituted 1*H*-tetrazoles under various conditions (Figure 40).[337] A series of 1-substituted 1*H*-tetrazoles was isolated in good to excellent yields through the reaction of triethyl orthoformate, sodium azide, and several amines at 100 °C under solvent-free conditions over 20 mg of catalyst containing 0.4 mol % Cu(II). Thirteen different 5-substituted 1*H*-tetrazoles in 80−92% yields were synthesized from cycloaddition of sodium azide and nitrile compounds containing a broad scope of substituents at 120 °C in DMF in the presence of 20 mg of $Fe_3O_4$@$SiO_2$−Salen Cu(II). Its catalytic recyclability was investigated based on the case of the cyclization of *p*-methoxy aniline, triethyl orthoformate, and sodium azide, and the nanocatalyst was magnetically collected and reused for seven subsequent reaction cycles without deterioration of the catalytic activity. ICP analysis revealed that the leaching amounts of Cu from the initial catalyst were 0.2% and 5.4% after the first and seventh repeated runs, respectively.

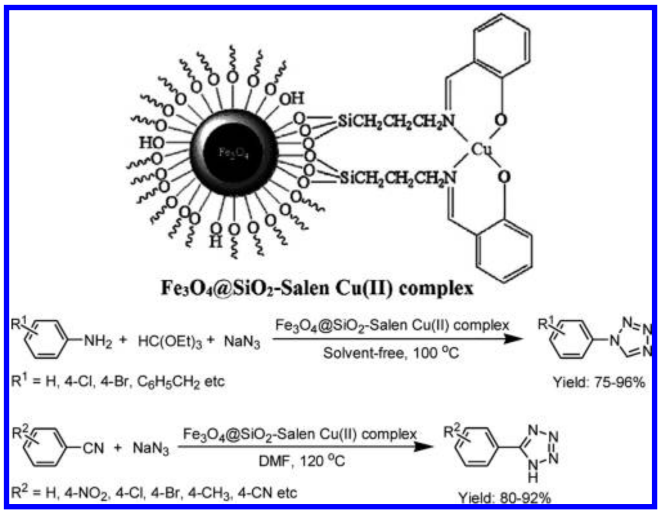


**Figure 40.** $Fe_3O_4$@$SiO_2$−Salen Cu(II)-catalyzed synthesis of 1- and 5-substituted 1*H*-tetrazoles.[337] Reprinted with permission from ref 337. Copyright 2013 Elsevier B.V.

Implantation of AgNPs into the mesoporous spheres of HMMS material was achieved via a six-step procedure using colloidal carbon spheres as templates.[338] Condensation of dicarbonyl compounds with amines forming *β*-enaminones was chosen as a model reaction to evaluate the catalytic property of Ag/HMMS (Figure 41). The reactions proceeded smoothly in methanol at 60 °C within a short time over 31 mg of catalyst, providing 84−100% yields.[338] In addition, the good magnetic recoverability and recyclability of the nanocatalys were verified via a catalytic recycling test.

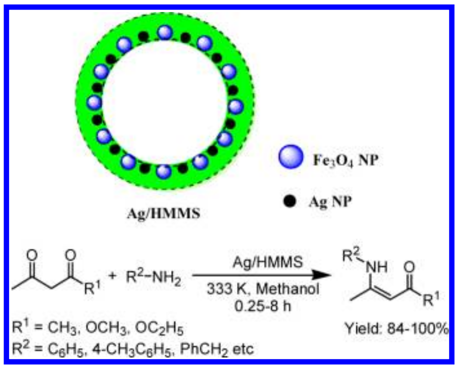


**Figure 41.** Synthesis of *β*-enaminones over Ag/hollow magnetic mesoporous spheres (Ag/HMMS).[338] Reprinted with permission from ref 338. Copyright 2013 Elsevier B.V.

The Ullmann-type coupling procedure has been shown to be a useful strategy to form carbon−oxygen bonds. Xu et al.[339] found that the stable, easily made, and low-cost magnetic catalyst $CuFe_2O_4$ showed high catalytic activity for the Ullmann C−O coupling reaction between phenols and aryl halides. Phenol and iodobenzene were chosen as model substrates, and diphenyl ether was synthesized in 99% yield when the reaction was promoted with 5 mol % $CuFe_2O_4$ and 10 mol % diketone ligand 2,2,6,6-tetramethylheptane-3,5-dione in NMP at 135 °C using $Cs_2CO_3$ as base. In the investigation of the substrate scope, a series of aryl ethers was obtained in good to excellent yields through reaction of various kinds of phenols with aryl iodides. Aryl bromides, instead of aryl iodides, were also suitable coupling partners of phenols. When 2-chloropyridine was used, the corresponding aryl ether was detected with 65% yield; unfortunately, chlorobenzene only gave traces of product. The reusability of the catalyst showed that $CuFe_2O_4$ was magnetically removed from the reaction medium and reused for 6 runs with obvious and steady decrease in yield under 5 mol % catalyst owing to a slight particle aggregation, decomposition of part $CuFe_2O_4$ NPs, and progressive loss during the recovery process. A 98% yield was obtained after the fifth reaction cycle over 10 mol % $CuFe_2O_4$. A carbon nanotube-supported $\alpha$-$Fe_2O_3$@CuO nanocomposite was another outstanding magnetic catalyst for cross-coupling of aryl halides with phenols to fabricate C−O bonds, and the catalyst was reused up to six reaction cycles without any loss of catalytic activity.[340]

$CuFe_2O_4$ MNPs with a particle size in the 10−30 nm range were an efficient catalyst for amination of iodides with ammonia in PEG.[341] Reactions involving various aryl or aliphatic iodides gave the corresponding arylamines in moderate to good yields, but the strategy was not amenable to aryl bromides. The catalyst was magnetically separable and used for at least five cycles with a slight decline in catalytic activity.[341]

## 2.2. Magnetically Recyclable Organocatalysts

Organocatalysis plays a decisive role in the field of catalysis, and the number of publications on MNPs-supported organocatalysis has dramatically increased during the past 2 years.

Direct asymmetric aldol reactions constructing C−C bonds are a popular strategy in the synthesis of chiral organic compounds. Since List et al. developed the asymmetric aldol reactions catalyzed by L-proline,[342] research on supported L-proline and its derivatives for aldol reactions has rapidly progressed. Recently, some proline-functionalized magnetic core−shell NPs were designed and used as efficient and recyclable organocatalysts for asymmetric aldol reactions. A novel hybrid consisting of a $Fe_3O_4$ core and polymer brush-like coating with acrylates or methacylates derived from *trans*-4-hydroxyproline was prepared. The organic nanocatalyst displayed excellent catalytic performance in asymmetric aldol reactions of ketones with aromatic aldehydes and performed very well in the recyclability test.[343] L-4-Hydroxyproline-grafted $Fe_3O_4@SiO_2$ MNPs promoted the asymmetric aldol reaction of ketone with aldehyde smoothly with good catalytic activity and selectivity (diastereoselectivity and enantioselectivity). In addition, the catalysts were magnetically separated and reused for at least five cycles without significant loss in activity.[344] $Fe_3O_4@SiO_2$ MNPs decorated by L-proline-functionalized imidazolium-based ionic liquid catalyzed the asymmetric aldol reaction that was processed in water without additive.[345] For the reaction between cyclohexanone and 2-nitrobenzaldehyde, 10 mol % of this catalyst provided excellent performance in terms of yield, diastereoselectivity, enantioselectivity, and recyclability, which was attributed to facilitation of the accessibility of the hydrophobic reactants to the active sites in water due to the existence of the ionic liquid moiety and its magnetic nature.

$\alpha$-Aminophosphonate compounds with a structural analogy to $\alpha$-amino acids have been exploited for remarkable applications in modern pharmaceutical chemistry. Acidic organocatalysts including phosphotungstic acid (PTA),[346] dehydroascorbic acid (DHAA),[347] and dendritic chlorosulfuric acid[348] supported on the MNPs were synthesized and applied to the synthesis of $\alpha$-aminophosphonates. The Pourjavadi group synthesized a new magnetically separable organocatalyst consisting of chlorosulfuric acid-functionalized PAMAM dendrimers (Figure 42). The immobilized dendritic chlorosulfuric acid was shown to be an efficient heterogeneous catalyst for synthesis of $\alpha$-aminophosphonates under neat conditions at rt. The catalyst was readily recovered by an external magnetic decantation and recycled for seven reaction cycles without decrease of activity.[348]

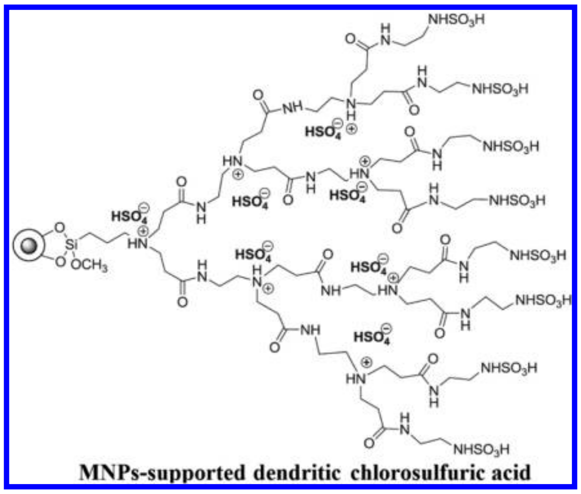


**Figure 42.** Synthesis of $\alpha$-aminophosphonates catalyzed by MNPs-supported dendritic chlorosulfuric acid.[348] Reprinted with permission from ref 348. Copyright 2012 Elsevier B.V.

Acidic organocatalysts immobilized on MNPs probably are the most common magnetic organocatalysts. Sulfonic acid,[349−359] polyphosphoric acid,[360] sulfonated-phenylacetic acid,[361] *N*-propylsulfamic acid,[362−364] chlorosulfuric acid,[365] phosphotungstic acid,[366] heteropolyacids,[367] amino acids,[368] sulphamic acid,[369] and dodecyl benzenesulfonic acid[370] were grafted onto MNPs and used as catalysts in esterification, Hantzsch reaction, one-pot synthesis of amidoalkyl naphthols, *N*-formylation reaction, Biginelli reaction, oxidation of sulfides to sulfoxides, synthesis of 2*H*-indazolo[2,1-*b*]phthalazine-triones, synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones, synthesis of 2,4,5-trisubstituted imidazoles, hydrolysis of cellulose, synthesis of 5-ethoxymethylfurfural, synthesis of imidazoles, and synthesis of a library of spirooxindole-pyrimidines in the past 2 years.

For example, Li et al.[349] synthesized nanosize or micosize magnetic catalysts containing an iron oxide core, poly(glycidyl methacrylate) (PGMA) shell, and sulfonic acid groups on the surface. The nanocatalyst with a diameter of 90 nm and high acid capacity was further used for esterification of free fatty acid (16 wt % in waste grease) to fatty acid methyl ester that was synthesized with 96% conversion within 2 h. This catalyst kept high catalytic performance in 10 successive runs. The size of the catalyst was shown to have profound effects on the catalytic property. The microsize catalyst (with a 60−350 $\mu$m diameter) provided far less catalytic performance regarding both activity and recyclability than the nanosize version. In comparison, benzenesulfonic acid-functionalized polystyrene−iron oxide (shell−core structure) MNPs and sulfonic acid-grafted silica−iron oxide (shell−core structure) were employed as catalysts for the same esterification reaction. The result showed that the catalyst with polystyrene as shell could not be recycled; the one with sulfonic acid as shell did not perform well concerning catalytic activity and recyclability.

Koukabi et al.[350] reported that a magnetic particle-immobilized solid acid with a high density of sulfonic acid groups was successfully used as catalyst in the Hantzsch reactions of various aromatic, aliphatic, and heteroaromatic aldehydes, acetoacetate derivatives, and ammonium acetate. 1,4-Dihydropyridines were isolated with 90−99% yields after reactions at 90 °C in a short time under solvent-free conditions using 25 mg of catalyst. After completion of the Hantzsch reaction of benzaldehyde, ethyl acetoacetate, and ammonium acetate, the MNPs-supported solid acid catalyst was simply collected by a hand-held magnet and reused five times; the observed yields were 98%, 98%, 98%, 96%, and 96%.

$\gamma$-$Fe_2O_3@SiO_2$ NPs-anchored dodecyl benzenesulfonic acid (DDBSA) ($\gamma$-$Fe_2O_3@SiO_2$-DDBSA) catalyzed the synthesis of spirooxindole−pyrimidine derivatives by three-component condensation reactions of cyclohexane-1,3-diones, barbituric acids, and isatins or acenaphthylene-1,2-dione in water (Figure 43).[370] Dozens of spirooxindole−pyrimidine compounds were synthesized with excellent yields using this catalytic system. $\gamma$-$Fe_2O_3@SiO_2$-DDBSA was reused for 6 runs without a decline of catalytic activity.

Ionic liquids (ILs) have attracted a great amount of attention in various areas, especially recently in the utilization as catalyst, due to their unique properties of safety, excellent solubility, high ionic conductivity, negligible vapor pressure, and wide liquid range, and MNPs-supported IL types have consequently been utilized in various organic syntheses.[371,372] Pourjavadi's group designed poly(basic ionic liquid)-coated MNPs to catalyze the synthesis of 4*H*-benzo[*b*]pyrans[373] and oxidation reactions.[374] As shown in Figure 44, MNPs were coated by multilayered tungstate-based poly(ionic liquid) cross-linked

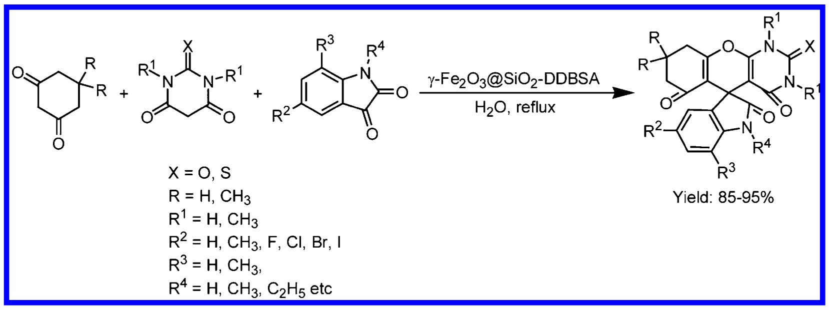


**Figure 43.** One-pot, three-component synthesis of a library of spirooxindole−pyrimidines catalyzed by MNPs-supported dodecyl benzenesulfonic acid in aqueous media.

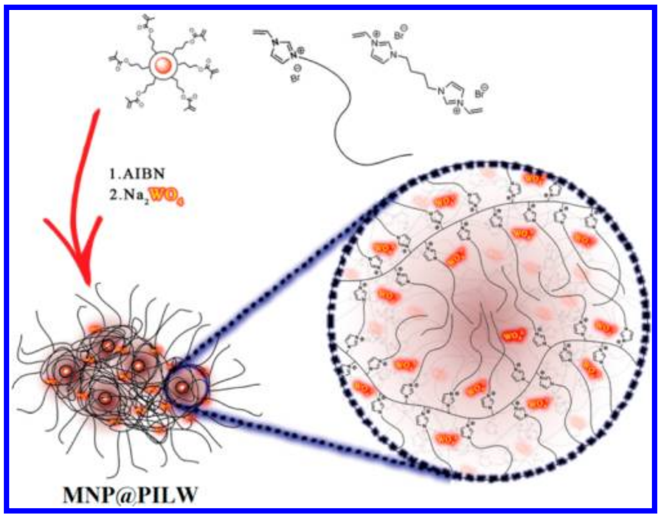


**Figure 44.** Oxidation of alcohols, sulfides, and olefins by $H_2O_2$ catalyzed by MNP@PILW.[374] Reprinted with permission from ref 374. Copyright 2013 Royal Society of Chemistry.

poly(ionic liquid) forming magnetic ionic liquid catalyst MNP@PILW that showed high performance in the selective oxidation of a wide range of alcohols, sulfides, and olefins using $H_2O_2$ as an oxidant under neat condition or in acetonitrile.[374] The excellent catalytic property was attributed to the hydrophobic surface and the multilayered nature of MNP@PILW. Product separation and catalyst recycling were easily accomplished with the assistance of an external magnet, and the catalyst was recycled several times without loss of catalytic activity.

An ionic liquid immobilized on MNPs was recently used as a magnetically recycled heterogeneous catalyst for multicomponent synthesis of aromatic heterocyclic compounds in one pot.[375] $Fe_3O_4$@$SiO_2$ MNPs-supported 3-sulfobutyl-1-(3-propyltriethoxysilane) imidazolium hydrogen sulfate was shown to be an efficient catalyst for the synthesis of benzoxanthenes by a three-component condensation of dimedone with aldehyde and 2-naphthol. A series of benzoxanthenes products was isolated with good to excellent yields from the one-pot reaction at 90 °C under solvent-free conditions within a short time. This "quasi-homogeneous" catalyst also exhibited excellent recyclability during six reaction cycles.[62]

Magnetic organocatalysts have been widely used to catalyze one-pot syntheses. Besides the above-mentioned examples, other reactions focused on the synthesis of pyrazolophthalazinyl spirooxindoles,[376] pyran-annulated heterocyclic compounds,[377] α-acyloxy carboxamides,[378] chromene derivatives,[379,380] triazolo[1,2-*a*]indazole-triones,[381] 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-dione derivatives[382] over $Fe_3O_4$-supported methylene dipyridine, $Fe_3O_4$@$SiO_2$-diazoniabicyclo-[2.2.2]octane dichloride (DABCO), $Fe_3O_4$@$SiO_2$-TEMPO, quinuclidine stabilized on $FeNi_3$ NPs, (3-aminopropyl)-triethoxysilane-modified $Fe_3O_4$ NPs, aminopropyl coated on magnetic $Fe_3O_4$ and SBA-15 NPs, etc.

TEMPO (2,2,6,6-tetramethyl-piperidin-1-oxyl) is a remarkable catalyst for oxidation reactions. SBA-15- and MNPs-supported TEMPO have been used to efficiently catalyze the aerobic oxidation of alcohols.[383−385] Karimi and co-workers[378] prepared TEMPO supported on the core−shell $Fe_3O_4$@$SiO_2$ MNPs (named MNST) and used this nanomaterial as catalyst in a new domino oxidative Passerini three-component reaction with either primary or secondary alcohols instead of their corresponding aldehydes or ketones (Figure 45). A wide range of α-acyloxy carboxamide compounds were obtained in toluene under a balloon pressure of oxygen at rt in the presence of 10 mol % *tert*-butyl nitrite (TBN) over 1 mol % MNST with moderate to good yields. The test of recyclability was conducted based on the reaction of benzyl alcohol and 4-methoxyphenylacetic acid, and MNST was magnetically removed from the reaction medium; after washing with $H_2O$ and EtOH it was repeatedly used for 14 consecutive cycles with a slight decline of catalytic activity.

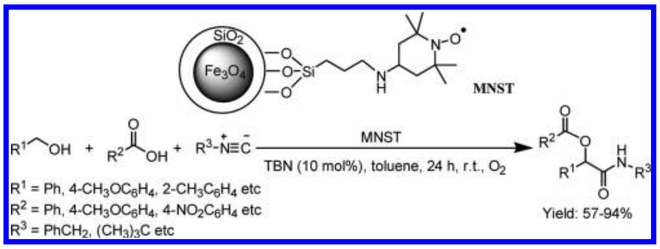


**Figure 45.** Oxidative Passerini reaction of alcohols using MNST.

Proline-stabilized $Fe_3O_4$ NPs were readily constructed in one pot without any supplemental linkers using commercially available Fe precursors and proline.[380] This catalyst with a mean diameter of around 43 nm was examined in the synthesis of chromene derivatives. The synthetic procedure was divided into two steps: condensation of benzaldehyde and malononitrile and ring annulations with 2-hydroxynaphthalene-1,4- dione or 4-hydroxycoumarin (Figure 46).[380] A series of functionalized chromene derivatives was synthesized under ambient conditions in excellent yields. The recyclability investigation revealed that use of a magnet allowed easy recovery of the catalyst that was successively reused for at least four times without loss in activity nor any iron leaching.

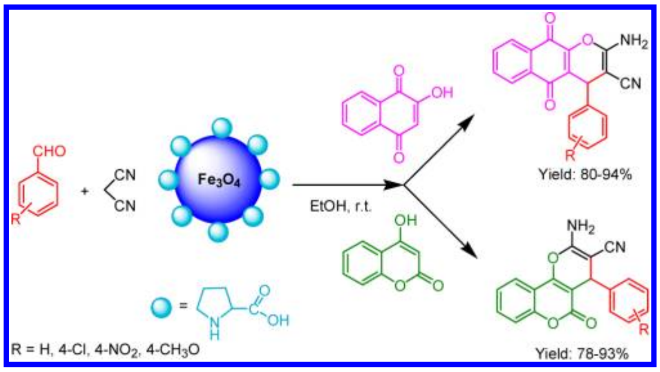


**Figure 46.** Synthesis of chromene derivatives using $Fe_3O_4$−proline MNPs.

As an essential catalyst for production of chemicals, β-cyclodextrin was grafted with MNPs, and this catalyst was then applied to promote the nucleophilic substitution reaction of benzyl halide[386] and selective oxidation of alcohols.[387] $Fe_3O_4$@$SiO_2$-anchored β-cyclodextrin (named $Fe_3O_4$@$SiO_2$−PGMACD) was readily prepared by polymerization on the surfaces of $Fe_3O_4$@$SiO_2$ and catalyzed the ring-opening reaction of epoxy groups. $Fe_3O_4$@$SiO_2$−PGMACD showed a high performance in the selective oxidation of alcohols using NaOCl as an oxidant, and its catalytic activity was similar to that of pure β-cyclodextrin.[388] Magnetic separation property and excellent recyclability of $Fe_3O_4$@$SiO_2$−PGMACD were obtained in the oxidation of benzyl alcohol (Figure 47).

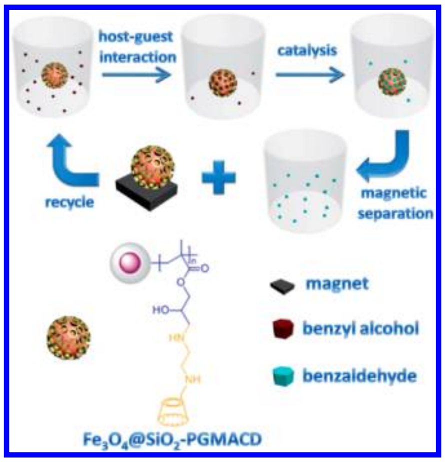


**Figure 47.** Schematic representation of the substrate-selective catalysis and recycling of the immobilized catalyst $Fe_3O_4$@$SiO_2$−PGMACD.[388] Reprinted with permission from ref 388. Copyright 2011 Royal Society of Chemistry.

Magnetic nanomaterials make a bridge between homogeneous and heterogeneous catalysts, and their use keeps the remarkable catalytic activity of homogeneous catalysts while providing recycling possibilities through simple magnetic separation. Dendrimers possess the same capability in catalysis.[389−392] Ouali et al.[393] prepared both magnetic nanomaterial- and dendrimer-supported organocatalysts. First, the Jørgensen−Hayashi catalyst [(*S*)-α,α-diphenylprolinol trimethylsilyl ether] was immobilized onto the surface of polymer-coated Co/C nanobeads and at the periphery of phosphorus dendrimers (generations 1−3). Both supported catalysts provided high performance in terms of activities and selectivities in the Michael additions of various aldehydes with nitroolefins (Figure 48). After completion of the reaction, these catalysts were recovered by magnetic decantation and precipitation with pentane, respectively. A phosphorus dendrimer (generation 3) supported catalyst was reused for at least 4 runs without loss of activity; however, an obvious decrease in activity of Co/C-immobilized catalyst was detected.

Other recent reactions catalyzed by magnetic organocatalysts include asymmetric Friedel−Crafts alkylation of *N*-substituted pyrroles with α,β-unsaturated aldehydes catalyzed by $Fe_3O_4$-supported MacMillan,[394] regioselective epoxide ring opening with phenol catalyzed by MNPs-immobilized dimethylaminopyridine,[395] phospha−Michael addition of diethyl phosphate catalyzed by γ-$Fe_2O_3$-pyridine,[396] C−S bond formation catalyzed by mPANI/$Fe_3O_4$ nanocomposite,[397] selective oxidation of sulfide catalyzed by $Fe_3O_4$-supported DABCO,[398] reduction of methylene blue dye catalyzed by yolk/shell $Fe_3O_4$@polypyrrole composites,[399] synthesis of phenylpyrido-[4,3-*d*]pyrimidins catalyzed by ($Fe_2O_3$)−MCM-41−*n*Pr$NH_2$,[400] acylation catalyzed vitamin B1 supported on γ-$Fe_2O_3$@$SiO_2$,[401] and Knoevenagel condensation catalyzed by polyvinyl amine-coated $Fe_3O_4$@$SiO_2$ NPs.[402]

## 2.3. Magnetically Recyclable Biocatalysts

Magnetically recyclable biocatalysts were developed during the past 2 years, and some new immobilization methods of enzymes and new magnetic supports were explored.

Silica-coated MNPs are still the most involved supports for biocatalysts.[403] Zhang et al.[404] demonstrated that α-amylase supported on amine-functionalized $SiO_2$@$Fe_3O_4$ NPs with high loading (235 mg/g) were readily prepared through adsorptive immobilization. The magnetic biocatalyst was evaluated in the hydrolysis of starch that is a polymer of many glucose units. The catalytic activities of immobilized and free α-amylase were measured by amylase activity units that were defined as the required amount of enzyme to hydrolyze 1 mg of starch in 1 h under appointed conditions. The activity of immobilized α-amylase was about 80% of that of the nonimmobilized counterpart. However, the presented magnetic α-amylase was recycled for at least three runs while maintaining similar enzymatic activity. Amine-functionalized $SiO_2$@$Fe_3O_4$ NPs were also used to anchor porcine pancrease lipase via covalent immobilization, from which the enhancement of stability (in terms of thermal, pH, and storage) and catalytic activity were observed.[405]

A recent study revealed that carbonic anhydrase (CA) provided excellent enzymatic activity in the catalytic conversion of $CO_2$ to bicarbonate.[406] Subsequently, bovine CA was successfully immobilized on (octa(aminophenyl)-silsesquioxane)-modified $Fe_3O_4$/$SiO_2$ NPs via covalent bonding (Figure 49).[407] This magnetic biocatalyst with good storage stability displayed satisfactory activity for sequestration of $CO_2$ even after 30 reaction cycles using an external magnetic field as a separating tool.

In addition to $SiO_2$-capped iron oxide NPs, other magnetic supports such as alpha chymotrypsin-coated $Fe_3O_4$,[408] iron oxide filled magnetic carbon nanotube,[409] a surfactant gum arabic-coated $Fe_3O_4$ NPs,[410] and silica-based β-cyclodextrin[411] were synthesized and used to bind enzymes via covalent[412,413] and noncovalent immobilization[414] to construct magnetically recyclable biocatalysts.

Since the discovery of carbon nanotubes (CNTs) in 1991,[415,416] they have received considerable attention to date

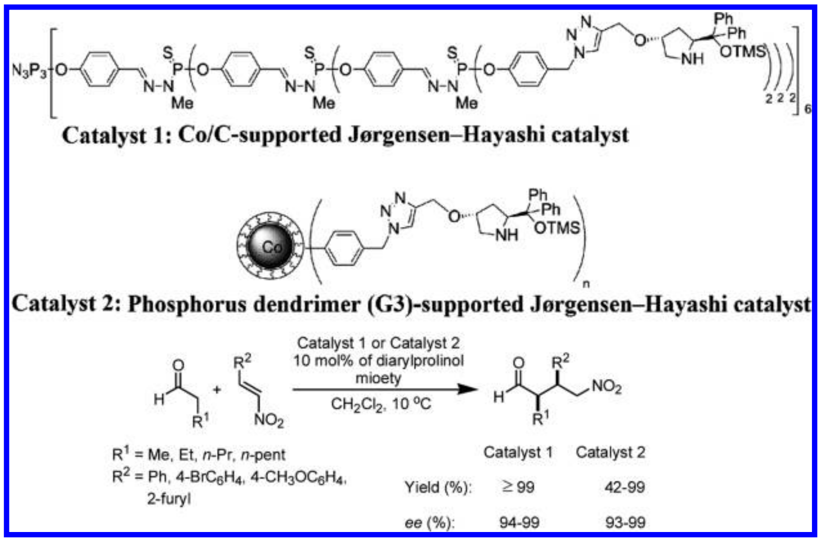


**Figure 48.** Addition of propanal *β*-nitrostyrene in the presence of dendrimer- and MNPs-supported Jørgensen−Hayashi catalysts.[393] Reprinted with permission from ref 393. Copyright 2013 Wiley-VCH Verlag GmbH & Co.

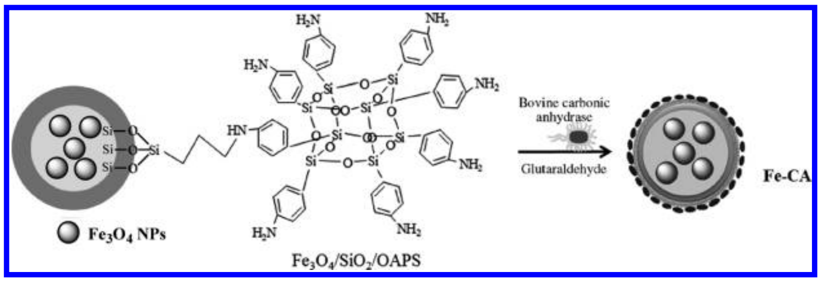


**Figure 49.** Immobilization of bovine carbonic anhydrase on encapsulated MNPs.[407] Reprinted with permission from ref 407. Copyright 2012 Wiley-VCHVerlagGmbH & Co.

toward various applications, in particular in catalysis because of their high surface area, strong adsorption ability, and great accessibility. CNTs-supported enzymes with high stability have been reported;[417] however, the inconvenient recovery restricted their industrial applications.[418] Use of MNPs-filled CNTs is a promising protocol to solve the issue. Pastorin's group[419] designed and synthesized Amloglucosidase (AMG) supported on CNTs and MNPs-filled CNTs, and immobilization was achieved through physical adsorption and covalent immobilization (Figure 50). The immobilized enzymes disclosed high storage stability in acetate buffer at 4 °C. Their activities were determined upon using starch as the substrate, and lower activity was found compared to free AMG; pristine CNTs provided better activity than magnetic CNTs. Excellent recyclability was observed in all cases of supported AMG. Owing to their magnetic property, magnetic CNTs-supported AMG were easily and efficiently recovered from the reaction medium using a magnet.

Use of *β*-cyclodextrin-grafted MNPs as support for immobilization of lipase was reported for the first time by Yilmaz et al.[411] In the synthetic process the presynthesized *β*-cyclodextrin-grafted $Fe_3O_4$ NPs were readily encapsulated with *Candida rugosa* lipase forming magnetic lipase that was applied as catalyst to the hydrolysis of *p*-nitro-phenylpalmitate and enantioselective hydrolysis of racemic Naproxen methyl ester (Figure 51). These reactions proceeded in an aqueous buffer solution/isooctane reaction system, providing high conversion and enantioselectivity (*E* value = 399). For comparison, the enantioselective hydrolysis reaction was also carried out over free lipase, and an *E* value of 137 was measured, which indicated that immobilization of lipase brought about a remarkable enhancement of enantioselectivity. In addition, the immobilized biocatalyst was magnetically collected and reused.

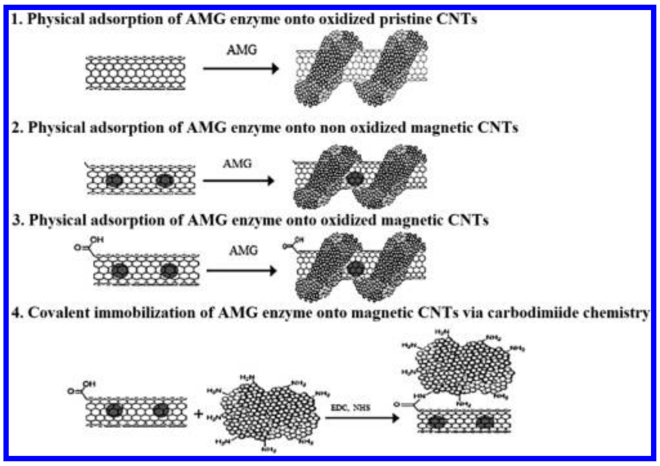


**Figure 50.** Immobilization of AMG on CNTs.[419] Reprinted with permission from ref 419. Copyright 2012 American Chemical Society.

The size of nanocatalysts is a crucial factor for their catalytic performance. In general, nanocatalysts with smaller diameter exhibit better activity compared to larger versions. In the catalytic application of MNPs-anchored catalysts, a shorter separation time is required especially for biocatalysts, which is

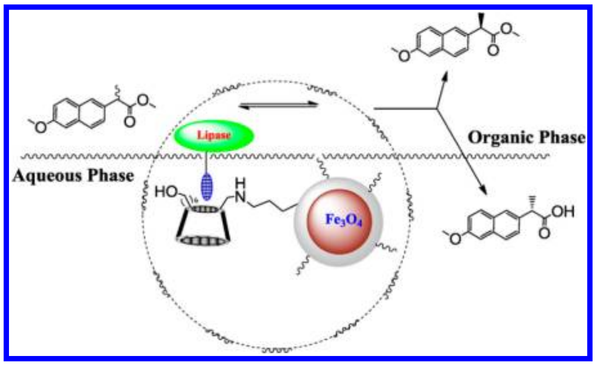


**Figure 51.** Catalysis of enantioselective hydrolysis of rasemic Naproxen methyl ester by $\beta$-cyclodextrin-grafted MNPs-supported lipase.[411] Reprinted with permission from ref 411. Copyright 2013 Elsevier B.V.

provided by the use of MNPs of small size. Li et al.[420,421] developed a practical method to reach this challenge. A novel cluster of magnetic nanobiocatalysts based on alcohol dehydrogenase (RDR) was successfully prepared via non-covalent immobilization. The cluster was reversibly formed and dissociated to individual enzyme-modified MNPs under general shaking conditions, and NPs of smaller size were potential biocatalysts with high activity. When shaking was stopped, the individual MNPs reclustered to form easily separated original clusters of magnetic biocatalysts (Figure 52). The reversible clustering of RDR-MNPs (RC RDR-MNPs) with high enzyme loading afforded the same activity and enantioselectivity as the free enzyme in the bioreduction of 7-methoxy 2-tetralone to produce (*R*)-7-methoxy-2-tetralol.[420,421] The presented biocatalyst was quickly and completely separated with a hand-held magnet and recycled for 15 runs with an acceptable decrease in activity and an enantioselectivity similar to that of the original catalyst (Figure 53).[421]

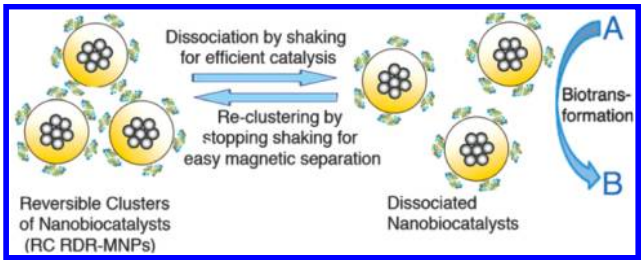


**Figure 52.** Reversible cluster formation of magnetic nanobiocatalysts.[420,421] Reprinted with permission from ref 421. Copyright 2012 Royal Society of Chemistry.

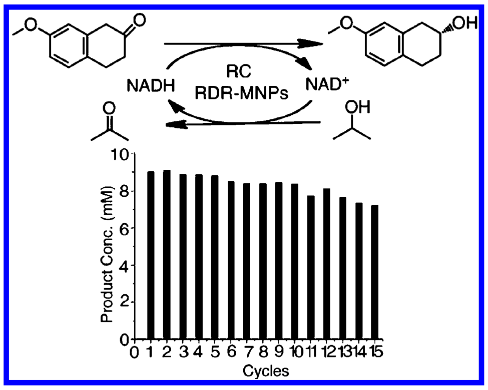


**Figure 53.** Enantioselective reduction of 7-methoxy-2-tetralone catalyzed by RC RDR-MNPs and recycling test.[421] Reprinted with permission from ref 421. Copyright 2012 Royal Society of Chemistry.

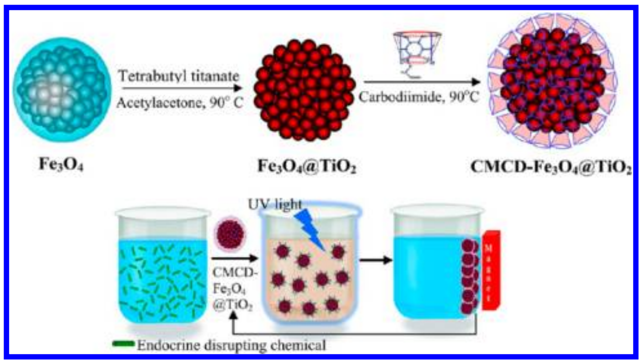


**Figure 54.** Synthesis of cyclodextrin-modified $Fe_3O_4@TiO_2$ NPs and their application to the photocatalytic degradation of endocrine-disrupting chemicals in water supplies.[424] Reprinted with permission from ref 424. Copyright 2013 American Chemical Society.

## 2.4. Magnetically Recyclable Photocatalysts in the Degradation of Pollutants

$TiO_2$ NPs are the most used catalysts in the photodegradation of pollutants, and a series of novel MNPs-supported $TiO_2$ NPs was designed and prepared. A core–shell structure of $Fe_3O_4/SiO_2/TiO_2$ composite was synthesized via the layer-by-layer technique.[422] In the process of immobilizing $TiO_2$ on presynthesized $SiO_2@Fe_3O_4$ it was found that treatment of silica surface with poly(acrylic acid) led to an enhanced stability of the photocatalyst through formation of a covalent bond between $TiO_2$ nanocrystals and silica. Moreover, the existence of the $SiO_2$ shell prevented photodissolution and transfer of electrons–holes from $TiO_2$ to core particle, and thus, the photocatalytic activity in the degradation of rhodamine B became promoted under UV illumination.[422] Another supported $TiO_2$ nanomaterial on $SiO_2@CoFe_2O_4$ showed excellent catalytic activity in the degradation of MB under UV irradiation, and 98.3% of MB was removed within 40 min.[423] Vasudevan et al.[424] demonstrated that cyclodextrin-modified $Fe_3O_4@TiO_2$ NPs (CMCD–$Fe_3O_4@TiO_2$) were easily prepared and used as photocatalyst in the decomposition of endocrine-disrupting chemicals. The reaction was successfully carried out in water thanks to the aqueous dispersibility of the nanocatalyst containing a cyclodextrin component. During the reaction process, the organic pollutant was captured and destroyed by CMCD–$Fe_3O_4@TiO_2$ under UV irradiation (Figure 54).[424] On the basis of the case of the photodegradation of bisphenol A, after completion of reaction, the catalysts were magnetically separated and reused 10 times with a slight decline of photocatalytic activity. As mentioned in the Introduction, both coupling with other semiconductors and doping with other elements are good ways to improve the photocatalytic property of $TiO_2$ NPs. In the past 2 years, samarium-doped mesoporous $TiO_2$ (Sm/$MTiO_2$) coated $Fe_3O_4$ photocatalysts,[425] magnetic and porous $TiO_2/ZnO/Fe_3O_4$/PANI,[426] core–shell nano-$TiO_2/Al_2O_3/NiFe_2O_4$ hybrid,[427] nano-$TiO_2$/C/$Fe_xO_y$,[428] and $Fe_3O_4@SiO_2@TiO_2$–Ag composites were prepared and used in degradation of MB, MO, MO, RB 5, and RhB, respectively, either under UV light or in

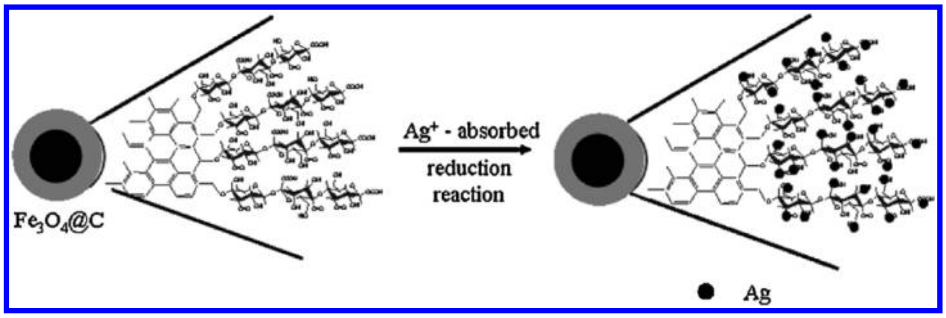


**Figure 55.** Schematic illustration of the synthetic process to Ag-loaded $Fe_3O_4$@C NPs.[433] Reprinted with permission from ref 433. Copyright 2013 Elsevier Ltd.

sunlight, and enhanced catalytic performance was observed in all cases.

A wide range of non-$TiO_2$-based metal oxides (including CuO, ZnO, $MnO_2$, $Fe_2O_3$, $Fe_3O_4$, and $Al_2O_3$) and metal sulfides (including CdS, CuS, ZnS, MnS, $Sb_2S_3$, $In_2S_3$, and $Bi_2S_3$) also exhibited good visible-light-driven catalytic activity. Several magnetic photocatalysts without $TiO_2$ were exploited and studied in degradation of organic pollutants, especially for effluents of textile wastewater. Sahu's group[429] assembled magnetic $SrFe_{12}O_{19}$ and $SrFe_{11.4}Al_{0.6}O_{19}$ by the microwave combustion method and followed by calcinations at high temperature. Both of them exhibited photocatalytic activity for decomposition of Congo red (CR) under visible and sun lights due to their low band gap. They were efficiently removed from the reaction medium using a magnetic field thanks to the reasonably high values of magnetization. Wang et al.[430] reported that the (Cu−$Fe_2O_3$/Fe)@C hybrid remarkably promoted oxidative photodegradation of MB (>90% of conversion in a short time) under UV−vis light irradiation. The high catalytic property was attributed to the surface-rich electrons of the carbon shell and the capacity of generation of photoelectrons and holes. $\gamma$-$Fe_2O_3$ NPs with a mean diameter of 35 nm displayed effective activity for the photodegradation of rose bengal (RB) and MB dyes under visible-light irradiation. The catalyst was recovered upon applying an external magnetic field to capture the $\gamma$-$Fe_2O_3$ NPs.[431] A Ni/ZnO nanomaterial was prepared by reduction of Ni ions via the solvothermal method followed by surface modification. The hexagonal Ni/ZnO nanostructure showed effective photocatalytic activity toward degradation MB molecules under visible-light irradiation and was easily recoverable in the presence of a magnetic field for successive reuses.[432]

Ag nanocrystals with a nearly spherical structure having a mean diameter of 10 nm were immobilized on carbonaceous polysaccharides shell-coated MNPs via direct adsorption of silver ions to core−shell MNPs followed by reduction of the silver ions (Figure 55).[433] Degradation of the pollutant neutral red was chosen as the model reaction for investigation of the photocatalytic activity. Photodegradation proceeded smoothly over this $Fe_3O_4$@C@Ag hybrid NPs under visible light, providing 93.7% of degradation within 30 min. In addition, the magnetic separation of the hybrid NPs was easily achieved using a hand-held magnet.

Graphene as catalyst support efficiently enhances the catalytic effect of these common photocatalysts. Graphene-supported metal oxides ($TiO_2$ and ZnO) have been identified as excellent heterogeneous photocatalysts in degradation of pollutants under UV irradiation.[434,435] Wang et al. found that the composites consisting of graphene and $MFe_2O_4$ (M = Zn, Co, Ni, Mn, and Cu)[436−439] exhibited good photoactivity in the degradation of dyes and were simply recovered upon applying an external magnetic field. The same group[440] fabricated a magnetically recoverable hybrid P25−$CoFe_2O_4$−graphene (P25, a sort of $TiO_2$ NPs) via hydrothermal approach in order to combine the advantages of each component in photocatalysis. This nanocomposite was utilized as catalyst in the visible-light-driven photodegradation of various organic dyes. P25−$CoFe_2O_4$−graphene was superior to $CoFe_2O_4$−graphene, P25−$CoFe_2O_4$, and P25−graphene photocatalysts, the enhancement of activity being caused by the synergistic effect among the individual components. The photocatalyst was collected with a hand-held magnet and reused. On the basis of the report on the fabrication of $Fe_{2.25}W_{0.75}O_4$ through doping in a $Fe_3O_4$ host matrix,[441] a novel bifunctional RGO-immobilized $Fe_{2.25}W_{0.75}O_4$ nanomaterial was synthesized through a one-pot hydrothermal method. The composite with excellent thermal stability displayed higher performance than pure $Fe_{2.5}W_{0.75}O_4$ NPs in the degradation of MO under UV-light irradiation, which was attributed to the enhancing effect of graphene. The hybrid displayed remarkable recyclability with an external magnet thanks to its magnetic property.[442]

## 3. CONCLUSIONS AND OUTLOOK

As shown here, catalysis with magnetically recyclable nanocatalysts is a rapidly growing field in the context of the high demands for development of sustainable and green chemistry. In order to prevent aggregation and achieve grafting catalyst species on presynthesized MNPs, modification and functionalization of MNPs with stabilizing ligands or coating/encapsulating materials (including small molecules, silica, polymers, carbon, ionic liquids, mesoporous materials, graphene, carbon nanotubes) are essential. Further covalent or noncovalent binding processes to transition metal catalysts, organocatalysts, and enzymes efficiently provided various magnetically recoverable catalysts that were used in a wide range of reactions during the past 2 years, such as Suzuki, Heck, Sonogashira, Hiyama, alkyne−azide cycloaddition, hydrogenation, reduction, oxidation, arylation, alkylation, epoxidation of alkenes, multicomponent "one-pot" synthesis, Fenton-like reaction, etc.

Although remarkable progress has been made using magnetically recoverable catalysts in terms of diversity of the reactions, activity, selectivity, and recyclability, both the intrinsic instability of MNPs over a long period of time and the leaching of catalysts under harsh conditions remain the major problems yet to be solved in many reported results. Development of new multifunctionalized materials and useful methods of immobilizing catalysts units are still required in order to overcome these problems.

Extension of the scope of the field by exploring more magnetically recyclable catalysts for more organic transformations is also called for. For instance, seeking magnetic plasmonic photocatalysts based on AuNPs, AgNPs, and CuNPs for promoting other organic transformations in environmentally friendly and energy sustainable protocol using the application of magnetically recyclable photocatalysts in the degradation of pollutants is a challenging goal.[89,90] Increased use of bimetals (Fe, Co, Mo) to replace expansive "noble" metals should be encouraged for increased sustainable processes. Further work is also required to push these magnetically recyclable catalysts to their use in multikilogram-scale synthesis toward industrial production. Given the fast pace of this area, progress, and perspectives it is most certainly only a matter of time before key industrial applications are realized.

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### Notes

The authors declare no competing financial interest.

### Biographies

Dong Wang studied organic chemistry with Professor Baohua Chen at the University of Lanzhou and received his doctoral degree in 2013. He is presently preparing his Ph.D. in the Nanosciences and Catalysis research group of Professor Didier Astruc at the Université de Bordeaux, where he is working on the synthesis and uses of magnetic nanoparticles-supported nanocatalysts.

Didier Astruc is Professor of Chemistry at the University of Bordeaux and Member of the Institut Universitaire de France. He did his Ph.D. work in Rennes with R. Dabard and his postdoctoral work at MIT with R. R. Schrock. His present interests are in nanomaterials and their applications in catalysis, sensing, and nanomedicine.

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Financial support from the Université de Bordeaux, the Centre National de la Recherche Scientifique (CNRS), and the Chinese Research Council (Ph.D. grant to D.W.) is gratefully acknowledged.

## ABBREVIATIONS

| | |
|---|---|
| $\beta$-CD | $\beta$-cyclodextrin |
| AAPTS | [3-(2-aminoethylamino)-propyl]-trimethoxysilane |
| AMG | amloglucosidase |
| APTS | 3-aminopropyltrimethoxysilane |
| CA | carbonic anhydrase |
| CDG | chemically derived graphene |
| DHAA | dehydroascorbic acid |
| CNTs | carbon nanotubes |
| CTAB | cetyltrimethylammonium bromide |
| CuAAC | copper-catalyzed cycloaddition of alkynes and azides |
| DABCO | diazoniabicyclo-[2.2.2]octane dichloride |
| DDBSA | dodecyl benzenesulfonic acid |
| DMEC | dimethylethynylcarbinol |
| DMP | 2,6-dimethylphenol; dimethylvinylcarbinol |
| DOPA | dopamine hydrochloride |
| DY | decolorization yield |
| EA | elemental analysis |
| *E* value | enantiomeric ratio for irreversible reactions, $E = \ln[(1 - x)(1 - ee_s)]/\ln[(1 - x)(1 + ee_s)]$ ($x$, conversion; $ee_s$, the enantiomeric excess of the substrate) |
| Fe CSNPS | iron@iron oxide core–shell nanoparticles |
| FT-IR | Fourier transform infrared spectroscopy |
| HMMS | hollow magnetic mesoporous silica spheres |

| | |
|---|---|
| HMS | hollow mesoporous silica spheres |
| HPG | hyperbranched polyglycidol |
| HPMC | hydroxypropylmethylcellulose |
| ICP | inductively coupled plasma analysis |
| ILs | ionic liquids |
| GO | graphene oxide |
| MagSilica | silica-coated magnetic nanoparticles |
| MB | methylene blue |
| MCF | magnetic $Fe_3O_4$@C |
| MCR | multicomponent reaction strategy |
| MMS | magnetic mesoporous silica spheres |
| MNPs | magnetic nanopartilces |
| MO | methyl orange |
| MVS | metal vapor synthesis |
| MW | microwave |
| MWCNT | multiwalled carbon nanotubes |
| MY | mineralization yield |
| NPs | nanoparticles |
| OA | oleic acid |
| OAPS | octa(aminophenyl)silsesquioxane |
| PAA | poly(acrylic acid) |
| PAMAM | polyaminoamido |
| PANI | polymer of aniline |
| PDA | PDMAEMA, polydopamine |
| poly(2-dimethylaminoethyl methacrylate) | |
| PEA | polyethylenimine |
| PEG | poly(ethylene glycol) |
| PFMN | phosphine-functionalized magnetic nanoparticles |
| PHEMA | poly(*N*,*N*′-methylenebis(acrylamide)-*co*-2-hydroxyethyl methacrylate), poly(glycidyl methacrylate) |
| PL | photoluminescence |
| PNP | paranitrophenol |
| PPO | poly(2,6-dimethyl-1,4-phenylene oxide) |
| PS | polystyrene |
| PTA | phosphotungstic acid |
| RB 5 | reactive black 5 |
| RDR | alcohol dehydrogenase |
| RGO | reduced graphene oxide |

| | |
|---|---|
| rt | room temperature |
| SEM | scanning electron microscopy |
| SQUID | superconducting quantum interference device |
| TEM | transmission electron microscopy |
| TEMPO | (2,2,6,6-tetramethyl-piperidin-1-oxyl) |
| TGA | thermal gravimetric analysis |
| VSM | vibrating sample magnetometer |
| XRD | X-ray diffraction (XRD) |
| XPS | X-ray photoelectron spectra (XPS) |

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## NOTE ADDED IN PROOF

Major contributions to the field of magnetically recyclable nanocatalysts have appeared since this paper was submitted concerning C−C coupling reactions,[443−446] reduction of nitroaromatics,[447−449] oxidation reactions,[450,451] epoxidation of alkenes,[452] Kabachnik−Fields reaction,[453] synthesis of arylsulfones,[454] esterification and transesterification,[455] and mini-reviews.[456,457]