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Nanoparticle-supported catalysts and catalytic reactions - a mini-review

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Nanoparticle-supported catalysts and catalytic reactions – a mini-review

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This article reviews recent developments of using nanometer-sized particular matrices for supporting catalysts and catalytic organic reactions. Immobilization of a catalyst onto the surface of an Au or magnetic (e.g. Fe_2O_3) nanoparticle allowed facile separation and recycling of the catalyst out of the reaction mixture. The activity and selectivity of the nanoparticle-supported catalytic species were found to be comparable to those of their parent catalysts in solution or their counterparts immobilized on the solid-phase. In addition, due to the unique surface structure of the nano-host, cooperative catalysis was observed in a dyad of amino acid residues and peptide analogues on the nanoparticle surface. Thereby, immobilization of catalysts on the surface of a nanoparticular matrix will not only facilitate the isolation and recovery of expensive catalysts, but also open a new avenue to regulate their activity and selectivity.

Keywords: Catalysis; Immobilization; Nanoparticle; Recycling; Support

1. Introduction

Developing novel materials for immobilizing a catalyst with the ability to maintain its activity and selectivity is a task of great economic and environmental importance in chemical and pharmaceutical industries, especially when expensive and/or toxic homogenous heavy metal complexes are employed [1]. This is because soluble transition metal composites are difficult to be separated from the product and any reaction solvent. The heavy metal contamination of a product is undesirable and must be limited to ppm or lower levels in large-scale pharmaceutical processes [2]. During recent years, solid-phase [3–5], perfluorinated tags [6, 7], ROMP gels [8, 9] and other types of synthetic polymers [10–12] have been extensively explored for supporting catalysts. Depending on the matrix used, the immobilized complexes can be isolated from reaction mixtures via either filtration (solid-phase) or the judicious selection of a second solvent for the selective precipitation of matrices out of the reaction mixtures (ROMP gels, etc.) or extraction of the scaffolds into an orthogonal liquid phase (perfluorinated

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tags). Thereby, immobilization of a soluble catalyst on a support allows the facile recovery and reuse of the expensive and toxic catalytic heavy metal species – which will cut costs and provide environmental protection benefits in industrial processes.

Recent advances in nanoscience and nanotechnology have led to a new research interest in employing nanometer-sized particles as an alternative matrix for supporting catalytic reactions. Compared with conventional supports like solid-phase, nanoparticular matrices could have a higher catalyst loading capacity due to their very large surface areas [13]. In addition, catalysts are usually immobilized on the surface of a nanocluster. Reactants in solution have easy access to the catalytic active sites of the nano-complex, avoiding the problems encountered in solid-phase resins where a great portion of catalysts are present deep inside the matrix backbones and reactants have the limited access to the catalytic sites [14]. Among nanomaterials examined, monolayer-protected Au nanoclusters (Au MPCs) and magnetic nanoclusters (e.g. maghemite nanoparticles) have received particular research attention due to their stability and tunable solubility in organic solvents. Au MPC-supported catalysts can be easily recovered after reaction via centrifugation or introduction of a second solvent for the select precipitation of Au MPC. In contrast, a catalyst immobilized on a magnetic nanoparticle can be easily recovered by applying a permanent magnet externally via magnetic concentration.

This mini-review article summarizes some recent developments on nanoparticle-supported catalysts and catalytic organic reactions. The catalysts discussed in this article include heavy metal complexes as well as organic catalysts, enzymes and biomimetic catalytic species. This article is divided into two sections focusing on Au and magnetic nanoparticle-supported catalytic reactions, respectively. In the present discussion, nanomaterials serve only as a carrier and they do not directly promote the reactions. Readers who are interested in organic transformations catalyzed by metal and metal oxide nanomaterials are directed to some recent review articles for the developments in that area [15–19].

2. Au nanoparticle-supported catalytic organic reactions

An Au nanoparticle-supported catalyst usually comprises of an Au nano-core wrapped with a monolayer of long-chained alkanethiolates and a catalyst tethered with a –SH or –S-S- terminus. The catalyst is attached to the Au surface due to the Au-S bonds [20]. Au MPCs showed remarkable stability under harsh reaction conditions including the use of strong bases or acids like trifluoroacetic acid [21, 22]. Reduction of the oxidized Au salts in the presence of alkanethiolate ligands is the method of choice for synthesizing Au nanoparticle matrices [23]. A surface-exchange reaction is usually followed to load the catalyst onto the Au nanoparticular matrices.

Tremel and coworkers have prepared an Au colloid particle supported-Ru catalyst (figure 1) [24]. FT-IR, ^{1}H NMR and surface plasmon resonance spectra were employed for analyzing and confirming the Ru catalyst on the Au particles. The Au nanoparticle-bound catalyst was then subjected to a ring-opening metathesis polymerization of norbornene in dichloromethane. The Au nanocluster-supported Ru catalyst was found to be much more active (TOF: 16,000 h^{-1}) than the unsupported counterpart
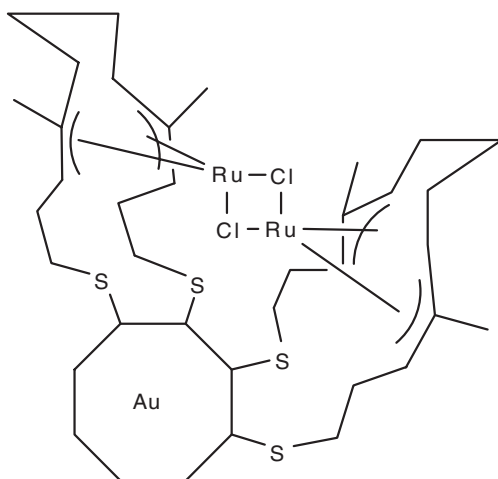
Figure 1. An Au nanoparticle-supported Ru catalyst for promoting ring-opening metathesis polymerization of norbornene.

(TOF: 3000 h^{-1}), but less active than the one on the flat Au surface (TOF: 80,000 h^{-1}). Authors suggested that the increase of the activity of the Ru catalyst immobilized on the Au nanoparticle was probably due to the orientation of the catalyst on the surface that favored its interaction with norbornene monomer molecules and the growing polymer chain. Recently, a different type of Au MPC-bound Ru catalyst (figure 2) has been examined for promoting ring-closing olefin metathesis for the synthesis of heterocyclic ring compounds [25]. It was found that the catalyst supported on the Au nanoparticle surfaces exhibited almost the same catalytic activity with that of the unbound Grubbs Ru catalyst.

The use of Au MPC-supported chiral catalysts for asymmetric induction reactions was also reported. Mrksich's laboratory has investigated the employment of a dihydroquinidine catalyst immobilized on Au nanoparticles (figure 3) for the sharpless asymmetric dihydroxylation of olefins [26]. Three substrates were examined and an average yield of 80% with an e.e. up to 90% was found. The dihydrolation of *trans*-stilbene and methyl *trans*-cinnamate under the Au catalyst was compared favorably in terms of yields and selectivities against those obtained using-polymer supported counterparts. The catalyst could be isolated and recovered by gel permeation chromatography. The recycled catalyst was found to promote the subsequent rounds of the dihydroxylation of *trans*-stilbene, however, with a modest loss in reaction yields and e.e. values of the reactions.

Another type of catalytic asymmetric reactions that have been examined under Au nanoparticle-supported chiral catalysts is the asymmetric alkylation of benzaldehyde with Et$_2$Zn (figure 4) [27]. (*R*)-1,1′-Bi-2-naphthol ((*R*)-BINOL) moieties were immobilized on the surface of Au clusters and such nano-composites were examined for catalyzing the asymmetric Et$_2$Zn alkylation of benzaldehyde by forming the Ti-BINOLate complex to afford the adduct in up to 98% yield with 86% e.e. Variations of the length of the ether linking the chiral ligand and the surface of an Au MPC host
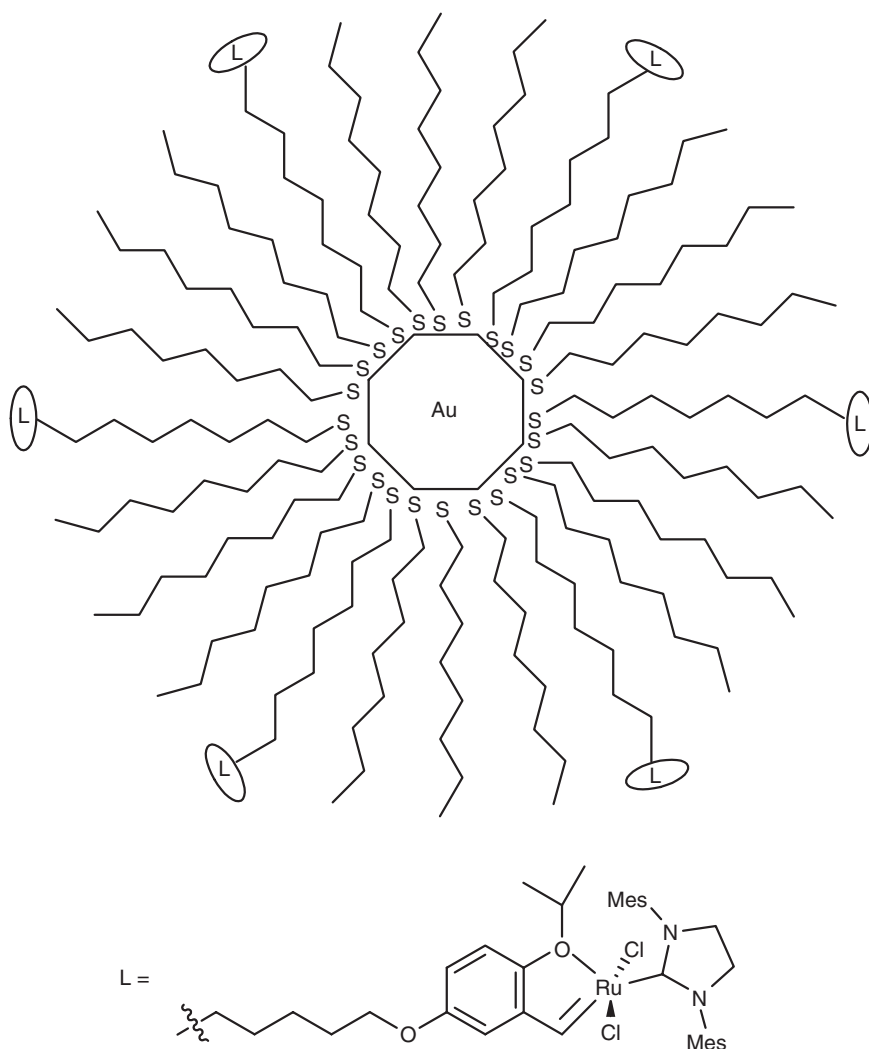
Figure 2.   An Au MPC-bound Ru-carbene catalyst employed for catalyzing ring-closing olefin metathesis.

led to slight changes of the reaction yields, but more significant variations of the e.e. values. In addition, Sasai's group has also found that the MPC was readily recovered from the reaction mixture and showed stability under acidic conditions. Similar catalysts immobilized on the surface of magnetic nanoparticles were also synthesized and investigated for catalyzing asymmetric alkylation reactions in our group (section 3) [28]. Unfortunately, lower conversion yields combined with moderate e.e. values were found. This might be due to the effects from the surface structure differences between the Au and iron oxide nanoparticles.

Stöhr and Pfaltz have incorporated chiral rhodium-diphosphine complexes into self-assembled thiolate monolayers on Au nanoparticles (figure 5) [29]. The results show
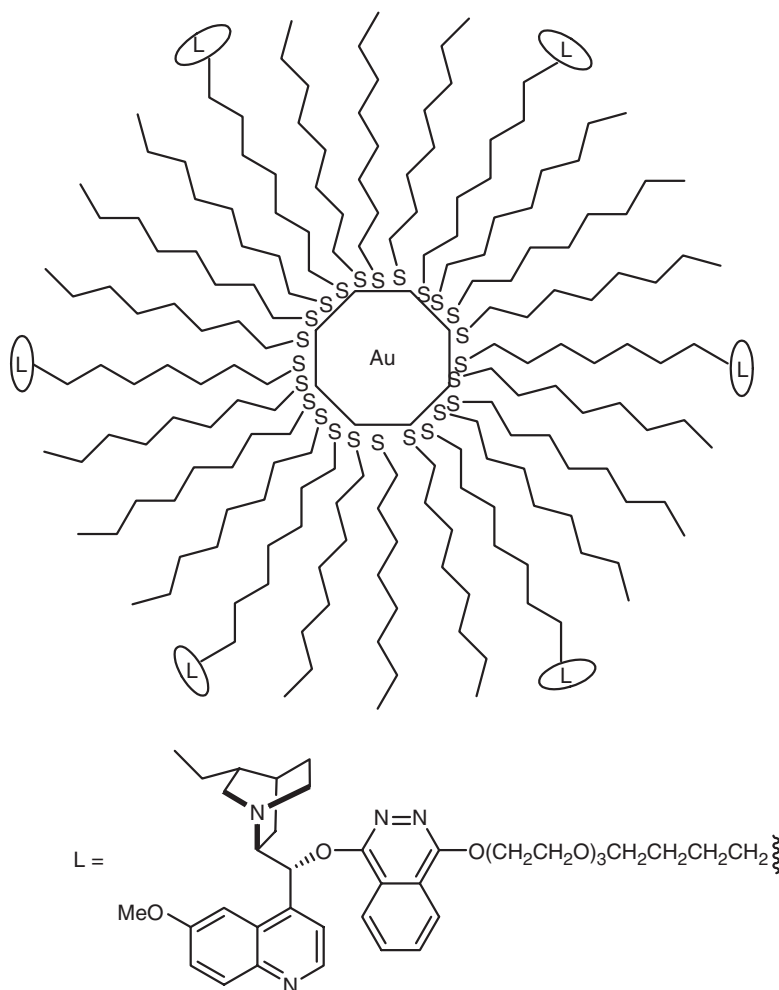
Figure 3. A dihydroquinidine catalyst immobilized on the surface of an Au nanocluster for the sharpless asymmetric dihydroxylation of olefins.

that these functionalized Au nanoparticles, coated with a mixed monolayer of *n*-octanethiolates and thiolates with chiral rhodium-diphosphine end groups, possess catalytic properties comparable to analogous homogeneous rhodium catalysts. In the hydrogenation of methyl R-acetamidocinnamate, the same enantioselectivities (up to 93% e.e.) and full conversion could be obtained as with the corresponding homogeneous [Rh(COD)-(PYRPHOS)]BArF catalyst. The colloids could be easily recovered by filtration and reused as catalysts three times without loss of enantioselectivity.

Kanemasa and coworkers reported the synthesis of reusable chiral bisoxazoline catalysts based on Au MPCs (figure 6) [30]. Such nanocatalysts promoted asymmetric ene reactions between 2-phenylpropene and ethyl glyoxylate in dichloromethane leading to (*s*)-ethyl 2-hydroxy-4-phenylpent-4-enolate with the reaction yield up to 99% and the
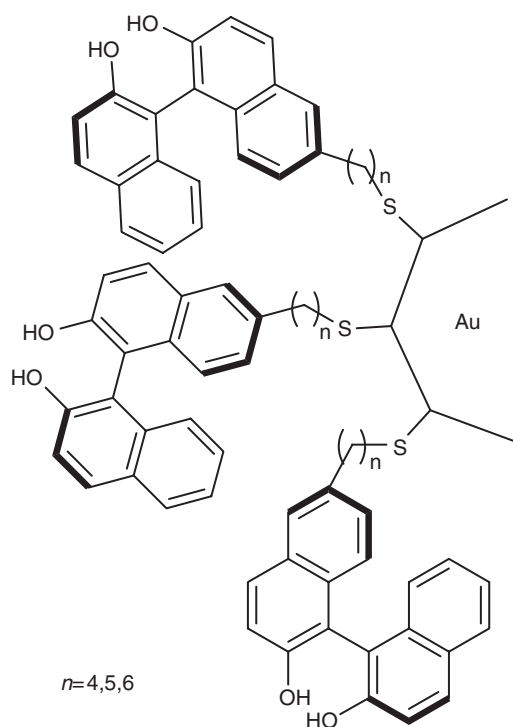
Figure 4. (*R*)-1,1-Bi-2-naphthol on an Au nanocluster employed for Ti-BINOLate-promoted catalytic asymmetric alkylation of benzaldehyde with Et_2Zn.
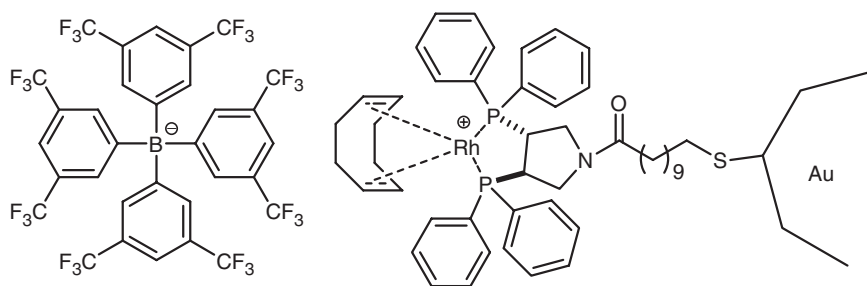

Figure 5. An Au nanoparticle-supported rhodium-diphosphine catalyst examined for an asymmetric hydrogenation reaction.

e.e. up to 86%. During work-ups, the catalyst could be recovered by repeated sequences of solvent exchange, centrifugation and decantation. Authors examined four subsequent repeated reactions using one of the Au nanoparticle-supported catalyst ($n = 4$). The reaction yields dropped from 99 to 80% and the e.e. value decreased from 86 to 84%.

In addition to supporting metal-promoted catalytic reactions, Au MPCs were also examined for aiding biomimetic and enzymatic catalyses. Pasquato *et al.* recently
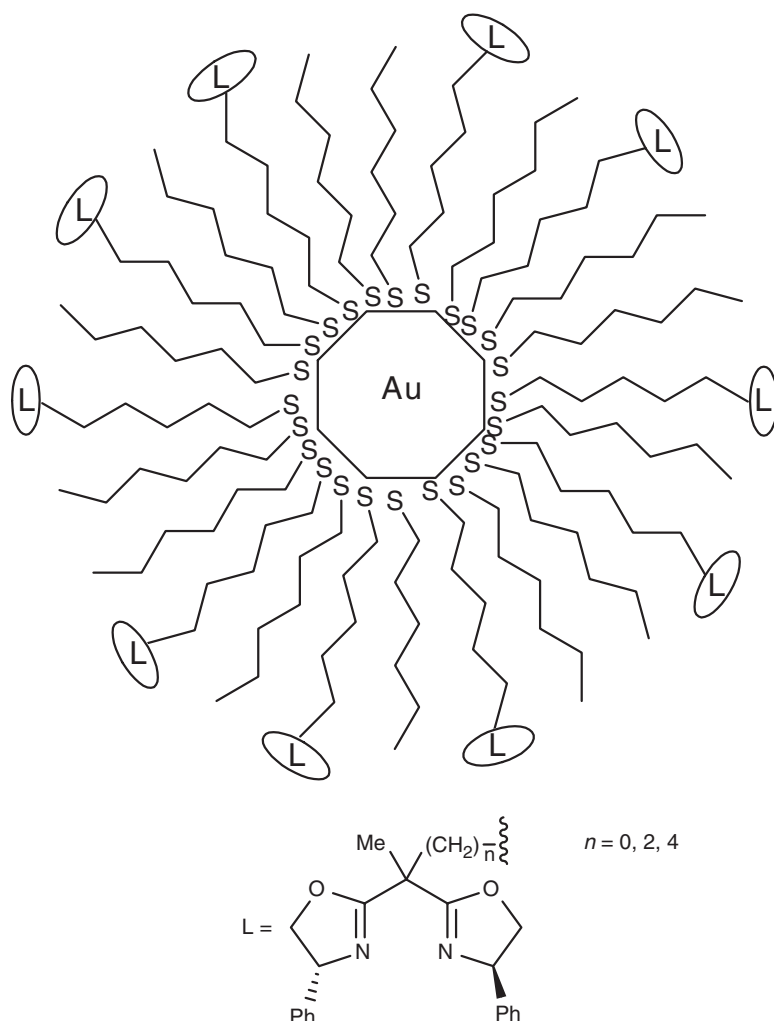
Figure 6.   Chiral bisoxazoline catalysts supported on Au MPCs for asymmetric ene reactions.

reported an Au MPC-supported Asp-His dipeptide (figure 7) for catalyzing the hydrolysis of two activated esters: 2,4-dinitrophenyl butanoate and *Z*-leucine-*p*-nitrophenyl ester [31]. The activity of such a nanocatalyst was found to be pH-dependent. A rate acceleration of more than 300-fold was observed when compared with an analogous un-supported dipeptide Asp-His in the low-pH regime. A cooperative hydrolytic mechanism that the carboxylate anion acted as a general base and the protonated imidazole served as a general acid was proposed to explain the rate acceleration phenomenon. This cooperative mechanism could also be supported by our recent hydrolysis studies using an amino acid dyad (Asp, His) immobilized on the surface of an iron oxide nanoparticle (section 3) [32]. A previous investigation from Pasquato and Scrimin employing a monomeric His derivative gave rise to much lower catalytic activity [33].
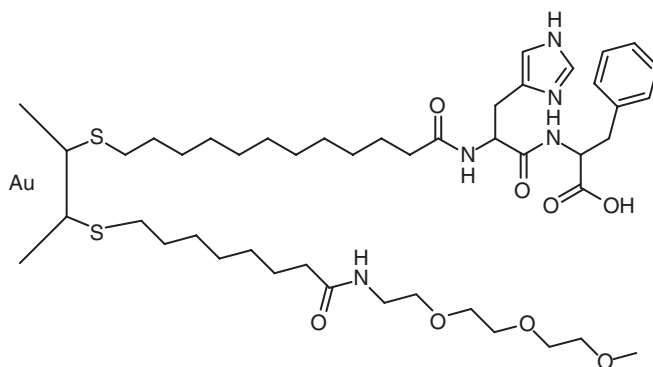
Figure 7.   An Au MPC-supported "esterase"-like catalyst.

3. Magnetic nanoparticle-supported catalytic organic reactions

Magnetic nanoparticles employed for supporting catalytic reactions usually have a superparamagnetic core [34] surrounded by a layer of organic coatings. Silanes or ethenediols are usually employed for anchoring catalysts onto the surface of iron oxide nanoparticles because silanes/ethenediols were known to have a large affinity for under-coordinated surface sites of metal oxide particles [35].

Our group has recently reported two types of maghemite nanoparticle-supported catalysts for C–C coupling reactions: (1) a Pd-carbene catalyst supported by a composite of iron oxide nanoclusters and polystyrene polymers (figure 8) was examined for catalyzing Suzuki cross-coupling reactions [36]. Such a nanocatalyst was easily isolated and recovered for the repeated uses simply via a magnetic concentration step using an external magnetic field (figure 9); (2) the Pd catalyst immobilized on the maghemite nanoparticles without a polymer layer (figure 10) for promoting Suzuki, Heck and Sonogashira cross-coupling reactions [37]. The cross-couplings between 4-iodoacetophone and phenylboronic acid were found to proceed much faster under the nanoparticle-supported Pd-carbene catalyst than the one promoted by the similar Pd catalyst supported on the solid-phase.

The use of magnetic nanoparticles for the immobilization of an Rh-based catalyst was reported by Lee *et al*. and the resultant complex (figure 11) was examined for catalyzing the hydroformylation of olefins [38]. An excellent reaction yield ($>99\%$) was reported for the hydroformylation of 4-vinylanisole and the recovered catalyst exhibited no loss of its catalytic activity for four more rounds of the reaction. Similarly, Ying's group has recently reported two types of iron oxide nanoparticle/sol gel-supported Pd catalyst (figure 12) [39]. Catalysts gave a 99% yield over six consecutive runs on the hydrogenation of nitrobenzene and preserved a good reactivity for run 14 with an 87% conversion yield. In addition, Cheon recently reported a core/shell Co/Pt nanocatalyst (figure 13) for catalytic hydrogenation of 1-decene [40]. The Co core allowed magnetic recovery of the catalyst and the Pt shell promoted the hydrogenation reactions. Complete conversions ($>100\%$) of the alkene were reported for seven repeated reactions using the recovered catalyst.
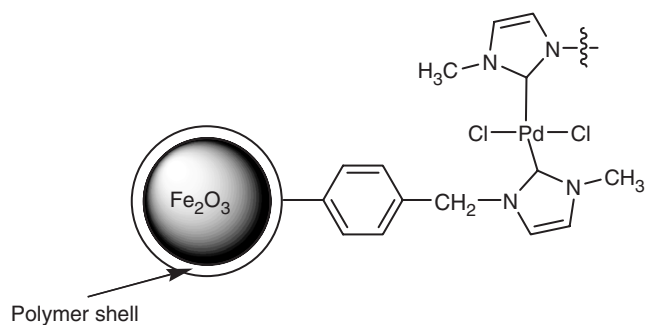
Figure 8. A Pd-carbene catalyst supported on iron oxide nanoparticle-polystyrene complexes investigated for catalyzing Suzuki cross-coupling reactions.
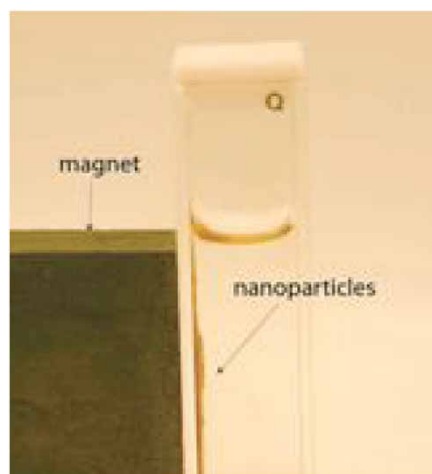

Figure 9. The maghemite nanoparticle-supported catalyst (figure 8) was isolated and recovered under an external magnetic field from the reaction mixture.
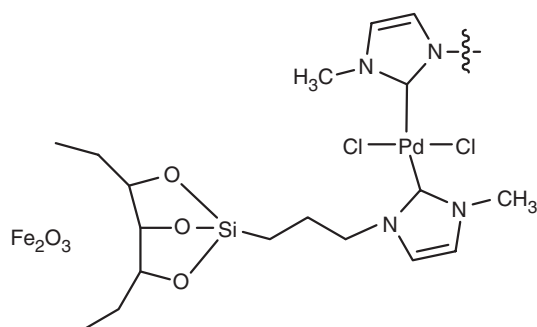

Figure 10. The Pd catalyst immobilized on the surface of a maghemite nanoparticle.
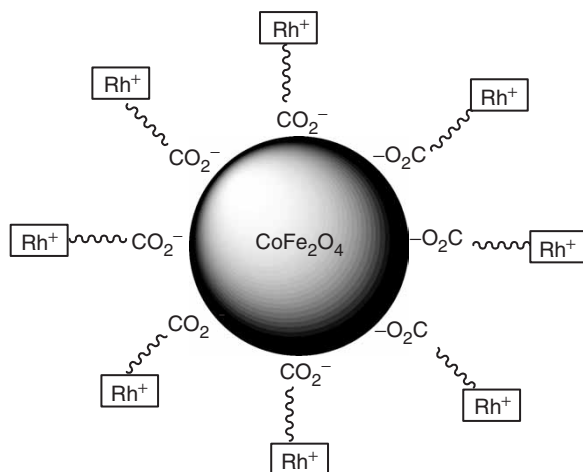
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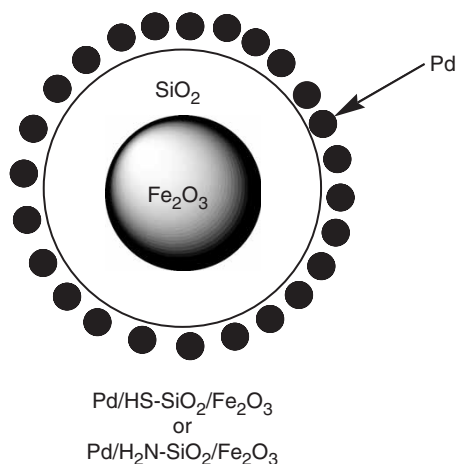Figure 11.   The $CoFe_2O_4$ nanoparticle-supported Rh catalyst.

Figure 12.   An iron oxide nanoparticle with a sol-gel coating for supporting the Pd catalyst.

Shen's group has recently reported a magnetic nanoparticle-supported catalyst for atom transfer radical polymerization (ATRP) reaction [41]. The iron oxide nanoparticle-supported ATRP catalyst (figure 14) was employed for the polymerization of methyl methacrylate with minimized adverse effect of catalyst support and easy catalyst separation. With the addition of $22\,mol\%$ of $CuBr_2$, the polymer molecular weights were well-controlled with an initiator efficiency of 0.85 and polydispersity lower than 1.2. The supported catalysts were separated using an external magnetic field and reused with slightly decreased activity but with further improved control.

Lin's laboratory has examined the magnetic nanoparticle-supported chiral Ru catalysts (figure 15) for asymmetric hydrogenation of a group of aromatic ketones [42]. Conversion yields greater than 99% were reported for all the substrates with the
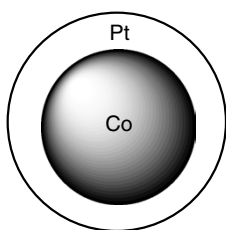
Figure 13.   A Co/Pt core/shell nanocatalyst.
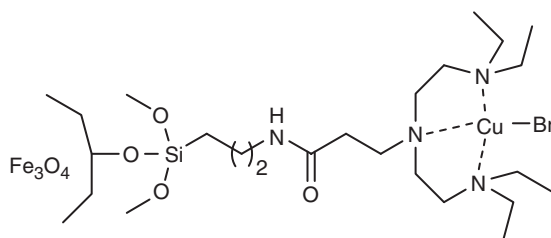
Figure 14.   An ATRP catalyst supported on a magnetic nanoparticle.
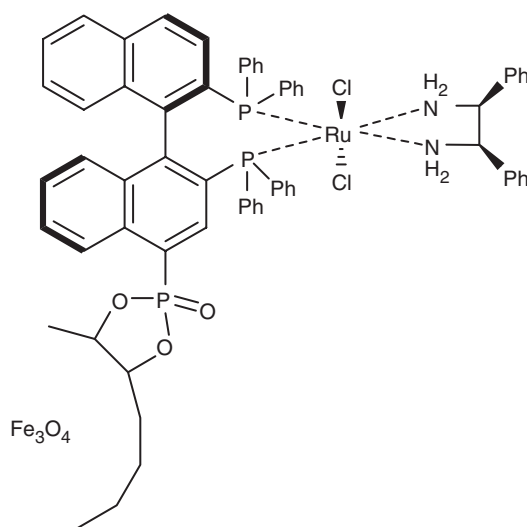
Figure 15.   A magnetic nanoparticle-supported chiral Ru catalyst.

e.e. values up to 98%. The recovered catalysts also showed remarkable conversion yields and enantiomeric selectivities.

However, our recent efforts on an iron oxide nanoparticle-supported chiral Ti-BINOLate catalyst only led to some disappointing results [28]. The chiral Ti-BINOLate complexes supported on iron oxide/polymer nanoparticles (figure 16)

Figure 16.   A magnetic/polymer nanoparticle-supported Ti-BINOLate catalyst for asymmetric alkylation reactions.

Figure 17.   A PAMAM dendron-functionalized magnetic nanoparticle for supporting an Rh catalyst.

were examined for catalyzing asymmetric alkylation of benzaldehyde with Et_2Zn – a similar study previously examined under an Au nanoparticle-supported Ti-BINOLate. Moderate reaction yields range from 47 to 55% with the e.e. values from 15 to 43% – lower than those (yield: 90%; 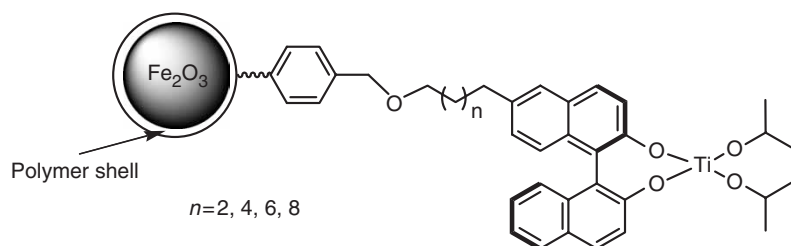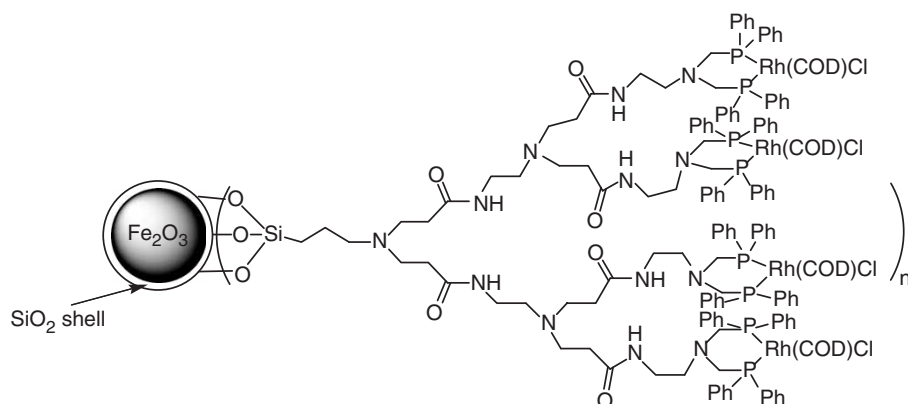e.e.: 84%) under unsupported Ti-BINOLate. The decreased conversion yields and e.e. values observed in our laboratory suggests that unlike the Au nanoparticle surfaces, the ionic nature of the iron oxide nanoclusters is detrimental to this nucleophilic addition reaction involving an anionic reagent. Thus, care needs to be taken for selecting an appropriate nanoparticle matrix for supporting a catalytic organic transformation.

To improve the solubility and stability of the magnetic nanoparticle-supported metal and metal oxide catalysts, a strategy using dendron polymer-functionalized magnetic nanoclusters as alternative matrices has been almost simultaneously developed in two research groups. Alper and coworkers have examined the use of polyaminoamido (PAMAM) dendrons for coating the surface of silica-iron oxide nanoparticles (figure 17) [43]. The dendron-functionalized magnetic nanoparticles were found to be more stable and more soluble in organic solvents. Such dendronized particles were phosphonated, complexed with $[Rh(COD)Cl]_2$, and investigated for promoting catalytic hydroformylation reactions. A group of substrates were examined and high reactivities (up to 100%) and high selectivities (up to 100%) were reported. On the other hand,
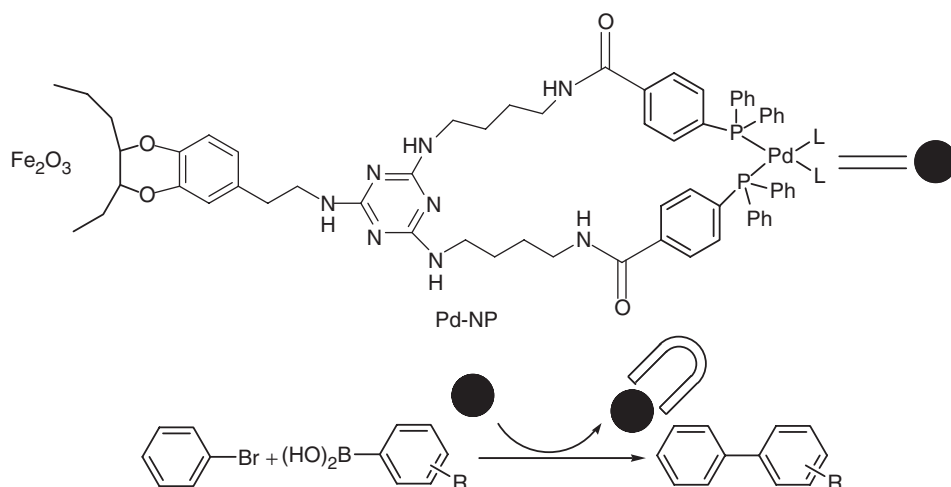
Figure 18. A Pd catalyst supported on a Simanek (melamine)-type dendron-functionalized magnetic nanoparticle for Suzuki cross-coupling reactions.

our research laboratory has recently examined a Simanek (melamine)-type [44] dendron-functionalized magnetic nanoparticle for supporting Pd-mediated Suzuki cross-coupling reactions (figure 18) [45]. The solubility of our dendron-coated nanoparticles could be tuned by varying the terminal groups of the dendron coatings so that hydrophobic and hydrophilic dendron-iron oxide nanoparticles were dissolved in organic and aqueous media, respectively for catalytic organic reactions (in organic solvents) and biomedical magnetic resonance imaging (in aqueous media).

In addition, our group has recently investigated the use of magnetic nanoparticle-supported Pd catalyst for facilitating solid-phase organic reactions (figure 19) [46]. Due to their small size (~4 nm), a magnetic nanoparticle-supported Pd catalyst was able to enter the pores of solid-phase (1% divinylbenzene-crosslinked polystyrene) for a three-phase Suzuki cross-coupling reaction. The work-up separating three components (the catalyst, product and remaining arylborate) is a chromatography-free process. The Pd catalyst was magnetically isolated and recycled from the reaction mixture by applying an external magnetic field. Then, a filtration process was followed to recover the excess borate reagent from the resins/product. Such chromatography-free work-up processes could be useful in robotic synthesis of combinatorial libraries and can potentially be adopted to fully automated organic syntheses. This orthogonal support strategy may also find its applications in process chemistry. Complicated separation and purification steps have frequently become a bottleneck in large-scale industrial processes that involve millions of tons of solvents, reagents and catalysts. Facile recovery and recycling of expensive homogeneous catalysts and excess reagents will cut costs and minimize chemical wastes – providing environmental protection benefits in chemical industry.

Jones and coworkers have investigated a similar strategy employing several different matrices for sequential catalytic reactions to facilitate work-up processes (figure 20) [47].
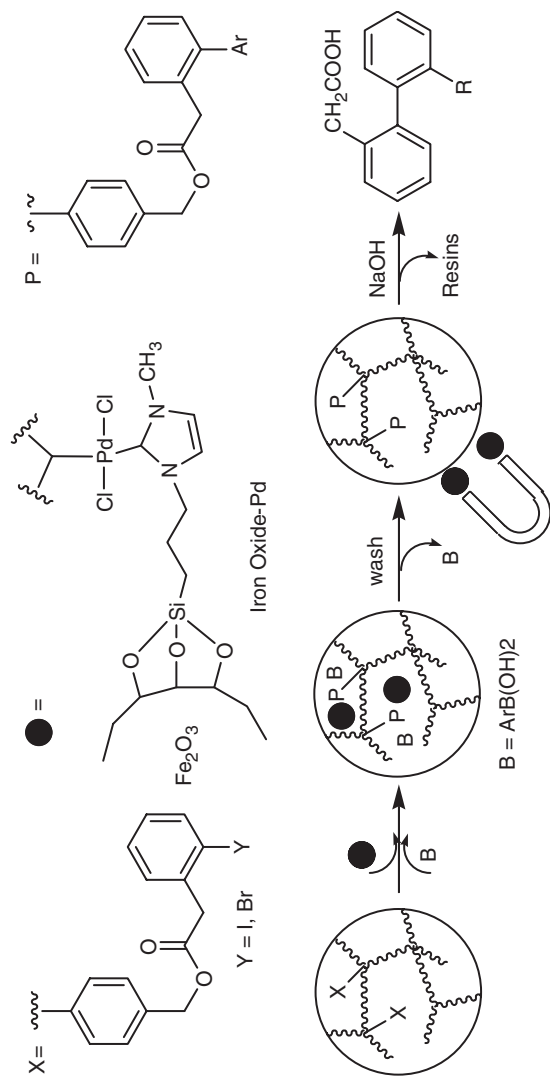
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Figure 19. A magnetic nanoparticle-bound Pd catalyst for supporting solid-phase Suzuki cross-coupling reactions.
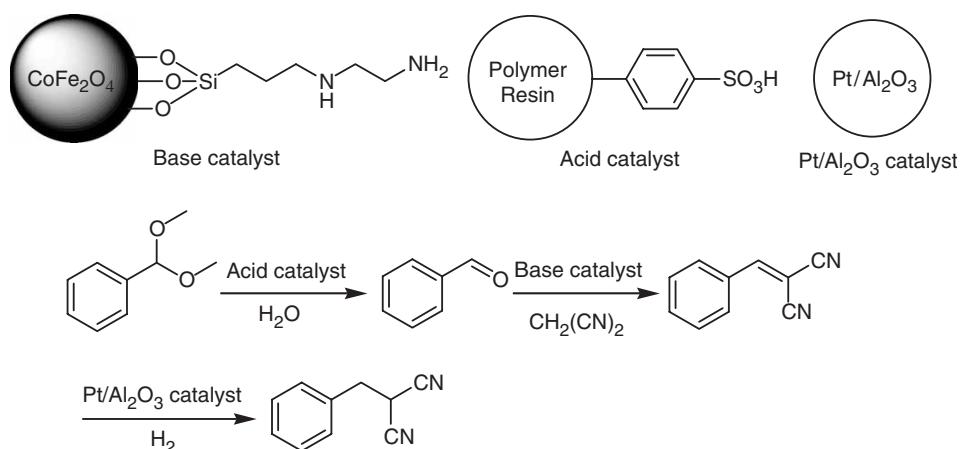
Figure 20. Multi-step reaction networks controlled by the combination of different catalysts including a magnetic nanoparticle-supported base catalyst in a single vessel.

A solid phase-supported sulfonate catalyst was first used for the hydrolysis of an acetal group followed by a magnetic nanoparticle-supported base-mediated condensation reaction. Finally, a hydrogenation reaction catalyzed by a heterogeneous Pt/Al_2O_3 catalyst was employed for achieving the product. Three sequential reactions were completed in one reaction vessel and the catalysts were recovered in pure forms and used in later manipulations. This multiple-steps, one-pot catalytic reactions strategy with the ability to steer the direction of the reaction and recover the catalyst at each step indeed could be of practical importance for real industrial applications.

Parallel with metal-mediated catalytic reactions, magnetic nanoclusters have also been examined for supporting enzymatic and biomimetic catalyses. Our group has recently examined the employment of a maghemite nanoparticle-supported lipase (figure 21) for catalyzing chiral resolution of racemic carboxylates [48]. An average yield of 78% was observed for three carboxylic acids with the e.e. values up to 99%. In addition, the long-term stability of lipase immobilized on the nanoparticles was found to be improved. This conclusion could be supported by similar studies reported from Tsang [49] and Ulman [50].

Hatton's group has reported a magnetic nanoparticle-supported catalyst for hydrolyzing organophosphates (figure 22) [51]. Magnetite nanoparticles coated with poly(4-vinylpyridine-*N*-phenacyloxime-*co*-acrylic acid) were found to be a very active catalyst in hydrolyzing diisopropyl fluorophosphates at 25°C, due to the presence of an α-nucleophile, the oximate group in their polymer coatings. Such nanocatalysts were colloidally stable at neutral pH and were readily recovered for reuse.

Our group has recently investigated a different type of magnetic nanoparticle-supported nanocatalyst for hydrolyzing activated phosphoester and carboxylate ester bonds under mild conditions (figure 23) [32]. Due to the unique surface structure of nanospheres, Asp and His residues supported on a 12 nm maghemite nanoparticle worked collaboratively as a biomimetic nanocatalyst for hydrolyzing paraoxon (phosphoester) and 4-nitrophenyl acetate (carboxylic ester) in Milli-Q water (pH 7.0)
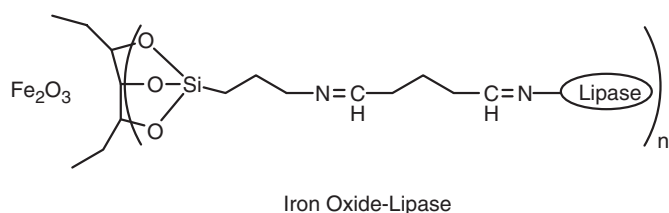
Iron Oxide-Lipase

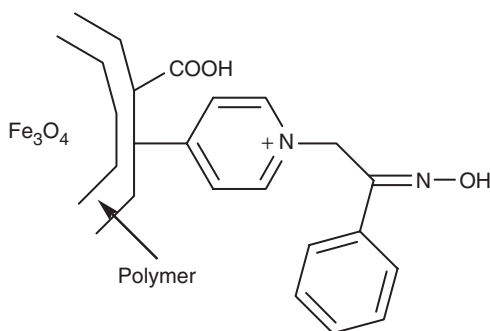Figure 21. Magnetic nanoparticle supported-lipase for chiral resolution reactions.

Figure 22. Magnetite nanoparticles coated with poly(4-vinylpyridine-*N*-phenacyloxime-*co*-acrylic acid) for hydrolyzing organophosphates.

at $37°C$ – without employing extremes of pH or heavy metals. The nanocatalyst could be easily recovered via magnetic concentration. Such biomimetic nanocatalysts might find their applications in national defense for neutralizing chemical warfare agents, pharmaceutical process chemistry for mild hydrolysis of esters, and novel antisense therapies for cleaving RNA molecules.

4. Conclusions

This article has reviewed recent developments of Au and magnetic nanoparticle-supported catalysts and catalytic organic reactions. Immobilization of a catalyst on nanoparticle matrices allowed facile separation and recycling of the catalytic species during work-ups. Most of the supported catalysts examined in this article were found to maintain their catalytic activity and selectivity – compatible to those of their parent complexes in solution or their polymer-supported counterparts. In addition, examples of utilizing magnetic nanoparticles to facilitate solid-phase catalytic reactions [46] and to support multiple-step, one-pot sequential reactions were discussed [47]. These proof-of-concept investigations suggest that the strategy of the combined use of a nanoparticle matrix with orthogonal supports (e.g. solid-phase) could be employed to simplify industrial processes with the ability to steer the direction of the reactions and recover the catalysts. More interestingly, a dyad of amino acid (Asp and His) analogues
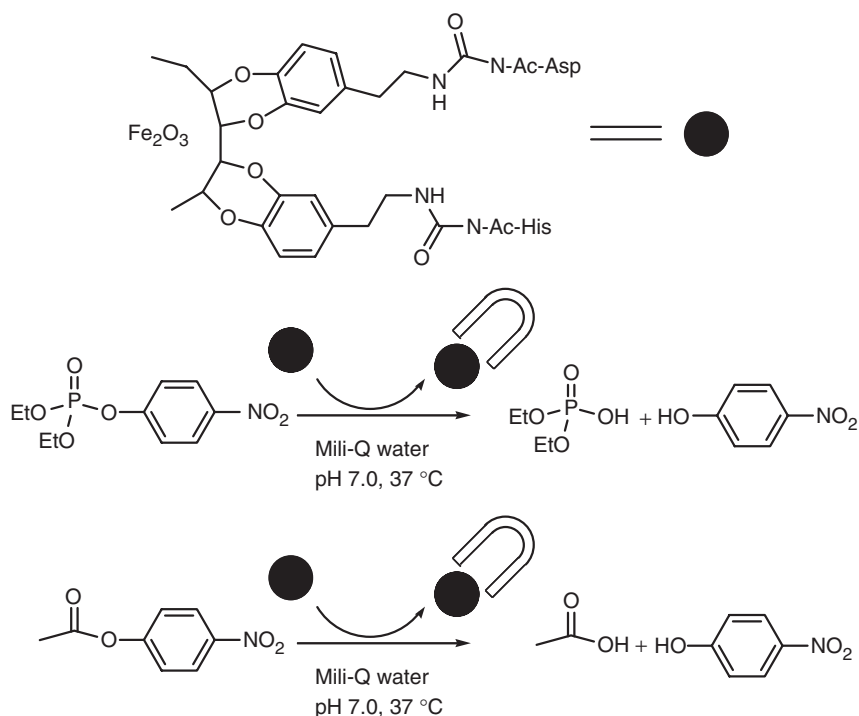
Figure 23. A maghemite nanoparticle-supported biomimetic nanocatalyst for hydrolyzing paraoxon and *p*-nitrophenyl acetate.

and a dipeptide (Asp-His) immobilized on the surface of nanoparticles were found to exhibit cooperative catalysis – giving rise to unique catalytic activities – otherwise not observed from their unsupported counterparts. Thereby, immobilization of catalysts on the surface of a nanoparticular matrix will not only facilitate the isolation and recovery of expensive catalysts, but also open a new avenue to tune their activity and selectivity for programmable catalyses of biological and organic reactions.

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