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Magnetic and Dendritic Catalysts

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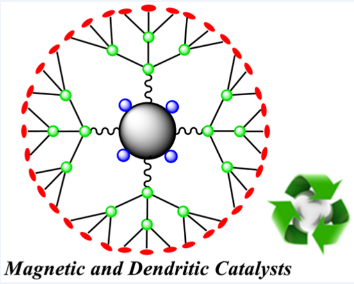

Magnetic and Dendritic Catalysts

CONSPECTUS: The recovery and reuse of catalysts is a major challenge in the development of sustainable chemical processes. Two methods at the frontier between homogeneous and heterogeneous catalysis have recently emerged for addressing this problem: loading the catalyst onto a dendrimer or onto a magnetic nanoparticle. In this Account, we describe representative examples of these two methods, primarily from our research group, and compare them. We then describe new chemistry that combines the benefits of these two methods of catalysis.

Classic dendritic catalysis has involved either attaching the catalyst covalently at the branch termini or within the dendrimer core. We have used chelating pyridyltriazole ligands to insolubilize catalysts at the termini of dendrimers, providing an efficient, recyclable heterogeneous catalysts. With the addition of dendritic unimolecular micelles olefin metathesis reactions catalyzed by commercial Grubbs-type ruthenium−benzylidene complexes in water required unusually low amounts of catalyst. When such dendritic micelles include intradendritic ligands, both the micellar effect and ligand acceleration promote faster catalysis in water. With these types of catalysts, we could carry out azide alkyne cycloaddition ("click") chemistry with only ppm amounts of $CuSO_4 \cdot 5H_2O$ and sodium ascorbate under ambient conditions.

Alternatively we can attach catalysts to the surface of superparamagnetic iron oxide nanoparticles (SPIONs), essentially magnetite (Fe_3O_4) or maghemite (γ-Fe_2O_3), offering the opportunity to recover the catalysts using magnets.

Taking advantage of the merits of both of these strategies, we and others have developed a new generation of recyclable catalysts: dendritic magnetically recoverable catalysts. In particular, some of our catalysts with a γ-Fe_2O_3@SiO_2 core and 1,2,3-triazole tethers and loaded with Pd nanoparticles generate strong positive dendritic effects with respect to ligand loading, catalyst loading, catalytic activity and recyclability. In other words, the dendritic catalysts were more efficient and more stable than their nondendritic γ-Fe_2O_3@SiO_2 analogues. The bulk at the dendritic periphery helps to localize the metal nanoparticles at the SPION core surface, which confers these advantages. We could also use sonification as a remarkably simple and efficient method to impregnate the SPIONs with dendrimer-encapsulated PdNPs. Catalysis within the hydrophobic dendrimer pockets that include ligands leads to rapid turnover with or without a γ-Fe_2O_3@SiO_2 core. In addition, catalytically active metal nanoparticles are more robust when they are loaded onto the surface of a γ-Fe_2O_3@SiO_2 dendritic core.

Herein, we illustrate this chemistry with examples including olefin metathesis, click chemistry, cross carbon−carbon bond forming reactions, and selective alcohol oxidation.

■ INTRODUCTION

Catalysis, recognized first by Baron J. J. Berzelius in 1835, is essential for most chemical processes, but catalyst recovery and reuse is a must for economical and ecological reasons; yet it remains a crucial problem. Homogeneous catalysts, present in the same (usually liquid) phase as reactants and products currently offers high selectivity and mechanistic understanding via kinetic data,[1,2] but not the possibility to isolate and reuse catalysts. Heterogeneous catalysis permits separation of the solid catalyst from the gas or liquid phase containing the reactants and products, and the catalysts are also much more thermally stable than homogeneous catalysts, but the advantages of homogeneous catalysis are lacking.[3,4] Among the remarkable modern approaches to combine the advantages of homogeneous and heterogeneous catalysis,[5] two new areas have recently introduced very advantageous methods for catalyst recovery and reuse: loading the catalyst onto a magnetic component[6−13] or onto a dendrimer.[14−24] The former is essentially relevant to heterogeneous catalysis, because the magnetic catalysts are usually insoluble. The later is rather relevant to homogeneous catalysis, because catalysts are often molecular species related to known homogeneous catalysts and covalently attached to molecular dendrimers. In this Account, we compare magnetic catalysts and dendritic catalysts in terms of recovery and recycling and show that magnetic and dendritic catalysis also meet each other in composite dendritic magnetic catalysts and that are involved in both late transition-metal complexes and zerovalent metal nanoparticles.

■ PRINCIPLES AND RECENT TRENDS IN DENDRIMER-SUPPORTED MOLECULAR CATALYSIS

The design of dendritic catalysts has mostly concerned the attachment of transition-metal catalytic complexes onto the termini of dendritic tethers or at the dendrimer core. This strategy has met some success,[23] because the catalyst has a

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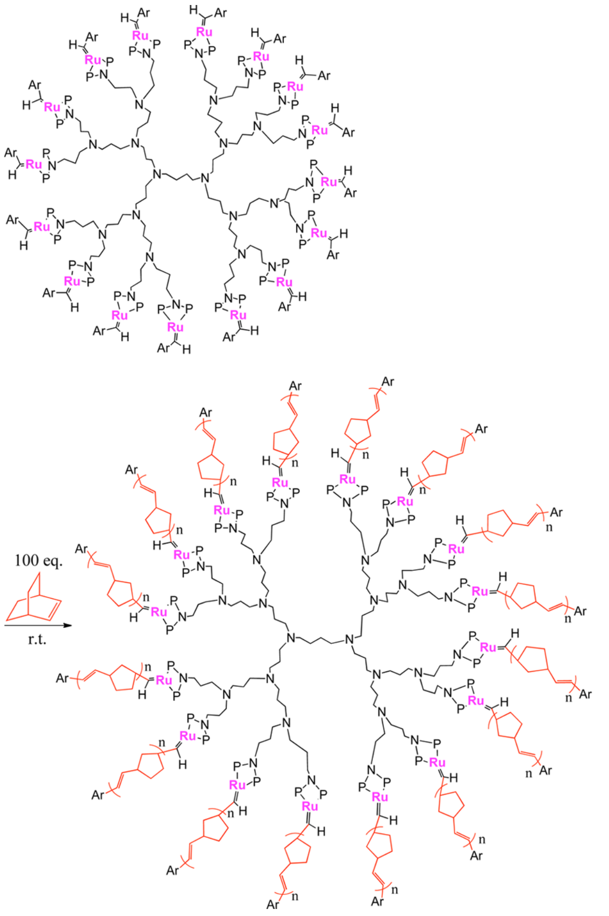
solubility that is different from those of substrates and products or is insoluble and thus can be easily separated and recycled.[24] It also has limits, because the approach of substrates onto the catalytic center is sterically inhibited by the other surrounding bulky catalytic centers at the dendrimer periphery or core.[23−25] For instance, diaminobutane dendrimers terminated by ruthenium benzylidene complexes $-N(CH_2PCy_2)_2\{Ru({=}CHC_6H_4\text{-}o\text{-}i\text{Pr})Cl_2\}$ undergo ring opening metathesis polymerization of norbornene with generation (G_n) rate order: $G_1 > G_2 > G_3$ (eq 1).[25]

The two Cl ligands of the Ru atoms and the two Cy substituents of the P atoms are omitted for clarity; Ar = *o*-*i*-PrC_6H_4.



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Depending on the organometallic mechanism involved in the catalytic reaction, however, the dendritic bulk at the dendrimer periphery is sometimes an advantage as shown by Gebbink and van Koten's group. These authors reported that a hexacationic triarylphosphine-based dendriphos ligands led to a highly active catalytic system in the Suzuki−Miyaura cross-coupling reaction of nonactivated aryl bromides and activated aryl chlorides at a low Pd loading (0.1 mol %). Dendriphos ligands behaved as very bulky phosphine ligands and led to a preferential formation of coordinatively unsaturated and catalytically active Pd(0) species, which explained the observed high catalytic activity and a positive dendritic effect with activated aryl chlorides for which oxidative addition is the rate-limiting step.[26]

The Gade group reported "catalysis in a tea bag" whereby bis- and tris-oxazolines containing a linker unit in the ligand backbone that allowed their covalent attachment to carbosilane dendrimers have been employed as polyfunctional ligands for recyclable Cu(II) Lewis acid catalysts that were immobilized in a membrane bag (Figure 1).

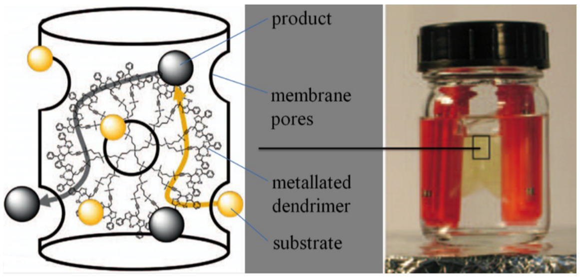


Figure 1. Gade's catalysis in a "tea bag". Reproduced with permission from John Wiley & Sons.[27]

The catalytic potential was assessed by studying the alpha-hydrazination of a beta-keto ester and the Henry reaction of 2-nitrobenzaldehyde with nitromethane, and catalytic activities and selectivities superior to those of nondendritic catalysts were obtained.[27] The same group also reported immobilization of the BINAP ligand on PPI dendrimers and showed a strong dependence of the enantioselectivity and activity on the generation of the dendrimer in the copper-catalyzed hydrosilylation of acetophenone. The macromolecular immobilized BINAP ligand was recycled several times without any observable loss of activity or enantioselectivity.[28]

Metallodendrimers terminated by Pd-pyridyltriazole ligands were particularly efficient catalysts for carbon−carbon cross coupling including the Suzuki−Miyaura, Sonogashira, and Heck reactions. The nonapalladium complex was insoluble in all the reaction media, whereas the tri- and tetranuclear Pd complexes were soluble, which allowed conducting catalysis under either homogeneous or heterogeneous conditions (Figure 2). Both types of catalysts showed excellent activity for these cross carbon−carbon bond formation involving aryl halides including activated aryl chlorides or acyl chlorides. Another key feature of these catalysts is their remarkable robustness that allowed recycling at least ten times in the example of the Heck reaction with excellent yields and without significant reduction of the conversion.[24]

Recently, different views on dendritic catalysts have involved dendritic molecular micelles for intradendrimer catalysis. For ring-closing metathesis (RCM) of hydrophobic terminal olefins, excellent yields were obtained for RCM in water with down to 4×10^{-2} mol % of the commercial Grubbs-II catalyst $[Ru({=}CHPh)(NHC)Cl_2(PCy_3)]$ (NHC = *N*-heterocyclic carbene) in the presence of the recyclable dendrimer micelle **1** (vide infra). This remarkable result was taken into account by the micellar effect and protection of the $Ru{=}CH_2$ intermediate in the hydrophobic interior of **1**.[29] Another remarkable example using the recyclable molecular dendritic micelle **1** involves the copper-catalyzed alcyne azide cycloaddition (CuAAC) "click" reactions whereby the dendrimer plays not only the role of a molecular micelle, but also that of an intradendritic multiligand. Indeed, the triazole ligands of the dendritic interior considerably activate the Cu(I) catalytic species. Both the micellar effect and the ligand influence were independently demonstrated, and these cumulative effects resulted in the possibility of using only ppm amounts of catalysts for various CuAAC reactions with application to biologically relevant molecules. Moreover, the reactions were carried out in water with hydrophobic substrates owing to the full micellar effect of

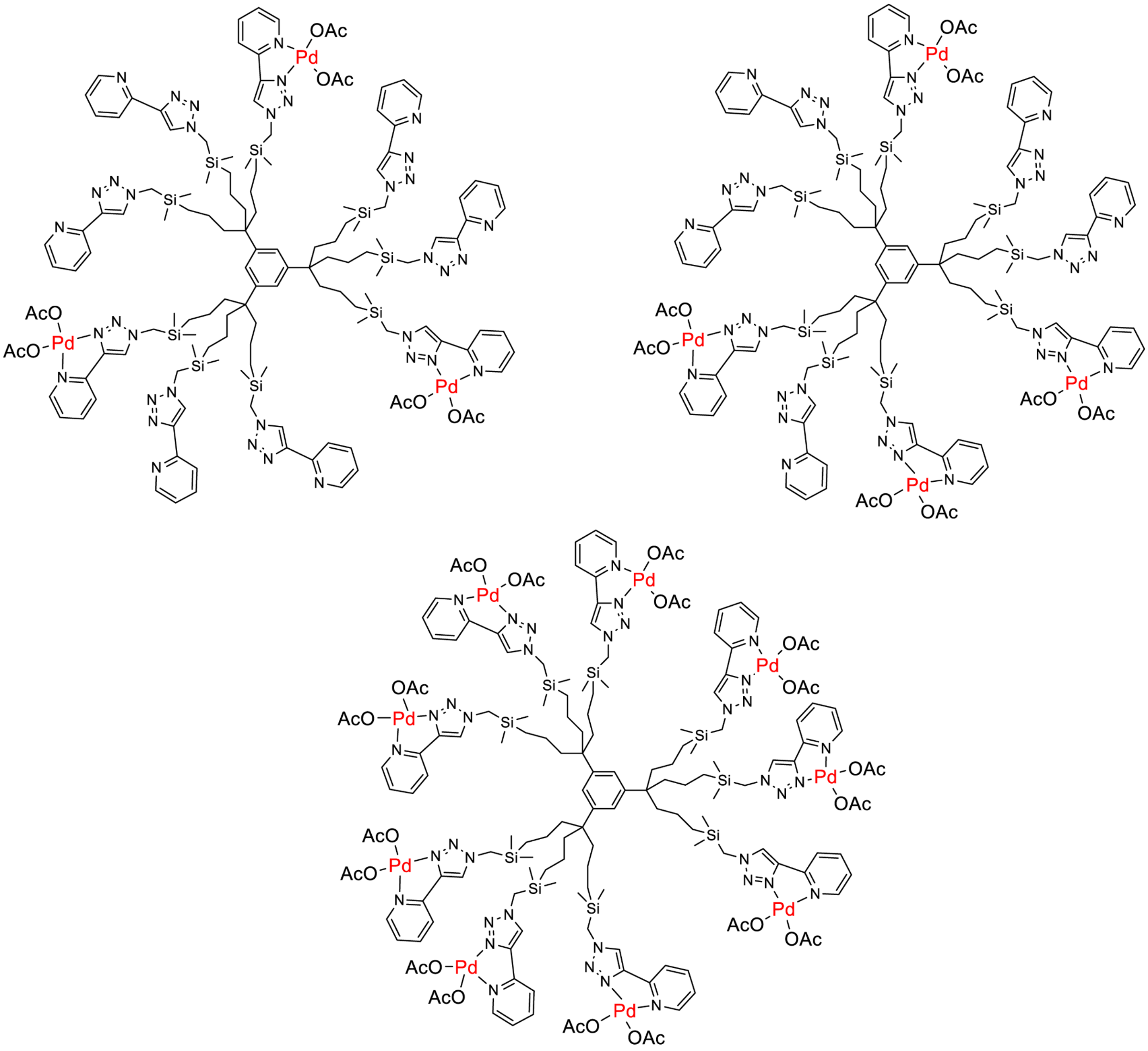


Figure 2. Isolated metallodendritic catalysts containing three, four, and nine metal centers with solubilities decreasing with increasing their number. Reproduced with permission from Wiley.[24]

the dendrimer that contained a hydrophobic interior and water solubilizing triethylene glycol branch termini (Figure 3).[30]

A useful concept was recently developed by the Fan group involving dendritic chiral phosphine ligands for asymmetric hydrogenation at the dendrimer core with recyclable catalysts. The dendritic structure provides both steric bulk for asymmetric induction and solubility difference for separation and recycling.[31] These recent examples show that astutely designed variations of the principle of dendrimer-support recovery gives very good results.

DENDRIMER-ENCAPSULATED NANOPARTICLE CATALYSTS

Another very fruitful approach pioneered by Crooks and coworkers[32−34] has involved dendrimer-encapsulated metal nanoparticles (DENs) that have been found with Pd nanoparticles (PdNPs) to catalyze various carbon−carbon cross-coupling and selective hydrogenation reactions,[32−36] the dendrimer periphery playing the role of a generation-dependent nanofilter. In this later case, a problem is that Pd DENs, as the PAMAM dendrimer themselves, do not withstand moderately high temperatures, that is, above 100 °C, and inter alia the PAMAM dendrimers decompose and Pd metal aggregates form, which does not allow to conduct the most difficult activation types.

With dendrimers synthesized by "click" chemistry,[37,38] the intradendritic 1,2,3-triazole ligands have been shown to provide ideal stabilization of catalytically active Pd[39−42] and Au NPs,[42−45] but recycling was not probed owing to the minute quantities of nanoparticle catalysts. Efficient catalysis was observed with Suzuki-Miyaura C−C coupling of bromoarenes, copper-free Sonogashira[42] and Heck cross C−C coupling of iodoarenes with PdNPs, and nitrophenol reduction with both PdNPs and AuNPs.[42−44] The dendrimer-templated synthesis of PdNPs was shown by the Meijboom group to be superior to

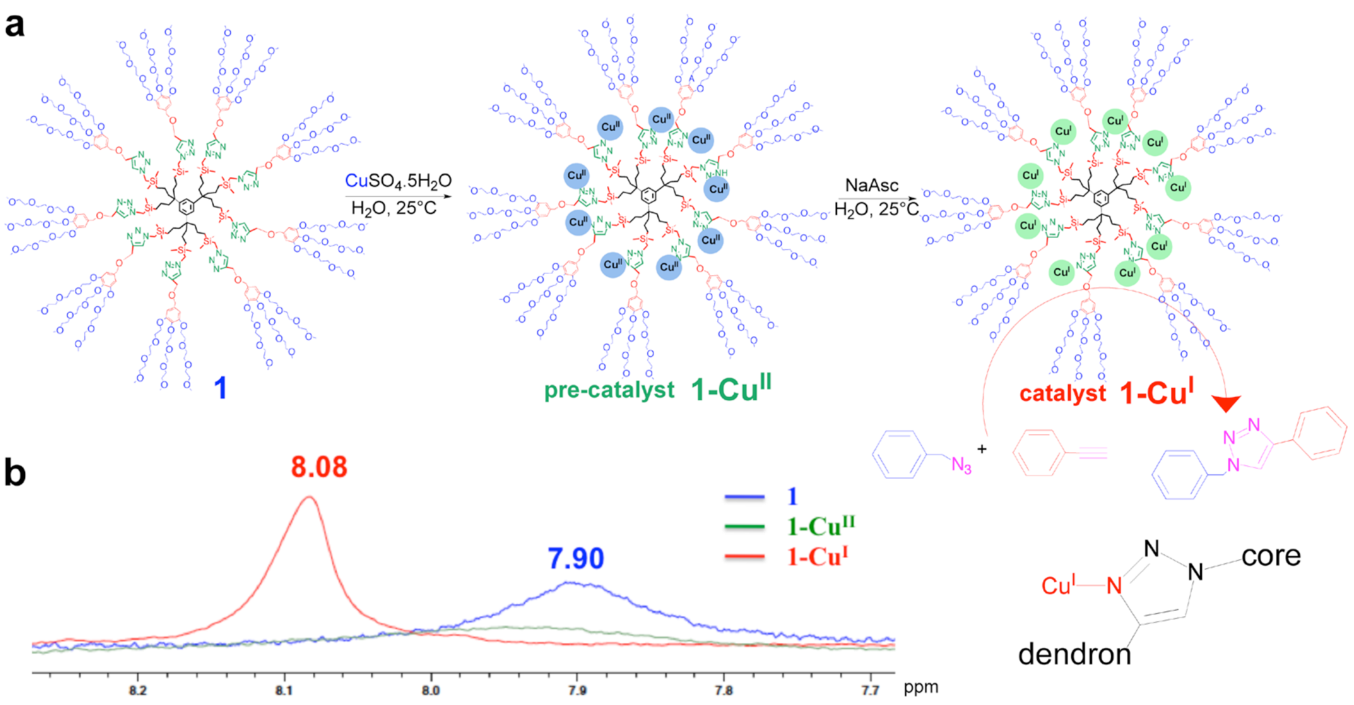


Figure 3. (a) Dendritic micelle **1** as nanoreactor/ligand for CuAAC catalysis. (b) Comparison of the NMR signals of the triazole proton of **1** alone (7.90 ppm), with Cu^{II} (very broad due to the paramagnetism) and Cu^{I} (shift to 8.08 ppm) showing the coordination of the intradendritic triazoles of **1** to the copper ions.

PdNPs synthesized by inverse microemulsions both in terms of PdNP dispersity and catalytic efficiency for the ligand-free Heck C−C coupling reaction of aryl halides, and the dendrimer template G5-OH(Pd-80) showed the best activity.[46]

In general, the comparison of dendrimers with other types of supporting structures such as reverse micelles, colloidal structures, sol−gel, atomic layer deposition chemistry, mixed-molecular nanostructures has been discussed and showed that dendrimers are one of the best catalysis means in terms of efficiency and recyclability.[47,48]

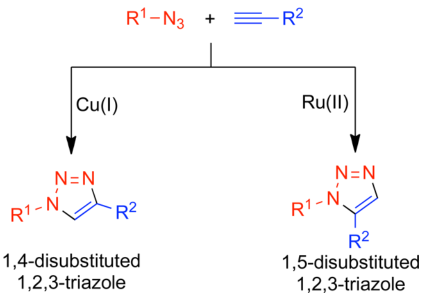
MAGNETICALLY RECYCLABLE CATALYSTS

Among magnetic nanoparticles (MNPs) including metals (Fe, Co, Ni), alloys (FePt, CoPt), iron oxides (FeO, Fe_2O_3, Fe_3O_4) and ferrites MFe_2O_4 (M: Co, Mn, Cu, Zn), the superparamagnetic iron oxide nanoparticles (SPIONs) magnetite (Fe_3O_4) and maghemite (γ-Fe_3O_4) are by far the most widely used supports of magnetically recoverable catalysts. This is due to their low cost, easy preparation, biocompatibility (SPIONs are also much used for biomedical applications[49,50]), stability, and ease of functionalization of their surface with other metal particle fragments (Au, Pd, Pt, Cu, Ni, Ir), inorganic and organometallic catalysts, organocatalysts,[51,52] and enzymes. Dopamine derivatives, triethoxysilyl-, phosphonic acid-functionalized molecules and glutathione are frequent linkers between the SPION surface and the catalyst. For instance, magnetite has recently been used for a range of reactions including Suzuki−Miyaura, Sonogashira, Heck, Hiyama, hydrogenation, reduction, oxidation, cycloaddition reactions, asymmetric synthesis,[6−13] ring-closing olefin metathesis,[53−55] and so forth.

Our group has been involved in research on molecular Cu,[30,39] Pd,[25,48] and Ru[26,55] molecular catalysts and on Pd[42,56] and Au NP[43−45] catalysts and in conducting SPION attachment to these catalysts in view of sustainable processes.[55,57]

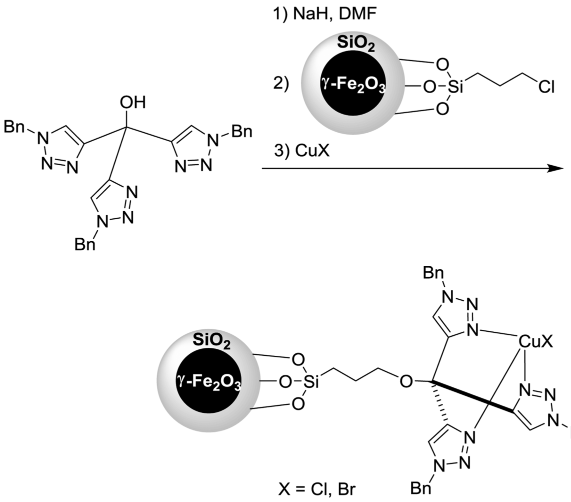
Metal-catalyzed alkyne azide cycloaddition (MAAC) was a priority to investigate using magnetic catalysts with both Cu(I) to form the 1,4-disubstituted 1,2,3-triazoles[58] and Ru(II) to form the isomeric 1,5-disubstituted 1,2,3-triazoles (Scheme 1).[59]

Scheme 1. Regioselective Metal-Catalyzed Azide Alkyne Cycloaddition Reactions



The 25 nm magnetic Cu catalyst (by transmission electron microscopy, TEM) was easily synthesized according to eq 2 whereby tris(triazolyl)CuX (X = Cl or Br) was attached to silica through 3-chloropropyltriethoxysilane that was immobilized on the surface of robust γ-Fe_2O_3@SiO_2.

Increasing yields of 1,4-disubstituted 1,2,3-triazoles were obtained with increasing catalytic amounts in the range of 0.17−1 mol %. The reactions proceeded in excellent yields (91% with X = Cl and 97% with X = Br) in the presence of 1 mol % (X = Cl) or 0.5 mol % (X = Br) catalyst in ROH/H_2O (R = Me or Et) or H_2O alone within 20 h at room temperature. These catalysts were easily separated from the reaction medium using an external magnet and kept the catalytic activity for six cycles. The amount of leaching copper from the initial catalyst to the reaction media, determined by inductively coupled



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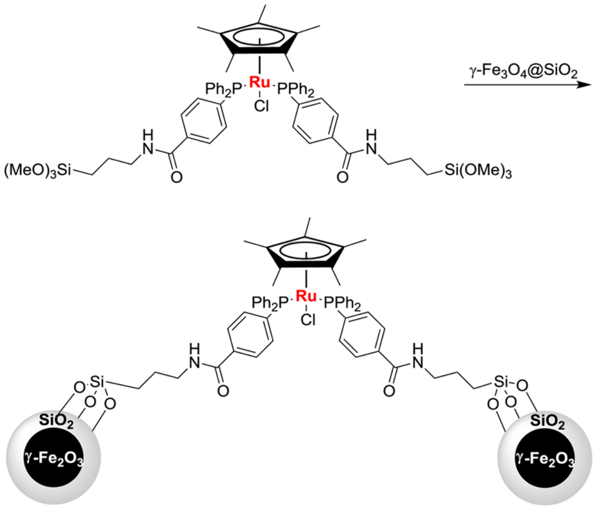
plasma (ICP) analysis, is negligible. This system is broad in substrate scope, and 25 1,4-disubstituted 1,2,3-triazoles were synthesized in good to excellent yields including dendrimers containing 27 allyl or 27 triethylene glycol termini.[60]



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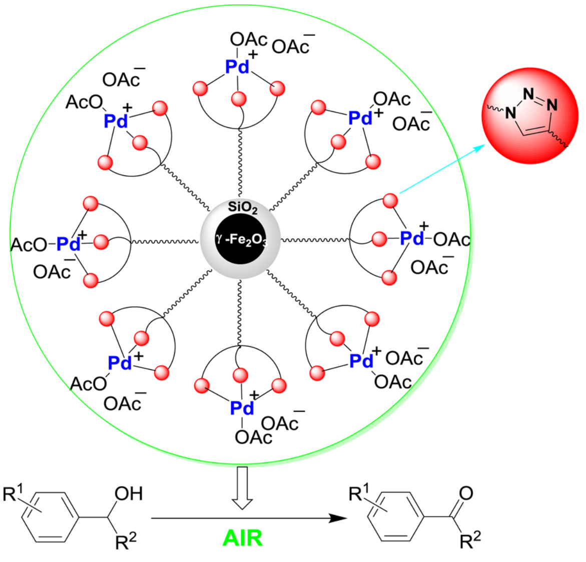
Likewise, the magnetic Ru(II) catalyst was synthesized according to eq 3 using monodisperse silica-coated γ-Fe_2O_3 nanoparticles (γ-Fe_2O_3@SiO_2).Tetraethoxysilane (TEOS) and aqueous NH_3 were used as silica source and hydrolyzing agent, respectively. TEM images showed the core–shell structure and the silica coating that has a uniform thickness of 9 nm. The dense silica shell has plenty of Si–OH units for potential derivatization with different functional groups and also prevents leaching of iron from the core under harsh shaking conditions. The silylated Cp*Ru(II) complex was obtained through coordination between the cluster $(Cp^*RuCl_2)_n$ and Si$(OMe)_3$-functionalized triarylphosphine and was immobilized on the surface of SiO_2/γ-Fe_2O_3 via the heterogenization with the Si–OH binding sites. The TEM images of the targeted magnetic nanoparticle catalyst (Cp*Ru/γ-Fe_2O_3@SiO_2) depicted relatively uniform core–shell nanoparticles with an average size of approximately 30 nm. The reaction between phenylacetylene and benzyl azide at 65 °C in 3 h with 2 mol % catalyst gave the 1,5-disubstituted 1,2,3-triazole with 100% selectivity and 91% yield, which was determined by both GC and NMR. The catalyst was reused five times by simple magnetic separation with only minimum decrease in catalytic activity and selectivity. The morphology and size of the nanoparticles did not change much even after five cycles, and the reaction was extended to 4-ethynyl-benzaldehyde, 2-ethynyl-pyridine, and 1-azidomethyl-4-bromo-benzene, with 100% selectivity and good to excellent yields.[61]

■ DENDRITIC MAGNETICALLY RECYCLABLE CATALYSTS

PAMAM dendrimers have been used as templates to encapsulate magnetic zerovalent transition-metal NPs such as Co[62,63] and Ni,[64] but these nanoparticles were not used as magnetic catalysts. After a seminal paper on selective hydroformylation reactions by Alper's group,[65] the area of magnetically recoverable dendritic catalysts has only appeared recently.[11,12,66−78] Our group has used SPION-cored dendritically encapsulated Pd NPs to efficiently catalyze a variety of reactions and shown that dendritic magnetic NPs are superior to nondendritic magnetic NPs in terms of catalyst loading, catalytic efficiency and catalyst recovery.[76−78]

An air-stable dendritic magnetic catalyst decorated with dendrons containing tris-triazole groups featuring 1 → 3 connectivity[79] at the end of branches connected to the termini of the γ-Fe_2O_3@SiO_2 core showed excellent catalytic results. Catalytic oxidation of alcohols was indeed achieved in air using these γ-Fe_2O_3@SiO_2-immobilized tris(triazolyl)–Pd(II) catalyst (eq 4) that provided impressive and better results concerning activity, selectivity, and recycling, compared to its PdNP counterpart. A series of primary and secondary benzyl alcohols were smoothly oxidized to afford the corresponding aldehydes and ketones in the presence of the magnetic tris(triazolyl)–Pd(II) catalyst (1.9 mol %) at 85–90 °C in toluene, with 81–97% conversions and 86–92% selectivity. In addition, the catalyst was easily recoverable and reusable for at least five cycles with only slight decrease in catalytic performance (eq 4).[76]Catalysts comprising intradendritic 1,2,3-triazole ligands were immobilized on γ-Fe_2O_3@SiO_2 magnetic nanoparticle interior with triethylene glycol terminal groups (Figure 4) and incorporating NPs.



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In dendrimers that contain triazoles, these heterocycles stoichiometrically bind Pd(II). The number of ligands around each iron oxide NP is, in average, approximately around 10^3. The approximate number of PdNPs loaded on one iron oxide

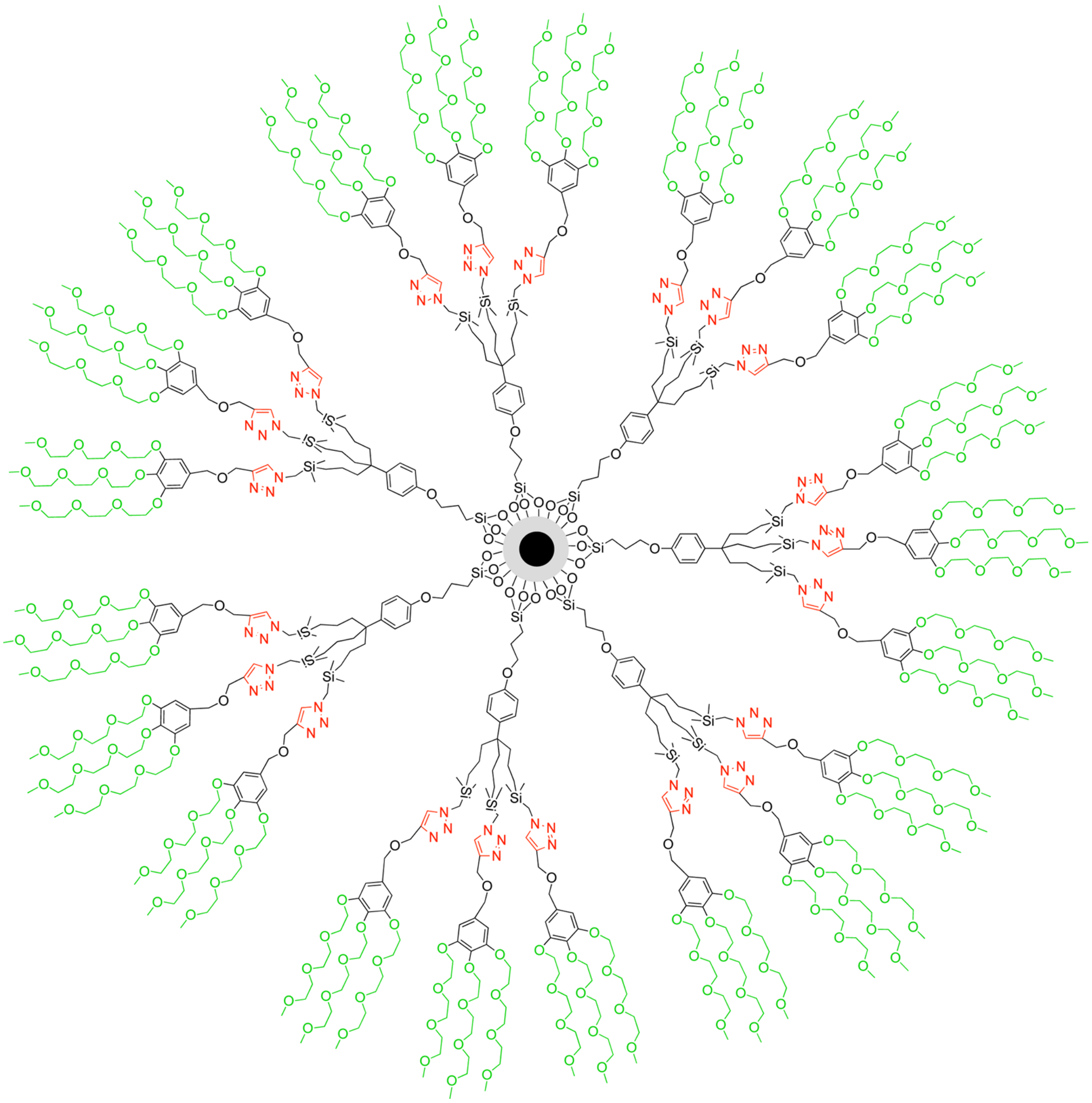

Figure 4. SPION-cored dendrimer. Reproduced with permission from Wiley.[77]

NP is, in average, 3.6. The SiOH moieties of the silica particle make a thick layer binding and stabilizing PdNPs, and PdNPs are fixed on the surface of silica. The stabilization of the PdNPs on the surface of silica proceeds both from the interior and by backfolding the triazole groups from the exterior (Figure 5), and XPS data confirm this hypothesis. The distance between the silica moieties and the triazole ligand groups is as expected toward the observed stabilization. Therefore, the PdNPs become better stabilized. In the same time, the triazole groups remain easily displaced by substrates in the outer surface.

This dendritic magnetic catalyst was highly active, dispersible, and recovered using an external magnet a large number of times in Suzuki–Miyaura and Heck reactions. Natural products and other compounds of pharmacological interest were made accessible using this magnetic dendritic catalyst. Relevant PdNP catalysts on γ-Fe_2O_3@SiO_2 containing linear 1,2,3-triazole PEGylated ligands were also prepared for comparison. Strongly positive dendritic effects were observed for ligand and catalyst loading, and for catalytic activity and recycling. Indeed the nondendritic analogues were much less efficient than the dendritic catalysts. Analysis by ICP for the Suzuki–Miyaura reactions showed that the quantity of leached Pd after eight cycles was negligible. The catalyst was recycled a large number of times without significant decrease in yield. All these benefits in terms of Pd loading, efficiency and stability of the dendritic γ-Fe_2O_3@SiO_2 compared to the nondendritic analogue, that is, the positive dendritic effects, are taken into account by the barrier that is formed by the dendronic frame at the framework periphery that protects the PdNP catalyst inside the dendrimer and induces its localization on the surface of the silica shell.[77]

Another method that is simpler and also efficient consists of impregnating dendritically preformed NPs on the magnetic support. Simple impregnation of maghemite γ-Fe_2O_3@SiO_2 with an aqueous solution of dendrimer **1** containing stabilized PdNPs is a new method of producing highly efficient heterogeneous catalysts (Figure 6).

It provides much better stability, recyclability, and activity in C–C cross coupling reactions and selective oxidation in water

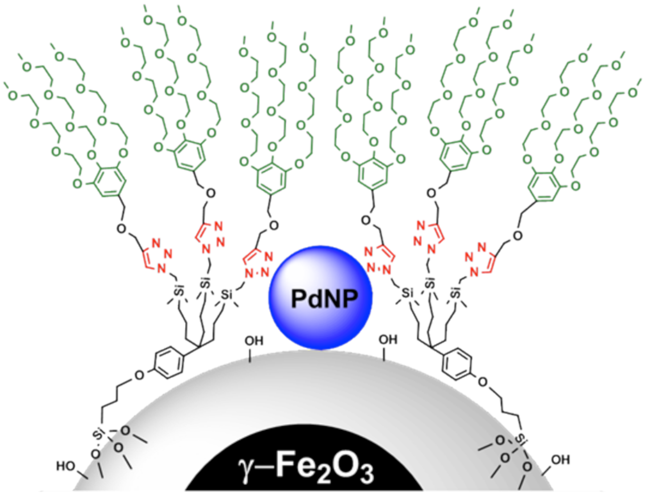

Figure 5. SPION with PdNP protected by dendronized triazole ligands attached to the silica surface. Reproduced with permission from Wiley.[77]

of benzyl alcohol to benzaldehyde than unsupported Pd nanoparticles. Thus, γ-Fe_2O_3 MNPs of approximately 10 nm diameter were synthesized by the coprecipitation method described by Shylesh et al.[67] These NPs are subsequently coated with a dense silica layer, in order to improve the water solubility and the biocompatibility and reduce iron leaching from the core. Therefore, tetraethoxysilane is used as the silica source and aqueous NH_3 as the hydrolyzing agent favor the ligandation of PdNPs at the SiO_2 surface.74 It is possible to obtain a quantitative loading of Pd upon mixing preformed dendrimer-encapsulated PdNPs and γ-Fe_2O_3@SiO_2 under optimized conditions. For the Suzuki−Miyaura reaction between phenyl boronic acid and bromobenzene, the catalyst was used five times without much activity loss, the yields decreasing from 99% yield (first run) to 91% (fifth run). Inductively coupled plasma optical emission spectrometry-optical emission spectrometry (ICP-OES) showed that only 0.3% of Pd composing the catalyst was lost after the first run. Copper-free Sonoganishra and Heck reactions of iodobenzene also proceeded quantitatively and full catalyst recovery. Finally, the oxidation of benzylic alcohol does not work at all in the presence of triazole dendrimer-stabilized PdNPs, because the PdNPs precipitate when dioxygen is bubbled. However, with 5 mn dioxygen bubbling with the γ-Fe_2O_3@SiO_2 impregnated dendrimer-stabilized PdNPs, the conversion to benzaldehyde is selective and quantitative with only 0.09−0.20 mol % of Pd from this catalyst in the presence of KOH as base in water, at 60 °C. In summary, this method produced a stable, versatile, efficient, and recyclable magnetic catalyst for a variety of crucial reactions under sustainable conditions.[78]

■ COMPARISON BETWEEN DENDRIMER CATALYSTS AND MAGNETIC CATALYST

Dendritic catalysts and magnetic catalysts share the recovery and recycling properties provided by the support, and both kinds of supports have been extensively developed. In terms of catalyst preparation, both methods require engineering that

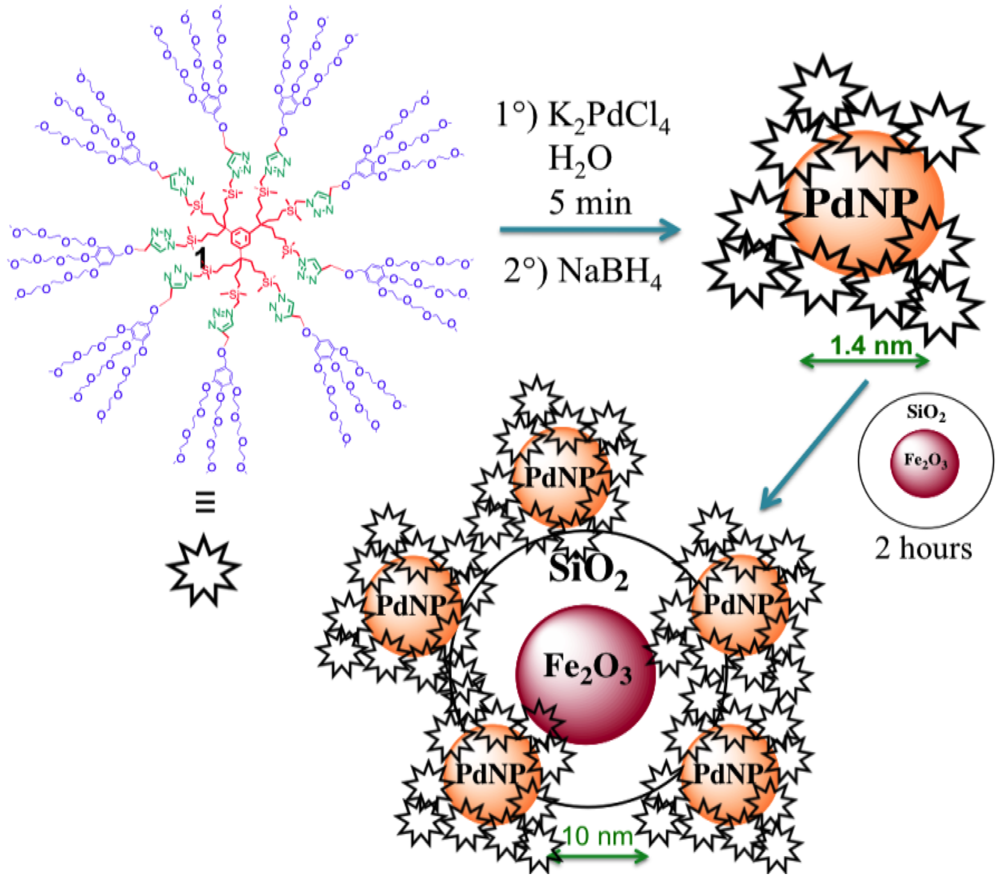

Figure 6. Impregnation of SPIONs with DENs.[79]

Table 1. Comparison between Dendritic and Magnetic Catalysts[a]

metallodendrimer	metal	reaction	recyclability	stability	activity
dendrimers of Figure 2	Pd	C−C cross-coupling	+++ by filtration	+++	+
dendrimer 1	Ru	olefin metathesis	++ by filtration	++	+++
dendrimer 1	Cu	CuAAC	+ by extraction	+++ (under N_2)	+++
dendrimer 1	Pd	C−C cross-coupling	+ by extraction	+	+++
γ-Fe_2O_3@SiO_2 (eq 3)	Ru	RuAAC	+++ with magnet	+++ (under N_2)	+++
γ-Fe_2O_3@SiO_2[60]	Cu	CuAAC	+++ with magnet	+++ (under N_2)	++
γ-Fe_2O_3@SiO_2 with tris-trz (eq 4)	Pd	alcohol oxidation	+++ with magnet	+++	++
γ-Fe_2O_3@SiO_2 with linear trz-PEG	Pd	C−C cross-coupling	++ with magnet	++	+
γ-Fe_2O_3@SiO_2 with dendritic trz-PEG	Pd	C−C cross-coupling	+++ with magnet	+++	+++
γ-Fe_2O_3@SiO_2 with dendrimer 1	Pd	C−C cross-coupling	+++ with magnet	+++	+++
γ-Fe_2O_3@SiO_2 with dendrimer 1	Pd	alcohol oxidation	+++ with magnet	+++	+++

[a]+, normal; ++, good; +++, excellent.

depends on the nature of the active catalyst. The synthesis of dendrimers is often time-consuming, but the PAMAM dendrimers are commercial and readily functionalized for catalytic purpose.[32−34] Dendritic properties are currently obtained with readily prepared zeroth- and first-generation dendrimers, and low-generation dendrimers are usually better catalyst supports than high-generation ones due to bulk problems.[23,24] It is also possible to use star-shape macromolecules with benefit rather than real dendrimers to avoid the periphery bulk problem periphery.[80,81] An advantage of magnetic supports over dendrimer ones is that the magnetic supports are insoluble solids, whereas dendritic catalysts are sometimes soluble as homogeneous catalysts, which makes separation occasionally tedious. Suitable design, however, allows avoiding this problem even with small insoluble dendrimer catalysts.[24] Recently, magnetic catalysts have become very popular, because suitable engineering allows relatively practical catalyst preparations with SPIONs, and separation from product using an external magnet is a very simple, efficient, and attractive method. Table 1 summarizes the compared performances of dendritic and magnetic catalysts discussed in this Account. Dendritic catalysts generally show higher avtivity than magnetic catalysts, whereas magnetic catalysts perform better than dendritic ones in terms of recyclability. Dendritic magnetic catalysts combine the advantages of both types of catalysts, and therefore, they are very promising.

■ CONCLUSION AND OUTLOOK

The emergence of dendritic architectures has generated many possibilities in catalysis including locating the catalyst at the dendritic termini or core with positive or negative effects in terms of catalyst stability, selectivity, and efficiency depending on the nature of the catalytic system and design parameters. For instance, insolubilization of the metallodendritic complexes provides efficient heterogeneous catalysts. The intradendritic formation of zerovalent transition-metal NPs allows stabilizing NPs for catalysis. Catalytic reactions involve leaching of the active metal with both molecular and NP catalysts, which is a drawback. Recent developments have introduced the concept of micellar dendritic ligands and catalysts whereby the dendritic periphery protects the catalytically active centers. The use of magnetic catalysts, in particular with SPIONs, has allowed a remarkable development of new heterogeneous supports allowing easy separation of the catalyst with a simple magnet. A recent sophistication of this attractive technique has involved the combination of dendritic and magnetic supports. In particular, as illustrated here, we have introduced SPION catalysts surrounded by dendronic ligands that allow encapsulating PdNP catalysts at the surface of the γ-Fe_2O_3@SiO_2 core. Positive dendritic effects concerning PdNP loading, stability and efficiency were shown to result from protection by the bulk of the dendronic periphery just as in dendritic micellar catalysis. The system can even be made simpler by impregnation of the SPION by the dendrimer-encapsulated PdNPs.

In conclusion, excellent results have been obtained with such dendrimer-encapsulated molecular or NP catalysts with or without γ-Fe_2O_3@SiO_2 core for olefin metathesis, CuAAC, various cross C−C coupling and selective alcohol oxidation reactions. Many more catalytic reactions should be much improved by sustainable procedures including catalyst recovery in the future using such catalyst design.

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Notes

The authors declare no competing financial interest.

Biographies

Dong Wang passed a doctorate with Professor Baohua Chen in Lanzhou, China, and a Ph.D. with Professor Didier Astruc in Bordeaux on dendrimer catalysis (2014) and is presently working as a postdoc with Professor Datong Song in Toronto.

Christophe Deraedt studied at the Univ. Bordeaux where he completed his Ph.D. on dendritic catalysis in December 2014 under the supervision of Didier Astruc and is now joining Professor Makoto Fujita's group in Tokyo for postdoctoral studies.

Jaime Ruiz studied at the Catholic University of Santiago, Chile, with Professor Enrique Roman, passed his PhD and habilitation in Bordeaux, did his postdoc in Austin with Professor Alan H. Cowley, and is presently an engineer in Didier Astruc's group.

Didier Astruc studied and passed his Ph.D. in Rennes with Professor René Dabard, did postdoctoral work with Professor Richard Schrock at MIT, and is Professor of Chemistry in Bordeaux and Member of the Institut Universitaire de France.

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