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Pd(0) encapsulated nanocatalysts as superior catalytic systems for Pd-catalyzed organic transformations

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In the last decade, Pd(0) nanoparticles have attracted increasing attention due to their outstanding utility as nanocatalysts in a wide variety of key chemical reactions. Remarkably, it has now been well-recognized that the encapsulation of Pd(0) nanoparticles as catalysts in various porous systems can protect the catalyst from deactivation, facilitate its separation and significantly increase its reusability. Encapsulated Pd(0) nanoparticles have also had great impact on the catalytic process in terms of reactivity and selectivity, through imposing confinement effects. In this review, we have tried to underscore the potential advantages associated with various organic, inorganic and hybrid porous systems, such as dendrimers, silica mesoporous systems, MOFs and zeolites, for Pd(0) encapsulation between 2005–2016 and disclose the role of confinement effects on the promotion of catalytic activity of the Pd(0) encapsulated species, which have been used as catalysts in some important organic transformations such as C–C coupling reactions, hydrogenation and oxidation reactions. The advantages and merits provided and observed using the encapsulated Pd(0) nanoparticles are compared with those of the corresponding conventional species. These qualities, particularly in terms of Pd leaching, reusability and activity, are systematically discussed.

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1. Introduction

Indisputably, palladium nanoparticles, Pd NPs, are among the most important catalysts in organic transformations,^{1–5} and have even found applications in pharmacology.⁶ In spite of their relatively high price, Pd catalysts are useful enough, and worth being widely used by organic chemists and being employed as catalysts in large scale productions.

Homogeneous Pd-catalyzed reactions are extensively used because of their solubility, which results in better reactivity, versatility, and tolerance of a wide range of functional groups. However, homogeneous catalysis meets some drawbacks, such as possible Pd contamination of the product, which necessitates costly additional purification. In addition, in homogeneous catalysis an appreciable amount of catalyst is lost during the reaction and work-up procedure. Thus, in industries where Pdcatalyzed reactions are a part of their daily programmed processes, usually at the same time, their R&D sections practically, but reasonably, try to make these reactions economically feasible. Along this line, in academia, investigations to modify and improve the catalytic activity of nano Pd-catalysts are at the centre of attention. Nowadays, it is well-recognized that performing a nano Pd-catalyzed reaction under heterogeneous catalysis is from different points of view, an achievement of great impact. In a fruitful heterogeneous catalysis, a simple and effective separation of the used catalyst is quite practical and thus, provides a promising, efficient reusability of this class of catalyst. In this regard, heterogeneous catalysis, which is generally accepted as more favourable catalysis, is of paramount importance, particularly in the relatively expensive Pd-catalyzed organic transformations.7,8 To accomplish such conditions nowadays, the catalysts are commonly immobilized on various types of supports.9-12

The advances in nanotechnology lead to the synthesis of various metal nanoparticles with definite shapes, sizes and morphologies. Currently, metallic nanoparticles, alloys and oxides are widely used as catalysts. In this regard, the progress in the fundamental understanding of the effects of structural features of nanoparticles on their catalytic performance result in growing applications of nanocatalysts.^{13,14}

Several Pd nanoparticles (Pd-NPs) have been immobilized on conventional supports, such as mesoporous silica and zeolites, in order to reduce the catalyst loading and prevent Pd species from agglomerating.¹⁵ Undoubtedly, this strategy circumvents some problems incorporated in several Pd-catalyzed reactions.¹⁶⁻¹⁹ The catalyst can be easily recovered by simple filtration and reused several times under optimized reaction conditions, usually without appreciable loss of activity; however, using conventional procedures only results in the immobilization of the Pd species on the surface of the support. Expectedly in such cases, during recovery and reusability, the Pd-species are subjected to undesired leaching to some extent.

Enzymes are natural catalysts with the capability of the encapsulation of multiple functionalities within their cavities; thus, they can efficiently promote catalytic processes in living organisms with excellent activity and selectivity. Their excellent, elegant and sophisticated catalytic behaviors have inspired and encouraged scientists to develop highly efficient catalysts that could mimic the enzymes' superior catalytic activities, including being recycled in different reaction runs without considerable loss of catalytic performance.^{20–22}

The microenvironment inside the enzyme cavity can effectively influence the reactions catalyzed by enzymes. Most of the effective parameters in enzyme operation, such as substrate preorganization, restricted substrate motion, protein dynamics, covalent binding of the transition state and desolvation of the substrate are induced by this microenvironment. Therefore, many efforts have been devoted to the design and synthesis of systems with a binding cavity,^{20,21} named the nanoreactor, which contains a restricted microcavity and can encapsulate guest species through binding interactions and the induced cavity effect.²⁰⁻²⁷ Although the nanoreactor concept is relatively new, there are several natural counterparts in nature, such as mitochondria, nucleus, Golgi apparatus, lysosomes, and the pores of channel proteins that inspired the researchers.²⁸ It is worth noting that the nanoreactor is different from a conventional nanometric reaction chamber like a bench-top or microreactor.29 The interior microenvironment of the nanoreactor can affect the process and result in new yields, kinetics, mechanism, activity and selectivity,23,30 which may be different from the bulk solvent reaction.29,31

Nanoreactors can possess active sites, such as transition metal species. Similarly, the confined space provided by nanoreactors can influence the reaction in terms of reaction mechanism and rate, via concentrating the substrates and additional interactions of the substrates and active sites.28,31 Moreover, a nanoreactor protects the catalyst from deactivation, facilitates its separation and improves its reusability. In the case of a nanometric system such as Pd NPs, the size and morphology of the catalyst are well controlled via encapsulation. In this way, the catalytic activity of the catalyst is improved and its agglomeration and deactivation are avoided. It is worth noting that although the concepts of catalyst immobilization and encapsulation are sometimes used interchangeably, these two concepts are different. A conventional support is usually a heterogeneous porous material with high surface area, which is used for immobilizing the catalytic species on the surface. A nanoreactor, however, is a heterogeneous or homogeneous compound with a designed cavity for hosting and embedding the catalyst to improve the catalytic performance and catalyst leaching. In recent years, several divergent organic, inorganic and hybrid nanoreactors, such as dendrimers, mesoporous silica, metal organic frameworks (MOFs) and zeolites have been developed^{21,31-33} and used for the encapsulation of Pd NPs. Nowadays, the utility of encapsulated PdNPs has been well recognized and practically applied for a wide range of chemical reactions.^{3,34-39} The advantages of using these encapsulated Pd catalysts are that the catalytic palladium sites in this system are accessed by diffusion through the porous material, while the left over Pd is trapped within, leading to a low level of metal remaining in the crude desired product. These merits have led to promising features for encapsulated PdNPs. Apart from high selectivity and reactivity, low Pd leaching37 and other

superiorities, such as the facile recovery of the catalyst by simple filtration, handling the Pd in a safe way, compatibility with a broad range of industrial processes and non-conventional, environmentally benign sources of heating, such as microwave irradiation (MWI), have been observed and well-recognized. These advantages have resulted in the development of some catalysts that are commercially available nowadays. One of the market purchasable encapsulated catalytic systems is Pd EnCat®, which is prepared by employing microencapsulation technology to immobilize the Pd diversely with activating ligands, on a highly cross linked polyurea matrix.⁴⁰ It has successfully catalyzed a plethora of organic reactions, including some important reactions like the Suzuki⁴¹ reaction and the hydrogenolysis of epoxides.⁴²

Catalysed organic reactions are of great importance.^{43–65} In 2016, a book concerning nanoreactors and their applications, including catalysis, was published.³¹ Taking the importance of these concepts into account, and in an attempt to propagate the concept of enzyme mimic catalysts,⁶⁶ herein, we highlight the recent advances (2005–2016) in the encapsulation of Pd in various porous compounds, such as dendrimers, polymers, zeolites, porous silica, carbon-based materials and MOFs, to prepare Pd encapsulated catalysts as superior catalysts and their advantageous utilities in various organic transformations.

It is worth mentioning that due to the huge number of relevant references concerning all kinds of Pd encapsulated catalysts, this review describes only the catalytic activity of nano Pd(0) encapsulated catalysts comprised of porous systems. It is worth noting that other reviews concerning the applications of other Pd species and encapsulated catalysts comprised of diverse supports are under preparation in our group, which will be published separately in due course.

2. Silica-encapsulated Pd NPs

Silica-based materials are among the most studied systems for embedding NPs.^{67–77} The structural properties of silica supports, such as pore (channel) size, pore volume and surface area render the encapsulated catalyst heterogeneous, more stable and active. To date, various kinds of silica materials have been applied for the confinement of catalysts.^{78–88}

Carbon thin film-lined SBA-15 was used as a nanoreactor for the encapsulation of Pd NPs. This hybrid system exhibited high catalytic activity for Suzuki–Miyaura cross coupling reactions in water in the presence of K_2CO_3 (Scheme 1).¹⁵ It was demonstrated that the addition of tetrabutylammonium bromide as



Scheme 1 The Suzuki-Miyaura cross coupling reaction.

a phase transferring agent could enhance the reaction rate. It is worth noting that the reaction did not proceed in the presence of Pd on earbon block (CP). This characterian was attributed to

of Pd on carbon black (CB). This observation was attributed to Pd agglomeration and the low accessible surface area of CB. The catalyst was reusable and could be recovered and reused for five reaction runs. Furthermore, ICP-AES analysis proved only a small amount of Pd leaching. A kinetic study indicated the crucial role of carbon thin film lining in achieving high reactivity of the catalyst and stability of the nanoreactor.

Yang *et al.* developed a novel catalyst for the aerobic oxidation of alcohols through the confinement of Pd NPs within the nanocavities of SBA-16.⁸⁹ The preparation was carried out by the modification of mesoporous silica, and the subsequent introduction of Pd(OAc)₂, followed by reduction. Various substrates, including 1-phenylethanol, benzylic and allylic alcohols could be oxidized efficiently under mild reaction conditions (*i.e.* ambient temperature, aqueous media and under O₂ atmosphere or air) in the absence of base. The catalyst exhibited outstanding reusability and was recovered and reused for twelve reaction cycles, with only negligible loss of activity and selectivity. The high reusability originated from the unique structure of SBA-16, which prevented Pd growth in the course of the catalytic reaction.

Pd NPs were confined within the pores of mesoporous SBA-15 of diverse textural properties and morphologies, through a novel and facile two-solvent procedure.⁹⁰ Investigating the catalytic oxidation of toluene demonstrated that the morphology of the catalyst support influenced the active phase dispersion, and the platelet-like morphology resulted in the best catalytic activity. Besides, Pd dispersion, pore properties (diameter and length) and CO_2 desorption capability affected the catalytic performance.

Toluene oxidation at low temperature was also reported by using Pd NPs confined within short column SBA-15 with controllable acidity and expanded microporosity.⁹¹ The observed high catalytic activity was attributed to active phase dispersion, as well as the synergetic effect of microporosity. It is worth noting that water vapor had a detrimental effect on catalytic activity, due to the formation of the inactive Pdhydroxide.

Two methods, grafting and impregnation were used for the confinement of Pd NPs in SBA-15. The effects of solvent on Pd dispersion and the catalytic activity of catalysts for the oxidation of toluene were investigated in terms of performance, selectivity, activity and stability.⁹² It was revealed that catalysts prepared *via* the grafting method were more efficient. However, both types of catalysts resulted in high CO₂ selectivity, toluene conversion and high stability. Moreover, solvent affected the particle size dramatically and DMF was the best solvent choice.

Jong *et al.* used a series of thiol-functionalized silica compounds, *i.e.* SBA-15, m-MCF, Aerosil-380 and plugged SBA-15 for confining ultra fine (\sim 2 nm) Pd NPs.⁹³ The authors investigated the catalytic activity of the confined NPs for the C–C coupling Suzuki and Heck reactions. In the case of the Heck reaction, although it was demonstrated that leached species had an essential role in catalytic activity, mesoporous silica could provide a more stable catalyst through limiting Pd



growth. For the Suzuki reaction, which was performed in stronger alkaline conditions, the catalyst based on plugged SBA-15 exhibited superior catalytic activity. Additionally, poor reusability was obtained for SBA-15.

Pd NPs were encapsulated within the channels of SBA-15. The synthesized Pd/SBA-15 with 3.01 wt% Pd loading and dispersion was used as the catalyst for performing the Heck coupling reaction in air and in the presence of triethylamine as base (Scheme 2).94 It is worth noting that the SBA-15 arrangement and pore ordering were not affected by metal loading. Excellent catalytic performance and good reusability are the advantages of this catalyst.

Highly-dispersed Pd NPs were anchored within the interior channels of MCM-41, via a one-pot convenient strategy.95 In this strategy, the surfactant, CTAB, not only served for the formation of MCM-41, but also played a role in grafting Pd species (Fig. 1). This system was used as a catalyst for the Suzuki coupling reaction of iodobenzene and phenylboronic acid. The results indicated the excellent catalytic activity of this catalyst. The reaction proceeded in the presence of 1.1 wt% catalyst and led to 91.42% conversion in a very short reaction time (5 min). The calculated TOF was 98.25 min⁻¹. Moreover, the catalyst was reusable and could be recovered and reused with preserving its catalytic activity. The ICP investigations ruled out the possibility of the leaching of Pd species.



Scheme 3 Selective hydrogenolysis of benzyl ether to primary alcohols.96

Lee et al. investigated the catalytic activity of ball-shaped Pd@MCM-48 nanocatalysts for the selective hydrogenolysis of benzyl ether to primary alcohols (Scheme 3).96 It was found that only unsubstituted benzyl ethers reacted in the presence of the new catalyst. Furthermore, the hydrogenolysis proceeded selectively and hydrogenation of a double bond was not observed. The comparison of catalytic activity and selectivity of this catalyst with those of Pd/SiO2, Pd/C and Pd(OH)2/C proved the superior catalytic performance of the former.

In another attempt, a novel nanoreactor based on Pd NPs encapsulated within mesoporous silica hollow spheres, with excellent catalytic activity for the Suzuki coupling reaction was synthesized by Song et al.97 The catalyst was obtained through a controlled three step procedure, in which carbon nanospheres were used for anchoring Pd NPs to afford a Pd/C composite with well-distributed Pd NPs with average size of 5 nm. Subsequently, the Pd/C composite was covered with a mesoporous silica shell. The final catalyst was obtained by calcinations and removing the carbon sphere and template. Investigating the catalytic activity of the nanoreactor for the Suzuki reaction confirmed that the novel catalyst could promote the reaction efficiently, in a very short reaction time. Moreover, good substrate tolerance was observed (Table 1). The authors



Fig. 1 One-pot synthetic route for Pd/MCM-41. CTAB played a double role as both the micelle template and the Pd grafting agent. Reprinted from ref. 95 with permission from the Royal Society of Chemistry.

Table 1 Suzuki reactions catalyzed by composite reactors.^a Adapted from ref. 97 with permission from the Royal Society of Chemistry

Substrate	Substrate	Time (min)	Yield (%)
Phenylboronic acid	Iodobenzene	3	99.5
Phenylboronic acid	Bromobenzene	3	32.4
HO ₂ C-B(OH) ₂	Iodobenzene	3	67.2
B(OH) ₂	Iodobenzene	3	86.3
Phenylboronic acid	1-Ethyl-4-iodobenzene	10	80.0
2,4-Difluorophenylboronic acid	Iodobenzene	3	50.6

^a Reaction conditions: 80 °C, ethanol (10 mL), iodobenzene (0.5 mmol), phenylboronic acid (1 mmol), K2CO3 (2 mmol), catalyst (10 mg, with Pd loading 4 wt%).

Table 2Hydrogenation of phenylacetylene to styrene with catalysts^a.Adapted from ref. 98 with the permission of the Royal Society of
Chemistry

Catalyst	Time (h)	Selectivity ^b (%)	Conversion ^b (%)	${{\operatorname{TOF}}^d} {\left({{{\mathrm{h}}^{ - 1}}} ight)}$
SiO ₂ @CuFe ₂ O ₄ -Pd	2.5	98	98	91
Lindlar catalyst ^c	2.5	92	82	64
Lindlar catalyst ^c	3.5	76	98	54
SiO ₂ @CuFe ₂ O ₄	2.5	_	_	0
SiO ₂ @Pd	2.5	98	3	3

 a Reaction conditions: phenylacetylene, 0.91 mmol; catalyst, 10 mg; hexane, 2 mL. H₂ balloon (about 1 atm). b Confirmed by ¹H NMR and GC. c Lindlar catalyst (*ca.* 5 wt% Pd on CaCO₃ poisoned with a lead complex, Aldrich, 10 mg). d [mol product]/[mol catalyst][hour].



Fig. 2 Schematic representation of the synthesis of SiO₂/Pd-NP/ porous-SiO₂ core-shell-shell nanospheres. Reprinted from ref. 99 with the permission of the Royal Society of Chemistry.

attributed the high catalytic activity of the catalyst to its structural properties, which could impose the confinement effect. The structure of the nanoreactor facilitated the adsorption of substrates by high surface area silica shell and their subsequent diffusion through the pores. This could concentrate the substrates in the proximity of interior residing Pd NPs. Measuring the Pd leaching of the nanoreactor and comparing the results with those of the Pd@carbon spheres proved its lower (about 8 times) Pd leaching.

Combining the confinement effect and the synergetic effects of bimetallic systems, Hur *et al.* designed a novel catalyst, $SiO_2@CuFe_2O_4$ -Pd, for the selective hydrogenation of phenylacetylene to styrene.⁹⁸ The catalyst was composed of copper ferrite and Pd encapsulated in a core/shell silica microsphere. The novel catalyst exhibited superior performance, compared to the Lindlar catalyst, in terms of selectivity and conversion (Table 2). The authors investigated the role of each NP in catalysis by examining the catalytic activity of individual $SiO_2@CuFe_2O_4$ and $SiO_2@Pd$. The results indicated that the former system was not active for hydrogenation. $SiO_2@Pd$ however, exhibited high selectivity and very low conversion. This observation implied that $CuFe_2O_4$ NPs could only promote the reaction when they were coupled with Pd NPs in the confined space.

Efficient heterogeneous and recyclable catalysts were developed based on SiO_2/Pd -NP/porous-SiO_2 core-shell-shell nanospheres for Heck coupling reactions and hydrogenation.⁹⁹ The procedure for preparing the catalyst (Fig. 2) consisted of the synthesis of octahedral Pd NPs, followed by anchoring them onto the amino functionalized silica nanospheres to afford SiO_2/Pd -NP core-shell nanospheres. These were subsequently coated with another silica shell to sandwich the Pd NPs. Finally, the exterior silica shell was etched to render the outer shell mesoporous, allowing the egress of substrates to access Pd NPs. Besides, high catalytic activity, catalyst reusability and insignificant Pd leaching were observed.

Using a wet-chemical process, Yin, Zhang *et al.* developed a novel and simple procedure for the preparation of graphenenanosheet-supported metal NPs, encapsulated by thin mesoporous SiO_2 layers.¹⁰⁰ The synthetic procedure (Fig. 3) consisted



Fig. 3 Synthesis of $M-RGO@mSiO_2$. Reprinted from ref. 100 with the permission of John Wiley and Sons.

of applying a deposition–precipitation method for loading metal NPs on graphene oxide sheets, followed by the formation of a silica layer by the hydrolysis of tetraethyl orthosilicate (TEOS). Finally, the hybrid system was obtained by annealing under H₂. The obtained NPs (such as Pd NPs) could be considered as reusable catalysts for both gas and liquid phase reactions, with high thermal stability and catalytic activity. In this hybrid system, the high surface area of graphene sheets improved the catalytic activity. Additionally, the exterior silica layer could confine the metal NPs and prevent them from sintering. Furthermore, strong π – π stacking interactions among graphene nanosheets would be avoided by the silica layer.

Efficient hydrogenation of olefins was achieved in aqueous media¹⁰¹ by using Pd NPs encapsulated within fluoro-functionalized yolk–shell mesoporous silica, y-Pd@mSiO₂-F. The catalyst was obtained by the impregnation of silica support with $Pd(OAc)_2$, followed by reduction with NaBH₄ to afford Pd/SiO₂, which was treated with CTAB and TEOS. Finally, etching was performed by using sodium carbonate under N₂ atmosphere to afford yPd@mSiO₂. The fluoro-functionalized species was prepared by treating yPd@mSiO₂ with 3,3,3-trifluoropropyltrimethoxysilane under N₂ atmosphere. The comparison of catalytic activities of both catalysts for the hydrogenation of methyl

Table 3 Results of hydrogenation of different substrates over the two catalysts. Adapted from ref. 101 with the permission of Elsevier

					Conversion ^a (%)	
Substrate	Product	Temp. (°C)	Time (min)	Pressure (MPa)	yPd@mSiO ₂	yPd@mSiO ₂ -F
Styrene	Ethylbenzene	25	45	0.15	45	88
\sim	\sim	30	30	0.15	48	96
\sim	γ^0	50	60	0.30	79	92
H ₂ N	H ₂ N H ₂ N	35	60	0.15	49	99
		30	45	0.15	65	94
\sim	γ^{0}	25	60	0.15	71	94
^{<i>a</i>} Determined by G	GC.					

acrylate proved the higher catalytic activity of y-Pd@mSiO₂-F (Table 3). This catalyst also exhibited high reusability and could be used for five reaction runs without significant loss of activity.

Silica nanotubes (SNT) were also used for the immobilization of Pd NPs. The catalytic activity of the hybrid system, Pd@SNT was investigated for Suzuki-Miyaura coupling and sp² C-H arylation of thiazoles (Schemes 4 and 5).¹⁰² To prepare the catalyst, anodized aluminum oxide (AAO) was deposited by a silica layer, followed by functionalization of the interior surface of SNTs and treatment with Na₂PdCl₄. Finally, the catalyst was obtained by baking at 120 °C and dissolving the template in phosphoric acid. One of the merits of the Pd@SNT system was the possibility of surface modification with various modification agents, such as trimethoxy octadecyl silane (C18), (3-aminopropyl)triethoxy silane (APTES) and 2-[methoxy-(polyethylenoxy)propyl]trimethoxy silane (PEG) in a simple manner. APTES-Pd@SNTs exhibited higher catalytic activity, compared with Pd@SNT. This higher activity emerged from the smaller size of Pd NPs and the higher number of Pd atoms at edges and vertexes. Moreover, the amino group in APTES could act as an anchoring ligand for Pd NPs residing within SNTs.

Paul *et al.* reported the synthesis of a novel catalyst composed of Pd NPs immobilized onto ethylene diamine functionalized silica-cellulose substrates [Pd(0)–EDA/SCs].¹⁰³ The authors explored the catalytic activity of this hybrid system for C–S and C–C coupling reactions in aqueous media. High catalytic activity, catalyst reusability and performing the reaction in the absence of base or in less basic conditions were the merits of this novel catalytic system.

Iranpoor and Firouzabadi *et al.* phosphorylated silica gel to obtain silica diphenylphosphinite (SDPP), which was subsequently treated with Pd(n) to furnish Pd(0)/SDPP nanocatalyst. This catalyst proved to be very efficient for C–S and C–O arylation of various aryl halides, thiophenols and phenols under mild reaction conditions (Scheme 6).¹⁰⁴ It can be noted that the catalyst was reusable and could be used for several reaction runs without significant loss of activity. Moreover, Pd leaching at the first reaction run was 3.2 and reached 7.4% at the fifth reaction run.



Scheme 4 Suzuki-Miyaura coupling reaction.¹⁰²



R₁ = H, 4-OMe, 4-Me R₂ = H, 4-Me, 4-OMe, 4-Cl, 4-Br, 4-CO₂Et, 2-F, 2-NO₂, 2-OMe

Scheme 5 sp² C–H arylation of thiazoles.¹⁰²



Scheme 6 C-S and C-O arylation of various aryl halides, thiophenols and phenols.104

Basu et al. disclosed the utility of Pd NPs supported on mesoporous silica, SiO₂@PdNP, for promoting phosphine-free Suzuki-Miyaura and Heck coupling reactions.¹⁰⁵ The reaction proceeded in the presence of low amounts of Pd catalyst (0.006 mol%). However, the catalyst did not exhibit high catalytic activity for the Heck reaction of bromoarenes and the Suzuki-Miyaura reaction of chloroarenes. High values of TON/TOF, reusability of the catalyst and the environmentally-benign procedure for catalyst preparation were other merits of the procedure.

Using the soft templating method, Liu et al. revealed the synthesis of yolk-shell NPs, YSNs, which were composed of a dense silica sphere as core, a shell of mesoporous periodic organosilica (PMO) and a hollow space between. The thickness of the shell and the dimensions of the void space could be controlled by adjusting the synthetic parameters. The authors proved the utility of this hybrid material, YS-PMO, for the encapsulation of various NPs such as Pd, Pt and Au, which could be considered as catalytic nanoreactors. In this regard, Pd-YS-PMO was synthesized by the impregnation and reduction of $Pd(NO_3)_2$ and applied for the selective oxidation of alcohols to the corresponding aldehyde (Table 4). As shown in this table, high selectivities and conversions were obtained for most substrates. The authors believe that the hollow space between

core and shell could effectively influence the catalytic activity and stability of Pd NPs.106

Song et al.¹⁰⁷ achieved reactant shape selectivity for Suzuki coupling reactions (Table 5) by applying a novel nanoreactorlike catalyst, Pd@meso-SiO2, composed of Pd NPs hosted at interior pore mouths surrounded by mesoporous silica walls. The authors proposed that the observed shape selectivity resulted from the diffusion barrier that arose from the nanoreactor and preferential adsorption of bulky phenylboronic acid.

The Suzuki coupling reaction was also catalyzed by Pd@porousSiO₂ (Pd@pSiO₂) yolk-shell nanocatalyst, composed of Pd core and porous silica hollow shell (Scheme 7).¹⁰⁸ The

Table 5 Suzuki reactions of phenylboronic acids and iodobenzene catalyzed by Pd@meso-SiO2 nanoreactor¹⁰⁷

Substrate	Conversion (%)	Time (min)
Phenylboronic acid	99.5%	3
<i>p</i> -Carboxyphenylboronic acid	67.2%	3
<i>m</i> -Carboxyphenylboronic acid	59%	3
o-Carboxyphenylboronic acid	Trace	180
n-C ₄ H ₉ —B(OH) ₂	85.9%	5
t-C ₄ H ₉ —B(OH) ₂	Trace	300
$(H_3C)_2HC$ $CH(CH_3)_2$ $CH(CH_3)_2$	Trace	180
B(OH) ₂	Trace	180
B(OH) ₂	86.3%	3

Table 4	Selective oxidation	of various	alcohols into	o aldehyde over	Pd-YS-PMO	nanoreactors ^{<i>a</i>106}
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Substrate	Product	Time (h)	T^{b} (°C)	Conversion (%)	Selectivity ^c (%)
Benzyl alcohol	Benzaldehyde	8	50	94	>99
4-Methyl benzyl alcohol	4-Methyl benzaldehyde	8	50	92	>99
4-Methoxy benzyl alcohol	4-Methoxy benzaldehyde	8	50	100	>99
Ph	Рһсно	8	50	100	>99
ОН	СНО	8	50	53	>99

^a The reaction was carried out in O₂ atmosphere in the presence of 5 mol% Pd with water as solvent. ^b T: reaction temperature. ^c Selectivity to aldehyde.



Scheme 7 Suzuki coupling reaction catalyzed by Pd@pSiO₂.¹⁰⁸

catalytic activity of this novel catalyst was higher than the $Pd@SiO_2$ core-shell catalyst. This was attributed to the fast diffusion of substrates through the porous shell. Broad substrate scope, excellent activity, good recyclability and high thermal stability were the merits of this nanocatalyst.

Au@Pd bimetallic NPs were encapsulated within a nanoreactor with a hollow mesoporous shell. To prepare the hybrid system, the yolk–shell structure composed of the Au core and –Ph-bridged periodic mesoporous organosilica shell, Au@Ph-PMO was synthesized and subsequently, the seed-growth of Pd NPs on Au was performed to afford an amphiphilic nanoreactor, Au@Pd@Ph-PMO (Fig. 4). The nanoreactor proved to be highly active for the aerobic oxidation of alcohols under mild and green reaction conditions (*i.e.* under atmospheric pressure, in aqueous media and in the presence of air as oxidizing agent) to furnish the products (aldehydes and ketones) in high yields (conversion: 56–100%, selectivity: 90–100%).¹⁰⁹

Impregnation in organic solvents was employed for the preparation of supported ionic liquid phases, SILPs, within macrocellular silica-based hybrid foams, Si(HIPE).¹¹⁰ This system was subsequently functionalized by 1-[3-(triethoxysilyl) propyl]-imidazole and used for the entrapment of Pd salt. Finally, reduction by dihydrogen furnished Pd@ionic liquid@g-imidazole–Si(HIPE). The catalytic activity of hybrid system was investigated for Heck coupling reaction of cyclohexylacrylate



Fig. 4 Schematic illustrating the preparation of the amphiphilic nanoreactor Au@Pd@Ph-PMO. Reprinted from ref. 109 with the permission of the Royal Society of Chemistry.



Fig. 5 Preparation of the core–shell-structured silica materials with encapsulated Pd NPs. Reprinted from ref. 111 with the permission of the American Chemical Society.

and iodobenzene. The recovery of this heterogeneous system was facile and Pd leaching was insignificant. Moreover, the obtained TONs and TOFs were competitive with the best reported catalysts.

Reduction of bromate, BrO_3^- , which is a drinking water contaminant, was effectively catalyzed in H₂-saturated water at room temperature by Pd NPs confined within core–shell silica, SiO₂@Pd@mSiO₂.¹¹¹ The catalyst was composed of a nanoporous silica core decorated with octahedral Pd NPs. The core–shell system was obtained by the formation of a surfactant-templated mesoporous silica shell (Fig. 5). The catalytic activity of this novel catalyst was compared with those of Pd NPs and SiO₂@Pd@mSiO₂ (by a factor of 10). It was suggested that well-defined mesopores restricted Pd NPs aggregation and release from support. Moreover, the silica shell played a role in increasing the catalytic activity through bringing BrO_3^- in proximity to catalytic sites.

Devi *et al.* suppressed the sintering and deactivation of Pd NPs *via* encapsulation within the silica nanoreactor.¹¹² Quaternary ammonium thiol was used as the protecting ligand for preparation of water-dispersible ultra-small clusters of Pd. The encapsulated species were obtained through the condensation process, followed by calcinations. This strategy led to a system with high thermal stability and catalytic performance, with potential utility for high-temperature processes, such as *trans*-stilbene hydrogenation under ambient temperature.

Zeolite encapsulated Pd NPs

Zeolites were also used for the confinement of metal clusters,¹¹³ including Pd(0) NPs.^{114,115} In this regard, Ozkar *et al.* reported¹¹⁶ the utility of zeolite-Y confined Pd NPs as an efficient and reusable catalyst for the Suzuki cross-coupling reaction (Scheme 8) at ambient temperature and pressure. The reaction showed



Scheme 8 Suzuki cross-coupling reaction.¹¹⁶

a broad substrate scope and various substrates with several functional groups tolerated the coupling reaction in very high yield and shorter reaction time.

Hydrogenation of *para*-nitro phenol to *para*-aminophenol was promoted in the liquid phase in the presence of Pd NPs (3.8 nm) encapsulated within ZSM-5 zeolite. Confinement of Pd NPs inhibited the aggregation and loss of catalytic active sites. The novel catalyst exhibited high sulfur tolerance and could be used for five consecutive reaction cycles.¹¹⁷

This research group also reported the catalytic activity of zeolite-Y confined Pd(0) NPs for production of H_2 through the hydrolysis of ammonia-borane.¹¹⁸ The catalyst was synthesized *via* a two-step process in which Pd²⁺ ions were introduced into the zeolite by ion-exchange, and subsequently reduced with NaBH₄. It was demonstrated that the novel catalyst was reusable and could be used for five reaction cycles. Using this catalyst, 15 600 turnovers in hydrogen generation at ambient temperature were obtained.

Combining MOF and zeolite, Zhang *et al.* developed a novel anti-poisoning core–shell catalyst Pd/ZSM-5@ZIF-8 for the size selective hydrogenation of alkene.¹¹⁹ To prepare the catalyst, high-crystalline ZSM-5 was initially synthesized and subsequently exchanged with Pd salt. The reduction was performed by using NaBH₄ to afford the Pd/ZSM-5 core. Prior to combination of the ZIF-8 shell, surface modification was carried out. Catalytic testing was performed by using 1-hexene and cyclohexene as model reagents. It was shown that the core–shell catalyst was less effective for the hydrogenation of a sterically more demanding substrate, cyclohexene, whose size is larger than the ZIF-8 aperture.

4. MOF-encapsulated Pd NPs

Table 6 Debalogenation of any chlorides a_{141}

The unique structural features of MOF^{120,121} not only provide a suitable cavity for the encapsulation of metallic species, but also cause synergetic effects between encapsulated species (catalyst) and organic linker or/and metal node. There are numerous reports on MOF-encapsulated nanoparticles¹²²⁻¹³¹ and their utility for catalysis.¹³²⁻¹⁴⁰

MIL-101(Cr) was modified with nitrating acid and SnCl₂ to afford amine-functionalized MIL-101(Cr)-NH₂, which was palladated by using a solution of H₂PdCl₄, followed by reduction with NaBH₄. Using various analyses such as TEM, BET and XRD, the similarity of Pd particle size (2.49 nm) and cage diameter (2.9 nm and 3.4 nm) was demonstrated. The obtained Pd NPs encapsulated within the cavities of functionalized MOF, Pd/ MIL-101(Cr)– NH_2 , were used as efficient and reusable catalysts for the dehalogenation of aryl chlorides in aqueous media under mild reaction conditions (Table 6).141 The superior activity of Pd/MIL-101(Cr)-NH₂ compared to Pd/C and Pd/MIL-53(Al)-NH₂ was observed and ascribed to accessible mesoporous cages and the higher surface area of the former. It is worth noting that both C-halogen bond energy and absorption strength of the substrate on the catalyst affected the activity of the substrate. In this regard, performing the reaction in the presence of tetrabutylammonium bromide, which acted as a phase-transfer agent, accelerated the reaction time remarkably.

Cao *et al.* reported the utility of Pd NPs encapsulated in MIL-101(Cr), Pd/MIL-101(Cr), for the direct arylation of indoles with various aryl halides (Scheme 9).¹⁴² The authors established that the reaction did not proceed in the presence of free MIL-101(Cr). Additionally, the Pd loading had a crucial role in the catalytic activity and amount of observed byproduct, biphenyl. The best Pd loading was reported as 0.1 mol%. Another influential reaction variable was reaction time, which was relatively long (about 24 h), due to low catalyst loading and the slow diffusion



Scheme 9 Direct arylation of indoles with various aryl halides.142

Substrate	Product	Time (h)	$\operatorname{Yield}^{b}(\%)$	Substrate	Product	Time (h)	$\operatorname{Yield}^{b}(\%)$
4-Chlorophenol	Phenol	3	98	4-Chloroaniline	Aniline	3	96
4-Chlorophenol ^c	Phenol	3	47	4-Nitrochlorobenzene	Aniline	6	91
4-Chlorophenol ^d	Phenol	3	64	4-Methyl chlorobenzene	4-Methyl benzene	6	96
4-Chlorobenzene	Benzene	6	92	Methyl 4-chlorobenzoate	Methyl benzoate	6	92
4-Chlorobenzene ^e	Benzene	3	89	4-Chlorobenzoic acid	Benzoic acid	6	93
4-Bromobenzene	Benzene	6	97	1-Chloronaphthalene	Naphthalene	6	91
4-Iodobenzene	Benzene	6	81	3-Chloropyridine	Pyridine	6	95
2-Chlorophenol	Phenol	3	93	1,2-Dichlorobenzene	Benzene	8	97
3-Chlorophenol	Phenol	3	97	1,3-Dichlorobenzene	Benzene	8	96
1,4-Dichlorobenzene	Benzene	8	97	2,4-Dichlorophenol	Phenol	8	95
1,2,4-Trichlorobenzene	Benzene	8	94	2,4,6-Trichlorophenol	Phenol	8	95

^{*a*} Reaction conditions: aryl chloride (1 mmol), HCOONH₄ (10 mmol), Pd/MIL-101–NH₂ (1 mol% Pd), H₂O (5 mL), room temperature. ^{*b*} GC yield (*n*-dodecane as internal standard). ^{*c*} 5 wt% Pd/C (1 mol% Pd). ^{*d*} Pd/MIL-53(Al)–NH₂ (1 mol% Pd). ^{*e*} Tetrabutylammonium bromide (0.1 mmol) as phase-transfer agent.



Scheme 10 Direct arylation of indole derivatives with aryl boronic acids.¹⁴³



Scheme 11 Tandem Knoevenagel reaction of malononitrile and 4nitrobenzaldehyde, and subsequent hydrogenation of the nitro functional group into the amino moiety.¹⁴⁴

of substrates to the Pd site within the pores. Comparison of the catalytic activity of this catalyst with those of other Pd-based catalysts, such as Pd/C and palladium-supported MIL-53(Al)–NH₂, proved the superior catalytic performance of the former. This observation was ascribed to high surface area and accessible mesoporous cages of MIL-101, as well as increased surface Lewis acidity.

Direct arylation of indole derivatives with aryl boronic acids at the C2 position was also achieved under mild reaction conditions by using Pd NPs encapsulated within mesoporous cages of MIL-101.¹⁴³ In this procedure O_2 or 2,2,6,6-tetramethylpiperidine *N*-oxyradical (TEMPO) was used as an external oxidant. The process had a broad range of substrates (Scheme 10) and substrates with various functional groups could be arylated. Furthermore, the catalyst could be recycled from the reaction mixture simply, and reused for six reaction runs. No leaching and loss of activity was observed.

Li and co-workers designed and synthesized a core-shell catalyst composed of a Pd NPs core, surrounded by amino functionalized isoreticular MOF-3 (IRMOF-3) shell.144 The authors proved the utility of this hybrid catalyst for the tandem Knoevenagel reaction of malononitrile and 4-nitrobenzaldehyde and the subsequent hydrogenation of the nitro functional group into the amino moiety. It was postulated that alkaline IRMOF-3 shells could promote the condensation reaction while the hydrogenation reaction was catalyzed with encapsulated Pd NPs (Scheme 11). The comparison of the catalytic activity of this core-shell catalyst with those of supported Pd/IRMOF-3 hybrids indicated the higher activity of the former (Table 7). This observation was also confirmed by density functional theory (DFT) calculations. The origin of higher catalytic activity, which was the result of preferential selective hydrogenation of nitro group of the compound B, was the unique core-shell structure of the catalyst.

In a pioneering study, Luque *et al.* reported a new procedure for the encapsulation of Pd NPs within the UiO-67 cage. This strategy was based on the controllable introduction of metal precursors, prior to UiO-67 assembly (Scheme 12).¹⁴⁵ The catalyst preparation was carried out by reacting ZrCl₄, biphenyldicarboxylic acid, H₂bpdc, which acted as bridging ligand of UiO-67 and metalloligand H₂L, followed by reaction with H₂ (Scheme 12). The loading of Pd was tuned by adjusting the H₂L/ H₂bpdc ratios. Hydrogenation of the bulky substrate that could not access the interior of the MOF framework did not lead to any product, indicating that Pd NPs were encapsulated within the MOF. The authors investigated the catalytic activity of the



Scheme 12 Preparation of catalyst; adapted from ref. 145 with the permission of the Royal Society of Chemistry.

Table 7Cascade reactions of Knoevenagel condensation coupling with selective hydrogenation reactions catalyzed by different catalysts^a.Adapted from ref. 144 with the permission of the American Chemical Society

Catalyst A (В		Sel. (%)				
	A (conv.) (%)	Form. ^{<i>b</i>} (%)	$(\text{Conv.})^{c}(\%)$	С	2-(4-Nitrobenzyl)malononitrile	2-(4-Aminobenzyl)-malononitrile		
Pd@IRMOF-3	100	100	100	86	8	6		
Pd/IRMOF-3	100	100	100	71	24	5		
IRMOF-3	100	100	0	0	0	0		
Pd NPs ^d	26	26	_	_	_	_		
Pd NPs ^e	_	_	82	68	32	0		
Blank ^f	26	26	_	_	_	_		

^{*a*} Reaction conditions: A (0.2 mmol), malononitrile (0.21 mmol), catalyst (10 mg). ^{*b*} B is formed *via* the condensation reaction. ^{*c*} Formed B is converted *via* the hydrogenation reaction. ^{*d*} For Knoevenagel condensation alone. ^{*e*} 0.2 mmol B is used as the raw material for the hydrogenation reaction. ^{*f*} No catalysts are used for the cascade reactions.

Table 8Results of the oxidation of cinnamyl alcohol;adapted fromref. 145 with the permission of the Royal Society of Chemistry

Solvent	Sel. ^b [%]	Conv. [%]
Talaan a	00	-1
Toluene	99	<1
Toluene	>99	73
Toluene	>99	83
Toluene	>99	>99
Toluene	90	>99
DMF	>99	11
CH ₃ CN	>99	10
o-Xylene	>99	95
Toluene	98	5
Toluene	97	52
Toluene	>99	99
Toluene	72	51
	Solvent Toluene Toluene Toluene DMF CH ₃ CN <i>o</i> -Xylene Toluene Toluene Toluene Toluene	Solvent Sel. ^b [%] Toluene 99 Toluene >99 Toluene >99 Toluene 90 DMF >99 CH ₃ CN >99 o-Xylene >99 Toluene 98 Toluene 97 Toluene 97 Toluene 97 Toluene 97 Toluene 97 Toluene 72

 a Reaction conditions: cinnamyl alcohol (1 mmol), catalyst (Pd 1 mol%), solvent (10 mL), 80 °C, 20 h, under air. b Yields were determined by GCMS analysis. c 0.6% Pd 0 /UiO-67 was prepared by the impregnation method. d 1 eq. NaOH was added. e Results of the catalyst reused after ten cycles.

novel catalyst for alcohol oxidation and compared the catalytic activity of the catalyst for a model reaction (aerobic oxidation of cinnamyl alcohol) with those of related catalysts obtained from the impregnation method (Table 8). The results established the superior catalytic activity and stability of the novel catalyst that originated from the synergetic effects of nano-confinement and electron-donation offered by the MOF framework. The substrate scope of this process was confirmed by using various substrates with a variety of functional groups (Table 9). It is worth noting that this catalyst was also active for nitrobenzene reduction.

In another approach, an incipient wetting procedure and subsequent reduction was used for embedding Pd NPs (<3 nm) in MIL-101. The obtained hybrid system was used as an efficient catalyst for indole synthesis *via* cycloadditions of 2-haloanilines with alkynes in aqueous media (Scheme 13).¹⁴⁶ The catalytic

Table 9Oxidation of various alcohols catalyzed by 1.0% Pd⁰-in-UiO- 67^a . Adapted from ref. 145 with the permission of the Royal Society ofChemistry

Substrate	Product	Time [h]	Yield ^b [%]
Dongyl alaahal	Dongoldohudo	20	>00
Benzyi alconoi	Belizaideliyde	20	>99
4-Methyl benzyl alcohol	4-Methylbenzaldehyde	15	>99
4-Methoxy benzyl alcohol	4-Methoxybenzaldehyde	12	>99
4-Chloro benzyl alcohol	4-Chlorobenzaldehyde	40	98
1-Phenylethanol	Acetophenone	20	99
(<i>E</i>)-3-Phenylprop-2-en-1-ol ^c	Cinnamaldehyde	20	>99
(E)-Hex-2-en-1-ol ^c	(E)-Hex-2-enal	30	>99
Cyclohexylmethanol ^d	Cyclohexanecarbaldehyde	30	96
Octan-2-ol ^d	Octan-2-one	30	98
(Thiophen-2-yl)methanol ^d	Thiophene-2-carbaldehyde	20	98
(Furan-2-yl)methanol ^d	Furan-2-carbaldehyde	20	97
(Pyridin-2-yl)methanol ^d	Picolinaldehyde	20	98

 a Reaction conditions: alcohol (1 mmol), 1.0% Pd⁰-in-UiO-67 (Pd 1 mol%), toluene (10 mL), 100 °C, under air. b Yields were determined by GC-MS analysis. c 80 °C. d Pd 2 mol%, 120 °C.



Scheme 13 Indole synthesis via cycloadditions of 2-haloanilines with alkynes.¹⁴⁶

activity of this catalyst was superior, compared to Pd/MCM-41. This observation was attributed to the Lewis acidity on MIL-101, as well as increased surface hydrophobicity. It can be noted that the catalyst showed high stability and could be reused for 10 reaction cycles.

Pd@MIL-101 was also used for the hydrolysis of ammonia borane at room temperature. The choice of MIL-101 was based on its good chemical stability in aqueous media, high specific surface area and thermal stability, as well as the existence of two cages of *ca.* 2.9 and 3.4 nm. In comparison with previously reported Pd-containing nanocatalysts, this hybrid system exhibited higher catalytic activity (Table 10).¹⁴⁷ It was also revealed that the catalyst was durable and the catalytic activity would be preserved after 5 reaction runs.

Cao *et al.* supported Pd NPs on amino functionalized MIL-53(Al)–NH₂ through a direct anionic exchange procedure, followed by reduction with NaBH₄. The catalyst was applied for catalyzing the Suzuki–Miyaura cross-coupling reaction (Scheme 14).¹⁴⁸ The results indicated the broad substrate scope of the procedure. To confirm the role of amine groups in the stabilization of Pd NPs and investigating the catalytic activity of this novel catalyst, its catalytic activity for a model reaction was compared with those of Pd supported MIL-53(Al) and commercial Pd/C. The results established the superior activity of the Pd catalyst supported on amino functionalized MIL-53(Al)–NH₂. The facile catalyst recovery and preservation of catalytic activity for five reaction runs and low Pd leaching were other advantages of this catalyst. Based on the results of the hotfiltration experiment, a heterogeneous catalysis was speculated.

Table 10 Catalytic activity of palladium nanoparticles with different supports $^{\rm 147}$

TOF (mol H ₂ per mol catalyst per min)	Metal/AB ratio (mol mol ⁻¹)	
35.7	0.024	
22.7	0.024	
26.3	0.006	
6.25	0.02	
5	0.02	
1.39	0.025	
0.67	0.05	
6.25	0.04	
40.89	0.02	
15.55	0.005	
19.1	0.03	
45	0.0189	
	TOF (mol H ₂ per mol catalyst per min) 35.7 22.7 26.3 6.25 5 1.39 0.67 6.25 40.89 15.55 19.1 45	

R₁ = 4-NO₂, 4-CN, 4-CF₃, 4-OMe, 2-OMe, 4-COMe, H R₂ = H, 4-NO₂, 2-OMe, 4-OMe

Scheme 14 Suzuki-Miyaura cross-coupling reaction.148



R = Ph, 4-Me-Ph, 4-OMe-Ph, 4-F-Ph, C₅H₁₁, 4-C₅H₁₁-Ph

R₁ = 4-Me, 2-OMe, 4-OMe, 2-CF₃, 4-CF₃, 4-Ac, H, 4-NO₂, 3,5-CF₃

Shu *et al.* developed a hybrid catalyst, Pd/MOF-5, consisting of Pd NPs and MOF-5 and confirmed its utility for catalyzing the ligand- and copper-free Sonogashira coupling reaction between terminal acetylene and aryl iodide derivatives (Scheme 15).¹⁴⁹ The generality of this procedure was confirmed by using various substrates with different steric and electronic properties. The authors optimized the reaction conditions by investigating the effects of reaction variables such as base, solvent, temperature and Pd loading. The optimum values for the aforementioned parameters were $K_3PO_4 \cdot 3H_2O$, methanol, 80 °C and 3 wt%, respectively. Besides high yields, the reusability of the catalyst and simplicity of catalyst preparation were the other merits of this synthetic procedure.

The Heck coupling reaction has also been catalyzed by MOFencapsulated Pd catalyst (Scheme 16). In this regard Cao *et al.*¹⁵⁰ made use of the attractive features of amine-functionalized, mixed-linker metal–organic frameworks (MIXMOFs), such as solvent tolerance, high surface area and high porosity for supporting Pd NPs with size of 3.2 nm. For this propose, the authors employed MIXMOFs based on MIL-53(Al) and supported Pd NPs *via* ion-exchange procedure. The catalytic activity of this novel catalyst was compared with some related catalysts,



Scheme 16 The Heck coupling reaction is also catalyzed by the MOFencapsulated Pd catalyst.¹⁵⁰

such as Pd/MIL-53(Al), Pd/C and Pd/MIL-53(Al) with different amount of NH₂. The results implied the superior activity of the prepared catalyst, compared to Pd/C and Pd/MIL-53(Al). Additionally, it was observed that the amine amount could influence the catalytic activity and the presence of amine group, to some extent, improve the catalytic performance, while the higher amount of amine groups would reduce the Pd activation for the reagent. Besides high catalytic activity and selectivity, the Pd leaching was insignificant and the catalyst could be recovered and reused with only negligible loss of activity. Furthermore, the catalyst had a good shelf-life and could be stored in air for 3 months.

The catalytic activity of the bifunctional Pd@MIL-101 catalyst, which possessed both Pd NPs and Cr^{3+} sites and could act as Lewis acid/hydrogenation catalyst, was investigated for the transformation of (–)-menthol to citronella in a two-step one pot procedure.¹⁵¹ It was proved that Cr^{3+} sites rendered the MIL-101 Lewis acid feature and promoted the cyclization of (–)-menthol under N₂ atmosphere, to afford the desired isopulegol diastereomer with high activity and diastereoselectivity. The encapsulated Pd could catalyze the second step of the reaction (that is, the hydrogenation of isopulegol) under H₂ atmosphere. It is worth noting that performing this two-step reaction in a one-step procedure and using H₂ atmosphere from the start of the reaction reduced the selectivity toward menthol remarkably.

Kempe *et al.* loaded MIL-101 with Pd NPs (up to 50 wt% Pd) of various sizes *via* metal–organic chemical vapor deposition,¹⁵² and used the obtained nano hybrid systems as catalysts for the hydrogenation of ketones (Table 11). Pd size can be tuned by altering the reduction conditions, such as temperature. The comparison of the catalytic activities of two catalysts that were prepared under different conditions (Table 11) established the size selectivity of the catalysts. It is worth noting that the catalysts were reusable and could be used for several reaction runs without significant loss of activity.

UiO-66(NH₂) was applied for the immobilization of the Pd NPs with diameter of 3-6 nm, to obtain Pd@UiO-66(NH₂) via the one-pot hydrothermal procedure.153 The novel nanocomposite proved to be an efficient and reusable photocatalyst that could promote the reduction of Cr(vi) under visible light irradiation. The results demonstrated the superior catalytic activity of Pd@UiO-66(NH₂), compared with UiO-66(NH₂). The higher catalytic activity was ascribed to the dispersion of Pd NPs and their close contact with the matrix. Moreover, the photocatalytic oxidation-reduction performance of Pd@UiO-66(NH₂) was investigated for the removal of organic pollutants, such as organic dyes, methylene blue and methyl orange and Cr(vi) reduction. The results indicated the higher activity of the nanocomposite. The observation was rationalized on the basis of the synergetic effect between photocatalytic oxidation and reduction.

Yamashita *et al.* developed novel catalysts based on the photo-assisted and ion exchange embedding of Pd NPs inside the cavities of titanium-based MOF MIL-125 and amine-functionalized MIL-125, NH₂–MIL-125.¹⁵⁴ The catalytic activity of the obtained nanocomposite was examined for dehydrogenation of

Table 11Reduction of various aryl alkyl ketones to the corresponding alcohol and/or arylalkane at 39–80 °C (pressure 20 bar: time: 24 h); left:LL4842, right: HH1545 (0.1 mol% Pd); $R_1 = aryl residue$, $R_2 = aliphatic residue$. Adapted from ref. 152 with the permission of John Wiley and Sons^a

$$R_1 \xrightarrow{O} R_2 \xrightarrow{OH} R_1 \xrightarrow{OH} R_2 + R_1 \xrightarrow{R_2} R_2$$

	LL4842		HH1545			
	80 (°C)	50 (°C)	80 (°C)	50 (°C)	89 (°C)	
Substrate	Conv. (sel_1/sel_2)					
Acetophenone	100 (<1/98)	100 (32/60)	100 (<1/95)	99 (90/8)	90 (98/1)	
Propiophenone	100 (<1/80)	100 (80/18)	99 (10/65)	98 (92/6)	95 (97/2)	
Valerophenone	98 (45/40)	57 (98/1)	100 (98/<1)	100 (97/2)	68 (99/<1)	
Heptanophenone	100 (25/72)	23 (90/8)	100 (50/48)	100 (99/<1)	70 (99/<1)	
Isopropylphenylketone	100 (<1/70)	72 (98/1)	100 (97/<1)	100 (98/<1)	_ `	
2,2-Dimethylpropiophenone	99 (70/20)	22 (98/1)	100 (95/4)	100 (97/2)	_	
4'-Fluoropropiophenone	100 (30/69)	100 (50/48)	100 (91/7)	100 (89/10)	_	
4'-Methylpropiophenone	100 (<1/98)	96 (25/72)	100 (12/83)	100 (20/79)	_	
4'-Methoxypropiophenone	100 (<1/98)	30 (40/58)	100 (<1/95)	100 (4/9)	_	
4-Methylbenzophenone	0 (0/0)	0 (0/0)	99 (88/10)	100 (95/4)	_	

 a LL4842, and HH1545: the first two letters indicate temperature and H₂ pressure conditions during the reduction of the Pd precursor, H = high, L = low; the following two digits indicate reduction time in hours, and the final two digits indicate the wt% Pd loading.

formic acid and hydrogen production at room temperature. The results exhibited superior catalytic activity of NH_2 -MIL-125. It was indicated that the amino groups in NH_2 -MIL-125 could stabilize Pd NPs. Moreover, the applied photo-assisted deposition procedure resulted in embedded Pd NPs with smaller size and better dispersion.

Using the pre-coordination method and amine-functionalized UiO-66(NH₂–UiO-66), the Ag–Pd alloy was supported and applied as catalyst for the dehydrogenation of formic acid at ambient temperature.¹⁵⁵ The results indicated excellent activity (TOF = 103 h⁻¹) and selectivity, which could be ascribed to the high dispersion of the alloy on the support, ultrafine particle sizes and the synergetic effect between the Ag–Pd alloy and the NH₂–UiO-66 support. The weakly basic amino functional groups on the support could promote the cleavage of the O–H bonds of formic acid, which is associated with the rate-determining C–H bond cleavage from the HCOO* intermediate, to release H₂. Furthermore, the catalyst was stable and could be reused.

Seed mediated growth was employed for the encapsulation of Pd@Ag core-shell NPs within the cavity of the MOF.¹⁵⁶ The synthetic procedure included the initial encasement of Pd NPs within the interior space of the MOF, followed by the deposition of the second metal, Ag, on the Pd NPs (Fig. 6). It is worth noting that the reducing agents for the latter process were provided through the dissociation and activation of hydrogen molecules on the surface of the palladium NPs. The obtained hybrid system, Pd@Ag-in-UiO-67, was used as an efficient and selective catalyst for partial hydrogenation of phenylacetylene at ambient temperature. The catalytic activity of this novel catalyst was superior, compared to Pd@Ag-in-UiO-67. This observation was ascribed to surface dilution, as well as electron modification influences of silver on the surface palladium sites. The catalyst exhibited high stability and could be reused with negligible loss of activity and metal leaching. Additionally, it was proved that catalysis was heterogeneous.

Recently, Jiang *et al.* reported a simple and rapid strategy for the synthesis of tiny Pd@Co core–shell NPs encapsulated within the cavity of ML-101 under mild reaction conditions.¹⁵⁷ Diffusion of metal precursors through the MIL-101 interior space was achieved by the double solvent approach (DSA). Subsequently, NPs were generated in the presence of ammonia borane as the



Fig. 6 Schematic illustration of the fabrication of Pd@Ag core-shell NPs encapsulated in the MOF pore. Reprinted from ref. 156.



Fig. 7 Synthesis of Pd@Co@MIL-101, Pd@Co/MIL-101, and PdCo@-MIL-101 catalysts by different procedures and reducing agents. Reprinted from ref. 157 with the permission of John Wiley and Sons.

reducing agent (Fig. 7). Pre-incorporation of metal precursors in MIL-101 and the reducing agent play important roles in obtaining the core-shell structure. The catalytic activity of this novel system was investigated for the hydrolytic dehydrogenation of ammonia borane and compared with those of monometallic Pd@MIL-101, Co@MIL-101 and PdCo@MIL-101. The results indicated the superior stability and activity of the Pd@Co core-shell. This observation could be attributed to the synergistic effect between the two metallic species, and the confinement and stabilization of the NPs in the interior space of MIL-101 (in PdCo@MIL-101 catalyst, the alloy NPs were dominantly located on the external surface of MIL-101).

5. Dendrimer-encapsulated Pd catalyst

Dendrimers are highly ordered, hyper branched, three-dimensional macromolecules with three distinguished architectural regions, including (i) core, (ii) layers of branched repeat units emanating from this core, and (iii) end groups on the outer layer of repeat units.³¹ Dendrimers have been extensively used for the encapsulation and immobilization of NPs.¹⁵⁸⁻¹⁶⁴ Dendrimer encapsulated NPs proved their use in the field of catalysis. To date, various reactions have been catalyzed with this class of compounds.^{17,165-171} Among the various metals encapsulated within dendrimers, Pd has attracted much attention and there are several reports and some review articles on this topic.¹⁷²⁻¹⁷⁷

Jesus *et al.* studied the catalytic efficiency of fourth-generation poly(amidoamine) (PAMAM) dendrimer encapsulated Pd(0), in which 40 Pd atoms were incorporated into each molecule, (G4-OH(Pd₄₀)), in the Stille reaction of iodoarenes and trichloro(phenyl)stannane in aqueous media (Scheme 17). To provide more insight into the role of dendrimers and the

PhSnCl₃ + Ar-I
$$\xrightarrow{0.3 \text{ mol}\% \text{ Catalyst}}_{\text{KOH/Water, 24h}}$$
 Ph-Ar + Ar-Ar
A B

Scheme 17 The Stille reaction of iodoarenes and trichloro(phenyl) stannane, in the presence of G4-OH(Pd₄₀).¹⁷⁸

nature of the catalyst in this process, the authors compared the catalytic activities of dendrimer encapsulated Pd with bare $Pd(OAc)_2$ and palladium(II)–PAMAM complexes, which were prepared by mixing the dendrimer and $Pd(OAc)_2$ or Na_2PdCl_4 . The results of this comparison are illustrated in Table 12. As is obvious, in most cases $Pd(OAc)_2$ resulted in the highest yield of desired products. Dendrimer containing Pd catalysts, however, had superior performance in terms of selectivity and reusability. Among these catalysts, G4-OH(Pd_{40}) proved to be the most efficient.¹⁷⁸

Using Pd NPs encapsulated within the cavity of the hydroxylterminated PAMAM dendrimers of generation 4, (G4-OH), Crooks et al. developed a mild and green procedure (aqueous media and room-temperature) for the Stille reaction (Scheme 18).¹⁷⁹ The catalyst (G4-OH(Pd₄₀)), had 40Pd atoms and a size of \sim 1.7 nm. It is worth noting that the reaction did not proceed in the presence of the dendrimer only (without Pd), unreduced dendrimer containing Pd $(G4-OH(Pd_{40}^{2+}))$ or dendrimerencapsulated Au nanoparticles. Interestingly, only low yield was obtained in the case of 2-iodobenzoic acid. To elucidate whether the dendrimer was responsible for this observation, the reaction was carried out in the presence of Pd catalysts (without dendrimer). The results showed that no product was formed in this condition, ruling out the converse effect of the dendrimer on the conversion. Examining the substrate with steric hindrance showed that only the substrate with iodine and carboxylic acid groups at the ortho-position led to low yields. Furthermore, the reaction of the active substrate in the presence of 2-iodobenzoic acid decreased the yield, confirming the role of 2-iodobenzoic acid in the irreversible passivation of the catalyst. Both close functional groups of 2-iodobenzoic acid (iodine and carboxylic acid groups) could interact with the Pd catalyst, and the bidentate interaction led to the irreversible attachment of the substrate and poisoning of the catalyst.

In a distinguished work from previous reports, in which poly(amidoamine) (PAMAM) was used for Pd encapsulation, Astruc and Heuze exploited diaminobutane dendrimers, DABdendrimers, of various generations (G1-G5) for preparing nearly monodisperse Pd NPs, and investigated their catalytic activities in the Suzuki-Miyaura reaction between phenylboronic acid and iodobenzene in water (Scheme 19).180 The results (Table 13) indicated the superior catalytic performance of Pd NPs encapsulated in dendrimers of low generations (G1-G3). However, the spacious structures of these dendrimers led to the formation of inactive palladium black. The low amounts of palladium black and lower catalytic activity of dendrimers of higher generation were ascribed to their compact structure that led to efficient catalyst encapsulation, while preventing the substrate from reaching the catalytic sites. It is worth noting that the catalytic activities of DAB-dendrimer based catalysts were similar to those of the PAMAM-dendrimer catalysts. The authors suggested derivatization of the exterior amine groups of dendrimer scaffold by functionalized alkyl chains as a way to promote the catalyst reusability and activity.

A hybrid series containing polyamidoamine (PAMAM) dendrimers and multiwall carbon nanotubes, MWCNT, was achieved by divergent synthesis of dendrimers of generation G1 to

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Table 12The yields and selectivity of various Pd-based catalysts in the cross-coupling reactions of trichloro(phenyl)tin, with aryl iodides in water.Adapted from ref. 178 with the permission of the American Chemical Society

	Iodoarene	Reaction temperature (°C)	Selectivity (A/B)	Yield (%)
Pd(OAc) ₂	CO ₂ H	40	95/5	87
G4-OH(Pd ₄₀)		40	100/—	100
G4-OH + 40Na ₂ PdCl ₄		40 80	100/— 100/—	18 81
G4-OH + 40Pd(OAc) ₂		40 80	100/— 100/—	46 91
Pd(OAc) ₂	COMe	40	90/10	91
G4-OH(Pd ₄₀)	COMe	40 80	17 66	100/— 100/—
G4-OH + 40Na ₂ PdCl ₄	COMe	80	100/—	66
G4-OH + 40Pd(OAc) ₂	COMe	80	100/—	68
Pd(OAc) ₂	OMe	80	95/5	44
G4-OH(Pd ₄₀)	OMe	80	96/4	15
G4-OH + $40Na_2PdCl_4$	OMe	80	70/30	6

	Iodoarene	Reaction temperature (°C)	Selectivity (A/B)	Yield (%)
G4-OH + 40Pd(OAc) ₂	OMe	80	70/30	4
Pd(OAc) ₂	N N	80	95/5	60
G4-OH(Pd ₄₀)	, N	80	100/—	3
G4-OH + 40Na ₂ PdCl ₄		80	_	Trace
$G4-OH + 40Pd(OAc)_2$		80	_	Trace





Scheme 19 The Suzuki–Miyaura reaction between phenylboronic acid and iodobenzene, using dendrimer encapsulated PdNPs. Adapted from ref. 180 with permission from Elsevier.

G3 on the surface of amino functionalized MWCNT (Fig. 8).¹⁸¹ This hybrid system was used for the *in situ* formation of palladium NPs through the sonication of an aqueous solution of PdCl₂ and PAMAM-grafted-MWCNTs, followed by reduction by NaBH₄. The authors investigated the catalytic activity of PAMAM-g-MWCNTs immobilized Pd NPs, PdNPs-PAMAM-g-MWCNTs, in the Heck reaction of olefinic compounds with aryl bromides, iodides and also chloride derivatives (Scheme 20). The results indicated that the high catalytic activities of the hybrids consist of G2 and G3. Recyclability of the catalyst as well as short reaction time were other merits of these catalysts.

Gao *et al.* developed a recyclable hydrogenation catalyst based on Pd(0) NPs stabilized by an organic–inorganic hybrid system (Fig. 9). The hybrid system consisted of mesoporous silica, SBA-15, and polyamidoamine (PAMAM) dendrimers and was obtained by the growth of dendrimers of various generations (G1–G4) on the inner surface of the amine-functionalized SBA-15. For this proposed, an iterative sequence of a Michaeltype addition reaction of amino functional groups to the methyl acrylates and amidation of the formed ester groups with ethylenediamine, were employed.¹⁸² Stabilization of Pd(0) NPs was carried out by using Pd(π) ions and their subsequent reduction by NaBH₄. The synthesized hybrid catalyst was used for the hydrogenation of allyl alcohol (Table 14). The results proved the high catalytic activities of the hybrid catalyst. Comparison of the

Table 13Suzuki-reaction with dendrimer encapsulated palladiumcatalysts. Adapted from ref. 180 with permission from Elsevier

Dendrimer generation (Gn)	Time (h)	$N\left(\mathrm{Pd}^{2+}\right)$ mol	Yield (%)	Formation of Pd black
G1	1	$4.2 imes10^{-6}$	100	Formed
G2	1	$4.2 imes 10^{-6}$	100	Formed
G3	1	$7.5 imes10^{-6}$	60	Formed
G3	4	$7.5 imes10^{-6}$	98	Formed
G4	1	$7.5 imes10^{-6}$	40	Little
G4	4	$7.5 imes10^{-6}$	66	Little
G4	24	$7.5 imes10^{-6}$	97	Little
G5	96	$7.5 imes10^{-6}$	40	Little



Fig. 8 Synthesis route of PdNPs-PAMAM-*g*-MWCNTs hybrid materials. Reprinted from ref. 181 with the permission of Elsevier.



 $\mbox{Scheme 20}$ The Heck reaction of olefinic compounds with aryl bromides, iodides and also chlorides. 181

catalytic performance of Pd(0)–G4-PAMAM–SBA-15 catalyst with the corresponding Pd(0)–G4-PAMAM showed that the hybrid system was 1.5 time more active. This observation was attributed to the presence of inorganic mesoporous silica, which could possibly decrease the aggregation of Pd(0)–G4-PAMAM. It is worth noting that the high selectivity for desired product and minimization of the isomerisation of the by-product, acetone, was achieved by using higher dendrimer generations. The authors believe that the reaction rate could be tuned by altering the dendrimer generation.

For the first time, Kaneda et al. studied the size-dependent geometric, electronic and catalytic characteristics of the poly(propylene imine) (PPI) dendrimers stabilized sub-nano palladium clusters (i.e. Pd₄, Pd₈, and Pd₁₆) by using XAFS and IR analyses.183 Phosphine-free allylic substitution reactions of benzoic acid with allylmethyl carbonate were selected for the investigation of the catalytic activity of G5-Pd $_n^0$ (where n = the number of Pd ions in one dendrimer). It was revealed that the catalyst can be recovered and reused without loss of activity. Additionally, the reaction solvent had an essential role in the catalytic activity and stability, and toluene was found to be the best choice (Table 15). This observation was attributed to the tight encapsulation of Pd clusters within the dendrimer in nonpolar solvents, which stem from the vigorous interaction of intramolecular hydrogen bonding between the amide functional groups of the periphery of the dendrimer. In polar solvents however, Pd cluster leaching is facilitated by the interaction of the amide groups with solvents, which weakened



Fig. 9 Pd(0) nanoparticles stabilized by the organic–inorganic hybrid system, Pd(0)–G1-PAMAM–SBA-15 and Pd(0)–G4-PAMAM–SBA-15. Reprinted from ref. 182 with the permission of the American Chemical Society.

the intramolecular hydrogen bonds. The larger the cluster size, the higher TOF was obtained.

Asefa *et al.* designed a novel hybrid core–shell catalyst, $SiO_2@Pd$ –PAMAM core–shell system, in which PAMAM dendrimer-encapsulated Pd NPs served as the shells of the SiO_2 microsphere cores.¹⁸⁴ The synthetic procedure (Fig. 10) consisted of the synthesis of silica microspheres, followed by etching with potassium hydroxide solution. In the next step, the etched silica was functionalized by vinyltriethoxysilane. Subsequently, epoxidation of vinylsilica was carried out. The ring opening of the latter was achieved by the amine groups of the PAMAM dendrimer of generation 4. Before Pd stabilization, which was performed by using K_2PdCl_4 solution, followed by reduction by NaBH₄, the exterior amine groups of the dendrimer were protonated by HCl solution to prevent Pd ions from growing on the outer surface of the dendrimer.

The catalytic activity of this hybrid catalyst was investigated in the hydrogenation of diverse substrates, such as olefins, nitro-benzenes and ketones (Table 16). Furthermore, the reusability of the catalyst and the catalytic activity were compared with SiO_2 @Pd and Pd/C indicated the superior performance of the SiO_2 @Pd–PAMAM core–shell catalyst.

Using poly(amido)amine (PAMAM) dendrimers of generations 4 and 6 as templates, monodisperse Pd NPs containing 10–200 atoms (with diameter less than 2 nm) were synthesized and used for studying the size- and template-dependent
 Table 14
 Hydrogenation activities and selectivities for 1-propanol, of the various hybrid catalysts. Reprinted from ref. 182 with the permission of the American Chemical Society

	Pd(0)-G1-PAMAM- SBA-15	Pd(0)-G2-PAMAM- SBA-15	Pd(0)-G3-PAMAM- SBA-15	Pd(0)-G4-PAMAM- SBA-15
TOF	$2185/2150^{a}$	2266/2288	711/705	739/734
Conversion (%)	>99.5%	>99.5%	>99.5%	>99.5%
Selectivity (%)	79.0/77.7	82.0/82.8	93.4/92.6	91.4/90.8

^a Duplicate measurements were performed to illustrate the levels of run-to-run reproducibility.

Table 15 Allylic substitution reactions using $G5-Pd_n^0$ in various solvents. Adapted from ref. 183 with the permission of the Royal Society of Chemistry



Catalyst	Cluster size (nm)	Solvent	Yield (%)	TOF
$G_{5}-Pd_{16}^{0}$	0.97	Toluene	91	3.1
$G_{5}-Pd_{16}^{0}$	0.97	DMF	62	_
$G_{5}-Pd_{16}^{0}$	0.97	Ethyl acetate	49	_
$G_{5}-Pd_{16}^{0}$	0.97	DMSO	23	_
$G_5-Pd_4^0$	0.50	Toluene	35	0.7
G_5 -Pd ⁰ ₈	0.76	Toluene	52	1.7

catalytic activity in *p*-nitrophenol hydrogenation to aminophenol¹⁸⁵ as the model reaction. The application of the dendrimer template prevented surface passivation and led to high catalytic activity. It was proved that most atoms in the studied NPs were located at the surface and participated in the catalysis. In the case of Pd clusters with 10 to 50 atoms, the rate constant normalized on a per atom basis showed little variability, indicating that all atoms were placed on the surface of Pd clusters, while for particles with 50 to 200 atoms, a decrease in per-atom activity was obtained with increasing particle size, implying that in this size range, some atoms were in the catalytically inactive core.

The dendrimer generation was another affecting factor. The catalysts prepared by using dendrimers of generation 4 resulted in the observed rate constant. Dendrimers of higher generation have more steric crowding at the periphery and the reagent had



Fig. 10 Schematic illustration of the synthesis of the $SiO_2@Pd-PAMAM$ dendrimer core-shell microsphere catalysts. Reprinted from ref. 184 with the permission of the American Chemical Society.

to pass a longer distance to get close to the encapsulated metallic catalyst.

Fan et al. reported the utility of phosphine dendrimers for the encapsulation of Pd NPs and the synthesis of an efficient and recyclable catalyst for hydrogenation and Suzuki coupling reactions (Scheme 21).186 Chemically inert Frechet-type polyaryl ether dendrons of three generations (1-3), $G_n \text{DenP}$ (n = 1-3)with coordination ability to palladium were employed for the synthesis of catalysts, G_n DenP-Pd, (n = 1-3). The catalysts were obtained by the reduction of Pd(acac)₂ in the presence of the dendritic ligand (Scheme 22). The reliability of the synthesized catalyst in the Suzuki coupling was established by using various aryl boronic acids and aryl halides. The comparison of the results of aryl bromides and aryl chlorides indicated that catalytic activity was independent of the type of halides, while the reaction of aryl bromides using PAMAM-encapsulated Pd NPs as the catalyst required elevated temperatures. To extend the scope of this procedure, Suzuki coupling of phenylboronic acid with various pyridyl bromides and even pyridyl chlorides and hydrogenation of olefins were studied. The former reaction under G₃DenP-Pd catalysis led to the desired products in good yields (44-94%). Hydrogenation catalyzed by G2DenP-Pd resulted in high selectivity and quantitative yields. Furthermore, Pd aggregation, which could happen by using thiol dendrimers, did not occur. The authors believe that dendritic wedges not only acted as stabilizers but also as ligands to promote the catalytic activity.

Astruc et al. developed poly-1,2,3-triazolylferrocenyl dendrimers containing triazole ligands for the stabilization and encapsulation (DEN or DSN) of Pd NPs.¹⁸⁷ The prepared Pd NPs were used a catalyst for the Suzuki reaction between phenylboronic acid and aryl halides under mild reaction conditions (25 °C) (Scheme 23 and Table 17). The results indicated a converse relationship between TOF, TON, reaction yield and the concentration of the reaction mixture. Moreover, the catalytic activities of both DSN-G0 and DEN-G1 were similar and slightly higher than DEN-G₂. This observation ruled out the possibility of dendrimer participation in catalysis. Extraction of catalysts with the bulky thiol, undodecanethiol, resulted only in the extraction of DSN-G₀, while using less bulky thiols resulted in the extraction of DEN-G1 as well. However, in the case of DEN-G₂, strict crowding of the dendrimer periphery prevented extraction. In the investigation of the catalytic performance of the extracted alkyl thiolate Pd NPs in the Suzuki reaction of PhI with PhB(OH)₂, quantitative or nearly quantitative yields were obtained at 25 °C, along with Pd black formation. Similar to the

Table 16 Hydrogenation of various substrates by the SiO₂@Pd-PAMAM dendrimer core-shell microsphere catalyst.^{*a*184} With permission of American Chemical Society

Substrate	Product	Time (min)	Selectivity (%)	Conversion (%)	TOF, h^{-1}
Styrene ^b	Ethvlbenzene	10	~ 100	9	1812
<u>,</u>	, see the second s	120	~ 100	80	
Styrene	Ethylbenzene	10	${\sim}100$	$\sim \! 100$	24 000
Styrene ^c	Ethylbenzene	10	${\sim}100$	${\sim}100$	10 840
5	·			40^d	4800
Ethynylbenzene	Ethylbenzene	15	${\sim}100$	${\sim}100$	16 000
Cyclohexene	Cyclohexane	20	${\sim}100$	${\sim}100$	12 000
Hexene	Hexane	60	${\sim}100$	${\sim}100$	4000
Acetone	Propan-2-ol	120	${\sim}100$	${\sim}100$	2000
Pentane-2,4-dione ^e	4-Hydroxypentan-2-one	120	${\sim}100^{f}$	95	2000
2-Phenyloxirane	1-Phenylethanol, 2-phenylacetaldehyde	180	$65^{g}: 35^{h}$	${\sim}100$	1333
1-Chloro-4-nitrobenzene	4-Chlorobenzenamine	150	96	${\sim}100$	1240
(E)-1,2-Diphenylethene	1,2-Diphenylethane	25	${\sim}100$	${\sim}100$	10 600
1-Nitro-4-vinylbenzene	1-Ethyl-4-nitrobenzene	90	${\sim}100^l$	${\sim}100^i$	1240
5	5		$\sim 35^m$	35 ^j	
			$\sim 88^n$	88^k	

^{*a*} Reaction conditions: substrate: 0.01 mol; methanol: 20 mL; catalyst: 5 mg (0.0053 wt% Pd in the SiO₂@Pd-PAMAM dendrimer core-shell microspheres); 10 bar H₂ pressure; temperature: 20 °C. ^{*b*} Catalyst used was Pd@SiO₂. ^{*c*} Catalyst used was 1% Pd/C. ^{*d*} Third recycling of 1% Pd/C. ^{*e*} Temperature: 50 °C. ^{*f*} 4-Hydroxypentan-2-one. ^{*g*} 1-Phenylethanol. ^{*h*} Phenylacetaldehyde. ^{*i*} In 15 min, all the double bonds were hydrogenated. ^{*j*} In 2.5 h, 35% of the nitro groups were additionally hydrogenated. ^{*k*} In 8 h, 88% of the nitro groups were additionally hydrogenated. ^{*k*} In 15 min, 100% selectively to 4-nitroethylbenzene product was obtained. ^{*m*} In 2.5 h, 35% of 4-ethylaniline and 65% 4-nitroethylbenzene were obtained. ^{*n*} In 8 h, 88% 4-ethylaniline and 12% 4-nitroethylbenzene were obtained.



Scheme 21 Suzuki coupling reaction.186



Scheme 23 The Suzuki reaction between phenylboronic acid and aryl halides. Adapted from ref. 187 with the permission of John Wiley and Sons.

former case, the kinetics were not influenced by Pd catalyst size. On replacing PhI with PhBr, neither Pd black nor the desired product was observed in the presence of DSN-G₀. It was concluded that in the presence of reactive reagent, Pd-atoms escaped from the Pd NPs. Pd escape was due to the oxidative addition of PhI to the PdNP surface, followed by the escape of Ph(Pd_x)I (x = 1 or 2) (similar to the high temperature Heck reaction). The lower yields obtained in the cases of DSNs or DENs were attributed to quenching of the catalytic species. In the case of thiolate PdNPs, however, inefficient quenching resulted in quantitative yields and catalyst recycling. The formation of Pd black was another quenching mechanism,

 $G_n \text{DenP} \xrightarrow{Pd(\text{acac})_2} G_n \text{DenP-Pd}$ $H_2 (25 \text{ atm}) (n = 1-3)$ $THF, 60 \ ^{\circ}\text{C}$

Scheme 22 Catalyst preparation procedure. Adapted from ref. 186 with the permission of the American Chemical Society.

which was much slower than other mechanism and did not limit the yields of the reactions catalyzed by alkyl thiolate PdNPs.

Crooks *et al.* studied the hydrogenation of allyl alcohol by using dendrimer encapsulated Pd NPs (1.3–1.9 nm) as catalyst.¹⁸⁸ The authors revealed that the rate of the process was dependent on the diameter of the Pd catalyst. The kinetic studies disclosed that the size effect (*i.e.* the relationship between the reaction rate and Pd NPs size) for particles with the smallest diameters (<1.5 nm diameter) originated from the electronic properties, while for particles with 1.5–1.9 nm diameter, geometric characteristics played the dominant role.

Click dendrimers, poly-1,2,3-triazolyl dendrimers containing ferrocenyl termini assembled and functionalized by click chemistry were used to stabilize and encapsulate Pd NPs with utility for the olefin hydrogenation reaction under ambient condition (Table 18).¹⁸⁹ As obvious in Table 18, the novel catalyst could promote the reaction of various substrates. However, sterically demanding ones such as ergosterol, which was too large to enter into the dendrimer could not be hydrogenated.

Catalyst amount (mol%)	PdNP	Diameter (nm)	Reaction time (h)	Yield (%)	TON	TOF
1	DSN-G ₀	2.8 ± 0.3	24	68	68	17
	DEN-G ₁	1.3 ± 0.2	24	70	70	18
	DEN-G ₂	1.6 ± 0.3	24	55	55	13
0.1	DSN-G ₀	2.8 ± 0.3	24	66	660	130
	DEN-G1	1.3 ± 0.2	24	69	690	140
	DEN-G ₂	1.6 ± 0.3	24	51	510	80
0.01	DSN-G ₀	2.8 ± 0.3	48	51	5100	375
	DEN-G1	1.3 ± 0.2	48	52	5200	363
	DEN-G ₂	1.6 ± 0.3	72	44	4400	225

Table 17 Comparison of TOF and TON values for three generations (0–2) of dendrimer-stabilized (DSN) and dendrimer-encapsulated nanoparticles (DEN). Adapted from ref. 187 with the permission of John Wiley and Sons

Table 18Hydrogenation of olefins catalyzed by Pd encapsulated in poly-1,2,3-triazolyl dendrimer with ferrocenyl termini with 36 triazole units(9 interior + 27 terminal) (methanol as reducing agent). Adapted from ref. 189 with the permission of John Wiley and Sons

Substrate	Product	Yield (%)	TOF	
Styrene	Ethylbenzene	100	1620	
Allyl alcohol	Propanol	100	1160	
Hexene	Hexane	43	1800	
	2-Hexene	57	2400	
2,5-Dimethylhexa-2,4-diene	2,5-Dimethylhex-2-ene	78	810	
	(E)-2,5-Dimethylhex-3-ene	22	230	
1,3-Cyclohexadiene	Cyclohexene	100	1150	
(Z,Z)-1,3-Cyclooctadiene	Cyclooctene	100	530	
1,3,5-Cycloheptatriene	Cycloheptene	100	130	
(4E,6E)-2,6-Dimethylocta-2,4,6-triene	(E)-3,7-Dimethyloct-2-ene		480	
• • •	2,6-Dimethyloct-2-ene			
H ₃ C CH ₃ H ₃ C H ₃ C	_	_	_	

The comparison of the catalytic activities of synthesized catalysts with those obtained from encapsulated Pd NPs in PAMAM indicated the superior catalytic activities of the former. Additionally, in comparison with Pd encapsulated in PPI-modified dendrimers, which were not stable under reaction conditions, the novel catalyst showed high stability and could be reused for several reaction cycles. The superior catalytic activity of this novel catalyst was attributed to the nature of the dendrimer and the presence of triazole moieties. Moreover, it was found that the reducing agent could influence the catalytic activity of the final DEN, and NPs prepared by using methanol exhibited better catalytic activities than NaBH₄. Among various generations, Pd NPs encapsulated in G₁ had superior activity.

Encapsulated Pd nanocatalysts have also found their applications in electrochemistry. On mixing aqueous solutions of K_2PdCl_4 and amine-terminated poly(amidoamine) dendrimer of generation 4, G4-NH₂ (Pd²⁺) was obtained and subsequently grafted to multi-wall CO₂H-functionalized carbon nanotubes (MWCNT). The final hybrid catalyst was obtained by reduction with NaBH₄. The dendrimer template rendered Pd NPs stable and well-dispersed. The peripheral amine functional groups of dendrimer were useful for tuning the solubility of the hybrid system and pairing it with MWCNT. Investigating the electrocatalytic activity of the catalyst was proved in the oxidation of hydrazine. The authors believe that this nanocomposite could be potentially used for fuel cells and promoting sensitive electrochemical sensors and biosensors.¹⁹⁰

'Mohammadpoor-Baltork *et al.* developed a novel support for Pd NPs immobilization, based on nano-silica triazine dendritic polymer (Pd_{np} -nSTDP). The catalyst preparation was initiated by modification of nano-silica with 3-aminopropyltrimethoxysilane (APTES) and formation of AP–nSiO₂, followed by treatment with cyanuric chloride (CC) to afford CC1–nSiO₂. The latter tolerated the reaction with bis(3-aminopropyl)amine to furnish G1, which would be transformed into CC2–nSiO₂ upon reaction with cyanuric chloride. Finally, nano-silica triazine dendritic polymer, nSTDP, was obtained through the reaction of CC2–nSiO₂ with bis(3-aminopropyl)amine. The Pd immobilization was achieved by reduction of Na₂Pd₂Cl₆ with methanol. The catalyst was applied for C–C coupling reactions including the Heck reaction styrene and aryl halide derivatives, and the Suzuki–Miyaura crosscoupling reaction between aryl halides and aryl boronic acids



Fig. 11 Amphiphilic dendritic nanoreactors. Reprinted from ref. 192 with the permission of John Wiley and Sons.

under conventional and microwave irradiation.¹⁹¹ The results established that low amounts (0.006 mol% and 0.01 mol%) of this novel and reusable catalyst could promote the reaction.

Astruc et al. developed amphiphilic dendritic nanoreactors consisting of hydrophilic triethylene glycol terminal groups and hydrophobic dendritic interior containing 1,2,3-triazole ligands for stabilization of very fine Pd NPs with size of 1-2 nm (Fig. 11).¹⁹² TEG termini render dendrimers water soluble, while the hydrophobic interior with 1,2,3-triazole ligands could stabilize Pd NPs. The obtained hybrid system was used as a catalyst for promoting C-C coupling reactions, including Heck, Sonogashira and Suzuki-Miyaura reactions, as well as reduction of 4-nitro phenol. Suzuki-Miyaura reactions of iodoarene and bromoarene derivatives were catalyzed remarkably by this dendrimer stabilized Pd NPs, the obtained TONs were equal to, or larger than 10⁶. The catalytic activity for Sonogashira coupling was also impressive and only 0.01% mol Pd was required. In the case of Heck coupling, promising results were obtained.31 However, 0.1 mol% catalyst was used due to the catalyst instability at high temperature (>100 °C). The catalytic activity of this catalyst for reduction of 4-nitrophenol was exceptional. The amount of Pd was quite low (down to 0.02 mol%) and the TOFs were very high.

6. PdNPs encapsulated in carbonbased materials

Pd NPs leaching and aggregation was prevented by their encapsulation within double-shelled hollow carbon spheres. The nanoreactor was composed of an interior shell of reduced graphene oxide (RGO) and exterior shell of carbon (C) layer. Encapsulated Pd NPs within this nanoreactor, RGO@Pd@C, exhibited high catalytic activity for reducing 4-nitrophenol to 4-aminophenol in the presence of sodium borohydrate and promoted the reaction in a very short reaction time (3 s).¹⁹³

Pd catalyst encapsulation was also performed by exploiting porous carbon (CMK-3). The catalyst (Pd@CMK-3) was prepared by immersion, ammonia hydrolysis, and heating procedures and applied for promoting Suzuki reactions (Scheme 24).¹⁹⁴ The reaction was carried out *via* three procedures, magnetic stirrer



R = H, 2-Me, 4-Me, 2-OMe, 4-OMe, 4-CN, 4-C(O)Me

Procedure 1: 60 °C, 3 mmol K₂CO₃, N₂ Procedure 2: 60 °C, 3 mmol K₂CO₃, N₂, homogenization by 2 min of US before heating Procedure 3: 30 °C, 1.5 mmol K₂CO₃, US

Scheme 24 Suzuki reactions.¹⁹⁴

or 2 min ultra-sonication (US) before heating and performing the reaction wholly under ultrasonic irradiation. In the third procedure, high catalytic activity at lower temperature, without using an inert atmosphere was observed. This was ascribed to the role of ultrasonic waves in improving mass-transfer.

Mesoporous carbon, CMK-5, was also employed for the encapsulation of Au–Pd sodium borohydrate with narrow size distribution *via* sequential incipient wetness impregnation. Investigation of catalytic activity of the hybrid system for the oxidation of benzyl alcohol demonstrated high selectivity and conversion (>99%) in a relatively short reaction time (3 h), under mild reaction conditions.¹⁹⁵ The high catalytic activity could be attributed to well-developed bimodal pore interconnectivity, as well as high surface area. Upon reusing the catalyst, high selectivity was preserved. However, the conversion dropped due to blockage of the catalyst active surface with benzaldehyde. To circumvent this problem, thermal treatment at 200 °C in air was suggested.

Oxidation of various alcohols, including primary benzylic and allylic alcohols (Table 19), was catalyzed by a novel thermally-stable core–shell Pd-based catalyst, (Pd@hmC), in which the Pd NPs resided in hollow carbon shells.¹⁹⁶ The comparison of the catalytic performances of this catalyst with conventional Pd/AC established the superior activity of the novel catalyst. It was believed that the reaction pathways of the two catalysts were similar and the particular structural features of Pd@hmC resulted in higher catalytic activity. Interestingly, this catalyst could be regenerated by heat treatment.

The wetness impregnation method and subsequent thermal treatment were used for the deposition of Pd NPs within multi walled carbon nanotubes, MWNTS. The hybrid was employed as a catalyst for the selective hydrogenation of a substrate that contained both C=C and C=O bonds, cinnamaldehyde.¹⁹⁷ The catalyst exhibited high selectivity toward the hydrogenation of C=C, which was attributed to the metal–support interaction and the absence of micropores and of oxygenated surface groups on the MWNT. Moreover, the catalyst was reusable and could be recovered and reused for several reaction runs.

Su *et al.* encased Pd NPs within hollow carbon sphere, HCS, through a simple method consisting of supporting Pd NPs on ZnO NPs, followed by coating a carbon layer *via* the fast coking method. The Pd@HCS was obtained through the removal of ZnO by HCl solution. The authors demonstrated that the composite exhibited high catalytic activity for the reduction of 4-nitrophenol to 4-aminophenol.¹⁹⁸ The observed catalytic

Table 19Aerobic oxidation of various alcohols over Pd@hmC and Pd/AC catalysts. $^{\alpha}$ Adapted from ref. 196 with the permission of theAmerican Chemical Society

Substrate	Catalyst	Time (h)	$\mathrm{TOF}^{b}/\mathrm{h}^{-1}$
CH ₂ OH	Pd@hmC	5	560
CH ₂ OH	Pd/AC	5	150
1-Phenylethanol	Pd@hmC	15	150
1-Phenylethanol	Pd/AC	15	50
Octanol	Pd@hmC	24	—
Octanol	Pd/AC	24	—
PhCD ₂ OH	Pd@hmC	2	340
PhCD ₂ OH	Pd/AC	2	200
4-Methoxybenzyl alcohol	Pd@hmC	1	4470
4-Methoxybenzyl alcohol	Pd/AC	1	2500
4-Methylbenzyl alcohol	Pd@hmC	1	3370
4-Methylbenzyl alcohol	Pd/AC	1	2150
4-Chlorobenzyl alcohol	Pd@hmC	5	540
4-Chlorobenzyl alcohol	Pd/AC	5	220

^{*a*} Reaction conditions: 0.15 μmol of Pd, 0.25 mmol of benzyl alcohol, 5 cm³ of 50 mM K₂CO₃ aqueous solution, 80 °C, 1 h, O₂ atmosphere. ^{*b*} Turnover frequency defined as the amount of benzaldehyde formed in 1 h per total amount of surface Pd atoms.

activity was superior to that of Pd NPs supported on commercial CNT.

In another attempt, Pd NPs were encapsulated within hollow carbon matrices and were used as a catalyst for the electrooxidation of methanol.¹⁹⁹ To elucidate the confinement effect, the catalytic activity of the encapsulated Pd NPs was compared with those of partially encapsulated Pd and Pd NPs deposited on the surface of activated charcoal. The results indicated the superior catalytic activity of exclusively confined Pd NPs. This observation was attributed to lower leaching and better closeness of Pd NPs to substrates.

Rance *et al.* investigated the effect of the confinement of Pd NPs in hollow graphitized nano-fibres (PdNP@GNF) on its catalytic activity for Suzuki–Miyaura cross-coupling reactions between aryl iodides and phenylboronic acids.²⁰⁰ The authors disclosed different preparation methods for optimization of this nanoreactor. It was demonstrated that the specific selectivity, as well as the yield of reaction, were influenced by the steric properties of the aryl iodide reactant, while the confinement effect was not detected for aryl boronic acid. The authors proved that the oxidative addition step of the Suzuki–Miyaura reaction occurred at the step-edge of the nanofibres.

Encapsulation of Pd NPs at the step-edges promoted the retention of catalytic centers. Moreover, the recovery of nanoreactors would be facilitated by insignificant loss of catalytic performance.

Apart from the discussed examples, Pd NPs encapsulated in carbon-based compounds were applied for various purposes. In this context, the encapsulation of Pd NPs within carbon nanocages was used for developing nanoenzymes with utility for the selective detection and multicolor imaging of cancer cells.²⁰¹ As another example, Pd NPs incorporated onto zeolite template carbon were used for improving hydrogen uptake and storage density.²⁰²

Zhou *et al.* reported a novel hybrid catalytic system composed of confined Pd NPs in grass-like graphene layers on monolithic cordierite for the hydrogenation of 4-carbox-ybenzaldehyde.²⁰³ The catalyst, Pd/Gr–N/cordierite was prepared by covering cordierite with a NH₂-ion liquid functionalized graphene (Gr) layer, followed by Pd loading. In comparison with Pd/AC, the novel catalyst led to higher stability, originating from the control of Pd leaching and aggregation. Moreover, the catalyst exhibited high corrosion resistance and mechanical strength.

Li *et al.* developed a novel catalyst, microencapsulated Pd NPs on cellulose, CelMcPd⁰, by reduction of Pd precursors, $PdCl_2$ or $Pd(OAc)_2$ in cellulosic ionic liquid solvent.²⁰⁴ The reduction can be achieved *in situ* by ionic liquid, or by using NaBH₄. The obtained nanocomposite was proved as a reusable and effective catalyst for phosphine-free Mizoroki–Heck and Suzuki–Miyaura reactions (Schemes 25 and 26). The catalyst could be recovered by filtration and reused for six runs without the loss of its activity.

In an innovative study, PdNPs were confined within doubleshelled graphene@carbon hollow spheres, RGO@Pd@C.¹⁹³ In this system, the carbon layer acted as the exterior shell and the double-shelled hollow carbon sphere with reduced graphene oxide served as the interior shell. The synthetic procedure for the nanoreactor is illustrated in Fig. 12. Initially, the SiO₂ nanospheres were functionalized by APTES and then enveloped by graphene oxide. Deposition of PdNPs was subsequently performed. The C shell was coated *via* pyrolysis of glucose. The final catalyst was obtained by thermal treatment, followed by etching of the SiO₂ core. It was proved that the nanocapsule



Scheme 25 Phosphine-free Mizoroki-Heck reaction.204



Scheme 26 Suzuki–Miyaura reaction.²⁰⁴

RSC Advances



Fig. 12 Schematic of the synthesis of RGO@Pd@C hollow spheres. Adapted from a scientific report. Reprinted from ref. 193 with the permission of the Nature publishing group.

prevented the PdNPs from aggregation and Pd leaching, and improved its stability and catalytic behavior. Investigation of the catalytic activity of the novel hybrid system for the reduction of 4-nitrophenol to 4-aminophenol with NaBH₄, showed that the catalyst, with even a low amount of Pd, could promote the reaction in a very short reaction time.

7. Polymer-incarcerated Pd NPs

Microencapsulated catalysts were initially introduced in 1998. They enjoy the advantages of heterogeneous catalysts, such as facile recovery, reusability, significant or no catalyst leaching and high catalytic activity.^{205,206} To date various catalysts,^{207–214} as well as palladium, such as Pd(0) NPs have been incarcerated in polymeric systems²¹⁵ and applied to a wide range of organic transformations.^{216–227}

7.1. Synthesis of heterocycles

Acridone derivatives were obtained under polymer incarcerated Pd and Sc catalysis.²²⁸ The preparation of catalyst was performed by making use of $Pd(PPh_3)_4$ and polystyrene-based copolymer (Scheme 27). The process included Pd-catalyzed amination and formation of *N*-phenyl anthranilic acid ester, followed by hydrolysis using an excess amount of basic resin Amberlite IRA 400 (OH), which provided *N*-phenyl anthranilic acid derivatives. The desired product was achieved through ring



Scheme 27 Catalyst preparation method. Reprinted from ref. 228 with permission of the American Chemical Society.





closure. The reaction was promoted by polymer-supported scandium catalyst as Lewis acid, and trifluoroacetic (TFAA) anhydride in $MeNO_2$ -LiClO₄ solution (Scheme 28). It was found that applying a mixture of toluene and H₂O as reaction media could suppress Pd leaching and improve the catalyst performance. The reaction of both aryl iodides and bromides proceeded smoothly to furnish the corresponding products in high yields. Aryl chlorides, however, gave the corresponding chlorides in moderate yields. The process could be extended to secondary amines. However, these amines gave the corresponding products in lower yields and more Pd leaching was realized.⁶⁶

7.2. Hydrogenation

Polysilane incarcerated Pd NPs on Al₂O₃ (PI Pd/PSi on Al₂O₃)²²⁹ was employed to promote some hydrogenation reactions. This new catalytic system did not suffer from the problems of Pd catalysts supported on polysilane (Pd/PSi), including solubility in some organic solvents and leaching of Pd. Scheme 29 illustrated the synthetic route to this catalyst. The catalytic performance on the other supports, such as TiO₂ and SiO₂, was also examined by these authors. It was found that alumina exhibited the best performance in terms of obtained yields and amounts of required catalysts. The catalyst preparation condition was optimized by adjusting reaction conditions, such as temperature and time. Moreover, the performance of the catalyst was examined by applying various substrates in the presence and absence of solvents (Table 20).⁶⁶

Immobilization of the Pd catalyst was also carried out by using the readily available poly(methylphenyl) silane without the phenyl moiety in its backbone.²³⁰ The precursors for catalyst



Scheme 29 Synthesis of PI Pd/PSi on Al_2O_3 . Reprinted from ref. 229 with the permission of the Royal Society of Chemistry.

Table 20	Hydrogenation of	various substrates using cataly	st. Adapted from ref. 22	29 with the permission of	the Royal Society of C	hemistry
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Substrate	Conc./mol L^{-1}	Solvent	Time/h	Product	Yield (%)	Leaching (%)
Ph	0.05 mol% 0.05 mol%	Neat-RT Neat, 50 $^{\circ}\mathrm{C}$	8 16	Ph OEt	>99.9 Quant.	<0.22 <0.1
	0.05 mol% 0.2 mol%	Neat 50 °C Neat-RT	1 1	0 N YO	58 79	_
	0.05 mol%	Neat 50 °C	24	Ph	80 (trace)	_
Pn 🕆 P	0.2 mol%	Neat 50 °C	24	Ph Ph	95 (5)	0.12
O Ph Ph	1.0	EtOH	24	Ph Ph OH Ph Ph	91 (6)	0.99
	0.50	EtOH	1	°₹ ^N ⊁°	97	0.48
HO ₂ CCO ₂ H	1.0	EtOH	3.5	HO ₂ CCO	Quant.	0.94
Ph	0.50	CH_2Cl_2	24	Ph	98	3.6
	1.0 0.33	EtOH Hexane	8 1.5		>99.9 >99.9	0.34 2.28

preparation with Pd loading of 56.6 μ mol g⁻¹ were poly(dimethyl)silane, Pd(OAc)₂ and Al₂O₃ (Scheme 30). The catalyst, [Pd/(DMPSi-Al₂O₃)], was characterized by various analytical techniques. The results demonstrated the presence of Pd NPs on silicon-rich areas, rather than on aluminum- or oxygen-rich areas. As a matter of fact, the polysilane support catalyzed the reduction and production of Pd NPs. The electronic interactions resulted in the immobilization of the formed Pd NPs on the polymer. This novel system was used to catalyze the reduction of phosphatidylcholine with hydrogen in a batch system. Interestingly, its catalytic activity was compared with that of Pd/C. Noticeably, in the first run, both catalysts exhibited high catalytic activities. In the second reaction run, however, Pd/(DMPSi-Al₂O₃) retained its catalytic activity, while the activity of Pd/C



Scheme 30 Synthesis of the catalyst. Reprinted from ref. 230 with the permission of Wiley-VCH.



Fig. 13 Schematic diagram of the continuous-flow reactor. PEEK = polyetheretherketone. Reprinted from ref. 230 with the permission of John Wiley and Sons.

dropped significantly. The catalytic activity of this catalyst was also examined in the continuous-flow hydrogenation (Fig. 13). The protocol showed broad substrate scope and various substrates, including simple liquid substrates (neat) and dissolved solid substrates, which were applied successfully (Table 21). Additionally, Pd leaching was not detected. It is worth mentioning that some vegetable oils could be hydrogenated on gram to kilogram scales, using the aforementioned catalyst system.⁶⁶

7.3. C-C coupling reactions

7.3.1. Suzuki–Miyaura coupling. Polymer incarcerated (PI) Pd catalysts were extensively studied by the Kobayashi research

Table 21 Continuous-flow hydrogenation of alkenes and 1-octyne. Reprinted from ref. 230 with the permission of John Wiley and Sons

Substrate	Substrate flow [µLmin ⁻¹]	H ₂ [equiv.]	$T [^{\circ}C]$	Product	Yield [g]	TON/TOF $[h^{-1}]$
\bigcirc	300	1.5	30		91.8	16 475/3295
	300	1.5	30		86.5	16 839/3368
\bigcirc	100	1.5	30	\bigcirc	26.5	6016/1203
\bigcup	50	2.0	70	\bigcirc	12.7	2516/498
	40	15.0	120		6.5	304/101
	100	3.0	30	\bigvee	23.2	3951/790

group.^{221,231} As an example, a heterogeneous PIPd catalyst was prepared for promoting the Suzuki-Miyaura coupling reaction, in which Pd NPs were immobilized into polystyrene-based polymers.²³² Although the catalyst exhibited high catalytic activity and could be easily filtered off and efficiently reused, the loss of phosphine ligand during filtration was realized, thus, addition of this ligand is required for recycling. To circumvent this problem, Kobayashi et al. developed a new catalyst by using $Pd(PPh_3)_4$ and a series of copolymers containing the PPh₂ group (Scheme 31).²³¹ During the synthesis of this catalyst, phosphine oxides were produced, which can be reduced in situ by HSiCl₃. The catalytic potentiality of phosphinated and non-phosphinated PI Pd catalysts was compared in Suzuki-Miyaura reaction (Scheme 32). The obtained results indicated the higher catalytic activity of phosphinated species, relative to non-phosphinated PI Pd, even when triphenylphosphine was added. It was demonstrated that phosphine groups in the polymer had an essential role in the catalytic activity and Pd leaching suppression. This novel catalyst could be recovered and reused several times, while retaining its catalytic activity.66



Scheme 31 Catalyst preparation procedure. Adapted from ref. 231 with the permission of the American Chemical Society.



Scheme 32 Suzuki–Miyaura coupling reaction. Adapted from ref. 231 with the permission of the American Chemical Society.

7.3.2. Sonogashira-type alkynylation of aryl halides. Ribecai *et al.* developed Sonogashira-type alkylation of aryl halides by using Pd EncatTM 40 or RPP30 under Cu-free conditions and a solvent-less system (Scheme 33).²³³ This approach exhibited good functional group tolerance. Various electron-rich and electron-deficient aryl iodides, as well as some aryl bromides, were successfully subjected to the aforementioned catalyzed reaction. The same authors also investigated the same reactions under microwave irradiation (MWI). Using the catalyst as low as 0.01 mol% Pd, not being sensitive to moisture, broad substrate



Scheme 33 Sonogashira-type alkylation of aryl halides.²³³

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 Table 22
 Scope of the PI/CB-Au/Pd/B-catalyzed one-pot sequential reaction. Reprinted from ref. 235 with the permission the of American Chemical Society

	$R_1 \xrightarrow{O}_{R_3} R_2 + \xrightarrow{OH}_{R_4} \frac{1 \mod 9 P}{\text{THF, O}_2(1)}$	/CB-Au/Pd/B (wrt Au) latm), 30 or 60 °C, 20h	
Donor	Alcohol	Product	Yield (%)
Ph OEt	OH	Ph CO ₂ Et	95
OMe	OH	CO ₂ Me	98
CO ₂ Et	OH		97
	OH	O O C(O)Me	82
мео	OH	MeO CO ₂ Me	88
MeO OMe	OH	Ph CO ₂ Me	87
Ph OEt	OH	Ph CO ₂ Me	83
Ph OEt	OH	Ph CO ₂ Me	95
Ph OEt	OH	Ph CO ₂ Me	94
Ph OEt	OH OMe	Ph CO ₂ Me OMe	89
Ph OEt	OH O	Ph CO ₂ Me	93
Ph OEt	OH CN	Ph CO ₂ Me CN	98
Ph OEt	OH CF3	Ph CO ₂ Me CF ₃	98

scope tolerance, obtaining products free from hazardous heavy metals, were the merits of this strategy. Comparison of the results indicated that the reactions being conducted under MWI are more favorable in terms of shorter reaction times and higher obtained yields of desired products.

Recently, Ishida et al. reported²³⁴ the utility of conjugated microporous polymers, CMPs, for the encapsulation of Pd NPs. This protocol involved the polymerization of 1,3,5-triethynylbenzene and 1,4-diiodobenzene in the presence of Pd(PPh₃)₄ to provide Pd/CMP-1. The latter was dried and treated in H₂ or N₂ to furnish Pd/CMP-1-N₂ and Pd/CMP-1-H₂. CMP-2 prepared from 1,3,5-triethynylbenzene and 4,4'-diiodobipheny was also used to generate Pd/CMP-2-H2 and Pd/CMP-1-N2. These catalytic systems were successfully used for the hydrogenation of 4nitrostyrene, N-benzylideneaniline and oxidation of benzyl alcohol. Pd/CMP-1-H2 exhibited high selectivity for the hydrogenation of 4-nitrostyrene into 4-ethylnitrobenzene. This reaction under Pd/Ketjen black catalysis furnished 4-ethylaniline. It was also found that catalytic activity was affected by substituents in CMP and benzyl alcohol oxidation. The better result was obtained when hydroxy-substituted CMP encapsulated Pd NPs was used instead of Pd/CMP-H₂.

7.4. Bimetallic systems

Tandem oxidation–addition reactions of allylic alcohols with 1,3-dicarbonyl derivatives was promoted by carbon-blackstabilized, polymer-incarcerated Au–Pd bimetallic nanocluster with boron, PI/CB–Au/Pd/B (Table 22).²³⁵ It was proposed that the B immobilization proceeded through the formation of a tetravalent boron complex through the esterification of NaBH₄, when the hydroxy functional groups were present on the polymer backbone (Scheme 34).

The catalytic activities of bimetallic and monometallic systems were compared. The results indicated the higher catalytic activity of PI/CB-Au/Pd/B. To elucidate the merit of the bimetallic system, its catalytic activity was also compared with that of a mixture of monometallic ones (Table 23). As can obviously be seen in this table, higher reaction rates in the case of the mixed catalyst system were obtained, which can be attributed to a decrease in the rate of the allylic oxidation, which arose from the reduced surface area of the polymer-CB composite material. Moreover, this catalyst exhibited efficient



Scheme 34 Immobilization of boron. Reprinted from ref. 235 with the permission of the American Chemical Society.

Table 23 Comparison between the bifunctional composite catalyst
and the mixed catalyst system for the sequential oxidation-Michael
reaction. Reprinted from ref. 235 with the permission of the American
Chemical Society

Ph OEt $Catalyst (1 m OEt OEt OEt O2 (1 atm), 0)$	$\begin{array}{c} \text{nol\% wrt Au)} \\ \text{esitylene,} \\ \text{50 °C, t (h)} \end{array} \begin{array}{c} 0 & 0 \\ \text{Ph} \\ CO_2 Et \end{array} \begin{array}{c} 0 \\ CO_2 Et \end{array}$
Yield (%)	
PI/CB-Au/Pd/B	PI/CB-Au/Pd + PI/CB-B
Not detected	Not detected
<5	6
13	18
35	49
>95	>95
	Ph $\stackrel{O}{\longleftarrow} O$ OEt $\frac{Catalyst (1 n)}{THF-d^8, M, O_2 (1 atm), G}$ <u>Yield (%)</u> <u>PI/CB-Au/Pd/B</u> Not detected <5 13 35 >95

reusability, due to the control of metal leaching.⁶⁶ The high efficiency and reusability of the catalyst, along with acting under mild reaction conditions, and the possibility of using air as the terminal oxidant can be mentioned as other advantages of this catalyst.

A novel catalytic system based on a layered heterogeneous bifunctional chiral catalyst containing metal NPs and a chiral Jorgensen-Hayashi-type organocatalyst (OC) supported on different polymers were developed. This catalytic system can efficiently catalyze the sequential aerobic oxidation. More importantly, this chiral catalytic system can successfully catalyze the asymmetric Michael reactions between primary allylic alcohols and dibenzyl malonate.²³⁶ In Scheme 35, the pathway for the preparation of the catalyst is illustrated. To obtain polymer bead 5 for use in the asymmetric Michael reaction, Jorgensen-Hayashi-type OC 1 was immobilized on acrylamides as co-monomers via suspension copolymerization with optimized amounts of N-tert-butylacrylamide, N,N' methylenebismethacrylamide and dimethyl 2,2'-azobis(2-methylpropionate) (V-601 as an initiator). Incorporation of Au-Pd bimetallic alloy NPs was achieved via 2 pathways, Scheme 35b and c, in which the order of the layers was reversed. In catalyst



Scheme 35 Catalyst preparation procedure. Adapted from ref. 236 with the permission of the Royal Society of Chemistry.

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Scheme 36 Sequential aerobic oxidation-asymmetric Michael reactions between primary allylic alcohols and dibenzyl malonate.²³⁶

(PI(Au/Pd)-CO) 4, polymer 2 formed a coating around polymer beads 3, while in (IOC/PI/CB-Au/Pd) 5, the PI/CB-Au/Pd catalyst was coated with polyacrylamide that contains OC 1. The optimized ratio of Au : Pd was determined as 1 : 1. Additionally, it was found that each metallic NPs as the sole catalyst is not appreciably effective. This catalyzed reaction showed wide substrate scope (Scheme 36). Interestingly, the order of the layers of catalyst affected the catalytic performance, dramatically (Table 24). IOC/PI/CB-Au/Pd, catalyst 7, (Table 24, entry 2) in which the core bimetallic alloy NPs was surrounded by the OC outer shell was not active. The same authors also examined the effect of unsupported OC on the bimetallic alloy NPs (Table 24). Although the deactivating effect of OC was confirmed, catalytic activity was obtained to some extent, implying that the poisoning of the bimetallic alloy NPs via some kind of coordination by acrylamides could result in zero catalytic activity (entry 2). As can be realized, by using the approach depicted in Scheme 35b, all unfavorable interactions were avoided.

In another attempt, a novel catalyst, PICB–Au/Pd, was developed. In this effective catalyst, Au/Pd NPs were immobilized onto styrene-based copolymer and carbon black (CB), which was used as a second or supportive support. The catalytic activity of this system was investigated for the imine synthesis from alcohol and amine derivatives *via* a cascade oxidative process, TOP (Scheme 37).²³⁷ The catalytic performance of PICB–Au/Pd was higher than PICB–Au/Co or PICB–Au/Pt. In this reaction, the effects of solvent were also studied. When THF was used, low selectivity toward imine, as well as high conversion was achieved; in contrast, by using MeOH, low reactivity and high selectivity were obtained. In conclusion, a mixture of THF–trifluoroethanol (TFE) was found as the best solvent system for



Scheme 37 Synthesis of the catalyst. Adapted from ref. 237 with the permission of the Royal Society of Chemistry.

R = Bn, Ph, 3-CIC₆H₄, 4-MeC₆H₄, C₈H₁₇, C₆H₁₃, C₂H₄(*i*-Pr), 4-OMeC₆H₄, 4-OMeBn

 R' = 4-MeC_6H_4, 4-NO_2C_6H_4, 4-OMeC_6H_4, 2-OHC_6H_4, Ph, 4-ClC_6H_4, 2-Pyridyl, 2-Furfuryl, C_7H_{15}, EthynylBn, VinylBn

Scheme 38 Direct synthesis of imines from the cascade oxidative process, TOP, of alcohols and amines.²³⁷

this reaction. Noticeably, TFE acted as a Brønsted acid and/or a hydrogen-bond donor, which could facilitate the dehydration step. The oxidation process proceeded smoothly by using this novel TOP in the presence of NaOH as base, and molecular oxygen as the terminal oxidant under mild reaction conditions. Importantly, no metal leaching was observed during the reaction. This protocol showed broad substrate scope (Scheme 38), being applicable to a wide range of substrates, including saturated as well as unsaturated alcohols, as well as those alcohols containing heterocycles.

The Kobayashi research group also disclosed their results of the *N*-alkylation of primary amides with benzyl alcohols by employing a the synergistic cascade catalytic system. In this system Lewis acid (Ca(OTf)₂/Ba(OTf)₂) and immobilized bimetallic Au/Pd NPs catalysts acted in a cascade manner. In the polymer incarcerated bimetallic catalyst, PI/CB–Au/Pd, carbon black, CB, was used as a secondary support (Fig. 14).²³⁸ The authors compared the catalytic activity of the bimetallic catalyst with that of the mixture of monometallic ones. The results

_CO₂Bn

ЪОН

Catalyst

AcO (20 mol%)

Ph ^{-//} + CO_2Bn EtOH/H ₂ O (1:1, C = 0.25 M) Ph ⁺ + CO_2Bn 30 °C, O ₂ (1atm), 24h CO_2Bn				
Entry	Catalyst	Conversion (%)	Yield (%)	ee (%)
1	6 (Au = 1, Pd = 1, OC = 5)	76	Not determined	91
2	7 (Au = 1, Pd = 1, OC = 5)	No reaction		_
3	PI/CB-Au/Pd (Au, $Pd = 1$) & 1 (5)	39	Not determined	85
4	6 (Au = 2, Pd = 2, OC = 10)	97	75	90



Fig. 14 Proposed dual catalysis for the challenging *N*-alkylation of primary amides *via* hydrogen autotransfer. Adapted from ref. 238.



proved the higher catalytic activity of the bimetallic system. The authors proposed that the vicinity of Au to Pd NPs could lead to more a profound effect of Au NPs on Pd. Moreover, the high catalytic activity could be attributed to the polarization of electric charge on the surface of the alloyed bimetallic NPs arising from the difference in electronegativity between Au and Pd. Among several examined additives, $Ba(OTf)_2$ was found to be the co-catalyst of choice. This strategy exhibited broad substrate scope. A wide range of appropriate substrates possessing different electronic and steric features were successfully subjected to this catalyzed reaction (Scheme 39).⁶⁶ The catalyst reusability, as well as suppressed leaching were studied and found to be advantageous for this novel catalytic system.

Polymer resins/gel-encapsulated Pd

Pd NPs were embedded onto macroporous Dowex Marathon ion-exchange resins and used as an efficient catalyst for promoting the Suzuki–Miyaura reaction between phenylboronic acid and bromobenzene derivatives in aqueous media (Scheme 40).²³⁹ The catalyst preparation procedure included the complexation of Pd(OAc)₂ and the subsequent reduction with NaBH₄. The generality of the process was confirmed by using a wide variety of substrates with different functional groups. Moreover, the catalyst showed good reusability and could be used for up to 10 runs with negligible loss of activity.

Kaur *et al.* resided Pd NPs within a commercial polystyrene– divinylbenzene cross-linked macroporous resin, Amberlite



 $\mathsf{R_1}$ = H, NH_2, OH, OMe, Me, NO_2, CF_3, COMe, CO_2H, CO_2Me, CHO, CONH_2 R_2 = H, OMe, Me, CI, F, NO_2, CHO, OMe

Scheme 40 The Suzuki–Miyaura reaction between phenylboronic acid and bromobenzenes.²³⁹

XAD-4, and used it as highly active and recyclable catalyst for a ligand-free Suzuki reaction with phenylboronic acid and allylbenzene and bromothiophene under microwave irradiation (Scheme 41).²⁴⁰ The catalytic activity of this catalyst was compared with those of Pd supported on previously reported supports, such as SBA-15/dendrimers, mesoporous starch, chitosan and mesoporous starch, *etc.* The results indicated that this novel catalyst, which could be prepared simply, exhibits superior reusability and catalyzes the reaction effectively with low Pd loading and most importantly, for its action as catalyst the phase transfer agent is not required.

The same research group also achieved and reported the preparation of Pd impregnated Amberlite XAD-4 resin and used it as an effective catalyst in the ligand-free Hiyama crosscoupling reaction between arylbenzene and bromothiophene with phenyltrimethoxysilane under MWI (Scheme 42).²⁴¹ The catalyst proved to be very efficient and reusable, tolerating a broad range of substrates.

Yusop *et al.* reported the immobilization of Pd NPs with size of 4–12 nm in HypoGel resin and its utility as an efficient catalyst for the Suzuki coupling reaction of aryl iodides or aryl



Scheme 41 Suzuki reaction between phenylboronic acid and allylbenzene and bromothiophene.²⁴⁰



Scheme 42 The Hiyama cross-coupling reaction between arylbenzene and bromothiophene with phenyltrimethoxysilane.²⁴¹



Scheme 43 Suzuki coupling reaction of aryl iodides or aryl bromides with phenylboronic acid.²⁴²



Scheme 44 Synthesis of the Pd NPs loaded on poly(ionic liquids). Adapted from ref. 243 with the permission of Elsevier.

bromides with phenylboronic acid in aqueous media (Scheme 43).²⁴² The catalyst, XL-HGPd, was prepared by heating Pd(OAc)₂ and HypoGel in toluene, followed by cooling and stirring. The cross-linking was achieved in the presence of triethylamine and succinyl chloride. Finally, hydrazine hydrate in methanol was used to furnish the desired catalyst. The obtained catalyst showed very low Pd leaching and was reused for at least five reaction cycles.

Recently, the utility of cross-linked mesoporous poly(ionic liquids) (MPILs) for the confinement of Pd NPs²⁴³ was disclosed. The catalytic activity of this system was investigated for the oxidation of benzyl alcohol to benzaldehyde in aqueous media with an O_2 balloon. Using azobisisobutyronitrile (AIBN) as the initiator, free radical copolymerization of the ionic liquid monomer and divinylbenzene, DVB, proceeded to afford the desired ionic copolymer (Scheme 44). Subsequently, Pd encapsulation was achieved by using Pd precursor and NaBH₄ as reducing agent. A series of MPILs with various functional groups were prepared and used for the encapsulation of Pd. Using carboxyl modified MPIL, which possesses high surface area and ionic density, highly uniform and narrowly dispersed Pd NPs were obtained. This catalytic system proved to be efficient and reusable for the above-mentioned reaction.

Hensen *et al.* reported²⁴⁴ the catalytic activity of Pd NPs entrapped within cross-linked ionic liquid polymers (microgels) for the hydrogenation of various substrates (Table 25). The route for the synthesis of catalyst is illustrated in Fig. 15. The microgel not only restricted the aggregation of Pd NPs, but also affected the catalytic activity, due to its physicochemical properties. Moreover, the size of the NPs could be tuned by adjusting the metal loading and altering the reduction method. It was proved that bromide was the best counter ion, due to the high swellability of the resulting catalyst in polar solvents. The catalyst exhibited high reusability and could be recovered and reused for at least 10 reaction runs with negligible loss of activity.

Basu and De *et al.*²⁴⁵ encapsulated Pd/Cu bimetallic NPs with average size of \sim 4.9 nm in cationic and macroporous Amberlite

Table 25Hydrogenation of various substrates by Pd entrapped inmicrogels. Reprinted from ref. 244 with the permission of Elsevier

Substrate	Product	Time (min)	Yield (%)	$_{\left(h^{-1}\right) }^{TOF}$
Styrene	Ethylbenzene	5	(First) 90	4320
		5	(Sixth) 100	4800
		5	(Tenth) 85	4080
Cyclohex-2-enone	Cyclohexanone	20	98	1176
•	·	25	100	
1-	Styrene ethylbenzene	10	88	2112
Ethynylbenzene			11	
Acetophenone	1-Phenylethanol	30	0	0



Fig. 15 Preparation procedure for palladium NPs entrapped in crosslinked polymeric ionic liquids. Reprinted from ref. 244 with the permission of Elsevier.

resins with formate (ARF), and used it as an efficient catalyst for the Sonogashira reaction of aryl iodides and terminal alkynes (Scheme 45). The authors proved the heterogeneous catalytic activity by metal-scavenger and hot-filtration methods. It is worth noting that the catalyst was reusable and could be reused for at least 5 reaction runs.

Core-shell microgels and spherical polyelectrolyte brushes (SPB) were used as colloidal carriers for encapsulation of Pd NPs (Fig. 16).²⁴⁶ The catalytic performances of these two systems were studied for *p*-nitrophenol reduction in the presence of NaBH₄ and compared with those of reported catalysts (Table 26). The rate constant of Pd NPs encapsulated in SPB was higher than that of microgels. The results indicated the dependence of



 $\begin{array}{l} \text{Ar-X}=4\text{-}O\text{MeC}_{6}\text{H}_{4}\text{I}, 4\text{-}\text{MeC}_{6}\text{H}_{4}\text{I}, 2\text{-}\text{MeC}_{6}\text{H}_{4}\text{I}, 3\text{-}\text{OMeC}_{6}\text{H}_{4}\text{I}, 3\text{-}\text{NO}_{2}\text{C}_{6}\text{H}_{4}\text{I}, 3\text{-}\text{Br}_{6}\text{H}_{4}\text{I}, 3\text{-}\text{S}_{6}\text{H}_{6}\text{H}_{6}\text{I}, 3\text{-}\text{S}_{6}\text{H}_{6}\text{H}_{7}, 1\text{-}\text{Br-3}\text{-}\text{IC}_{6}\text{H}_{4}, \text{C}_{6}\text{H}_{5}\text{B}(\text{OH})_{2}, 3\text{-}\text{MeC}_{6}\text{H}_{4}\text{Br}, 1\text{-}\text{Br-3}\text{-}\text{IC}_{6}\text{H}_{4}, \text{C}_{6}\text{H}_{5}\text{B}(\text{OH})_{2}, 3\text{-}\text{MeC}_{6}\text{H}_{4}\text{Br}, 1\text{-}\text{Br-3}\text{-}\text{IC}_{6}\text{H}_{4}, \text{C}_{6}\text{H}_{5}\text{B}(\text{OH})_{2}, 3\text{-}\text{MeC}_{6}\text{H}_{4}\text{Br}, 1\text{-}\text{Br-3}\text{-}\text{IC}_{6}\text{H}_{4}, 1\text{-}\text{B}_{6}\text{-}\text{B}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_{6}\text{H}_$

 $\mathsf{R}=\mathsf{C}_{6}\mathsf{H}_{5},\,\mathsf{C}\mathsf{H}_{2}\mathsf{OCOMe},\,\mathsf{C}\mathsf{H}_{2}\mathsf{OCOEt},\,\mathsf{C}\mathsf{H}_{2}\mathsf{C}\mathsf{H}_{2}\mathsf{C}_{6}\mathsf{H}_{5},\,\mathsf{C}_{6}\mathsf{H}_{4}(4\text{-}\mathsf{C}\mathsf{H}_{3})$

 \mbox{Scheme} 45 Sonogashira reaction of aryl iodide and terminal alkynes. $^{\rm 245}$



Fig. 16 Schematic representation of the formation of palladium NPs in spherical polyelectrolyte brushes (SPB) or microgels. The upper part shows the SPB that has a shell of poly((2-methylpropenoyloxyethyl) trimethylammonium chloride). The metal ions, namely, $PdCl_4^{2-}$, are confined within the brush layer. Reduction of the metal ions by NaBH₄ leads to nanosized palladium particles bound on the PS surface. The lower part shows the microgel particles, which have a network-like shell consisting of PNIPA cross-linked by BIS. Palladium nanoparticles were generated and confined within the PNIPA network-like shell. Reprinted from ref. 246 with the permission of the American Chemical Society.

catalytic activity on the type of carrier and diffusional barriers. It is worth noting that no specific interaction was detected between Pd NPs and polymer chains.

Ye *et al.* synthesized encapsulated Pd NPs in polyethylene (PE) gel as an efficient and reusable catalyst for the Suzuki and Heck coupling reactions of aryl bromides or iodobenzene.²⁴⁷ The PE gel was obtained by the one pot copolymerization of ethylene with 1,6-hexanediol diacrylate, promoted by Pd–diimine, followed by the reduction of the Pd(π) species to Pd(0) by methanol. A low amount of Pd leaching rendered the catalyst highly active and reusable. The measured average TOF for the Heck reaction was 460 h⁻¹, while the maximum TOF for the Suzuki reaction was 3.33 × 104 h⁻¹.

Miscellaneous encapsulated Pd NPs

The porous systems used for the encapsulation of Pd(0) NPs are not limited to the discussed compounds.^{248,249} A variety of



Fig. 17 Scheme of the synthetic procedure for the preparation of Pd/ Fe_3O_4 @hTiO₂. Reprinted from ref. 264 with the permission of the Royal Society of Chemistry.

catalytic systems were developed by confining Pd(0) NPs in a broad range of nanoreactors. $^{250\text{-}263}$

Li *et al.* reported the use of a TiO₂ hollow mesoporous system as a novel, cost-effective host, with low toxicity and good chemical stability and photocatalytic activity for the encapsulation of Pd(0) NPs.²⁶⁴ The synthesis was carried out in six steps, including the preparation of SiO₂ nanospheres and its surface loading by Fe₃O₄. The latter was deposited by Sn²⁺ in the third step. Pd NPs were loaded and subsequently, the Pd/Fe₃O₄/ SiO₂@TiO₂ core-shell compound was prepared. Removal of the template was performed *via* etching with Na₂CO₃ (Fig. 17). The authors investigated the catalytic activity of the novel catalyst for the hydrodechlorination of chlorophenols. The results indicated the excellent catalytic activity of this catalyst for the hydrodechlorination of 4-chlorophenols. Moreover, the catalyst could be easily recovered by using an external magnet and reused for several reaction runs with negligible loss of activity.

Semi-hydrogenation of alkynes was promoted under mild reaction conditions by a novel core-Pd/shell-Ag nanocatalyst, Pd@Ag (Fig. 18), in a very selective manner (*Z*-selectivity) (Scheme 46).²⁶⁵ The high catalytic performance was attributed to the synergetic effects of metallic components. The role of the Ag shell was to prevent over-hydrogenation, while the Pd core provided hydrogen to the shell. It is worth noting that the catalyst could be recovered easily and reused without loss of catalytic performance.

Wang *et al.* reported the decoration of carbon nanotubes with V–P–O compounds encapsulated Pd NPs, with core–shell structure, Pd@V–P–O/CNT, and their utility as electrocatalyst

 Table 26
 Catalytic activity of the palladium nanoparticles: comparison with the literature^a. Reprinted from ref. 246 with the permission of the American Chemical Society

Catalyst	T (°C)	$k_{\mathrm{app}}(\mathrm{s}^{-1})$	$k_1^{b} (s^{-1} m^{-2} L)$	$c \pmod{\mathrm{L}^{-1}}$	<i>d</i> (nm)	$S^b \left(\mathrm{m}^2 \mathrm{L}^{-1} \right)$
Microgel-1-Pd9	15	$1.50 imes 10^{-3}$	$1.01 imes 10^{-1}$	2.15×10^{-3}	3.8 ± 0.6	$1.49 imes 10^{-2}$
SPB-30-Pd3	15	$3.47 imes10^{-3}$	$5.62 imes10^{-1}$	$6.60 imes10^{-4}$	2.1 ± 0.4	$8.58 imes10^{-3}$
SPB-30-Pd9	15	$4.41 imes10^{-3}$	1.10	$3.66 imes10^{-4}$	2.4 ± 0.5	$4.00 imes10^{-3}$
PAMAM dendrimer G 4.0	15	$1.79 imes10^{-3}$	3.07×10^{-3}	$2.00 imes10^{-2}$	1.8 ± 0.42	$5.83 imes10^{-1}$
PPI dendrimer G 3.0	15	4.07×10^{-3}	7.76×10^{-1}	$2.00 imes10^{-2}$	2.0 ± 0.41	$5.25 imes10^{-1}$

^{*a*} k_{app} : apparent rate constant; k_1 : rate constant normalized to the surface of the particles in the system; *d*: diameter of the palladium particles; *S*: surface area of palladium nanoparticles normalized to the unit volume of the system; *c*: total amount of palladium particles in the system. ^{*b*} Calculated from the data given in the respective papers.



Fig. 18 Design concept of complementary bimetallic core-Pd/shell-Ag catalyst for the selective semihydrogenation of alkynes. Reprinted from ref. 265 with the permission of the American Chemical Society.



R = Hex, Cyclohexyl, Benz, Pr, Ph, CO₂Et, Me, Et, PhC₂H₄, C₂H₄CN, CH₂CO₂, C₃H₇O, C₄H₈Cl

 $R'' = H, Pr, Ph, NEt_2, CO_2Et, CH_3OH, C_2H_5O$

Scheme 46 Semi hydrogenation of various alkynes.²⁶⁵

for the oxygen reduction reaction (ORR).²⁶⁶ Comparison of the catalytic performance of the novel catalyst with those of conventional ones (Pd/C, Pd/CNT, Pt/C) proved the considerable catalytic activity and increased methanol tolerance of the catalyst. The authors believe that the shell would protect active Pd sites from MeOH oxidation.

The novel Pd-encapsulated catalyst, Pd@void@ZrO₂, was developed and used for H_2O_2 synthesis from H_2 and O_2 .²⁶⁷ To prepare the catalyst, Pd nano crystals were encapsulated within the silica shell to produce the core-shell Pd@SiO₂. The latter would be encapsulated for second time with zirconia, to afford Pd@SiO₂@ZrO₂. The final yolk-shell system was formed by etching the silica layer with KOH (Fig. 19). The catalytic activity of this catalyst was higher (1.2 times) than the core-shell Pd@SiO₂. It was believed that the hollow space in the yolk-shell system improved gas transfer and the accessibility of gases to the catalytic surface. Moreover, the shell oxide effect could also influence the catalytic activity. The concentration of halide ions also affected the catalytic performance. 0.1–0.3 mM was found to be the best concentration of Br⁻.



Fig. 19 The steps for the preparation of $Pd@void@ZrO_2$ catalyst. Reprinted from ref. 267 with the permission of Elsevier.



Fig. 20 Synthetic scheme of four distinct catalyst structures: $Pd@SiO_2$ core-shell (1), $Pd@SiO_2-Niphy$ (2, 3), and Pd@Niphy yolk-shell (4) nanoparticles. Reprinted from ref. 268 with the permission of the American Chemical Society.

Table 27Suzuki coupling reactions of 1-bromo-4-ethylbenzene withphenylboronic acid yielding 4-ethylbiphenyl. Reprinted from ref. 268with the permission of the American Chemical Society



Catalysts	Pd [mol%]	Time [h]	Conv. ^{<i>a</i>} [%]
Dd@SiQ_core_shall_1	2	15	40
$Pu(a)SiO_2$ core-siten, 1	2	15	42
$Pd(a)SiO_2$ -Niphy, 2	2	15	81
Pd@SiO ₂ -Niphy, 3	2	15	89
Pd@Niphy yolk–shell, 4	2	15	100 (92)
Pd@SiO ₂ core-shell, 1	1	36	71
Pd@SiO ₂ -Niphy, 2	1	36	76
Pd@SiO ₂ -Niphy, 3	1	36	87
Pd@Niphy yolk–shell, 4	1	36	>99 (98)
SiO ₂ -Niphy	—	24	0

 a All conversion yields were estimated by $^{1}\mathrm{H}$ NMR, except the isolated yields in parentheses.

Park and Song developed a novel catalyst based on the $Pd@SiO_2$ yolk–shell NPs with Ni phyllosilicate branches.²⁶⁸ The procedure for the synthesis of the catalyst included the preparation of $Pd@SiO_2$ core–shell NPs, 6, followed by the formation of pores in the shell by using Ni phyllosilicate to afford $Pd@SiO_2$ –Niphy, 2 and 3 (total pore volume for 7 and 8 were 0.585 and 0.744 cm³ g⁻¹, respectively). The final catalyst, Pd@Niphy yolk–shell nanocatalyst, 9, was obtained by removing silica (Fig. 20). The catalytic activities of the synthesized series of catalysts, 1–4, were investigated for the Suzuki coupling reaction (Table 27). The results demonstrated the superior catalytic activity of 4 and proved the correlation of the reaction rate and shell porosity and surface exposure of the metal cores. The catalyst could be recovered and reused for 5 reaction runs while maintaining its activity.

10. Conclusions

Confinement of Pd NPs within the cavity of a nanoreactor not only prevents the NPs from agglomeration and improves their reusability, but also promotes the catalytic performances of encapsulated catalysts in terms of selectivity, reactivity and Pd leaching. Several organic, inorganic and hybrid systems can be used for the encapsulation of Pd NPs, including mesoporous silica, zeolites, MOFs, dendrimers, carbon materials, *etc.* We hope this review article discloses the potential utility of encapsulated Pd NPs for various organic reactions.

Note added after first publication

This article replaces the version published on 16th September 2016, in which the biography texts were interchanged through editorial error.

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