Metal Nanoparticles for Catalysis

Advances and Applications

CHAPTER 6-1

Pd Nanoparticles in C–C Coupling Reaction

Intelligent Organometallic Chemistry Lab

Pusan National University

College of Natural Sciences, Department of Chemistry

History

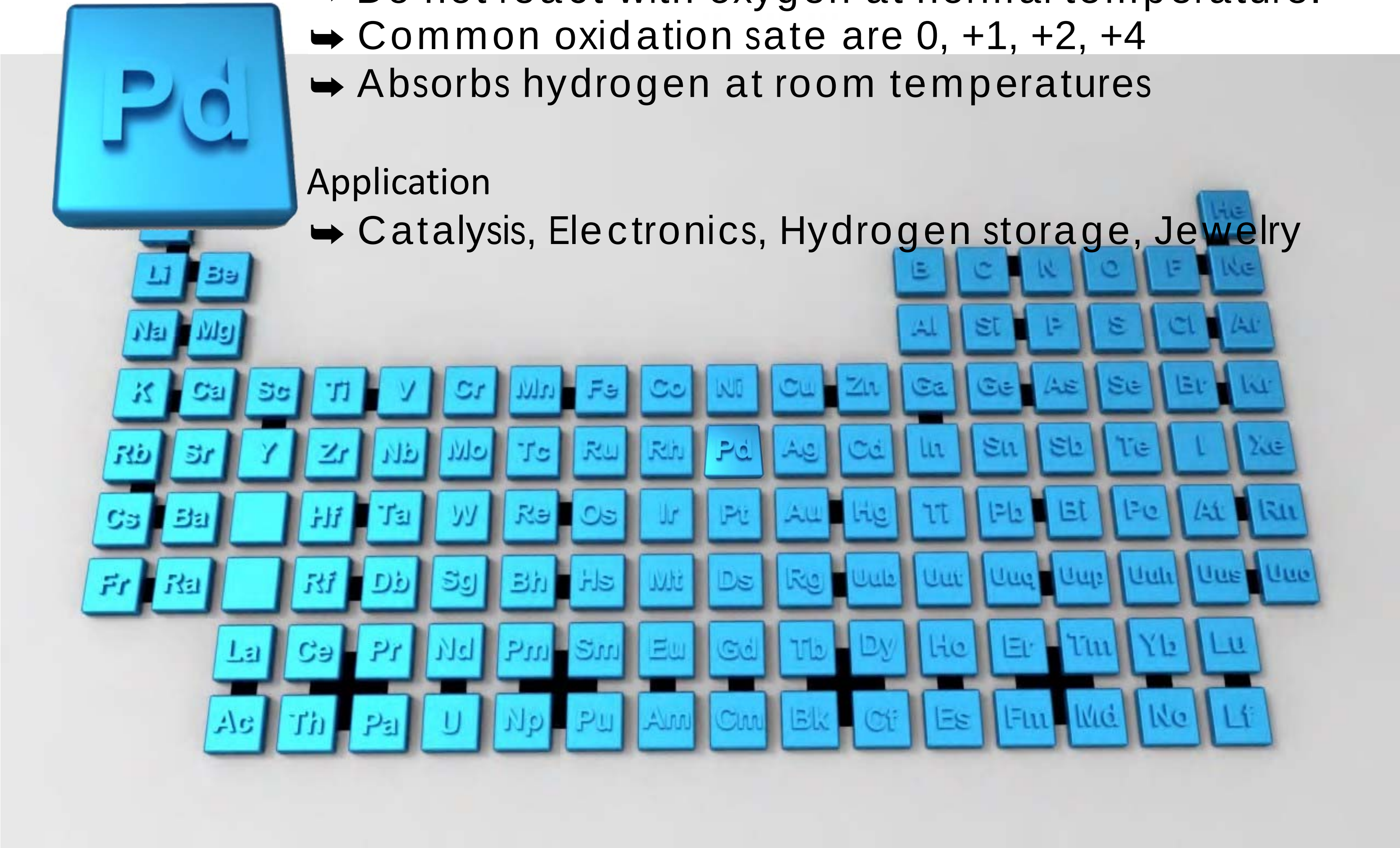
- It was named by Wollaston in 1802

Property

- Do not react with oxygen at normal temperature.
- Common oxidation sate are 0, +1, +2, +4
- Absorbs hydrogen at room temperatures

Application

- Catalysis, Electronics, Hydrogen storage, Jewelry



The Nobel Prize in Chemistry 2010

Great art in a test tube: the Molecule Makers

*The Nobel Prize in Chemistry 2010 was awarded jointly to Richard F. Heck, E and Suzuki “for **palladium**-catalyzed cross couplings in organic synthesis".*

Richard F. Heck
American citizen. Born 1931 in Springfield, MA, USA. Ph.D. 1954 from University of California Los Angeles (UCLA), CA, USA. Willis F. Harrington Professor Emeritus at University of Delaware, Newark, DE, USA.

Ei-ichi Negishi
Japanese citizen. Born 1935 in Changchun, China. Ph.D. 1963 from University of Pennsylvania, Philadelphia, PA, USA. Herbert C. Brown Distinguished Professor of Chemistry at Purdue University, West Lafayette, IN, USA.

Akira Suzuki
Japanese citizen. Born 1930 in Mukawa, Japan. Ph.D. 1959, Distinguished Professor Emeritus, both at Hokkaido University, Sapporo Japan.

www.nobelprize.org

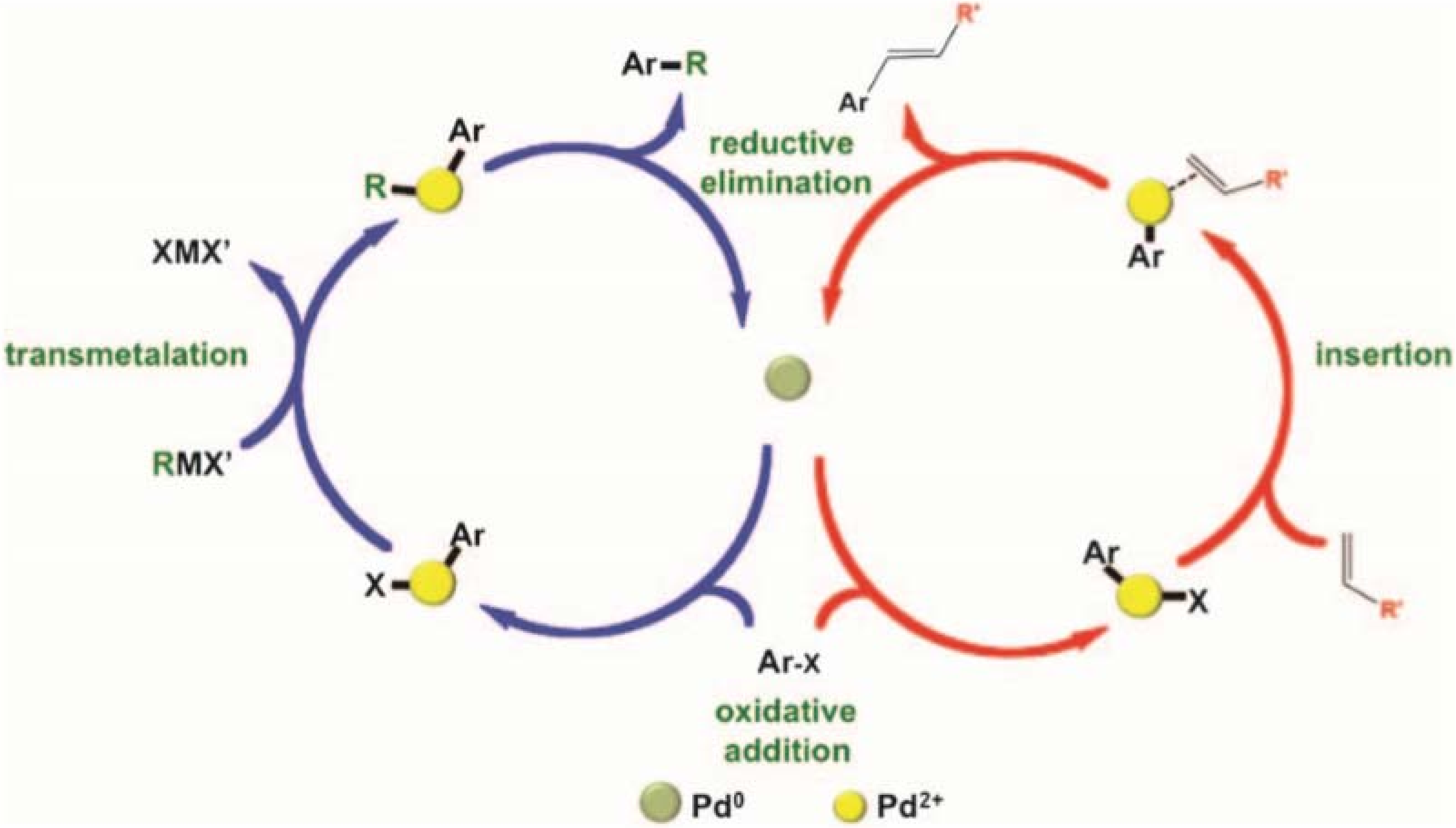
6.1Introduction

Transition metals have played an important role in synthetic chemistry as they have the unique capacity of activating various organic compounds towards chemical transformation and/or generation of new bonds. As such, organic ligand-stabilized metal catalysts based on Mg, Fe, Ni, Au, Ag, Pd, and Pt have been synthesized to afford industrially important transformations such as carbon–carbon (C–C) coupling reactions, alkylation, hydrogenation, oxygen and nitro-group reduction, and carbon dioxide oxidation.

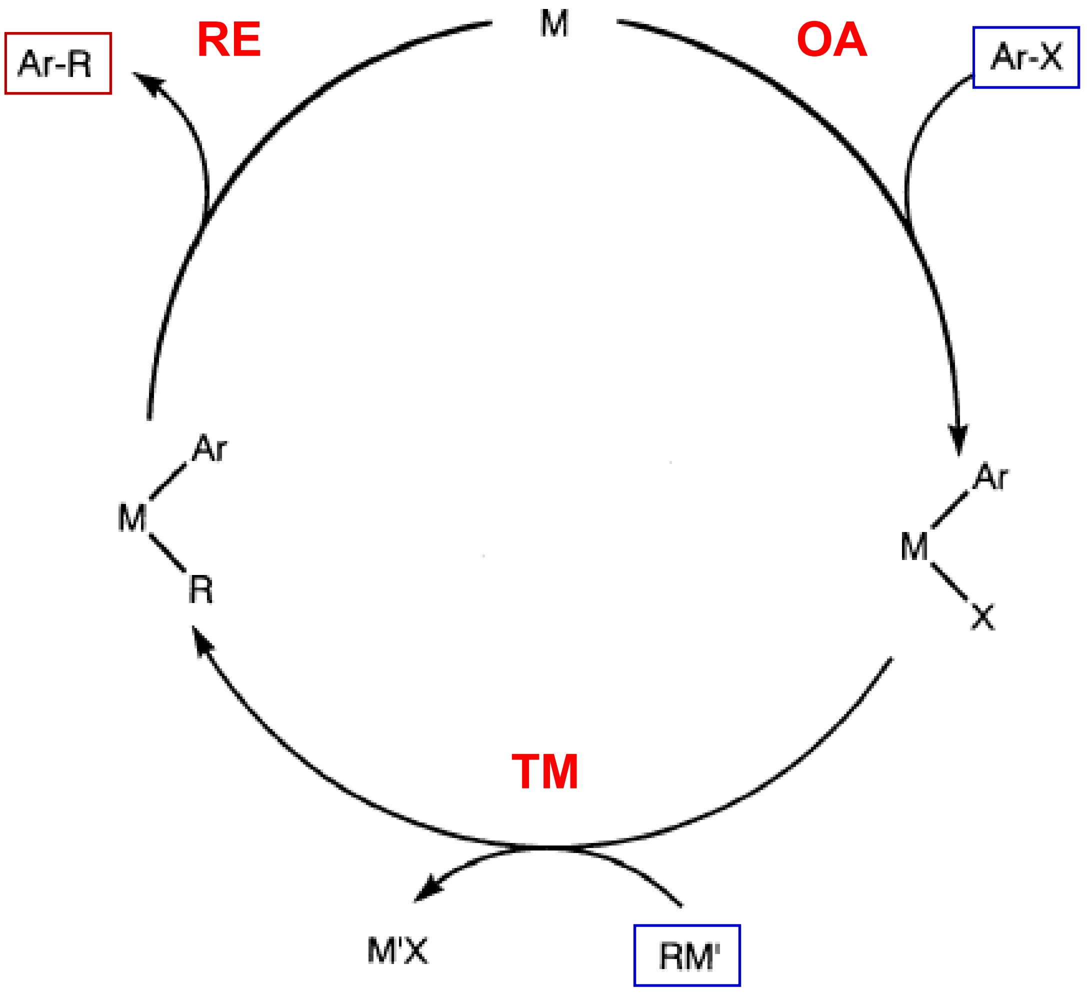
These reactions, however, typically involve the use of organic solvents, high temperatures, and high metal loadings. Furthermore, these processes also produce toxic by-products and are becoming economically unsustainable and environmentally unviable. As such, new processes are being developed to reduce the energy consumption and ecological impact of these reactions that are essential to maintain current technological advances.

One reaction that has garnered significant attention over the past decade is the C–C coupling reaction using Pd-based catalysts due to its applications in pharmaceutical, natural products, and materials synthesis. The coupling reaction, shown in Scheme 6.1, typically involves the formation of a new C–C bond between an electrophile (usually an aryl or vinyl halide) and a nucleophile (either an olefin or organometallic reagent), using zerovalent Pd metal to drive the reaction.

The first step in the coupling is oxidative addition wherein Pd^0 reacts with the electrophile by insertion between the C–X bond to form an organopalladate complex, oxidizing the Pd^0 to Pd^{2+}. The nucleophilic component will then attack the organopalladate complex either through transmetalation or alkene insertion, positioning the two carbon groups closer to each other on the metal surface. After reductive elimination, the new C–C bond is formed, the product is released, and the Pd^{2+} is reduced back to Pd^0.



Scheme 6.1 General mechanism of Pd-catalyzed C–C coupling.

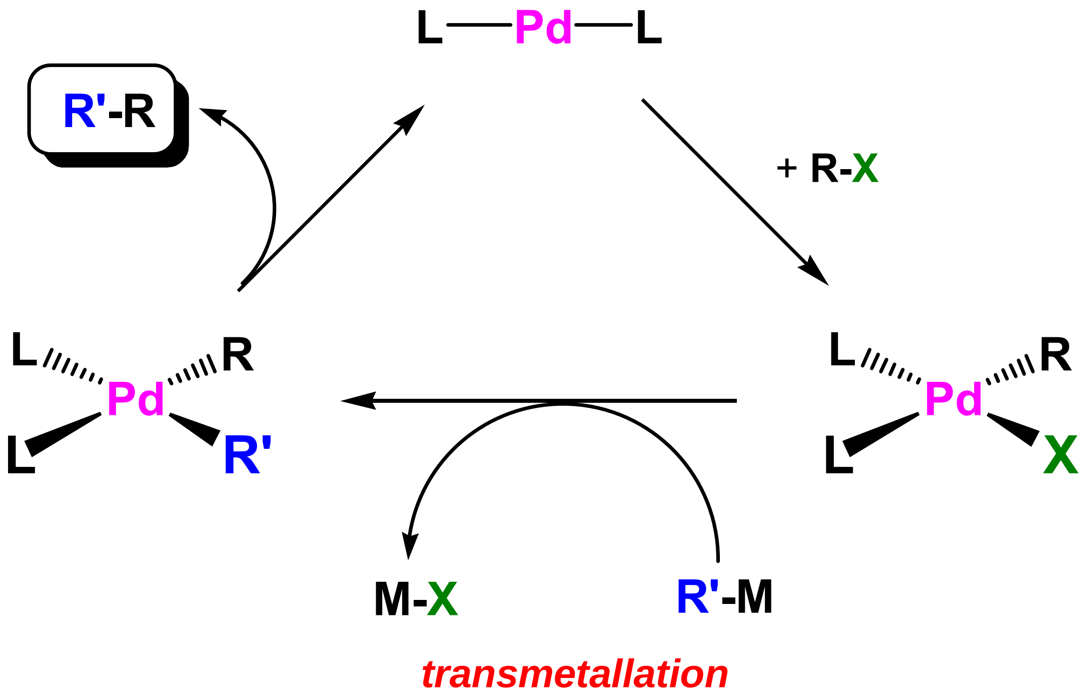

M
OA
Ar-X
Ar
M
X
TM
RM'
M'X
Ar
M
R
RE
Ar-R

Cross-Coupling of Organometallics and Halides

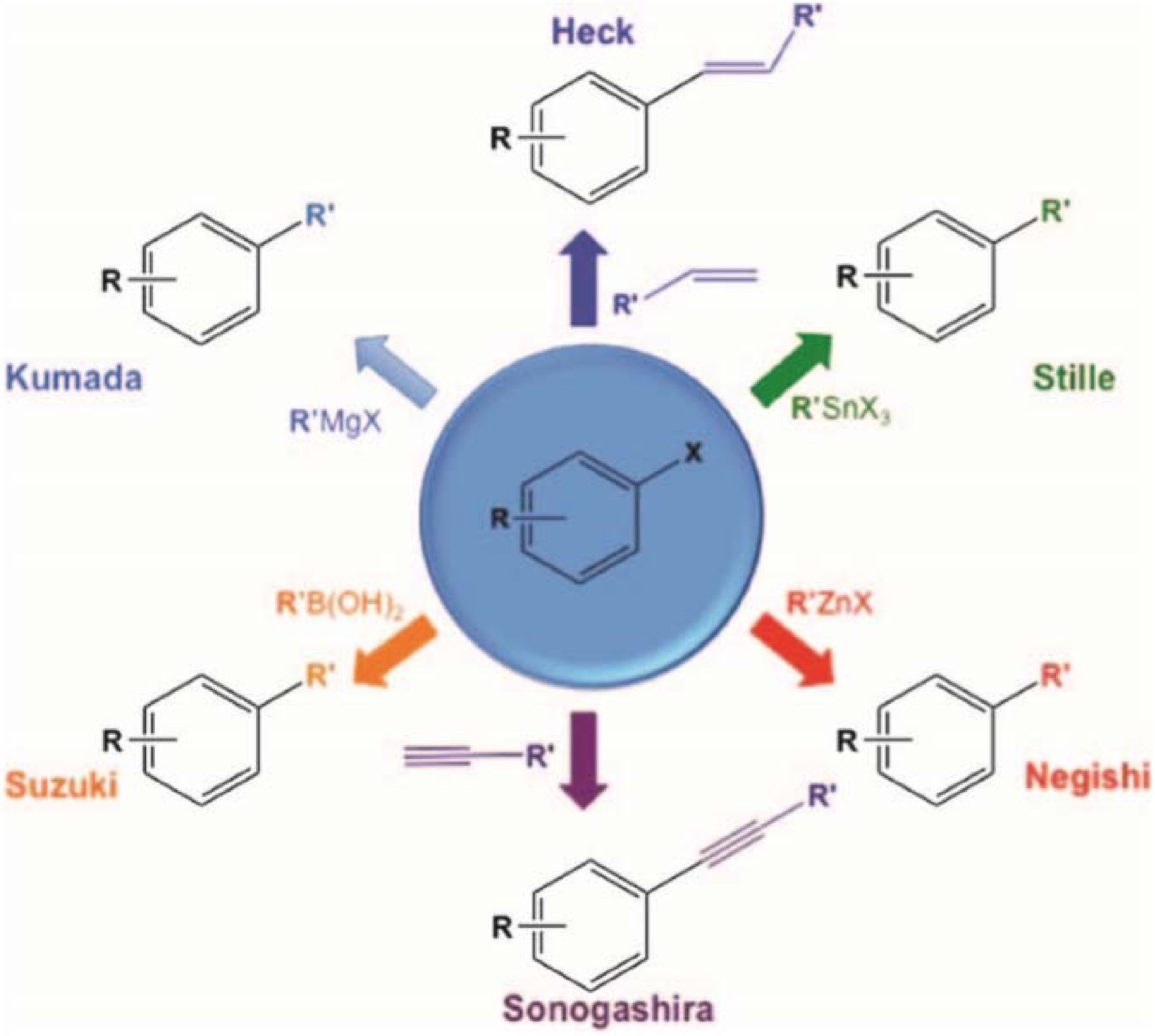
$$R\text{-}X \quad + \quad R'\text{-}M \xrightarrow{Pd(0)} R\text{-}R' \quad + \quad MX$$

M = MgX, $ZrCp_2Cl$, ZnX, SnR_3, $B(OR)_2$, $AlMe_2$, SiR_3, Cu,…

The mechanism involves oxidative addition of the halide or triflate to the initial Pd(0) phosphine complex to form a Pd(II) species. The key slow step is a **transmetallation**, so called because the nucleophile (**R'**) is transferred from the metal in the organometallic reagent to the palladium and the counterion (**X** = halide or triflate) moves in the opposite direction. The new Pd(II) complex with two organic ligands undergoes reductive elimination to give the coupled product and the Pd(0) catalyst ready for another cycle.



The halide partner (**R**–**X**) must be chosen with care, as β-hydride elimination would decompose the first intermediate during the slow transmetallation step. The choice for **R** is restricted to substituents without β-hydrogen atoms: vinyl, allyl, benzyl, and polyfluoroalkyl halides, triflates, and phosphates have all been coupled successfully.



Scheme 6.2 Select Pd-catalyzed C–C coupling reactions.

The modern use of Pd catalysts for C–C coupling reactions was pioneered by Heck with the publication of his work in 1972 on Pd-catalyzed arylation of olefins to produce substituted olefinic compounds. In this reaction, catalytic quantities of Pd were used to form new C–C bonds between aromatic and olefinic compounds producing a standard protocol for metal-catalyzed coupling reactions. For many years thereafter, several Pd-catalyzed coupling reactions (Scheme 6.2) were developed by different groups by modifying the nucleophilic component of the reaction. Sonogashira used alkynes instead of alkenes for cross-coupling reactions with aryl halides. Stille, on the other hand, initiated the use of organometallic reagents as the nucleophile by using organostannane compounds for the Pd-catalyzed coupling reaction with aryl halides; however, the toxic nature of tin compounds limited their large-scale use.

As an alternative to tin reagents, less toxic organometallic compounds such as organozinc was used by Negishi in the coupling reaction generating a mild and highly selective transmetalation agent that can tolerate a variety of functional groups. Kumada used organomagnesium reagents for transmetalation, although the highly reactive Grignard reagent also restricted their applications to a selection of functionalities. As an alternative to highly toxic tin and highly reactive Grignard transmetalation agents, Suzuki developed boron-based organometallic reagents for coupling reactions with aryl halides, generating a non-toxic and practical alternative that can be used under mild reaction conditions. In this reaction, activation of organoboron by a base is required to produce the boronate intermediate that initiates transmetalation, where a wide variety of functional groups can be employed.

The importance of Pd-catalyzed C–C coupling reactions in organic and material synthesis, as well as industrial applications, was recognized by the 2010 Nobel prize in chemistry for the pioneering works of Heck, Suzuki, and Negishi. In more recent times, technological advancements have led to novel synthetic approaches for producing highly active Pd catalysts by using different types of organic-based stabilizers that can control the reactivity and selectivity of the metal catalyst. Furthermore, these new Pd materials have unique characteristics and properties that enable their use in catalytic transformations for a wide array of applications in material,natural products, and pharmaceutical synthesis.

With the advent of nanotechnology, new synthetic strategies for the generation of *Pd nanocatalysts have been developed with particular emphasis on the control of the particle size, shape, and functionality.*

Since nanomaterials encompass the gap between the atomic level and bulk materials, interesting physical, chemical, electronic, and optical properties can be obtained, thereby generating a new class of structures for specific applications. Modern synthetic methods allow for the production of nanosized catalysts with optimized surface-to-volume ratios, allowing for more efficient catalytic reactivity as compared to traditional small molecule materials. The use of Pd nanoparticles for C–C catalysis marks a transition from using traditional organic solvent-based and high temperature reactions toward more ambient conditions such as aqueous solutions, mild temperatures, and low catalyst loadings. This is achieved by employing highly functionalized stabilizers such as dendrimers, proteins, peptides, and other small molecules. These materials allow for size-specific interactions, as well as control over the nanoparticle shape, thereby generating solution stability, but at the same time exposing active sites for interaction with substrates.

6.2 Synthetic Scheme for the Fabrication of Pd Nanoparticles

There are several common methods employed for the synthesis of Pd nanoparticles such as chemical reduction, vapor phase deposition, laser ablation, sonochemical reduction, electrochemical methods, seed-mediated approaches, and microwave reduction. However, we will focus on the chemical reduction approach, which typically involves the use of metal salts as a precursor, organic and/or biological ligands as surface passivants, and a reductant to reduce the metal ions to the zerovalent state. Using this method, the metal precursor, which is usually K_2PdCl_4 or K_2PdCl_6 is dissolved in aqueous solution and added to a separate ligand solution. In this process, the interaction of metal ions and ligands can lead to a ligand to-metal charge transfer band in UV-vis analysis. Upon addition of a reducing agent, typically $NaBH_4$, the metal ions are reduced to form metallic Pd nanoparticles as evidenced by the formation of a dark brown solution with a broad absorbance spectrum.

During the reduction process, several nucleation sites are generated, thus resulting in rapidly growing nanoparticles that can ripen and precipitate as bulk metal in the absence of stabilizing agents. As such, the ligands present in the reaction prevent particle agglomeration and control the size and shape of the resulting nanoparticles. By design, these stabilizing agents do not completely coat the nanoparticles, which, therefore, allows for surface accessibility by the substrates in the reaction; however, the porous network of ligands can also be designed to control access to the metal surface to develop catalytic selectivity. Commonly used stabilizers in Pd nanoparticle synthesis are amine-, thiol-, and phosphorus-based ligands, polymers, dendrimers, surfactants, ionic liquids, and biomacromolecules such as peptides.

While this method has produced a variety of homogeneous nanocatalysts for different C–C coupling reactions, their wide scale application in industry has not yet been realized due to the difficulty in recovering and recycling the catalyst. In this regard, attaching the nanoparticles to a solid support offers an alternative process for easier catalyst recovery and recyclability. *Although there are many advantages for homogeneous catalysts such as efficiency and selectivity, supported nanocatalysts can be more practical, easily separated, and cost-effective in large-scale use. They also greatly reduce the amount of metal impurities in the isolated products, thus lowering the degree of separation required post reaction.*

Solid supports such as carbon nanotubes, metal oxides, silica, alumina, zeolites, clays, polymer coatings, molecular sieves, aerogels, and naturally occurring porous diatomite have been used to immobilize Pd nanoparticles. The synthesis of a solid-supported nanocatalyst generally involves the adsorption, grafting, or attachment of the stabilizing agent to the solid material, after which Pd ions are introduced to interact with the ligands, followed by reduction. The solid materials can be easily separated via filtration, washed to remove excess ligands, and redispersed in various solvents for catalytic application.

6.3 Pd Nanoparticles in the Suzuki Coupling Reaction

The Suzuki reaction was first reported in 1979 where the cross-coupling of alkenylboranes with aryl halides was performed using a phosphine-stabilized Pd catalyst in the presence of a base. This provided a new synthetic strategy to produce stereoselective arylated alkene products from different aryl halides with activated alkenylboranes as the nucleophilic partner. The main advantages of this coupling reaction are the ability to tolerate different functional groups attached to the aryl ring, as well as the relatively low toxicity of the boron reagent. In this reaction, the presence of a base is important as it converts the boronate species into its active form for transmetalation to occur; absence of the base results in no product formation. In a separate paper, Suzuki and coworkers reported the coupling of alkenylboranes with alkenyl halides in the presence of a base and a catalytic amount of tetrakis(triphenylphosphine) Pd to produce decent yields of conjugated dienes and enynes with high regio- and stereoselectivity. From these simple borane compounds, the application of the Suzuki reaction was expanded to different organoboranes such as boronic acids, boronate ester, and arylboranes, providing a wide array of applications in organic synthesis.

THE SUZUKI REACTION

In 1979 Akira Suzuki started to use boron in palladium-catalyzed cross coupling. This element is the mildest activator, and it is even less toxic than zinc, which is an advantage in large-scale applications. The Suzuki reaction is for example used in the industrial synthesis (thousands of tons) of a substance that protects crops from fungi. The reaction is also used in research and development; a few examples are shown below.

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German scientists are using the Suzuki reaction to create organic polymers that emit light when a current runs through them. The goal is to improve super-thin OL ED (organic light-emitting diode) displays.

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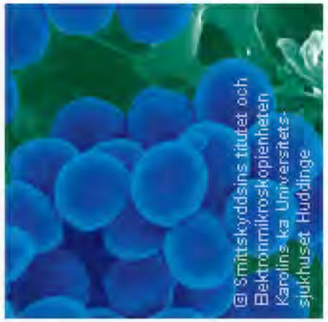
Swedish scientists are using the Suzuki reaction to develop n,ew light-capturing molecules. These can be spray-painted onto a surface and could become a part of future flat solar cells.



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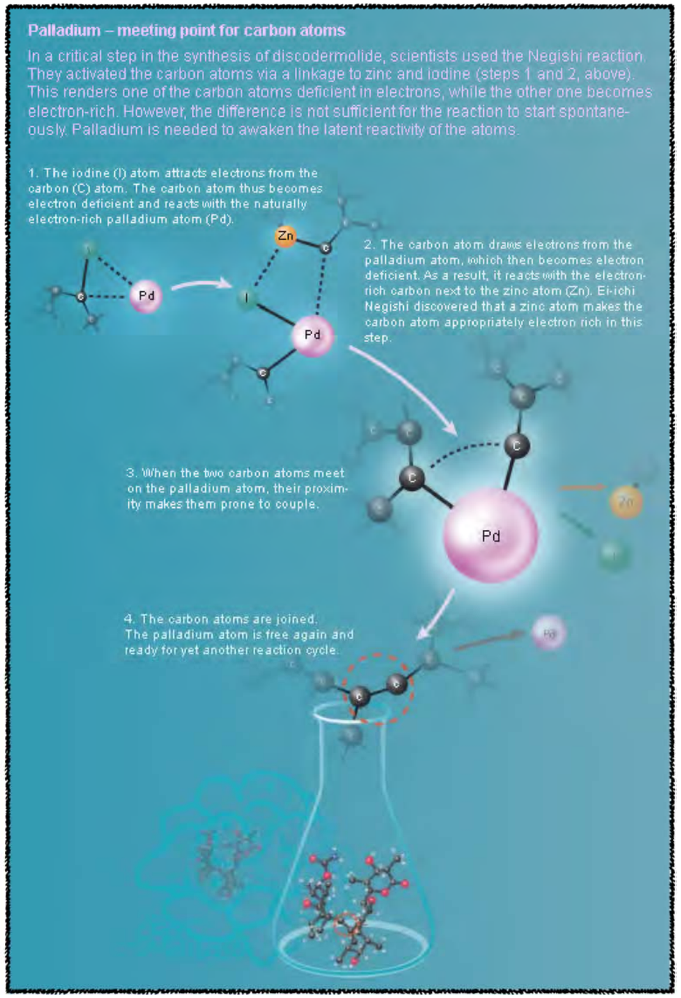
The Suzuki reaction has been used to develop variants of the antibiotic vancomycin. These variants are effective against strains of bacteria that are otherwise resistant (MRSA).



Palladium – meeting point for carbon atoms

In a critical step in the synthesis of discodermolide, scientists used the Negishi reaction. They activated the carbon atoms via a linkage to zinc and iodine (steps 1 and 2, above). This renders one of the carbon atoms deficient in electrons, while the other one becomes electron-rich. However, the difference is not sufficient for the reaction to start spontaneously. Palladium is needed to awaken the latent reactivity of the atoms.

1. The iodine (I) atom attracts electrons from the carbon (C) atom. The carbon atom thus becomes electron deficient and reacts with the naturally electron-rich palladium atom (Pd).

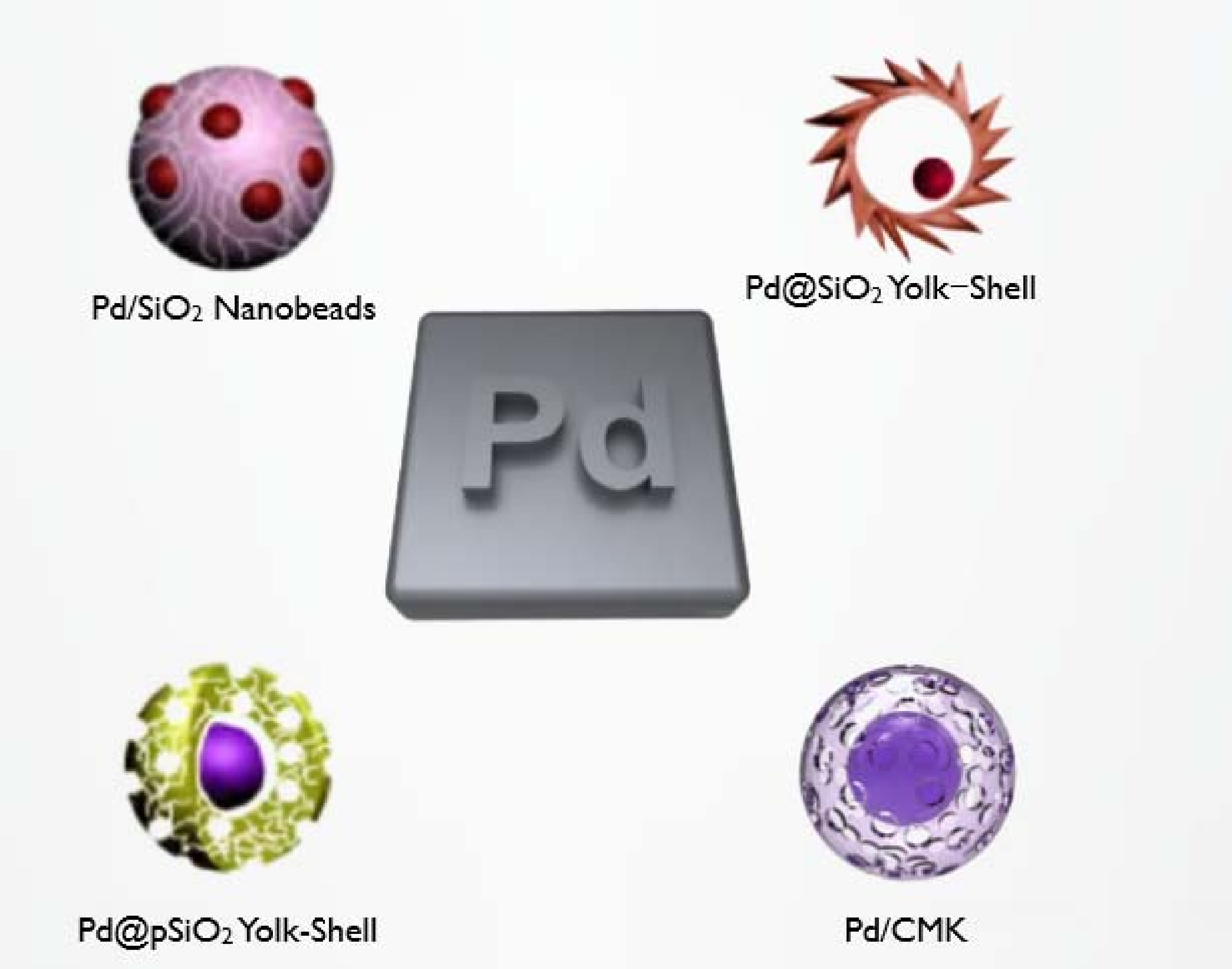
2. The carbon atom draws electrons from the palladium atom, which then becomes electron deficient. As a result, it reacts with the electron-rich carbon next to the zinc atom (Zn). Ei-ichi Negishi discovered that a zinc atom makes the carbon atom appropriately electron rich in this step.

3. When the two carbon atoms meet on the palladium atom, their proximity makes them prone to couple.

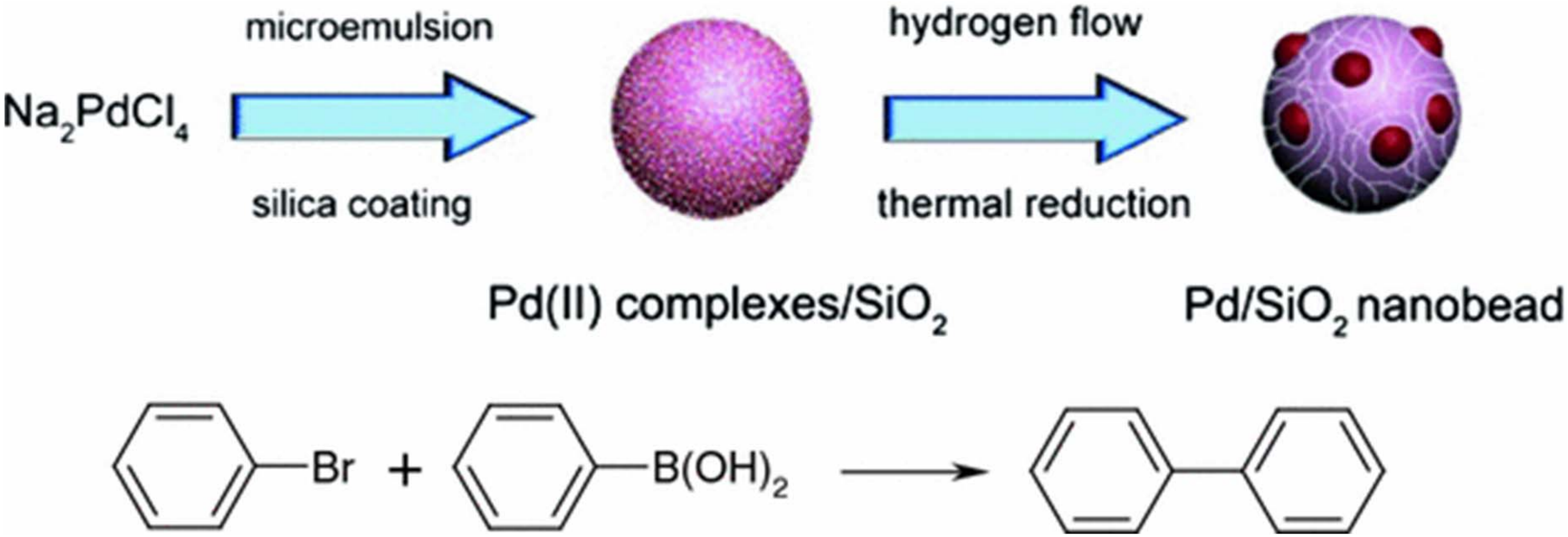
4. The carbon atoms are joined. The palladium atom is free again and ready for yet another reaction cycle.

The application of Pd nanoparticles for Suzuki coupling was first introducedby the Reetz group (M. T. Reetz, R. Breinbauer and K. Wanninger, *Tetrahedron Lett.*, 1996, *37*, 4499–4502). For this,tetrabutylammonium(R_4N^+)-or (PVP)stabilized Pd nanocatalysts were employed for the reaction between aryl bromides and aryl chlorides with phenylboronic acid producing biaryl products. The R_4N^+ Pd clusters of 2–3 nm were initially employed for the Suzuki coupling reaction between bromobenzene and phenylboronic acid in DMF at 100 ^{o}C for 3.5 h. The results of these studies demonstrated 100% conversion of the starting material based on GC and thin layer chromatography (TLC) analyses with a 53% isolated yield for the product.

Our Research



1. Synthesis of Pd/SiO_2 Nanobeads for Use in Suzuki Coupling Reactions by Reverse Micelle Sol–gel Process



Scheme 6.3. The proposed procedures for the formation of encapsulated Pd/ SiO_2 nanobead

Catalysis Letters, **2012**, *142*, 588-593

Pd/SiO_2 nanobeads containing tiny Pd clusters with a diameter of about 2 nm were prepared via a sol–gel process for SiO_2 by using a water-in-oil microemulsion with Pd complexes and subsequent hydrogen reduction by heat treatment. The Pd/SiO_2 nanostructures were employed in Suzuki coupling reactions with various substrates, and they served as good catalysts in these reactions.

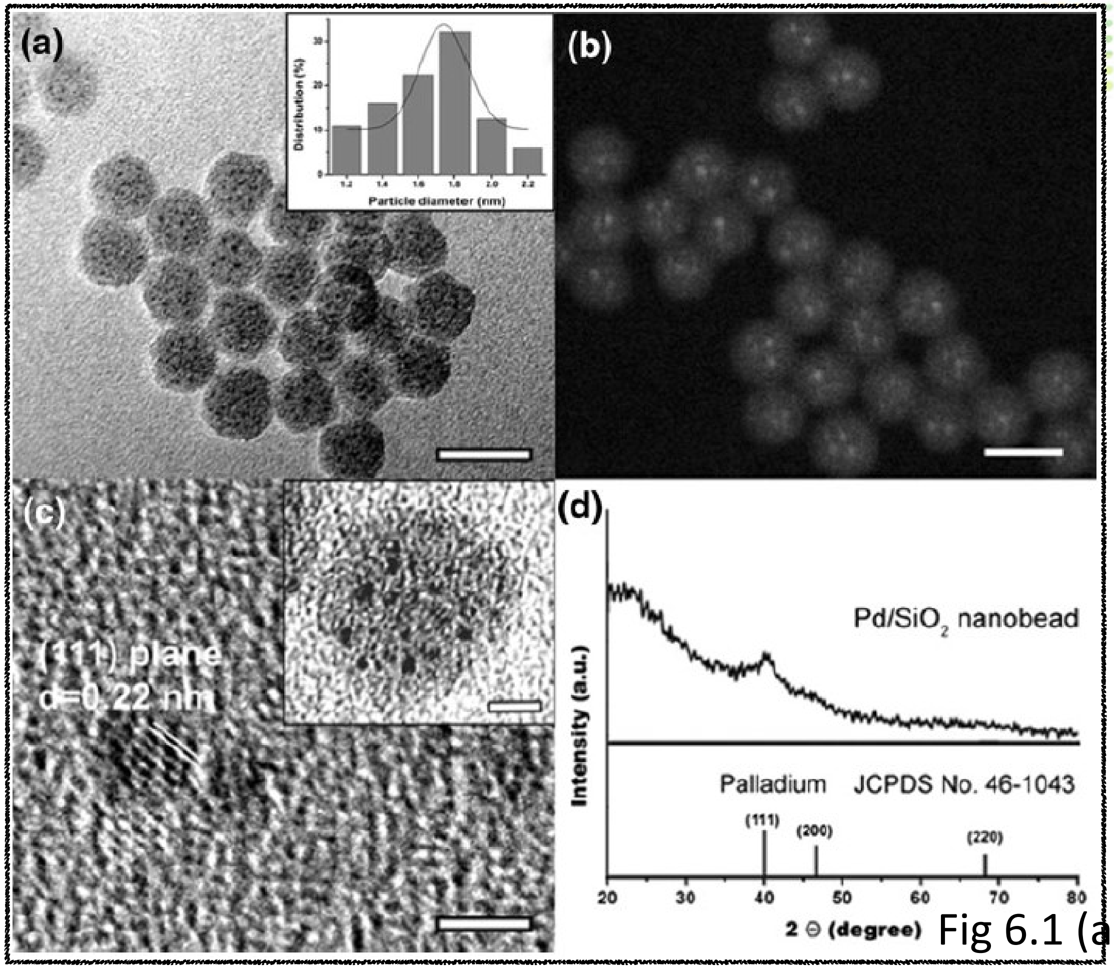
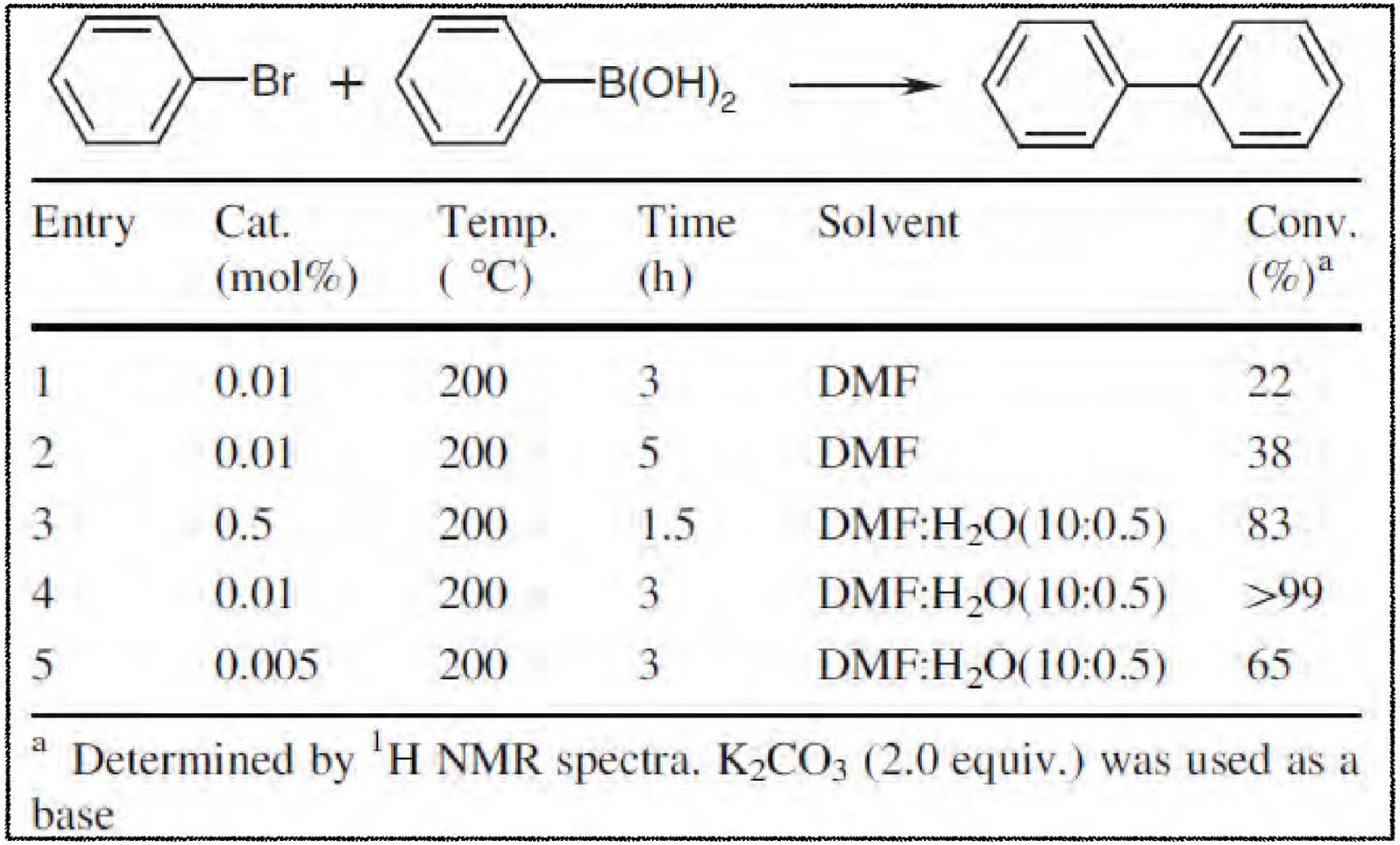


Fig 6.1 (a) TEM, (b) HAADF–TEM, and (c) HRTEM images of Pd/SiO_2 nanobeads. (d) XRD spectrum of Pd/ SiO_2 beads. The inset images of a and (c) show a histogram of Pd NP size distribution and single Pd/SiO_2 nanobead, respectively. The bars represent 20 nm ((a), (b)), 5 nm (inset of (c)), and 2 nm (c), respectively

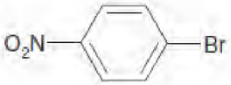
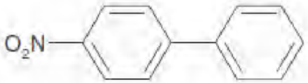
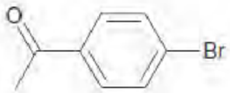
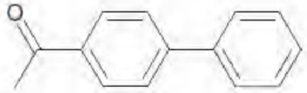
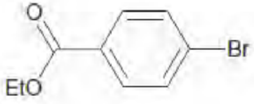
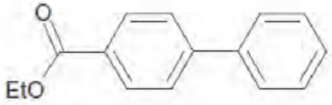
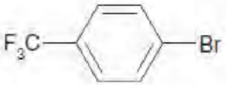
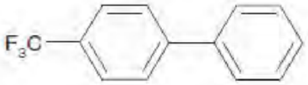
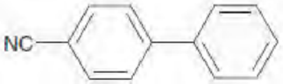
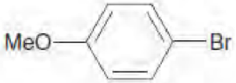
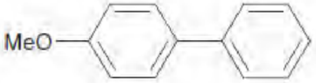
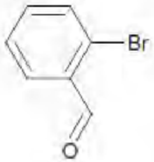
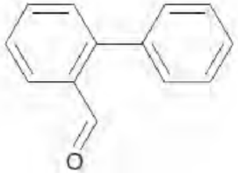
Table 6.1 Optimization of reaction condition for Suzuki reaction of bromobenzene with phenylboronic acid



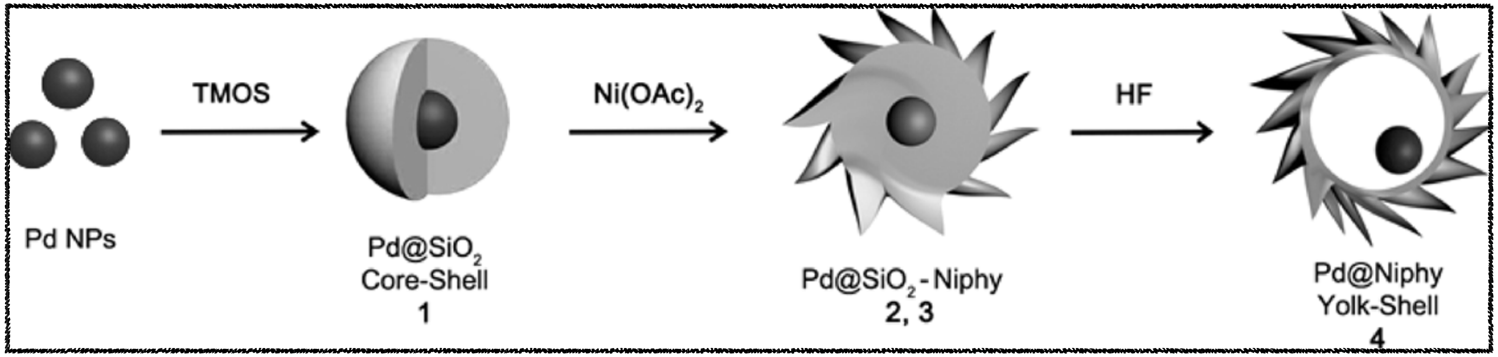
Entry	Cat. (mol%)	Temp. (°C)	Time (h)	Solvent	Conv. (%)[a]
1	0.01	200	3	DMF	22
2	0.01	200	5	DMF	38
3	0.5	200	1.5	$DMF:H_2O(10:0.5)$	83
4	0.01	200	3	$DMF:H_2O(10:0.5)$	>99
5	0.005	200	3	$DMF:H_2O(10:0.5)$	65

[a] Determined by ^1H NMR spectra. K_2CO_3 (2.0 equiv.) was used as a base

Table 6.2 Pd/SiO$_2$ catalyzed Suzuki coupling reaction of various substrates with phenyl boronic acid

Entry	Substrate	Product	Conv. (%)[a]
1			82
2			82
3			66
4			59
5			100
6			53
7			100

2. Porosity Control of Pd@SiO_2 Yolk−Shell Nanocatalysts by the Formation of Nickel Phyllosilicate and Its Influence on Suzuki Coupling Reactions

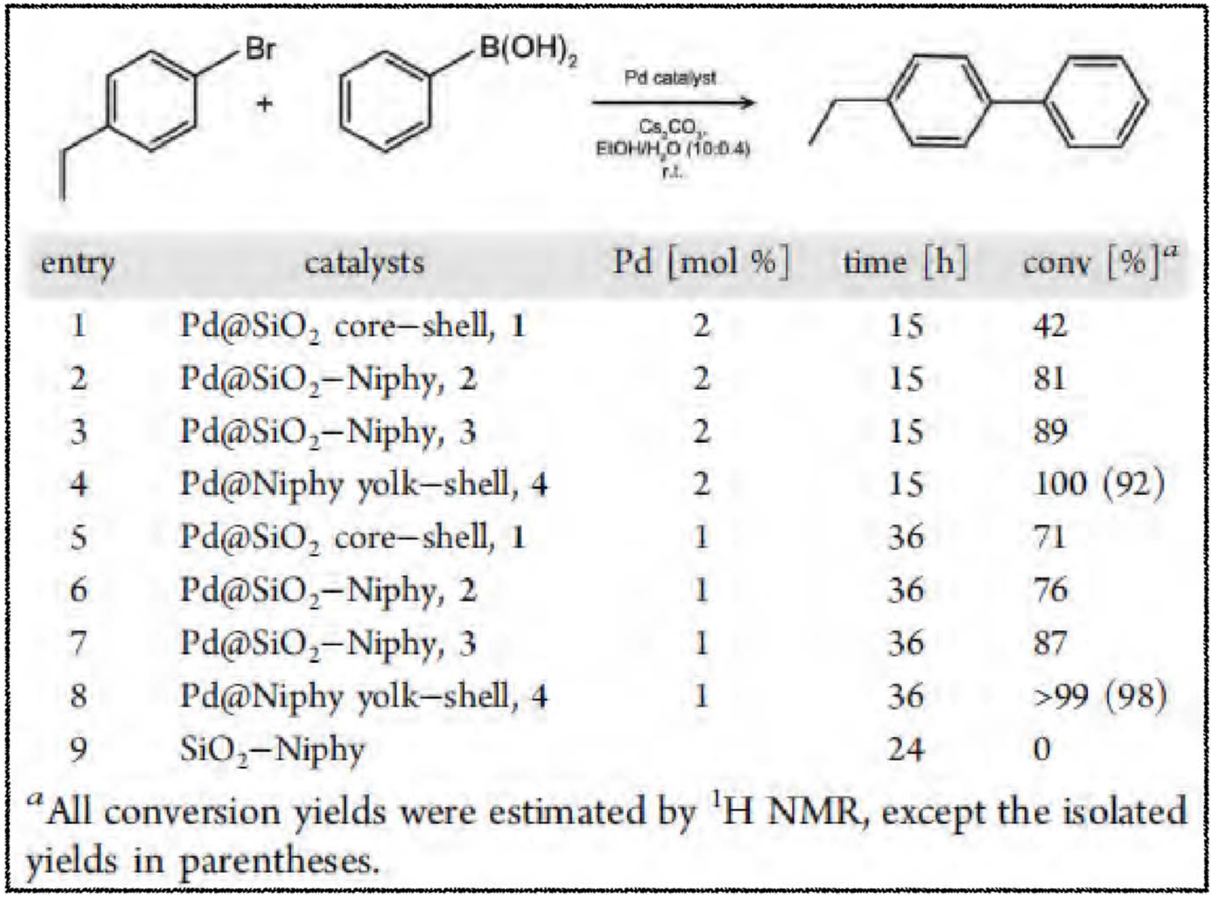


Scheme 6.4 Synthetic scheme of four distinct catalyst structures Pd@SiO_2 core−shell (1), Pd@SiO_2−Niphy (2, 3), and Pd@Niphy yolk−shell (4) nanoparticles

Langmuir, **2012**, *28*, 6441-6447

The surface of Pd@SiO_2 core–shell nanoparticles (1) was simply modified by the formation of nickel phyllosilicate. The addition of nickel salts formed branched nickel phyllosilicates and generated pores in the silica shells, yielding Pd@SiO_2–Niphy nanoparticles (Niphy = nickel phyllosilicate; 2, 3). By removal of the silica residue, Pd@Niphy yolk–shell nanoparticles (4) was uniformly obtained. The four distinct nanostructures (1–4) were employed as catalysts for Suzuki coupling reactions with aryl bromide and phenylboronic acid, and the conversion yields were in the order of $1 < 2 < 3 < 4$ as the pore volume and surface area of the catalysts increased. The reaction rates were strongly correlated with shell porosity and surface exposure of the metal cores. The chemical inertness of nickel phyllosilicate under the basic conditions rendered the catalysts reusable for more than five times without loss of activity.

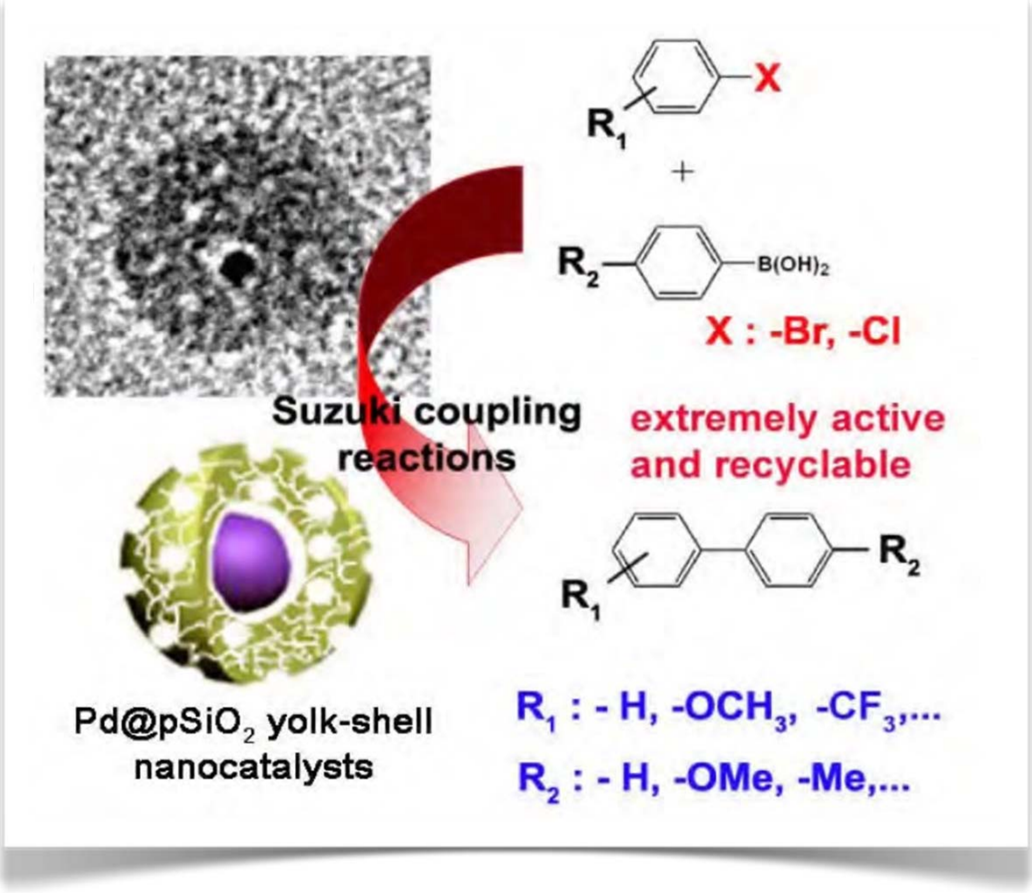
Table 6.3. Suzuki coupling reactions of 1-bromo-4ethylbenzene with phenylboronic acid yielding 4-ethylbiphenyl



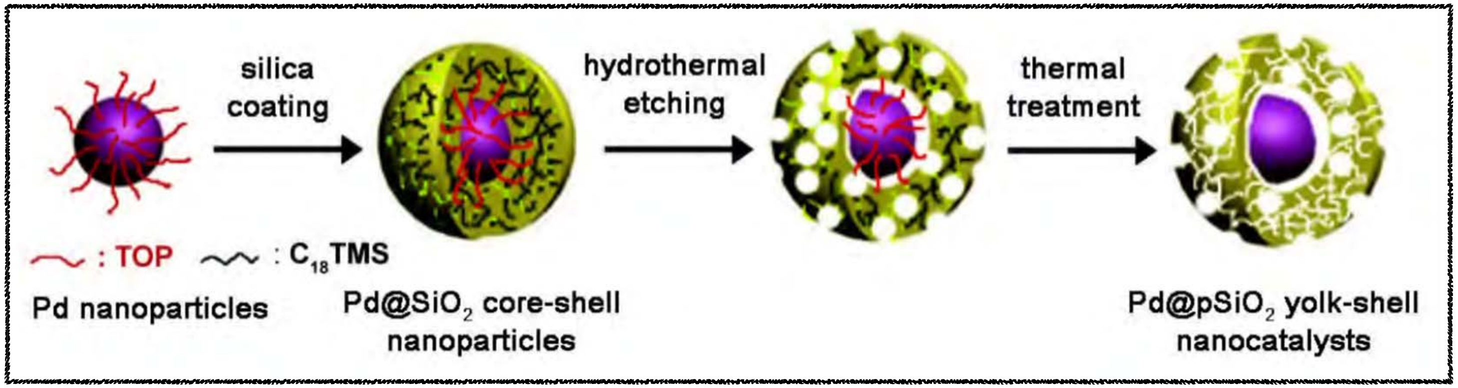
entry	catalysts	Pd [mol %]	time [h]	conv [%][a]
1	Pd@SiO_2 core–shell, 1	2	15	42
2	Pd@SiO_2–Niphy, 2	2	15	81
3	Pd@SiO_2–Niphy, 3	2	15	89
4	Pd@Niphy yolk–shell, 4	2	15	100 (92)
5	Pd@SiO_2 core–shell, 1	1	36	71
6	Pd@SiO_2–Niphy, 2	1	36	76
7	Pd@SiO_2–Niphy, 3	1	36	87
8	Pd@Niphy yolk–shell, 4	1	36	>99 (98)
9	SiO_2–Niphy		24	0

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

3. Extremely Active Pd@pSiO$_2$ Yolk-Shell Nanocatalysts for Suzuki Coupling Reactions of Aryl Halides



J. Phys. Chem. C, **2011**, *115*, 15772–15777 we optimize the yolk–shell nanostructure in a palladium–silica system for the purpose of attaining high activity in Suzuki cross-coupling reactions. Pd@porous SiO_2 (Pd@pSiO_2) yolk–shell nanoparticles, bearing tiny palladium cores and highly porous silica hollow shells, were synthesized by direct silica coating and partial etching of the silica layers. High temperature treatment removed all surfactants around the catalyst surface and generated large pores on the silica shells. The resulting Pd@pSiO_2 yolk–shell catalysts exhibited extremely high initial turnover frequency of 78000 h^{-1}, as well as excellent reusability of more than 10 times in a standard Suzuki coupling reaction. The catalysts also catalyzed Suzuki reactions with various substrates including bromo- and chlorobenzene very well.



Sheme 6.5 Synthetic procedure of Pd@pSiO_2 yolk-shell Nanocatalysts.

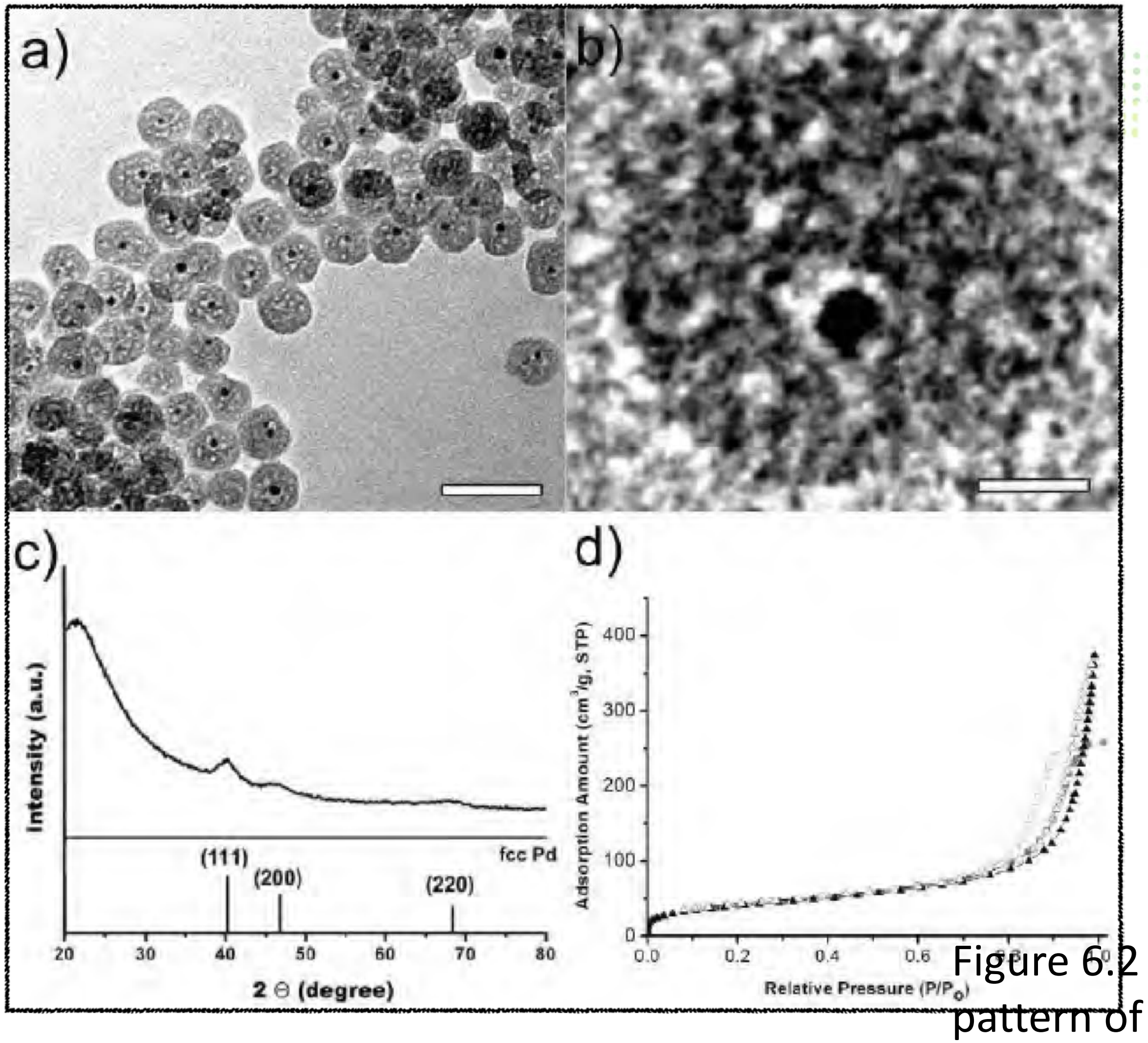
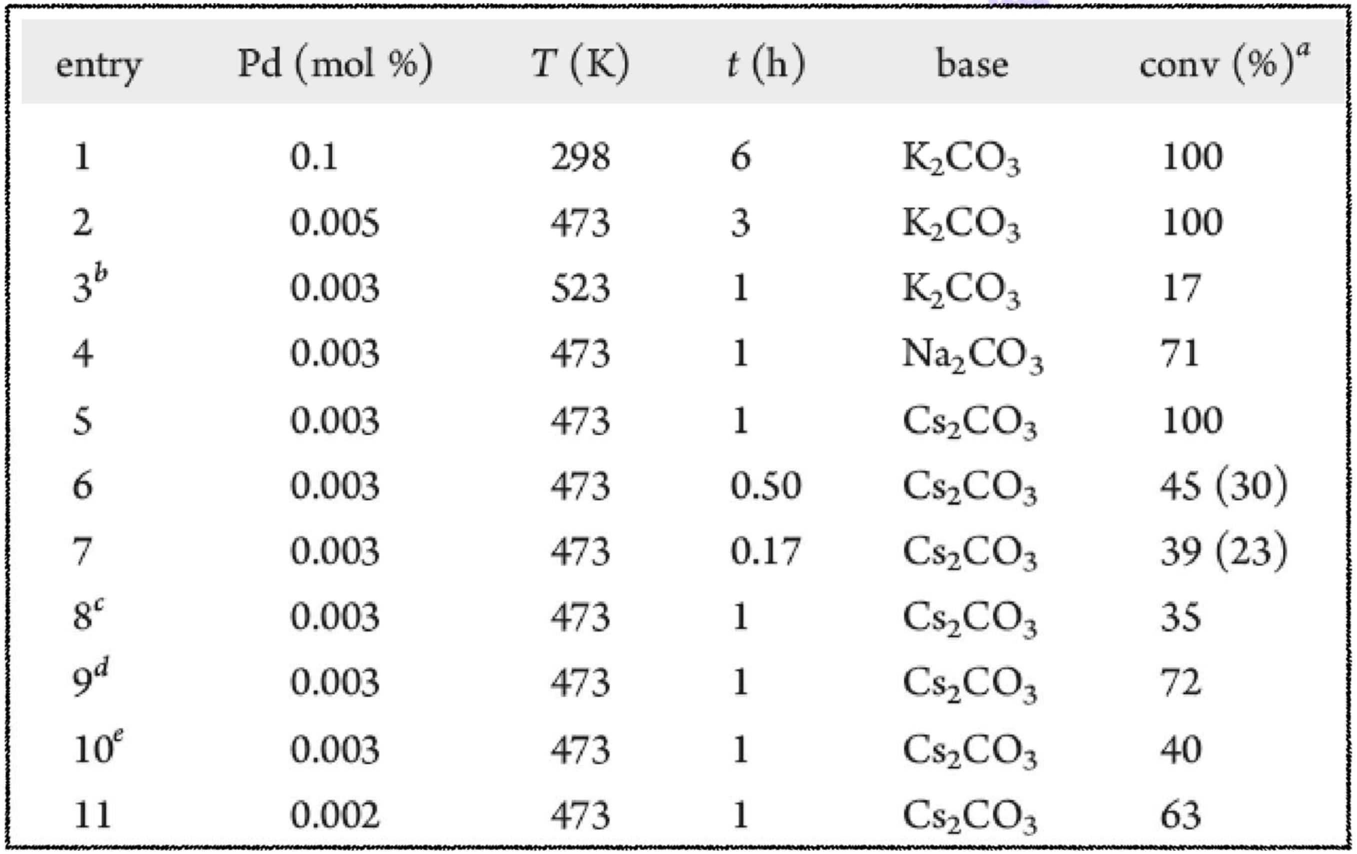


Figure 6.2 (a,b) TEM images and (c) XRD pattern of Pd@pSiO2 yolk-shell nanocatalysts after thermal treatment. (d) N2 adsorption-desorption isotherms of Pd@SiO2 core-shell nanoparticles (■, □) and Pd@pSiO2 yolk-shell nanocatalysts (▲, Δ) after thermal treatment. The bars represent (a) 50 nm and (b) 5 nm.

Table 6.4 Suzuki coupling reactions of bromobenzene with phenylboronic acid



entry	Pd (mol %)	*T* (K)	*t* (h)	base	conv (%)[a]
1	0.1	298	6	K_2CO_3	100
2	0.005	473	3	K_2CO_3	100
3[b]	0.003	523	1	K_2CO_3	17
4	0.003	473	1	Na_2CO_3	71
5	0.003	473	1	Cs_2CO_3	100
6	0.003	473	0.50	Cs_2CO_3	45 (30)
7	0.003	473	0.17	Cs_2CO_3	39 (23)
8[c]	0.003	473	1	Cs_2CO_3	35
9[d]	0.003	473	1	Cs_2CO_3	72
10[e]	0.003	473	1	Cs_2CO_3	40
11	0.002	473	1	Cs_2CO_3	63

a Determined by ^{1}H NMR spectra. bNMP/H_2O (20:1) as a solvent mixture. c Free-standing Pd nanoparticles. d Pd@pSiO_2 yolk-shell nanoparticles before thermal treatment. e Pd@SiO_2 core-shell nanoparticles. The values inside the parentheses are isolated yields of the product.

YIELD

Pd@pSiO$_2$ yolkshell nanocatalysts (100%)

∨

Pd@pSiO$_2$ yolkshell nanoparticles before thermal treatment (72%)

∨

Pd@SiO$_2$ coreshell nanoparticles (40%)

∨

free-standing Pd nanoparticles (35%)

RECOVERY

For easy recovery, the Pd@pSiO$_2$ yolk-shell nanocatalysts were diluted with MCFs (siliceous mesostructured cellular foams) to reduce a possible loss during the separation procedure. The resulting catalysts exhibit high recyclability with a substrate/Pd molar ratio of 1000:1. The initial activity is completely maintained for more than 10 cycles.

4. Ordered Mesoporous Carbon Supported Colloidal Pd Nanoparticle Model Catalysts for Suzuki Coupling Reactions : Impact of Organic Capping Agents

The OA-Pd/CMK-3 catalyst was treated with acetic acid to generate a supported catalyst with surfactant-free Pd NPs (OA-Pd/CMK-3-A). Structural characterization revealed that the Pd NPs were uniformly dispersed throughout the mesopores of the CMK-3 support and the particle size and crystallinity of the Pd NPs were preserved following the incorporation. All of the Pd/CMK-3 nanocatalysts exhibited higher activity than commercial activated carbon supported Pd catalysts in Suzuki coupling reactions. The catalytic activities of the three Pd/CMK-3 nanocatalysts were in the following order: OA-Pd/CMK-3-A>OA-Pd/CMK-3>TOP-Pd/CMK-3. This result suggested that the presence and type of surfactants had a significant effect on the catalytic activity. The OA-Pd/CMK-3-A catalyst also showed high activity for various substrates and good recycling ability in Suzuki coupling reactions.

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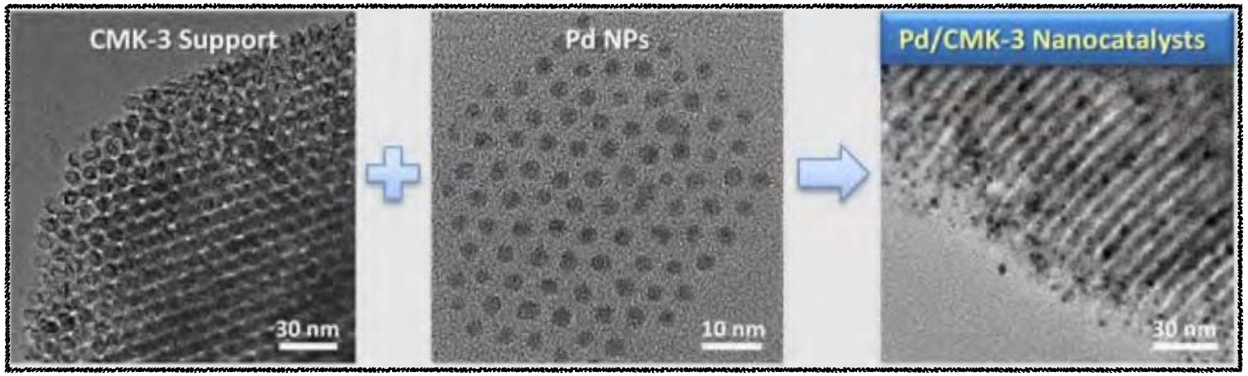
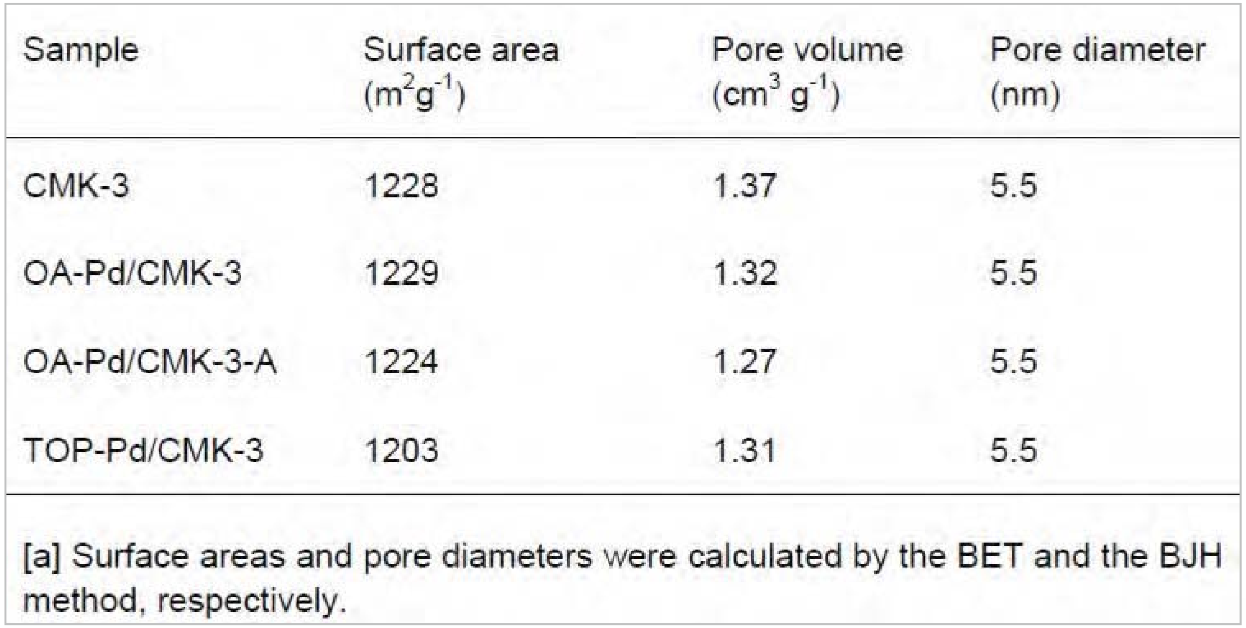
Table 6.5 Surface areas, pore volumes, and pore diameters of CMK-3 and Pd/CMK-3 samples

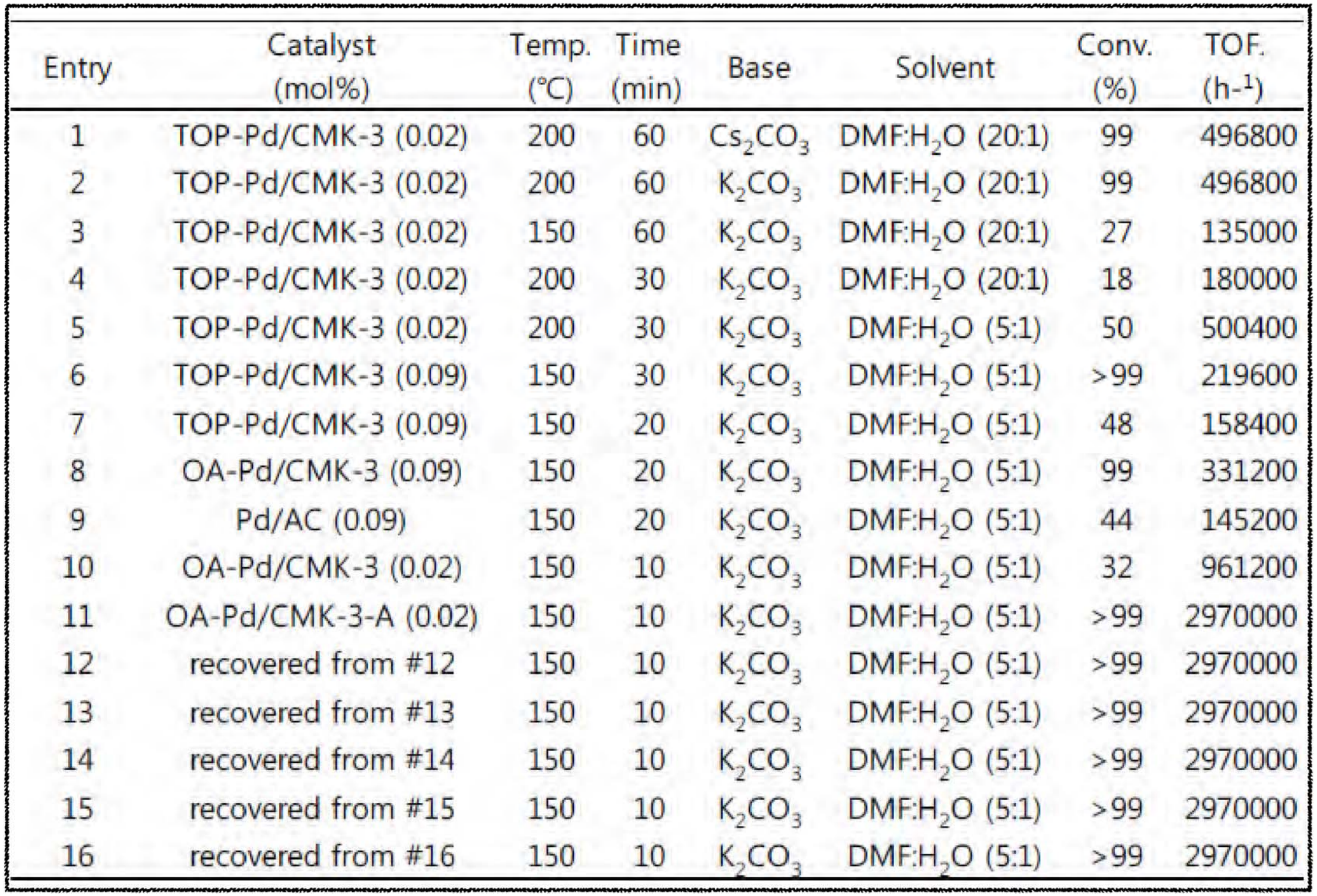




Sample	Surface area (m^2g^{-1})	Pore volume (cm^3 g^{-1})	Pore diameter (nm)
CMK-3	1228	1.37	5.5
OA-Pd/CMK-3	1229	1.32	5.5
OA-Pd/CMK-3-A	1224	1.27	5.5
TOP-Pd/CMK-3	1203	1.31	5.5

[a] Surface areas and pore diameters were calculated by the BET and the BJH method, respectively.

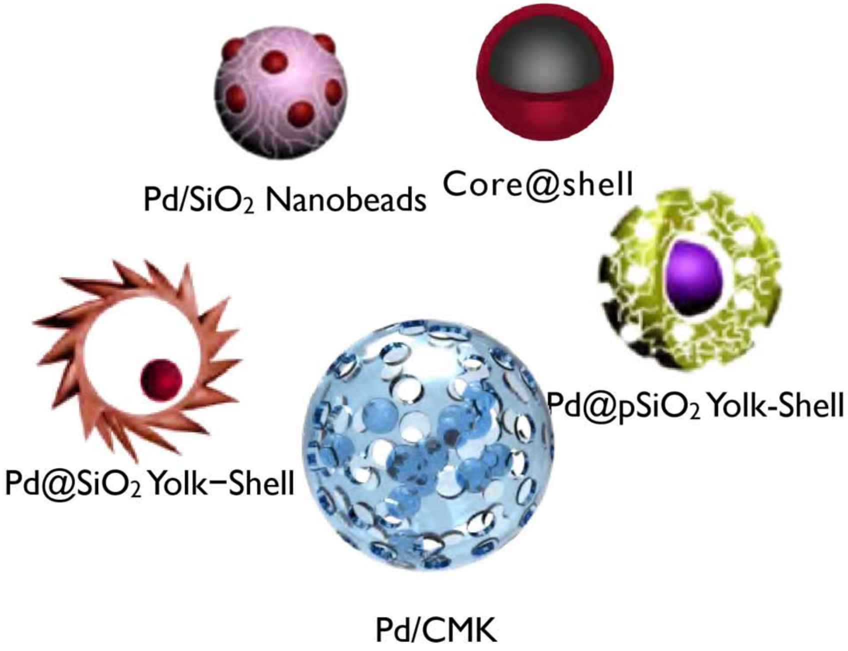
Table 6.6 Suzuki coupling reaction of bromobenzene with phenylboronic acid.



Entry	Catalyst (mol%)	Temp. (℃)	Time (min)	Base	Solvent	Conv. (%)	TOF. (h-^{1})
1	TOP-Pd/CMK-3 (0.02)	200	60	Cs_2CO_3	DMF:H_2O (20:1)	99	496800
2	TOP-Pd/CMK-3 (0.02)	200	60	K_2CO_3	DMF:H_2O (20:1)	99	496800
3	TOP-Pd/CMK-3 (0.02)	150	60	K_2CO_3	DMF:H_2O (20:1)	27	135000
4	TOP-Pd/CMK-3 (0.02)	200	30	K_2CO_3	DMF:H_2O (20:1)	18	180000
5	TOP-Pd/CMK-3 (0.02)	200	30	K_2CO_3	DMF:H_2O (5:1)	50	500400
6	TOP-Pd/CMK-3 (0.09)	150	30	K_2CO_3	DMF:H_2O (5:1)	>99	219600
7	TOP-Pd/CMK-3 (0.09)	150	20	K_2CO_3	DMF:H_2O (5:1)	48	158400
8	OA-Pd/CMK-3 (0.09)	150	20	K_2CO_3	DMF:H_2O (5:1)	99	331200
9	Pd/AC (0.09)	150	20	K_2CO_3	DMF:H_2O (5:1)	44	145200
10	OA-Pd/CMK-3 (0.02)	150	10	K_2CO_3	DMF:H_2O (5:1)	32	961200
11	OA-Pd/CMK-3-A (0.02)	150	10	K_2CO_3	DMF:H_2O (5:1)	>99	2970000
12	recovered from #12	150	10	K_2CO_3	DMF:H_2O (5:1)	>99	2970000
13	recovered from #13	150	10	K_2CO_3	DMF:H_2O (5:1)	>99	2970000
14	recovered from #14	150	10	K_2CO_3	DMF:H_2O (5:1)	>99	2970000
15	recovered from #15	150	10	K_2CO_3	DMF:H_2O (5:1)	>99	2970000
16	recovered from #16	150	10	K_2CO_3	DMF:H_2O (5:1)	>99	2970000

NEW CHALLENGES IN NANO CATALYSIS

- SIZE
- SHAPE
- SUPPORT
- MULTIPLE CATALYTIC FUNCTIONALITY
- MOLECULAR FUNCTIONALIZATION



6.4 Pd Nanoparticles in the Stille Coupling Reaction

The Stille coupling process was first reported in 1978 as a reaction between acid chlorides and organostannane reagents in the synthesis of ketones, catalyzed by phosphine-stabilized Pd catalysts. Since then, various modifications to the phosphine ligands have been reported for this reaction, which takes advantage of the *air- and moisture-stable* nucleophilic partner to afford C–C bond formation with substrates containing different functional groups. Typically, this transformation is performed at elevated temperatures (70–120 ^oC), in organic solvents, and with catalyst loadings of > 1 mol% Pd, which can be reduced in situ. For example, using dendritic materials for the synthesis of Pd nanoparticles, Stille coupling was performed in water at room temperature with only 0.10 mol% Pd as the catalyst.

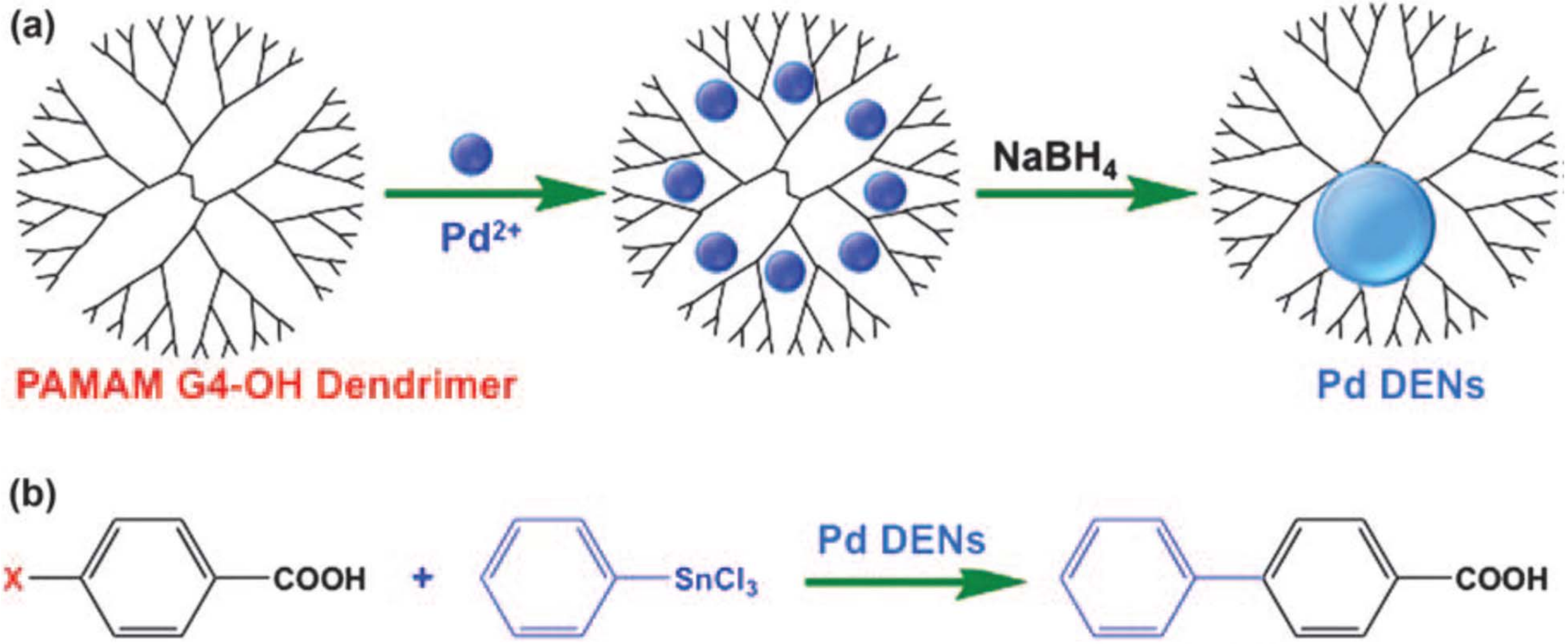


Figure 6.3 (a) Synthesis of dendrimer-encapsulated Pd nanoparticles, (b) Stille coupling reaction using Pd DENs.