

Heterogeneous & Homogeneous & Bio- & Nano-

CHEM **CAT** CHEM

CATALYSIS

Accepted Article

Title: Carbon-Derived Supports for Palladium Nanoparticles as Catalysts for Carbon-Carbon Bonds Formation

Authors: Carmen Nájera, Mohammad Gholinejad, and Zhwan Naghshbandi

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *ChemCatChem* 10.1002/cctc.201802101

Link to VoR: <http://dx.doi.org/10.1002/cctc.201802101>

WILEY-VCH

www.chemcatchem.org



Carbon-Derived Supports for Palladium Nanoparticles as Catalysts for Carbon-Carbon Bonds Formation

Mohammad Gholinejad,^{*[a,b]} Zhwan Naghshbandi,^[a] Carmen Nájera,^{*[c]}

Abstract: The review considers the variety allotropes of carbon to be used as supports for palladium and investigation of the resulting catalysts for carbon-carbon forming reactions with focus on the effect of the solvent, base and catalyst loading in the catalyst recovery. Specially, carbon nanotubes, C₆₀ and graphene allowed the covalent functionalization with different ligands for palladium facilitating a lower leaching. Magnetic iron nanoparticles can be easily covered by charcoal, graphene oxide and carbon quantum dots facilitating the recovery of the supported catalyst. These heterogeneous catalysts are able to activate even aryl chlorides in cross-coupling reactions such as Suzuki-Miyaura, Mizoroki-Heck and Sonogashira-Hagihara in organic but also in aqueous media. All these features favoured the applicability of the materials for industrial processes.

1. Introduction

Carbon-carbon bond formation is the 'backbone' of most organic molecules and is an essential step for the synthesis of a broad variety of chemicals and natural products. There is an ever-growing number of approaches available for carbon-carbon bond formation. However, the science of organic synthesis including C-C bond synthesis has intensely changed by the emergence of transition metals chemistry in the 1960s. Among different transition metals, palladium is showed excellent reactivity and selectivity in many organic transformations specially in carbon-carbon cross-coupling reactions. Palladium-catalyzed reactions for carbon-carbon bond formation such as Suzuki, Negishi, Stille, Hiyama, Glaser, Heck, Sonogashira, Tsuji-Trost, Fukuyama, Liebeskind-Srogle and C-H functionalization have gained a crucial place in the arsenal of organic chemists.^[1-8] These reactions are typically performed under homogeneous conditions in the presence of different palladium salts or palladium complexes including different ligands. However, due to the price

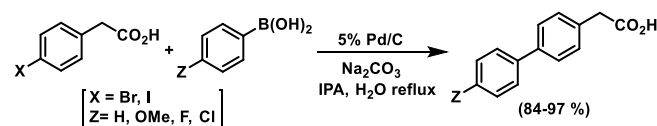
of palladium and its toxic property, separation, recovery and reutilization of the palladium catalyst represents a crucial factor for the sustainable development of C-C bond forming reactions. In recent years, many heterogeneous palladium catalysts supported on various solids such as polymers, magnetic nanoparticles, silica, polysaccharides etc. have been developed for various Pd-catalysed coupling reactions. However, among the different materials for preparation of heterogeneous palladium catalysts, carbon which is the main component of coal and coke and naturally abundant can be considered as an excellent support for stabilization of palladium species.

In this review, we wish to provide an overview of the most important milestones in the development of palladium nanoparticles (NPs) supported on carbon based materials and their applications in carbon-carbon bond forming reactions and therefore the text is divided by the nature of the carbon support.

2. Palladium on Carbon Black

Palladium metal supported on charcoal (Pd/C) contains a Pd concentration in the range 5 to 20 wt%. The use of this material as catalyst in C-C bond forming reactions was described in the 90's, in particular a review about its use in Suzuki reactions was due to Felpin and co-workers.^[9]

In 1997 Gala and co-workers, from Schering-Ploug, used 5 % Pd/C as catalyst in the large scale Suzuki reaction of (4-iodo or bromophenyl)acetic acids with arylboronic acid in aqueous isopropanol (IPA) with Na₂CO₃ as base under reflux resulting pharmaceutical important biphenyl acetic acids in high yields (Scheme 1).^[10] They found that this method is a direct, unexpensive and efficient method for the large scale preparation of these compounds. The catalyst can be recovered by simple filtration, low contamination of Pd in the products and degassing of the solvents was not necessary.



Scheme 1. Synthesis of biphenyl acetic acids.

Ennis and co-workers,^[11] from SmithKlineBeechman Pharmaceuticals, also used similar reaction conditions for the synthesis of an intermediate of the antidepressant SB-245570, 2'-methyl-4'-(2-oxo-1-pyrrolidinyl)biphenyl-4-carboxylic acid, by

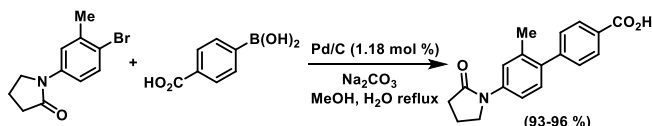
[a] Mohammad Gholinejad, Zhwan Naghshbandi
Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), P. O. Box 45195-1159, Gavazang, Zanjan 45137-6731, Iran
E-mail: gholinejad@iasbs.ac.ir

[b] Mohammad Gholinejad,
Research Center for Basic Sciences & Modern Technologies (RBST), Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan 45137-66731, Iran

[c] Carmen Nájera
Centro de Innovación en Química Avanzada (ORFEO-CINQA).
Universidad de Alicante, Apdo. 99, E-03080-Alicante, Spain
Email: cnajera@ua.es

FULL PAPER

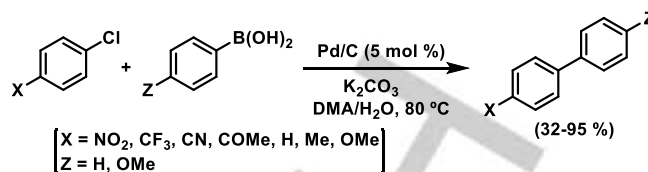
Suzuki reaction of 1-(4-bromo-3-methylphenyl)pyrrolidin-2-one with 4-carboxyphenylboronic acid in 82% overall yield from 4-bromo-3-methylaniline (Scheme 2). This process was performed in multikilogram scale in refluxing aqueous MeOH the residual Pd being less than 6 ppm.



Scheme 2. Synthesis of 2'-methyl-4'-(2-oxo-1-pyrrolidinyl)biphenyl-4-carboxylic acid.

Ligand less Heck reaction of iodobenzene with methyl acrylate was investigated by Arai and co-workers using different supported Pd catalysts such as Pd/SiO₂, Pd/C and Pd/SM (Mg) (a magnesium-containing smectite-like porous material).^[12] Results indicated that significant amounts of palladium leach out into the solvent and these dissolved Pd species are responsible for the catalytic activity. After the reaction has been completed, almost all the palladium species in the solution can redeposit onto the surface of the supports completed (at 100 % conversion of iodobenzene) when mixed bases of Et₃N and Na₂CO₃ were used in NMP at 140 °C. When the Heck reaction was carried out between bromobenzene or chlorobenzene with methyl acrylate using Pd/C (0.0752 mmol Pd) as catalyst and mixed bases Et₃N and Na₂CO₃ at 160 °C methyl cinnamate was isolated in 96 or 69 % yield, respectively. In the case of 10% Pd/C the catalyst was recycled four times for the reaction of iodobenzene with methyl acrylate. Hagiwara and co-workers^[13] reported in 2001 the use of 10 % Pd/C (3 mol%) as catalyst in the Heck reaction in the ionic liquid [bmim]PF₆. The arylation of ethyl acrylate took place in good yields for aryl iodides having electron-withdrawing or -donating substituents (53-95 %) and lower yields (25-85 %) for aryl bromides. This catalyst system was easily re-usable for six runs without loss of catalytic activity in the reaction of iodobenzene and ethyl acrylate. Aryl iodides gave moderate results with other alkenes (16-92 %). The catalytic process occurs in the surface of the Pd supported on the C and not in the ionic liquid.

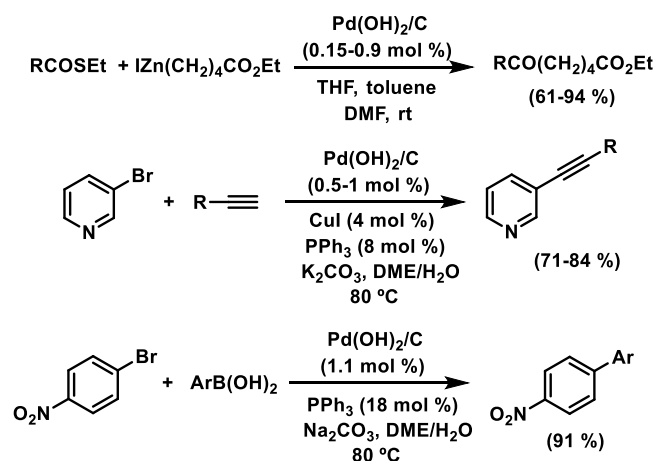
A library of chiral 4-arylmandelic acids has been synthesized by Tiffin and co-workers^[14] at Roche by using the Suzuki coupling reaction of enantiopure 4-bromomandelic acid with arylboronic acids in the presence of 10% Pd/C (2 mol%) in aqueous IPA and Na₂CO₃ as base at 62 °C in 75-99 % yields and total retention of the configuration. During the same year, Yongkui Sun and co-workers^[15] have studied 5 % Pd/C (5 mol%) as catalyst in the Suzuki reaction of aryl chlorides with arylboronic acids. These cross-couplings in aqueous ethanol gave very low yields but using a mixture of *N,N*-dimethylacetamide (DMA): water (20:1) as solvent at 80 °C and K₂CO₃ as base biphenyls were obtained in 32-95 % yields (Scheme 3). Results showed good to high yields for aryl chlorides with electron-withdrawing groups and low yields for electron-rich aryl chlorides.



Scheme 3. 5 % Pd/C-catalyzed Suzuki reaction of aryl chlorides.

In 2002, using 10% Pd/C (0.3 mol%) as a catalyst, Hirao and co-workers^[16] performed the Suzuki reaction of halophenols with arylboronic acids in aqueous media with K₂CO₃ as base at room temperature in good to high yields (70-99 %). Also, Kohler and co-workers^[17] accomplished Heck, Suzuki and Sonogashira reactions using Pd/C as catalyst with low Pd concentrations (down to 0.0025 mol% for Heck coupling, 0.005 mol% for Suzuki coupling and 0.125 mol% for the Sonogashira alkylation). Good results were obtained in general for the arylation of styrene with for bromoarenes in NMP at 140 °C with NaOAc as base (10-90 % yields). In the case of the Suzuki reaction aryl bromides and activated chlorides reacted with phenylboronic acid in aqueous NMP at 120 °C using Na₂CO₃ or NaOH as bases (43-99 % yields). Iodobenzene was allowed to react with phenylacetylene in NMP at 80 °C using pyrrolidine as base in 80 % yield.

Pearlman's catalyst, Pd(OH)₂/C, was used in Fukuyama, Sonogashira and Suzuki reactions.^[18] Reactions of thioesters with 4-(ethoxycarbonyl)butylzinc iodide were performed with Pd(OH)₂/C and Pd/C with 0.15 mol% of catalyst in DMF at room temperature affording the δ -keto esters in 61-83 % and 19-67 % yields, respectively (Scheme 4). The use of Pd(OH)₂/C (1.1 mol%) was further applied to the Sonogashira reaction of 3-bromopyridine with terminal alkynes with K₂CO₃ as base, CuI as co-catalysts and PPh₃ as ligand with 0.5 or 1 mol% Pd loading in aqueous DME at 80 °C producing the desired products in 71-84 % yields. Also in aqueous DME at 80 °C, the Suzuki reaction of 1-bromo-4-nitrobenzene with arylboronic acids in aqueous DME at 80 °C with Na₂CO₃ as base and PPh₃ as ligand gave similar yields than with Pd/C (91 %).

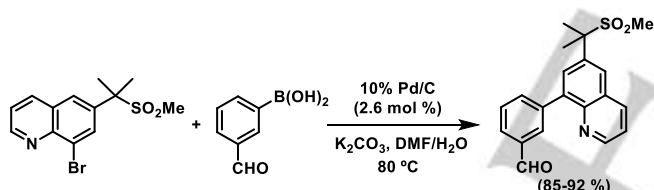


Scheme 4. Fukuyama, Sonogashira and Suzuki reactions using Pearlman's catalyst.

FULL PAPER

Kohler and co-workers investigated the effects of the Pd dispersion, Pd oxidation state, Pd distribution, the water content (wet and dried catalyst) and the conditions of catalyst preparation (saturation method, pretreatment conditions) on the catalytic activity of different Pd/C catalysts in the Heck reaction of aryl bromides with styrene.^[19] This study concludes that high Pd dispersion, low degree of Pd reduction, higher water content (>50 %) and uniform Pd saturation have higher catalytic activity. The effect of thermal treatment indicated that the higher the treatment temperature and the lower the dispersion resulted a lower catalytic activity in the Heck reaction. The arylation of styrene with bromobenzene in DMA with NaOAc as base at 140 °C could be carried out down to 0.005 mol% Pd loading. Several reaction parameters influenced the leaching and redeposition of Pd during the reaction. Results indicated that the Pd concentration in solution is highest at the beginning of the reaction and is a minimum (<1 ppm) at the end of the reaction.

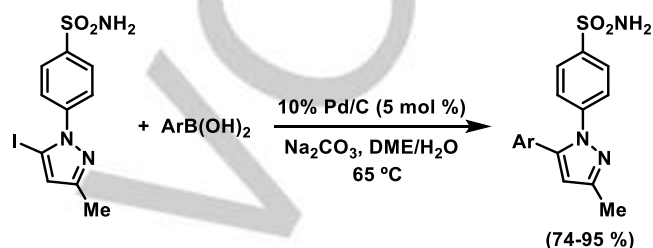
The relationship between the carbon support and the concentration of soluble Pd on the catalytic activity was investigated by Conlon and co-workers.^[20] By comparison of 5 % and 10 % Pd/C catalysts in the ligand-free Suzuki cross-coupling reaction of bromoquinoline with 3-formylphenylboronic acid. The reaction was performed with K₂CO₃ or KF as base, 2.6 mol% of Pd in aqueous DMF at 80 °C giving the corresponding drug intermediate at Merck (Scheme 5). Results showed that the 10 % Pd/C catalyst although has less the amount of carbon support, produced twice the amount of soluble palladium and reached a maximum conversion in the Suzuki reaction.



Scheme 5. Pd/C catalyzed synthesis of a drug intermediate by Suzuki cross-coupling.

In 2003, Nishida and co-workers at Koei Chemical Company reported the use of Pd/C in the presence PPh₃ or 2-(dicyclohexylphosphino)biphenyl as ligands in the Suzuki reaction of halopyridines and haloquinolines with phenylboronic acid.^[21] For bromopyridines, bromoquinolines, 2-chloropyridine and 2-chloroquinoline, Pd/C in the presence of PPh₃, Na₂CO₃ and DME at 80 °C provided good 60 % to quantitative yields. In the case of 3-chloropyridine, 4-chloropyridine, and 6-chloroquinoline the presence of 2-(dicyclohexylphosphino)biphenyl as a ligand gave 77-92 % yields. Under aqueous media, Arcadi and co-workers employed Pd(PPh₃)₄ or Pd/C as catalyst in the Suzuki reaction of aryl halides (iodides, bromides and chlorides) with arylboronic acid in the presence of cetyltrimethylammonium bromide (CTAB) as a surfactant.^[22] Excellent yields were obtained for aryl iodides, aryl bromides including electron-rich derivatives at room temperature and for electron-poor aryl chlorides was necessary to heat at 100 °C. Recycling experiments for the reaction of 4-bromoanisole with phenylboronic acid, aqueous 0.1 M solution of

CTAB, K₂CO₃ as base and 5 mol% of Pd/C at rt gave during four cycles 95, 88, 85 and 80 % yield. A library of Celecoxib [4-(5-iodo-3-methylpyrazolyl) phenylsulfonamide] analogues were prepared in high yields via a Pd/C catalyzed Suzuki coupling reaction of the iodopyrazole, 4-(5-iodo-3-methyl-1H-pyrazol-1-yl)sulfonamide, with different arylboronic acids.^[23] Cross-coupling of this iodopyrazole was performed in aqueous DME, with Na₂CO₃ as base 10 % Pd/C (5 mol% Pd loading) as catalyst at 65 °C giving the corresponding products in 74 to 95 % yield (Scheme 6). The metal was eliminated after purification by means of silica gel chromatography.



Scheme 6. Synthesis of Celecoxib analogues.

The Heck reaction of aryl halides with alkene has been performed under Pd/C catalysis in the presence of 1-octanyl-3-methylimidazolium tetrafluoroborate ([OMIm]BF₄) as ionic liquid in the absence of phosphine under microwave irradiation.^[24] In the presence of Bu₃N as base and 3 mol% loading of 5 % Pd/C at 225 or 375W for 1.5 min, good yields (30-86 %) were obtained for aryl iodides and bromides, whereas aryl chlorides failed. This catalyst was recycled for five times in the reaction of iodobenzene with butyl acrylate in the range of 86 to 67 % yield. Cravotto and co-workers, also used Pd/C as catalyst under microwave irradiation (MW) and under ultrasound (US) conditions in the Suzuki reaction of aryl iodides and bromides with arylboronic acids.^[25] Suzuki reaction under combining US in aqueous media and MW in DME have better efficiency than individually ultrasound and microwave conditions. Under US technique and in the presence of oxygen, aryl iodides and bromides underwent Ullmann-type Zn-mediated homocoupling reaction in aqueous media.

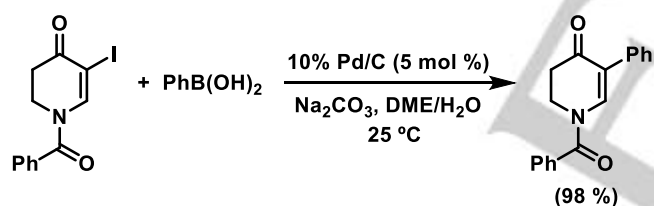
Djakovitch and co-workers applied Pd/C as the only catalyst in several tandem or domino reactions such as Heck-hydrogenation, Sonogashira-intramolecular heteroannulation to form indoles and in Heck-Suzuki reactions.^[26] The results of Heck reaction exhibited 92 % yield for the reaction of bromobenzene with styrene and 94 % yield in the case of 2-bromo-nitrobenzene using NaOAc, NMP, 0.01-0.1 mol% Pd at 135-140 °C. The Sonogashira reaction performed between 2-iodoaniline and phenylacetylene with Et₃N as base, CuI (1 mol%) and Pd/C (1 mol%) as catalysts in DMF/H₂O (1:1) at 120 °C provided 2-phenylindole in 72 % yield. A representative example using both Heck and Suzuki reactions of 4-iodobromobenzene with styrene and further cross-coupling with phenylboronic acid afforded 4-styrylbiphenyl in 86 % yield.

Ultrasounds has been employed by Toma and co-workers in the Suzuki coupling reaction of aryl halides with arylboronic acids under Pd/C catalysis.^[27] Under the optimized reaction conditions involving KF as a base, aqueous MeOH as solvent and 10 mol%

FULL PAPER

of Pd loading in the reaction of iodobenzene with 4-methoxyphenylboronic acid provided 4-methoxybiphenyl in 95 % yield. However, bromobenzene afforded the best results using PdCl₂ as catalyst in aqueous solvents in the presence of benzyltriethylammonium chloride (BTEAC) as phase-transfer catalyst. Leadbeater and co-workers have performed the Suzuki coupling reaction of aryl chlorides with phenylboronic acid using (1 mol%) Pd/C, Na₂CO₃ as base, 1 equiv. of tetra-*n*-butylammonium bromide (TBAB) and water as solvent under microwave heating (120 °C).^[28] This group investigated the use of simultaneous cooling in conjunction with microwave heating, results showed that this method increased the lifetime of the aryl chloride substrates during the reaction avoiding their reduction. 4-Chorotoluene gave 75 % yield under simultaneous cooling conditions 35 % higher than without the simultaneous cooling conditions.

The Suzuki reaction was performed using tetraarylborates and arylbromides in the presence of (0.1-0.005 mol%) Pd/C catalyst under ligand free conditions and water reflux with Na₂CO₃ as base.^[29] Pd/C showed excellent yields (74-99 %) and was recycled for five runs in the case of the reaction of 4-bromobenzoic acid and sodium tetraphenylborate with yields in the range 76-95 %. Felpin and co-workers used 10 % Pd/C (5 mol% Pd loading) as catalyst for the cross-coupling of 2-iodocycloalkenones with arylboronic acids using Na₂CO₃ as base in aqueous DME (1:1) at 25 °C (Scheme 7).^[30] Moderate recyclability of Pd/C was observed for the reaction of 2-iodocyclohexenone with phenylboronic acid at rt during three cycles with yields in the range 86-79 %.



Scheme 7. Suzuki arylation of a 2-iodocyclohexenone derivative.

The use of Pd/C as a catalyst in the Sonogashira reaction of aryl iodides and bromides with phenylacetylene in oligo(ethylene glycol) or Triton X10 (TX10) microemulsions at 70 °C under ligand-, copper- and amine-free conditions has been reported by Cai and co-workers.^[31] Aryl iodides and activated aryl bromides reacted with phenylacetylene and the corresponding products were obtained quantitatively within 30-150 min. The reactivity in the microemulsion was higher than in biphasic systems.

In 2007, several authors reported the catalytic activity of Pd/C in the Suzuki reaction. Khinast and co-workers investigated Pd-leaching and Pd-removal in Pd/C catalyzed Suzuki reaction. By using hot filtration and poly(4-vinylpyridine) (PVPy) tests it was concluded that the activity of Pd/C is only due to leached Pd(II) species.^[32] Sajiki and co-workers used 10 % Pd/C as catalyst in the Suzuki reaction for the preparation of heterobiaryl derivatives.^[33] Good to excellent yields were obtained for the cross-coupling of aryl bromides with heteroarylboronic acids (72-98 % yield) and of heteroaryl bromides with arylboronic acids (27-

98 %) in H₂O and isopropanol (IPA) as solvents, K₃PO₄·12H₂O as base at 80 °C. The same group have applied Pd/C as catalyst in the Suzuki and Sonogashira reactions of aryl bromides with arylboronic acids and aryl iodides with terminal alkynes, respectively.^[34-35] The Pd/C showed good to high catalytic activity in the ligand-free Suzuki reaction in aqueous media at room temperature. In the Sonogashira reaction, aryl alkynes were obtained with moderate to excellent yields in aqueous IPA at 80 °C in the presence of 0.4 mol% Pd loading.

Choi and co-workers prepared carbon supported bimetallic Pd-M (Pd-M/C) materials (M= Ag, Cu and Ni) by γ -irradiation at room temperature without reducing agent.^[36] These materials were applied as catalysts in the Suzuki reaction in EtOH at 78 °C using K₃PO₄ as base and in acetonitrile for the Heck and Sonogashira reactions with Et₃N as base at 82 °C. Moderate to high yields were observed for the Suzuki, Heck and Sonogashira reactions using aryl iodides and high loadings. The catalytic activity declined in the order Pd-Cu/C > Pd/C > Pd-Ag/C > Pd-Ni/C. The most efficient material Pd-Cu/C was recycled for five consecutive runs in the reaction of iodobenzene and phenylboronic acid with small decrease in the activity.

A new form of Pd/C was described by Lipshutz and co-workers, palladium-on-charcoal (UC Pd), prepared by dissolving Pd(NO₃)₂ in water and adding activated charcoal followed by ultrasonication during 20 h.^[37] The catalytic efficiency was studied in the Sonogashira reaction of aryl bromides with terminal alkyne in EtOH as solvent at 50 °C under copper-free conditions. Comparative studies about catalytic activity and recyclability of UC Pd compared with several commercially available sources of Pd/C showed the higher performance of UC Pd, nevertheless the higher size of the Pd NPs.

Bhagwat and co-workers reported the used of Pd/C as catalyst in the Sonogashira reaction of iodobenzene with phenylacetylene.^[38] This group studied the effect of various cationic and anionic surfactants such as cetyltrimethylammonium bromide (CTAB), benzalkonium chloride (BKC), cetylpyridinium chloride (CPC) and sodium dodecylbenzene sulfonate (DBS) in the above mentioned reaction. The alkylation reaction was found to be promoted using cationic surfactants only. Among these surfactants, CTAB exhibited excellent yield in water and aerobic conditions.

The bimetallic Pd-Au/C have used in the Sonogashira reaction of activated 4-iodoacetophenone with phenylacetylene in aqueous *i*-PrOH at 80 °C by Felpin and co-workers.^[39] Moderate to high yields and recyclability were achieved with Pd-Au/C (2 mol% Pd) in the Sonogashira reaction. Comparison of the bimetallic Pd-Au/C with monometallic Pd/C and Au/C showed that Pd-Au/C has higher catalytic activity and recyclability than the monometallic catalysts.

In 2014, Li and co-workers introduced carbon-supported Fe@Pd core-shell as catalyst in the Suzuki reaction of aryl iodides, bromides and chlorides with phenylboronic acid in water.^[40] This catalyst was obtained from the reduction of Pd and Fe on the active carbon (Figure 1). Fe@Pd/C (0.5 mol% Pd loading) in water with K₂CO₃ as base, has displayed good to excellent yields for aryl iodides and bromides at 70-80 °C and low yields for aryl chlorides even at 100-130 °C. This catalyst was recovered by an

FULL PAPER

external magnet and recycled for five runs with low loss in catalytic activity.

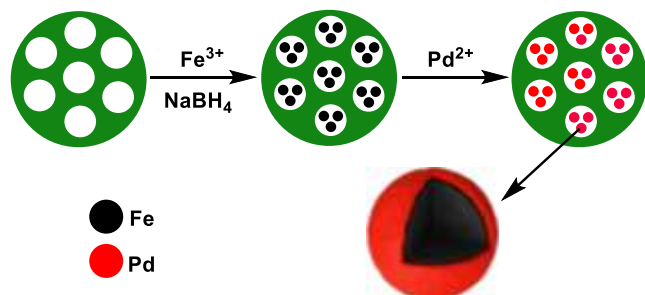


Figure 1. Preparation of Fe@Pd/C.

The Suzuki reaction of aryl bromides and heteroaryl bromides with potassium aryltrifluoroborates^[41] and with arylboronic acids^[42] in the presence of Pd/C as catalyst has been described by Liu and co-workers. Moderate to excellent yields (44-97 %) for aryl and heteroaryl bromides with potassium aryltrifluoroborates were obtained using 0.5 mol% Pd loading, K₂CO₃ as base in EtOH/H₂O (3:1) at 80 °C. In the Suzuki reaction with arylboronic acids a higher loading was used (1.5 mol%), diisopropylamine as base under refluxing water to achieve moderate to good yields (53-99 %). The catalyst was recycled during seven times in the case of potassium aryltrifluoroborates with small loss in activity. However, in the cross-coupling with arylboronic acids only during 3 runs the yield could be maintained.

For the synthesis of 3-vinylindoles as potential cytotoxic agents, Rao and co-workers used Pd/C-PPh₃ as catalyst in the Heck reaction of 3-iodo-1-methyl-1*H*-indole with terminal alkenes under ultrasound irradiation.^[43] The resulting products 3-vinylindoles were obtained with good yields during 2-3 h in the optimized conditions, DMF as solvent, Et₃N as base at 30 °C with 5 mol% of Pd loading and 10 mol% of PPh₃.

Recently, Amali, Pitchumani and co-workers have synthesized a core-shell nanospheres of cubical Pd supported C and Fe₃O₄ (Pd/C@Fe₃O₄).^[44] This material was employed in the Stille and Heck coupling reactions of aryl iodides, bromides and chlorides with tri-*n*-butylphenylstannane and styrene, respectively, using K₂CO₃ as base, DMF as solvent and 0.73 mol% of Pd loading. In the Stille reaction, good to excellent yields were obtained at room temperature for aryl iodides and bromides (82-99 %) and moderate to good yields for aryl chlorides (55-82 %) in the presence of TBAB. In the Heck reaction, good to excellent yields were achieved for aryl iodides and bromides (70-99 %) and moderate yields (48-58 %) for aryl chlorides, even in the presence of TBAB. This catalyst was reused for five times in the reaction of iodobenzene and styrene with little leaching of Pd.

Comparison of the catalytic activity for the some Pd/C catalysts in the Suzuki reaction of aryl bromides with phenylboronic acid has been presented in Table 1.

Table 1. Comparison of the catalytic activity of some reported Pd/C catalysts for Suzuki coupling reaction.

Catalyst	T (°C)	T (h)	Pd (mol %)	Yield (%)
Pd/C ^[17]	120	2	0.005	100 ^a
Pd/C ^[22]	25	3	0.25	90 ^a
Pd/C ^[34]	25	48	1.5	98 ^a
Pd/C ^[41]	100	0.3	1.5	93 ^a
Pd/C ^[27]	30	1	15	67 ^b
Fe@Pd/C ^[40]	80	1	0.5	91 ^b
Pd/C ^[41]	100	0.5	1.5	85 ^b
Pd/C ^[16]	50	12	0.3	76 ^c
Pd/C ^[17]	120	2	0.01	100 ^c
Pd/C ^[34]	25	11	1.5	90 ^c
Pd/C ^[41]	100	0.3	1.5	96 ^c
Pd/C ^[22]	25	3	0.25	89 ^d
Fe@Pd/C ^[40]	80	1	0.5	90 ^d
Pd/C ^[41]	100	0.3	1.5	97 ^d

^a R = OCH₃

^b R = CH₃

^c R = OH

^d R = COCH₃

Several composites based on Pd NPs supported on nitrogen-doped carbon (N-C) have been described. Coville and co-workers have prepared Pd NPs loaded on nitrogen-doped carbon spheres, which were prepared by chemical vapor deposition and then by bubbling acetylene through an alkali solution of ammonia and carbonization at 900 °C.^[45] This material Pd@N-C has been used as catalyst in the Heck reaction of iodo, bromo and chlorobenzene with methyl acrylate using Et₃N as base in DMF at 120 °C and in the Suzuki reaction with phenylboronic acid, K₂CO₃ as base under toluene reflux. Recycling experiments have been carried out for the alkenylation of iodobenzene with styrene during 3 runs. Wang and co-workers have prepared Pd@N-C by carbonization of nitrogen containing containing Al-based MOFs^[46] and of Zn-MOFs (zeolitic imidazole framework: ZIF-8).^[47] By using 0.2 mol% of Pd loading the Suzuki reaction with aryl bromides with arylboronic acids takes place at rt with K₂CO₃ as base in aqueous EtOH (1:1) in high yields (90-99 %). Recycling experiments in both cases were performed for the cross-coupling of phenylboronic acid with bromobenzene during 6 runs. The composite prepared by Pd salts as Pd NPs precursors, colloidal silica^[48] as template or polyethylene glycol polymer^[49] and chitosan as precursor of nitrogen-doped carbon gave Pd@N-C with large porosity. These materials have been employed by Zeng and co-workers as

FULL PAPER

heterogeneous catalyst in Heck^[48] and Ullmann^[49] reactions. In the case of the Heck reaction, aryl iodides and bromides reacted with *n*-butyl acrylate and styrene using 0.001 mol % Pd, KOAc as base in DMSO and ethylene glycol as solvents at 110 °C in 89–98 % yields for aryl iodides and in 72–74 % yield for aryl bromides. The composite Pd@N-C^[48] was 16 times recycled in the reaction of iodobenzene with *n*-butyl acrylate, whereas Pd/C could be recycled only 11 times. On the other hand, the homocoupling of aryl iodides and bromides with composite Pd@N-C^[49] was performed at 120 °C with 5 mol % of Pd loading and using the same reaction conditions as above yielding the biaryls in 29–91 % for aryl iodides and 59–70 % for bromides. In the recycling experiments using iodobenzene this material could be reused 10 times better than Pd/C. Nitrogen-doped carbon black supported PdCu alloy nanocatalysts have been synthesized by Sun and Wang group.^[50] The PdCu NPs were dispersed on the N-C surface. In the case of the Suzuki reaction the Pd₅Cu₅@N-C material was the best catalyst working under conventional reaction conditions (K₂CO₃ in EtOH/H₂O) at rt with a 0.24 mol % Pd loading for aryl iodides, bromides and chlorides with 7-fold higher activity than Pd@N-C. This catalyst could be recovered 5 times in the cross-coupling of iodobenzene and phenylboronic acid.

Nitrogen-doped magnetic carbon nanoparticles, namely Pd@N-MNCPs, were described by Jang and co-workers.^[51] Pd NPs were deposited on N-doped magnetic carbon NPs by a simple impregnation procedure. This material was used as catalyst in three types of C-C bond forming reactions, Heck, Suzuki and Sonogashira, which were repeated during 3 cycles with the same yields by magnetic separation recovery. Thus, iodobenzene reacts with styrene at 120 °C in 97 % yield, 2-iodoanisole was allowed to react with phenylboronic acid at 80 °C in 94 % yield and 4-bromoacetophenone with phenylacetylene at 100 °C using CuI as co-catalyst in 91 % yield. Recently, double-shelled hollow nanospheres supported Pd NPs in which iron species was the inner shell and N-doped carbon the outer shell has been described by Xi and Wang groups.^[52] This Pd@N-C@Fe material has been used as catalyst in the reduction of 4-nitrophenol and in the Suzuki reaction of iodobenzene with phenylboronic acid with K₂CO₃ as base under aqueous EtOH reflux with TOF 52.7 min⁻¹. Yang and co-workers have used Pd NPs supported on N,O-dual doped porous carbon in the Sonogashira reaction of 2-iodoanisole with arylboronic acids to afford 2-benzofurans.^[53] This carbon has been prepared by renewable biomass-bamboo shoots by hydrothermal treatment and carbonization process. These reactions took place with 0.3 mol % Pd loading under copper- and amine-free conditions using K₃PO₄ as base in DMF at 160 °C with similar yields (57–92 %) than Pd/C but with better recyclability.

Nanoporous carbon hollow tubes have been used as support for Pd NPs.^[54] This material Pd@CHTs was prepared by carbonization of hyper crosslinked polymer tubes under nitrogen flow followed by reduction of Pd(OAc)₂ with NaBH₄. The high catalytic efficiency was studied in the Sonogashira reaction of aryl iodides and bromides with phenylacetylene with 0.00023 mol % of Pd loading, Cs₂CO₃ as base in DMF at 80 °C under copper- and amine-free conditions giving the internal acetylenes in 70–85 % yields. Pd NPs supported on N-doped carbon microtubes

Pd@N-CTs have been developed by Wang and co-workers for the hydrogenation of 4-nitrophenol and the Suzuki reaction of iodobenzene with phenylboronic acid.^[55]

As a summary, Pd/C has shown along the years a moderate to very good efficiency in many Pd-catalyzed reactions, namely C-C bond forming reactions working in organic and also in aqueous solvents in large scale processes. Due to the leaching of Pd to the solution during the catalysis clearly it has been suggested to work by means of a homogeneous catalytic mechanism. On the other hand, after the reaction is concluded the leached Pd is able to reprecipitate onto the carbon support allowing not only a good recovery of Pd/C but also its moderate to good recyclability.

3. Palladium-Supported on Carbon Nanotubes

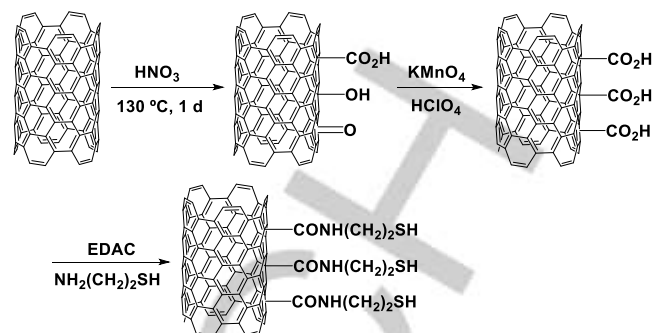
Carbon nanotubes (CNTs) have been extensively used as support for Pd NPs due to the large surface area to volume ratio and high thermal stability. However, CNTs are chemically inactive and surface functionalization is an excellent strategy to enhance Pd NPs release-redeposition and to increase the stability to the palladium catalyst. This Pd@CNTs has been used efficiently in C-C bond forming reaction.^[56]

Unfunctionalized CNTs were described as supports for Pd NPs by Wai and co-workers. The palladium-multiwalled carbon nanotubes (MWCNTs) were prepared by reduction of Pd(II) hexafluoroacetylacetonate with hydrogen under supercritical fluid CO₂ at 80 °C and 150 atm in the presence of the MWCNTs.^[57–59] Transmission electron microscopy (TEM) images showed spherical Pd NPs attached to the surface with a 3% weight of Pd(0). This ligand-less Pd@MWCNTs was employed in the Suzuki reaction of iodo- and bromoarenes with phenylboronic acid using NaOAc as base under MeOH reflux in the air. High yields and moderate TOF between 27 and 709 h⁻¹, in general higher than with Pd/C. The catalytic activity of the recycled material for the reaction of 4-iodobenzene and phenylboronic acid were excellent during six runs with little change on the Pd density on the MWCNTs surface. In the presence of sodium dodecyl sulfate (SDS) as surfactant He and co-workers deposited Pd NPs by reduction of Na₂PdCl₄ in ethylene glycol in the presence of MWCNTs by heating at 110 °C during 3 h.^[60] The generated 5–20 μm microparticles according to scanning electron microscopy (SEM) showed that the Pd NPs (7 wt%) have a narrow size distribution ranging from 2 to 5 nm due to the presence of controlled amount of SDS. Suzuki cross-coupling reactions using this material as catalyst was carried out with aryl iodides, K₃PO₄ as base under EtOH reflux in higher TOF (1520 h⁻¹) than the previously described Pd@MWCNTs. This Pd@MWCNTs has been recovered by simple filtration and its catalytic activity was maintained during 5 cycles for the reaction of 4-iodoacetophenone with phenylboronic acid. Independently, Tagmatarchis and co-workers prepared similar Pd@MWCNTs in refluxing SDS using Pd(OAc)₂ as Pd source during 6 h.^[61] This material was evaluated in hydrogenation of C-C double bonds, Stille and Suzuki cross-coupling reactions. The Suzuki reaction of iodobenzene and 4-iodoanisole with phenylboronic acid was performed with 0.25 mol % of Pd loading in DMF and with Na₂CO₃

FULL PAPER

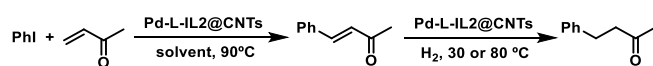
as base at 110 °C during 2 h. Recycling experiments were carried out during five runs without appreciable lowering of yields. In 2010, Chu and co-workers reported the preparation and catalytic activity of Pd supported on double CNTs in Heck reaction.^[62] They used a chemical reduction technique and a conventional impregnation method to generate Pd@CR-MWCNT and Pd@MWCNT, respectively. The former hybrid material gave slightly better results than the later one for the reaction of bromobenzene with acrylic acid using Et₃N as base and DMF as solvent at 120 °C due to a better dispersion of the Pd NPs. Similar results were observed with both materials when the more reactive iodobenzene was allowed to react with acrylic compounds or styrene at 100 °C with 0.004 mol % Pd loading. Both catalysts were reused during 5 cycles with yields in the range 70 to 63 %. Homogeneous dispersion of tris(dibenzylideneacetone) dipalladium into MWCNTs was performed under toluene reflux and Ar atmosphere either under conventional heating or microwave (MW) irradiation.^[63] Higher Pd deposition was obtained under MW heating, around 40 wt %, and according to TEM images uniform distribution of Pd NPs smaller than 7 nm were formed. Catalytic studies in Heck, Suzuki and hydrogenation reactions gave high TOF values. Iodobenzene reacted with methyl acrylate under MW heating in acetonitrile at 140 °C in 15 min quantitative yield with TOF 8x10⁴ h⁻¹ and was recycled four times with quantitative yield. However, only 72 % of Pd was retained in the MWCNTs in the last fourth run. In the case of the reaction of iodobenzene with phenylboronic acid, biphenyl was obtained quantitatively under MW heating at 80°C during 15 min using aqueous EtOH and K₃PO₄ as base with 10⁻⁴ mol % of Pd loading.

Functionalized MWCNTs by thiol groups,^[64] prepared by a modified previously procedure described by Sainsbury and Fitzmaurice (Scheme 8),^[65] were allowed to react with 4-(dimethylamino)pyridine (DMAP) stabilized Pd NPs giving Pd-DMAP@MWCNT. The thiol group displaced the stabilizing DMAP ligand in complex Pd(DMAP)₄(OH)₂. This composite acted as reservoir for dissolved Pd species, which are the catalyst in the Suzuki reaction of 4-halogen substituted benzoic acids with phenylboronic acid using 0.05 mol % of Pd loading for 4-iodo and 4-bromobenzoic acid for 1 h and 20 d, respectively. However, 4-chlorobenzoic acid needed 0.4 mol % of Pd to achieve 43-55 % yields after 16 d. In all these cross-coupling reactions, Na₂CO₃ was used as base under water reflux. Performing a hot filtration test no Pd was detected in the solution. Choi and co-workers used also MWCNTs functionalized by thiol groups as linkers for Pd NPs generated from Pd(dba)₂ dissolved in THF.^[66] In this case, the carboxylic group was treated with an aqueous solution of NaSH and then Pd NPs (3-10 nm) were anchored. The prepared catalyst was used in Stille and Hiyama cross-coupling reactions. The reaction of 4-iodotoluene with tri-*n*-butylphenylstannane promoted by CsF in dioxane at 50 °C for 40 h with 0.3 mol % of Pd loading provided 4-methylbiphenyl in 60 % yield. In the Hiyama reaction 4-iodotoluene was allowed to react with trimethoxysilylbenzene in the presence of tetra-*n*-butylammonium fluoride (TBAF) at 50 °C during 20 h affording the same product in 98 % yield.



Scheme 8. Preparation of functionalized MWCNT-SH.

By covalent grafting of poly(lactic acid) (PLA) onto MWCNTs and subsequent deposition of Pd NPs resulted the corresponding hybrid material.^[67] In this case pristine MWCNTs were treated with a mixture of HNO₃/H₂SO₄ and then with SOCl₂ followed by esterification with PLA. These functionalized f-MWCNTs were treated with an aqueous solution of PdCl₂ and stirred for 2 h at room temperature followed by addition of an aqueous solution of NaBH₄. The catalytic efficiency of this material was assayed in the Heck reaction of iodo-, bromo- and chlorobenzene with alkyl acrylates affording the corresponding cinnamates using Et₃N as base in DMF at 100 °C. Recycling experiments performed with bromobenzene and methyl acrylate were carried out during three consecutive cycles with ca. 2 % lower yield in each run. However, Pd-supported NPs on vertically aligned MWCNTs (Pd@VA-MWCNT) showed lower catalytic activity in the Heck reaction.^[68] Only the very reactive 4-nitroiodobenzene was able to react with styrene and ethyl acrylate under MW heating at 180 °C using EtOH as solvent and Et₃N as base. Superior results were obtained than with Pd/C and lower Pd leaching. The platelets Pd@VA-MWCNT were recovered with tweezers and reused four times without loss of catalytic activity. Similar recyclability has been found for Pd NPs, prepared in ionic liquids (IL) in the presence of 4-(3-phenylpropyl)pyridine under hydrogen atmosphere, immobilized onto f-MWCNTs with imidazolium units.^[69] The supported ionic liquid phase (SILP) catalyst using 1-ethyl-3-methylimidazolium hydrogenphosphonate (IL2) gave Pd-L-IL2@f-MWCNTs, which catalyzed the Heck reaction of iodobenzene with methyl vinyl ketone using IL2 as solvent without base at 90 °C for 1 d. A similar material supported on silica Pd-L-IL2@SiO₂ was less efficient than the MWCNTs hybrid. For the regeneration of the Pd NPs and their corresponding recycling was necessary to perform a hydrogenation process affording saturated 4-phenyl-2-butanone (Scheme 9).



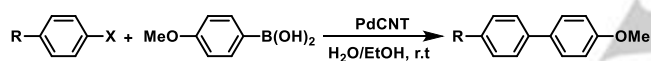
Scheme 9. Tandem Heck and Hydrogenation reactions catalyzed by Pd-L-IL2@MWCNTs.

Single walled carbon nanotubes (SWCNTs) decorated with carboxylic moieties have been employed for supporting Pd NPs, generated by pyrolysis of Pd(OAc)₂.^[70] This Pd@SWCNTs has

FULL PAPER

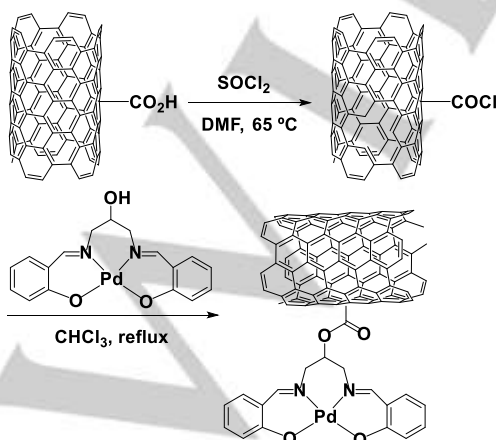
been tested in the Cu-free acyl Sonogashira reaction for the synthesis of ynones from acyl chlorides and terminal alkynes using Et_3N as base in acetonitrile at 25 to 90 °C. In the case of the acylation of phenylacetylene with thiophene-2-carbonyl chloride at 25 °C quantitative yields were obtained during 4 cycles.

A very efficient catalyst formed by Pd NPs supported on MWCNTs prepared by a layer-by-layer approach has been used in the Suzuki reaction.^[71] In the first step, hemi-micelles on MWCNTs were prepared from amphiphilic nitrilotriacetic diacetylene lipid (DANTA). The resulting nanoring-like structures with the hydrophobic part of DANTA are adsorbed by van der Waals interactions on the MWCNTs surface. Photopolymerization of the diyne moieties followed by stirring of this coated nanotube with cationic poly(diallyldimethylammonium chloride) (PDADMAC) afforded a double coated nanotube by electrostatic interactions with the anionic DANTA rings. Final addition of freshly prepared Pd NPs provided a robust material (Scheme 10). Cross-coupling of boronic acids with aryl iodides, bromides and chlorides were carried out in aqueous EtOH with K_2CO_3 as base and with 1.2 mol % of Pd loading at room temperature. This robust material is the most efficient catalyst for the Suzuki reaction. The catalytic activity (97-98 %) was maintained during five cycles for the reaction of 4-iodonitrobenzene with 4-methylphenylboronic acid. No changes were detected in the recycled nanohybrid catalyst.



Scheme 10. Suzuki coupling reaction using of PdCNT.

Pd-Schiff base complex supported on MWCNTs, Pd-Schiff-base@MWCNT, has been prepared by reaction of commercially available MWCNT- CO_2H with SOCl_2 followed by addition of the Pd(II)-Schiff base complex (Scheme 11).^[72] Good yields were obtained in the Suzuki reaction of aryl iodides and bromides in aqueous DMF with 0.1 mol % of Pd and K_2CO_3 as base at 60 °C, whereas aryl chlorides gave moderate yields. The reusability was studied in the case of 4-bromoanisole and phenylboronic acid during four cycles (99 to 82 % yields). For the copper-free Sonogashira alkynylation only good yields were obtained with aryl iodides using 1.2 mol % of Pd, Et_3N as base and water as solvent at 90 °C. Recycling experiments were not performed in this case.

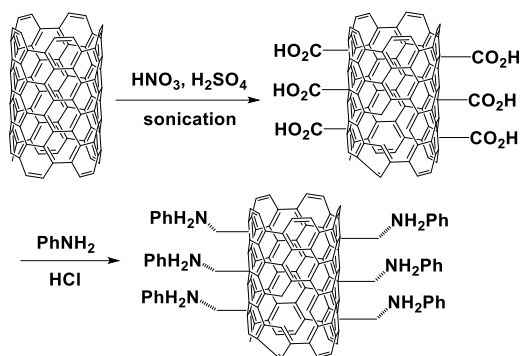


Scheme 11. Preparation of Pd-Schiff base@MWCNT.

Rance and co-workers have shown that the catalytic properties of Pd NPs on CNTs superstructures in the Suzuki reaction critically depend on morphological features.^[73] They synthesized these composites by two ways including ex situ and in situ methodologies and compared the obtained materials as catalysts. In the case of ex situ strategy, separate synthesis and deposition of the Pd NPs onto carbon nanostructures was performed. For the in situ method simultaneous nucleation and growth of Pd NPs directly onto the MWCNTs sidewall were performed. Results indicated that a catalyst prepared by ex situ method using dodecanethiol as nanoparticle stabilizer showed high activity in the Suzuki coupling reaction of 1-bromo-4-nitrobenzene and 1-iodo-4-nitrobenzene with phenylboronic acid. Alternative catalysts prepared using other carbon nanostructures (CNS), such as single- and double-walled carbon nanotubes (SWCNTs and DWCNTs, respectively) and graphitized carbon nanofibers (GNF) were studied. It can be foreseen that MWCNTs were able to uptake the highest number of NPs per unit surface in comparison to other carbon nanostructures (MWCNTs > DWCNTs > SWCNTs ~ GNF). The extent of growth is dependent on the type of nanocarbon support, with wider MWCNTs possessing lower curvature and thus retarding the growth and coalescence of NPs to a greater extent than other carbon nanostructures (SWCNTs > DWCNTs > MWCNTs ~ GNF). In addition, MWCNTs showed not only higher catalytic activity but also stability and recyclability (up to 3 runs) for the cross-coupling of 4-iodonitrobenzene and phenylboronic acid in MeOH with NaOAc as base at 70 °C with 2 mol% Pd loading.

Polyaniline (PANI) on MWCNTs with Pd NPs deposited via in situ polymerization have been prepared by Cui and co-workers.^[74] The procedure for the synthesis of Pd@MWCNT-PANI involves the polymerization of aniline on the surface of MWCNTs at 0 to 5 °C followed by Pd decoration onto the MWCNT-PANI surface. PANI was used as a reducing agent as well as for the stabilization of Pd NPs (Scheme 12). The catalytic activity of Pd-MWCNTs-PANI has been tested in several Heck reactions of aryl iodides, bromides and chlorides with acrylic acid or styrene that the catalyst is efficient for aryl iodides and bromides, but only aryl chlorides having electron-withdrawing groups gave moderate yields. This alkenylation reactions were carried out with 0.9 mol% Pd loading in DMF and with Bu_3N as base at 90 °C. Recycling experiments for the reaction of iodobenzene and acrylic acid were successfully performed during seven cycles with yield in the range of 93 to 91%.

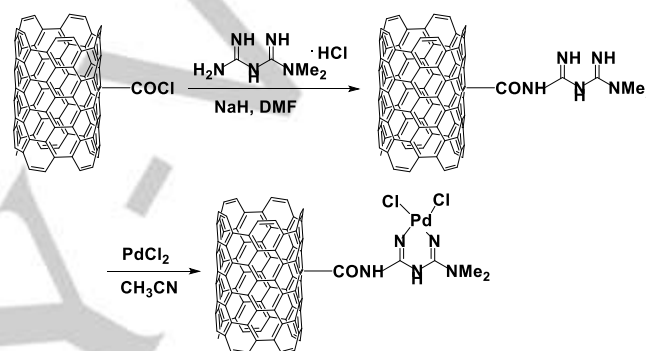
FULL PAPER



Scheme 12. Preparation of MWCNTs-PANI.

Gupton and co-workers employed a rapid and solvent-less mechanochemical ball-milling and thermal methods for the preparation of Pd NPs supported on SWCNTs or MWCNTs.^[75] The catalytic activity of Pd@MWCNT and Pd@SWCNT were studied in the Suzuki coupling reaction of bromobenzene with phenylboronic acid at room temperature. Although, both (Pd@MWCNT) and (Pd@SWCNT) exhibited good catalytic activity in Suzuki cross-coupling reactions under ambient conditions, the former showed a slightly better reactivity and recyclability. The results of hot filtration test and recycling study of the Pd@MWCNT catalyst, confirmed evidence for the interfacial release-redeposition mechanism, in which leached Pd from this hybrid material catalyzes the reaction and re-deposit onto the surface. Recycling experiments were carried out for the reaction of bromobenzene with phenylboronic acid using 0.5 mol% of Pd and K_2CO_3 as base in aqueous EtOH at 80 °C during fourth cycles under MW heating and during nine cycles for iodobenzene. Modified MWCNTs with different defect density and oxygen-containing groups have been used as new carriers of Pd NPs as catalysts for the Heck reaction.^[76] These defects on CNTs become nucleation center for Pd NPs and efficiently improve the stability of the catalyst. Treating raw MWCNTs with different concentration of nitric acid such as 12.1 mol/L, 7.5 mol/L and 2.8 mol/L, and their subsequently reaction with $PdCl_2$ afforded three types of catalysts, CNT-12.1, CNT-7.5 and CNT-2.8, respectively. Applications of the prepared catalysts were investigated in the reaction of iodobenzene with different alkenes. The Pd@MWCNT-12.1 was found to be the most stable catalysts among the three samples. Recycling studies using the three catalysts in the reaction of iodobenzene with acrylic acid showed high amount of Pd leaching to the reaction mixture during the Heck reaction. Thus, in the reaction of iodobenzene with acrylic acid and Pd@MWCNT-12.1 during five runs the yields were maintained. On the other hand, Pd leaching studies indicated that after completion of the reaction the leached Pd decreased notably. Therefore, they suggested that the reaction proceed via a leaching and re-deposition of Pd mechanism. The process seems to be divided onto three steps: i) the leached palladium is coordinated with polar solvents; ii) the complexes suffer oxidative addition with iodobenzene and continuation of reaction to give desired product and iii) palladium re-deposited to the supports when iodobenzene was completely consumed.

Palladium supported on metformine drug functionalized SWCNTs Pd@SWCNT-Met hybrid materials has been synthesized by Veisi and co-workers.^[77] For the synthesis of this hybrid material metformine was attached on modified SWCNTs surface and the complexation with Pd of SWCNT-Met was performed with $PdCl_2$ (Scheme 13). Finally, to reduce Pd^{2+} to Pd^0 , the obtained complex was treated with $NaBH_4$. TEM images exhibited that Pd NPs were uniformly dispersed on f-SWCNTs and some of them appeared twinned together. The catalytic behavior of SWCNT-Met- Pd^{2+} has been evaluated in the Suzuki cross-coupling of aryl halides (ArI, ArBr and ArCl) with phenylboronic acid. The yields of the products were in the range from 80% to 95%. Recycling experiments were performed for the reaction of iodobenzene with phenylboronic acid in aqueous EtOH at 50 °C with 1 mol % of Pd loading during 5 cycles.



Scheme 13. SWCNT-Met-Pd(II).

Uniformly embedded Pd NPs in the inner cavity of CNTs has been achieved by using a simple ZnO nanowires template-based procedure.^[78] The ZnO nanowires were prepared by a modified physical vapor deposition process under atmospheric pressure. Then the formed ZnO nanowires were dispersed into an aqueous solution of $Pd(NO_3)_2$ and the pH of the solution was adjusted between 8 and 9 to form Pd/ZnO. After deposition of Pd NPs onto the ZnO surface, the carbon layer was coated onto the surface of ZnO by a fast coking process with diluted ethylbenzene under high pressure. In the final step, ZnO was removed via gas flow of ethylene at 700 °C and Pd/C nanocomposite having uniform distribution of Pd NPs was obtained (Figure 2). The prepared Pd/C nanocomposite demonstrated higher catalytic activity in the Suzuki cross-coupling reaction than Pd@CNTs. Recycling experiments were carried out for the reaction of iodobenzene with phenylboronic acid in aqueous EtOH, K_2CO_3 as base at 85 °C during four cycles with quantitative yields, whereas Pd@CNTs gave only 63 % yield in the fourth run.

FULL PAPER

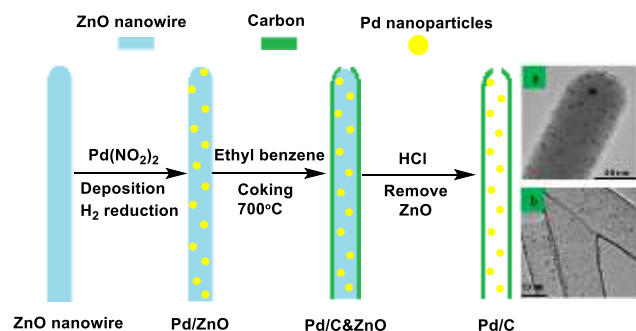


Figure 2. Pd NPs embedded in the inner surface of CNTs and TEM of (a) Pd/C/ZnO and (b) Pd/C composite.

After successful application in the Sonogashira and Suzuki reaction, Movassagh and co-workers investigated the catalytic activity Pd-Salen@MWCNT in Heck and Hiyama reactions.^[79] The Heck reaction was performed between aryl iodides and bromides with styrenes and acrylic derivatives in the presence of triethylamine using 0.6 mol % of catalyst in DMF at 130 °C. However, for aryl bromides and activated aryl chlorides 1 equiv of TBAB was added. To perform the Hiyama reaction, 0.8 mol % Pd loading was used for the reaction of aryl iodides and bromides with phenyltrialkoxysilanes in the presence of TBAF, in toluene at 90 °C. The catalyst was reused for four consecutive runs in both reactions with yields in the range 95-81 % for the reaction of iodobenzene with styrene and between 93-78 % for iodobenzene and phenyltriethoxysilane.

Zhang and co-workers reported that f-MWCNTs modified with 3-aminopropyltriethoxysilanes (APTES) through grafting can be used as the carrier to immobilize Pd NPs by a impregnation method.^[80] The obtained material was used as a catalyst in the Heck reaction of aryl halides with olefins. Iodobenzene was allowed to react with acrylic acid giving cinnamic acid in 78 % yield, whereas bromobenzene gave the same product in 35 % yield. It should be noted that using this catalyst aryl chlorides failed in the Heck reaction. Comparing catalytic activity of Pd@APTES-MWCNT with Pd@MWCNT, showed that the former one exhibited higher product yields for the Heck reaction of iodobenzene as well as better recyclability. This higher performance was attributed to the presence of APTES on MWCNTs and its significant role in homogeneous dispersion of Pd NPs.

An one-pot gas-liquid interfacial plasma (GLIP) method has been used by Li and co-workers for the synthesis of Pd/PdO NPs on different types of CNTs, such as MWCNTs, weakly oxidized MWCNTs and strongly oxidized SWCNTs.^[81] Pd/PdO NPs supported on oxidized MWCNTs showed better morphology and catalytic activity compared to MWCNTs and SWCNTs supports. Oxidized MWCNTs did not changed, but the length of the SWCNTs becomes shorter, which is due to the introduction of nitric acid in the oxidation step. The reduced length of the SWCNTs, led to the decrease of the MWCNTs surface and existence of larger Pd/PdO particle size on the surface of SWCNTs resulting lower catalytic activity. The Pd/PdO@oxidized MWCNT was applied in the Suzuki cross-coupling reaction of

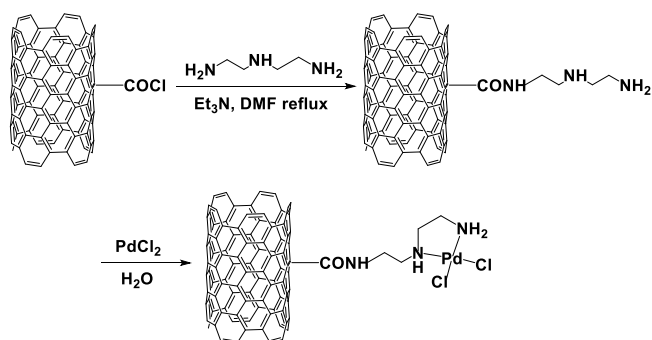
challenging substrates such as heteroaryl bromides and *ortho*-substituted aryl bromides as well as activated aryl chlorides in water at 90 °C with diisopropylamine as base and 0.1 mol % of Pd loading.

Chen and co-workers have developed a simple one-pot hydrothermal approach for the preparation of three-dimensional (3D) graphene/MWCNTs/Pd (Pd@G/MWCNT) composite hydrogel.^[82] This Pd@G/MWCNT composite hydrogel interconnects porous microstructure via self-assembled GO and MWCNTs, in which Pd NPs simultaneously grown in situ on the 3D framework. During the formation of the composite hydrogel, several reactions could happen. Initially, the surface of GO and MWCNTs having oxygen-containing functional groups and structural defects promote nucleation sites for Pd²⁺ ions by electrostatic force. Then, the Pd²⁺ ions could be in situ reduced to Pd(0) NPs by glucose. The presence of glucose increased the mechanical strength of the self-assembled structure under the hydrothermal condition. This material was applied as catalyst for the Suzuki coupling of aryl iodides and bromides with phenylboronic acid under mild aerobic conditions. Recycling experiments for the cross-coupling of iodobenzene with phenylboronic acid using 0.5 mol% of Pd, K₂CO₃ as base, in aqueous EtOH at 60 °C gave yields in the range 99 to 94 % during six runs.

Ignaszak and co-workers have prepared Pd@MWCNTs by an electrodeposition method.^[83] Soluble Pd NPs obtained by electrochemical reduction were deposited on MWCNTs and the obtained material was employed as a catalyst in the Suzuki and Sonogashira reaction of iodobenzene or 4-nitroiodobenzene with phenylboronic acid and phenylacetylene, respectively, under aqueous MeOH reflux. This catalyst was gave products in yields of 84-87 % for Suzuki reaction, similar to Pd/C, and 71-78 % yields for the Sonogashira reaction. Very poor recovery and recycling results were observed during 3 cycles.

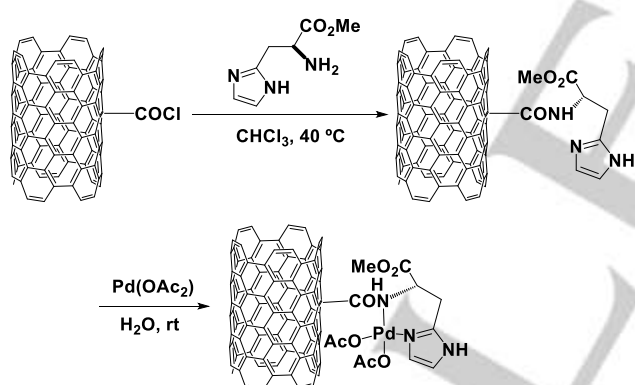
In 2015, Ghorbani-Vaghei and co-workers synthesized f-SWCNTs with diethylenetriamine (DETA) and its Pd(II) complex SWCNT-DETA-Pd(II) hybrid material (Scheme 14)^[84] and studied the catalytic activity in the Suzuki cross-coupling reaction of aryl iodides and bromides with phenylboronic acid. The SEM analysis confirmed that the f-SWCNTs with DETA coordinate Pd(II) ions. When, phenylboronic acid in the presence of the catalyst was coupled with aryl iodides and bromides containing both electron-donating and electron-withdrawing groups at the *para* position, the corresponding biphenyls being obtained in excellent yields. However, the *ortho*-substituted aryl iodides and bromides gave the corresponding products in slightly lower yields due to steric effects. The catalyst was recovered and reused up to seven consecutive cycles for the reaction of bromobenzene with phenylboronic acid under typical aqueous reaction conditions, K₂CO₃ as base EtOH/H₂O (1:1) at 60 °C, during 7 runs with yields in the range of 98 to 80 %.

FULL PAPER



Scheme 14. Preparation of SWCNT-DETA-Pd(II).

Hajipour and co-workers were reported the synthesis Pd NPs immobilized on a f-MWCNTs bearing (S)-methyl histidinate (Scheme 15).^[85] The synthesized catalyst offered high activity and reusability in the Heck and Suzuki reactions in polyethylene glycol (PEG) 200 and aqueous ethanol as solvents, respectively. Heck coupling of aryl iodides and bromides were performed with styrene using KOH as base, 0.0022 mol % Pd at 50 °C and gave corresponding olefins in high to excellent yields. The Suzuki coupling reaction accomplished between aryl iodides and bromides with phenylboronic acid at room temperature using 0.0022 mol % Pd and the corresponding biphenyls were obtained in high to excellent yields. This catalyst was recycled for six consecutive cycles without any significant loss of its activity.

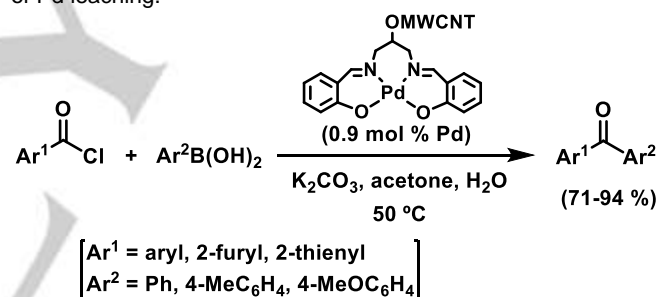


Scheme 15. Synthesis of MWCNT-(S)-methyl histidinate-Pd(II).

Palladium and bimetallic Pd-Ni NPs protected by polyvinylpyrrolidone (PVP) and supported on MWCNTs (Pd-Ni@MWCNT) via a solvent reduction method.^[86] Pd-Ni@MWCNT with different amount of Pd and Ni ratios were applied as catalyst for carbon-carbon bond forming reactions such as Suzuki, Hiyama, Heck, and Sonogashira in neat water. Bimetallic Pd₅₀Ni₅₀@MWCNT (0.1 mol % Pd) was employed as the best catalyst for the Suzuki reaction of 4-bromoanisole with phenylboronic acid or potassium phenyltrifluoroborate using K₂CO₃ as base and TBAB as additive at 120 °C giving 4-methoxybiphenyl in quantitative yields. For the Heck reaction of 4-iodoanisole with styrene KOH was employed as a base and

TBAB as an additive at 120 °C affording quantitative yield with the same catalyst loading. On the other hand, Pd@MWCNTs (0.1 mol %) was the best catalyst for the Hiyama cross-coupling reaction of 4-iodoanisole with trimethoxyphenylsilane under fluoride-free conditions using 50 % NaOH as a base at 120 °C in 99 % yield. For the Sonogashira reaction Pd@MWCNT (0.1 mol%) was also the best catalyst for the alkylation of 4-iodoanisole with phenylacetylene under copper-free conditions using pyrrolidine as a base at 120 °C. Recycling experiments of Pd₅₀Ni₅₀@MWCNT were successfully performed in the Suzuki reaction only with phenylboronic acid during 4 runs with yields in the range 99 to 87%. Also in the Sonogashira reaction the best catalyst Pd@MWCNT was recycled for only 3 runs with yields decreasing from 99 to 64%.

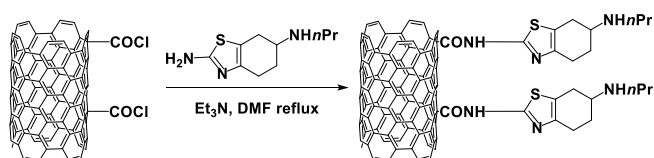
In 2016, Movassagh and co-workers employed Pd-Salen@MWCNT catalyst (Scheme 11) for the acylation reaction of arylboronic acids with aroyl chlorides.^[87] This catalyst previously was prepared and applied by same group in Suzuki, Sonogashira, Heck and Hiyama reactions.^[72,79] The acylation reaction was performed with 0.9 mol % Pd loading, K₂CO₃ as a base in aqueous acetone at 50 °C affording the corresponding diaryl ketones in 71 to 94 % yields (Scheme 16). The catalyst can be easily recovered by a simple filtration and reused for three consecutive runs without significant loss of its activity with 1.2 % of Pd leaching.



Scheme 16. Synthesis of diaryl ketones catalyzed by Pd-Salen@MWCNT.

Recently, Hekmati and Abbasi reported the synthesis of pramipexole drug f-MWCNTs for the immobilization of Pd NPs.^[88] For the preparation of Pd@MWCNT-pramipexole, the MWCNTs bearing carboxylic groups in the surface was treated with SOCl₂ and the resulting acyl chlorides were allowed to react with the primary amine group of pramipexole (Scheme 17). In the next step, MWCNT-pramipexole was treated with PdCl₂ solution followed by chemical reduction using hydrazine hydrate. This material showed high catalytic activity in the copper-free Sonogashira reactions of aryl halides (iodides, bromides and chlorides) in DMF, using Et₃N at 80 °C in 65-96% yields. The catalyst was recycled successfully for the reaction of iodobenzene with phenylacetylene during six times with the same yield.

FULL PAPER



Scheme 17. Synthesis of MWCNT-pramipexole.

Functionalization of MWCNTs by non-covalent π - π stacking interactions with two tetraazamacrocyclic ligands has been performed by Garzon and co-workers.^[89] In the first step, the MWCNTs were subjected to spontaneous chemisorption by the pyrimidine moieties of macrocycles HL1 and HL2 (Figure 3) in water as solvent at room temperature. Then, Pd(II) was coordinated to the azamacrocycle of MWCNT-HL1 and MWCNT-HL2 by addition of a 1M aqueous KCl solution of K_2PdCl_4 giving the corresponding MWCNT-HL1-Pd(II) and MWCNT-HL2-Pd(II) catalysts. The obtained heterogeneous catalysts were employed in the copper-free Sonogashira reaction of iodobenzene with phenylacetylene affording excellent yields in the presence of both catalysts. The reusability of these catalysts was examined for the above Sonogashira coupling reaction. Results indicated that using the MWCNT/HL1-Pd catalyst yield decreases to 80 % in the third and fourth cycles. In the case of MWCNT/HL2-Pd, the yield dropped to 66 % in fourth cycle. The observed decreasing of the catalytic activity of MWCNT/HL2-Pd was attributed to a higher lost of nitrogen ligand in MWCNT/HL2-Pd than MWCNT/HL1-Pd due to high solubility of HL2 in water.

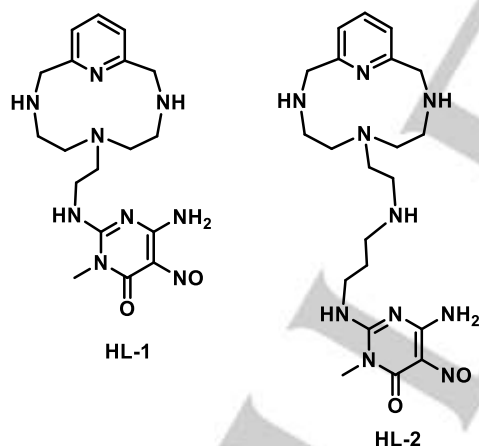
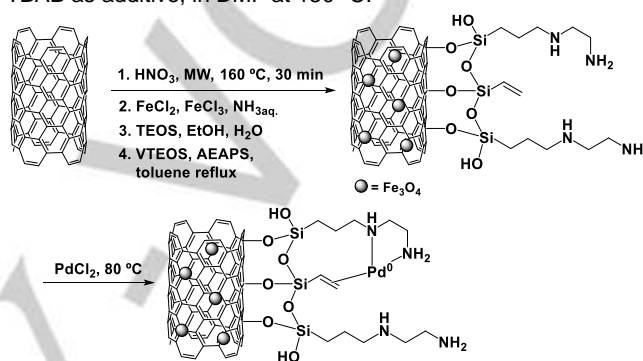


Figure 3. Tetraazamacrocyclic ligands HL-1 and HL-2.

Pd NPs supported on amino-vinyl silica functionalized magnetic CNTs ($CNT@Fe_3O_4@SiO_2$ -Pd) have been reported by Khalili and co-workers.^[90] For the preparation of this material, CNTs were treated with HNO_3 under MW heating at 160 °C for 30 min after isolation were treated with $FeCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 6H_2O$ at 50 °C in order to support Fe_2O_3 in the surface by this co-precipitation method. Afterwards, $CNT@Fe_3O_4$ were treated with tetraethyl orthosilicate (TEOS) and then with a mixture of [3-(2-aminoethylamino)propyl]trimethoxysilane (AEAPS) and vinyltriethoxysilane (VTEOS) and heated for 12 h under toluene

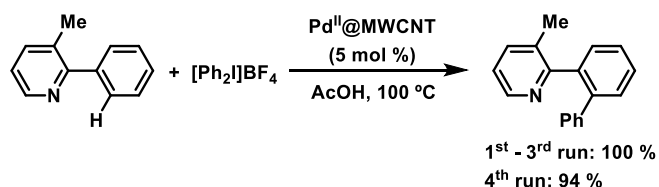
reflux. The resulting nanocomposite $CNT@Fe_3O_4@SiO_2$ was treated with 1M H_2SO_4 solution of $PdCl_2$ and heated at 80 °C for 20 min to afford $Pd@CNT@Fe_3O_4@SiO_2$ (Scheme 18). This magnetic Pd nanocomposite showed high efficiency as a catalyst towards Suzuki and Heck coupling reactions of aryl halides. Aryl iodides, bromides, chlorides and tosylates react with phenylboronic acid using Cs_2CO_3 as a base under EtOH reflux with 1.5 mol % of Pd loading. This catalyst was magnetically separated and recycled for seven runs in the Suzuki reaction of bromobenzene with phenylboronic acid with yields in the range 92 to 89 %. The Heck reaction was carried out with aryl iodides, bromides and chlorides with the same Pd loading, K_2CO_3 as base, TBAB as additive, in DMF at 130 °C.



Scheme 18. Synthesis of $Pd@CNT@Fe_3O_4@SiO_2$.

The deposition of Pd NPs in N-doped CNTs has been described by Zhu and co-workers as catalyst in the Heck reaction and in the oxidation of benzyl alcohol.^[91] N-doped CNTs were synthesized by a chemical vapor deposition with iron-containing SBA-15 molecular sieve as the catalyst and ethylene diamine as the N and C sources. Pd NPs were deposited by employing sodium dodecyl sulfate as a salt and polyvinylpyrrolidone as surface modified and a stabilizing agent. Quantitative yield was observed in the arylation of ethyl acrylate with iodobenzene in DMF with Et_3N as a base at 80 °C.

Ellis and co-workers has recently described the preparation of $Pd^{II}@MWCNT$ which was used in C-C bond forming reactions by C-H activation via a Pd(II)/Pd(IV) catalytic cycle.^[92] The arylation reactions of biphenyls and other substrates with heteroatom-chelating groups, previously described using $Pd(OAc)_2$,^[93] were carried out with $[Ph_2I]BF_4$ and other $[ArI]BF_4$ arylating agents in AcOH at 100 °C with 5 mol % of Pd loading. The catalyst was recovered and recycled up to four times in the reaction of 2-phenyl-3-methylpyridine with $[Ph_2I]BF_4$ with a range of 100 to 94 % yields (Scheme 19).



Scheme 19. C-H functionalization catalyzed by $Pd^{II}@MWCNT$.

FULL PAPER

Carbon nanotubes and cyclodextrin nanosponge (CDNS) have been used by Sajadi and co-workers as a support for embedding Pd(0) NPs (Pd@CDNS-CNT).^[94] The catalytic activity of Pd@CDNS-CNT was investigated in the Sonogashira and Heck reactions. Results of Sonogashira and Heck reactions showed formation of high to excellent yield, while the products of aryl chlorides and bromides were obtained with lower yields in longer reaction times compared to aryl iodides. The catalytic activity Pd@CDNS-CNT was compared with Pd@CNT and Pd@CDNS that the results demonstrated the catalytic activity in order of Pd@CDNS-CNT > Pd@CNT > Pd@CDNS. CDNS was acted as an accommodation of the organic reagent into its hydrophobic cavities and bringing them near the catalytic active sites. In addition, due to the presence of hydroxyl groups on the surface of CDNS, it can act as phase transfer agent and facilitate the reaction performance in aqueous media. Recycling experiments for the reaction of iodobenzene with phenylacetylene was carried out using K₂CO₃ as a base, and water as solvent at 50 °C during six cycles with yields in the range 93 to 83 %. In the arylation of methyl acrylate with iodobenzene with K₂CO₃ in water at 100 °C, recycling during six runs gave 94 to 83 % yields.

Other strategy for the preparation of Pd NPs supported on polyaniline (PANI) coated CNTs^[74] has been reported by Sun and co-workers.^[95] The resulting material was prepared using the polymerization of aniline monomer onto the CNTs surface, afterward the Pd NPs were deposited onto the PANI@CNTs. The N-species in PANI coordinated with Pd clusters prevents the aggregation of NPs and limited the Pd leaching during the catalytic reaction. The Pd-PANI@CNTs was applied as catalyst for the Heck reaction of iodobenzene with styrene using Et₃N as a base in DMF at 110 °C in >97 % yield. The thickness of PANI on the CNTs impressed the catalytic stability and recyclability of the composite. Upon increasing the PANI coating, the PANI units tend to form bulky structures, and separate from the CNTs surface. The catalyst with a PANI/CNT ratio of 0.5:1 exhibited the best recycling performance, with only a small loss of activity observed after 10 cycles.

Comparison of the catalytic performance of some reported carbon nanotubes supported Pd catalysts in Suzuki reaction of aryl bromides with phenyl boronic acid has been shown in Table 2.

Table 2. Comparison of the results obtained for different catalysts of carbon nanotubes supported Pd in Suzuki coupling reaction.

Catalyst	T (°C)	T (h)	Pd (mol %)	Yield (%)
Pd Schiff base@MWCNTs ^[72]	60	6	0.1	98 ^a
SWCNT-Met/ Pd ²⁺ ^[77]	50	0.5	1	92 ^a
Pd/PdO/WCNT ^[81]	90	4	0.1	99 ^a

G/MWCNTs/Pd ^[82]	60	1	0.5	98 ^a
SWCNT-DETA/Pd ²⁺ ^[84]	60	2	1	90 ^a
Pd-(S)-methyl histidinate@MWCNT ^[85]	25	1	0.0022	92 ^a
CNT@Fe ₃ O ₄ @(A-V)-silica-Pd MNPs ^[90]	80	5	1.5	90 ^a
PdSchiff base@MWCNTs ^[72]	60	3	0.1	99 ^b
SWCNT-Met/ Pd ²⁺ ^[77]	50	1	1	90 ^b
Pd/PdO/WCNT ^[81]	90	4	0.1	99 ^b
G/MWCNTs/Pd ^[82]	60	1.5	0.5	92 ^b
SWCNT-DETA/Pd ²⁺ ^[84]	60	1.3	1	96 ^b
Pd-(S)-methyl histidinate@MWCNT ^[85]	25	1	0.0022	80 ^b
CNT@Fe ₃ O ₄ @(A-V)-silica-Pd MNPs ^[90]	80	15	1.5	91 ^b

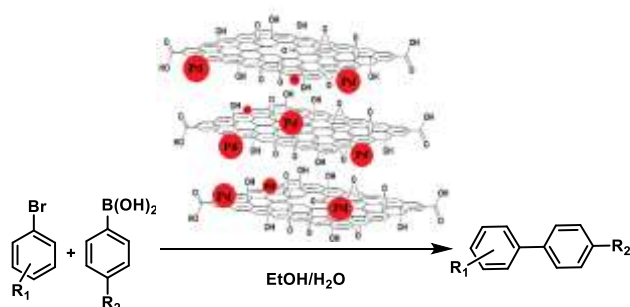
^a R= NO₂
^b R= OCH₃

4. Palladium-Supported on Graphene or Graphene Oxide

The thermal, chemical, mechanical stability and excellent dispersability of graphene or graphene oxide (GO) and specially its high surface area as two-dimensional layers convert this material in an excellent support for metallic NPs. In 2009, Mülhaupt and co-workers prepared graphite oxide and chemically derived graphene (CDG) as supports for Pd NPs.^[96] Pd²⁺@GO was synthesized by immobilization of Pd²⁺ on the graphite oxide surface via cation exchange, while in the case of Pd/CDG after immobilization of Pd²⁺ on the graphite oxide, the material was subjected to chemical reduction with hydrazine hydrate. The prepared Pd²⁺@GO and Pd@CDG were applied for Suzuki-Miyaura coupling reaction of aryl bromides with arylboronic acids using Na₂CO₃ as a base in aqueous EtOH at 80 °C, that the former one (0.25 mol % Pd) displayed high catalytic activity with very low palladium leaching (Scheme 20). Modest recycling, 3 runs, were carried out by centrifugation of Pd²⁺@GO for the cross-coupling of 3-bromobenzaldehyde with 4-methoxyphenylboronic acid with yields in the range 99 to 74 %. The same group^[97] has applied this catalyst (1 mol % Pd) in the Suzuki reaction of aryl chlorides with phenylboronic acid in aqueous DMA at 80 °C during 1 d to give biphenyls in 28-95 % yields. For the Sonogashira reaction of aryl iodides with phenylacetylene, 0.25 mol % of Pd was employed in aqueous IPA and Na₃PO₄ as a base at 80 °C affording the corresponding diaryl acetylenes in 25-95 % yields. In the case of the Heck reaction between aryl bromides and *n*-butyl acrylate, 0.1 mol % of Pd and NaOAc as a base were used

FULL PAPER

in NMP at 140 °C giving the corresponding cinnamates in 73-93 % yields.



Scheme 20. Pd@CDG as catalysts in Suzuki reaction.

El. shall and co-workers have reported the synthesis of Pd NPs supported on graphene and graphene oxide by microwave-assisted chemical reduction and they were applied as catalysts in the Suzuki and Heck reactions of aryl bromides with arylboronic acid and alkene, respectively.^[98] The most active catalyst Pd@G, afforded high yields for both reactions under microwave heating using 0.3 mol % of Pd in aqueous EtOH and K₂CO₃ as a base at 80 °C for the Suzuki and at 180 °C during 10 min for the Heck reaction. Pd@G was recycled for eight times with small loss of activity in the Suzuki coupling of bromobenzene with phenylboronic acid with yields in the range of 100-96 %, whereas Pd@GO was reused 5 times. The same group reported the synthesis of Pd NPs supported on partially reduced graphene oxide nanosheets (PRGO) by using a facile laser reduction method.^[99] The obtained Pd@PRGO (0.5 mol % Pd) was employed for Suzuki, Heck and Sonogashira coupling reactions in aqueous EtOH and with K₂CO₃ as base. In the Suzuki reaction, bromobenzene reacted quantitatively with phenylboronic acid at room temperature with good recyclability (four cycles). In the case of Heck and Sonogashira reactions bromobenzene and iodobenzene were allowed to react with styrene and phenylacetylene, respectively, under microwave irradiation at 180 °C. In the both coupling reactions, the products were formed with excellent yields for iodobenzene and lower conversion for bromobenzene.

Pd NPs on the graphene oxide surface Pd@GO, have been used by Lyubimov and co-workers as catalyst for the Suzuki-reaction of bromobenzene with phenylboronic acid in aqueous EtOH at 80 °C using 2 mol % Pd loading.^[100] The Pd@GO nanocomposite has been prepared by treatment of GO with H₂PdCl₄ followed by reduction with sodium formate and hydroxide giving 2 nm Pd NPs. Nishina and co-workers have developed a new technique for the synthesis of Pd@G composites via intercalation of metal cations into graphene oxide (GO) layers followed by thermal exfoliation.^[101] This material was applied as a catalyst (0.18 mol % Pd) in the Suzuki reaction of bromobenzene with phenylboronic acid in EtOH/H₂O at 80 °C. Modest recyclability, 3 runs, with yields in the range 98 to 58 % and low Pd leaching were observed.

Wang and co-workers have reported the preparation of noble metal (Rh, Au, Rh-Pt and Pd) nanostructures on graphene using

Ti³⁺ as a reducing agent for both the metal and GO and investigated the roles of graphene on tuning the growth behaviors of nanostructures.^[102] For the preparation Pd nanocrystals on graphene, to dispersed GO in EtOH/H₂O (9:1) was alternatively added dropwise PdCl₂ and TiCl₃ under sonication. This Pd@G was used as a catalyst in the Suzuki and Heck reactions of aryl iodides with arylboronic acid and methyl acrylate, respectively. Pd@G composites demonstrated excellent yields for both coupling reactions. However, recycling experiments were not reported.

Mandal and co-workers have synthesized PdNPs supported on GO using pyrolysis of Pd(OAc)₂ in the absence of reducing agent.^[103] This Pd@GO material was prepared by mixing Pd(OAc)₂ with GO in toluene under sonication for 1 h at rt and then heated at 100 °C under N₂ atmosphere for 4 h. This material has been employed in the Suzuki reaction of aryl halides (I, Br) with arylboronic acids in two solvents including IPA (K₂CO₃ as a base) and dioxane (NaOMe as a base). This catalyst showed excellent yields for the cross-coupling of aryl iodides and bromides containing electron-donating and withdrawing groups such as -NO₂, -C(O)Me, -CN, -OH and -NH₂ with arylboronic acid in dioxane in nearly quantitative yields. Whereas in IPA, the reaction of heteroaryl halides with arylboronic acids in the presence of afforded heterobiaryls in better yields (58-99 %). Pd@GO exhibited impressive recyclability over 16 runs without any loss in activity for the synthesis of 4'-chloro-2-nitrophenyl (boscalid nucleus) from 2-iodonitrobenzene and 4-chloroboronic acid using dioxane, NaOMe as a base at 100 °C. In the case of 2'-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)biphenyl-4-carbaldehyde (telmisartan nucleus) the catalyst was recycled during 12 runs using K₂CO₃ in IPA at 85 °C for 1 d. Wang and co-workers have prepared a Pd NPs supported on GO via intercalation of PdCl₂ into the GO layers followed by reduction with hydrazine hydrate of both components.^[104] Thus, to an aqueous suspension of GO was added PdCl₂ and then hydrazine hydrate and then heated at 100 °C for 1 h. The obtained Pd@GO nanocomposite was applied in the Heck reaction of aryl halides (I, Br, Cl) with styrene and *n*-butyl acrylate with K₂CO₃ as a base in NMP at 100 °C. The reaction afforded excellent yields for aryl iodides and activated bromides with 0.05 mol % Pd loading, whereas chlorobenzene gave low yields. Additionally, the catalyst was recycled for 7 runs in the reaction of bromobenzene with *n*-butyl acrylate using 0.1 mol % Pd loading with yields in the range 96 to 80 %.

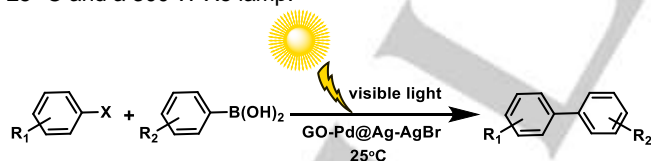
In 2013, Nagarkar and co-workers reported an electrochemical co-deposition method of Pd NPs (Pd@ERGO) on graphene of 3 to 9 nm size.^[105] This supported catalyst was applied as an efficient catalyst for the Suzuki reaction of aryl bromides and iodides with K₂CO₃ as base under EtOH reflux. This catalyst was successfully recycled up to five runs for the cross-coupling of iodobenzene and phenylboronic acid with small decrease in activity.

The introduction of nitrogen decreases the size of the Pd NPs and improves the catalytic efficiency. Li and co-workers have synthesized hybrids of nitrogen-doped porous graphene (N-PG) and Pd NPs (Pd@N-PG) by a plasma method.^[106] For the preparation of this material, Pd(OAc)₂ was added to the sonicated nitrogen-doped graphene in EtOH and the resulting N-PG

FULL PAPER

decorated with Pd was dispersed in the IL [BMIM]BF₄. For the formation of Pd NPs, electrons were irradiated towards the IL for 10 min. The Suzuki reaction was performed between aryl bromides and arylboronic acid in the presence of Pd@N-PG (0.5 mol % of Pd) as catalyst, K₂CO₃ as a base in EtOH at 60 °C. Pd@N-PG catalyst was recycled for four times without Pd leaching and catalytic behavior deactivation. In the case of the Heck reaction, iodobenzene and styrene in NMP at 100 °C using 0.6 mol % of Pd gave stilbene in 93 % yield. Fu and co-workers used N-doped G as support for Pd@PdO.^[107] This Pd@PdO-NG has been employed in the Suzuki reaction of aryl bromides with phenylboronic acid under typical reaction conditions (K₂CO₃, EtOH reflux) giving the corresponding biphenyls in 90-96 % yields and can be recycled during 5 runs. Graphene doped with 11.24 wt % of nitrogen as support for Pd NPs gave the best catalytic efficiency in Suzuki and Ullmann reactions.^[108] Aryl iodides, bromides and chlorides react with arylboronic acids under typical reaction conditions giving high yields for iodides and bromides (73-98 %) and lower for chlorides (57-76 %) with 0.025 and 0.1 mol % Pd loading, respectively. In the case of the homocoupling of aryl iodides, bromides and chlorides a higher Pd loading (0.25 to 2 mol %) was compulsory to obtain high yields (87-98 %).

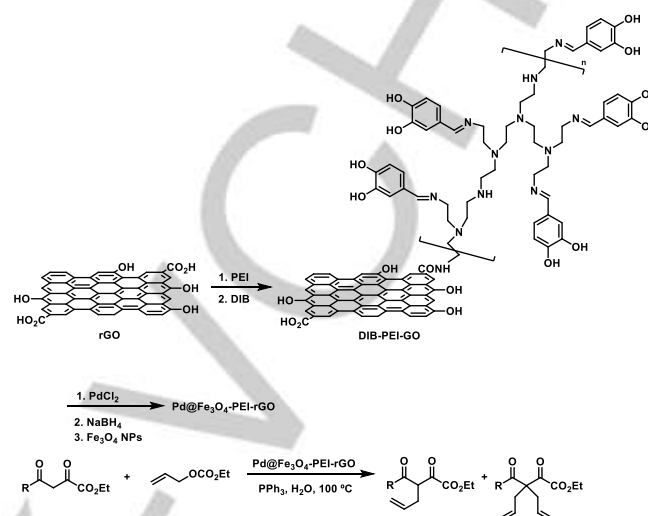
A plasmonic Ag-AgBr photocatalyst functionalized with graphene oxide-Pd (Pd@GO-Ag-AgBr) have fabricated by Wang and co-workers.^[109] The Pd@GO-Ag-AgBr was used as an efficient visible-light-responsive photocatalyst for the Suzuki reaction of aryl halides (iodides and bromides) with arylboronic acids. The combination of plasmonic Ag-AgBr with Pd NPs supported on GO allowed efficient visible light harvesting for the catalytic reaction. Results showed that Pd-free Ag-AgBr and Ag-AgBr-free GO-Pd were inactive in the photocatalytic coupling reaction. The results of this study demonstrated that the intrinsic catalytic activity of Pd increased by visible light irradiation of Ag-AgBr, by the photo-induced energetic electrons located at the surface of Pd sites. Moreover, the photo-induced holes could activate the phenylboronic acid (Scheme 21). The results of Suzuki coupling showed excellent yields for aryl iodides, good to excellent yields for aryl bromides in aqueous EtOH, with K₂CO₃ at 25 °C and a 300 W Xe lamp.



Scheme 21. Pd@GO-Ag-AgBr photocatalytic Suzuki reaction.

Wang and co-workers have introduced Fe₃O₄ and Pd NPs to reduced graphene oxide (rGO) sheets by employing polyethyleneimine as the coupling linker.^[110] This nanocomposite Pd@Fe₃O₄-PEI-rGO was prepared using a multistep method, firstly the PEI was grafted on the GO surface by amide bonds. The obtained material PEI-rGO was treated with 3,4-dihydroxybenzaldehyde (DIB) and then a solution of PdCl₂ in EtOH was added. In the next step, in situ reduction to Pd NPs was carried out with NaBH₄ and finally Fe₃O₄ was added to provide Pd@Fe₃O₄-PEI-rGO. The resulting nanocomposite was applied for the Tsuji-Trost reaction of 1,3-dicarbonyl compounds with allyl

ethyl carbonate (Scheme 22) in water and under air atmosphere and compare with Pd@rGO. Mixtures of mono and diallylated compounds were obtained. The catalyst displayed good magnetic recycling properties with very low leaching of Pd.



Scheme 22. Synthesis of Pd@Fe₃O₄-PEI-rGO and used as catalyst in the Tsuji-Trost reaction.

In 2014, Yan and co-workers prepared a hydrogel of 3D formed by reduced graphene oxide and Pd NPs (Pd@rGO) by two simple steps method. Firstly, Pd NPs were growth over GO in an aqueous solution using vitamin C as reducing agent, after heating at 70 °C the corresponding hydrogel was formed.^[111] The catalytic activity of 3D Pd@rGO hydrogel has been tested in the Suzuki reaction of bromobenzene and iodobenzene with phenylboronic acid in H₂O/EtOH as solvent, Na₂CO₃ as base at 80 °C giving 83 and 91 % yields, respectively. Recycling experiments showed that the yield rose up to the four run.

Park and co-workers introduced Pd and PdO NPs dispersed on graphene and graphene oxide, respectively, by an impregnation method combined with thermal treatments.^[112] The Pd@G and PdO@GO were employed in Sonogashira reaction of aryl iodides with phenylacetylene under solvent-free and microwave heating at 120 °C. Comparison studies about both catalysts showed similar yields, and confirm that the oxidative states of Pd NPs and graphene do not significantly influence the good catalytic efficiency.

Calf thymus DNA-modified graphene has been prepared by Qu and co-workers for the stabilization of Pd NPs (Pd@G-DNA).^[113] The ctDNA was heated at 95 °C for 1 to 2 h to obtain single stranded DNA. Then, it was mixed with a GO dispersion in water and hydrazine was added the resulting mixture being heated at 100 °C for 1 h. To the resulting G-DNA was added H₂PdCl₄ in water and afterwards NaBH₄ at rt affording Pd@G-DNA. The Suzuki reaction of iodobenzene with phenylboronic acid catalyzed by Pd@G DNA (1.1 mol % Pd) provided 100 % yield in 4 min using water in the presence of sodium dodecyl sulfate (SDS) and K₃PO₄ as a base at 100 °C. This catalyst was reused for seven times with small loss in activity (100 to 82%).

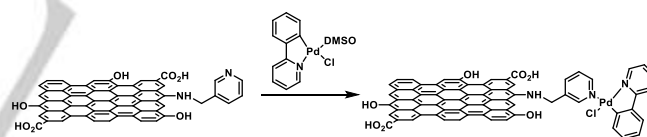
FULL PAPER

Graphene nanosheets (GNS) coated with 1-pyrene carboxylic acid (PCA) has been used for the immobilization of Pd NPs by Ghosh and co-workers affording Pd@GNS-PCA.^[114] GNS-PCA was prepared by treatment of GO in water with NaOH and PCA followed by $N_2H_4 \cdot H_2O$ and heated at 80 °C for 1 h. The obtained GNS-PCA was ultrasonicated in EtOH for 30 min and the PdCl₂ was added and the mixture refluxed for 1 h. The catalytic activity of Pd@GNS-PCA (0.2 mol % Pd) was assayed in the Suzuki and Heck reactions of aryl halides (Br and Cl) with phenylboronic acid and styrene or acrylic systems, respectively, using Na₂CO₃, water at 90 °C. In the Suzuki reaction, the catalyst was exhibited good to excellent yields for aryl bromides and moderate efficiency for aryl chlorides, whereas recycling experiments between 4-bromobenzaldehyde and phenylboronic acid were rather disappointed, 5 runs with 100 to 48 % yields. In the case of the Heck reaction the corresponding arylated alkene products were obtained in moderate to good yields for aryl bromides and moderate yields for aryl chlorides in the presence of TBAB as additive. Again, poor recyclability was observed for the reaction of 4-bromobenzaldehyde and styrene for 5 runs with yield in the range 100 to 31 %. Pd NPs supported on β -cyclodextrin (CD) functionalised graphene nanosheets (Pd@GNS-CD) has been also used by the same group in the Suzuki and Heck reactions of aryl bromides and aryl chlorides under similar reaction conditions.^[115] In the presence of Pd@CD-GNS (0.2 mol % Pd), aryl bromides and chlorides reacted with phenylboronic acid in H₂O at 90 °C to provide the products in good to excellent yields. The Heck reactions accomplished smoothly to generate the corresponding products in moderate to good yields. Better reusability than with the previous catalyst was achieved 100 to 84 % for 4 runs in the Suzuki reaction and 100 to 80 % yield for the Heck reaction.

In 2014, Fan and co-workers described the immobilization of Pd(II) onto graphene oxide surface through the in situ coordination interaction with aminosilane ligand (Pd(II)@GO-2N).^[116] For the preparation of this material, firstly the GO functionalized with N-[3-(trimethoxysilyl)propyl]ethylenediamine (AATPTS) and then Pd²⁺ was attached to nitrogen atoms in the ligand. Pd(II)@GO-2N exhibits good catalytic activity in the Suzuki reaction using 0.5 mol % of Pd, K₂CO₃ as base under refluxing EtOH. For the reaction of aryl iodides with phenylboronic acid excellent yields and for aryl bromides and chlorides moderate to good yields were achieved. The obtained catalyst was recycled and reused for six times without loss of its catalytic activity in the cross-coupling of iodobenzene with phenylboronic acid. Other facile strategy for combined an organic amine with a palladium complex supported on GO was reported by the same group.^[117] In this work, a tertiary amine, [3-(diethylamino)propyl]trimethoxysilane (DEAPMS), and a diamine bearing a secondary and a primary amino groups, 3-(2-aminoethylamino)propyltrimethoxysilane (AEAPMS) were immobilized on GO dispersed in EtOH by refluxing for 12 h giving GO-NEt₂-2N. This material was treated with PdCl₂ affording Pd(II)@GO-NEt₂-2N, which was applied as very efficient catalyst (0.4 mol % Pd) in the Tsuji-Trost allylation of allyl methyl carbonate with ethyl acetoacetate in 1,4-dioxane as a solvent at 70 °C. Jonnalagadda and co-workers have reported the use of Pd NPs on functionalized GO with

AEAPMS as catalyst in Suzuki reaction.^[118] Aryl halides (I, Br, Cl) reacted with phenylboronic acid catalyzed by Pd@GO-AEAPMS using K₃PO₄ as base, in water at 90 °C. The catalyst efficiency for the coupling of aryl iodides (96-98 %) is comparable to aryl bromides (79-84 %) and lower for to aryl chlorides (33-43 %). This catalyst was recycled after reactivation by calcination and reused for six times without a loss in activity and leaching of Pd.

The tertiary amine was demonstrated to show a synergistic catalyst effect with the palladium-diamine complex in this allylation. The Pd(II)@GO-NEt₂-2N was recycled and recovered for five consecutive times without loss catalytic activity. In 2015, Hoseini and co-workers described the synthesis of GO also amino functionalized with 3-aminomethyl pyridine (3-AMPY) and used for the immobilization of Pd NPs (Pd@GO-3-AMPY) and employed as catalyst for the Suzuki reaction.^[119] This nanocomposite was applied as catalyst in the Suzuki reaction of aryl iodides, bromides and chlorides with phenylboronic acid under conventional reaction conditions (K₂CO₃ under H₂O/EtOH reflux) with high yields. Reusability of the catalyst has been also examined in the Suzuki reaction of bromobenzene with phenylboronic acid showing that Pd@GO-3-AMPY can be recycled for eight times with a small decrease in activity. The same group used GO-3-AMPY as support for palladacycles complexes [Pd(C[^]N)Cl(DMSO)] and [Pd(C[^]N)Cl(PPh₃)] in which C[^]N = N(1), C(2')-chelated deprotonated 2-phenylpyridine and DMSO = dimethyl sulfoxide and used as catalysts for the Suzuki reaction at room temperature (Scheme 23).^[120] For the preparation of these materials the two palladium complexes were bonded by coordination to the amino group of the functionalized GO-3-AMPY. Higher TON and TOF were obtained for the formed supported complex in comparison to the second one.

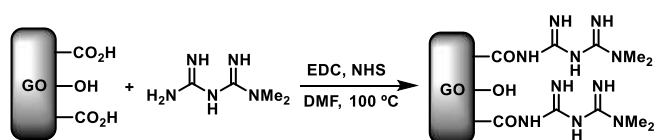


Scheme 23. Synthesis of cyclopalladacycle@GO-3-AMPY.

Also in 2015, the application of PdCl₂ coordinate to rGO functionalized with *N*-propylethane-1,2-diamine, Pd(II)@rGO-2N, was employed as catalyst for different reactions such as Suzuki, Heck, C-H bond functionalization of 2-ethylthiophene and Glaser of terminal alkynes have been developed by Jia and co-workers.^[121] To prepare Pd(II)@rGO-2N, GO was allowed to react with *N*-propylethane-1,2-diamine and then reduced with hydrazine hydrate followed by addition of a DMF solution of PdCl₂. This catalyst has demonstrated high efficiency in the Suzuki reaction of aryl bromides with arylboronic acids at rt (0.25 mol % Pd, Na₂CO₃, in aqueous EtOH). The Heck reaction also takes part with aryl bromides and with styrene and butyl acrylate with 1 mol % of Pd loading, Et₃N as base and tetra-*n*-butylammonium acetate in DMF at 100-120 °C. In the case of the C-H bond functionalization 2-ethylthiophene was arylated at the 5 position with aryl bromides using 0.5 mol % Pd loading, CsOAc as a base in DMF at 140 °C. The Sonogashira alkynylation failed with aryl bromides instead the Glaser reaction of terminal acetylenes

FULL PAPER

occurred. Veisi and Mirzaee have reported the use of GO modified with metformine as a support for Pd NPs, Pd@GO-Met.^[122] The catalytic activity of this material was studied in the Heck reaction of aryl halides (I, Br, Cl) with styrene and acrylates under the optimized reaction conditions (Et₃N in DMF at 110 °C). The results showed excellent yields for aryl iodides, bromides and even for aryl chlorides in the presence of 0.1 mol % of the catalyst (Scheme 24). Pd@GO-Met was reused for seven times in the reaction of bromobenzene with styrene with low loss in activity.



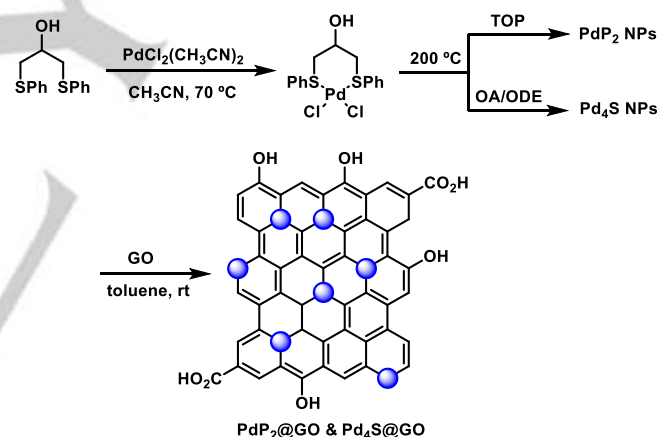
Scheme 24. Synthesis of Pd@GO-Met.

Recently, Oliveira and co-workers have introduced catalysts comprising Pd NPs on the surface of non-functionalized and functionalized GO with organosilanes bearing amine or thiol groups Pd@GO-NH₂ or Pd@GO-SH, respectively.^[123] These new materials were employed as catalysts (0.5 mol % Pd loading) for Heck and Suzuki reactions under microwave irradiation. For the Suzuki reaction aryl bromides reacted efficiently with phenylboronic acid using Na₂CO₃, aqueous EtOH at 70 °C. In the case of the Heck reaction *n*-butyl acrylate was allowed to react with aryl iodides and 4-bromoanisole with Et₃N as base in DMF/toluene at 150 °C. Model reactions of 4-iodoanisole with *n*-butyl acrylate and 4-bromoanisole with phenylboronic acid, respectively, were carried out with Pd@GO-NH₂ and Pd@GO-SH and compared with commercial available catalysts 5% Pd/C and 5 % Pd/Al₂O₃ and unfunctionalized Pd@GO. Results indicated that in the both reactions Pd@GO showed a better performance compared to other catalysts as well as the functionalized GO supported Pd catalysts. However, recycling studies indicated that Pd@GO-NH₂ and Pd@GO-SH were active during five cycles with small decrease in activity, but Pd@GO lost significantly its catalytic activity. It can be concluded that presence of functional groups reduces the metal particle growth and aggregation of Pd NPs.

A phosphine functionalized GO was synthesized by Fareghi-Alamdari and co-workers for the stabilization of Pd NPs.^[124] First, synthesized GO with several epoxy groups was treated with KOH and the resulting polyhydroxylated GO was functionalized with phosphine groups through reaction with chlorodiphenylphosphine (ClPPh₂) giving GO-PPh₂. Further treatment with Pd(OAc)₂ in EtOH gave Pd NPs on the surface of this functionalized GO, Pd@GO-PPh₂. The catalytic activity of Pd@GO-PPh₂ was evaluated in Heck, Suzuki and N-arylation reactions of aryl halides (I, Br, Cl). For the Heck reaction with styrenes and acrylates 1.7 mol % of Pd loading was used, K₂CO₃ base, in DMF at 120 °C. Recycling experiments for the reaction of 4-bromotoluene with styrene were performed during five runs (90 to 85 % yields). For the Suzuki reaction with different arylboronic acids, 1.2 mol % of Pd loading under conventional reaction conditions (K₂CO₃, EtOH/H₂O, 80 °C) gave good yields of

products for aryl iodides and bromides and moderate yields for aryl chlorides. Recycling experiments for the cross-coupling of 4-bromotoluene with phenylboronic acid were carried out during five cycles with yields from 93 to 85 %. In the case of the N-arylation reaction, Na^tBuO as a base under toluene reflux with 1.7 mol % Pd loading gave in general good yields. This catalyst was reused for 5 times for the reaction of 4-bromotoluene with indol with yields in the range 92 to 88 %.

PdP₂ and Pd₄S NPs have been by Singh and co-workers and anchored to GO.^[125] For the synthesis of Pd₄S@GO and PdP₂@GO firstly, the ligand 1,3-bis(phenylsulfanyl)propan-2-ol (L) was prepared by reaction of Na₂S with 1,3-dibromo-2-propanol. In the next step, L was treated with [PdCl₂(CH₃CN)₂] in acetonitrile at 70 °C and the obtained Pd-L was allowed to react at 200 °C with oleic acid-octadecane (OA-ODE) and trioctylphosphine (TOP) producing Pd₄S and PdP₂ NPs, respectively. Finally, Pd₄S@GO and PdP₂@GO were obtained from grafting PdP₂ and Pd₄S NPs to GO under sonication at the mixture was stirred at rt for 1 d (Scheme 25). These composite and were applied as catalysts (0.5 mol % Pd) in the Suzuki reaction of aryl bromides with phenylboronic acid under typical reaction conditions (K₂CO₃, EtOH/H₂O, 80 °C) showing that PdP₂@GO displayed higher catalytic activity than Pd₄S@GO. However, PdP₂@GO was recycled only twice because in the third run the yield decreased from 100 to 83 %.

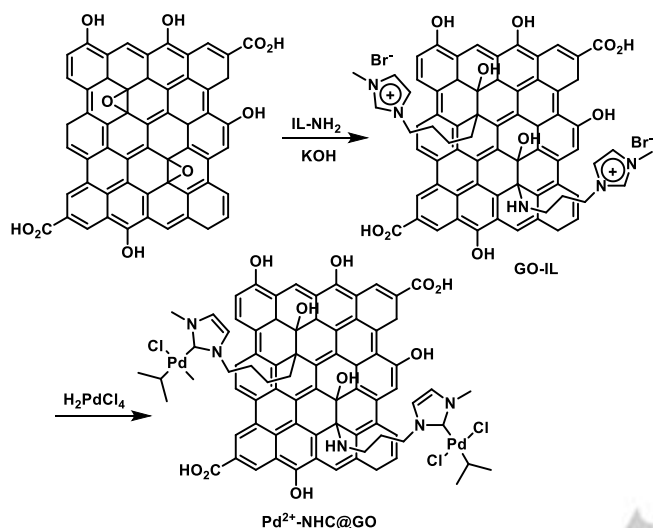


Scheme 25. Synthesis of Pd₄S@GO and PdP₂@GO.

Functionalized GO with imidazolium salts have been used for the coordination of Pd(II) forming N-heterocyclic carbenes in the surface of GO. N-Heterocyclic carbene-palladium complex (NHC-Pd²⁺) was immobilized by Wang and co-workers, onto the surface of graphene oxide by a chemical bonding method and the synthesized catalyst was used for the Suzuki reaction.^[126] For the preparation of this catalyst, firstly, ionic liquid-NH₂ (IL-NH₂) was synthesized via reaction of bromopropylamine and 1-methylimidazole. Then IL-GO was prepared by reaction of IL-NH₂ with epoxy groups of GO by a nucleophilic ring-opening reaction. Finally, IL-GO was treated with H₂PdCl₄ resulting Pd²⁺-NHC@GO-IL, which was reduced with hydrazine hydrate and vitamin C to afford Pd-NHC-N₂H₄@GO and G-Pd-NHC-Vc@GO, respectively (Scheme 26). The three GO-NHC supported Pd

FULL PAPER

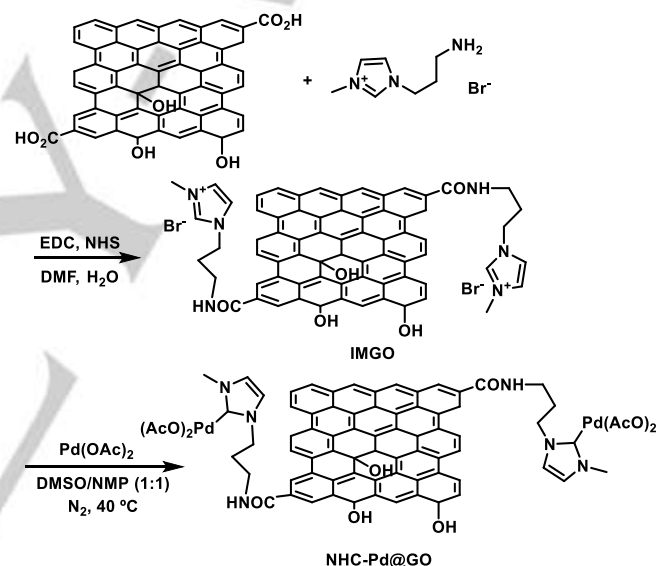
catalysts were assayed as catalysts in the Suzuki reaction of aryl bromides with arylboronic acids. Among the three catalysts tested, Pd²⁺-NHC@GO was found to be the most effective giving biphenyl in 93 % yield. Recycling experiments showed that this composite (0.25 mol % of Pd) in aqueous EtOH and with K₂CO₃ at 80 °C can be reused for six times for the reaction of bromobenzene with phenylboronic acid without a significant loss of the catalytic activity and low Pd leaching.



Scheme 26. Synthesis of Pd²⁺-NHC@GO.

NHC derived from 3-(3-aminopropyl)-1-methylimidazolium bromide ([APMIm][Br]), has been used by Kim and co-workers as ligand for Pd immobilization on GO (Scheme 27).^[127] The resulting material NHC-Pd@GO was applied as catalyst to the Suzuki reaction of aryl iodides, bromides, and chlorides under the optimized conditions, Cs₂CO₃, H₂O:DMF (1:1) at 50 °C. Results indicated that excellent catalytic activity was observed for aryl iodides and bromides and lower catalytic activity for aryl chlorides. Recycling experiments for the reaction of 4-chlorotoluene with phenylboronic acid was efficient for 5 cycles with yields in the range of 89 to 79 %. Bazgir and co-workers reported a NHC Pd complex immobilized on GO with an ionic liquid framework, NHC-Pd@GO-IL.^[128] For the preparation of this nanocomposite, the NHC-palladium complex, with a trimethoxysilylpropyl unit, was grafted to GO under EtOH reflux. This material showed good catalytic activity in the Suzuki reaction of aryl iodides and bromides with 0.1 mol % Pd loading under typical reaction conditions at 60 °C. In the case of aryl chlorides a 0.2 mol % of Pd was used at 90 °C. This catalyst was successfully recycled for five runs for the reaction of iodobenzene with phenylboronic acid, using K₂CO₃ as base in aqueous EtOH at 60 °C, with small decrease in the catalytic activity. Kuang and co-workers reported the synthesis of Pd NPs supported on reduced GO grafted with 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF₆) ionic liquid (rGO-IL) by a phase-transfer method from water.^[129] The Pd@rGO-IL showed good catalytic activity in the Heck reaction of aryl iodides with acrylates and styrene at 130 °C. This catalyst can be reused for ten cycles without a significant loss in

activity. TEM images of reused catalyst after tenth runs showed uniform dispersion of Pd NPs with average size of about 2.0 nm without significant agglomeration. Lee and co-workers have used a bulky NHC as ligand for Pd NHC-Pd@GO and applied this material as catalyst in the Heck, Suzuki and Sonogashira reactions of aryl and heterocyclic iodides with styrene, phenylboronic acid and phenylacetylene, respectively, in H₂O with 1 mol % Pd loading.^[130] For the preparation GO/NHC-Pd, the synthesized GO was allowed to react with the precursor of 1-(2,6-diiodopropylphenyl)-3-(propyltrimethoxysilyl)imidazol-2-ylidene in THF at 60 °C. In the next step, Pd(OAc)₂ was added and chelated with NHC under the same reaction conditions. The activity as reusable catalyst for the Suzuki and Sonogashira reactions was studied. In the case of the Suzuki reaction, 4-iodoacetophenone reacted with phenylboronic acid with K₃PO₄ as base at 100 °C during 5 cycles in 99.9 to 79 % yield. In the Sonogashira reaction, the reaction of 2-iodothiophene with phenylacetylene in H₂O with piperidine as base and CuI as co-catalyst at 80 °C was performed for 5 runs with moderate yields in the range 70 to 50 %.



Scheme 27. Synthesis of NHC-Pd@GO.

Recently, three-dimensional (3D) amine-terminated ionic liquid (IL) covalently functionalized graphene/Pd composite aerogel has been prepared prepared by Wang and co-workers.^[131] For the preparation of this 3D Pd@GO-IL aerogel, GO was functionalized with 1-(3-aminopropyl)-3-methylimidazolium bromide (NH₂-IL) in water and then KOH was added under US for 30 min. To the resulting solution, Na₂PdCl₄ was added and stirred at rt overnight. Next, ascorbic acid was added and the mixture was heated at 90 °C for 6 h. Pd@GO-IL aerogel (0.5 mol % Pd) was employed as a catalyst in the Suzuki reaction of aryl halides (I, Br, Cl) with phenylboronic acid at 80 °C under conventional reaction conditions. Excellent results were obtained except for chlorobenzene. The catalytic activity 3D Pd@GO-IL aerogel was compared with IL-free 3D Pd@GO, the former being better than the last one. This catalyst was reused at least for ten cycles for the cross-coupling of iodobenzene with

FULL PAPER

phenylboronic acid without obvious loss of activity. Pahlevanneshan and co-workers reported the synthesis a Pd(II) complex containing bis(imidazolium) ligand, PdBIM, immobilized on GO via non-covalent method PdBIM@GO.^[132] For the preparation of PdBIM@GO, 1,3-bis(1-methylimidazolium-3-yl)propan-2-one diiodide was allowed to react with Pd(OAc)₂ in DMSO and to the resulting PdBIM was added GO in aqueous DMSO. The catalytic activity of PdBIM@GO (0.35 mol % Pd) was investigated in the Suzuki reaction of aryl halides (I, Br, Cl) with arylboronic acid in H₂O/DMF as a solvent at 60 °C. This material demonstrated high catalytic activity, and good reusability for the cross-coupling of 4-iodoanisole with phenylboronic acid during 5 cycles (100-95 % yield) with low leaching of Pd.

In order to reduce the consumption of Pd, Xu and co-workers reported the synthesis of different ratios of Pd-Co bimetallic NPs supported on rGO, PdCo@rGO, by a chemical reduction method.^[133] A mixture of Co(OAc)₂, PdCl₂ and GO were treated with 0.1 M aqueous solutions of N₂H₄ and NH₃ and stirred at 80 °C for 4 h. The resulting powders were heated in atmosphere of N₂ and H₂, successively at 200 and 500 °C to give different PdCo@rGO. These nanocomposites were employed as catalysts in Sonogashira (2 mol % Pd, 2 mol % PPh₃, 0.3 mol % CuI and Et₃N in THF/H₂O at 80 °C) and Suzuki reaction (4 mol % Pd, Na₂CO₃ in EtOH/H₂O at 80 °C) of aryl iodides with phenylacetylene and phenylboronic acid, respectively. Results showed that the Pd-Co (1:1) NPs were found to be the most active catalyst in both cross-coupling reactions. The catalytic activity of this catalyst in the reaction of iodobenzene with phenylboronic acid was maintained during five runs. Hoseini and co-workers have prepared bimetallic Pd-Cu NPs also supported on reduced GO as well as PtPdCu NPs thin films via chemical reduction of [PtCl₂(cod)], [PdCl₂(cod)] (cod = *cis,cis*-1,5-cyclooctadiene) and [Cu(acac)₂] (acac = acetylacetonate) using NaBH₄ as reductant.^[134] In the case of PdCu@GO, to the toluene solution of PdCl₂(cod) and Cu(acac)₂ was added GO in water and finally the reductant. After characterization with different techniques, these materials have been employed as catalysts in the Suzuki reaction of aryl halides (I, Br, Cl) with phenylboronic acid using K₂CO₃ as base under water reflux with conventional or MW heating. The PtPdCu thin film displayed higher catalytic activity compared with PdCu and PdCu@GO thin films. Due to donation of electrons from the Pt metal to the Pd centre, the presence of Pt in the PtPdCu thin film enhanced the catalytic activity in the cross-coupling reaction. These three catalysts were showed excellent yields for aryl iodides and good efficiency for aryl bromides and chlorides in the Suzuki reaction. Concerning recovery experiments for the reaction of bromobenzene with phenylboronic acid using very low 0.0006 mol % Pd loading, only the PdCu@GO material gave the same yield during 7 runs.

Several groups have reported several types of Pd/Fe₃O₄ NPs on GO as easily recoverable magnetic materials. As in the case of MWCNTs,^[77] metformine (Met) has been used to support Pd NPs on magnetic GO by Shafiee and co-workers.^[135] By a co-precipitation method Fe₃O₄ NPs were deposited in then surface of GO, which was further modified by the *N*-aminoguanidine Met using diethylene glycol (DEG) giving MGO-Met. The resulting material was used for the stabilization and immobilization of Pd

Pd@Fe₃O₄-GO-Met. This material has been applied as a catalyst in Heck and Suzuki cross-coupling reactions of aryl halides (I, Br) with styrene or *n*-butyl acrylate and arylboronic acids, respectively, at rt in excellent yields using 0.009 mol % Pd loading. Park and co-workers reported the synthesis of Fe₃O₄@amin-functionalized GO composite as a support for immobilization of Pd NPs.^[136] For the synthesis of Pd/Fe₃O₄@GON, firstly, the synthesized Fe₃O₄ by a solvothermal method was functionalized with 3-aminopropyltrimethoxysilane (APTMS), and the resulting solid was allowed to react with GO giving Fe₃O₄@GO. The obtained magnetic material was aminated by addition of *N*-hydroxysuccinimide (NHS) and then of ethylene dicarbonate in DMF affording Fe₃O₄@GON. Pd NPs were immobilized on this material by addition of K₂PdCl₄ under sonication. The catalytic activity of Pd/Fe₃O₄@GON (0.5 mol % Pd) was investigated in the Sonogashira reaction of aryl iodides and bromides with arylacetylenes in DMSO as a solvent and NaOAc as a base at 130 °C. The results showed high catalytic activity for aryl iodides, whereas aryl bromides gave moderate yields. This catalyst was reused for five times in the reaction of iodobenzene with phenylacetylene with yields in the range 99 to 77 %. In 2015, Hoseini and co-workers have prepared a similar Pd/Fe₃O₄@rGO nanohybrid.^[137] For this purpose, the prepared Fe₃O₄ NPs were allowed to react with γ -aminopropyl-triethoxysilane (APTES) in toluene at 60 °C for 12 h. To the resulting isolated solid was added GO and aqueous NaOH and heated at 80°C in N₂ atmosphere. Then to Fe₃O₄@GO, a solution of PdCl₂ in HCl was added and afterwards NaBH₄ and the mixture was heated at 60 °C for 12 h. This material Pd/Fe₃O₄@GO (0.36 mol % Pd) showed moderate to excellent activity in the Suzuki reaction of aryl halides (I, Br, Cl) with phenylboronic acid in H₂O at 80 °C. Recycling tests for the cross-coupling of bromobenzene with phenylboronic acid indicated that this catalyst can be reused for eight consecutive times without significant loss of activity. Gupton and co-workers have fabricated several Pd/Fe₃O₄ NPs with different Pd/Fe₃O₄ ratio which were supported on graphene nanosheets Pd@Fe₃O₄@GO.^[138] By mixing Pd(NO₃)₂ with Fe(NO₃)₃·6H₂O and GO in water following by addition of hydrazine hydrate as reducing agent and heating under MW, this material was obtained. The best catalyst was prepared from 50 % wt of Pd and Fe₃O₄ or 7.5 % wt Pd NPs according to its catalytic activity in the Suzuki reaction. With this catalyst in hand through microwave heating Suzuki and Heck reactions were performed of aryl bromides with arylboronic acids and styrenes, respectively. Both reactions were carried out in H₂O/EtOH with 0.3 mol % Pd loading, K₂CO₃ as base at 80 °C and 150 °C, respectively, for 10 min. This catalyst can be reused over 10 cycles in the reaction of bromobenzene with phenylboronic acid with 0.5 mol % of Pd loading and yields in the range 100 to 80 %. In the case of the Heck reaction the reusability was possible during 8 cycles with low lost in activity. Recently, Zhao and colleagues have introduced a facile one pot hydrothermal method for the preparation of Pd nanoparticles supported on NiFe₂O₄@GO.^[139] To a GO suspension on EtOH and ethylene glycol was added first NiCl₂·6H₂O and Fe(NO₃)₃·6H₂O and after 30 min stirring PdCl₂ and the mixture was heated in a autoclave at 120 °C for 1 d giving PdNiFe₂O₄@GO. The prepared catalyst was used in the Heck

FULL PAPER

reaction of aryl iodides and bromides with styrene and acrylates in H₂O/EtOH with K₂CO₃ as base at 80 °C with only 0.08 mol % of Pd loading. The catalytic activity of PdNiFe₂O₄@GO compared with PdNiFe₂O₄ showed that the former one exhibited higher catalytic performance. It has been suggested that the presence of GO could be preventing aggregation of nanoparticles. This catalyst system afforded excellent yield (90-99 %) for aryl iodides, good to excellent efficiency for aryl bromides and low yields for an activated aryl chlorides. The catalyst can be reused for the reaction of bromobenzene with styrene during six times (99 to 95 % yields) without a significant decrease in the activity with only 0.15 wt% of Pd leaching. Also Shen and co-workers have prepared Pd NPs on the magnetic reduced GO nanosheet (Pd/Fe₃O₄@GO) via a one-pot hydrothermal method.^[140] Firstly, to a solution of FeCl₂·4H₂O in aqueous ammonia was added K₂PdCl₄ and GO in EtOH and heated in a autoclave at 140 °C for 4 h. The obtained Pd/Fe₃O₄@GO nanocomposite was employed as a catalyst for Suzuki and Heck reactions of aryl iodides and bromides with phenylboronic acid and aryl iodides with styrene, respectively. The magnetic catalyst (0.06 mol % Pd) was used in the Suzuki reaction under conventional reaction conditions and in the Heck reaction using Et₃N in toluene at 120 °C. This Pd/Fe₃O₄@GO catalyst was used six times without significant loss of its activity on the cross-coupling of 4-iodoanisole and phenylboronic acid with 0.25 mol % of Pd giving the corresponding 4-methoxybiphenyl in 95 to 70 % yield. In the case of the arylation of styrene with 4-iodoanisole during 6 cycles lower yields (92-65 %) were observed. Elazab and co-workers prepared Pd NPs with Fe₃O₄, Co₃O₄ and Ni(OH)₂ NPs supported on GO by a simple microwave heating method.^[141] This material was prepared by treatment of mixtures of Pd(NO₃)₂ with Fe(NO₃)₃·9H₂O, or Co(NO₃)₂·6H₂O or Ni(NO₃)₂·6H₂O and then treated with hydrazine hydrate giving Pd/Fe₃O₄ or Co₃O₄ or Ni(OH)₂ NPs which were supported on GO. The most active Pd bimetallic NPs supported on GO was Pd/Fe₃O₄@GO (0.5 mol % Pd) in the Suzuki reaction of aryl bromides with phenylboronic acid under microwave irradiation at 80 °C under conventional reaction conditions. Among these catalysts, Pd@Fe₃O₄@GO demonstrated excellent catalytic activity in the cross coupling reaction and recycled for up to four times without loss of catalytic activity. Recently, Sheibani and co-workers reported a novel and green approach for the synthesis of Pd NPs on magnetic GO by using *Origanum vulgare* leaf plant extract as reductant.^[142] This nanocomposite Pd@GO@Fe₃O₄ was synthesized by reaction of GO by SOCl₂ and then with 1,4-phenylene diamine (1,4-PDA) and Et₃N affording GO-NH₂. In the next step, 2-pyridine carboxaldehyde was attached to GO-NH₂ and the resulting material employed for coordination of Pd²⁺. The obtained Pd²⁺@GO-NH₂ was reduced by leaf extract of *Origanum vulgare* to form Pd NPs. Finally, this catalyst was magnetized by treating Fe₃O₄ NPs with Pd@GO. The catalytic activity Pd@GO@Fe₃O₄ (0.5 mol % Pd) was investigated in the Suzuki reaction of aryl halides (I, Br, Cl) with phenylboronic acid at 80 °C under conventional reaction conditions. This catalyst demonstrated excellent yield for aryl iodides, good efficiency for aryl bromides and moderate yield for aryl chlorides. Pd@GO@Fe₃O₄ catalyst

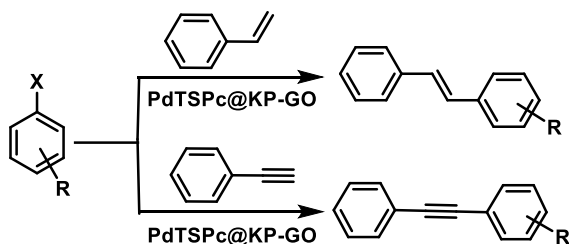
was reused for six times for the cross-coupling of iodobenzene with phenylboronic acid with yields in the range 95 to 80 %.

Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (P123) has been used by Rostamnia and co-workers for the preparation of Pd NPs supported on GO nanosheets.^[143] First GO was treated with Na₂PdCl₄ followed by NaBH₄ selective reduction of Pd²⁺ species (Pd@GO), then P123 was used as a suitable surfactant for the exfoliation of this GO-based catalytic system affording Pd@GO-P123. The resulting material was applied as catalyst (0.5 mol % Pd) in the Hiyama reaction of aryl iodides and bromides with triethoxyphenylsilane in aqueous dioxane and in the presence of TBAF and NaOH at 80 °C. Pd@GO-P123 was recycled for five runs for the cross-coupling of 4-bromoacetophenone with triethoxyphenylsilane, yields being in the range 85-72 %. Gogoi, Das and co-workers have developed a new strategy for the synthesis of Pd NPs onto reduced GO sheets (Pd@rGO-H₂).^[144] For the preparation of this material Pd(OAc)₂ was added to a dispersion of GO in EtOH in the presence of an alkene and stirred under H₂ atmosphere overnight. During the synthesis of the Pd@GO-H₂ and stabilization of Pd NPs onto the rGO nanosheets under hydrogen atmosphere, reduction of olefins to saturated hydrocarbons was also studied. The prepared catalyst was applied in the Suzuki reaction of aryl iodides, bromides and chlorides with arylboronic acid in H₂O/EtOH at 80 °C with Na₂CO₃ as base. The catalytic performance of Pd@GO-H₂ compared with other catalysts Pd@GO-As (ascorbic acid as reductant) and Pd@GO-Gl (glucose as reductant) confirmed that Pd@GO-H₂ displayed higher catalytic activity in the Suzuki reaction than the two other catalysts. The Pd@GO-H₂ catalyst demonstrated catalytic activity and recyclability during 4 runs (96-88 % yields) in the Suzuki reaction of bromobenzene with phenylboronic acid without leaching of Pd to the solution. The same group has used Pd@GO-H₂ as catalyst for the copper-free Sonogashira reaction.^[145] Aryl iodides and activated aryl bromides reacted with arylacetylenes in ethanol, K₂CO₃ as base, in the presence 5 wt % of Pd at room temperature. The Pd@GO-H₂ afforded excellent to good yields in the case of both electron-withdrawing and electron-donating aryl iodides and low yields for aryl bromides. The catalyst can be recycled for the reaction of phenylacetylene with 4-bromonitrobenzene up to six runs with yields in the range 92-80 %.

Hezarkhani and Shabani have prepared Pd(II) tetrasulfophthalocyanine (TSPc) supported on wool keratin protein (KP) modified GO nanosheets PdTSPc@GO-PK.^[146] For the preparation of PdTSPc@GO-KP, phthalic anhydride was allowed to react with urea, PdCl₂ and ammonium heptamolybdate under microwave heating giving PdTSPc. Afterwards, PdTSPc was grafted on KP modified GO (Scheme 28). PdTSPc@GO-KP was employed as a catalyst in the Heck and Sonogashira reactions of aryl iodides and bromides with styrene and phenylacetylene, respectively, with K₂CO₃, under water reflux. In the Heck reaction 0.8 mol % of Pd loading was used. In the Sonogashira reaction 1 mol % of Pd and also 4 mol % of CuI were needed. For both reactions, this catalyst displayed good to excellent performance for aryl bromides and iodides and low efficiency for aryl chlorides. The catalyst was recycled in the

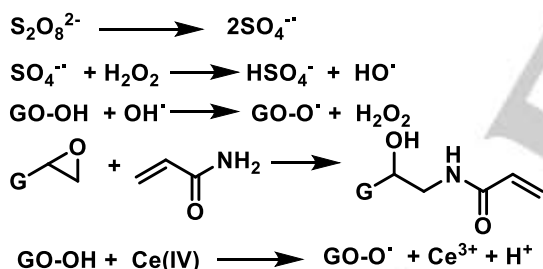
FULL PAPER

arylation of styrene with bromobenzene during five runs with only minor decreases in the reaction yields.



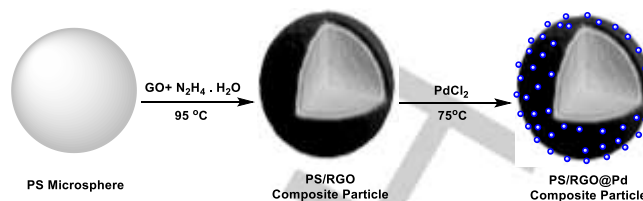
Scheme 28. The Heck and Sonogashira reactions by PdTSPc@KP-GO.

Different GO supports linked to polymers have been also described. Thus, Mahdavi and Rahmani have synthesized polyacrylamide (PAM) grafted on GO via a redox polymerization method for the immobilization of Pd NPs (Pd@GO-PAM).^[147] Polymerization of acrylamide (AM) monomer on the GO was performed in the presence of Ce(IV) and $K_2S_2O_8$ in H_2O at 65 °C (Scheme 29). The catalytic activity of Pd@GO-PAM (0.015 mol % Pd) has been investigated in the Suzuki reaction of aryl halides (I, Br, Cl) with arylboronic acids with K_2CO_3 as base in H_2O at rt or 50 °C producing the corresponding products in high to excellent yields. Recovery and reusability of Pd@GO-PAM catalyst for the cross-coupling of iodobenzene with phenylboronic acid at rt were achieved without significant loss of catalytic activity during eight cycles just by increasing the reaction time from 20 to 130 min and with low leaching of Pd.



Scheme 29. Radical formation on the surface of GO sheets using Ce(IV) and $S_2O_8^{2-}$ as polymerization initiators.

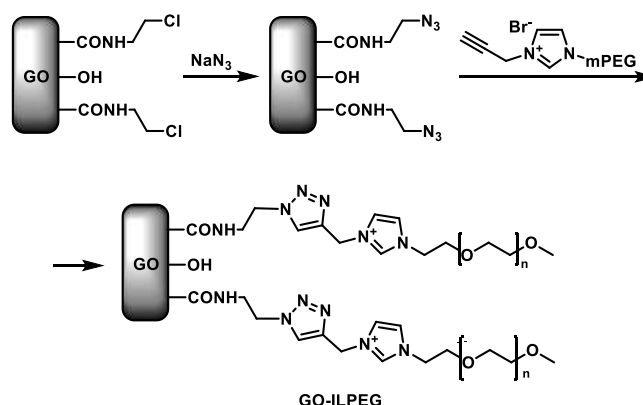
In the case of polystyrene (PS) microspheres, they were coated by GO and Pd NPs by Li and co-workers.^[148] To prepare this Pd@GO-PS, PS microspheres were coated with GO in the presence of hydrazine hydrate as a reducing agent. Then, Pd NPs were grown in situ on the surface of GO@PS composite through a spontaneous redox reaction between $PdCl_2$ and rGO (Scheme 30). Using Pd@GO-PS, the Suzuki reaction was performed efficiently between aryl halides (I, Br) and phenylboronic acid under conventional reaction conditions ($EtOH/H_2O$, K_2CO_3 at 80 °C). Pd@GO-PS was easily recovered by centrifugation for five cycles without decreasing of the catalytic activity.



Scheme 30. Preparation of Pd NPs supported on GO-PS microspheres.

Recently, Kim and co-workers have reported the synthesis of Pd NPs on ionic polymer-doped GO (Pd@GO-IP) nanocomposite through one-pot and one-shot-injection method using benzoic acid (BA) as a structure-directing agent.^[149] The pyrene was functionalized with poly(dimethylaminoethyl methacrylate)-b-poly[(ethylene glycol) methyl ether methacrylate] as an ionic polymer-doped GO and the resulting material was used as support for Pd NPs. Pd@GO-IP (0.3 mol % Pd) was applied as a catalyst in the Suzuki coupling reaction of aryl iodides with arylboronic acids in $H_2O/EtOH$, NaOH at 60 °C. The catalytic behavior of Pd@GO-IP compared with Pd@GO, demonstrated that the catalytic efficiency of Pd@GO were significantly lower for all substrates than that of Pd@GO-IP. This catalyst showed high yield and high reusability during 10 cycles for the cross-coupling of iodobenzene with phenylboronic acid with no significant leaching of the Pd during hot-filtration test in the Suzuki coupling reaction.

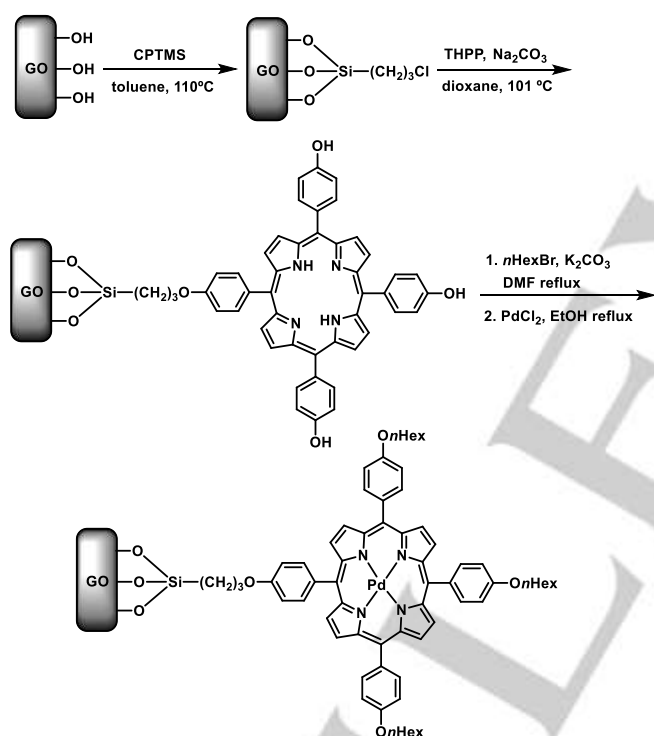
Shi and Cai have used Pd NPs on reduced GO functionalized by mPEGylated imidazolium-based ionic liquid containing polyethylene glycol monomethyl ether moieties (Pd@GO-ILPEG) as a catalyst in the Suzuki reaction.^[150] For the preparation of Pd@GO-ILPEG, the azide-functionalized rGO was allowed to react with mPEG200-3-propargyl-imidazolium bromide ionic liquid by CuAAC click reaction. The IL-functionalized rGO was treated with $Pd(OAc)_2$ generating the Pd@GO-ILPEG catalyst (Scheme 31). This catalyst gave good to excellent yields of products in the Suzuki reaction of aryl bromides with arylboronic acid at room temperature in aqueous $EtOH$ with K_2CO_3 as base and 0.5 mol % Pd loading. In recycling experiments for the reaction of 4-bromoanisole with phenylboronic acid, this catalyst was reused for five times without significant decrease in catalytic activity.



Scheme 31. Synthesis of GO-ILPEG.

FULL PAPER

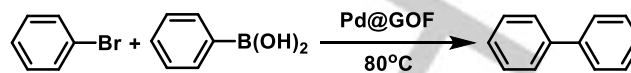
Recently, Bahrami and Kamrani designed Pd(II) complex coordinated to 5,10,15,20-tetrakis-(4-hexyloxyphenyl)-porphyrin (THPP) grafted to the surface of graphene oxide (Pd-TKHPP@GO-CPTMS) with covalent bond.^[151] To prepare this material, (3-chloropropyl)trimethoxysilane (CPTMS) modified GO was linked to THPP resulting THPP@GO-CPTMS. The obtained material was allowed to react with 1-bromohexane for the alkylation of the phenol units and finally PdCl₂ was added in EtOH and heated at 80 °C (Scheme 32). The obtained Pd-TKHPP@GO-CPTMS was applied as a catalyst for the Suzuki and Heck reactions of aryl halides (I, Br, Cl) with phenylboronic acid and styrene, respectively. In the presence of high Pd loading (10 mol %) of Pd-TKHPP@GO-CPTMS, K₂CO₃ in aqueous EtOH at 80 °C, excellent yields were obtained. For the recycling experiments, the cross-coupling of bromobenzene and phenylboronic acid was performed during 5 runs with yields in the range of 99 to 91 %. In the Heck reaction, this catalyst (10 mol % Pd) showed high yields in DMF with K₂CO₃ at 120°C.



Scheme 32. Synthesis of Pd-TKHPP@GO-CPTMS.

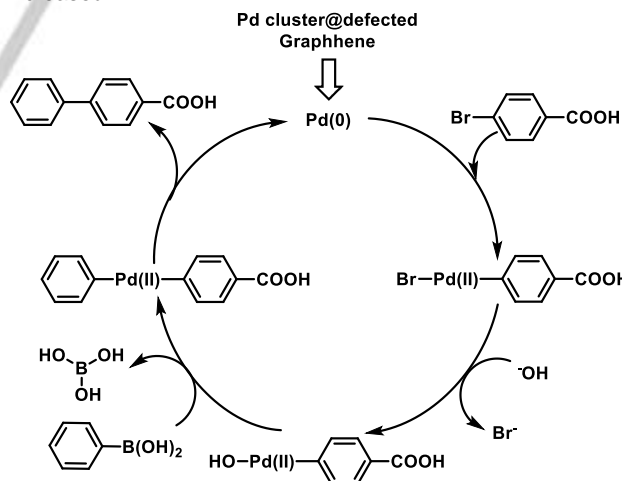
Recent developments in this field by Taniike and co-workers comprised the encapsulation of Pd NPs inside a porous structure of graphene oxide framework (GOF). GO layers were intercalated by two-side covalent links with benzene-1,4-diboronic acid to give GOF with uniform interlayer spaces (Scheme 33).^[152] The porous GOF was allowed to react with PdCl₂ in toluene at 80 °C for 4 h giving Pd@GOF, which was used as an efficient catalyst (2.1 mol% Pd) in the Suzuki reaction of bromobenzene and phenylboronic acid with K₂CO₃ as base in toluene at 80 °C. The

catalytic activity of Pd@GOF was superior to Pd@GO or Pd/C, even the recyclability during five cycles.



Scheme 33. Pd@GOF and its catalytic activity in the Suzuki reaction.

The role of graphene as support in the particle size of Pd NPs was studied by Khanna and co-workers.^[153] They also studied the particle support interactions on both oxidative and reductive steps and the catalytic activity on the Suzuki reaction (Scheme 34). For this purpose, Pd@G was prepared by three ways: (1) in the co-precipitation method (CO), graphene was impregnated with Pd(NO₃)₂ followed by reduction using hydrazine under MW [Pd@G CO (MW)], (2) in the strong electrostatic adsorption (SEA), graphene was added to an aqueous solution of H₂PdCl₄ at pH = 3.25 and the resulting solid was heated at 180 °C under H₂ atmosphere to give Pd@G SEA-H, and (3) strong electrostatic adsorption stabilization of Pd on G followed by solventless MW heating reduction affording Pd@G SEA-MW. Results indicated that the material containing a weakly bound Pd NPs to graphene support showed low catalytic activity but when the Pd precursor and graphene was reduced through microwave irradiation (method 3) an increase of the efficiency resulted due to a stronger interaction between Pd NPs and the support. The microwave irradiation induced defects into the graphene that strongly bind the PdNPs. The catalytic activity was performed in the Suzuki reaction of 4-bromobenzoic acid with phenylboronic acid with 0.5 mol % Pd loading under conventional reaction conditions. Furthermore, results showed that using the MW irradiation method the leaching of Pd was reduced, the activation energy is drastically decreased, and the reaction rates are significantly increased.



Scheme 34. Pd NPs supported on graphene.

Shendage and co-workers have introduced Pd NPs supported on reduced GO using aloe vera extract as reducing agent.^[154] The obtained material was employed in the Suzuki reaction of aryl halides (I, Br, Cl) with arylboronic acids in EtOH/H₂O. Pd@GO demonstrated excellent yields for aryl iodides and bromides and

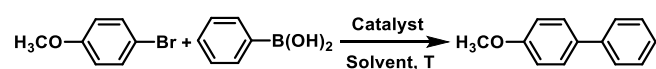
FULL PAPER

low reactivity for chlorobenzene under conventional reaction conditions. The recyclability this catalyst investigated in the reaction of iodobenzene with phenylboronic acid being reused for seven times with yields in the range 110 to 89 %.

As summary for this section, GO usually obtained by Hummers method^[155] from graphite, has been demonstrated to be an excellent support for Pd NPs and for bimetallic NPs.

Comparison of the catalytic activity for the some graphene and graphene oxide supported Pd catalysts in Suzuki and Heck reactions of aryl bromides with phenyl boronic acid and styrene have been shown in Table 3 and Table 4, respectively.

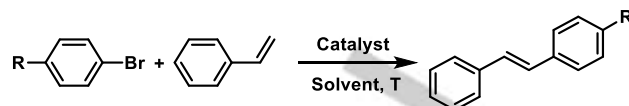
Table 3. Comparison of the catalytic activity for different catalysts of graphene or graphene oxide supported Pd in Suzuki cross coupling reaction.



Catalyst	T (°C)	t (h)	Pd (mol %)	Yield (%)
Pd ²⁺ /GO ^[96]	80	4	0.25	99
Pd@PdO-NDG ^[107]	80	1	20 ^a	90
GO-Pd@Ag-AgBr ^[109]	25	2	25 ^a	99
GO-NH ₂ Pd ^[123]	70	0.17	0.6	80
GO-PdP ₂ ^[125]	80	2	0.5	94
GO-NHC-Pd ²⁺ ^[126]	80	18	0.25	89
GO-NHC-Pd ^[127]	80	1	1	93
Pd ^{II} (BIM)@GO ^[132]	60	0.5	0.35	89
PdCu/RGO ^[134]	80	1.9	0.006	70
Pd-Fe ₃ O ₄ /rGO ^[140]	80	1	0.06	89
GO/Fe ₃ O ₄ /Pd ^[142]	80	0.5	0.5	85
PdNPs-rGO-H ₂ ^[144]	25	2	25 ^a	95
RGO-IL-Pd ^[150]	25	3	0.5	95
GO-CPTMS@Pd-TKHPP ^[151]	80	0.67	10	97

^a Pd catalyst according to mg.

Table 4. Comparison of the results obtained for different catalysts of graphene or graphene oxide supported Pd in Heck coupling reaction.



Catalyst	T (°C)	t (h)	Pd (mol %)	Yield (%)
Pd/G ^[96]	180	0.17	0.3	97 ^a
Pd/PRGO ^[99]	180	0.17	0.5	60 ^a
Pd/Met/GO ^[122]	110	3	0.1	96 ^a
PFG-Pd ^[124]	120	6	1.7	88 ^a
NiFe ₂ O ₄ @GO-Pd ^[139]	80	24	0.3	75 ^a
PdTSPc@KP-GO ^[146]	100	9	0.8	87 ^a
GO-CPTMS@Pd-TKHPP ^[151]	120	40	10	88 ^a
Pd/Met/GO ^[122]	110	3	0.1	95 ^b
PFG-Pd ^[124]	120	8	1.7	90 ^b
NiFe ₂ O ₄ @GO-Pd ^[139]	80	5	0.08	88 ^b
GO-CPTMS@Pd-TKHPP ^[151]	100	1	0.1	85 ^b

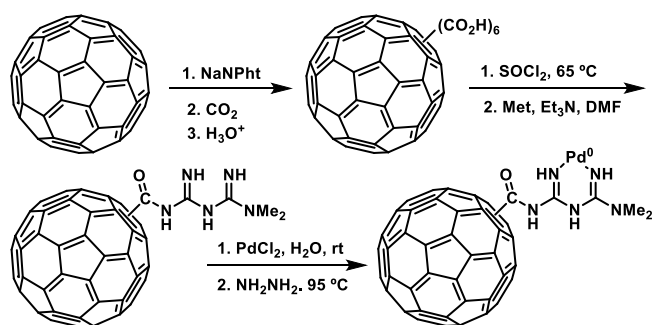
^a R= H

^b R= CH₃

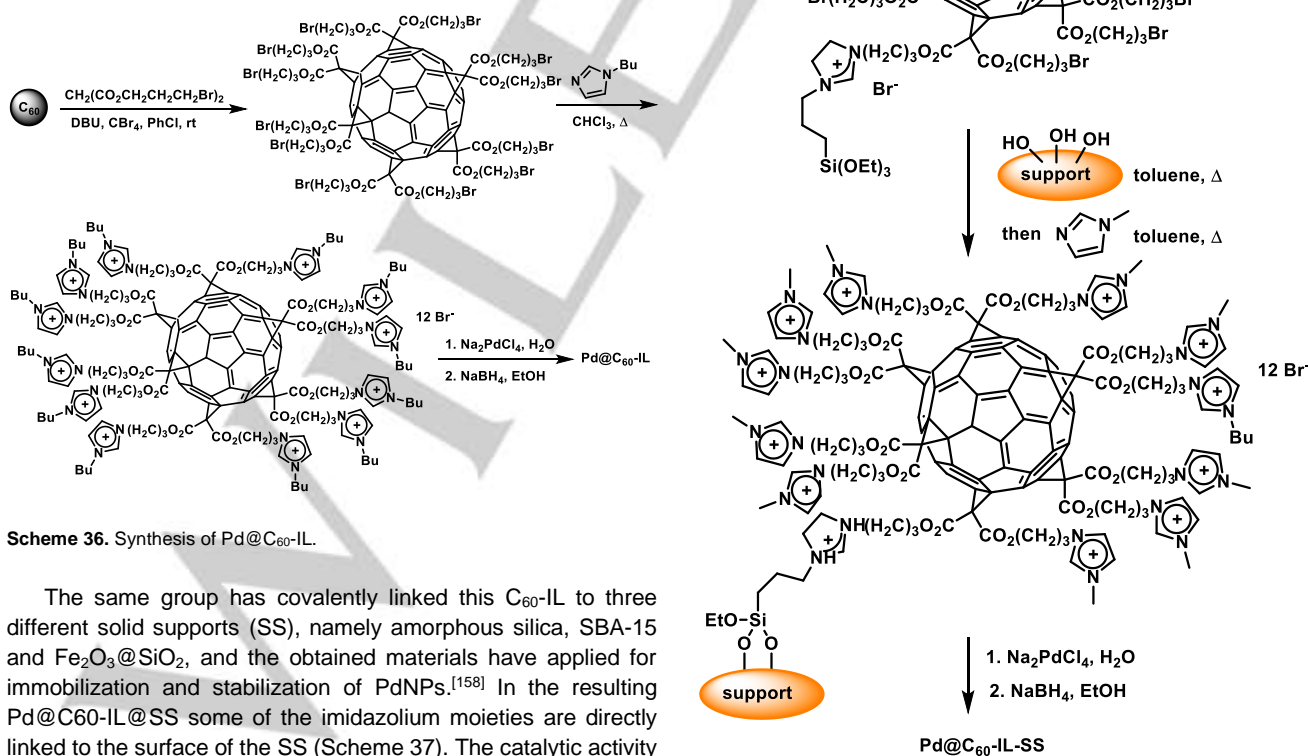
5. Palladium-Supported on C₆₀

Fullerenes can be easily functionalized through a covalent bond with a ligand able to coordinate Pd NPs. Veisi and co-workers have synthesized a heterogeneous palladium nanocatalyst on biguanide (metformine)-functionalized C₆₀ fullerene (Pd@C₆₀-Met) and used as catalyst in the Suzuki reaction.^[156] To the preparation of C₆₀-Met, C₆₀ was first modified with sodium naphthalenide in the presence of carbon dioxide gas giving C₆₀-(COOH)₆, and then the carboxylic groups were allowed to react with thionyl chloride and then with metformine. This material was treated with PdCl₂ in water at rt for 1 d and then treated with hydrazine hydrate at 90 °C for 2 h (Scheme 35). The resulting Pd@C₆₀-Met was employed as catalyst in the Suzuki reaction between aryl halides (I and Br) and phenylboronic acid using 1 mol % Pd in aqueous ethanol at rt. This catalyst provided good to excellent yields for both types of substrates and the recovering experiments were carried out during six cycles for the cross-coupling of iodobenzene with phenylboronic acid with low loss of catalytic activity (98-88 %) and without leaching of Pd.

FULL PAPER

Scheme 35. Synthesis of Pd@C₆₀-Met.

Giacalone, Gruttaduria and co-workers have reported a C₆₀-ionic liquid hybrid C₆₀-IL as support for PdNPs through ion exchange.^[157] C₆₀ was submitted to Bingel cyclopropanation with 3-bromopropyl malonate followed by S_N reaction with 1-butylimidazole under CHCl₃ reflux. This methodology allows the synthesis of the hexakis adduct with twelve ionic liquid moieties (Scheme 36). Through ion metathesis the tetrachloropalladate anion was introduced, which was reduced with NaBH₄ in EtOH affording Pd@C₆₀-IL with Pd NPs mainly with a mean diameter of 1.4±0.5 nm. This hybrid material was used as catalyst in the Suzuki and Heck reactions with 0.2 mol % of Pd loading. In the case of the Suzuki reaction, aryl bromides and chlorides reacted efficiently with phenylboronic acid in the presence of K₂CO₃ as a base in EtOH/H₂O at 50 °C. Recycling experiments for the cross-coupling of 4-bromobenzaldehyde with phenylboronic acid showed that the yield could be maintain during 5 cycles. The arylation of methyl acrylate with iodoarenes using Et₃N as base in DMF/H₂O at 90 °C took place in excellent yields.

Scheme 36. Synthesis of Pd@C₆₀-IL.

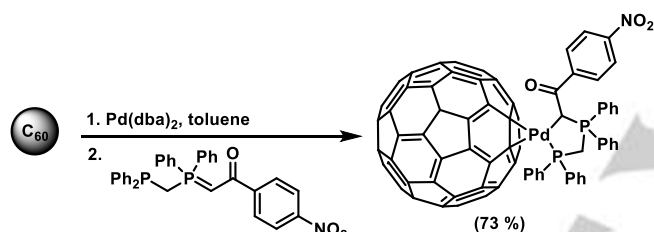
The same group has covalently linked this C₆₀-IL to three different solid supports (SS), namely amorphous silica, SBA-15 and Fe₂O₃@SiO₂, and the obtained materials have applied for immobilization and stabilization of PdNPs.^[158] In the resulting Pd@C₆₀-IL@SS some of the imidazolium moieties are directly linked to the surface of the SS (Scheme 37). The catalytic activity

of three obtained materials were assessed in the Heck and Suzuki reactions. Aryl iodides reacted with styrene or methyl acrylate with 0.1 mol % Pd and Et₃N as base in DMF at 120 °C affording the corresponding products in excellent yields. Recycling experiments with the best catalyst, Pd@C₆₀-IL@SiO₂ for the reaction of 4-iodoanisole with methyl acrylate was performed during nine cycles in quantitative yields. In the case of the Suzuki reaction, 0.01 mol % Pd under the previous described reaction conditions gave excellent yields with remarkable TOF values (up to 3,640,000 h⁻¹). Silica supported catalyst (0.1 mol % Pd) was recycled for ten consecutive runs in the reaction of 4-bromobenzaldehyde with phenylboronic acid with quantitative yields.

FULL PAPER

Scheme 37. Synthesis of Pd@C₆₀-IL@SS.

Mono- and bidentate Pd(0)-C₆₀ complexes prepared by reaction of α -keto phosphorous ylides have been prepared by Sabounchei and co-workers.^[159] These complexes have been prepared by reaction of C₆₀ with Pd(dba)₂ in toluene followed by addition of the phosphorous ylide at rt. The most active catalyst in the Heck reaction was the palladacycle complex working with aryl chlorides and styrene at rt (Scheme 38). The reaction was performed in MeOH with Cs₂CO₃ as a base and 1 mol % of Pd loading not only with electron-withdrawing aryl chlorides but also with deactivated ones in high yields under homogeneous catalysis. The complex has also the beneficial effects of heterogeneous catalysts because it can be recycled during five cycles in the Heck reaction of chlorobenzene with styrene at rt with yields in the range of 90 to 81 %. The same group have used the same palladacycle and also platinacycle as catalysts in the Suzuki reaction of aryl chlorides with phenylboronic acid.^[160] The reactions were carried out with K₂CO₃ as a base in DMF at 130 °C. Parallel experiments with both catalysts demonstrated a better performance of the Pd than the Pt complex in this cross-coupling reaction. However, no recycling experiments were described.

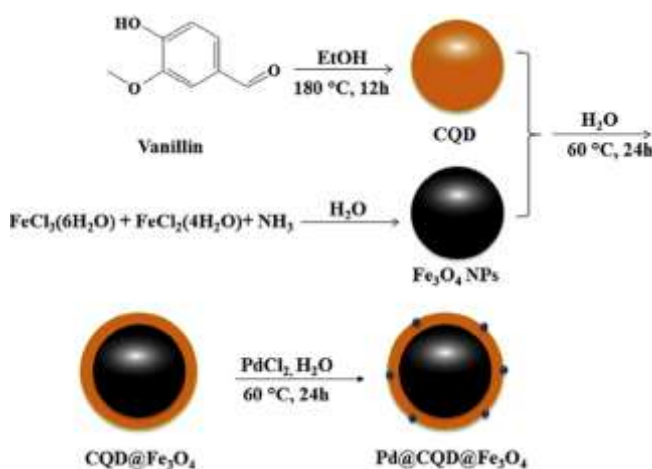
**Scheme 38.** Synthesis of Pd(0)-C₆₀-P,C complex.

6. Palladium-Supported on Carbon Quantum Dots

Fluorescent carbon quantum dots (CQD) are a new class of carbon nanomaterials with size below 10 nm with interesting physical features and applications.^[161] The presence of carboxylic and hydroxy groups in their surface induces high solubility in water and act as nucleation center for the formation of metal NPs. In addition, they are abundant, inexpensive and nontoxic materials appropriate conditions to act as support. They can be prepared by several methods such as pyrolysis, oxidation, ultrasound and microwave-induced synthesis, hydrothermal synthesis and electrochemical etching. Their application as reducing agent for metals, namely palladium, as well as stabilizing material for Pd NPs, due to the formation of layers around the NP surface, was described by Dey, Sharma and co-workers.^[162] They used Pd@CQD as catalyst for the Heck and Suzuki reactions of aryl iodides with styrene and aryl bromides with arylboronic acid, respectively. CQD were prepared by thermal simmering of clotted cream source. The brown residue was separated from the butter oil and dried and was allowed to react with H₂PdCl₄ under water reflux giving Pd@CQD, which was treated with a PVP solution in

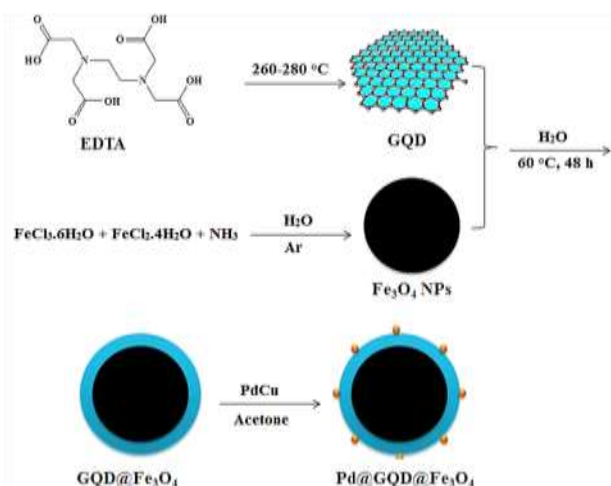
water giving Pd@CQD-PVP for a better stabilization. The Pd NPs were coated by ultrathin CQD shells of ca. 4 nm. The hydroxy, carboxy and epoxy groups on the CQD surface act as efficient reducing agents for the reduction of ionic Pd(II) to Pd NPs. The Suzuki reaction was carried out with 0.5 mol % Pd and KOH as a base in water at 60 °C affording biphenyls in 67-95 % yields. This material was recycled for 3 runs without appreciable agglomeration of the Pd NPs and the CQD layers were intact in the Pd NPs. For the Heck reaction K₂CO₃ in water at 40 °C, using also 0.5 mol % of Pd, gave the corresponding stilbenes in 79-95 % yields.

In 2016, Gholinejad and co-workers reported the synthesis of CQD modified by Fe₃O₄ NPs and used for the reduction of Pd^{II} and the formation of Pd NPs (Pd@Fe₃O₄@CQD).^[163] To prepare this material, CQD were formed from citric acid source and urea by a hydrothermal method in a teflon autoclave at 160 °C. The obtained CQD were allowed to react with Fe₃O₄ NPs in water at 60 °C affording Fe₃O₄@CQD. Treating PdCl₂ and Fe₃O₄@CQD with sonication and heating in water at 60 °C for 1 d, produced Pd@Fe₃O₄@CQD containing mostly reduced Pd(0) species. The catalytic activity of this magnetic material (0.22 mol % Pd) was investigated in the Suzuki reaction of aryl halides (Br, Cl) with arylboronic acids in the aqueous ethanol with K₂CO₃ at rt for ArBr and at 80 °C for ArCl in good yields. This catalyst was reused for nine cycles with small decrease in activity (100-89 %) and 1.26 % Pd leaching. The same group reported the preparation of CQD from vanillin as an ecofriendly and naturally abundant source for modification of magnetic NPs.^[164] CQD were prepared by heating an ethanolic solution of vanillin in an autoclave at 180 °C for 12 h. Freshly prepared Fe₃O₄ NPs were added CQD and heated at 60 °C for 1 d. To this new CQD@Fe₃O₄ magnetic solid was added PdCl₂ in water and heated at 60 °C for 1 d affording Pd@CQD@Fe₃O₄ (Scheme 39). This material was applied as an efficient catalyst (0.1 mol % Pd) for the Suzuki reaction under the previous described reaction conditions. In the case of aryl bromides, the reaction was carried out at room temperature in aqueous EtOH, whereas for aryl chlorides was used PEG 200 as solvent at 120 °C. The recyclability of this catalyst was investigated using 4-bromobenzonitrile and phenylboronic acid for up eight runs with low loss activity (12% in the last cycle).

**Scheme 39.** Synthesis of Pd@CQD@Fe₃O₄.

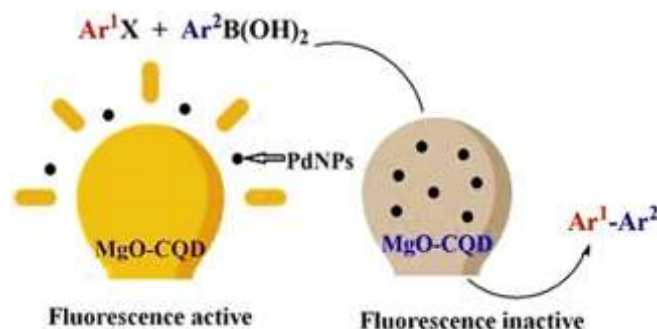
FULL PAPER

Gholinejad and co-workers reported the synthesis of PdCu bimetallic NPs supported on graphene quantum dots (GQD)-modified Fe_3O_4 NPs ($\text{PdCu@GQD@Fe}_3\text{O}_4$) (Scheme 40).^[165] This material is used as an efficient catalyst for the Sonogashira reaction of aryl iodides, bromides, and chlorides in toluene or *N,N*-dimethylacetamide at 60–110 °C in very high yields with 0.3 mol % of Pd loading. Notably, the catalyst can be reused for at least six times without any decline in activity.



Scheme 40. Preparation steps of $\text{PdCu@GQD@Fe}_3\text{O}_4$.

Very recently, also Gholinejad and co-workers have prepared MgO-CQD for the formation and stabilization of Pd NPs (Pd@MgO-CQD).^[166] MgO-CQD was prepared by dissolving $\text{Mg}(\text{NO}_3)_2$ in PEG 200 at rt and then aqueous solutions of Na_2CO_3 and urea were added and the mixture was heated in an autoclave at 160 °C for 2 h. To this MgO-CQD was added aqueous EtOH and then a sonicated solution of PdCl_2 in water and the mixture was heated at 60 °C for 1 d. Using Pd@MgO-CQD (0.3 mol % Pd), the Suzuki reaction of aryl bromides with arylboronic acids was performed in water with K_2CO_3 as base at room temperature in high yields. Only activated aryl chlorides reacted at 80 °C in water affording corresponding biphenyls in 72–98 % yields. In this report for the first time, fluorescence emission of MgO-CQD was applied for determining Pd loading and leaching in the catalyst preparation and recycling process. Results showed that by increasing Pd loading on MgO-CQD, fluorescence emission due to electron-transfer from the CQD to metallic ions decreased. Using a linear equation between content of supported Pd and emission, it is possible to determine the amount of Pd on the support in each stage of a catalytic reaction (Scheme 41). This catalyst was recycled for six runs in the case of the cross-coupling of 4-bromobenzonitrile with phenylboronic acid with yields in the range 100 to 80 %.



Scheme 41. The use of Pd@MgO-CQD in the Suzuki reaction.

6. Palladium-Supported on Other Allotropes of Carbon

Carbon nanofibers (CNFs) as in the case of CNTs are well-defined nanostructures with high surface area and easy separation of the catalyst than conventional active carbon. However, the preparation of CNFs by chemical vapor deposition requires a quartz reactor, the use of H_2 and CO and very high temperatures (600 °C). Yuan and co-workers reported for the first time, CNF-supported Pd NPs and their use as catalyst in the Heck reaction.^[167] The 5 % Pd@CNF was prepared by the incipient wetness impregnation method. Thus, to CNFs was added a solution of PdCl_2 in 2M HCl and the wet solid was dried at 80 °C overnight and then calcinated at 150 °C to 350 °C. The resulting material was reduced under flowing Ar/H_2 at 100–300 °C for 2 h. Study of prepared materials structure indicated that the dispersion of Pd on CNF is strongly dependent on both the calcination and reduction temperatures. By increasing calcination temperature from 150 °C to 250 °C followed by Ar/H_2 reduction at 150 °C, the respective dispersion of Pd/pCNF is increased from 18.0 % to 34.5 %. Results indicated that the obtained Pd@CNF under calcination and reduction temperatures of 250 and 150 °C respectively, is the most efficient catalyst in the Heck reaction of bromobenzene with styrene. The Heck reaction was carried out with 0.01 mol % of Pd, Na OAc as base in NMP at 80 °C for ArI and at 120 °C for ArBr and ArCl with styrene or methyl acrylate. Pd@GNF was reused for six cycles in the reaction of iodobenzene with styrene with quantitative yields.

Bai et al. have prepared Pd@CNFs by combining the electrospinning, gas-phase hydrogenation reduction and subsequent calcination processes.^[168] For preparation of Pd@CNF , firstly polyacrylonitrile (PAN) was allowed to react with PdCl_2 in DMF. Then, CNFs and the resulting PAN- PdCl_2 -DMF were passed through a winding copper wire under the positive voltage. The resulting material was reduced using hydrogen gas at 100 °C and carbonized in a furnace at 270–350 °C under flowing of nitrogen and finally annealed at high temperature. The obtained Pd@CNF were employed as catalyst in the Heck reaction of iodobenzene and acrylates with Et_3N as base in DMF at 125 °C. This group investigated the effect of the different carbonization temperatures (500, 600, 700, 800 and 900 °C) on the yields of the desired products. Results confirmed that the optimal

FULL PAPER

carbonization temperature of 600 °C gave the highest yields. This catalyst was recycled for five consecutive runs maintaining the quantitative yield.

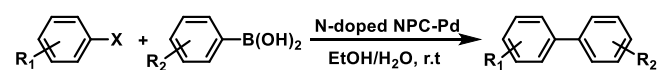
The use of Pd NPs supported on an ionic liquid derived nanofibrillated mesoporous carbon, Pd@IFMC, as catalyst in the Ullmann homocoupling reaction has been described by Karimi and co-workers.^[169] To prepare Pd@IFMC, initially mesoporous silica SBA-15 was prepared from the reaction of pluronic P123 and tetraethyl orthosilicate (TEOS). Then, an acetonitrile solution of 1-methyl-3-phenethyl-1*H*-imidazolium hydrogen sulfate (MPIHS) was allowed to react with SBA-15 and heated at 160 °C and this procedure was repeated. Finally the resulting solid was carbonized at 900 °C giving IFMC. For the immobilization of Pd NPs, Pd(OAc)₂ and IFMC were treated with hydrazine hydrate in THF at rt. This catalyst exhibited excellent yields for aryl iodides and bromides using 0.3 to 1 mol % of Pd, Cs₂CO₃ as a base in water at 80 °C. In the case of the homocoupling of aryl chlorides 1.5 mol % of Pd must be used. The recyclability of Pd@IFMC for the Ullmann reaction of 4-iodoanisole took place efficiently during five runs with yields in the range 99 to 85 %. The same group have used a ionic liquid derived nitrogen-rich mesoporous carbon for supporting Au-Pd bimetallic NPs, AuPd@NMCI, as an efficient catalyst for Ullmann coupling reaction of aryl halides (Br and Cl) at rt.^[170] The Ullmann reaction was carried out with 0.7 to 1.2 mol % Pd and a 2.8:1 Au/Pd ratio, K₂CO₃ as base in EtOH/H₂O (1:4). AuPd@NMCI was reused for five runs without any significant loss in activity in the Ullmann coupling of chlorobenzene to give biphenyl. Leaching of the metals in the solution support a homogeneous reaction pathway.

Carbon aerogels have high mesoporosity and high surface area, have also appropriate carbon materials to support Pd NPs. Vallribera and co-workers have prepared Pd@C-aerogels and tested their catalytic activity in different carbon-carbon bond forming reactions.^[171] The aerogel was prepared by copolymerization of 2,4-dihydrobenzoic acid in water with K₂CO₃ and with formaldehyde at rt for 24 h and at 70 °C for 96 h. To the resulting gel was added Pd(OAc)₂ in acetone for 1 d and dried with supercritical CO₂ and pyrolyzed at 1050 °C. In the case of the Heck reaction of iodobenzene with ethyl acrylate with Et₃N as base under acetonitrile reflux recycling experiments could not be performed. However the hydroxycarbonylation reaction of aryl iodides, with lithium formate and acetic anhydride, as source of CO, with 5 mol % Pd@C-aerogel, LiCl, and diisopropylethylamine (DIPEA) in DMF at 100 °C giving the corresponding benzoic acids with good yields (77-94 %).^[172] Recycling experiments were performed with 4-iodotoluene and ethyl 4-iodobenzoate during twelve and ten runs, respectively. The Sonogashira reaction of aryl iodides and terminal alkynes has been carried out with 6 mol % of Pd loading, CuI (12 mol %), PPh₃ (12 mol %), diisopropylamine as base in DMF at 100 °C giving the corresponding internal alkynes in excellent yields. Recycling experiments for the reaction of 3-iodoanisole and hept-1-yne were performed during 15 runs without leaching of Pd from the catalyst.^[173] This type of material has been also used as catalyst for the Suzuki reaction of aryl iodides and bromides with arylboronic acids with 1 mol % Pd loading, K₂CO₃ as a base under water reflux.^[174] These catalysts demonstrated good to high

catalytic activity and yields for aryl iodides and moderate yields for aryl bromides. Comparison studies about the catalytic activity of Pd@C-aerogel with Ni@C-aerogel showed that the Ni material has slightly higher catalytic activity than the Pd one. These catalysts were recycled for six times without metal leaching.

Colloidal carbon spheres (CSP) are highly dispersible in solvents and have high surface. In 2011, Ghosh and co-workers synthesized Pd@CSP through an *in situ* reducing process in EtOH.^[175] CSP are prepared, following the method described by Sun and co-workers,^[176] from a solution of glucose in EtOH using an autoclave at 180 °C and then PdCl₂ were added in EtOH and heated at 70 °C for 6 h. The TEM image of Pd@CSP showed that the Pd NPs on amphiphilic CSP had spherical shape with an average diameter of ~12 nm and the size of CSP was typically 400–600 nm. The resulting material was applied as catalyst in the Suzuki reaction of aryl halides (I, Br and Cl) with arylboronic acids using 0.2 mol % Pd, K₂CO₃ as a base in aqueous DMF at 90 °C. Good to excellent yields for aryl iodides and bromides and moderate efficiency for aryl chlorides were observed. Recycling studies of this nanocatalyst for the reaction of 4-bromobenzaldehyde with phenylboronic acid in DMF or in water have been successfully performed for four runs with low loss of activity.

Nanoporous carbon material has been recently prepared from MOFs under thermolysis conditions. Wang et al. have reported the synthesis of N-doped nanoporous carbon (NPC) as a support for stabilization Pd NPs, Pd@NPC, by an impregnation method.^[177] This catalyst was obtained from Al-based MOFs (Al-MOF), which was prepared by reaction of AlCl₃·6H₂O and 2-amino-1,4-benzenedicarboxylic acid (H₂N-H₂bda) in methanol by hydrothermal method.^[178] The resulting Al-MOF was carbonized at 800 °C with flowing N₂ giving NPC. Afterwards, Pd NPs were immobilized on NPC by addition of PdCl₂ in water followed by NaBH₄ reduction under water reflux for 2 h (Scheme 42). The Pd@NPC was used as a catalyst in the Suzuki reaction at rt of aryl iodides and bromides with arylboronic acids, in the presence of 0.2 mol % Pd and under conventional reaction conditions giving excellent yields. The catalyst was reused for the reaction of bromobenzene with phenylboronic acid during six runs without leaching of Pd and decreasing in activity.

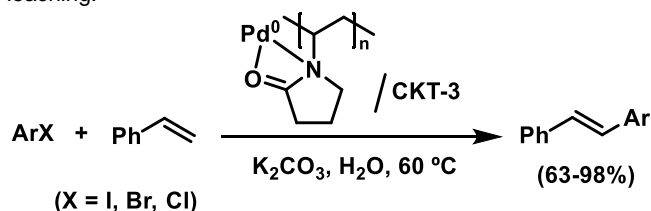


Scheme 42. N-doped Pd@NPC catalyst in Suzuki reaction.

In 2012, Kalbasi and co-workers introduced poly(N-vinyl-2-pyrrolidone)/mesoporous carbon nanocage (CKT-3) for the immobilization of Pd NPs, Pd@PVP/CKT-3.^[179] The procedure used for the fabrication of PVP/CKT-3 involves the preparation of CKT-3 from mesoporous silica (SBA-15) as a template and sucrose as a carbon precursor and CKT-3 was allowed to react with PVP via polymerization.^[180] The resulting material was treated with Pd(OAc)₂ and with hydrazine hydrate as reducing agent. Pd@PVP/CKT-3 was applied in the Heck reaction of aryl halides with styrene with K₂CO₃ as a base in water at 60 °C giving the corresponding stilbenes in excellent yields (Scheme 43). This

FULL PAPER

catalyst was reused for the arylation of styrene with iodobenzene over 10 cycles without any loss in activity and negligible Pd leaching.



Scheme 43. The Heck reaction catalyzed by Pd@PVP/CKT-3.

Hu and co-workers^[181] synthesized Pd NPs embedded in carbon thin film-lined (SBA-15) nanoreactors, through the reaction of the enediyne grafted SBA-15^[182] with Pd. An aqueous solution of H_2PdCl_4 was added to SBA-15 and after stirring for 1 h the water was evaporated and the resulting solid calcinated at 400 °C under H_2/Ar atmosphere during 3 h to afford Pd@SBA-15. The performance of Pd@SBA-15 in the Suzuki reaction has been studied, giving excellent yields for aryl iodides and bromides and moderate yields for aryl chlorides with phenylboronic acid using 0.005 to 0.08 mol % Pd in the presence of K_2CO_3 , TBAB in water at 80 °C (120 °C for PhCl). The Pd@SBA-15 catalyst was easily recovered during five times for the reaction of iodobenzene with phenylboronic acid. Hot filtration test showed that the Pd NPs were tightly attached to the SBA-15 nanoreactor without any leaching of Pd during the recycling process.

Conclusions

Reusable Pd NPs that promote carbon-carbon forming reactions was possible thanks to the existing variety of carbon materials as supports. Carbon-based materials have several advantages as supports of Pd NPs, mainly high surface area and large porosity. In addition, in many cases such as MWCNTs, GO and C_{60} fullerene is possible to bond covalently ligands forming Pd(II) or Pd(0) complexes or NPs. Due to economical, safety and availability properties of Pd/C and the facile separation from the product by simple filtration with low Pd contamination of the product, it has been used in several high scale industrial processes. However, rather high catalyst loading has to be employed in Heck and Sonogashira reactions. Concerning availability, there is a problem related to the different commercially available sources of Pd/C in order to obtain reproducible results. For these reasons, the readily accessible preparation of Pd developed by Lipshutz and co-workers^[37] can be an excellent alternative to the classical palladium-on-charcoal. The functionalization of CNTs allows the covalent bonding of Pd complexes increasing the solubility, catalytic activity and reusability of these type of materials. With respect to GO as carbon support, several magnetic nanocomposites have been prepared using Fe_3O_4 NPs with simplification of the recovery of the corresponding material. Different ligands have been covalently bonded to GO for the complexation of Pd(II) specially nitrogenated compounds as well as NHCs. Several polymers bonded to the support have been also prepared for non-covalent interactions with Pd NPs. In general, these GO derived materials showed high catalytic activity in different carbon-carbon bond

forming reactions specially as easily recovered catalysts. The use of C_{60} derived materials or complexes have shown excellent catalytic performance in Heck and Suzuki reactions including recyclability. However, few applications have been described due to the availability problems of C_{60} . CQDs are very accessible and inexpensive supports for the formation and stabilization of Pd NPs giving very stable materials allowing the determination of Pd content by fluorescence emission. The catalytic activity in the Suzuki reaction is very good in aqueous media and also the recyclability.

Acknowledgements

The authors are grateful to Institute for Advanced Studies in Basic Sciences (IASBS) Research Council and Iran National Science Foundation (INSF-Grant number of 94010666) for support of this work. C. Nájera is also thankful to the Spanish Ministerio de Economía, Industria y Competitividad, Agencia Estatal de Investigación (AEI) and Fondo Europeo de Desarrollo Regional (FEDER, EU) (projects CTQ2016-76782-P and CTQ2016-81797-REDC), the Generalitat Valenciana (PROMETEOII/2014/017) and the University of Alicante for financial support.

Keywords: Cross-coupling reactions • Carbon • Palladium • Nanoparticles • Fullerenes • Graphene

- [1] A. Bej, K. Ghosh, A. Sarkar, D. W. Knight, *RSC Adv.* **2016**, *6*, 11446 – 11453.
- [2] P. Taladriz-Blanco, P. Hervés, J. Pérez-Juste, *Top. Catal.* **2013**, *56*, 1154 – 1170.
- [3] E. J. García-Suárez, P. Lara, A. B. García, K. Philippot, *Recent Pat. Nanotech.* **2013**, *7*, 247 – 264.
- [4] Á. Molnár, *Palladium-Catalyzed Coupling Reactions: Practical Aspects, Future Developments*, Wiley-VCH, Weinheim, **2013**.
- [5] R. Jana, T. P. Pathak, M. S. Sigman, *Chem. Rev.* **2011**, *111*, 1417– 1492.
- [6] A. Fihri, M. Bouhrara, B. Nekoueshahraki, J.-M. Basset, V. Polshettiwar, *Chem. Soc. Rev.* **2011**, *40*, 5181 – 5203.
- [7] M. Lamblin, L. Nassar-Hardy, J. C. Hierso, E. Fouquet, F. X. Felpin, *Adv. Synth. Catal.* **2010**, *352*, 33 – 79.
- [8] M.A.Zolfigol, V. Khakyzadeh, A.R. Mossavi-Zare, A. Rostami, A. Zare, N. Iranpoor, M.H. Beyzavi, R. Luque, *Green Chemistry.* **2013**, *15*, 2132– 2140.
- [9] F.-X. Felpin, T. Ayad, S. Mitra, *Eur. J. Org. Chem.* **2006**, 2679 – 2690.
- [10] D. Gala, A. Stamford, J. Jenkins, M. Kugelman, *Org. Process Res. Dev.* **1997**, *1*, 163 – 164.
- [11] D. S. Ennis, J. McManus, W. Wood-Kaczmar, J. Richardson, G. E. Smith, A. Carstairs, *Org. Process Res. Dev.* **1999**, *3*, 248 – 252.
- [12] F. Zhao, B. M. Bhanage, M. Shirai, M. Arai, *Chem. Eur. J.* **2000**, *6*, 843 – 848.
- [13] H. Hagiwara, Y. Shimizu, T. Hoshi, T. Suzuki, M. Ando, K. Ohkubo, C. Yokoyama, *Tetrahedron Lett.* **2001**, *42*, 4349 – 4351.
- [14] U. C. Dyer, P. D. Shapland, P. D. Tiffin, *Tetrahedron Lett.* **2001**, *42*, 1765 – 1767.

FULL PAPER

- [15] C. R. LeBlond, A. T. Andrews, Y. Sun, J. R. Sowa, *Org. Lett.* **2001**, *3*, 1555 – 1557.
- [16] H. Sakurai, T. Tsukuda, T. Hirao, *J. Org. Chem.* **2002**, *67*, 2721 – 2722.
- [17] R. G. Heidenreich, K. Koehler, J. G. Krauter, J. Pietsch, *Synlett* **2002**, 1118 – 1122.
- [18] Y. Mori, M. Seki, *J. Org. Chem.* **2003**, *68*, 1571 – 1574.
- [19] K. Köhler, R. G. Heidenreich, J. G. Krauter, J. Pietsch, *Chem. Eur. J.* **2002**, *8*, 622 – 631.
- [20] D. A. Conlon, B. Pipik, S. Ferdinand, C. R. LeBlond, J. R. Sowa Jr, B. Izzo, P. Collins, G. J. Ho, J. M. Williams, Y. J. Shi, *Adv. Synth. Catal.* **2003**, *345*, 931 – 935.
- [21] T. Tagata, M. Nishida, *J. Org. Chem.* **2003**, *68*, 9412 – 9415.
- [22] A. Arcadi, G. Cerichelli, M. Chiarini, M. Correa, D. Zorzan, *Eur. J. Prg. Chem.* **2003**, 4080 – 4086.
- [23] M. G. Organ, S. Mayer, *J. Comb. Chem.* **2003**, *5*, 118 – 124.
- [24] X. Xie, J. Lu, B. Chen, J. Han, X. She, X. Pan, *Tetrahedron Lett.* **2004**, *45*, 809 – 811.
- [25] G. Cravotto, M. Beggiato, A. Penoni, G. Palmisano, S. Tollari, J.-M. Lévêque, W. Bonrath, *Tetrahedron Lett.* **2005**, *46*, 2267 – 2271.
- [26] M. Gruber, S. Chouzier, K. Koehler, L. Djakovitch, *Appl. Catal. A: Gen.* **2004**, *265*, 161 – 169.
- [27] V. Polácková, M. Hut'ka, S. Toma, *Ultrasonics Sonochemistry* **2005**, *12*, 99 – 102.
- [28] R. K. Arvela, N. E. Leadbeater, *Org. Lett.* **2005**, *7*, 2101 – 2104.
- [29] G. Lu, R. Franzén, Q. Zhang, Y. Xu, *Tetrahedron Lett.* **2005**, *46*, 4255 – 4259.
- [30] F.-X., Felpin, *J. Org. Chem.* **2005**, *70*, 8575 – 8578.
- [31] J.-z. Jiang, C. Cai, *Colloids Surf. A: Physicochem. Eng. Asp.* **2006**, *287*, 212 – 216.
- [32] J.-S. Chen, A. N. Vasiliev, A. P. Panarello, J. G. Khinast, *Appl. Catal. A: Gen.* **2007**, *325*, 76 – 86.
- [33] Y. Kitamura, S. Sako, T. Udzu, A. Tsutsui, T. Maegawa, Y. Monguchi, H. Sajiki, *Chem. Commun.* **2007**, 5069 – 5071.
- [34] T. Maegawa, Y. Kitamura, S. Sako, T. Udzu, A. Sakurai, A. Tanaka, Y. Kobayashi, K. Endo, U. Bora, T. Kurita, *Chem. Eur. J.* **2007**, *13*, 5937 – 5943.
- [35] S. Mori, T. Yanase, S. Aoyagi, Y. Monguchi, T. Maegawa, H. Sajiki, *Chem. Eur. J.* **2008**, *14*, 6994 – 6999.
- [36] S.-J. Kim, S.-D. Oh, S. Lee, S.-H. Choi, *J. Ind. Eng. Chem.* **2008**, *14*, 449 – 456.
- [37] C. Duplais, A. J. Forman, B. A. Baker, B. H. Lipshutz, *Chem. Eur. J.* **2010**, *16*, 3366 – 3371.
- [38] M. M. Shinde, S. S. Bhagwat, *Colloids Surf. A: Physicochem. Eng. Asp.* **2011**, *380*, 201 – 206.
- [39] C. Rossy, J. Majimel, E. Fouquet, C. Delacôte, M. Boujtita, C. Labrugère, M. Tréguer-Delapierre, F.-X. Felpin, *Chem. Eur. J.* **2013**, *19*, 14024 – 14029.
- [40] W. Tang, J. Li, X. Jin, J. Sun, J. Huang, R. Li, *Catal. Commun.* **2014**, *43*, 75 – 78.
- [41] X. Rao, C. Liu, Y. Zhang, Z. Gao, Z. Jin, *Chin. J. Catal.* **2014**, *35*, 357 – 361.
- [42] C. Liu, C. Liu, X.-M. Li, Z.-M.; Gao, Z.-L. Jin, *Chin. Chem. Lett.* **2016**, *27*, 631 – 634.
- [43] S. Bhavani, M. A. Ashfaq, D. Rambabu, M. B. Rao, M. Pal, *Arab. J. Chem.* **2016**, doi:10.1016/j.arabic.2016.02.002
- [44] B. S. Kumar, R. Anbarasan, A. J. Amali, K. Pitchumani, *Tetrahedron Lett.* **2017**, *58*, 3276 – 3282.
- [45] A. A. Deshmukh, R. U. Islam, M. J. Witcomb, W. A. L. van Otterlo, N. J. Coville, *ChemCatChem* **2010**, *2*, 51 – 54.
- [46] L. Zhang, C. Feng, S. Gao, Z. Wang, C. Wang, *Catal. Commun.* **2015**, *61*, 21 – 25.
- [47] L. Zhang, W.-H. Dong, N.-Z. Shang, C. Feng, S.-T. Gao, C. Wang, *Chin. Chem. Lett.* **2016**, *27*, 149 – 154.
- [48] M. Zeng, Y. Wang, Q. Liu, X. Yuan, R. Feng, Z. Yang, C. Qi, *Int. J. Biol. Macromol.* **2016**, *89*, 449 – 455.
- [49] M. Xu, J. Zhao, G. Shu, X. Zheng, Q. Liu, Y. Wang, M. Zeng, *Int. J. Biol. Macromol.* **2019**, doi: 10.1016/j.ijbiomac.2018.12.013.
- [50] J. Xia, Y. Fu, G. He, X. Sun, X. Wang, *MATER CHEM PHYS* **2018**, *209*, 86 – 94.
- [51] H. Yoon, S. Ko, J. Jang, *Chem. Commun.* **2007**, 1468 – 1470.
- [52] X. Duan, J. Liu, J. Hao, L. Wu, B. He, Y. Qiu, J. Zhang, Z. He, J. Xi, S. Wang, *Carbon* **2018**, *130*, 806 – 813.
- [53] G. Ji, Y. Duan, S. Zhang, Y. Yang, *Catal. Today* **2019**, doi: 10.1016/j.cattod.2018.04.036.
- [54] A. Modak, A. Bhaumik, *J. Mol. Catal. A: Chem.* **2016**, *425*, 147 – 156.
- [55] Y. Duan, M. Xiao, S. Liang, Z. Zhang, Y. Zeng, J. Xi, S. Wang, *Carbon* **2017**, *119*, 326 – 331.
- [56] A. H. Labulo, B. S. Martincigh, B. Omondi, V. O. Nyamori, *J. Mater. Sci.* **2017**, *52*, 9225 – 9248.
- [57] X. R. Ye, Y. H. Li, C. M. Wai, *Chem. Commun.* **2003**, 642 – 643.
- [58] X. R. Ye, Y. H. Li, C. Wang, M. H. Engelhard, Y. Wang, C. M. Wai, *J. Mat. Chem.* **2004**, *14*, 908 – 913.
- [59] H. B. Pan, C. H. Yen, B. Yoon, M. Sato, C. M. Wai, *Synth. Commun.* **2006**, *36*, 3473 – 3478.
- [60] X. Chen, Y. Hou, H. Wang, Y. Cao, J. He, *J. Phys. Chem. C* **2008**, *112*, 8172 – 8176.
- [61] N. Karousis, G.-E. Tsotsou, F. Evangelista, P. Rudolf, N. Ragoussis, N. Tagmatarchis, *J. Phys. Chem. C* **2008**, *112*, 13463 – 13469.
- [62] Y. Zhang, W. Chu, L. Xie, W. Sun, *Chin. J. Chem.* **2010**, *28*, 879 – 883.
- [63] M. Cano, A. Benito, W. K. Maser, E. P. Urriolabeitia, *Carbon* **2011**, *49*, 652 – 658.
- [64] J. A. Sullivan, K. A. Flanagan, H. Hain, *Catal. Today* **2009**, *145*, 108 – 113.
- [65] T. Sainsbury, D. Fitzmaurice, *Chem. Mater.* **2004**, *16*, 2174 – 2179.
- [66] J. Y. Kim, Y. Jo, S.-K. Kook, S. Lee, H. C. Choi, *J. Mol. Catal. A: Chem.* **2010**, *323*, 28 – 32.
- [67] G. M. Neelgund, A. Oki, *Appl. Catal. A: Gen.* **2011**, *399*, 154 – 160.
- [68] I. Janowska, K. Chizari, J.-H. Olivier, R. Ziessel, M. J. Ledoux, C. Pham-Huu, *CR Chim.* **2011**, *14*, 663 – 670.
- [69] L. Rodríguez-Pérez, C. Pradel, P. Serp, M. Gómez, E. Teuma, *ChemCatChem* **2011**, *3*, 749 – 754.
- [70] S. Santra, P. Ranjan, P. Bera, P. Ghosh, S. K. Mandal, *RSC Adv.* **2012**, *2*, 7523 – 7533.
- [71] D. V. Jawale, E. Gravel, C. Boudet, N. Shah, V. Geertsen, H. Li, I. N. Namboothiri, E. Doris, *Catal. Sci. Technol.* **2015**, *5*, 2388 – 2392.
- [72] M. Navidi, N. Rezaei, B. Movassagh, *J. Organomet. Chem.* **2013**, *743*, 63 – 69.
- [73] B. Cornelio, G. A. Rance, M. Laronge-Cochard, A. Fontana, J. Sapi, A. N. Khlobystov, *J. Mater. Chem. A* **2013**, *1*, 8737 – 8744.
- [74] G. Nie, L. Zhang, Y. Cui, *React. Kinet. Mech. Cat.* **2013**, *108*, 193 – 204.
- [75] A. R. Siamaki, Y. Lin, K. Woodberry, J. W. Connell, B. F. Gupton, *J. Mater. Chem. A* **2013**, *1*, 12909 – 12918.
- [76] W. Sun, Z. Liu, C. Jiang, Y. Xue, W. Chu, X. Zhao, *Catal. Today* **2013**, *212*, 206 – 214.

FULL PAPER

- [77] H. Veisi, A. Khazaei, M. Safaei, D. Kordestani, *J. Mol. Catal. A: Chem.* **2014**, *382*, 106 – 113.
- [78] H. Liu, L. Zhang, N. Wang, D. S. Su, *Angew. Chem., Int. Ed.* **2014**, *53*, 12634 – 12638.
- [79] B. Movassagh, F. S. Parvis, M. Navidi, *Appl. Organomet. Chem.* **2015**, *29*, 40 – 44.
- [80] H. Zhang, F. Huang, C. Yang, X. Liu, S. Ren, *React. Kinet. Mech. Cat.* **2015**, *114*, 489 – 499.
- [81] F. Yang, C. Chi, S. Dong, C. Wang, X. Jia, L. Ren, Y. Zhang, L. Zhang, Y. Li, *Catal. Today* **2015**, *256*, 186 – 192.
- [82] H.-q. Song, Q. Zhu, X.-j. Zheng, X.-g. Chen, *J. Mater. Chem. A* **2015**, *3*, 10368 – 10377.
- [83] M. Radtke, S. Stumpf, B. Schröter, S. Höppener, U. S. Schubert, A. Ignaszak, *Tetrahedron Lett.* **2015**, *56*, 4084 – 4087.
- [84] R. Ghorbani-Vaghei, S. Hemmati, M. Hashemi, H. Veisi, *CR Chim.* **2015**, *18*, 636 – 643.
- [85] A. R. Hajipour, Z. Khorsandi, *Appl. Organomet. Chem.* **2016**, *30*, 256 – 261.
- [86] A. Ohtaka, J. M. Sansano, C. Nájera, I. Miguel-García, A. Berenguer-Murcia, D. Cazorla-Amorós, *ChemCatChem* **2015**, *7*, 1841 – 1847.
- [87] E. Mohammadi, Z. Hajilou, B. Movassagh, *Helv. Chim. Acta* **2016**, *99*, 747 – 752.
- [88] S. Abbasi, M. Hekmati, *Appl. Organomet. Chem.* **2017**, *31*, 3600-3608.
- [89] M. Savastano, P. Arranz-Mascarós, C. Bazzicalupi, M. P. Clares, M. L. Godino-Salido, M. D. Gutiérrez-Valero, M. Inclán, A. Bianchi, E. García-España, R. López-Garzón, *J. Catal.* **2017**, *353*, 239 – 249.
- [90] D. Khalili, A. R. Banazadeh, E. Etemadi-Davan, *Catal. Lett.* **2017**, *147*, 2674 – 2687.
- [91] L.-L. Wang, L.-P. Zhu, N.-C. Bing, L.-J. Wang, *J. Phys. Chem. Solids* **2017**, *107*, 125 – 130.
- [92] S. Korwar, M. Burkholder, S. E. Gilliland, K. Brinkley, B. F. Gupton, K. C. Ellis, *Chem. Commun.* **2017**, *53*, 7022 – 7025.
- [93] D. Kalyani, N. R. Deprez, L. V. Desai, M. S. Sanford, *J. Am. Chem. Soc.* **2005**, *127*, 7330 – 7331.
- [94] S. Sadjadi, M.M. Heravi, M. Raja, *Carbohydr. Polym.* **2018**, *185*, 48 – 55.
- [95] R. Yu, R. Liu, J. Deng, M. Ran, N. Wang, W. Chu, Z. He, Z. Du, C. Jiang, W. Sun, *Catal. Sci. Technol.* **2018**, *8*, 1423 – 1434.
- [96] G. M. Scheurmann, L. Rumi, P. Steurer, W. Bannwarth, R. Mülhaupt, *J. Am. Chem. Soc.* **2009**, *131*, 8262 – 8270.
- [97] L. Rumi, G. M. Scheurmann, R. Mülhaupt, W. Bannwarth, *Helv. Chim. Acta* **2011**, *94*, 966 – 976.
- [98] A. R. Siamaki, S. K. Abd El Rahman, V. Abdelsayed, M. S. El-Shall, B. F. Gupton, *J. Catal.* **2011**, *279*, 1 – 11.
- [99] S. Moussa, A. R. Siamaki, B. F. Gupton, M. S. El-Shall, *ACS Catal.* **2012**, *2*, 145 – 154.
- [100] Y. V. Ioni, S. Lyubimov, A. Korlyukov, M. Y. Antipin, V. Davankov, S. Gubin, *Russ. Chem. B.* **2012**, *61*, 1825 – 1827.
- [101] Y. Nishina, J. Miyata, R. Kawai, K. Gotoh, *RSC Adv.* **2012**, *2*, 9380 – 9382.
- [102] G. Xiang, J. He, T. Li, J. Zhuang, X. Wang, *Nanoscale* **2011**, *3*, 3737 – 3742.
- [103] S. Santra, P. K. Hota, R. Bhattacharyya, P. Bera, P. Ghosh, S. K. Mandal, *ACS Catal.* **2013**, *3*, 2776 – 2789.
- [104] P. Wang, G. Zhang, H. Jiao, L. Liu, X. Deng, Y. Chen, X. Zheng, *Appl. Catal. A: Gen.* **2015**, *489*, 188 – 192.
- [105] S. S. Shendage, A. S.; Singh, J. M. Nagarkar, *Tetrahedron Lett.* **2014**, *55*, 857 – 860.
- [106] L. Ren, F. Yang, Y. Li, T. Liu, L. Zhang, G. Ning, Z. Liu, J. Gao, C. Xu, *RSC Adv.* **2014**, *4*, 26804 – 26809.
- [107] B. Jiang, S. Song, J. Wang, Y. Xie, W. Chu, H. Li, H. Xu, C. Tian, H. Fu, *Nano Res.* **2014**, *7*, 1280 – 1290.
- [108] S. K. Movahed, M. Dabiri, A. Bazgir, *Appl. Catal. A-Gen.* **2014**, *488*, 265 – 274.
- [109] S. Gao, N. Shang, C. Feng, C. Wang, Z. Wang, *RSC Adv.* **2014**, *4*, 39242 – 39247.
- [110] J. Liu, X. Huo, T. Li, Z. Yang, P. Xi, Z. Wang, B. Wang, *Chem. Eur. J.* **2014**, *20*, 11549 – 11555.
- [111] X. Wang, W. Chen, L. Yan, *Mater. Chem. Phys.* **2014**, *148*, 103 – 109.
- [112] M. Lee, B.-H. Kim, Y. Lee, B.-T. Kim, J. B. Park, *Bull. Korean Chem. Soc.* **2014**, *35*, 1979 – 1984.
- [113] K. Qu, L. Wu, J. Ren, X. Qu, *ACS Appl. Mater. Interf.* **2012**, *4*, 5001 – 5009.
- [114] C. Putta, V. Sharavath, S. Sarkar, S. Ghosh, *RSC Adv.* **2015**, *5*, 6652 – 6660.
- [115] V. Sharavath, S. Ghosh, *RSC Adv.* **2014**, *4*, 48322 – 48330.
- [116] C. Bai, Q. Zhao, Y. Li, G. Zhang, F. Zhang, X. Fan, *Catal. Lett.* **2014**, *144*, 1617 – 1623.
- [117] Q. Zhao, Y. Zhu, Z. Sun, Y. Li, G. Zhang, F. Zhang, X. Fan, X. *J. Mater. Chem. A* **2015**, *3*, 2609 – 2616.
- [118] S. Rana, S. Maddila, K. Yalagala, S. B. Jonnalagadda, *Appl. Catal. A-Gen.* **2015**, *505*, 539 – 547.
- [119] S. J. Hoseini, H. G. Khozestan, R. H. Fath, *RSC Adv.* **2015**, *5*, 47701 – 47708.
- [120] R. H. Fath, S. J. Hoseini, *J. Organomet. Chem.* **2017**, *828*, 16 – 23.
- [121] S. Wang, D. Hu, W. Hua, J. Gu, Q. Zhang, X. Jia, K. Xi, *RSC Adv.* **2015**, *5*, 53935 – 53939.
- [122] H. Veisi, N. Mirzaee, *Appl. Organomet. Chem.* **2018**, *32*, 4067-4073.
- [123] Oliveira, R. L.; Oliveira, C. S.; Landers, R.; Correia, C. R., *ChemistrySelect* **2018**, *3*, 535 – 543.
- [124] R. Fareghi-Alamdari, M. G. Haqiqi, N. Zekri, *New J. Chem.* **2016**, *40*, 1287 – 1296.
- [125] H. Joshi, K. N. Sharma, A. K. Sharma, A. K. Singh, *Nanoscale* **2014**, *6*, 4588 – 4597.
- [126] N. Shang, S. Gao, C. Feng, H. Zhang, C. Wang, Z. Wang, *RSC Adv.* **2013**, *3*, 21863 – 21868.
- [127] J. H. Park, F. Raza, S.-J. Jeon, H.-I. Kim, T. W. Kang, D. Yim, J.-H. Kim, *Tetrahedron Lett.* **2014**, *55*, 3426 – 3430.
- [128] S. K. Movahed, R. Esmatpoursalmani, A. Bazgir, *RSC Advances* **2014**, *4*, 14586 – 14591.
- [129] D. Liu, C. Zhang, F. Wang, Z. Huang, N. Zhang, H. Zhou, Y. Kuang, *J. Mater. Chem. A* **2015**, *3*, 16583 – 16589.
- [130] S. Kim, H.-J. Cho, D.-S. Shin, S.-M. Lee, *Tetrahedron Lett.* **2017**, *58*, 2421 – 2425.
- [131] Y. Huang, Q. Wei, Y. Wang, L. Dai, *Carbon* **2018**, *136*, 150 – 159.
- [132] M. Moghadam, H. Salavati, Z. Pahlevanneshan, *J. Iran. Chem. Soc.* **2018**, *15*, 529 – 536.
- [133] Y.-S. Feng, X.-Y. Lin, J. Hao, H.-J. Xu, *Tetrahedron* **2014**, *70*, 5249 – 5253.
- [134] S. J. Hoseini, H. A. Agahi, Z. S. Fard, R. H. Fath, M. Bahrami, *Appl. Organomet. Chem.* **2017**, *31*, 3607-3615.
- [135] L. Ma'mani, S. Miri, M. Mahdavi, S. Bahadorikhalili, E. Lotfi, A. Foroumadi, A. Shafiee, *RSC Adv.* **2014**, *4*, 48613 – 48620.

FULL PAPER

- [136] M. Kim, H. Kang, K. H. Park, *Catal. Commun.* **2015**, *72*, 150 – 155.
- [137] S. J. Hoseini, V. Heidari, H. Nasrabadi, *J. Mol. Catal. A: Chem.* **2015**, *396*, 90 – 95.
- [138] H. A. Elazab, A. R. Siamaki, S. Moussa, B. F. Gupton, M. S. El-Shall, *Appl. Catal. A-Gen.* **2015**, *491*, 58 – 69.
- [139] X. Liu, X. Zhao, J. Zhu, J. Xu, *Appl. Organomet. Chem.* **2016**, *30*, 354 – 359.
- [140] W. Fu, Z. Zhang, P. Zhuang, J. Shen, M. Ye, *J. Colloid Interf. Sci.* **2017**, *497*, 83 – 92.
- [141] H. A. Elazab, S. Moussa, A. R. Siamaki, B. F. Gupton, M. S. El-Shall, *Catal. Lett.* **2017**, *147*, 1510 – 1522.
- [142] N. Seyedi, K. Saidi, H. Sheibani, *Catal. Lett.* **2018**, *148*, 277 – 288.
- [143] S. Rostamnia, B. Zeynizadeh, E. Doustkhah, H. G. Hosseini, *J. Colloid Interf. Sci.* **2015**, *451*, 46 – 52.
- [144] N. Hussain, A. Borah, G. Darabdhara, P. Gogoi, V. K. Azhagan, M. V. Shelke, M. R. Das, *New J. Chem.* **2015**, *39*, 6631 – 6641.
- [145] A. Mahanta, N. Hussain, M. R. Das, A. J. Thakur, U. Bora, *Appl. Organomet. Chem.* **2017**, *31*, 3679-3684.
- [146] Z. Hezarkhani, A. Shaabani, *RSC Adv.* **2016**, *6*, 98956 – 98967.
- [147] H. Mahdavi, O. Rahmani, *Catal. Lett.* **2016**, *146*, 2292 – 2305.
- [148] X. Ni, Z. Wu, X. Gu, D. Wang, C. Yang, P. Sun, Y. Li, *Langmuir* **2017**, *33*, 8157 – 8164.
- [149] T. H. Kwon, K. Y. Cho, K.-Y. Baek, H. G. Yoon, B. M. Kim, *RSC Adv.* **2017**, *7*, 11684 – 11690.
- [150] X. Shi, C. Cai, *New J. Chem.* **2018**, *42*, 2364 – 2367.
- [151] K. Bahrami, S. N. Kamrani, *Appl. Organomet. Chem.* **2018**, *32*, 4102 – 4111.
- [152] T. P. N. Tran, A. Thakur, D. X. Trinh, A. T. N. Dao, T. Taniike, *Appl. Catal. A: Gen.* **2018**, *549*, 60 – 67.
- [153] Y. Yang, A. C. Reber, S. E. Gilliland, C. E. Castano, B. F. Gupton, S. N. Khanna, *J. Catal.* **2018**, *360*, 20 – 26.
- [154] P. A. Kulkarni, S. S. Shendage, A. G. Awale, *Orient. J. Chem.* **2018**, *34*, 881 – 886.
- [155] W. S. Hummers, R. E. Offemann, *J. Am. Chem. Soc.* **1958**, *80*, 1339 – 1340.
- [156] H. Veisi, R. Masti, D. Kordestani, M. Safaei, O. Sahin, *J. Mol. Catal. A Chem.* **2014**, *385*, 61 – 67.
- [157] V. Campisciano, V. Parola, L. F. Liotta, F. Giacalone, M. Gruttadauria, *Chem. Eur. J.* **2015**, *21*, 3327 – 3334.
- [158] F. Giacalone, V. Campisciano, C. Calabrese, V. Parola, L. F. Liotta, C. Aprile, M. Gruttadauria, *J. Mater. Chem. A*, **2016**, *4*, 17193 – 17206.
- [159] S. J. Sabounchei, A. Hashemi, M. Hosseinzadeh, S. Salehzadeh, F. Maleki, *Catal. Lett.* **2017**, *147*, 2319 – 2331.
- [160] S. J. Sabounchei, K. Badpa, A. Hashemi, S. Salehzadeh, F. Maleki, L. Hosseinzadeh, *Appl. Organometal. Chem.* **2018**, *32*, 4382-4397.
- [161] S. Y. Lim, W. Shen, Z. Gao, *Chem. Soc. Rev.* **2015**, *44*, 362 – 381.
- [162] D. Dey, T. Bhattacharya, B. Majumdar, S. Mandani, B. Sharma, T. K. Sarma, *Dalton Trans.* **2013**, *42*, 13821 – 13825.
- [163] M. Gholinejad, M. Seyedhamzeh, M. Razeghi, C. Nájera, M. Kompany-Zareh, *ChemCatChem* **2016**, *8*, 441 – 447.
- [164] M. Gholinejad, C. Nájera, F. Hamed, M. Seyedhamzeh, M. Bahrami, M.; Kompany-Zareh, *Tetrahedron* **2017**, *73*, 5585 – 5592.
- [165] M. Gholinejad, J. Ahmadi, C. Nájera, M. Seyedhamzeh, F. Zareh, M. Kompany-Zareh, *CemCatChem* **2017**, *9*, 1442-1449.
- [166] M. Gholinejad, M. Bahrami, C. Nájera, *Mol. Catal.* **2017**, *433*, 12 – 19.
- [167] J. Zhu, J. Zhou, T. Zhao, X. Zhou, D. Chen, W. Yuan, *Appl. Catal. A Gen.* **2009**, *352*, 243 – 250.
- [168] L. Guo, J. Bai, C. Li, H. Liang, W. Sun, Q. Meng, T. Xu, *New J. Chem.* **2013**, *37*, 4037 – 4044.
- [169] B. Karimi, H. Behzadnia, H. Vali, *ChemCatChem* **2014**, *6*, 745 – 748.
- [170] B. Karimi, H. Barzegar, H. Vali, *Chem. Commun.* **2018**, *54*, 7155 – 7158.
- [171] S. Martínez, A. Vallribera, C. L. Cotet, M. Popovici, L. Martín, A. Tpig, M. Moreno-Mañas, E. Molins, *New J. Chem.* **2005**, *29*, 1342 – 1345.
- [172] S. Cacchi, C. L. Colet, G. Fabrizi, G. Forte, A. Goggiamani, L. Martín, S. Martínez, E. Molins, M. Moreno-Mañas, F. Petrucci, A. Roig, A. Vallribera, *Tetrahedron*, **2007**, *63*, 2519 – 2523.
- [173] R. Soler, S. Cacchi, G. Fabrizi, G. Forte, L. Martín, S. Martínez, E. Molins, M. Moreno-Mañas, F. Petrucci, A. Roig, R. M. Sebastian, A. Vallribera, *Synthesis* **2007**, 3068 – 3072.
- [174] L. Martín, E. Molins, A. Vallribera, *Tetrahedron* **2012**, *68*, 6517 – 6520.
- [175] C. B. Putta, S. Ghosh, *Adv. Synth. Catal.* **2011**, *353*, 1889 – 1896.
- [176] X. Sun, Y. Li, *Angew. Chem., Int. Ed.* **2004**, *43*, 597 – 601.
- [177] L. Zhang, C. Feng, S. Gao, Z. Wang, C. Wang, *Catal. Commun.* **2015**, *61*, 21 – 25.
- [178] T. Ahnfeldt, N. Guillou, D. Gunzelmann, I. Margilaki, T. Loiseau, G. Ferrey, J. Senker, N. Stock, *Angew. Chem., Int. Ed.* **2009**, *48*, 5163 – 5166.
- [179] R. J. Kalbasi, N. Mosaddegh, A. Abbaspourrad, *Tetrahedron Lett.* **2012**, *53*, 3763 – 3766.
- [180] R. J. Kalbasi, N. Mosaddegh, *Mat. Chem. Phys.* **2011**, *130*, 1287 – 1293.
- [181] J. Zhi, D. Song, Z. Li, X. Lei, A. Hu, *Chem. Commun.* **2011**, *47*, 10707 – 10709.
- [182] X. Yang, Z. Li, J. Zhi, J. Ma, A. Hu, *Langmuir* **2010**, *26*, 11244 – 11248.

Biographies:



Mohammad Gholinejad was born in Tabriz (Iran). He took a Ph.D. degree in Organic Chemistry from Shiraz University under the supervision of Professor Habib Firouzabadi and Professor Nasser Iranpoor, followed by a six months sabbatical period at the University of Alicante under the supervision of Professor Carmen Najera. In September 2012, he joined the Department of Chemistry at the Institute for Advanced Studies in Basic Sciences (IASBS University), Zanjan, Iran as an Assistant Professor. His research interests include organic reactions catalyzed by organometallic reagents and nanoparticles.

FULL PAPER



Zhwan Naghshbandi was born in 1991 in Sanandaj (Iran). She received her BSc and MSc in chemistry from Kurdistan University (2013) and Tabriz University (2016), respectively. She is currently a Ph.D. candidate at the Institute for Advanced Studies in Basic Sciences, Zanjan (Iran), working under the supervision of Dr. Mohammad Gholinejad. Her current research is about the synthesis and characterization of metal catalysts.



Carmen Nájera was born in Nájera (La Rioja) in 1951 and was graduated from the University of Zaragoza in 1973, obtaining her doctorate in chemistry from the University of Oviedo in 1979. She

spent postdoctoral stays at the ETH (Zurich), the Dyson Perrins Laboratory (Oxford), Harvard University, and Uppsala University. She became Associate Professor in 1985 at the University of Oviedo and Full Professor in 1993 at the University of Alicante. She is coauthor of more than 400 papers (h 64), 6 patents and 30 book chapters and has supervised more than 45 PhD students. She has been awarded with the 2006 Organic Chemistry Prize from the Spanish Royal Chemical Society of Chemistry, the 2006 Rosalind Franklin International Lectureship from the English Royal Society, the SCF 2010 French-Spanish Prize from the Société Chimique de France, the IUPAC 2015 Distinguished Women in Chemistry or Chemical Engineering Award and the 2018 Serratosa lectureship. In 2012 she was named full Member of the Royal Spanish Academy of Sciences and was appointed as Active Member of the European Academy of Sciences and Arts. In 2016-2017 was named ChemPubSoc Europe Fellow. Professor Nájera has been in the Advisory Board of several international journals including ChemCatChem and also of the GADEA for Science Foundation.

FULL PAPER

Layout 2:

FULL PAPER

Fashion carbon: supported palladium nanoparticles on carbon-based materials such as carbon black, carbon nanotubes, graphene and graphene oxide, C₆₀, carbon quantum dots, carbon nanofibers and other allotropes of carbon show excellent performance as recoverable catalysts in several carbon-carbon bonds forming reactions, mainly in Suzuki-Miyaura, Mizoroki-Heck and Sonogashira-Hagihara reactions.

Mohammad Gholinejad, Zhwan Naghshbandi and Carmen Nájera

Page No. - Page No.

Carbon-Derived Supports for Palladium Nanoparticles as Catalysts for Carbon-Carbon Bonds Formation

