Polymeric Catalysts Hot Paper

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A Polyphenylene Support for Pd Catalysts with Exceptional Catalytic Activity**

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Dedicated to the MPI für Kohlenforschung on the occasion of its centenary

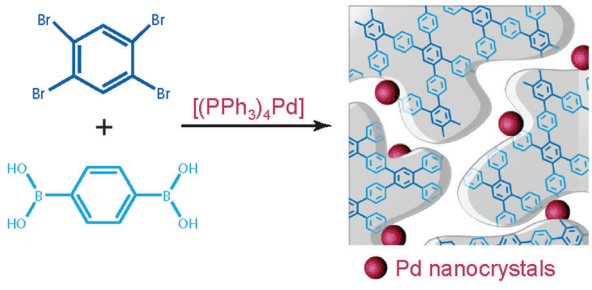
Abstract: *We describe a solid polyphenylene support that serves as an excellent platform for metal-catalyzed reactions that are normally carried out under homogeneous conditions. The catalyst is synthesized by palladium-catalyzed Suzuki coupling which directly results in formation of palladium nanoparticles confined to a porous polyphenylene network. The composite solid is in turn highly active for further Suzuki coupling reactions, including non-activated substrates that are challenging even for molecular catalysts.*

A major goal in catalysis is to combine the advantages of molecular catalysts and heterogeneous processes, ideally maintaining—or even improving—the reactivity and selectivity of the molecular catalysts, while facilitating product recovery and catalyst recycling.[1–3] However, in fine-chemicals synthesis molecular catalysts are predominantly used, partly because typical solids do not provide the nonpolar environments often required for organic reactions. This is often easier realized with metal complexes and suitable ligands and solvents, which provide the required geometry and stabilize the transition state of the reaction.[4–6] Polymers as less conventional supports could provide a "solvent"-like reaction environment, onto which ligands and metal complexes can be grafted to provide the catalytic functionality.[7,8] Polymeric solids based on polystyrene,[9,10] polydivinylbenzene (PDVB),[11] polyacrylate derivatives,[12] covalent organic frameworks (COF),[13] and hybrid metal–organic frameworks[14–16] have recently been explored as carriers for catalytic metal nanoparticles.

Commercially, polymeric catalyst supports are limited to ion-exchange resins, for example, the Amberlyst series based on polystyrene-*co*-divinylbenzene. Also carbon materials are widely applied when an apolar carrier material is required to host metal catalytic species.[17] In our search for intermediate materials between carbons and the polymers listed above, we decided to study the performance of polyphenylene (PPhen) in catalysis. In this polymer, all the carbon atoms are sp^2 hybridized. The thermal and chemical stability of PPhen is higher than those of most other polymers, while it still provides a "solvent-like" reaction environment, suggesting its suitability for organic transformations.

The catalyst consists of Pd nanocrystals supported on a porous polyphenylene network, and is synthesized by the palladium-catalyzed cross-coupling of 1,2,4,5-tetrabromobenzene and benzene-1,4-diboronic acid.[18,19] The cross-coupling catalyst, tetrakis(triphenylphosphine)palladium [$Pd(PPh_3)_4$], was found to decompose at 150 °C in dimethylformamide into palladium nanocrystals with a broad particle size distribution, from less than 5 nm to several tens of nanometers (Figure S1). Combining the decomposition of the palladium complex with the in situ catalyzed polymerization reaction enables confinement of the nascent Pd particles in the developing polymer network (Scheme 1).

After 20 h of reaction at 150 °C, the cross-coupling reaction results in a gray solid which can be readily isolated from the reaction medium. All reflections in the X-ray



Scheme 1. Formation of Pd/PPhen by [$(Ph_3P)_4Pd$]-catalyzed coupling of 1,2,4,5-tetrabromobenzene and benzene-1,4-diboronic acid.

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diffraction (XRD) pattern can be assigned to palladium nanocrystals, indicating the amorphous character of the polyphenylene polymer (Figure S2). Under standard reaction conditions, the palladium loading in the resulting solid is 2.7 wt%; this can be varied by simply adjusting the molar ratio of $[Pd(PPh_3)_4]$ to C–C coupling substrates in the reaction media (Figure S3). Performing the reaction at a lower temperature of 100°C produced the Pd-free polymer[20] (Figure S4). Figure 1 provides an overview of the structure of a 2.7 wt% Pd/PPhen composite. Scanning electron microcopy (SEM) shows irregularly shaped particles with a smooth, highly curved surface. High-resolution scanning transmission electron microscopy (HR-STEM)[21,22] reveals very small Pd nanoparticles in the size range of 0.5–4 nm (Figure S5), evenly distributed throughout the polymer host. Quantitative analysis of the tomograms shows that 87% of the Pd nanoparticles are confined within the polymer network. A representative tilt series of HR-STEM images is given as Movie S1.

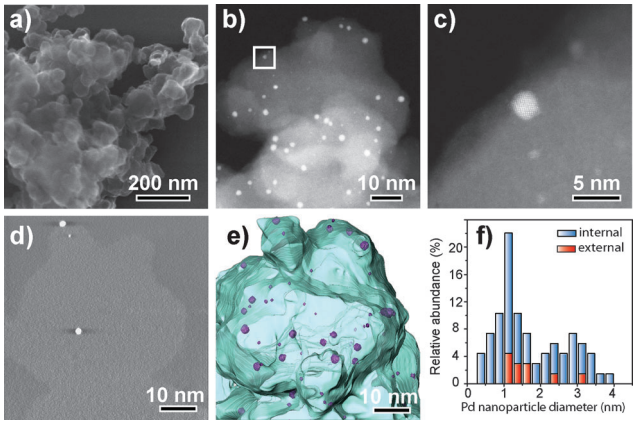


Figure 1. Structure of a Pd/PPhen solid composite (2.7 wt% Pd). a) Scanning electron micrograph, b) high-angle annular dark-field scanning transmission electron micrograph (HAADF-STEM), c) high-magnification detail of the region framed in (b). d) Cross-sectional slice (0.12 nm thick) through the reconstructed HAADF-STEM tomogram. Carbon film of the microscopy grid (darker gray background), PPhen (light gray silhouette), Pd (white). e) Three-dimensional, surface-rendered view of the reconstructed HAADF-STEM tomogram after segmentation of the different phases. f) Histogram of Pd particle size and spatial location.

The solid-state ^{13}C NMR spectrum of the solid shows two signals at 140.3 and 129.6 ppm, which correspond to the connecting and nonconnecting carbon atoms of the polyphenylene, respectively (Figure 2a). Thermogravimetric analysis (TGA) proves the outstanding stability, with no evident mass loss up to 400°C in air and up to 600°C in argon, respectively (Figure 2b). The BET-equivalent specific surface area is 1010 $m^2 g^{-1}$, of which roughly 10% corresponds to the external surface of the polymer particles. A total pore volume of 0.46 $cm^3 g^{-1}$ results from equal contributions in the micropore (< 1.5 nm) and supermicropore (1.5–2 nm) size ranges. The palladium is accessible, since treatment of the Pd/PPhen composite in solutions of H_2O_2 and HCl[23] results in the quantitative leaching of the metal, so that a Pd-free polymer

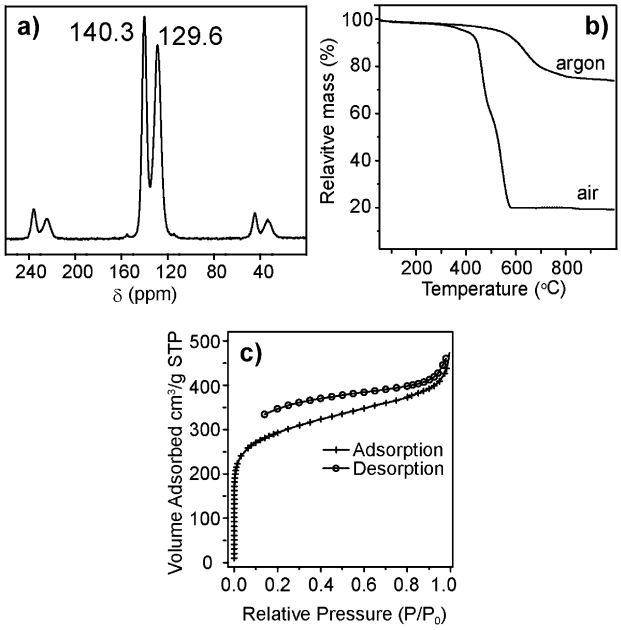


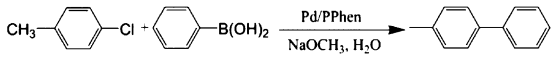
Figure 2. a) Solid-state ^{13}C NMR spectrum. b) TGA profiles in air and argon flow. c) N_2-physisorption isotherm.

residue is obtained (Figure S6). The accessibility is due to the micropores and swelling of PPhen. The Pd/PPhen composite has a density of (1.38 ± 0.01) g cm^{-3} and is readily dispersed in all common organic solvents (Table S1). The synthesis has been repeated many times and properties were found to be highly reproducible even at the gram scale.

Suzuki coupling reactions are among the most important reactions in organic synthesis.[4,24] They are mostly carried out in homogeneous phase, catalyzed by palladium complexes such as $[Pd(PPh_3)_4]$. Due to the exclusively aromatic backbone of the polyphenylene carrier, favorable interaction of the substrates with the surface of the porous support was expected, which should lead to good catalytic performance.

Initially, coupling between 4-chlorotoluene and phenylboronic acid was studied, where steric requirements are not very demanding; however, chloroaromatic compounds are difficult to activate.[25] $[Pd(PPh_3)_4]$ is known to be active for this reaction in organic phase. Similar to its molecular counterpart, Pd/PPhen is highly active for this reaction (Table 1, entry 1). In addition to ethanol/water, pure water was also studied as solvent, which facilitates workup of the reaction mixture. Polyvinylpyrrolidone (PVP, MW = 55000) was added to facilitate the dispersion of Pd/PPhen in water, and similar activity was observed (entry 2). A loading of 5.9 wt% Pd/PPhen results in a lower yield (entry 3), indicating that the larger Pd nanocrystals, (3.3 ± 0.8) nm, in this composite (Figure S3) are less efficient catalysts. The reactivity of the Pd/PPhen solids cannot be attributed to residual $[Pd(PPh_3)_4]$ species, since solid-state ^{31}P NMR spectroscopy ruled out the presence of $[Pd(PPh_3)_4]$ residues in the solid catalyst (Figure 3). Moreover, XPS of the Pd/PPhen solid shows two signals corresponding to Pd^0 $3d_{5/2}$ (335.9 eV) and $3d_{3/2}$ (341.2 eV) (Figure S7), confirming the metallic character of the palladium species.

Table 1: Suzuki coupling reactions using different Pd catalysts.[a]



Entry	Catalyst	Yield [%]
1	Pd/PPhen 2.7 wt% in C_2H_5OH/H_2O (1:1)	82
2	Pd/PPhen 2.7 wt%	82
3	Pd/PPhen 5.9 wt%	27
4	$[Pd(PPh_3)_4]$[b]	< 0.5
5	Na_2PdCl_4[b]	< 0.5
6	Pd/C from Sigma Aldrich	< 0.5
7	Pd/C[c]	< 0.5
8	Pd/PDVB[c]	< 0.5

[a] Reaction conditions: chlorotoluene 0.5 mmol, phenylboronic acid 0.75 mmol, $NaOCH_3$ 1.5 mmol, catalyst (0.8 mol% Pd to aryl chloride), PVP 0.5 mg, water 5 mL, 80°C, under argon, 3 h. [b] Tetrabutylammonium bromide (TBAB)[30] 0.3 mmol is added as phase transfer catalyst. [c] Pd/C and Pd/PDVB are prepared by methods indicated in Supporting Information.

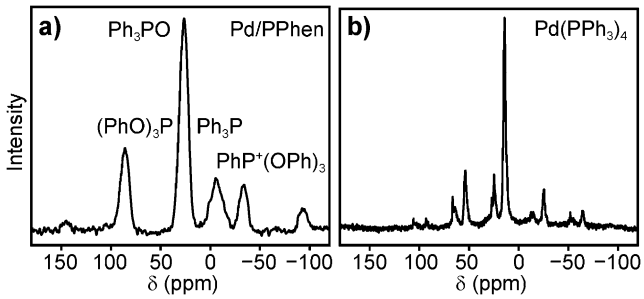
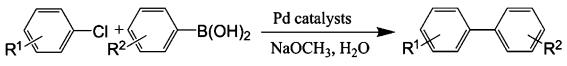


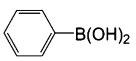
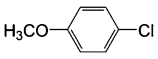
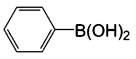
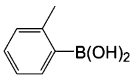
Figure 3. Phosphorus speciation as studied by solid-state ^{31}P NMR spectroscopy. a) Pd/Phen composite. b) commercial solid $Pd(PPh_3)_4$.

Other solid and molecular Pd catalysts, including Pd nanoparticles (2.7 wt%, Pd particle size in the range of 0.5–3.5 nm) on either carbon or PDVB carriers prepared through impregnation with the $[Pd(PPh_3)_4]$ precursors followed by reduction in H_2 (Figures S8 and S9), gave rather poor results (entries 4–8). Pd/C and Pd/PDVB obtained by precipitation in DMF at 150°C also gave no conversion. The superior performance strongly suggests a synergistic role of the PPhen support material in this reaction. This might be attributed to its unique conjugated aromatic structure, which is absent in carbon and PDVB, and which might allow for strong π–π interactions with the substrates in the vicinity of the catalytic palladium species, similar to the proposed effect of conjugated aromatic ligands in C–C coupling reactions catalyzed by palladium complexes.[25]

The superior catalytic activity of the Pd/PPhen composite over all other systems studied[26,27] encouraged us to explore the performance with more challenging Suzuki coupling reactions, such as with 2-chloro-1,3-dimethylbenzene and 4-chloroanisole. These substrates require more effective ligands in molecular catalysis, such as N-heterocyclic carbenes, P-(tBu)$_3$, and the phosphine family developed by Buchwald and co-workers.[25,28,29] These substrates are known to pose an even greater challenge to heterogeneous catalysis.[26] Pd/PPhen as the catalyst in the Suzuki coupling reaction of 2-chloro-1,3-dimethylbenzene with arylboronic acid results in a yield above 50% after only three hours (Table 2, entry 1). Yields exceeding 80% are obtained for other unactivated substrates after 20 h (entries 3 and 5). The results indicate that PPhen may act as a conjugated ligand in a similar manner as the Buchwald ligands to stabilize the transition state of the oxidative addition and/or reductive elimination.

Table 2: Suzuki coupling reactions using different substrates.[a]



Entry	Aryl choride	Arylboronic acid	t [h]	Yield [%]
1			3	55
2			3	20
3			20	80
4			3	51
5			20	87

[a] Reaction conditions: aryl chloride 0.5 mmol, arylboronic acid 0.75 mmol, $NaOCH_3$ 1.5 mmol, catalyst (0.8 mol% Pd to aryl chloride), PVP 0.5 mg, water 5 mL, 80°C, under argon.

The nature of the "true" catalytic species in Suzuki coupling reactions has been long debated. Very recently, Corma and co-workers showed that ligand-free, very small palladium clusters are responsible for the catalytic activity in aqueous media.[30] Under our experimental conditions, removal of the solid catalyst from the reaction media by hot filtration revealed that neither product nor 4-chlorotoluene was present in the remaining solution (for analysis, reactants and products were extracted, see the experimental details in the Supporting Information). This supports the notion that the PPhen solid carrier locally provides an organic solvent-like environment. When fresh 4-chlorotoluene and phenylboronic acid substrates and base were added into this solid-free solution, along with TBAB to transfer 4-chlorotoluene into the aqueous phase, no reaction was detected after 3 h at 80°C. Elemental analysis of the hot-filtered solution gave palladium concentrations below 10 ppm. Accordingly, the Pd/PPhen catalyst could be recycled, retaining product yields in the range of 78–84% for four cycles (Table S2 and Figure S10).

The Pd/PPhen catalyst thus holds high promise as a C–C coupling catalyst and for different gas-phase reactions, which are currently being explored in our laboratory.

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