Surface Catalysis

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The Role of Palladium Dynamics in the Surface Catalysis of Coupling Reactions**

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Ever since its discovery, the carbon–carbon cross-coupling reaction has contributed greatly to increasing the chemical complexity of molecules, which is crucial for organic synthesis and pharmaceutical drug development.[1–4] Surface-catalyzing carbon–carbon bond formation on supported Pd nanoparticles (PdNPs)[5–8] can decrease product contamination and aid the development of "greener" routes in organic synthesis. On the nanoscale, unlike in the bulk phase, PdNPs exhibit a large specific surface area and have abundant low coordination sites that enable increased catalytic activity. However, the catalytic reaction mechanisms on supported PdNPs surfaces remain a controversial topic of discussion. Some reports[9–11] suggest that surface sites on PdNPs may play a crucial role in catalyzing coupling reactions, while others propose that the Pd species leached from support into solution govern the reaction pathways.[12,13]

Surface analysis of supported PdNPs used during cross-coupling reactions with atomic precision is difficult.[14,15] Recent work suggests that PdNPs smaller than 1 nm are commonly missed during most microscopic studies.[14] In addition, signal collection on highly dispersed particles after cross-coupling reactions is challenging owing to geometric and electric interference with the surface of bulk support.[15]

Herein, we set out to investigate the catalytic performance of PdNPs, in the Suzuki–Miyaura reaction, supported on materials with various levels of functionalization. The Pd dynamics were investigated in terms of changes to the surface of the PdNPs and to the support and correlated with catalytic results. Unlike previous reports applying active carbon,[16,17] silica,[18,19] alumina,[20,21] or zeolites[22,23] in the heterogeneous catalysis of coupling reactions, the current work exploits functionalized carbon nanotubes (CNTs) as a support. To study the influence of the chemical properties of the supporting materials on the Pd dynamics, CNTs were functionalized to different degrees before being loaded with PdNPs for use in coupling reactions.

After synthesis the CNTs underwent annealing treatments at 700 °C and 1500 °C to improve the graphitization.[24] For functionalization the CNTs were added to vigorously stirred concentrated nitric acid at 120 °C. CNTs annealed at 700 °C have more defects than CNTs annealed at 1500 °C, HNO_3 treatment introduced a high functionalization (H-CNTs) on defective CNTs and a low functionalization (L-CNTs) on graphitized CNTs. The functionalities act as sites for anchoring metal cations during impregnation.[25] Vacancies and cavities in the CNTs may also play entrap PdNP precursors.[26]

The STEM image in Figure 1 a shows the dispersion of PdNPs (2 % wt palladium) on H-CNTs (Pd/H-CNTs) with a size distribution of (1.8 ± 0.2) nm. Figure 1 b shows a poor dispersion of PdNPs (2 % wt palladium) on L-CNTs (Pd/L-CNTs) with a larger size distribution of (14.5 ± 0.2) nm. Figure 1 c shows plots of conversion versus reaction time for the Suzuki–Miyaura reaction of iodobenzene with phenylboronic acid in the presence of these PdNP/CNT catalysts. Quantitative conversion was obtained within one hour when Pd/H-CNTs was used, whereas reactions with Pd/L-CNTs required 8 h to reach quantitative conversion. The turnover frequency (TOF) at completion of the reaction is 990 h^{-1} for Pd/H-CNTs and 124 h^{-1} for Pd/L-CNTs. Figure 1 d shows the Suzuki–Miyaura reaction solution of Pd/H-CNTs after one hour reaction time. This black solution could be left to stand for 10 min and no precipitate was observed. Filtration using normal filter papers collected all the Pd/H-CNTs and result in a clear filtrate (Figure 1 e). The reaction solution of Pd/L-CNTs after one hour reaction time, precipitated completely on being allowed to stand for 10 min (Figure 1 f).

The significant differences in reactivity prompted a detailed analysis of the catalysts by electron microscopy. Reactions were stopped at 1 hour for Pd/H-CNTs and Pd/L-CNTs. Although the majority H-CNTs were intact (Supporting Information, Figure S1), some showed damage after catalyzing the coupling reaction. The morphology changes to the Pd/H-CNTs are shown in Figure 2 a,b. The STEM image in Figure 2 a shows the dispersion of PdNPs on a structurally damaged H-CNT. Although some PdNPs have a larger size, PdNPs with a diameter of 1–2 nm are still visible. A detailed view of the damaged H-CNTs after reaction, was obtained by TEM (Figure 2 b). "Tracks" from the movement

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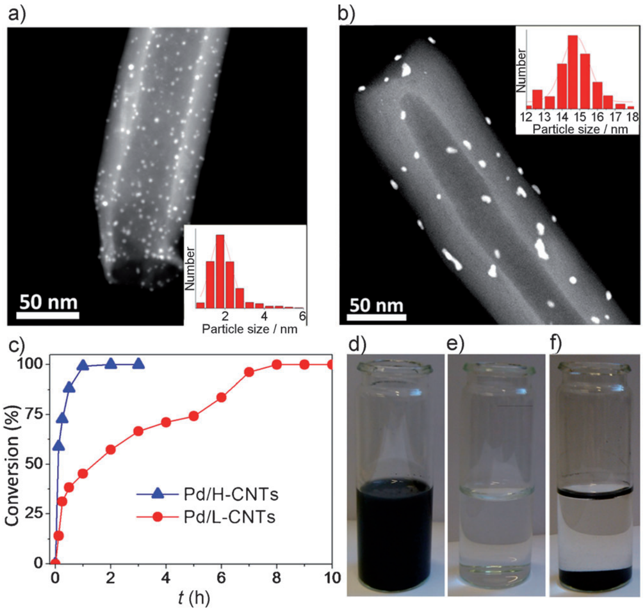

Figure 1. a) Scanning transmission electron (STEM) image of Pd/H-CNTs. b) STEM image of Pd/L-CNTs. c) Suzuki–Miyaura reactions between iodobenzene and phenylboronic acid, conversion as a function of reaction time when using Pd/H-CNTs and Pd/L-CNTs as catalysts. Reactants together with K_2CO_3 were heated to 60 °C in a mixture of water and DMF (1:1). d) Solution of Pd/H-CNTs after 1 h reaction and then being left to stand for 10 min. e) Filtrate of the solution in Figure 1d. f) Solution of Pd/L-CNTs after 1 hour reaction and then being left to stand for 10 min.

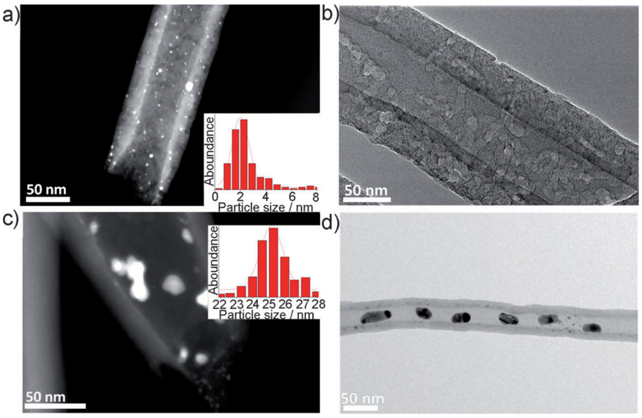

Figure 2. After 1 hour catalysis: a) STEM image of Pd/H-CNTs. b) TEM image of Pd/H-CNTs. c) STEM image of Pd/L-CNTs. d) TEM image of Pd/L-CNTs.

of PdNPs can be seen on the H-CNTs. X-ray diffraction (XRD) analyses (Figure S2) are consistent with the microscopic studies, that the carbon structure changes shown in Figure 2 occurred to only some H-CNTs, but not to the majority.

For the Pd/L-CNTs after one hour, although reaction was not complete, leaching of PdNPs from the outer walls of L-CNTs was clearly observed, and PdNPs inside the L-CNT channels sintered into larger aggregates (Figure 2c,d). In addition, no damage to the graphitic structure L-CNTs was observed.

The morphological changes to the Pd/H-CNTs during their use as catalysts are remarkable, as illustrated by the movement tracks made by the catalytically active PdNPs on H-CNTs. Our evidence may provide information about the dynamics of catalytically active species under reaction conditions, thus contributing to a better understanding of catalysis pathways. Moreover, the established physical and mechanical properties of CNTs indirectly demonstrate the magnitude of the observed effect. Standard CNTs can withstand a pressure up to 24 GPa without deformation. Bulk modulus studies revealed that CNTs composed of a hard phase can withstand a pressure even higher than diamond.[27] The engraving and channel forming on CNTs vividly reveals the reaction-driven migrations of PdNPs. The electron-microscope results indicate a strong interaction between the metal and the support H-CNTs and are consistent with previous studies that PdNPs can be leached from unmodified inorganic substrates and form aggregates during coupling reactions.[28,29]

The morphological changes to the supporting H-CNTs prompt a more in-depth examination of the surface and crystalline structure of the supported PdNPs. Before catalyzing the coupling reactions, as-prepared Pd/H-CNTs and Pd/L-CNTs have metallic Pd phases. Pd/L-CNTs are still in the Pd metallic phase after the catalytic reaction (Figure 3a), whereas after one hour of catalysis, HRTEM analyses of the Pd/H-CNTs (Figure 3b) show changes in their crystallinity in regions near the surface of the PdNPs. The distorted crystalline phases were observed only in the near surface regions, the cores of the PdNPs remained as palladium metallic phases. Clear boundaries between the metallic cores

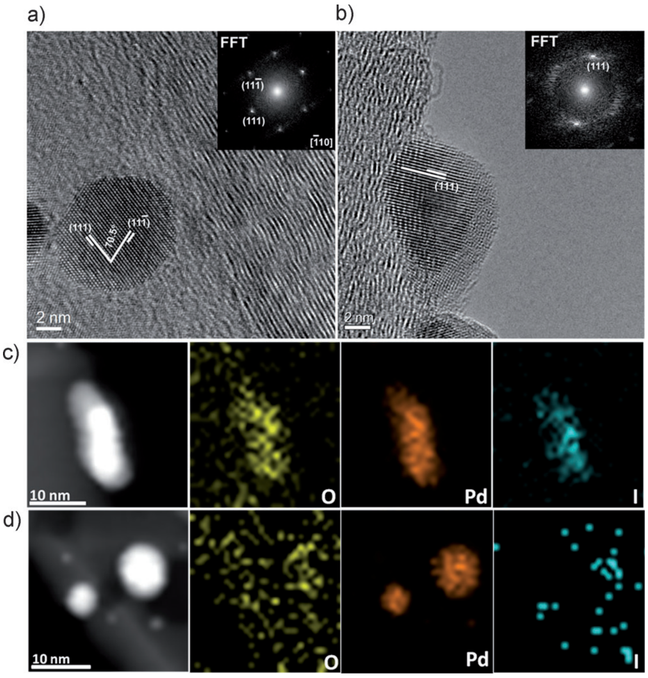

Figure 3. HRTEM images after 1 hour catalysis of: a) a Pd nanoparticle on L-CNTs, b) a Pd nanoparticle on H-CNTs. STEM-EDX maps of a Pd nanoparticle supported on c) H-CNT, d) L-CNT.

and the distorted crystalline surfaces indicate that phase changes occurred on the Pd surfaces during the coupling reaction. Crystalline changes took place on PdNPs, which are supported on both damaged and structurally intact H-CNTs. The observation of surface changes on supported PdNPs was surprising as normally aggregated Pd is obtained after Suzuki–Miyaura reactions in homogeneous and heterogeneous systems.[8,15,30,31] This situation indicates that surface changes taken place on PdNPs that remain trapped on H-CNTs. Re-adsorption of PdNPs after the reaction is possible, but generally results in the formation of Pd aggregates. Even if PdNPs re-adsorb prior to the completion of a coupling reaction, no nanoparticles with the observed "half core–shell" structures would result, because on a re-adsorbed Pd nanoparticle, the distorted surface (shell) would be present between the core and H-CNTs, thus, the metallic Pd core could not be in direct contact with the H-CNTs surface as observed in Figure 3 b. There is an interesting analogy with carbon catalysts in the oxidative dehydrogenation of butane. Starting from nanodiamonds, a surface-induced recrystallization to graphitic carbon occurs resulting in an increase in both activity and selectivity to butenes.[32]

Significant crystalline changes (Figure 3 b) indicate a change in the elemental compositions of supported PdNPs during catalysis. Element maps of a Pd nanoparticle supported on H-CNTs, obtained by STEM-EDX (Figure 3 c; EDX = energy dispersive X-ray spectroscopy), after 1 hour of catalysis show homogeneous distributions of O and Pd. More importantly, an iodine signal was clearly traced to the PdNPs. In contrast, maps of PdNPs on L-CNTs after a 1 hour reaction show elemental signals with significantly reduced intensities (Figure 3 d). In line with HRTEM analyses of metallic phase Pd/L-CNTs and of the distorted crystalline phase of Pd/H-CNTs, contrasting oxygen intensities in the elemental maps indicate an appearance of oxidatively added complex on the PdNPs on H-CNTs.

The reaction, based on our analytical data, is shown in Figure 4. Added to water, H-CNTs have an enriched surface charge, and repulse each other in an aqueous solution to form a stabilized CNT dispersion. In the course of Suzuki–Miyaura reactions, the oxidative-addition step requires the participation of Pd nanospecies and possibly causes leaching and formation of Pd aggregates. In our work, we confirmed that most of the PdNPs are strongly bound to H-CNT under the reaction conditions. As shown in Figure 4, the reactants are co-dispersed with Pd/H-CNTs, they adsorb on the embedded PdNPs which have high surface areas, thus enhancing the possibility of surface catalysis on the supported PdNPs. PdNPs that had undergone crystalline changes were observed on H-CNTs with and without structural damage. Structural damage (engraving of the graphitic walls) to the H-CNTs could be caused by the catalyst preparation, in which PdNP loading varies depending upon the distribution of functional groups on the H-CNTs. Thus, higher PdNPs loadings on small-diameter H-CNT with thin (less graphitic layers) multiwalls could result in greater movement of PdNPs causing more damage to the H-CNTs during catalytic reactions. Although leaching becomes possible under these circumstances, the engraved CNT structures show the high magnitude of the force that drives the movement of PdNPs and overcomes the metal–support interactions.

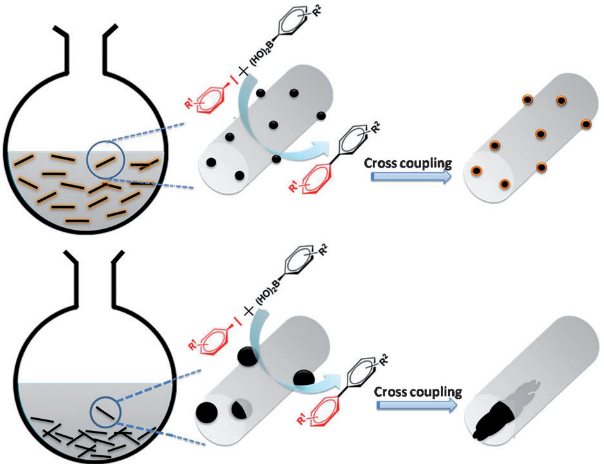

Figure 4. Proposed reaction based on analytical data for catalysis with Pd/H-CNTs (top) and Pd/L-CNTs (bottom).

In this work, the functionality and dispersibility of supporting materials were exploited to alter the metal–support interaction between PdNPs and functionalized CNTs. Thus, the role of PdNP dynamics in the surface catalysis of coupling reactions can be studied. The observed high reactivity did not lead to leaching of PdNPs during the Suzuki–Miyaura reaction, however, it resulted in surface changes on PdNPs and the supporting H-CNTs. Corresponding to the commonly reported high reactivity in homogeneous catalysis, carbon–carbon couplings with high efficiency can be achieved on supported PdNPs by improving surface functionalization and the dispersibility of the catalyst. Such a system, in addition, offers opportunities for characterizing surface catalysis with atomic precision, which is crucial for detecting dynamic changes on catalytically active species and understanding catalysis pathways. This approach may also be applicable to systems using other inorganic substrates for supporting PdNPs. Future work will focus on modifying supporting materials with various surface properties of interest for studying the role of Pd dynamics in surface catalysis.

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