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Metal vapor synthesis of ultrasmall Pd nanoparticles functionalized with N-heterocyclic carbenes

Received 00th January 20xx, Accepted 00th January 20xx Patricia Tegeder,^a Marcello Marelli,^b Matthias Freitag,^a Laura Polito,^b Sebastian Lamping,^a Rinaldo Psaro,^b Frank Glorius,^a Bart Jan Ravoo,^{a*}and Claudio Evangelisti^{b*}

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The synthesis of N-heterocyclic carbene (NHC)-stabilized palladium nanoparticles (PdNPs) by an entirely new strategy comprising the NHC functionalization of ligand-free PdNPs obtained by metal vapor synthesis is described. Detailed characterization confirms the formation of very small monodisperse PdNPs (2.3 nm) and the presence of the NHC ligand onto the Pd surface. The stable NHCfunctionalized PdNPs dispersed onto carbon support showed high activity in the hydrogenation of limonene with enhanced regioselectivity in comparison to bare PdNPs on carbon.

Ligand stabilized metal nanoparticles (MNPs) attract a large interest as alternative to classical homogeneous and heterogeneous transition metal catalyst due to their unique activity and selectivity.¹⁻³ The surface chemistry of the MNPs plays a crucial role in their performance as catalyst. On the one hand, surface ligands can activate the metal they are binding to by electronic effects. On the other hand, the adsorbed ligands can influence the number and location of active sites on the MNP, which can have in turn a huge impact on the selectivity. In the recent years, N-heterocyclic carbenes (NHCs) have attracted increasing attention as a new type of MNP ligands.^{4,5} Similar to thiols, they form strong covalent bonds to many transition metals, but contrary to thiols, do not tend to inhibit the catalytic properties of the metal. Moreover, they are structurally very versatile, feature a facile synthesis and can induce catalytic activity by their outstanding donor ability.⁶

NHC-stabilized MNPs have been so far synthesized by four different strategies: 1) reduction of an NHC metal complex,^{7–12} 2) deprotonation of an azolium metalate and subsequent reduction,^{13,14} 3) degradation of a metal(0) complex in the presence of the free NHC^{15–17} and 4) ligand exchange with



Scheme 1: Synthetic approaches to NHC-stabilized MNPs.

preformed ligand stabilized MNPs.¹⁸⁻²¹ By using the first three approaches, the particles are formed in presence of the NHC ligand, which consequently governs the size of the MNPs. Since the catalytic performance of MNPs is strongly influenced by the particle diameter and the ligand structure,² it is highly desirable to tune both parameters individually. To the best of our knowledge, the ligand exchange procedure is the only method that allows the synthesis of MNPs with defined size and shape independent from the used NHC ligand. However, the disadvantages of this approach are the excess of NHC needed to replace the precursor ligand, the elaborate and timeconsuming work-up to purify the particles and the instable mixed ligand shell during the exchange process which can lead to irreversible aggregation.²² Therefore, it would be highly beneficial to develop a synthetic protocol in which the MNPs are formed with defined properties and further functionalized with the NHC ligand avoiding the use of additional ligands.

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Scheme 2: PdNPs synthesis by metal vapor synthesis (1) and subsequent NHC immobilization (2).

The metal vapor synthesis (MVS) potentially enables this approach.²³ By using MVS, very small (< 5 nm) solvent-stabilized MNPs of a variety of transition metals can be generated.²⁴⁻²⁶ MNPs are weakly stabilized by solvent molecules, thus the NHC coordination is effective and an excess of NHC is not necessary for surface functionalization. Since only the solvent and the pure metals are used in the MVS method, the number of possible impurities is reduced to a minimum and the subsequent purification is facilitated.

We describe in this communication the synthesis of ultrasmall NHC-stabilized PdNPs by the MVS technique. To the best of our knowledge this is the first report on the immobilization of NHC ligands on preformed, ligand-free MNPs. We selected PdNPs as a first test system because their functionalization with NHC ligands by means of other methods is already known. As ligand, we selected a NHC with long alkyl chains in the backbone of the heterocycle (**LC-NHC**), which forms a protective monolayer around the MNPs and was successfully used before for MNP stabilization.^{27,28}

The solvent-stabilized PdNPs were synthesized by the MVS technique according to a previously reported procedure (see ESI).²⁹⁻³¹ Briefly, Pd vapor generated in high-vacuum by resistive heating of the pure metal was co-condensed with a 1:1 mixture of mesitylene and 1-hexene in a liquid nitrogen cooled glass reactor. The melting of the solid matrix afforded a brown solution of PdNPs which was handled and stored at low temperature (-20°C) under argon atmosphere. For the surface modification with LC-NHC, the free carbene was first generated in situ by deprotonation of the corresponding imidazolium salt with KO^tBu in mesitylene. The PdNPs were added to the NHC and the solution was stirred at room temperature. After 18 h, the absence of any precipitate indicated the successful coordination of LC-NHC on the particle surface (LC-NHC@Pd). As a matter of fact, the solvent-stabilized PdNPs are not stable in air and precipitation of Pd powder takes places after few hours (ca. 2 h) at 25°C even under inert atmosphere. The particles were then purified in air by precipitation in acetonitrile and subsequent centrifugation. The thus prepared LC-NHC@Pd



Figure 1: ¹H (top) and ¹³C NMR (bottom) spectra of LC-NHC@Pd measured in benzenzed₆.

were re-dispersed in toluene and were stable at room temperature for a very long time (> 6 months).

Transmission electron microscopy (TEM) analysis revealed the presence of very small NPs with a size distribution ranging from 1.5 to 3.0 nm (mean diameter of 2.3 nm ± 0.4 nm) (Fig. S1). High resolution TEM micrographs (Fig. S2) confirmed the presence of crystalline lattice planes exhibiting spots in the fast Fourier transform pattern at 2.3 Å, which are ascribed to the spacing of {111} planes of face centered cubic (fcc) structure of metallic Pd. The presence of the NHC ligand on the particle surface was investigated by NMR measurements. In the ¹H NMR spectrum of LC-NHC@Pd, the expected proton signals of the alkyl chains are visible in the aliphatic region (Fig. 1 top). The signals are broadened due to the immobilization on the particle surface, as expected for ligands anchored on NPs.32 The signal of the methyl groups at 4.1 ppm is particularly weak due to the close distance of the protons to the particle surface. The formation of the carbene species is attested by the absence of a signal at 10.1 ppm corresponding to the proton at the C2 position of the imidazolium salt. In the ¹³C NMR spectrum only the signals of the aliphatic alkyl chains can be observed (Fig. 1 bottom). The carbon signals of the heterocycle are not visible in the spectrum which is in agreement with our previous report on NPs functionalized with LC-NHC.28 For the determination of the metal-to-ligand ratio, the PdNPs were investigated by thermogravimetric analysis (TGA) (Fig. S3). Taking the residual toluene in the sample into account, the particles contain 38% Pd and 62% ligand corresponding to a metal-to-ligand ratio of 2.3 : 1. Elemental analysis carried out on LC-NHC@Pd revealed a carbon-to-nitrogen atomic ratio of 17.9 in good agreement with the theoretical value of the free NHC ligand (C/N atomic ratio = 16.1).

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In order to effectively use the NPs as heterogeneous catalyst, LC-NHC@Pd was quantitatively deposited on a carbon support (Vulcan® XC72) by simple impregnation, yielding LC-NHC@Pd/C. For comparison, the unmodified PdNPs synthesized by the same MVS procedure were also deposited on the carbon material, denoted as Pd/C (Fig. S4).

HAADF-STEM and TEM analysis of the NHC-functionalized PdNPs deposited onto the support (Fig. 2a, Fig. S5a) revealed the presence of MNPs with identical size and shape compared to the unsupported MNPs, proving that no reconstruction of the metal core or coalescence takes place during the immobilization step. Likewise, the MVS-derived supported unfunctionalized PdNPs (Pd/C) have a similar size of 2.1 ± 0.4 nm indicating that the NHC ligand does not affect the particle dimensions (Fig. 2b, Fig. S5b).



Figure 2: Representative HAADF-STEM micrograph and corresponding histogram of particle size distribution of LC-NHC@Pd/C (a) and Pd/C (b). MNPs can be observed as bright spots in the micrographs.

X-ray photoelectron spectroscopy (XPS) analysis of **LC-NHC**@Pd/C provided evidence that the NHC ligand is on the Pd surface after immobilization on the carbon support, since characteristic signals of nitrogen can be found (see Fig. S6). The binding energy of the N1s signal at 401.2 eV matches well with previously reported values for NHC stabilized PdNPs.²² For Pd/C, no signal can be observed in this region. The binding energies measured in the Pd3d region of both NHC functionalized and unfunctionalized Pd/C compare well with previously reported values for Pd⁰.³³ However, small shoulders at higher binding energies indicate partial oxidation to Pdⁿ⁺ (see Fig. S7).³⁴

The catalytic properties of **LC-NHC**@Pd/C were studied and compared with those of the bare Pd/C prepared by the same approach in the selective hydrogenation of limonene, a monocyclic terpene, which is the main component of essential oils derived from the rinds of various citrus fruits (Fig. 3 and Table S1 and S2).³⁵ In particular, the selectivity towards the



Catalyst	T (min)	Conv. (%)	Sel. 1 (%)ª	TOF (h⁻¹) ^ь
LC-NHC@Pd/C	8	68.3	65.5	2.6·10 ⁴
	15	86.4	66.5	-
Pd/C	8	67.5	47.6	2.5·10 ⁴
	15	85.4	42.9	-

Figure 3. Reaction conditions: (*R*)-(+)-Limonene (1.1 mL), Pd catalyst 1 wt.% (35 mg), Sub/Pd molar ratio = 2000, $p(H_2) = 4$ bar; T = 30°C. ^a Selectivity (Sel 1) calculated as mol of *p*-(1)-menthene/ mol limonene conv. ^b Normalized TOF (i.e. mmol substrate (converted) x (mmol Pd(surface) x h)⁻¹.

Both MVS-derived Pd/C catalysts are very active for the reduction of limonene to *p*-1-menthene (1), *p*-3-menthene (2) and *p*-menthane (a mixture of *cis*- (3) and *trans*- (4) isomers) with a normalized TOF [38] higher than 2.10⁴ h⁻¹. Noteworthy, LC-NHC@Pd/C led to a marked increase of the p-1-menthene selectivity (66.5% at 86.4% of limonene conversion) respect to the unmodified Pd/C (42.9% at 85.4 % of limonene conversion), partially inhibiting the Pd-catalyzed isomerization of 1 to 2. The differences in regioselectivity between the two catalysts were found both in neat conditions and in toluene as solvent (see Table S1 and S2). Moreover, the lower regioselectivity of unmodified Pd/C is comparable with that found for less active commercial and previously reported Pd/C catalysts (see Table S1 and refs. 36 and 37). These results demonstrate that the presence of NHC ligand influences the reactivity of the Pd surface.

The stability of **LC-NHC**@Pd/C was analyzed by recyclability studies as well as evaluating the Pd leaching in reaction conditions. The system was effectively recycled for five reaction runs in neat conditions with only a slightly decrease of the catalytic activity (Conv. = 75.0 % after 15 min during the 5th cycle) (Fig. S8). Remarkably, the selectivity towards *p*-1-menthene was almost identical (67-69%) during the five runs. Moreover, ICP-OES evidenced no Pd leaching into the reaction mixture.

In summary, ligand-free PdNPs synthesized by the MVS method were successfully functionalized with an aliphatic NHC ligand leading to air-stable NPs. Characterization of the particles by TEM, NMR, TGA, XPS and elemental analysis clearly confirm their very small size, the presence of the NHC on the particle surface and a high ligand density. The functionalized PdNPs can be easily immobilized on carbon support in order to use them as recyclable catalyst. The particles show high activity in the hydrogenation of limonene with *p*-1-menthene as main product. By comparison with the performances of unfunctionalized Pd catalysts, an evident ligand effect was

observed on the regioselectivity, probably due to electronic modification of the Pd surface and/or steric effects by ligand binding. Finally, we expect that the metal vapor synthesis approach to obtain NHC-immobilized PdNPs can be easily

different NHC ligands. We are grateful for financial support by the Deutsche Forschungsgemeinschaft (DFG SFB 858). We thank Dr. Vassilios Siozios from the MEET (WWU Münster) for TGA measurements.

extended to other homo- and heterometallic MNPs as well as

Conflicts of interest

There are no conflicts to declare.

Notes and references

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