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Enhancing catalytic activity in hydrogenation reaction by decorating Pd nanoparticles with N-heterocyclic carbenes

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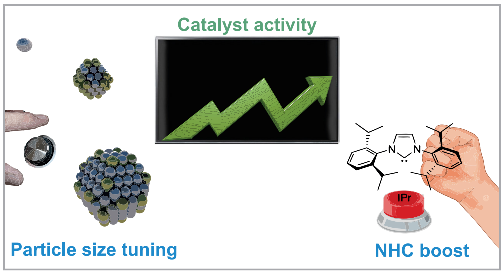
A method for the preparation of a heterogeneous palladium catalyst is proposed, which allows controlling the size and activity of the resulting particles. Materials prepared from $Pd_2(dba)_3$ by deposition at 80 °C showed high catalytic activity in the reaction of diphenylacetylene hydrogenation. The catalytic activity can be further enhanced by pre-activation involving the addition of the carbene ligand 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) into the reaction mixture.



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Of the entire array of heterogeneous catalysts based on palladium, one can single out the subtype of ‘nanosized palladium on carbon materials’ (Pd/C), which is used for hydrogenation in the synthesis of dyes, fragrances, pharmaceuticals and biologically active compounds.[1–3] Recently, the intensive development of catalytic hydrogenation processes has generated significant interest among researchers in the synthesis of highly active catalysts.[4–7] It has been repeatedly demonstrated that the efficiency and selectivity of the heterogeneous hydrogenation reaction using molecular hydrogen is affected by the size of nanoparticles (NPs), and the dependence of the total activity on the size of NPs has a dome-shaped form.[8–11]

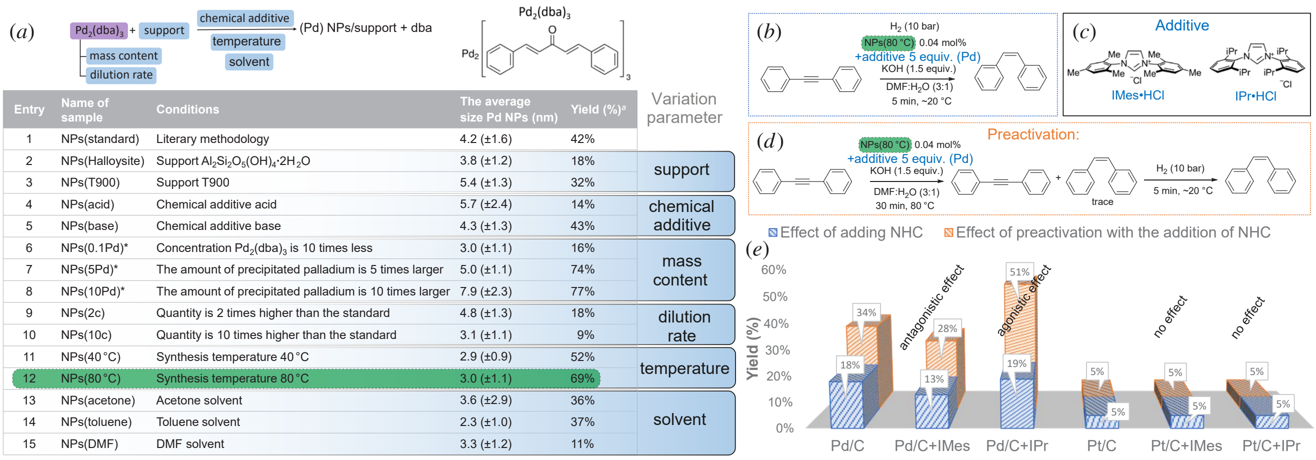
The catalytic efficiency of Pd NPs can be improved by carefully controlling the chemical transformations at different stages of catalyst preparation or by modifications induced by the reaction medium [Figure 1(*a*)].[12–14] It has been previously demonstrated that the palladium(0) complex $Pd_2(dba)_3$ is unstable in solution and generates Pd NPs.[14] Increasing the palladium-to-carbon ratio allows controlling the surface coverage and the size of the resulting particles. It is interesting to study the relationship between the structure and properties of the catalyst used in the hydrogenation reaction in order to achieve the desired reaction parameters. Another method for changing the catalytic activity described in the literature is to modify the metal surface with ligands. Coordination of carbene ligands with metal NPs or clusters can change not only the local spatial environment but also contribute to a change in the electron density, which significantly affects the catalytic activity of the system in an as yet unpredictable manner.

In particular, it has been recently shown that surface decoration of palladium NPs with N-heterocyclic carbenes (NHCs) can significantly enhance the catalytic activity in a number of important reactions, including the Buchwald–Hartwig amination reaction,[15] the Mizoroki–Heck reaction, the Suzuki–Miyaura reaction[16] and transfer hydrogenation.[17] Self-formation of such systems from soluble Pd–NHC complexes in the hydrogenation reaction with molecular hydrogen has also been found.[18,19] Moreover, even *in situ* generation of NHCs allows for decorating the obtained NPs.[16] However, surface treatment of metal NPs with NHC ligands to enhance the catalytic activity of a heterogeneous palladium catalyst for hydrogenation with molecular hydrogen has not yet been studied.

This work highlights the importance of NP size and NP surface modification using NHCs for optimizing catalytic processes of industrially and biologically significant reactions using the model reaction of diphenylacetylene hydrogenation as an example.

In this work, Pd/support catalyst samples with different active center morphologies were prepared. For this purpose, the decomposition conditions of the $Pd_2(dba)_3$ complex were tested, including the solvent, temperature, complex concentration, support nature and medium acidity [see Figure 1(*a*)]. The average NP sizes were measured for each sample by averaging over at least 400 points. The resulting catalysts were used in the hydrogenation reaction shown in Figure 1(*b*). Conversions ($C^{10\,\mathrm{min}}$) were measured after 10 min. In the model reaction of diphenylacetylene hydrogenation, only one reaction product is formed in the given time interval (see Online Supplementary Materials). Varying the solvent showed that the best catalyst activity values were observed for Pd NPs (particle size 4.2 ± 1.6 nm, $C^{10\,\mathrm{min}} = 42\%$) [Figure 1(*a*), entry 1] prepared in chloroform as described in the original methodology,[14] but acceptable activity values were also obtained for Pd NPs prepared in acetone (particle size 3.6 ± 2.9 nm, $C^{10\,\mathrm{min}} = 36\%$) (entry 13) and toluene (particle size 2.3 ± 1.0 nm, $C^{10\,\mathrm{min}} = 37\%$) (entry 14).

DMF was found to be the worst solvent for the preparation of Pd NPs (particle size 3.3 ± 1.2 nm, $C^{10\,\mathrm{min}} = 11\%$) for the hydrogenation reaction [Figure 1(*a*), entry 15]. A possible explanation for such a solvent effect is the different ability of solvents to stabilize metal particles on the support surface and the dependence of the wettability of the support surface on the nature of the solvent, thus forming active centers from groups of metal atoms on the NPs surface. It should be noted that the



Entry	Name of sample	Conditions	The average size Pd NPs (nm)	Yield (%)[a]	Variation parameter
1	NPs(standard)	Literary methodology	4.2 (±1.6)	42%	
2	NPs(Halloysite)	Support $Al_2Si_2O_5(OH)_4{\cdot}2H_2O$	3.8 (±1.2)	18%	support
3	NPs(T900)	Support T900	5.4 (±1.3)	32%	
4	NPs(acid)	Chemical additive acid	5.7 (±2.4)	14%	chemical additive
5	NPs(base)	Chemical additive base	4.3 (±1.3)	43%	
6	NPs(0.1Pd)*	Concentration $Pd_2(dba)_3$ is 10 times less	3.0 (±1.1)	16%	mass content
7	NPs(5Pd)*	The amount of precipitated palladium is 5 times larger	5.0 (±1.1)	74%	
8	NPs(10Pd)*	The amount of precipitated palladium is 10 times larger	7.9 (±2.3)	77%	
9	NPs(2c)	Quantity is 2 times higher than the standard	4.8 (±1.3)	18%	dilution rate
10	NPs(10c)	Quantity is 10 times higher than the standard	3.1 (±1.1)	9%	
11	NPs(40 °C)	Synthesis temperature 40 °C	2.9 (±0.9)	52%	temperature
12	NPs(80 °C)	Synthesis temperature 80 °C	3.0 (±1.1)	69%	
13	NPs(acetone)	Acetone solvent	3.6 (±2.9)	36%	solvent
14	NPs(toluene)	Toluene solvent	2.3 (±1.0)	37%	
15	NPs(DMF)	DMF solvent	3.3 (±1.2)	11%	

Figure 1 (*a*) Scheme for preparing Pd NPs on supports indicating the variable parameters controlling the deposition of NPs on the support, and a table of particle sizes and yields of the hydrogenation product depending on the catalyst preparation method. [a] The yield of 1,2-diphenylethene in the diphenylacetylene hydrogenation reaction for 10 min. * The weight of the catalyst was the same in all cases. (*b*) Scheme of the diphenylacetylene hydrogenation reaction to study the effect of the NHC additive on the catalytic activity. (*c*) Structures of NHC additives. (*d*) Scheme of the diphenylacetylene hydrogenation reaction to study the effect of the NHC additive and pre-activation on the catalytic activity. (*e*) Comparison of the efficiency of Pd/C and Pt/C catalysts after adding NHC with and without pre-activation.

solvent can react with metals, thereby contaminating the surface with reaction products. For example, both the reactivity of DMF at high temperatures (120 °C) towards metal particles, leading to the formation of palladium cyanide complexes, and the formation of palladium chlorides during the preparation of the catalyst in chloroform were previously noted.[20] In an acidic medium, protonation of dba occurs and the complex is destroyed within seconds, which makes the rate of NPs formation orders of magnitude higher than deposition in a neutral medium.[18] The addition of acetic acid (entry 4) resulted in a wider particle size distribution and a larger average particle size, which negatively affected the catalytic activity (particle size 5.7 ± 2.4 nm, $C^{10\,\mathrm{min}} = 14\%$). The introduction of an oxygen-free base (triethylamine) as a chemical additive (entry 5) led to an improvement in the catalytic activity, with no noticeable change in the particle size (particle size 4.3 ± 1.3 nm, $C^{10\,\mathrm{min}} = 43\%$). Varying the temperature showed that the optimal condition for obtaining the catalyst for hydrogenation is 80 °C. At the same time, the higher the temperature, the faster the degradation of $Pd_2(dba)_3$ occurs, as in an acidic medium, which, however, led to a deterioration in activity, as shown previously. Pd NPs obtained at room temperature have a larger average particle size (4.2 ± 1.6 nm) (entry 1) compared with the catalysts obtained at 40 °C (2.9 ± 0.9 nm) (entry 11) and at 80 °C (3.0 ± 1.1 nm) (entry 12).

Examination of the effect of the support nature showed that graphite is the optimal material to deposit Pd NPs for the hydrogenation reaction. Dilution of the initial solution of the complex with a concentration of 9.5 mmol dm^{-3} by 2 and 10 times resulted in a 2.5-fold decrease in the catalytic activity, from $C^{10\,\mathrm{min}} = 42\%$ [see Figure 1(*a*), entry 1] for the standardly prepared catalyst to $C^{10\,\mathrm{min}} = 18\%$ (entry 9) for both 2- and 10-fold dilutions. The particle size was 4.8 ± 1.3 nm in the case of 2-fold dilution (entry 9), 3.1 ± 1.1 nm in the case of 10-fold dilution (entry 10) and 4.2 ± 1.6 nm for the catalyst prepared according to the standard procedure (entry 1). The ratio of the concentration of the initial complex to the amount of the support material allows controlling the catalyst activity. The average particle sizes are 3.0 ± 1.1 nm for 0.1% Pd/graphite (Pd/C) [Figure 1(*a*), entry 6], 4.2 ± 1.6 nm for 1% Pd/C (entry 1), 5.0 ± 1.1 nm for 5% Pd/C (entry 7) and 7.9 ± 2.3 nm for 10% Pd/C (entry 8). Meanwhile, the TON values are 4000, 1050, 370 and 192, and the TOF values are 24010, 6303, 2229 and 1152 h^{-1}, respectively.

The catalyst activity depends not only on the size of its NPs but also on the method of their preparation and modification. Therefore, at this stage of the work, we synthesized NHC ligands in solution and performed *in situ* surface decoration of NPs(80 °C) in the 1% Pd/C catalyst with these ligands to improve its catalytic activity [Figure 1(*a*), entry 12].

Decoration of palladium NPs was achieved using NHC ligands [Figure 1(*c*)] having different steric hindrance, the more hindered 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) and the less hindered 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene (IMes). This decoration improves the catalytic activity through several mechanisms. First, NHCs can stabilize palladium NPs by coordinating with the surface metal atoms, which reduces aggregation and maintains a large surface area of the catalyst. This effect is especially important in reactions involving small molecules such as hydrogen. Second, NHC ligands can alter the electronic environment of the palladium particles by injecting electron density into the metal, which enhances the activation of specific bonds in the substrate molecules, thereby improving the reaction kinetics. In particular, the sterically hindered IPr ligand provides better surface coverage without excessively blocking the active catalytic sites, allowing an optimal balance between NPs stabilization and substrate accessibility. In contrast, the IMes ligand, due to its smaller size, binds more strongly to palladium particles, potentially leading to higher surface coverage, which may inhibit the catalytic activity by reducing the number of exposed active sites. The catalytic activity of 1% Pt/C (see Online Supplementary Materials) was measured as a comparative standard. In the first experiment [Figure 1(*b*)], 5 equiv. of NHC relative to palladium was introduced into the hydrogenation reaction and the obtained results were compared with those of samples without added NHC. To study the general applicability of the NHC modification method, a Pt-based catalyst was chosen. Platinum, being catalytically active in hydrogenation reactions and belonging to the same group as Pd but one period lower, was an interesting object for investigation. The aim was to determine whether the introduction of NHC could enhance its activity and to compare the effect of NHC modification on Pt with that observed for Pd catalysts. The diphenylacetylene hydrogenation reaction uses a base (KOH) which serves as a good reagent for converting NHC · HCl salts into carbenes which are then able to bind to the metal surface. Figure 1(*e*) shows a comparison of the measured activities of Pd/C, Pt/C and samples decorated with the corresponding NHC ligands. In the case of the platinum catalyst the activity did not change indicating the absence of the effect of NHC. The reaction mixture with Pd/C + IMes showed a slight decrease in activity, while for the mixture with Pd/C + IPr the activity did not change within the measurement error.

It is known from the literature that NHC ligands are capable of removing metal atoms from NPs[21] and that the resulting (NHC)PdL_n complexes exhibit catalytic activity in the hydrogenation reaction with molecular hydrogen.[19] Therefore, one explanation for the increase in the catalytic activity of the system may be the formation of soluble palladium complexes. To test this hypothesis, an experiment was carried out on the pre-activation of the Pd/C catalyst by treatment with a solution containing NHC ligand at 80 °C for 30 min. It turned out that in the case of the IMes ligand, the catalytic activity decreased to 28% compared to 34% activity of the conventional Pd/C catalyst, while in the case of the IPr ligand, on the contrary, it increased up to 51% [see Figure 1(*e*)]. On the other hand, the Pt catalyst did not show any shift in catalytic activity when treated with NHC ligands in a similar study. This raises an interesting question about the mechanism of the hydrogenation reaction. It is known that in alkaline media, DMF in the presence of palladium can act as a hydrogen source for transfer hydrogenation.[22] However, even though high temperatures are required to activate this process, it is necessary to ensure that there is no contribution of transfer hydrogenation to the overall process. For this purpose, the experiments were carried out in fully deuterated DMF (DMF-d_7). The absence of hydrogenation product with deuterium atoms confirmed the hypothesis of preferential hydrogenation due to molecular hydrogen. The effect of NHC can be considered from different aspects. In the case shown in Figure 1(*b*), it is likely that the surface decoration of metal NPs occurs, the coverage of which remains to be determined. It can be hypothesized that IMes, being less sterically hindered, will be more strongly attached to the palladium particles compared to IPr. As a result, IMes and IPr provide different surface coverage due to steric effects, which affects the catalytic activity. It is also known that Pd NPs carrying excess negative charge have lower initial activity for acetylene hydrogenation than those with excess positive charge.[23] NHC will inject electron density at the expense of aryl moieties coordinated to Pd NPs, which has an antagonistic effect. During pre-activation, metal leaching occurs, which increases the catalytic activity of Pd/C in all cases. When using IPr, an agonistic effect is observed, which is explained by the fact that sterically hindered IPr is less anchored on the surface of Pd NPs. In this case, no significant effect is observed from the surface decoration of metal particles, but the catalytic activity is enhanced by leaching of the metal. IMes binds strongly to NPs, due to which an antagonistic effect is observed even upon leaching. To investigate the role of NHCs and to determine whether their introduction during pre-activation leads to the formation of active palladium complexes, a hot filtration test was conducted. It was shown that pre-activation resulted in 0.19, 0.35 and 0.33% Pd leaching in the cases of Pd/C, Pd/C + IMes and Pd/C + IPr, respectively. The product yields after pre-activation and hot filtration were less than 3% in all cases (see Online Supplementary Materials). This indicates that the main catalytic activity is provided by the palladium particles rather than the leached palladium complexes. This suggests that the role of NHCs during pre-activation is likely to be more efficient surface decoration, which ultimately modifies the catalytic activity.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7693.

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