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Facile Synthesis of NHC-Stabilized Ni Nanoparticles and their Catalytic Application in the Z-selective Hydrogenation of Alkynes

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Well defined Ni nanoparticles (NiNPs) stabilized by N-heterocyclic carbenes (NHCs) have been synthesized through a new methodology involving the decarboxylation of a zwitterionic CO_2 adduct. Their catalytic performance was tested in the partial hydrogenation of alkynes into (Z)-alkenes under very mild reaction conditions (50 °C and 5 bar H₂ pressure) providing excellent activities and selectivities.

Metal nanoparticles (MNPs) display unique physical and chemical properties, which confers them high potential for applications in diverse areas such as medicine and catalysis, among others.^{1, 2} To enhance their performance in catalysis, the selective formation of well-defined nano-objects is required. Furthermore. they should be stabilized by species that will restrict the approach of the substrate and as such induce selectivity. Nowadays, Nheterocyclic carbenes (NHCs) are recognized as one of the most versatile families of compounds in modern chemistry and are employed as ligands in metal transition catalysed transformations in both academy and the chemical industry.³ Although these ligands were used for the preparation of Au,⁴⁻⁸ Pd, 9 Ir¹⁰ and Ru^{11, 12} nanoparticles, to the best of our knowledge, there is only one report on the use of NHCs for the stabilization of Ni NPs.¹³ To date, NHC-stabilized MNPs have been obtained by three main methodologies: i) by direct reduction of NHC-organometallic complexes.⁶ ii) by procedures using the isolated free carbene (either by ligand exchange¹⁴ or by the organometallic approach developed by Chaudret¹¹), and iii) using non-isolable carbenes via in situ generation of the free carbenes (Scheme 1).¹²

In all cases, a basic pre-treatment of an imidazolium salt precursor is required, either for the isolation of the free carbene or for its *in-situ* generation. Crabtree et al. reported the utilization of 1,3-dialkylimidazolium-2-carboxylate (R_2Im-CO_2) as an efficient carbene precursor for the synthesis of NHC-based organometallic complexes.¹⁵



Scheme 1 Synthetic approaches to NHC-stabilized metal nanoparticles.

These imidazolium carboxylates are water-stable, synthetically readily available, and efficiently transfer the corresponding NHC ligand by decarboxylation in non-polar solvent.^{16, 17} It was therefore thought that the use of such NHC-precursor could be applied in the synthesis of MNPs and as such, neither the filtration of inorganic salts nor the isolation of carbenes would be required.

The hydrogenation of alkynes to selectively produce (*E*)- or (*Z*)alkenes is a useful synthetic tool for the production of valuable compounds.¹⁸ Since classical heterogeneous catalysts are usually based on noble metals such as Pd, Pt or Au,¹⁹⁻²² new approaches employing abundant and low-cost metals is therefore desirable. Recently, Prechtl and co-workers reported the use of NiNPs stabilised by ionic liquids for the selective hydrogenation of alkynes to the corresponding (*Z*)-alkenes.²⁰

Here, we report a new and straightforward methodology to prepare small and well defined NHC-stabilized nickel nanoparticles, both colloidal and supported in carbon nanotubes (CNTs), using a simple "one-pot" procedure based on the decarboxylation of 1,3-dialkylimidazolium-2-carboxylate $(R_2 Im-CO_2)$.²³ This procedure

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⁺ Footnotes relating to the title and/or authors should appear here.

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avoids basic pre-treatment. The catalytic performance of these latter species was evaluated in the selective hydrogenation of internal alkynes into Z-alkenes under mild conditions.

To evaluate Me_2Im-CO_2 as ligand precursor for the stabilization of Ni-NPs, the organometallic precursor Ni(COD)₂ (COD=cyclooctadiene) was reduced in THF under 3 bar of hydrogen at 60°C in the presence of Me_2Im-CO_2 (Scheme 2). The amount of NHC-based ligand used during the synthesis was varied using 0.1, 0.2, 0.5 and 1 equivalent per Ni.



Scheme 2 Synthetic methodology used for the preparation of NHCstabilized Ni-NPs using **Me_Im-CO_2** as stabilizer precursor.

In the presence of 0.1 equivalent of ligand, nickel particles were not efficiently stabilized. When the amount of ligand was increased, the NPs **Ni-0.2**, **Ni-0.5** and **Ni-1** were formed and could be isolated. The TEM images of these particles are shown in Fig. 1.



Fig. 1 TEM micrographs and size distributions of Ni-0.2,Ni-0.5 and Ni-1 nanoparticles.

As previously observed with NHCs,¹¹ smaller NPs were formed upon increasing the amount of the ligand from 0.2 to 0.5 equivalent per Ni. Indeed, in sample **Ni-0.2**, the NPs exhibited a mean diameter of *ca.* $2.4\pm$ 0.9 nm, whilst for **Ni-0.5**, the mean size of *ca.* $2.0\pm$ 0.4 nm. Under these conditions, particles were well separated and neither agglomeration nor coalescence was detected on the carbon grid, indicating that the NHC-based ligand is strongly adsorbed on the nickel surface. However, for Ni-1 NPs a mean diameter of *ca*. 2.9 ± 0.7 nm was measured and a high degree of agglomeration was observed.

TGA analysis of the samples revealed that the NHC content for these NPs ranges from ca. 15 wt.% (Ni-0.2 NPs) to 44 wt.% (Ni-1.0 NPs) (Fig. S1, SI). Ni-0.5 NPs presented a ligand content of 27 wt.%. Similar NHC contents were previously reported for Ru²⁴ and Pt²⁵NPs. In addition, no weight loss associated to the presence of imidazolium carboxylate (at ca. 200 °C) was observed, confirming that this species is not acting as stabilizer. XRD patterns of a selected sample (Ni-0.5 NPs, Fig. S3, SI) revealed the presence of crystalline Ni with fcc packing. XPS measurements (Fig. S4, SI) showed a high percentage of NiO on the surface of Ni nanoparticles (67.6 at.%), which was attributed to nanoparticle oxidation during the sample preparation for XPS analysis. Indeed, nickel nanoparticles are very reactive and burn spontaneously in the presence of air producing white clouds of the oxide which is explained by their very small size and clean surface state. Upon Ar sputtering, the Ni content substantially increased (from 32.4 to 95.5 at.%) confirming the presence of metal core nanoparticles. This new route was first validated by comparing two batches of NiNPs stabilized with 1,3-dimethyimidazol-2-ylidene (Me,1m), prepared by i) the above mentioned methodology and ii) the reported in situ generation of non-isolable NHC,12 which is first employed here for the preparation of Ni nanoparticles. Following the last protocol, Me₂Im·HCl (0.5 molar equiv/Ni) was deprotonated via the addition of a slight excess of KOtBu in THF, and the resulting suspension (Me₂Im) was filtered through celite prior to its transfer into a solution of Ni(COD)₂ in THF. The reaction mixture was then pressurized with 3 bar of H₂, leading to a colloidal solution of nickel NPs with a mean size of 2.0± 0.5 nm (Fig. S5, SI). Comparison with the TEM data obtained by the new methodology clearly revealed similar dispersion of the particles on the grid and size (2.0±0.4 nm). In addition, the IR spectra recorded from the two batches of Ni-Me₂Im NPs were similar. In the sample of NPs prepared via the decarboxylation method, the characteristic features of the compound Me2Im-CO2 were not detected, confirming that this species does not participate to the NP stabilization (Fig. S6, SI). Furthermore, the TGA analysis recorded from the two batches of Ni/Me₂Im NPs showed similar profiles (Fig. S7, SI). Based on these results, it was concluded that both synthetic procedures yield very similar Ni nanoparticles, and thus evidenced that the new methodology developed in this work allows a rapid access to NHCstabilized nanoparticles without the need of a basic pre-treatment. With these results in hand, supported Ni nanocatalysts were synthesized following the same methodology in the presence of multiwalled carbon nanotubes (MWCNTs). The amount of NHCbased ligand used during the synthesis was varied from 0.2, 0.5 to 1 equivalent per Ni. TEM analysis of the resulting hybrid material is shown in Fig. 2. Interestingly, the TEM micrographs of Ni-0.2 NPs@CNTs and Ni-0.5 NPs@CNTs revealed the formation of very similar nanoparticles with no significant differences in size, shape and distribution since both exhibited a diameter of ca. 3.6± 0.8 nm.

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Fig. 2 TEM micrographs and size distributions of supported Ni-0.2,Ni-0.5 and Ni-1 NPs@CNTs.

It is remarkable that an increase of the mean particle size and size distribution was observed in comparison with the colloidal systems. When the amount of the NHC-based stabilizer was increased to 1 equivalent per Ni (Ni-1NPs@CNTs), a wider distribution was observed with no significant difference in size with respect to the colloidal system. In general, the small Ni nanoparticles were mostly deposited in the inner cavity of CNTs, as confirmed by STEM (Fig. 3). The supported nanoparticles were characterized by XRD analysis, evidencing the presence of Ni crystalline systems with fcc packing (Fig. S11, SI). XPS measurements (Fig. S12, SI) again revealed a high surface NiO content (82.9 at.%) due to the strong oxygen sensitivity of the nanoparticles even after immobilization onto CNTs. However, after Ar sputtering the metal content increased (72.7 at.%). Finally, TGA and ICP revealed a nickel content in Ni-Me2Im@CNTs that was similar to the nominal loading (10 wt.%) with values of 10.0 wt.% and 8.8 wt.%, respectively.



Fig. 3 STEM micrographs of Ni-0.5 NPs@CNTs.

Next, the catalytic performance of the NPs was evaluated in the *semi*-hydrogenation of internal alkynes. The results are summarized

in Table 1. First, the catalytic performance of Ni-0.2NPs@CNTs, Ni-0.5NPs@CNTs and Ni-1NPs@CNTs were compared using diphenylacetylene as model substrate using 3 mol% of Ni at 50°C and under 5 bar of H₂. After 16h, full conversion was achieved for 0.2NPs@CNTs and Ni-0.5NPs@CNTs while a lower value was measured using Ni-1NPs@CNTs (Table 1, Entries 1-3). This indicated that the large amount of NHC used during the synthesis of the latter nanocatalyst could hinder the substrate coordination at their surface. In all cases, no over-hydrogenation product was detected while distinct degree of stereoselectivity was measured: using 0.2NPs@CNTs, excellent selectivity (94%) to the Z-alkene was observed while using Ni-0.5NPs@CNTs as the catalytic system, diphenylacetylene was selectively converted to (Z)-stilbene in quantitative yield (Table 1, entry 2). In contrast, using Ni-1NPs@CNTs, a drop in selectivity was detected.

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Table 1 Catalytic <i>semi</i> -hydrogenation of internal alkynes using NiMe₂lmNPs@CNTs ^a						
E.	NiNPs@CNT	R1	R ₂	Conv. ^b (Yield B) ^c	$\mathbf{B/C}^{b}$	% D ^b
1	Ni-0.2@CNT	Ph	Ph	100	94/6	0
2	Ni-0.5@CNT	Ph	Ph	100(97)	97/3	0
3	Ni-1@CNT	Ph	Ph	78	78/22	0
4	Ni-0.5@CNT	$(CH_2)_2CH_3$	$(CH_2)_2CH_3$	100(91)	99/1	0
5	Ni-0.5@CNT	CH₃	$(CH_2)_4CH_3$	81(90)	98/2	10
6	Ni-0.5@CNT	CH_2CH_3	Ph	100(70)	94/6	12
7	Ni-0.5@CNT	CH₂OH	Ph	100(80)	96/4	13

^{*a*}General conditions: 1 mmol of substrate, 3 mol% of Ni, 10 ml of THF, 50°C, 5 bar H₂, t = 16h. ^{*b*}Determined by GC-MS spectrometry and NMR analysis. ^CIsolated yeld.

In view of these results, the reaction using **Ni-0.5NPs@CNTs** as catalytic system was repeated and monitored over time (Fig. 4). Total conversion of the substrate was observed after a reaction time of 7 hours with total selectivity for the corresponding (Z)-alkene. Interestingly, no over-hydrogenation of the substrate into the corresponding alkane was observed even after 24 hours of reaction.



Fig. 4 Evolution in time of diphenylacetylene semi-hydrogenation in the presence of NiMe₂Im-0.5 NPs@CNTs at 50°C, 5 bar H₂ for 24h.

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The remaining solution after catalytic reaction was analysed by inductively coupled plasma (ICP) revealing a nickel content of 0.008% with respect to all Ni initially introduced. Furthermore, no evolution of the reaction was observed when the *semi*-hydrogenation of diphenylacetylene was tested using the remaining solution of a catalytic test after filtration of the heterogeneous catalyst. These results indicated that no relevant leaching had taken place under the reaction conditions.

Next, we examined the application of the optimized catalyst system for a broader scope of internal alkynes (Table 1, Entries 4-7). When 4-octyne was tested as substrate (Entry 4), the corresponding (*Z*)-alkene was again obtained in quantitative yield. However, when 2-octyne was used (Entry 5), 81% conversion was measured and a mixture of alkene and alkane was observed. However, the Z/E ratio remained at *ca*. 98%. In the case of 1-phenyl-1-butyne substrate, a greater amount of alkane was obtained (12%) at 100% conversion and the selectivity Z/E was slightly lower (ca. 92%) (Entry 6). In the hydrogenation of 3-phenyl-2-propyn-1-ol (Entry 7), the selective formation of the (*Z*)-alkene was observed but 10% of the overhydrogenated product was detected with full conversion.

To evaluate the robustness of these catalysts, the NiMe₂Im-0.5 NPs@CNTs was recycled several times in the hydrogenation of diphenylacetylene as model substrate (Fig. 5). No relevant loss of activity nor selectivity was observed over 3 runs although a slight decrease in activity was observed in the last run.



Fig. 5 Recycling experiment of the hydrogenation of diphenylacetylene over NiMe_2Im-0.5 NPs@CNTs at 50° C, 5 bar H₂ for 7h.

In conclusion, a new procedure to synthesize small and defined NHC-stabilized NiNPs well based on the decarboxylation of the corresponding imidazolium carboxylate zwitterionic salt has been developed. This methodology was employed for the synthesis of colloidal NiNPs and for the immobilization of NiNPs onto carbon nanotubes by a simple "one-pot" procedure without surface modification. These NPs were thoroughly characterised and the supported NPs revealed efficient catalysts in the selective hydrogenation of terminal alkynes into the corresponding (Z)-alkenes under very mild reaction conditions. Furthermore, these heterogeneous catalysts can be readily recovered by simple filtration and reused 3 times without relevant decrease in activity.

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