A New Straightforward and Mild Preparation of Nickel(0) Nanoparticles

Francisco Alonso, José Juan Calvino,[†] Iñaki Osante, and Miguel Yus*
Departamento de Química Orgánica, Facultad de Ciencias, and Instituto de Síntesis Orgánica (ISO),
Universidad de Alicante, Apdo. 99, 03080 Alicante, Spain
[†]*Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica,*
Facultad de Ciencias, Campus Río San Pedro, 11510 Puerto Real, Cádiz, Spain

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Very fine nickel nanoparticles with diameters of 2.5 ± 1.5 nm have been prepared by reduction of anhydrous nickel(II) chloride with lithium powder and a catalytic amount of 4,4′-di-*tert*-butylbiphenyl (DTBB) in THF at room temperature.

In the recent years, considerable attention has been devoted to the development of uniform nanometer-sized metal particles because of their unique properties and potential applications in a variety of fields including electronics, optics, magnetism, energy technology or chemistry, among others.[1] In particular, transition-metal nanoparticles, in different forms, have emerged as a novel family of catalysts able to promote more efficiently a variety of organic transformations.[2] Despite the diverse methodologies available for the synthesis of metal nanoparticles,[3] the less nobel metal Fe, Co, and Ni nanoparticles are more difficult to generate but of special interest due to their ferromagnetic and catalytic properties.[4] Concerning the preparation of nickel nanoparticles, only few works have been reported, the reduction of a nickel salt being the most practiced method. In this context, it is worth of mention the contributions of the groups of Schmid,[5] Kurihara,[6] Yanagida,[7] Chen,[8–10] and Tsuji.[11] All the methodologies have in common the presence of an additive (Ph_3P, polyvinylpyrrolidone, or cetyltrimethylammonium bromide) as protective agent in order to prevent particle agglomeration. In fact, it is well known that in its absence, the resultant particles can be in the micrometre or submicrometre size range. In addition, most of the methodologies available involve high temperatures and long reaction times.

We want to present herein a new and mild methodology that allows the fast preparation of nickel(0) nanoparticles, most of them between 1.5–4.0 nm, in the absence of any antiagglomeration additive or nucleation catalyst. The methodology involves anhydrous $NiCl_2$ as the metallic nickel source, metal lithium as the reducing agent, catalytic 4,4′-di-*tert*-butylbiphenyl (DTBB) as an electron carrier (the reaction failed in its absence), and THF as solvent. In a typical experiment, THF (20 mL) was added to lithium powder (4.0 mmol) and DTBB (0.05 mmol) at room temperature, and the mixture was stirred until formation of a deep blue suspension (ca. 5 min). Then, $NiCl_2$ (1.0 mmol) was added with concomitant formation of a black suspension, which was stirred for ca. 10 min.

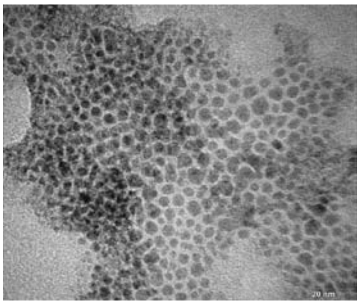

Figure 1. TEM micrograph of nickel nanoparticles.

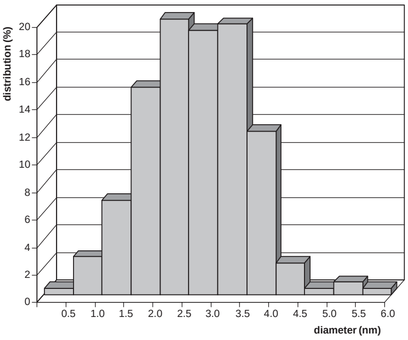

Figure 2. Size distribution of nickel nanoparticles determined by TEM. The sizes were determined for 220 nanoparticles selected at random.

Dropplets of the solution containing the nickel nanoparticles were first analyzed by transmission electron microscopy (TEM), a typical TEM micrograph and size distribution graphic being depicted in Figures 1 and 2, respectively. Very fine spherical and monodispersed nanoparticles were observed with a narrow distribution range (ca. 2.5 ± 1.5 nm). Interestingly, a considerable amount of nickel nanoparticles could be measured with diameters <2 nm (25%), whereas only three particles out of 220 were >5 nm.

Energy-dispersive X-ray (EDX) analysis on various regions confirmed the presence of nickel, with energy bands of 7.46, 7.48, and 8.26 keV (K lines) and 0.74, 0.76, 0.85, and 0.87 keV (L lines). A maximum absorbance at 208 nm in the UV–vis spectrum could be also ascribed to nickel nanoparticles.[12] However, the nanoparticles experienced partial oxidation upon exposure to air, as confirmed by X-ray photoelectron spectroscopy (XPS), which showed the Ni $2p_{3/2}$ (852.2 eV) and Ni $2p_{3/2}$ (855.5 eV) peaks at an estimated 47:53 Ni(0)/Ni(II) ratio (Figure 3). The X-ray diffraction spectrum (XRD) did not show any significant peak, what might be due to the amorphous character of the sample and/or to the fact that the crystal domains are <10 nm. At any rate, the presence of narrow and wide peaks in nearby angular regions could be attributed to a multiphasic sample, containing more than one crystal phase under different microstructural conditions. In fact, the selected area electron diffraction (SAED) pattern (Figure 4) shows two reflections at 0.203 and 0.176 nm which can be assigned, respectively,

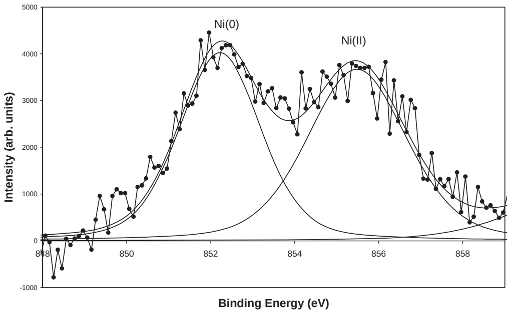

Figure 3. X-ray photoelectron spectrum of nickel nanoparticles corresponding to the Ni $2p_{3/2}$ region.

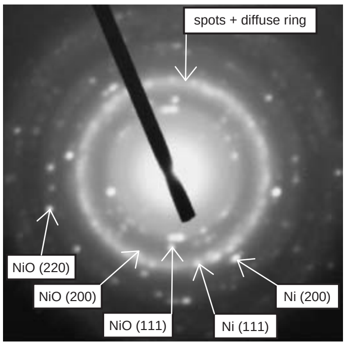

Figure 4. Electron-diffraction pattern of nickel nanoparticles.

to the (111) and (200) planes of a face-centered cubic (fcc) nickel phase. However, because of the coexistence of both discrete points and a diffuse intensity ring in the 0.203 nm region of all the SAED patterns recorded for this sample, the presence of some amorphous nickel particles can not be ruled out. Other spots observed in this pattern at 0.256, 0.208, and 0.147 nm are consistent with the presence of cubic NiO. Thus, the reported *d* values could be assigned to the (111), (200), and (220) planes of this phase, respectively. The observation of NiO is in agreement with the XRD and XPS results reported above.

Very little concentration effect on the size and distribution of the nanoparticles was observed. Thus, by performing the reaction under the above-described conditions but with 5 mL of THF (0.2 M) instead of 20 mL (0.05 M), 125 nanoparticles analyzed showed diameters within the range 1.2–4.8 nm. It is notheworthy that the particle agglomeration phenomenon was minimun after stirring for 8 h, with a size range of 1.1–4.0 nm. In contrast, agglomeration turned dramatic after 24 h, the only monodispersed particles detected being in the range 2.5–7.1 nm.

Alternatively, the nickel nanoparticles were also analyzed after filtration. In this case, practically no deviation from the above-reported diameter range was observed (0.6–4.5 nm). However, the longer time required for handling and the consequent longer exposure to air led to a higher proportion of oxidized nickel, Ni(0)/Ni(II) 14:86.

The high reactivity of the generated nickel nanoparticles was demonstrated in the catalytic hydrogenation of a variety of organic compounds.[13,14] Thus, different alkenes, dienes, and alkynes were reduced to alkanes; carbonyl compounds and imines to alcohols and amines, respectively; alkyl and aryl halides to the corresponding hydrocarbons; aryl hydrazines to anilines; the partial reduction of aromatic compounds and the deoxygenation of azoxy compounds and *N*-oxides was also achieved. Reductions were carried out with lithium powder and catalytic $NiCl_2$ in THF at room temperature under 1 atm H_2 atmosphere, using a catalytic amount of naphthalene or polymer-supported naphthalene as the electron carrier.

More recently, nickel(0) nanoparticles, generated under very similar reaction conditions to those described in this report, have been successfully applied to the semireduction of alkynes to alkenes.[15]

In summary, a fast, mild, and simple preparation of very fine and reactive nickel nanoparticles has been described, in the absence of any antiagglomeration additive or nucleation catalyst. Further studies on the generation and reactivity of nickel nanoparticles from related systems[16] as well as the development of systems more resistant to oxidation are under way.

References and Notes

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16 During the preparation of this manuscript we have discovered that the reduction of $NiCl_2 \cdot 2H_2O$, under the same conditions described above, led to the formation of nickel nanoparticles within a diameter range that has been estimated to be equal or even lower than that reported herein. This result could explain the successful application of the system $NiCl_2 \cdot 2H_2O$–Li–arene (cat.) to the reduction of a variety of functional groups: For a review, see: F. Alonso and M. Yus, *Chem. Soc. Rev.*, **33**, 284 (2004).