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## Preparation of nickel(0) nanoparticles by arene-catalysed reduction of different nickel chloride-containing systems

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Nickel(0) nanoparticles with diameters < 6 nm have been prepared in a straightforward manner by reduction of different nickel(II) chloride-containing systems with lithium powder and a catalytic amount of an arene in THF at room temperature. The properties and reactivity of the different nickel nanoparticles have been studied and compared.

*Keywords:* Nickel; Nanoparticles; Reduction

### 1. Introduction

Nanoparticles have chemical and physical properties different from those of the bulk and isolated atoms or molecules with the same chemical composition. 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 [1–8]. 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 because of their small size and extremely large surface-to-volume ratio [9–14]. Despite the diverse methodologies available for the synthesis of metal nanoparticles [15, 16], the less noble metal Fe, Co, and Ni nanoparticles are more difficult to generate but of special interest due to their ferromagnetic and catalytic properties [17, 18]. As regards the preparation of nickel nanoparticles, the reduction of a nickel salt is the most practiced method, which has

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been applied by the groups of Schmid [19], Kurihara [20], Yanagida [21], Chen [22–24], and Tsuji [25]. In general, the presence of an additive (such as  $\text{Ph}_3\text{P}$ , polyvinylpyrrolidone, or cetyltrimethylammonium bromide), as protective agent, is necessary and a common feature in all these methodologies in order to prevent particle agglomeration. In fact, it is well known that in its absence, the resultant particles can be in the micrometer or sub-micrometer size range, thus conditioning their physical and chemical properties. In addition, most of the methodologies available involve high temperatures and long reaction times.

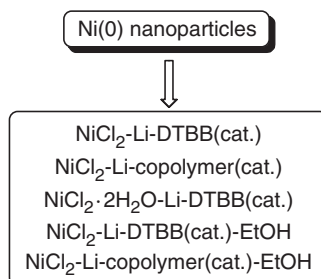
Due to our ongoing interest in the development of new reducing systems for organic compounds based on the use of active nickel(0), we have recently communicated about a new and mild methodology that allows the fast preparation of nickel(0) nanoparticles, most of them between 1.5–4.0 nm, in the absence of any anti-agglomeration additive or nucleation catalyst [26]. We want to present herein a comparative study on the preparation and reactivity of nickel(0) nanoparticles, obtained by the reduction of nickel(II) chloride present in different reaction systems, using lithium powder and a catalytic amount of an arene as an electron carrier. The different systems studied are:  $\text{NiCl}_2\text{-Li-DTBB}$ ,  $\text{NiCl}_2\text{-Li-copolymer}$ ,  $\text{NiCl}_2 \cdot 2\text{H}_2\text{O-Li-DTBB}$ ,  $\text{NiCl}_2\text{-Li-DTBB-EtOH}$ , and  $\text{NiCl}_2\text{-Li-copolymer-EtOH}$ .

## 2. Experimental section

### 2.1 Materials

Anhydrous nickel(II) chloride, lithium powder, and 4,4'-di-*tert*-butylbiphenyl (DTBB) were commercially available (Aldrich, Fluka, and MEDALCHEMY S. L., respectively). Dry THF was directly used without any purification (Acros, 99.9%).  $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$  was obtained from commercially available  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  by heating in vacuo (ca. 0.5 Torr) at 100°C in Kugelrohr during 2 h [27]. The polymer-supported electron carrier 4'-vinylbiphenyl(VBP)/divinylbenzene(DVB) copolymer was prepared by radical copolymerisation according to the published procedure [28, 29].

Five different nickel(II) chloride-containing systems, with a varied applicability in organic functional group transformations, have demonstrated to generate highly reactive nickel nanoparticles. The nature and properties of these nanoparticles as well as the stabilisation effect of the different components have been studied and compared.



## **2.2 Preparation of Ni(0) nanoparticles from the system NiCl<sub>2</sub>-Li-DTBB (procedure A)**

THF (20 mL) was added to lithium powder (28 mg, 4.0 mmol) and 4,4'-di-*tert*-butylbiphenyl (DTBB) (13 mg, 0.05 mmol) at room temperature and the mixture was stirred until formation of a deep blue suspension (ca. 5 min). Then, anhydrous NiCl<sub>2</sub> (130 mg, 1.0 mmol) was added with concomitant formation of a black suspension that was stirred for ca. 10 min. Droplets of the solution containing the nickel nanoparticles were taken out at different reaction times (0.5, 8 and 24 h) and analysed by the means described below. Alternatively, some samples were analysed after filtration.

## **2.3 Preparation of Ni(0) nanoparticles from the system NiCl<sub>2</sub>-Li-copolymer (procedure B)**

As described in procedure A but using a VBP/DVB copolymer (44 mg, 0.05 mmol) as an electron carrier instead of DTBB.

## **2.4 Preparation of Ni(0) nanoparticles from the system NiCl<sub>2</sub>·2H<sub>2</sub>O-Li-DTBB (procedure C)**

THF (2 mL) was added to lithium powder (28 mg, 4.0 mmol) and DTBB (13 mg, 0.05 mmol) at room temperature and the mixture was stirred until formation of a deep blue suspension (ca. 5 min). Then, NiCl<sub>2</sub>·2H<sub>2</sub>O (166 mg, 1.0 mmol) was added with concomitant formation of a black suspension, which was stirred for ca. 10 min, followed by the addition of THF (18 mL).

## **2.5 Preparation of Ni(0) nanoparticles from the system NiCl<sub>2</sub>-Li-DTBB-EtOH (procedure D)**

As described in procedure C but using anhydrous NiCl<sub>2</sub> (130 mg, 1.0 mmol) instead of NiCl<sub>2</sub>·2H<sub>2</sub>O and adding ethanol (0.12 mL, 2 mmol) at the end.

## **2.6 Preparation of Ni(0) nanoparticles from the system NiCl<sub>2</sub>-Li-copolymer-EtOH (procedure E)**

As described in procedure D but using the VBP-DVB copolymer (44 mg, 0.05 mmol) as an electron carrier instead of DTBB.

## **2.7 Characterisation**

TEM images were recorded using a JEOLJEM2010 microscope, equipped with a lanthanum hexaboride filament, operated at an acceleration voltage of 200 kV. For their observation, the powder samples were mounted on holey-carbon coated 300 mesh copper grids (a gold grid was utilized in some cases). X-EDS analyses were carried out with an Oxford Inca Energy TEM100 attachment. For samples in solution, a drop was added to the grid allowing the solvent to evaporate before being introduced into the microscope. For samples in the solid state, a small portion was suspended in hexane and

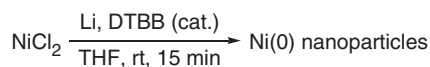
sonicated for a few seconds, a drop of the resulting suspension was added to the grid allowing the solvent to evaporate before being introduced into the microscope. The XRD diagrams were collected in the  $\theta$ - $\theta$  mode using a Bruker D8 Advance X-ray diffractometer: Cu  $K\alpha_1$  irradiation,  $\lambda = 1.5406 \text{ \AA}$ ; room temperature ( $25^\circ\text{C}$ );  $2\theta = 4$ – $80$ . The XPS spectra were measured with a VG-Microtech Multilab 3000 electron spectrometer using a non-monochromatised Mg- $K\alpha$  (1253.6 eV) radiation source of 300 W and a hemispheric electron analyser equipped with 9 channeltron electron multipliers. The pressure inside the analysis chamber during the scans was about  $5 \cdot 10^{-7} \text{ Nm}^{-2}$ . After the survey spectra were obtained, higher resolution survey scans were performed at pass energy of 50 eV. The intensities of the different contributions were obtained by means of the calculation of the integral of each peak, after having eliminated the baseline with S form and adjusting the experimental curves to a combination of Lorentz (30%) and Gaussian (70%) lines. All the bond energies were referred to the line of the C 1s to 284.4 eV, obtaining values with a precision of  $\pm 0.2 \text{ eV}$ .

### 3. Results and discussion

#### 3.1 $\text{NiCl}_2$ -Li-DTBB

In this system, anhydrous  $\text{NiCl}_2$  was used as the metallic nickel source, lithium metal as the reducing agent, catalytic 4,4'-di-*tert*-butylbiphenyl (DTBB) as the electron carrier, and THF as the solvent at room temperature (scheme 1). It is worthy to note that the generation of nickel nanoparticles failed in the absence of the electron carrier. Following the procedure A described in the experimental section, droplets of the solution after 0.5 h containing the nickel nanoparticles were first analysed by transmission electron microscopy (TEM), a representative TEM micrograph and size distribution graphic being depicted in figure 1. Well defined spherical and monodispersed nanoparticles were observed with a narrow distribution range (ca.  $2.5 \pm 1.5 \text{ nm}$ ). Interestingly, a considerable amount of nickel nanoparticles could be measured with diameters  $< 2 \text{ nm}$  (25%), whereas only three particles out of 220 were  $> 5 \text{ nm}$ .

Energy-dispersive X-ray (EDX) analysis on various regions confirmed the presence of nickel, with energy bands of 7.46, 7.48, 8.26 keV (K lines) and 0.74, 0.76, 0.85, 0.87 keV (L lines). A maximum absorbance at 208 nm in the UV-Vis spectrum could be also ascribed to nickel nanoparticles [30]. 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 2). The X-ray diffraction spectrum (XRD), however, 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  $< 10 \text{ nm}$ . 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



Scheme 1. Preparation of Ni(O) nanoparticles.

different microstructural conditions. In fact, the selected area electron diffraction (SAED) pattern (figure 3) shows reflections at 2.03 and 1.76 Å which can be assigned, respectively, to the (111) and (200) planes of a face-centered cubic (fcc) nickel phase. However, and due to the coexistence of both discrete points and a diffuse intensity ring in the 2.03 Å 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 2.56, 2.08, and 1.47 Å 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 concentration seemed to have very little effect on the size and distribution of the nanoparticles. 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 analysed showed diameters within the range 1.2–4.8 nm. It is noteworthy that the particle agglomeration phenomenon was minimum after stirring for 8 h, with a size range

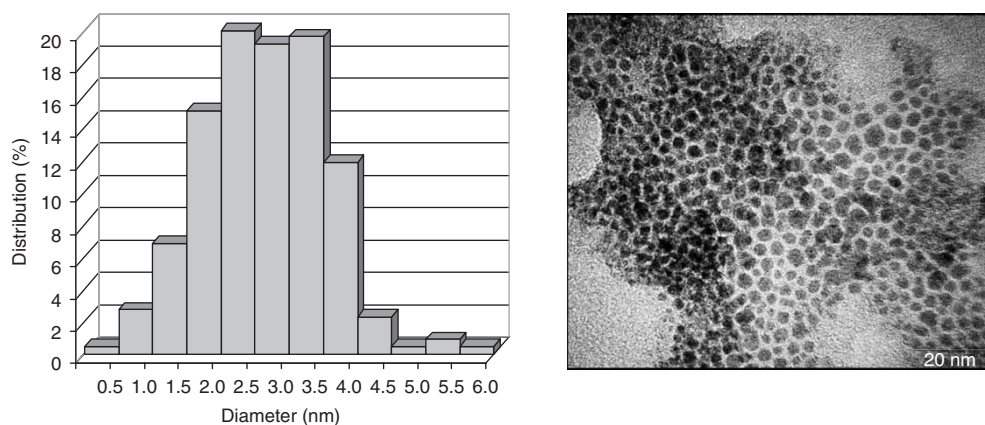


Figure 1. TEM micrograph and size distribution of the nickel nanoparticles obtained from the system  $\text{NiCl}_2\text{-Li-DTBB}$ . The sizes were determined for 220 nanoparticles selected at random.

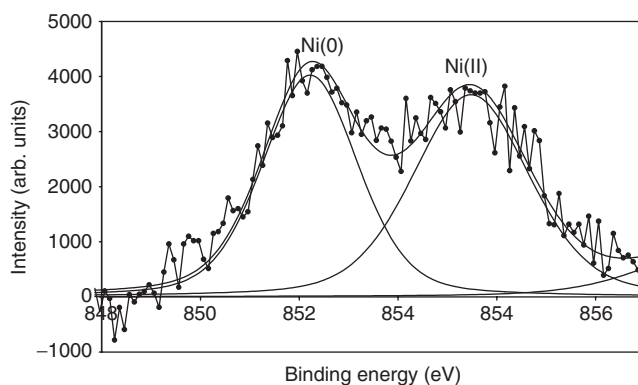


Figure 2. X-ray photoelectron spectrum of nickel nanoparticles, obtained from the system  $\text{NiCl}_2\text{-Li-DTBB}$ , corresponding to the  $\text{Ni } 2p_{3/2}$  region.

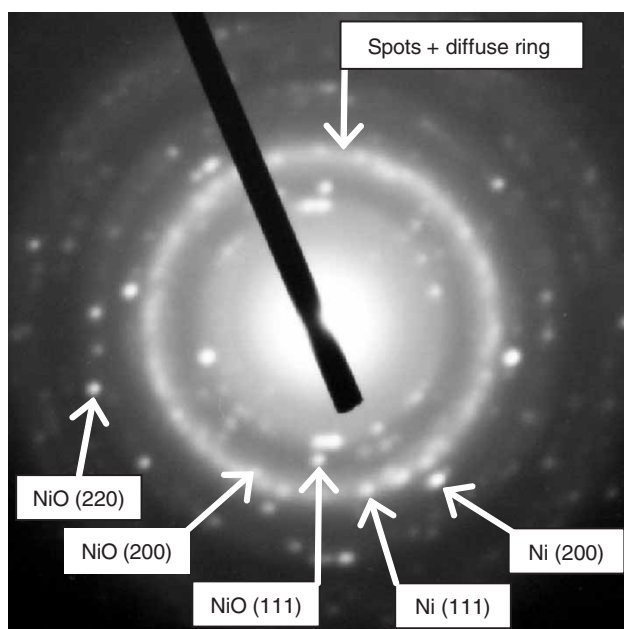


Figure 3. Electron-diffraction pattern of nickel nanoparticles obtained from the system  $\text{NiCl}_2\text{-Li-DTBB}$ .

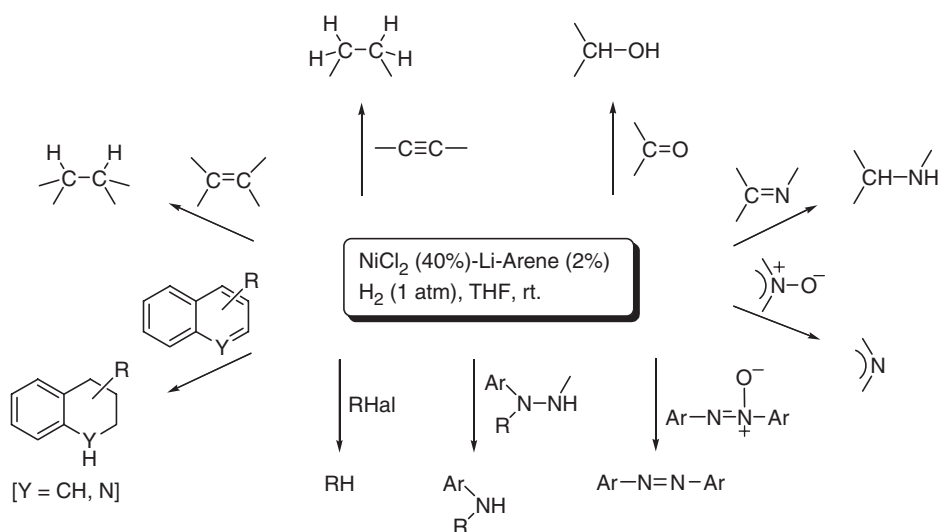
of 1.1–4.0 nm. In contrast, agglomeration turned dramatic after 24 h, the only monodispersed particles detected being in the range 2.5–7.1 nm.

Alternatively, the nickel nanoparticles were also analysed 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 oxidised 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 [31, 32]. 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 (scheme 2). Reductions were carried out with lithium powder and a catalytic amount of  $\text{NiCl}_2$  in THF at room temperature under 1 atm  $\text{H}_2$  atmosphere, using a catalytic amount of naphthalene as the electron carrier. The reactivity observed resembles somewhat that of Raney nickel.

### 3.2 $\text{NiCl}_2\text{-Li-copolymer}$

Alternatively, the catalytic hydrogenations depicted in scheme 2 could be carried out with a polymer-supported naphthalene or biphenyl (DVB-VBP copolymer) as electron carriers [28]. This fact represents an important advantage since they can be easily removed from the reaction medium by simple filtration. Following the procedure B



Scheme 2. Hydrogenation of organic compounds catalysed by Ni(O) nanoparticles generated from the system N:Cl<sub>2</sub>-Li-arene.

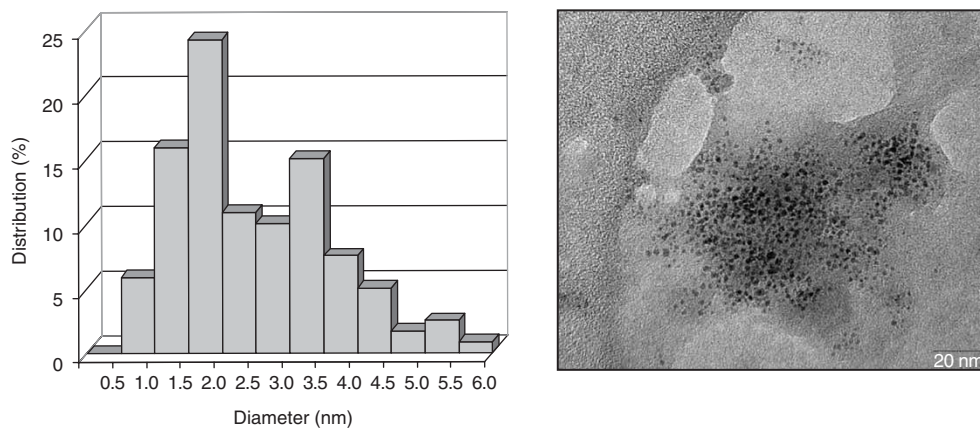


Figure 4. TEM and size distribution of nickel nanoparticles obtained from the system NiCl<sub>2</sub>-Li-copolymer. The sizes were determined for 120 nanoparticles selected at random.

described in the experimental section, droplets of the solution containing the nickel nanoparticles were analysed by TEM after 0.5 h. The obtained spherical and monodispersed nanoparticles showed a similar distribution range compared to that of the NiCl<sub>2</sub>-Li-DTBB system (figure 4), though the increase in size from 2.0 to 6.0 nm was more progressive in the latter, with a larger amount of nanoparticles > 4 nm. Additional stirring until a total time of 24 h slightly increased the number of nanoparticles > 4.5 nm, the presence of the copolymer showing a certain stabilisation on the size of the particles.



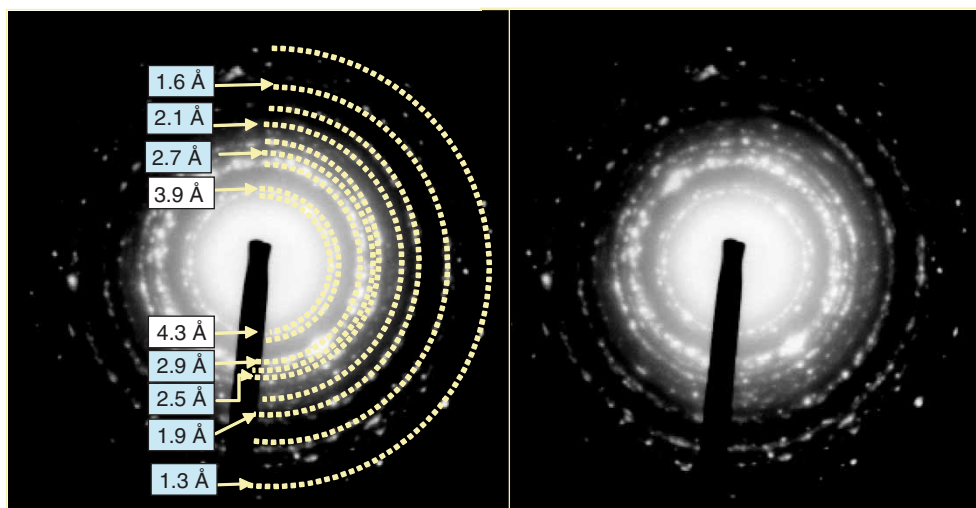


Figure 5. Electron-diffraction pattern of the nickel nanoparticles obtained from the system  $\text{NiCl}_2$ -Li-copolymer.

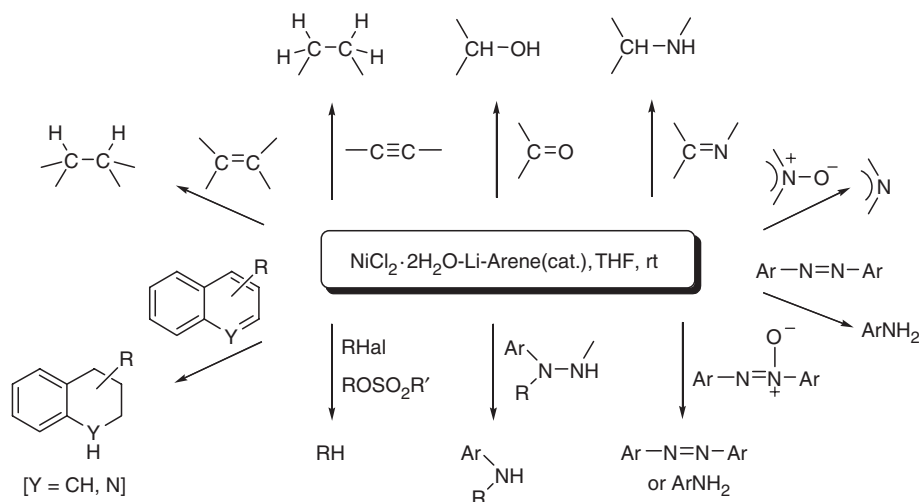
The XRD spectrum did not show any significant peak. The surface of these nanoparticles seemed to be completely oxidized after a short exposure to air since XPS analysis showed the O 1s (531.1 eV) and Ni  $2p_{3/2}$  (855.9 eV) peaks corresponding to an oxygenated form of Ni(II). The SAED pattern shows three reflections at 1.90, 1.29, and 1.08 nm which could be assigned, respectively, to the (200), (220) and (311) planes of a fcc nickel phase (figure 5). The presence of cubic NiO could be correlated with the peaks at 2.12 Å (200) and 1.49 Å (220), whereas other reflections can be assigned to lithium-containing compounds such as LiCl, LiOH or  $\text{LiOH}\cdot 2\text{H}_2\text{O}$ . Therefore, the presence of the copolymer does not seem to prevent the oxidation of the Ni(0) nanoparticles during the time of analysis.

### 3.3 $\text{NiCl}_2\cdot 2\text{H}_2\text{O}$ -Li-DTBB

The main feature of this reducing system is the fact that molecular hydrogen is generated *in situ* by the reaction of the excess of lithium powder with the hydration water of the nickel salt, thus avoiding the handling of molecular hydrogen. It found application in the reduction of alkenes, alkynes, carbonyl compounds and imines, halogenated materials, sulfonates, aromatic and heteroaromatic compounds, hydrazines, azo compounds, azoxy compounds, *N*-oxides, and nitrones (scheme 3) [33].

In this case, the lithium hydroxide generated in the reaction medium (procedure C, experimental section) seems to affect the particle size, making the particle distribution narrower at the time that decreases the average particle diameter (92% of the particles with 1.0–3.0 nm) (figure 6). A stabilizing effect has also been observed, since the particle distribution remains practically unaltered after 24 h.

As occurred in the previous systems, the XRD spectrum did not show any significant peak. In this case, the SAED pattern apparently did not show any reflection



Scheme 3. Reduction of organic compounds promoted by Ni(O) nanoparticles generated from the system  $\text{NiCl}_2 \cdot 2\text{H}_2\text{O-Li-arene}$ .

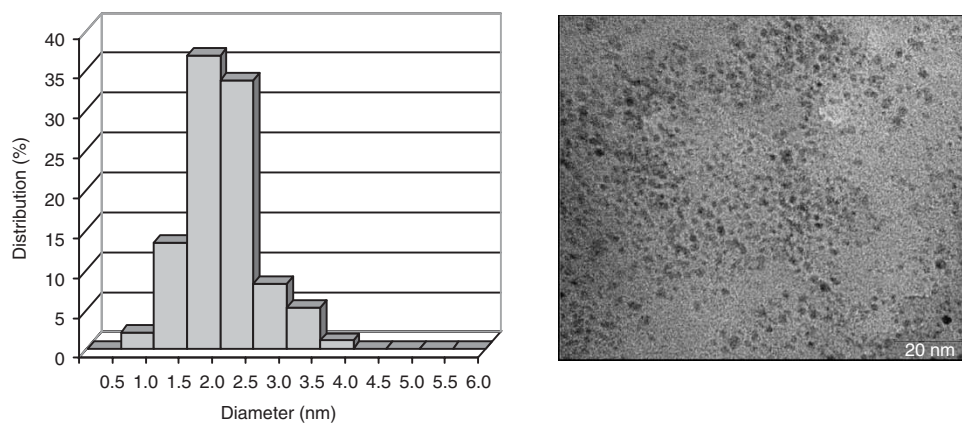


Figure 6. TEM micrograph and size distribution of nickel nanoparticles obtained from the system  $\text{NiCl}_2 \cdot 2\text{H}_2\text{O-Li-DTBB}$ . The sizes were determined for 98 nanoparticles selected at random.

corresponding to cubic NiO but only Ni and several reflections that could be assigned to cubic lithium [ $2.59 \text{ \AA}$  (111),  $2.19 \text{ \AA}$  (200), and  $1.34 \text{ \AA}$  (311)] (figure 7). This observation could be in agreement with the fact that the unreacted lithium prevented somewhat the oxidation of the Ni(0) nanoparticles. Nonetheless, longer exposure to air resulted in complete oxidation of the surface, the XPS analysis showing the O 1s ( $531.1 \text{ eV}$ ) and Ni  $2p_{3/2}$  ( $856.1 \text{ eV}$ ) peaks corresponding to oxidized Ni(II).

### 3.4 $\text{NiCl}_2\text{-Li-DTBB-EtOH}$

Very recently, we have discovered that the introduction of an alcohol (ethanol or isopropanol) as a source of hydrogen in the reducing system is a very convenient

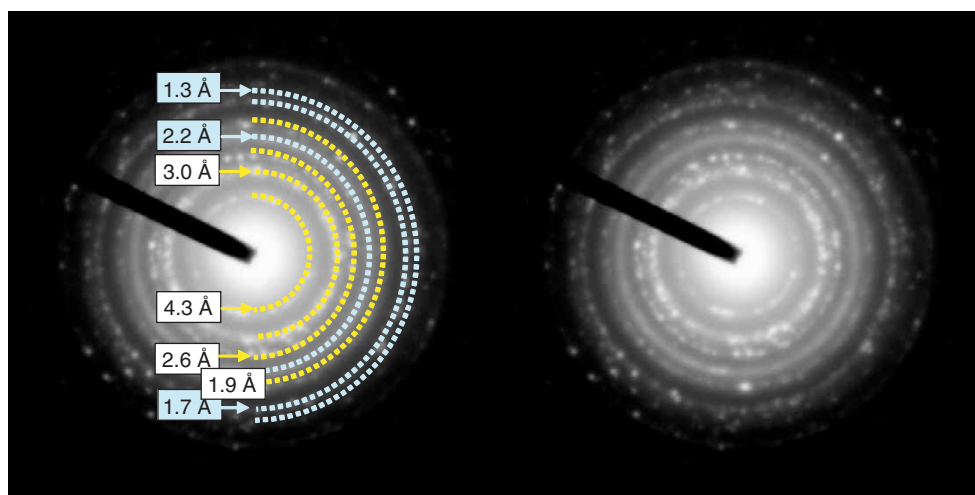
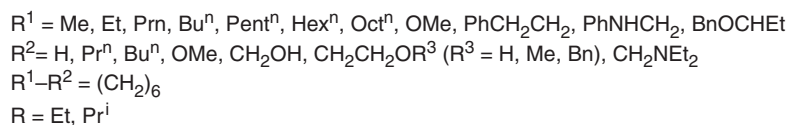
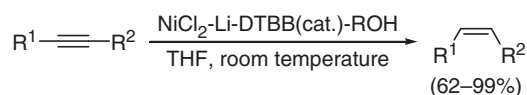
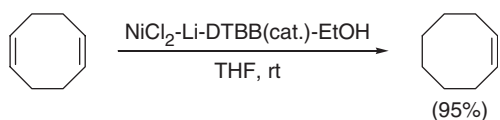


Figure 7. Electron-diffraction pattern of the nickel nanoparticles obtained from the system  $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ -Li-DTBB.



Scheme 4. Semihydrogenation of alkynes promoted by Ni(O) nanoparticles generated from the  $\text{NiCl}_2$ -Li-DTBB-ROH.



Scheme 5. Semihydrogenation of 1,5-cyclooctadiene promoted by Ni(O) nanoparticles generated from the system  $\text{NiCl}_2$ -Li-DTBB-EtOH.

method for the highly stereoselective *cis* semihydrogenation of internal alkynes and the semihydrogenation of terminal alkynes (scheme 4) [34]. Furthermore, this reducing system also found application in the complete reduction of alkenes and alkynes, and semi-reduction of dienes [35]. As an example, 1,5-cyclooctadiene was selectively reduced to cyclooctene in high isolated yield (scheme 5).

In this case, TEM analysis also revealed the presence of nanoparticles with even a narrower particle distribution range and lower average particle diameter (98% of the particles with 1.0–2.5 nm) compared with the above described systems (figure 8). Almost identical particle distribution was observed after 24 h. According to the

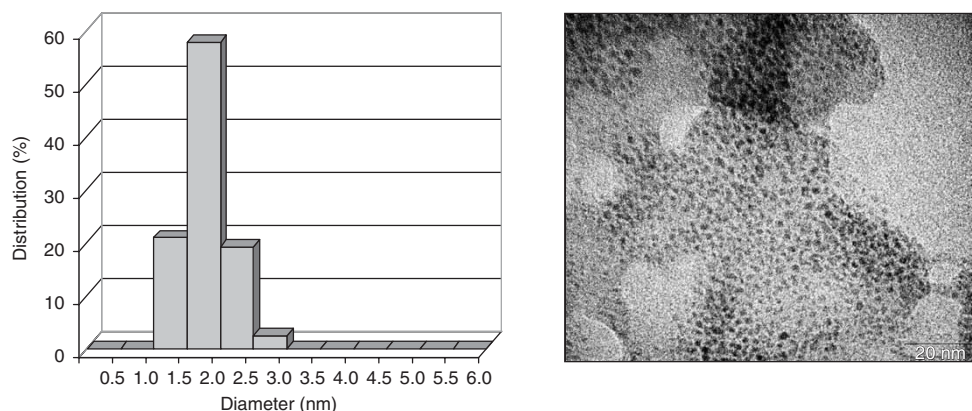


Figure 8. TEM micrograph and size distribution of nickel nanoparticles obtained from the system  $\text{NiCl}_2\text{-Li-DTBB-EtOH}$ . The sizes were determined for 120 nanoparticles selected at random.

behaviour observed for the  $\text{NiCl}_2\cdot 2\text{H}_2\text{O-Li-DTBB}$  system, we believe that in the present system the small particle size and stabilizing effect on the size of the nickel nanoparticles could be attributed to the presence of lithium ethoxide generated *in situ* from lithium and ethanol. This feature was somewhat confirmed by the addition of externally generated lithium ethoxide to a suspension of  $\text{NiCl}_2\text{-Li-DTBB}$ . Under these conditions, an improvement in the size distribution respect to the original  $\text{NiCl}_2\text{-Li-DTBB}$  system was observed after 30 min. Moreover, under these conditions, the dramatic particle agglomeration observed for the  $\text{NiCl}_2\text{-Li-DTBB}$  system for longer reaction times (i.e., 24 h) was prevented. In fact and surprisingly, even a narrower particle distribution and smaller average size was observed after 24 h.

As occurred in the previous systems, the XRD spectrum did not show any significant peak. The SAED pattern recorded for this sample, however, showed diffuse intensity rings in the 2.15 and 1.77 Å, and 2.52 and 1.56 regions, which suggest a very small size for the crystalline domains of Ni(0) and NiO, respectively (figure 9). The presence of oxidized nickel was confirmed by XPS analysis, which showed the O 1s (531.2 eV) and Ni 2p<sub>3/2</sub> (855.4 eV) peaks.

### 3.5 $\text{NiCl}_2\text{-Li-copolymer-EtOH}$

Alternatively to the previously described nickel(II) chloride-containing reducing system, the DVB-VBP copolymer was introduced as an electron carrier, making the process more efficient, with easier work-up and no need of product purification. Under these conditions, the selective conjugate reduction of a variety of carbonyl compounds has been successfully accomplished [36]. As an example, isophorone was transformed into 3,3,5-trimethylcyclohexanone in high isolated yield (scheme 6).

The incorporation of EtOH in the  $\text{NiCl}_2\text{-Li-copolymer}$  system (see the experimental procedure E) showed a similar behavior to the incorporation of EtOH in the  $\text{NiCl}_2\text{-Li-DTBB}$  system. Thus, narrower particle distribution range and lower average particle

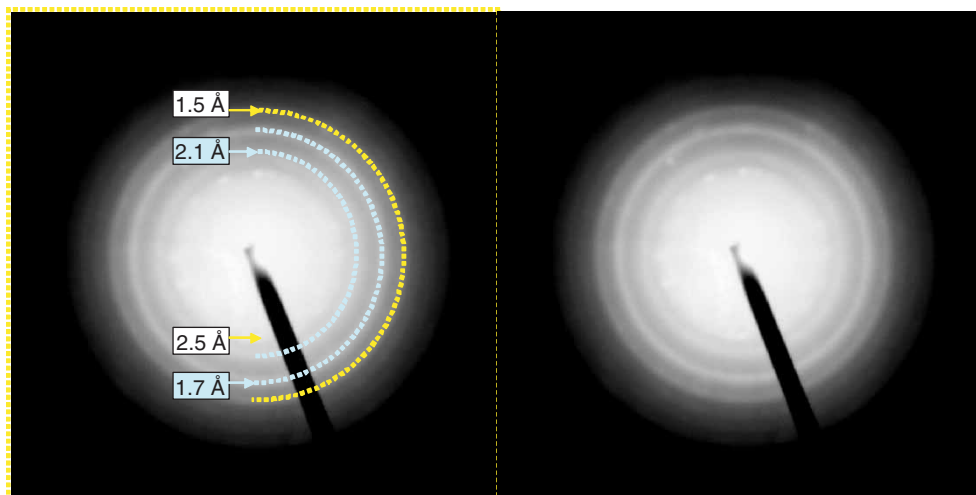
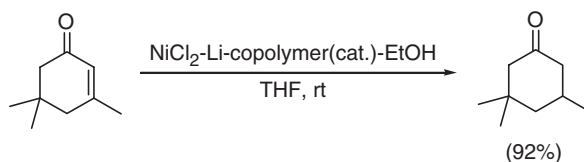


Figure 9. Electron-diffraction pattern of the nickel nanoparticles obtained from the system  $\text{NiCl}_2\text{-Li-DTBB-EtOH}$ .



Scheme 6. Conjugate reduction of isophorone promoted by  $\text{Ni(O)}$  nanoparticles generated from the system  $\text{NiCl}_2\text{-Li-copolymer-EtOH}$ .

diameter was observed in the presence of EtOH (figure 10). Also in this case, the particle distribution remained practically invariable after 24 h.

No significant peak was observed in the XRD spectrum. The SAED pattern clearly shows the reflections corresponding to fcc  $\text{Ni(0)}$  [ $2.07 \text{ \AA}$  (111),  $1.84 \text{ \AA}$  (200), and  $1.24 \text{ \AA}$  (220)] and cubic  $\text{NiO}$  [ $2.40 \text{ \AA}$  (111),  $2.07 \text{ \AA}$  (200), and  $1.45 \text{ \AA}$  (220)] (figure 11). The surface, however, after exposure to air seems to be completely oxidized as confirmed by XPS analysis, which showed the O 1s ( $531.4 \text{ eV}$ ) and Ni  $2p_{3/2}$  ( $856.2 \text{ eV}$ ) peaks.

We believe that the stabilising effect on the nickel nanoparticles exerted by the *in situ* generation of LiOH or LiOEt is mainly of an electrostatic nature. It is known that, even in organic media, in which electrostatic effects might not normally be considered important, the development of charge has been demonstrated on inorganic surfaces, including metals, in contact with organic phases such as solvents and polymers. In our case, this phenomenon could promote the formation of an electrical double layer formed by adsorbed anions and cations ( $\text{Li}^+$  and  $\text{OH}^-$  or  $\text{EtO}^-$ ) which would be attracted to the nickel nanoparticles. If the electric potential associated with the double layer were sufficiently high, the resulting Coulombic repulsion between nanoparticles would prevent their agglomeration [37]. Although the exact role of hydroxides and

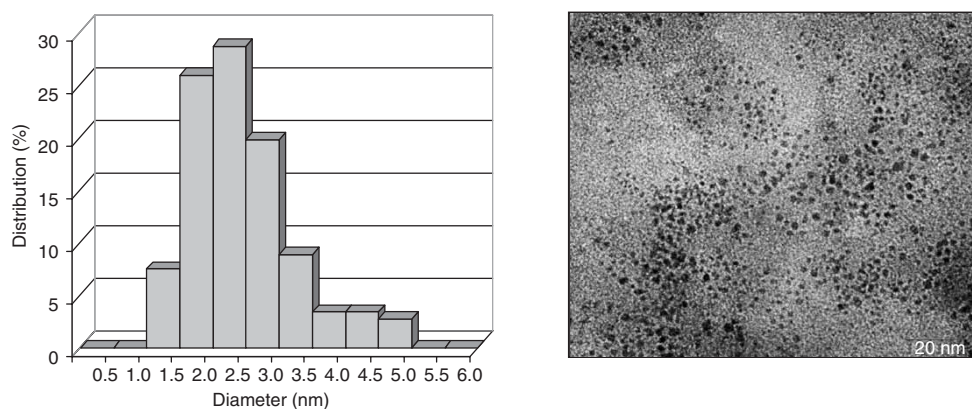


Figure 10. TEM micrograph and size distribution of nickel nanoparticles obtained from the system  $\text{NiCl}_2$ -Li-copolymer-EtOH. The sizes were determined for 147 nanoparticles selected at random.

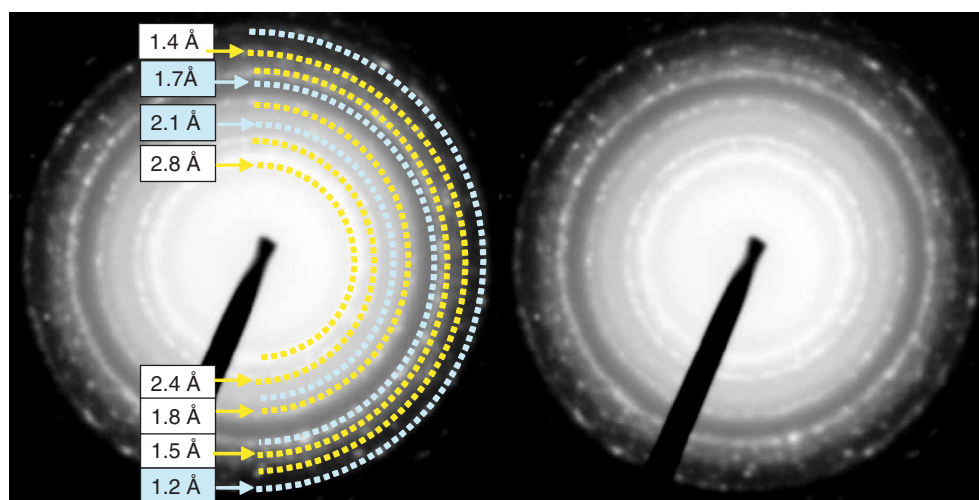


Figure 11. Electron-diffraction pattern of the nickel nanoparticles obtained from the system  $\text{NiCl}_2$ -Li-copolymer-EtOH.

alkoxides in the metal particle growth has not been studied in detail, it has been reported that NaOH might act as a catalyst and was indispensable for the formation of pure nickel nanoparticles by hydrazine reduction in ethylene glycol [38]. The group by Caubère *et al.* reported in the early eighties that metallic nickel prepared by reduction of  $\text{Ni}(\text{OAc})_2$  with NaH only showed catalytic activity in the presence of an alkoxide [39]. Recently, it was also suggested that  $\text{KOBu}^t$  acted as an effective protective agent for the formation and size control of nickel nanoparticles [40]. At any rate, in the case of the  $\text{LiOEt}$  *in situ* generated in our systems, an electrosteric stabilising effect can not be ruled out.

#### 4. Conclusion

The different nickel chloride-containing systems, NiCl<sub>2</sub>-Li-DTBB, NiCl<sub>2</sub>-Li-copolymer, NiCl<sub>2</sub>·2H<sub>2</sub>O-Li-DTBB, NiCl<sub>2</sub>-Li-DTBB-EtOH, and NiCl<sub>2</sub>-Li-copolymer-EtOH, with a varied applicability in organic functional group transformations, have shown to generate nickel(0) nanoparticles in a fast manner under very mild reaction conditions. The presence of a VBP-DVB copolymer, but above all the presence of LiOH or LiOEt, either *in situ* or externally generated, seems to exert certain stabilisation on the particle size avoiding the agglomeration phenomenon even under prolonged stirring. Moreover, the systems containing H<sub>2</sub>O and EtOH led to narrower size distribution and lower average diameter. These systems, however, also seem to experience faster oxidation when exposed to air, furnishing a core mainly composed of metallic nickel and a surface of nickel(II) oxide. Further synthetic applications of the above systems are under way.

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