

Ni-nanoparticles: an efficient green catalyst for chemoselective reduction of aldehydes

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Abstract—A novel method for reduction of aromatic and heteroaromatic aldehydes with ammonium formate using Ni-nanoparticles is described. The Ni-nanoparticles act as a green catalyst for selective reduction of the aldehydic group in the presence of other functional groups, viz.: $-\text{NO}_2$, $-\text{CN}$ and alkenes to give the corresponding alcohols in excellent yields.

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The reduction of carbonyl compounds to the corresponding alcohols is an important transformation in organic synthesis^{1,2} and an important step in the synthesis of biologically active compounds.^{3,4} A variety of reducing systems are available to carry out reductions, which include Raney nickel,^{5,6} Ni-MCm-41,⁷ nickel-aluminium (Ni–Al) alloy,⁸ nickel–aluminium hydrotalcite,⁹ Al_2O_3 – NaBH_4 ,^{10,11} Cu/Ru complexes,^{12–14} HCO_2 – Na/Δ /pressure,^{15,16} Meerwein–Ponndorf–Verley (MPV) reductions,^{17,18} Fe/HCl¹⁹ and Sn/HCl.²⁰ The selective reduction of aldehydes in the presence of other functional groups vulnerable to reduction constitutes a major task in organic synthesis, and in many such cases, it is necessary to use the expensive reagents and/or work at low temperatures. This can be circumvented by using aminoborane,^{21,22} tributylstannane,²³ low valency titanium,²⁴ tetrabutylammonium triacetoxycobalt(II) hydride,²⁵ potassium triphenylborohydride²⁶ and lithium trialkoxyaluminium hydrides.²⁷

All these methods have their own drawbacks which include the use of high pressure/temperature or both, long reaction times,⁷ low yields,⁷ toxic solvents^{28,29} and non-selective stoichiometric amounts of reagent, that could lead to the formation of quantitative amounts of undesirable salts or require the use of a pyrophoric catalyst.

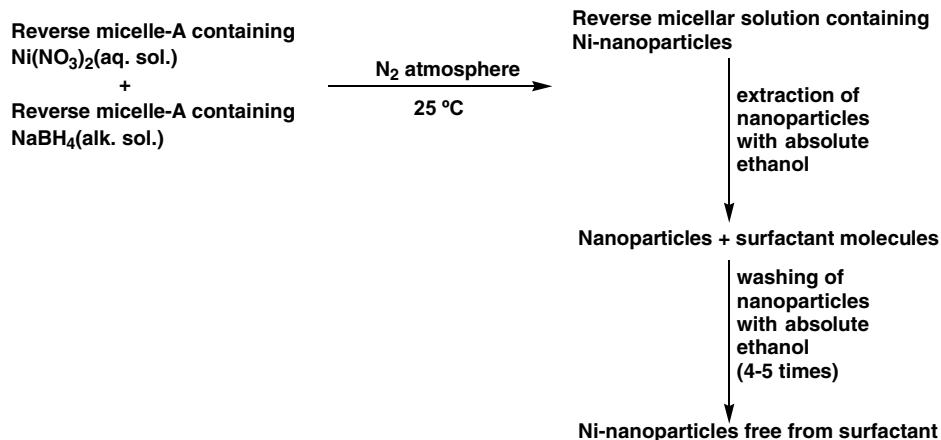
However, there is strong need to develop new green catalysts^{30,31} that should be efficient, involve an easy work-up and afford greater yields in shorter reaction times. In this regard, Raney-Ni has extensively been used for catalytic reduction. However, reactions catalysed by Raney-Ni are very slow owing to the large surface area of the catalyst. It was therefore worthwhile to develop a new green catalyst that could enhance the reaction rate.

Work in the field of metal nanoparticles as catalysts in synthetic organic chemistry has gained much attention.^{32–50} Pioneering work includes the Mizoroki–Heck reaction using palladium nanoparticles,^{32–34} Suzuki cross-coupling reactions using palladium nanoparticles,^{32,34–41} Stille type reactions,^{42–44} Sonogashira coupling reactions,³⁹ Tsuji–Trost allylation and Pauson–Khand reactions,^{45,46} aza-Michael reactions⁴⁷ and nanoparticle catalysed reactions.^{48–50} Recent literature has shown that the application of nanoparticles as catalysts in organic synthesis has been little explored. Ni-nanoparticles, in particular being cheap, need mild reaction conditions for high yields of products in short reaction times as compared to the traditional Raney-nickel catalysts.

We report herein a novel protocol that employs Ni-nanoparticles^{51–54} as an efficient and selective catalyst for the reduction of aldehydes. The Ni-nanoparticles selectively and catalytically reduce aldehydic groups in the presence of other functional groups such as $-\text{NO}_2$, $-\text{CN}$, and double bonds at α,β positions. Reduction of

Keywords: Ni-nanoparticles; Chemoselective; Catalytic reduction; Aldehydes.

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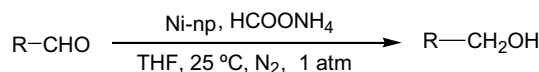
Scheme 1. Preparation of Ni-nanoparticles.

Ni^{2+} ions to Ni(0) in a reverse micellar system was employed to prepare the nickel nanoparticles (Scheme 1).^{55,56}

The sizes of the Ni-nanoparticles prepared at $W_0 = 3\text{--}15$ (the water content parameter W_0 defined as the molar ratio of water to surfactant, $W_0 = [\text{H}_2\text{O}]/[\text{surfactant}]$) were confirmed as 10 ± 2 nm to 85 ± 2 nm through quasi-elastic light scattering data (QELS) (Fig. 1a) and transmission electron microscopy (TEM) (Fig. 1b). The Ni-nanoparticles prepared were round in shape and black in color (colloidal state).

Ni-nanoparticles (Ni-np), 10–85 nm in size have been used efficiently for the catalytic reduction of aromatic and heteroaromatic aldehydes (Scheme 2).⁵⁷ A control experiment was conducted in the absence of catalyst and it was observed that the reduction of aromatic aldehydes using ammonium formate produced the required products in 72 h in 15–20% yield. In contrast, our protocol reduces various aromatic and heteroaromatic aldehydes with significantly shorter reaction times and very high yields (Table 1).

The solvent used plays an important role in deciding the reaction path and the nature of the product. Changing the solvent in the heterogeneous catalytic reduction from methanol to *n*-hexane resulted in a steep drop in



Scheme 2. Catalytic reduction of aromatic aldehydes using Ni-nanoparticles (18–62 nm) employing ammonium formate as a hydrogen donor.

activity due to the sparingly soluble nature of ammonium formate which acts as a hydrogen donor. Non-polar solvents such as *n*-hexane were unsuitable for the reactions. However, polar solvents such as methanol gave promising results (Table 2).

Ni-nanoparticles of different sizes from 10 nm to 85 nm diameters were prepared in the aqueous cores of reverse micellar droplets. The mechanism of the catalytic action of the nanoparticles is dependent on the nanoparticle size.

The maximum reaction rate has been observed for an average particle diameter of about 20 nm. With a decrease in particle size, a trend of decreasing reaction rate has been found for particles less than a diameter of 20 nm, while those above this diameter show a steady decline of reaction rate with increasing size. It has been postulated, that in the case of particles of average size less than 20 nm, a downward shift of Fermi level takes

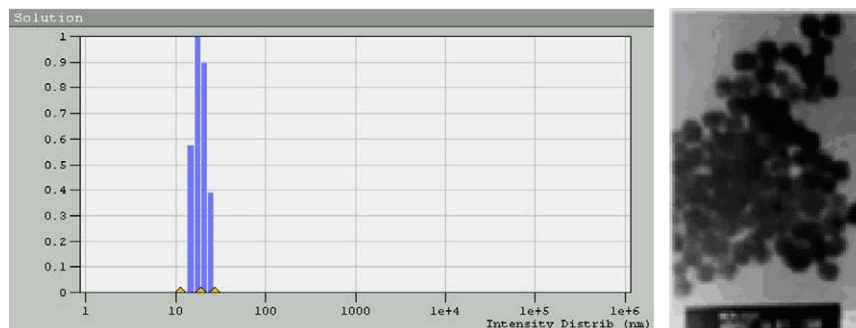
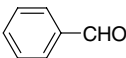
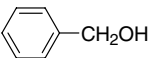
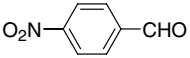
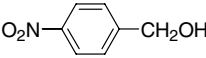
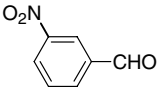
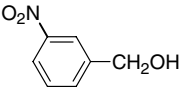
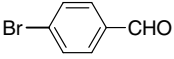
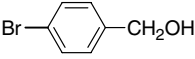
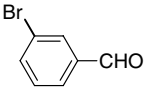
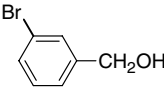
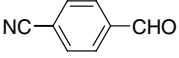
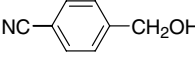
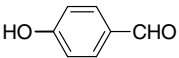
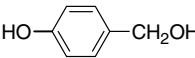
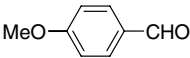
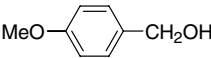
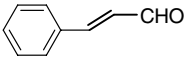
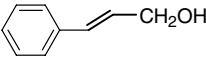
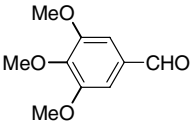
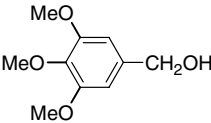
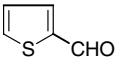
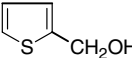
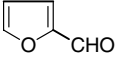
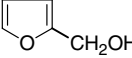


Figure 1. (a) QELS data of Ni-nanoparticles: plot of population distribution in percentile versus size distribution in nm, (b) TEM image of Ni-nanoparticles. The scale bar corresponds to 20 nm in the TEM image.

Table 1. The heterogeneous catalytic reduction of aldehydes to alcohols using Ni-nanoparticles (10 mol %)^a

Entry	Substrate	Time (h)	Product	Yield (%) ^b
1		1.5		85
2		3.0		72
3		3.5		78
4		4.0		89
5		3.6		90
6		2.8		76
7		1.7		93
8		2.2		97
9		6.0		92
10		1.4		95
11		2.3		88
12		4.6		60

^a Reaction conditions: 1.0 equiv of aldehyde, 1.0 equiv of ammonium formate, 10 mol % of Ni-nanoparticles (45 nm) in THF at room temperature stirred under an inert atmosphere.

^b Isolated yields.

place, consequently, with an increase of band gap energy. As a result, the particles require more energy to pump electrons to the adsorbed ions for the electron transfer reaction. This leads to a reduction in reaction rate when catalysed by smaller particles. On the other

hand, for nanoparticles >20 nm in diameter, the change of Fermi level is not appreciable. As these particles exhibit less surface area for adsorption with increased particle size, a decrease in catalytic efficiency results (Table 3).

Table 2. Effect of solvents on the catalytic reduction of 4-methoxybenzaldehyde and 3,4,5-trimethoxybenzaldehyde using Ni-nanoparticles (18 nm)

Solvent	4-Methoxybenzaldehyde		3,4,5-Trimethoxybenzaldehyde	
	Yield (%) ^a	Time (h)	Yield (%) ^a	Time (h)
Methanol	97	1.5	96	1.2
Tetrahydrofuran	97	2.2	95	1.4
Acetonitrile	93	2.8	89	2.2
<i>n</i> -Hexane	81	6.2	68	5.7

^a Isolated yields.

Table 3. Effect of size of the nanoparticles on catalytic reduction of 4-methoxybenzaldehyde and 3,4,5-trimethoxybenzaldehyde using 10 mol % Ni-nanoparticles

Particle size (± 2 nm)	4-Methoxybenzaldehyde		3,4,5-Trimethoxybenzaldehyde	
	Yield (%) ^a	Time (h)	Yield (%) ^a	Time (h)
10	89	2.5	87	2.7
20	92	2.2	95	1.4
30	93	2.8	91	2.0
85	71	3.2	69	2.6

^a Isolated yields.

In summary, these results demonstrate that Ni-nanoparticles (20 nm) can reduce various aromatic and hetero-aromatic aldehydes chemoselectively. Moreover, our method avoids the use of expensive reagents and high temperatures and leads to improved yields of products in shorter reaction times. Additional applications of this technology are currently under investigation.

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57. General procedure for the reduction of aldehydes (Scheme 2): To a suspension of aldehyde (5 mmol), Ni-nanoparticles (18–62 nm, 10 mol %), in tetrahydrofuran (THF, 3 ml), ammonium formate (5 mmol) was added at room temperature and the resulting mixture stirred under a nitrogen atmosphere. After completion of the reaction (monitored by TLC), the mixture was filtered and THF was removed in vacuo. The residue was extracted with dichloromethane (2 × 15 ml). The organic layer was dried over anhydrous Na₂SO₄ and after removal of the solvent in vacuo, the residue was purified by column chromatography (silica gel 250–400 mesh size). The structure of the product alcohol was confirmed from IR (KBr or Nujol) and ¹H NMR data.