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Short communication

The colloidal synthesis of unsupported nickel-tin bimetallic nanoparticles with tunable composition that have high activity for the reduction of nitroarenes

Mazloom Shah, Qing-Xiang Guo *, Yao Fu *

Department of Chemistry, University of Science and Technology of China, Hefei 230026, PR China

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ABSTRACT

Ni-Sn bimetallic nanoparticles with controllable size and composition were prepared by facile method in ambient air using inexpensive metal salts. Adjusting stoichiometric ratio of Ni and Sn precursors afforded nanoparticles with different compositions, such as Ni₁₀₀, Ni₇₄-Sn₂₆, Ni₅₉-Sn₄₁, and Ni₅₀-Sn₅₀. The characterization of nanoparticles was performed by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HR-TEM), and energy dispersive X-ray analysis (EDX). Ni₇₅-Sn₂₅ and Ni₆₀-Sn₄₀ nanoparticles showed enhanced catalytic activity towards 2-nitroaniline reduction as compared with Ni nanoparticles. Furthermore, Ni₇₅-Sn₂₅ nanocatalyst exhibited excellent activity for the reduction of a number of nitro aromatic compounds under mild conditions along with high level of reusability.

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1. Introduction

In recent years, research has been directed towards the synthesis and application of metal nanoparticles owing to their unique properties compared to bulk materials [1]. Among various metal nanoparticles, nickel nanoparticles have received considerable attention because of their applications as catalytic and magnetic materials [2]. The magnetic properties of nickel nanoparticles make them to be effective and easily separated from the reaction mixture by applying an external magnetic field. The nanoparticles composed of two metals are of great importance from the scientific and technological points of view for the enhancement of the catalytic activities of monometallic nanoparticles for industrial production of chemicals. The enhancement derived from the combination of two metal elements into bimetallic nanoparticles can arise from an ensemble effect, a modified electronic structure, or the formation of new catalytic sites [3-6]. Nanoparticles composed of a noble metal and a non-noble metal have an increasing interest among researchers because of their high possibility of tailoring electronic and geometric structures, which in turn can enhance the catalytic activity [7–9]. Bimetallic nanoparticles involving tin and late transition metals are useful industrial catalysts for various hydrocarbon reactions. Several authors have studied the deposition of tin on nickel which highlighted its actual importance for the bimetallic system [10–13]. The formation of surface alloys appears to be determinant in the

* Corresponding authors. E-mail addresses: qxguo@ustc.edu.cn (Q.-X. Guo), fuyao@ustc.edu.cn (Y. Fu). nanoparticles were mostly prepared directly on catalyst supports or substrates by coimpregnation, sequential impregnation or surface organometallic chemistry [10-14]. On the contrary side, reports on the colloidal synthesis of unsupported Ni-Sn bimetallic nanoparticles with advanced structural, size or composition control are very limited. Therefore, the synthesis of Ni-Sn nanoparticles with narrow size-distribution and well controlled composition/structure still remains a challenge. The nickel nanoparticles exhibit lower activity than bimetallic Ni-Sn nanoparticles but higher selectivities for the production of hydrogen by aqueous phase reforming of oxygenated hydrocarbons [15,16]. Adding tin to nickel catalysts influence the dehydrogenation of cyclohexane, hydrogenation of acetylene, H₂-D₂ equilibration and H-D exchange between C_2D_4 and H_2 [17,18]. The addition of tin to modify metal catalysts prevents metal carbide formation and therefore, it reduces cooking [19]. The reduction of nitro compounds to amino compounds is industrially important as the amines obtained are versatile synthetic intermediates due to their application in the preparation of dyes, pharmaceuticals, agricultural products, surfactants and polymers [20-22]. In this regard, a variety of methods and catalyst system have been well documented for the catalytic reduction of nitro compounds [23–30], however, some of these protocols bear drawbacks such as long reaction time, high reaction temperature, use of complicated method for catalyst synthesis, use of toxic and expensive catalyst, carcinogenic solvent, and unavailability and reusability of the catalyst. Therefore, development of fast, cost effective, and mild catalytic route for the reduction of nitroaromatics is needed. In the present study, the Ni-Sn nanoparticles

chemical behavior of the bimetallic system. In these works, Ni-Sn alloy







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Table 1

Nanoparticles	Precursors (mol L ⁻¹)	PVP (g)	$NaBH_4(g)$	T ₁ (°C)	T ₂ (°C)	Reaction time (min)
Ni	Nickel (II) formate dehydrate (0.03)	0.35	0.15	69	195	150
Ni-Sn	Nickel (II) formate dehydrate (0.03)	0.35	0.17	50	198	150
	Tin (II) chloride dehydrate (0.01)					
Ni-Sn	Nickel (II) formate dehydrate (0.036)	0.35	0.17	50	198	150
	Tin (II) chloride dehydrate (0.02)					
Ni-Sn	Nickel (II) formate dehydrate (0.03)	0.35	0.17	50	198	150
	Tin (II) chloride dehydrate (0.03)					
Sn	Tin (II) chloride dehydrate (0.03)	0.25	0.15	25	25	60

Reaction conditions for the preparation of nanoparticles.

with tunable composition having different particle sizes were prepared by facile method using inexpensive metal salts such as nickel format dihydrate (Ni (HCOO)₂·2H₂O) and tin chloride dihydrate (SnCl₂·2H₂O). Furthermore, Ni-Sn nanoparticles with different particle sizes and metal compositions were tested for reduction of 2-nitroaniline by NaBH₄ in water. The nanocatalyst which exhibited best performance was used for the reduction of a number of nitro aromatic compounds under mild reaction conditions.

2. Experimental

2.1. Materials

Tin chloride dihydrate (SnCl₂·2H₂O \geq 98%), sodium borohydride (NaBH₄ \geq 96%), ethylene glycol (HOCH₂CH₂OH 99%), polyvinylpyrrolidone with an average molecular weight of 10,000 (PVP 100%), nitrobenzene (NO₂C₆H₅ \geq 99%), 3-nitroaniline (NH₂C₆H₄NO₂ \geq 98.5%), 4-chloronitrobenzene (ClC₆H₄NO₂), acetone (CH₃COCH₃ \geq 99%) and ethanol (C₂H₅OH \geq 99%) were purchased from Sinopherm chemical reagent Co. Ltd., 4-nitroaniline (NH₂C₆H₄NO₂) from Aladdin, petafluoronitrobenzene (NO₂C₆F₅) and 4-nitroanisole (CH₃OC₆H₄NO₂) from TCI Mark and nickel (II) formate dihydrate (Ni (HCOO)₂·2H₂O), 2-nitroaniline (NO₂C₆H₄NH₂ 98%) from Alfa Aesar.

2.2. Methods

2.2.1. Preparation and catalytic application of nanoparticles

For preparation of Ni nanoparticle 0.24 g Ni (HCOO)₂·2H₂O was dissolved in 35 mL of ethylene glycol. Calculated amount of PVP was added and the solution was heated to 342 K while stirring until the formation of a completely homogeneous blue solution. Once at this temperature, 0.15 g of NaBH₄ was added under magnetic stirring. The resultant solution was refluxed at 468 K for 2.5 h. In case of Ni-Sn nanoparticle preparation calculated amount of Ni (HCOO)₂·2H₂O, SnCl₂·2H₂O and PVP were added in 35 mL of ethylene glycol and the solution was heated to 323 K while stirring until the formation of a completely homogeneous blue solution. Once at this temperature, 0.18 g of NaBH₄ was added under magnetic stirring. The resultant solution was refluxed at 470 K for 2.5 h. The nanoparticles were precipitated in acetone, washed with acetone, ethanol and dried in air at room temperature.

In a typical reduction, 0.0019 g of catalyst was dispersed in 15 mL of aqueous solution containing 0.5 mmol of NaBH₄. The mixture was vigorously stirred for 10 min at room temperature. 10 mL of 0.0036 M 2nitroaniline aqueous solution was added and the resulting mixture

Table 2

Particle size and composition as determined by TEM-EDX for the as prepared Ni-Sn nanoparticles.

Entry	Sample name	Average particle size (nm)	Nominal composition (atom % Ni)	Ni-Sn composition determined by EDX (atom % Ni)
1	Ni-Sn (3:1)	4.5	75	73.6
2	Ni-Sn (3:2)	8	60	58.8
3	Ni-Sn (1:1)	7.2	50	49.5

was stirred at room temperature until the yellow solution became colorless. After the completion of the reaction, the reaction mixture was filtered. Then, the residue was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4 and the solvent was removed under vacuum. The products were identified with GC-MS analysis.

3. Results and discussion

The nickel-tin nanoparticles with tunable composition were synthesized in air using Ni (HCOO)₂·2H₂O and SnCl₂·2H₂O as precursors and NaBH₄ as reducing agent. Nanoparticles composed up of reactive metals such as Ni and Sn typically degrade in the presence of air. However, Ni-Sn nanoparticles described here were synthesized, dried and stored in ambient condition. It is well known that the morphology and size distribution of metallic particles produced by the reduction of precursor salts in solution depend on various reaction conditions such as concentration, temperature, time, molar ratio of precursor salt/reducing agent, mode and order of addition of reagents, presence and type of protective agents, degree and type of agitation, and whether nucleation is homogeneous or heterogeneous [31]. The synthesis conditions used for the production of nanoparticles are summarized in Table 1. The nominal particle-composition was controlled by varying the ratio between the nickel and tin precursors. The compositions of Ni-Sn nanoparticles, as determined by EDX analysis, were Ni₇₄-Sn₂₆, Ni₅₉-Sn₄₁, and Ni₅₀-Sn₅₀ which corresponded to the precursor Ni/Sn molar ratios of 3:1, 3:2, and 1:1, respectively shown in Table 2. The XRD patterns of as-synthesized Ni and Ni-Sn nanoparticles are shown in Fig. 1. Three main characteristic diffraction peaks at $2\theta = 44.38$, 51.67, and 76.57° correspond to the (111), (200), and (220) crystal planes of metallic Ni, confirming the formation of Ni nanoparticles with no visible impurity phases such as NiO. The broadening of peaks in the XRD diffractogram is inversely correlated with short crystallite size of the nanoparticles. X-ray diffraction patterns of Ni-Sn show a crystalline structure, where two broad diffraction lines at 30.41° and 43.05° were clearly observed. The broadening of peaks in the diffraction patterns is because of very small crystallite size [32–34]. The Ni-Sn XRD patterns indicated the presence of hexagonal Ni₃Sn and orthorhombic Ni₃Sn₂ phases. Although, the hexagonal Ni₃Sn phase showed diffraction lines



Fig. 1. Powder XRD patterns for Ni, Sn and Ni-Sn nanoparticles.

corresponding to the (002) and (201) planes at 42.54 and 44.95°, respectively that may account for the broad peaks observed at 43.41, the line at 30.41 cannot be associated to this phase since the closer possible diffraction line corresponding to the (101), (220) and (310) plane appears at 28.61, 71.21 and 74.67 respectively far away from that experimentally observed. However, the Ni₃Sn₂ phase revealed diffraction lines corresponding to the (1 1 2), (2 1 1), (0 2 0), (1 2 2) and (3 0 2), appears at 30.32, 32.36, 34.35, 42.96 and 44.07, respectively. With a gradual increase in tin content, the peaks progressively shifted to higher intensity and low 20 values without forming any discrete Sn reflections, which suggested that the nanoparticles were bimetallic alloys, as opposed to a physical mixture of separately nucleated monometallic Ni and Sn particles. Representative TEM images and the corresponding particle size distributions of the as-prepared, Ni₇₄-Sn₂₆, Ni₅₉-Sn₄₁, and Ni₅₀-Sn₅₀ nanoparticles are shown in Figs. 2, 3 (a, b) and Fig. 3 (c, d), respectively. Ni, Ni74-Sn26, Ni59-Sn41, and Ni50-Sn50 nanoparticles were observed to have a mixture of irregular shape and spherical morphology with an estimated average size of 13 nm, 4.5 nm, 8 nm and 7.2 nm, respectively. The mean diameter of the nanoparticles was estimated by counting about 100 metal particles. The size estimated from TEM micrographs agrees well with the crystallite size calculated from XRD, which may reveal nearly single crystalline character of metallic Ni nanoparticles. However in case of Ni-Sn nanoparticles, well-dispersed nanoparticles are single crystals while the elongated particles are polycrystals. The EDX analysis of the Ni-Sn nanoparticles showed that Sn concentration on the agglomerated particles was higher than on the well dispersed nanoparticles. It means that the material formed is quite heterogeneous having particles with different compositions. It is found that the reducibility of Ni²⁺ in the synthesis conditions was easier than that of Sn²⁺ favouring the initial formation of nickel rich particles. Furthermore, a closer observation of Ni74-Sn26 nanoparticles in Fig. 2(d) indicated that they are crystalline with visible lattice fringes of d = 0.20 nm and 0.228 nm, correspond to Ni₃Sn (201) and (200) planes, respectively.

To investigate the catalytic performance of Ni₇₄-Sn₂₆, Ni₅₉-Sn₄₁, and Ni₅₀-Sn₅₀ nanoparticles as compared to Ni nanoparticles, the reduction of 2-nitroaniline using sodium borohydride as the hydrogen source was initially studied. The reduction of 2-nitroaniline does not occur without coinage metals [35]. The peak at 411 nm completely diminished when all the 2-nitroaniline was converted to 1,2-benzenediamine in Fig. 4. In the presence of the Ni and Sn nano-catalysts, it takes about 6.5 min, and 42 min respectively to complete a reduction reaction. While using the Ni₇₄-Sn₂₆, Ni₅₉-Sn₄₁, and Ni₅₀-Sn₅₀ nano-catalyst, the reaction lasts only about 2.5 min, 5.0 min and 8.0 min respectively shown in Fig. 5 and Table S.1. Ni74-Sn26 and Ni59-Sn41, nano-catalysts reported here exhibited higher catalytic activity for the reduction of 2-nitroaniline as compared to Ni, Sn and Ni₅₀-Sn₅₀ nano-catalysts. When the reaction temperature was decreased from room temperature to 8 °C, Ni₇₄-Sn₂₆ nano-catalyst takes 34 min, for the reduction reaction to complete. The order of activity at room temperature was Ni₇₄-Sn₂₆ > Ni₅₉- $Sn_{41} > Ni > Ni_{50}-Sn_{50} > Sn$ nano-catalyst in water. With the increase in the concentration of tin up to 41 mol% the catalytic activity towards the reduction of 2-nitroaniline was increased, and further increase in the tin concentration up to 50% decreases catalytic activity of Ni-Sn nanoparticles as compared with nickel nanoparticles. The high catalytic activity of Ni₇₄-Sn₂₆ nano-catalyst is because of having small crystallite size, small particle size and high surface area as compared to other nano-catalysts. The Ni₅₀-Sn₅₀ nano-catalyst has low crystallite size, low particle size and high surface area as compare to Ni₅₉-Sn₄₁ and Ni nano-catalysts. But the catalytic activity of Ni₅₀-Sn₅₀ nano-catalyst is lower than Ni₅₉-Sn₄₁ and Ni nanocatalysts mean that addition of tin up to some extent enhances catalytic activity of Ni-Sn nanoparticle.



Fig. 2. (a) The TEM images of Ni-Sn nanoparticles with different magnifications, (b) size distribution histogram of Ni-Sn nanoparticles obtained from the TEM micrographs (c) EDX profile of Ni-Sn nanoparticles (d) HR-TEM image of Ni-Sn nanoparticles.



Fig. 3. (a) and (c) The TEM micrographs of Ni-Sn (3:2) and Ni-Sn (1:1) nanoparticles respectively, (b) and (d) size distribution of Ni-Sn (3:2) and Ni-Sn (1:1) respectively; obtained from the TEM micrographs.

The reduction of 2-nitroaniline by NaBH₄ in the absence of catalyst did not show any conversion after 72 h. Subsequently, the catalyst which showed the best performance towards reduction of 2-nitroaniline, was tested for the reduction of a number of nitro aromatic compounds under mild reaction conditions. Results, in Table 3, show that different nitro aromatic compounds can be converted to the corresponding amines at high yields and selectivity, regardless of the electrondonating or electron-withdrawing ability of the substituent group.



Fig. 4. Absorption spectra of aqueous solution of, A; 2-nitro-aniline; B, C, D, E and F; after reaction completion by using bimetallic Ni-Sn (3:1), Ni-Sn (3:2), Ni-Sn (1:1), Ni and Sn nanoparticles as catalyst, respectively.

When nitrobenzene was subjected to hydrogenation it yielded 98% of aniline in 8.5 min (Table 3, entry 1). The rate of reaction was increased by increasing concentration of sodium borohydride (NaBH₄). As its concentration was increased from 3-equivalent to 4-equivalent the time of reduction reaction decreased significantly from 8.5 min to 4.5 min with 99% product yield (Table 3, entry 1 and entry 2). Clearly, the presence of



Fig. 5. Comparison of reduction of 2-nitroaniline into benzene-1,2-diamine at various nano-catalysts in water. Where Ni-Sn 1 (3:1), Ni-Sn 2 (3:2), Ni-Sn 3 (1:1). Reaction conditions; 37 mmol 2-nitroaniline aqueous solution, 19 mg catalysts, 0.4 mol NaBH₄ aqueous solution, room temperature.

Table 3

Reduction of various nitro aromatic compounds into corresponding amines with NaBH₄ catalyzed by Ni-Sn^a.

Entry	Reactant	Product	NaBH4 (Equiv.)	Time (min)	Vield ^b (%)
1	NO ₂	NH ₂	3	8.5	98
2	NO ₂	NH ₂	4	4.5	99
3	NO ₂	NH ₂	4	12	95
4	NO ₂	\widetilde{NH}_2	4	7	98
		NH			
5	NO ₂	NH ₂	4	15	91
6	NH ₂	NH ₂	4	30	95
0			7	30	35
7			4	7	91
			-	·	
8	ĊI ŅO ₂	ĊI ŅH2	4	5	92
	F	F F			
	F	F			

Reaction conditions: substrate (1 mmol), ^a (Ni₇₄:Sn₂₆) Catalyst (0.026 g), NaBH₄(4 mmol), H₂O (5 mL), room temperature. ^bIsolated yield.

an amino group at different positions on the phenyl ring afforded the corresponding aniline in excellent yields (Table 3, entries 3-5). Nitroarenes possessing electron donating groups such as 4-nitroanisole (Table 3, entry 6) was also reduced to the desired amines in high yield (>95%). Similar reduction of 1-chloro-4-nitrobenzene and petafluoronitrobenzene compounds containing the electron-acceptor group (Table 3, entries 7 and 8) gives above 91% of the corresponding amines. Notably, we have not observed any secondary reaction affecting the dehalogenation functionalities under the selected reaction conditions, suggesting the high chemoselectivity of the present Ni₇₄-Sn₂₆/ NaBH₄ reduction system.

4. Conclusions

The unsupported Ni-Sn bimetallic nanoparticles with controllable size and composition were successfully prepared by a simple method using nickel formate dihydrate (Ni (HCOO)₂·2H₂O), tin chloride dihydrate (SnCl₂·2H₂O) and sodium borohydride (NaBH₄). The obtained nanoparticles have been confirmed by XRD, TEM, HR-TEM and EDX analysis. Ni, Ni₇₄-Sn₂₆, Ni₅₉-Sn₄₁, and Ni₅₀-Sn₅₀ nanoparticles were observed to have a mixture of irregular shape and spherical morphology with an estimated average size of 13 nm, 4.5 nm, 8 nm and 7.2 nm,

respectively. The well-dispersed Ni-Sn nanoparticles were found to have single crystals while the elongated particles have polycrystals. The Ni₇₄-Sn₂₆ nanoparticles exhibited excellent catalytic performance as compared with Ni, Ni₅₉-Sn₄₁, and Ni₅₀-Sn₅₀ nanoparticles. The replacement of the nickel content with tin up to 41% improved catalytic performance while further its addition decreased catalytic activity of the nickel-tin nanoparticles. Furthermore, Ni₇₄-Sn₂₆ nanocatalyst showed excellent activity for the reduction of a number of nitroarenes carrying activated and deactivated groups under mild conditions.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.catcom.2015.02.026.

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