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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

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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 Ni_{100}, Ni_{74}-Sn_{26}, Ni_{59}-Sn_{41}, and Ni_{50}-Sn_{50}. 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). Ni_{75}-Sn_{25} and Ni_{60}-Sn_{40} nanoparticles showed enhanced catalytic activity towards 2-nitroaniline reduction as compared with Ni nanoparticles. Furthermore, Ni_{75}-Sn_{25} nanocatalyst exhibited excellent activity for the reduction of a number of nitro aromatic compounds under mild conditions along with high level of reusability.

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 chemical behavior of the bimetallic system. In these works, Ni-Sn alloy 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, H_2-D_2 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

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Table 1
Reaction conditions for the preparation of nanoparticles.

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) Tin (II) chloride dehydrate (0.01)	0.35	0.17	50	198	150
Ni-Sn	Nickel (II) formate dehydrate (0.036) Tin (II) chloride dehydrate (0.02)	0.35	0.17	50	198	150
Ni-Sn	Nickel (II) formate dehydrate (0.03) Tin (II) chloride dehydrate (0.03)	0.35	0.17	50	198	150
Sn	Tin (II) chloride dehydrate (0.03)	0.25	0.15	25	25	60

with tunable composition having different particle sizes were prepared by facile method using inexpensive metal salts such as nickel format dihydrate (Ni $(HCOO)_2 \cdot 2H_2O$) and tin chloride dihydrate ($SnCl_2 \cdot 2H_2O$). Furthermore, Ni-Sn nanoparticles with different particle sizes and metal compositions were tested for reduction of 2-nitroaniline by $NaBH_4$ 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 ($SnCl_2 \cdot 2H_2O \geq 98\%$), sodium borohydride ($NaBH_4 \geq 96\%$), ethylene glycol ($HOCH_2CH_2OH$ 99%), polyvinylpyrrolidone with an average molecular weight of 10,000 (PVP 100%), nitrobenzene ($NO_2C_6H_5 \geq 99\%$), 3-nitroaniline ($NH_2C_6H_4NO_2 \geq 98.5\%$), 4-chloronitrobenzene ($ClC_6H_4NO_2$), acetone ($CH_3COCH_3 \geq 99\%$) and ethanol ($C_2H_5OH \geq 99\%$) were purchased from Sinopherm chemical reagent Co. Ltd., 4-nitroaniline ($NH_2C_6H_4NO_2$) from Aladdin, petafluoronitrobenzene ($NO_2C_6F_5$) and 4-nitroanisole ($CH_3OC_6H_4NO_2$) from TCI Mark and nickel (II) formate dihydrate (Ni $(HCOO)_2 \cdot 2H_2O$), 2-nitroaniline ($NO_2C_6H_4NH_2$ 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 $(HCOO)_2 \cdot 2H_2O$ 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 $NaBH_4$ 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 $(HCOO)_2 \cdot 2H_2O$, $SnCl_2 \cdot 2H_2O$ 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 $NaBH_4$ 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 $NaBH_4$. The mixture was vigorously stirred for 10 min at room temperature. 10 mL of 0.0036 M 2-nitroaniline aqueous solution was added and the resulting mixture 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.

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

3. Results and discussion

The nickel-tin nanoparticles with tunable composition were synthesized in air using Ni $(HCOO)_2 \cdot 2H_2O$ and $SnCl_2 \cdot 2H_2O$ as precursors and $NaBH_4$ 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 Ni_{74}-Sn_{26}, Ni_{59}-Sn_{41}, and Ni_{50}-Sn_{50} 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 Ni_3Sn and orthorhombic Ni_3Sn_2 phases. Although, the hexagonal Ni_3Sn phase showed diffraction lines

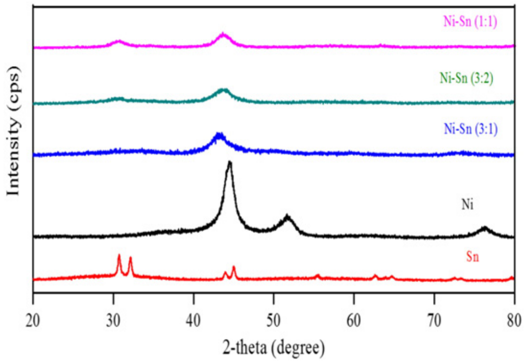

Fig. 1. Powder XRD patterns for Ni, Sn and Ni-Sn nanoparticles.