Precisely Composition Controlled Synthesis of Cu0.5Ni0.5 Alloy with Optimum Catalytic Activity postprint

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Abstract

Alloys based on non-noble metals could be the next generation of high-performance catalysts for many chemical reactions. However, precisely composition controlled synthesis of non-noble alloys remains a significant challenge. In this work, we report a simple synthesis of Cu0.5Ni0.5 alloys without any component segregation. Its success relies on the use of Cu–Ni oxalate precursors, which are chelated in the proximity by oxalate ligands. One of the attractive features for the oxalate routes of catalyst preparation is that no classical support material is needed. The actual component ratios of the obtained Cu0.5Ni0.5 alloy are consistent with the initial ratio. Cu0.5Ni0.5 alloy shows a higher catalytic activity than pure Cu and Ni catalysts in the reduction of p-nitrophenol (4-NP) to p-aminophenol (4-AP) by sodium borohydride (NaBH4) in an aqueous solution, and the performance depends strongly on the strong interaction between Cu and Ni. The findings reported here are highly helpful to understand the relationship between the synergistic effects in alloys and their catalytic performance, and therefore could provide appropriate strategies to obtain desirable catalysts with improved activity in various catalytic applications.

Full Text

Preamble

Precisely Composition Controlled Synthesis of Cu . Ni . Alloy with Optimum Catalytic Activity

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ABSTRACT

Alloys based on non-noble metals could represent the next generation of high-performance catalysts for many chemical reactions. However, precisely composition-controlled synthesis of non-noble alloys remains a significant challenge. In this work, we report a simple synthesis of Cu . Ni . alloys without any component segregation. The success of this approach relies on the use of Cu–Ni oxalate precursors, in which the metals are chelated in close proximity by oxalate ligands. One attractive feature of this oxalate-based catalyst preparation route is that no classical support material is required. The actual component ratios of the obtained Cu . Ni . alloy are consistent with the initial ratio. The Cu . Ni . alloy shows higher catalytic activity than pure Cu and Ni catalysts in the reduction of p-nitrophenol (4-NP) to p-aminophenol (4-AP) by sodium borohydride (NaBH) in aqueous solution, and this performance depends strongly on the strong interaction between Cu and Ni. The findings reported here are highly helpful for understanding the relationship between synergistic effects in alloys and their catalytic performance, and could therefore provide appropriate strategies for obtaining desirable catalysts with improved activity in various catalytic applications.

Keywords: catalytic reduction; CuNi bimetallic alloy; p-nitrophenol; NaBH

1. INTRODUCTION

Alloys have received considerable interest due to their potential applications in various chemical and physical processes, such as hydrogen storage, magnetic sensors, hydrogenation, fuel cells, ammonia decomposition, catalytic reforming, water-gas shift reactions, and so on [1-4]. Noble metal alloys have been widely utilized in catalytic reactions across various fields [5-8]. However, due to the high cost and limited supply of noble metals, improving catalytic efficiency and reducing costs are top priorities.

Alloys based on non-noble metals could serve as the next generation of high-performance catalysts for many chemical reactions. Noble-metal-free alloys are considered promising catalysts with low cost, high activity, and selectivity [9-11]. Owing to the synergistic effect of alloying between different metals, the activity and selectivity of alloys can be optimized by controlling the elemental composition. Consequently, non-noble metal alloys (involving Cu, Fe, Co, and Ni) with different compositions have been synthesized by diverse methods [12]. Among these alloys, CuNi alloys are particularly promising candidates [12-14]. Nevertheless, the reduction potentials for Cu and Ni metals are generally much lower than those of noble metals. As a result, more strenuous reaction conditions are required to prepare CuNi alloys [15-17]. For instance, toxic organic capping agents, solvents, reducing agents, and organometallic compounds have been utilized to increase the reduction potentials. Additionally, the differences in reduction potentials for Cu and Ni metals also limit alloy formation [18-20]. Therefore, it is necessary to develop simple and green methods to synthesize CuNi alloys with desired compositions.

Based on these considerations, we report a simple synthesis of Cu . Ni . alloy without any component segregation. The success of this method relies on the use of Cu-Ni oxalate precursors, in which the metals are chelated in close proximity by oxalate ligands [21-23]. Using this strategy, the actual component ratio of the obtained Cu . Ni . alloy is consistent with the initial ratio. The Cu . Ni . alloy exhibits high activity in the reduction of p-nitrophenol (4-NP) by sodium borohydride (NaBH) in aqueous solution.

2. EXPERIMENTAL

2.1 Chemicals and Materials

Cu(NO) ·3H O (>98%), Ni(NO) ·6H O (>98%), H C O ·2H O (>99%), sodium borohydride (NaBH), and acetone were purchased from Shanghai Chemical Reagent Company, and p-nitrophenol (4-NP) was purchased from Sigma-Aldrich Chemicals Company. All chemical reagents were used as received without further purification.

2.2 Synthesis of Cu . Ni . Alloys

Cu . Ni . alloy was prepared by thermal decomposition of Cu-Ni oxalate precursors. In a typical synthesis, oxalic acid (4 mmol) was dissolved in 20 mL acetone at room temperature. Cu(NO) ·3H O (0.5 mmol) and Ni(NO) ·6H O (0.5 mmol) were dissolved in 10 mL acetone at room temperature. Then, the metal nitrate solution was added to the oxalic acid solution, and the mixed solution was stirred for 2 h. Finally, the obtained Cu-Ni oxalate precipitate was filtered, washed with acetone several times, and dried overnight at 80 °C.

The Cu-Ni oxalate was calcined in a temperature-programmed manner (10% H in Ar as carrier gas at a volumetric flow rate of 30 mL min ^{1} using a ramp of 3 °C min ^{1} up to 450 °C for 3 h). The product thus obtained was passivated in a mixed atmosphere (1% O and 99% Ar) at 25 °C for 30 min, after which the alloy sample was obtained. For comparison, pure Cu and Ni metals were also prepared using a similar procedure.

2.3 Sample Characterization

X-ray diffraction (XRD) patterns of the samples were recorded using a D/MAX 2550 Advance X-ray diffractometer with CuK radiation source operated at 30 kV and 20 mA. Data were collected from 2 between 40° and 80° with a step of 0.02° at a scanning speed of 5 °/min. FT-IR spectra of the samples were examined using a Jasco FT/IR-410 in air at room temperature using 420 Herschel series in KBr dispersion.

X-ray photoelectron spectroscopy (XPS) measurements were performed using an ESCALAB250 photoelectron spectrometer equipped with a charge neutralizer and an MgK X-ray source. Thermogravimetry (TG: Perkin-Elmer) was carried out for the precursor powder in air from 25 to 800 °C at a constant heating rate of 10 °C·min ^{1}. Morphologies of the as-synthesized samples were recorded using a field emission scanning electron microscope (FE-SEM) equipped with EDX. Transmission electron microscopy (TEM) images were recorded on a JEOL 3010 with 300 kV acceleration voltages. UV-Vis absorption spectroscopy was carried out on a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer in a wavelength range of 300–1000 nm.

2.4 Catalytic Activity Test

10 mL of 4-NP aqueous solution (200 ppm) and 10 mL of freshly prepared aqueous NaBH (0.06 M) were successively added to 20 mL of deionized water in a beaker. Next, 2 mg of catalyst was added to the mixture. The color of the solution changed gradually from yellow to transparent as the reaction proceeded. UV-Vis spectrometry was used to monitor the change in absorbance at time intervals of 1 min.

3. RESULTS AND DISCUSSION

3.1 Characterization of the Obtained Cu-Ni Oxalates

Cu-Ni oxalates were first prepared prior to the formation of CuNi alloy. The crystal structures of the obtained Cu-Ni oxalates were characterized by XRD. The fresh Cu . Ni . oxalate was composed of copper oxalate hydrate and nickel oxalate hydrate phases, as the XRD peaks could be indexed to CuC O ·xH O (JCPDS 21-0297) and orthorhombic phase NiC O ·2H O (JCPDS 25-0582), respectively [23]. From the data comparison between nickel oxalate (Fig. 1c [Figure 1: see original paper]) and Cu . Ni . oxalate (Fig. 1b) with higher nickel content, the peaks of Cu . Ni . oxalate were characteristic of nickel oxalate hydrate in an orthorhombic phase. The XRD peak at 2 = 18.580° became more pronounced with increasing Ni content, which could be ascribed to the diffraction of the (202) plane of nickel oxalate.

To further determine the coordination environment of Cu-Ni oxalates, FT-IR spectra of the oxalate samples were recorded (Fig. 2 [Figure 2: see original paper]). All samples showed similar absorption spectra. The strong band located at 3370 cm ^{1} is assigned to the stretching vibration of the O-H group. The presence of the carboxylate group in oxalate samples is confirmed by two bands at 1620 cm ^{1} for asymmetric stretching vibrations and 1360 cm ^{1} for symmetric stretching vibrations [24]. The band at 1317 cm ^{1} is assigned to symmetric (C-O), indicating the presence of bridging oxalates with all four oxygen atoms coordinated to metal atoms [25, 26].

In this work, Cu . Ni . alloy was synthesized by thermal decomposition of oxalates. To determine the suitable calcination temperature, all samples were studied by thermogravimetric (TG) analysis (Fig. 3 [Figure 3: see original paper]). The TG curves clearly showed that all oxalates underwent three stages. The first stage, observed in the temperature range of 35–100 °C, corresponds to the loss of adsorbed water. The second stage begins at about 100 °C and ends at about 250 °C, attributed to the release of crystal water from MeC O · mH O to MeC O . The third stage begins at about 250 °C and ends at about 450 °C, showing a mass loss close to the theoretical value for the decomposition of MeC O to Me O and Me with release of CO and CO gases [27-29]. Based on the reduction temperature of oxalates in TG analysis, the calcination temperature was set at 450 °C for subsequent alloying.

3.2 Characterization of the Obtained Cu . Ni . Alloy

The crystal structures of pure Cu and Ni metals and Cu . Ni . alloy were monitored by XRD. Fig. 4 [Figure 4: see original paper] shows the standard diffraction data for metallic Cu and Ni. The diffraction peaks of all samples are assigned to the (111), (200), and (220) planes, respectively, as confirmed by the standard data for the fcc structure of Cu . Ni . alloy [12, 30]. The diffraction peaks for the alloy sample are distributed between those of pure copper and pure nickel, confirming the formation of a solid solution between Cu and Ni. Further, the Cu content in Cu . Ni . alloy was estimated based on Vegard' s law, which claims a linear relationship between the lattice parameter of an alloy and its composition. For most catalytic reactions, the surface area of the catalyst is important due to its relevance to the adsorption and desorption of reactants. BET data of the as-prepared sample are extremely low ($<5\ m^2/g$), which helps eliminate the influence of contact area on catalytic performance.

Fig. 5a [Figure 5: see original paper] shows an SEM image of Cu . Ni . alloy. The SEM image clearly illustrates that the bimetallic particles are primarily spherical in nature, and small particles self-assembled to form larger aggregates. TEM images further confirm that the obtained Cu . Ni . alloy has spherical morphology. Fig. 5f shows a high-resolution TEM (HRTEM) image of Cu . Ni . alloy. The interfringe distance of 0.205 nm is slightly smaller than the 0.208 nm spacing for Cu (111), but larger than the 0.203 nm spacing for Ni (111). To analyze the structure and elemental composition of the alloys, SEM-energy dispersive X-ray (EDX) elemental mapping images of the Cu . Ni . alloy are presented in Fig. 5(c–e), which confirm the high dispersion of Cu and Ni in forming alloy structures without significant segregation of each component. As shown in Fig. 5b, the molar ratio of Cu to Ni is about 50:50, which agrees well with the initial ratio. This suggests that the metal precursors were completely reduced and transformed into Cu . Ni . alloy. These analyses further confirm the successful preparation of Cu . Ni . alloy.

The chemical states of Cu and Ni in Cu . Ni . alloy were further determined by XPS spectra. In the full spectrum of Cu . Ni . alloy (Fig. 6a [Figure 6: see original paper]), signals for C 1s, O 1s, Ni 2p, and Cu 2p can be clearly seen in the binding energy region from 0 to 1200 eV. XPS spectra of Cu 2p (Fig.

6b) exhibit two strong peaks at 932.3 and 952.5 eV, corresponding to Cu 2p / and Cu 2p / , respectively. The binding energy values indicate the presence of metallic Cu [13, 31], whereas minor peaks located at 934.4 eV and low-intensity satellites at 940–945 eV can be attributed to Cu^{2} , as reported elsewhere [32-34]. Ni 2p spectra (Fig. 6c) also exhibited spin-orbital peaks. The photoelectron peak at 852.5 eV is assigned to Ni [30]. Additionally, a signal related to Ni^{2} was also detected at a binding energy of 855.8 eV [30, 35, 36]. Therefore, Ni species were partially oxidized to form NiO. In addition to these peaks, a shake-up satellite peak in the region of 860–865 eV also confirms the existence of a small amount of NiO [37]. The presence of copper and nickel oxides in the alloy suggests that a thin oxidized layer was formed, which is conducive to alloy stability.

3.3 Application of Cu . Ni . Alloy for Catalytic Reduction of 4-NP

The reduction of 4-NP by NaBH in aqueous solution is a model reaction [38, 39] that can be used to examine the catalytic activity of the as-prepared catalyst. For this purpose, the advantages of Cu . Ni . alloy were explored in studying the reduction of 4-NP to p-aminophenol (4-AP) in the presence of NaBH at room temperature. As observed in Fig. 7a [Figure 7: see original paper], the 4-NP solution exhibited a strong absorption peak at 317 nm, which remarkably red-shifted to 400 nm when treated only with an aqueous solution of NaBH [40]. Simultaneously, the color of the solution changed from light to dark yellow. The absorption peak immediately shifted from 317 to 400 nm, probably due to the formation of p-nitrophenolate ions under alkaline conditions with NaBH [41]. It should be noted that NaBH cannot reduce 4-NP without catalysts, even though it is considered an electron donor and hydrogen source. The peak at 400 nm remained unchanged for over 4 min in the absence of catalyst (Fig. 7b), demonstrating that the reduction reaction did not proceed without a catalyst.

The catalytic activities of the as-prepared Cu . Ni . alloy and pure Cu and Ni metals were compared in the 4-NP reduction reaction. Fig. 8 [Figure 8: see original paper] shows the time-dependent absorption of the solution over the catalyst in the presence of excess NaBH . The maximum absorbance peak at 400 nm gradually declines as the reduction reaction proceeds. Meanwhile, the color of the solution gradually changes from dark yellow to colorless, accompanied by a concomitant increase in the peak at 300 nm, indicating the reduction of 4-NP to 4-AP. The UV-Vis absorption spectra show an isosbestic point between the two absorption peaks, suggesting that 4-NP was gradually converted to 4-AP without any side reaction.

As indicated by the UV-Vis absorption spectra in Fig. 8a, Cu required 24 min to complete the catalytic reaction. For Ni (Fig. 8b), more than 40 min was needed to complete the catalytic reaction, demonstrating that Ni’ s catalytic activity was significantly lower. In comparison, for Cu . Ni . alloy (Fig. 8c), the complete reaction time dramatically decreased to 10 min, showing a great enhancement in catalytic activity. The reduction reaction completes in much shorter time for bimetallic alloy nanocrystals compared to monometallic Cu and Ni.

To determine the role of Cu . Ni . alloy in this reduction conversion, kinetic analysis of these reactions was carried out based on the temporal decay of these peaks. The ratio of C to C (where C and C are 4-NP concentrations at time t and 0, respectively) was measured from the relative intensity of the respective absorbance A /A . As shown in Fig. 8d, without catalysts, the maximum absorption peak remains unchanged, indicating that the presence of NaBH alone cannot initiate the conversion reaction even in large excess. In contrast, introducing pure Cu or Ni into the reaction system provides moderate conversion, showing that pure Cu or Ni is active for 4-NP reduction. It is observed from Fig. 8d that the reduction reaction completes in much shorter time over Cu . Ni . alloy compared to monometallic Cu and Ni particles.

To study catalyst activity, a pseudo-first-order reaction with respect to 4-NP concentration was used to evaluate the kinetic rate constant. The kinetic equation for the reduction can be written as:

$$\frac{dC_t}{dt} = kC_t \quad \text{or} \quad \ln\left(\frac{C_t}{C_0}\right) = -kt \quad (1)$$

where C is the concentration of 4-NP at time t and k is the rate constant, which can be obtained from the decrease in peak intensity at 400 nm with time. The catalytic performance of Cu . Ni . alloy and monometallic Cu and Ni particles was obtained by calculating the rate constants from UV-Vis absorption spectra. The rate constants (k) for the reduction of 4-NP to 4-AP were estimated from diffusion-coupled first-order reaction kinetics. The k value obtained for 4-NP reduction over Cu . Ni . alloy is 0.31 min ^{1}, about twice as high as 0.15 min ^{1} for Cu and 0.12 min ^{1} for Ni. According to the rate constant, the catalytic activity of Cu . Ni . alloy for 4-NP reduction is higher than other noble metals reported in the literature [42, 43]. This could be due to the synergistic effect between Cu and Ni in the alloy that plays a leading role in improving catalytic properties. In the reduction of aromatic nitro-compounds, it is believed that p-nitrophenolate ions are adsorbed by the catalyst, and borohydride ions react with the catalyst and transfer surface hydrogen species and electrons to them, thereby resulting in efficient reduction of the -NO group [44]. The interaction between Cu and Ni here may facilitate the formation of intermediate species and the transition of electrons.

Stability and reusability are of great importance for practical catalyst applications. The recyclability of catalytic reduction was carried out for Cu . Ni . alloy over five successive cycles, as presented in Fig. 9 [Figure 9: see original paper]. After five cycles, the catalytic activity remains high at 82%, showing high stability for Cu . Ni . alloy. The slight decreases in catalytic activity during the fourth and fifth cycles are probably due to catalyst loss during separation and reuse.

4. CONCLUSION

Cu . Ni . alloy was prepared by thermal decomposition of Cu–Ni oxalates. The key was the use of Cu–Ni oxalate precursors, which allowed the metal precursors to be completely reduced and transformed into alloys. The actual component ratios of the obtained Cu . Ni . alloy are consistent with the initial ratios. Compared with monometallic Ni and Cu, Cu . Ni . alloy exhibits excellent catalytic activity and selectivity for the reduction of p-nitrophenol by sodium borohydride in aqueous solution, which might be related to the strong interaction between Cu and Ni. Therefore, CuNi alloys, with their low cost, simple preparation, and high activity, are shown to have great potential for replacing noble metals in other catalytic applications.

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Figure Captions

Fig. 1. X-ray diffraction patterns of oxalate precursors: (a) cupric oxalate, (b) Cu . Ni . oxalate, and (c) nickel oxalate

Fig. 2. FT-IR spectra of oxalate precursors: (a) cupric oxalate, (b) Cu . Ni . oxalate, and (c) nickel oxalate

Fig. 3. TG curves of the given oxalate precursors

Fig. 4. XRD patterns of (a) Cu, (b) Cu . Ni . alloy, and (c) Ni

Fig. 5. SEM images of (a) Cu, (b) Ni, and (c) Cu . Ni . alloy; (d–e) TEM image of Cu . Ni . alloy; (f) HRTEM image of Cu . Ni . alloy; (g) SEM-EDS spectrum; SEM-EDS elemental mapping images of (h) Cu and (i) Ni for Cu . Ni . alloy

Fig. 6. XPS analysis of Cu . Ni . alloy: (a) Full spectrum in the binding energy region from 0 to 1200 eV; detailed spectra of (b) Cu 2p and (c) Ni 2p

Fig. 7. (a) UV-visible absorption spectra of 4-NP with and without NaBH , and (b) time-dependent UV-visible absorption spectra for the reduction of 4-NP

with NaBH in the absence of catalyst

Fig. 8. Evolution of UV-Vis spectra of 4-NP solution with various catalysts: (a) Cu, (b) Ni, (c) Cu . Ni . ; (d) variation of relative intensity of 4-NP with reaction time in the presence of excess NaBH over various catalysts. Square dots represent data without any catalyst

Fig. 9. Conversion of 4-NP for five successive cycles of reduction with the Cu . Ni . alloy

Note: Figure translations are in progress. See original paper for figures.