



# $\alpha$ - and $\beta$ -CoNi binary hydroxides nanostructures: Synthesis, characterization, and application as heterogeneous catalysts



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## ABSTRACT

The aim of this study is to show that  $\alpha$ - and  $\beta$ -CoNi binary hydroxides nanostructures can be used as heterogeneous catalysts in the oxidation of benzyl alcohol, *N*-formylation of aniline, and the Claisen–Schmidt condensation. The catalysts were synthesized by hydrothermal method and characterized by XRD, FE-SEM/EDX, FT-IR, TGA, UV–vis and  $N_2$  adsorption-desorption techniques. The  $\alpha$ -phase is similar to layered double hydroxide (LDH), while  $\beta$ -phase is isostructural with brucite. In all of the three reactions, the conversion enhanced by increasing the amount of catalysts from 10 to 30 mg, and the catalytic activity of  $\alpha$ -phase was better than  $\beta$ -phase. In benzyl alcohol oxidation, the best conversion for  $\alpha$ - and  $\beta$ -phases was 90% and 80%, respectively, under solvent-free conditions. In *N*-formylation, the best yield for both catalysts was obtained 95% in solvent-free conditions. However, the time required for  $\alpha$ -phase to reach this amount was a quarter of that for  $\beta$ -phase. For the Claisen–Schmidt condensation, the best yield was obtained at 90 °C, which was 70% and 50% for  $\alpha$ - and  $\beta$ -CoNi binary hydroxides, respectively. Both catalysts were stable and subsequent to each step of recovery and reuse, no significant loss in activity was observed.

## 1. Introduction

The hydroxides of cobalt and nickel are found well in two polymorphs of  $\alpha$  and  $\beta$  [1,2]. The metal hydroxide layers in both phases have a hexagonal structure. However, there are differences between the two forms. The  $\beta$ -phase similar to brucite,  $Mg(OH)_2$ , has neutral surface layers without the presence of any species in the interlayer spacing [3]. In contrast, in the  $\alpha$ -form, positively-charged surfaces are separated from each other by water and interlayer anions. This leads to maintaining electroneutrality and greater stability of the structure [4]. Therefore, basal spacing in the  $\alpha$ -hydroxide is larger than of  $\beta$ -hydroxide. Furthermore, layers in the  $\beta$ -phase are perfectly stacked in the *c*-axis direction, while they have a random orientation in the  $\alpha$ -phase (turbostratic disordered structure). The  $\alpha$ -hydroxides without trivalent cations in the hexagonal layers can be synthesized by the generic formula  $[M^{2+}_{1-x}M^{3+}_x(OH)_{2-y}](A^{n-})_{y/n}\cdot mH_2O$ , where *M* could be written as:  $Co^{2+}$  and  $Ni^{2+}$ , and  $A^{n-}$  is the interlayer anion [5]. A positive charge on the metallic surface is produced by partial protonation of the hydroxyl ions according to the equation of  $[M(OH)_2] + xH^+ \rightarrow [M(OH)_{2-x}(H_2O)_x]^{x+}$  [6]. The structure of  $\alpha$ -hydroxides is analogous to that of the layered double hydroxides (LDHs) in which the positive charge results from the partial substitution of trivalent cations instead

of some divalent cations [7]. The composition of LDHs are represented by the general formula  $[M^{2+}_{1-x}M^{3+}_x(OH)_2](A^{n-})_{x/n}\cdot mH_2O$ , where  $M^{2+}$  and  $M^{3+}$  are di- and trivalent cations, respectively and  $A^{n-}$  is the interlayer anion. In recent decades, the products of organic reactions have received much attention in laboratory research, industrial synthesis and pharmaceutical compounds. The majority of reactions without catalysts are not associated with a good yield. Therefore, it is essential that inexpensive catalysts with easy preparation, high selectivity, and excellent recovery be applied [8,9]. In this study, we synthesized  $\alpha$ - and  $\beta$ -CoNi binary hydroxides nanostructures and investigated their activity as heterogeneous catalysts in the oxidation of benzyl alcohol, *N*-formylation of aniline, and the Claisen–Schmidt condensation. Not only the products of these reactions are important intermediates in the preparation of other organic compounds [10,11] but also some of them have biological activities such as anti-bacterial [12], anti-diabetic [13], anti-inflammatory [14], anticancer [15]. In the last two decades, hydroxides of cobalt and nickel were used as supercapacitor electrode materials and rechargeable alkaline batteries [16,17]. They also have been used as high-performance catalyst for water oxidation [18,19]. However, according to our study, there is no report of catalytic activity of these compounds in organic reactions. Choudhary et al. [20] applied various LDHs and binary metal hydroxides containing the first series of

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transition metals in order to oxidation of benzyl alcohol. Moreover, a comprehensive review of catalytic oxidation of alcohols over the LDHs as a catalyst or supported catalysts has been reported by Crocker et al. [21]. Compared with the oxidation of alcohols, there is no report on the catalytic activity of the LDHs and binary metal hydroxides in *N*-formylation of amines. Finally, the calcined and rehydrated Mg-Al LDHs have been extensively applied as effective solid-base catalysts in aldol condensations such as the Claisen–Schmidt condensation reaction [22,23]. In the recent years, more attention has been paid to the catalytic activity of LDHs and binary metal hydroxides containing transition metals [24,25].

## 2. Experimental section

### 2.1. Materials and instruments

Cobalt (II) nitrate hexahydrate, Nickel (II) nitrate hexahydrate, and ammonia solution (25%, w/v) were purchased from Chem-Lab Analytical. Benzyl alcohol was purchased from Scharlau. Aniline, formic acid, acetophenone, tert-butyl hydrogen peroxide (TBHP), acetonitrile, and urea were obtained from Merck. All chemicals were of analytical grade and were used without further purification. Purity of products was checked by a digital melting point apparatus (Electrothermal model IA9300). A Shimadzu gas chromatograph model GC 2014 with a flame ionization detector (FID) and Agilent HP-5 GC Capillary Column (30 m, 0.25 mm, 0.25  $\mu$ m) was used to calculate the reaction selectivity.

### 2.2. Synthesis of $\alpha$ -CoNi binary Hydroxide

A facile hydrothermal route under ambient atmosphere was utilized for synthesizing the catalysts. In a typical experiment, 2.91 g  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 2.91 g  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 0.9 g urea in 70 ml of deionized water were mixed under vigorous stirring for 20 min. The solution obtained was transferred into a 120 ml, Teflon-lined, stainless steel autoclave and then was heated at 150  $^\circ\text{C}$  for 10 h. Subsequently, the autoclave was allowed to cool down naturally to room temperature. Finally, the precipitation obtained was filtered and washed several times with deionized water and absolute ethanol and dried in an oven at 60  $^\circ\text{C}$ .

### 2.3. Synthesis of $\beta$ -CoNi binary hydroxide

The catalyst was synthesized in a similar way to the above-mentioned procedure, except that instead of urea, 10 ml of an aqueous solution containing 50 mmol of  $\text{NH}_3 \cdot \text{H}_2\text{O}$  was dropwisely added. In this case, a suspension was formed by adding the ammonia solution.

### 2.4. Characterization of catalysts

The powder X-ray diffraction (XRD) pattern of catalysts was obtained by a PW 1800 X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.542 \text{ \AA}$ ) at 40 kV and 30 mA current. The surface morphology and EDX spectra were recorded, using Tescan Mira 3 field emission scanning electron microscopy (FE-SEM) equipped with energy dispersive X-ray analysis system (Accelerating Voltage: 20.0 kV). Fourier-transform infrared (FT-IR) absorption spectra were recorded at room temperature with the KBr pellet technique by a Perkin Elmer Spectrum One spectrophotometer in the range of 4000–450  $\text{cm}^{-1}$ . The thermogravimetric analysis (TGA) of catalysts was carried out through a BAHR STA 503 thermal analyzer in air atmosphere. UV–vis–diffuse reflectance spectra of catalysts were performed by a Shimadzu UV Mini 1240 spectrophotometer in the region 200–800 nm at room temperature. The textural properties including BET specific surface area, total pore volume, and average pore volume were calculated from the nitrogen adsorption–desorption measurements using BELSORP in-

strument (BELSORP-mini II, BEL, Japan) at 77 K. The BJH pore size distributions were determined from the adsorption branch of nitrogen adsorption–desorption isotherms. The micropore size distributions were determined by micropore analysis (MP method). The basicity of catalysts was determined by acid–base titration method [26]. In this method 100 mg of catalysts were vigorously shaken with 10 ml deionized water for 24 h in room temperature and catalyst was separated. Then, filtrate was neutralized with 0.05 M of HCl. The remaining acid was titrated with 0.1 M of standard NaOH.

### 2.5. Oxidation of benzyl alcohol

Benzyl alcohol (1 mmol), catalyst (10 and 30 mg), and TBHP (2 mmol; 70% in water) were added into a 50-ml two-neck, round-bottomed flask equipped with a magnetic stirrer, reflux condenser, thermometer. The reaction was performed in solvent-free and acetonitrile conditions at the temperature of 40  $^\circ\text{C}$  for 6 h and monitored by TLC.

### 2.6. *N*-formylation of aniline

Aniline (1.5 mmol), formic acid (4.5 mmol) and catalyst (10 and 30 mg) were added into a 10-ml vial and the mixture was stirred at room temperature for an appropriate amount of time. The reaction was performed in solvent-free and acetonitrile conditions and monitored by TLC.

### 2.7. Claisen–Schmidt condensation

Benzaldehyde (1 mmol), catalyst (10 and 30 mg), and acetophenone (1 mmol) were added into a 25-ml two-neck, round-bottomed flask equipped with a magnetic stirrer, reflux condenser, thermometer. The reaction was performed in toluene at 40  $^\circ\text{C}$  and 90  $^\circ\text{C}$  for 8 h and monitored by TLC.

### 2.8. Catalyst recycling

After the reaction, the catalysts were separated by centrifugation, washed with water and ethanol and then dried at 60  $^\circ\text{C}$ . The recovered catalysts were reused for the next runs under the same conditions without further purification.

## 3. Results and discussion

### 3.1. Characterization of catalysts

The typical XRD pattern of the  $\alpha$ -CoNi binary H consists of four broad peaks appearing at  $2\theta$  values of 12.27 $^\circ$ , 24.72 $^\circ$ , 33.29 $^\circ$ , and 59.4 $^\circ$  is shown in Fig. 1a. The diffraction peaks are indexed as (003), (006), (101), and (110) planes, respectively, suggesting that  $\alpha$ -Co(OH) $_2$  (JCPDS No.46-0605) and  $\alpha$ -Ni(OH) $_2$  (JCPDS No. 38-0715) with weak crystallinity were synthesized. No impurities originating from  $\beta$  phases

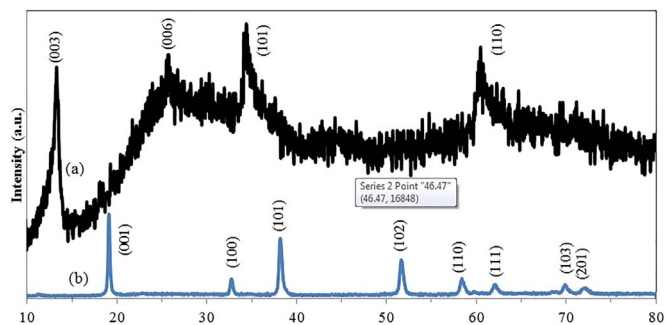


Fig. 1. XRD patterns of (a)  $\alpha$ - and (b)  $\beta$ -CoNi binary Hs.

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