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α - and β -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 α - and β -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 N₂ adsorption-desorption techniques. The α -phase is similar to layered double hydroxide (LDH), while β -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 α -phase was better than β -phase. In benzyl alcohol oxidation, the best conversion for α - and β -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 α -phase to reach this amount was a quarter of that for β -phase. For the Claisen–Schmidt condensation, the best yield was obtained at 90 °C, which was 70% and 50% for α - and β -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 α and β [1,2]. The metal hydroxide layers in both phases have a hexagonal structure. However, there are differences between the two forms. The β -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 α -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 α -hydroxide is larger than of β -hydroxide. Furthermore, layers in the β -phase are perfectly stacked in the c-axis direction, while they have a random orientation in the α -phase (turbostratic disordered structure). The α -hydroxides without trivalent cations in the hexagonal layers can be synthesized by the generic formula $[M^{2+}_{1-x} M^{2+}_{x} (OH)_{2-y}] (A^{n-})_{y/n}.mH_2O$, where M could be written as: Co²⁺and Ni²⁺, and Aⁿ⁻ 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} (H₂O)_x]^{x+} [6]. The structure of α -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 $[M^{2+}_{1-x} M^{3+}_{x} (OH)_{2}] (A^{n-})_{x/n} .mH_{2}O$, where M^{2+} and M³⁺ are di- and trivalent cations, respectively and Aⁿ⁻ is the interlaver 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 α - and β-CoNi binary hydroxides nanostructures and investigated their activity as heterogeneous catalysts in the oxidation of benzyl alcohol, Nformylation 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 μ m) was used to calculate the reaction selectivity.

2.2. Synthesis of a-CoNi binary Hydroxide

A facile hydrothermal route under ambient atmosphere was utilized for synthesizing the catalysts. In a typical experiment, $2.91 \text{ g Co}(\text{NO}_3)_2$ · $6\text{H}_2\text{O}$, $2.91 \text{ g Ni}(\text{NO}_3)_2$ · $6\text{H}_2\text{O}$ 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 °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 °C.

2.3. Synthesis of β -CoNi binary hydroxide

The catalyst was synthesized in a similar way to the abovementioned procedure, except that instead of urea, 10 ml of an aqueous solution containing 50 mmol of $\rm NH_3 \cdot H_2O$ 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 α radiation $(\lambda = 1.542 \text{ Å})$ 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). Fouriertransform 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 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 instrument (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, roundbottomed flask equipped with a magnetic stirrer, reflux condenser, thermometer. The reaction was performed in solvent-free and acetonitrile conditions at the temperature of 40 °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 °C and 90 °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 °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 α -CoNi binary H consists of four broad peaks appearing at 20 values of 12.27°, 24.72°, 33.29°, and 59.4° is shown in Fig. 1a. The diffraction peaks are indexed as (003), (006), (101), and (110) planes, respectively, suggesting that α -Co(OH)₂ (JCPDS No.46-0605) and α -Ni(OH)₂ (JCPDS No. 38-0715) with weak crystallinity were synthesized. No impurities originating from β phases





Fig. 2. SEM images of (a, b) α- and (c, d) β-CoNi binary Hs.

have been observed. The lattice parameters were obtained as a = 3.10 Å and c = 21.6 Å. These values indicate that the metal hydroxide layers in the catalyst are stacked rhombohedrally [27]. The basal spacing of 7.2 Å is obtained directly from the (003) plane. Fig. 1b shows the XRD pattern of the β -CoNi binary H, where eight diffraction planes of (001), (100), (101), (102), (110), (111), (103), and (201) are located at 2θ 19.1°, 32.7°, 38.1°, 51.6°, 58.3°, 62.1°, 69.8°, and 71.8°, respectively. These peaks can be attributed to β -Co(OH)₂ (JCPDS No. 30–0443) and β -Ni(OH)₂ (JCPDS No.14–0117) without any trace of α -phase. The cell parameters of a = 3.16 Å and c = 4.64 Å show the presence of a hexagonal lattice with good crystallinity in the catalyst [28]. The latter parameter is identical to the basal spacing. Fig. 2 shows the typical SEM images of as-synthesized catalysts. In α -phase (Fig. 2a), a number of nanosheets are connected to each other and present a 2D structure. It is also observable that nanosheets are non-uniform and their different thicknesses are estimated to range from 24 nm to 50 nm (Fig. 2b). The uniform hexagonal nanoplatelets with nearly equal size, smooth surface and corner sharp were stacked regularly in the (001) direction (c-axis) as shown in Fig. 2c. This can be responsible for the high crystallinity of catalyst, which is in agreement with the XRD pattern. The lateral observation (Fig. 2d) showed that nanoplatelets,

with approximate thickness of 24-30 nm, were vertically aligned. FT-IR spectra of α - and β -CoNi binary Hs are illustrated in Fig. 3. In the case of α -phase (Fig. 3a), the broad peak around $3459 \, \mathrm{cm}^{-1}$ can be assigned to the O-H stretching modes of the interlayer water molecules and the H-bound O-H groups and the peak at 1632 cm⁻¹ is attributed to the bending mode of the interlayer water molecule [29]. A sharp absorption peak at 2196 cm^{-1} is attributed to the vibration of C=N triple-bond interlayer OCN anions which were produced from the decomposition of urea [30]. The absorptions around 1497 and 1352 cm⁻¹ can be assigned to the intercalated carbonate anions [29,31]. The bands at 1000, 1295 and 1384 cm⁻¹ are attributed to the nitrate groups located in the interlayer space [32]. The peaks below 1000 cm⁻¹ were resulted from the vibrations of M–O, and M–OH (M= Co, Ni) in the brucite-like layers. The FT-IR spectrum of α -phase is shown in Fig. 3b. The narrow peak at 3635 cm⁻¹ can be attributed to the non-hydrogen-bonded hydroxyl groups in the brucite-like structures. The broad bands around 3434 and 1633 cm⁻¹ can be ascribed to the water absorbed by the surface and hydrogen-bonded O-H groups [33]. The sharp peak at 1384 cm^{-1} and the weak band at 1353 cm^{-1} can be attributed to the surface-absorbed nitrate and carbonate ions, respectively. The peaks located below 1000 cm⁻¹ correspond with M-







Fig. 4. TGA curves of α - and (b) β -CoNi binary Hs.

O and M-OH (M=Co, Ni) stretching and bending vibrations. TGA curves of as-synthesized catalysts at the temperature range of 25-800 °C show two-step weight loss (Fig. 4). The first weight loss (about 10%) for α-phase between 25 °C and 260 °C is due to the evaporation of water adsorbed on surface and interlayer water molecules. The main weight loss (about 23%) at the temperature range between 260 °C and 320 °C is attributed to the dehydroxylation of the brucite-like layers as well as the loss of intercalated anions [34]. For β -phase, the first weight loss (about only 2%) below 240 °C corresponds to the removal of the water adsorbed, while the main weight loss (about 12%) between 240 °C and 304 °C is assigned to the dehydroxylation of the brucite-like layers and afterwards the formation of metal oxides [35]. Many models have been suggested in the explanation of the origin positive charge of metal layers in the α phase of Co-Ni hydroxide [6]. The two of these, contain the partial oxidation of Co^{2+} ions to Co^{3+} [36] and the presence of hydroxyl vacancies in the metal layers (without Co^{3+}) [6] are more important than others. In the latter model, some of Co²⁺ ions occupy tetrahedral sites and remains are found in octahedral sites. Also, Ni²⁺ ions only occupy octahedral sites [6]. The study of the electronic transitions is one of the experiments that can be used to determine the nature and coordination of Co²⁺, Co³⁺ and Ni²⁺ species in Co-Ni binary Hs especially in the α -phase. The UV-vis diffuse reflectance spectra of as-synthesized catalysts are shown in Fig. 5. The peak at ~ 375 nm is attributed to the transition ${}^{3}A_{2}g(F) \rightarrow {}^{3}T_{1}g(P)$ (v₃) of Ni²⁺ ions at octahedral sites [37]. The broad bands at ~ 530 and ~ 515 nm for $\alpha\text{-}$ and β -Co-Ni binary Hs, respectively, are attributed to octahedral Co²⁺



Fig. 5. UV–vis diffuse reflectance spectra of α - and β -CoNi binary Hs.

ions originating from ${}^{4}T_{1}g$ (F) $\rightarrow {}^{4}T_{1}g$ (P) (v₃) transition [38]. Additionally, the strong peaks at ~ 594 and ~ 640 nm for α -phase are assigned to ${}^{4}A_{2}$ (F) $\rightarrow {}^{4}T_{1}$ (P) (v₃) transition of Co²⁺ ions in tetrahedral coordination [38,39]. Co³⁺ ions with nitrogen donors as ligand in the octahedral coordination show d-d absorption in the 400-500 nm region [40]. As is clear from Fig. 5a, there is no band corresponding to octahedral Co^{3+} for α -phase in this region. On the basis of EDX analysis (Table 1), the atomic percentage of oxygen in αphase is several times higher than that of β -phase. This is consistent with the basal spacing of the catalysts and confirms the presence of water and interlayer anions between the brucite-like layers in α -phase. The textural parameters of as-synthesized catalysts were calculated by the N₂ adsorption-desorption isotherms. The results are reported in Table 1. A larger specific surface area was obtained for α -phase $(40.7 \text{ m}^2 \text{ g}^{-1})$ than that of β -phase $(7.05 \text{ m}^2 \text{ g}^{-1})$. The values of pore diameter (α -phase is 7.98 nm, β -phase is 6.23 nm) and pore volume (α phase is $0.081\,\text{cm}^3~\text{g}^{-1}$ $\beta\text{-phase}$ is $0.011\,\text{cm}^3~\text{g}^{-1})$ show that both catalysts have characteristics of mesoporous materials. N2 adsorptiondesorption isotherms of α - and β -CoNi binary Hs are shown in Fig. 6. The isotherms can be categorized as type IV isotherms according to IUPAC classification with H3 hysteresis loop and reveal that there is slit-like mesopores in both catalysts [41]. The mesopore and micropore size distributions obtained by the BJH and MP methods are shown in Fig. 7a and b, respectively. As can be seen from Fig. 7a, the pore size distribution centered at ~ 10.6 nm and ~ 4.6 nm for α -and β -Co-Ni binary Hs, respectively, suggesting the catalysts have the mesoporous structure. However, for both plots an abrupt increase near to the micropore region (< 2 nm) is observed. This indicates that in addition to mesopores, there are micropores in both catalysts. For further investigation pore size distribution of micropore the MP-plot was used as shown in Fig. 7b. The plots of both catalysts are nonuniform and show a distribution range with the majority concentrates in ~ 1.9 nm and ~ 1.7 nm for α -and β -CoNi binary Hs, respectively. The Lewis and Bronsted basic properties have known for the mixed metal layered hydroxides. For uncalcined form the Bronsted basicity is more important than the other, while the Lewis basicity is increased by calcination of these compounds at an appropriate temperature. It is found that the Bronsted basic sites in uncalcined form are originated from OH⁻ group on the metal surface layers. In addition, the electronegativity of metals on the layer has an influence on basicity. If the electronegativity of metals is low, the electron density is pulled toward to oxygen atom, resulting in the weakening of the M-OH, so the basicity of mixed metal layered hydroxides is increased. The basic properties of for α-and β-Co-Ni binary Hs obtained by acid-base titration method are reported in Table 1. The basicity of α -phase is higher than that of β -phase. The electronegativity values for Co²⁺ and Ni²⁺ reported by Zhang [42] are 1.467 and 1.502, respectively. The EDX results in Table 1 show that the Co/Ni atomic ratio for α -phase is higher of that than β -phase and this could possibly be the reason to higher basicity of a-phase compared to β-phase. The Lewis acid strengths of cations in the metal layers have an important effect on

Table 1

Catalyst	Specific surface area (m 2 g $^{-1}$)	Pore volume (cm ^{3} g ^{-1})	Pore diameter (nm)	Atomic content (%)				
				Co	Ni	0	Co/Ni ratio	Basicity (mmol g^{-1})
α-CoNi binary H β-CoNi binary H	40.7 7.05	0.081 0.011	7.98 6.23	16.1 36.3	23.60 62.05	48.4 1.40	0.68 0.58	0.35 0.05



Fig. 6. N_2 adsorption-desorption isotherms (a) α - and (b) β -CoNi binary Hs.



Fig. 7. Pore size distribution curves (a) and MP plot (b) of α - and β -CoNi binary Hs.

acidity of the mixed metal layered hydroxides. Zhang [43] reported correlation Lewis Acid strengths with electron configurations for metal ions. The presence of some trivalent metal cations such as Al³⁺ increases the Lewis acidity and catalytic activity of the mixed metal layered hydroxides [44]. However, in absence of trivalent metal cations these properties can be determined by the Lewis acid strengths of divalent metal cations. Lewis Acid strengths for Co²⁺ and Ni²⁺ were calculated to be 0.356 and 0.293, respectively. In α -CoNi binary H with a Co/Ni atomic ratio larger than that of β -CoNi binary H (Table 1), possibly there is more acidic sites for α -phase than β -phase.

3.2. Oxidation of benzyl alcohol

In the absence of the catalysts, the conversion of benzyl alcohol is less than 10%. This could be due to the noncatalytic oxidation. Since H₂O₂ is decomposed faster than TBHP in the presence of metal hydroxides having transition elements in the brucite layers, TBHP was employed as the oxidizing agent in our study. As shown in Table 2, the conversion of benzyl alcohol and selectivity of the benzaldehyde under solvent-free conditions was greater than of that acetonitrile solvent. Furthermore, the conversion and selectivity depend on the amount of catalysts. Increasing the amount of catalysts from 10 to 30 mg increased the conversion and selectivity in the both media. Drawing a comparison between the two catalysts demonstrates that α -phase has a better activity than β -phase. The best result was observed using of $30 \text{ mg} \alpha$ -phase under solvent-free conditions (Table 2, Entry 3). It should be noted that in order to investigate the performance and the difference between the two catalysts, the reactions were conducted only in about 6 h. To improve the benzyl alcohol conversion, some reactions (Table 2, Entries 1, 2) were continued for 2 more hours. The conversion was increased to 90% and 65% (Table 2, Entries 9, 10) by further increasing the reaction time to 8 h. However, no significant change in the selectivity was observed. The reusability of α -and β -CoNi binary Hs was examined in three consecutive runs with the same reaction conditions for 6 h as shown in Fig. 8. For α -phase, the results revealed no losses in the conversion after three consecutive runs. In the case of β -phase, the reusability was accomplished no losses of conversion after two consecutive runs and then it decreased to 55% in three consecutive runs. These observations demonstrate that α -and β -CoNi binary Hs have high stability in the oxidation of benzyl alcohol. It has been found that generally, the oxidation of benzyl alcohol over the surface of the catalysts in the presence of H₂O₂ and TBHP proceeds through a free-radical pathway [45]. We propose a four-step mechanism based on radical routes for this reaction (Scheme 1) [46]. Initially, due to the interaction with Co²⁺ and Ni²⁺ on the surface of the catalysts, TBHP is decomposed into t-butoxide and hydroxyl radicals. Following that, by the abstraction of the hydrogen from benzyl alcohol by t-butoxide, the intermediate benzylic radical and t-butyl alcohol are produced. In the third step, hydroxyl radical generated from the decomposition of TBHP is combined with benzylic radical, and dihydroxyl intermediate is formed. Finally, in the last step, the benzaldehyde is simply produced by the loss of water molecule from the dihydroxyl compound [47].

Table 2

Oxidation of benzyl alcohol by $\alpha\text{-}$ and $\beta\text{-CoNi}$ binary Hs^a

Entry	Catalyst	Amount (mg)	Solvent	Conversion of benzyl alcohol (%)	Selectivity of benzaldehyde (%)	Yield (%)
1	α-CoNi binary H	10	Solvent-free	70	98	69
2	β-CoNi binary H	10	Solvent-free	50	95	48
3	α-CoNi binary H	30	Solvent-free	90	95	86
4	β-CoNi binary H	30	Solvent-free	80	95	76
5	α-CoNi binary H	10	CH ₃ CN	50	90	45
6	β-CoNi binary H	10	CH ₃ CN	30	92	28
7	α-CoNi binary H	30	CH ₃ CN	70	90	63
8	β-CoNi binary H	30	CH ₃ CN	60	91	55
9 ^b	α-CoNi binary H	10	Solvent-free	90	99	89
$10^{\rm b}$	β-CoNi binary H	10	Solvent-free	65	93	61

^a Reaction conditions: Benzyl alcohol (1 mmol), TBHP (2 mmol), solvent-free or CH₃CN (10 ml), 40 °C, 6 h.

^b Reaction was carried out for 8 h.



Fig. 8. Reusability of (a) α - and (b) β -CoNi binary Hs for the oxidation of benzyl alcohol.



Scheme 1. The proposed mechanism for oxidation of benzyl alcohol by α -CoNi binary H.

Table 3

Formylation of aniline by $\alpha\text{-}$ and $\beta\text{-CoNi}$ binary $\text{Hs}^a.$

Entry	Catalyst	Amount (mg)	Solvent	Time (min)	Yield (%)
1	α-CoNi binary H	10	Solvent-free	10	95
2	β-CoNi binary H	10	Solvent-free	25	95
3	α-CoNi binary H	30	Solvent-free	5	95
4	β-CoNi binary H	30	Solvent-free	20	95
5	α-CoNi binary H	10	CH ₃ CN	90	90
6	β-CoNi binary H	10	CH ₃ CN	130	70
7	α-CoNi binary H	30	CH ₃ CN	55	90
8	β-CoNi binary H	30	CH_3CN	105	90

 $^{\rm a}$ Reaction conditions: Aniline (1.5 mmol), formic acid (4.5 mmol), solvent-free or CH_3CN (5 ml), room temperature.



Fig. 9. Reusability of (a) $\alpha\text{-}$ and (b) $\beta\text{-CoNi}$ binary Hs for the N-formylation of aniline.

Table 4

The effect of increasing the amount of formic acid on time and yield^a.

Entry	Catalyst	Solvent	Time (min)	Yield (%)
1	α-CoNi binary H	Solvent-free	15	95
2	α-CoNi binary H	CH ₃ CN	100	90
3	β-CoNi binary H	Solvent-free	60	95

^a Reaction	conditions:	Aniline	(1.5 mmol),	formic	acid	(9 mmol),	solvent-free	01
CH ₃ CN (5 ml), room temp	perature.						



Scheme 2. The proposed mechanism for N-formylation of aniline by α-CoNi binary H.

3.3. N-formylation of aniline

Among the formylating agents, formic acid (98-100%) has attracted a lot of attention owing to its availability, low toxicity, and low cost. Moreover, against aqueous formic acid, Dean-Stark trap is not required under reflux conditions. No reaction progress was observed without the catalysts. The details and the results obtained from the Nformylation reaction are shown in Table 3. With both catalysts, aniline was converted in to the corresponding N-formyl amine in a very short time under the solvent-free conditions (Table 3 entries 1-4) than acetonitrile (Table 3 entries 5–8). The results show that α -phase has a better activity than β -phase. The best result was observed with 30 mg of α -phase (Table 3 entry 3). Drawing a comparison between the amounts of catalysts and the time of the reaction progress show that by increasing α -phase to 30 mg, the conversion period of aniline to the corresponding product was further reduced (Table 3 entries 3 and 7). Fig. 9 shows the reusability of α -and β -CoNi binary Hs in five consecutive runs with the same reaction conditions. In the case of α form, the reusability was accomplished without loss of activity after three consecutive runs. Then yield decreased to 85% in four and five consecutive runs. For β -phase, loss of activity was not observed in the two consecutive runs. Then yield started to decrease to 90% and 85% in next consecutive runs. These results show that α -and β -CoNi binary Hs have high stability in the N-formylation of aniline. The effects of amount of formic acid on the time of the reaction progress and yield were studied. 30 mg of both catalysts were selected (optimized amount) for N-formylation of 1.5 mmol aniline with 9 mmol formic acid (Table 4). The results revealed that the yield does not significantly change along with the increase the amount of formic acid. However, the reaction period increases. A proposed mechanism for the reaction

Table 5	
Claisen–Schmidt condensation by α- and β-CoNi binary Hs ^a .	

Entry	Catalyst	Amount (mg)	Temperature (°C)	Yield (%)
1	α-CoNi binary H	10	40	30
2	β-CoNi binary H	10	40	20
3	α-CoNi binary H	30	40	40
4	β-CoNi binary H	30	40	35
5	α-CoNi binary H	10	90	45
6	β-CoNi binary H	10	90	30
7	α-CoNi binary H	30	90	70
8	β-CoNi binary H	30	90	50

 $^{\rm a}$ Reaction conditions: Benzyl alcohol (1 mmol), acetophenone (1 mmol), toluene (5 ml), 8 h.

using catalysts is shown in Scheme 2. The metal surface layer in both catalysts can act as a Lewis acid in the *N*-formylation. However, as mentioned earlier, Lewis acid strength of α -phase is stronger than that of β -phase. This could be due to the higher Co²⁺/Ni²⁺ ratio for α -phase in comparison with β -phase. Consequently, the intermediate (I) is probably formed faster over the positive surfaces of α -phase. Thus, the electrophilic character of the carbonyl group in the formic acid further increases by α -phase toward β -phase. Finally, with the nucleophilic attack of aniline on this intermediate and the elimination of water molecule, the *N*-formylation product (II) is constituted [48].

3.4. Claisen-Schmidt condensation

At first, this reaction was carried out by taking 1 mmol of benzaldehyde, 1 mmol of acetophenone, and 30 mg of catalysts for 24 h at room temperature in 5 ml of toluene as the solvent. No conversion of the reactants into chalcone was observed in toluene. In order to investigate the effect of temperature on the yield, the reaction was performed at temperatures of 40 °C and 90 °C. The results obtained are summarized in Table 5. It is obvious that a dramatic increase in the yield of chalcone was observed when benzaldehyde and acetophenone were mixed and heated under reflux. The yield of



Fig. 10. Reusability of (a) $\alpha\text{-}$ and (b) $\beta\text{-CoNi}$ binary Hs for the Claisen–Schmidt condensation.



Scheme 3. The proposed mechanism for the Claisen–Schmidt condensation by α -CoNi binary H.

chalcone was enhanced by increasing the amount of two catalysts from 10 to 30 mg in both temperatures (Table 5 entries 1-8). However, the vield of chalcone at the temperature of 40 °C is less than 50% (Table 5 entries 1-4). As the temperature of the reaction mixture rose from 40 °C (Table 5 entries 1-4) to 90 °C (Table 5 entries 5-8), a relative improvement in the yield of chalcone was noticed. The best result occurred in the presence of 30 mg of α -phase at 90 °C (Table 5 entry 7). Fig. 10 shows the reusability of α - and β -CoNi binary Hs in three consecutive runs at 90 °C under the same reaction conditions. In the presence of α -phase, the reusability was accomplished without loss of activity after two consecutive runs. Then yield reached 75% in three consecutive runs. In the case of β -phase, no reduction in the yield of chalcone was observed after two consecutive runs. Then yield decreased to 50% in three consecutive runs. These results show that theses catalysts have high stability in the Claisen-Schmidt condensation similar to the previous two reactions. There is no doubt that calcined and rehydrated the mixed metal layered hydroxides as base catalysts in the aldol condensations have a higher activity than the parent form. However, we cannot completely ignore the surface basicity of mixed metal layered hydroxides. Costantino et al. [49] prepared a Ni-Al LDH with interlayer carbonate and used it as the base catalyst at 60 °C in the absence of solvent in the Knoevenagel condensation. The results indicated that the catalyst had a high activity for the condensation of aldehydes with malononitrile and ethylcyanoacetate. However, it was not active for the condensation between aldehydes with dimethylmalonate. The yield of the Claisen-Schmidt condensation reaction is strongly dependent on the basicity of catalysts. The abstraction of H⁺ from acetophenone is a key step that would be promoted by basic sites on the catalysts surface. The mechanism of product formation during the reaction between acetophenone and benzaldehyde using α-CoNi binary H is shown in Scheme 3. First the Bronsted basic site on the surface of catalyst deprotonates the α -carbon atom of acetophenone. Simultaneously the carbonyl group of benzaldehyde can be polarized by co-ordination of oxygen with Lewis acidic sites of the catalyst (I). Then the enolate anion with nucleophile attack is added to the carbonyl group of benzaldehyde and the intermediate alkoxide is formed (II). This intermediate is protonated and the corresponding β -hydroxy ketone is obtained (III). Finally, with removal of water molecule (dehydration) from β -hydroxy ketone the desired product is formed (IV) [50].

4. Conclusion

In summary, we synthesized nanosized micro and mesoporous aand β-Co-Ni binary Hs by hydrothermal method as heterogeneous catalysts for benzyl alcohol oxidation, N-formylation of aniline, and Claisen-Schmidt condensation. To the best of our knowledge, this paper is first report on the catalytic activity of α -and β -CoNi binary Hs in these reactions. UV–vis spectroscopy demonstrated that the α -phase of Co-Ni binary H was synthesized without trivalent cations in the metal hydroxide layer. The Co²⁺/Ni²⁺ ratio had a significant effect on the acidic and basic surface sites of both catalysts. Co²⁺ has the lower electronegativity and the greater Lewis acid strength than Ni²⁺. The Co^{2+}/Ni^{2+} ratio for α -phase was higher than that of β -phase, suggesting the greater basicity and acidity there is for α-CoNi binary H. Our findings demonstrated that α -phase has a higher catalytic activity than β -phase in all three reactions. This arises from the fact that α -phase showed higher porosity, specific surface area, basicity and acidity than β-phase.

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