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Research article

Cobalt chromium-layered double hydroxide, α - and β - Co(OH)₂ and amorphous Cr(OH)₃: synthesis, modification and characterization

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ABSTRACT

Cobalt-chromium layered double hydroxide (CoCr LDH), α - and β - Co(OH)₂ and amorphous Cr(OH)₃ have been synthesized under different reaction conditions. The obtained CoCr LDH was modified by stearic acid (SA) and sodium stearate (SS). The obtained samples have been characterized by X-ray diffraction (XRD), Scanning electron microscope (SEM), Ultraviolet-visible- (UV-Vis), Fourier transform infrared- (FTIR) and Energy-dispersive X-ray-(EDX) spectroscopy. The influence of reaction conditions on product composition, structural and optical properties of the samples have been discussed in detail. The basal spacing of CoCr-LDH increased from 7.366 Å to 7.428 Å and 25.214Å after the intercalation by stearic acid and sodium stearate, respectively. The average particles size by SEM analyze was estimated to be approximately 100–150 nm and 30–50 nm for CoCr-LDH_{0.6M(90°C)} and CoCr-LDH_{0.6M(90°C)}/SS nanostructures, respectively. Mixed hydroxides like α - and β - Co(OH)₂ have been obtained along with LDH at lower pH value (pH \sim 7). The number of diffraction peaks corresponding to β -Co(OH)₂ has increased with relatively decreasing of Co²⁺ ions in the reaction medium. At high chromium concentrations (Co²⁺:Cr³⁺ = 1:3 and 1:5), amorphous Cr(OH)₃ were formed in the experiment.

1. Introduction

Layered double hydroxides (LDHs) can be represented by the general formula: $M_a^{2+}M_b^{3+}(OH)_{2a+2b}(X^-)_b.xH_2O$ where, M^{2+} and M^{3+} are cations, and X^- is an exchangeable interlayer anion [1, 2]. These perspective materials can be used as a catalyst [2], pharmaceutical [3], biochemical [4], photochemical [5], electrochemical [6] materials, ion-exchanger and adsorbent [7], etc. The anion-exchange capability of LDH changes in following sequence $CO_3^{2-} > SO_4^{2-} > OH^- > F^- > CI^- > Br^- > NO_3^- > I^-$ [8]. The modification of LDH with different organic anions like 4-(12-(Methacryloylamino) dodecanoylamino) benzenesulfonate (basal spacing (b.s.) in Zn–Al-LDH is 3.75 nm) [9], Oleate (b.s. is 3.96 nm) [10], Stearate (b.s. is 3.05 nm) [11], 4-dodecyl benzene sulfonate (b.s. in MgAl-LDH is 2.80, 2.96, 2.99 nm) [12] are of great importance to get highly wide basal spacing.

Depending on the composition, well-crystallized hydrotalcite-like structures can be obtained at a different precipitation condition. pH of the reaction medium, the concentration and the nature of the base solution, aging time and temperature, total cation concentration and the molar ratios of M^{2+}/M^{3+} highly influence the product properties [13].

Co-based materials, such as Co_3O_4 [14], $LaCoO_3$ [15], CoFe LDH [16], NiCoLDH [17], etc., are considered as promising candidates for low-cost and highly active oxygen evolution reaction (OER) catalysts [18, 19]. Chenlong Dong et al. have synthesized CoCr layer double hydroxide (CoCr LDH) electrocatalyst by co-precipitation method and investigated it as an OER catalyst [19]. Their CoCr LDH achieved an onset potential of 1.47 V corresponding to an over potential of 240 mV, and a low Tafel slope of 81.0 mV dec⁻¹. They have studied that OER activity of CoCr LDH is among the best of cobalt-based materials.

In another work, cobalt/chromium-layered double hydroxide (Co/Cr (NO³)-LDH) nano-sheets were synthesized by simple co-precipitation method and employed as a packed in-tube solid phase microextraction sorbent [24]. Authors have investigated that, nanometer-sized Co/Cr (NO³)-LDH is a good choice for the separation and preconcentration of acidic pesticides in aqueous samples as a result of its simple synthesis procedure, high anion-exchange capacity and low cost compared with other commercially available sorbents [24].

But there is very little work on the synthesis, physicochemical

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characterization and investigation of CoCr-based LDH. Herein applying different reaction conditions CoCr-LDH have been synthesized, modified using functional molecules and characterized by detailed interpretation. Effect of molar ratios of metal ions, pH, reaction temperature, time and the nature of the modified agents on the structural and optical properties of CoCr-LDHs and mixed hydroxides are also investigated in detail.

2. Experimental

2.1. Materials and instrumentation

Cobalt (II) nitrate hexahydrate $[Co(NO_3)_2 \cdot 6H_2O]$, chromium (III) nitrate nonahydrate $[Cr(NO_3)_3 \cdot 9H_2O]$, sodium hydroxide (NaOH), urea $[CO(NH_2)_2]$, stearic acid $(C_{17}H_{35}COOH)$, sodium stearate $(C_{17}H_{35}COONa)$ and ethyl alcohol (C_2H_5OH) were used in the experiment without further purification and all these chemicals were of analytical grade. Double-distilled water was used in the preparation of suspensions and solutions, washing the products and cleaning.

Powder X-ray diffractometer (XRD) (Bruker D2 Phaser) in CuK α radiation ($\lambda = 0.1541$ nm) was used in the angular range $2\theta = 5-80^{\circ}$ to characterize the structural properties of the samples. The average size of nanoparticles has been calculated using Debye–Scherrer equation [20]. (1):

$$D = \frac{\alpha \lambda}{\beta \cos \theta} \tag{1}$$

where, *D* is the particle diameter, α is the Scherrer constant (0.9), λ is the X-ray wavelength (1.5418 Å), β is full width of half maximum (FWHM) and θ is the Bragg's angle.

Basal spacing is determined by Bragg's Law equation from (003) reflection [21] (2):

$$d_{(hkl)} = \frac{n\lambda}{2sin\theta} \tag{2}$$

where, θ is the scattering angle, *n* is a positive integer and λ is the wavelength of the incident wave.

Because LDH structures are hexagonal particles with high aspect ratio [22] the lattice parameters 'a' and 'c' were calculated in $a = b \neq c$; $\alpha = \beta = 90^{\circ}$; $\gamma = 120^{\circ}$ condition, according to Eq. (3) [23].

$$\frac{1}{d_{(hkl)}^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$
(3)

Lattice parameters "a" and "c" were calcullated using (110) and (003) reflections, respectively.

Optical characterization was carried out by Varian 3600 Fouriertransform infrared (FTIR) and Specord 250 UV–vis spectrometers. JEOL JSM-7600F Scanning electron microscope (SEM) and X-max 50 energy dispersive X-ray spectrometer (EDX) were used to characterize the surface morphology and chemical composition of the products.

2.2. Synthesis of CoCr-LDH-NO3 and metal hydroxides

Synthesis of CoCr-LDH-NO₃ was carried out by co-precipitation and homogeneous precipitation by urea hydrolysis methods. 40mL of 0.375M Co(NO₃)₂·6H₂O and 40mL of 0.125M Cr(NO₃)₃·9H₂O solutions were mixed and titrated with 0.6M (10M and 20M) of NaOH/water solutions under vigorous stirring. 0.1 mol urea was added to get well-precipitated LDHs where 0.6 M of NaOH solution was used in the experiment. The obtained slurry solutions were aged at three different temperatures (25°C, 90°C and 100°C) and denoted as CoCr-LDH_{0.6M,25°C}, CoCr-LDH_{0.6M,90°C}, CoCr-LDH_{0.6M,100°C}, CoCr-LDH_{10M,90°C} and CoCr-LDH_{20M,90°C} corresponding to the respective reaction preceding. Using different molar ratio of Co and Cr ions like Co:Cr = 1:1, 1:3, 1:5, 3:1 and 5:1 the co-precipitation method was also used to synthesize the samples. The pH of these samples was maintained constant at 7 by adding NaOH simultaneously. All the products synthesized at different reaction proceedings were washed well with double-distilled water, air-dried and ground into the powder. For the modification of obtained CoCr-LDH-NO₃, 0.5g of CoCr-LDH_{0.6M,90°C}–NO₃ powder was treated with 0.3% of stearic acid (SA)/ethanol and 0.3% of sodium stearate (SS)/water solutions, separately and aged for a week at 75°C temperature. The modified CoCr-LDHs are called as CoCr-LDH_{0.6M,90°C}–SA and CoCr- LDH_{0.6M,90°C}-SS.

3. Results and discussion

3.1. XRD study

The XRD patterns of obtained LDHs under different temperatures, pH and methods were shown in Fig. 1. The characteristic reflection planes (003), (006), (009), (012) and (110) corresponding to hydrotalcite-like crystal structures (JCPDS file 38–0487) [24] were observed at $2\theta = 11.86^{\circ}$, 23.1°, 34.13°, 38.76°, 60.34° diffraction angles (Fig. 1a).

The purpose of the modification is to intercalate the layered structure with an organic compound and increase the basal spacing. The basal spacing of CoCr-LDH increased from 7.366 Å to 7.428 Å and 25.214Å after the intercalation by stearic acid and sodium stearate, respectively. The XRD pattern of CoCr-LDH_{0.6M, 90°C}-SA shows partial changes in basal spacing after the modification by stearic acid (Table 1). Due to the solubility of sodium stearate in water, we could achieve a wide basal plane spacing (d₍₀₀₃₎ = 25.214 Å) with sodium stearate.

Mixed hydroxides like α - and β - Co(OH)₂ have been obtained along with LDH at lower pH value (pH ~ 7) (Fig. 2a,b). It is explained that a small amount of hydroxide ions causes the formation of α - and β -Co(OH)₂ and amorphous Cr(OH)₃ in reaction medium. Cobalt hydroxide crystallizes in two polymorphs, α -Co(OH)₂ and β -Co(OH)₂ depending on cobalt ion concentration and pH [25, 26]. The number of diffraction peaks corresponding to β -Co(OH)₂ has increased with relatively decreasing of Co²⁺ ions in the reaction medium. These results are consistent with the investigation demonstrated by Zhaoping Liu et al. [25].

At high chromium concentrations (Co^{2+} : $\text{Cr}^{3+} = 1:3$ and 1:5), amorphous Cr(OH)₃ were formed in the experiment (Fig. 2d,e). Svetozar Music et al. have investigated the hydrolyzed product synthesized from 0.1 M Cr(NO₃)₃ solution and 0.5 M urea at 100°C for 9 h at pH_{final} = 7.05 was completely amorphous [27]. After the heating it up to 360°C,



Fig. 1. XRD patterns of a) CoCr- LDH_{0.6M,90^{\circ}C}, b) CoCr- LDH_{0.6M,90^{\circ}C} –SS, c) CoCr- LDH_{0.6M,90^{\circ}C} –SA, d) CoCr- LDH_{20M,90^{\circ}C}, e) CoCr- LDH_{10M,90^{\circ}C}.

Table 1

Structural parameters of CoCr-LDHs determined from XRD pattern.

Parameters (Å)	CoCr-LDH _{0.6M,}	CoCr-LDH _{0.6M,}	CoCr-LDH _{0.6M,}	CoCr-LDH _{0.6M} , 90° C ⁻	CoCr-LDH _{0.6M} , 90°C-	CoCr-LDH _{10M,}	CoCr-LDH _{20M,}
	25°C	90°C	100°C	SA	SS	90°C	90° C
$\begin{array}{l} d_{(003)} \\ d_{(006)} \\ d_{(110)} \\ a = 2d_{110} \mbox{ (latt.par.)} \\ c = 3d_{003} \mbox{ (latt.par.)} \\ D \mbox{ (particle size)} \end{array}$	7.490	7.459	7.366	7.428	25.214	7.554	7.491
	3.789	3.821	3.794	3.813	19.186	3.797	3.797
	1.551	1.532	1.544	1.532	1.540	1.517	1.521
	3.102	3.064	3.088	3.064	3.08	3.034	3.042
	22.470	22.377	22.098	22.284	105.891	22.662	22.473
	37.9	41.7	29.3	33.4	27.7	166.9	111.3



Fig. 2. XRD patterns of mixed hydroxides obtained at different molar ratios (a) 5:1, (b) 3:1, (c) 1:1, (d) 1:3 and (e) 1:5 of Co^{2+} and Cr^{3+} ions (pH = \sim 7).

crystalline Cr2O3 has appeared [27].

The XRD patterns of CoCr-LDHs synthesized with 10M and 20M NaOH are shown in Fig.1d,e. In spite of XRD pattern of CoCr-LDH_{0.6M}, 90° C shows low-intensity peaks (Fig. 1a), the intensity of peaks has increased for CoCr-LDH_{10M}, 90° C and decreased for CoCr-LDH_{20M}, 90° C. As can be seen from Table 1, the (003) basal plane spacing of CoCr-LDH_{10M}, 90° C has increased and for CoCr-LDH_{20M}, 90° C decreased. It is explained by the structure change during the experiment in high concentrated base solution. The average particle size of the samples obtained with 10 M and 20M NaOH solution were higher than using 0.6M NaOH. It could be explained by the fact that, in high concentrated base solution the system could not reach its stable state immediately. This explanation is also shown in the reactions (4)–(7). At the start of the reaction a completely transparent dark blue solution has obtained using 20M NaOH in the experiment and it could be explained by the formation of amphoteric compounds [28].

$$Cr(NO_3)_3 \cdot 9H_2O + 6NaOH \rightarrow Na_3[Cr(OH)_6] + 3NaNO_3 + 9H_2O$$
(4)

$$Co(NO_3)_2 \cdot 6H_2O + 4NaOH \rightarrow Na_2[Co(OH)_4] + 2NaNO_3 + 6H_2O$$
(5)

But well-dispersed suspension has formed after heating the solution at 90°C. In the meantime, the Na₃[Cr(OH)₆] compound has decomposed at 90°C and amorphous Cr(OH)₃ and CoCr-LDH have obtained due to the concentration of NaOH was higher in the solution.

$$Na_{3}[Cr(OH)_{6}] \rightarrow Cr(OH)_{3} + 3NaOH$$
(6)

The formation of CoCr-LDH could be shown by the following reaction (7):

$$3\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} + 6\text{NaOH} \rightarrow$$

 $\text{Co}_3\text{Cr}[(\text{OH})_6]^{+3} \cdot 3(\text{NO}_3)^- \cdot \text{y H}_2\text{O} + 6\text{NaNO}_3$ (7)

Using the high concentrated base solution well crystallized LDH structures can be form if the ionic radii of the two metal ions are different [29]. We have observed in this experiment that CoCr-LDH also crystallizes better using extremely high concentrated base solution even where these two ions have similar ionic radii (0.790 Å for Co²⁺ and 0.755 Å for Cr³⁺ [30]. A possible reason is shown in the above reaction mechanism (4)–(7). Here, the crystallization manifested itself more clearly with using 10M NaOH solution (Fig. 1e). The diffraction peak intensity, (003) basal spacing of CoCr-LDH structure and the average particle size has also increased using 10 M NaOH in the experiment.

3.2. Morphology and chemical composition

The surface morphology of CoCr-LDH_{0.6M}, $90^{\circ}C/SS$ and CoCr-LDH_{0.6M}, $90^{\circ}C$ were characterized by SEM and EDX techniques. According to Fig.3a and 3c, unmodified CoCr-LDH_{0.6M}, $90^{\circ}C$ demonstrate hexagonal nanoplates. The average particle size by SEM analyze was estimated to be approximately 100–150 nm and 30–50 nm for CoCr-LDH_{0.6M}, $90^{\circ}C$ and CoCr-LDH_{0.6M}, $90^{\circ}C/SS$ nanostructures, respectively. According to this result, the average particles size was decreased after the modification by



Fig. 3. SEM analysis (A, C) and EDX spectrum (B, D) of CoCr-LDH_{0.6M, 90°C}/SS (A, B) and CoCr-LDH_{0.6M, 90°C} (C, D).

sodium stearate and it coincides with crystal size has been achieved by XRD. The decreasing of particle size after the modification could be explained by the influence of organic groups on the stability of the structure. Particles size by SEM is higher than crystal size calculated by XRD which could be explained by the coalescence of LDH crystallites has led to the hexagonal nanoplates to low Gibb's free energy [31, 32].

According to the elemental composition by EDX analysis (Fig.3 b and d), the cobalt and chromium content in both samples was 3/1 which corresponds to the initial reaction processing. The number of elements on per surface unit for CoCr-LDH_{0.6M, 90°C}/SS compound was less (Co/Cr = 4.6/1.7) than CoCr-LDH_{0.6M, 90°C} (Co/Cr = 19.6/6.7). This is due to the expansion of the structure and the growth of gaps.

3.3. Optical properties by FTIR and UV-vis spectroscopy

The FTIR spectra of CoCr-LDH_{0.6M, 25°C}, CoCr-LDH_{0.6M, 90°C}, CoCr-LDH_{0.6M, 90°C}/SA, and CoCr-LDH_{0.6M, 90°C}/SS were shown in Fig. 4. The broadband at 3430–3450 cm⁻¹ frequency observed at the spectra is attributed to the stretching vibration of hydroxyl group which exist in LHD layers and inter-lamellar water molecules [24, 33, 34].

To get well-crystallized LDH, urea hydrolysis method has been applied in the experiment. The reaction undergoes by the formation of ammonium cyanate (NH_4CNO) (8) before the formation of ammonium

and carbonate ions (9) [35].
CO(NH₂)₂
$$\rightarrow$$
NH₄CNO

$$NH_4CNO + 2H_2O \rightarrow 2NH_4^+ + CO_3^2$$
⁽⁹⁾

(8)

The characteristic absorption corresponding to the C-H bond stretching saturated hydrocarbons was observed with 3 intense IR bands at 2941cm⁻¹, 2902 cm⁻¹ and 2841 cm⁻¹ [36] for CoCr-LDH_{0.6M}, 90°C-SA and CoCr-LDH_{0.6M.} 90°C-SS because they contain organic groups. FTIR spectra of CoCr-LDH_{0.6M, 90°C}-SA and CoCr-LDH_{0.6M, 90°C}-SS shows that, the characteristic bands corresponding to C-H and -(CH₂)_n groups shifted from 715cm⁻¹ to 670cm⁻¹ after the modification. A shift in the bands corresponding C-H and -(CH₂)_n groups to lower wavenumber. It is explained by the fact that, due to the interaction between organic functional groups and positively charged layers, the energy of the hydrocarbon chain weakened. Decrease in band intensity of the NO3 stretching at 1370-1380 cm⁻¹ after the modification and shift to higher wavenumber (to 1384 cm⁻¹) could be explain that the anion exchange has happened into the structure which causes faster rotation of NO3 anion [37]. The band at 1355 cm^{-1} corresponding NO₃ anions is slightly broader for CoCr-LDH_{0.6M} is related to the impact of "n" number in NO₃. (H₂O)_n and hydrogen bonding which produces significant band broadening [37, 38]. The low-frequency intense bands at 440 and 527 cm⁻¹ are attributed to the Co-O and Cr-O bound for CoCr-LDH layers [39] (Fig. 4).



Fig. 4. FTIR spectra of the samples obtained at different temperature and modified by sodium stearate and stearic acid.

The direct electronic transition band-gap of CoCr-LDH_{0.6M}, $90^{\circ}C$ and CoCr-LDH_{0.6M}, $90^{\circ}C$ /-SS were calculated using Kubelka-Munk equation (10) [40]:

$$\left[F(R_{\infty})h\nu\right]^{1/n} = k(h\nu - E_g) \tag{10}$$

Where, $F(R_{\infty})$ is Kubelka–Munk function; $h\nu$ is photon energy, (eV); k is a constant depends on samples diffuse reflectance ($R_{\infty} = R_{sample}/R_{standard}$) [41] and not depends on the thickness of bulk materials [42]. The values of n are $\frac{1}{2}$, 3/2, 3 for direct allowed, indirect allowed, direct forbidden and indirect forbidden, respectively. The calculated bandgap (E_g) in the case of n = 1/2 is similar to the E_g based on the extrapolation of the absorption edge (Fig. 5). Thus, the electronic transition of CoCr-LDH is a direct allowed process from oxygen 2p to metal ns or nd levels [43]. Two transition bandgap values ($E_g(high)$ and $E_g(low)$) were determined by extrapolating the straight-line portion of [$F(R_{\infty})h\nu$]² curves with $h\nu$ axes. $E_g(high)$ values of CoCr-LDH_{0.6M}, 90°C and CoCr-LDH_{0.6M}, 90°C-SS were estimated to be 6.2 and 5.95 eV and $E_g(low)$

values were estimated to be 3.5 and 3.7 eV, respectively. Thus, the intercalation with SS and increasing the interlamellar space influence the transition band gap. With increasing interlamellar space the electronic transition from oxygen 2p to cobalt and chromium metal's 4s or 3d (Cr) levels band gap decreases, which are explained with the decrease of physical forces between the LDH lamellar.

CoCr-LDH_{0.6M, 90°C}/SS and CoCr-LDH_{0.6M, 90°C} compounds describe very high–value band gap energy, that attributed to the presence of organic and inorganic anions in LDH galleries. This result is in good agreement with XRD results described in Fig. 1. The diffuse reflectance UV–vis absorption maximum was shifted (~13nm) towards the low energy level is explained by the replacing of inorganic anions into the organic group.

4. Conclusions

In this paper, we have discussed the synthesis and modification of cobalt chromium-layered hydroxide and mixed hydroxides under



Fig. 5. Diffuse reflectance UV-visible absorption spectra (A) and variation of $[F(R_{\infty})h\nu]^2$ versus $h\nu$ of CoCr-LDH_{0.6M}. 90°C and CoCr-LDH_{0.6M}. 90°C SS.

different reaction proceedings. Mixed hydroxides like α - and β - Co(OH)₂ have been obtained along with LDH at lower pH value (pH ~ 7). At high chromium concentrations (Co²⁺:Cr³⁺ = 1:3 and 1:5), amorphous Cr(OH)₃ were formed from the experiment. The basal spacing of CoCr-LDH increased from 7.366 Å to 7.428 Å and 25.214Å after the intercalation by stearic acid and sodium stearate, respectively. We have observed in this experiment that CoCr-LDH also crystallizes well using extremely high concentrated base solution even where these two ions have similar ionic radii (0.790 Å for Co²⁺ and 0.755 Å for Cr³⁺). The average particles size by SEM analyze was estimated to be approximately 100–150 nm and 30–50 nm for CoCr-LDH_{0.6M, 90°C} and CoCr-LDH_{0.6, M90°C}/SS nanostructures, respectively. The decreasing of particle size after the modification could be explained by the influence of organic groups on the stability of the structure.

Declarations

Author contribution statement

Ofeliya O. Balayeva: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Abdulsaid A. Azizov, Mustafa B. Muradov & Rasim M. Alosmanov: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.

Goncha M. Eyvazova & Sevinj J. Mammadyarova: Analyzed and interpreted the data.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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