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# Synthesis and Characterization of Nano-structured Mixed Oxides

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**Abstract.** Nano-structured hydrotalcite based mixed oxides have been synthesized using coprecipitation method under variable pH and low supersaturation condition. XRD technique has been used to confirm the hydrotalcite structure and its derived different phase of mixed oxides. The metal dispersion of mixed oxides was analyzed using ICP-MS. The nanostructures of the mixed oxides have been investigated using FESEM and HRTEM. The textural properties of mixed oxides were analyzed using $N_2$ adsorption-desorption (BET) technique. The Characterizations have revealed that the developed mixed oxides were consisted with hexagonal/rhombohedral well dispersed nano-particles. Polycrystalline mixed oxides formed mesopore surface and narrower pore size distribution.

## Introduction

Material synthesis conditions are the key factors to develop nano-structured materials. Nano-structured materials show high specific surface area, high surface energy, improves the catalytic activity of the materials, high proportion of metals on the surface, high thermal stability and electrical conductivity and high absorption/adsorption capacity. Different functional nano-structured material attracted high demand for various applications. Regenerable layered material (hydrotalcite) shows attractive functional properties for different practical uses. The standard formula of hydrotalcite-like structures(HTlcs) can be written as $\left[M^{II}_{1-x}M^{III}_{x}(OH)_2\right][\ A^{q-}_{\frac{x}{q}}.nH_2O]$, where $\left[M^{II}_{1-x}M^{III}_{x}(OH)_2\right]$ and $[\ A^{q-}_{\frac{x}{q}}.nH_2O]$ represent the layer and the interlayer composition, respectively. $M^{II}$ and $M^{III}$ are divalent and trivalent metal cations, $A^{q-}$ is a $q$-valent anion, and molar ratio of $x$ varies between 0.25 to 0.33 [1].

Nano-structured hydrotalcite can be synthesized by tuning the influencing factors such as mixing rate, synthesis temperature and pH of the precursor's solution and controlling low supersaturation condition. [2]. Several synthesis methods have been developed for the synthesis of hydrotalcite. These include co-precipitation, the urea method, the sol-gel method and the microwave irradiation method. The co-precipitation method is the most commonly used method for the synthesis of hydrotalcite and it does not require any volatile solvents or other harsh and expensive chemicals or apparatus. The size, shape and morphology of the hydrotalcite can be controlled by controlling pH, temperature, types of salt and their ionic strength, as well as the ratio of the constituent metal cations [3]. The variable pH method is efficient to form fine grained crystals with rough surfaces and relatively high surface areas [4]. Synthesis under supersaturation condition is essential in order to simultaneous precipitation of two or more cations. Low supersaturation has been performed by slow addition of mixed solutions of divalent and trivalent metal salt with required ratios and alkali solution with a fixed pH in such a rate as to maintain the pH at a certain range which help to careful control of charge density of ($M^{(II)}/M^{(III)}$ ) of the hydroxide layers to coprecipitate of the two or more metallic salts [5]. This conditions give rise to precipitates with higher crystalline particle than those obtained under high supersaturation conditions [6] due to the rate of the crystal growth is higher than the rate of nucleation. At higher calcination temperatures, HTlcs are transformed to mixed metal oxides, which serve as good catalysts and adsorbents because of their large surface area, high metal dispersions, and good thermal stability [7].

In this work, hydrotalcite based nano-structured mixed oxides containing nickel, cobalt and chromium were synthesized under variable pH and low supersaturation conditions and studied mixed oxides phases, morphology and textural properties.

## Experimentation

**Synthesis:** - The mixed oxides containing nickel, cobalt, and chromium were synthesized by using coprecipitation method from metal nitrate precursors and $Na_2CO_3$ as the precipitating agent. Three solutions, each containing appropriate quantities of the metal nitrate precursors of nickel, cobalt and chromium, were prepared. Mixed nitrate solutions were added drop wise (80 ml/h) into a 0.5M sodium carbonate solution maintained the temperature 55$^o$C with a vigorous stirring. At temperature 55$^o$C, anion exchange occurs moderately and formation of hydrotalcite is homogenous due to better neutralization [8]. The resulting precipitates were washed several times to remove the excess $Na^+$ and $NO_3^-$ ions, and then the precipitates were filtered and dried. The fresh dried material was calcined at 500$^o$C for eight hours to convert the mixed oxides. The mixed oxides samples were designated by NCCM-xyz, respectively; NCCM stands for Ni-Co-Cr mixed oxides, and xyz stands for the molar ratios of the Ni:Co:Cr samples. Same symbolic technique was followed for hydrotalcite such as NCCH-xyz.

**Characterizations:** X-ray diffraction (XRD) technique has been applied using a Bruker D8 advanceddiffractometer with Cu-Kα radiation (λ =0.154 nm. An elemental chemical analysis has been carried out using the ICP-MS (Inductively coupled plasma mass spectrometry), from Agilent 7500 series. The surface morphology was studied by using field emission scanning electron microscopy (FESEM), CARL Zeiss Supra 55VP instrument and High resolution transmission electron microscopy (HRTEM),CARL Zeiss LIBRAR 200FE electron microscope with an acceleration voltage of 200 kV. The textural properties of the materials were studied by nitrogen adsorption-desorption technique using a micromeritics ASAP 2020 sorptometer.

## Results and discussion

**Nano-structured hydrotalcite and mixed oxides**-The group of peaks at 2θ angle of 11$^o$, 22.5$^o$, and 34$^o$ are corresponding to the diffractions by (003), (006), and (009) crystal planes, respectively. These peaks indicate the typical hydrotalcite-like layered structure (JCPDS 15- 0087). The peaks at 2θ angle of 38$^o$, 44$^o$, and 61$^o$ represent diffraction from the (015), (018) and (110) plane, respectively of the hydrotalcite structure [20]. Additionally, the two peaks just over 60$^o$ correspond to the (110) and (113) crystal planes of hydrotalcite (SS-NNN PDF 89-0460). Similar XRD patterns of hydrotalcites are shown in literature [9], which showed sharp and symmetric peaks at low $2\theta$ angles and broad and asymmetric peaks at higher $2\theta$ angles, and which is characteristics of clay materials with a layered structure. So the synthesized materials successfully formed hydrotalcite (Figure 1a). The cell parameter 'a' of binary hydrotalcite of Ni-Cr is higher than that of Co-Cr (Table 1). The diffraction of $d_{110}$ for Co-Cr hydrotalcite is at higher $2\theta$ angle. Besides, the parameter 'c' is increased with incorporation of increasing amount of cobalt to chromium containing hydrotalcites (Table 1). The resultant positive charges due to the substitution of cobalt by chromium are higher where more anion and water are needed to balance the interlayer charges. Nickel containing hydrotalcite formed with bigger size crystal than that of cobalt hydrotalcite is due to the higher cations radii of cobalt and rate of nucleation to form crystal. Derived Mixed oxides are in the range of 8-16 nm.

The Ni-Co-Cr hydrotalcite were decomposed fully at calcination temperature of 500$^o$C with crystalline phase. The well crystalline mixed oxides were formed at high calcination temperature (500$^o$C) that is shown in Figure 1.b. Different phases were compared with the joint committee of powder diffraction standard (JCPDS) file and determined.

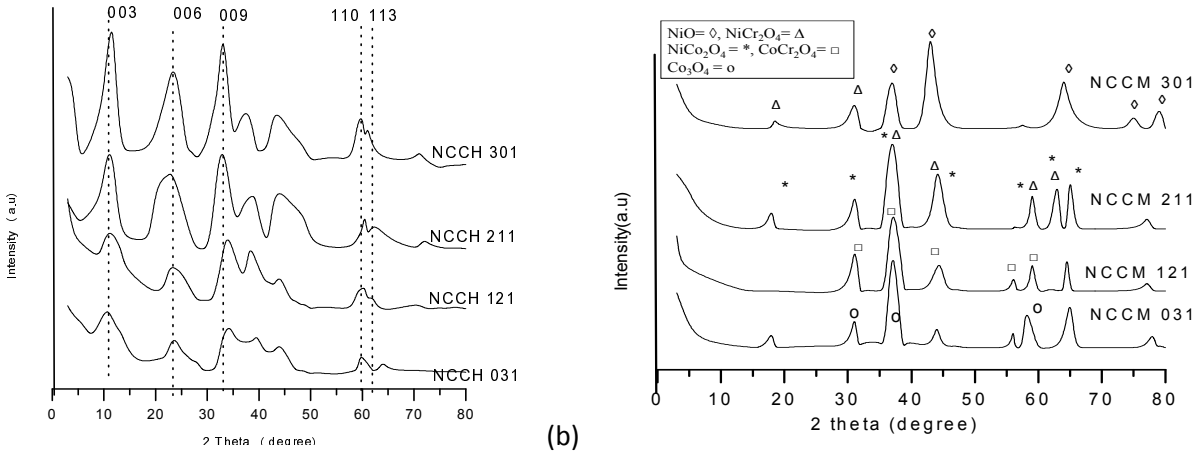



Fig.1: XRD pattern of NCCH and NCCM with different molar ratios.

Table-1: Crystallographic data of Ni-Co-Cr hydrotalcite

| HTlcs Name | Basal spacing/nm | | | Crystal parameter/nm | | Crystal size/nm | |
|---|---|---|---|---|---|---|---|
| | $d_{003}$ | $d_{006}$ | $d_{110}$ | a | c | HTlcs | Mixed oxide |
| NCCM 301 | 0.74 | 0.38 | 0.15 | 0.308 | 2.27 | 6.29 | 12.60 |
| NCCM 211 | 0.76 | 0.38 | 0.15 | 0.308 | 2.29 | 5.87 | 7.22 |
| NCCM 121 | 0.76 | 0.38 | 0.15 | 0.306 | 2.30 | 4.96 | 10.72 |
| NCCM 031 | 0.77 | 0.38 | 0.15 | 0.307 | 2.30 | 2.94 | 16.89 |

The decomposition of binary hydrotalcite lead to oxide phases of cobalt oxides ($Co_3O_4$) [JCPDS42-1467], nickel oxides (NiO) [JCPDS01-1239(D)] and nickel chromites $NiCr_2O_4$ [JCPDS23-1272(N)],cobalt chromites ($CoCr_2O_4$) [JCPDS 780711]. Additionally, ternary hydrotalcite showed characteristic diffraction peaks of $NiCo_2O_4$ [JCPDS 02-1074(N)] that are at $2\boldsymbol{\theta}$ angle of 19°, 31°, 36.5°, 44°, 56°, 59° and 65° [10].

**Homogenous Metal Dispersed Mixed Oxides.**

The formation of hydrotalcite is a simultaneous precipitation of both cations, the pH being greater than the precipitation pH of both $Ni(OH)_2$, $Co(OH)_2$ and $Cr(OH)_3$ [11]. The precipitation of $Cr(OH)_3$ easily occur in this condition and react with other cations to form hydrotalcite. The iso-electric point of chromium hydroxides (=8.5) which is less than nickel hydroxide (11.1) and cobalt hydroxide (11.4) and high pH environment is needed to coprecipitation. Therefore, chromium hydroxides precipitate earlier and react with other cations to form hydrotalcite structure. The trend of result correspond that nickel precipitates with chromium as nickel-chromium hydroxyl-carbonate which precipitate with aluminium. it can be clearly observed from the results of ICP-MS analyses (Table 2) that the molar ratios [$x$=$M^{III}$/ ($M^{II}$+ $M^{III}$)] of the cations in the mixed oxides are close to the value in the starting solutions (synthesis molar ratio). The results demonstrate that the degrees of the precipitation of the metals are about 95% of synthesis solution, and the cations were distributed homogenously in the mixed oxides.

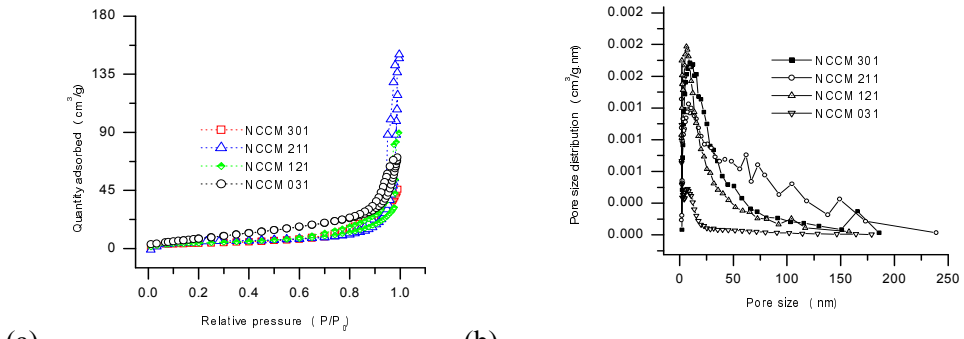
Table 2: Cations distribution in mixed oxides

| Adsorbent Name | $M^{II}/M^{III}$ | Metal composition (wt%) | | |
|---|---|---|---|---|
| | | Ni | Co | Cr |
| NCCM-301 | 3.04 | 76.50 | --- | 23.50 |
| NCCM-211 | 2.96 | 50.95 | 26.00 | 23.05 |
| NCCM-121 | 2.99 | 25.06 | 52.94 | 23.00 |
| NCCM-031 | 2.95 | --- | 77.00 | 23.00 |

**Textural Properties**

The isotherm of nickel, cobalt and chromium containing (NCCM) mixed oxides (Figure 2a) showed considerably sharp $N_2$ uptakes at high relative pressure and the presence of hysteresis loop indicated

that mesoporosity originated due to the aggregation of the nano-particles [12]. The completion of mesopores filling at high relative pressure values indicating that the mesopores were likely formed between platelets and capillary condensation was delayed. The hysteresis loops are vertical and parallel at high relative pressure which suggested the aggregates of plate-like particles leading to slit-shape pores of mixed oxides. [13] Specific surface area of NCCM 211 and NCCM 121 are 135 and 85 $m^2/g$ whereas binary mixed oxides NCCM 301 and NCCM 031 displayed 44 and 42 $m^2/g$.



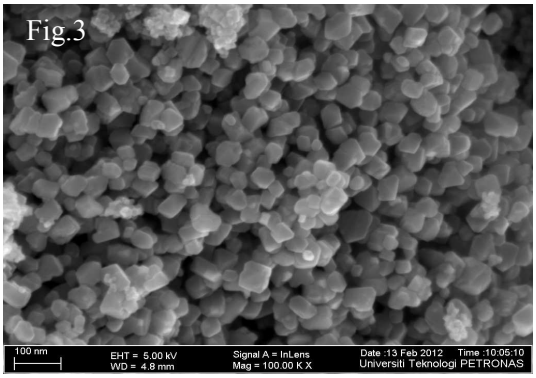

(a) (b)

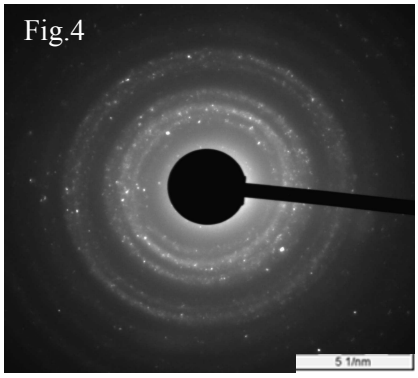
Fig.2: (a) Isotherm curves (b) PSD of NCCM with different molar ratios.

The pore size distribution plot (Figure 2b) showed narrow distribution for NCCM with peak pore width of 8-11 nm. The mixed oxides showed higher mesopores volume. The smaller pore distribution is corresponding to inter-crystalline distance within the aggregates whereas the large pore size distribution are likely originates from the inter-aggregate distances.

**Morphology of Mixed Oxides**

The Ni-Co-Cr hydrotalcite derived mixed oxides showed well defined hexagonal and rhombohedral crystal particle (Figure 3). After calcination at temperature 500°C, the mixed oxides still retained it shape of the crystal.




FESEM image of NCCM-121 was generated in sharp and in uniform (hexagonal shape oriented in different angle) through calcination due to removal of impurity and water and strongly bonded hydroxyl. The 'memory effect' of shape is because of the trivalent cations $Cr^{3+}$ substitutes the divalent cations ($Ni^{2+}$ or $Co^{2+}$) to the burucite sheets, and is converted to periclase-like solid solution [14]. The formation of nano-crystalline hydrotalcite derived mixed oxides could be due to the nickel influence on the nucleation and crystal growth process during coprecipitation. The HRTEM of mixed oxides of Ni-Co-Cr 121 showed rhombohedral particles (Not shown here) that are formed at high pH during synthesis. The solid solution of Ni(CoCr)O was reconstructed to hydrotalcite structure due to the memory effect. The thickness of the particle is around 5 nm. The ring of the SAED diffraction patter (Figure 4) with bright spot indicates that mixed oxides are polycrystalline.

**Conclusion**

The coprecipitation under variable pH and low supersaturation is efficient method to synthesize nano-structured hydrotalcite derived mixed oxides. The mixed oxides are homogenous and well dispersed that are potential properties for catalysis and for adsorbent. Uniform size crystal and clean and high specific surface area can be achieved in this synthesis conditions. Moreover, the poly crystalline mixed oxides are highly interactive which enhance the thermal stability and can be used to the different industrial application.

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