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Chemical & Environmental  
Engineering  
19 – 21 April 2016

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### PCEA -3

## Synthesis and structural characterization of CuCoFe-layered double hydroxides

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### Abstract

Layered double hydroxides (LDHs) are a class of anion clays consisting of brucite-like host layers and interlayer anions, with versatility in composition, morphology and architecture. The CoFe-LDH catalyst with  $\text{Co}^{2+}/\text{Fe}^{3+}$  molar ratio of 2 was synthesized via simple co-precipitation method. The binary CoFe-LDH catalyst was modified by insertion of  $\text{Cu}^{2+}$ , within the brucite-like sheets to obtain ternary CuCoFe-LDH with different  $\text{Cu}^{2+}/(\text{Cu}^{2+}+\text{Co}^{2+})$  molar contents of 35%, 60% and 100%. To investigate the impact of the copper content, a detailed characterization study was done to maximize the structural information through XRD, FT-IR, thermogravimetric measurements &  $\text{N}_2$  adsorption. The XRD results revealed that the CoFe, copper containing CoFe and CuFe prepared samples have typical layered structure with 3R layer & were well-crystallized. The copper rich LDH sample has  $\text{Cu}(\text{OH})_2$  &  $\text{Cu}_2\text{O}$  as impurity phases beside LDH phase formation in opposite to authors reported the impossibility of CuFe-LDH phases formation due to strong Jahn–Teller effect.

**Keywords:** Layered double hydroxides compounds (LDHs); heterogeneous catalysis; structural characterization

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19 – 21 April 2016

## 1. Introduction

Layered double hydroxides (LDHs) consists of positively charged hydrotalcite- like layers of compounded metal hydroxides that are located in the center of an edge-sharing octahedral network with charge-balancing anions and water molecules located in the interlayer spaces (Fig.1). The chemical composition of LDHs is expressed by the general formula  $[M^{+2}_{1-x}M^{+3}_x(OH)_2]^{x+}(A^{m-x/m})^x \cdot nH_2O$ , where  $M^{+2}$  and  $M^{+3}$  are divalent and trivalent metal cations and  $A^{n-}$  is a n-valent anion used to balance the positive charge in the brucite like layer [1–4].

LDHs have been studied as scavengers for anionic contaminants because of their high capacity and affinity for a wide range of anions. Also LDHs attracted interests due to their potential applications in catalysis, catalyst precursors [5–7], super capacitors [8] and adsorbents [9]. The wide range applications of LDHs comes from the salient features of their structure, as: possibility of accommodation of cations of different natures in the sheets, atomic scale homogeneity, possibility of intercalation of several types of anions and formation of mixed oxides under thermal treatment [10]. LDHs containing Cobalt or copper transition metals tend to exhibit enhanced catalytic activity owing to the presence of redox and Lewis sites that have found important environmental applications, such as the removal or decomposition of  $SO_x$  and  $NO_x$  [11-12].

Accordingly, the interest in modifying Co–Fe-based hydrotalcite as a function of  $Cu^{2+}$  addition is the aim of our study.

## 2. Experimental procedure

### 2.1. Materials

For preparing the ternary HT all the starting materials,  $Co(NO_3)_2 \cdot 6H_2O$ ,  $Cu(NO_3)_2 \cdot 3H_2O$ ,  $Fe(NO_3)_3 \cdot 9H_2O$ ,  $Na_2CO_3$  and NaOH were reagent grade, of 99.9% purity.

### 2.2. Preparation of ternary hydrotalcites catalysts

The layered double hydroxides with molar ratio  $(Co^{2+}+Cu^{2+})/Fe^{3+} = 2$  were prepared by using the co-precipitation method [13]. In a typical procedure, 200 ml of an aqueous solution containing  $Co^{2+}$ ,  $Cu^{2+}$  and  $Fe^{3+}$  with  $Cu^{2+}/(Cu^{2+}+Co^{2+})$  molar contents of 0, 35, 60 and 100% (the relation  $Co^{2+}+Cu^{2+} = 0.06$  mol was kept constant) was slowly added dropwise under vigorous mechanical stirring into 200 ml of another solution containing  $0.1 \text{ mol L}^{-1}$  NaOH and  $0.30 \text{ mol L}^{-1}$   $Na_2CO_3$ . The obtained samples were submitted to an ageing treatment at  $60^\circ C$  for 7d (the pH of the slurry after the ageing process was 10). The slurry was centrifuged and washed several times with deionized water until the pH reached 7.0. After that the precipitates were dried at  $60^\circ C$  for 24 h.

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Engineering  
19 – 21 April 2016

### 2.3. Characterization methods

#### 2.3.1. X-Ray Diffraction Analysis (XRD)

The structure and phase purity of the prepared materials were analyzed via X-ray diffraction (XRD). The experiments were carried out using a Shimadzu XD-1 diffractometer using Cu K $\alpha$  radiation ( $\lambda=0.1542$  nm) at a beam voltage of 40 KV and 40 mA beam current. The intensity data were collected at room temperature in a  $2\theta$  range of 10-70° with a scan rate of 0.7° s<sup>-1</sup>. The phase identification was made by comparing to the Joint Committee on Powder Diffraction Standards (JCPDS). The average crystallite size of the samples was determined from the XRD peaks using the Scherrer equation.

#### 2.3.2 Fourier transforms infrared spectroscopy (FTIR)

The interlayer space was investigated on spectrometer Perkin-Elmer-Spectrum no.1 in the range of 4000-400 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup>. The samples were grounded to fine powder and dispersed in KBr to compress into pellets before measurements.

#### 2.3.3. Thermal analysis

Thermogravimetric (TGA) and Differential thermal analysis (DTA) were performed to study the structural changes of the prepared materials with thermal treatment. A 10 mg of sample was heated up to 700 °C, with a heating rate of 10 °C min<sup>-1</sup> in an air flow at a rate of 100 ml min<sup>-1</sup> on SDTQ-600 (TA-USA) thermo balance instrument.

#### 2.3.4. Surface analysis using N<sub>2</sub> adsorption technique

The textural properties were determined from the N<sub>2</sub> adsorption-desorption isotherms at liquid nitrogen temperature (-196°C) using NOVA 3200 S Unite, automates gas sorption analyzer (Quantachrome Corporation) system. All samples were degassed at 300°C for 12h in nitrogen atmosphere prior each measurement to ensure a dry clean surface. The pore size distributions were determined from Barrett–Joyner–Halenda (BJH) method applied to the desorption branch of the isotherm.

#### 2.3.5. High resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray (EDX) spectroscopy

These instruments were conducted using a JEOL 2100F TEM at an accelerating voltage of 200 kV. To prepare the TEM samples, a dilute particle–ethanol colloidal mixture was ultrasonicated for 30 min and a drop of solution was placed on a carbon coated Cu TEM grid.

## 3. Results and discussion

### 3.1. Structural phase changes of the prepared samples

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8<sup>th</sup> International Conference  
on  
Chemical & Environmental  
Engineering  
19 – 21 April 2016

### 3.1.1. X-ray diffraction analysis

The XRD patterns of the Co-Fe and copper-containing Co-Fe synthesized samples are graphically illustrated in Fig.2.

For the Co-Fe synthesized sample (Fig.2-a), three intense reflection peaks appeared at  $2\theta = 12^\circ, 25^\circ, 35^\circ$ , corresponded to the interlayer d-spacings 6.92416 Å at (0 0 3) plane, 3.45936 Å at (0 0 6) plane and 2.45847 Å at (0 0 9) plane, respectively. This insures the synthesized CoFe-sample was well crystallized and had a layered structure with 3R layer (JCPDS card 25–0521) in agreement with that reported in the literatures [14], LDH structure Fig.1

The diffractograms for copper containing Co-Fe synthesized samples (Fig.2-b&c), exhibit the same peaks appeared for CoFe-LDH sample at about  $12^\circ, 25^\circ, 35^\circ, 39^\circ, 43^\circ, 60^\circ$ , and  $61^\circ$ , attributed to the (0 0 3), (0 0 6), (0 1 2), (0 1 5), (0 1 8), (1 1 0), and (1 1 3) planes, respectively, indicating typical signature of crystalline layered LDH materials belonging to the space group 3R layer (JCPDS card 25–0521). Neither impurity phases nor changes in the baseline of the diffractograms are observed for 35% CuCoFe and 60% CuCoFe samples as compared with CoFe-LDH emphasizing that these HT samples exhibit a single crystalline phase. Furthermore, the diffraction lines intensity decreases slightly for the 35% Cu-Co-Fe LDH sample (crystallite size ~ 20 nm), meanwhile on increasing the copper content to 60% Cu-Co-Fe the intensity increased (crystallite size ~ 31 nm), compared to Co-Fe LDH (crystallite size ~ 27 nm-Table 1).

This behavior can be explained upon that, for low  $\text{Cu}^{2+}$  content, a small distortion maybe occurred in the brucite-like layers due to the larger ionic radius of the  $\text{Cu}^{2+}$  compared to  $\text{Co}^{2+}$  and  $\text{Fe}^{3+}$  which can't be accommodated in the crystalline lattice leading to a broadening of the (110) plane, indicating that the layers are becoming more disordered. However, with the  $\text{Cu}^{2+}$  content, the crystalline lattice can accommodate such distortions as the  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  cations are well separated from each other and they are arranged in a typical octahedral network.

The XRD patterns for 100%CuFe sample (Fig.2-d), showed peaks at  $12^\circ, 25^\circ$  and  $35^\circ$  which fitted well to layered double hydroxide phase formation. In addition, the presence of several impurity peaks marked with (● and \*), which were indexed to a  $\text{Cu}(\text{OH})_2$  and  $\text{CuO}$  phases, respectively. The  $\text{CuO}$  phase found resulted from the decomposition of the  $\text{Cu}(\text{OH})_2$  phase that is formed during the precipitation step which is very unstable in highly basic media and easily transformed into  $\text{CuO}$  [15]. The formation of the 100%CuFe LDH phase using this synthesis method is opposite to that reported by Iglesias [13].

From the a and c cell parameters that calculated from X-ray data (Table 1), The c unit cell parameter corresponds to three times the (003) diffraction peak at  $2\theta = 12^\circ$ . It can be observed that the c parameter is constant for all the synthesized samples (2.08 nm), corresponds well with values reported previously for LHDs containing  $\text{CO}_3^{2-}$  as the interlamellar anion [16]. At the same time, the (a) unit cell parameter stands for the  $\text{Cu}^{2+}$ - $\text{Co}^{2+}$

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on  
Chemical & Environmental  
Engineering  
19 – 21 April 2016

average distance inside the layers and can be determined from the (110) reflection at  $2\theta = 60^\circ$ . it was found that all the synthesized LDH samples have similar values (0.3 nm) for the (a) parameter (see Table 1). This is reasonable since  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  have very similar ionic radius.

Thus, the XRD results clearly indicated the successful formation of CoFe, 35%CuCoFe, 60%CuCoFe and 100%CuFe-LDH samples.

Table 1 Structural characteristics and porosity data for the studied LDHs nanomaterials

LDH samples	Crystal size (nm)	c, nm	a, nm	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$TV_p$ (cc/g)	$D_p$ (nm)
Co-Fe	26	2.08	0.3	175	0.12	1.7
35%CuCoFe	20	2.08	0.3	196	0.18	1.7
60% CuCoFe	30	2.08	0.3	173	0.11	1.6
100%CuFe	101	2.07	0.31			

$$c = 3d_{003}, a = 2d_{110},$$

Crystallite sizes calculated using the Scherrer equation,  $S_{\text{BET}}$  – specific surface area calculated using the BET method,  $TV_p$  – total pore volume measured at  $p/p^0$  of 0.95,  $D_p$  – pore diameter calculated using the BJH method.

### 3.1.2. FTIR spectra

The FTIR spectra of the prepared CoFe and copper containing CoFe layered hydroxide samples (Fig.3) proved that all samples are typical HT compounds containing mainly  $\text{CO}_3^{2-}$ . [13]

For the CoFe LDH sample (Fig.3-a), the broad band observed at about  $3453 \text{ cm}^{-1}$  is assigned to O–H stretching ( $\nu_{\text{O-H}}$ ) due to the presence of hydroxyl as well as both adsorbed and interlayer water. The bending mode of H–O–H from  $\text{H}_2\text{O}$  was observed at  $1625 \text{ cm}^{-1}$  which confirming the presence of water in the interlayer space. The shoulder observed at  $2923 \text{ cm}^{-1}$  (marked with a black dot) can be assigned to hydrogen bonds between water and  $\text{CO}_3^{2-}$  [17]. The presence of a narrow mode at  $3547 \text{ cm}^{-1}$  (marked with an up arrow) is remarkable; this mode has been assigned to the O–H stretching of free metallic hydroxide. The sharp band observed at about  $1355 \text{ cm}^{-1}$  (Fig. 3-a) in the FTIR spectrum is attributed to the  $\nu_3$  asymmetric stretching of the  $\text{CO}_3^{2-}$ . the  $\nu_3$  mode observed appears down shifted by  $60 \text{ cm}^{-1}$  when compared with free  $\text{CO}_3^{2-}$  ( $\nu_3 = 1415 \text{ cm}^{-1}$ ) due to interaction of these anions with water molecules through hydrogen bonds. However, these interactions are not strong enough to distort the  $\text{CO}_3^{2-}$  anions from their  $D_{3h}$  free molecule symmetry. The  $\nu_2$  bending mode of the carbonate anions was confirmed by the shoulder observed at  $854 \text{ cm}^{-1}$  (marked with a dashed line). The IR bands below  $800 \text{ cm}^{-1}$  can be attributed to the (Co - Fe) –OH and (Co - Fe) –O (Fig. 3-a) vibrations.

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8<sup>th</sup> International Conference  
on  
Chemical & Environmental  
Engineering  
19 – 21 April 2016

For the copper containing CoFe & 100%CuFe-LDH samples (Fig.3-b-d), exhibit the same IR spectrum represented by CoFe LDH sample. The intensity of the broad band related to the O–H group become a little more intense as copper loading percent increases, indicating a small increase in the hydroxyl group amount as copper percent increased. The intensity of the narrow mode assigned to the O–H stretching of free metallic hydroxide at  $3547\text{ cm}^{-1}$  (marked with an up arrow), decreased first for 35%CuCoFe sample and then increased as the copper content increase in agreement with XRD results where we observed the presence of  $\text{Cu}(\text{OH})_2$  phase for 100%CuCoFe-LDH sample. The position of the sharp band observed at about  $1355\text{ cm}^{-1}$  (Fig. 3-b-d) due to the  $\nu_3$  asymmetric stretching of the  $\text{CO}_3^{2-}$  does not depend on Cu content in the prepared hydrotalcite layered samples, [18], The IR bands below  $800\text{ cm}^{-1}$  can be attributed to the (Co, Cu & Fe) –OH and (Co, Cu & Fe) –O (Fig. 2) vibrations. The band centered at  $785\text{ cm}^{-1}$  is assigned to the (Co, Cu & Fe- OH) mode. Since Cu–O, Co–O and Fe–O vibration frequencies are very close, the Cu content does not significantly affect the energy of the (Co, Cu & Fe) –O position.

### 3.2. Thermal behavior of the prepared hydrotalcites

The thermal stability of CoFe, copper containing CoFe and 100% CuFe-LDH samples was determined by thermogravimetric analysis and represented in Fig. 4.

The TGA and DTA scans are qualitatively the same for all the prepared LDH samples, differing only in the temperatures where the thermal events minimums occur.

The TGA profiles of the prepared samples show a continuous weight loss from room to  $220\text{ }^\circ\text{C}$  temperature, that is the most important event occurring with  $\sim 18.3, 18.6, 16.3$  &  $18.8\%$  weight loss for CoFe, 35%CuCoFe, 60% CuCoFe & 100% CuFe-LDH samples, respectively. From  $220$  to  $650\text{ }^\circ\text{C}$  the weight loss is found to be only  $6.4, 5.92, 9.7$  &  $5.60\%$  for CoFe, 35% CuCoFe, 60% CuCoFe & 100% CuFe-LDH samples, respectively. The weight losses may be attributed to the following thermal events: (i) release of the interlamellar and adsorbed water, keeping the layered structure; and (ii) release of hydroxyl groups from the brucite-like layers (as water) and the release of the interlamellar anion  $\text{CO}_3^{2-}$  as  $\text{CO}_2$  [19], At this stage, there is a collapse of the layered structure.

The DTA scans (Fig.4) shows an intense endothermic peak located at  $215\text{ }^\circ\text{C}$  for CoFe,  $230\text{ }^\circ\text{C}$  for 35% CuCoFe,  $216\text{ }^\circ\text{C}$  for 60% CuCoFe &  $231\text{ }^\circ\text{C}$  for 100% CuFe-LDH samples. The intensity of the endothermic peak decreases significantly for 35% Cu-Co-Fe prepared LDH sample and shifted to a relatively higher temperature ( $230\text{ }^\circ\text{C}$ ), Whereas, it becomes weak intense (a little broad) for the prepared 60% Cu-Co-Fe LDH sample and then become intense again for 100% CuFe-LDH sample. This endothermic peak accompanied with the release of both interlamellar and adsorbed water, keeping the layered structure. The  $\Delta H$  value of the dehydration event is low for the 35% CuCoFe sample ( $38\text{ J/g}$ ) as compared with the  $\Delta H$  values of the CoFe ( $80\text{ J/g}$ ), 60% CuCoFe ( $83\text{ J/g}$ ) & 100% CuFe ( $123\text{ J/g}$ ) -LDH samples, which

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8<sup>th</sup> International Conference  
on  
Chemical & Environmental  
Engineering  
19 – 21 April 2016

suggests that the water dehydration process is more easier for 35% CuCoFe-LDH prepared sample and is difficult for 100% CuFe-LDH prepared sample, confirming the FT-IR data which indicate that the 100% CuFe-LDH sample have more amount of hydroxyl groups caused by the presence of Cu(OH)<sub>2</sub> phase detected by XRD patterns leading the desorption process to become very difficult because of strong hydrogen bonding.

In addition, an exothermic peak is observed at ~ 522°C for Co-Fe, 509°C for 35% CuCoFe, 521°C for 60% CuCoFe, and 533°C for 100% CuFe-LDH samples, which attributed to the formation of cobalt and or (copper) oxy-carbonate, like phase, and hence hydrotalcite layered collapse.

### 3.3. N<sub>2</sub> adsorption –desorption isotherms and porosity analysis

The nitrogen adsorption–desorption isotherms, pore size distributions (PSD) calculated from the desorption branch & the textural properties of all the prepared LDH samples are included in Fig.5 and Table 1.

The nitrogen adsorption–desorption isotherms of the prepared CoFe & copper containing CoFe -LDH samples (Fig.5a-c) show that the adsorption-desorption isotherms are related to type II according to Brunauer classification [20]. The inflection point or knee of the isotherm ( $p/p^0 > 0.35$ ) indicates the stage at which monolayer coverage is completed and multilayer adsorption begins to occur. The isotherms of the samples exhibit H3- type hysteresis loops according to IUPAC classification [21]. This type indicates the presence of non-rigid aggregates (assemblage of particles which are loosely coherent) of plate like particles giving rise to slit-shaped mesopores [22]. These mesoporous come from the interconnected CoFe and or CuCoFe-LDH sheets. Generally, the LDH-type materials are characterized by an external surface mesoporosity since the N<sub>2</sub> diameter is larger than the interlamellar space for carbonate-containing LDHs. So the measured pore volumes are corresponding to the interparticle pores [23].

From the above data (Table 1) It is clear that the values of BET surface area ( $S_{BET}$ ), total pore volume ( $TV_p$ ) and average pore diameter ( $D_{p, nm}$ ) of CoFe and 60% CuCoFe -LDH samples are similar irrespective of substitution of Co<sup>2+</sup> cations with Cu<sup>2+</sup> cations within the CoFe-LDH lattice. While for the 35% CuCoFe-LDH prepared sample has higher  $S_{BET}$  surface area compared with CoFe and 60% CuCoFe -LDH samples and relatively higher pore volume this can be explained in terms of crystallite size calculated by sherrer equation from XRD data.

## 4. Conclusion

In summary, The CoFe, 35% CuCoFe, 60% CuCoFe & 100% CuFe-brucite- like layered double hydroxides of mixed hydroxides carbonates as interlayer anions were successfully

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on  
Chemical & Environmental  
Engineering  
19 – 21 April 2016

synthesized via simple co-precipitation method with varying copper content, at aging time 7d and constant PH=10. Which conflict with that reported by Iglesias et al [13]. This may be due to:

- The aging time may offer the chance of double layered to grow dispersal, regarding their aggregation and contraction. Also, the directed slow substitution of  $\text{Cu}^{2+}$  by  $\text{Co}^{2+}$  avoid the lattice distortion (elongation) and hence, the contribution of the Jahn-teller effect.
- The roughly equal radius of  $\text{Cu}^{2+}$  (0.73) and  $\text{Co}^{2+}$  (0.70),  $\text{Cu}^{2+}$  could replace a portion of  $\text{Co}^{2+}$  to form CuCoFe-LDH with stable structure, as the dispersive and isolated effect of  $\text{Co}^{2+}$  and  $\text{Fe}^{3+}$  enable  $\text{Cu}^{2+}$  achieving high dispersion in the layer. This is in agreement with Behrens et al.,[24] who prepared CuZnAl-LDH successfully.
- From XRD analysis, increased crystallinity was obtained by insertion of 60% and 100% copper cations within the CoFe-LDH network.
- From the FT-IR spectra, All the synthesized LDH samples exhibit typical FT-IR spectrum of layered double hydroxide compounds containing  $\text{CO}_3^{2-}$  as an interlayer anion and the 100% CuCoFe-LDH prepared sample has higher amount of free metallic hydroxide group which match XRD data that confirms the presence of  $\text{Cu}(\text{OH})_2$  as an impurity phase.
- From the thermal behavior of the prepared LDH samples, all the samples exhibit major weight loss from room temperature to 220°C, accompanied with a successive endothermic peaks due to release of the interlamellar and adsorbed water, keeping the layered structure. The 35% CuCoFe-LDH sample has the lowest  $\Delta H$  and hence indicates easy dehydration process. A second weight loss accompanied by the appearance of exothermic peak occurred at temperatures higher than 500 °C, caused by the total removal of carbonate and release of hydroxyl groups from the brucite-like layers indicating the formation of a metal oxy-carbonate, like phase, and hence hydroxalcite layered structure collapse.
- From the  $\text{N}_2$  adsorption analysis, all the prepared LDH samples exhibit type II  $\text{N}_2$  adsorption – desorption isotherms with H3 type hysteresis loop indicating the presence of non-rigid aggregates ( assemblage of particles which are loosely coherent ) of plate like particles giving rise to slit-shaped mesopores coming from the interconnected CoFe and or CuCoFe-LDH sheets.

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19 – 21 April 2016

## 5. References

- [1] F. Cavani, F. Trifirò, A. Vaccari, *Catal. Today* 11 (1991) 173.
- [2] V. Rives, M. Aulibarri, *Coord. Chem. Rev.* 181 (1999) 61.
- [3] A.I. Khan, D. O'Hare, *J. Mater. Chem.* 12 (2002) 3191.
- [4] F.M. Vichi, O.L. Alves, *J. Mater. Chem.* 7 (1997) 1631.
- [5] F. Li, Q. Tan, D.G. Evans, X. Duan, *Catal. Lett.* 99 (2005) 151.
- [6] D. Carriazo, C. Martı́n, V. Rives, *Eur. J. Inorg. Chem.* 2006 (2006) 4608.
- [7] G. Centi, S. Perathoner, *Microporous Mesoporous Mater.* 107 (2008) 3.
- [8] Y. Dou, T. Pan, A. Zhou, S. Xu, X. Liu, J. Han, M. Wei, D.G. Evans, X. Duan, *Chem. Commun.* 49 (2013) 8462.
- [9] S. Mandal, S. Mayadevi, *Appl. Clay Sci.* 40 (2008) 54.
- [10] A.I. Khan, D. O'Hare, *J. Mater. Chem.* 12 (2002) 3191.
- [11] A.E. Palomares, J.M. Lopez-Nieto, F.J. Lazaro, A. Lopez, A. Corma, *Appl. Catal. B* 20 (1999) 257.
- [12] F. Mårquez, A.E. Palomares, F. Rey, A. Corma, *J. Mater. Chem.* 11 (2001) 1675.
- [13] A. H. Iglesiasa, O. P. Ferreira, D. X. Gouveia, A. G. S. Filhob, J. A.C. de Paiva, J. M. Filhob, O. L. Alves, *J. Solid State Chem.* 178 (2005) 142.
- [14] J.J. Yu, Z. Jiang, L. Zhu, Z.P. Hao, Z.P. Xu, *J. Phys. Chem. B* 110 (2006) 4291.
- [15] Y. Cudenneq, A. Lecerf, *Solid State Sci.* 5 (2003) 1471.
- [16] M. Vucelic, W. Jones, G.D. Moggridge, *Clays Clay Miner.* 45 (1997) 803.
- [17] F.M. Labajos, V. Rives, M.A. Ulibarri, *J. Mater. Sci.* 27 (1992) 1546.
- [18] M.J. Hernandez-Moreno, M.A. Ulibarri, J.L. Rendon, C.J. Serna, *Phys. Chem. Miner.* 12 (1985) 34.
- [19] J. Pérez-Ramírez, G. Mul, F. Kapteijn, J.A. Moulijn, *J. Mater. Chem.* 11 (2001) 821.
- [20] Brunauer S., Deming L. S., Deming W. E., Teller E. E., *J. Am. Chem. Soc.* 62 (1940) 1723.
- [21] Gregg S.J, Sing K.S.W. IUPAC, *coll.sur.chem.* 31 (1972) 578.
- [22] Lecloux A., Pirard J.P., *J. coll. Interface sci.* 70 (1979) 265.
- [23] P. Benito, F.M. Labajos, J. Rocha, V. Rives, *Micropor. Mesopor. Mater.* 94 (2006) 148.
- [24] S. Kühn, J. Schumann, I. Kasatkin, M. Hävecker, R. Schlögl, M. Behrens, *J. Catal. Tod.* 246 (2015) 92.
- [25] J. Perez-Ramirez, G. Mul, J.A. Moulijn, *Vib. Spectrosc.* 27 (2001) 75.

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19 – 21 April 2016

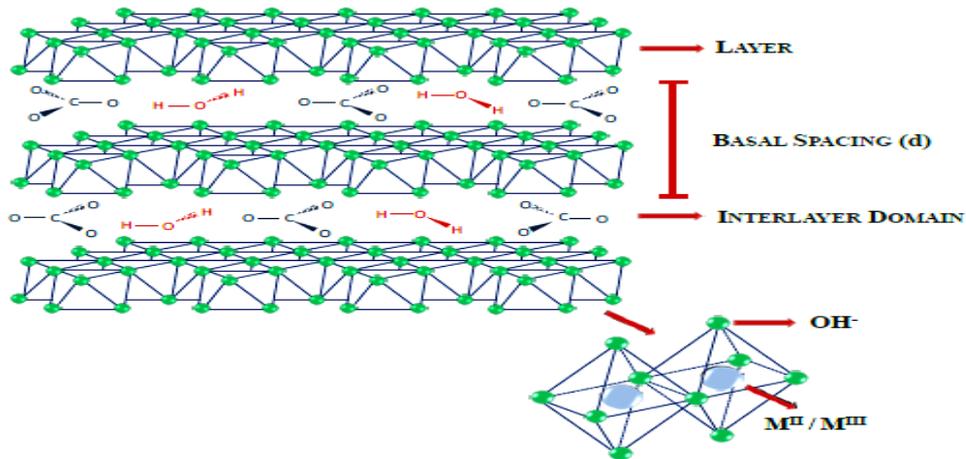


Fig.1. Layered double hydroxide structure

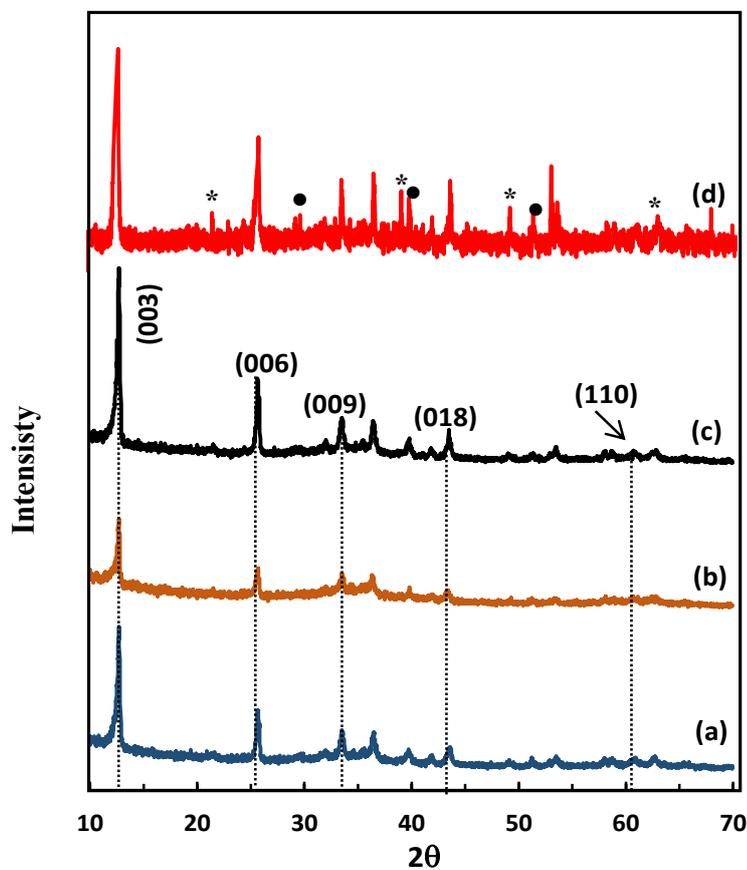


Fig.2. XRD patterns of (a) CoFe , (b) 35%CuCoFe , (c) 60%CuCoFe & (d) 100%CuFe – LDH samples.

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19 – 21 April 2016

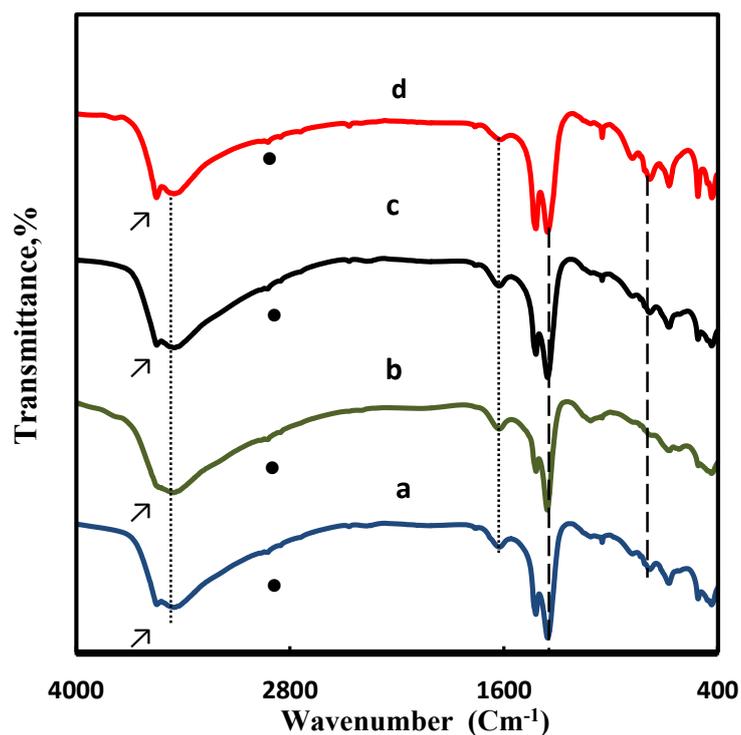


Fig.3. the FT-IR spectra of (a) CoFe, (b) 35%CuCoFe, (c) 60%CuCoFe &(d) 100%CuFe- LDH samples.

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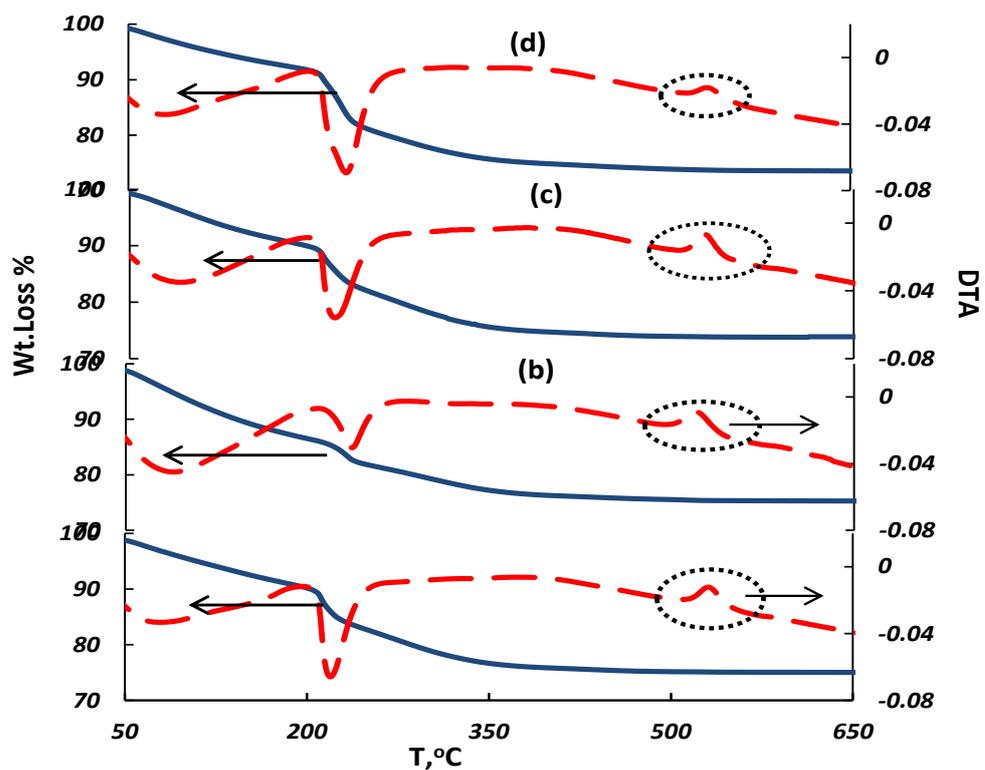


Fig.4. the TGA & DTA profiles of (a) CoFe, (b) 35%CuCoFe, (c) 60%CuCoFe & (d) 100% CuFe-LDHs.

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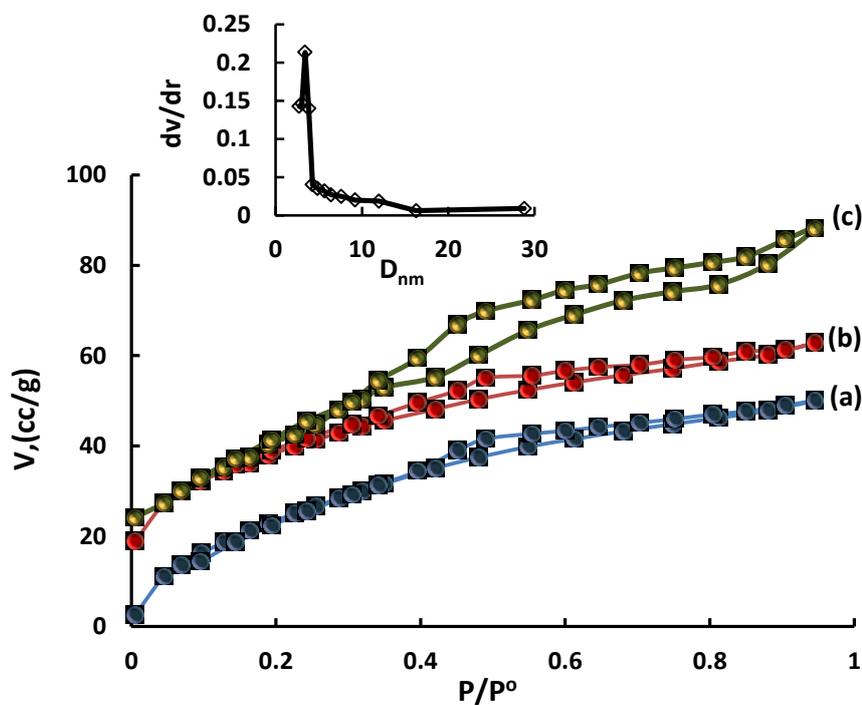


Fig.5. the nitrogen adsorbed- desorbed isotherms and PSD curves of (a) CoFe, (b) 60%CuCoFe & (c) 35% CuCoFe-LDHs.