Nano sized Nickel and Copper Layered Hydrotalcite Catalysts For the Sonochemical Synthesis of Pyrazolo [1,5-a] Pyrimidine Derivative: I. Structural Characterization

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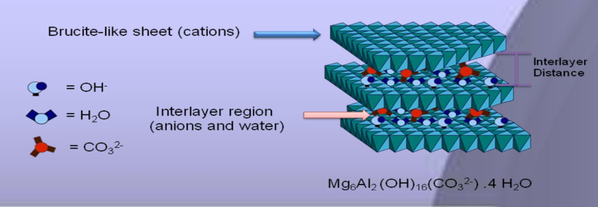
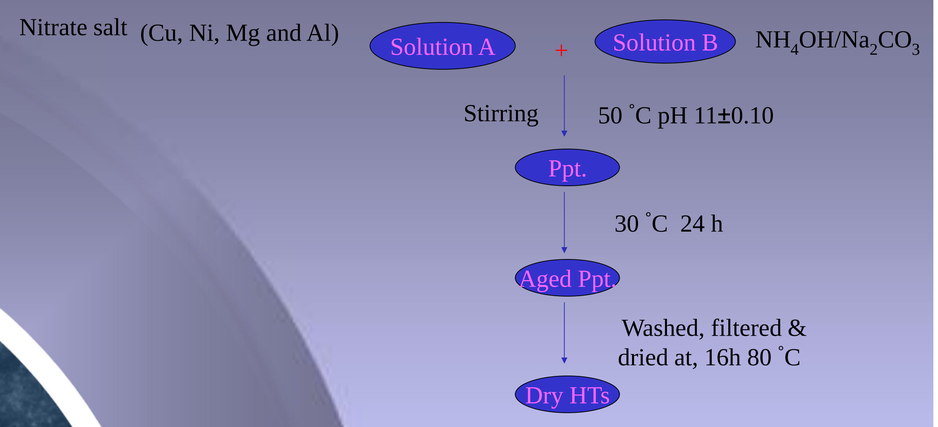
Introduction

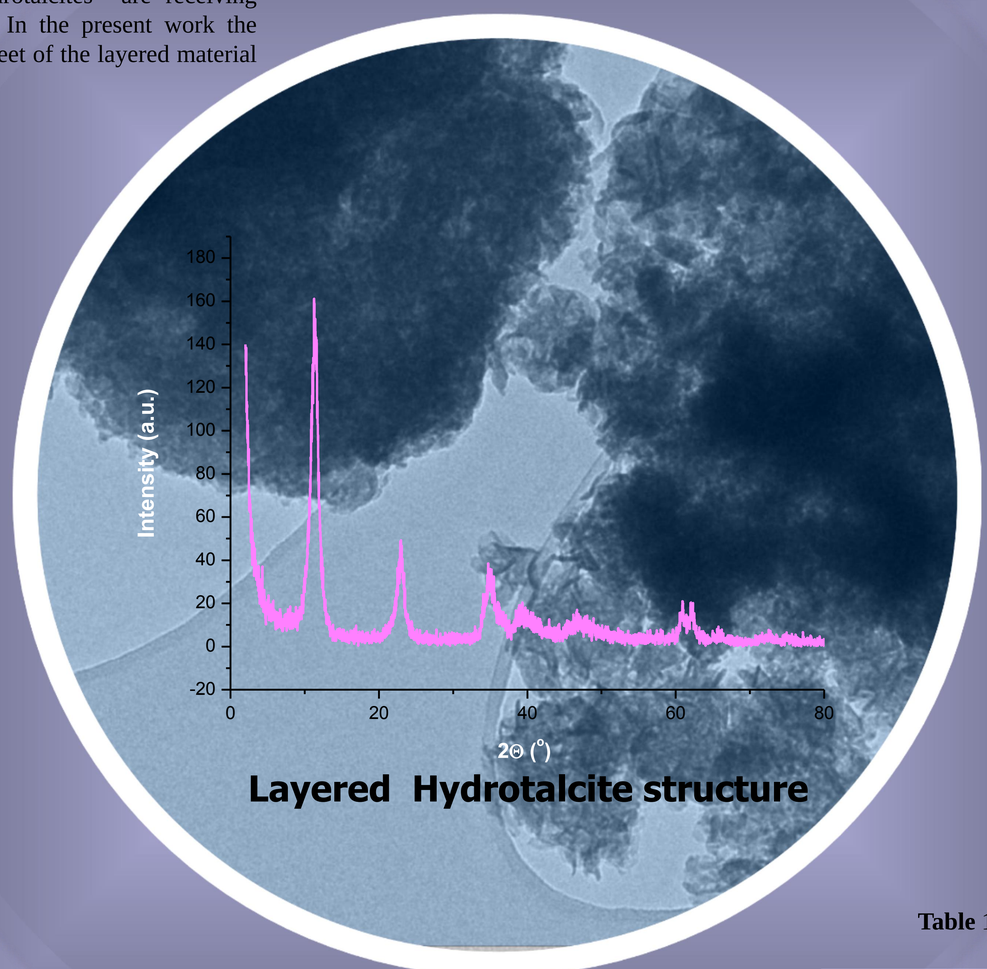
Layered double hydroxides (LDH) are a class of synthetic two dimensional nanostructured anionic clays, containing a positively charged layer and exchangeable anions in the interlayer. The best-known compound in this class of materials is the double hydroxide of Mg with Al, known as hydrotalcite [1]. The general formula for these LDHs is $(M^{2+}_{1-x}M^{3+}_{x}(OH)_2)^{x+}\cdot(A^{n-})_{x/n}.mH_2O$ where M^{2+} and M^{3+} are divalent and trivalent cations, respectively; the value of x is equal to the molar ratio of $M^{3+}/(M^{2+}+M^{3+})$, A is the interlayer anion of valence n. The identities of M^{2+}, M^{3+}, x, and A^{n-} may vary over a wide composition and/or preparation variables, low cost, etc [4]. Transition metal containing hydrotalcites, particularly copper and nickel-containing hydrotalcites are receiving increasing attention owing to their diverse catalytic applications [5-7]. In the present work the isomorphic substitution of Mg^{2+} with Cu^{2+} and Ni^{2+} ions in the cationic sheet of the layered material was studied.



Experimental



Results



XRD

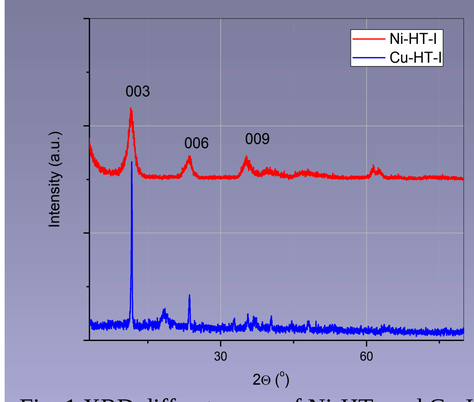


Fig. 1 XRD diffractogram of Ni-HTs and Cu-HTs samples.

XRD diffractograms show the formation of single Ni-hydrotalcite and Cu-hydrotalcite phases. The average crystallite sizes , estimated from Scherrer equation using the FWHM of the basal reflection plane (003), were 9 and 20 nm for Ni-HTs and Cu-HTs, respectively . The term “nanosheets” has been accepted to describe these materials. So, Ni^{2+} and Cu^{2+} were isomorphically substiute Mg^{2+} in the cationic nanosheets.

TGA

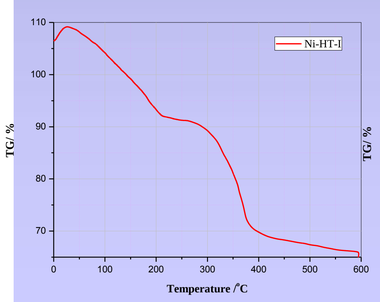


Fig. 2 TGA of Ni-HT-I

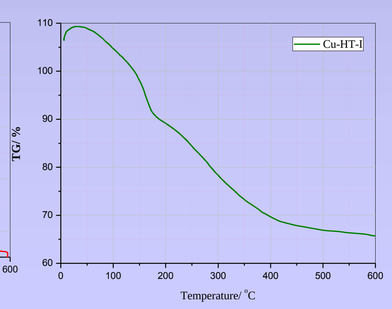


Fig. 3 TGA of Cu-HT-I

TGA of each sample shows two main mass losses, which are associated with two endothermic transitions. The first, at ~200 ºC, amounting to *ca.* 10-15% of total mass, is indicative of removal of interlayer water molecules (dehydration). The second, across a range of 280-420 ºC, amounting of a further *ca.* 10-20% of the total mass, is indicative of further water loss, via the dehdroxylation of the brucite-like sheets, and decomposition of compansating carbonate anions in the interlayer space.

TEM

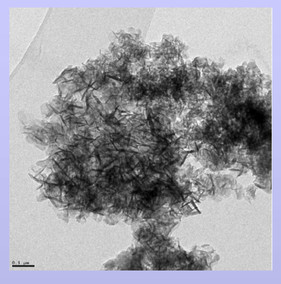


Fig. 4 TEM of Cu-HT-I

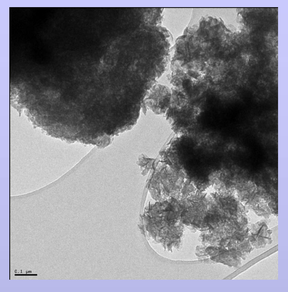


Fig. 5 TEM of Ni-HT-I

TEM images indicate a heterogeneous distribution of Cu^{2+} and Ni^{2+} in the nanosized cationic sheets of the layered HTs.

FTIR

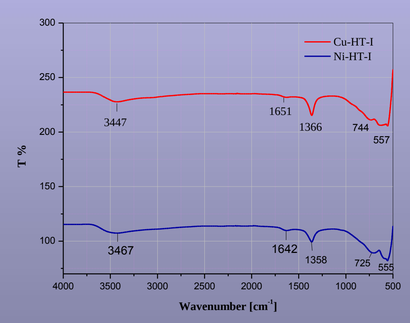


Fig. 6 FTIR spectra of different investigated samples

- The infrared spectra showed a broad peak at about 3447 cm^{-1} was due to ν_{HOH} from the hydroxyl groups of water molecules existing in the interlayer space.
- Bands due to interlayer carbonate are also observed. Thus, the maxima at 1366 cm^{-1} is ascribed to mode ν_3 (anti-symmetric stretching) of carbonate species, which splits because of the lowering symmetry and hydrogen bonding with hydroxyl groups in the interlayer space.
- The peak at 1642 cm^{-1} can be attributed to the bending mode of interlayer water.

Results

Estimating the Chemical Composition

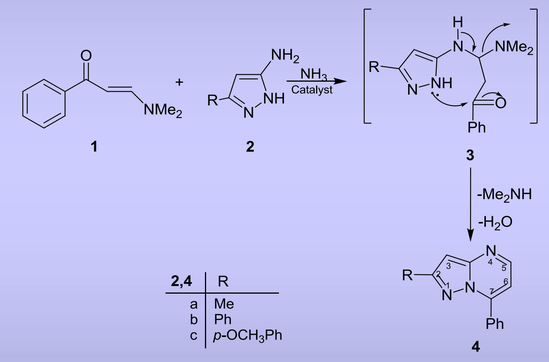
Hydrotalcites and hydrotalcite- like compounds have the basic chemical formula: $M(II)_{1-x}M(III)_x(OH)_2^{x+}(A^{n-}_{x/n}).mH_2O$. Using this basic formula and some simple calculations using the data gained from TGA, ICP and EDX analyses, we have estimated the chemical formulas for the two hydrotalicte samples – see Table 1.

Table 1 chemical formula Hydrotalcite samples using TGA, ICP and EDX measurements

Sample	Composition (EDX)	Composition (ICP)
Ni-HT-I	Mg0.225Ni0.45Al0.225(OH)2(CO3)0.11•0.6H2O	
Cu-HT-I	Mg0.33Cu0.45Al0.22(OH)2(CO3)0.11•0.7H2O	Mg0.345Cu0.11Al0.345(OH)2(CO3)0.17•0.6H2O

Future Outlook

The main goal of the present research work is the use of hydrotalcite catalysts as assisted by sonocation irradiation to prepare the pyrazolo[1,5-a] pyrimidine derivatives. Synthesis , physicochemical, structural and surface properties of hydrotalcite catalysts will cover the first part of this work.The application of the prepared solid base catalysts in the preparation of the Pyrazolo [1,5-a] pyrimidine derivatives is the aim of the second part of the proposed research work.



Scheme 1 Synthesis of Pyrazolo[1,5-a]Pyrimidine derivatives

References

[1] A. Vaccari, Catal. Today., 41, (1998), 53–71.
[2] K. H. Goha, T. T. Lima, Z. Dongb, A review Water Research. 42 (2008) 1343–1368.
[3] D. T. Tran, P. Y. Zavalij, S. R. J. Oliver, J. Am. Chem. Soc. 124, (2002) 3966-3969.
[4] D. G. Cantrell et al, Lisa J. Gillie, Adam F. Lee, Applied Catalysis A. 287 (2005) 183–190.
[5] D. Meloni, R. Monaci, V. Solinas, A. Auroux, E. Dumitriu, Appl. Catal. A:Gen. 350 (2008) 86–95.
[6] V. R. Choudhary ,P. A. Chaudhari,V. S. Narkhede, Catal. Comm.4 (2003) 171–175.
[7] R. Adriana, M. Jobba, M. Laborde, G. Baronetti, N. Amadeo, Catal. Today. 149 (2010) 407–412.