Synthesis, Characterization and Catalytic Properties of Nickel Substituted Copper Ferrospinel nanoparticles

Prabhulkar S.G. and Patil R.M.
Department of Chemistry, the Institute of Science, 15, Madam Cama Road, Mumbai, INDIA

Abstract

The nickel substituted copper ferrite nanoparticles ($Ni_xCu_{1-x}Fe_2O_4$), where x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) were prepared by simple and economic coprecipitation method and characterized by various physicochemical methods such as XRD analysis, IR spectrometry, FEG-SEM and EDS. The XRD analysis showed that all the samples formed have single-phase cubic structure. The FEG-SEM analysis data reveals that the particle size of the compounds lie in the range 13.9 to 31.8nm. The nanoparticles synthesized are useful in the catalytic reactions and are ~100% selective for the acetylation of selected phenols. The catalysts were found to be magnetically separable and reusable without any further treatment. These ferrospinel nanoparticles were found to have better catalytic activity as compared to the corresponding metal oxides. The present nanoparticle catalysts offer high yields in a short reaction time and moderate reaction conditions.

Keywords: Nanoparticles, chemical synthesis, XRD, FEG-SEM, catalytic properties.

Introduction

The metal ferrite spinel compounds of the type AB_2O_4 due to their large expansion coefficient, low saturation magnetic moment and low magnetic transition temperature have been found to be an attracting class of materials[1,2]. The structural, electrical, magnetic and catalytic properties of spinels of the type AB_2O_4 are found to have potential industrial applications[3-5]. Ferrite spinel compounds have been found to be selective and active catalysts[6,7] and are found to sustain over various reaction conditions[5,8]. Spinel ferrites have also found to be the useful materials due to their technical applications such as in magnetic pigments[9], nano devices[10], photoelectric devices[11], sensors[12] and microwave devices[13,14].

Acetylation reactions in organic synthesis are of crucial importance to protect the phenolic hydroxyl group in various organic reactions. Traditionally these reactions are often carried with acid chloride or anhydrides[15-18] as acetyl source in various environmentally hazardous reaction conditions using catalysts such as Lewis acids like $AlCl_3$, BF_3, $TaCl_5$[19,20], inorganic acids[21] and organic bases[22] that leads to the generation of large amount of toxic and corrosive materials as bi-products. The acetylation of phenols and other aromatic compounds is an important reaction in the synthesis of various industrially important organic compounds like fragrances and flavones[23-27], fine chemicals and surfactants[28].

The present work deals with the synthesis and characterization of the nickel substituted copper ferrospinel nanoparticles prepared by simple and economic coprecipitation method and their applications to the catalytic reactions. These nanoparticles were characterized by XRD analysis for their phase determination and crystallinity, IR spectrometry for the metal oxygen bonding, FEG-SEM for size determination and EDS for elemental composition.

Material and Methods

Materials: The analytical reagent grade nickel nitrate [$Ni(NO_3)_2.6H_2O$], copper nitrate [$Cu(NO_3)_2.3H_2O$], ferric nitrate [$Fe(NO_3)_3.9H_2O$], sodium hydroxide [NaOH] and hydrogen peroxide [H_2O_2] 30% (100 volumes); ($\geq$ 99%) were used as starting materials. Double distilled water was used throughout to prepare the solutions of metal nitrates and sodium hydroxide and washings of the filtered products.

Methods: Nanocrystalline powders of $Ni_xCu_{1-x}Fe_2O_4$ were prepared by co-precipitation method[29]. The stoichiometric solutions of the metal salts were prepared and mixed slowly with constant stirring. The pH of the solution was brought to and maintained between 9.0 and 9.5 by using 10% NaOH solution with the help of Equiptronics digital pH meter. The product obtained was digested on a boiling water bath for 3 hours and *in situ* oxidized by 30% (100 volumes) hydrogen peroxide solution. The digested product was further aged overnight, filtered and washed several times with double distilled water and dried in hot air oven at 110°C. The compounds obtained were ground finely in agate mortar and pestle. The samples were investigated for optimization of the reaction temperature on Rigaku TG/DT Analyzer at heating rate of 10ºC min^{-1}. The TG/DTA thermograms showed no weight loss after 600°C and therefore, the present compounds were uniformly sintered in Eurocon automated programmable furnace at 650°C at the heating rate of 4°C for 3 hours to get the crystalline single phase.

The prepared samples have been designated as follows

Sr. No.	Nanoparticle composition	Designation
1	$Cu_{1.0}Ni_{0.0}Fe_2O_4$	CFe
2	$Cu_{0.8}Ni_{0.2}Fe_2O_4$	CNFe–1
3	$Cu_{0.6}Ni_{0.4}Fe_2O_4$	CNFe–2
4	$Cu_{0.4}Ni_{0.6}Fe_2O_4$	CNFe–3
5	$Cu_{0.2}Ni_{0.8}Fe_2O_4$	CNFe–4
6	$Cu_{0.0}Ni_{1.0}Fe_2O_4$	NFe

Instrumental techniques: The prepared materials were characterized on 'Rigaku Miniflex II DESKTOP X-ray DIFFRACTOMETER' (Cu Kα_1 radiation source with λ = 1.5419 Å) for the confirmation of crystallinity of the sintered compounds. Infra-Red spectra of the samples were scanned on Perkin Elmer *precisely* Spectrum-100 FT-IR Spectrometer for confirmation of the metal-oxygen bonds.

The series of $Ni_xCu_{1-x}Fe_2O_4$ particles were coated with Au-Pd plasma coating with the help of JEOL JFC–1600 Auto-fine coater and analyzed for their size determination in JEOL JSM–7600 F Field Emission Gun – Scanning Electron Microscope inbuilt with X-Max 80 mm^2 (Oxford instruments) Energy Dispersive X-ray Analyzer (EDS) for the study of elemental analysis.

Catalytic activity: The nanoparticles were used for their catalytic activity towards some selected phenols like 2-Cresol, 4-Cresol, 1-Naphthol and 2-Naphthol for acetylation reaction with acetyl chloride in the presence of 0.05g of catalyst by refluxing at 80°C for 90 min in water bath. The optimized reaction conditions were obtained by using copper ferrite as a model catalyst. The progress of the reaction was monitored on TLC. After completion of the reactions, the catalysts were separated by magnetic separation and washed initially with warm double distilled water followed by acetone. The reaction products were analyzed by TLC and DATALAB GC 9000 Series (Gas chromatograph) instrument with silica capillary column, FID, column temperature as 120°C for 5 min followed by heating rate 10°C/min up to 220°C, detector temperature 250°C. The products were confirmed by IR and NMR spectral data. The reactions were also carried out in absence of catalysts under optimized reaction conditions.

Results and Discussion

Thermal analysis: The TG curve results of all the samples have shown the weight loss of the samples up to the temperature ~600ºC, after which all the samples evidently shown no further decrease in their weight content. Thus, the calcination temperature for all the compounds was optimized at the 650ºC for all the samples to heat in an Eurocon automated programmable furnace at the rate of 4ºC hour^{-1} for 3 Hrs.

X-Ray diffraction studies: The literature survey reveals that the X-ray diffraction patterns of sintered samples at the temperature of 650ºC are in good agreement for the existence of single-phase cubic spinel structures for all the samples as shown in figure-1 (a) to (f).
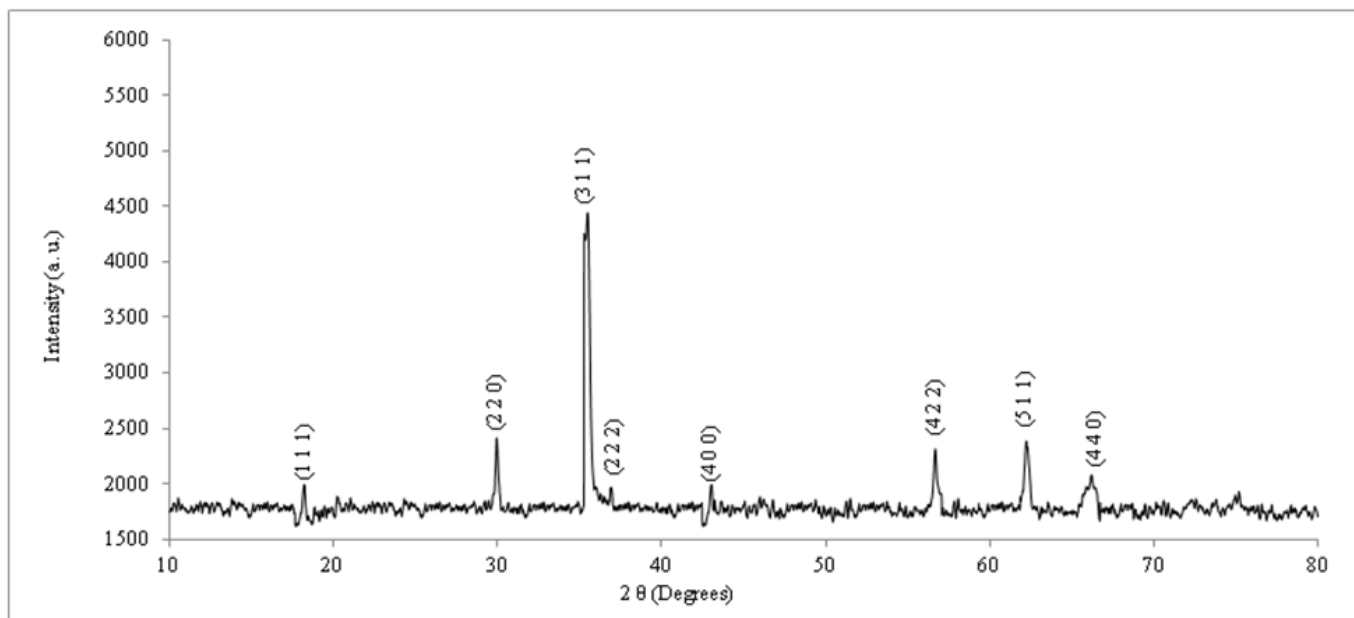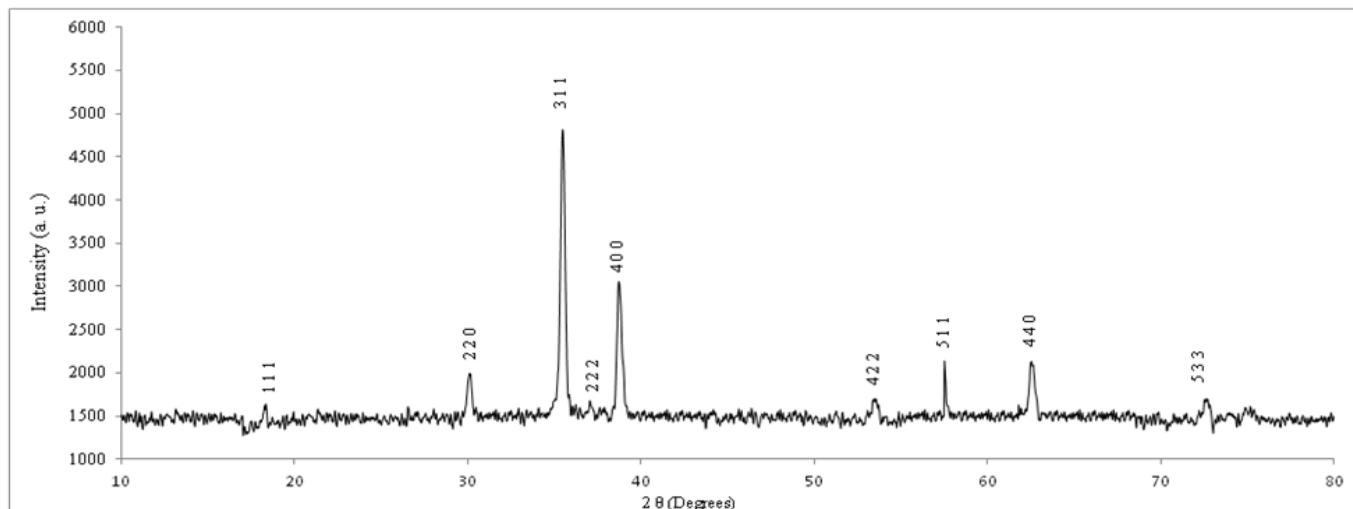

Figure-1(a)
XRD pattern of CFe
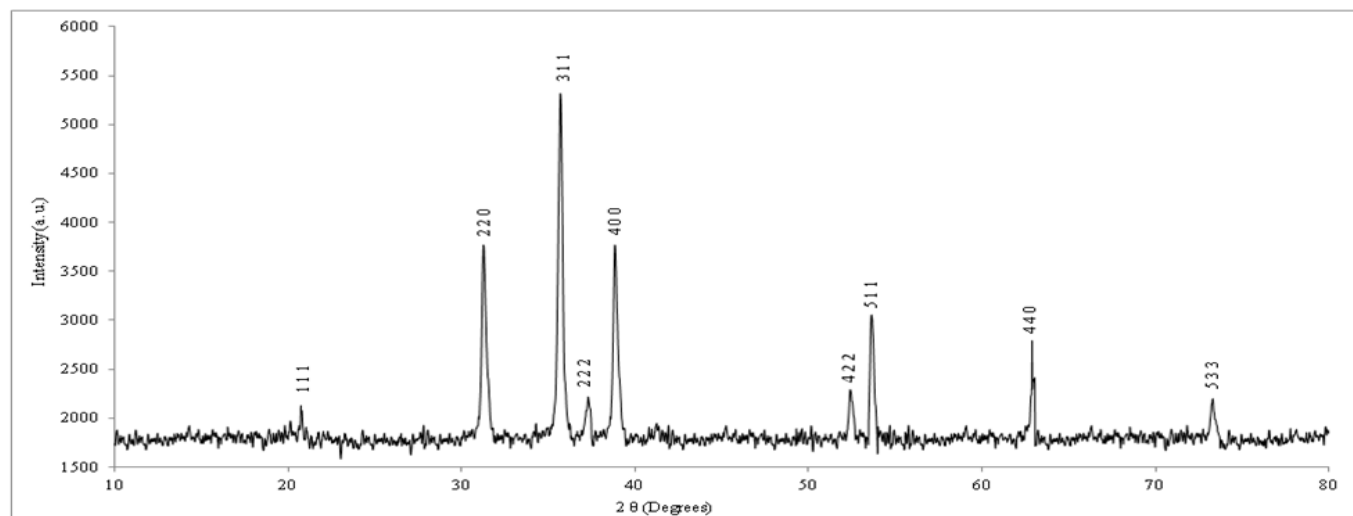
Figure-1(b)
XRD pattern of CNFe-1
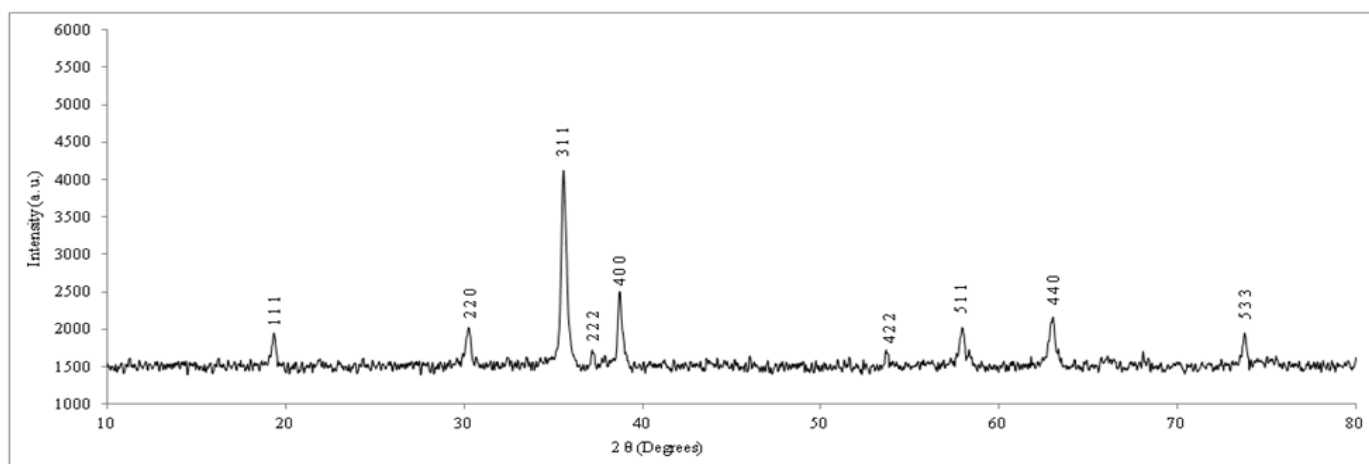

Figure-1(c)
XRD pattern of CNFe-2

Figure-1(d)
XRD pattern of CNFe-3
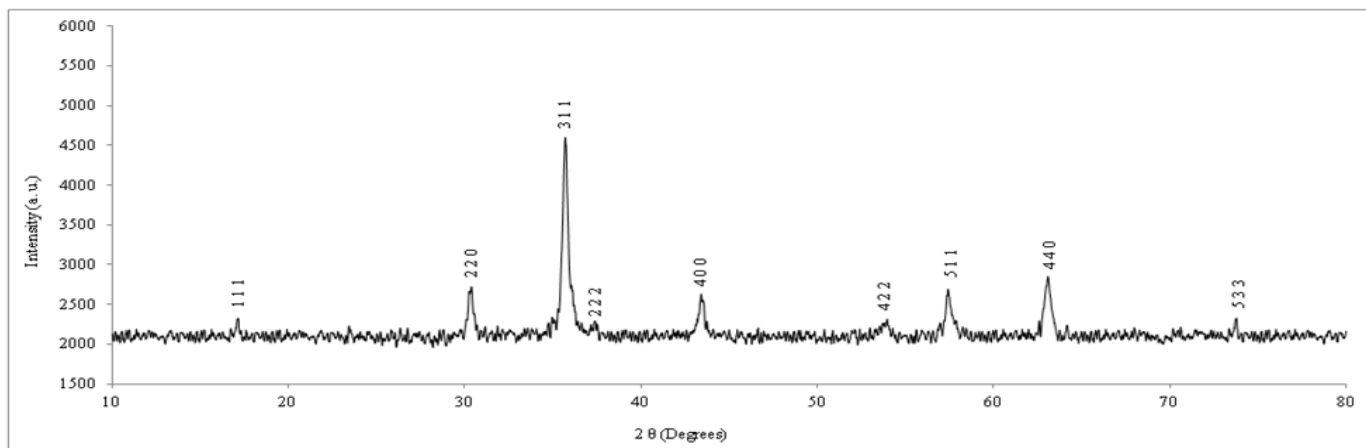
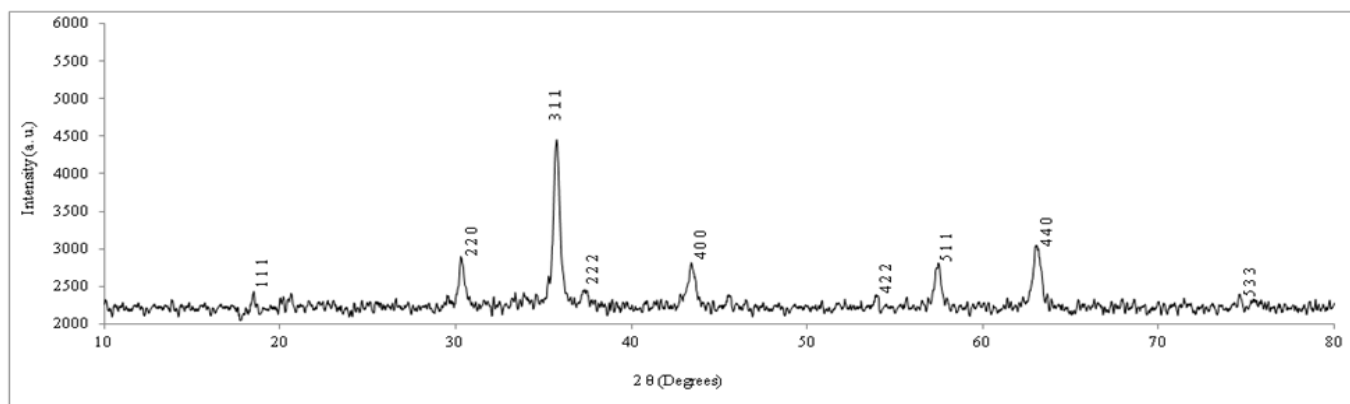**Figure-1(e)**
XRD pattern of CNFe-4

Figure-1(f)
XRD pattern of NFe
Figure-1
X-ray diffraction patterns of the compounds CFe to NFe

Indexing of X-ray diffraction patterns of most intense peaks are given in the table-1 shown below:

Energy Dispersion Spectroscopy and Field Emission Gun – Scanning Electron Microscopy for particle size analysis: The metal content stoichiometry of the compounds used for the preparation of the samples was taken as theoretical composition while the observed stoichiometry was calculated from EDS studies. The theoretical and calculated values of metal content stoichiometry are in good agreement with the chemical composition shown in table 2.

FT-IR studies: The FT-IR spectra of the samples in KBr powder were scanned. The vibrational frequencies depend upon the cation mass, cation-oxygen bond length and the bond strength. The values of vibrational frequencies for tetrahedral (v_1), octahedral sites (v_2) and differences ($v_1 - v_2$) are given in the table 3.

Table-1
Indexing of the X-ray diffraction patterns of peaks with $I/I_0 = 100$ %

Sr. No.	Sample	2θ Values	Intensity	d- Value
1	CFe	35.500°	4439	2.5266
2	CNFe – 1	35.480°	4816	2.5280
3	CNFe – 2	35.720°	5284	2.5116
4	CNFe – 3	35.560°	4131	2.5225
5	CNFe – 4	35.700°	4600	2.5129
6	NFe	35.740°	4462	2.5102

Table-2
Elemental composition by EDS and particle size of the nanoparticles from FEG-SEM

Sample	Atom percentage (Theoretical)				Atom percentage by EDS				Particle size (nm)
	Cu	Ni	Fe	O	Cu	Ni	Fe	O	
CFe	26.56	00.00	46.69	26.75	25.95	00.00	47.26	26.79	21.1
CNFe–1	21.34	04.93	46.88	26.85	21.02	05.00	47.31	26.67	31.8
CNFe–2	16.07	09.89	47.07	26.97	16.18	09.78	47.09	26.95	28.8
CNFe–3	10.76	14.90	47.26	27.08	10.96	14.83	47.01	27.20	18.9
CNFe–4	05.40	19.95	47.46	27.19	05.51	19.91	47.45	27.13	13.9
NFe	00.00	25.04	47.65	27.31	00.00	24.95	47.77	27.28	17.8

Table-3
**Values of vibrational frequencies for tetrahedral (v_1), octahedral sites (v_2)**

Sr. No.	Nanoparticle	v_1 cm^{-1} (Td)	v_2 cm^{-1} (Oh)	v_1 - v_2 cm^{-1}
1	CFe	596	413	183
2	CNFe–1	598	414	184
3	CNFe–2	604	419	185
4	CNFe–3	618	420	198
5	CNFe–4	623	423	200
6	NFe	629	425	204

The bands at higher and lower wavelength regions are assigned by Yu'eva et. al.[30] to the vibrations of tetrahedral metal-oxygen bond (Fe-O) and octahedral metal-oxygen bond (Fe-O, Ni-O and Cu-O) respectively. A comparison of the observed vibrational frequencies of all the compositions indicates that the v_1(corresponding to tetrahedral unit) remains almost unmodified with increasing Ni^{2+} content. However, v_2(corresponding to octahedral unit) is observed to increase smoothly with increase in Ni^{2+} content. The increase in vibrational frequency (v_2) with Ni^{2+} content can be attributed to the increasing force constant and shortening of M-O bonds of the octahedral unit. The Ni^{2+} preferably enters the octahedral site increasing the force constant of Ni-O bond. This is also reflected in the v_1 - v_2 difference which decreases with increase in Ni^{2+} substitution.

Size of the particles: The results of particle size for the series $Ni_xCu_{1-x}Fe_2O_4$ in JEOL JSM – 7600 F Field Emission Gun – Scanning Electron Microscope inbuilt with X-Max 80 mm^2 (Oxford instruments) Energy Dispersive X-ray Analyzer (EDS) are in the range of 13.9 to 31.8 nm can be termed as 'Nanoparticles' throughout[31]. FEG-SEM images and the histogram showing the size of the prepared nanoparticles are shown in figure-2 and 3 respectively.

Catalytic performance: The materials thus characterized for structure, composition and particle sizes were then used as catalysts to evaluate their catalytic efficiency. The reaction of 4-Cresol with acetyl chloride was used as the model reaction as the catalytic results obtained were in good yield of the corresponding 4-cresyl acetate. The results indicated that the yield of 4-cresyl acetate with CuO (40%), NiO (48%) and Fe_2O_3 (56%) while the reaction without catalyst have low yield below 50%. The effects of time, temperature, solvents, 4-Cresol:acetyl

chloride mole ratio and selectivity over other catalysts have been successively carried out.
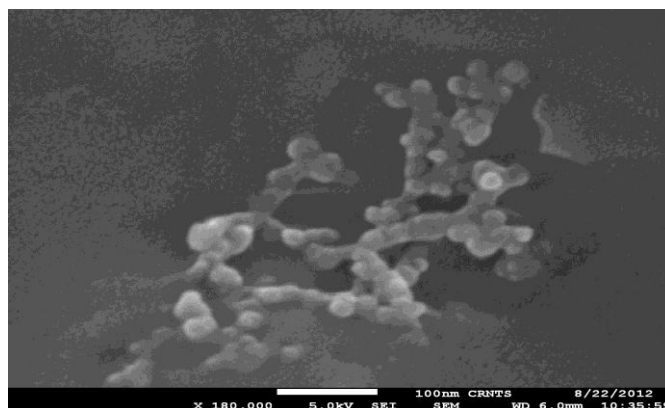
Figure-2(a)
FEG-SEM image of CFe
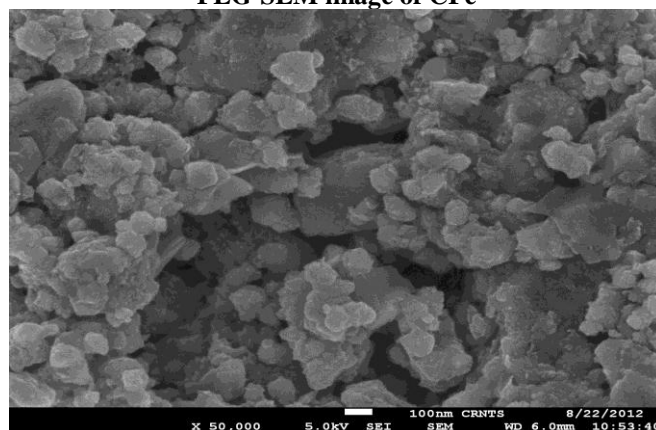
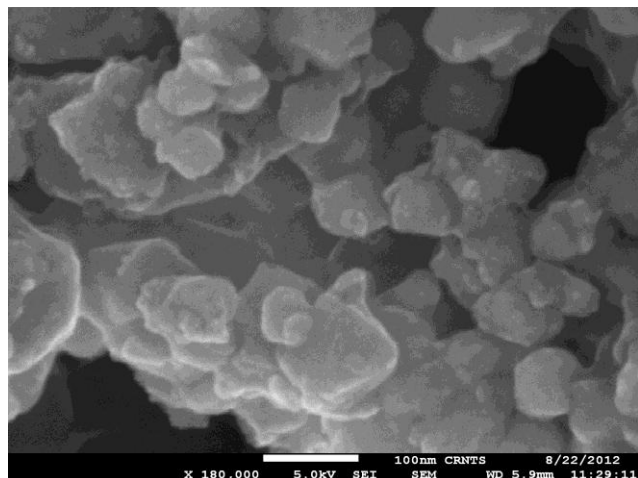**Figure-2(b)**
FEG-SEM image of CNFe-1
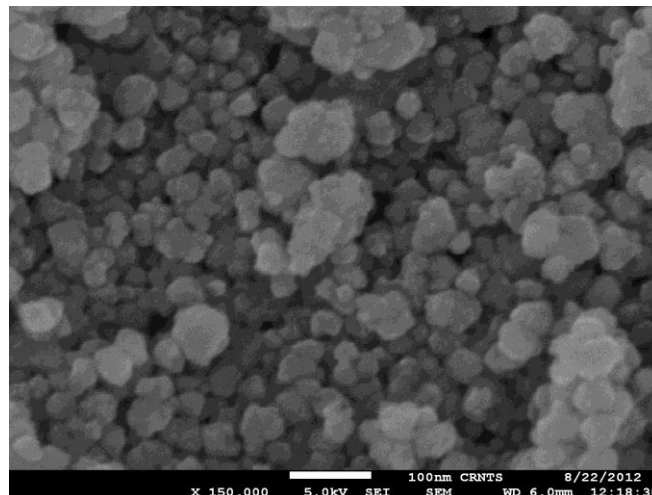
Figure-2(c)
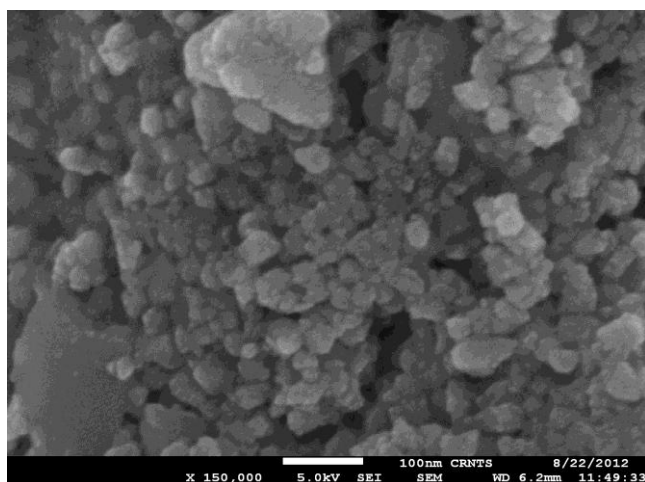**FEG-SEM image of CNFe-2**

Figure-2(f)
FEG-SEM image of NFe
Figure-2
**Field Emission Gun–Scanning Electron Microscopic images
of the compounds CFe to NFe**
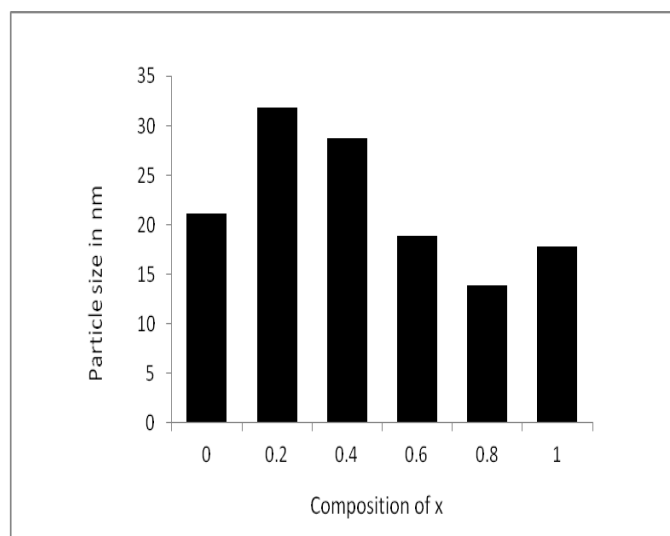

Figure-2(d)
FEG-SEM image of CNFe-3

Figure-3
**Histogram of the size of the nanoparticles of the system
$Ni_xCu_{1-x}Fe_2O_4$**

The effect of contact time was studied with 0.05 g of catalyst and it was observed that 90 min contact time gives maximum yield (96.8 %) of the product. There was no change in % yield of the product, above 90 min. The effect of amount of catalyst was also studied to optimize the reaction conditions. The results show the maximum conversion was obtained by 0.05 g of catalyst. Hence, reaction time of 90 min and 0.05 g of catalyst was fixed for further studies.

Catalyst selectivity: The variable compositions of the system $Ni_xCu_{1-x}Fe_2O_4$ was tested under optimized reaction conditions (0.05 g of catalyst by refluxing at 80°C for 90 min in water

Figure-2(e)
FEG-SEM image of CNFe-4

bath) for the acetylation of 4-cresol. The 4-cresyl acetate yields obtained were varying in the range 55.8 % to 96.8 % for different compositions. The $Cu_{0.2}Ni_{0.8}Fe_2O_4$ system gave maximum yield of the product with better selectivity among the various compositions. The smaller particle size of $Cu_{0.2}Ni_{0.8}Fe_2O_4$ is an effective parameter to give maximum yield of the product. The results obtained are tabulated in table 4. Thus, the $Cu_{0.2}Ni_{0.8}Fe_2O_4$ catalyst was used as model catalyst for further acetylation reactions and it gives maximum yield with 4-cresol among the other phenols under study the results of which are tabulated in table 5.

Table-4
The formation of 4-Cresyl acetate by the reaction of 4-Cresol and acetyl chloride over different compositions of the nanoparticles of the $Ni_xCu_{1-x}Fe_2O_4$ system

Nanoparticles used	Percentage Yield
CFe	78.1
CNFe–1	55.8
CNFe–2	65.3
CNFe–3	88.7
CNFe–4	96.8
NFe	89.2

Table-5
Acetylation of selected phenols with selected catalyst $Cu_{0.2}Ni_{0.8}Fe_2O_4$

Reactant	Product	Yield of the product
2-Cresol	2-Cresyl acetate	95.3 %
4-Cresol	4-Cresyl acetate	96.8 %
1-Naphthol	1-Naphthyl acetate	93.2 %
2-Naphthol	2-Naphthyl acetate	94.3 %

Reaction Mechanism: In the proposed mechanism, an acetylation reaction takes place through the formation of complex between acetyl chloride and catalyst. The coordination complex is formed between acidic center of catalyst and oxygen of acetyl chloride. The complex further interacts with oxygen of phenol and forms an intermediate, thereby releasing the chloride ion. The intermediate undergoes rearrangement resulting in the formation of acetylated product. The probable reaction mechanism is shown in figure 4.

Catalyst reusability: The catalyst was separated from the reaction by magnetic separation as shown in its photograph in figure-5, washed with hot double distilled water followed by acetone. The catalyst was annealed at 110^oC and reused. It is observed that, per cent yield decreased with increase in number of cycles of the catalyst indicating slight decrease in catalytic activity. These results are tabulated in table 6.
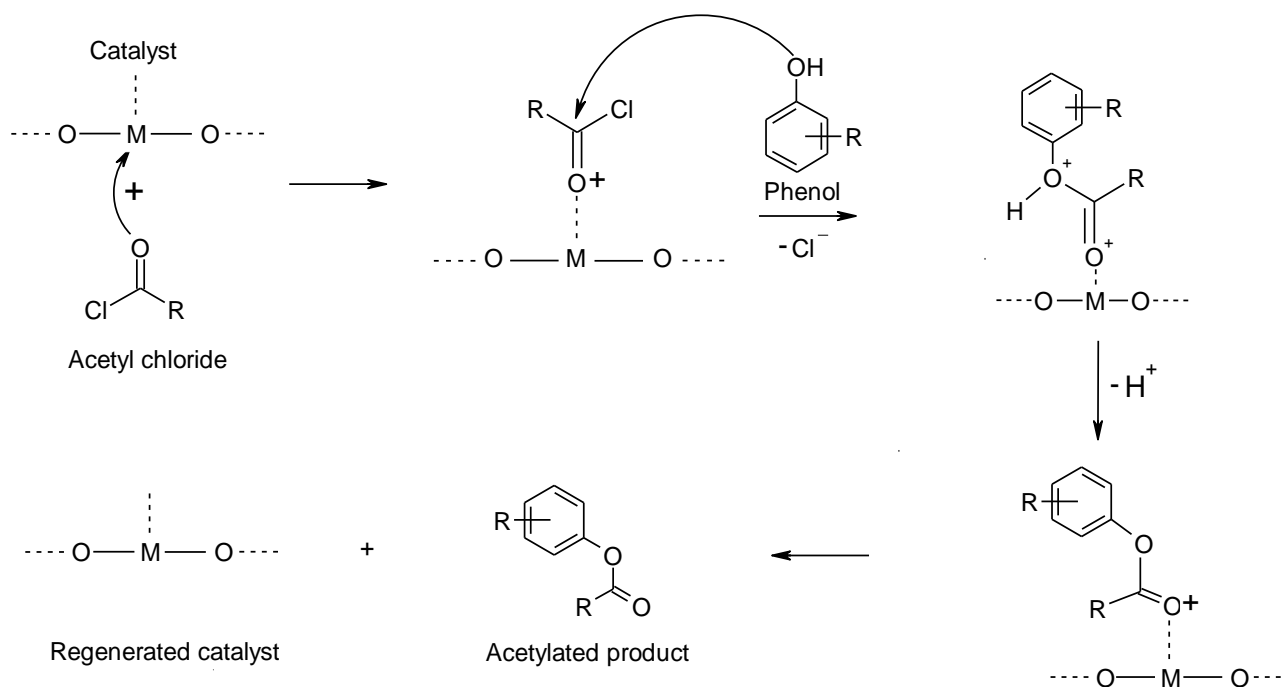
Figure-4
Probable catalytic reaction mechanism for acetylation of phenols

Figure-5
Catalyst nanoparticles in reaction (left) and its separation by simple magnet (right)

Table-6
Number of cycles of $Cu_{0.2}Ni_{0.8}Fe_2O_4$ catalyst with 4-cresol

Sr. No	Number of cycles	Percentage Yield
1	0	96.8
2	1	96.3
3	2	95.8
4	3	95.4
5	4	95.1
6	5	94.7

Conclusion

From the results obtained we conclude that nickel substituted copper ferrospinel nanoparticle catalysts obtained by the safest, economic, convenient and eco-friendly coprecipitation method provides a widely acceptable synthesis technique. These nanoparticles, favor the acetylation of 2- and 4- cresols and 1- and 2- naphthols with acetyl chloride. Nickel substituted ferrites $Cu_{0.2}Ni_{0.8}Fe_2O_4$ nanoparticles show better activity among all the compounds investigated. The product 4-cresyl acetate is obtained with more selectivity than all other acetylation products. This study reveals that the prepared nickel substituted copper ferrospinel nanoparticles $Cu_{0.2}Ni_{0.8}Fe_2O_4$ are the convenient eco-friendly substitutes over the hazardous stoichiometric reagents and thus are highly recommended to be used in synthetic chemical industries.

References

1. Xu Q., Wei Y., Liu Y., Ji X., Yang L. and Gu M., *Solid State Sci.,* **11(2)**, 4/2-4/8 **(2009)**

2. Iian M.B., *Magnetic Material Beijng*, I Singhua University Press, **(2001)**

3. Blasse G., *Philips Res. Rep*. Suppl., **3,** 96 **(1964)**

4. O'Keefe M., *J. Phys. Chem. Solids,* **(1961)**

5. Ghorpade S.P., Darshane V.S. and Dixit S.G., *Appl. Catal. A: Gen.,* **166,** 135 **(1998)**

6. Narsimhan C.S. and Swamy C.S., *Appl. Catal.,* **2,** 315 **(1982)**

7. Sloczynski J., Janas J., Machej I., Rynkowski J. and Stoch J., *Appl. Catal B,* **24(1)**, 45 **(2000)**

8. Lee H., Jung J., Kim H., Chung Y., Kim T.J., Lee S.J., Oh S., Kim Y.S., Song L.K., *Catal. Lett.,* **122,** 281 **(2008)**

9. Wang X., Yang G., Zhang Z., Yan L. and Meng J., *Dyes Pigm.,* **74 (2)**, 269 **(2007)**

10. Ajayan P.M., Redlich P. and Ru"hle M., *J. Micro,* **185 (2)**, 2/5-282 **(1997)**

11. Hu J., Li L-s, Yang W., Manna L. and Wang L-w, Alvisatos A.P., *Science,* **292 (5524),** 2060 **(2001)**

12. Pena M.A. and Pierro J.L.G., *Chem. Rev.,* **101(7),** 1981 **(2001)**

13. Baykal A., Kasapoglun, Durmus Z., Kalvas H., Ioprak M.S. and Koseogla Y., *Iurk J. chem.,* **33,** 33 **(2009)**

14. Gunjakar J.L., More A.M., Gurav K.V. and Lokhande C.D., *Appl. Surf. Sci.,* **254(18),** 5844 **(2008)**

15. Vedejs E., Bennets N.S., Conn L.M., Diver S.T., Gingras M., Lin S., Oliver P.A. and Peterson M. J., *J. Org. Chem.,* **58,** 7286 **(1993)**

16. Sano T., Ohashi K. and Oriyama T., *Synthesis,* 1141 **(1999)**

17. D'Sa B.A. and Verkade J.G., *J. Org. Chem.,* **61,** 5702 **(1996)**

18. Vedejs E. and Daugulis O., *J. Org. Chem.,* **61,** 2963 **(1996)**

19. Olah G.A., *Friedel-Craft's and Related Reactions,* **Vol. III**, Interscience Publishers, New York, 1606 **(1964)**

20. Lee S. and Park J.H., *J. Mol. Catal. A: Chem.,* **194,** 49 **(2003)**

21. Spagnol M., Gilbert L., Alby D., Desmurs J.R. and Rattoy S. (Eds.), *The Roots of Organic Development,* Elsevier, Amsterdam, 29 **(1996)**

22. Li C., Liu W. and Zhao Z., *Catal. Commun.,* **8,** 1834 **(2007)**

23. Tamaddon F., Ali Amrollahi M. and Sharafat L., *Tetrahedron Lett.,* **46,** 7481 **(2005)**

24. Ghosh R.B., Maiti S. and Chakraborty A., *Tetrahedron Lett.,* **46,** 147 **(2005)**

25. Zhdanov R.I. and Zhenadavora S.R., *Synthesis,* 222 **(1975)**

26. Green T.W. and Wutz P.G.M., *Protective Groups in Organic Synthesis,* second edn., Wiley, New York, **(1991)**

27. Bauer K., Garbe D. and Sturburg H., *Commmon Fragrance and Flavor Materials: Preparation and Uses,* fourth edn., Wiley – VCH, **(2001)**

28. Choudhary B.M., Lakshmi Kantam M., Neerja V. and Bandyophadhyay T., Reddy P.N., *J. Mol. Catal. A: Chem.,* **140,** 25 **(1999)**

29. Dube G.R. and Darshane V.S., *Bull. Chem. Soc. Jpn.,* **64,** 2449 **(1991)**

30. Yur'eva T.M., Boreskov G.K., Zharkov V.I., Karakchivev L.G., Popovski V.V. and Chigrina V.A., *Kinet. Katal.,* **9** 1063 **(1968)**

31. Poole Charles P. and Owens F.J. Jr., *Introduction to Nanotechnology,* John Wiley and Sons, **(2003)**