Global Journal of Science Frontier Research
Chemistry
Volume 13 Issue 7 Version 1.0 Year 2013
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals Inc. (USA)
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

Methylation of Aniline over Mn-Cu Ferrites Catalysts

By Rajeev Dixit, P Gupta, Samidha Saxena & Reena Dwivedi

Devi Ahilya University, Indore

Abstract- The structural and catalytic properties of the mixed spinel ferrite system $Mn_{1-x}Cu_xFe_2O_4$ (x=0, 0.25, 0.5,0.75, 1.0) have been investigated by X-Ray diffraction, Mössbauer and catalytic activity measurements. The variation of lattice parameter, crystallite size, and Mössbauer parameters of the product formed with the variation in the concentration of Cu has been studied. XRD Study revealed the formation of phase pure spinels with FCC cubic structure with particle size ranging from 5.21 nm to 20 nm. Lattice constant values showed constant decrease with increasing concentration. Mössbauer spectra showed the presence of Fe^{3+} at both octahedral and tetrahedral sites. These ferrites were used as catalysts in the alkylation of Aniline. A maximum conversion of 80.5 % of aniline with selectivity of 98.6 % towards N-methylaniline (NMA) has been obtained at a temperature 673 K, Methanol : Aniline molar ratio of 5:1 and weight hour space velocity (WHSV) of 0.2 h-1. It was found that the yield is maximum for $CuFe_2O_4$. The result is supported by acidity measurements.

Keywords: mn-cu ferrites; ferrospinel; methylation; aniline; cubic structure.

GJSFR-B Classification : FOR Code: 030601

METHYLATION OF ANILINE OVER MN-CU FERRITES CATALYSTS

Strictly as per the compliance and regulations of :

Methylation of Aniline over Mn-Cu Ferrites Catalysts

Rajeev Dixit [α], P Gupta [σ], Samidha Saxena [ρ] & Reena Dwivedi [ω]

Abstract- The structural and catalytic properties of the mixed spinel ferrite system $Mn_{1-x}Cu_xFe_2O_4$ (x=0, 0.25, 0.5,0.75, 1.0) have been investigated by X-Ray diffraction, Mössbauer and catalytic activity measurements. The variation of lattice parameter, crystallite size, and Mössbauer parameters of the product formed with the variation in the concentration of Cu has been studied. XRD Study revealed the formation of phase pure spinels with FCC cubic structure with particle size ranging from 5.21 nm to 20 nm. Lattice constant values showed constant decrease with increasing concentration. Mössbauer spectra showed the presence of Fe^{3+} at both octahedral and tetrahedral sites. These ferrites were used as catalysts in the alkylation of Aniline. A maximum conversion of 80.5 % of aniline with selectivity of 98.6 % towards N-methylaniline (NMA) has been obtained at a temperature 673 K, Methanol : Aniline molar ratio of 5:1 and weight hour space velocity (WHSV) of 0.2 h-1. It was found that the yield is maximum for $CuFe_2O_4$. The result is supported by acidity measurements.

Keywords: mn-cu ferrites; ferrospinel; methylation; aniline; cubic structure.

I. INTRODUCTION

Alkyl anilines are valuable intermediates for the manufacture of pharmaceuticals, drugs, dyes and agrochemicals. These compounds may be prepared by catalytic alkylation of aniline with various alkylating reagents: There are reports on alkylation of aniline in liquid phase under pressure[1], in vapour phase using oxides[2], Raney-Nickel[3], zeolites[4], AEL type molecular sieves[5], clays[6-10] and few spinels[11-14].

The unusual properties exhibited by nanoparticle and their promising technological applications have attracted much interest in recent years. [15]. There particles are shown to posses low saturation magnetization, Ms, enhance coercivity, H_c, and higher curie temperature, T_c, as compared to bulk materials, [16-21]. This phenomenon have been ascribed to random canting of surface spins [22], pinning of spins at particles surface or presence of a dead layer around magnetic core materials [23] and interparticle interactions [24]. It has been shown that certain ferrites with nanosized particles, posses metastable state and the cation distribution is different from that of bulk ferrites, where divalent metal occupies only tetrahedral, A, site and Fe^{+3} occupies only octahedral, B, site. In addition to these physical effects, nanoparticle ferrites are found to be excellent catalyst of alkylation and cyclization reactions with very high conversion and selectivity. The high performances of ferrite cata1yst have been attributed to cations distribution of different particles size, lattice parameters and acido-basic characters of ferrite catalyst. To the best of our know1edge, there is no report on the methylation of aniline over copper-manganese ferrites (Cu-Mn ferrite). The present problem of the methylation of aniline over Cu-Mn ferrites was there fore undertaken with a view to optimize the Cu-Mn-Fe composition and process conditions over the catalyst for maximum conversion of aniline. Besides these, catalysts have been characterized by XRD and Mössbauer spectroscopy, BET surface area and acidity measurements. The cation distribution obtained from Mössbauer study has been used to explain acidity and cata1ytic activity of the catalysts.

II. EXPERIMENTAL

a) Preparation of the Sample

Nanoparticle of $Cu_{1-x}Mn_x\ Fe_2O_4$ (x = 0, 0.25, 0.5, 0.75, 1.0) were prepared by co- precipitation method. Required quantities of $MnCl_2$, Fe $(NO_3)_3.9H_2O$ and $Cu(NO)_3.3H_2O$ were dissolved in excess of distilled water. The pH of the solution was adjusted to 9 with dilute solution of NaOH. Excess of water fast stirring and slow addition of NaOH solution are must for getting small size particles. The resulting mixture was heated at a temperature of 333 K along with stirring for one hour. Then, it was kept for settling in the heating mode at 333 K for half an hour for digestion. The product was washed by repeated decantation with 1.5 dm^3 portions of water until the supernatant is free of Cl^- (about 10-15 washings was required). The precipitate was filtered through Buchner funnel, dried in oven at 393 K and calcined at 673 K. The material was sieved through a 6/10 mesh sieve. After sieving the bigger size clusters were kept for acidity and catalytic activity evaluation while smaller size clusters obtained after sieving, were ground into fine powders and were used fur XRD and Mössbauer experiment.

b) Characterization of Samples

X-Ray diffraction pattern were recorded using Cu - K_α radiation (angle range 20° to 65°) as the source

---

Authors α ρ ω : Catalysis and Nanomaterials Research Laboratory School of Chemical Sciences, Devi Ahilya University, Indore.
Author σ : IPS Academy, Indore. e-mail: rajeevdixit08@gmail.com

on a Rigaku X-Ray diffractometer. Diffraction patterns show the sharp lines corresponding to single-phase spinel for the samples as the entire peaks match well with the characteristic reflections of the corresponding ferrite. The average particle size was measured by broadening of the (311) peak and applying Debye - Scherer equation. Lattice cell parameters were also calculated using Bragg's equation.

c) *Mössbauer Measurements*

Samples were crushed to obtain fine powder in order to observe Mössbauer spectra. The Mössbauer absorber was prepared by spreading the paste of powdered sample and vacuum grease over perplex glass that is used as the sample holder. The absorption spectra were recorded in transmission geometry at room temperature with constant acceleration Mössbauer drive along with a 256 multichannel analyzer, using Austin Science Inc, USA Mössbauer. A single line source $^{57}Fe(Rh)$ with initial activity of 10 mCi was used. Several runs were taken in order to check the reproducibility of the spectra. Total counts collected were about 10^6 or more. The Mössbauer spectrometer was calibrated using a 0.001 inch enriched α-Fe foil. The outer lines are separated through 10.68 mm/s. This is an excellent agreement with an ideal absorption spectrum and calibration was done accordingly. The experimental data were computer fitted using the least square-fitting program assuming Lorentzian line shape with χ^2 minimization technique. The solid line through the data points is the result of the computer fit of the data.

d) *Acidity Measurement*

Acidity measurement were performed by ammonia desorption method. This experiment was carried out in order to measure the acidity of the ferrite catalyst using ammonia as an adsorbate. 1 g of the catalyst was packed in between two plugs of glass wool in a Pyrex tube down flow fixed bed reactor and heated to 773 K under a nitrogen gas flow rate of 0.5 cm^3/s for 1.5 hour. The reactor wag coo1ed to room temperature and adsorption was conducted at this temperature during which the sample was exposed to ammonia for 1.5 hours. In order to remove physically adsorbed ammonia from the purged sample again nitrogen gas was allowed to pass through it at the rate of 0.5 $cm^3\ h^{-1}$as the same rate at 353 K for 1 hour. The acid strength distribution was obtained raising the catalyst temperature from 353 K -773 K during the flow of nitrogen gas and absorbing the evolved ammonia in distilled water containing phenolphthalein as an indicator. Titrating the water solution with standard 0.1 M HCl solution in different temperature ranges lead to quantitative estimation.

e) *Catalytic Activity*

The alkylation unit consists of three parts i.e. feed system, reactor and product recovery unit. The reactor was charged with a known weight (5g) of catalyst and was clamped in the assembly holder. The tubular heater was also clamped in the stand. The reactor was then joined to the product recovery unit and syringe pump filled with known volume of reactant mixture. The catalyst was activated at 773 K by passing air and then brought down to desired temperature by cooling down in the current of N_2. The mixture of reactant was fed by a 10 ml syringe pump. The liquid product was condensed with the help of cold-water condenser, a cold trap and was analyzed by shimadzu gas chromatography using SE-30 column and FID detector.

III. RESULTS AND DISCUSSION

a) *XRD analysis*

XRD patterns shown in Fig 3.1 reveals the formation of spinel phase of ferrite as all the composition showed the characteristic reflection of the spine1 phase. All the peaks of $MnFe_2O_4$ and $CuFe_2O_4$ matched well with those as reported for the same in JCPDS Card No.10-319; 3-864. The reflections at the planes (111), (220), (311), (222), (400), (422), (511), (440) can be detected with d values of 4.89, 2.97, 2.53, 2.42, 2.08, 1.71, 1.61, 1.49 respectively. Accordingly the lattice cell parameters were also calculated that matched well with the values as reported in the JCPDS card numbers given above. Lattice cell parameter shows a linear decrease from 8.49 A^0 to 8.39 A^0 with the introduction of Cu in $MnFe_2O_4$ as could be seen clearly from the fig 3.2 and may be attributed to the replacement of Mn^{2+} (0.80 A) by smaller Cu^{+2} (0.69 A). This also confirms the formation of solid solution. The mean crystallite size was calculated by broadening of the (311) diffraction peak and applying Scherer formula and the range is in between 7.2 nm - 20 nm. Surface area was also estimated from the crystallite size data assuming the crystallites to be of spherical shapes. They depend on the size of the particle as is clear from the reported values in Table 3.1. The average particle size and lattice cell parameter for the above mixed ferrite nanoparticles are also reported in Table 1.

b) *Mössbauer*

Mössbauer absorption spectra for the samp1es i.e. x = 0, 0.5, 1.0 were recorded at room temperature as shown in Fig. 3. The spectra were fitted using NORMOS fitting program and hyperfine parameters e.g. isomer shift δ, quadrupole splitting, Δ, line width, Γ, and hyperfine field, H_{int}, thus obtained are listed in Table 3.2. The Mössbauer spectra exhibit broad magnetic hyperfine sp1it sextets. In case of $MnFe_2O_4$ an additional doublet is seen which can be attributed to super paramagnetic behavior exhibited by smaller size particles. The doublet was fitted with two sub spectra . The isomer shift was found to be 0.24-0.27 mm/s which can be attributed to Fe^{3+} ions in tetrahedral and octahedral sites. The sextets were fitted with two sub spectra. One sextet is due to Fe^{3+} ion at the tetrahedral A site and the outer sextet is due to Fe^{3+} at the octahedral B sites, which indicates the ferrimagnetic behavior of the samples. All of them shows isomer shift values in the range 0.22 mm/s to 0.34 mm/s, which could be attributed to the Fe^{3+} ions present at both the A and B sites of the spinel structure. This indicates that Mn^{2+} is also distributed between tetrahedral site and octahedral site. Similar metastable structure has been proposed by Rath et al [25] in nanocrystalline Mn ferrite. However, the case is different in bulk ferrites where Mn^{2+} prefers tetrahedral site while Fe^{3+} prefers octahedral site.

Distribution of Mn^{2+} on both the sites has also been reported for $MnFe_2O_4$ nanoparticles by Mahmoud et al. [26]. On addition of Cu^{2+} which can occupy both the sites but prefers the octahedral site, slight broadening of the line width and reduction in the intensity of the central lines is observed. These results agree with those reported earlier in the literature. The tetrahedral and octahedral positions of iron in the ferrospinels could also be distinguished on the basis of Magnetic hyperfine field, MHF. It has been mentioned that the internal MHF field experienced at A sites is smaller than that exerted at B sites: Usually, contribution of Fe^{2+} to the hyperfine field is significantly smaller than that of Fe^{3+} i.e. ferric ions. Also the isomer shift values for ions located at the tetrahedral site are generally smaller than those at octahedral site. It has also been reported that Fe^{3+} ions are at A site while Fe^{3+}/ Fe^{2+} both can reside at B site alternately. The observed isomer shift value confirms the presence of Fe^{3+} ions at both the sites while no Fe^{2+} is present in any of the composition. The intensity ratio A and B sites gives the ratio of the number of Fe atoms at A and B sites respectively. Quadrupole splitting has value near by zero for both the sites. As in the presence of strong magnetic interaction, the distribution of quadrupole interaction that arises from chemical disorder, produces an appreciable broadening of the individual Zeeman lines for both tetrahedral and octahedral patterns, but doesn't produces an observable quadrupole line shifts. Data extracted from the fits are reported in table 2.

c) *Effect of acidity and process variable*

The performance of various Mn-Cu ferrite catalysts along with their acidity, XRD surface area, particle size, and lattice constants is presented in Table 3.1. It can be seen that conversion of aniline as well as acidity of different catalysts increase with increase in copper content of the ferrites. Similar trend can be seen for surface area. The increase XRD surface is due to decrease in particle size of the sample with increase in Cu content. Consistency in lattice parameters of all the ferrites confirms them to possess same lattice type as concluded in section.

The order of catalytic activity of ferrospinels towards overall conversion was found to be CF> MCF-3>MCF-2>MCF-I>MF. It can be concluded from these results that. catalytic performance of the ferrites under consideration is proportional to surface area as well as acidity. An examination of the acidity reveals CF to be the better catalyst as its acidity value is larger and it also increases with increasing x as is clear from the reported values in Table 3.1. It also shows CF to be the better catalyst, as its aniline conversion (%) is larger.

The effect of methanol to aniline molar ratio on the performance of copper ferrite is depicted in Figure 3.4. The conversion increases at lower molar ratio and tends towards limiting conversion at higher molar ratio, Maximum conversion of 82 % of aniline was obtained at methanol to aniline molar ratio of 5 with NMA selectivity of 80 %.

The temperature effect on alkylation for MF at constant molar ratio was also studied in the temp range 473-773 K and results are presented in Table 3.5. Negligible conversion can be seen below 473 K while the conversion effectively occurs in the range 673 K - 700 K. The best performance by the catalyst was shown at temperature 673 K with conversion of 62 and 15 % for N-methyl aniline and N-N-dimethyl aniline respectively, and selectivity of 79 and 62 % for NMA and NNDMA respectively. Conversions decreased due to charring and deposition of carbon on the catalyst surface at temperature higher than 673 K.

IV. CONCLUSION

$Mn_{l-x}Cu_xFe_xO_4$ (x = 0., 0.25 0.5 0.75 1.0) mixed ferrite nanoparticles were obtained in a broad range of Cu concentration 0.0 < x <1.0 by coprecipitation and digestion method. Room temperature Mössbauer spectra of these fine particles exhibit slightly high value of hyperfine field and broadening of the zeeman spectral lines shows strong ferromagnetic behavior of the three compositions. The occupancy ratio between Fe cation at A and B sites of the spinel structured is deduced from the fitted data of the Mössbauer spectra.

These mixed ferrite spinel systems were also studied for the alkylation of aniline using methanol as the alkylating agent. These systems effectively alkyl ate aniline to N-methyl aniline and N-N-dimethyl aniline under optimized reaction condition. Highest activity is obtained for CF whereas MF and MCF-1 were mildly activated. Substitution of Cu in MF leads to the increase in value of acidity and the aniline conversion. This behavior suggests for Mn-Cu mixed ferrite system to be a good catalyst.

V. ACKNOWLEDGEMENTS

The Authors wish to express their appreciation to UGC-DAE-CSR, Indore for recording XRD, Mössbauer measurements.

REFERENCES RÉFÉRENCES REFERENCIAS

1. Battacharya A K, Nandi D K, Pressure Synthesis of N, N-Diethylaniline. Ind. Eng. Chem, *Prod. Pros. Dev*. 14, **1975**, 162-167.
2. Narayanan S, Prasad B P, Characterization and aniline alkylation activity of vanadia and silica-supported vanadia catalysts, *J. Mol. Catal*. 96(1), **1995**, 57-64.
3. Rice R G, Kohn E J, Raney Nickel Catalyzed N-Alkylation of Aniline and Benzidine With Alcohols, *J. Am. Chem. Soc*. 77,**1955**, 4052- 4054.
4. Narayanan S, Asima S, Acidity dependence of isopropylation activity over zeolites of Different structures and si/al ratios, *Stud. Surf. Sci. Catal.* 113, **1998**,667-673.
5. Elangovan S, Kannan P C, Arabindoo B, Murugeshan M, Aniline methylation over AFI and AEL type molecular sieves, *Appl. Catal A*: 174(1-2), **1998**, 213- 219.
6. Narayanan S, Deshpande K, Mechanism of aniline alkylation over vanadia and supported Vanadia, *J.Mol. Catal*. 104(2), **1995**, I09-113.
7. Narayanan S, Deshpande K, A comparative aniline alkylation activity of montmorillonite and vanadia-montmorillonite with silica and vanadia-silica, *Appl. Catal*: A. 135(1), **199**6, 125-135.
8. Narayanan S, Deshpande K, *N*-Alkylation of aniline over silica and montmorillonite K10: The influence of oxide impregnation. *Microporous Mater*. 11(1-2), **1997**, 77-82.
9. Narayanan S, Deshpande K, Acid activation of montmorillonite : Effect on structural and catalytic properties Stud, *Suif. Sci. Catal*. 113, **1998**, 773-778.
10. Radhcshyam A, Dwivcdi R, Reddy V. S, Chary KVR, Prasad R, Vapour phase methylation of pyridine with methanol over the $Zn_{1-x}Mn_xFe_2O_4$ ($x = 0, 0.25, 0.50, 0.75$ and 1) ferrite system, *Green Chem*. 4(6), **2002**, 558-561.
11. Sreekumar K, Mathcws T, Rajgopa I R, Vetrivcl R, Rao B S, Selective synthesis of 3-picoline via the vapor-phase methylation of pyridine with methanol over Ni-Co-Fe ternary spinel systems, *Catal. Lett*. 65, **2000**, 99-105.
12. Sreekumar,K, Jyothi TM, Mathcw T, Talawar M B, SugunaS N, Rao B S, Selective *N*- methylation of aniline with dimethyl carbonate over $Zn_{1-x}Co_xFe_2O_4$ (x=0, 0.2, 0.5, 0.8 and type systems, *J. Mol. Catal*. 159(2), **2000**, 327-334.
13. Sreekumar K, Mathcw T, Dcvassy B M, Rajgopa R I, Vetrivel R, Rao.B S, Vapor-Phase methylation of pyridine with methanol to 3-picoline over Zn1−xCoxFe2O4 (*x*D0, 0.2,0.5, 0.8 and 1.0)-type ternary spinels prepared via a low temperature method, *Appl. Catal.* 205, **2001**, 11-18.
14. Hadjjpanayis G C, Siegel R W, Properties- Applications, Nanophase Materials (Kluver, Dordreeht) **1994**.
15. Gajbhiye N. S, Trends in Research on Nanostructured, *Magnetic Materials. Metels. Materials Processes,* 10, **1998**, 247-264.
16. Kodama R H, Berkowitz A E, Mcniff E J, Foner S, Surface Spin Disorder in $NiFe_2O_4$ Nano, *Phys. Rev. Lett*. 77(2), **1996**, 394-397.
17. Chen P, Sorensen C M, Klabund K J, Hadjipanayis G C, Delvin E, Kostikas, A Size-dependent magnetic properties of $MnFe_2O_4$ fine particles synthesized by coprecipitation, *Phys. Rev.* B-54(13), **1996**, 9288-9296.
18. Pal M, Brahma P, Chakravorty D, Bhattacharya D, Maiti H S, Nano crystalline nickel-zinc ferrite prepared by glass-ceramic route, *J. Magn. Magn. Mater*. 164(1-2), **1996**, 256-260.
19. Cullity B. D Elements of X-Ray Diffarction. Wesley Publishing Company New York (1978).
20. Toledo J, Bosch A. P, Valenzuela M. A, Montoya A, Nava N, Oxidative dehydrogenation of 1-butene over Zn-Al ferrites, *J. Mol. Cata. A. Chemical*. 125, **1997**, 53-62.
21. Klug H. P. L, Alexander E (1974). X-Ray Diffraction procedures wiley, New York 562.
22. Lazar K, Mathew T, Koppany Z, Megyeri J, Subhash V S, Mirajkar P, Rao B S L, $Cu_{1-x}Co_xFe_2O_4$ ferrospinels in alkylation: Structural changes upon reaction, *Phys. Cem*. 4(14), **2002**, 3530-3536.
23. Tang Z X, Sorensen C M, Klabunde K J, Hadjipanayis G C, Preparation of manganese ferrite fine particles from aqueous solution, *J. colloid and interface science* 146(1), 1991, 38-52.
24. Rath C, Anand S, Das R P, Sahu K K, Kulkarni D, Date S K, Mishra N C, Dependence on cation distribution of particle size, lattice parameter, and magnetic properties in nanosize Mn–Zn ferrite, *J.of Appli. Phy*, 91(4), 2002, 2211-2215.
25. Mahmoud M H, Hamdeh H H, Ho J C, Shea M J O, Walker Mössbauer studies of manganese ferrite fine particles processed by ball-milling. *J. M ag. Mag. Mat.* 220 (2-3), 2000, 139-146.

Table 1 : Particle size, Lattice parameter, acidity and catalytic activity of $Mn_{1-x}\,Cu_xFe_2O_4$ catalyst. Temperature = 673 K, Mole ratio = 5.0

Composition	Aniline conversion	Particle Size (nm)	XRD Surface area (m^2/g)	Lattice parameter (A^0)	Acidity (m mole/g)
MF	28	13.9	86.16	8.49	1.2
MCF-1	32.2	20.9	56.15	8.45	1.2
MCF-2	40.4	14.6	78.67	8.43	1.3
MCF-3	58.0	13.9	81.29	8.40	1.4
CF	80.5	7.2	155	8.39	1.5

Table 2 : Mössbauer parameters extracted from the fitting for the composition $Mn_{1-x}Cu_xFe_2O_4$. Where I.S-Isomer shift, Q.S- Quadrupole splitting, MHF- Magnetic hyperfine field, H.L. W-half line width, RI -Relative intensity for A and B sites

Composition		Site	I.S (±0.03 mm/s)	Q.S (±0.02 mm/s)	MHF (± I T)	H.L.W. (± 0.01)	RI (%)
$MnFe_2O_4$	[D]	A	0.27	1.07	-	0.48	12.50
	[D]	B	0.24	0.82	-	0.36	12.50
	[S]	A	0.38	-0.212	50.12	0.47	37.50
	[S]	B	0.14	-0.12	50.00	0.41	37.50
$Mn_{0.5}Cu_{0.5}Fe_2O_4$	[D]	A	0.25	0.015	47.77	0.68	38
	[S]	B	0.32	-0.22	51.90	0.45	62
$Cu_{0.5}Fe_2O_4$	[S]	A	0.22	-0.04	48.15	0.71	45
	[S]	B	0.29	-0.1	51.14	0.67	55

Table 3 : Performance of various catalysts in the alkylation of aniline. Methanol/Aniline molar ratio = 5; Temperature = 673 K, WHSV = 0.2 h^{-1}.

Catalyst (%)	Aniline Conversion (%)	Product distribution		
		Aniline	NMA	NNDMA
MF	28.0	70.0	21.8	8.2
MCF-1	32.2	65.2	27.6	7.8
MCF-2	40.4	62.4	34.0	3.6
MCF-3	58.0	50.6	47.4	2.0
CF	80.5	19.4	79.4	1.2

Table 4 : Effect of mole ratio (Methanol to Aniline) on alkylation of Aniline Temperature = 673 K, WHSV = 0.2 h^{-1}, Catalyst = $CuFe_2O_4$

Mole ratio	Aniline Conversion (%)	NMA (yield)	NNDMA (yield)	NMA (Selectivity)	NNDMA (Selectivity)
2.5	64.2	20.6	10.0	67.3	32.7
5.0	82	61.2	15.3	80.0	20.0
7.5	79.2	63.6	8.2	88.5	11.5
1.0	73.4	71.2	5.2	93.2	6.8

Table 5 : Effect of temperature on alkylation of Aniline Methanol/aniline molar ratio = 5, WHSV = 0.2h^{-1}, Catalyst = $CuFe_2O_4$

Temperature	Aniline Conversion (%)	Product distribution (%)			
		Aniline	NMA	NNDMA	Others
473	06.0	96.0	-	-	4.0
573	38.2	51.2	20.8	22.0	6.0
673	80.1	23.2	62.4	14.4	-
773	42.8	39.8	42.2	18.0	-

FIGURE CAPTIONS

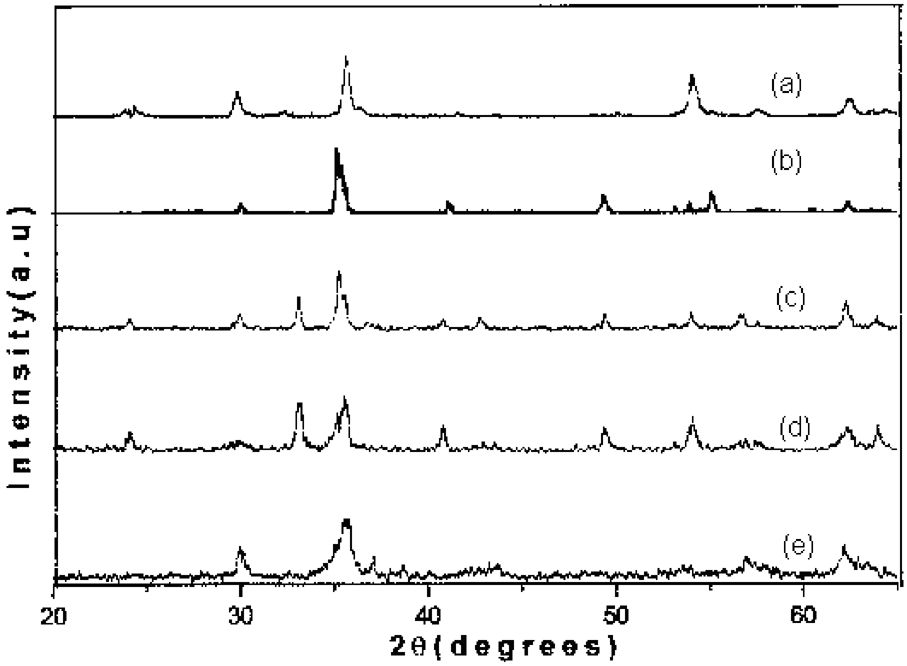

Figure 1 : XRD Pattern of Mn-Cu Ferrites

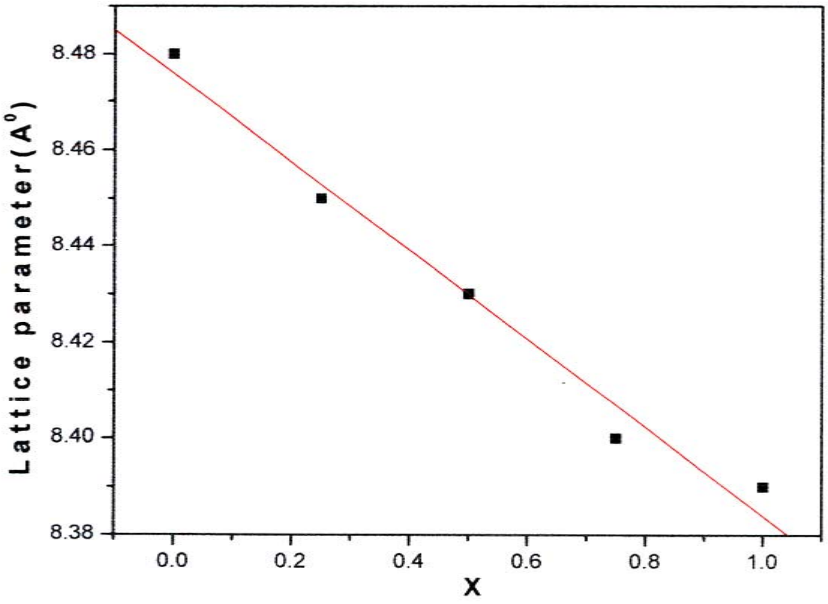

Figure 2 : Change in lattice parameter due to induction of Cu in Mn-ferrite

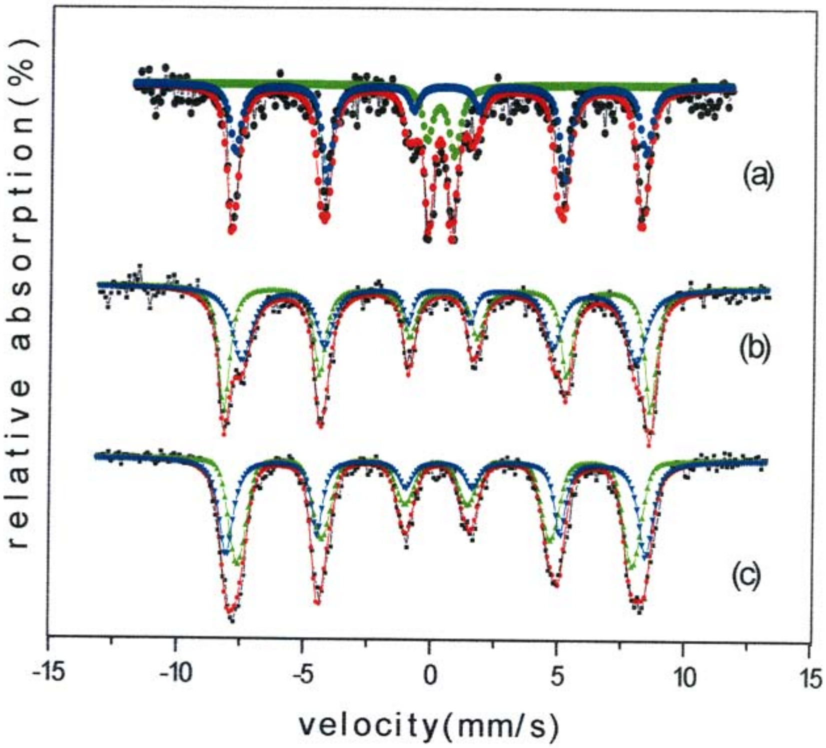

Figure 3 : Mössbauer Spetra of Samples

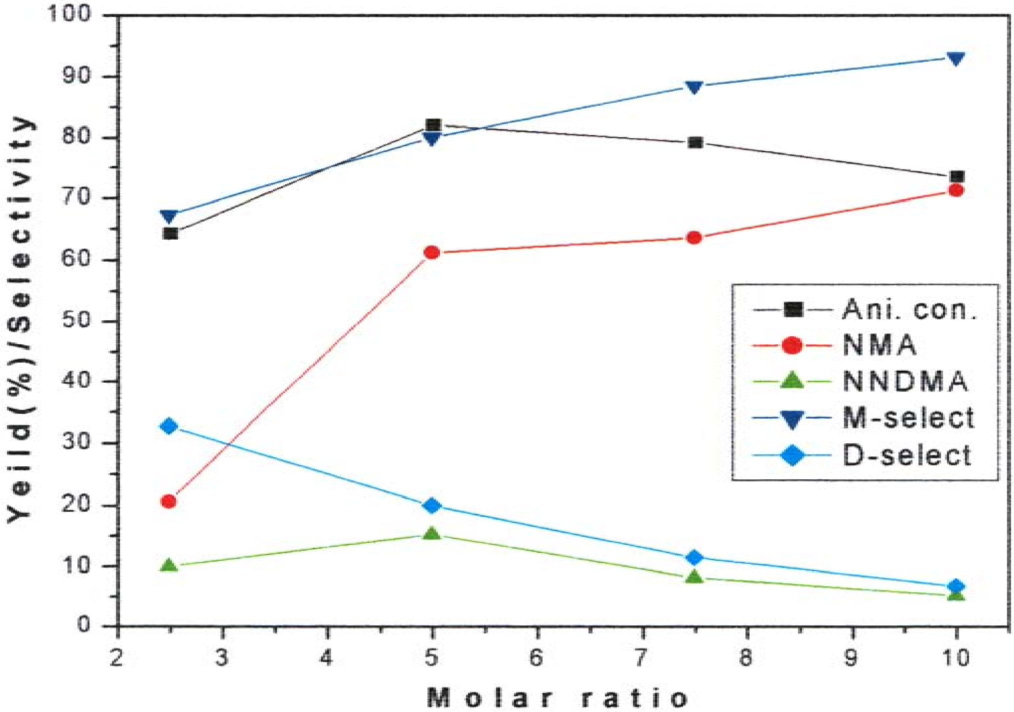

Figure 4 : Effect of molar ratio (methanol to aniline) on product selectivity

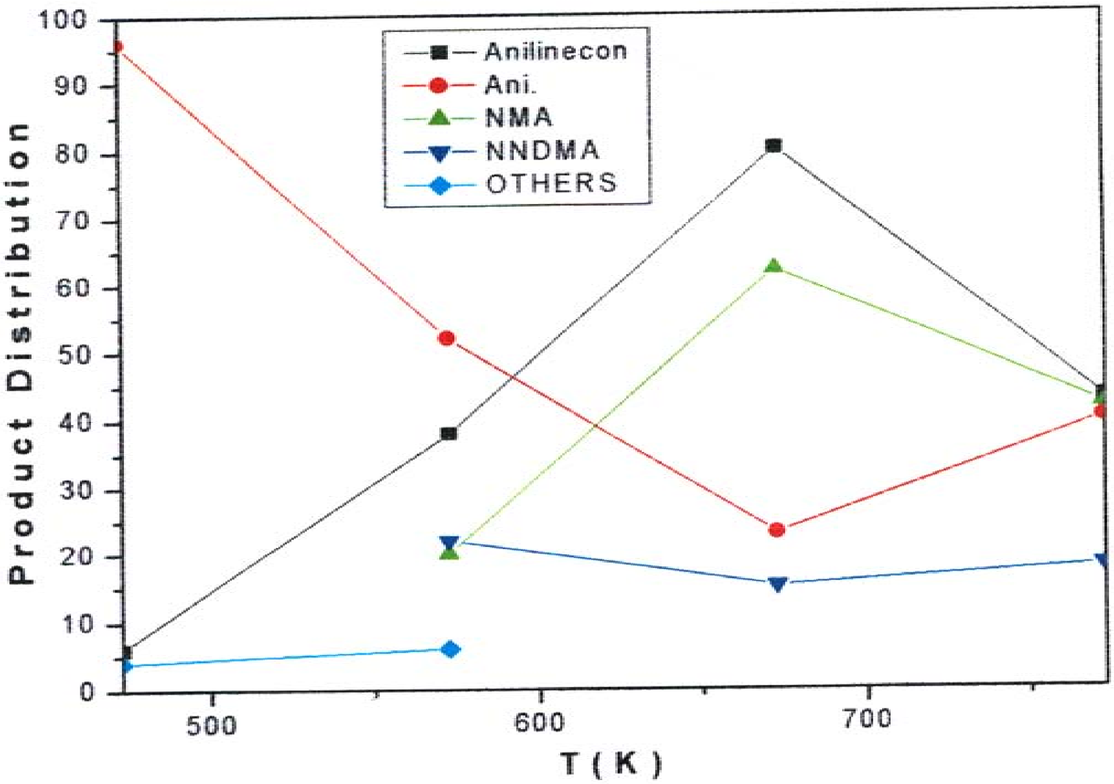

Figure 5 : Effect of temperature on product distribution

Global Journals Inc. (US) Guidelines Handbook 2013

www.GlobalJournals.org