Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2015, 7(6):663-671

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Vapor phase alkylation of 1-naphthol with methanol over Ni-Co ferrites

Alka Rani, Vinod Sharma, Surander Singh and R. K. Gupta*

Department of Chemistry, Guru Jambheshwar University of Science and Technology, Hisar, Haryana, India

---

ABSTRACT

Vapor phase alkylation of 1-naphthol with methanol has been carried out over $Ni_{1-X}Co_XFe_2O_4$ (x = 0.0, 0.50, 0.75, 1.0) type ferrospinels prepared via. low temperature co-precipitation method in a down flow fixed bed reactor. 2-Methyl-1-naphthol was found to be the major product. The activity of the catalysts was varied with acidity of the ferrospinels systems studied. It was observed that system possessing higher 'x' values were highly selective for 2-methyl-1-naphthol. The maximum yield of 59.6% with 84.5% selectivity of 2-methyl-1-naphthol was obtained under optimized conditions of temperature 573 K, methanol to 1-naphhthol molar ratio 3:1 and WHSV 0.4 h^{-1}.

Key words: Alkylation; Ferrospinels; 1-Naphthol; 2-Methyl-1-naphthol.

INTRODUCTION

2-Methyl-1-naphthol is widely used as an intermediate in the preparation of pharmaceuticals, dyes, polymers and agrochemicals. It can easily be oxidized to 2-methyl-1, 4-naphthoquinone (vitamin K3, menadione) by peroxides [1, 2]. Menadione is an intermediate in the production of vitamin K1, K2 and K4. Till now, a usual process of producing menadione comprises 2-methylnaphthalene oxidation with chromic acid in liquid phase [3]. The synthesis of 2-methyl-1-naphthol was reported over various modified zeolites [4]. Conventionally Friedel-Crafts alkylation reaction using homogenous acid catalysts are used to produce the alkylated aromatic compounds. Due to stringent environmental concern over the disposal of spent catalysts, it is difficult to continue with these catalysts. In this context, several heterogeneous catalysts, which include metal oxides, zeolites, heteropoly acids and their salts, have been studied due to their ecofriendly nature and their potential to replace the conventional Friedel-Crafts catalysts. In recent years ferrospinels are used as catalysts for alkylation due to their reusability, easy separation, high thermal stability and ecofriendly nature [5-7].

Ferrites have attracted much attention due to their remarkable electrical, magnetic and catalytic properties [8-12]. The general structure of ferrite having spinel structure is AB_2O_4 (A is divalent ion, B is trivalent ion). Most of the ferrite properties depend on the distribution of metal ion in tetrahedral and octahedral sites. The adequate selection of the substituting ion and suitable chemical composition changes the catalytic properties of ferrites [13, 14]. Alkylation of 1-naphthol to 2-methyl-1-naphthol with methanol over $N_{1-X}Co_XFe_2O_4$ type ferrite in vapor phase is reported for the first time.

EXPERIMENTAL SECTION

2.1. Preparation of catalysts

2.1.1. Preparation of $NiFe_2O_4$ (NF)

A solution of 1.2 mol of NaOH in 150 mL of water was allowed to react with a solution of 0.075 mol of $NiCl_2.6H_2O$ in 50 mL of water. The resulting solution was added to a 5 L beaker containing 0.15 mol of $FeCl_3.6H_2O$ in 2500 mL of 0.6 M HCl and stirred for 2 h. The resulting mixture was further heated for 0.5 h at 333 K. The mixture was allowed to settle and reacted with 2 M NaOH till a permanent pink color was obtained with phenolphthalein. The product was washed by repeated decantation with 2.5 L portions of water until the supernatant was free of Cl^- (about 15 washings were required), filtered through a sintered glass filter, dried in an oven at 393 K overnight and calcined at 773 K for 16 h. Finally the product was sieved through a sieve of size 6/10 mesh.

2.1.2. Preparation of other catalysts

Preparation of $CoFe_2O_4$ (CF) was similar to $NiFe_2O_4$ (NF), described above, except that now 0.075 mol of $CoCl_2.6H_2O$ were used in place of $NiCl_2.6H_2O$. Similarly $Ni_{0.5}Co_{0.5}Fe_2O_4$ (NCF-1), $Ni_{0.25}Co_{0.75}Fe_2O_4$ (NCF-2), were prepared using 0.0375 mol, 0.0188 mol of $NiCl_2.6H_2O$ and 0.0375 mol, 0.0562 mol of $CoCl_2.6H_2O$ respectively.

2.2. Apparatus and Procedure

1-Naphthol was alkylated with methanol in a continuous fixed bed down flow reactor. The upper halves worked as pre-heater and lower half as reactor. 9.0 g of catalyst sieved through a sieve of size 6/10 mesh, was placed in the middle of reactor. The reactants were fed from the top of reactor with a current of N_2 gas @ 30 mL/min. The gaseous products were collected using an ice cold water coiled condenser at the bottom of reactor. Gas Chromatograph Nucon, Model-5700 with flame ionization detector having fused silica capillary column of film thickness 30 m x 0.25 mm x 0.25 um was used to determine the composition of the product mixture. The conversion was given with respect to 1-naphthol.

RESULTS AND DISCUSSION

3.1. Catalyst *characterization, surface area and acidity measurements*

XRD spectra of composite samples CF, NCF-2, NCF-1, NF were obtained with a Rigaku-Miniflex-II instrument using $CuK_{\alpha1}$ radiation (λ =1.54 Å) and reproduced in Figure 1.

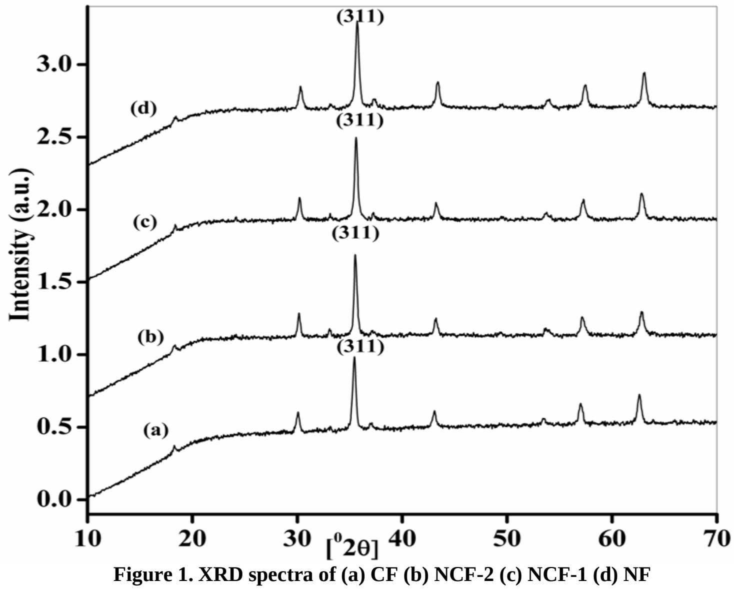


Figure 1. XRD spectra of (a) CF (b) NCF-2 (c) NCF-1 (d) NF

All the peaks in the pattern match well with the characteristics reflections of CF and NF ferrites reported in JCPDS file no: 22-1086 and 10-325 respectively and confirm the phase purity, thus indicating the exclusive formation of a single spinel structure for all compositions of the catalyst. From the XRD data, Average particle size (*D*) was determined w.r.t. intense peak (311) using the Scherrer's formula [15] and presented in Table 3.

$$D = \frac{k\lambda}{\beta \cos\theta}$$

k is shape factor, which takes a value of about 0.9, β is the full width at half maxima of most intense diffraction peak, λ is the wavelength of x-ray source used in the XRD and θ is the angle of Bragg diffraction. The cubic unit cell length (Table 3.) have been calculated by using the formula given in Eq. (1) [16], is plotted against the compositional parameter 'x' in Figure 2.

$$a_0 = \frac{\lambda}{2}\frac{[h^2 + k^2 + l^2]^{1/2}}{\sin\theta} \qquad (1)$$

Where *h*, *k* and *l* are miller indices.

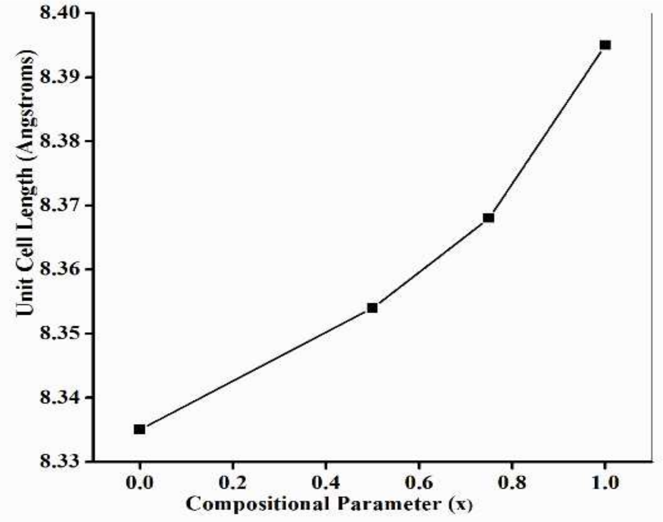


Figure 2. Unit cell length plotted against the compositional parameter 'x'

The unit cell length is found to increase linearly as the Co^{2+}content increases. This is because the ionic radius of Co^{2+} ($0.78A^0$) is greater than the ionic radius of Ni^{2+} ($0.74A^0$) and Fe^{3+} ($0.67A^0$) ions [17].

Infrared spectra of ferrites were recorded on Shimadzu IR Affinity 8000 FT-IR spectrometer and are shown in Figure 3.

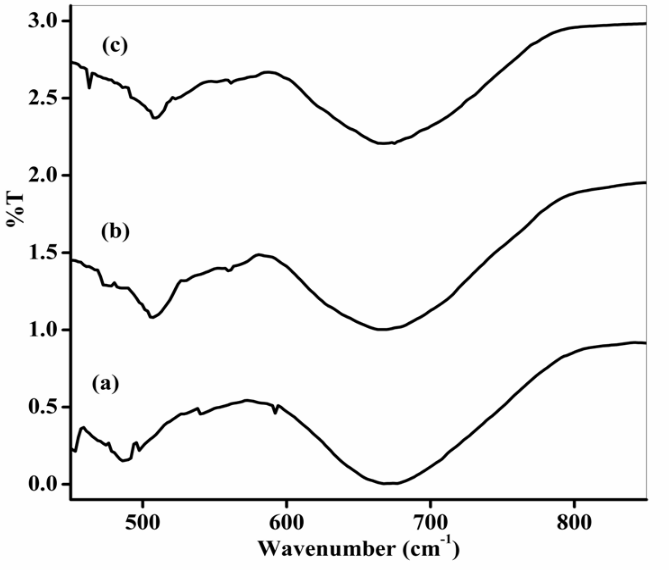
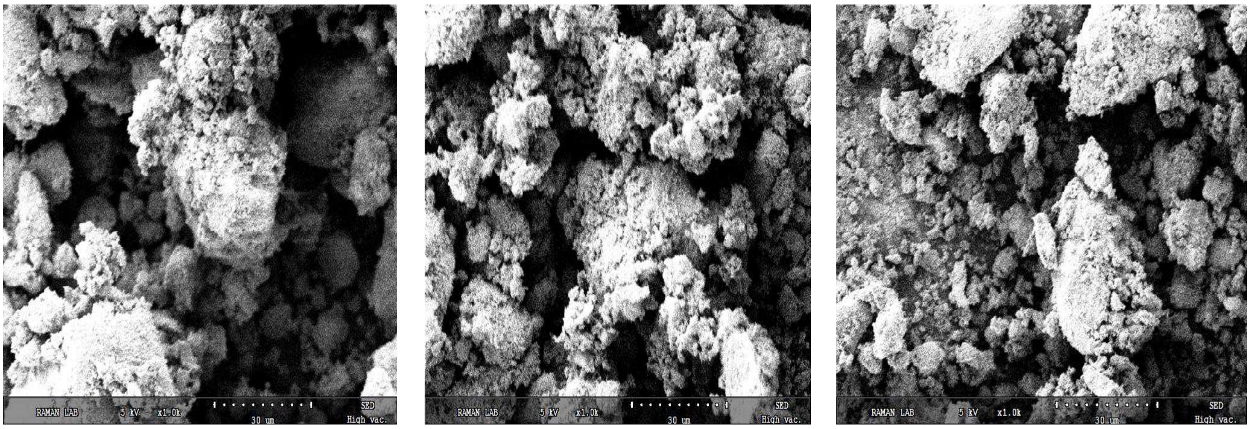


Figure 3. IR spectra of (a) CF (b) NCF-1 (c) NF

The spectrum consists of two major bands. One with the higher wave number, ν_1, around 700 cm^{-1}, which corresponds to stretching vibration of the M-O bond at the tetrahedral site, whereas, ν_2, the lower band , around 500 cm^{-1}, is attributed to octahedral M-O stretching mode of vibration [18, 19]. The difference in the band position is due to the difference in metal-oxygen bond distance at tetrahedral and octahedral sites of the spinel.

To determine morphology of ferrite nanopowders SEM was recorded for freshly calcined samples on Instrument-SEMTRAC MINI and is shown in Figure 4. (a), (b) and (c).



(a) **(b)** **(c)**

Figure 4. SEM Micrograph of (a) CF (b) NCF-1 (c) NF

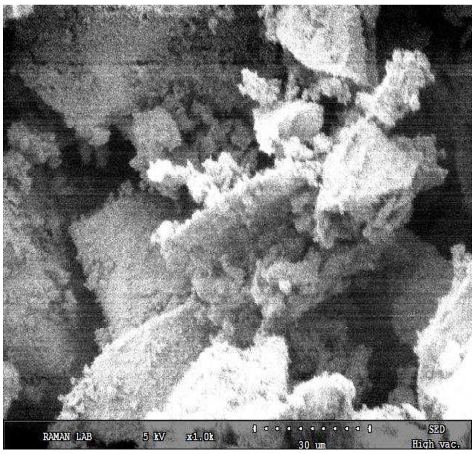


Figure 4. (d) CF sample

It is evident from SEM studies that ferrites give the appearance of sponge structure, highly dense, with different grain size along with large number of pores. However, from the SEM shown in Figure 4. (d) for $CoFe_2O_4$ after its use as a catalyst for alkylation, it is found that its morphology is different from that of freshly calcined $CoFe_2O_4$.

The chemical composition of ferrites was determined using X-ray fluorescence (XRF) Instrument- Rigaku ZSX (Primus). The results (Table 1.) indicate good agreement between the experimental and theoretical wt% values of Ni, Co, Fe.

Table 1. Chemical analysis of ferrite catalysts by XRF

Catalysts	Metal Concentration (wt %)^a			Ni : Co : Fe (Mole Ratio)^b		
	Ni	Co	Fe	Ni	Co	Fe
NF	36.02 (34.45)	-	63.98 (65.55)	1.04 (1.0)	-	1.95 (2.0)
NCF-1	17.38 (17.23)	17.29 (17.27)	65.33 (65.50)	0.50 (0.50)	0.50 (0.50)	1.99 (2.0)
NCF-2	7.21 (8.61)	24.45 (25.90)	68.34 (65.49)	0.21 (0.25)	0.70 (0.75)	2.08 (2.0)
CF	-	34.66 (34.54)	65.34 (65.46)	-	1.0 (1.0)	1.99 (2.0)

^{a} *Theoretical wt% in parentheses*
^{b} *Theoretical mole ratio in parentheses*

The results also show that relative molar ratio of Ni, Co, Fe is close to the desired stoichiometric composition of the prepared ferrites, thus confirming the formation of ferrites with desired composition.

The acidity data of all the ferrites were measured by a temperature-programmed desorption of ammonia method using procedure given elsewhere [19] and results of which are presented in Table 2.

Table 2. Catalytic acidity at different temperatures

Acidity (NH_3 uptake in mmol/g)				Total acidity
Catalysts	423-523 K	523-623 K	623-723 K	
NF	0.35	0.29	0.37	1.01
NCF-1	0.39	0.31	0.38	1.08
NCF-2	0.40	0.33	0.42	1.15
CF	0.45	0.36	0.43	1.24

The BET surface area of ferrites was determined on Quantachrome, Model: Nova 2000e instrument; the results are presented in Table 3.

Table 3. XRD parameter, BET surface area of ferrite catalysts

Catalysts	Particle Size (nm)	(A^0)	BET Surface area (m^2/g)
NF	22.46	8.335	58.05
NCF-1	23.18	8.354	40.01
NCF-2	26.71	8.368	32.73
CF	27.71	8.395	24.70

3.2. Acidity, surface area, unit cell length and catalytic activity of various catalysts in methylation of 1-naphthol

Acidity, surface area and unit cell length of various ferrite catalysts are presented in Table 2 and 3. The catalytic activity (Table 4.) with respect to 1-naphthol conversion was found to increase with increase in 'x'value of $Ni_{1-X}Co_XFe_2O_4$ series. The order of catalytic activity of various catalysts were found to be CF > NCF-2 > NCF-1 > NF.

Table 4. Catalytic activity of various catalysts in the methylation of 1-naphthol (at temperature 573 K, methanol to 1-naphthol molar ratio 3:1, WHSV 0.4 h^{-1})

Catalysts	1-Naphthol Conversion (%)	2-Methyl-1-naphthol Yield (%)	Others*	2-Methyl-1-naphthol Selectivity (%)
NF	60.8	38.5	22.3	63.3
NCF-1	63.1	42.0	21.1	66.6
NCF-2	64.0	49.3	14.7	77.0
CF	70.5	59.6	10.9	84.5

*Naphthalene, 2-methylynaphthalene, 1-methoxynaphthalene and polymethylnaphthalenes.

The catalytic activity order reveals that acidity of catalyst increases as the value of ‘x’ increases. The better catalytic activity of CF as compared to NF can be ascribed due to its higher acidity. At higher ‘x’ value the yield and selectivity of 2-methyl-1-naphthol reaches maximum because acidic sites favor 2-methyl-1-naphthol formation. From this we conclude that there exists direct relationship between acidity and alkylation activity. We also conclude that increase in unit cell length values with increase in Co^{2+} content can lead to higher bond distances between the metal and oxygen atoms, which can reduce the electron density on the metal atom, thus leading to higher Lewis acidity of the catalysts. It explains the increase in acidity of the catalysts with increasing content of Co^{2+} ions, as revealed by the NH_3-TPD desorption method.

3.3. Effect of temperature

The effect of temperature on alkylation of 1-naphthol was studied on $CoFe_2O_4$ in the temperature range 533 K to 653 K and results are shown in Table 5.

Table 5. Effect of reaction temperature on 1-naphthol methylation (catalyst-$CoFe_2O_4$, methanol to 1-naphthol molar ratio 3:1, WHSV 0.4 h^{-1})

Temperature (K)	1-Naphthol Conversion (%)	2-Methyl-1-naphthol Yield (%)	Others*	2-Methyl-1-naphthol Selectivity (%)
533	40.3	26.3	14.0	65.3
573	70.5	59.6	10.9	84.5
613	74.0	34.4	39.6	46.5
653	63.2	27.0	36.2	42.7

*Naphthalene, 2-methylnaphthalene, 1-methoxynaphthalene and polymethylnaphthalenes.

The maximum yield of 2-methyl-1-naphthol was obtained at 573 K. Below 573 K, the alkylating activity is low. Above 573 K, the yield and selectivity of 2-methyl-1-naphthol decreases. This may be due to the deep ring methylation and deposition of coke at higher reaction temperature, hence decreasing the yield and selectivity of 2-methyl-1-naphthol.

3.4. Effect of molar ratio

Effect of molar ratio on alkylation of 1-naphthol was studied over $CoFe_2O_4$, at 573 K and 0.4 h^{-1} WHSV. The results are shown in Figure 5. 1-Naphthol conversion and selectivity of 2-methyl-1-naphthol increased with increase in methanol to 1-naphthol molar ratio, reaching a maximum at 3:1 and then decreased. At higher molar ratio, the selectivity of 2-methyl-1-naphthol was reduced. This was probably due to the unavailability of active sites for 1-naphthol over the catalyst surface, because of competition between methanol and 1-naphthol for adsorption.

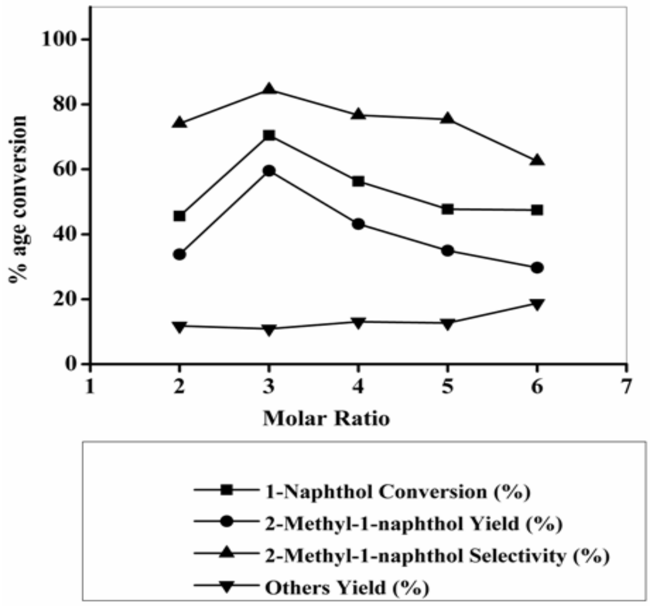


Figure 5. Effect of methanol to 1-naphthol molar ratio on the methylation of 1-naphthol (catalyst-$CoFe_2O_4$, temperature 573 K, WHSV 0.4 h^{-1})

3.5. Effect of WHSV

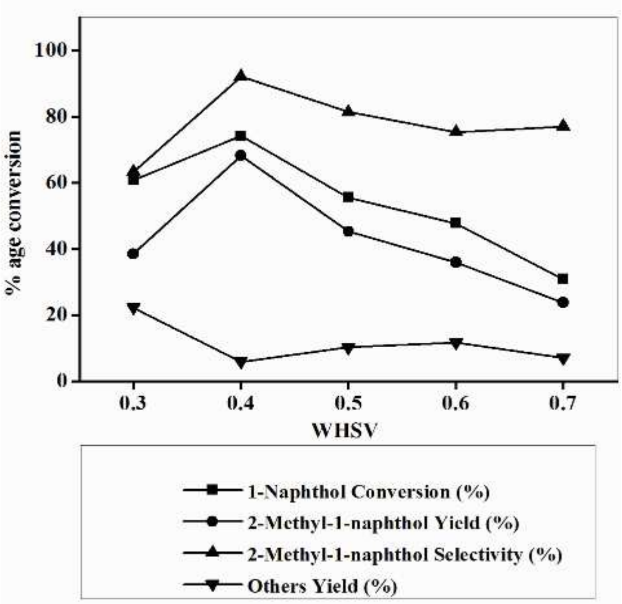
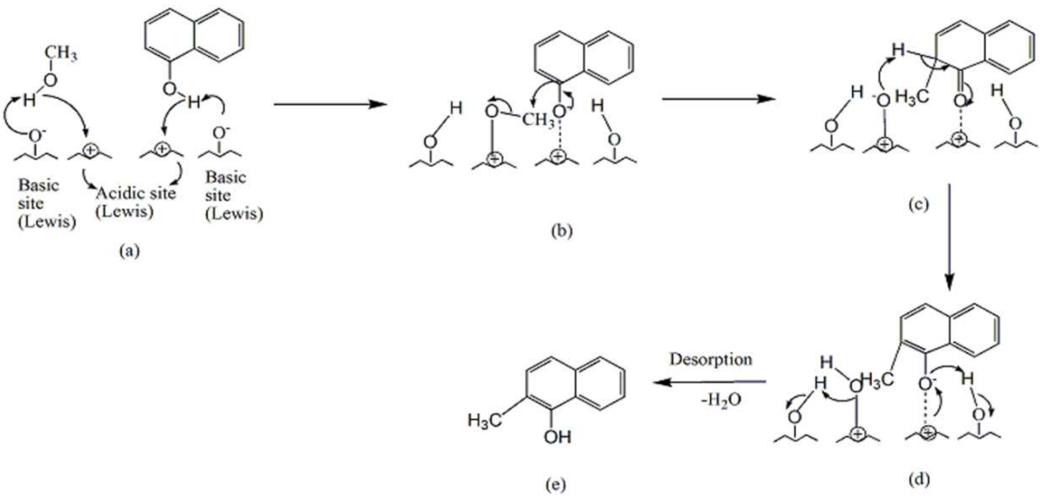


Figure 6. Effect of WHSV on the methylation of 1-naphthol (catalyst-$CoFe_2O_4$, temperature 573 K, methanol to l-naphthol molar ratio 3:1)

The influence of WHSV on alkylation of 1-naphthol was studied over $CoFe_2O_4$ catalyst at 573 K and molar ratio of methanol to 1-naphthol 3:1. With WHSV increase from 0.3, 0.4 h^{-1} and so on, conversion of 1-naphthol increased first and subsequently it decreased as shown in Figure 6. This perhaps indicates that the reaction is diffusion controlled. The high contact time causes charring of catalyst over active sites at 0.3 h^{-1}. WHSV above 0.4 h^{-1}, 1-naphthol conversion decreases due to decrease in contact time.

4. Mechanism



Scheme 1. Possible Reaction mechanism for the alkylation of 1-naphthol with methanol

1-Naphthol is a nucleophilic heterocycle and it reacts very easily with electrophiles. High C-2 methylation selectivity can be explained by assuming vertical orientation of adsorbed 1-naphthol on the Lewis acidic site as postulated by Klemm *et al* [20]. The mechanism is given in Scheme 1. In scheme 1 (a), an ensemble of four sites (two acidic Lewis and two basic Lewis sites) serve to adsorb methanol and 1-naphthol. According to which the naphthoxide and methoxide ion are adsorbed on the Lewis acidic sites and hydrogen ion is bound to the Lewis basic site. Methylation of adsorbed naphthoxide ion at C-2 by adjacently adsorbed methoxide ion and proton transfer from a hydroxide group leads to the formation of 2-methyl-1-naphthol. At higher reaction temperature, dehydroxylation activity of cations, repeated methylation of naphthoxide ion leads to the formation of polymethylnaphthalenes.

CONCLUSION

A catalytic activity experiment reveals that the maximum yield of 59.6% with selectivity 84.5% of 2-methyl-1-naphthol was obtained over $CoFe_2O_4$ ferrite under the optimized conditions of temperature 573 K, molar ratio 3:1 and WHSV 0.4 h^{-1}.The catalytic activity of the system was dependent on the reaction parameters. The activity of the catalysts was found to increase with increasing the acidity. High reaction temperature results in decrease of 2-methyl-1-naphthol yield.

Acknowledgements

One of the authors, Alka Rani is highly grateful to UGC, New Delhi for financial assistance. The authors are also thankful to the Director of CIRB, Hisar for providing GC facilities.

REFERENCES

[1] I Yuranov; L Kiwi-Minsker; A Renken, *Appl. Catal*., **2002**, A 226, 193-198.
[2] H Grabowska; W Mista; L Syper; J Wrzyszcz; M Zawadzki, *J. Catal.*, **1996**, 160, 134.
[3] LF Fieser, *J. Biol. Chem*., **1940**,133, 391.
[4] SJ Kulkarni; KVVSBSR Murthy; K Nagaiah; M Subrahmanyam; KV Raghavan, *Micropor. Mesopor. Mater*., **1998** 21, 53-57.
[5] RA Sheldon, *J. Mol. Catal.*, **1996**, A 107, 75.
[6] A Kotsuki; M Teraguch;, N Shimomoto; M Ochi, *Tetrahedron Lett*., **1996,** 37, 3727.
[7] P Siwach ; S Singh ; R K Gupta, *Catal. Comm*., **2009,** 10, 1577-1581.
[8] K Sreekumar; S Sugunan; *J. Mol. Catal*., **2002**, A 185, 259-268.
[9] K Sreekumar; TM Jyothi; T Mathew; MB Talawar; S Sugunan; BS Rao, *J. Mol. Catal.*, **2000**, A 159, 327-334.
[10] A Radhe Shyam; R Dwivedi; VS Reddy; KVR Chary; R Prasad, *Green Chem*., **2002**, 4, 558-561.
[11] VS Reddy; A Radhe Shyam; R Dwivedi; RK Gupta; VR Chumbale; R Prasad, *J.Chem. Technol. Biotechnol.*, **2004**, 79, 1057-1064.

[12] K Sreekumar; T Raja; BP Kiran; S Sugunan; BS Rao, *J. Appl. Catal.*, **1999,** A 182, 327-336.
[13] JP Jacob; A Maltha; JCH Reintjes; J drimal; V Ponec; HH Brogersma, *J. Catal.*, **1994,** 147, 294.
[14] CG Ramankutty; S Sugunan, *Appl. Catal.*, **2001**, A 218, 39.
[15] NM Deraz; A Alarifi; *Int. J. Electrochem. Sci.*, **2012**, 7, 3809.
[16] Y Koseoglu; F Alan; M Tan; R Yilgin; M Ozturk, *Ceramics International,* **2012**, 38, 3625-3634.
[17] NK Dung; NH Tuan, *VNU J. Sci. Math. Phys.*, **2009**, 25, 153-159.
[18] RD Waldern, *Phys. Re*., **1995,** 99, 1727-1735.
[19] P Siwach ; S Singh ; RK Gupta, *Appl. Catal.*, **2009**, A 366, 65-70.
[20] LH Klemm; CE Klopefenstein, *J. Org. Chem*., **1970,** 35, 1069.