

Catalytic alkylation of 1-naphthol with Methanol Over $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ Type Ferrites

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Abstract: Vapor phase alkylation of 1-naphthol with methanol was investigated over $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.50, 1.0$) type ferrites system. 2-Methyl-1-naphthol was found to be the major product. The maximum yield 53.0% of 2-methyl-1-naphthol with 78.2% selectivity was obtained under optimized parameters at a temperature of 573 K, molar ratio 3:1 and WHSV 0.4 h^{-1} .

Keywords: Ferrospinels, 1-Naphthol, 2-Methyl-1-naphthol

1. Introduction

Alkylations are the most important reactions while heterogeneously catalyzed alkylation by Friedel-Crafts reaction is one of the most studied and utilized reactions for C-C bond formation in organic chemistry. Many studies have been reported on the conventional Lewis acid catalysts such as sulfuric acid, phosphoric acid, TiCl_4 , AlCl_3 , BF_3 and FeCl_3 . These catalysts should be replaced because of their corrosive nature, non-reusability, non-shape selectivity and non-ecofriendly nature [1-5]. Ferrites have attracted much attention due to their remarkable electrical, magnetic, catalytic properties and their reusability, easy separation, high thermal stability, ecofriendly nature [6-8]. Recently, there has been an upsurge on the alkylation of aromatics over ferrospinels catalysts [9-11], having general formula $\text{M}^{+2}[\text{Fe}_2^{+3}]\text{O}_4$, formed due to close packing of oxygen anions having tetrahedral and octahedral interstitial sites filled by M^{+2} and Fe^{+3} ions respectively. Metal ion in the bracket represents octahedral sites. Depending upon the position of metals in the tetrahedral and octahedral sites ferrospinels can be normal $\text{M}^{+2}[\text{Fe}_2^{+3}]\text{O}_4$, inverse $\text{Fe}^{+3}[\text{M}^{+2}\text{Fe}^{+3}]\text{O}_4$ or mixed spinel in which the divalent cations are distributed between both sites. This type of cations distribution significantly affects acido-basic [11] and surface properties of ferrospinels [12]. The adequate selection of the substituting ion and suitable chemical composition changes the catalytic properties of ferrites [13, 14]. K.V.V.S.B.S.R. Murthy et al reported alkylation of 1-naphthol over molecular sieves and modified silicoaluminophosphate and 2-methyl-1-naphthol was found as major product with 44.8% yield over CoSAPo-5 under optimum reaction conditions [15]. Grabowska et al reported the synthesis of 2-methyl-1-naphthol over modified iron oxide catalysts with high yield and selectivity. K3-vitamin can be synthesized by the oxidation of 2-methyl-naphthalene and oxidation of 2-methyl-1-naphthol. Microwave assisted solid liquid phase alkylation of naphthol has been carried with various alkyl halide out by E. Balint et al and alkylation were O-selective in the presence of K_2CO_3 in acetonitrile as a solvent [16]. Alkylation of 1-naphthol with camphene in presence of aluminium phenoxide and isopropoxide has been reported by I. Yu. Chukicheva et al. The yield of 2-alkylated product was varied 12-62% [17]. The synthesis of 2-methyl-1-naphthol was carried out over alumina. The selectivity was lower due to parallel reactions. 2-Methyl-1-naphthol is widely used as an intermediate in the preparation of pharmaceuticals,

polymers, dyes, and agrochemicals [18]. In this paper, alkylation of 1-naphthol to 2-methyl-1-naphthol with methanol over $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ type ferrite in vapor phase.

2. Experimental Work

2.1. Catalyst synthesis and characterization

A series of ferrospinels of compositions viz. MnFe_2O_4 (MnF), NiFe_2O_4 (NiF), $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ (NiMnF) were synthesized by low temperature co-precipitation method as reported earlier [19].

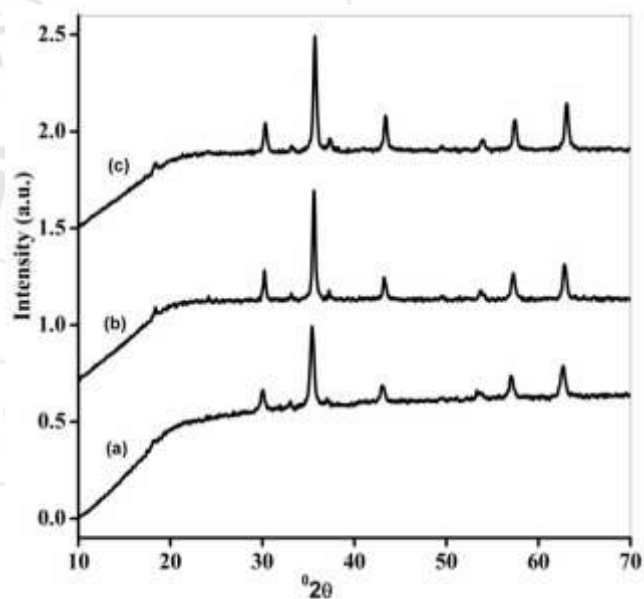


Figure 1: XRD spectra of (a) MnF (b) NiF (c) NiMnF

XRD pattern of $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ferrospinels were studied with a Rigaku-Miniflex-II instrument using $\text{CuK}_{\alpha 1}$ radiation ($\lambda = 1.54 \text{ \AA}$) as shown in Fig. 1. All the peaks in the pattern match well with the characteristics reflections of MnF and NiF ferrites and reveal a single phase spinel structure for all the compositions of ferrospinels.

The FTIR spectra were recorded on Shimadzu IR Affinity 8000 FT-IR spectrometer and spectrum consists of two major bands 700 cm^{-1} , 500 cm^{-1} . Band around 700 cm^{-1} , which corresponds to stretching vibration of the M-O bond

at the tetrahedral site, band around 500 cm^{-1} , is attributed to octahedral M-O stretching mode of vibration [19, 20].

The acidity of all the ferrites were measured by a temperature-programmed desorption of ammonia method using procedure given elsewhere [21] and results of which are presented in Table 1.

Table 1: Catalytic acidity at different temperatures and surface area data

Catalysts	Acidity (NH ₃ uptake in mmol/g)			Total acidity	BET Surface area (m ² /g)
	423-523K	523-623K	623-723K		
NiF	0.35	0.29	0.37	1.01	58.05
NiMnF	0.39	0.31	0.38	1.06	45.01
MnF	0.4	0.33	0.42	1.2	33.31

The BET surface area of ferrites was determined on Quantachrome, Model: Nova 2000e instrument; the results are presented in Table 1.

To determine morphology of ferrites SEM was recorded for freshly calcined samples on Instrument-SEMTRAC MINI and result is shown in Fig. 2. (a) and (b).

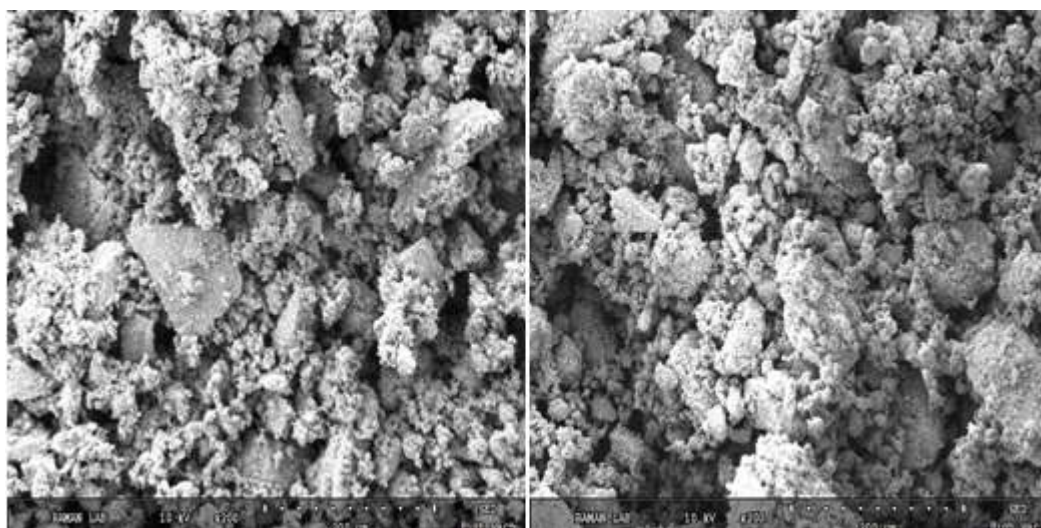


Figure 2: SEM Micrograph of (a) MnF (b) NiMnF

From SEM studies is revealed that ferrites give the appearance of highly dense structure with different grain size along with large number of pores.

The composition of metal ion was determined using X-ray fluorescence (XRF) Instrument- Rigaku ZSX (Primus). The results (Table 2.) indicate that the experimental and theoretical wt% values of Ni, Mn, and Fe are very comparable.

Table 2: Chemical analysis of ferrite catalysts by XRF

Catalysts	Metal Concentration (wt %) ^a			Ni: Mn : Fe (Mole Ratio) ^b		
	Ni	Mn	Fe			
NiF	36.02 (34.45)	-	63.98 (65.55)	1.04 (1.0)	-	1.95 (2.0)
NiMnF	17.57 (17.42)	16.16 (16.30)	66.25 (66.28)	0.50 (0.50)	0.50 (0.50)	1.99 (2.0)
MnF	-	32.78 (32.97)	67.21 (67.03)	-	0.99 (1.0)	2.0 (2.0)

^a Theoretical wt% in parentheses

^b Theoretical mole ratio in parentheses

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

2.2. Apparatus and Procedure

Vapor phase alkylation of 1-Naphthol with methanol was carried out in a continuous fixed bed down flow reactor. An amount 9.0 g of catalyst sieved through a sieve of size 6/10 mesh, was placed in the middle of reactor and was activated at 773K for 2 h under a flow of air and then brought down to the desired temperature by cooling in a current of N₂ gas of 30 ml/min. The reactants were fed from the top of reactor with a current of N₂ gas of 30 ml/min. The gaseous products were collected using an ice cold water coiled condenser at the bottom of reactor. Dhruva Gas chromatograph with flame ionization detector was used to determine the composition of the product mixture.

3. Results and Discussion

3.1. Acidity, surface area and performance of various catalysts in methylation of 1-naphthol

Acidity, surface area of various ferrite catalysts are presented in Table 1. The catalytic activity (Table 3) with respect to 1-naphthol conversion was found to increase with increase in 'x' value of Ni_{1-x}Mn_xFe₂O₄ series. The order of performance of various catalysts were found to be MnF > NiMnF > NiF.

Table 3: Performance 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 (%)
NiF	61	39.0	22	63.9
NiMnF	65.4	43.0	22.4	65.7
MnF	67.7	53.0	14.7	78.2

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

The better catalytic activity of MnF as compared to NiF can be ascribed due to its higher acidity. With the increase of 'x' value the yield and selectivity of 2-methyl-1-naphthol reaches maximum because acidic sites favor 2-methyl-1-naphthol formation.

3.2 Effect of reaction temperature

A series of 1-naphthol alkylation reactions were performed in the temperature range of 548-673 K over MnF and the results are shown in Table 4. It has been found that the temperature has a marked influence on the 1-naphthol conversion and product distribution. The maximum yield of 2-methyl-1-naphthol was obtained at 573 K. However, further increase in temperature reduced the yield and selectivity of 2-methyl-1-naphthol probably due to the deep ring methylation and coke deposition at higher reaction temperature.

Table 4: Effect of reaction temperature on 1-naphthol methylation (catalyst-MnFe₂O₄, methanol to 1-naphthol molar ratio 3:1, WHSV 0.4 h⁻¹)

Temperature	1-Naphthol Conversion (%)	2-Methyl-1-naphthol Yield (%)	Others*	2-Methyl-1-naphthol Selectivity (%)
548	47.5	29.7	17.8	62.5
573	67.7	53	14.7	78.2
623	74.4	32.3	42.1	43.4
673	61.1	21.5	39.6	35.1

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

3.3. Effect of methanol to 1-naphthol molar ratio

In order to understand the optimum feed mixture ratio, a series of experiments were performed at temperature of 573 K and 0.4 h⁻¹ WHSV with different molar ratio of methanol to 1-naphthol over MnF. The results are depicted in Fig. 3. 1-Naphthol conversion and selectivity of 2-methyl-1-naphthol increased with increase in molar ratio, reaching a maximum at 3:1 and further increase in feed ratio, decrease in the selectivity of 2-methyl-1-naphthol was probably due to the unavailability of active sites for 1-naphthol over the catalyst surface.

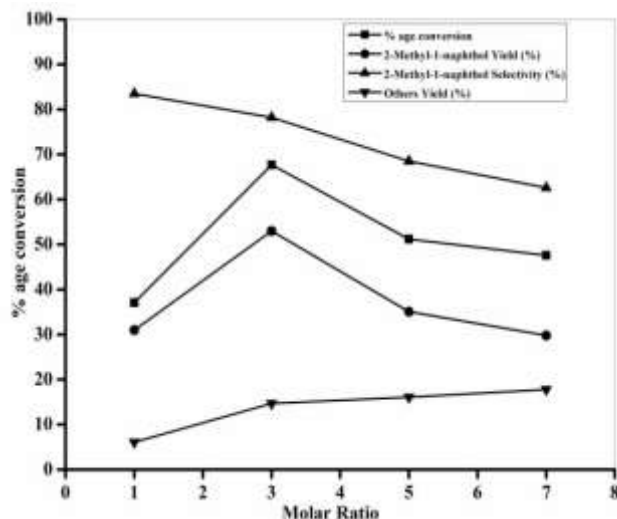


Figure 3: Effect of methanol to 1-naphthol molar ratio on the methylation of 1-naphthol (catalyst-MnF, temperature 573 K, WHSV 0.4 h⁻¹)

3.4. Effect of weight hour space velocity (WHSV)

The effect of WHSV on methylation of 1-naphthol was studied over MnF catalyst at 573 K and 3:1 molar ratio in the range 0.2 to 0.6 h⁻¹ WHSV as shown in Fig. 4. 1-Naphthol conversion increases with increase in WHSV and reaches a maximum at 0.4 h⁻¹, further increase in WHSV results decrease in 1-Naphthol conversion probably due to 1-naphthol gets less time to go into the product side.

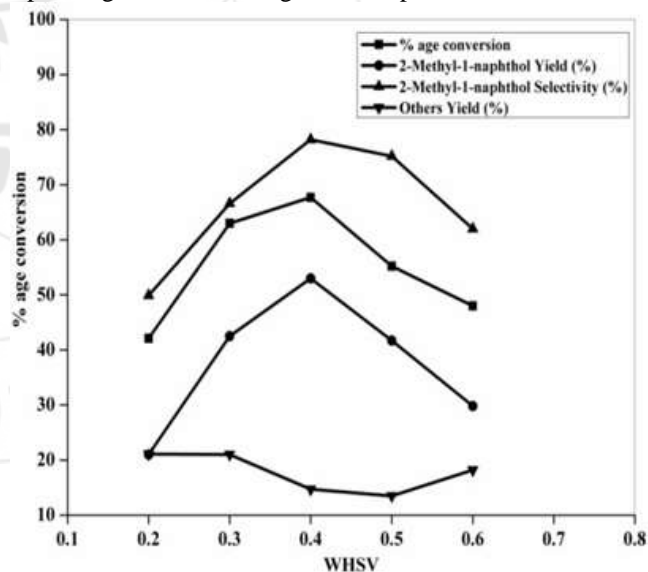
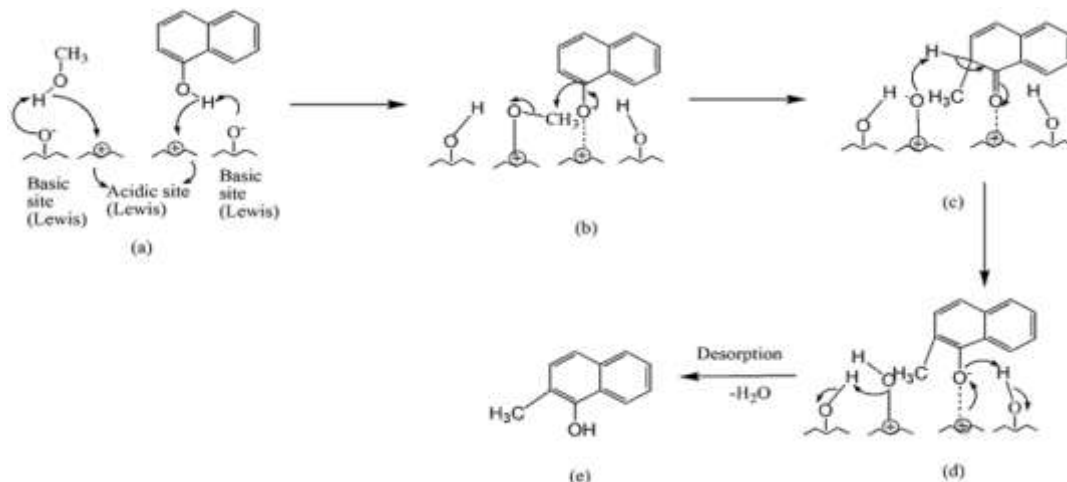


Figure 4: Effect of WHSV on the methylation of 1-naphthol (catalyst-MnF, temperature 573 K, molar ratio 3:1)

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* [22]. 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. Dehydroxylation activity of cations, repeated methylation of naphthoxide ion leads to the formation of polymethylnaphthalenes at high reaction temperature.

5. Conclusions

The maximum yield of 53.0% with selectivity 78.2% of 2-methyl-1-naphthol was obtained over MnFe_2O_4 ferrite under the optimized parameters at temperature 573 K, molar ratio 3:1 and WHSV 0.4 h^{-1} . The performance of the system was dependent on the reaction parameters.

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