

Vapour Phase Methylation of Phenol Over $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ Type Ferrites

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Methylation of phenol with methanol has been studied over $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.25, 0.5, 0.75, 1.0$) type ferrites prepared via low temperature co-precipitation method. Alkylation of phenol in vapour phase leads to *o*-methylation of phenol yielding *o*-cresol and 2,6-xyleneol as the major products. A maximum yield of 18.3 and 62.1 % were obtained for *o*-cresol and 2,6-xyleneol, respectively with total *ortho*-selectivity ≥ 97 % under optimized conditions of temperature 598 K, methanol/phenol ratio 6 and weight hour space velocity (WHSV) 0.5 h^{-1} . Phenol conversion and selectivity for *o*-cresol and 2,6-xyleneol depends on the acidic-basic properties of the catalysts. The selectivity for *o*-cresol was maximum when $x = 0$, whereas 2,6-xyleneol selectivity increases as the value of x increases and become maximum when $x = 1$. The catalyst characterization was made by XRD, FTIR, NH_3 -TPD and BET-SA measurements.

Key Words: Ferrites, *o*-Cresol and 2,6-Xyleneol.

INTRODUCTION

Ortho-alkylated phenols like *o*-cresol and 2,6-xyleneol are industrially important compounds, which are extensively, used as starting materials in agrochemicals, polymers and other industries¹⁻⁴. The stringent specifications and demand for these compounds necessitate the development of better catalytic systems for the selective synthesis of *o*-cresol and 2,6-xyleneol. In past, a variety of catalysts based on zeolites, metal oxides such as MgO-based^{5,6}, V_2O_5 based^{7,8}, Al containing hydrotalcites^{9,10} and rare earth metal oxides such as CeO_2 , La_2O_3 ¹¹, etc. has been employed to produce *o*-cresol and 2,6-xyleneol. Recently methylation of phenol has been investigated over ferrites^{11,12}. Ferrites are well known for their magnetic, electrical and catalytic properties¹³⁻¹⁵. The general structure of ferrites with spinel structure is $\text{M}^{2+}_{\text{tet}}[\text{Fe}^{3+}_{\text{octa}}]_2\text{O}_4$. The introduction of a third metal modifies the distribution of ions in the spinel structure. The nature and distribution of metal

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ions among tetrahedral and octahedral sites significantly influence the acidic-basic properties of ferros spinels¹¹⁻¹⁴. The present study is based on the ferrite system having composition $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.25, 0.5, 0.75, 1.0$). Varying the $\text{Ni}^{2+}/\text{Mn}^{2+}$ ratio can increase the selectivity for a particular product, *viz.*, *ortho*-cresol or 2,6-xyleneol. During the experimental conditions only traces of O-alkylated products like anisole and hardly any other xyleneol or cresol isomers were detected.

EXPERIMENTAL

Catalyst preparation

Preparation of NiFe_2O_4 (NF-1): A solution of 1.2 mol of NaOH in 150 cm³ of water was allowed to react with a solution of 0.075 mol of NiCl_2 in 50 cm³ of water. The resulting solution was added to a 5 dm³ beaker containing 0.15 mol of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 2.5 dm³ 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 phenolphthalein colour was obtained. The product was washed by repeated decantation with 2.5 dm³ portions of water until the supernatant was free of Cl^- (*ca.* 15 washings were required), filtered through a sintered glass filter, dried in an oven at 393 K and calcined at 773 K for 16 h. Finally the product was sieved through a sieve of 6/10 mesh size.

Preparation of other catalysts: Preparation of MnFe_2O_4 (MF-5) was similar to that of NiFe_2O_4 (NF-1) described above, except that now 0.075 mol of MnCl_2 were used in place of NiCl_2 . Similarly, $\text{Ni}_{0.75}\text{Mn}_{0.25}\text{Fe}_2\text{O}_4$ (NMF-2), $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ (NMF-3) and $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{Fe}_2\text{O}_4$ (NMF-4) by taking 0.0562, 0.0375 and 0.0188 mol of NiCl_2 salt and 0.0188, 0.0375 and 0.0562 mol of MnCl_2 salt, respectively.

Catalyst characterization, surface area and acidity measurements

Catalysts were characterized by X-ray diffraction (XRD), BET surface area, infrared spectroscopy and NH_3 -TPD methods.

X-ray diffraction of NF-1, NMF-3 and MF-5 was recorded on a Rigaku diffractometer with $\text{Cu-K}\alpha$ radiation and is reproduced in Fig. 1. All the peaks in the pattern match well with the characteristic reflections of corresponding ferrites and confirm the phase purity of samples.

The FTIR spectra of the ferrites were recorded on Shimadzu FTIR 8000 series and are reproduced in Fig. 2. Two broad bands at 700 and 500 cm^{-1} can be assigned to metal-oxygen stretching frequencies. Both metal-oxygen bonds can be assumed to have same force constants. Since tetrahedral metal-oxygen ($T_d \text{ M-O}$) bonds are associated with the metal of lower mass¹¹, this stretching frequency is expected to appear at higher frequency compared to metal-oxygen stretching of octahedral ($O_h \text{ M-O}$) sites. Hence

the band appearing at 700 cm^{-1} is assigned to the metal-oxygen stretching mode of the tetrahedral group, whereas band at 500 cm^{-1} can be assigned to the metal-oxygen stretching mode of the octahedral group.

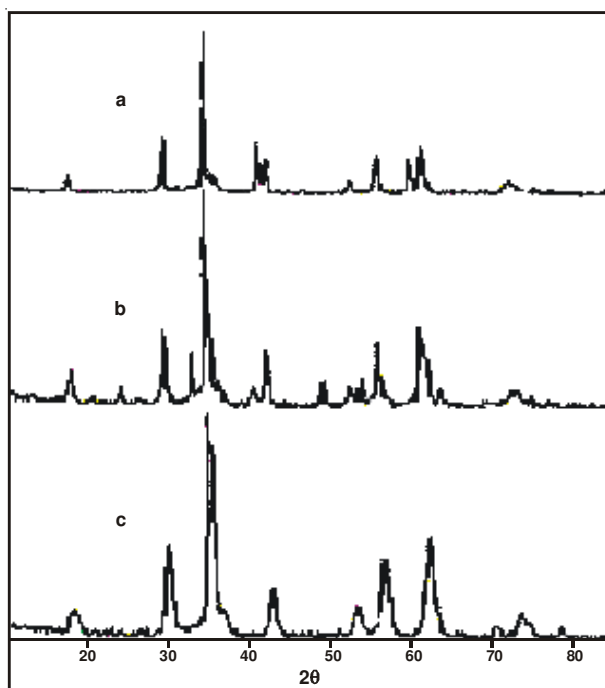


Fig. 1. X-ray diffractograms of (a) NF-1 (b) MF-5 (c) NMF-3

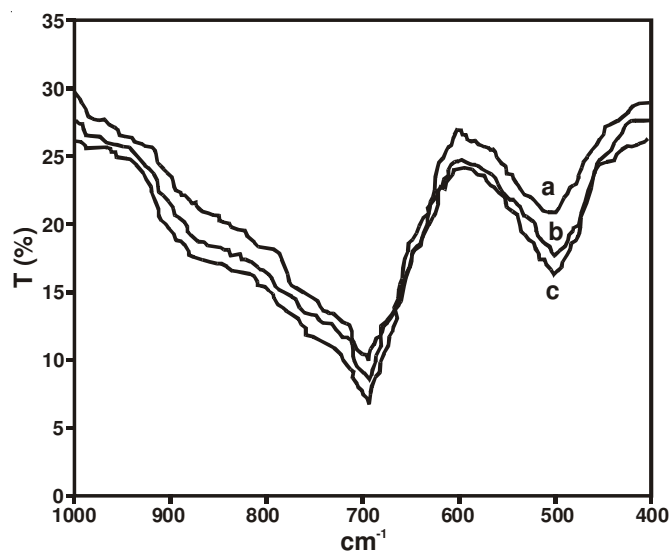


Fig. 2. IR spectra of (a) MF-5 (b) NF-1 (c) NMF-3

Temperature programmed NH_3 desorption (TPD) experiments were carried out to measure the acidity of catalysts using procedure given elsewhere¹¹ and results are presented in Table-1. The BET surface areas of ferrites were determined on OMNISORP 100 CX instrument and the results are presented in Table-1.

TABLE-1
COMPOSITIONAL PARAMETER 'x' ($\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$), ACIDITY AT DIFFERENT TEMPERATURES, CATALYTIC ACTIVITY (PHENOL CONVERSION AT TEMPERATURE 598K, WHSV 0.5 h^{-1} , MOLAR RATIO 6) AND BET SURFACE AREA (m^2/g) OF FERRITE CATALYSTS

x	Acidity (NH_3 uptake in mmol/g)			Total acidity	Catalytic acidity (phenol conversion)	BET surface area (m^2/g)
	423-523 K	523-623 K	623-723 K			
0.00	0.38	0.34	0.36	1.08	45.7	73.25
0.25	0.39	0.34	0.37	1.10	60.9	67.26
0.50	0.40	0.35	0.38	1.13	73.6	60.34
0.75	0.42	0.36	0.40	1.18	79.8	50.17
1.00	0.43	0.37	0.42	1.22	82.5	43.73

Apparatus and procedure: Catalytic activities were determined by using a tubular fixed-bed micro reactor of 0.45 m length and 13 mm diameter. The upper half worked as preheater and lower half worked as reactor, where catalyst was packed between two plugs of glass wool and was activated at 773 K for 4 h under a flow of air and then brought down to the desired temperature by cooling in a current of nitrogen, exposed to a feed stream mixture of methanol and phenol. The gaseous products were condensed using a cold water coiled condenser. A gas chromatograph with FID, SE-30 and capillary column was used to analyze the liquid product mixture.

RESULTS AND DISCUSSION

Acidity, surface area and performance of various catalysts in the alkylation of phenol: Acidity and surface area data of various ferrite catalysts NF-1, NMF-2, NMF-3, NMF-4 and MF-5 are presented in Table-1. The performance of various catalysts in the alkylation of phenol is presented in Table-2. The order of catalytic activity of various catalysts were found to be MF-5 > NMF-4 > NMF-3 > NMF-2 > NF-1. The catalytic order reveals that acidity of catalysts increases as the value of x increases and better performance of MF-5 compared to NF-1 can be ascribed due to its higher acidity.

Catalytic activity and effect of catalysts composition on alkylation of phenol: Catalytic activity as a function of catalyst composition is shown in Figs. 3 and 4 and Table-2. The catalytic activity with respect to phenol

conversion was found to increase with increasing x values of $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ series. At lower x values the yield and selectivity of *o*-cresol was higher because *o*-cresol formation is favoured over catalysts with weak acid sites, whereas on increasing x values yield and selectivity of 2,6-xylenol was increased and reached to a maximum when $x = 1$, because 2,6-xylenol formation is favoured over catalysts with stronger acid sites¹¹. This is supported by gradual increase in yield and selectivity of 2,6-xylenol with increasing x values.

TABLE-2
PERFORMANCE OF VARIOUS CATALYSTS IN THE METHYLATION OF PHENOL (AT TEMPERATURE 598 K, WHSV 0.5 h⁻¹, MOLAR RATIO 6)

Catalysts	Phenol conversion	<i>o</i> -Cresol yield	2,6-Xylenol yield	<i>o</i> -Cresol selectivity	2,6-Xylenol selectivity	Others	Total <i>ortho</i> selectivity
NF-1	45.7	35.1	6.7	76.8	14.7	3.9	91.5
NMF-2	60.9	32.0	26.6	52.5	43.7	2.3	96.2
NMF-3	73.6	28.7	43.0	39.0	58.4	1.9	97.4
NMF-4	79.8	23.3	53.9	29.1	67.5	2.6	96.3
MF-5	82.5	18.3	62.1	22.1	75.2	2.1	97.3

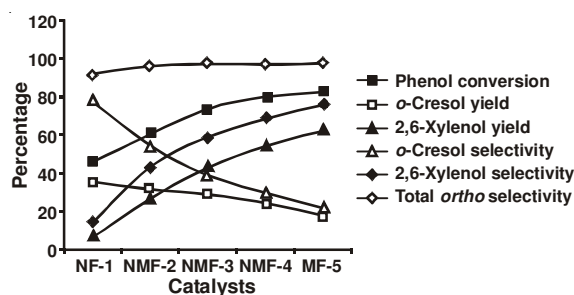


Fig. 3. Performance of various catalyst in phenol conversion (at temperature 598K, WHSV 0.5 h⁻¹, molar ratio 6)

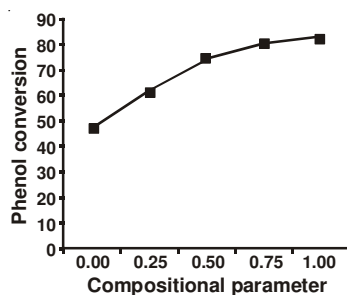


Fig. 4. Effect of compositional parameter ' x ' ($\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$) on phenol conversion (at temperature 598K, WHSV 0.5 h⁻¹, molar ratio 6)

Effect of temperature: Effect of temperature on methylation of phenol over MF-5 at methanol to phenol molar ratio 6 and WHSV 0.5 h^{-1} was investigated in the temperature range of 523-673 K and results are presented in Fig. 5. Phenol conversion increased with increase in the reaction temperature. The catalyst was most effective in the temperature range 573-598 K, with a maximum *o*-cresol yield 18.3 % and 2,6-xylene yield 62.1 % with total *ortho* selectivity 97.3 %. The selectivity for 2,6-xylene increased with temperature and reached to a maximum at 598 K, beyond 598 K yield and selectivity of 2,6-xylene decreased due to decrease in consecutive methylation of *o*-cresol¹¹. At higher temperature phenol conversion decreased due to charring and decomposition of carbon on the catalyst active sites.

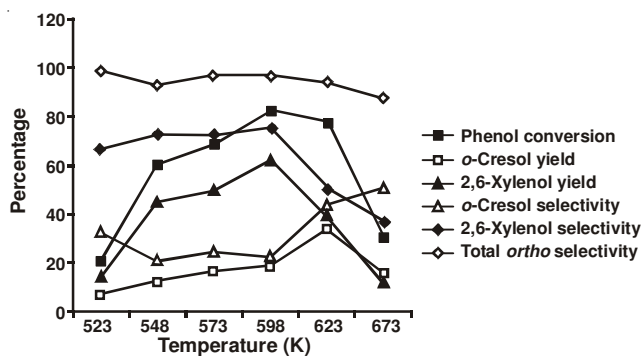


Fig. 5. Effect of temperature on methylation of phenol (Catalyst MnFe_2O_4 , WHSV 0.5 h^{-1} , methanol/phenol molar ratio 6)

Effect of molar ratio: The influence of methanol to phenol molar ratio on phenol methylation over MF-5 is shown in Fig. 6. Phenol conversion and selectivity for *o*-cresol and 2,6-xylene increased with increase in methanol to phenol molar ratio, reaching a maximum at 6:1 (methanol/phenol) and then reduced at higher molar ratio probably due to unavailability of active sites for phenol over catalyst surface. The increase in phenol conversion then decrease at higher molar ratio suggests Langmuir-Hinshelwood type bimolecular reaction.

Effect of weight hour space velocity (WHSV): The influence of WHSV on the methylation of phenol is reproduced in Fig. 7. Phenol conversion increased as the WHSV increased from 0.3 to 0.5 h^{-1} and decreased thereafter. The high contact time causing charring over catalyst active sites at 0.3 h^{-1} , hence low phenol conversion. Above 0.5 h^{-1} phenol conversion decreased due to decrease in contact time. Yield and selectivity for 2,6-xylene increased with decrease in flow rate and reached a maximum of 62.1 and 75.2 %, respectively at WHSV 0.5 h^{-1} . At higher WHSV

selectivity for *o*-cresol increased due to lack of consecutive methylation of *o*-cresol.

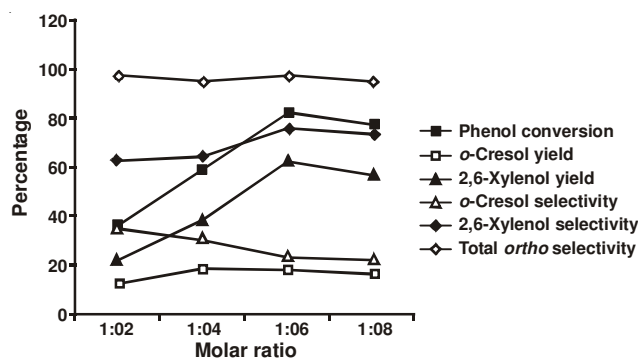


Fig. 6. Effect of methanol/phenol molar ratio on methylation of phenol (Catalyst MnFe_2O_4 , WHSV 0.5 h^{-1} , temperature 598 K)

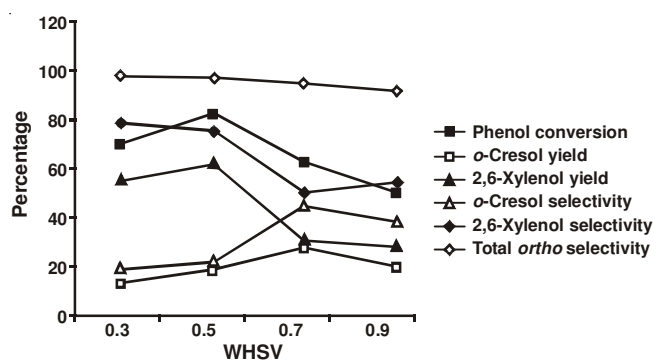
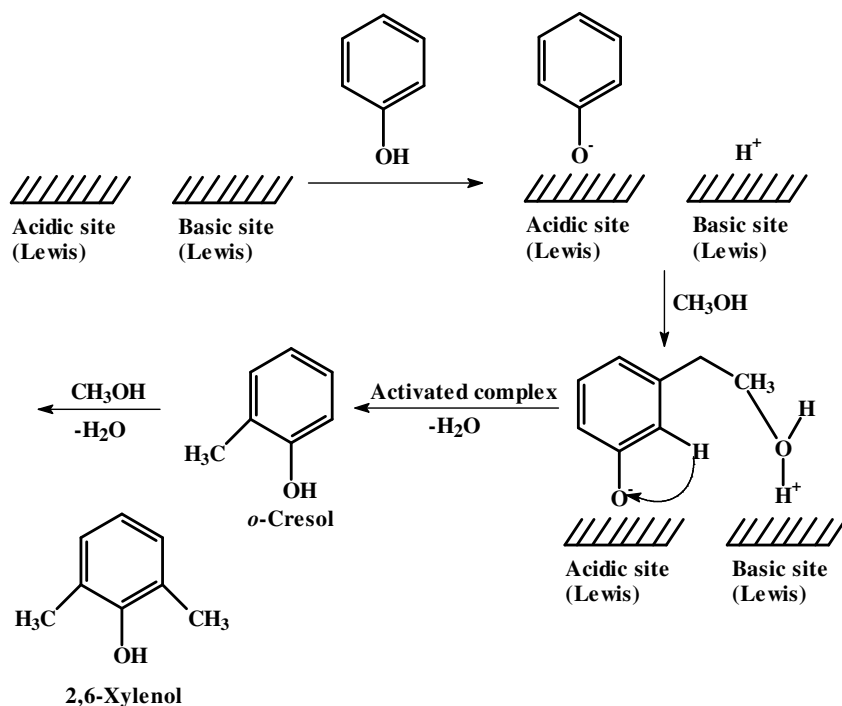


Fig. 7. Effect of WHSV (h^{-1}) on methylation of phenol (Catalyst MnFe_2O_4 , methanol/phenol molar ratio 6, temperature 598 K)

Mechanism: In general alkylation of phenol occurs at a ring position over acidic catalysts and at oxygen over basic catalysts¹⁷⁻¹⁹. Phenol can adsorb over catalyst surface either in a parallel¹² or perpendicular orientation¹⁶, the former promote *O*-alkylation and *p*-substituted products whereas later give *ortho*-substituted products. Since major products in the present study are *ortho*-substituted therefore, it may be concluded that phenol is perpendicularly adsorbed on the catalyst surface. Thus it seems phenol is perpendicularly to a Lewis acid site while methanol is adsorbed on the neighboring basic site. Methanol abstracts a proton from phenol and converts to a carbonium ion by losing a water molecule. The carbonium ion thus formed attack on the *ortho*-position of phenol leads to the formation of *o*-cresol. Further adsorption of *o*-cresol and methanol leads to the formation of 2,6-xylenol. The mechanism is shown in **Scheme-I**.



Scheme-I Mechanism of methylation of phenol

Conclusions

$Ni_{1-x}Mn_xFe_2O_4$ ($x = 0, 0.25, 0.5, 0.75, 1.0$) type ferrite system prepared *via* low temperature co-precipitation method was studied for the alkylation of phenol. The catalyst was found to have excellent selectivity for *ortho*-alkylation of phenol. The total *ortho*-selectivity was $\geq 97\%$. A maximum yield of 62.1% for 2,6-xyleneol and 18.3% for *o*-cresol was observed at 598 K temperature, methanol/phenol molar ratio 6 and WHSV 0.5 h^{-1} .

The catalytic activity and product selectivity strongly depends on the acidic-basic properties of catalysts. It was found that acidity of catalysts increased with increasing value of x . System possessing low x value were more selective for *o*-cresol, whereas increase in x values gave 2,6-xyleneol. Thus consecutive methylation increases as the value of x increased.

A tentative mechanism for *ortho*-selective methylation of phenol over $Ni_{1-x}Mn_xFe_2O_4$ catalyst system has been proposed *i.e.* phenol is perpendicularly adsorbed on a Lewis acid site by a lone pair of electron on the oxygen atom and is alkylated by methanol, which is possibly in the form of methyl carbonium ion.

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