



## Alkylation of Aniline using Methanol over Ferros spinels

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**ABSTRACT**

Various compositions of nickel manganese ferros spinels were tested as catalysts for the vapour phase alkylation of aniline with methanol. The samples were prepared by room temperature co-precipitation technique and characterized by various physico-chemical methods. All the ferrite samples were proved to be active for N-monoalkylation of aniline leading to N-methyl aniline.  $Ni_{0.8}Mn_{0.2}Fe_2O_4$  and  $NiFe_2O_4$  exhibited remarkable activity and cent percent selectivity for N-methyl aniline. Neither C-alkylated products nor any other side products were detected for all catalyst samples. The catalytic activity of the samples towards the alkylation of aniline is related their acid-base properties and also on the cation distribution. Under the optimized reaction conditions all the prepared ferros spinel systems showed constant activity, remarkable selectivity for N-monoalkylation and persistent stability for a long duration.

**KEYWORDS :** Ferros spinels, nickel manganese ferros spinels, Surface acidity, Surface basicity, Aniline alkylation, N-methyl aniline

**INTRODUCTION:**

Methylation of aniline is industrially important owing to the wide uses of various substituted anilines like N-methylaniline (NMA), N,N-dimethylaniline (NNDMA), toluidines and xylydines<sup>1,2</sup>. It is possible to selectively synthesize N-alkylated products, which are industrially more important by controlling the reaction parameters and acidity of the catalysts. Traditionally, these catalysts were carried out by the alkylation of aniline in liquid phase using mineral aids as catalysts ad alkyl halides or dimethyl sulphides as alkylating agents<sup>3,4</sup>. The intrinsic drawbacks coupled with the processes are very distinct to prevent their wised use in aniline alkylation. Consequently, use of various heterogeneous catalysts and non toxic alkylating agents such as methanol and dimethyl carbonate<sup>5-8</sup> are introduced. The results suggest that the aniline conversion and ad product selectivity depend on the nature of the catalysts and on the reaction conditions employed. The catalysts tried for the reaction yield better selectivity for N-alkylation than C-alkylation. But the selectivity for more important mono alkylated product is poor as both mono and di-substitution on nitrogen atom is viable. Besides high methanol to aniline molar ratio ad high temperature are required for a satisfactory aniline conversion. More-over these systems lack in maintaining a constant activity after a certain reaction period due to their reduced catalytic stability.

This paper reports on the activity and selectivity of  $Ni_xMn_{(1-x)}Fe_2O_4$  ( $x=0.0, 0.2, 0.4, 0.6, 0.8$  and  $1.0$ ) type ferros spinel systems in the vapour phase aniline alkylation using methanol as the alkylating agent in different reaction conditions. The catalysts are inexpensive and their preparation method is simple. The ferros spinel systems, of  $Ni_{0.8}Mn_{0.2}Fe_2O_4$  and  $NiFe_2O_4$  exhibited remarkable activity and selectivity for

The stoichiometry of the catalysts checked by inductively coupled plasma (ICP) analysis. The thermal stability of the samples was determined by TG analysis at a heating rate of  $10^\circ\text{C}/\text{min}$ . The BET surface area and pore volume of the samples were measured by nitrogen adsorption at liquid nitrogen temperature using a Micrometrics Gemini Analyser. The DRIFT spectra of the samples were taken in the  $400\text{--}1000\text{ cm}^{-1}$  region using Schimkadazu DR-IR.

**Surface properties – acidity/basicity**

The strength and distribution of acidity of the samples were determined by temperature programmed desorption (TPD) of ammonia. About 0.75 g of the samples were pelleted and activated at  $500^\circ\text{C}$  for 2 h. To remove the surface impurities further, the pellets were activated in the reactor at  $300^\circ\text{C}$  in a flow of nitrogen for half an hour. After cooling to the room temperature, ammonia gas was injected into the reactor and was allowed to adsorb on the samples in a uni-

form manner. The physisorbed ammonia was desorbed by a run of nitrogen gas. The acid strength distribution was obtained from  $100$  to  $600^\circ\text{C}$  in a flow of nitrogen in a number of steps. The ammonia evolved was trapped in dilute  $\text{H}_2\text{SO}_4$  solution and was titrated with standard NaOH solution. The ammonia desorbed in the temperature range of  $100^\circ\text{C}$ – $600^\circ\text{C}$  is divided into three different temperature regions ( $^\circ\text{C}$ ) such as  $100\text{--}200^\circ\text{C}$ ,  $201^\circ\text{C}$ – $400^\circ\text{C}$  and  $401^\circ\text{C}$ – $600^\circ\text{C}$  and assigned as weak, medium and strong acid sites respectively.

The thermodesorption studies of the samples of 2,6-dimethylpyridine (2-DMP) were implemented to investigate the relative amount of Bronsted acid sites in ferros spinel samples. For this the TG analysis of the 2-DMP absorbed samples at a heating rate of  $10^\circ\text{C}/\text{min}$  was take and the weight loss between  $300^\circ\text{C}$  and  $600^\circ\text{C}$  gave the measurement of Bronsted acidity.

**RESULTS & DISCUSSION****Structural analysis**

The XRD data well ascertained the formation of single spinel phase and crystallinity of the ferrites. The space lattice was found to be cubic. In the systems studied, the compositional differences are due to different proportion of Ni and Mn in pure  $\text{MnFe}_2\text{O}_4$ . These atoms have close atomic numbers and so, much alike XRD patterns. Using Scherrer equation<sup>12</sup>, the crystallite structure of each sample has been estimated to be in between 17 and 46 nm, establishing the fine structure of ferrite powders. The stoichiometry of the samples prepared by low temperature co-precipitation technique was in good agreement with the theoretical values as evident from inductively coupled plasma analysis (Table 1). The ferrite samples prepared by low temperature co-precipitation technique possess high surface area (Table 1). All compositions of the ferrite samples showed two strong IR bands,  $\nu_1$  and  $\nu_2$  at around  $700\text{ cm}^{-1}$  and  $500\text{ cm}^{-1}$  respectively, confirming the spinel phase formation<sup>13</sup>. The TG analysis revealed that all these ferrite systems are thermally stable in the range of  $150^\circ\text{C}$ – $800^\circ\text{C}$  without creating major weight loss and decompositions. Cation distributions between tetrahedral and octahedral sublattices characteristic of  $Ni_xMn_{(1-x)}Fe_2O_4$  system are also included in Table 1.

**Surface properties-acidity/basicity**

The study of surface acidity and basicity of solids are important as these properties have decisive roles in determining the catalytic activities and selectivities in reactions. The strength of the sites exposed on the surface and their distribution depends greatly upon the catalytic composition. The present system of ferrites studied contains normal spinels, inverse spinels and mixed spinels. According to Jacob et.al<sup>14</sup>, whatever be the type of spinel, the octahedral sites are

incorporation of nickel ions into the manganese ferros spinels in mixed Ni-Mn series. Thus the enhancement in the weak Lewis acidity is responsible for the improved weak plus medium acidity as evident from the NH<sub>3</sub>-TPD studies and TGA of 2,6-dimethyl pyridine adsorbed samples.

Since TCNQ is a strong electron acceptor it can form anion radicals adsorbed from strong as well as weak donor sites where as chloranil, a weak electron acceptor can accept electrons only from strong and moderately strong basic sites. As a result the limiting amount of TCNQ gives a measure of total amount of basic sites whereas limiting amount of chloranil signifies the measure of moderate and strong basic sites. The total basicity of this series (Table 2), as evident from the limiting amount of TCNQ adsorbed follows the order: M <<< NM-1 < NM-2 < NM-3 < NM-4 < N. Thus the increment in nickel content in the octahedral positions of pure manganese ferros spinels enhanced the basicity in the various types of basic sites as evident from the limiting amounts of TCNQ and chloranil adsorbed. The increment in nickel content in the octahedral sites did not alter the concentration of more acidic Fe<sup>3+</sup> in the octahedral site. The variation of basicity in different compositions of Ni-Mn series depend strongly on the Ni<sup>2+</sup>/ Mn<sup>3+</sup> ratio in the octahedral sites.

**CATALYTIC ACTIVITY**

**Alkylation of aniline using methanol:**

Aniline alkylation with methanol is a consecutive reaction, the primary product being NMA, which gets further alkylated to NNDMA and to C-alkylated anilines (intra molecular transformation). The formation of NNDMA and C-alkylated amines usually takes place at high temperature and high contact time.

**We could observe that with the**

The spinel compositions and cation valency distribution of the mixed Ni-Mn spinel ferrites are depicted in the Table 1. All the ferrites in this series are inverse in nature and the inverse nature increases with increase in 'x' values. The concentration of the Fe<sup>3+</sup> ions in the octahedral sites is same for all the compositions. Hence the catalytic activity is mainly determined by the amount of incorporated nickel ions in the octahedral sites. Thus, the improved catalytic activity of the

NM-4	4.68 (4.70)	20.07 (20.09)	85.78	Mn <sub>0.1</sub> <sup>2+</sup> Fe <sub>0.9</sub> <sup>3+</sup>	Fe <sub>0.1</sub> <sup>2+</sup> Fe <sub>1</sub> <sup>3+</sup> Mn <sub>0.1</sub> <sup>3+</sup> Ni <sub>0.8</sub> <sup>2+</sup>
N	--	25.03 (25.04)	75.63	Fe <sup>3+</sup>	Fe <sup>3+</sup> Ni <sup>2+</sup>

<sup>a</sup>Quantities in the parentheses indicate the theoretical value.

**Table 2.**

**The amount of ammonia desorbed, the amount of 2,6-DMP desorbed and limiting amounts of electron acceptors adsorbed over Ni<sub>x</sub>Mn<sub>(1-x)</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0)**

Catalyst	NH <sub>3</sub> desorbed (10 <sup>3</sup> mmol m <sup>-2</sup> )				2,6-DMP desorbed (wt.% loss)	Limiting amounts of electron acceptors adsorbed (10 <sup>-4</sup> mmol m <sup>-2</sup> )	
	Weak	Medium	TCNQ Strong	Chloranil Total			
M	3.85	4.27	8.38	16.50	0.825	10.71	2.6
NM-1	3.86	4.70	7.80	16.36	0.824	20.81	6.41
NM-2	3.88	4.86	7.53	16.27	0.823	22.47	7.00
NM-3	3.90	4.90	7.33	16.13	0.820	23.13	7.58
NM-4	3.93	5.00	7.14	16.07	0.817	24.97	7.92
C	3.95	5.04	7.04	16.03	0.814	25.52	8.91

**Table 3. Alkylation of aniline with methanol over Ni<sub>x</sub>Mn<sub>(1-x)</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 0, 0.2, 0.4, 0.6, 0.8 and 1.0)- type systems**

Catalyst	Aniline conversion (%)	NMA Yield (wt %)	Product distribution (%)		
			NMA	NNDMA	Toluidine
MnFe <sub>2</sub> O <sub>4</sub>	22.45	13.12	78.72	13.73	7.55
Ni <sub>0.2</sub> Mn <sub>0.8</sub> Fe <sub>2</sub> O <sub>4</sub>	23.73	35.36	91.12	7.28	1.60
Ni <sub>0.4</sub> Mn <sub>0.6</sub> Fe <sub>2</sub> O <sub>4</sub>	25.57	39.37	93.01	5.81	1.18
Ni <sub>0.6</sub> Mn <sub>0.4</sub> Fe <sub>2</sub> O <sub>4</sub>	27.16	45.52	95.32	3.71	0.97
Ni <sub>0.8</sub> Mn <sub>0.2</sub> Fe <sub>2</sub> O <sub>4</sub>	28.79	58.73	100	---	---

Ni-Mn series is due to the enhancement in weak Lewis acidity by the successive nickel doping.

**CONCLUSIONS**

Various compositions of nickelmanganese ferros spinels with general formula Ni<sub>x</sub>Mn<sub>(1-x)</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) can be effectively used for the alkylation of aniline with methanol as the alkylating agent. The acid-base properties of the catalysts vary with the successive incorporation of nickel ions into the pure manganese ferros spinel. All the catalyst samples especially NM-4 and N exhibited high activity, remarkable selectivity and persistent stability for aniline conversion and NMA selectivity. Large excess of alkylating agent and very high temperature are not required for the reaction. These catalysts were found to be reusable even after repeated use.

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**Table 1. ICP analysis data, surface areas and cation distribution of the system, of Ni<sub>x</sub>Mn<sub>(1-x)</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0)**

Catalyst	ICP analysis data <sup>a</sup>		Surface area (m <sup>2</sup> /g)
	Mn%	Ni%	
M	23.82 (23.82)	--	153.3
NM-1	18.98 (18.99)	5.05 (5.07)	112.95
NM-2	14.18 (14.19)	10.09 (10.11)	105.28
NM-3	9.43 (9.43)	15.12 (15.10)	97.23

NiFe <sub>2</sub> O <sub>4</sub>	30.29	56.78	100	---	---
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Reaction temperature-350°C, MeOH/ aniline-5, TOS- 2 h and flow rate -5mL/h.

Cations at	
Tetrahedral site	Octahedral site
Mn <sub>0.5</sub> <sup>2+</sup> Fe <sub>0.5</sub> <sup>3+</sup>	Fe <sub>0.5</sub> <sup>2+</sup> Fe <sub>0.5</sub> <sup>3+</sup> Mn <sub>0.5</sub> <sup>3+</sup>
Mn <sub>0.4</sub> <sup>2+</sup> Fe <sub>0.6</sub> <sup>3+</sup>	Fe <sub>0.4</sub> <sup>2+</sup> Fe <sub>1</sub> <sup>3+</sup> Mn <sub>0.4</sub> <sup>3+</sup> Ni <sub>0.2</sub> <sup>2+</sup>
Mn <sub>0.3</sub> <sup>2+</sup> Fe <sub>0.7</sub> <sup>3+</sup>	Fe <sub>0.3</sub> <sup>2+</sup> Fe <sub>1</sub> <sup>3+</sup> Mn <sub>0.3</sub> <sup>3+</sup> Ni <sub>0.4</sub> <sup>2+</sup>
Mn <sub>0.2</sub> <sup>2+</sup> Fe <sub>0.8</sub> <sup>3+</sup>	Fe <sub>0.2</sub> <sup>2+</sup> Fe <sub>1</sub> <sup>3+</sup> Mn <sub>0.2</sub> <sup>3+</sup> Ni <sub>0.6</sub> <sup>2+</sup>

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