

Selective alkylation of aniline to *N*-methyl aniline using chromium manganese ferros spinels

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Abstract

Various compositions of chromium 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. The acidity–basicity determination revealed that the samples possess greater amount of basic sites than acidic sites. All the ferrite samples proved to be selective and active for *N*-monoalkylation of aniline leading to *N*-methyl aniline; $\text{Cr}_{0.6}\text{Mn}_{0.4}\text{Fe}_2\text{O}_4$, $\text{Cr}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$ and CrFe_2O_4 exhibited 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 studied in this reaction is related to their acid–base properties and also on the cation distribution. Under the optimized reaction conditions all the systems showed constant activity for a long duration.

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1. Introduction

N-Methyl aniline is an industrially important product as it is an essential intermediate in the manufacture of paper and textile dyes, drugs, perfumes and explosives [1]. Traditionally, these reactions were carried out by the alkylation of aniline in liquid phase using mineral acids as catalysts and alkyl halides or dimethyl sulphate as alkylating agents [2–4]. The intrinsic drawbacks coupled with the processes are very distinct to prevent their wide use in aniline alkylation. Consequently, use of various heterogeneous catalysts and non-toxic alkylating agents such as methanol and dimethyl carbonate [5–13] are introduced. The results suggest that the aniline conversion and product selectivity depend on the nature of the catalysts and on the reaction conditions employed. The metal oxides tried for the reaction yield better selectivity for *N*-alkylation than C-alkylation. But the selectivity for synthetically more important monoalkylated product is poor as both mono and di-substitution on nitrogen atom is viable in majority of the cases. Besides high methanol to aniline molar ratio and high reaction temper-

ature are needed for a satisfactory aniline conversion and product selectivity. More to the point most of the systems lack in maintaining a constant activity after a certain reaction period due to their reduced catalytic stability.

Many of the reports available in the literature reveal the dependence of acid–base properties of the catalysts and aniline alkylation [14–26]; the type and strength of acidic and basic sites have been an area under discussion. Though small amount of basic sites in zeolites exhibit more activity in the methylation of aniline, an excessive amount of basicity might cover the active sites and deactivate the catalyst [15–18]. Woo et al. [15,16] investigated the selective alkylation of aniline with methanol over several metallosilicates. They suggested that weak and moderate acid sites are sufficient for the *N*-alkylation whereas strong sites are mandatory for ring alkylation and coke formation. According to Narayanan and Deshpande [19–21], a combination of Brønsted and Lewis acid sites on the catalyst surface is more favourable for aniline alkylation. Ko et al. [22] proposed a mechanism in which aniline and methanol are adsorbed undissociatively on the Lewis acid–base dual sites of γ -alumina and electrophilic attack of the methyl group of methanol on the nitrogen atom of aniline results in favourable formation of *N*-methylated products. Ferros spinels possess a variety of acid and basic sites and can be

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used as catalysts for numerous reactions including aniline alkylation.

This paper reports on the activity and selectivity of $\text{Cr}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8$ and 1.0) type ferrosipinel 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. Interestingly, ferrosipinel systems such as $\text{Cr}_{0.6}\text{Mn}_{0.4}\text{Fe}_2\text{O}_4$, $\text{Cr}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$ and CrFe_2O_4 exhibited remarkable activity and selectivity for *N*-monomethylation of aniline. Furthermore, large excess of alkylating agent or high reaction temperature are not required for the appreciable aniline conversion and *N*-methyl aniline selectivity. We detected no C-alkylated products for chromium substituted manganese ferrosipinels, which is another significant feature of the system. Unlike the other conventional systems the catalyst samples showed a persistent activity for a long reaction period. A thorough investigation of the physico-chemical characterisation of prepared systems giving prominence on the acidity–basicity estimation is also accounted.

2. Experimental

2.1. Catalyst preparation

In the present study, various spinel compositions viz. MnFe_2O_4 (MF), $\text{Cr}_{0.2}\text{Mn}_{0.8}\text{Fe}_2\text{O}_4$ (CMF-1), $\text{Cr}_{0.4}\text{Mn}_{0.6}\text{Fe}_2\text{O}_4$ (CMF-2), $\text{Cr}_{0.6}\text{Mn}_{0.4}\text{Fe}_2\text{O}_4$ (CMF-3), $\text{Cr}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$ (CMF-4) and CrFe_2O_4 (CF) were prepared by a low temperature co-precipitation technique [27]. Initially, calculated amounts of the corresponding nitrate salts were dissolved in doubly distilled water and the precipitation of the hydroxide was carried out at a controlled pH of 9–10 using 5 M NaOH solution at room temperature with vigorous stirring. The precipitate was washed several times with doubly distilled water to remove the excess nitrate ions and alkali. It was then filtered, washed, dried in an air oven at 80°C for 36 h, powdered, sieved below $100\text{ }\mu\text{m}$ mesh and calcined at 500°C for 5 h to achieve the spinel phase.

2.2. Catalyst characterisation

2.2.1. Structural analysis

The catalyst samples were activated at 500°C for 2 h before each characterisation technique. The X-ray diffractograms of the samples were taken using RIGAKU D/MAX-C instrument with Cu $\text{K}\alpha$ radiation. The stoichiometry of the catalyst was checked by inductively coupled plasma (ICP) using ARL 3410 ICP atomic emission spectrometer. The thermal stability of the oven-dried samples was determined by Shimadzu Thermogravimetric analyser (TGA-50) in nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$. The BET surface area of the samples was measured by nitrogen adsorption at liquid nitrogen temperature using a Micrometrics Gemini Analyser. The DRIFT

spectra of the samples were taken in the $400\text{--}1400\text{ cm}^{-1}$ region using Shimadzu DR-IR.

2.2.2. 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 pelletised and activated at 500°C for 2 h. To remove the surface impurities further, the pellets were activated in the reactor at 300°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 uniform manner. The physisorbed ammonia was desorbed by a run of nitrogen gas. The acid strength distribution was obtained from temperature programmed desorption of ammonia from 100 to 600°C in a flow of nitrogen in a number of steps. The ammonia evolved was trapped in dilute H_2SO_4 solution and was titrated with standard NaOH solution.

The thermodesorption studies of the samples after adsorption of 2,6-dimethylpyridine (2-DMP) were implemented to investigate the relative amount of Brönsted acid sites in ferrosipinel samples. In this case the TG analysis of the 2-DMP adsorbed samples at a heating rate of $10^\circ\text{C}/\text{min}$ was taken and the weight loss between 300 and 600°C gave the measure of Brönsted acidity.

The evaluation of the Lewis basicity of the systems by the adsorption of the electron acceptors having different electron affinity values has been well established [28–30]. 7,7,8,8-Tetracyanoquinodimethane (TCNQ); 2,3,5,6-tetrachloro-4-benzoquinone (chloranil) and *p*-dinitrobenzene (PDNB) with electron affinity values 2.84, 2.4 and 1.77 eV, respectively, in acetonitrile as solvent were employed for the present study. The catalysts were activated at 500°C and were placed in an airtight cylindrical glass vessel. A 10 ml solution of the electron acceptor of choice in the acetonitrile solution was added. The solution was stirred for 4 h at room temperature. The amount of electron acceptor adsorbed was determined by means of UV-Vis spectrophotometry by noting the absorbance of the solution of electron acceptor before and after adsorption at the λ_{max} of electron acceptor in acetonitrile.

2.3. Catalytic activity

The alkylation reactions were carried out in a fixed-bed down—flow silica reactor of 1 cm i.d. and 30 cm length in the temperature range $250\text{--}450^\circ\text{C}$ under atmospheric pressure. 0.5 g of the catalyst activated at 500°C for 2 h was sprinkled over loosely packed glass wool placed at the center of the reactor. The temperature was controlled by a Cr-Al thermocouple placed inside the reactor. The feed mixture (aniline and methanol) was admitted to the reactor by means of a syringe pump. Evolved gases from the reactor were passed through a condenser and on to a collector that allowed liquids to be withdrawn at required time intervals. The products were analysed by gas chromatography (Chemito GC 8610),

and were identified by GC-MS. A blank run was carried out at 350 °C in the reactor indicated negligible thermal reaction.

3. Results and discussion

3.1. Structural analysis

The XRD data 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 Cr and Mn in pure MnFe_2O_4 . These atoms have close atomic numbers and so, much alike XRD patterns. The X-ray diffractogram of mixed Cr-Mn spinel, CMF-4 is presented in Fig. 1. Using Scherrer equation [31], the crystallite size of each sample has been estimated to be in between 17 and 46 nm, establishing the fine nature of the ferrite powders. The stoichiometry of the samples prepared by the low temperature

co-precipitation technique was in good agreement with the theoretical values as evident from the inductively coupled plasma analysis (Table 1). The TG analysis revealed that all these ferrite systems are thermally stable in the temperature range of 150–800 °C without creating major weight loss and decompositions. The ferrosinels prepared by the low temperature co-precipitation technique possess high surface area (Table 1). All compositions of the ferrite system showed two strong IR bands, ν_1 and ν_2 at around 700 and 500 cm^{-1} , respectively, confirming the spinel phase formation [32,33]. Cation distributions between tetrahedral and octahedral sublattices characteristic of $\text{Cr}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ system are also included in Table 1.

3.2. Surface properties—acidity/basicity

Ferrosinels possess both Lewis and Brönsted acid sites and Lewis basic sites. According to Jacob et. al [34] the spinel surface sites are exposed with octahedral cations. The

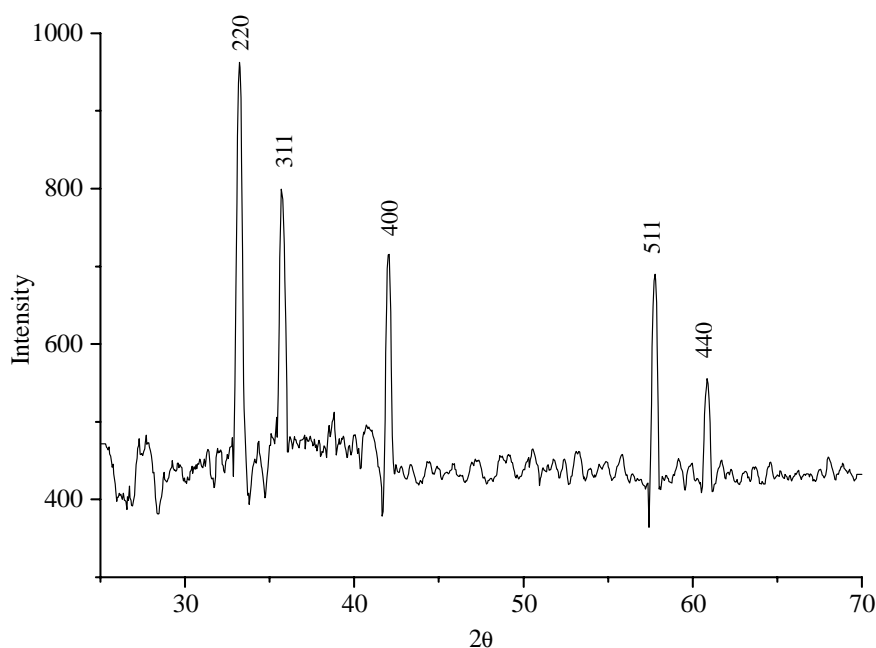


Fig. 1. X-ray diffractogram of CMF-4 calcined at 500 °C.

Table 1

ICP analysis data, surface area and cation distribution of the system $\text{Cr}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8$ and 1)

x	ICP analysis data ^a		Surface area (m^2/g)	Cations at	
	Mn%	Cr%		Tetrahedral site	Octahedral site
0.0	23.82 (23.82)	—	153.30	$\text{Mn}_{0.5}^{2+}\text{Fe}_{0.5}^{3+}$	$\text{Fe}_{0.5}^{2+} \text{Fe}^{3+}\text{Mn}_{0.5}^{3+}$
0.2	19.09 (19.10)	4.50 (4.52)	65.32	$\text{Mn}_{0.4}^{2+}\text{Fe}_{0.6}^{3+}$	$\text{Fe}_{0.6}^{2+} \text{Fe}_{0.8}^{3+}\text{Mn}_{0.4}^{3+} \text{Cr}_{0.2}^{3+}$
0.4	14.35 (14.36)	9.05 (9.06)	54.31	$\text{Mn}_{0.3}^{2+}\text{Fe}_{0.7}^{3+}$	$\text{Fe}_{0.7}^{2+} \text{Fe}_{0.6}^{3+}\text{Mn}_{0.3}^{3+} \text{Cr}_{0.4}^{3+}$
0.6	9.59 (9.60)	13.63 (13.63)	47.58	$\text{Mn}_{0.2}^{2+}\text{Fe}_{0.8}^{3+}$	$\text{Fe}_{0.8}^{2+} \text{Fe}_{0.4}^{3+}\text{Mn}_{0.2}^{3+} \text{Cr}_{0.6}^{3+}$
0.8	4.80 (4.81)	18.22 (18.22)	41.06	$\text{Mn}_{0.1}^{2+}\text{Fe}_{0.9}^{3+}$	$\text{Fe}_{0.9}^{2+} \text{Fe}_{0.2}^{3+}\text{Mn}_{0.1}^{3+} \text{Cr}_{0.8}^{3+}$
1.0	—	22.83 (22.83)	35.76	Fe^{3+}	$\text{Fe}^{2+} \text{Cr}^{3+}$

^a 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 $\text{Cr}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8$ and 1)

x	NH ₃ desorbed (10 ⁻³ mmol m ⁻²)				2,6-DMP desorbed (wt.% loss)	Limiting amount of electron acceptor adsorbed (10 ⁻⁴ mmol m ⁻²)	
	Weak	Medium	Strong	Total		TCNQ	Chloranil
0.0	3.85	4.27	8.38	16.5	0.825	10.71	2.60
0.2	3.88	4.31	2.37	10.6	0.300	55.52	22.79
0.4	3.97	4.39	2.12	10.5	0.261	56.28	25.19
0.6	4.02	4.41	1.95	10.4	0.233	57.58	30.67
0.8	4.08	4.45	1.80	10.3	0.208	59.01	35.29
1.0	4.15	4.50	1.61	10.2	0.187	60.61	38.58

octahedral M–O bond is weaker and more polar than the tetrahedral M–O bond [35] and hence acidic sites in spinels are mostly dependent on the nature of octahedral cations. Electron donor properties or basicity of the catalysts come from the surface hydroxyl groups or from the coordinately unsaturated oxygen anion or from the electron trapped in intrinsic defects [36]. In the $\text{Cr}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ system varying x from 0 to 1 has a profound effect on the catalyst structure in that chromium replaces both Mn^{3+} and Fe^{3+} ions in octahedral sites. Thus, the successive incorporation of chromium ions into the pure manganese ferros spinel show significant variation in the acid–base properties of the system.

Ammonia is frequently used as a probe molecule because of its small molecular size, stability and strong basicity. TPD of ammonia can be used to characterise the strength and distribution of acidic sites and furthermore to obtain the quantitative amount of acid sites in a particular temperature range [37]. The amount of ammonia desorbed in weak (100–200 °C), medium (201–400 °C) and strong (401–600 °C) acid regions are shown in Table 2. The progressive addition of chromium ions into the pure manganese ferros spinel decreases the total acidity as well as acidity in the strong region whereas the weak and the medium acidic sites were pronounced. NH₃-TPD method lacks in discriminating the type of acid sites (Brönsted and Lewis). However, it is generally accepted that evacuation of ammonia adsorbed surface at 400 °C removes most of the Brönsted acid sites [38]. Thus, it can be inferred that the acidity in the weak plus medium region is due to the Brönsted and weak Lewis acid sites. The cation distribution reveals that this series of ferrites contain Mn^{3+} , Fe^{3+} , Fe^{2+} and Cr^{3+} ions in the octahedral site and relative concentration of these ions are mainly responsible for the acidity of the individual systems. The successive substitution of Mn by Cr decreased the amount of more acidic Fe^{3+} and Mn^{3+} ions in the octahedral sites and this is the reason for the decrease in the strong acidity values and subsequent increase in the weak plus medium acidity.

2,6-Dimethylpyridine (2,6-DMP) adsorbs strongly on Brönsted acid sites and forms weak bonds with Lewis acid sites [39]. According to Satsuma et al. [40] the 2,6-DMP weakly bound to Lewis acid sites, get desorbed below 300 °C. Hence, thermodesorption study of 2,6-dimethylpyri-

dine adsorbed samples beyond 300 °C can give the measure of Brönsted acid sites. The detection of Brönsted acid sites by 2,6-DMP may be due to its stronger basicity (higher $\text{p}K_a$ value) than that of pyridine [37]. It is assumed that the weak plus medium acidity obtained from NH₃-TPD studies is mainly due to Brönsted as well as weak Lewis acid sites. From Table 2, it is clear that the relative amount of Brönsted acidity is reduced by the successive incorporation of chromium ions into the manganese ferros spinels in mixed Cr-Mn series. Thus, the enhancement in the weak Lewis acidity is responsible for the improved weak plus medium acidity as evident from the NH₃-TPD studies.

Since TCNQ is a strong electron acceptor it can form anion radicals adsorbed from strong as well as weak donor sites whereas 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: MF \ll CMF-1 < CMF-2 < CMF-3 < CMF-4 \approx CF. It can be seen that the incorporation of Cr^{3+} ions into the octahedral sites of the pure manganese ferros spinel enhanced the moderate to strong basic sites very significantly as evident from the steady increase in the limiting amount of the chloranil adsorbed. From the cation distribution, it is seen that MF is a partially inverse spinel and the inverse nature increases with progressive incorporation of chromium ions into the octahedral sites. This isomorphically replaces the more acidic Fe^{3+} from the more active octahedral sites to the hindered tetrahedral sites and increased the amount of less acidic Fe^{2+} ions in the octahedral sites. The creation of new electron donor site increased the basicity of the catalyst samples. If we evaluate the data in Table 2, it can be noticed that when the amount of strong acid sites decreases the number of basic sites increases.

3.3. Catalytic activity

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 at high contact time.

We could observe that with the different compositions of the ferrosin systems studied, the catalysts with higher 'x' values showed remarkable activity and selectivity towards *N*-monomethylation of aniline leading to NMA, while the catalytic activity found to have a considerable dependence with their composition. The catalyst with lower 'x' values yielded NNDMA. No C-alkylated anilines and no other side products were detected, which is the significant feature of the system. Also the activities of the present ferrosin systems remained for longer durations.

3.3.1. Effect of methanol to aniline molar ratio

The change in conversion and product distribution for aniline alkylation at different molar ratios of MeOH to aniline at 350 °C and volume space velocity of 5 ml h⁻¹ is shown in Fig. 2. It is obvious from the figure that the major reaction product is *N*-methyl aniline and its selectivity remained cent percent from a MeOH/aniline molar ratio of 3 up to a molar ratio of 5. Further increase in the molar ratio decreased the selectivity for NMA with corresponding increase in the selectivity for NNDMA. This suggests that higher molar ratios, favour the consecutive methylation of NMA owing to the presence of large amount of methanol. A similar trend on the results from aniline alkylation was reported elsewhere [22]. Neither any C-alkylated product nor other side products were observed even at high molar ratios. When the molar ratio was 3, the aniline conversion was 38.44%, improved significantly up to a molar ratio of 5 (58.51%). However, excess of methanol beyond the molar ratio of 5 lowered the aniline conversion because the alcohol probably undergoes side reactions leading to the forma-

tion of coke. Therefore, MeOH/aniline molar ratio of 5 was selected as the optimum feed mix ratio in the subsequent experiments.

3.3.2. Effect of reaction temperature

A series of aniline alkylation reactions were performed in the temperature range of 200–450 °C over CMF-4. Fig. 3 shows the influence of reaction temperature on aniline conversion and product distribution. It can be seen that temperature has a marked influence on the aniline conversion. The aniline conversion showed a significant increase with the rise of temperature from 200 to 350 °C. However, further increase in temperature rather reduced the aniline conversion, due to the coke deposition in this temperature range. Another possible reason for the reduced conversion is that methanol decomposition to C-oxides will be larger at higher temperatures. At all the temperatures, *N*-methyl aniline was observed to be the major product. Negligible amount of NNDMA is formed by the successive alkylation of NMA at temperatures beyond 350 °C. These results indicate that the optimum temperature range is 300–350 °C for high aniline conversion and high selectivity for NMA.

3.3.3. Effect of flow rate

Fig. 4 shows the influence of flow rate (VHSV) over CMF-4 at 350 °C and a MeOH/aniline molar ratio of 5. Increase in feed rate increases the diffusion of the reactant molecules through the catalyst. So aniline gets much less time to go into the product side, which will result in a decrease in aniline conversion and higher alkylated products of aniline. Yuvaraj et al. observed a similar trend over zeolites Y and β [26]. The ferrite samples follow the same drift as it can be seen from Fig. 4. With the increase of VHSV, aniline conversion decreased dramatically. The lower flow rate

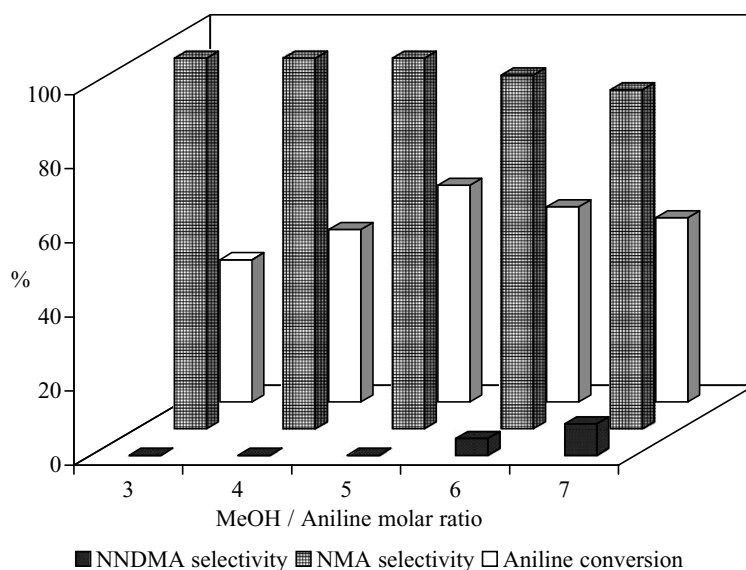


Fig. 2. Effect of MeOH/aniline molar ratio on conversion and selectivity of methylation of aniline over Cr_{0.8}Mn_{0.2}Fe₂O₄. Reaction temperature: 350 °C; TOS: 2 h; VHSV: 5 ml h⁻¹.

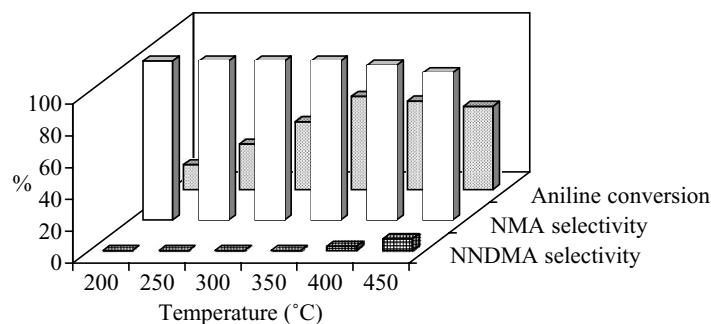


Fig. 3. Effect of reaction temperature on aniline alkylation. Catalyst: $\text{Cr}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$; TOS: 2 h; VHSV: 5 ml h^{-1} ; MeOH/aniline molar ratio: 5.

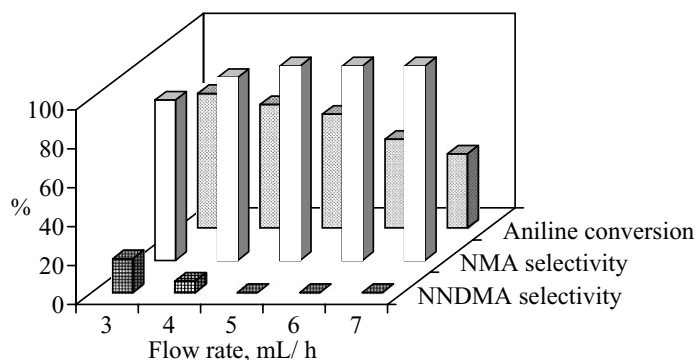


Fig. 4. Effect of flow rate on conversion and selectivity of methylation of aniline over $\text{Cr}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$. Reaction temperature: 350°C ; MeOH/aniline molar ratio: 5 and TOS: 2 h.

enhances the formation of dialkylated product, NNDMA. As the flow rate was increased from 3 to 7 ml h^{-1} , the reaction shifted completely towards *N*-monoalkylation leading to NMA.

3.3.4. Effect of time on stream

The catalytic stability of different Cr-Mn systems was ensured by observing NMA yield over a reaction period of 7 h. The reactions were carried out at 350°C at a MeOH/aniline molar ratio of 5 and the product analysis was done at regular intervals of 60 min. All the catalysts showed excellent stability and good yield for NMA for a long reaction period. Even though reduction of Fe^{3+} ions takes place during the reaction it does not alter the spinel lattice configurations. Due to this the reduced Fe^{3+} ions can regain their original state by means of oxidative transfer with the neighbouring metal cations. This electron hopping mechanism is more pronounced in the case of inverse spinels. All the catalyst samples are inverse spinels and the inverse nature increases progressively by the incorporation of chromium ions into the pure manganese ferros spinel. The presence of Fe^{3+} ions in both the octahedral and tetrahedral sites make the electron hopping more facile. Thus, the inverse spinel lattice imparts extra stability to the catalyst under various reaction conditions so that these systems have sustained activity for longer durations.

3.3.5. Effect of catalyst composition

Table 3 presents the comparison of the results of the methylation of aniline between Cr-Mn ferrite systems. *N*-Alkylated products were observed for all the systems. We detected no C-alkylated or other secondary products, which is consistent with the weak surface acidity of the chromium manganese ferros spinels. The catalysts with higher 'x' values are remarkably active and selective for the NMA formation; CMF-3, CMF-4 and CF performed cent percent NMA selectivity. The NMA yield enhanced from 13.12% for MF to 61.78% for CMF-4. Thus, it can be seen that the successive incorporation of chromium into the pure manganese

Table 3
Alkylation of aniline with methanol over $\text{Cr}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ -type systems

Catalyst	Aniline conv. (%)	NMA yield (wt.%)	Selectivity (%)	
			NMA	NNDMA
MnFe_2O_4	22.45	13.12	78.72	21.28
$\text{Cr}_{0.2}\text{Mn}_{0.8}\text{Fe}_2\text{O}_4$	47.37	42.36	98.72	1.28
$\text{Cr}_{0.4}\text{Mn}_{0.6}\text{Fe}_2\text{O}_4$	49.66	49.37	99.01	0.99
$\text{Cr}_{0.6}\text{Mn}_{0.4}\text{Fe}_2\text{O}_4$	53.37	56.52	100	–
$\text{Cr}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$	58.51	61.78	100	–
CrFe_2O_4	51.27	54.73	100	–

Reaction temperature: 350°C ; MeOH/aniline-5; TOS: 2 h; flow rate: 5 ml h^{-1} .

ferrospinel increased both the aniline conversion and NMA yield.

Regarding the surface acid–base properties, the population of basic sites exceeds the acid sites. The successive substitution of Mn by Cr decreased the amount of Fe^{3+} ions in the octahedral sites and this is the reason for the decreased acidity values corresponding to strong acid sites and subsequent increase in the weak plus medium acidity of the solids. The enhanced weak plus medium acidity is due to the weak Lewis acidity. The chromium substitution in manganese ferrospinel also increased the number of Lewis basic sites. The catalytic activity follows the order: $\text{MF} \ll \text{CMF-1} < \text{CMF-2} < \text{CMF-3} < \text{CMF-4} > \text{CF}$. The gradation in catalytic activity fairly pursue the trend in weak plus medium acidity and basicity of the solids, although CF performed differently.

Though aniline alkylation is an acid–base catalyzed reaction, it is observed that acid–base properties of the catalysts are not the sole factors determining the catalytic activity. The decisive role in determining the catalytic activity of the spinels is their cation distribution. The partially inverse MF is shifted to the more inverse nature by the incorporation of chromium ions in the octahedral sites. This resulted in the isomorphic replacement of Fe^{3+} ions from the more exposed and active octahedral sites to the hindered tetrahedral sites. The cation valency distribution of the mixed Cr–Mn series reveals that $\text{Fe}_{\text{oct}}^{3+}/\text{Fe}_{\text{tet}}^{3+}$ ratio decreases with increase in ‘x’ value. The octahedral cations are more polar and more accessible to the reactant molecules than the tetrahedral cations [34]. But due to the easy electron hopping between the sites [41], tetrahedral ions can also influence the overall activity of the system, and this hopping mechanism

is more pronounced in inverse spinels. The participation of Fe^{3+} ions in the octahedral sites as the alcohol adsorbing centers has already been reported [42]. Except for CF, all the other systems in this series possess some amount of Fe^{3+} ions in the octahedral sites and this may be the reason for reduced catalytic activity of CF compared to CF-4 and CF-3. Since aniline is a strong base, even the weak Lewis acid sites on the catalyst surface can make effective coordination with this molecule. It is also believed that only weak to moderate acidity and basicity [15–17] favour the reaction and the enhanced catalytic activity of mixed Cr–Mn systems is due to the improved weak Lewis acidity and basicity.

4. Mechanism of the reaction

It is concluded from Table 3 that moderate amounts of both acidic and basic Lewis sites on the catalyst surface are favorable for the *N*-alkylation of aniline. Based on this a reaction mechanism of aniline alkylation is proposed in Fig. 5. Aniline and methanol are adsorbed on neighbouring sites and are in equilibrium with the catalyst surface. Since aniline being a strong base even the weak Lewis acid sites can interact well with the molecule; the adsorption of alcohol on the catalyst surface is more significant. If the catalyst surface is exposed with sufficient acidic and basic sites then the methoxy species could be bonded to Lewis acid sites and hydrogen atom of the undissociated hydroxyl group interact with the Lewis basic site. Thus, methanol could compete for adsorption to generate the electrophile ($\text{CH}_3^{\delta+}$). The adsorption behaviour of aniline or *N*-methyl aniline follows

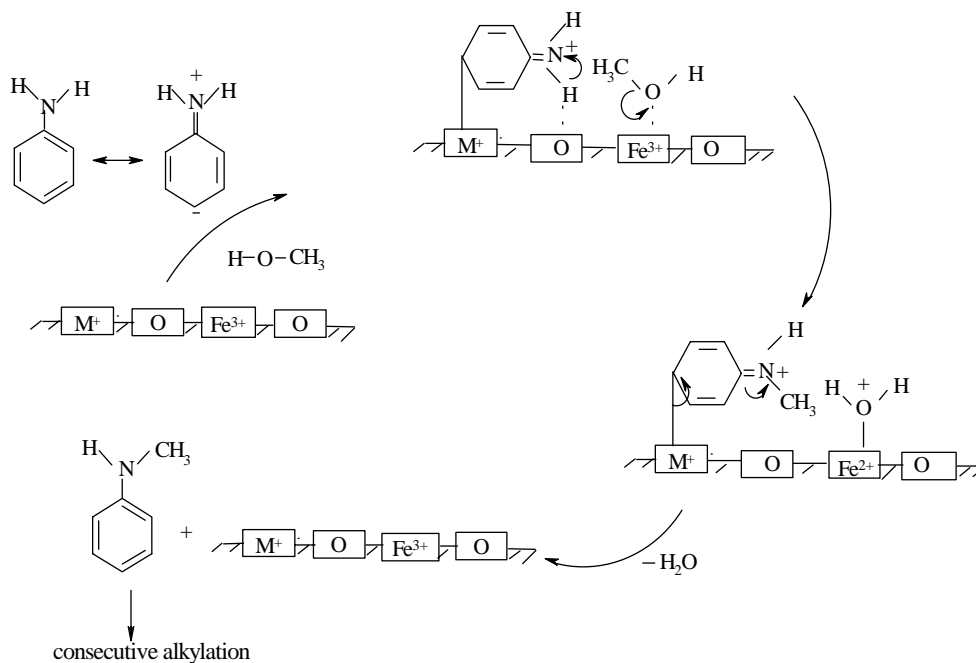


Fig. 5. Reaction mechanism for aniline alkylation over ferrospinel system.

the similar pattern. The electrophilic attack of $\text{CH}_3^{\delta+}$ on the nitrogen atom of the aniline gives *N*-methyl aniline. In a similar mode *N,N*-dimethyl aniline is produced from the methylation of *N*-methyl aniline. Due to presence of electron donating methyl group on nitrogen atom the adsorption of *N*-methyl aniline is more probable over the catalyst surface than aniline. Since number of basic sites than acidic sites inhibited the strong adsorption of *N*-methyl aniline to produce *N,N*-dimethyl aniline, thus, the more basic catalyst samples such as CF-3, CF-4 and CF yielded only *N*-methyl aniline with cent percent selectivity.

5. Conclusions

Various compositions of chromium manganese ferrosinels with general formula $\text{Cr}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8$ and 1.0) can be effectively used for the alkylation of aniline with methanol as the alkylating agent. The acid–base properties of the catalyst vary with the successive incorporation of chromium ions into the pure manganese ferrosinels. All the catalyst samples especially CMF-3, CMF-4 and CF exhibited high activity, remarkable selectivity and persistent stability for *N*-monoalkylation. Moderate amount of acid as well as basic sites are mandatory for the appreciable aniline conversion and NMA selectivity. Large excess of the alkylating agent and very high reaction temperature are not needed for the reaction. Since all the catalyst samples are inverse spinels the reduced Fe^{3+} ions can easily regain their original state easily; maintained a constant activity after 7 h on stream.

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