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Alkylation of aniline with ethanol over $Zn_{1-x}Mn_xFe_2O_4$ (x= 0, 0.25, 0.50, 0.75 and 1) ferrite system

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N-Alkylation of aniline with ethanol has been studied in vapour phase, in a fixed bed reactor over $Zn_{1-x}Mn_xFe_2O_4$ (X= 0, 0.25, 0.50, 0.75 and 1) ferrospinel system. N-ethylaniline (NEA) and N,N-diethylanilines (NNDEA) were found to be the major products. It was observed, that, systems possessing low x values are highly selective for *N*-ethylaniline. Reaction parameters were optimized over $ZnFe_2O_4$ catalyst. A maximum yield of 53% of *N*-ethylaniline with selectivity of 97% and 1.79% of *N*, *N*-diethylaniline with selectivity of 3% was obtained over $ZnFe_2O_4$ catalyst at a temperature of 503 K, ethanol to aniline molar ratio 6 and weight hour space velocity of 0.17 h^{-1}. Catalyst characterization has been made by XRD, IR spectroscopy and ammonia desorption methods. All catalysts show their characteristic M-O stretching bands around 700 and 500 cm^{-1} associated with tetrahedral and octahedral sites respectively. All catalysts were found to show weak, medium and strong acidic sites corresponding to ammonia desorption at different temperature ranges 423-523, 523-623 and 623-723 K. A tentative mechanism for production of *N*-ethylanilines has been proposed.

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Ferrospinels as magnetic and catalytic materials are widely used in electronic and in catalytic industries. The unit cell of these materials, formed by 32 oxygen and 24 cations is of face centered cubic symmetry with unit cell length a_0 of ~ 0.84 nm. There are 64 tetrahedral and 32 octahedral possible positions for cations in the unit cell, out of which only 8 tetrahedral and 16 octahedral positions are occupied by cations. Their general formula is $A{+2}[B_2^{+3}]O_4^{-2}$. B positions represent octahedral sites and are usually shown by square brackets.

Alkylation of aniline produces *N*-ethylaniline and *N*, *N*-diethylaniline. Former is an important dyestuff while latter finds application as co-catalyst in polymerization reaction, anticorrosive agent in acidic medium and as antioxidant for lubricating oils. 2,6-diethylaniline is needed for manufacture of weedicide, butachlore.

Alkylation of aniline by ethanol is an electrophilic substitution reaction. The electrophile i.e., carbonium ion is formed from ethanol with the help of acid sites on the catalyst surface. The traditional, corrosive, costly and environmentally unfriendly Friedel-Crafts catalyst is slowly being replaced with more stable and environmental friendly catalysts, such as, metal oxides (SiO_2, Al_2O_3), clays, and zeolites, possessing Brönsted or Lewis-Brönsted sites. Although, these catalysts produce $C_2H_5^+$ and promote alkylation, they protonate aniline molecule as well and reduce the extent of reaction. These catalysts get deactivated at higher temperature and high aniline/ethanol molar ratio, because of coke formation by alcohol. Because of these disadvantages with Brönsted/Lewis-Brönsted catalysts, attempts are being made to develop catalysts possessing mild Lewis acidity/basicity, so that deactivation of aniline and charring of ethanol can be reduced.

Ferrospinels, possessing only Lewis sites can prove to be ideal catalysts for alkylation. Doping these spinels with transition metal can further improve their acido-basic character to suit the requirement of a particular reaction.

Although, there are few reports on alkylation of

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aniline in liquid phase under pressure [1], in vapour phase using oxides[2], Raney-Nickel,[3] zeolites[4], AEL type molecular sieves[5], clays [6-10] and few spinels[11-14], there is no report on alkylation of aniline with ethanol on $Zn_{1-x}Mn_xFe_2O_4$ (X= 0, 0.25, 0.50, 0.75 and 1) ferrospinel system. The present study of the alkylation of aniline was therefore undertaken with a view to [i] search for a suitable ferrite catalytic system, [ii] to optimize the composition of catalyst and to [iii] optimize the process for maximum yield to *N*-ethylanilines. Besides, catalysts have been characterized using XRD, IR and ammonia desorption methods with a view to understand the structure, nature of bonding and acido-basic properties of the catalysts.

Experimental Procedure

Catalyst preparation

Preparation of $ZnFe_2O_4$(ZF)

16.35 g of $ZnCl_2$ was dissolved in 150 mL of distilled water and allowed to react with 76.80 g of NaOH dissolved in 100 mL of water (solution A). A solution of 68.87 g of $FeCl_3.6H_2O$ was prepared in 2L of 0.96 molar HCl in a 5L beaker (solution B). Solution A was mixed with solution B and stirred for two hours and further heated for half an hour at 333K. The mixture was allowed to settle and its pH adjusted to 7.5 with 2N NaOH. The product was washed by repeated decantation till free from Cl^- ions, filtered through a sintered glass filter, dried in an oven at 393K. and calcined at 773K for 5 h. Finally the product was sieved through a 6/10 size mesh.

Preparation of $MnFe_2O_4$ (MF) was similar to that of $ZnFe_2O_4$ described above, except that now 23.75 g of $MnCl_2.6H_2O$ was taken in place of $ZnCl_2$. Similarly, $Zn_{0.75}Mn_{0.25}Fe_2O_4$ (ZMF-1), $Zn_{0.5}Mn_{0.5}Fe_2O_4$ (ZMF-2) and $Zn_{0.25}Mn_{0.75}Fe_2O_4$ (ZMF-3) were prepared by taking 0.0562, 0.0375 and 0.0187 mol of Zn salt and 0.0187, 0.0375 and 0.0562 mol of Mn salt.

Catalyst characterization and surface acidity measurements

The XRD diffractogram of ZF, ZMF-2 and MF were recorded on Rigaku diffractometer with Cu Kα radiation and are reproduced in Fig, 1. All peaks in the pattern match well with the characteristic reflections of corresponding ferrites reported in JCPDS card and confirm the phase purity of the samples. The FTIR spectra of these ferrite catalysts were recorded on Perkin-Elmer Series 1600 FTIR spectrometer and are reproduced in Fig. 2. Two broad bands appearing at 700 and 500 cm^{-1} are ascribed to M-O stretching modes of tetrahedral and octahedral sites respectively.

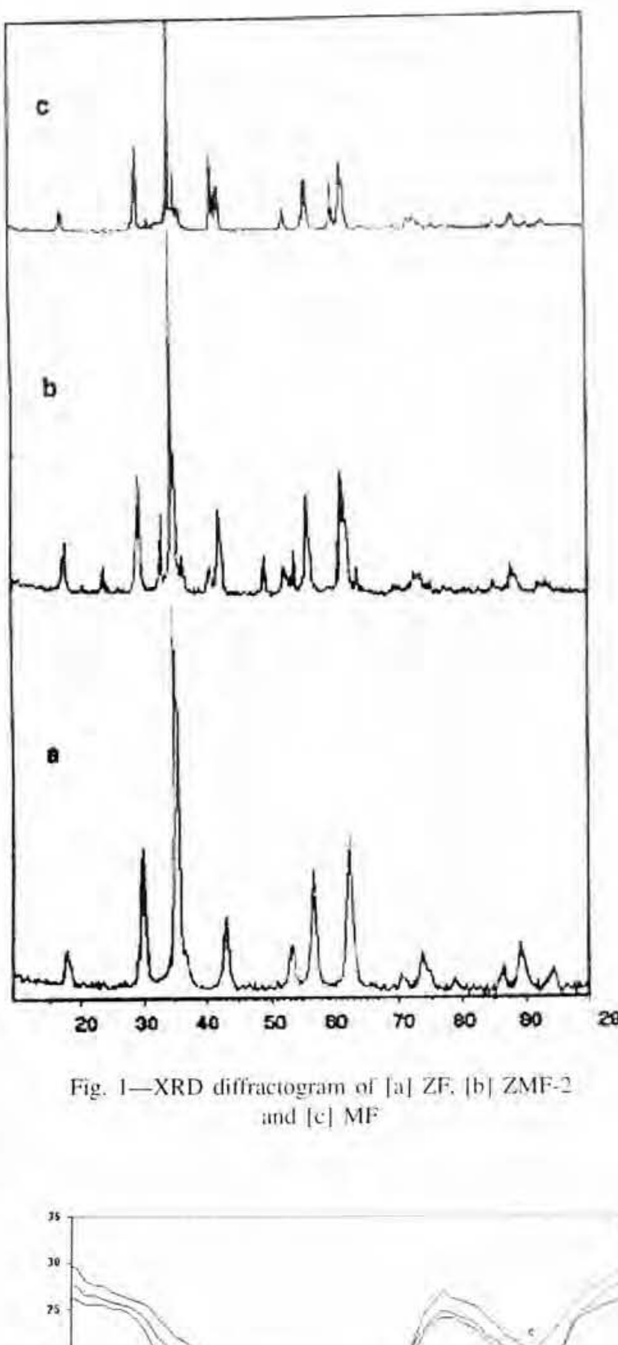


Fig. 1—XRD diffractogram of [a] ZF, [b] ZMF-2 and [c] MF

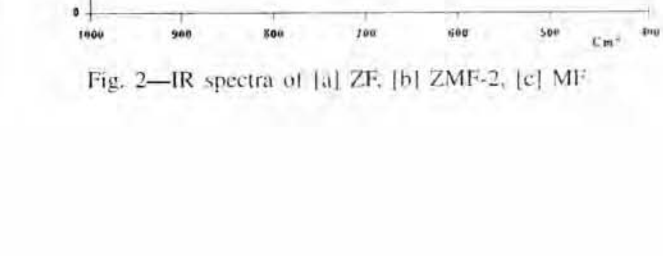


Fig. 2—IR spectra of [a] ZF, [b] ZMF-2, [c] MF

Acidity of catalysts was measured by ammonia desorption method and results are presented in Table 1. Surface area measurements were made using BET method and results are shown in Table 1.

Apparatus and procedure

The reaction was carried out in a fixed bed down flow pyrex glass tubular reactor (0.45 m in length and 0.025 m ID) at atmospheric pressure. The upper half worked as preheater and the lower half worked as reactor, where the catalyst was packed between two plugs of pyrex glass wool. It was activated at 773 K by passing air and then broughtdown to the desired temperatures by cooling down in a current of nitrogen. The mixture of aniline and ethanol was fed by a 10 cm^3 pressure-equalizing funnel. The liquid products were condensed with the help of a cold-water condenser a cold trap and were analyzed by Shimadzu 14B Gas Chromatograph using SE-30 column and FID detector.

Results and Discussion

Acidity, surface area and performance of various catalysts in the alkylation of aniline

An elaborate comparative discussion of the performance of various solid acid catalysts such as oxides, clays, and zeolites and their modified forms in the aniline alkylation is presented by Narayanan and Deshpande[16]. It has been observed that physico-chemical properties of the catalysts, specifically acidity plays important role in the performance of these catalysts. Most of these catalysts produce either high conversion and low selectivity or low conversion and high selectivity. Contrary to this, ferrite catalysts produce reasonably high conversion (> 67%) and very high selectivity (> 99%) for *N*-methyl aniline[17]. The acidity and surface area data of various ferrite catalysts $ZnFe_2O_4$ (ZF), $Zn_{0.75}Mn_{0.25}Fe_2O_4$ (ZMF-1), $Zn_{0.5}Mn_{0.5}Fe_2O_4$ (ZMF-2), $Zn_{0.25}Mn_{0.75}Fe_2O_4$ (ZMF-3) and $MnFe_2O_4$ (MF) used in the present study are listed in Table 1. Performance of various ferrite catalysts in the alkylation of aniline is presented in Table 2. The order of catalytic activity of ferrite spinel systems toward overall conversion was found to be ZF > ZMF-1 > ZMF-2 > ZMF-3 >MF. It was observed that, systems possessing low x values are highly selective for *N*-ethylaniline (NEA) and increasing x value led to the increased selectivity for *N, N*-diethylaniline (NNDEA). An examination of Table 1 reveals that increasing the acidity with increasing x value, concomitantly decreases the activity of the ferrite systems. Insertion of Mn in $ZnFe_2O_4$ did not improve its performance; further activity test work was therefore undertaken over ZF catalyst. ZF has been found to be

Table 1—Acidity and surface area of ferrite catalysts

S.No	Catalyst	Acidity (NH_3 uptake/mmol g^{-1}) 423-523K	523-623K	623-723K	Total	Surface area (m^2/g)
1	ZF	0.36	0.33	0.34	1.03	32.21
2	ZMF-1	0.38	0.32	0.36	1.06	32.96
3	ZMF-2	0.40	0.28	0.41	1.09	39.72
4	ZMF-3	0.41	0.34	0.40	1.15	42.45
5	MF	0.43	0.37	0.42	1.22	43.27

Table 2—Performance of various catalysts in the alkylation of aniline

Ethanol/aniline molar ratio = 6, Temperature = 503 K, WHSV = 0.17 h^{-1}

Catalyst	Aniline Conversion (%)	Product distribution (%) Aniline	NEA	NNDEA
ZF	54.79	45.21	53.00	01.79
ZMF-1	47.26	52.74	39.94	07.32
ZMF-2	39.20	60.80	20.86	18.34
ZMF-3	36.60	63.40	15.54	21.06
MF	25.96	74.04	02.24	23.72

the most efficient catalyst for selective monomethylation of aniline over $Zn_{1-x}Ni_xFe_2O_4$ (x= 0, 0.2, 0.5, 0.8 and 1) type system as well[17]. Contrary to Zn-Mn ferrite system in which acidity increases with Mn concentration. In Zn-Ni ferrite system acidity decrease with increasing Ni concentration. Best performance of ZF shows that this catalyst has the most appropriate acidity among Zn-Ni ferrite Zn ferrite and Zn-Mn ferrites.

Effect of temperature on alkylation of aniline

Effect of temperature on alkylation of aniline over ZF, at constant ethanol/aniline molar ratio, was investigated in the temperature range 473-723 K and the results are presented in Fig. 3. Negligible conversion was obtained below 473 K, which increased effectively in the temperature range 503-573 K. NNDEA was not formed below 503 K. At higher temperature NNDEA and others were formed along with NEA. The best performance by the catalyst was shown at 503 K with product distribution of 53 and 1.79% for NEA and NNDEA respectively and selectivity of 97 and 3% for NEA and NNDEA respectively in the product. At temperatures higher than 503 K, conversion decreased due to charring and deposition of carbon on the catalyst surface.

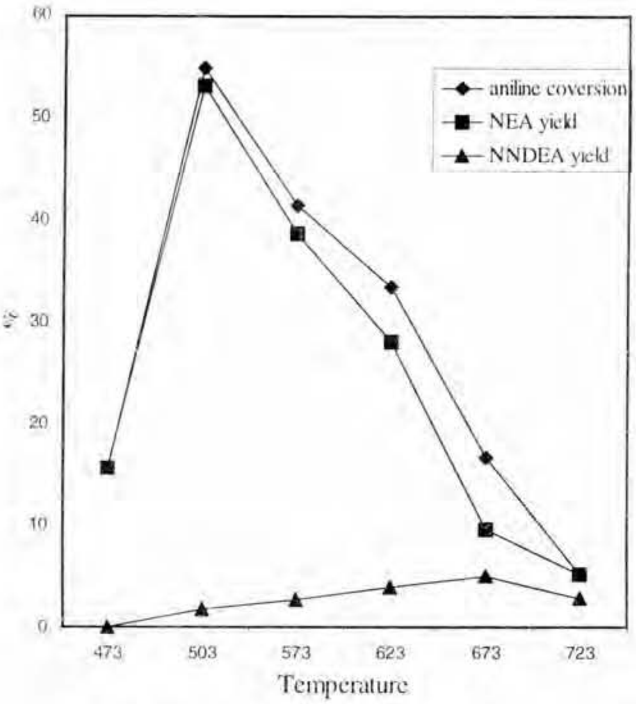


Fig. 3—Effect of temperature on alkylation of aniline, ethanol/aniline molar ratio = 6 and WHSV = 0.17 h^{-1}

Effect of ethanol/aniline molar ratio on alkylation of aniline

The effect of ethanol/aniline molar ratio on alkylation of aniline over ZF catalyst at 503 K is represented graphically in Fig. 4. With the increase in ethanol/aniline molar ratio conversion of aniline increases, reaches a maximum and then decreases. Selectivity and production of NEA and NNDEA increases with increasing the molar ratio, reaching a maximum and then decreasing at higher molar ratio. This suggests a Langmuir-Hinshelwood type of bimolecular reaction. A maximum yield of 53 and 1.79 % respectively for NEA and NNDEA was obtained at an ethanol/aniline molar ratio of 6. The selectivity for NEA and NNDEA in the product was 97 and 3% respectively at this molar ratio of 6.

Effect of weight hourly space velocity on alkylation of aniline

The effect of weight hour space velocity on alkylation of aniline over MF catalyst at 503 K and constant ethanol/pyridine molar ratio, was investigated in the ranges 0.1 to 0.8 h^{-1} and results are represented graphically in Fig. 5. Yield of *N*-ethylanilines and conversion of aniline increases with increasing WHSV, reaches a maximum and then decreases with further increasing the weight hour space velocity, due to the decreased contact time. The best catalytic activity was observed at 0.17 h^{-1} with production of 53 and 1.79% NEA and NNDEA respectively and selectivity of 97

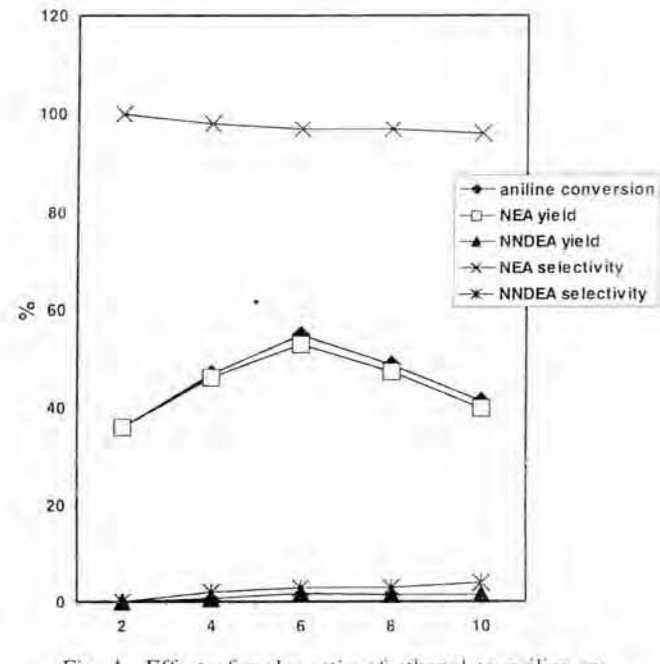


Fig. 4—Effect of molar ratio of ethanol to aniline on conversion, selectivity and yield over $ZnFe_2O_4$ catalyst. WHSV 0.17 h^{-1}; reaction temperature 503K

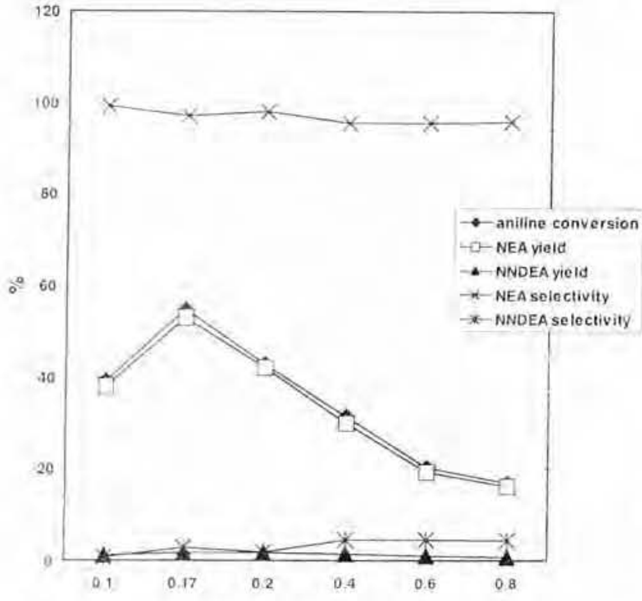


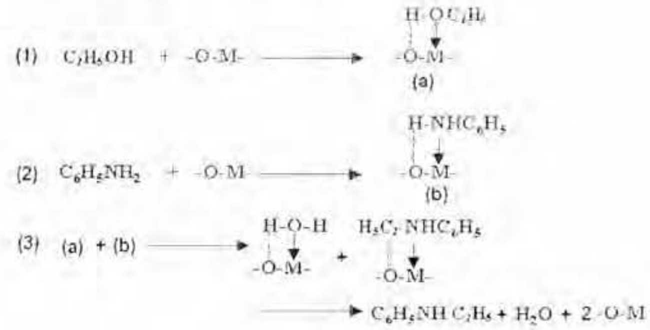
Fig. 5—Effect of weight hour space velocity on alkylation of aniline over $ZnFe_2O_4$ catalyst. Reaction temperature 503K; molar ratio of ethanol to aniline 6

and 3% for NEA and NNDEA respectively in the product.

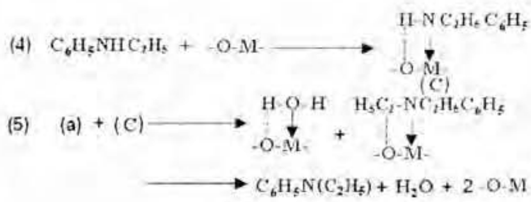
Mechanism

Ethylene was identified as one of the products, whose concentration increased with increase in ethanol/aniline mole ratio. Passing hydrogen peroxide with feed suppressed the yield to *N*-ethylanilines, which rules out possibility of a free radical mechanism. Passing ethylene along with aniline over ferrite catalyst reduce the yield of *N*-ethylanilines considerably. This rules out the possibility of ethylene as the intermediate. Obviously, ethylene is produced due to dehydration of alcohol over Brönsted acidic sites and is not involved in the mechanism of alkylation of aniline with ethanol. From the study of effect of ethanol/aniline molar ratio on the yield of NEA presented in section 3.3, it is clear that reaction follows a Langmuir-Hinshelwood type of bimolecular reaction involving competitive adsorption, requiring one molecule of both the reactants. At lower concentrations, where there are enough number of catalytic sites to accommodate aniline as well as ethanol molecules, the yield of NEA is proportional to concentration of ethanol and aniline. At higher ethanol/aniline molar ratio, ethanol molecules displace aniline molecules, causing a decrease in the rate and production of NEA. It seems, the reaction follows a consecutive mechanism. NEA is formed first which is further alkylated to *N*, *N*-diethylaniline. A mechanism consistent with the above results can be suggested as follows.

Mechanism of N-ethylaniline:



Mechanism of N-ethylaniline:



Conclusions

(i) $Zn_{1-x}Mn_xFe_2O_4$ (x= 0, 0.25, 0.50, 0.75 and 1) ferrite spinal systems were studied for alkylation of aniline using ethanol as the alkylating agent. It was found that these systems could effectively alkylate aniline to produce *N*-ethylaniline selectively. 97% of selectivity for NEA in the product was obtained under optimized reaction conditions. Activity increases as *x* value decreases. Highest activity was observed for ZF, whereas MF was only mildly active. As *x* increases, the acidity and surface area of the systems also increases.

(ii) substitution of Zn by Mn leads to higher acidity and surface area of the ferrite catalysts as is supported by the present surface area and ammonia desorption measurements. Similar trends have been reported by others as well[12-14].

(iii) a tentative mechanism for production of *N*-ethylanilines has been proposed.

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