ALKYLATION OF ANILINE WITH ETHANOL OVER NANOCRYSTALLINE $ZnFe_{2-X}Al_XO_4$ (X = 0, 0.25, 0.50, 0.75 AND 1) FERRITE SYSTEM

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Abstract. N-alkylation of aniline with ethanol has been studied in vapour phase in a fixed bed reactor over $ZnFe_{2-x}Al_xO_4$ (X= 0, 0.25, 0.50, 0.75 and 1). N-ethylaniline (NEA) and N, N-diethyl anilines (NNDEA) were found to be major products. It was observed that systems possessing high 'x' values are highly selective for N-ethylaniline. Reaction parameters were optimized over $ZnFeAlO_4$ catalyst. A maximum yield of 74 % of N-ethyl aniline with selectivity of 98% and 1.5 % of N, N-diethylaniline with selectivity of 2 % was obtained over $ZnFeAlO_4$ catalyst at a temperature of 523K, ethanol to aniline molar ratio 6 and weight hour space velocity of 0.17 h^{-1}. Catalyst characterization has been made by XRD, IR, Mössbauer spectroscopy, ammonia desorption and BET surface area measurements. 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 in different temperature ranges 423-523, 523-623 and 623-723 K. Mössbauer measurement suggests formation of homogenous solid solution in all the samples and increase in acidity of the samples with increasing incorporation of aluminum. A tentative mechanism for production of N-Ethyl anilines has been proposed.

Keywords: aluminium ferrite, ferrospinels, ethylation of aniline, N-ethylaniline

Introduction

Recently, there has been an upsurge on the alkylation of aromatics over ferrospinel catalysts [1-3], having general formula $M^{+2}[Fe_2^{+3}]O_4$, 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 ferrospinel can be normal $M^{+2}[Fe_2^{+3}]O_4$, inverse $Fe^{+3}[M^{+2}Fe^{+3}]O_4$ or mixed spinel in which the divalent cations are distributed between both sites. This type of cation distribution significantly affects acido-basic [3] and surface properties of ferrospinels [4-5].

C- and N-alkylated anilines are pivotal in synthesis of many dye chemicals, pharmaceuticals, explosives and pesticides. N, N-diethylaniline is employed in the synthesis of triphenyl methane dyes such as basic green, acid blue and basic violet. Nitration of N, N-dimethyl aniline produces tetryl (2,4,6-trinitrophenylmethyl nitramine) used as booster explosive. 2,6-Diethylaniline is starting material for synthesis of pesticide butachlor. N-alkylamines are used for synthesis of pharmaceutical compounds.

Although, there are few reports on alkylation of aniline [6-12], some of these studies are on C-alkylation [7], and few of these processes are carried out in liquid phase / slurry phase [6-8]. There are reports on alkylation of aniline in liquid phase under pressure [13], in vapour phase using oxides [14], Raney-Nickel [15], zeolites [16], AEL type molecular sieves [17], clays [18-21] and few spinels [22-25].There seems to be no detailed report on synthesis of N-ethylanilines by N-alkylation of aniline with ethanol over $ZnFe_{2-x}Al_xO_4$ (X = 0, 0.25, 0.50, 0.75 and 1) ferrospinal system.

The present study of the alkylation of aniline was therefore undertaken with a view to: (1) search for a suitable ferrite catalytic system, (2) to optimize the composition of catalyst and to (3) optimize the process for maximum yield to N-ethyl anilines. 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

Different compositions of ferrospinels series viz. $ZnFe_2O_4$ (ZF), $ZnFe_{1.75}Al_{0.25}O_4$ (ZAF-1), $ZnFe_{1.5}Al_{0.5}O_4$ (ZAF-2) and $ZnFe_{1.25}Al_{0.75}O_4$ (ZAF-3) and $ZnFeAlO_4$ (ZAF-4) were prepared by co-precipitation method. Calculated amounts of nitrates of metals were dissolved in large excess of distilled water and pH was adjusted to 8.5 with the help of a dilute solution of NaOH. Thus in a typical preparation of $ZnFe_{1.5}Al_{0.5}O_4$ (ZAF-2), 4.8 g of Zn $(NO_3)_2.6H_2O$, 9.7 g of Fe $(NO_3)_3.9H_2O$ and 3.0 g of Al $(NO_3)_3.9H_2O$ were dissolved in 2 L of water at room temperature and 0.5 N NaOH was added slowly with constant stirring till precipitation was complete. The precipitate was washed, filtered and dried in oven at 383K. The dried mass was calcined at 773 K to obtain the ferrites.

Catalyst characterization and surface acidity measurements

The XRD diffractogram of ZF, ZAF-2 and ZAF-4 were recorded on Rigaku diffractometer with Cu K_{α} 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 No. 22-1012, 10-319 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 appeared at 700 and 500 $cm.^{-1}$ can be assigned to metal-oxygen stretching frequencies. Both M-O bonds can be assumed to have almost same force constants and since tetrahedral M-O bond (T_d M-O) is associated with metal of lower mass, this stretching frequency is expected to appear at higher frequency compared to M-O stretching frequency of octahedral (O_h M-O) site. In view of this, the band appeared at 700 $cm.^{-1}$ is assigned to M-O stretching mode of tetrahedral group and that appeared at 500 $cm.^{-1}$ is assigned to M-O stretching mode of octahedral group.

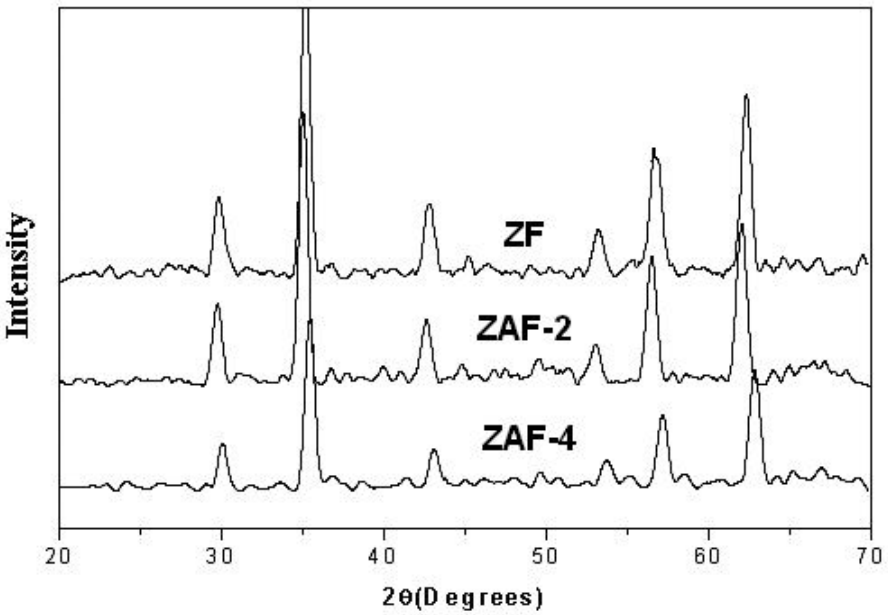


Fig. 1. XRD spectra of ZF, ZAF-2 and ZAF-4 ferrites

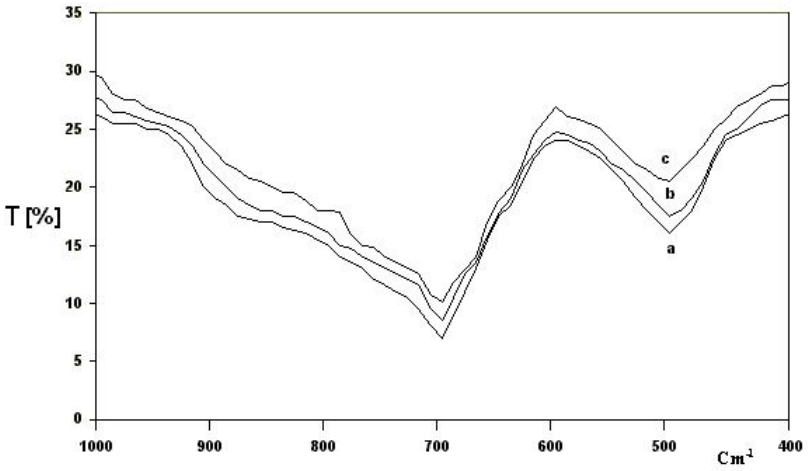


Fig. 2. IR spectra of [a] ZF, [b] ZAF-2 and [c] ZAF-4 ferrites

Mössbauer spectra of this series were recorded using a conventional PC based constant acceleration Mössbauer spectrometer in transmission mode at a velocity of ±5 mm/s equipped with a proportional detector. The gamma radiation source was Co in Rhodium matrix. Velocity calibration was done at room temperature at a velocity of 5 mm/s. The source velocity was varied in the range ±5mm/s with constant acceleration. All the Mössbauer parameters are relative to aFe and the accuracy in the range of 0.01mm/s.

Ammonia desorption experiments were carried out to measure the acidity of the catalyst using ammonia as an adsorbate. 5 g of catalyst was packed in a Pyrex tube down flow reactor and heated to 673K under a nitrogen gas flow rate of 0.5 $cm^3\ s^{-1}$ for 3 hours. The reactor was then cooled to 298K and adsorption conducted at that temperature by exposing the sample to ammonia for 2 h. Physically adsorbed ammonia was removed by purging the sample with a nitrogen gas flow rate 0.5 $cm^3 s^{-1}$ at 353 K for 1 h. The acid strength distribution was obtained by raising the catalyst temperature from 353 – 773K in a flow of nitrogen gas 0.5 $cm^3 s^{-1}$and absorbing the ammonia evolved in double distilled water containing phenolphthalein as indicator. Quantitative estimation was made by titrating the water solution by standard 0.1 N HCl solutions in different temperature ranges. The results are presented in Table 1. Surface area measurements were made using BET method and results are shown in Table1.

Table 1. Acidity, surface area and Mössbauer parameters of ferrite catalysts

S.No	Catalyst	Acidity (NH_3 uptake m mol. g^{-1})				Surface Area (m^2/g)	Mössbauer parameters		
		423-523K	523-623K	623-723K	Total		I.S.	Q.S.	HLW
1	ZF	0.36	0.33	0.34	1.03	32.21	0.32	0.29	0.25
2	ZAF-1	0.79	0.69	0.78	2.26	68.2	0.29	0.30	0.29
3	ZAF-2	1.15	1.08	1.14	3.37	101.7	0.26	0.32	0.29
4	ZAF-3	1.41	1.34	1.40	4.15	108.1	0.16	0.33	0.32
5	ZAF-4	1.77	1.69	1.76	5.22	124.3	0.14	0.38	0.38

Apparatus and procedure

The reaction was carried out in a fixed bed down flow Pyrex glass tubular reactor (0.45m in length and 0.025m 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 773K by passing air and then brought down 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, Mössbauer parameters and performance of various catalysts in the alkylation of aniline

The acidity, surface area, Mössbauer parameters of various ferrite catalysts $ZnFe_2O_4$ (ZF), $ZnFe_{1.75}Al_{0.25}O_4$ (ZAF-1), $ZnFe_{1.5}Al_{0.5}O_4$ (ZAF-2), $ZnFe_{1.25}Al_{0.75}O^4$ (ZAF-3) and $ZnFeAlO_4$ (ZAF-4), 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 ZAF-4 > ZAF-3 > ZAF-2 > ZAF-1 >ZF. It was observed that, systems possessing high 'x' values are highly selective for N-ethylaniline and concomitantly decreases the N, N-diethylaniline formation. An examination of Table 1 will reveal that the acidity as well as surface area increases with increasing 'x' value and better performance of ZAF-4 catalyst can be ascribed to its higher acidity and surface area, compared to Zn ferrite. Further process development work was therefore undertaken over ZAF-4 catalyst.

The room temperature Mössbauer Spectra for all samples were found to be doublet in the velocity range 0.0-0.6 mm/s, characteristic of Fe^{3+} ions at octahedral sites. For different samples, although there was no considerable shift in the position of

doublets, the interval between the peaks increases perhaps due to qudropole splitting. The values of isomer Shift (IS), qudropole splitting (QS) and half line width (HLW) are listed in Table 1. It can be seen that IS, QS as well as HLW date are found to be almost proportional to substitution degree x of Fe^{3+} by Al^{+3}, conforming formation of solid solution. The IS values of all sample were found to be characteristic of Fe^{3+} in octahedral environment. It was found that while IS values decreased with increasing x due to increased s-electron density at Fe^{3+} nucleus, QS values increased with increasing x due to isomorphic substitution of Fe^{3+} by Al^{+3} in octahedral sites, giving rise to decreased symmetry in electron distribution around Fe^{3+} and lattice distortion. This replacement of Fe^{3+} ions by Al^{3+} ions in the octahedral sites produces charge transfer from iron to oxygen in Fe-O bond and Fe atom becomes more electrons deficient and acidic [12]. Thus, Mössbauer data also suggest increase in acidity of the catalysts with increase in Al^{3+} content.

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

Catalysts	Aniline Conversion [%]	Product distribution [%]		
		Aniline	NEA	NNDEA
ZF	54.79	45.21	53.00	01.79
ZAF-1	57.26	42.74	55.53	01.73
ZAF-2	59.20	40.80	57.54	01.66
ZAF-3	66.60	33.40	65.01	01.59
ZAF-4	75.96	24.04	74.46	01.50

Ethanol/ Aniline molar ratio = 6, Temperature = 523 K. WHSV = 0.17 h^{-1}

Effect of temperature on alkylation of aniline

Effect of temperature on alkylation of aniline over and $ZnFeAlO_4$ catalyst at constant ethanol/aniline molar ratio, was investigated in the temperature range 473-723K and results are presented in Table 3. Negligible conversion is obtained below 473 K and occurs effectively in the temperature range 523-573K. NNDEA was not formed bellow 523 K. At higher temperature NNDEA and others were formed along with NEA. The best performance by the catalyst was shown at 523 K with conversion of 74 and 1.5 % for NEA and NNDEA respectively and selectivity of 97 and 3% for NEA and NNDEA respectively. At temperatures above 523 K, conversions decrease due to charring and deposition of carbon on the catalyst surface.

Table 3. Effect of temperature on alkylation of aniline

Temperature K	Aniline Conversion [%]	Product distribution [%]			
		Aniline	NEA	DDNEA	Others
473	16.13	83.87	16.13	Nil	Nil
523	75.96	24.04	74.46	01.50	Nil
573	52.23	48.76	48.43	03.80	
623	35.39	64.61	29.91	03.16	Nil
673	18.74	81.26	13.22	02.06	02.32
723	09.57	95.43	05.00	Nil	03.46
					04.57

Ethanol / Aniline molar ratio = 6, WHSV = 0.17 h^{-1}

Effect of ethanol/aniline molar ratios on alkylation of aniline

The effect of ethanol/aniline molar ratios on alkylation of aniline over $ZnFeAlO_4$ catalyst at 523K is represented graphically in Fig. 3. With increase in ethanol/aniline molar ratio conversion of aniline increases, reaches a maximum and then decreases. Selectivity and conversions to NEA and NNDEA increased with increasing the molar ratio, reaching a maximum and then decrease at higher molar ratio suggests a Langmuir-Hinshelwood type of bimolecular reaction. A maximum yield of 74 and 1.5 % respectively for NEA and NNDEA was obtained at an ethanol/aniline molar ratio of 6. The selectivity for NEA and NNDEA was 98 and 2 % respectively at this molar ratio of 6.

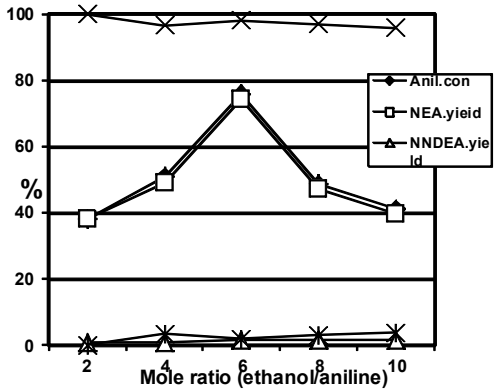


Fig. 3. Effect of ethanol to aniline molar ratio on alkylation of aniline over $ZnFeAlO_4$ catalyst. WHSV 0.17 h^{-1}; reaction temperature 523 K

Effect of weight hour space velocity on alkylation of aniline

The effect of weight hour space velocity on alkylation of aniline over and $ZnFeAlO_4$ catalyst at 523 K and constant methanol/Aniline molar ratio, was investigated in the weight hour space velocity ranges 0.1 to 0.8 h^{-1} and results are represented graphi-

cally in Fig. 4. Yield of N-ethylanilines and conversion of aniline increased with increasing WHSV, reached a maximum and then decreases with increasing the weight hour space velocity, perhaps due to decrease in contact time. The best catalytic activity was observed at 0.17 h^{-1} with conversion of 74 % and 1.5 % for NEA and NNDEA respectively and selectivity of 97% and 3 % for NEA and NNDEA respectively.

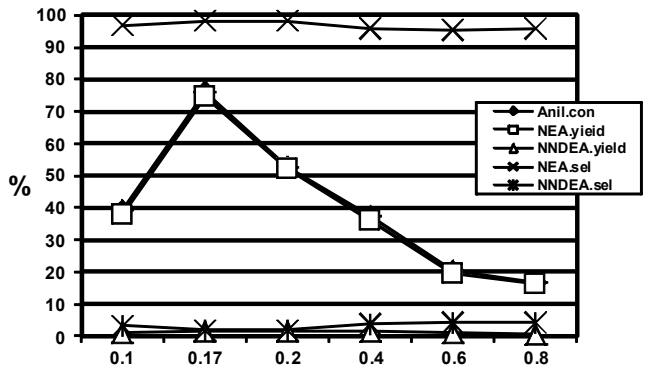


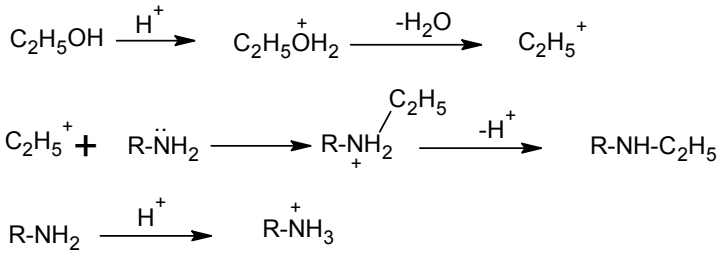
Fig. 4. Effect of weight hour space velocity on alkylation of aniline over $ZnFeAlO_4$ catalyst; reaction temperature 523K; molar ratio of ethanol to aniline 6

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. A comparative performance of few catalysts for alkylation of aniline is presented in Table 4. This Table reveals that with increasing ethanol/aniline molar ratio performance of Al_2O_3 catalyst increases. This can be explained on the basis of presence of Broensted sites in Al_2O_3. At low ethanol/aniline molar ratio, aniline as well as ethanol is adsorbed at the catalyst surface producing anilinium ion and ethyl carbonium ions, respectively which discourages the reaction and results into low conversion. At higher ethanol/aniline molar ration, aniline is flushed away by excess ethanol and conversion increases. It is unlikely that ferrite catalysts possessing exclusively Lewis sites will follow this mechanism. It seems in the beginning few Broensted sites are formed due to adsorption water molecules produced due to reaction of aniline and ethanol. After generation of Broensted sites, the mechanism follows the same course as that on alumina. The mechanism is shown in Schemes 1 and 2.

Table 4. Comparative performance of few catalysts in the alkylation of aniline at temperature 523 K

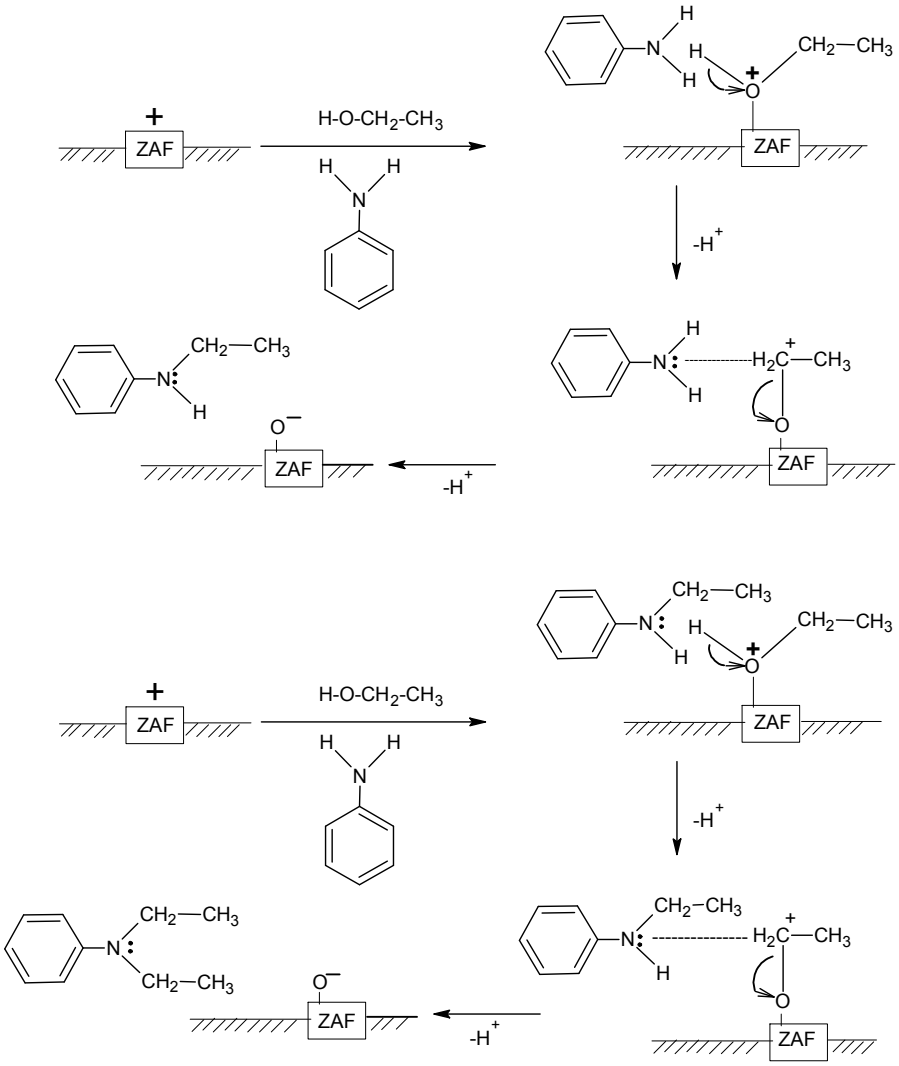
Catalysts	Mole Ratio E: M	Aniline Conversion [%]	Product distribution [%]		
			Aniline	MEA	NNDEA
Al_2O_3	1:1	47.7	45.21	40.1	7.6
Al_2O_3	6:1	65.26	34.74	56.05	9.21
ZF	6:1	54.79	52.3	53.00	01.79
ZAF-4	6:1	75.96	24.02	74.46	01.50



H^+ comes from Alumina Possesing Bronsted Sites

R= C_6H_5

Scheme 1. Mechanism of aniline alkylation over alumina possessing Broensted sites



Scheme 2. Mechanism of aniline alkylation over ZAF possessing Lewis sites only

Conclusion

$ZnFe_{2-x}AlxO_4$ (X= 0, 0.25, 0.50, 0.75 and 1) ferrite spinal system was studied for alkylation of aniline using ethanol as the alkylating agent. It was found that catalysts could effectively alkylate aniline to give N-ethyl aniline selectively. 98 % of selectivity for NEA was obtained under optimized reaction conditions. Activity increases as 'x' value increases. Highest activity was observed for ZAF, whereas ZF was only mildly active. As 'x' increases, the acidity and surface area of the systems also increases.

Substitution of Fe by Al leads to higher acidity and surface area of the ferrite catalysts as is supported by the present surface area and ammonia desorption measurements. Others [1-3] have reported similar trends as well. A tentative mechanism for production of N-ethylanilines has been proposed.

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