

Selective *N*-monomethylation of aniline using $\text{Zn}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.5, 0.8$ and 1.0) type systems

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Abstract

A series of ferrites having the general formula $\text{Zn}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.5, 0.8$ and 1.0) were prepared by soft chemical route. The materials were characterized by adopting various physico-chemical methods. The reaction of aniline with methanol was studied in a fixed-bed reactor system as a potential source for the production of various methyl anilines. It was observed that systems possessing low ' x ' values are highly selective and active for *N*-monoalkylation of aniline leading to *N*-methylaniline. Reaction parameters were properly varied to optimize the reaction conditions for obtaining *N*-methylaniline selectively and in better yield. Among the systems $\text{Zn}_{0.8}\text{Co}_{0.2}\text{Fe}_2\text{O}_4$ is remarkable due to its very high activity and excellent stability. Under the optimized conditions *N*-methylaniline selectivity exceeded 98%. Even at a methanol to aniline molar ratio of 2, the yield of *N*-methylaniline was nearly 50%, whereas its yield exceeded 71% at the molar ratio of 5. ZnFe_2O_4 , though executed better conversion than $\text{Zn}_{0.8}\text{Co}_{0.2}\text{Fe}_2\text{O}_4$ in the initial period of the run, deactivates quickly as the reaction proceeds. The Lewis acidity of the catalysts is mainly responsible for the good performance. Cation distribution in the spinel lattice influences their acido-basic properties and, hence, these factors have been considered as helpful parameters to evaluate the activity of the systems. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Ferrites; Spinel systems; Aniline conversion; *N*-alkylation of aniline

1. Introduction

Methylation of aniline is industrially important owing to the numerous uses of various substituted anilines like *N*-methylaniline, *N,N*-dimethylaniline and toluidines [1,2]. These are

essential intermediates for the manufacture of a wide class of compounds viz. agrochemicals, dyes, pharmaceuticals and explosives. Initially aniline was alkylated using dimethyl sulphate or alkyl halides as the alkylating agents [3]. Continuous efforts have been made to replace the traditional Friedel–Crafts type systems due to the inherent drawbacks associated with the process. As a result, solid acids or bases are recommended as safe and active systems and toxic

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alkylating agents are replaced by non-toxic alkylating agents such as methanol and dimethyl carbonate. By performing alkylation in vapour-phase reactors, the tedious and expensive procedures associated with liquid-phase reactions can also be avoided.

Recently, a quite wide variety of catalysts have been tested for the alkylation of aniline with methanol, and some of them became viable alternative to the conventional homogeneous systems. However catalyst selectivity is often poor and not still developed enough for industrial applications. Different systems studied include zeolites such as HZSM-5, ALPO and SAPO [4–13]; clays and metal oxides such as Al_2O_3 and MgO [14–20]. Systems like $\text{AlPO}_4\text{--Al}_2\text{O}_3$ and $\text{CrPO}_4\text{--AlPO}_4$ were reported for alkylation of aniline by Bautista et al. [21,22]. Usually zeolites with large pores were found to favor both ring- and *N*-alkylation. Moreover, in the case of strong acid catalysts, activity for this reaction might be suppressed by the adsorption of aniline since it is a strong base. Therefore strong solid acid catalysts cannot be employed for this reaction [22]. Metal oxides usually show better selectivity for *N*-alkylation, however, a majority of such systems reported so far afforded both di- and mono-substitution on nitrogen. In addition to this, in almost all cases, large methanol to aniline molar ratio was employed and, usually, the reactions were performed at sufficiently higher temperatures. Therefore, for the industrial convenience of the process, the choice of a suitable catalyst and of the proper operating conditions are needed.

As a result of our experiments over $\text{Zn}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.5, 0.8$ and 1.0) type systems, we could realize that $\text{Zn}_{0.8}\text{Co}_{0.2}\text{Fe}_2\text{O}_4$ is remarkably active and selective for *N*-monomethylation of aniline using methanol as the alkylating agent. High NMA selectivity, catalyst stability and high activity even at comparatively low temperature and methanol to aniline molar ratio are the remarkable features of the system. The spinel structure and, hence, the cation distribution between tetra-

hedral (Tet.) and octahedral (Oct.) sites are supposed to play a major role towards the activity and stability of the system. All other members in the spinel series, except CoFe_2O_4 ($x = 1.0$), were also found to be selective for *N*-monoalkylation even though activity showed much difference with the variation in the '*x*' value.

2. Experimental

2.1. Synthesis

Different compositions of the spinel series viz. ZnFe_2O_4 (ZF-1), $\text{Zn}_{0.8}\text{Co}_{0.2}\text{Fe}_2\text{O}_4$ (ZCF-2), $\text{Zn}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ (ZCF-3), $\text{Zn}_{0.2}\text{Co}_{0.8}\text{Fe}_2\text{O}_4$ (ZCF-4) and CoFe_2O_4 (CF-5) were prepared according to procedure reported earlier [23]. Unlike the spinels synthesized by some conventional solid state high temperature routes, which produce systems with inherent drawbacks like poor compositional control, chemical inhomogeneity and low surface areas, this method provides chemically homogeneous, reproducible ferrite particles with sufficiently high surface areas. Metals were precipitated from their nitrate solution using sodium hydroxide. Aging, washing and drying were done as reported in the literature. The materials were calcined at 300°C for 8 h.

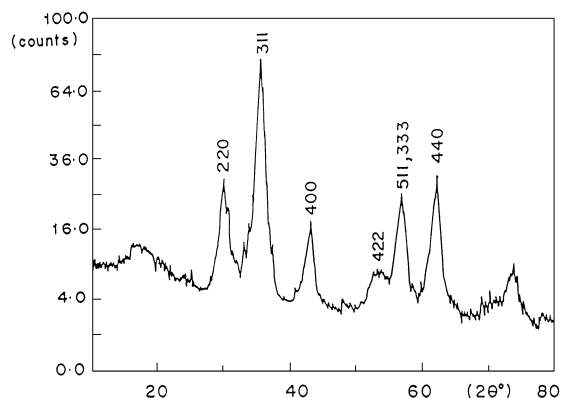


Fig. 1. Powder X-ray diffractogram of ZnFe_2O_4 (ZF-1) calcined at 500°C .

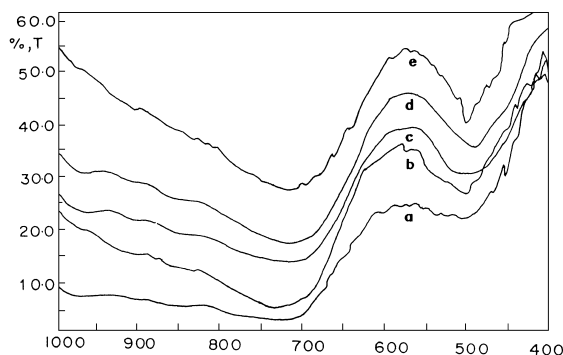


Fig. 2. Diffuse reflectance infrared spectra of different Zn–Co–ferrite systems. (a) CF-1 (b) ZCF-4 (c) ZCF-3 (d) ZCF-2 (e) ZF-1.

2.2. Characterization

2.2.1. Structural analysis

The phase purity and crystallinity of the materials were ensured by XRD (Rigaku, model D/MAX-VC) with Cu K α radiation. All peaks in the pattern matched well with the characteristic reflections of standard values reported for Zn–Co–ferrites. The X-ray diffractograms of some samples are presented in Fig. 1. Thermal analysis (SETARAM-TG-DTA-92) using finely powdered α -alumina as a reference material revealed that ferrite systems are thermally stable in the temperature range of 150°C–1000°C without creating major weight loss, decomposition or phase transformations. Scanning electron micrographs showed fine grains of uniform size \approx 50 nm, which was very much less than the grains of the spinels prepared by the conventional high temperature methods. The diffuse

reflectance infrared (DR-IR) spectra of the samples are presented in Fig. 2. All compositions of the system showed two strong IR bands, ν_1 and ν_2 around 700 and 500 cm^{-1} , respectively. It was systematically assigned by Waldron [24] and White and De Angelies [25] that the high-frequency band at 700 cm^{-1} is due to the stretching vibration of the tetrahedral group and the lower frequency band at 500 cm^{-1} is due to the vibration of the octahedral M–O group. In a spinel lattice each oxygen anion is bonded to 3 octahedral and 1 tetrahedral cation. According to Waldron [24], the tetrahedral bonds have the effect of substantially increasing the frequency of vibration, since these cations introduces a supplementary restoring force in a preferential direction along the $M_{\text{Tet-O}}$ bond. The BET surface areas of the different compositions of the ferrite systems were determined using an OMNISORP 100 CX instrument; the results are presented in Table 1.

2.2.2. Surface properties — acidity/basicity

Acidity and basicity of the systems were evaluated using two independent methods. The multipathway conversion (i.e., dehydration and dehydrogenation) of alcohol can be used as a test reaction to understand the nature of the active sites on oxide surface [26]. According to the widely accepted concept, dehydration is influenced mainly by the acid centers on the surface [27]; hence, the dehydration activity can be correlated with surface acidity. In the present case one such experiment using cyclohexanol as

Table 1
Physico-chemical characteristics of Zn–Co–ferrite systems

Composition (x)	Cation at		Concentration (%) ^a		Surface area ^b (m ² /g)
	Tet. site	Oct. site	Zn ²⁺	Co ²⁺	
0	Zn ²⁺	Fe ₂ ³⁺	27.0 (27.1)	–	30.01
0.2	Zn _{0.8} ²⁺ Fe _{0.2} ³⁺	Co _{0.2} ²⁺ Fe _{1.8} ³⁺	21.7 (21.8)	4.6 (4.8)	33.57
0.5	Zn _{0.5} ²⁺ Fe _{0.5} ³⁺	Co _{0.5} ²⁺ Fe _{1.5} ³⁺	13.7 (13.7)	12.3 (12.4)	39.46
0.8	Zn _{0.2} ²⁺ Fe _{0.8} ³⁺	Co _{0.8} ²⁺ Fe _{1.2} ³⁺	5.7 (5.5)	20.0 (20.0)	39.82
1.0	Fe ₃ ³⁺	Co ₂ ²⁺ Fe ₃ ³⁺	–	24.7 (24.8)	40.06

^aQuantities in the parantheses indicate the theoretical value.

^bSpecific surface areas of the samples calcined at 500°C.

the substrate has been performed. The amphoteric character of cyclohexanol permits their interaction with acid and base centers. The reaction was carried out in a down-flow vapour-phase silica reactor. The detailed reaction procedure is given elsewhere [28]. The mol.% of cyclohexene formed has been taken as the direct measure of the acidity of the system (Table 2).

For the determination of the basicity of the system, adsorption studies of electron acceptors (EA) were performed. The utility of EA adsorption for the study of the electron donor properties of the surface has been well established [29–31]. The limiting amount of EAs adsorbed depends on two factors: (1) the strength and distribution of donor sites (Lewis basic sites) on the surface and (2) the electron affinity values of the EAs used. Thus, from a comparison of limiting concentrations of EAs adsorbed and the electron affinity values of the respective EAs used, valuable information regarding the strength and distribution of the donor sites can be obtained. 7,7,8,8-Tetracyanoquinodimethane (TCNQ), 2,3,5,6-tetrachloro-1,4-benzoquinone (chloranil) and *p*-dinitrobenzene with electron affinity values 2.84, 2.40 and 1.77 eV were employed for this study. Catalysts were activated at 500°C prior to each experiment. The adsorption study was carried out over 0.5 g catalyst placed in a cylindrical glass vessel fitted with an air tight stirrer. A solution of EA in acetonitrile was then admitted to the catalyst. Stirring was continued for 4 h at room temperature. The amount of EA adsorbed was deter-

mined from the difference in concentration of EA in solution before and after adsorption, which was measured by means of a UV–VIS spectrophotometer (λ_{max} of EA in solvent: 393.5 nm for TCNQ, 288 nm for chloranil and 262 nm for PDNB).

The limiting amounts adsorbed for TCNQ and chloranil are presented in Table 2. The adsorption of PDNB was negligible. The limiting concentrations were expressed in mol m⁻²; the surface areas being determined using BET method for each sample. Langmuir type of adsorption isotherms obtained for TCNQ and chloranil are shown in Figs. 3 and 4, respectively. The limiting amount value is higher for TCNQ than for chloranil. Since TCNQ is a strong EA (electron affinity value 2.84 eV) it forms anion radicals adsorbed from strong as well as weak donor sites. In other words, the limiting amount of TCNQ adsorbed will give a measure of strong as well as weak donor sites on the catalyst surface. However, chloranil (electron affinity value 2.40 eV) can accept electrons from strong and moderately strong donor sites. Negligible adsorption of PDNB (electron affinity value 1.77 eV) in all systems indicates absence of very strong donor sites. This suggests that the adsorption sites on Zn–Ni–ferrites act as electron donors to the adsorbed molecule with electron affinity values less than 2.40 eV but greater than 1.77 eV. A survey of the limiting amount adsorbed (Table 2) indicates that basicity of the system follows the order: ZF-1 \approx ZCF-2 > ZCF-3 > ZCF-4 \approx

Table 2

Cyclohexanol dehydration activity and the limiting amounts of electron acceptors (EA) adsorbed over different Zn–Co–ferrite systems

Catalyst composition	Cyclohexene (%) ^a	Limiting amount of EA adsorbed ($\times 10^{-5}$ mol m ⁻²)	
		TCNQ	Chloranil
ZF-1	39.72	1.66	0.66
ZCF-2	40.40	1.56	0.48
ZCF-3	49.80	1.55	0.43
ZCF-4	52.40	1.47	0.37
CF-5	55.30	1.40	0.31

^aReaction conditions: WHSV 2 h⁻¹, reaction temperature 325°C.

CF-5, which indicates that basicity shows a decreasing trend with progressive substitution of zinc by cobalt, even though the decrease is very slow, as evident from the nearly close limiting amount values for the neighbouring members. The decrease in basicity is associated with a concomitant increase in their acidity, as revealed from the dehydration activity. From these results it can be inferred that either Co^{2+} or Fe^{3+} ions are responsible for the acidity of the systems. Since cobalt-substitution replaces an equivalent amount of Fe^{3+} ions from more active Oct. sites to less accessible Tet. sites, and also since cobalt-substitution increased acidity of the systems, we believe that the stronger Lewis acid centers are created mainly by Co^{2+} ions.

2.3. Reaction procedure

Catalytic measurements were carried out in a fixed-bed down-flow silica reactor (20 mm i.d.)

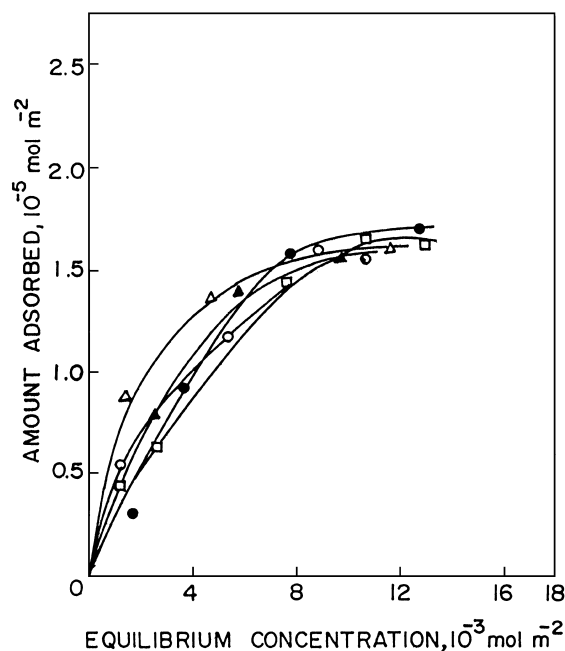


Fig. 3. Adsorption isotherms of TCNQ in acetonitrile on different Zn–Co–ferrite systems calcined at 500°C. ● ZF-1; □ ZCF-2; ▲ ZCF-3; △ ZCF-4; ○ CF-5.

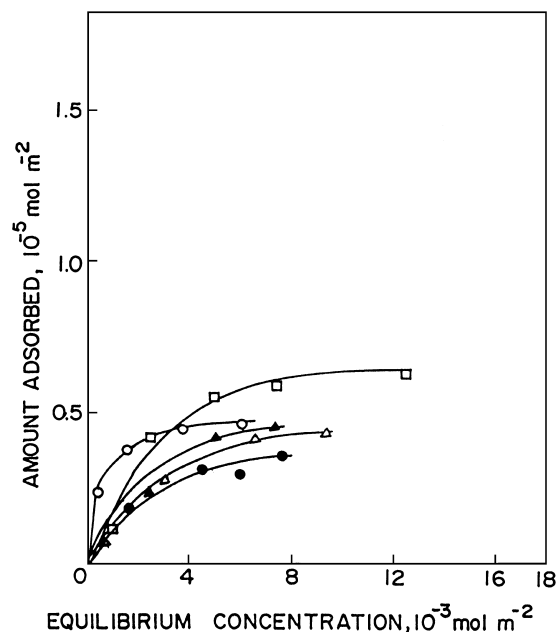


Fig. 4. Adsorption isotherms of chloranil in acetonitrile on different Zn–Co–ferrite systems calcined at 500°C. □ ZF-1; ○ ZCF-2; ▲ ZCF-3; △ ZCF-4; ● CF-5.

at atmospheric pressure. Pre-treatment of the catalysts consisted of heating in a stream of air for about 5 hours at 500°C, and then brought down to the corresponding reaction temperatures by cooling under a current of nitrogen gas of high purity. After terminating the nitrogen flow, the feed consisting of a mixture of aniline and methanol was fed into the reactor by a ISCO-Model 500 D syringe pump. The reactions were performed as a function of temperature, mole ratios of the reaction mixture and feed rates (WHSV varied from 0.7 h^{-1} to 3.3 h^{-1}). Liquid products were condensed and were analyzed by a Shimadzu GC-15 A gas chromatograph using FID and 2 M, 2% carbowax 20 M + 5% KOH on a chromosorb W column. The gaseous products were analyzed using a porapak-Q column with TCD. A blank run without any catalyst indicated negligible thermal reaction. The material balance of our experimental system was in the range of 95–96 wt.%, while the reproducibility of the experimental system was better than $\pm 5\%$.

3. Results and discussion

The multistep sequential reaction of aniline and methanol leads to a variety of products. NMA and/or toluidines are the primary alkylated products. NMA on further alkylation gives NNDMA and/or *N*-methyl toluidines. Another possibility is the transalkylation between a molecule of NNDMA and another molecule of aniline, giving two molecules of NMA. Toluidines on further alkylation give products like xylidines and *N*-methyltoluidines.

Among the various compositions of the system, the ones possessing low ‘*x*’ values (0, 0.2 and 0.5) were found to be highly selective for *N*-monomethylation of aniline. But catalytic activity depends strongly on catalyst composition and reaction conditions. Considerable difference in the activity was observed as the composition varies from one extreme to the other. Systems possessing the lower ‘*x*’ values (0, 0.2 and 0.5) were found to be more active and selective, compared to those having ‘*x*’ values 0.8 and 1.0. In the latter case, a large quantity of aniline was converted into products like benzene and

toluene, owing to the interaction with the strong acidic sites present on these systems. Details regarding the optimization of various process parameters are presented systematically in the following sections.

3.1. Effect of molar ratio of methanol to aniline

In order to understand the optimum feed mix ratio, a series of experiments were performed at 350°C with different molar ratios of methanol to aniline over ZCF-2 (Fig. 5). In all cases NMA has been formed as the major product. Some amount of NNDMA was detected at higher feed-mix ratio. However, neither any toluidine isomers nor any condensed products of aniline or alkylanilines were formed throughout the experiment. Both aniline conversion and NMA yield improved with feed molar ratio (methanol to aniline) and at the molar ratio of 5 the yield of NMA was maximized ($\approx 72\%$). Even at a methanol to aniline molar ratio of 2, the catalyst executed excellent NMA yield ($\approx 52\%$) with selectivity more than 99%.

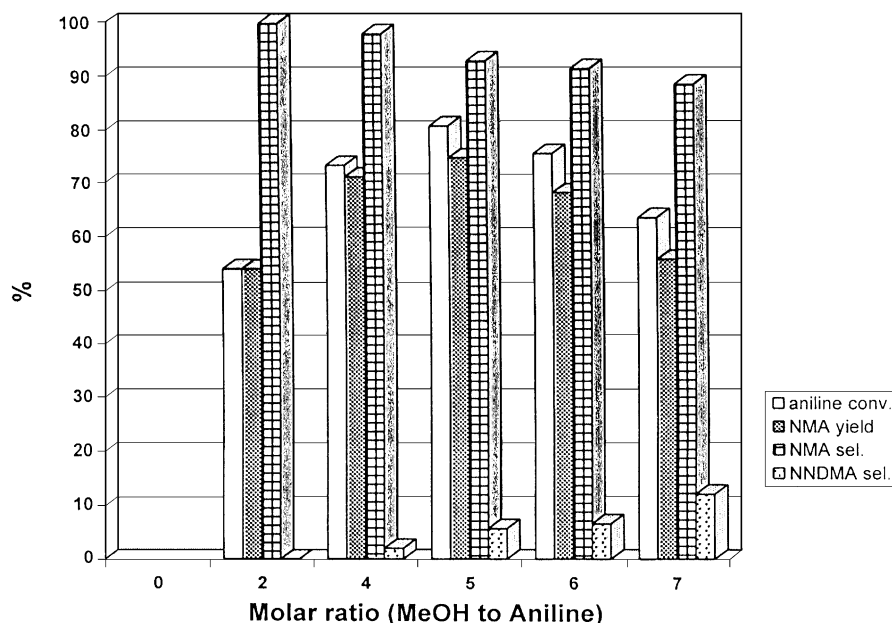


Fig. 5. Influence of feed (methanol to aniline) molar ratio on conversion and selectivities over ZCF-2. WHSV 2 h^{-1} ; reaction temperature 350°C; TOS 1 h.

3.2. Effect of catalyst composition

Another series of experiments were performed to relate the activity with composition. Product distribution data as a function of composition is represented in Fig. 6. It can be seen that zinc–cobalt ratio is an important factor which can greatly influence selectivity as well as conversion. At lower ‘*x*’ values the selectivity of NMA increased; ZF-1, ZCF-2 and ZCF-3 executed nearly 99% NMA selectivity. The influence of ‘*x*’ on NMA yield was much more pronounced. Even at a methanol to aniline molar ratio of 2 both ZF-1 and ZCF-2 exhibited very high activity for the *N*-monoalkylation of aniline (NMA yield nearly 53% and 51%, respectively). However, with pure cobalt ferrite (CF-5), selectivity for NMA was only 11%. Large amounts of secondary products viz. benzene and toluene, as a result of deamination of aniline, were also detected in this system.

3.3. Effect of time on stream

The performance of these catalysts were studied over a period of 6 h. Reactions were per-

formed at 350°C and the product analysis has been done at regular intervals of 60 min. In Fig. 7, the yield of NMA is plotted as a function of time on stream in hours. Except ZF-1, all other members of the spinel series displayed excellent stability. ZF-1 deactivates in the initial period of the run (up to 4 h) and thereafter it maintained a steady value of activity. This result is particularly interesting if one considers the normal spinel lattice of ZF-1, where electron hopping is constrained due to the nonavailability of Fe³⁺ ions in the Tet. sites. Others are inverse in nature and all such systems showed prolonged stability.

3.4. Effect of reaction temperature and feed flow rate

Catalyst runs have been performed on ZCF-2, in the temperature range between 250°C and 400°C. Temperature has a marked influence on aniline conversion. Alkylation of aniline takes place effectively at temperatures above 250°C (Table 3). It has been seen that in the temperature range between 300°C and 350°C hardly any

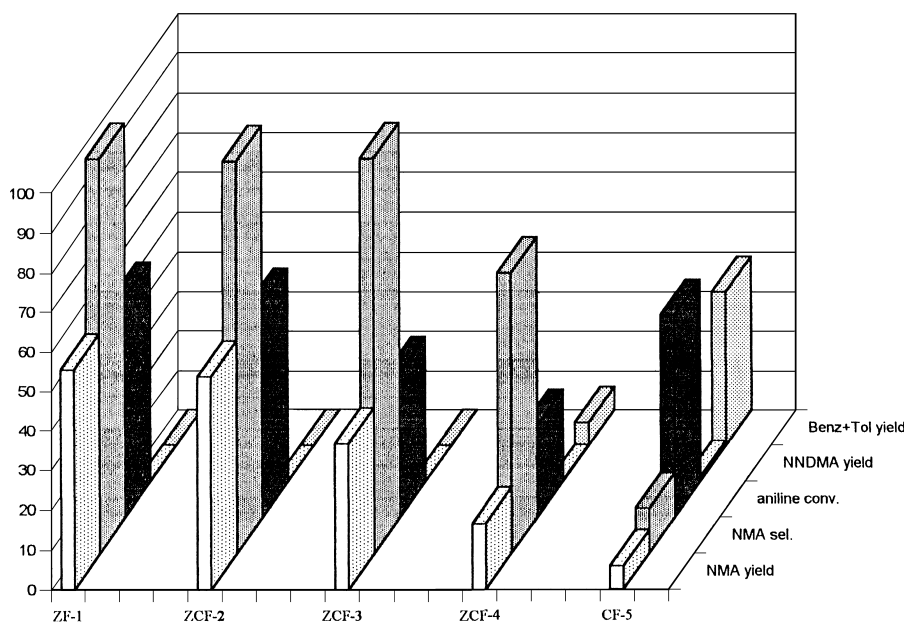


Fig. 6. Product distribution and selectivity pattern of aniline alkylation over different Zn–Co–ferrite systems. Reaction temperature 350°C; WHSV 2 h⁻¹; methanol:aniline 2:1; TOS 1 h.

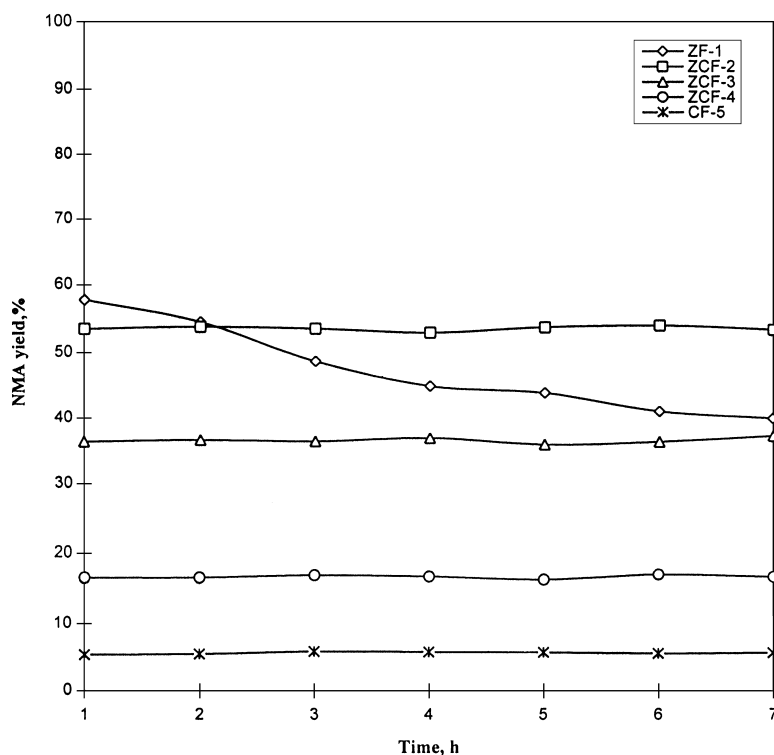


Fig. 7. Evaluation of catalyst stability: WHSV 2 h^{-1} ; reaction temperature 350°C ; methanol:aniline 2:1. Concentration of *N*-methylaniline is plotted as a function of reaction time in hours.

ring alkylated products were formed and only *N*-alkylation takes place with NMA selectivity always greater than 90%. Up to 350°C , both aniline conversion and NMA yield improved with rise in temperature. Maximum yield of NMA (71.8%) was observed at 350°C with selectivity more than 91%. The temperature range providing maximum yield of NNDMA was 350°C – 370°C , however its yield was not exceeded 6%. Further increase in temperature did not show any enhancement in the alkylation rate, but high temperature favoured decomposition of methanol yielding products like oxides of carbon and C_1 and C_2 hydrocarbons. The high decomposition rate of methanol was further clarified by passing methanol alone over these catalysts in the temperature range selected for the alkylation experiments. This indicates that the optimum temperature range for selective formation of NMA is 300°C – 350°C .

Fig. 8 shows the effect of contact time on aniline conversion and NMA selectivity. Selectivity and conversion first increased and reached a maximum at a WHSV of 2 h^{-1} (flow rate 6

Table 3

Performance of ZCF-2 for aniline methylation at different reaction temperatures. WHSV 2 h^{-1} ; methanol to aniline molar ratio 6; TOS 1 h

Reaction temperature ($^\circ\text{C}$)	250	300	350	400
<i>Aniline Conversion (wt.%)</i>	14.35	56.52	77.62	59.40
<i>Product distribution (wt %)</i>				
Benzene + Toluene	Nil	0.73	1.28	3.00
NMA	14.05	54.30	71.82	50.95
NNDMA	Nil	1.34	4.40	5.45
Toluidines	Nil	Nil	Nil	Nil
Others	0.30	0.15	0.12	
<i>Product selectivity (wt.%)</i>				
NNDMA	97.90	96.07	92.52	85.77
	–	–	5.67	9.17

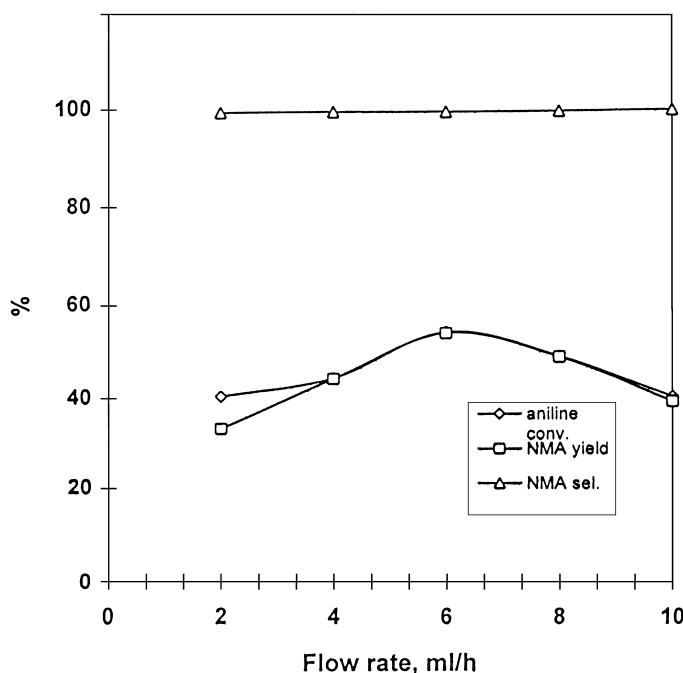


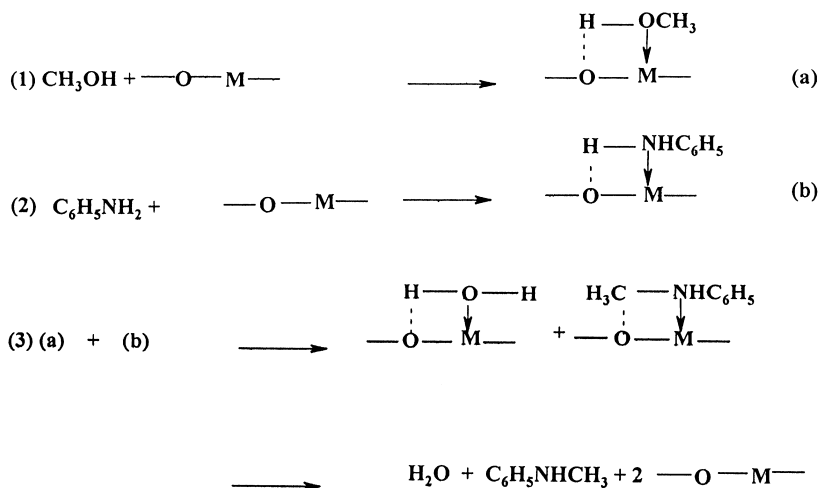
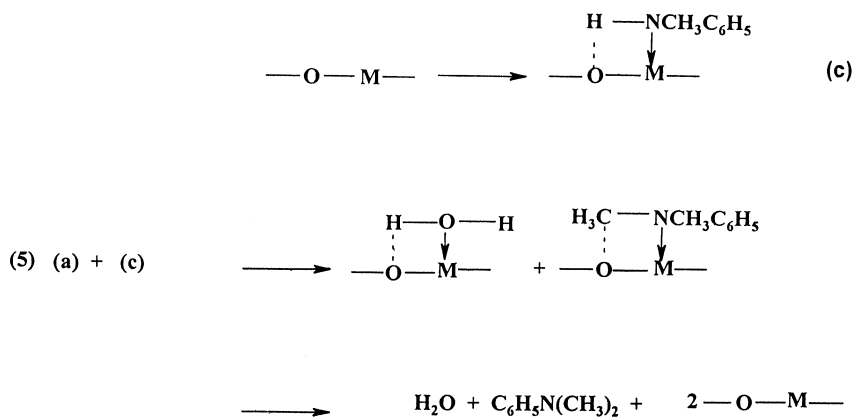
Fig. 8. Effect of feed flow rate on aniline methylation: Catalyst ZCF-2, WHSV 2 h^{-1} ; reaction temperature 350°C ; TOS 1 h.

ml/h) and then declined. The low aniline conversion rate at high contact time regions can be attributed to the increased rate of methanol decomposition as a side reaction. Since the methanol to aniline ratio is only 2, such side reactions of methanol will seriously affect aniline conversion. As contact time decreases, the rate of this side reaction also decreases, resulting in more aniline conversion and NMA yield.

4. Catalytic pathway

Alkylation of aniline over oxide systems occurs through a concerted mechanism involving simultaneous participation of both acidic and basic centers on the catalyst surface. The mechanism of aniline alkylation over oxide systems has been well established by An Nanko et al. [16], according to which Lewis acid sites of the metal oxide systems interact with the methoxy species and, the hydrogen atoms of the undissociated hydroxyl groups interact with the Lewis basic sites (Fig. 9). Electrophilic attack of the

methyl group of methanol on the nitrogen atom of the adsorbed aniline leads to NMA, which on subsequent methylation leads to NNDMA. Thus the mechanism accounts the need of moderate amounts of both acidic and basic Lewis sites for the system. The acidity and basicity of the tested catalysts were measured according to the methods previously described (Table 2). Catalytic activity follows the order: ZF-1 > ZCF-2 > ZCF-3 > ZCF-4 > CF-5. From the cyclohexanol dehydration activity, it has been concluded that Co-substitution has increased the acidity of the system. In other words, the substitution of Fe^{3+} ions by Co^{2+} ions in the octahedral sites creates stronger acid sites than due to Fe^{3+} ions. Creation of acidic sites by octahedral ions can also be explained in another way: Due to the lower coordination number of the tetrahedral cations, the effective attractive force for a single Tet. M–O bond will be strong [32]. Since each octahedral cation is surrounded by more number of anions, the Oct. M–O bond will be weaker, and hence will be more polar. Additionally, Jacobs et al. [33] in a study, using LEIS (Low

Mechanism of N-monoalkylation**Mechanism of N,N-dialkylation**Fig. 9. Mechanism of *N*-methylation of aniline using methanol.

Energy Ion Scattering, a technique which is sensitive to the outermost atomic layer), revealed that spinel surface sites are mainly octahedral and, hence, the Oct. cations are exposed on the surface. The acidity and basicity depend on the extent of polarity of the metal cation and oxygen anion respectively. As reported by Narasimhan and Swamy . [27], weak Oct. M–O bonds act as strong alcohol adsorption centers. From the adsorption experiments using electron acceptors and their dehydration activities, we could understand the trend in acid–base site

distribution with composition. We have observed that, as ‘*x*’ increased the dehydration activity increased, whereas the limiting concentration of EAs adsorbed decreased. In other words, acid–base properties mutually dependant and creation of new acidic centers occurs via. the removal of existing basic centers. This clearly indicated that the acido-basic property depends up to a major extent on the variation of M–O bond polarity with composition.

Even though replacement of Zn^{2+} by Co^{2+} increased acidity, alkylation activity shows a

trend not commensurating with their acidity. In this sense, unlike other typical acid–base reactions, acidity cannot be considered as the sole factor deciding the catalytic activity. Since aniline itself is a strong base, even the weak Lewis acid sites on the catalyst surface can effectively coordinate with this molecule and, therefore, the liability of the systems towards alcohol adsorption becomes more important. It is believed that the stronger Lewis acid sites are provided by the octahedral ions (either Fe^{3+} in ZF-1 or Fe^{3+} and Co^{2+} in the substituted spinels). ZF-1 being a normal spinel, all Fe^{3+} ions are available in the active Oct. sites and the Tet. sites are occupied exclusively by stable Zn^{2+} (d^{10} configuration) ions. Hence, the high NMA yield of the system can be due to the moderate acidity created by surface Fe^{3+} ions. A similar conclusion regarding acidity was reported by Ghorpade et al. [34] for Cu–Cr–Fe ternary spinel systems, since they observed a progressive decrease in the activation energy for Friedel–Crafts benzylation reaction as the iron content of the system increases. Oct. M–O bond is weaker and, hence, the Oct. Fe^{3+} ions act as the alcohol adsorbing centers in ZF-1. Adsorption of alcohol and the subsequent electron transfer from adsorbate to catalyst can change the oxidation state of iron. A characteristic feature of spinel system which has been stressed by many workers is their unique property to withstand reducing conditions via. electron hopping between adjacent ions. Since, in ZF-1, the neighbouring sites are occupied by stable Zn^{2+} ions, the reduced Fe^{3+} ions are unable to regain their original state through oxidative transfer, resulting in progressive deactivation of the system.

As ‘ x ’ increases, Co^{2+} ions replace equivalent amounts of Fe^{3+} ions from Oct. to Tet. sites. Thus the spinel gradually becomes inverse in nature. Presence of Fe^{3+} ions in both sites facilitates fast redistribution of electrons and, thus, the reduced Fe^{3+} ions can regain their original state quite easily. All inverse systems showed persistent activity for a long period. But Co-substitution increased the acidity of the sys-

tem, and acidity significantly improved with increase in ‘ x ’ value beyond 0.5. This leads to strong interaction of acid centers and aniline, and, if acidity is sufficiently more, deamination of aniline occurs giving products like benzene and toluene. This has happened in the case of ZCF-4 and CF-5. Owing to their strong acidity, a large quantity of aniline decomposed as indicated by the significant amounts of benzene and toluene in the product distribution data (Fig. 5).

5. Conclusions

The main conclusions drawn from this work are summarised below.

(a) The systems possessing lower ‘ x ’ values (i.e., ‘ x ’ between 0 and 0.5) in the ferrite series $\text{Zn}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ can be used for the selective synthesis of NMA. Aniline conversion and product selectivities vary with reaction parameters. NMA selectivity of 99% or more was observed under the optimized reaction conditions.

(b) Among the spinel series, ZCF-2 ($x = 0.2$) is remarkable due to its high activity, selectivity and excellent stability towards *N*-monoalkylation. Large excess of alkylating agent is not required and appreciable conversion was observed even at a methanol to aniline molar ratio of 2. ZF-1 shows activity slightly higher than ZCF-2 in the initial period of the run, however deactivates as the reaction proceeds.

(c) ZF-1 is a normal spinel system. As ‘ x ’ increases, the system progressively approaches to an inverse lattice. All inverse systems ($x \neq 0$) displayed prolonged stability. This is due to the presence of redox ions in both octahedral and tetrahedral sites of inverse systems. Nonavailability of Fe^{3+} ions in the Tet. sites of ZF-1 causes deactivation, since the reduced Fe^{3+} ions in the Oct. sites are unable to exchange electrons and thereby regain their original states.

(d) Optimum concentration of acidic as well as basic sites are essential for the reaction. Cobalt addition increased the acidity of the

system with a concomitant decrease in its basicity. When 'x' exceeds 0.5 acidity increased substantially. Exposure of more Co^{2+} ions together with Fe^{3+} ions in the active Oct. sites facilitates deamination of aniline. In CF-5 ($x = 1.0$) the major products were toluene and benzene.

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References

- [1] S. Narayanan, V. Durgakumari, A. Sudhakar Rao, Appl. Catal. A 111 (1994) 133.
- [2] P.R. Hari Prasad Rao, P. Massiani, D. Barthomeuf, Catal. Lett. 31 (1995) 115.
- [3] Y. Ono, Cat. Tech. (1997) .
- [4] P.Y. Chen, M.C. Chen, H.Y. Chu, N.S. Chang, T.K. Chuang, Proc. 7th Int. Zeolite Conf., Kodasha Tokyo (1986) 739.
- [5] W.W. Kaeding, R.E. Holland, J. Catal. 109 (1988) 212.
- [6] K. Kunikata, Japan Kokai 78 (1978) 128.
- [7] C.V. Kilkhtyanin, K.G. Ione, L.V. Malesheva, A.V. Toktarev, Proc. Int. Symp. Chem. Microporous Crystals, Elsevier, Amsterdam.
- [8] P.Y. Chen, M.C. Chen, H.Y. Chen, N.S. Chang, T.K. Chuang, Stud. Surf. Sci. Catal. 28 (1986) 739.
- [9] S. Prasad, B.S. Rao, J. Mol. Catal. 62 (1990) L17.
- [10] O. Mokoto, I. Koji, I. Yusuke, J. Inclusion Phenom. 2 (1984) 359.
- [11] P.S. Singh, R. Bandyopadhyay, B.S. Rao, Appl. Catal. A 136 (1996) 177.
- [12] O. Onaka, K. Ishikawa, Y. Isumi, Chem. Lett. (1992) 1783.
- [13] S. Narayanan, A. Sulthan, K. Krishna, React. Kinet. Catal. Lett. 52 (1994) 1783.
- [14] H. Matsushashi, K. Arata, Bull. Chem. Soc. Jpn. 64 (1991) 2605.
- [15] A.G. Hill, J.H. Ship, A.J. Hill, Ind. Eng. Chem. 43 (1951) 1579.
- [16] A. Nanko, C.L. Yang, W. Zhu, H. Lin, Appl. Catal. A 134 (1996) 53.
- [17] N. Takamiya, Y. Koinuma, K. Ando, S. Murai, Nippon Kagakukaishi (1979) 1452.
- [18] A.N. Ko, C.L. Yang, W. Zhu, H. Lin, Appl. Catal. A 134 (1996) 53.
- [19] C.M. Naccache, Y.B. Tarit, J. Catal. 22 (1971) 171.
- [20] J.M. Parera, A. Gonzalez, M.A. Barral, Ind. Eng. Chem. Proc. Res. Dev. 7 (1968) 259.
- [21] F.M. Bautista, J.M. Campelo, A. Garcla, D. Luna, J.M. Marrinas, A.A. Romero, M.R. Urbano, J. Catal. 172 (1997) 103.
- [22] F.M. Bautista, J.M. Campelo, A. Garcla, D. Luna, J.M. Marrinas, A.A. Romero, Appl. Catal. A 166 (1998) 39.
- [23] P.S. Anilkumar, J.J. Schotri, S.D. Kulkarni, C.E. Deshpande, S.K. Date, Mat. Lett. 27 (1996) 293.
- [24] R.D. Waldron, Phy. Rev. 99 (1955) 1727.
- [25] W.B. White, B.A. De Angelies, Spectrochim Acta A23 (1967) 985.
- [26] M.P. Rosynek, R.J. Koprowski, G.N. Dellisante, J. Catal. 122 (1990) 80.
- [27] C.S. Narasimhan, C.S. Swamy, Appl. Catal. 2 (1982) 315.
- [28] W.S. Chin, M.D. Lee, Appl. Catal. A 83 (1992) 201.
- [29] B.D. Folkhart, I.R. Leith, R.C. Pink, Trans. Faraday Soc. 65 (1969) 542.
- [30] K. Meguro, K. Esumi, J. Colloid Interface Sci. 59 (1) (1977) 93.
- [31] K. Esumi, H. Shimada, K. Meguro, Bull. Chem. Soc. Jpn. 50 (10) (1977) 2795.
- [32] F.C. Romeijn, Philips Res. Rep. 8 (1953) 304.
- [33] J.P. Jacobs, A. Maltha, J.R.H. Reintjes, T. Drimal, V. Ponec, H.H. Brogersma, J. Catal. 147 (1994) 294.
- [34] S.P. Ghorpade, V.S. Darshane, S.G. Dixit, Appl. Catal. A 166 (1998) 141.