

# Selective *N*-methylation of aniline with dimethyl carbonate over $Zn_{1-x}Co_xFe_2O_4$ ( $x = 0, 0.2, 0.5, 0.8$ and $1.0$ ) type systems

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## Abstract

The alkylation of aniline with dimethyl carbonate (DMC) is reported over  $Zn_{1-x}Co_xFe_2O_4$  ( $x = 0, 0.2, 0.5, 0.8$  and  $1.0$ ) type systems prepared via coprecipitation route. The influence of surface acid–base properties, cation distribution in the spinel lattice and various reaction parameters are discussed. It was observed that systems possessing low  $x$  values are highly selective and active for *N*-alkylation leading to *N*-methyl aniline as the major product. Since the authors have already reported the alkylation reaction using methanol as the alkylating agent over the same ferros spinel systems, in some cases both data are compared to highlight the merits and demerits of the choice of the two alkylating agents. DMC is acting as a better alkylating agent at comparatively low temperature, where methanol shows only mild activity. However, on the selectivity basis DMC as an alkylating agent could not compete with methanol, since the former executed appreciable amount of *N,N*-dimethylaniline (NNDMA) even at low temperature where methanol gave nearly 99% *NMA* selectivity. Cation distribution in the spinel lattice influences its acido-basic properties, and hence, these factors have been considered as helpful to evaluate the activity and stability of the systems. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Ferrites; Spinel structure; Aniline conversion; *N*-Alkylation; Dimethyl carbonate

## 1. Introduction

Spinel type mixed oxides ( $AB_2O_4$ ) are interesting systems due to the peculiar nature of cation distribution in tetrahedral (Tet.) and octahedral (Oct.) sites. Spinel oxides containing iron are called ferros spinels. Based on the distribution of cations, spinels can be either normal  $M_{Tet}^{2+}[Fe^{3+}Fe^{3+}]_{Oct}O_4$  or inverse with half of the

trivalent ions in the Tet. position and the other half together with the divalent ions in the Oct. site. Crystal field stabilization energy, Madung constant and cation size are the principal factors in deciding the structure of the systems [1,2]. The catalytic effectiveness of ferrites for many reactions arises because of the ease with which iron can change its oxidation state between 2 and 3 [3]. Another important attribute of these materials, from the commercial point, is that spinel structure provides high stability so that these materials can withstand extremely

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reducing conditions. However, the conventional routes using solid-phase calcination methods cannot usually provide materials with essential requirements needed for good catalysts. Recently reported low temperature, controlled coprecipitation routes overcome this drawback since these methods produce homogeneous, fine and reproducible ferrite particles with sufficiently large surface areas. Several authors have reported that the major influence in the activity comes from the Oct. ions, probably due to the large exposure of these ions on the surface, as shown by Jacobs et al. [4] using low energy ion scattering experiments.

As a result of our experiments on vapour-phase alkylation of aniline using methanol as the alkylating agent over ferrosinels containing Zn, Ni and Co prepared via low temperature method, we could understand that systems possessing lower  $x$  values in the spinel systems  $Zn_{1-x}Co_xFe_2O_4$  and  $Zn_{1-x}Ni_xFe_2O_4$  ( $x = 0, 0.2, 0.5, 0.8$  and  $1.0$ ) are highly selective and active for  $N$ -monomethylation of aniline leading to  $N$ -methylaniline (NMA) [5,6]. NMA is an important chemical for the production of dyes, pharmaceuticals and explosives [7–10]. Dimethyl carbonate (denoted as DMC hereafter) is a substitute for methanol as a methylating agent because of its low toxicity [11–14]. In this work, we will report that NMA is obtained in a high yield by vapour-phase methylation of aniline with DMC over various compositions of  $Zn_{1-x}Co_xFe_2O_4$ -type systems. The influence of the various reaction variables on the NMA formation is systematically studied. In the present series of compounds, all except  $ZnFe_2O_4$  are inverse in nature.  $Co^{2+}$  ions replace  $Fe^{3+}$  ions from the Oct. sites progressively as  $x$  increases. In other words, as  $x$  varies, the metal ion concentration in the Tet. as well as in the Oct. sites isomorphically varies and, thus, this type of cation distribution significantly affects their acido-basic properties. Hence, in the present work, alkylation activity is evaluated as a function of composition and the subsequent variation in acidity and basicity.

## 2. Experimental

### 2.1. Synthesis

The ferrosinels systems having the general formula  $Zn_{1-x}Co_xFe_2O_4$  ( $x = 0, 0.2, 0.5, 0.8$  and  $1.0$ ) were prepared following a coprecipitation route reported by Anilkumar et al. [15]. The important feature of the method over the conventional solid state calcination route is the exclusive formation of spinel phase at sufficiently low temperature, leading to homogeneous, fine and reproducible ferrite powders with sufficiently high surface areas. Drying and calcination were done as reported in the procedure. Catalyst pellets of the required mesh size were then obtained by pressing under 10 t of pressure. The catalyst systems were designated as:  $ZnFe_2O_4$  (ZF-1);  $Zn_{0.8}Co_{0.2}Fe_2O_4$  (ZCF-2);  $Zn_{0.5}Co_{0.5}Fe_2O_4$  (ZCF-3);  $Zn_{0.2}Co_{0.8}Fe_2O_4$  (ZCF-4);  $CoFe_2O_4$  (CF-5).

### 2.2. Characterization

#### 2.2.1. Structural analysis

The phase purity has been evaluated using powder X-ray diffraction (XRD) (Rigaku, model D/MAX-VC) with Cu K $\alpha$  radiation. The XRD patterns of various spinel compositions are presented in Fig. 1. All peaks in the pattern matched

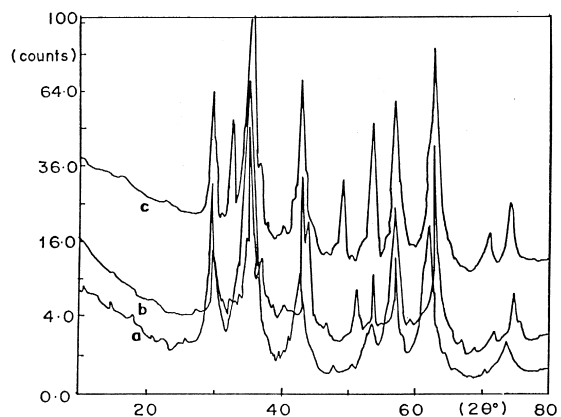


Fig. 1. Powder XRD patterns of (a) ZF-1 (b) ZCF-3 (c) CF-5 calcined at 500°C.

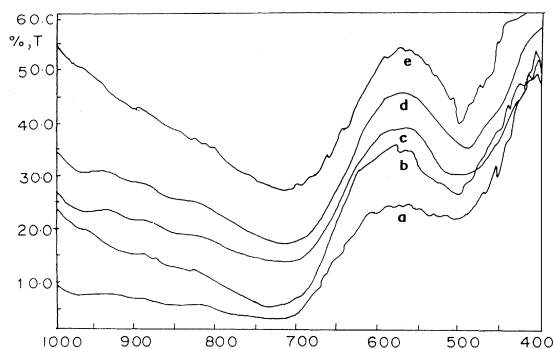


Fig. 2. Diffuse reflectance infrared spectra of (a) CF-5, (b) ZCF-4, (c) ZCF-3, (d) ZCF-2, (e) ZF-1.

well with the characteristic reflections of Zn–Co ferrites reported in the ASTM card. Diffuse reflectance infrared (DR-IR) spectra of the samples, shown in Fig. 2, consisted of two distinct broad peaks around 500 and 700  $\text{cm}^{-1}$ , respectively. In a spinel lattice every oxygen anion is bonded to three Oct. and one Tet. cations [16]. Vibration of the Tet. metal–oxygen group corresponds to the highest restoring force and thus assigned to the highest frequency band (i.e. at 700  $\text{cm}^{-1}$ ), and the band at 500  $\text{cm}^{-1}$  indicates the vibration of the Oct. metal–oxygen group [17,18]. Thermal analysis using a TG-DTA instrument (SETARAM-TG-DTA-92) indicated that ferrite systems are thermally stable in the temperature range of 150–1000°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

spinel prepared by the conventional high temperature methods. 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

Two independent methods were adopted to evaluate the acidity and basicity of the systems. Dehydration activity of the systems can be correlated with their surface acidity. In the present case, one such experiment using cyclohexanol as the substrate has been performed. The reaction is carried out in a down-flow vapor-phase silica reactor. The detailed reaction procedure is given elsewhere [19]. Mole percent of cyclohexene formed has been taken as the direct measure of the acidity of the system (Table 2).

The basic strength has been evaluated using adsorption studies of electron acceptors (EAs). The utility of EA adsorption for the study of the electron donor properties of the surface has been well established [20–23]. The most suitable way is to measure the limiting concentrations of EAs adsorbed from inert solvents. 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. The adsorption properties were studied with the following EAs, (electron affinity values in parentheses): 7,7,8,8-tetracyanoquinodimethane [TCNQ (2.84 eV)], 2,3,5,6-tetrachloro 1-4-benzoquinone

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

x	Cation distribution		Elemental analysis (%) <sup>a</sup>		Surface area <sup>b</sup> ( $\text{m}^2/\text{g}$ )
	Tet. site	Oct. site	Zn <sup>2+</sup>	Co <sup>2+</sup>	
0	Zn <sup>2+</sup>	Fe <sub>2</sub> <sup>3+</sup>	27.0 (27.1)	–	30.01
0.2	Zn <sub>0.8</sub> <sup>2+</sup> Fe <sub>0.2</sub> <sup>3+</sup>	Co <sub>0.2</sub> <sup>2+</sup> Fe <sub>1.8</sub> <sup>3+</sup>	21.6 (21.8)	4.6 (4.8)	33.57
0.5	Zn <sub>0.5</sub> <sup>2+</sup> Fe <sub>0.5</sub> <sup>3+</sup>	Co <sub>0.5</sub> <sup>2+</sup> Fe <sub>1.5</sub> <sup>3+</sup>	13.7 (13.8)	12.3 (12.4)	39.46
0.8	Zn <sub>0.2</sub> <sup>2+</sup> Fe <sub>0.8</sub> <sup>3+</sup>	Co <sub>0.8</sub> <sup>2+</sup> Fe <sub>1.2</sub> <sup>3+</sup>	5.7 (5.5)	20.0 (20.0)	39.82
1.0	Fe <sub>3</sub> <sup>3+</sup>	Co <sub>2</sub> <sup>2+</sup> Fe <sub>3</sub> <sup>3+</sup>	–	24.7 (24.8)	40.06

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

<sup>b</sup>Specific surface areas of the samples calcined at 500°C.

Table 2

Cyclohexanol dehydration activity and the limiting amounts of EAS adsorbed over different Zn–Co ferrite systems

Catalyst composition	Cyclohexene (%) <sup>a</sup>	Limiting amount of EA adsorbed ( $\times 10^{-5} \text{ mol m}^{-2}$ )	
		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

<sup>a</sup>Reaction conditions: WHSV  $2 \text{ h}^{-1}$ , reaction temperature  $325^\circ\text{C}$ .

[chloranil (1.77 eV)] and *p*-dinitrobenzene [PDNB (1.77 eV)]. The catalysts were activated at  $500^\circ\text{C}$  prior to each experiment. The adsorption study was carried out over 0.5 g catalyst placed in cylindrical glass vessel and outgassed at  $1.3 \times 10^{-3} \text{ Pa}$  for an hour. Subsequently, 20 ml of a solution of the EA in acetonitrile was added, and the solution was stirred at  $28^\circ\text{C}$  for 4 h in a thermostated bath. The amount of EA adsorbed was determined from the difference in the concentration of EA in solution before and after adsorption, which was measured by means of a UV–VIS spectrophotometer ( $\lambda_{\text{max}}$  of EA in solvent: 393.5 nm for TCNQ, 288 nm for chloranil and 262 nm for PDNB).

The Langmuir type of adsorption isotherms obtained for TCNQ and chloranil are given in Figs. 3 and 4, respectively. The limiting amounts adsorbed for TCNQ and chloranil are presented in Table 2 (the limiting concentrations were expressed in  $\text{mol m}^{-2}$ ; the surface areas being determined using BET method for each sample). In all cases, the adsorption of PDNB was negligible. Since the electron affinity value of TCNQ is more, its anion radicals are expected to form on strong as well as weak basic sites. Chloranil with intermediate electron affinity value cannot accept electrons from very weak donor sites. The negligible adsorption of PDNB for all systems indicates the absence of very strong donor sites, and hence the limiting amount of TCNQ

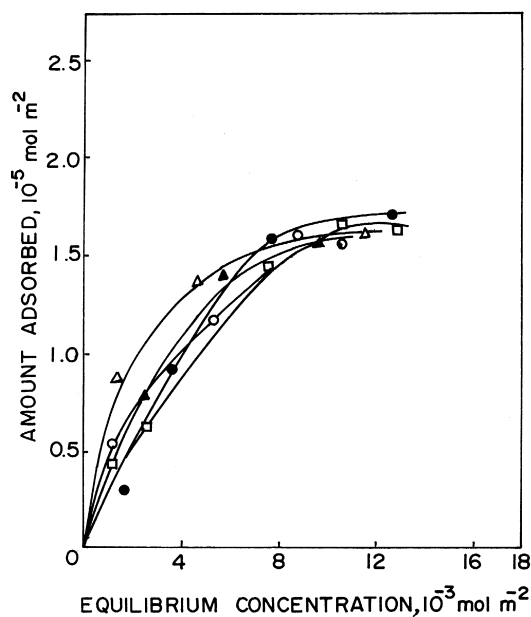


Fig. 3. Adsorption isotherms of TCNQ in acetonitrile on different Zn–Co ferrite systems calcined at  $500^\circ\text{C}$ . ● ZF-1; □ ZCF-2; ▲ ZCF-3; △ ZCF-4; ○ CF-5.

and chloranil would be an estimate of the weak or moderate basic sites. Basicity of the system

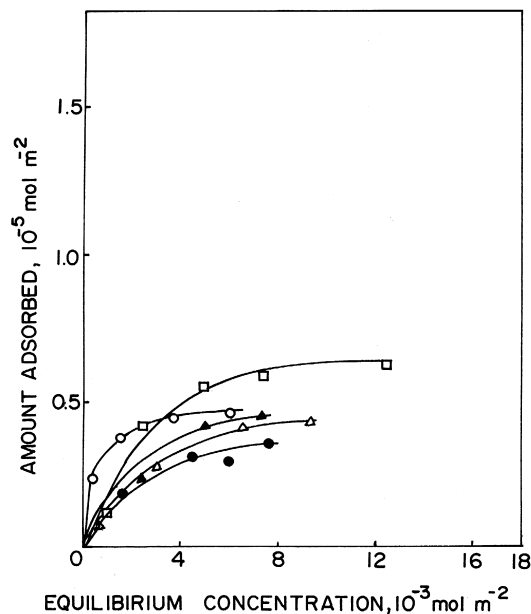


Fig. 4. Adsorption isotherms of chloranil in acetonitrile on different Zn–Co ferrite systems calcined at  $500^\circ\text{C}$ . □ ZF-1; ○ ZCF-2; ▲ ZCF-3; △ ZCF-4; ● CF-5.

follows the order: ZF-1  $\approx$  ZCF-2 > ZCF-3 > ZCF-4  $\approx$  CF-5. The decrease in basicity during Co-substitution is associated with a concomitant increase in their acidity, as revealed from the dehydration activity. It is well established that  $\text{Co}^{2+}$  ions always prefer an octahedral environment and accommodation of  $\text{Co}^{2+}$  ions in the Oct. sublattices occurs after transferring an equivalent amount of  $\text{Fe}^{3+}$  from Oct. to Tet. sites. Thus the decrease in basicity on Co-substitution can be rationalized on the basis of the substitution of Oct.  $\text{Fe}^{3+}$  ions by  $\text{Co}^{2+}$  ions.  $\text{Zn}^{2+}$  being a  $d^{10}$  system and also since it occupies in less accessible Tet. sites, the major influence on acid–base property comes from the  $\text{Co}^{2+}/\text{Fe}^{3+}$  ratio in the Oct. sites.

### 3. Catalytic reactivity

#### 3.1. Apparatus and procedure

The catalytic test was carried out on 3 g catalyst, retained by inert porcelain beads at almost the center of a vapor-phase down-flow silica reactor (20 mm ID) (gèomècanique, France) at atmospheric pressure. The materials were pretreated for 12 h at 500°C under oxygen and brought down to the respective reaction temperatures using flowing dry nitrogen. The feed containing aniline and DMC was delivered using a liquid syringe pump (ISCO-Model 500D). Liquid products were condensed with a cold trap and were analyzed by a Shimadzu GC-15A 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 porapack-Q column with TCD. A blank run without any catalyst indicated negligible thermal reaction.

#### 3.2. Results and discussion

The multistep sequential reaction of aniline with DMC gives products like NMA, *N,N*-di-

methylaniline (NNDMA) and toluidines. NMA and NNDMA can be formed by the direct electrophilic substitution of methyl groups on the hetero atom. NMA can also be formed by the *trans*-alkylation between adsorbed NNDMA and aniline.

Alkylation experiments revealed that in the ferrispinel series,  $\text{Zn}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ , the systems possessing low  $x$  values, viz. 0, 0.2, and 0.5, are selective for *N*-methylation of aniline. NMA was formed as the major product over all compositions, even though catalytic activity showed a significant gradation with their  $x$  values. Maximum activity was observed over ZF-1 and even in this most active catalyst the percentage of C-alkylated product was found to be less than 0.8% under the optimized reaction conditions. But the most significant advantage of using DMC is its low operation temperature (below 280°C), compared to using methanol as the alkylating agent, where we have already reported the optimum temperature for the selective formation of NMA is 350°C [5,6].

Table 3 shows the activities and selectivities of various compositions of the system in methylation of aniline with DMC. In contrast with methylation with methanol, every catalyst gave both mono- and di-*N*-alkylated products. As  $x$  increased, more amount of NNDMA was formed. ZF-1 and ZCF-2 executed nearly similar activities and both these systems afforded more amount of NMA. Aniline conversion increased

Table 3  
Aniline conversion and selectivity data of aniline methylation using DMC over different Zn–Co ferrites. Reaction temperature 250°C; WHSV 1.2 h<sup>-1</sup>; molar ratio (DMC to aniline) 2; TOS 1 h

Catalyst composition	Product distribution (wt.%)			
	Aniline conversion	NMA selectivity	NNDMA selectivity	Others <sup>a</sup>
ZF-1	50.00	75.31	10.87	13.82
ZCF-2	50.53	73.83	11.93	14.24
ZCF-3	55.47	67.21	16.01	16.78
ZCF-4	57.75	62.22	20.05	17.73
CF-5	60.05	61.17	21.87	16.96

<sup>a</sup>Others include DMC fractions, benzene, toluene and traces of unidentified products.

progressively with increase in the  $x$  value, however, the activity of higher members ( $x > 0.5$ ) was much lower than the more Zn-substituted systems. In an earlier work, using methanol as the alkylating agent over Zn–Co systems, we have reported a similar activity pattern for NMA formation [6]. The similarity of aniline conversion and total alkylation (both *N*-mono- and *N,N*-di-alkylations) activity pattern using methanol and DMC suggests the involvement of same active sites of the catalyst surface irrespective of the alkylating agent. However, the considerable difference in the yield and selectivities of the respective products over same catalyst suggest that the adsorbed active alkylating species formed from methanol and DMC are different. Due to the lower coordination number of the tetrahedral cations, the effective attractive force for a single Tet. M–O bond will be strong [3]. Since each octahedral cation is surrounded by more number of anions, the Oct. M–O bond will be weaker, thus will be more polar. Additionally, Jacobs et al. [4] after a series of Low Energy Ion Scattering (LEIS — a technique highly sensitive to probe surface atomic layer) experiments have shown that in a spinel lattice the surface layer is mainly Oct. and, therefore, Oct. cations are exposed on the surface whereas the Tet. ones are not easily assessable. Thus it is reasonable to conclude that in the adsorption and subsequent reaction of aniline with DMC, the  $\text{Fe}_{\text{Oct}}^{3+}/\text{Co}_{\text{Oct}}^{2+}$  ratio of the systems is an important factor. As the ratio decreases, acidity increases, resulting a sharp variation in the activity pattern.

In order to understand the influence of various process parameters, further studies have been performed using ZCF-2 as a model system.

A series of experiments were performed in the temperature range of 200–300°C using a feed composition (DMC/aniline) of 2 and WHSV of 1.2 h<sup>-1</sup>. Unlike the experiments using methanol, here temperature showed a marked influence on selectivities of the products. At low temperature NMA selectivity was high, but

quickly decreased with increase in temperature. Increase in temperature increased *N,N*-dialkylation rate upto 280°C and thereafter, it suddenly decreased. The other products include DMC fractions, benzene and toluene. The results are summarized in Table 4. Increase in temperature above 280°C increased the decomposition rate of DMC substantially, and above 300°C, concentration of DMC fractions exceeded above 35%.

Fig. 5 shows the effect of DMC/aniline molar ratio on the conversion of aniline and the yield of various products at 250°C. At low DMC concentration, the selectivities of NMA and NNDMA were nearly 74% and 12%, respectively. At high DMC/aniline ratio more amount of NNDMA was formed. When the ratio was 4, the selectivity of NMA was about 40%, whereas that of NNDMA was increased up to 28%.

Optimum feed flow rate for NMA formation was 4 ml/h (WHSV 1.2 h<sup>-1</sup>). At low flow rate more amount of NNDMA was formed due to the high contact time with the catalyst. At sufficiently high flow rate, aniline conversion and alkylation activity significantly diminished. The results are shown in Fig. 6.

The above discussion clearly indicates that DMC can act as an effective *N*-alkylating agent at sufficiently low temperature, where methanol shows only mild activity. However, unlike our

Table 4

Product distribution and selectivity data of aniline alkylation using DMC as a function of reaction temperature over ZCF-2. WHSV 1.2 h<sup>-1</sup>. TOS 1 h and molar ratio (DMC to aniline) 2

Product distribution (wt.%)	Reaction temperature (°C)			
	200	250	280	300
Aniline conversion	31.30	50.53	62.30	50.35
NMA	24.99	37.31	32.78	22.30
NNDMA	1.07	6.03	16.74	7.21
Others <sup>a</sup>	5.24	7.20	12.78	20.85
Selectivity				
NMA	79.84	73.83	52.62	44.29
NNDMA	4.28	11.93	26.87	14.32

<sup>a</sup>Others include DMC fractions, benzene, toluene and traces of unidentified products.

previous experiments using methanol, alkylation with DMC afforded both mono- and di-substitution on aniline leading to comparatively less selectivity for NMA. It is interesting to note more amount of *N,N*-dialkylated product at sufficiently low temperature where methanol afforded nearly 99% NMA selectivity. This result is contrary to that obtained for systems like  $\text{Al}_2\text{O}_3$ , MgO [24] and alkali exchanged EMT zeolites [25] because such systems executed high selectivity for NMA using DMC than with methanol.

Aniline alkylation over oxide surface involves a concerted mechanism as suggested by Nanko et al. [26]. Optimum concentration of acid–base centers is needed for the adsorption and subsequent polarization of aniline. However, since aniline is a strong base, it can easily coordinate even with weak acid centers. Hence, it is the change in the basicity of the system, rather than acidity, that controls the overall performance of the catalysts. From the adsorption study of EAs and their dehydration activity, it is clearly understood that substitution of  $\text{Zn}^{2+}$  by  $\text{Co}^{2+}$  creates an increase in acidity with a

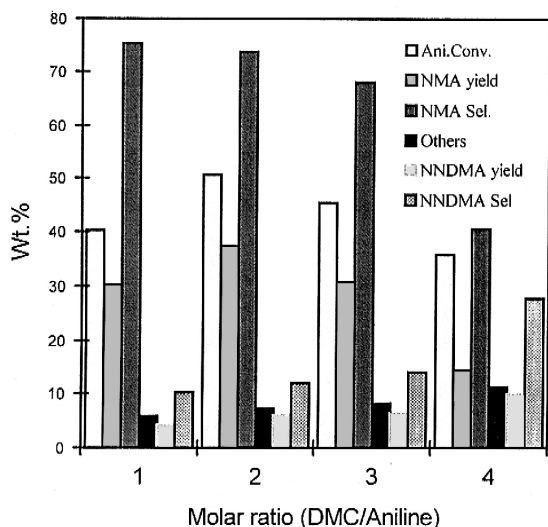


Fig. 5. Effect of DMC to aniline molar ratio on aniline conversion and product selectivities over ZCF-2. Reaction temperature 250°C; WHSV 1.2  $\text{h}^{-1}$ ; TOS 1 h.

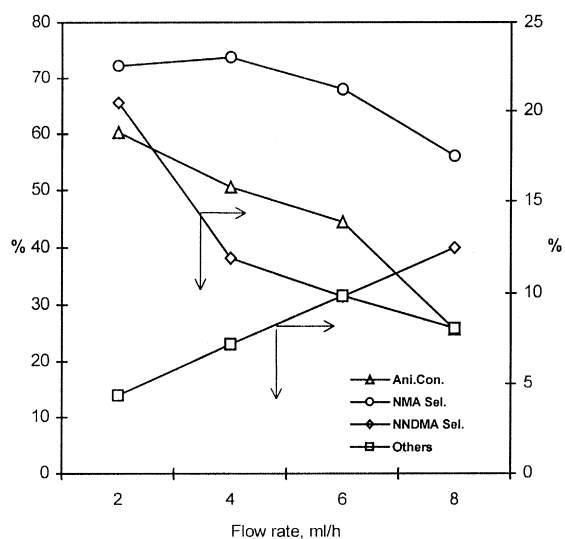


Fig. 6. Effect of feed flow rate on conversion and selectivities over ZCF-2. Reaction temperature 250°C; molar ratio (DMC to aniline) 2; TOS 1 h.

concomitant decrease in basicity. Alkylation activity (total yield of *N*-methylated products) follows the order: ZF-1 > ZCF-2 > ZCF-3 > CF-4  $\approx$  CF-5, and this trend is nearly opposite to that of the acidity pattern. Pure zinc ferrite (i.e. ZF-1) possess optimum acid–base centers and well suited for the proper adsorption and the subsequent polarization of the N–H bond. However, increase in the  $x$  value progressively removes  $\text{Fe}^{3+}$  from the active Oct. sites and correspondingly increases the concentration of acidic  $\text{Co}^{2+}$  ions in the same positions. Thus, the low activity on cobalt substitution can be accounted due to the removal of basic centers originally present on ZF-1 by cobalt substitution. However, when  $x$  exceeds 0.5 (i.e. ZCF-4 and CF-5), it seems that acidity substantially increases and, subsequently, results in the decomposition of the adsorbed aniline and DMC, leading to large quantity of side products viz. benzene, toluene, methane and oxides of carbon. Additionally, when we passed aniline and DMC separately over these systems, decomposition products were maximum over more cobalt-containing systems.

#### 4. Conclusion

$Zn_{1-x}Co_xFe_2O_4$  ( $x = 0, 0.2, 0.5, 0.8, 1.0$ ) type systems were studied for alkylation of aniline using DMC as the alkylating agent. The lower members of the series ( $x = 0 \leq 0.5$ ) are active for *N*-methylation of aniline. Activity decreases as  $x$  increases. As  $x$  increases, the acidity of the system also increases due to the progressive substitution of Oct.  $Fe^{3+}$  ions by  $Co^{2+}$  ions. When  $x$  exceeded 0.5, acidity of the surface substantially increased and, thereby, such systems facilitated decomposition of aniline as well as DMC leading to less activity. Higher activity was observed in the temperature range of 200–250°C. However, unlike the experiments using methanol for alkylation, DMC afforded both mono- and di-substitutions on aniline, lead to comparatively less selectivity for NMA. Increase in temperature as well as molar ratio (DMC/aniline) increased the dialkylation rate. The main advantage of the reaction is that alkylation is possible at significantly low temperature where methanol cannot work properly. As in the case of methanol, DMC also did not give any C-alkylated products.

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