

Vapor-phase methylation of pyridine with methanol to 3-picoline over $Zn_{1-x}Co_xFe_2O_4$ ($x=0, 0.2, 0.5, 0.8$ and 1.0)-type ternary spinels prepared via a low temperature method

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Abstract

The reaction of pyridine with methanol was carried out over $Zn_{1-x}Co_xFe_2O_4$ ($x=0, 0.2, 0.5, 0.8$ and 1.0)-type systems in a fixed-bed down-flow reactor. The influences of surface acidity, cation distribution in the spinel lattice and various reaction parameters are discussed. The activity and selectivity were shown to be strongly dependent on the surface acidity of the systems. Over all compositions of the systems, 3-picoline was formed as the major product, even though the activity and selectivity show a strong dependence on composition and reaction conditions. Generally, the systems possessing more acidic sites ($x \geq 0.5$) favor the production of 3-picolines and 3,5-lutidine. Pyridine conversion increased with the progressive substitution of Zn^{2+} ions by Co^{2+} ions. Cation distribution in the spinel lattice influences their acidic properties. These factors have been adequately considered as helpful to evaluate the activity of the systems. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Mixed metal oxides possessing spinel structure have been investigated by a number of workers, since they exhibit interesting structural, electrical, magnetic and catalytic properties [1,2]. Their peculiar type of cation distribution among the tetrahedral (Td) and octahedral (Oh) sites of the coordinated oxygen is an important factor in explaining the catalytic effectiveness. For a binary oxidic spinel containing divalent M cations and trivalent N cations, two extreme distributions of cations between the Oh and Td sites available

are possible: the 'normal' $M[N_2]O_4$ and the 'inverse' $N[MN]O_4$ [3,4]; in each case the ions in the Oh sites are in square brackets. Iron-containing spinels are called ferrosinels, and in ternary spinel systems Fe^{3+} ions can be easily shifted between Oh and Td sites by stoichiometrically varying the concentrations of other cations. This type of structural feature of ferrosinels systems, compared to ordinary oxide systems, enables ferrosinels to withstand extremely reducing atmosphere [5], and even if reduction of Fe^{3+} to Fe^{2+} occurs, in many cases the original state can be regained by mild activation procedures. Several authors have reported that the major activity comes from the Oh ions, probably due to the large exposure of these ions on the surface. Sensitive surface analysis techniques

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like low energy ion scattering (LEIS) and differential neutron diffraction (DND) are giving strong evidence for this conclusion [6,7].

Alkylpyridines like picolines (methyl pyridines) and lutidines (dimethyl pyridines) are a class of industrially valuable compounds for the production of useful synthetic intermediates in the fine chemical, pharmaceutical and dye industries [8,9]. Electrophilic substitution on pyridine is extremely difficult and commercial synthetic procedures of picolines mostly involve condensation of carbonyl compounds with ammonia over Pt, Pd or Rh exchanged zeolite systems [10,11]. Several groups have studied gas-phase alkylation of pyridine using several kinds of alcohols as the alkylating agents [12–14]. Myerley and Weinberg [15] showed that a CO–H₂ mixture could be used as the methylating agent for the alkylation of pyridine. In a recent work, Fujiata and co-workers [16] claimed that pyridine can be methylated to 2-methylpyridine with high selectivity over various Ni-supported metal oxide systems. As a part of our investigation of M_{1-x}N_xFe₂O₄ (where M and N are transition elements like Cr, Co, Ni and Zn, and $x=0, 0.2, 0.5, 0.8$ and 1.0)-type ferros spinels as versatile alkylating catalysts, we have reported previously the selective formation of *N*-monomethylaniline over Zn_{1-x}Co_xFe₂O₄ [17] and Zn_{1-x}Ni_xFe₂O₄ [18]-type systems. The present study deals with direct methylation of pyridine with methanol in a vapor-phase down-flow reactor over Zn_{1-x}Co_xFe₂O₄-type systems. Systems possessing higher ‘*x*’ values are selective and active for 3-picoline formation. A systematic catalytic evaluation study as a function of various process parameters is carried out and an attempt has been made to explain the observed trends considering the surface acidity and the structural properties of the various spinel compositions.

2. Experimental

2.1. Catalyst synthesis

Different compositions of the ferros spinel series viz ZnFe₂O₄ (ZF-1), Zn_{0.8}Co_{0.2}Fe₂O₄ (ZCF-2), Zn_{0.5}Co_{0.5}Fe₂O₄ (ZCF-3), Zn_{0.2}Co_{0.8}Fe₂O₄ (ZCF-4), CoFe₂O₄ (CF-5) were prepared by a low temperature controlled coprecipitation method reported by Date

and co-workers [19], using aqueous solutions of (1) ferric nitrate 2.6 M, (2) zinc nitrate 3.4 M, (3) cobalt nitrate 3.4 M and (4) sodium hydroxide 5.3 M. The stoichiometric amounts of the premixed nitrate solutions were rapidly added to the sodium hydroxide solution. Excess alkali was not used for the precipitation in order to avoid the formation of soluble sodium zincate which might disturb the stoichiometry of the ferrite precursor. Due to the exothermic nature of the chemical reaction forming the mixed hydrated oxides, the temperature of the slurry was around 50°C. After an aging of 8 h, the precipitate was washed free of nitrate and sodium ions. The precipitate was initially dried in air at 80°C for 24 h. The materials were powdered and calcined at 300°C for 36 h. The catalyst pellets of the required mesh size were then obtained by pressing under 10 Torr of pressure.

Unlike the spinels synthesized by the solid state high temperature methods, which produce systems with some inherent drawbacks like poor compositional control, chemical inhomogeneity and low surface area, this method provides chemically homogeneous and fine ferrite particles.

2.2. Structural analysis

The prepared systems were well characterized by techniques such as XRD, TG-DTA, diffuse reflectance infrared spectral analysis, scanning electron microscope, energy dispersive X-ray (EDX) analysis and BET surface area measurements.

2.3. Surface acidity

Dehydration of cyclohexanol is an acid catalyzed reaction, and is often recommended as the test reaction for qualitatively measuring the surface acidity of the systems. In the present case, one such experiment is carried out in a down-flow vapor-phase reactor. The detailed reaction procedure is given elsewhere [20]. Mole percent of cyclohexene formed has been qualitatively correlated as a measure of the acidity of the systems (Tables 1 and 2).

2.4. Catalytic reactions

The catalytic experiments were performed in a fixed-bed down-flow silica reactor. The catalysts were

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

Composition (x)	Cation at		Concentration ^a (%)		Surface area (m ² /g) ^b
	Td site	Oh site	Zn ²⁺	Co ²⁺	
0	Zn ²⁺	Fe ₂ ³⁺	27.0 (27.1)	–	30.1
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)	33.6
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)	39.5
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)	39.8
1.0	Fe ³⁺	Co ²⁺ Fe ³⁺	–	24.7 (24.8)	40.1

^a Quantities in the parentheses indicate the stoichiometric values.

^b Specific surface area of the samples calcined at 500°C.

pressed, pelleted and sieved to a size of 10–20 mesh. The amount of catalyst used every time was 3 g. The catalyst was placed at the center of the reactor; it was activated at 500°C in flowing air, and then brought down to the corresponding reaction temperatures by cooling under a current of nitrogen gas of high purity. The mixture of pyridine and methanol was fed by an ISCO-Model 500 D syringe pump. The reaction liquid products collected by traps cooled with ice cold water were analyzed by GC with FID by using a HP-ultra capillary column. The gaseous products were analyzed using a porapack-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

3.1. Structural analysis

Powder X-ray diffraction (XRD) patterns of the calcined samples were recorded on a computer-controlled

Table 2
Cyclohexanol dehydration activity of Ni–Co ferrite systems

Catalyst composition	Cyclohexene ^a (mol%)
ZF-1	39.72
ZCF-2	40.40
ZCF-3	49.80
ZCF-4	52.40
CF-5	55.30

^a Reaction conditions: WHSV 1.4 h⁻¹; activation temperature 500°C; reaction temperature 325°C.

automated diffractometer (Rigaku Model, D/MAX III VC). Ni-filtered Cu K α radiation was used with a curved graphite crystal monochromator and NaI scintillator. Data were collected in the 2θ range, 10–80° at a scan rate of 1°/min with silicon as an internal standard. The XRD pattern of ZF-1 is presented in Fig. 1. Thermal stability of the samples was established by TG-DTA analysis using finely powdered α -alumina as a reference material. Scanning electron micrographs (SEM) showed fine grains of uniform size ≈ 50 nm, which was very much smaller than the grain size of the spinels prepared by the conventional high temperature methods. The chemical analysis of the samples were performed with wet gravimetric analysis in combination with EDX analysis. Diffuse reflectance infrared (DR-IR) spectra of the samples, shown in Fig. 2, consisted of two distinct broad peaks around 500 and 700 cm⁻¹, respectively. Waldren [21] and White and DeAngelies [22] assigned the high frequency band at 700 cm⁻¹ as due to the stretching vibration of the Td group and the lower frequency band at 500 cm⁻¹ as due to the vibration of the Oh M–O group. According to Waldren [21], the Td coordination has the effect of substantially increasing the frequency for vibration, since these cations introduce a supplementary restoring force in a preferential direction along the M_T–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.

3.2. Alkylation of pyridine

The methylation of pyridine with methanol has been studied by varying the reaction parameters. The electron-deficient nature of the pyridine ring makes

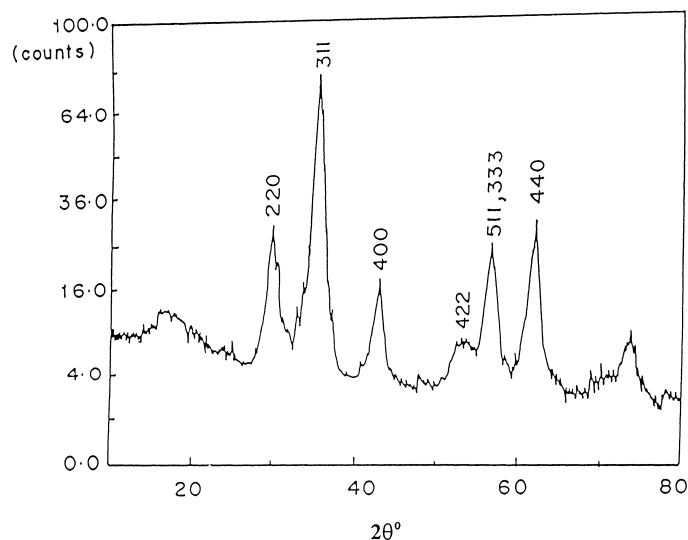


Fig. 1. Powder X-ray diffractogram of ZnFe_2O_4 (ZF-1) calcined at 500°C .

direct electrophilic substitution less feasible. Thus, only very few works have been reported for the direct methylation of pyridine using suitable alkylating agents. Vapor-phase methylation, over an active catalyst, can give products such as methylpyridines (picolines), dimethylpyridines (lutidines), and trace amounts of polyalkylated and dense products. Selectivity for a particular isomer of picoline is strongly influenced by the acid strength of the catalyst.

A series of experiments were performed to relate the activity with composition. Product distribution

data obtained at 400°C over different compositions are shown in Table 3. Among the various compositions of the system ($\text{Zn}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$), the systems with 'x' value ≥ 0.5 were found to be more active for the reaction. Pyridine conversion was highest in the case of CF-5 (49.8%) and lowest in ZF-1 (4.3%). When 'x' exceeds 0.5, 3,5-lutidine was formed as a side product and its yield also progressively increased with the 'x' value of the composition. Even though pyridine conversion was less over ZF-1 ($x=0$), unlike other compositions here a trace amount of 2-picoline was formed as a

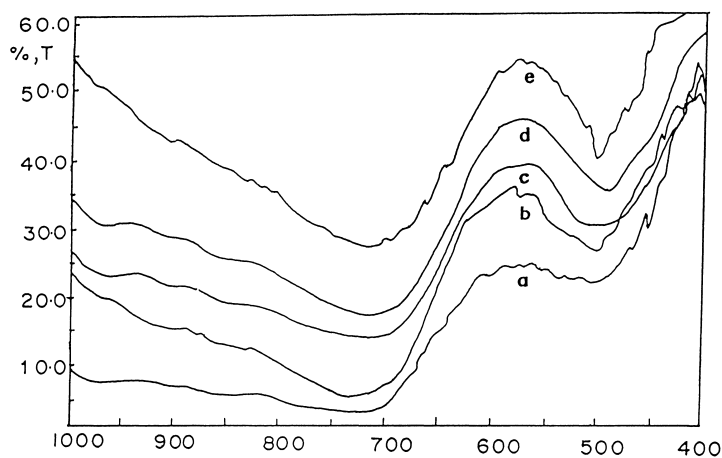


Fig. 2. Diffuse reflectance infrared spectra of different Zn–Co ferrite systems. (a) CF-5; (b) ZCF-4; (c) ZCF-3; (d) ZCF-2 and (e) ZF-1.

Table 3
Effect of catalyst composition of pyridine conversion and product selectivities^a

Catalyst composition	ZF-1	ZCF-2	ZCF-3	ZCF-4	CF-5
Pyridine conversion (wt.%)	4.30	22.17	31.50	45.00	49.80
Selectivity (%)					
3-Picoline	97.67	97.60	97.41	97.30	95.38
2-Picoline	1.00	Nil	Nil	Nil	Nil
3,5-Lutidine	1.00	1.52	1.75	2.00	3.61
Others	0.33	0.87	0.80	0.70	1.00

^a WHSV 1.3 h⁻¹, reaction temperature 400°C, methanol to pyridine molar ratio 1:7.

side product. The results clearly indicate that pyridine conversion and surface acidity follow an order represented as: ZF-1 < ZCF-2 < ZCF-3 < ZCF-4 < CF-5 and the selectivity for a particular isomer is influenced by the variation of the surface acid-base properties during the gradual change of the spinel matrix from a completely 'normal' (i.e. ZF-1) to a completely 'inverse' (i.e. CF-5) form.

The alkylation reaction is performed at different temperatures ranging from 325 to 450°C over CZF-4. Pyridine conversion increases with the increase of temperature. Negligible conversion was observed below 375°C, and conversion occurs effectively in the temperature range of 400–425°C. Table 4 shows the influence of temperature over the product distribution. 3-Picoline was the major product in the range of temperature studied. 3,5-Lutidine was the only

Table 4
Performance of ZCF-4 for pyridine methylation at different reaction temperatures^a

	Reaction temperature (°C)				
	325	350	375	400	425
Pyridine conversion	1.80	4.10	14.75	45.00	48.00
Product yield					
3-Picoline	1.80	4.10	14.30	43.80	40.21
2-Picoline	Nil	Nil	Nil	Nil	Nil
3,5-Lutidine	Nil	Nil	0.25	0.90	6.30
Others	Nil	Nil	0.15	0.32	1.49
Selectivity					
3-Picoline	100	100	96.95	97.30	83.77
3,5-Lutidine	–	–	1.69	2.00	14.00

^a (WHSV 1.3 h⁻¹; methanol to pyridine molar ratio 7; TOS 2 h).

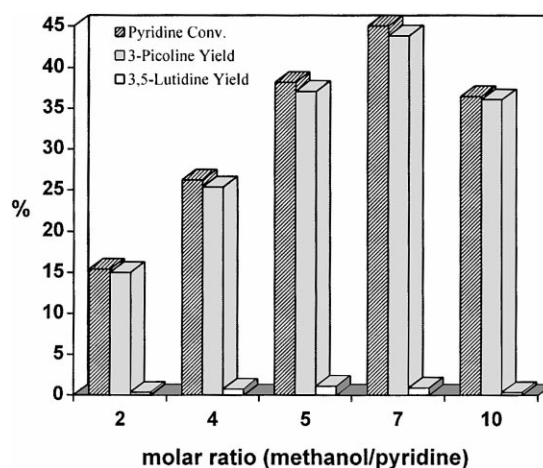


Fig. 3. Influence of feed (methanol to pyridine) molar ratio on pyridine conversion and product yields over ZCF-4. WHSV 1.3 h⁻¹; reaction temperature 400°C; TOS 1 h.

dialkylated product observed throughout the experiment. The maximum yield of 3-picoline (43.8%) was observed at 400°C with selectivity more than 97%. However, as temperature increases from 400°C onwards, selectivity towards 3-picoline decreases, whereas that of 3,5-lutidine increases. At 425°C the selectivity of 3-picoline was 83.8%, whereas that of 3,5-lutidine increased up to 14.0%. It is notable that since 3,5-lutidine is formed by the alkylation of an initially formed 3-picoline, whenever selectivity towards 3-picoline decreases the selectivity towards 3,5-lutidine increases and vice versa. With further rise in temperature, methanol decomposition predominates over alkylation activity, and thus leads to a decrease in the overall alkylation activity of the systems.

In order to understand the optimum feed mix ratio, a series of experiments were performed at 400°C with different molar ratios of methanol to pyridine over ZCF-4 (Fig. 3). Pyridine conversion as well as the yield of 3-picoline reach a maximum value at a methanol/pyridine molar ratio of 7. 3,5-Lutidine yield also improved along with 3-picoline yield up to a molar ratio of 5 (1.0%) and thereafter it decreased. Further increase in molar ratio lowers the conversion of pyridine without affecting 3-picoline selectivity.

The reaction was also studied as a function of space velocity ranging from 0.65 to 3.2 h⁻¹. A typical activity profile of pyridine methylation as a function of feed rate over ZCF-4 is shown in Fig. 4. Yield of 3-picoline

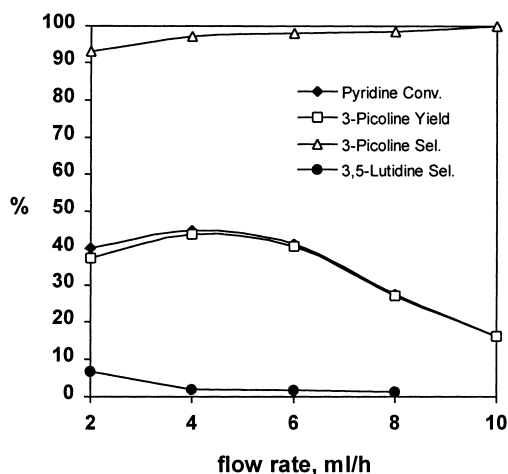


Fig. 4. Influence of feed flow rate on pyridine alkylation over ZCF-4. Reaction temperature 400°C; methanol to pyridine molar ratio 7; TOS 1 h.

and conversion of pyridine first increased and reached a maximum at WHSV 1.3 h^{-1} (feed rate 4 ml/h) and thereafter decreased linearly due to decrease in contact time. The low pyridine conversion rate at high contact time region can be attributed to the increased rate of methanol decomposition as a side reaction. As contact time decreases, the rate of this side reaction also decreases, resulting in more pyridine conversion and 3-picoline yield.

3.3. Catalytic pathway

Methylation of pyridine in all catalysts leads to 3-picoline as the major product, with selectivity more than 93%. Both pyridine conversion and acidity follow the order ZF-1 < ZCF-2 < ZCF-3 < ZCF-4 < CF-5. However, the yield of cyclohexene on various spinels did not differ so much as in the pyridine conversion, which indicates that the reaction of pyridine might be controlled by some other factors in addition to acidity. The gradation in activity can be explained by considering factors like variation of acid-base properties during Co^{2+} substitution and its direct influence on the distribution of active Fe^{3+} ions in the coordinated sites of oxygen anions of the spinel lattice. Considerable enhancement in the yield of 3-picoline has been observed with the substitution of Zn^{2+} ions by Co^{2+} ions. Systems possessing higher 'x' values (0.8 and 1.0) are found to be more active, compared to the sys-

tems possessing high zinc concentration. ZF-1 is the only system in the series which afforded the formation of a small amount of 2-picoline along with 3-picoline. 3,5-Lutidine is the only dialkylated product observed throughout the experiment and its yield appears to be favoured mainly on the compositions containing high $\text{Co}^{2+}/\text{Fe}^{3+}$ ratios.

Co^{2+} ion always prefer an Oh site, and as 'x' increases, Co^{2+} ions replace Fe^{3+} ions isomorphically from Oh sites to Td sites. In other words, the substitution of Fe^{3+} ions by Co^{2+} ions in the Oh sites creates stronger acid sites than those due to the Fe^{3+} ions which initially occupied the same sites. Creation of acidic sites by Oh ions can be explained in another way: due to the lower coordination number of the Td cations, the effective attractive force for a single $\text{Td}_{\text{M-O}}$ bond will be strong [23]. Since each Oh cation is surrounded by a higher number of anions, the $\text{Oh}_{\text{M-O}}$ bond will be weaker and hence will be more polar. Additionally, Jacobs and coworkers [7] in a study using LEIS, a technique which is sensitive to the outermost atomic layer, revealed that spinel surface sites are mainly octahedral and, hence, the Oh cations are exposed on the surface. Direct ring-substitution of pyridine on an acid catalyst would give 3 and 3,5-substituted products only [24]. The two possible routes for the formation of 3-picoline involve direct ring alkylation by an initially formed formaldehyde from methanol or by the rearrangement of 2-picoline at the reaction temperature [24]. However, in the present case, the formation of 3-picoline is not via the rearrangement of the 2-isomer; this was confirmed by the independent attempts to isomerize 2-picoline on these systems at the reaction temperature. A blank run of methanol alone over the catalyst systems revealed that the HCHO concentration was maximum in the temperature range of 380–400°C (Fig. 5). Negligible amounts of HCHO were observed below 350°C and above 425°C. The similar dependence of both HCHO and 3-picoline yield on reaction temperature suggests that 3-picoline formation occurs via the initial formation of formaldehyde (HCHO) by the interaction of methanol with pyridine on strong acidic centers of the catalyst, as reported by Kameswari and co-workers [13]. As reported by Narasimhan et. al. [5], weak $\text{Oh}_{\text{M-O}}$ bonds act as strong alcohol adsorption centers. Since pyridine is a strong base, even the weak Lewis acid centers on the catalyst surface can

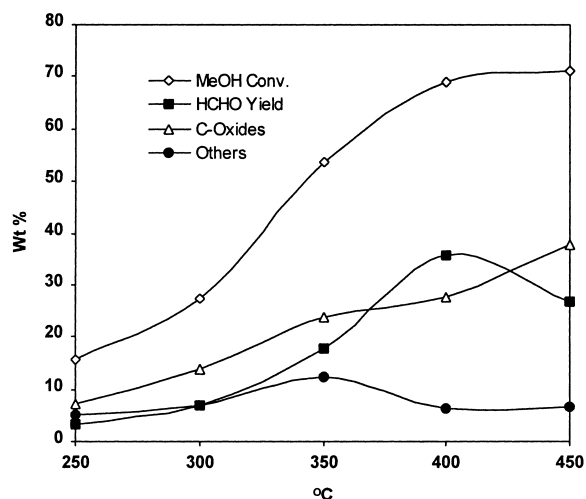
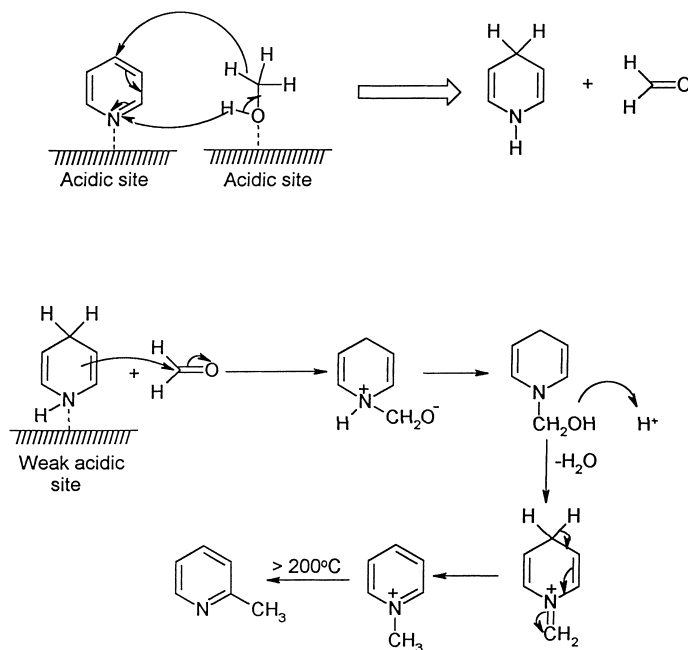


Fig. 5. Decomposition of methanol over ZCF-4 as a function of reaction temperature. WHSV 2 h^{-1} ; TOS 1 h. ('Others' in the figure include lower hydrocarbons and traces of dimethyl ether).

effectively coordinate with this molecule. Methanol adsorbed on an acidic site can get oxidized to HCHO [25]. We have observed that both acidity and catalytic activity increase during 'Co' substitution. Formation of HCHO from methanol is accompanied by the

reduction of pyridine to dihydropyridine intermediate. It is believed that the Lewis acid sites are provided by the Oh ions (either Fe^{3+} in ZF-1 or Fe^{3+} and Co^{2+} in the substituted spinels). The better activity of the 'Co' substituted systems can be attributed to the presence of $\text{Co}^{2+}\text{-Fe}^{3+}$ pair in the Oh site, which can act as the active sites where methanol and pyridine can be converted into HCHO and dihydropyridine. Another molecule of HCHO can attack the dihydropyridine intermediate at 3-position, leading to the formation of 3-picoline. However, direct methylation of pyridine in the 2-position is impossible due to the electron deficient nature of the ring. The trace amount of 2-picoline formed over ZF-1 can be accounted for by a mechanism similar to that of the Ladenberg rearrangement of an initially formed *N*-methyl pyridinium ion at the reaction temperature [9]. ZF-1 being a normal spinel, all Fe^{3+} ions are available in the active Oh sites and the Td sites are occupied exclusively by stable Zn^{2+} ions (d^{10} configuration). Due to the mild acidity of the system, some formaldehyde will directly interact with the lone pair of electrons on the nitrogen of pyridine, yielding *N*-methyl pyridinium ion. The mechanism of the formation of 2-picoline involving Ladenberg rearrangement is shown in Scheme 1.



Scheme 1. Mechanism for 2-picoline formation through Ladenberg rearrangement (on a weakly acidic site).

4. Conclusions

The main conclusions drawn from this work are summarized below.

1. The Zn–Co ferrites represented by the general formula $Zn_{1-x}Co_xFe_2O_4$ ($x=0, 0.2, 0.5, 0.8$ and 1.0) can be used for the selective synthesis of 3-picoline via the methylation of pyridine with methanol in a vapor-phase down-flow reactor. Systems possessing high Co^{2+}/Fe^{3+} ratio in the Oh sites are found to be more active.
2. Under optimized conditions, 3-picoline selectivity was better than 95%. 3,5-Lutidine was the only dialkylated product observed throughout the experiment and its yield also increased with the 'x' value of the system. ZF-1 is the only system which afforded a small amount of 2-picoline, whereas its formation is completely suppressed by the substitution of zinc by cobalt.
3. Although acidity is an important factor in the reaction of pyridine with methanol, the variation in the cation distribution with spinel composition is another strong influencing factor for the reaction. Generally, more Co-containing systems are found to be highly active for 3-picoline formation. Both acidity and oxidizing properties (methanol to HCHO) increased with Co-substitution.
4. The presence of a $Co^{2+}-Fe^{3+}$ pair in the Oh site provides active sites where methanol and pyridine can be converted into HCHO and dihydropyridine. Another molecule of HCHO attacks dihydropyridine intermediate at 3-position, leading to 3-picoline selectively. The trace amount of 2-picoline over ZF-1 can be accounted by a mechanism similar to the Ladenberg rearrangement, which involves the rearrangement of an *N*-methylpyridinium ion at the reaction temperature, leading to the formation of 2-picoline.

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