Selective synthesis of 3-picoline via the vapor-phase methylation of pyridine with methanol over $Ni_{1-x}Co_xFe_2O_4$ ($x = 0$, 0.2, 0.5, 0.8 and 1.0) type ferrites

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A series of Ni–Co ferrites with the general formula $Ni_{1-x}Co_xFe_2O_4$ ($x = 0$, 0.2, 0.5, 0.8 and 1.0) was prepared by a low-temperature hydroxide coprecipitation route. The catalyst systems were characterized by adopting various physico-chemical techniques. Alkylation of pyridine with methanol was carried out in a down-flow vapor-phase reactor. The influence of surface acid–base properties, cation distribution in the spinel lattice and various reaction parameters are discussed. It was observed that the systems possessing x values $\geqslant 0.5$ are selective for 3-picoline formation, whereas the ones with x values 0 and 0.2 give a mixture of 2- and 3-picolines. Pyridine conversion increased with the progressive substitution of Ni^{2+} ions by Co^{2+} ions. Cation distribution in the spinel lattice influences their acidic and basic properties, and these factors have been adequately considered as helpful to evaluate the activity of the systems.

Keywords: spinel structure, ferrites, pyridine methylation, electron acceptors

1. Introduction

Binary and ternary oxides possessing spinel structure have attracted much attention due to their remarkable transport, magnetic and catalytic properties. For a binary oxidic spinel containing divalent M and trivalent N cations, two extreme distributions of cations between the octahedral (Oh) and tetrahedral (Td) sites available are possible: the “normal” $M[N_2]O_4$ and the “inverse” $N[MN]O_4$ [1,2]; in each case the ions in the Oh sites are in square brackets. Iron-containing spinels are called ferrospinels, and in ternary spinel systems Fe^{3+} ions can be easily replaced between Oh and Td sites by stoichiometrically varying the concentrations of other cations. This peculiar structural feature enables ferrospinels to withstand even extremely reducing atmosphere. Even if reduction of Fe^{3+} to Fe^{2+} occurs, the lattice configuration remains unaltered and upon reoxidation, the original state can be regained [3]. Several authors have reported that the major influence in the activity comes from the Oh ions, probably due to the large exposure of these ions on the surface of the materials [4].

As a part of our continuing investigation of $M_{1-x}N_xFe_2O_4$ (where M and N are transition elements such as Cr, Co, Ni and Zn, and $x = 0$, 0.2, 0.5, 0.8 and 1.0) ferrospinel systems as versatile alkylating catalysts, we have reported previously the selective formation of N-monomethylaniline over $Zn_{1-x}Co_xFe_2O_4$ [5] and $Zn_{1-x}Ni_xFe_2O_4$ [6] type systems. As an extension of this work into the ability of such systems to alkylate various heterocyclic compounds, we have now carried out a detailed study on the alkylation of pyridine with methanol in vapor phase. The reaction was carried out in a silica reactor using $Ni_{1-x}Co_xFe_2O_4$ ($x = 0$, 0.2, 0.5, 0.8 and 1.0) as the catalyst system. Methylation of pyridine over all the catalysts leads to 3-picoline as the major product. Picolines are a class of useful synthetic intermediates in fine chemical, pharmaceutical and dye industries [7,8]. Electrophilic substitution of 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 [9,10]. The present study deals with the selective synthesis of 3-picoline from pyridine by direct electrophilic substitution, using methanol as the alkylating agent. Considerable difference in the activity was observed as the x value of the composition, $Ni_{1-x}Co_xFe_2O_4$, varies from 0 to 1.0. Cation distribution in the spinel lattice influences their acid–base properties, and hence, these factors have been considered as helpful to evaluate the activity and stability of the systems.

2. Experimental

2.1. Catalyst synthesis

The five compositions of the Ni–Co ferrites viz. $NiFe_2O_4$ (NF-1), $Ni_{0.8}Co_{0.2}Fe_2O_4$ (NCF-2), $Ni_{0.5}Co_{0.5}Fe_2O_4$ (NCF-3), $Ni_{0.2}Co_{0.8}Fe_2O_4$ (NCF-4) and $CoFe_2O_4$ (CF-5) were prepared by a low-temperature controlled coprecipitation method using aqueous solutions of ferric nitrate (2.6 M), nickel nitrate (3.4 M), cobalt nitrate (3.4 M) and sodium hydroxide (5.3 M). The metal ion solutions were premixed

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in the required stoichiometric ratio and rapidly added to sodium hydroxide solution. The precipitate was separated and washed free off nitrate and sodium ions with distilled water. 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. Catalyst pellets of the required mesh size were then obtained by pressing under 10 t of pressure.

2.2. Physical characterization

The phase purity and crystallinity of the samples were first ensured by XRD (Rigaku, model D/MAX-VC) with Cu Kα radiation. The X-ray diffractograms of some samples are presented in figure 1. Thermal stability of the samples was established by TG-DTA analysis on an automatic derivatograph (SETARAM-TG-DTA-92) using finely powdered α-alumina as a reference material. All compositions of the system showed two strong IR bands ν_1 and ν_2, around 700 and 500 cm^{-1}, respectively. In a spinel every oxygen anion is bonded to three Oh and one Td cations [11]. Vibration of the Td metal–oxygen group corresponds to the highest restoring force and is thus assigned to the highest frequency band (i.e., at 700 cm^{-1}), and the band at 500 cm^{-1} indicates the vibration of the Oh metal–oxygen group [12,13]. According to Waldren [12], the tetrahedral coordination has the effect of substantially increasing the frequency of vibration, since these cations introduce a supplementary restoring force in a preferential direction along the $M_{\mathrm{Tet.}}$–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.

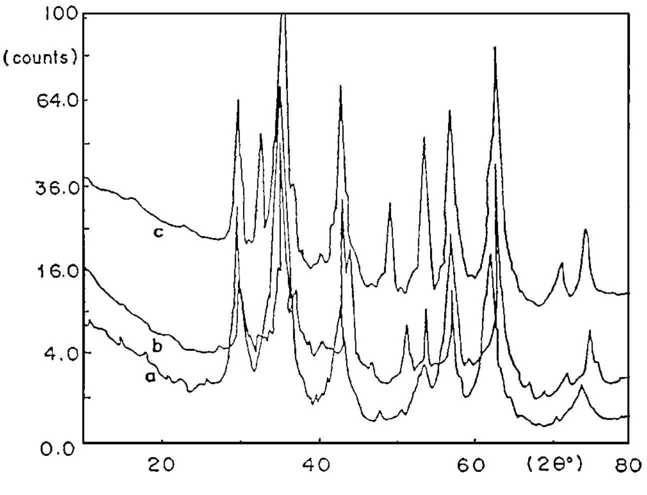

Figure 1. Powder X-ray diffractogram: (a) CF-5, (b) NCF-3, (c) NF-1, calcined at 500 °C.

2.3. Evaluation of surface acidity and basicity

Cyclohexanol dehydration reacion has been carried out to correlate the acid strength of the systems. The detailed reaction procedure is given elsewhere [14]. Mol% of cyclohexene formed has been qualitatively correlated as a measure of the acidity of the systems (table 2).

The basic strength has been evaluated using adsorption studies using different electron acceptors (EA). The adsorption study was carried out over 0.5 g catalyst placed in a cylindrical glass vessel and outgassed at 1.3×10^{-3} Pa for 1 h. Subsequently, 20 ml of a solution of a suitable EA in acetonitrile was added, and the solution was stirred at 28 °C for 4 h in a thermostated bath. Adsorption of the EA was meausred using a UV-vis spectrophotometer.

2.4. Catalytic activity studies

The pyridine alkylation reaction was carried out on 3 g of 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 air and brought down to the respective reaction temperatures using flowing dry nitrogen. The feed containing pyridine and methanol was delivered using a syringe pump (ISCO model 500 D). Liquid products were condensed with a cold trap and were analyzed by a Shimadzu GC 15A gas chromatograph using a HP-ultra-capillary column and FID. 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 94–95 wt%, while the reproducibility of the experimental system was better than ±5%.

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

Composition	Cation at		Concentration[a] (%)		Surface area[b]
(x)	Td site	Oh site	Ni^{2+}	Co^{2+}	(m^2/g)
0	Fe^{3+}	$Fe^{3+}Ni^{2+}$	25.1 (25.1)	–	60.9
0.2	Fe^{3+}	$Fe^{3+}Ni^{2+}_{0.8}Co^{2+}_{0.2}$	19.9 (20.0)	4.9 (5.0)	58.3
0.5	Fe^{3+}	$Fe^{3+}Ni^{2+}_{0.5}Co^{2+}_{0.5}$	12.5 (12.5)	12.5 (12.6)	38.9
0.8	Fe^{3+}	$Fe^{3+}Ni^{2+}_{0.2}Co^{2+}_{0.8}$	5.1 (5.0)	19.9 (20.2)	35.7
1.0	Fe^{3+}	$Fe^{3+}Co^{2+}$	–	24.7 (24.8)	40.1

[a] Quantities in the parentheses indicate the theoretical value.

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

Table 2
Cyclohexanol dehydration activity and limiting values of electron acceptors (EA) adsorbed over different Ni–Co ferrite systems.[a]

Catalyst composition	Cyclohexene[a] (%)	Limiting amount of EA adsorbed ($\times 10^{-5}$ mol m^{-2})	
		TCNQ	Chloranil
NF-1	12.03	2.382	1.060
NCF-2	16.70	2.017	0.970
NCF-3	24.66	1.921	0.874
NCF-4	37.27	1.913	0.711
CF-5	55.30	1.536	0.315

[a] Reaction conditions: WHSV 1.4 h^{-1}, activation temperature 500 °C, reaction temperature 325 °C.

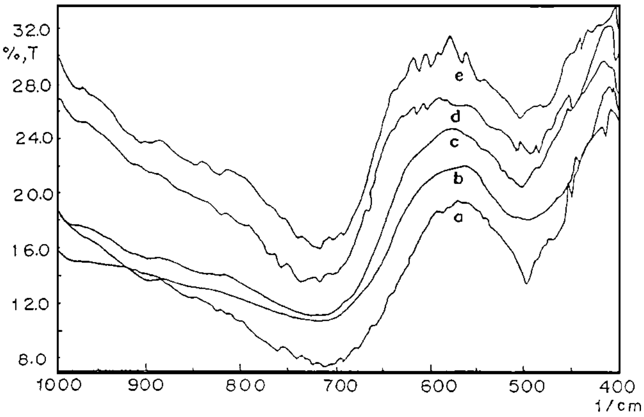

Figure 2. Diffuse reflectance infrared spectra of different Ni–Co ferrite systems: (a) CF-5, (b) NCF-4, (c) NCF-3, (d) NCF-2 and (e) NF-1.

3. Results and discussion

3.1. Acid–base strength distribution

The utility of electron acceptor adsorption for the study of the electron donor properties of the surface has been well established [15–19]. 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 (chloranil (2.40 eV)) and p-dinitrobenzene (PDNB (1.77 eV)). The catalysts were activated at 500 °C prior to each experiment. 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 ($\lambda_{\max}$ of EA in solvent: 393.5 nm for TCNQ, 288 nm for chloranil and 262 nm for PDNB).

The Langmuir type of adsorption isotherms are plotted for TNNQ and chloranil (figures 3 and 4, respectively) for calculating the limiting amounts adsorbed; the values are presented in table 2 (the limiting concentrations were expressed in mol m^{-2}; the surface areas being determined using the BET method for each sample). The adsorption of PDNB was negligible in all cases (electron affinity value 1.77 eV). TCNQ being a strong EA (electron affinity value 2.84 eV), its anion radicals are expected to form on strong as well as weak basic sites, whereas chloranil with intermediate electron affinity value (2.40 eV) 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 limit-

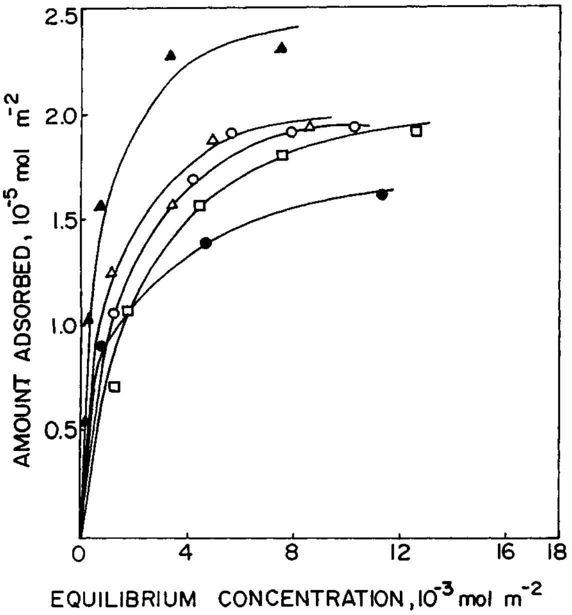

Figure 3. Adsorption isotherms of TCNQ in acetonitrile on different Ni–Co ferrite systems calcined at 500 °C: (▲) NF-1, (△) NCF-2, (○) NCF-3, (□) NCF-4 and (●) CF-5.

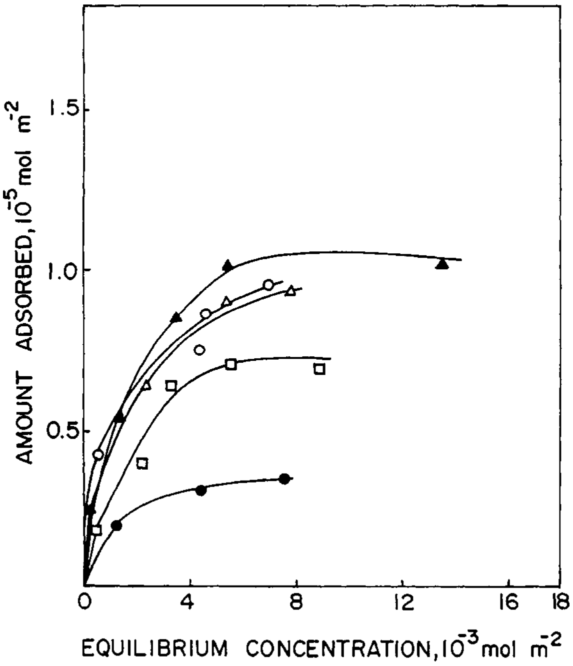

Figure 4. Adsorption isotherms of chloranil in acetonitrile on different Ni–Co ferrite systems calcined at 500 °C: (▲) NF-1, (○) NCF-2, (△) NCF-3, (□) NCF-4 and (●) CF-5.

ing amount of TCNQ and chloranil would be an estimate of the weak or moderate basic sites. The study reveals that the basic strength of the system follows the order NF-1 > NCF-2 > NCF-3 > NCF-4 > CF-5, showing a decreasing trend with progressive substitution of Ni^{2+} ions by Co^{2+} ions. The decrease in basic strength is associated with a concomitant increase in the acidity, as revealed from the dehydration activity. All compositions of the $Ni_{1-x}Co_xFe_2O_4$ type system are inverse in nature. From the above results it can be inferred that either Co^{2+} or Fe^{3+} ions are responsible for the acidity of the systems. As the composition varies the Fe^{3+} ion concentrations in the Td sites and the Oh sites remain unaltered (equally distributed) and only the Co^{2+}/Ni^{2+} ratio in the Oh sites isomorphically varies. Since the Fe^{3+} concentration is the same for all compositions and also since the acidity–basicity values have been substantially influenced during Co-substitution, we believe that the stronger Lewis acid centers are created by Co^{2+} ions.

3.2. Alkylation of pyridine

The electron withdrawing nature of the N atom in the pyridine ring makes it inert towards electrophilic substitution and very few works have been reported for the direct methylation of pyridine using suitable alkylating agents. Vapor-phase methylation of pyridine, if at all possible, can give products such as methylpyridines (picolines) and dimethylpyridines (lutidines), in addition to traces of polyalkylated and dense products. Selectivity for a particular isomer of picoline or lutidine is strongly influenced by the acid strength of the catalyst.

3.2.1. Effect of feed molar ratio

Among the various compositions of the system ($Ni_{1-x}Co_xFe_2O_4$), the systems with x values 0.5, 0.8 and 1.0 were found to be selective for 3-picoline formation, even though the catalytic activity showed a significant gradation with their x values. Figure 5 shows the influence of methanol to pyridine molar ratio on the activity over CF-5. In all cases 3-picoline has been formed as the major product. Both pyridine conversion and 3-picoline yield improved with higher methanol to pyridine feed molar ratio and at the molar ratio of 7 : 1 the yield of 3-picoline was nearly 47%. 3,5-lutidine yield also improved along with 3-picoline yield up to a molar ratio of 5 (3.6%) and thereafter it decreased.

3.2.2. Effect of reaction temperature

The alkylation experiments were performed in the temperature range 325–450 °C over CF-5. The temperature has a marked influence on pyridine conversion. Negligible conversion was observed below 375 °C, and occurs effectively in the temperature range of 400–425 °C (table 3). Maximum yield of 3-picoline (47.5%) was observed at 400 °C with selectivity more than 95%. But above 400 °C, selectivity for 3-picoline gradually decreased owing to the formation of more amount of polyalkylated pyridine. At 425 °C the selectivity of 3-picoline was 83%, whereas that of 3,5-lutidine increased upto 16%. Further increase in temperature did not show any enhancement in the alkylation rate, but high temperature favored decomposition of methanol to products like oxides of carbon as well as C_1 and C_2 hydrocarbons.

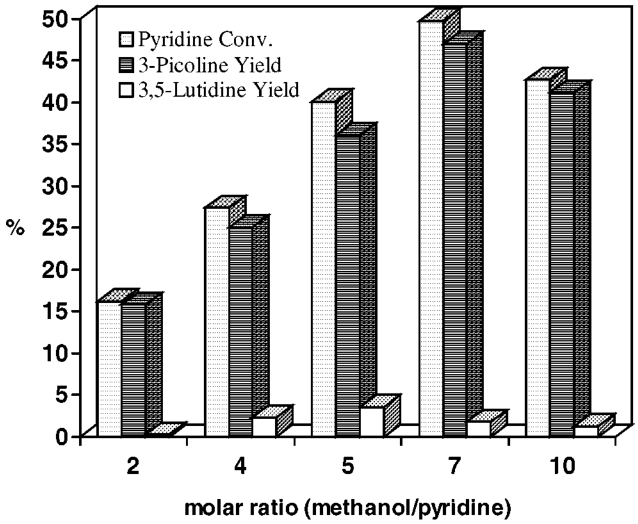

Figure 5. Influence of methanol to pyridine feed molar ratio on pyridine conversion and product yields over CF-5. WHSV 2 h^{-1}, reaction temperature 400 °C, TOS 1 h.

Table 3
Performance of CF-5 for pyridine methylation at different reaction temperatures.[a]

Product distribution (%)	Reaction temperature (°C) 325	350	375	400	425
Pyridine conversion	2.50	4.27	16.87	49.80	53.40
3-picoline	2.50	4.27	16.41	47.50	44.32
2-picoline	Nil	Nil	Nil	Nil	Nil
3,5-lutidine	Nil	Nil	0.40	1.80	8.54
Others	Nil	Nil	0.06	0.50	0.54
Selectivity					
3-picoline	100	100	97.27	95.38	83.00
3,5-lutidine	–	–	2.37	3.61	16.00

[a] Reaction conditions: WHSV 1.3 h^{-1}, methanol to pyridine molar ratio 7, TOS 2 h.

3.2.3. Effect of catalyst composition

The effect of catalyst composition on activity and selectivity is shown in table 4. It can be seen that the cobalt–nickel ratio is an important factor which can greatly influence selectivity as well as conversion. At high x values the selectivity for 3-picoline was more, whereas at lower x values 2-picoline formation also was noticed along with 3-picoline, as evident from table 4. Catalytic activity follows the order: CF-5 > NCF-4 > NCF-3 > NCF-2 > NF-1. Since the acidity values of the systems were also found to follow the same order, the gradation in the activity can be explained by considering the variation of acidity with Co^{2+} substitution in the $NiFe_2O_4$ matrix.

Table 4
Effect of catalyst composition of pyridine conversion and product selectivities.[a]

Catalyst composition	Pyridine conversion (%)	Selectivity (%)			Others (%)
		3-picoline	2-picoline	3,5-lutidine	
NF-1	17.41	82.61	15.71	1.30	0.38
NCF-2	25.06	92.34	5.30	1.60	0.66
NCF-3	26.36	96.31	1.80	1.67	0.22
NCF-4	32.80	96.43	Nil	2.87	0.70
CF-5	49.80	95.38	Nil	3.61	1.00

[a] Reaction conditions: WHSV 1.3 h^{-1}, reaction temperature 400 °C, methanol to pyridine molar ratio 1 : 7.

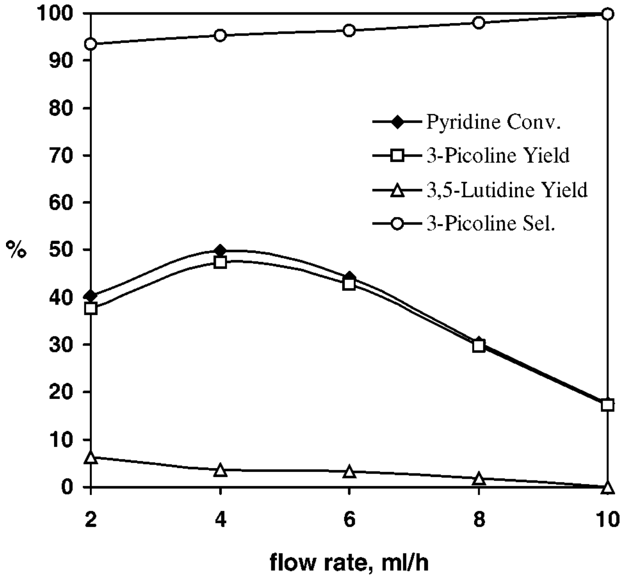

Figure 6. Effect of feed flow rate on pyridine methylation: catalyst CF-5, reaction temperature 400 °C, TOS 1 h.

3.2.4. Effect of contact time

A typical activity profile of pyridine methylation as a function of feed rate (WHSV varies from 0.65 to 3.2 h^{-1}) over CF-5 is shown in figure 6. Yield of 3-picoline and conversion of pyridine first increased and reached a maximum at WHSV 2 h^{-1} (4 ml h^{-1}) and then declined. The low pyridine conversion at high contact time region can be attributed to the preferential decomposition of methanol at the reaction temperature of 400 °C.

3.3. Catalytic pathway

Methylation of pyridine in all catalysts, except NF-1, leads to 3-picoline as the major product, with selectivity more than 90%. A considerable change in the yield of 3-picoline was observed as Ni^{2+} is substituted by Co^{2+} ions. Systems possessing higher x values (0.8 and 1.0) were found to be more active and selective, compared to those having x values of 0 and 0.2, where alkylation leads to a mixture of 2- and 3-picolines. 3,5-lutidine was the only dialkylated product observed throughout the experiment. Methylation of pyridine on an acid catalyst would give 3- and 3,5-substitution only [20]. 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 [21]. However, in the present case, the formation of 3-picoline is not via the rearrangement of the 2-isomer, which was confirmed by independent attempts to isomerize 2-picoline on these systems at the reaction temperature. Our study based on effluent gas analysis revealed 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. Methanol on an acidic catalyst can get oxidized to HCHO [22]. Formation of HCHO from methanol is accompanied by the reduction of pyridine to a dihydropyridine intermediate. Another molecule of HCHO can attack the dihydropyridine intermediate at the 3-position leading to the formation of 3-picoline. From the adsorption study of EAs and their dehydration activity, it is clear that substitution of Ni^{2+} by Co^{2+} creates an increase in acidity with a concomitant decrease in basicity. In the present series of catalysts as x increases the Co^{2+}/Ni^{2+} ratio in the Oh sites uniformly varies whereas the metal ion concentration in the Td sites remains unaltered. It was reported that the lower valency and coordination number of Td ions lead to a strong M–O interaction [1,3]. In ferrites, the Fe^{3+}–O distance is more when Fe^{3+} is in Oh symmetry than in the Td symmetry. This suggests that the Fe^{3+} ions in the Oh symmetry will be more acidic than in the Td symmetry. Recent works based on advanced surface analysis techniques such as low-energy ion scattering (LEIS), a technique used for identifying the surface atomic layer of solid surfaces [4], have revealed that the outermost atomic layer of spinels contains mainly Oh cations, and hence, the Oh cations play a dominating role in determining the catalytic properties. We have observed that both acidity and catalytic activity increase during Co substitution. The presence of a Co^{2+}–Fe^{3+} pair in the octahedral site provides active sites where methanol and pyridine can be converted into HCHO and dihydropyridine. The possibility of effective adsorption and subsequent reactions of pyridine and methanol, due to the presence of a Co^{2+}–Fe^{3+} pair, is believed to play an important role towards the catalytic activity. The dihydropyridine thus formed may again adsorb on the strong acidic site and undergoes 3-alkylation by another molecule of HCHO leading to 3-picoline, as represented by figure 7.

Direct methylation of pyridine in the 2-position is impossible due to the electron deficient nature of the ring. Hence, a different mechanism should be considered for the formation of 2-picoline. It is well established that, on a weak acidic site the lone pair electrons on N are more freely available and, hence, formaldehyde can directly attack to form an N-alkyl pyridinium ion [20]. Both NF-1 and NCF-2 possess mild acidity and are thus suitable for direct N-methylation. The Ladenberg rearrangement [8] of the N-alkyl pyridinium ion at the reaction temperature can give 2-picoline as shown in figure 8.

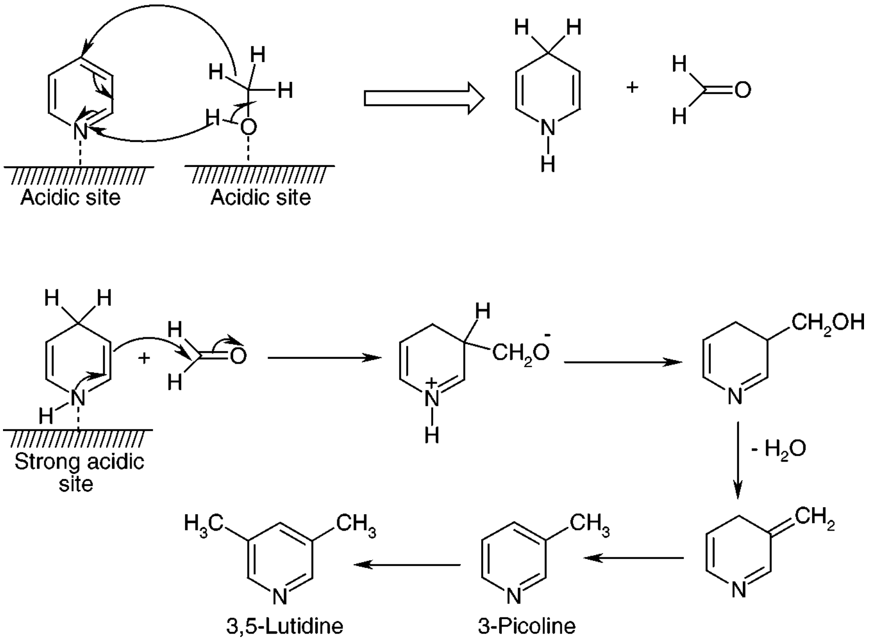

Figure 7. Mechanism of 3-alkylation of dihydropyridine intermediate by HCHO (on a strong acidic site).

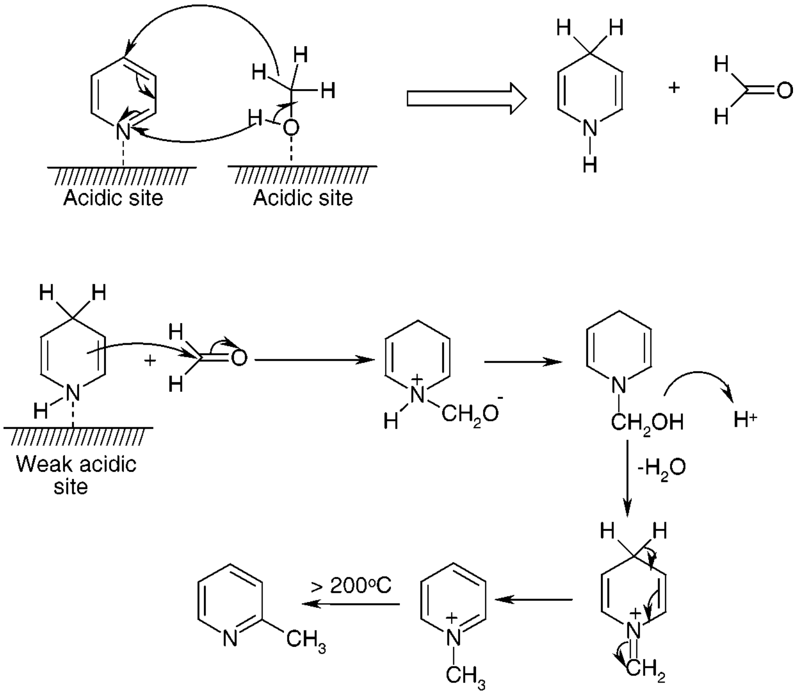

Figure 8. Mechanism for 2-picoline formation through Ladenberg rearrangement (on a weak acidic site).

4. Conclusions

(1) $Ni_{1-x}Co_xFe_2O_4$ ($x = 0$, 0.2, 0.5, 0.8 and 1.0) type systems were studied for alkylating pyridine using methanol as the alkylating agent. Systems possessing x values $\geqslant 0.5$ can effectively alkylate pyridine to give 3-picoline selectively. Under optimized conditions, 3-picoline yield was better than 95%. 3,5-lutidine was the only dialkylated product formed and its yield also increased with the x value of the system.

(2) Systems possessing x values $\leqslant 0.2$ give a mixture of 2- and 3-picolines, though selectivity for the latter was high. Pyridine conversion improves directly with substitution of Ni^{2+} ions by Co^{2+} ions.

(3) Selectivity for a particular isomer of picoline or lutidine is strongly influenced by the acid strength of the catalyst. Systems possessing high acid strength are more active for 3- and 3,5-alkylations, whereas the ones possessing mild acid strength lead to formation of 2-picoline.

(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 the dihydropyridine intermediate at the 3-position leading to 3-picoline selectively.

(5) Both NF-1 and NCF-2 possess mild acidity and, hence, the lone pair electrons on N are more freely available for an electrophile. The appreciable amount of 2-picoline over these systems can be accounted for by a mechanism similar to the Ladenberg rearrangement which involves the rearrangement of an N-methyl pyridinium ion at the reaction temperature leading to the formation of 2-picoline.

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