



SELECTIVE SYNTHESIS OF 2-PICOLINE VIA VAPOUR PHASE METHYLATION OF PYRIDINE OVER NANOCRYSTALLINE FERROSPINELS OF $Cd_{1-x}Cr_xFe_2O_4$ TYPE (X = 0, 0.25, 0.5, 0.75 and 1.0)

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ABSTRACT

Methylation of pyridine with methanol was investigated over $Cd_{1-x}Cr_xFe_2O_4$ ($x = 0, 0.25, 0.5, 0.75$ and 1.0) type ferros spinels prepared via low temperature co-precipitation method. 2-Picoline and 3-picoline were found to be major products. Products distribution and individual selectivity depends on the acido-basic properties of catalysts. It was observed that system possessing high 'x' value were highly selective for 2-picoline. Cd/Cr ionic composition in spinel lattice influences the acido-basic properties of catalysts. The influence of surface acid-base properties, cation distribution in the spinel lattice and various reaction parameters are discussed.

Key Words: Ferros spinels, Spinel structure, 2-Picoline, 3-Picoline.

INTRODUCTION

Alkylated pyridines and their derivatives are industrially important compounds for the production of pharmaceuticals, herbicides, insecticides, fungicides and as fine chemicals¹. Traditionally these compounds are obtained from the coal-tar distillation. Several groups studied gas phase alkylation of pyridine using alcohols as alkylating agents. Recently alkylation of pyridine has been reported over ferrites. Ferrites are well known materials, often used as high frequency circuits, pigments or heterogeneous catalysts. They have shown adequate activity and selectivity towards alkylation reaction²⁻⁹. Ferros spinel structure presents two types of interstitial sites: tetrahedral and octahedral. These sites are surrounded by four and six oxygen atoms, respectively.

The formula of spinel oxides is AB_2O_4 , where A^{2+} ions occupy the tetrahedral and

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B³⁺ ions the octahedral positions. Most of the ferrite properties depend upon the ion distribution among the tetrahedral and octahedral sites in the spinel structure. It has been observed that catalytic properties of ferrites can be modified with the introduction of third metal ion. In this context, tertiary spinels take relevance because the introduction of third metal should change or modify the ion distribution in the spinel. Therefore, through an adequate selection of a substituting ion and appropriate chemical composition, the catalytic properties of the ferrites could be improved¹⁰⁻¹².

EXPERIMENTAL

Catalyst preparation and characterization

The different compositions of Cd_{1-x}Cr_xFe₂O₃ ferrites viz. CdFe₂O₄ (CF-1), Cd_{0.75}Cr_{0.25}Fe₂O₄ (CF-2), Cd_{0.5}Cr_{0.5}Fe₂O₄ (CF-3), Cd_{0.25}Cr_{0.75}Fe₂O₄ (CF-4) and CrFe₂O₄ (CF-5) were prepared by low temperature co-precipitation method using procedure given elsewhere⁵.

Table 1. Compositional parameter ‘x’, acidity, catalytic activity (pyridine conversion), and BET surface area (m²/g) of ferrite catalysts.

x	Acidity (Total NH ₃ uptake in mmol/g)	Catalytic activity (Pyridine conversion)	BET Surface area (m ² /g)
0.00	1.15	27.5	66.25
0.25	1.28	31.9	62.26
0.50	1.45	39.1	58.34
0.75	1.66	58.3	50.17
1.00	1.75	80.3	43.73

The phase purity of the samples was established by XRD, recorded on Rigku X-ray diffractometer with Cu-K α radiations. All the ferrites showed two strong IR-Bands around 700 cm⁻¹ and 500 cm⁻¹. The high frequency band at 700 cm⁻¹ is due stretching vibration of tetrahedral group and lower frequency band at 500 cm⁻¹ is due to vibration of octahedral M-O group. The tetrahedral bonds have 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 bond¹³⁻¹⁴. FTIR of CF-1, CF-3, CF-5 is presented in Fig. 2. BET surface areas of different ferrites were determined on OMNISORP 100 CX instrument and

results are presented in Table 1.

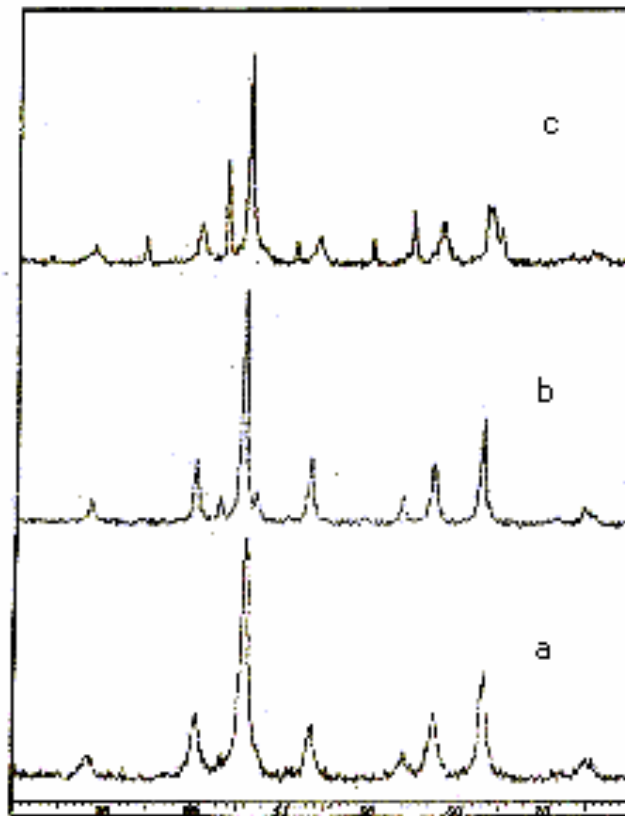


Fig. 1: X-ray diffractograms of (a) CF-1 (b) CF-3 (c) CF-5

Acidity evaluation

Acidity of the systems was determined by NH_3 -TDP. Temperature programmed ammonia desorption (NH_3 -TPD) experiments were carried out to measure the acidity of catalysts. 2.0 g of catalyst was packed in a pyrex tube in down flow reactor and heated to 673 K under a nitrogen flow rate of 30 mL/min for 3 h. The reactor was then cooled to 298 K and adsorption is conducted at this temperature by exposing the sample to NH_3 for 2 h. The physically adsorbed NH_3 was removed by purging the sample with nitrogen gas flow rate of 30 mL/min. at 323 K for 1 h. The acidity was obtained by raising the catalyst temperature from 323-773 K and absorbing the NH_3 evolved in double distilled water. Quantitative estimation was made by titrating the resulting solution with a standard 0.1 M HCl solution. The results are presented in the Table 1.

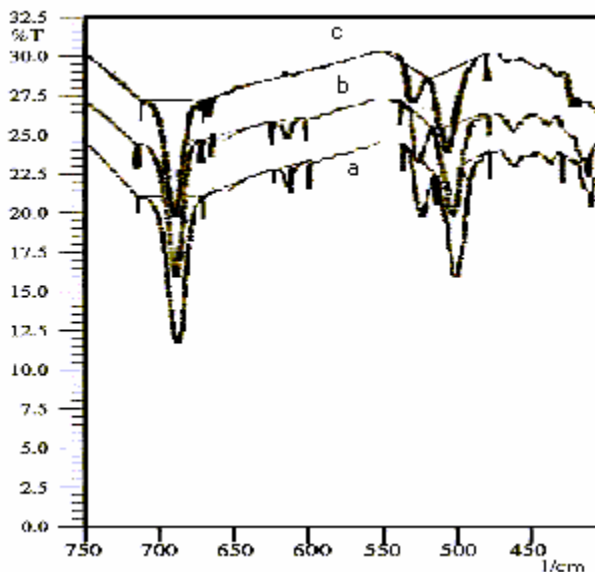


Fig. 2: IR spectra of (a) CF-1 (b) CF-3 (C) CF-5

Apparatus and procedure

Catalytic activities were determined by using a tubular fixed-bed micro reactor of 0.45 m length and 13 mm diameter. The upper half worked as pre-heater and lower half worked as reactor, where 5 g of catalyst was packed between two plugs of glass wool and was activated at 773 K for 4 h under a flow of air and then brought down to the desired temperature by cooling in a current of nitrogen gas, exposed to a feed stream mixture of methanol and pyridine. The gaseous products were condensed using a cold water coiled condenser. A gas chromatograph with FID, SE-30 column was used to analyze the liquid product mixture.

RESULTS AND DISCUSSION

Acidity and performance of various catalysts in methylation of pyridine

The effect of catalyst composition on activity and selectivity is shown in table 2. NH_3 -TPD experiment reveals that substitution of Cd ion by Cr ion creates an increase in acidity. Both acidity and catalytic activity of the system follow the order: CF-5 > CF-4 > CF-3 > CF-2 > CF-1; since the acidity of the systems was also found in the same order. The gradation in the activity can be explained by variation in acidity of various systems. It

has been observed that system possessing high 'x' value were highly active and better performance of CF-5 can be described due to its higher acidity. The high strength Lewis acidity is probably due to Fe^{3+} ions in the octahedral sites because of the stable nature of Cd ions and also due to their occupancy in the less accessible tetrahedral sites. As 'x' increases, Cr ion replace Fe^{3+} ions isomorphically from octahedral to tetrahedral sites. In other words, high activity on Cr substitution can be accounted for as due to the replacement of basic sites by acidic sites during Cr ion substitution. This is clearly evidenced from ammonia desorption study, since Cr ion substitution progressively increased the ammonia uptake. It has been observed that lower valency and coordination number of tetrahedral ions led to a strong M-O interaction¹⁵. In the ferrites, the Fe^{3+} -O distance is more when Fe^{3+} ion is at octahedral site than in tetrahedral sites. Hence, Fe^{3+} ions will be readily available for the adsorption of methanol; thus, Fe^{3+} ions in the octahedral sites are mainly responsible for catalytic activity.

Table 2. Performance of various catalysts in methylation of pyridine

Catalysts	Pyridine conversion	2-Picoline yield (%)	3-Picoline yield (%)	Others
CF-1	27.5	25.2	2.1	0.2
CF-2	31.9	27.6	4.2	0.1
CF-3	39.1	31.5	7.3	0.3
CF-4	58.3	45.7	11.4	0.2
CF-5	80.3	70.1	10.1	0.1

Effect of reaction parameters on methylation of pyridine

Methylation experiments were carried out in the temperature range 250-450°C over CF-5. The results are reproduced in table 3. As the temperature was increased, pyridine conversion, yield and selectivity of 2-picoline was increased. A maximum yield of 70.1% with selectivity 87.3% was observed for 2-picoline at 400°C. Beyond 400°C, pyridine conversion declined probably due to decomposition of carbon on the catalytic surface.

Influence of pyridine to methanol molar ratio on the activity over CF-5 is shown in Fig. 3. Over all catalyst compositions 2-picoline has been detected as the major products. Pyridine conversion yield and selectivity of 2-picoline increased with methanol to pyridine molar ratio and at the molar ratio 6 (methanol/pyridine), the yield of 2-picoline was maximized. Increase in pyridine conversion with methanol/pyridine molar ratio and then a

decrease at higher molar ratio suggests a Langmuir-Hinshelwood type of bimolecular reaction.

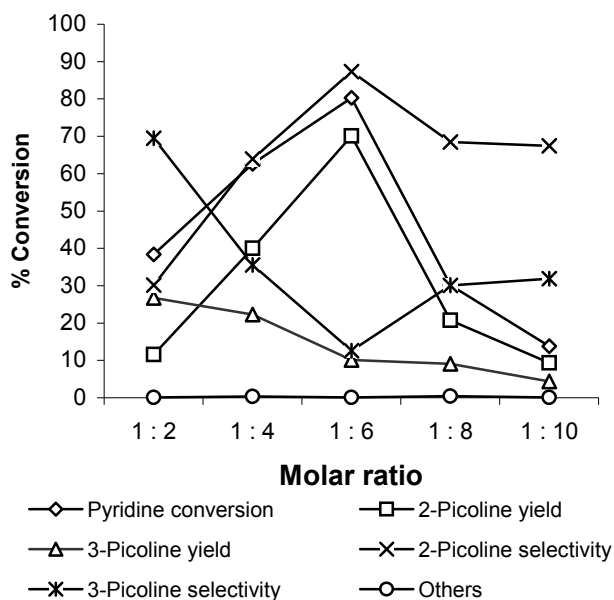


Fig. 3: Effect of methanol/pyridine molar ratio on pyridine methylation

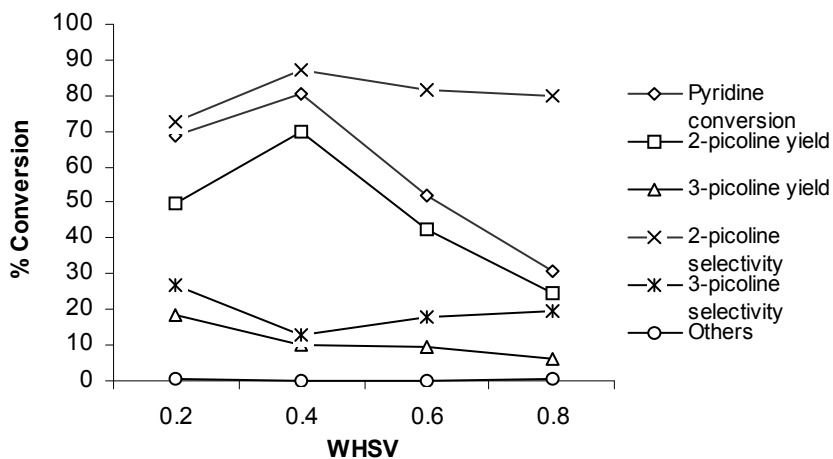


Fig. 4: Effect of WHSV on pyridine methylation

In another set of experiments, the effect of contact time on methylation of pyridine was studied over CF-5. The results are shown in fig. 4. WHSV was varied from 0.2-0.8 h⁻¹. As the WHSV was increased, pyridine conversion also increased reaching a maximum at 0.4 h⁻¹ and then decreased on increasing the flow rate.

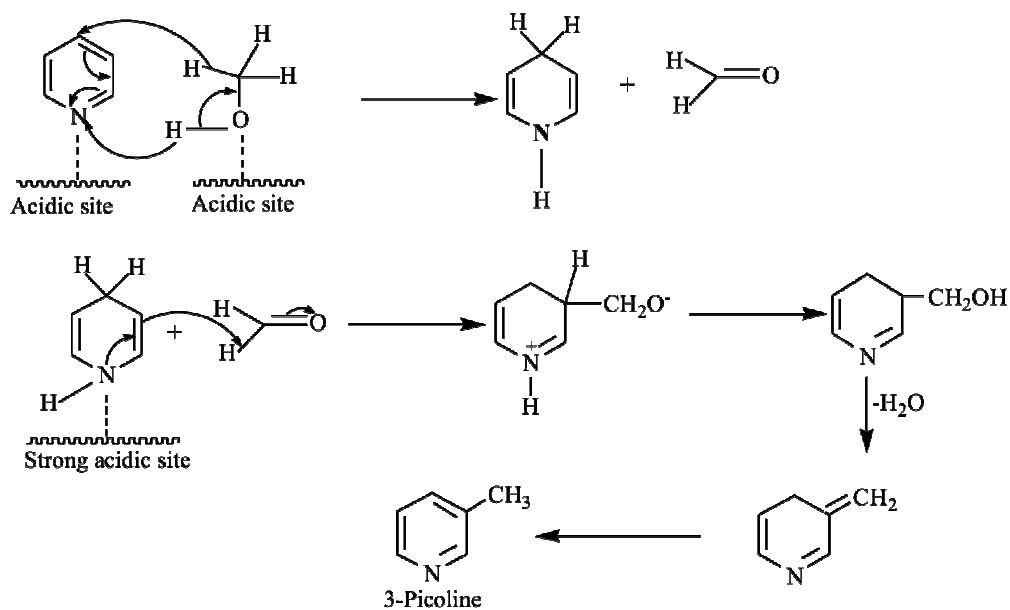
Table 3. Effect of reaction temperature on methylation of pyridine.

Temperature (°C)	Pyridine conversion	2-Picoline yield (%)	3-Picoline yield (%)	Others
250	12.3	3.8	8.3	0.2
300	33.9	14.6	18.9	0.4
350	57.8	43.0	14.5	0.3
400	80.3	70.1	10.1	0.1
450	68.2	57.4	10.4	0.4

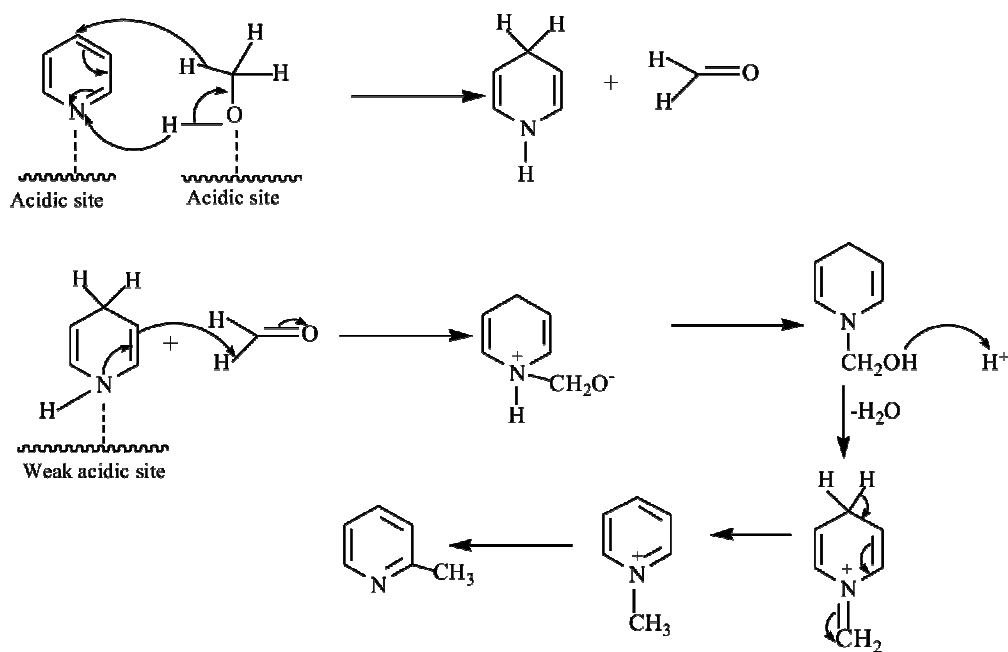
MECHANISM

3-Picoline formation may involve direct ring alkylation by formaldehyde formed from methanol dehydrogenation over acidic sites of catalysts or by isomerisation of 2-picoline.

Passing 2-picoline over catalyst bed at reaction temperature did not produce 3-picoline, which rule out the formation of 3-picoline by rearrangement of 2-picoline. It seems that pyridine abstracts the hydrogen atoms produced from methanol dehydrogenation and converted into dihydropyridine. Electrophillic attack of formaldehyde at 3-position of dihydropyridine leads to the formation of 3-picoline as shown in **scheme 1**. In an experiment, equal amounts of formaldehyde and pyridine were passed over catalyst along with hydrogen gas, where all the formaldehyde converted to 3-picoline. This experiment further confirmed formation of dihydropyridine intermediate. Direct methylation of pyridine at 2-position is not possible due to electron deficient nature of ring. It seems that the formaldehyde interacts with lone pair of electron on the nitrogen atom of pyridine to form N-alkyl pyridinium ion, which rearranges to give 2-picoline as shown in **Scheme 2**.



Scheme-1 Mechanism for 3-Picoline formation



Scheme-2 Mechanism for 2-Picoline formation

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