$Cu_{1-x}Co_xFe_2O_4$ Ferrospinels: Synthesis, Characterisation and Investigation of Catalytic activity in Vapor phase Methylation of Aniline

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Abstract

The vapor phase alkylation of aniline with methanol was investigated over $Cu_{1-x}Co_xFe_2O_4$ (x=0, 0.25, 0.5, 0.75 and 1.0) type ferrospinels in a fixed-bed down-flow reactor. Reaction parameters were optimized and a maximum yield of 81.32% of NMA at 84.13% aniline conversion was obtained over $CuFe_2O_4$ at a temperature of 623 K, aniline/methanol molar ratio of 1:5 and WHSV of 0.5 h^{-1}. Product distribution and individual selectivity are shown to be strongly dependent on acido-basic properties of the catalysts.

Keywords: Ferrospinels, Alkylation, Aniline, NMA, NNDMA.

Introduction

Alkylated anilines such as n-methylaniline, n,n-dimethylaniline and toluidines are valuable intermediates for the synthesis of pharmaceuticals, drugs, dyes and explosives [1-2].Conventionally Friedel-Craft alkylation reaction using homogeneous acid catalysts were used but due to stringent environmental concern over the disposal of spent catalysts, it is difficult to continue with these catalysts. Mixed metal oxides possessing spinel structure have attracted the attention of chemists and technologists due to their peculiar cation distribution among the tetrahedral (Td) and octahedral (Oh) sites of the co-ordinated oxygen, high thermal and mechanical stability, interesting electrical and magnetic properties, reusability, easy seperation and ecofriendly nature [3-5]. The formula of spinel oxides is AB_2O_4 where A^{2+} occupy the tetrahadral sites and B^{3+} occupy the octahedral sites. Most of the ferrite properties depend upon the ion distribution among the tetrahedral and octahedral sites and the introduction of third metal significantly change or modify the ion distribution in the spinel and affects the acido basic properties of the ferrospinels [5-7]. Earlier, a wide variety of catalysts have been tested for the alkylation of aniline with methanol including zeolites, clay, metal oxides such as MgO and Al_2O_3 [8] and ferrites [8-10]. Metal oxides usually show better selectivity for N-alkylation but required large feed mixture ratio and high temperature. Therefore from the industrial point of view, choice of the better catalyst and the proper reaction parameters are required. The present problem of methylation of aniline over $Cu_{1-x}Co_xFe_2O_4$ (x=0, 0.25, 0.5, 0.75 and 1.0) type ferrospinels was therefore taken with a view to optimize the reaction parameters and the Cu-Co-Fe composition to get maximum aniline conversion with highs selectivity of NMA.

Experimental work

Catalyst synthesis and characterisation

Various spinel compositions viz. $CuFe_2O_4$ (CF-1), $Cu_{0.75}Co_{0.25}Fe_2O_4$ (CF-2), $Cu_{0.5}Co_{0.5}Fe_2O_4$ (CF-3), $Cu_{0.25}Co_{0.75}Fe_2O_4$ (CF-4), $CoFe_2O_4$ (CF-5) were synthesized by low temperature co-precipitation method as reported earlier [6].

The composition of the series of $Cu_{1-x}Co_xFe_2O_4$ ferrospinels were determined by X-ray fluorescence (XRF) and are presented in table 1. The results obtained from X-ray fluorescence were found to be in close agreement with the theoretical values.

Table 1 Chemical analysis results obtained from XRF
(the quantities in the parenthesis indicate the theoretical values)
surface area data and acidity values (total NH_3 uptake in mmol /g) Metal concentratio(wt.%)

X	$Cu_{1-x}Co_xFe_2O_4$	Co	Cu	S_{BET} (m^2/g)	Acidity (m mol/g)
0	$CuFe_2O_4$	-	26.8 (26.56)	41.0	1.06
0.25	$Cu_{0.75}Co_{0.25}Fe_2O_4$	5.8 (6.18)	20.2 (20.11)	45.9	1.10
0.5	$Cu_{0.5}Co_{0.5}Fe_2O_4$	12.41(12.43)	13.37(13.41)	48.2	1.14
0.75	$Cu_{0.25}Co_{0.75}Fe_2O_4$	18.37(18.74)	7.11 (6.73)	51.6	1.20
1.0	$CoFe_2O_4$	24.80(25.11)	-	54.0	1.27

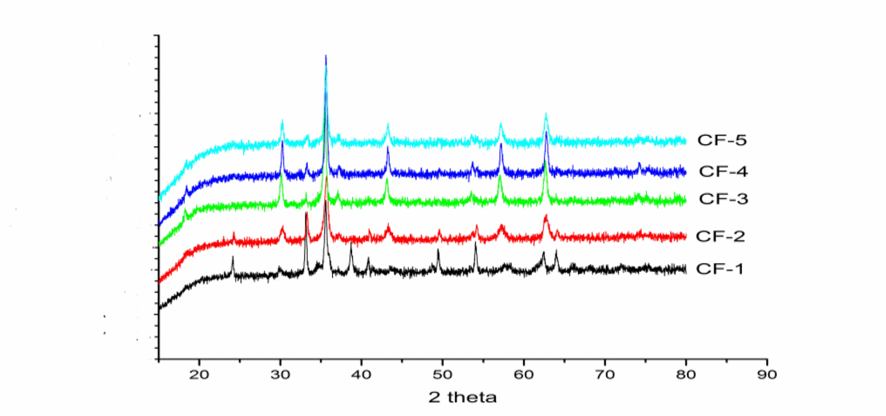

Fig.1- X-ray diffractograms of $CuFe_2O_4$ (CF-1), $Cu_{0.75}Co_{0.25}Fe_2O_4$ (CF-2), $Cu_{0.5}Co_{0.5}Fe_2O_4$ (CF-3), $Cu_{0.25}Co_{0.75}Fe_2O_4$ (CF-4), $CoFe_2O_4$ (CF-5)

X-ray diffraction pattern of $Cu_{1-x}Co_xFe_2O_4$ ferrospinels was studied by Rigaku X-ray diffractometer in the 2θ range of 15-80° using Cu Kα radiations (λ=1.54A°) at a scan rate of 2°/min and are presented in fig.1. XRD analysis reveals a single phase spinel structure for all the compositions of ferrospinels. The morphological characteristics of the $Cu_{1-x}Co_xFe_2O_4$ ferrospinels were investigated by scanning electron microscope (SEM) analysis. From the SEM micrographs, it is clear that Cu1-xCoxFe2O4 nanoparticles have almost uniform spherical structure with a narrow size distribution of the particles [11] as shown in Fig.2. The average size calculated using SEM micrographs were found to be in the range of 20-50 nm.The FTIR spectra of Cu1-xCoxFe2O4 ferrospinels showed two strong IR bands at 700 cm-1 and 500 cm-1 due to stretching vibration of tetrahadral M-O group and the stretching vibration of octahedral M-O group respectively. The tetrahadral M-O bond have the effect of substantially increasing the frequency of vibration as compared to octahedral M-O bond, since these cations introduce a restoring force in preferential direction along the Mt-O bond [12-13].

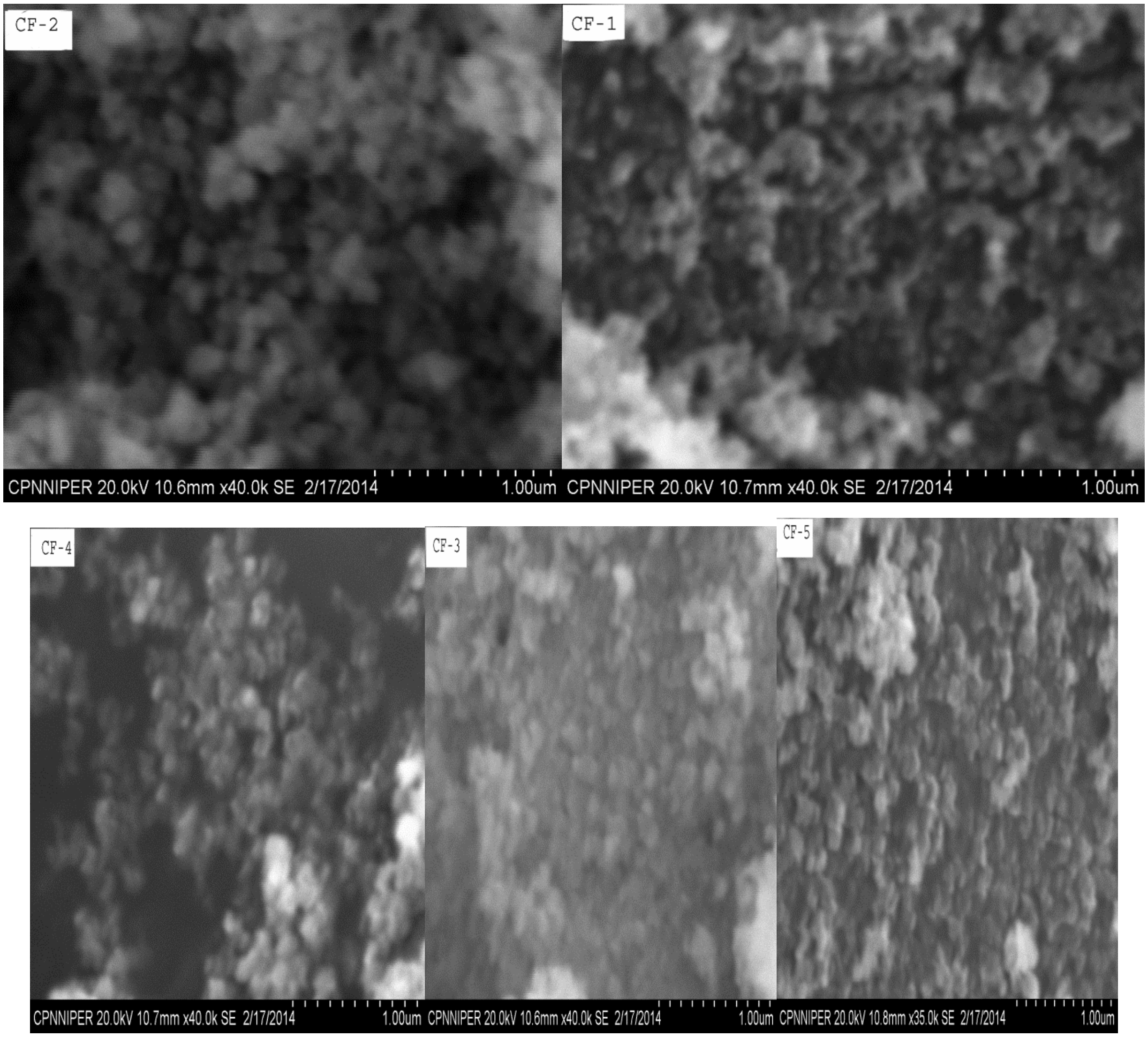

Fig. 2. SEM images of $CuFe_2O_4$ (CF-1), $Cu_{0.75}Co_{0.25}Fe_2O_4$ (CF-2), $Cu_{0.5}Co_{0.5}Fe_2O_4$ (CF-3), $Cu_{0.25}Co_{0.75}Fe_2O_4$ (CF-4), $CoFe_2O_4$ (CF-5).

Temperature -programmed ammonia desorption (NH3-TPD) method was used to measure the acidity values of all the ferrospinels. Exactly 3.0 g of the sample was introduced in a pyrex tube and under a nitrogen flow, it was pre-heated to 673 K for 2 h. The reactor was then cooled to 298 K and adsorption is conducted at this temperature by exposing the sample to NH_3 at a flow rate of 30 mL/min for 2 h. The physically adsorbed NH_3 was removed by exposing the sample with a nitrogen gas flow rate of 30 mL/min at 323 K for 1h. The acidity was measured by increasing the temperature from 323 K to 773 K and absorbing the NH_3 evolved in double distilled water. Quantitative estimation was done by titrating the resulting solution with a standard 0.01M HCl, results are depicted in Table1. The BET surface area of the $Cu_{1-x}Co_xFe_2O_4$ ferrospinels were determined with the help of Thermo-electron corporation make sorptomatic 1990 instrument and the results are shown in Table 1.

Apparatus and Procedure

The vapor phase alkylation reaction was carried out in a fixed-bed down-flow reactor. An amount of 9 gm of 6/10 mesh sized catalyst was packed between two plugs of glass wool and was activated at 773K for 2 h under a flow of air and then brought down to the desired temperature by cooling in a current of nitrogen gas of 30 mL/min. The reactants were fed from the top of the reactor through a syringe pump with a current of nitrogen gas of 30 mL/min. The gaseous products were collected by using a cold water coiled condenser at the bottom of the reactor. Dhruva Gas chromatograph with flame ionisation detector was used to determine the composition of the product mixture.

Results and Discussion

Surface area, acidity and performance of various catalysts in alkylation of aniline

The performance of various catalysts in the alkylation of aniline is presented in table 2. NH_3-TPD experiment reveals that acidity of the ferrospinels increases with progressive substitution of Cu ions by Co ions as depicted in table.1 and basicity values follow exactly the opposite trend.The order of acidity values of various catalysts were found to be CF-5> CF-4> CF-3> CF-2> CF-1, however the catalytic activity follow the opposite trend CF-5< CF-4< CF-3< CF-2< CF-1. It can be seen that copper-cobalt ratio is an important factor which can greatly influence aniline conversion as well as selectivity of the desired product. Systems possessing lower □ x □ values (0, 0.25, 0.5) were found to be more active and selective for n-methylaniline formation. Unlike other acid-base reactions, here acidity values cannot be considered as a sole factor in determining the catalytic activity of various ferrospinels. Since aniline is a strong base so even weak lewis acid sites on the catalyst surface can make effective co-ordination with this molecule, therefore the activity of the system towards methanol adsorption becomes more important.

Effect of reaction temperature

A series of Aniline alkylation reactions were performed in the temperature range of 523-673 K over CF-1 and the results are shown in Fig. 3. It has been found that the temperature has a marked influence on the aniline conversion and product distribution. Both aniline conversion and NMA yield improved with increase in temperature from 523K to 623K.Maximum yield of 81.32% of NMA at 84.13% aniline conversion was obtained over $CuFe_2O_4$ at a temp. of 623 K. However, further increase in temperature reduced the aniline conversion since high temperature favour the decomposition of methanol.

Table 2 : Performance of various catalysts in the methylation of aniline
(at temperature 623 K , WHSV 0.5 h^{-1} and aniline/Methanol molar ratio 1: 5)

Catalyst composition	Aniline conversion (%)	NMA Yield (%)	NNDMA Yield (%)	NMA Selectivity (%)	NNDMA Selectivity (%)	Others Yield (%)
CF-1	84.13	81.32	1.61	96.66	1.91	1.20
CF-2	68.97	65.76	1.84	95.34	2.67	1.37
CF-3	56.54	52.37	2.49	92.62	4.40	1.68
CF-4	53.22	47.58	3.38	89.40	6.35	2.26
CF-5	41.98	35.39	3.90	84.30	9.29	2.69

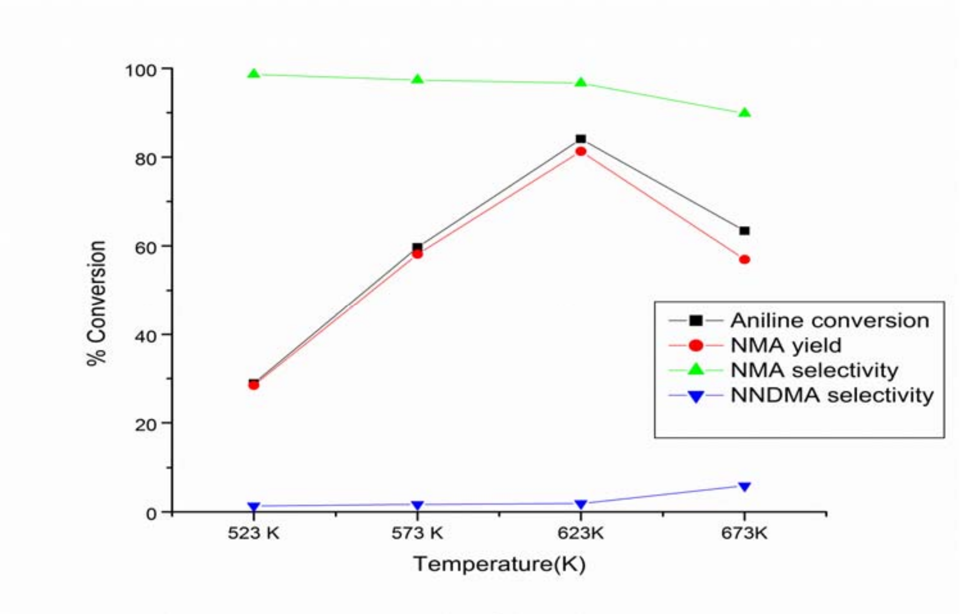

Fig. 3 : Effect of rection temperature in the methylation of aniline over $CuFe_2O_4$, WHSV 0.5 h^{-1} and aniline/Methanol molar ratio1: 5.

Effect of weight hour space velocity (WHSV)

The effect of WHSV on alkylation of aniline was studied over $CuFe_2O_4$ at a temperature of 623 K, aniline to methanol molar ratio of 1:5 in the range of 0.1 to 0.7 h^{-1} WHSV and the results are shown in fig-4. Aniline conversion increases with increase in WHSV reaches a maximum at 0.5 $h^{-1}$and further increase in WHSV results in low aniline conversion since aniline gets less time to go into the product side. At low flow rate more NNDMA was formed since due to long contact time NMA was futher alkylated to form NNDMA.

Effect of molar ratio of aniline to methanol

In order to understand the optimum feed mixture ratio, a series of experiments were performed at temperature of 623 K, WHSV 0.5 h^{-1} with different molar ratio of aniline to methanol over CF-1. The results are shown in fig-5. In all the experiments, it can be seen that NMA has been formed as a major product with high selectivity. Aniline conversion increases with increase in aniline to methanol molar ratio, reaching a maximum at 1:5(maximum yield of 81.32% of NMA at 84.13% aniline conversion). Further increase in feed mixture ratio decreased the selectivity for NMA with subsequent increase in the selectivity of NNDMA since high aniline to methanol molar ratio favours the consecutive methylation of NMA to NNDMA owing to the presence of large amount of methanol but at high molar ratio aniline conversion decreases because methanol undergoes side reaction resulting in coke formation.

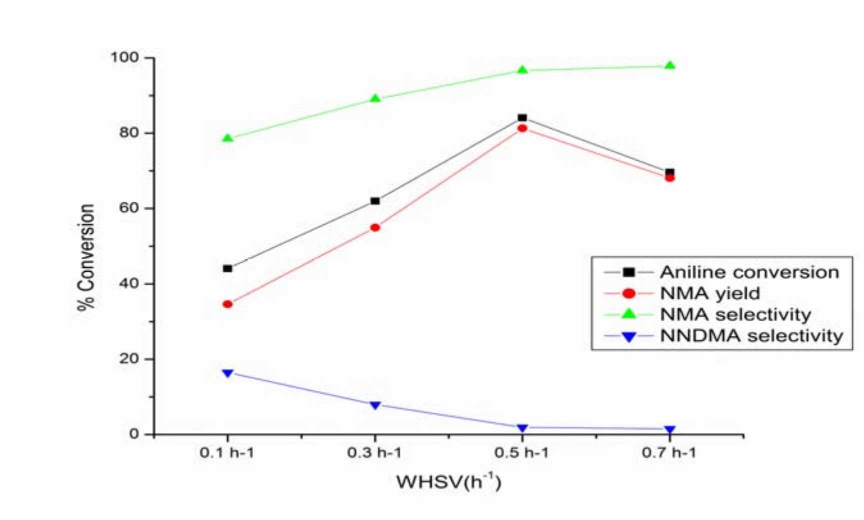

Fig. 4 : Effect of weight hour space velocity in the methylation of aniline over $CuFe_2O_4$, temperature 623 K and aniline/Methanol molar ratio1: 5.

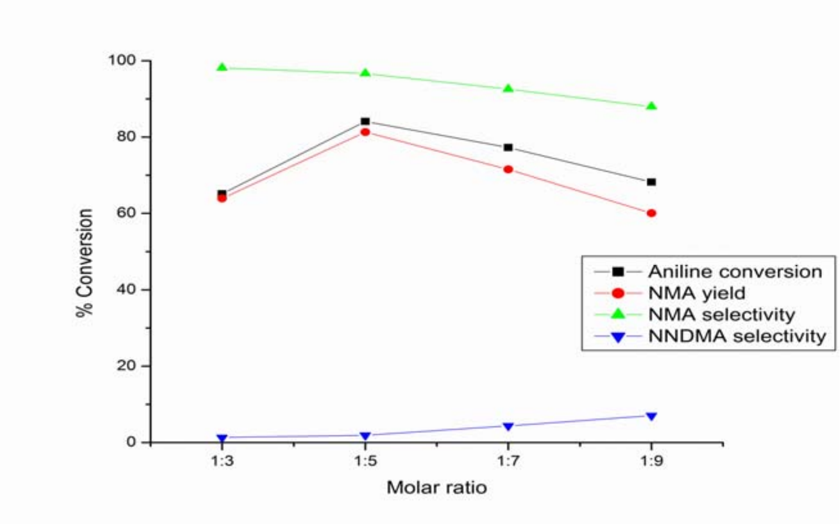

Fig. 5 : Effect of molar ratio in the methylation of aniline over $CuFe_2O_4$, WHSV 0.5 h^{-1} and temperature 623 K.

Mechanism

From table 2, it can be seen that moderate amount of both acidic and basic sites are required on the surface of catalyst for N-alkylation of aniline. Since aniline is a strong base so even weak lewis acid sites on the catalyst surface can effectively interact with this molecule, therefore the activity of the system towards methanol adsorption becomes more important. Reaction mechanism for the alkylation of aniline is presented in Fig.6. It seems that methoxy species interact with the lewis acid sites while the hydrogen atom of the undissociated hydroxyl group interacts with the lewis basic sites. The electrophile CH_3 attack on the nitrogen atom of the aniline leading to n-methylaniline formation which on subsequent methylation leads to n,n-dimethylaniline in a similar way [9].

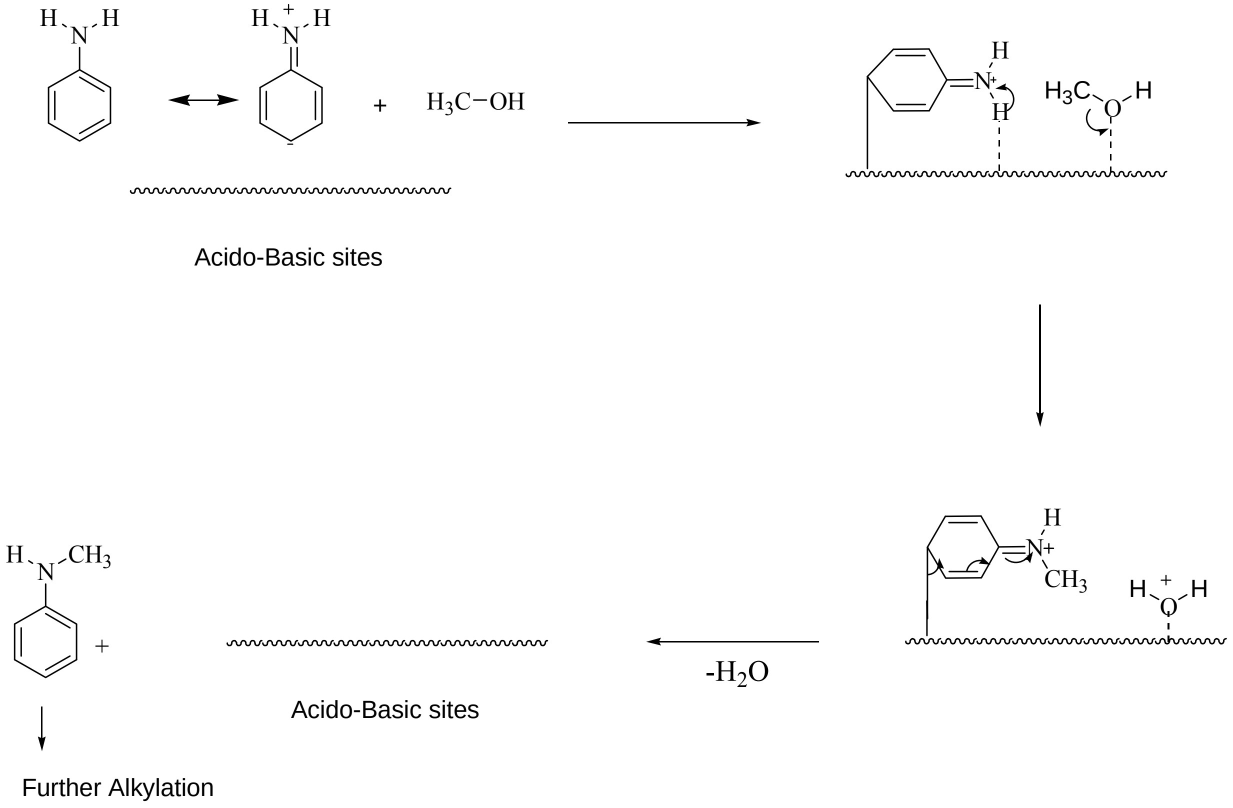

Fig.6: Reaction mechanism for the alkylation of aniline

Conclusion

A series of $Cu_{1-x}Co_xFe_2O_4$ (x= 0, 0.25, 0.5, 0.75 and 1.0) type ferrospinels were prepared by low tempeature co-precipitation method and characterised by various physico-chemical techniques.The acid–base properties of the ferrospinels vary with the progressive substitution of Cu ions by Co ions. Systems possessing lower □ x □ values are found to be more active and selective for NMA formation. Aniline conversion and NMA selectivity vary with the reaction parameters. Under the optimized condition, a maximum yield of 81.32% of NMA at 84.13% aniline conversion was obtained over $CuFe_2O_4$ at a temperature of 623 K, aniline/methanol molar ratio of 1:5 and WHSV of $0.5h^{-1}$. It is believed that only weak to moderate lewis acidity and basicity favour the reaction,therefore the enhanced catalytic activity of $CuFe_2O_4$ can be ascribed to its weak lewis acidity and basicity.

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