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Vapor Phase Methylation of Indole over Nanocrystalline $Cd_{1-x}Cr_xFe_2O_4$ (x = 0, 0.25, 0.5, 0.75 and 1.0) Ferrospinels

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Vapor phase methylation of indole has been carried out over nanocrystalline $Cd_{1-x}Cr_xFe_2O_4$ (x = 0, 0.25, 0.5, 0.75 and 1.0) ferrospinels in a fixed bed down-flow reactor. Catalyst characterization was performed by Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy with EDX, BET surface area and temperature programmed ammonia-desorption method. Product selectivity is shown to be strongly influenced by acidic properties of the catalyst. A maximum yield of 64.29 % of 3-methyl indole with 91.46 % selectivity at 70.3 % indole conversion was obtained under optimized reaction conditions.

Keywords: Ferrospinels, Alkylation, Indole, 3-Methyl indole.

INTRODUCTION

The discovery of mixed metal oxides possessing spinel structure has drawn a lot of attention owing to their high thermal stability, easy separation, re-usability and environmentally benign nature [1-3]. In recent years, abundant research has been conducted on ferrospinels because of their fascinating structural, electrical, magnetic and catalytic properties [4-7]. They have peculiar cation distribution among the two interstitial sites *i.e.*, tetrahedral (T_d) and octahedral (O_h) sites of the co-ordinated oxygen atom. Indole and its derivatives are extensively used in perfumery, in tryptophan synthesis (an amino acid commonly found in animal protein) and as an intermediate within the synthesis of plant growth hormone like auxin, anti-inflammatory agents, dyes, agrochemicals and antibiotics. 3-Methyl indole also known as skatole have been intensively used as an antidiuretic, stimulant, antihypertensive, muscular relaxant, heart stimulant and respiratory inhibitor and have additionally been found to stimulate the dimerization of butadiene [8-10]. The current study is based on nanocrystalline $Cd_{1-x}Cr_xFe_2O_4$ (x = 0, 0.25, 0.5, 0.75 and 1.0) ferrospinels for extremely selective synthesis of skatole *via* vapor phase methylation of indole.

EXPERIMENTAL

Preparation of $CdFe_2O_4$ (CC-1): A solution of 1.2 mol of NaOH in 150 cm^3 of water was allowed to react with a solution of 0.075 mol of $CdCl_2·H_2O$ in 50 cm^3 of water. The ensuing $Na[Cd(OH_3)]$ solution was added to a 5 dm^3 beaker containing 0.15 mol of $FeCl_3·6H_2O$ in 2.5 dm^3 of 0.6 M HCl and stirred for 2 h. The resulting mixture was further heated at 333 K for 0.5 h. The mixture was allowed to settle down at room temperature and then reacted with 2 M NaOH till a permanent pink colour of phenolphthalein was obtained. Then product was washed by continual decantation with distilled water till the supernatant was freed from Cl^-. The product was filtered, dried in an oven at 393 K and further calcined at 773 K for 16 h and finally sieved through a 6/10 mesh size sieve.

Preparation of other catalysts: Preparation of $CrFe_2O_4$ (CC-5) was similar to CC-1 as described above, except that now 0.075 mol of $CrCl_3·6H_2O$ was used. Similarly $Cd_{0.75}Cr_{0.25}Fe_2O_4$ (CC-2), $Cd_{0.5}Cr_{0.5}Fe_2O_4$ (CC-3), $Cd_{0.25}Cr_{0.75}Fe_2O_4$ (CC-4) was prepared by taking 0.0562, 0.0375 and 0.0187 mol of $CdCl_2·H_2O$ and 0.0187, 0.0375 and 0.0562 mol of $CrCl_3·6H_2O$, respectively.

The vapor phase methylation of indole was carried out in a continuous fixed bed down-flow glass reactor. The upper half worked as a pre-heater and the lower half worked as a reactor where 9 g of 6/10 mesh size catalyst was placed between two plugs of glass wool, activated at 773 K for 2 h under a flow of air and then brought down to the desired temperature by cooling in a current of N_2 gas of 30 cm^3/min. The reactants were fed from the top with a current of N_2 gas of 30 cm^3/min and the products were collected from an ice-cold trap at the bottom of the reactor. Gas chromatogram was used to determine the composition of the product mixture.

Catalyst characterization: The different compositions of the $Cd_{1-x}Cr_xFe_2O_4$ ferrospinels were characterized by various physico-chemical techniques *i.e.*, FTIR, XRD, SEM with EDX, BET surface area and ammonia desorption methods. FTIR spectra for all the compositions of $Cd_{1-x}Cr_xFe_2O_4$ ferrospinels consist of two significant bands around 700 cm^{-1} and 500 cm^{-1} due to stretching vibration of the tetrahedral M-O group and the octahedral M-O group respectively [11]. The difference in the band position is due to the difference in the Fe^{3+}–O^{2-} distance for tetrahedral and octahedral sites. X-ray diffraction pattern of $Cd_{1-x}Cr_xFe_2O_4$ ferrospinels was studied by Rigaku X-ray diffractometer in the 2θ range of 10-80° using Cu K_α radiations (λ = 1.54 Å) at a scan rate of 2°/min as shown in Fig. 1. All the peaks in the XRD analysis match well with the characteristic reflections of corresponding ferrites and this reveals a single phase spinel structure.

The BET surface area of $Cd_{1-x}Cr_xFe_2O_4$ ferrospinels was determined with the help of OMNISORP 100 CX instrument and the results are represented in Table-1. The micro-structure and the suface morphology of the $Cd_{1-x}Cr_xFe_2O_4$ ferrospinels were investigated by using scanning electron microscopy (SEM model HITACHI S-3700 N). SEM micrographs are shown in Fig. 2. From the micrographs, it is clear that the obtained ferrospinels are highly dense and have almost spherical structure with different grain size. The particle size calculated using scanning electron microscopy was found to be in the nanometer range. The compositional analysis of the obtained $Cd_{1-x}Cr_xFe_2O_4$ ferrospinels was carried out using EDX as shown in Fig. 3. The results of EDX confirm the formation

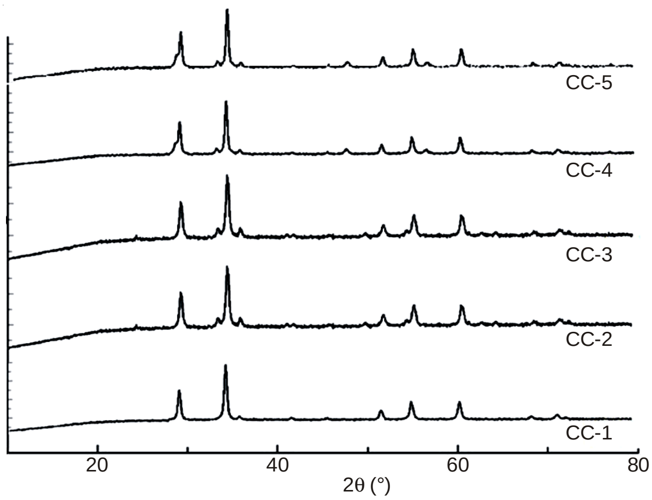


Fig. 1. X-ray diffractogram of $Cd_{1-x}Cr_xFe_2O_4$ ferrospinels

TABLE-1
COMPOSITIONAL PARAMETER 'x', ACIDITY, CATALYTIC ACTIVITY IN TERMS OF % INDOLE CONVERSION AND BET SURFACE AREA OF $Cd_{1-x}Cr_xFe_2O_4$ FERROSPINELS

X	$Cd_{1-x}Cr_xFe_2O_4$	Acidity (Total NH_3 uptake in mmol/g)	Catalytic activity (% Indole conversion)	BET surface area (m^2/g)
0.00	$CdFe_2O_4$	1.14	49.8	65.52
0.25	$Cd_{0.75}Cr_{0.25}Fe_2O_4$	1.31	53.1	61.09
0.50	$Cd_{0.5}Cr_{0.5}Fe_2O_4$	1.47	56.9	56.63
0.75	$Cd_{0.25}Cr_{0.75}Fe_2O_4$	1.65	62.4	49.84
1.00	$CrFe_2O_4$	1.73	70.3	43.26

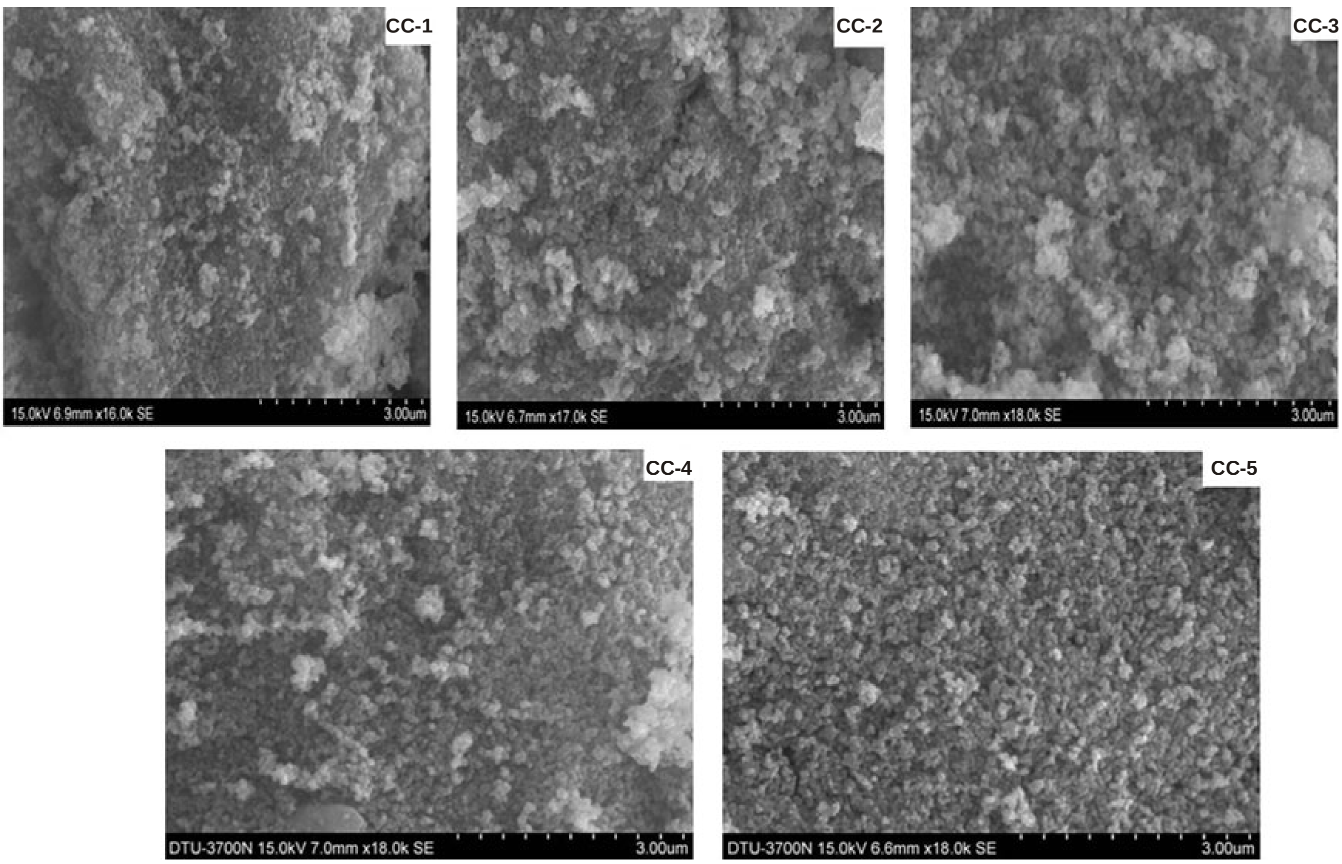


Fig. 2. SEM images of $Cd_{1-x}Cr_xFe_2O_4$ ferrospinels

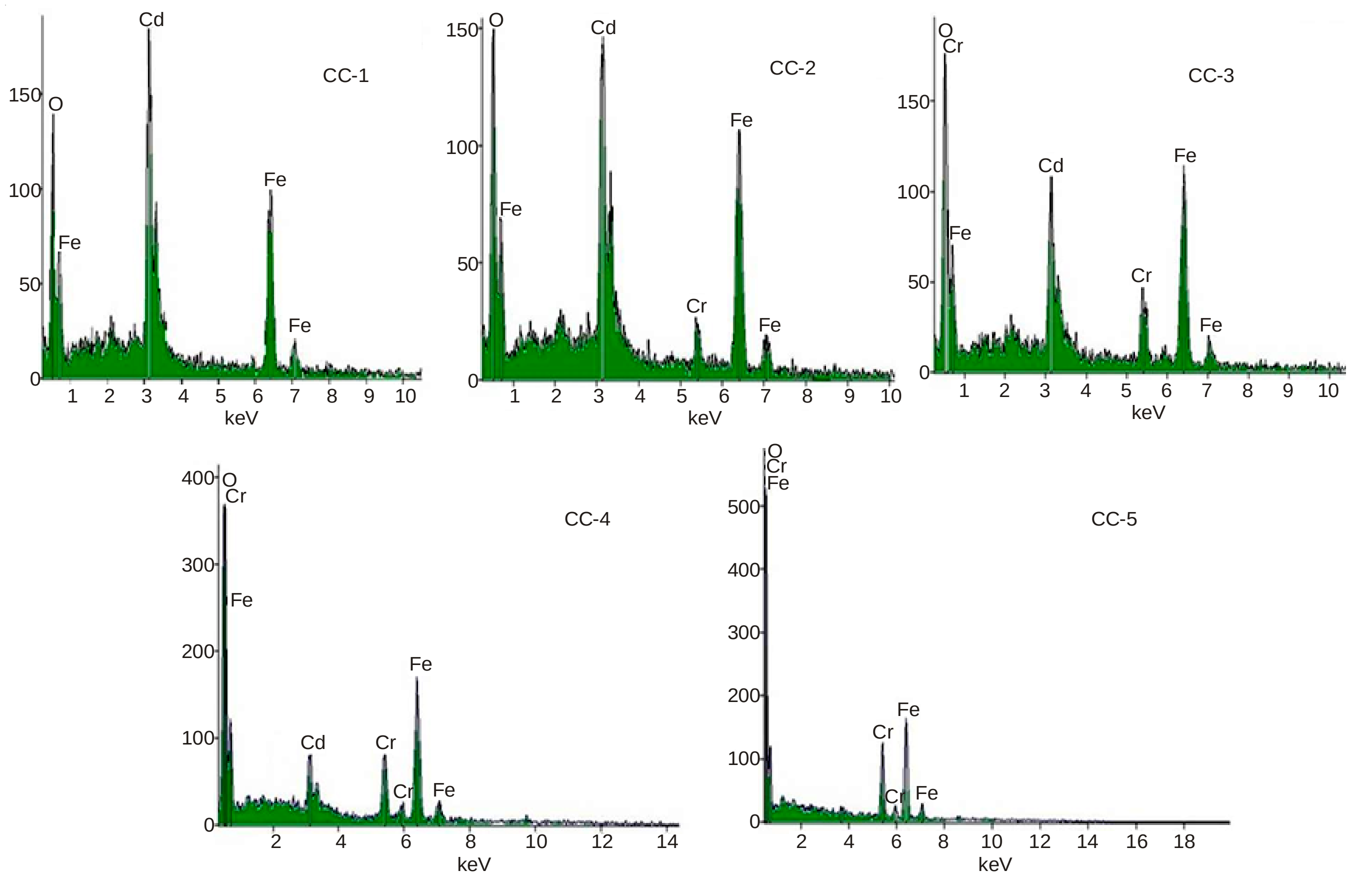


Fig. 3. EDX Spectra of $Cd_{1-x}Cr_xFe_2O_4$ ferrospinels

of ferrites with desired composition. Acidity values of all the $Cd_{1-x}Cr_xFe_2O_4$ ferrospinels were determined by temperature programmed ammonia-desorption method and the values are shown in Table-1.

RESULTS AND DISCUSSION

The present study involves the vapor phase alkylation of indole with methanol as the alkylating agent for the highly selective synthesis of 3-methyl indole. The surface area data, acidity values and performance of various catalysts in the alkylation of indole is presented in Table-1. It has been found that acidity of the system follows the order CC-5 > CC-4 > CC-3 > CC-2 > CC-1. The order of catalytic activity of ferrospinels toward overall conversion was found to be CC-5 > CC-4 > CC-3 > CC-2 > CC-1. An examination of Table-1 reveals that the acidity and surface area of $Cd_{1-x}Cr_xFe_2O_4$ ferrospinels increases with increasing 'x' values and the better performance of CC-5 as compared to CC-1 can be ascribed to its higher acidity.

Effect of catalyst composition: Catalytic activity as a function of composition of catalyst is shown in Table-2. Among the various composition of the system, the catalytic activity with reference to indole conversion increases with increase in 'x' value of $Cd_{1-x}Cr_xFe_2O_4$ ferrospinels. Systems possessing higher 'x' values were found to be more active and selective for 3-methyl indole formation since acidic sites favour 3-methyl indole formation.

Effect of reaction temperature: A series of indole alkylation reactions were performed in the temperature range of 548-673 K over CC-5 and the results are shown in Fig. 4. The maximum yield of 3-methyl indole was obtained at 598 K. Indole conversion and selectivity for 3-methyl indole formation increases with rise in temperature from 548 to 598 K and above 598 K, indole conversion increases but selectivity of 3-methyl indole decreased due to the generation of strong lewis acid sites at higher reaction temperature [12] and such sites enhance the formation of polyalkylated product, hence decreasing the selectivity of 3-methyl indole.

TABLE-2
PERFORMANCE OF VARIOUS CATALYSTS IN METHYLATION OF INDOLE AT 598 K, WHSV 0.5 h^{-1} AND INDOLE/METHANOL MOLAR RATIO OF 1:6

Catalyst	Indole conversion (%)	3-Methyl-indole yield (%)	3-Methyl-indole selectivity (%)	Others yield (%)
CC-1	49.8	34.45	69.18	15.35
CC-2	53.1	38.76	72.95	14.34
CC-3	56.9	45.84	80.57	11.06
CC-4	62.4	53.25	85.34	9.15
CC-5	70.3	64.29	91.46	6.01

Effect of molar ratio of indole to methanol: The effect of molar ratio of reactants on the vapor phase methylation of indole was carried out over CC-5 at temperature 598 K and 0.5 h^{-1} weight hour space velocity (WHSV) and the results are represented in Fig. 5. It has been found that the indole conversion and the selectivity of 3-methyl indole increases with increase in indole to methanol molar ratio and reaches a maximum at 1:6. At higher molar ratio selectivity of 3-methyl indole decreased due to unavailability of active sites.

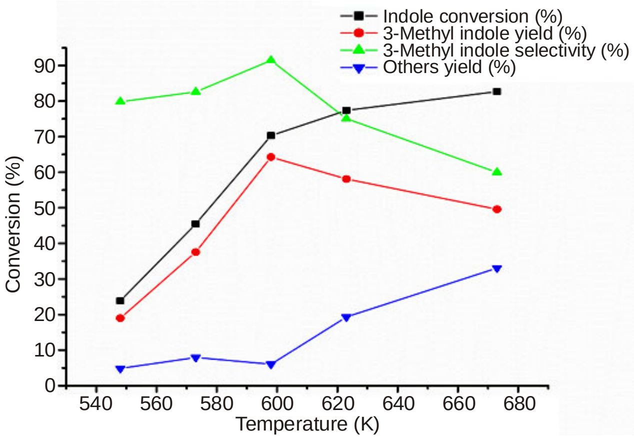


Fig. 4. Effect of reaction temperature on indole methylation (Catalyst: CC-5, WHSV: 0.5 h^{-1}, indole/methanol molar ratio 1: 6)

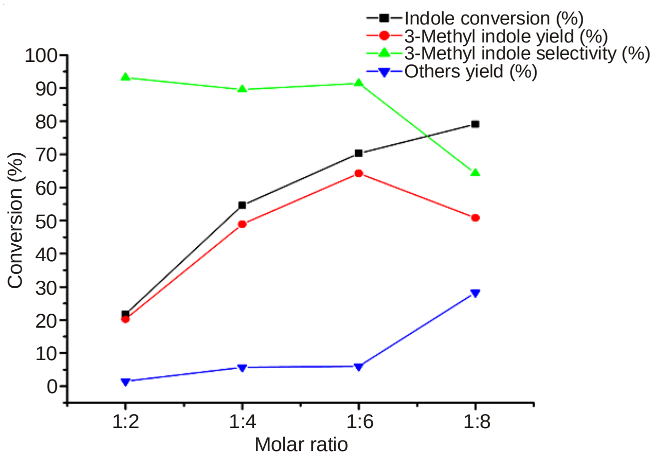


Fig. 5. Effect of molar ratio on indole methylation (catalyst: CC-5, WHSV: 0.5 h^{-1}, Temperature: 598 K)

Effect of weight hour space velocity (WHSV): The effect of WHSV on methylation of indole was studied over CC-5 at 598 K, indole to methanol molar ratio of 1:6 in the range of 0.1 to 0.7 h^{-1} WHSV and the results are shown in Fig. 6. Indole conversion increased with increase in WHSV and reaches a maximum at 0.5 h^{-1} and thereafter decreased. The high contact time causes charring over active sites, therefore decreasing the indole conversion below 0.5 h^{-1} and above 0.5 h^{-1} indole conversion further decreases due to reduced contact time.

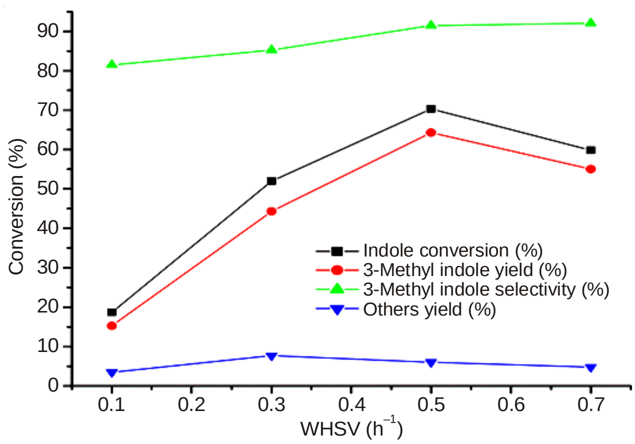
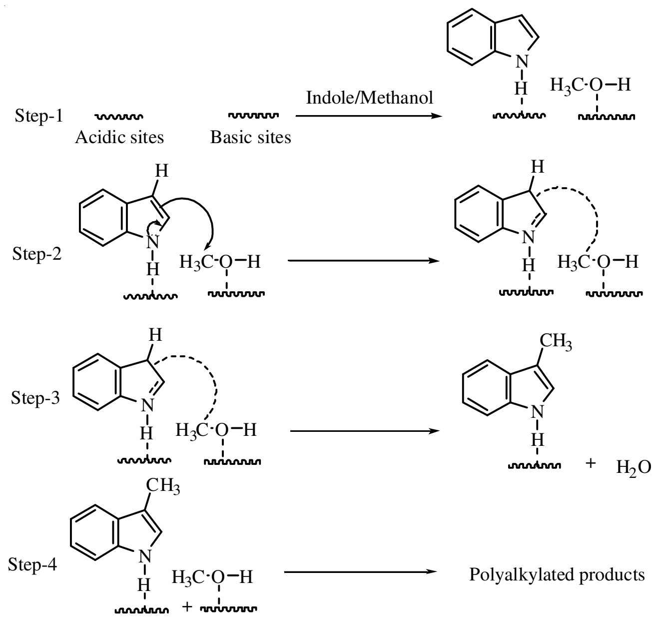


Fig. 6. Effect of WHSV on indole methylation (catalyst: CC-5,Temp: 598 K, molar ratio of 1:6)

Mechanism: Indole is a nucleophilic heterocycle and its excessive π-character makes indole more susceptible to electrophilic substitution reactions at 3-position of indole ring to form 3-methyl indole as the major product. The preferred site for electrophilic substitution is C-3 rather than C-2, since the cation formed by attack at C-3 is more stable as compared to C-2 because the positive charge can be delocalized without involving the benzenoid part of the molecule [13,14]. Further alkylation results in the formation of polyalkylated products as shown in **Scheme-I**.



Scheme-I

Conclusion

Nanocrystalline $Cd_{1-x}Cr_xFe_2O_4$ (x = 0, 0.25, 0.5, 0.75 and 1.0) ferrospinels prepared *via* low temperature coprecipitation method were studied for the alkylation of indole using methanol as the alkylating agent. It was found that these nanocrystalline ferrospinels can effectively alkylate indole to give a maximum yield of 64.29 % of 3-methyl indole with 91.46 % selectivity at 70.3 % indole conversion over $CrFe_2O_4$ (CC-5) at 598 K, WHSV 0.5 h^{-1} and indole/methanol molar ratio of 1:6. Indole conversion increases with progressive substitution of Cd by Cr ions due to increase in the acidity of the catalyst.

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