

Vapor Phase Methylation of *m*-Cresol over Ce-Impregnated $\text{Cd}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.25, 0.50, 0.75$ and 1.0) Ferrospinel

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Cd-Cr ferrospinel prepared by co-precipitation method were impregnated with cerium as promoter. Ce-impregnated ferrospinel were tested for the vapor phase alkylation of *m*-cresol with methanol. It has been observed that with increase in value of 'x' in Ce-impregnated $\text{Cd}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$ ferrospinel, the selectivity of 2,5-dimethyl phenol increases considerably. The reason for the improved catalytic selectivity may be due to the preferential adsorption, the strong synergistic effects among the different metal components and the relative changes in the redox nature of catalysts.

Keywords: Impregnated ferrospinel, Alkylation, *m*-Cresol.

INTRODUCTION

Alkylated phenol derivatives find numerous industrial applications for the synthesis of several intermediates [1,2]. 2,5-Dimethyl phenol (2,5-DMP) is used as an intermediate for the synthesis of antiseptics, antioxidants and dyes. 2,3,6-Trimethyl phenol (2,3,6-TMP) is used as a starting material for the synthesis of vitamin E. Starting from *m*-cresol and methanol as the alkylating agent, 2,5-dimethyl phenol can be selectively synthesized.

The increasing demands for catalyst materials with desired properties in the field of environmental legislation continues to prompt the researchers worldwide for developing better and environmentally safe catalysts. Ferrospinel possessing spinel structure acts as an efficient catalyst for the large number of industrially important alkylation reactions [3-6]. Supported metal particles also play a vital role in heterogeneous catalysis [7,8]. In order to further enhance the catalytic effectiveness, the catalysts have been modified by impregnated with suitable metal ion. Impregnation consists in contacting a solid catalyst with the solution containing the components to be deposited on the surface of the catalyst. Impregnated ferrospinel shows improved catalytic activity due to preferential absorption, strong synergistic effects and relative redox changes in the catalyst [9]. In the present investigation, an attempt has been made to synthesize and characterise Ce-impregnated $\text{Cd}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$ ferrospinel in order to study their catalytic role in the vapor phase alkylation of *m*-cresol with methanol.

EXPERIMENTAL

Synthesis of Ce-impregnated CrFe_2O_4 (Ce-CC-5): A series of $\text{Cd}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$ ferrospinel prepared by low temperature co-precipitation method were impregnated with 0.2 mol Ce by wet impregnation method. Co-precipitated CrFe_2O_4 (CC-5) ferrospinel were impregnated with aqueous solutions containing 0.2 mol cerium chloride heptahydrate in 50 mL of water. After standing at room temperature for 24 h, water was evaporated by heating the samples at 393 K for 24 h in oven. Subsequently the dried solids were calcined at 773 K for 16 h. Finally, the product was sieved through a sieve of 6/10 mesh size [10].

Similarly, Ce-impregnated CdFe_2O_4 (Ce-CC-1), Ce-impregnated $\text{Cd}_{0.75}\text{Cr}_{0.25}\text{Fe}_2\text{O}_4$ (Ce-CC-2), Ce-impregnated $\text{Cd}_{0.5}\text{Cr}_{0.5}\text{Fe}_2\text{O}_4$ (Ce-CC-3) and Ce-impregnated $\text{Cd}_{0.25}\text{Cr}_{0.75}\text{Fe}_2\text{O}_4$ (Ce-CC-4) were synthesized.

Catalyst characterization: The synthesized Ce-impregnated $\text{Cd}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$ ferrospinel were characterized by X-ray diffraction (XRD) technique primarily used for the phase determination of crystalline materials. The XRD diffractogram were recorded on a Rigaku X-ray diffractometer in the 2θ range of $10-80^\circ$ using $\text{CuK}\alpha$ radiations ($\lambda = 1.54 \text{ \AA}$) at a scan rate of $2^\circ/\text{min}$ as shown in Fig. 1. The peak intensities were found to be almost same as those of the parent sample thus revealing the crystalline nature of Ce-impregnated $\text{Cd}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$ ferrospinel.

Catalytic activity studies: The vapor phase methylation of *m*-cresol was carried out on 9 g of 6/10 mesh sized Ce-impregnated $\text{Cd}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$ ferrospinel placed between two

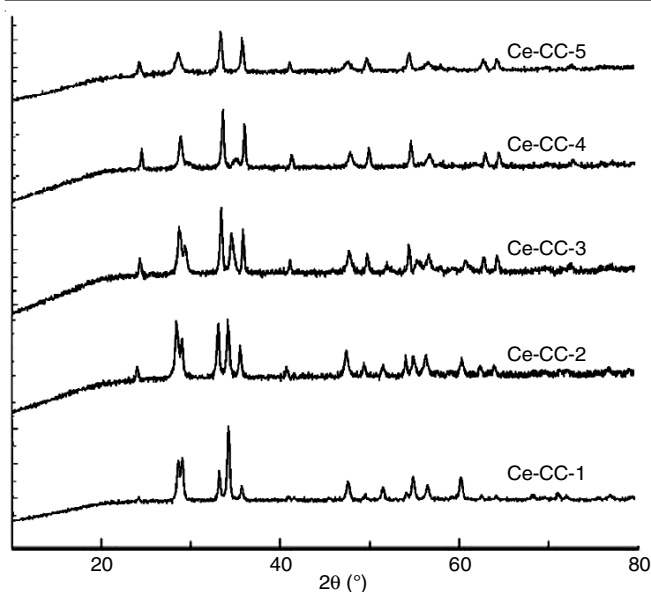


Fig. 1. X-ray diffractogram of Ce-impregnated $\text{Cd}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$ ferrospinel

plugs of glass wool in a continuous fixed bed down-flow reactor. The catalyst was activated at 773 K in a flow of dry air for 2 h and then brought down to the desired reaction temperature by cooling in a current of N_2 gas of 30 mL/min. The reactant mixture containing *m*-cresol and methanol was fed through a 10 mL pressure equalizing funnel into the reactor and the products were condensed with the help of an ice-cold trap at the bottom of the reactor. The phenolic products obtained were

finally analyzed by gas chromatography with flame ionization detector.

RESULTS AND DISCUSSION

The vapor phase alkylation of *m*-cresol with methanol as the alkylating agent has been carried out over Ce-impregnated $\text{Cd}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$ ferrospinel. A mixture of O- and C-alkylated products *i.e.* 3-methyl anisole (3 MA), 2,5- and 2,3-dimethyl phenols (DMP) and 2,3,6-trimethyl phenol (2,3,6-TMP) and various other alkylated phenols were obtained as represented in Fig. 2. Further, position 5 of the aromatic ring is favoured because in order to minimize the steric hindrance, methyl group of *m*-cresol will settle in opposite direction. As a result, the selectivity of 2,5-dimethyl phenol increases.

The effect of Ce-impregnated $\text{Cd}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$ ferrospinel on the vapor phase alkylation of *m*-cresol with methanol was studied at 598 K, weight hour space velocity (WHSV) of 0.4 h^{-1} and *m*-cresol to methanol molar ratio of 1:3 and the results obtained are reported in Table-1 and shown by Fig. 3. It can be seen that with increase in 'x' values in Ce impregnated ferrospinel, the *m*-cresol conversion decreases but the selectivity of the desired product 2,5-dimethyl phenol increases considerably. Over Ce-CC-5 catalyst, the maximum selectivity of 82.57 % of 2,5-dimethyl phenol with 63.23 % *m*-cresol conversion was obtained. This enhanced selectivity upon Ce impregnation may be attributed to preferential adsorption, strong synergistic effects between the different metal components and modified redox properties of $\text{Cd}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$ ferrospinel.

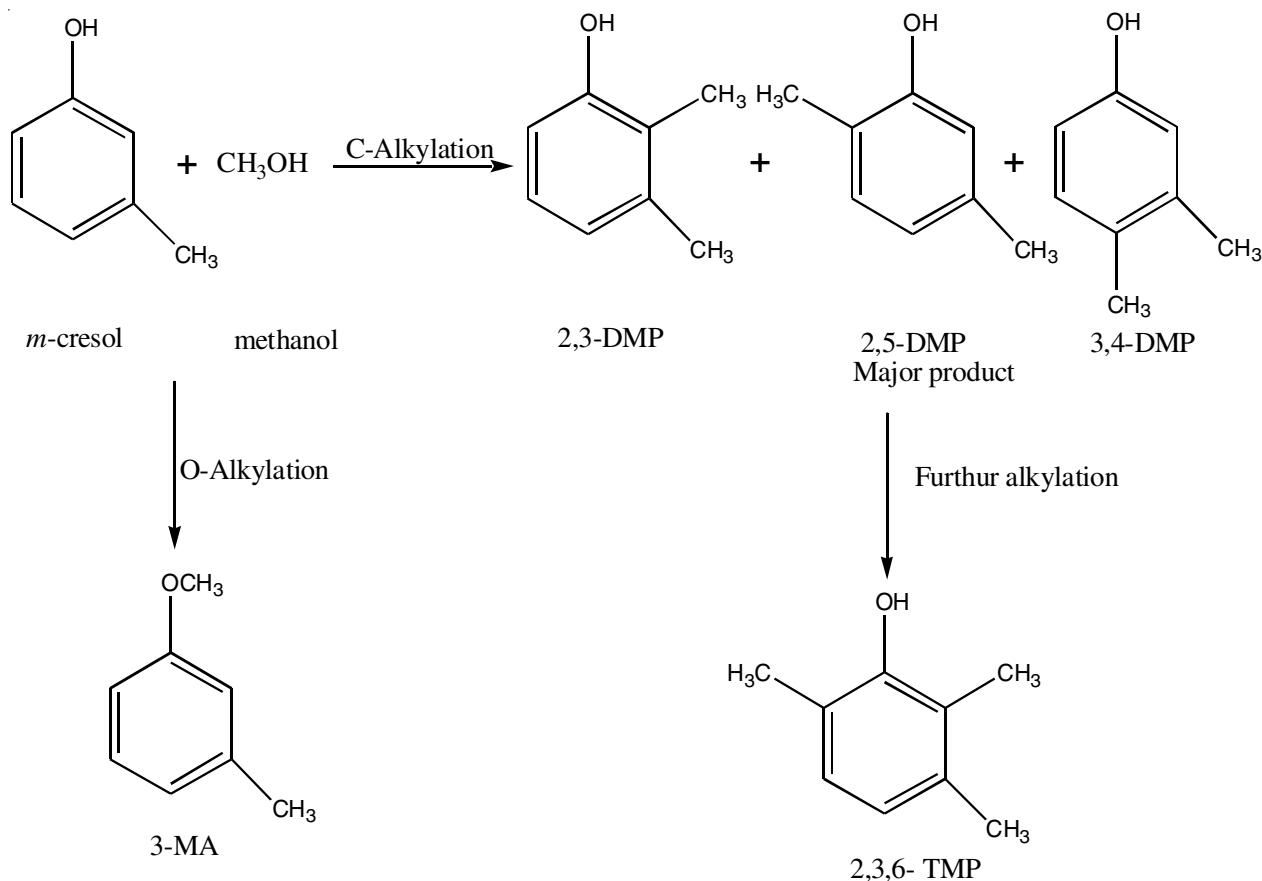


Fig. 2. Probable reaction for the methylation of *m*-cresol

TABLE-1
PERFORMANCE OF Ce-IMPREGNATED $\text{Cd}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$ FERROSPINELS IN THE ALKYLATION OF *m*-CRESOL WITH METHANOL AT 598 K, WHSV 0.4 h^{-1} AND *m*-CRESOL/METHANOL MOLAR RATIO OF 1:3

Catalyst	<i>m</i> -Cresol conversion (%)	2,5-DMP yield (%)	2,3,6-TMP yield (%)	2,5-DMP selectivity (%)	Others yield (%)
Ce-CC-1	72.34	51.67	17.50	71.43	3.170
Ce-CC-2	71.48	52.80	17.27	73.84	1.413
Ce-CC-3	65.97	50.86	12.51	77.08	2.602
Ce-CC-4	63.49	50.48	12.47	79.49	0.544
Ce-CC-5	63.23	52.21	10.31	82.57	0.707

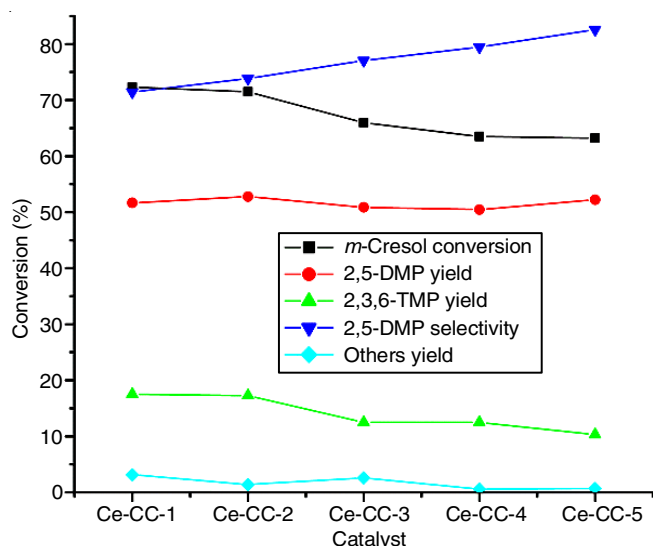


Fig. 3. Performance of Ce-impregnated $\text{Cd}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$ ferrites in the alkylation of *m*-cresol with methanol at 598 K, WHSV 0.4 h^{-1} and *m*-cresol/methanol molar ratio of 1:3

Conclusion

The effect of Ce-impregnated $\text{Cd}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$ ferrospinel prepared *via* wet impregnation method on the vapor phase catalytic alkylation of *m*-cresol with methanol has been examined. It has been observed that the *m*-cresol conversion decreases while the selectivity of 2,5-dimethyl phenol increases

significantly upon Ce impregnation. On a large scale application, selectivity of desired product is more important than activity. A maximum selectivity of 82.57 % of 2,5-dimethyl phenol with 63.23 % *m*-cresol conversion was obtained over Ce-CC-5 at 598 K, WHSV of 0.4 h^{-1} and *m*-cresol/methanol molar ratio of 1:3.

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