

## Research Article

## Alkylation of m-Cresol over Ferrospinels of Varying Cd/Cr Ionic Composition

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**Abstract**

The alkylation of m-cresol with methanol was carried out over Cd-Cr ferrites ( $x=0, 0.25, 0.5, 0.75$  and  $1.0$ ) in the temperature range  $548-623$  K in a fixed bed, down flow reactor. A mixture of O- and C- alkylated products i.e 3-methyl anisole, 2,3- and 2,5 -dimethylphenols and 2,3,6-trimethylphenol and various other alkylated phenols were obtained. 2,5-dimethylphenol (2,5-DMP) is found to be the major product. Maximum yield of 57.36 % of 2,5-DMP with selectivity of 70.13 % at 81.79 % conversion was obtained at 598 K, methanol to m-cresol molar ratio of 3 and  $0.4 \text{ h}^{-1}$  weight hour space velocity over  $\text{CrFe}_2\text{O}_4$ .

**Keywords:** Ferrospinels, Alkylation, m-cresol, Optimization, 2,5-dimethylphenol

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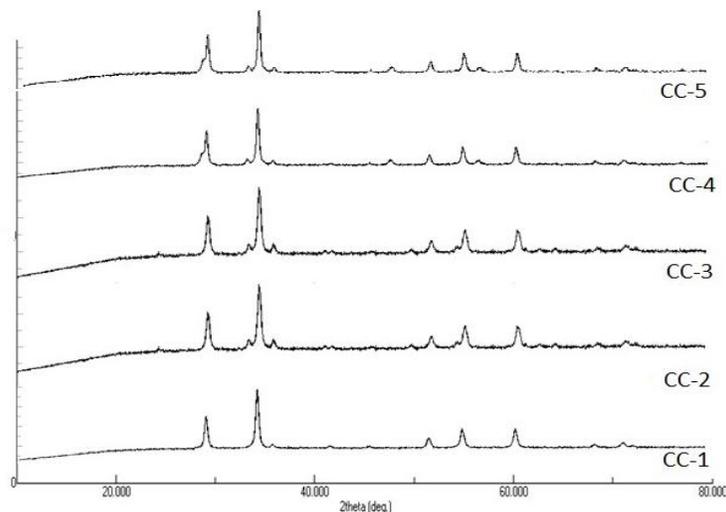
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**Introduction**

Alkylated phenol derivatives are industrially important compounds used for the synthesis of intermediates for the fine chemical, agrochemicals and polymer industries [1–3]. For example, 2,5-dimethylphenol (2,5-DMP) is used as an intermediate for antiseptics, dyes and antioxidants. 2,6-dimethylphenol (2,6-DMP) is used for the synthesis of polyphenylenoxide resin (PPO Resin) and 2,3,6-trimethylphenol (2,3,6-TMP) is used as an intermediate for antioxidants, plastics and also used as a precursor to synthetic vitamin E. The stringent specifications and high demand of these chemicals necessitate the development of better catalytic systems. As a result, global demand for mixed metal oxides possessing spinel structure have increased considerably in recent years in order to replace the conventional Friedel-Crafts type system due to the inherent drawbacks associated with them [4]. Ferrospinels are well known for their high thermal and mechanical stability [5], remarkable catalytic activity and are used extensively as magnetic materials owing to their high electrical resistivity [6–9]. They are represented by the general formula  $\text{AB}_2\text{O}_4$  where  $\text{A}^{2+}$  occupy the tetrahedral and  $\text{B}^{3+}$  ions occupy the octahedral sites [10, 11]. The catalytic effectiveness of these ferrospinels is due to the ability of the metal ion to migrate between the sublattices without altering the structure [12] and this makes the catalyst more efficient for various alkylation reactions [12–18]. Recently, a variety of catalysts including hydrotalcites and various mixed oxides have been tested for the selective synthesis of 2,5 DMP and 2,3,6-TMP [3, 19, 20]. In the current investigation attempt has been made for vapor phase alkylation of m-cresol with methanol over  $\text{Cd}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$  ferrospinels.

**Experimental****Catalyst Synthesis and Physico-chemical characterisation**

The five different compositions of Cd-Cr ferrospinels viz.  $\text{CdFe}_2\text{O}_4$  (CC-1),  $\text{Cd}_{0.75}\text{Cr}_{0.25}\text{Fe}_2\text{O}_4$  (CC-2),  $\text{Cd}_{0.5}\text{Cr}_{0.5}\text{Fe}_2\text{O}_4$  (CC-3),  $\text{Cd}_{0.25}\text{Cr}_{0.75}\text{Fe}_2\text{O}_4$  (CC-4) and  $\text{CrFe}_2\text{O}_4$  (CC-5) were synthesized by low temperature co-precipitation method [21]. Their physico-chemical properties were characterised by using Fourier Transform Infrared Spectroscopy (FTIR), X-Ray diffraction (XRD), Scanning electron microscope (SEM), Energy Dispersive X-ray spectroscopy (EDX), BET surface area and temperature programmed ammonia-desorption method ( $\text{NH}_3$ -TPD). The phase purity and crystallinity of the synthesized  $\text{Cd}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$  ferrospinels were first ensured by XRD (Rigaku X-ray diffractometer) in the  $2\theta$  range of  $10-80^\circ$  using  $\text{Cu K}\alpha$  radiations ( $\lambda=1.54\text{Å}$ ) at a scan speed of  $2^\circ/\text{min}$  as shown in **Figure 1**. Each crystalline material exhibits its unique X-ray diffraction pattern used for its identification. All the peaks in the X-ray diffraction analysis match well with the characteristic reflections of corresponding ferrites, thus revealing a single phase spinel structure. All the compositions of the  $\text{Cd}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$  ferrospinels showed two significant FTIR bands around  $700 \text{ cm}^{-1}$  and  $500 \text{ cm}^{-1}$  due to intrinsic vibrations of the tetrahedral M-O group and the octahedral M-O group respectively [22–24].

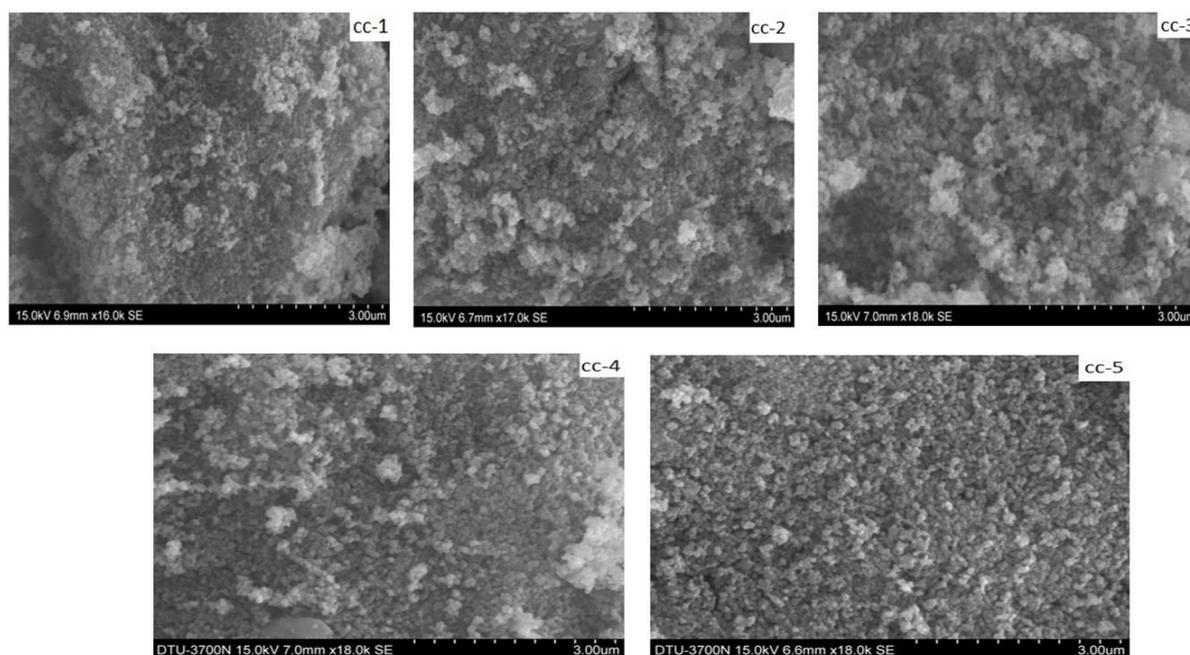


**Figure 1** X-Ray diffractogram of  $\text{Cd}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$  ferrispinels

The BET surface area of the synthesised  $\text{Cd}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$  ferrispinels was determined with the help of OMNISORP 100 CX instrument and the results are shown in **Table 1**. The size and the surface morphology of the synthesised  $\text{Cd}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$  ferrispinels were analysed by scanning electron microscopy (SEM model HITACHI S-3700 N). The SEM pictures of these catalysts are shown in **Figure 2**. From the SEM pictures, it is clear that all the catalysts have almost spherical structure with different grain size. The particle size calculated using scanning electron microscopy was found to be within the nanometer range. The compositional analysis of the synthesised  $\text{Cd}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$  ferrispinels was carried out using EDX [25] and the results of EDX ensure the formation of ferrites with desired composition.

**Table 1** Compositional parameter 'x', Acidity, Catalytic activity in terms of % m-cresol conversion and BET Surface area of  $\text{Cd}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$  ferrispinels

X	$\text{Cd}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$	Acidity (Total $\text{NH}_3$ uptake in m mol/g)	Catalytic activity (%m-cresol conversion)	BET Surface area ( $\text{m}^2/\text{g}$ )
0.00	$\text{CdFe}_2\text{O}_4$	1.14	53.43	65.52
0.25	$\text{Cd}_{0.75}\text{Cr}_{0.25}\text{Fe}_2\text{O}_4$	1.31	69.26	61.09
0.50	$\text{Cd}_{0.5}\text{Cr}_{0.5}\text{Fe}_2\text{O}_4$	1.47	74.50	56.63
0.75	$\text{Cd}_{0.25}\text{Cr}_{0.75}\text{Fe}_2\text{O}_4$	1.65	78.44	49.84
1.00	$\text{CrFe}_2\text{O}_4$	1.73	81.79	43.26



**Figure 2** SEM images of  $\text{Cd}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$  ferrispinels

### Evaluation of surface acidity

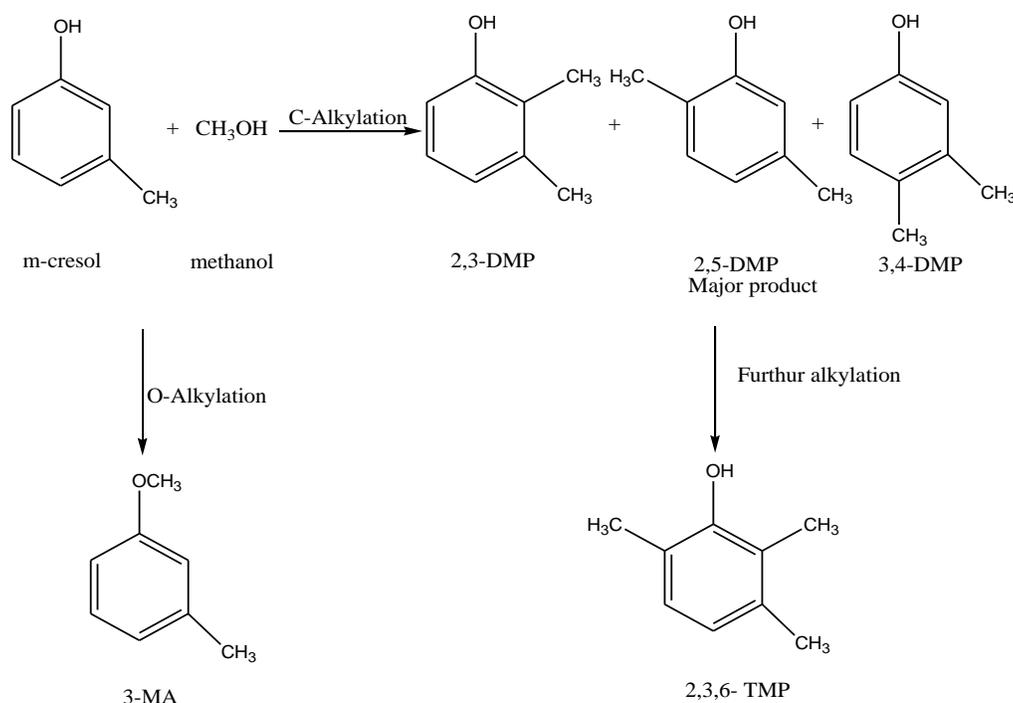
Acidity of all the synthesised  $\text{Cd}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$  ferrospinels were determined by temperature programmed ammonia-desorption method ( $\text{NH}_3$ -TPD). Exactly 3.0 g of the catalyst was introduced in a pyrex tube that was pre-heated to 673 K for 2 h under  $\text{N}_2$  flow. The reactor was then cooled to 298 K and adsorption is conducted at this temperature by exposing the sample to  $\text{NH}_3$  at flow rate of 30 mL/min for 2 h. The physically adsorbable  $\text{NH}_3$  was removed by exposing the sample with  $\text{N}_2$  at a flow rate of 30 mL/min at 323 K for 1h. The acidity was determined by increasing the temperature from 323 K to 773 K and absorbing  $\text{NH}_3$  evolved in double distilled water. Quantitative estimation was done by titrating the ensuing solution with a standard 0.01 M HCl, as depicted in Table 1.  $\text{NH}_3$ -TPD experiment reveals that acidity of the synthesised  $\text{Cd}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$  ferrospinels increases with progressive substitution of Cd ions by Cr ions.

### Catalytic activity studies

The vapor phase alkylation of m-cresol with methanol was carried out on 9 g of 6/10 mesh size catalyst placed between two plugs of glass wool in a continuous fixed bed down-flow glass reactor. Before carrying out the reaction, the catalyst was activated in a flow of dry air at 773 K for 2 h and then cooled to the desired reaction temperature in presence of  $\text{N}_2$  gas of 30 mL/min. The reactant mixture containing m-cresol and methanol was fed from the top using pressure equalizing funnel with a flow rate of  $\text{N}_2$  gas of 30 mL/min and the products were condensed with an ice-cold trap at the bottom of the reactor. The phenolic products were analysed by gas chromatography with flame ionization detector.

### Results and Discussion

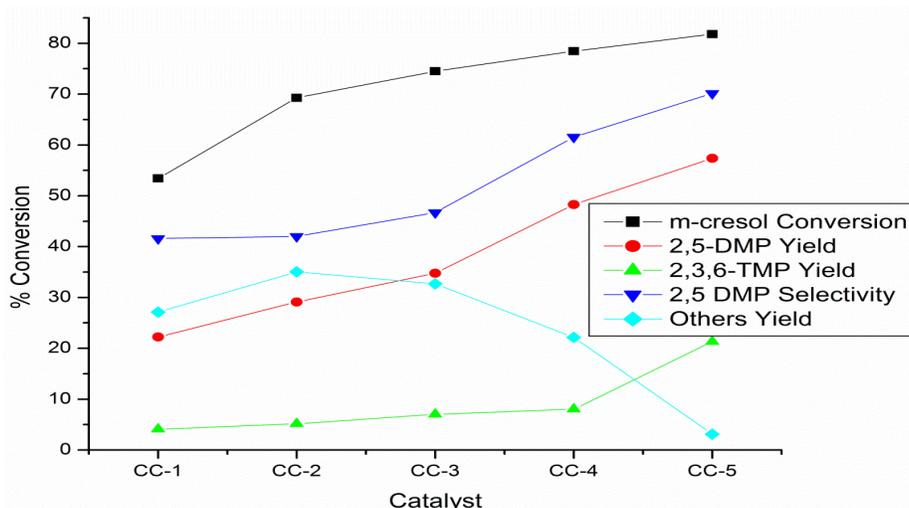
The vapor phase alkylation of m-cresol with methanol was carried out over  $\text{Cd}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$  ferrospinels. A mixture of O- and C-alkylated products i.e 3-methyl anisole (3 MA), 2,3- and 2,5 -dimethylphenols (DMP) and 2,3,6-trimethylphenol(2,3,6-TMP) and other alkylated phenols were obtained as shown in **scheme 1**. Moreover, position 5 of the aromatic ring is favoured because, to reduce the steric hinderance, methyl group of m-cresol will settle in opposite direction. As a consequence, the selectivity of 2,5-DMP increases. The m-cresol conversion and the products selectivity depends on m-cresol/methanol molar ratio, temperature, WHSV and the composition of the synthesised  $\text{Cd}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$  ferrospinels. The surface area data, acidity values and performance of various catalysts in the methylation of m-cresol is presented in Table 1. It has been found that acidity of the catalyst follows the order CC-5> CC-4> CC-3> CC-2> CC-1. The order of catalytic activity of ferrospinels towards overall conversion was found to be CC-5> CC-4> CC-3> CC-2> CC-1.



**Scheme 1** Probable reaction for the methylation of m-cresol

### Effect of Catalyst Composition

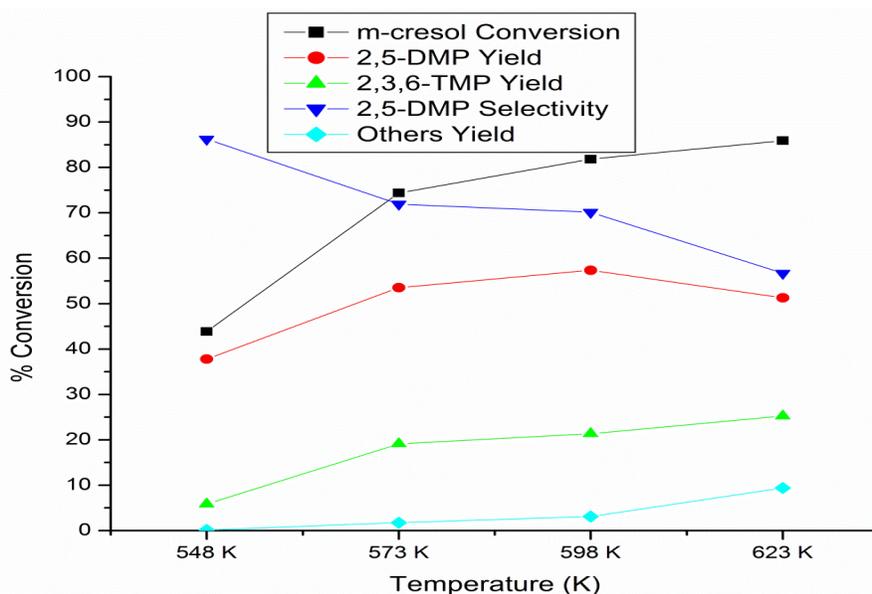
The effect of catalyst composition on the m-cresol conversion and the product selectivity is shown in **Figure 3**. It can be seen that at higher 'x' values, the selectivity of 2,5-DMP was more whereas at lower 'x' values, other alkylated products have also been obtained in addition to 2,5-DMP. The catalytic activity follows the order CC-5 > CC-4 > CC-3 > CC-2 > CC-1. Since the acidity values also follow the same order, the gradation in catalytic activity can be explained by considering the acidity variation with Cr substitution in the  $\text{CdFe}_2\text{O}_4$  matrix. Basic catalysts have been found to be less active than the acid ones and they prefer o-alkylation resulting in higher yield of other alkylated products instead of 2,5-DMP.



**Figure 3** Performance of various catalysts in the alkylation of m-cresol with methanol at Temperature 598 K, WHSV  $0.4 \text{ h}^{-1}$  and m-cresol/methanol molar ratio of 1:3

### Effect of Reaction Temperature

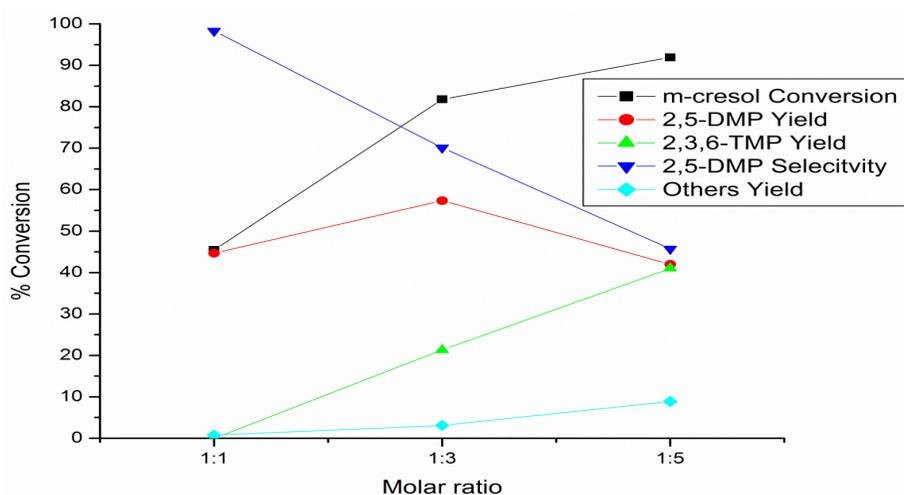
The vapor phase alkylation of m-cresol with methanol was performed in the temperature range of 548–623K over CC-5 as reported in **Figure 4**. It is found that temperature has marked influence on overall m-cresol conversion and selectivity of 2,5-dimethylphenol. With increase in temperature, m-cresol conversion will increase considerably however the selectivity of 2,5-dimethylphenol decreases because high temperature predominantly favors the consecutive methylation to 2,3,6-trimethylphenol and other alkylated products.



**Figure 4** Effect of reaction temperature on alkylation of m-cresol over Catalyst CC-5, WHSV  $0.4 \text{ h}^{-1}$  and m-cresol / methanol molar ratio of 1: 3

### Effect of Molar ratio

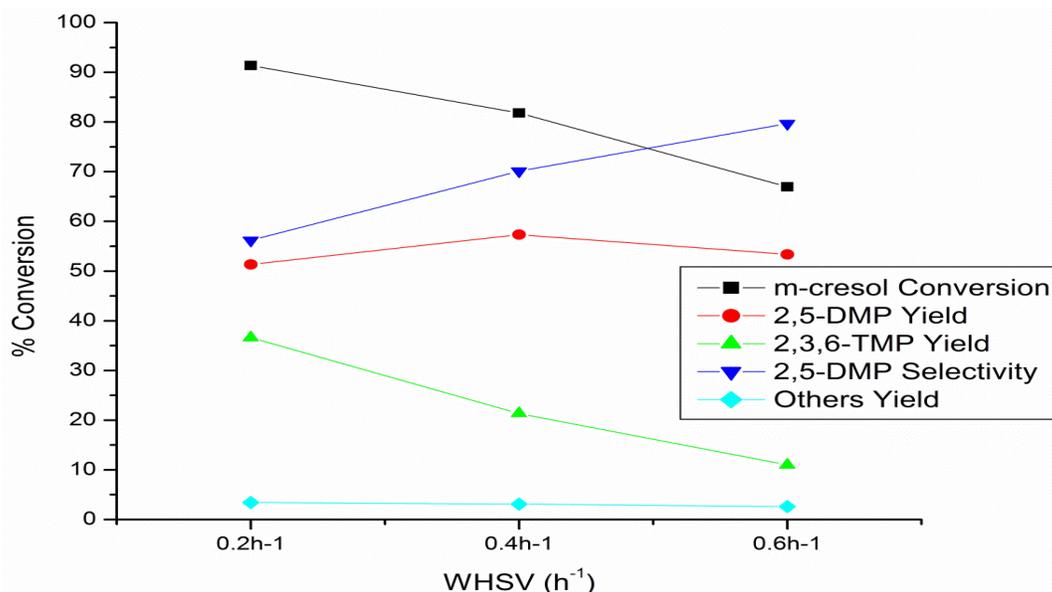
Alkylation of m-cresol with methanol was carried out at 598 K over CC-5 catalyst with varying m-cresol to methanol molar ratio (1:1, 1:3 and 1:5) at WHSV of  $0.4 \text{ h}^{-1}$  in order to study the effect of molar feed ratio on m-cresol conversion and products selectivity. The m-cresol conversion and the products distribution at various molar feed ratios is shown by **Figure 5**. It is observed that the m-cresol conversion is found to increase with increasing m-cresol content in the feed. With increase in molar feed ratio from 1:1 to 1:5, m-cresol conversion increases from 45.44% to 91.94% over CC-5, however the selectivity of 2,5-dimethylphenol decreases from 98.33% to 45.70% because higher molar feed ratio leads to polyalkylation and other alkylated products. Considering the m-cresol conversion and the selectivity of the 2,5-dimethylphenol, the optimum m-cresol to methanol ratio of 1:3 was followed for further studies.



**Figure 5** Effect of molar ratio on alkylation of m-cresol with methanol over Catalyst CC-5, WHSV  $0.4 \text{ h}^{-1}$  and Temperature 598 K

### Effect of WHSV

The effect of WHSV ( $0.2 \text{ h}^{-1}$ ,  $0.4 \text{ h}^{-1}$ ,  $0.6 \text{ h}^{-1}$ ) on the m-cresol conversion and the products distribution was studied at 598 K over CC-5 with molar feed ratio of 1:3 and the results obtained are shown in **Figure 6**. It is observed that m-cresol conversion decrease while the selectivity of 2,5-DMP increases with increase in WHSV. The low m-cresol conversion at higher weight hour space velocity (WHSV) can be accounted for in terms of the shorter contact time at higher WHSV of m-cresol.



**Figure 6** Effect of WHSV on alkylation of m-cresol with methanol over Catalyst CC-5, temperature 598 K and m-cresol/methanol molar ratio of 1: 3

## Conclusion

In summary, CrFe<sub>2</sub>O<sub>4</sub> (CC-5) catalyst exhibits better performance for the vapor phase catalytic alkylation of m-cresol with methanol. The Cd/Cr ratio can considerably influence the surface area and acidity values of the Cd<sub>1-x</sub>Cr<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> ferros spinels, thus varying the catalytic activity and selectivity for the m-cresol alkylation reaction. Under the optimized conditions, a maximum yield of 57.36 % of 2,5-DMP with 70.13 % selectivity at 81.79 % m-cresol conversion was obtained at 598 K temperature, 0.4 h<sup>-1</sup>WHSV, 1:3 m-cresol to methanol molar ratio over CrFe<sub>2</sub>O<sub>4</sub>.

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