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Selective C-methylation of phenol to o-cresol and 2, 6-xyleneol in high yields have been carried out with methanol over mesoporous ceria modified by transition metals. The maximum conversion of 68% with 98% selectivity for corresponding ortho-alkylated products (o-cresol and 2, 6-xyleneol) was obtained with 2% anisole as O-alkylated product. A series of catalysts with 2–10weight% metal loading were prepared and calcined at 350°C. The XRD results reveal the formation of single phase cubic fluorite structure after addition of metals. Metals and their compositions were found to influence the conversion and selectivity. The influence of various experimental parameters on phenol conversion and product selectivity has been investigated. The catalyst was active without any deactivation showing its longer life. The catalytic activity and selectivity is correlated with its acidity and structure.

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## **7.1 Introduction**

There is currently a significant world-wide interest in the use of solid acid and base catalysts to promote various organic reactions of industrial importance, since such systems often give value-added products with improved selectivity without creating major burdens to the environment. Alkylation of aromatic substrates catalysed by solid acids such as zeolites and metal oxides constitutes a class of reactions important both academically and industrially. Among alkylation reactions, methylation of phenol has attracted considerable attention due to industrial importance of methyl phenols as chemical intermediates in the manufacture of pharmaceuticals, agrochemicals, resins, various additives, polymerization inhibitors, antioxidants and various other chemicals [1]. In particular, ortho-alkylated phenols such as o-cresol, 2, 6-xyleneol and trialkyl substituted phenols are more important alkyl phenols. For example, epoxy cresol novolac (ECN) and polyphenylene oxide (PPO) used in the electronic industries and automobile industries are derived from o-cresol and 2, 6-xyleneol, respectively [2]. After suitable processing, o-cresol is used in the synthesis of herbicides as well as in sealing material for integrated circuits, whereas 2, 6-xyleneol is used in manufacture of disinfectant and in high impact resistant resins [3]. Trimethyl phenols are precursors for the synthesis of Vitamin-E. Anisole and methyl aryl ethers (MAE) are considered as octane number booster for gasoline. It was found that a mixture of MAE can effectively substitute for the non-metallic additives such as methyl tertiary butyl ether (MTBE) [4]. C-alkylated phenols, in particular, tert-butyl-, iso-octyl-, and iso-decyl- phenols, are widely used in the chemical industry as drilling oil additives, antioxidants, and polymer stabilizers. The isomeric O-alkylated phenols also have

numerous industrial applications, particularly in the production of dyes and agrochemicals. The selective synthesis of alkyl phenols especially o-cresol and 2, 6-xyleneol is receiving increasing interest in recent years because of their importance as intermediates for the synthesis of a variety of resins, herbicides, insecticides and other chemicals[ 5]. o-Cresol is used in the manufacture of insecticides and herbicides and 2, 6-xyleneol is a precursor for poly 2, 6 dimethyl phenoxide, a thermo resistant polymer used in special grade paints.

The catalytic alkylation of aromatic hydrocarbons is of significant fundamental and practical importance and has been intensively investigated in recent years. Although current homogeneous catalysts are efficient, their corrosive and toxic nature provide potential environmental hazards and their operational problems, including difficulty in separation, recovery, and reutilization result in higher capital costs. Friedel–Crafts catalysts such as  $\text{AlCl}_3$ ,  $\text{BF}_3$ ,  $\text{TiCl}_4$ , liquid HF, various types of zeolites,  $\gamma$ -alumina, silica-alumina, Nafion-H, phosphoric acid, ALPO, SAPO, metal phosphates, acidic and basic oxides; etc. producing a mixture of C- and O- alkylated products have been used for the alkylation of phenol [6]. Selective alkylation of phenol on the aromatic carbon atoms has not been very successful [7]. Furthermore, several problems are associated with these catalysts such as low selectivity, separation of the catalyst from reactants and products, and disposal of effluents. Alkylation of phenols is generally carried out using a liquid acid catalyst, giving wide product distribution. Typical strong acid catalysts promote a range of undesirable side reactions. A review covering the various aspects of the shape-selective catalysts in alkylation were published recently [8].

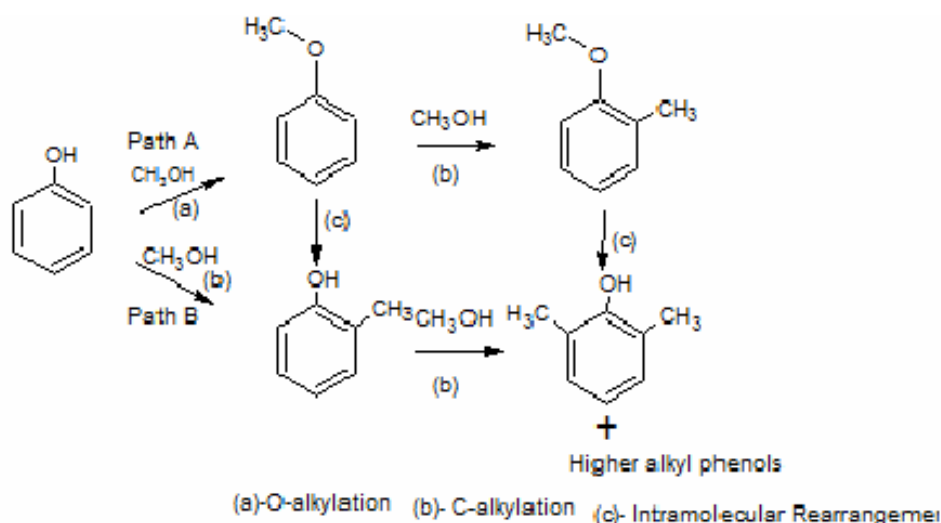
The formation of alkylated phenols is a major area of chemistry and clean processes are required. Alkyl phenols are valuable industrial chemicals. Both C- and O-alkylation of phenol is possible depending on reaction conditions such as temperature, source of reagent, and type of catalyst. The combination of some weakly acidic centres, along with basic sites, can lead to very good selectivity and a clean process. The use of highly corrosive and polluting liquid acids are major environmental problems and, therefore, heterogeneous solid acids like anion exchange resins, NaX and Y zeolites, hetero polyacids, acid-treated clays, and titania-supported  $\text{AlPO}_4$  have replaced them.

Anisole is used as an additive in gasoline to boost octane number. The conversion of anisole to 2, 6- xylenol is an important target, and heterogeneous catalysts may provide the answer. The synthesis of 2, 6-xylenol by the alkylation of phenol with methanol has been attempted over different metal oxide catalysts [9, 10, 11, 12]. Alkylation of phenol, in general, leads to thermodynamically favourable m-isomer rather than the o- and/or p-isomers. However, the presence of a phenolic group in the reactant under consideration kinetically favours the latter. Although the o-isomer is kinetically more favourable than the p-isomer, the former isomerizes easily into stable p-isomer owing to steric hindrance at the ortho position.

The increasing demand for new and selective catalysts with larger molecular dimensions led to the discovery of mesoporous catalytic materials. Unlike in the case of microporous and macroporous solids, catalysts with a mesoporous structure can achieve an optimum compromise of high site density and good transport characteristics. Acidic and redox functionalities were generated in these materials by the incorporation of transition metals or by the encapsulation of well-defined homogeneous

complexes inside the pores. Also, they opened up many new strategies for shape-selective, enantioselective, and regioselective conversions [8]. Further, the selectivity of the products depends mainly on the nature of the acidic sites present on the catalyst as well as the reaction temperature. Bautista and co-workers found that dealkylation to phenol is predominant over  $\text{AlPO}_4\text{-Al}_2\text{O}_3$  catalysts in the alkylation of anisole with methanol [13]. Apart from the acid–base properties of the catalysts, the product selectivity is often influenced by the operating conditions and the nature of alkylating agent.

The process using solid catalysts and fixed bed reactors offer many advantages such as catalyst reusability, ease of product work up and continuity of operation. The vapour phase methylation of phenol with methanol using metal oxide or zeolite as catalysts has been done extensively. The products are usually mixtures of anisole (the product of O-methylation) and the products of ring methylation (cresols and xylenol), the selectivity being strongly depended on the catalyst. There can be two important pathways for the formation of 2, 6-xylenol and o-cresol. In the first pathway anisole formed first, react with methanol to form 2, 6-xylenol. In the second pathway direct C-alkylation takes place forming o-cresol which reacts further with another molecule of methanol to give 2, 6-xylenol. It is known that anisole can undergo intramolecular rearrangement reaction to o-cresol or intermolecular rearrangement between two molecules to methyl anisole and phenol [14].



**Fig.7.1 Pathways for the formation of 2, 6-xyleneol and o-cresol**

Oxide catalysts are found to be more selective for the synthesis of 2, 6-xyleneol and o-cresol [12]. Reports on the selective O-methylation, however, have been very limited. Pierantozzi and Nordquist obtained 94% selectivity for anisole at a 12% yield over  $\text{La}_2(\text{HPO}_4)_3$  at 573K. Renaud et al. obtained 80% selectivity with an anisole yield in the range of 20-30%. It is generally accepted that the acid-base properties of the catalysts employed have a significant influence on the product distribution. Alkylation of phenol with methanol is catalysed by both Brønsted and Lewis acid sites as well as by basic sites. Phenol is adsorbed both on acidic and basic sites. For example, O-alkylation can easily occur on basic sites, while C-alkylation requires the presence of weak or stronger acid sites [15]. The formation of polyalkylated products requires more severe reaction conditions, i.e., higher reaction temperatures, longer contact times, an excess of methanol in the feed, and/or a sufficiently high acid strength of the catalyst. To prove that the secondary products stem to a large extent from anisole, Marczewski et al. [16] studied the reactions of anisole and of

a mixture of anisole and methanol on H-USY (ultra stable zeolite Y). They proposed that the direct isomerization of anisole to cresols does not occur and that the alkylation of phenol by anisole leads to cresols and methyl anisoles as primary products. Anisole has been suggested to be an intermediate in the formation of cresols during phenol methylation [17]. Studying the methylation of phenol with methanol on zeolite H-Beta by conventional GC analysis, Xu et al. [18] came to the conclusion that anisole is an unstable primary product and an important reaction intermediate. The formation of the predominant product o-cresol was enhanced by lower temperature, less amount of alkylating agent in the feed and lower acidity of the catalyst. It is proposed that at lower temperature and lower residence time anisole is formed which undergoes rearrangement and further alkylation at higher temperature and high residence time to give o-cresol and 2, 6-xyleneol at the expense of anisole. Methylating agents such as methyl carbonates favours O-alkylation and almost quantitative yields of anisole has been reported with dimethyl carbonate [19, 20]. Hence it can be concluded that basicity or very low acidity favours O-alkylation at lower temperature whereas moderate or high acidity favours C-alkylation.

The selective C-alkylation of phenol with methanol over basic MgO has also been explained on the basis of vertical orientation of phenoxide aromatic ring on the catalyst surface and O-alkylation due to its parallel orientation on acid catalyst surface [21]. Preferential C-alkylation can be attributed to large number of weak and medium acid sites whereas preferential ortho-alkylation is due to perpendicular orientation of phenol aromatic ring on catalyst surface. Selectivity in phenol alkylation (O- or C-alkylation) is reported to depend on the acid–base properties of the catalyst [22]. While basic catalyst favours C-alkylation, acidic catalyst does not

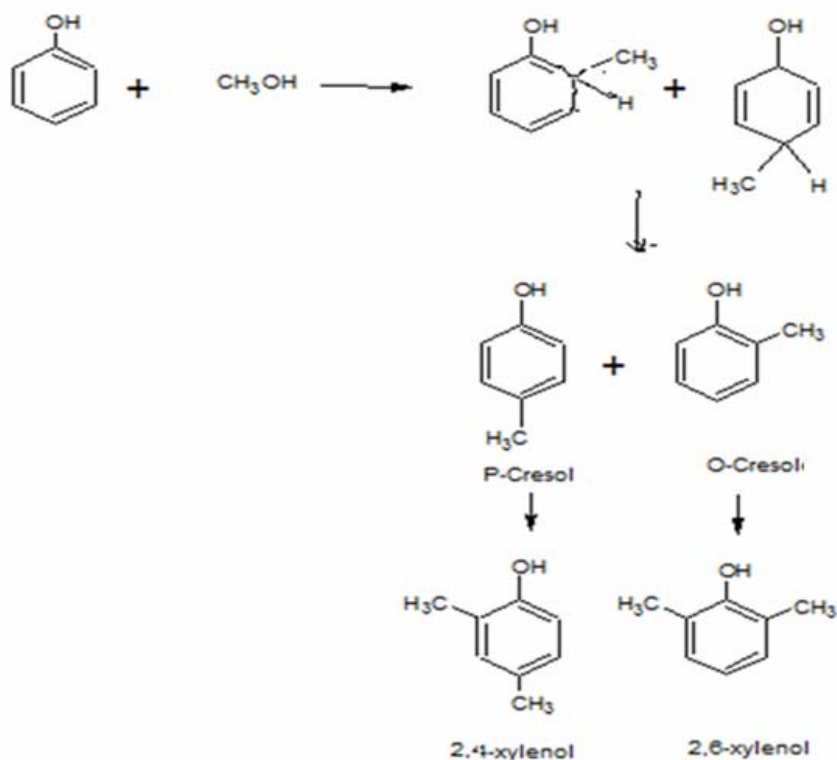
favour this reaction (it gives O-alkylation) due to the orientation of phenol aromatic ring with respect to the catalyst surface as shown in Fig.7.1 a & b [23]. After adsorption on the catalyst surface, phenol dissociates into phenoxide ion and proton. In case of basic catalyst the aromatic ring is shown to be perpendicular to the catalyst surface facilitating ortho-alkylation. However in case of acidic catalyst the aromatic ring is parallel to the catalyst surface and the electrons of the ring interact with the catalyst surface. It can be said that aromatic ring is perpendicular to the catalyst surface minimizing the interaction of  $\pi$  electrons with the surface. This orientation facilitates the attack of adsorbed alkyl moiety at ortho position giving high yields of o-cresol and 2, 6-xylenol. In general, cresols can be formed both by direct C-alkylation of phenol with methanol and by conversion of the anisole formed by O-methylation of phenol [24]. Over the more acidic catalysts, phenol molecule may adsorb by interaction of its electron cloud, while on a more basic catalyst, it may adsorb by the  $-OH$  group [25].

Satoshi Sato et al. studied the vapour phase alkylation of phenol-methanol over  $CeO_2$ -MgO at temperature range between 450 -550°C and got excellent selectivity to the sum of o-cresole and 2, 6 -xylenol more than 98% [26]. Pure  $CeO_2$  also showed excellent ortho cresol selectivity. The selectivity generally determined by Brønsted acidity of the molecular sieves, are also affected by other factors such as pore size and geometry. In the case of the AlPO-5 having initially high alkylation activity, a different mechanism is likely operative [27]. During alkylation of phenol with methanol using AlPO-5 exclusively C-alkylated (alkylation proceeds through ring) products were formed [28]. K.V.R. Chary et al. reported the alkylation of phenol with methanol over a series of pure zirconia and



vanadium oxide catalyst supported on zirconia to produce selectively valuable o-cresol and 2, 6-xyleneol (C-alkylated products).

The earlier reports indicate lot of discrepancies in correlation of acidic and basic nature of catalyst and its influence on C or O-alkylation of phenol. The presence of substantial amounts of anisole in the products with cresols to anisole ratio of 2 indicates that in the mechanism, both the schemes - scheme C and scheme D- are operating simultaneously with scheme C being the predominant one.



**Fig.7.2 Reaction scheme C -for methylation of phenol with methanol**

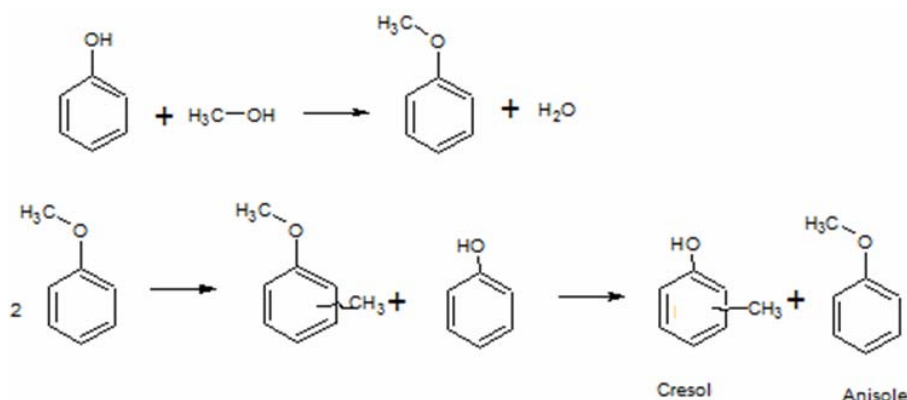
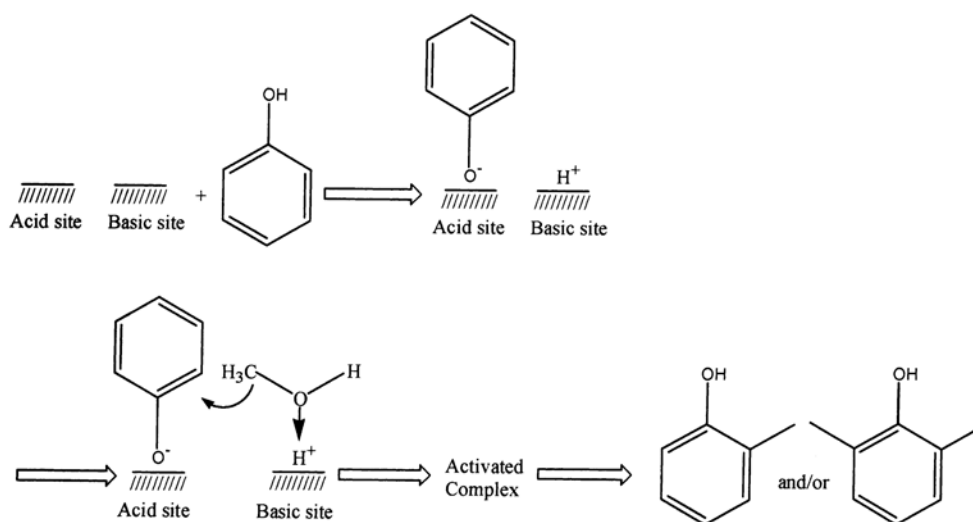


Fig.7.3 Reaction scheme O- methylation of phenol with methanol

## 7.2 Reaction Pathway

Phenol can adsorb on the surface perpendicularly as well as parallel. While perpendicular adsorption is expected to give ortho products, parallel adsorption will facilitate formation of para or oxygen substituted products. In the present study, major products were ortho substituted products. The formation of ortho substituted products rules out the parallel adsorption of phenol on catalyst surface. The ortho selectivity of the catalysts (formation of o-cresol, 2, 6-xyleneol) can be attributed to perpendicular adsorption of phenol over catalyst surface. The shifting of electron cloud of the M-O bond towards oxygen makes it more basic and proton attracting. The phenol molecule is vertically absorbed on the surface with oxygen attached to  $\text{M}^{\text{n}+}$  (Lewis acid site) as a phenoxide ion and hydrogen to the oxide ion (Lewis base site). Methanol absorbed on the Lewis base site through proton, abstracts the phenol proton, gets protonated and is converted to carbonium ion by releasing water molecule. An electrophilic attack by carbonium ion on the ortho position of phenoxide ion leads to formation of o-cresol and completing the catalytic cycle. Almost constant conversion to o-cresol and

increased conversion to 2, 6-xylenol with increasing mole ratio of methanol to phenol, suggests the reaction to follow a consecutive mechanism. Due to presence of negative charge on the phenoxide ion, strength of the bond between this ion and Lewis site will increase with increasing acidity of the catalyst due to increasing  $M^{n+}$  content. This will permit phenoxide ion to remain on the surface for longer time and help formation of 2, 6-xylenol. the mechanism is shown in scheme A of Fig. 7.4.



**Fig.7.4 Scheme A. Perpendicular orientation of aromatic ring on the catalyst surface-- Reaction mechanism of ortho methylation of phenol using methanol as the alkylating agent [29]**

Fig. 7.4. represents the reaction scheme for ortho methylation of phenol using methanol as the alkylating agent. According to this scheme, the phenolate ion is adsorbed on the Lewis acid site and the hydrogen ion is bound to the basic site. Such a protonated site accelerates methanol to produce carbonium ion, which then reacts with the aromatic ring of the adjacently adsorbed phenolate species at its ortho position.

### 7.3 Reaction procedure

Vapour phase methylation experiments were performed in a fixed-bed continuous down flow glass reactor at the atmospheric pressure. A tubular glass reactor of 10 mm diameter and 25 cm length was loaded with 0.25g of the modified mesoporous ceria catalyst in powder form. The upper part of the reactor was packed with inert ceramic beads as the preheating zone. The catalyst was preheated at 300°C for 1 hour. The reactions were carried out by passing a mixture of phenol and methanol using syringe pump in the temperature range of 300–500°C at the rate of 4 ml/h. The weight hourly space velocity (WHSV) was varied from 13 to 35 h<sup>-1</sup>. The products were collected in an ice-cooled condenser and analysed by a gas chromatograph fitted with an OV-17 column and a flame ionization detector. The identity of the products was established by the comparison of retention times of authentic samples and also by GC-MS.

#### 7.3.1 Process Optimization

For any reaction, % conversion and product selectivity are influenced by catalyst composition, reaction conditions like temperature, time of reaction, substrate to reagent ratio, time and flow rate. So before carrying out the reaction, it is essential to optimize the reaction conditions. The results of the observations are given in the following section.

##### 7.3.1.1 Effect of temperature

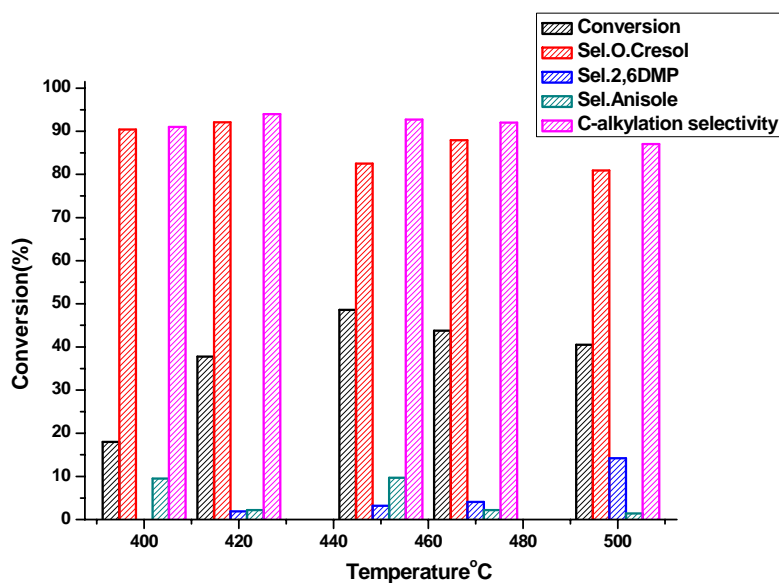
To study the effect of temperature on activity of the catalysts, the reaction was carried at different temperatures from 400 to 500°C. The results of the phenol methylation carried out at various temperatures showed maximum conversion (50.5%) at 500°C with 87% selectivity for ortho-alkylated products (Fig. 7.3.) for the catalyst CeFe(10%). But at

temperature (450°C) the maximum selectivity of 92.7% was observed however with a slight low conversion (48.6%). As expected the rate of reaction and % conversion increases with temperature. The selectivity of 2,6-DMP increases with the increase of reaction temperature, indicating that reaction

$\text{o-cresol} + \text{methanol} \rightarrow 2,6\text{-DMP} + \text{H}_2\text{O}$  is more temperature sensitive than reaction

$\text{Phenol} + \text{methanol} \rightarrow \text{o-cresol} + \text{H}_2\text{O}$

The formation of poly-methylated products is the reason for decrease in selectivity at higher temperature. Also methanol undergoes decomposition in greater extent at very high temperature decreasing the reaction rate.



**Fig.7.5 Effect of temperature on methylation of phenol**

*Reaction conditions: Catalyst -0.25g CeFe (10%),*

*Phenol: methanol – 1:5,*

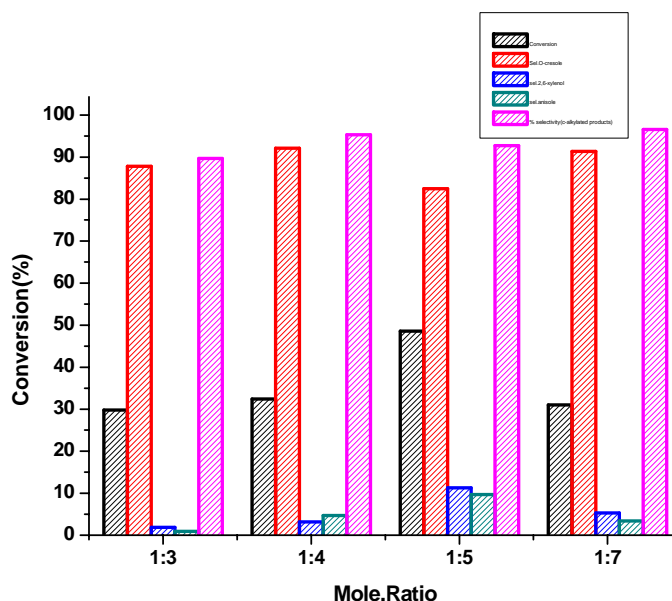
*Flow Rate: 4mL/h, Time of flow: 2 hrs*

According to literature basic catalysts favour O-alkylation at lower temperature and lower residence time, whereas C-alkylation is favoured by strong or medium acid sites. High temperature also favours C-alkylation. According to K. M. Malshe et al. basic Mg–Al–HT shows higher selectivity for anisole at low residence time whereas at higher residence time selectivity for C-alkylation increases at the expense of anisole [30]. Hence it is proposed that at lower temperature and lower residence time anisole is formed which undergoes rearrangement and further alkylation at higher temperature and high residence time to give o-cresol and 2, 6-xylenol at the expense of anisole. Our results are in good agreement with the literature. Mesoporous ceria catalyst which is moderately acidic, gives selective C-alkylation at high temperature (350–450°C). Hence it can be concluded that basicity or very low acidity favours O-alkylation at lower temperature whereas moderate or high acidity favours C-alkylation.

#### **7.3.1.2 Effect of methanol: phenol mole ratio on conversion and selectivity for C- Alkylated products**

In order to choose an optimum feed mix ratio, the experiments were conducted at different molar ratio using different volumes of methanol keeping the volume of phenol constant. The reaction was done at optimised temperature of 450°C using CeCr (10%) catalyst at a flow rate of 4ml /hr. The time of flow was selected as 2hr. The C-alkylated products such as o-cresol and 2, 6- xylenol were obtained as major reaction products. % Phenol conversion and product selectivity are plotted against phenol/methanol molar ratio Effect of change in methanol: phenol mole ratio on conversion and selectivity is shown in Fig.7.4. Conversion % of phenol goes up as the mole ratio is increase from 3 to 5 due to the availability of additional methyl groups for the reaction, however with further increase in

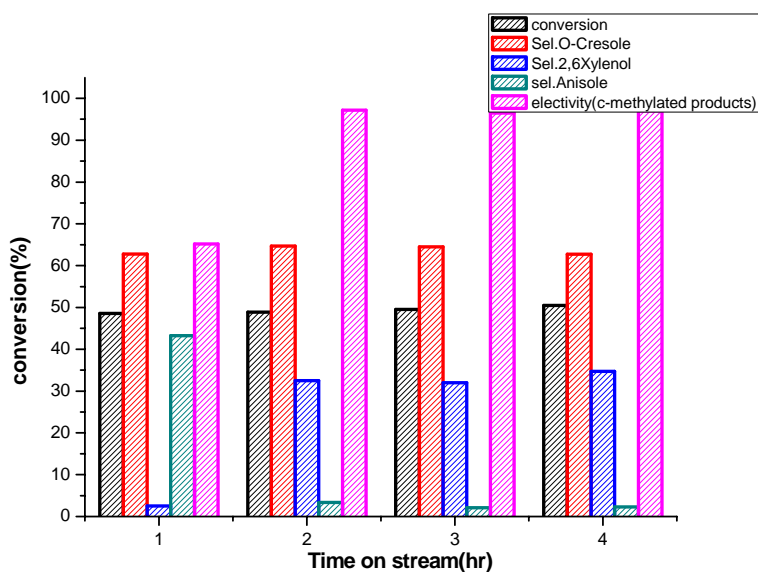
mole ratio there is a decrease in % conversion, and selectivity of o-cresole but selectivity for ortho-alkylated products increases as the yield of 2, 6-xylenol increased with more methanol concentration.



**Fig.7.6 Effect of mole ratio on methylation of phenol**

*Reaction conditions: Catalyst -0.25g CeFe (10%), Flow Rate: 4mL/h, Time of flow: 2 hrs, Temperature: 450°C*

This is due to the consecutive methylation at higher mole ratio. This result indicates that o-cresol is the primary alkylated product, the one which on further alkylation produces 2, 6-xylenol. An increase in mole ratio retains the initially formed o-cresol on the catalyst surface and facilitates consecutive methylation to give 2, 6-xylenol [31]. The linear increase in the conversion of phenol at lower molar ratio suggests a Langmuir–Hinshelwood bimolecular reaction [32].



**Fig.7.7 Effect of time on methylation of phenol**

*Reaction conditions: Catalyst -0.25g CeFe (10%), Phenol: methanol – 1:5, Flow Rate: 4mL/h*

### 7.3.1.3. Effect of time on methylation of phenol

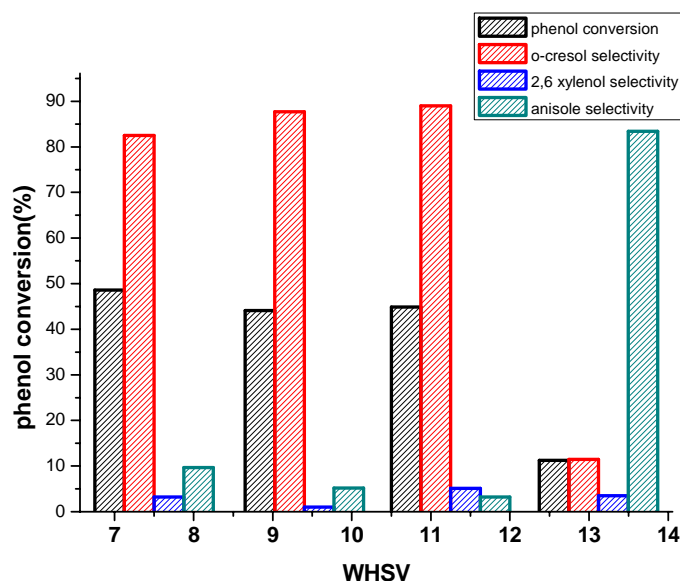
The time on stream studies using CeCr (10%) catalyst for methylation of phenol was done by carrying out the reaction for 4hrs. Results are shown in fig 7.5. Up to 4 hours of reaction there is steady rate in the conversion of phenol. The effect of contact time on product selectivity (Fig.7. 5) showed that, at low contact times, anisole was also a major product. As the contact time increased, the anisole selectivity decreased and o-cresol and 2, 6-xylenol increased. This shows that, anisole is to a large extent responsible for the formation of o-cresol and 2, 6-xylenol. It is proposed that at lower temperature and lower residence time anisole is formed which undergoes rearrangement and further alkylation at higher temperature and high residence time to give o-cresol and 2, 6-xylenol at the expense of anisole. The selectivity towards C-alkylated products varies with time on stream and maximum selectivity is obtained at 2 hours. The catalyst is found to be



active up to this period which shows better stability, no obvious activity loss occurs within the running time. However the deactivation of catalyst after prolonged use may be due to the formation of a layer of carbon as coke on catalyst surface.

#### **7.3.1.4 Effect of WHSV**

Effect of contact time of the reactant molecules on catalyst surface is expressed in terms of weight hourly space velocity (WHSV). When (WHSV) is  $7.5 \text{ h}^{-1}$ , optimum result in terms of % conversion was observed (Fig. 7.6). At lower WHSV although conversion is high, selectivity for C-alkylated products is less. As WHSV increases there is a decrease in the conversion whereas the C- alkylation selectivity increases up to a WHSV of  $11.25 \text{ h}^{-1}$ . When it is above 13 both conversion and selectivity drastically decreased. At high WHSV the conversion is getting decreased, which suggests the attainment of high rate of diffusion of the reactants reducing the chemisorption on the catalyst surface. At higher flow rate the residence time of the reactant molecules on the catalyst surface is less compared to the lower flow rates which results in the lower conversion. Ortho-alkylated products are very low due to longer residence time at the catalyst surface leading to the formation of C-alkylated product by rearrangement reaction and polyalkylated products. The low conversion at very high contact time can be attributed to the increased rate of methanol decomposition as a side reaction. As contact time decreases, the rate of this side reaction also decreases, resulting in high phenol conversion. At higher WHSV, selectivity for o-cresol increased due to lower contact time resulting in lack of consecutive methylation of cresol [32].



**Fig.7.8 Effect of WHSV on methylation of phenol**

*Reaction conditions: Catalyst -0.25g CeFe (10%), Phenol: methanol – 1:5, Temperature-450°C, Time-2hrs*

### 7.3.1.5 Effect of amount of catalyst

To study the effect of amount of catalyst on conversion and selectivity of methylation of phenol vapour phase reaction was done at 450°C with phenol to methanol ratio of 1:5. The feed at a flow rate of 4ml/hr. is introduced at the top of a preheated reactor packed with different amounts of pre activated catalyst packed between silica beads. The products are collected after 2 hours of reaction and analysed by GC. The results are given in the Table7.1

When the catalyst amount is increased from 0.1 to 0.25g, the conversion increases from 45.4 to 48.6 wt%. Further when the amount doubled the increase in conversion is only by 1%. The change in the selectivity was also not appreciable. So the amount was optimised to be 0.25g.

**Table 7.1 Effect of amount of catalyst on methylation of phenol**

Weight of catalyst(g)	Conversion (Weight %)	% selectivity (C-alkylated products)
0.1	45.4	90.1
0.25	48.6	85.7
0.5	49.6	86.5
1	49	91

Reaction conditions: Catalyst –CeFe (10%), Phenol: methanol – 1: 5, Temperature-450°C, Time-2hrs, Flow rate- 4mL/hr.

#### 7.4 Comparison of catalytic activities of prepared systems

Methylation of phenol was done under optimized reaction conditions using mesoporous ceria and all the prepared systems of ceria modified by transition metals. C-alkylated products mainly o-cresol and small amount of 2, 6-xylene were obtained as the major products under optimized condition for most of the samples confirming perpendicular orientation of phenol on catalyst surface.

**Table 7.2 Optimized parameters for the methylation of phenol.**

Parameters	Optimised conditions
Temperature	450°C
Molar ratio of phenol to methanol	1:5
WHSV	7.5 h. <sup>-1</sup>
Weight of catalyst	0.25g
Time on stream	2hours

A comparative evaluation of all the prepared systems is given in the Table 7.3.

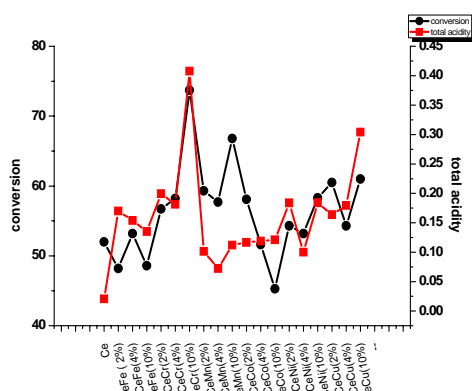
**Table 7.3 Methylation of phenol over mesoporous ceria and modified systems**

sample	Phenol conversion	o- cresol selectivity	2,6-xylenol selectivity	C-alkylated selectivity	Anisole selectivity
Ce	52	83.2	6.9	90.1	9.9
CeFe (2%)	48.2	72.3	5.4	77.7	25.9
CeFe (4%)	53.2	74.8	3.2	78	13.1
CeFe (10%)	48.6	82.3	3.4	85.7	9.7
CeCr (2%)	56.7	62.8	2.6	65.4	31.1
CeCr (4%)	58.2	54	39.5	93.5	5.8
CeCr (10%)	73.7	91	6.2	97.2	2.1
CeMn (2%)	59.3	50.6	28	78.6	21.6
CeMn (4%)	57.7	34.9	0.6	35.5	56
CeMn(10%)	66.8	30.3	0.7	31	63.2
CeCo (2%)	58.1	52.3	40.9	93.2	3.8
CeCo(4%)	51.6	41.6	53.8	95.4	2.6
CeCo(10%)	45.3	56.7	41.4	98.1	1.9
CeNi(2%)	54.3	50.8	46.2	97	2
CeNi (4%)	53.2	55.8	41.9	97.7	1.9
CeNi(10%)	58.3	62.8	34.2	97	2.5
CeCu (2%)	60.5	48.4	47.6	96	3.5
CeCu (4%)	54.3	55.8	34.9	90.7	5.3
CeCu(10%)	61	61.4	36	97.4	2.3

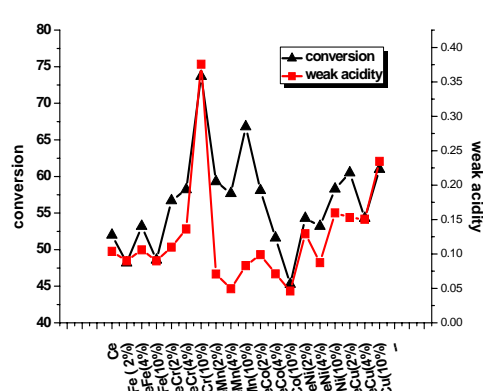
*Reaction condition: - Catalyst wt-0.25g, Phenol: methanol – 1:5, Temperature-450°C, Time-2hours, Flow rate- 4mL/h*

## 7.5 Acid-base property and catalytic activity

Among different transition metal modified samples, the catalytic activity and product selectivity strongly depend upon acid-basic properties of the catalyst, especially; the strength of the acidic sites plays a vital role in *o*-selective phenol alkylation. It was observed that the acidity increased with increasing content of the metal ion. This is due to decreased electron density on metal atom, which favours the adsorption of the phenoxide ion, leading to higher conversion of phenol. Phenol itself is highly polar, even very weak basic sites can easily bind with  $H^+$  ion from the phenolic O–H bond. Moreover, the phenoxide ion is resonance-stabilized and a stronger acid site is required to interact with a phenoxide ion. Thus, in the case of phenol alkylation, it is the acidity rather than the basicity which controls the catalytic activity.



**Fig.7.9a** Correlation of phenol conversion with total acidity



**Fig.7.9b** Correlation of phenol conversion with weak acidity

Here the conversion of phenol is correlated with total acidity (Fig.7.7a) and also with weak acidity (Fig.7.7b). A good correlation obtained between conversion and the acidity values shows agreement with reported literature. Among different samples prepared, CeCr (10%) got 73.7% phenol conversion with 97% selectivity of C-alkylated products.

This is highly correlated with the fact that this catalyst has the maximum acidity value among the different prepared samples.

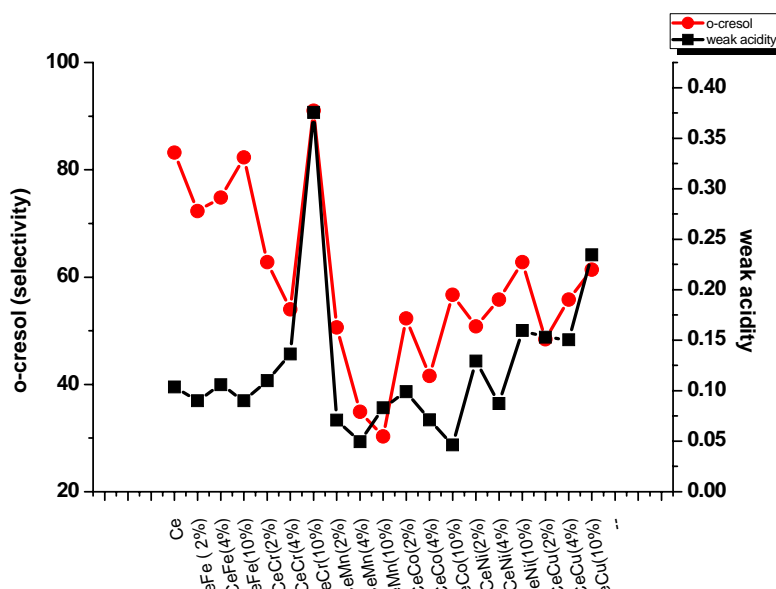


Fig.7.10 Correlation of o-cresol selectivity with weak acidity

But for all the other samples though a positive correlation is maintained between acidity and % conversion of phenol, the quantitative increase in % conversion is not found with the increase in acidity between different metals.

That is in the case of different samples of same the metal, there is linear change between acidity and % conversion. This is not maintained between different metals. This may be due to the fact that though acidity is a factor controlling the phenol methylation reaction, the catalyst activities also depend upon certain other factors like surface area, pore volume, structure of the catalyst etc.

In order to confirm the importance of acidity a regression equation was proposed by (32) Reddy et al. for the methylation of phenol over ferro spinel systems.

$$\ln(\text{activity}) = -0.18 \ln(\text{surface area}) + 0.27(\text{acidity}) + 4.05$$

A large value of acidity coefficient suggests the reaction to be acidity directed. According to this equation surface area does not seem to contribute much to the activity.

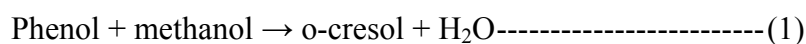
The catalytic activity of metal promoted systems may be correlated with Lewis acidity. The increase in acidity was rather sharp when the metal loading varied. However such a change could not be observed in conversion. This indicates that the metal content or acidity is not the only the criteria favouring the reaction. The leveling off of the conversions at higher loading indicates that there exists a critical value for the acidity beyond which the reaction seems to be independent of acidity.

Preferential C-alkylation can be attributed to large number of weak and medium acid sites whereas preferential ortho-alkylation is due to perpendicular orientation of phenol aromatic ring on catalyst surface. Selectivity in phenol alkylation (O- or C-alkylation) is reported to depend on the acid–base properties of the catalyst [22]. The O & C-selectivity of the catalysts (formation of o-cresol, 2, 6-xyleneol and 2- methyl anisole but not meta- or para-cresols or 4-methyl anisole) can be attributed to the nature of adsorption of phenol on these catalysts. As described by Tanabe [33] the phenolate ion is adsorbed on these catalysts such that the ortho-position is very near to the catalyst surface, hence only the ortho-position can be methylated. In our work the o-cresol selectivity of different samples are found to be in good correlation with weak acidity which support the reports [31]. The undesired side reactions such as the dealkylation to phenol and formation of poly methylated products are suppressed over these catalysts due to the unavailability of strong acid sites.

## 7.6 Rate of phenol methylation: Kinetic parameters

The heterogeneous model is based on the Langmuir–Hinshelwood–kinetics wherein the main reaction forming o-cresol & 2, 6-xylene(C-alkylated products) is catalysed by the active sites on the catalyst. According to this, phenol and methyl alcohol are chemisorbed on dual adjacent active sites of the catalyst to form different carbonium ions. Both chemisorbed phenol and methanol react with each other to form C-alkylated products followed by desorption of products from the active sites. Here, the dual-site surface reaction is the rate controlling step [34].

For the synthesis of o-cresol and 2, 6-dimethylphenol (2, 6-DMP) from phenol, the reactions occur according to the following stoichiometry:



Phenol methylation is highly exothermic with a standard heat of reaction of 146 kJ/mol for the formation of 2, 6-DMP. To determine the reaction rate parameters, the following differential equations were established to describe the reaction system by assuming a pseudo-first-order equation for phenol methylation:

$$-dC_{\text{phenol}}/d(1/\text{WHSV}) = k_1 C_{\text{phenol}} \text{-----(3)}$$

$$dC_{\text{o-cresol}}/d(1/\text{WHSV}) = k_1 C_{\text{phenol}} - k_2 C_{\text{o-cresol}} \text{-----(4)}$$

$$dC_{\text{2, 6-DMP}}/d(1/\text{WHSV}) = k_2 C_{\text{o-cresol}} \text{-----(5)}$$

Integration of eqn. (3) yields

$$-\ln(1 - X) = k / \text{WHSV} \text{-----(6)}$$



Experimental results were plotted according to equation(6), and a straight line passing through origin was obtained, indicating a good fit of the data to Equation (6), as illustrated in Fig. 7.9. Therefore, the rate of phenol disappearance (reaction 1) is first-order with respect to phenol concentration and zero order with respect to methanol. The rate equation can be written as'

$$r = kC_{\text{phenol}} \text{-----(7)}$$

### 7.6.1 Test of pseudo-first-order kinetic model for reaction at 450°C over CeFe (10%)

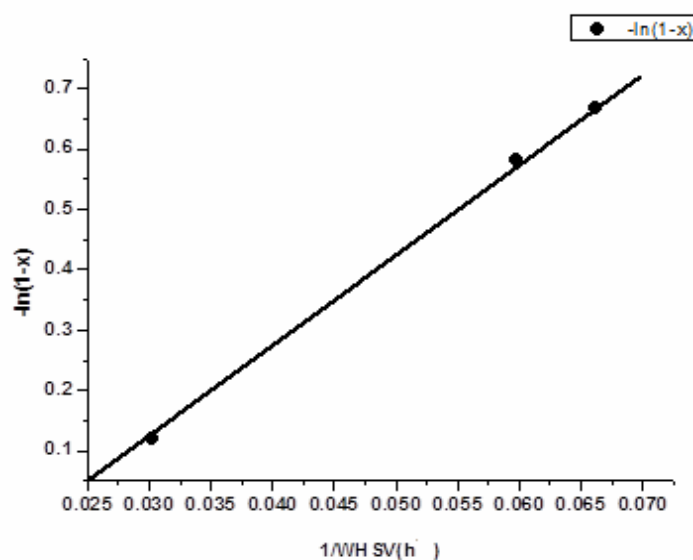


Fig.7.11 First order kinetic plot of phenol methylation

Considering the reaction as pseudo unimolecular, the intrinsic rate constants in the units of ( $\text{min}^{-1}\text{m}^{-2}$ ) was determined for each catalyst using the formula

$$k(\text{min}^{-1}\text{m}^{-2}) = \frac{2.303}{twA} \log \frac{100}{100-\% \text{yield}}$$

Where,  $t$  = time of the reaction in minutes,  $w$  = weight of the catalyst (g) and  $A$  = BET surface area of the catalyst ( $\text{m}^2/\text{g}$ )

The kinetic parameters ( $E_a$  and  $\ln A$ ) were evaluated from the phenol conversion values in the temperature range 400-500°C, assuming the diffusion and mass transfer effects were insignificant. Rate constant  $k$  is calculated for the reaction at different temperatures using CeFe (10%) catalyst under the same reaction conditions. Based on the Arrhenius equation,

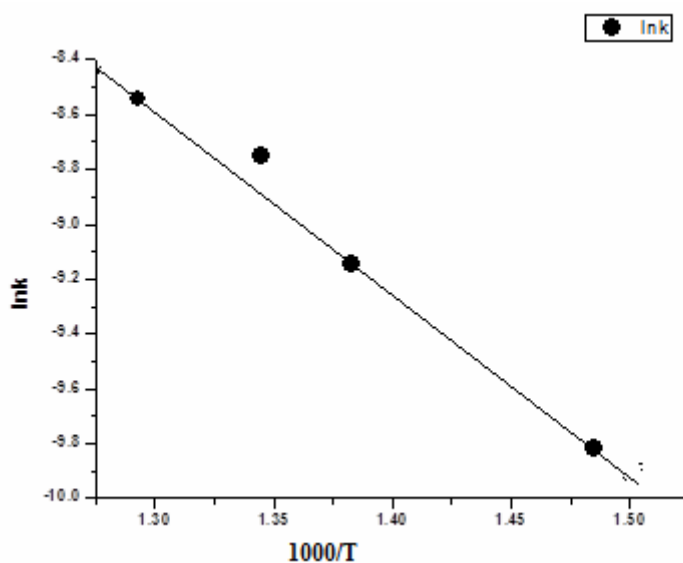
$$k = A \exp (-E_a/RT)$$

using 'least square method', the frequency factor  $A$  and the activation energy  $E_a$  were evaluated as  $9.6 \times 10^6 (\text{kg of catalyst})^{-1} \text{ h}^{-1}$  and 51 kJ/mol, respectively. The values of  $E_a$  vary in the same range (30-130 kJ mol<sup>-1</sup>) as reported recently by several authors for phenol conversion over different catalyst. Recently Li et al. [35] have reported the  $E_a$  value of 115.0 kJ mol<sup>-1</sup> for the conversion of phenol over manganese oxide catalyst, while Bautista et al. [36] has found it to be 20-60 kJ mol<sup>-1</sup> over various anions loaded AlPO<sub>4</sub>-Al<sub>2</sub>O<sub>3</sub>. Santacesaria et al. [37] have estimated the same to be 50-70 kJ/mol over the H-ZSM-5 zeolite. The  $E_a$  calculated in the present study also varies in the same range (30-130 kJ mol<sup>-1</sup>) indicating the validity of the model assumed for the evaluation of kinetic parameters.

Employing the power law equation from Power law kinetics the rate of reaction for the present system would be [38].

$$-r = A \exp (-E_a / RT) C_{\text{phenol}}, \text{-----(3)}$$

Where,  $E_a$ - the apparent activation energy and  $A$ - is the Arrhenius frequency factor.



**Fig.7.12** Arrhenius plot with CeFe (10%) as the catalyst

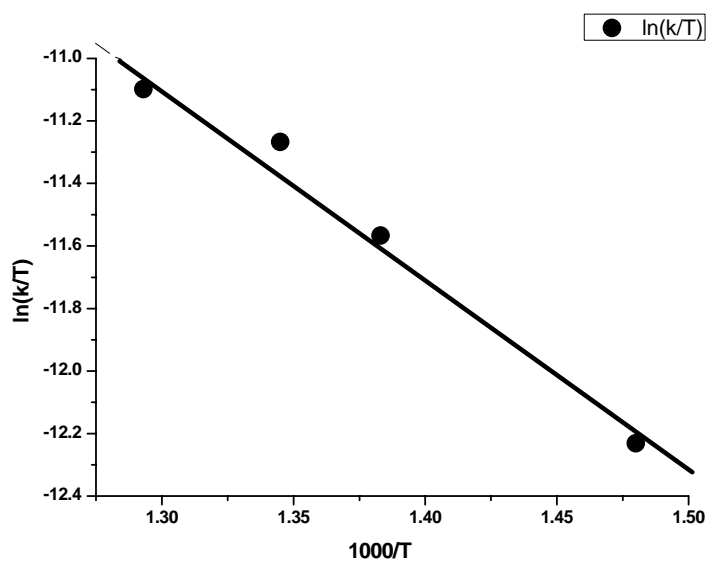
$E_a$ - the apparent activation energy is calculated from the above plot is 57.2 kJ/mol which is approximately same as that calculated by 'least square method'. The rate constant for the catalyst CeFe (10%) at the reaction temperature of 723K is found to be  $6.85 \times 10^{-3} \text{ min}^{-1}$ .

From the Arrhenius plot,

$$E_a = 57.2 \text{ kJ/mol},$$

$$\text{So } \Delta H^\ddagger = E_a - RT = 51.2 \text{ kJ/mol}$$

$$\Delta S^\ddagger = R [\ln A - \ln(kT/h) - n] = -230 \text{ J/mol /K}$$



**Fig.7.13** Eyrings plot with CeFe (10%) as the catalyst

The values of different kinetic parameters calculated according to Arrhenius equation and Eyrings equation are given in the Table 7.4

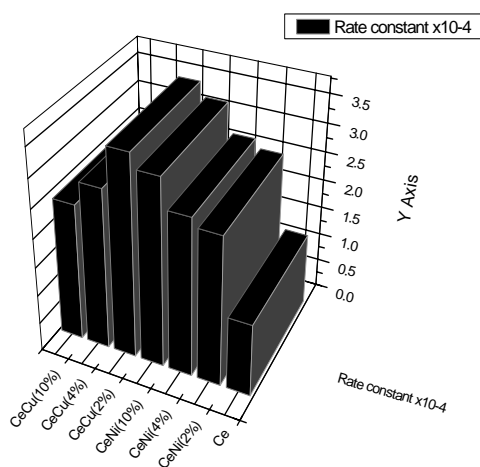
**Table 7.4** Values of different kinetic parameters

<b>Kinetic parameters</b>	<b>Values</b>
Activation energy $E_a$	57.2 kJ/mol
Frequency factor A	$9.6 \times 10^6$ (kg of catalyst) $^{-1}$ h $^{-1}$
Enthalpy of activation $\Delta H^\ddagger$	51.2 kJ/mol
Entropy of activation $\Delta S^\ddagger$	-230 J/Mol /K

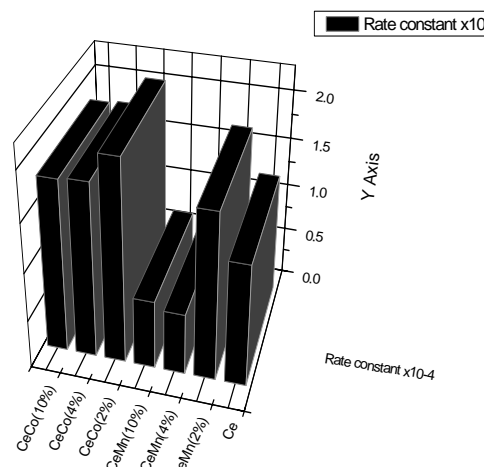
Table 7.5 Effect of metal loading on phenol methylation reaction

sample	Rate constant ( $\text{m}^{-2} \text{min}^{-1}$ ) $\times 10^{-4}$	TON	TOF( $\text{h}^{-1}$ )	Catalyst activity ( $\text{mmol m}^{-2} \text{h}^{-1}$ )
Ce	1.26	-	-	-
CeFe (2%)	1.55	5944	2972	0.0265
CeFe (4%)	1.78	3284	1642	0.0296
CeFe (10%)	3.36	1199	599	0.051
CeCr (2%)	1.24	6496	3248	0.025
CeCr (4%)	2.15	3350	1675	0.027
CeCr (10%)	4.37	1692	846	0.043
CeMn (2%)	1.72	7200	3600	0.027
CeMn (4%)	0.63	3503	1752	0.0268
CeMn (10%)	0.705	1622	811	0.034
CeCo (2%)	2.08	7570	3785	0.024
CeCo (4%)	1.8	3362	1681	0.023
CeCo (10%)	1.78	1181	590	0.023
CeNi (2%)	2.59	7059	3530	0.031
CeNi (4%)	2.74	3450	1725	0.033
CeNi (10%)	3.25	1512	756	0.037
CeCu (2%)	3.5	8571	4286	0.041
CeCu (4%)	2.8	3846	1923	0.038
CeCu (10%)	2.4	1728	864	0.046

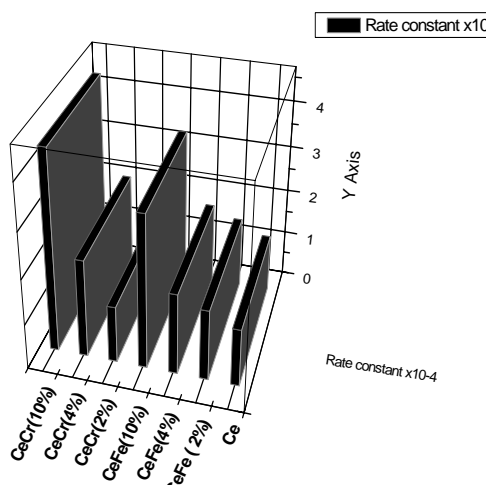
Reaction condition: - Catalyst weight-0.25g, Phenol: methanol – 1:5,  
Temperature-450°C, Time-2hours, Flow rate- 4mL/hr



**Fig.7.14a** Effect of loading of Cu & Ni on phenol conversion



**Fig.7.14.b** Effect of loading of Co & Mn on phenol conversion



**Fig.7.14.c** Effect of loading of Cr & Fe on phenol conversion

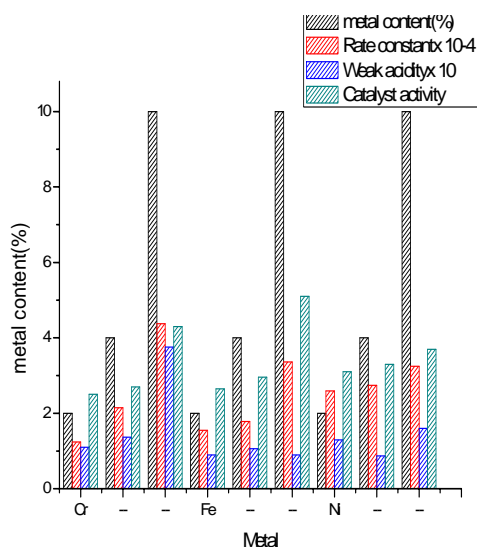
For Cr, Fe & Ni modified samples, the rate constants increases as the metal content increases. For Co & Mn loaded samples the rate constant initially decreases with metal loading then it increases. However with Cu loading, the rate constant decreases steadily. Effect of metal loading on

phenol conversion may be due to the higher uniform dispersion of metal ions on ceria support as well as moderate acidity.

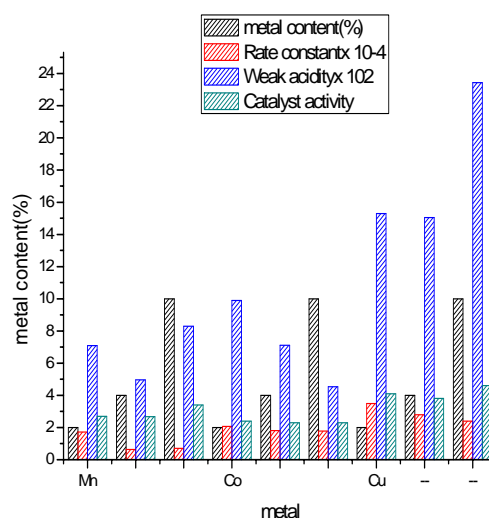
At higher metal loading, the decrease in the conversion could be due to the non-uniform distribution of metal ions on ceria support as well as higher acidity. These results suggest that the moderate acidity is more favourable for this reaction than strong acidity.

The catalyst activity of Cr, Fe, Mn & Ni modified samples increase with metal concentration. As metal concentration increases, the acidity of the system increases with a corresponding reduction in the basicity. In other words, acid–base properties are mutually dependent and creation of new acidic centres occurs through the removal of existing basic centers [29]. In the case of phenol alkylation, for the Cr, Fe & Ni modified mesoporous ceria catalysts the catalytic activity progressively increased as metal content increased (Fig.7.13a). For Co samples the activities are almost same with negligible change with increase in metal loading (Fig.7.13b). The TON & TOF are inversely related to the metal concentration. This is because the change in conversion with metal loading is not that much pronounced with increase in the metal content.

The catalytic activity of metal promoted systems may be correlated with Lewis acidity. The increase in acidity was rather sharp when the metal loading varied. However such a change could not be observed in conversion. This indicates that the metal content or acidity is not the only the criteria favouring the reaction. The leveling off of the conversions at higher loading indicates that there exists a critical value for the acidity beyond which the reaction seems to be independent of acidity.



**Fig.7.15a** Effect of Cr, Fe & Ni loading on phenol methylation reaction



**Fig.7.15.b** Effect of Co, Cu & Mn loading on phenol methylation reaction

## 7.7 Summary and conclusions

Mesoporous ceria permit the alkylation of bulk molecules for which micro porosity of zeolite imposes limitations to the reaction. It is important to control both porosity and acidity to get the desired product. It is a challenge to develop a satisfactory solid alkylation catalyst that makes the chemical transformation economically feasible and environmentally friendly, which has a high yield of alkylate, selectivity to the desired product, a long life cycle, regenerability, and greatly reduced environmental and safety risks. We report herein the development of an environmentally friendly process for C-methylation of phenol derivatives with methanol using mesoporous ceria modified solid acid catalysts. In summarizing the results, the following conclusions can be deduced:



- These systems are highly efficient for alkylating phenol in the ortho position, leading to o-cresol as the major product. Under optimized conditions, for the best catalyst among the prepared samples (CeCr10%) the total ortho selectivity was higher than 97% with a phenol conversion of 74%.
- Preferential C-alkylation can be attributed to large number of weak and medium acid sites whereas preferential ortho-alkylation is due to perpendicular orientation of phenol aromatic ring on catalyst surface. The undesired side reactions such as the dealkylation to phenol and formation of poly methylated products are suppressed over these catalysts due to the unavailability of strong acid sites.
- Formation of poly methylated products is suppressed over these catalysts due to the unavailability of strong acid sites. Direct C-alkylation over the prepared catalysts is due to the higher acidity of catalysts. The catalyst is highly stable and does not deactivate even after a number of cycles.
- A tentative mechanism for the ortho selective methylation of phenol over the catalyst has been proposed. Phenol is adsorbed perpendicularly on Lewis acidic site by lone pair electrons of oxygen atom and is alkylated by methanol, which is possibly in the form of methyl carbonium ion.
- The reaction is proved to be following first order kinetics with phenol conversion with the frequency factor A and the activation energy  $E_a$  evaluated as  $9.6 \times 10^6$  (kg of catalyst)<sup>-1</sup> h<sup>-1</sup> and 57.2 kJ/ mol, with (CeFe10%)catalyst. The values of  $E_a$

vary in the same range (30-130 kJ mol<sup>-1</sup>) as reported recently by several authors for phenol conversion over different catalyst. The kinetic parameters like  $\Delta H$ ,  $\Delta S$  of activation for the reaction are calculated.

- For Cr, Fe & Ni modified samples, the rate constants increases as the metal content increases. For Co & Mn loaded samples the rate constant initially decreases with metal loading up to a higher concentration then it increases. However with Cu loading, the rate constant decreases steadily. Effect of metal loading on phenol conversion may be due to the higher uniform dispersion metal ions on ceria support as well as moderate acidity.
- The activity of Cr, Fe, Mn & Ni modified samples increase with metal concentration. For Co samples the activities are almost same with negligible change with increase in metal loading.
- The TON & TOF are inversely related to the metal concentration. This is because the change in conversion with metal loading is not that much pronounced with increase in the metal content.

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