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Selective C-methylation of phenol with methanol over transition metals modified mesoporous ceria catalysts

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ABSTRACT

The demand for selective catalysts with larger molecular dimensions led to the discovery of mesoporous catalytic materials. We report herein the development of an environmentally friendly process for C-methylation of phenol derivatives with methanol using mesoporous ceria modified with transition metals. Selective C-methylation of phenol, has been investigated over transition metals loaded mesoporous ceria. Catalyst reaction rates at various reaction parameters were also investigated. 98% selectivity for ortho-alkylated products (o-cresol and 2, 6-xylenol) was obtained. The reaction is proved to be first order with phenol conversion. The frequency factor A and the activation energy Ea were also evaluated with (CeFe10%) catalyst.

Key words: Mesoporous ceria, C-alkylation, ortho alkylated products, Kinetic order, Frequency factor

Academic Discipline And Sub-Disciplines

Chemistry, catalysis and kinetics

SUBJECT CLASSIFICATION

Chemistry, heterogeneous catalysis

TYPE (METHOD/APPROACH)

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1. INTRODUCTION

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]. Alkylation of phenols is generally carried out using a liquid acid catalyst, giving wide product distribution. 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 neutralisation result in higher capital costs. Friedel–Crafts catalysts such as $AlCl_3$, BF_3, $TiCl_4$, liquid HF, various types of zeolites, ɣ-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 [2]. Both C- and O-alkylation of phenol is possible depending on reaction conditions such as temperature, source of reagent, and type of catalyst. 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 with transition metals as solid acid catalysts. 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 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 reaction is proved to be following first order kinetics with phenol conversion with the frequency factor A and the activation energy Ea evaluated as 9.6×10^{6} (kg of catalyst)$^{-1}$ h^{-l} and 57.2 kJ/ mol, with (CeFe10%)catalyst. The values of Ea vary in the same range (30-130 kJ mo1^{-1}) as reported recently by several authors for phenol conversion over different catalyst [3].

2. MATERIALS AND METHODS

2.1. Experimental

2.1.1. Synthesis

The modified mesoporous ceria catalysts were prepared via templated method (surfactant assisted route) using cerium nitrate [Ce $(NO_3)_3$. $6H_2O$] as the precursor. Iron nitrate hexahydrate (Alfa 98.5%), chromium nitrate (S. D. Fine chemicals Ltd), manganese acetate (Merck), cobalt nitrate (S. D. Fine chemicals Ltd), nickel nitrate (S. D. Fine chemicals Ltd), copper nitrate (S. D. Fine chemicals Ltd) hexadecyl amine (Aldrich), and ammonia were used as sources for iron, chromium, manganese, cobalt, nickel, copper, surfactant and alkali respectively. Mesoporous ceria was synthesized, according to literature procedure [4] and modified with 3 different compositions of each of the metals by wet impregnation method. 0.5M solution of the corresponding metals [Cr $(NO_3)_3.9H_2O$, $Mn(AC)_2.4H_2O$, $Fe(NO_3)_3$, $Co(NO_3)_2.4H_2O$, $Ni(NO_3)_2.6H_2O$ and $Cu(NO_3)_2.3H_2O$] containing required amount of metal (2, 4 and 10wt% of metal) were added to the previously prepared mesoporous ceria and mechanically stirred for 6h, kept overnight and dried at 80°C which were further dried at 110°C. They are powdered and calcined at 350°C to obtain metals incorporated cerium oxide.

2.1.2. Characterization

Powder X-ray diffractograms of the materials were recorded on a Rigaku D MAX III VC Ni-filtered Cu Kα radiation, $\lambda = 1.5404$ A° 2θ range 10-80 º at a speed of 1º/min. Low angle XRD was also done to confirm the mesoscopic nature of the sample. N_2 adsorption–desorption isotherms, pore size distributions as well as the textural properties of the materials were determined at -196 ^{o}C by a *Micromeritics Tristar 3000* surface area and porosity analyser. Pore size distribution and average pore size of the samples were obtained from the adsorption branch of the isotherms using the Barret-Joyner-Halenda (BJH) method. FT-IR spectra of the solid samples were taken in the range of 4000–400 cm^{-1} on a Shimadzu FT-IR 8201 instrument by diffuse reflectance scanning disc technique. Diffuse reflectance UV–Vis spectra were recorded in the range 200–800nm with a Shimadzu UV-2101 PC spectrometer equipped with a diffuse reflectance attachment, using BaSO4 as the reference. SEM analysis of the samples was done using *JEOL* JSM-840 A (Oxford make) model16211 scanning electron microscope analyser with a resolution of 13 eV. The HR-TEM of the samples were carried out in ultrahigh resolution analytical electron microscope JEOL3010. Perkin Elmer TG analyser instrument was used for carrying out thermo gravimetric studies. Elemental composition was confirmed by ICP-AES. The acidity measurements of the prepared samples were done by Temperature Programmed Desorption (TPD) using ammonia as probe molecule by desorbing ammonia at various temperatures after adsorption on the catalyst at room temperature. The values obtained were tested by vapour phase cumene cracking reaction. Vapour phase cumene cracking reaction is a test reaction for identifying the Lewis to Bronsted acid ratio of a catalyst.

2.1.3. 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 25 mg of the modified mesoporous ceria catalyst in powder form. The upper part of the reactor packed with inert ceramic beads was the preheating zone. The catalyst was preheated at 300^{o}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^{o}C at the rate of 4 ml/h. The weight hourly space velocity (WHSV) was varied from 13 to 35 h^{-1}. 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.

3. RESULTS AND DISCUSSION

A detailed results of the characterization of the present catalyst systems have been already reported elsewhere[5, 6].The crystalline phases were identified by comparison with standard JCPDS (Joint Committee on Powder Diffraction Standards) data file. Wide angle XRD analysis clearly shows peaks corresponding to the crystalline cubic fluorite ceria phase. With loading of metals no additional metal oxide phase was formed up to a 10wt%metal loading except for copper. This points to the fact that the metal species are highly dispersed or exist as microcrystalline material below the XRD detection limit. A peak at low-angle region confirms the mesoporous nature of the sample prepared. FT-IR shows the successful removal of surfactant at a lower calcination temperature (350^{o}C) which is effective for a high surface area for the calcined sample free of surfactant. The samples exhibits N_2 adsorption–desorption of Type IV isotherm with steps between partial pressures P/Po of 0.3 to 0.8, and a hysteresis loop, due to capillary condensation in the mesoporous channels and/or cages. Narrow BJH pore size distribution suggests an open pore channel with a regular mesopore structure. The H3 hysteresis loop obtained were characteristic of mesoporous materials with narrow slit-like pores. The pore volume, pore diameter & surface area were calculated by desorption studies. Surface area decreases with metal loading. Crystallite size and lattice parameters were calculated from XRD data using Scherrer equation. Crystallite sizes obtained show decrease with metal incorporation. It is clear that with incorporation of heteroatom in the framework of ceria, a slight decrease in the d111 spacing is observed, indicating the presence of the heteroatom within the framework [5, 6]. The acidities of the samples measured by TPD of ammonia indicate an increase in the total acidity with the metal loading in the sample [Table 1]. Upon modification with metals, there is enhancement in the amount of weak, medium and strong acid sites. But as the metal concentration increases though there is a change in the total acidity, there is no steady increase in the acidity with increase in the concentration of the metals.

Table 1.Distribution of acid sites of pure ceria and transition metals incorporated ceria.

Sample	Weak [mmol/g] (100-200℃)	Medium [m mol/g] (201-400℃)	Strong [mmol/g] (401-600℃)	Medium + strong	Total [mmol/g] (100-600℃)
Ce	0.10	0.02	**Nil**	0.021	0.12
CeFe(2%)	0.09	0.07	0.01	0.08	0.17
CeFe(4%)	0.11	0.02	0.03	0.05	0.16
CeFe(10%)	0.09	0.02	0.02	0.04	0.13
CeCr(2%)	0.11	0.05	0.03	0.09	0.19
CeCr(4%)	0.13	0.02	0.02	0.04	0.17
CeCr(10%)	0.37	0.02	0.01	0.03	0.40
CeMn(2%)	0.07	0.02	0.01	0.03	0.10
CeMn(4%)	0.05	0.01	0.01	0.023	0.07
CeMn(10%)	0.08	0.02	0.01	0.03	0.11
CeCo(2%)	0.1	0.01	0.01	0.02	0.12
CeCo(4%)	0.07	0.015	0.01	0.022	0.09
CeCo(10%)	0.05	0.05	0.02	0.07	0.12
CeNi(2%)	0.13	0.03	0.02	0.05	0.18
CeNi(4%)	0.09	0.01	0.003	0.013	0.10
CeNi(10%)	0.16	0.01	0.01	0.02	0.18
CeCu(2%)	0.15	0.01	0.002	0.01	0.16
CeCu(4%)	0.15	0.02	0.01	0.03	0.18
CeCu(10%)	0.23	0.04	0.03	0.07	0.30

4. CATALYTIC STUDY

4.1. 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.

4.1.1. 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. For the catalyst CeFe (10%), at temperature (450°C) the maximum selectivity of 92.7% was observed with a conversion (48.6%) (Fig.1). As expected the rate of reaction and % conversion increases with temperature. The selectivity of 2, 6-DMP increases with the increase of reaction temperature. 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

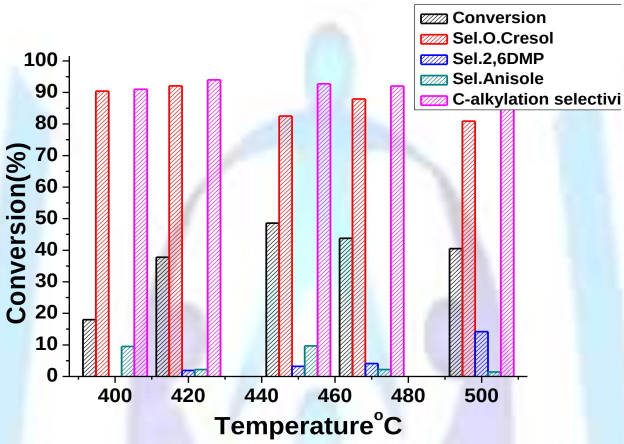

Fig.1. Effect of temperature on methylation of phenol

Reaction conditions: Catalyst -0.25g CeFe (10%),Phenol: methanol – 1:5,

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

4.1.2. 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 CeFe (10%) catalyst at a flow rate of 4ml /hr. The time of flow was selected as 2hrs. The C-alkylated products such as o-cresol and 2, 6- xylenol were obtained as major reaction products. %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. This result indicates that o-cresol is the primary alkylated product, the one which on further alkylation produces 2, 6-xylenol.

4.1.3 Effect of time on methylation of phenol

The time on stream studies using CeFe (10%) catalyst for methylation of phenol was done by carrying out the reaction for 4hrs. Up to 4 hours of reaction there is steady rate in the conversion of phenol. The effect of contact time on product selectivity (Fig.3) showed that, at low contact times, anisole was also a major product. As the contact time increased, the selectivity of anisole 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

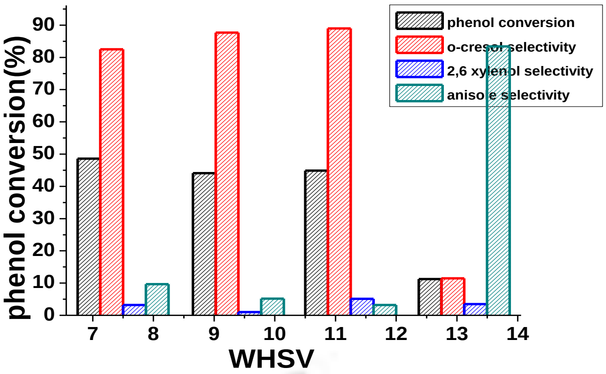

Fig.4. Effect of WHSV on methylation of phenol

Reaction conditions: Catalyst -0.25g CeFe (10%), Phenol: methanol – 1:5,Temp.-450^{o}C, Time-2hrs

4.1.4. 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 h^{-1}, optimum result in terms of % conversion was observed (Fig.4). At lower WHSV although conversion is high, selectivity for C-alkylated products is less. As WHSV increases there is decrease in the conversion whereas the C- alkylation selectivity increases up to a WHSV of 11.25 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 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 [7].

4.1.5. 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^{o}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. 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 2. Optimized parameters for the methylation of phenol

Parameters	**Optimised conditions**
Temperature	450^{o}C
Molar ratio (phenol to methanol)	1:5
WHSV	7.5 h.$^{-1}$
Weight of catalyst	0.25g
Time on stream	2h

4.2Comparison of catalytic activities of prepared systems

Table 3. Conversion of different systems

sample	Phenol conversion	O-cresol selectivity	2,6-xylenol selectivity
Ce	52	83.2	6.9
CeFe (2%)	48.2	72.3	5.4
CeFe (4%)	53.2	74.8	3.2
CeFe (10%)	48.6	82.3	3.4
CeCr (2%)	56.7	62.8	2.6
CeCr (4%)	58.2	54	39.5
CeCr (10%)	73.7	91	6.2
CeMn (2%)	59.3	50.6	28
CeMn (4%)	57.7	34.9	0.6
CeMn(10%)	66.8	30.3	0.7
CeCo (2%)	58.1	52.3	40.9
CeCo(4%)	51.6	41.6	53.8
CeCo(10%)	45.3	56.7	41.4
CeNi(2%)	54.3	50.8	46.2
CeNi (4%)	53.2	55.8	41.9
CeNi(10%)	58.3	62.8	34.2
CeCu (2%)	60.5	48.4	47.6
CeCu (4%)	54.3	55.8	34.9
CeCu(10%)	61	61.4	36

Methylation of phenol was done under optimized reaction conditions (Table 2) 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–xylenol were obtained as the major products under optimized condition for most of the samples confirming perpendicular orientation of phenol on catalyst surface. A comparative evaluation of all the prepared systems is given in the Table3.

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. 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 [8].

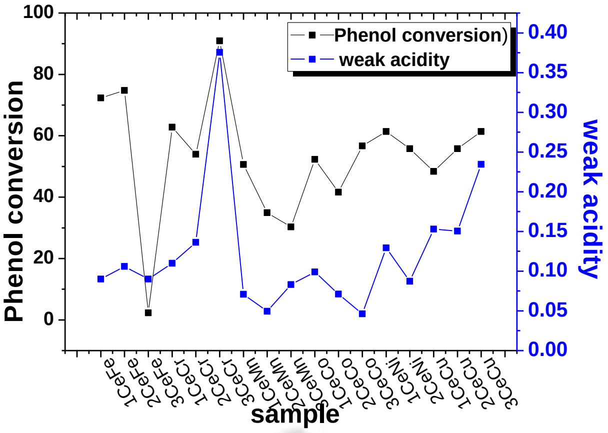

Fig.5.Correlation of weak acidity with conversion

Here the conversion of phenol is correlated with weak acidity (Fig.5). A good correlation obtained between conversion and the acidity values. 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. 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.

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–xylenol(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 [9].

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

Phenol + methanol → o-cresol + H_2O (1)

o-cresol + methanol → 2, 6-DMP + H_2O (2)

To determine the reaction rate parameters, differential equations were established to describe the reaction system by assuming a pseudo-first-order equation for phenol methylation: Experimental results were plotted according to equation(3), and a straight line passing through origin was obtained, indicating a good fit of the data to Equation (3), as illustrated in (Fig. 6). 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’

$r = k\ C_{phenol}$ (3)

6.1 Test of pseudo-first-order kinetic model for reaction over CeFe (10%)

The kinetic parameters (Ea and In 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,

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

using ‘least square method’, the frequency factor A and the activation energy Ea were evaluated as 9.6 x 10^6(kg of catalyst)$^{-1}$ h^{-l} and 51 kJ/mol, respectively. The values of Ea vary in the same range (30-130 kJ mo1^{-1}) as reported recently by several authors for phenol conversion over different catalyst. Recently Li et al. [10] have reported the Ea value of 115.0 kJ mol^{-1} for the conversion of phenol over manganese oxide catalyst, while Bautista et al. [11] has found it to be 20-60 kJ mol-1 over various anions loaded AlPO4-Al2O3. Santacesaria et al. [12] have estimated the. same to be 50-70 kJ/mol over the H-ZSM-5 zeolite. The Ea calculated in the present study also varies in the same range (30-130 kJ mol-1) indicating the validity of the model assumed for the evaluation of kinetic parameters.

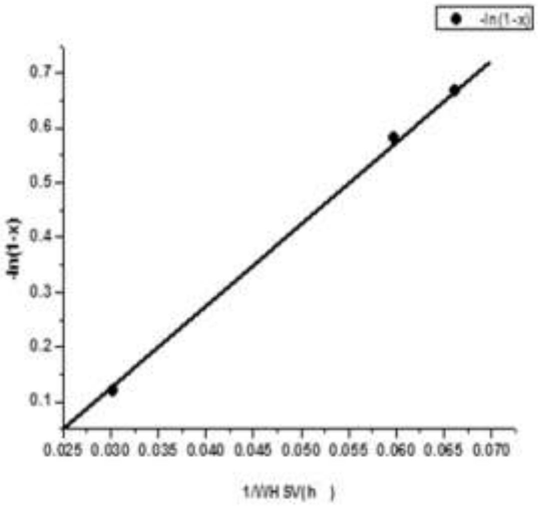

Fig.6. First order kinetic plot of phenol methylation

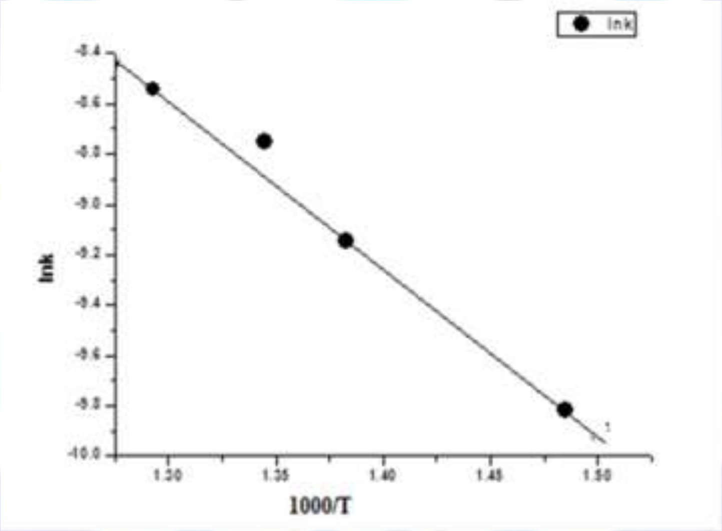

Fig.7. Arrhenius plot with CeFe (10%) as the catalyst

The values of different kinetic parameters calculated according to Arrhenius equation and Eyrings equation are given in the Table 4.

Table 4. Values of different kinetic parameters

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

7. SUMMARY AND CONCLUSIONS

sites. The catalyst is highly stable and does not deactivate even after a number of cycles. 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 x 10^6 (kg of catalyst)$^{-1}$ h^{-l} and 57.2 kJ/ mol, with (CeFe10%)catalyst. The values of E_a vary in the same range (30-130 kJ mo1^{-1}) as reported recently by several authors for phenol conversion over different catalyst.

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Author’s biography with Photo

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