

## OXIDATION OF ETHYL BENZENE

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Recently there has been an increased interest in the development of clean and economical processes for the selective oxidation of ethyl benzene to the higher value added product acetophenone. The current industrial production of acetophenone is via the oxidation of ethyl benzene with molecular oxygen using cobalt cycloalkane carboxylate or cobalt acetate as catalyst in acetic acid solvent. This method suffers from its corrosive form and environmentally unfriendly nature. For the present investigation, oxidation of ethyl benzene was carried out in liquid phase using the mesoporous ceria and different transition metals modified ceria systems using tert-butyl hydroperoxide (TBHP) as the oxidizing agent. The reaction was studied at different temperatures to find out the kinetic parameters of the optimized catalyst.

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## 6.1 Introduction

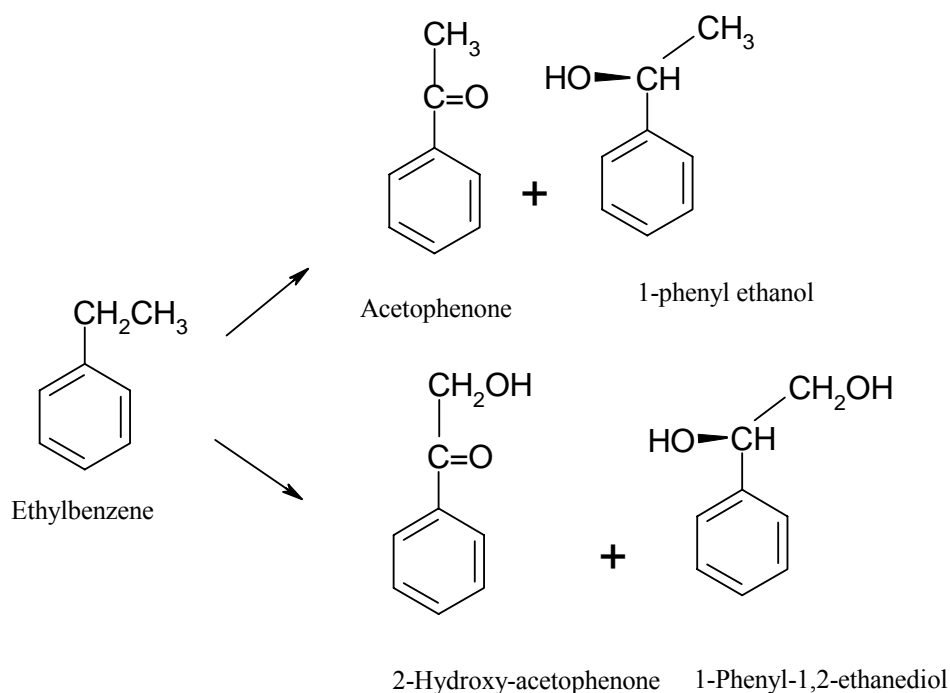
One of the foremost challenges currently facing the chemical industry is the need for alternative production technologies that are cleaner, safer, and environmentally friendly. Processes should be efficient both in terms of economy and energy consumption. Catalytic oxidation of hydrocarbons in general is employed in the manufacture of fine chemicals. The selective catalytic oxidation of organic compounds using environmentally friendly and cheap oxidants, such as molecular oxygen and aqueous  $\text{H}_2\text{O}_2$ , and a heterogeneous, easily recyclable catalyst is a challenging goal of the fine chemical industry [1]. Site isolation of discrete redox metal centres in inorganic matrices can afford oxidation catalysts with unique activities and selectivity by circumventing the oligomerization of the active monomeric species. One way of designing stable, solid catalysts with unique activities is through incorporation of redox metal ions or complexes into the framework or cavities of the molecular sieves.

Autoxidation reactions are very important milestones in the development of new petrochemical processes. These kinds of reactions use the most abundant and cheapest oxidant that minimizes the production and use of pollutants. The use of mesoporous materials is recommended highly if one oxidizes organic compounds of large molecular sizes with a bulky oxidant such as tert-butyl hydroperoxide (TBHP). Side chain oxidation of alkyl aromatics using cleaner peroxide oxidants catalysed by heterogeneous catalysts still attracts interest. Classical laboratory procedures preferably use stoichiometric oxidants such as permanganates and dichromate, which are hazardous [2]. Hence there has been an interest to develop eco-friendly catalysts for the oxidation of alkyl aromatics. As these reactions follow a complex radical mechanism, it is difficult to reach high selectivity at high

conversion levels. The development of catalytic systems that allows good yields could be a great challenge in the “green chemistry”. Oxygenated products are the required intermediates for many chemical feed stocks, agrochemicals, fragrances, pharmaceuticals, and polymers, but traditional methods for their preparation often require stoichiometric amounts of Cr(VI), Mn(VII) or Os(VIII) that generate large quantities of toxic metal waste [3]. A substantial amount of research was focused on the homogeneous catalytic oxidation of alkyl aromatic substrates with cobalt salts and dioxygen under corrosive conditions [4]. But a more environmentally benign and selective catalytic process is clearly desirable. Metal supported heterogeneous catalysts that can operate in conjunction with an amenable oxidant in the liquid phase are advantageous in that they are recoverable and have minimal environmental impacts [5]. Effective utilization of ethylbenzene, available in the xylene stream of the petrochemical industry to more value added products is an interesting proposition. Well known are the isomerization of ethylbenzene to xylenes and dehydrogenation to styrene monomer. Oxidation of ethylbenzene has not drawn much attention due to the complexity of the products [6].

The selective catalytic oxidation is the main route to obtain monomers and intermediates for organic synthesis. The catalysts used are solids, most often mixed oxides with elements of different oxidation states, with redox properties. The lattice oxygen is inserted in the hydrocarbon molecule while the so-reduced solid is oxidized by the gaseous oxygen. This mechanism is described by Mars and van Krevelen as a two steps mechanism: the first one involves the hydrocarbon oxidation by lattice oxygen and the second one, the catalyst re-oxidation by gaseous oxygen. In chemical processes where catalytic reactions are involved, several

strategies can be taken in order to enhance efficiency, energy balance, environmental aspects and the economics of the process. In view of these issues, the improvement of the catalyst physico-chemical properties, in order to extend the scope of the applications of existing catalysts are of high interest. Oxidation of ethyl benzene to different products can take place in two ways. One is the aromatic ring hydroxylation under which the hydroxylation at the para position is preferred to some extent to ortho position. The other is the side chain oxidation at primary and secondary carbon atoms. The primary and secondary carbinols formed from the side chain oxidation undergo further oxidation to the respective aldehydes and ketones. The pathways of ethyl oxidation are shown in Fig. 6.1.



**Fig.6.1 Reaction Scheme for ethylbenzene oxidation**

Production of acetophenone, which is used as a component of perfumes and as an intermediate for the manufacture of pharmaceuticals,

resins and alcohols is an important reaction in organic chemistry [7]. The presence of molecular oxygen or single oxygen donors such as tert-butyl hydroperoxide (TBHP) for the oxidation of alkanes to ketones are shown to be important [8]. Earlier, synthesis of acetophenone was performed using stoichiometric quantities of oxidizing agents like  $\text{KMnO}_4$  or  $\text{K}_2\text{Cr}_2\text{O}_7$ , or via Friedel–Crafts acylation reaction of aromatics by acid halide/anhydride, using stoichiometric amounts of corrosive  $\text{AlCl}_3$  catalyst. The current industrial production of benzylic ketones is based on the oxidation of alkyl benzenes with molecular oxygen using cobalt acetate as the catalyst in acetic acid [9]. Zeolite encapsulated Co(II), Ni(II) and Cu(II) complexes gave acetophenone as the only partial oxidation product during ethylbenzene oxidation with  $\text{H}_2\text{O}_2$  [10]. Titano silicates mainly catalyse ring hydroxylation of arenes with  $\text{H}_2\text{O}_2$ , whereas vanadium and chromium substituted zeolites and alumino phosphate molecular sieves have been known to favour side-chain oxidation selectively [11]. Chromium substituted aluminophosphates are found to favour the formation of ketones from alkyl arenes with TBHP as the oxidant [12]. Aromatic ketone acetophenone is an important intermediate for perfumes, drugs and pharmaceuticals [13]. Production of this aromatic ketone by Friedel Craft's acylation of aromatic compound by acid halide or acid anhydride using stoichiometric amount of anhydrous aluminium chloride or a homogeneous acid catalyst leads to the formation of a large volume of highly toxic and corrosive wastes [14, 15, 16]. In the past, efforts have been made to produce aromatic ketones by oxidizing the methylene group attached to an aromatic ring using stoichiometric quantities of oxidizing agent eg.the oxidation of ethyl benzene to acetophenone by  $\text{KMnO}_4$  [17]. In this the waste produced is very large and the separation of reactants and the products from the reaction mixture is difficult. Acetophenone can also be

produced by the liquid phase oxidation of ethyl benzene by oxygen in air using heterogeneous transition metals (viz. Co, Mn, Cu or Fe) compounds as catalysts [18, 19, 20, 21, 22]. In this reaction, the conditions are harsh, the product selectivity is poor, separation of the catalysts from the reaction mixture is difficult and catalyst cannot be reused. A lot of tarry waste products are also formed. It is therefore of great practical interest to develop a more efficient easily separable, reusable and environmental friendly catalyst for the production of aromatic ketone. In this study, we used transition metal modified mesoporous ceria as catalysts in the oxidation of ethylbenzene with TBHP as oxidant in the liquid phase reaction.

Ethyl benzene oxidation was conducted in a 50ml glass round bottom flask fitted with a water cooled condenser and a magnetic stirrer, placed in a thermostated oil bath. In a typical reaction, required amounts of ethyl benzene, solvent and catalyst were taken in the R.B. flask. It is stirred till a particular temperature is attained and then calculated amount of TBHP is added drop wise with stirring. The products are withdrawn at certain intervals and analysed using Chemito 8610 GC fitted with FID Detector and using SE-30 column. The products were identified by GC-MS.

## 6.2 Optimization of reaction parameters

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

### 6.2.1 Effect of oxidant

Oxidation of ethyl benzene was conducted using *tert*-butyl hydroperoxide (TBHP) and hydrogen peroxide as oxidants. The data obtained is given in the Table 6.1

**Table 6.1 Effect of oxidant on oxidation of ethyl benzene**

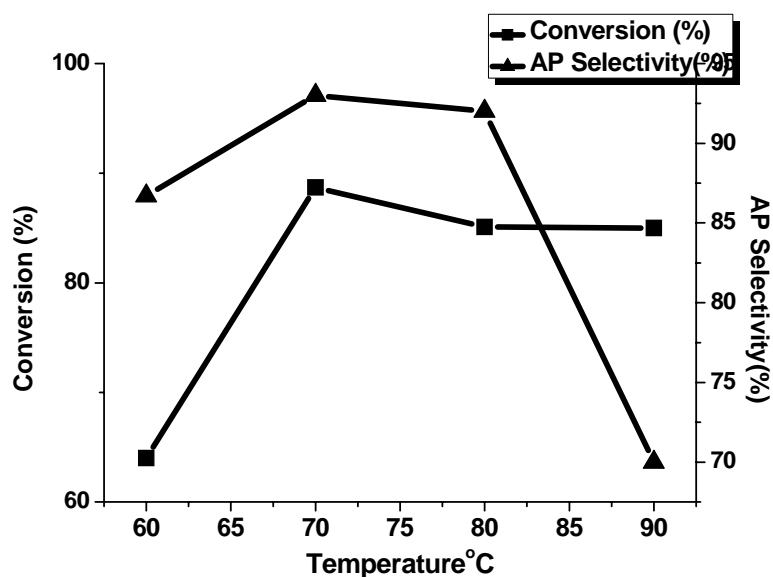
oxidant	Conversion (%)	Selectivity	
		Acetophenone	1-phenyl ethanol
H <sub>2</sub> O <sub>2</sub>	41	62.5	37.5
TBHP	88.7	93	7

*Reaction conditions: Ethyl benzene to oxidant mole ratio-1: 4, Acetonitrile-5mL, Time-6h, CeCr (10%)-0.05g, Temperature-70°C*

When H<sub>2</sub>O<sub>2</sub> was used as the oxidant the conversion was 41% with 62.5 % acetophenone selectivity, while TBHP gave 88.7 % conversion with 93% selectivity of acetophenone. According to Sheldon et al. [23] metal ions which catalyse oxygen transfer reactions with H<sub>2</sub>O<sub>2</sub> or RO<sub>2</sub>H are divided into two types based on the active intermediate: a peroxometal or oxometal complex. Transition metals, like Mo (VI), W (VI), Ti (IV), follow peroxometal pathways and first row transition metals like Cr(VI), V(V), Mn(V), Ru(VI), Ru(VIII), Os(VIII) use oxometal pathways. The prepared samples of mesoporous ceria modified with first row transition metals follow oxometal pathway with TBHP as oxidant. Since the oxidation with TBHP is more selective and efficient, TBHP is selected for further study.

### 6.2.2 Effect of reaction temperature

To study the effect of temperature on ethylbenzene oxidation, reactions were carried out at different temperatures: 60 to 90°C with 1:4 molar ratios of ethyl benzene and TBHP using 5ml of acetonitrile solvent and 0.05g of CeCr (10%) catalyst.



**Fig.6.2 Effect of temperature on oxidation of ethyl benzene**

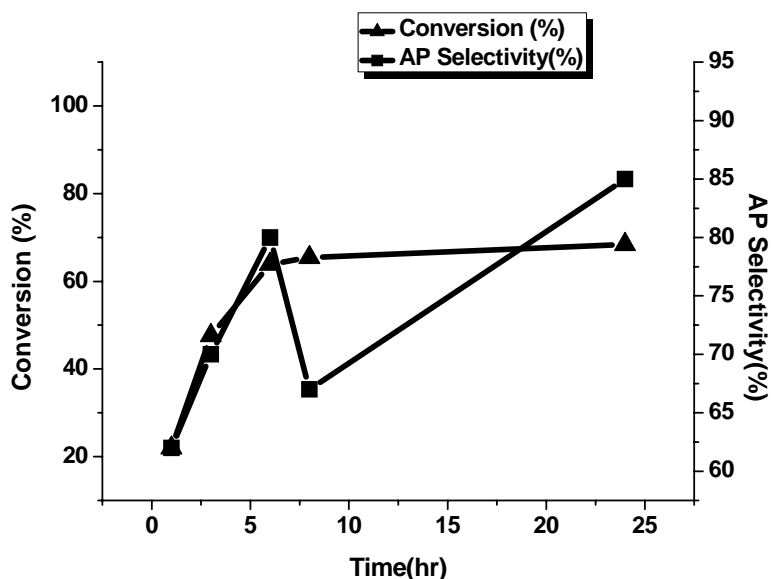
*Reaction conditions: Ethyl benzene to oxidant mole ratio-1: 4, Acetonitrile-5mL, Time-6h, CeCr (10%)-0.05g*

From figures 6.2 it is clear that the conversion increases as the temperature rises from 60°C to 70°C for the catalyst and then decreases at 80°C. The increase in conversion as the temperature increased from 70 to 80°C may be due to the activation of t-butyl hydroperoxide at 70°C. The lower conversion at 90°C might be attributed to the decomposition of t-butyl hydroperoxide at higher temperature. Similar to conversion of ethyl benzene, the selectivity towards acetophenone also increases as the temperature increases from 60°C to 70°C. So 70°C is the optimized temperature for the reaction.



### 6.2.3 Effect of reaction time

To study the influence of reaction time on the efficiency of the catalyst the reaction was done at 70°C using 1:4 molar ratio of ethyl benzene to TBHP in the presence of 0.05 g CeCr (4%) catalyst and 5 ml of acetonitrile solvent. The result (Fig. 6.3) shows that the percentage conversion increased when the reaction was carried out for 6 hours. After that the increase in %conversion was very small for next 2 more hours of reaction, and the trend is continued. The selectivity also decreased after 6 hours. At prolonged reaction for 24 hours, the conversion and selectivity are found to be increased, but the change is only 5% after 18 more hours of reaction. Hence further reactions were done for 6 hours.

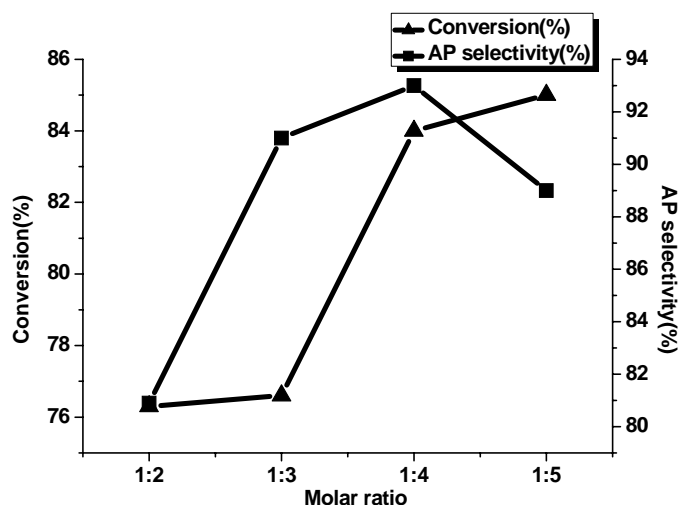


**Fig. 6.3 Effect of time on ethylbenzene oxidation**

*Reaction conditions: Ethyl benzene to TBHP mole ratio -1: 4,  
Temperature- 70°C, Acetonitrile-5mL, Catalyst -0.05g CeCr (4%)*

### 6.2.4 The effect of mole ratio of ethylbenzene to TBHP

To study the effect of mole ratio of ethylbenzene to TBHP, the reaction was carried out in previously optimized conditions of temperature and time, i.e., at 70°C for 6 hours at different molar ratios of ethyl benzene and TBHP, keeping the volume of ethyl benzene as 1ml.



**Fig. 6.4 Effect of ethyl benzene to TBHP mole ratio on ethylbenzene oxidation**

*Reaction conditions: Temperature- 70°C, Acetonitrile-5mL, Catalyst-0.1g CeCr (10%)*

From the Fig. 6.4, it is found that the oxidation of ethyl benzene is sensitive to the molar ratio of the reactants. As the molar ratio increases, selectivity and the % conversion increases. When ratio is 1:5 the selectivity of acetophenone is found to be decreased. So the molar ratio of the reactants is optimized as 1:4 for conducting further reactions.

### 6.2.5 Effect of solvent

It has been reported in several articles that the liquid phase oxidation reactions are sensitive to the nature of the solvent used. The role of solvent

on the reaction is very complex, especially on product distribution [24]. Among a series of solvents like acetonitrile, acetone, methanol, water, acetonitrile is found to give high conversion. Beliefa et al. observed that the presence of polar solvents makes vanadia- Titania catalyst more active for cyclohexane oxidation [25]. So we employed different solvents such as acetonitrile, acetone, methanol and water. The influence of the solvent on the oxidation of ethyl benzene is summarized in the Table 6.2.

**Table 6.2 Effect of solvent on reaction**

Solvents	Conversion (wt. %)	Acetophenone selectivity (%)
Water	24	84
Acetone	26.6	49
Acetonitrile	63	85
Methanol	30.4	81

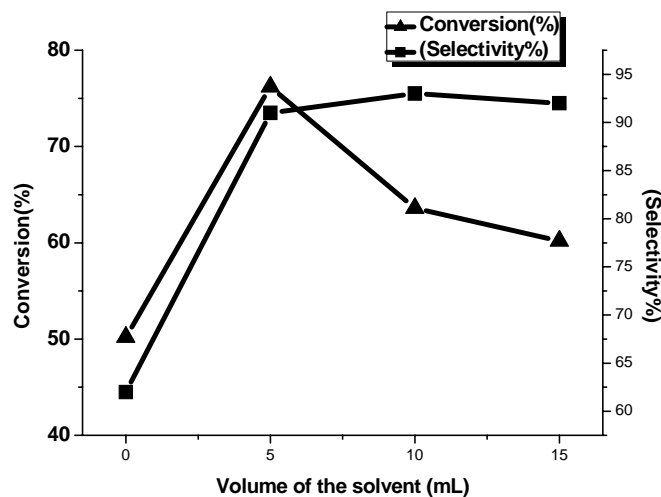
*Reaction conditions: Ethyl benzene to TBHP mole ratio-1:4, Temperature- 70°C, Solvent- 5mL, Catalyst -0.05g CeCr (4%)*

The catalytic reaction shows much higher conversion when acetonitrile was used as the solvent. Maximum percentage conversion and selectivity was obtained when acetonitrile was used as the solvent.

With water, conversion was very low. So for the oxidation of ethyl benzene using TBHP, acetonitrile was found to be the suitable solvent. The oxidation of ethyl benzene was found to be influenced by the polarity of the solvent. The catalysts are persistently deactivated by strong interaction of the polar solvents thereby preventing diffusion of the reactants to the active sites. As a result the more polar solvents lead to lower conversion [26].

### 6.2.6 Effect of volume of the solvent

After optimizing acetonitrile as the suitable solvent for the oxidation of ethyl benzene using TBHP, the effect of volume of the solvent was studied. The reaction was carried out at a temperature of 70°C, for 6 hours using 1:4 molar ratios of ethyl benzene and TBHP. The relation between the volume of the solvent and percentage conversion and selectivity are shown in the Fig. 6.5



**Fig. 6.5 Effect of volume of the solvent on ethyl benzene oxidation**

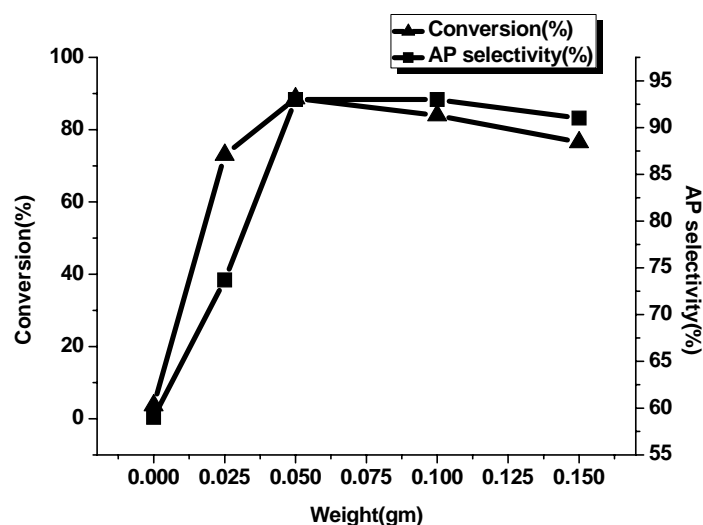
*Reaction conditions: Temperature- 70°C, Time -6h, Catalyst - 0.1g CeCr(10%), Ethyl benzene to TBHP mole ratio-1: 4, Solvent -Acetonitrile*

The results show that a noticeable conversion and selectivity is obtained in the absence of solvent. But in the presence of catalyst, the % conversion and selectivity of acetophenone is increased to a considerable extent. When the volume of the solvent is increased from 0 to 5ml there was a two fold increase both in the percentage conversion of ethyl benzene and the selectivity of acetophenone. After that the conversion is decreased. Increase in the selectivity is not much pronounced by change in solvent

amount after 5ml acetonitrile. This suggests that there is an optimum solvent concentration for maximum conversion. This may be due to the blocking of active sites of the catalyst by solvent molecules, and also may be due to the dilution of the reaction system. So 5ml acetonitrile was optimized for solvent in the reaction.

### 6.2.7 Effect of the weight of the catalyst

In heterogeneous catalysis the amount of catalyst plays a crucial role in determining the rate of the reaction. The oxidation was done using different weights of the catalyst (0.05, 0.1 and 0.15 g) for 6hours using CeCr (10%) catalyst and the results are represented in Fig. 6.6.



**Fig. 6.6 Effect of the weight of the catalyst**

*Reaction conditions: Temperature- 70°C, Time- 6h, Acetonitrile-5mL, Catalyst- CeCr (10%), Ethyl benzene to TBHP mole ratio -1: 3,*

From the data it can be seen that the amount of catalyst has an imperative function in the oxidation of ethyl benzene. It is found that when the weight of the catalyst is increased the conversion also increased establishing that the reaction proceeds through a pure heterogeneous

mechanism. But when the catalyst weight was 0.05g, the selectivity and conversion were maximum. Then the conversion and selectivity decreases. So 0.05g of the catalyst is taken as the optimum catalyst amount for the effective performance for the reaction.

### 6.2.8 Optimized conditions

The optimization procedures reveal that the reaction parameters have strong influence on the oxidation activity and acetophenone selectivity of the catalyst systems. The optimized reaction conditions are summarized in Table 6.3.

**Table 6.3 Optimized conditions**

<b>Time</b>	<b>6hours</b>
Reaction temperature	70 °C
Molar ratio	1:4
Solvent	Acetonitrile
Volume of the solvent	5 ml
Weight of the catalyst	0.05g

### 6.3 Leaching and reusability studies: Structural stability of the catalysts

An important requisite for a heterogeneous catalyst for the better catalytic performance is the stability of its active sites under the reaction conditions. Major causes that can lead to the deactivation of a catalyst include the disruption of the crystalline structure and changes in chemical composition during the reaction. The leached metal cation in solution can enhance the reaction rate whereby the pure heterogeneity of the reaction is lost. The regeneration of the catalyst after several repeated reaction runs also gives an idea about the stability of the system towards a particular reaction. Thus it becomes important to test the metal leaching on the catalytic activity and

regeneration ability of the present systems. CeMn (10%) and CeCr (10%) are taken as the representative sample for these investigations.

### 6.3.1 Effect of metal leaching

A very important subject to be considered for the solid catalyst is the leaching phenomenon to find out the true nature of the catalytic reaction whether it is homogeneous or heterogeneous. Leaching can take place during a catalyzed reaction without an induction period and the nature of the reaction may gradually change from heterogeneous to homogeneous without any indication in the reaction profile. To prove the heterogeneous nature of the reactions, the solid catalyst was removed by filtration after 1 hour from the reaction mixture at the reaction temperature. The mother liquor is again subjected for further reaction at the same conditions for five more hours. The results obtained using CeMn (10%) and CeCr (10%) are shown in Table 6.4

**Table 6.4 Effect of metal leaching in oxidation of ethyl benzene**

Catalyst	Time(h)	Conversion (Wt %)
CeMn(10%)	1 hour	25.3
	5hrs	29
CeCr (10%)	1 hour	52.7
	5hrs	76

From the results it is clear that in the case of CeMn (10%) the conversion remains more or less constant after the removal of the catalyst showing that metal ions are not leaching from the catalyst surface during the oxidation process. The investigation reveals the true heterogeneous nature of the reaction over modified ceria catalysts. But for CeCr (10%) there is increase in the conversion after the quenching by removal of the catalyst. It is clear that the Cr catalyst loses traces of Cr which catalysed the further reaction

in a homogeneous manner. It is reported that no heterogeneous Cr catalyst have been prepared which have been stable under liquid phase oxidation conditions by performing tests for leaching [23].

### 6.3.2 Catalyst regeneration

One of the major objectives guiding the development of solid acid catalysts includes the easy separation of final products from the reaction mixture and efficient catalyst recovery. The recycling of the used catalyst for the same reaction is also a measure of catalyst structural stability. The reusability is tested for representative systems CeMn (10%) and CeCr (10%). The catalyst was removed by filtration from the reaction solution, washed thoroughly with acetone and then dried and calcined at 350 °C for 4 hours. The same catalyst was again used for carrying out the subsequent run under similar reaction conditions.

**Table 6.5 Regeneration of the catalyst**

catalyst	Number of cycles	Conversion (Wt %)
CeMn (10%)	1	56.5
	2	54
CeCr (10%)	1	88.7
	2	77

*Reaction conditions: Ethyl benzene to TBHP mole ratio -1:4, Temperature- 70°C, time -6h, Acetonitrile-5mL, Catalyst weight- 0.05g*

From the Table 6.5., it is evident that the reuse of the catalyst gave %conversion without appreciable change. Thus the catalyst can be recycled without loss of activity.

### 6.4 Catalyst efficiency of different systems

We have prepared pure mesoporous ceria and three series of manganese, chromium, iron, cobalt, copper and nickel modified ceria systems. Under the



optimized process parameters of temperature, time, molar ratio, catalyst weight and volume of the optimized solvent, all the prepared systems were tested for the oxidation of ethyl benzene using TBHP as the oxidizing agent. The activity of different catalytic systems in terms of percentage conversion and acetophenone selectivity are given in the Table 6.6.

**Table 6.6 Activity of the catalyst systems in the oxidation of ethyl benzene**

Catalyst	Ethylbenzene Conversion (Weight %)	Selectivity (%)		TON <sup>a</sup>	TOF <sup>b</sup> (h <sup>-1</sup> )	Catalyst activity <sup>c</sup> (mmol/m <sup>2</sup> /h) x10 <sup>-3</sup>
		Acetophenone	(*Others)			
Without catalyst	3.7			-	-	-
Ce	4.7	74.1	25.9	-	-	0.4
CeFe (2%)	18.0	99.0	1.0	8700	1450	2.4
CeFe (4%)	12.1	99.0	1.0	2900	483	1.6
CeFe (10%)	18.9	59.7	40.3	1820	303	4.9
CeCr(2%)	26.2	78.6	21.4	11300	1883	2.9
CeCr (4%)	63.0	85.0	15.0	13600	2267	7.2
CeCr (10%)	88.7	93.0	7.0	7700	1283	12
CeMn (2%)	56.5	76.0	24.0	23700	3950	6.4
CeMn (4%)	51.7	89.5	10.5	11800	1967	5.9
CeMn (10%)	33.0	7.0	29.0	5200	867	4.1
CeCo (2%)	36.5	80.0	20.0	17600	2933	3.7
CeCo (4%)	28.4	86.6	13.4	6900	1150	3.1
CeCo (10%)	36.1	77.0	23.0	3500	583	4.5
CeCu (2%)	44.0	53.6	46.4	24100	4017	7.3
CeCu (4%)	51.2	76.5	23.5	14000	2333	8.7
CeCu (10%)	68.7	31.0	69.0	7500	1250	13
CeNi (2%)	15.0	72.0	28.0	7200	1200	2.1
CeNi (4%)	13.0	99.2	0.8	3100	517	1.99
CeNi (10%)	26.4	71.8	28.2	2600	433	4.2

Reaction conditions: Ethyl benzene to TBHP mole ratio -1: 3, Temperature- 70°C, Time - 6h, Acetonitrile-5mL

(\* Others mainly include 2-phenyl ethanol traces of o/p-hydroxy acetophenone & Phenyl acetaldehyde etc)

The Table 6.6. shows that compared to ceria, the modified systems are more active. In the absence of catalyst the conversion was only 3.7% with less acetophenone selectivity. In the case of the iron modified systems, though there is not much conversion, the acetophenone selectivity is very high. With the increase in the metal content, in the case of Fe, Co and Ni doped systems, conversion first decreases and then increases. For Cr and Cu modified systems there is a steady increase with increase in the metal content. In the case of Cr modified systems the metal content plays a crucial role in catalytic activity. On increasing the metal content from 2 to 4% a two-fold increase in activity is observed. For Mn doped systems the conversion decreases with % of metal doping. According to B. Viswanathan et al. [27], mesoporous Cr- $\text{AlPO}_4$  exhibits both acidic and redox properties by promoting dealkylation and oxidation in a concerted manner, whereas, under identical conditions, Cr-MCM-48 promotes only oxidation. Here among all the systems, Cr, Cu and Mn doped ones are giving % conversion more than 50%. CeCr (10%) is more active than the other two systems. Among the prepared catalyst systems 10% chromium doped ceria is found to be the most active catalyst with 88.7% conversion and 93% selectivity in the oxidation of ethyl benzene. Comparing the activities of Mn, Cu and Cr modified systems, Cr modified ones are most active and selective towards acetophenone. Next to chromium the better system is CeCu (10%). For ceria modified with Cr prepared by sol-gel method, the % conversion for ethyl benzene oxidation reaction was only 59% [28]. So Cr doped mesoporous ceria prepared by surfactant route is much more active than that prepared by sol-gel route.

From Table 6.6., it is evident that as the metal loading increases, the TON and TOF are getting decreased. This is because of the reason that with the increase in the metal loading, % conversion is not increased in a proportional manner.

It is reported that the oxidation of toluene with TBHP in the presence of chromium silicate catalyst proceeds through the reversible transformation of  $\text{Cr}^{3+}$  and  $\text{Cr}^{5+}$ . Parentis et al. [29] suggested that in the presence of TBHP,  $\text{Cr}^{3+}$  is oxidised to  $\text{Cr}^{5+}$  in  $\text{Cr}/\text{SiO}_2$  catalysts which oxidises the substrate via redox mechanism. The C-H bond activation at the benzylic position by transition metal complexes under mild conditions is an important transformation in the synthetic organic chemistry. Hexavalent chromium catalysts are extensively used for the transformation of alkyl aromatics to aromatic ketones and acids in homogeneous phase [30]. Sivasanker et al. [31], reported an efficient catalytic method for benzylic oxidation of alkyl arenes to the corresponding carbonyl compounds in good yields using Cr-MCM-41 catalyst and 70% tert-butyl hydroperoxide (TBHP) in MeOH as oxidant. Imamura et al. concluded that the effect of ceria was to produce Mn species with lower oxidation states ( $\text{Mn}^{3+}$ ,  $\text{Mn}^{2+}$ ) and combination of  $\text{Mn}^{4+}$  with  $\text{Mn}^{3+}$  or  $\text{Mn}^{2+}$  was assumed to be the cause for the high activity of the catalyst [32].

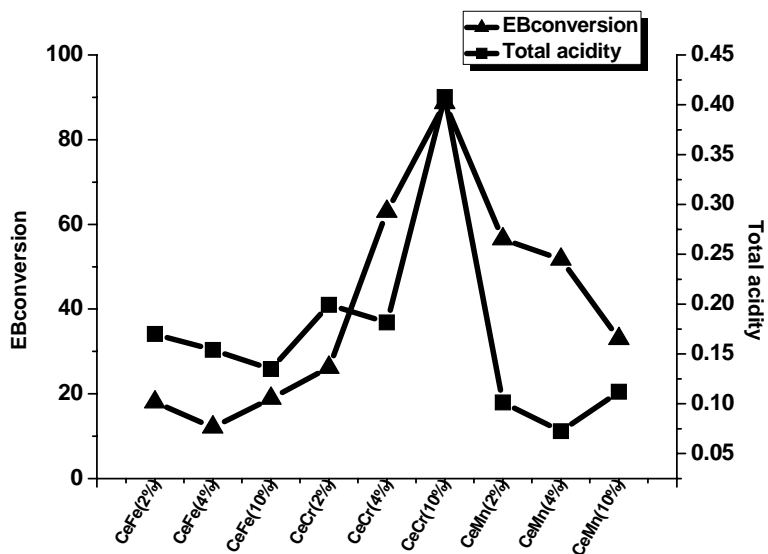


Fig.6.5a Correlation between the surface acidity and catalytic activity for Fe, Cr & Mn doped systems

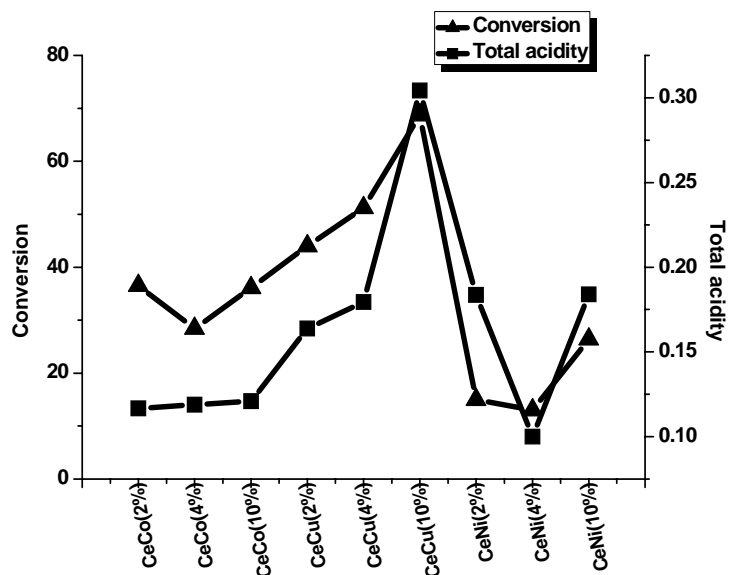


Fig.6.5b Correlation between the surface acidity and catalytic activity for Co, Cu & Ni doped systems

According to Sheldon et al. first row transition metals generally employ oxometal pathway which involves two-electron redox reactions of the metal ion. The highest activity for Cr, Mn, & Cu modified catalysts which can easily undergo redox reactions through oxometal path way. A correlation is also noticed between the surface acidity and catalytic activity. This is shown in the Fig. 6.5a & b.

## 6.5 Kinetic Parameters

### 6.5.1 Test of pseudo-first-order kinetic model for reaction at 70°C over CeCr (10%)

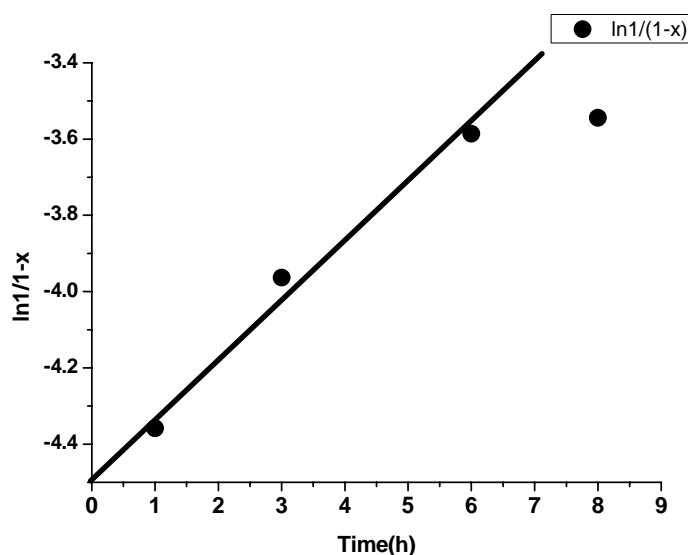


Fig.6.6 First order kinetic plot of ethyl benzene oxidation

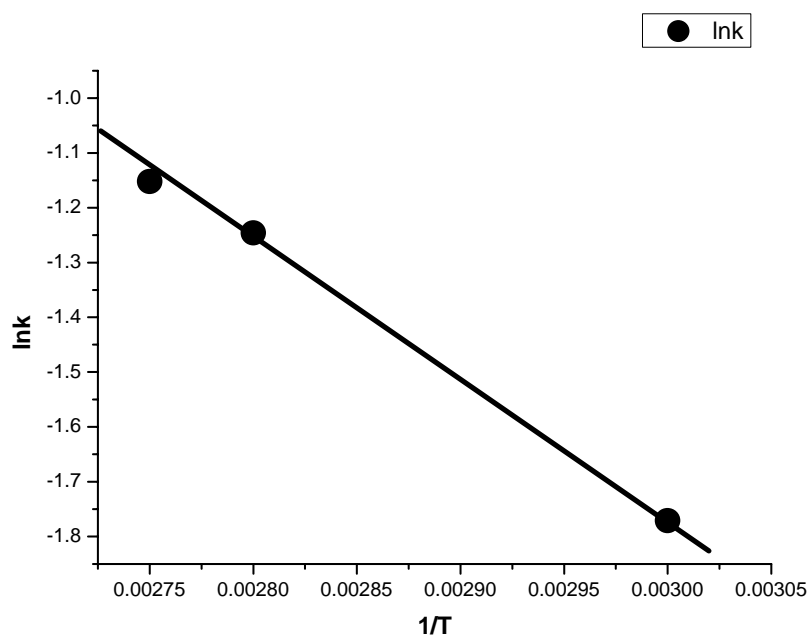
Since the reaction is found to be pseudo unimolecular, the intrinsic rate constants in the units of ( $\text{min}^{-1}\text{m}^{-2}$ ) was determined for each catalyst using the formula,

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

The kinetic parameters ( $E_a$  and the frequency factor  $A$ ) were evaluated from the ethyl benzene conversion values in the temperature range 60-90°C, assuming the diffusion and mass transfer effects were insignificant. Rate constant  $k$  is calculated for the reaction at different temperatures using CeCr (10%) catalyst under the same reaction conditions. Based on the Arrhenius equation,  $k = A \exp(-E_a/RT)$  using 'slope and intercept' of Arrhenius plot, the frequency factor  $A$  and the activation energy  $E_a$  were evaluated as  $15.3 \times 10^8(\text{kg of catalyst})^{-1} \text{ h}^{-1}$  and 21.37 kJ/mol, respectively.

$$\Delta H^\ddagger = E_a - RT = 18.52 \text{ kJ/mol}$$

$$\Delta S^\ddagger = R [\ln A - \ln(kT/h) - n] = -206.4 \text{ J/mol/K}$$



**Fig.6.7** Arrhenius plot with CeCr (10%) as the catalyst

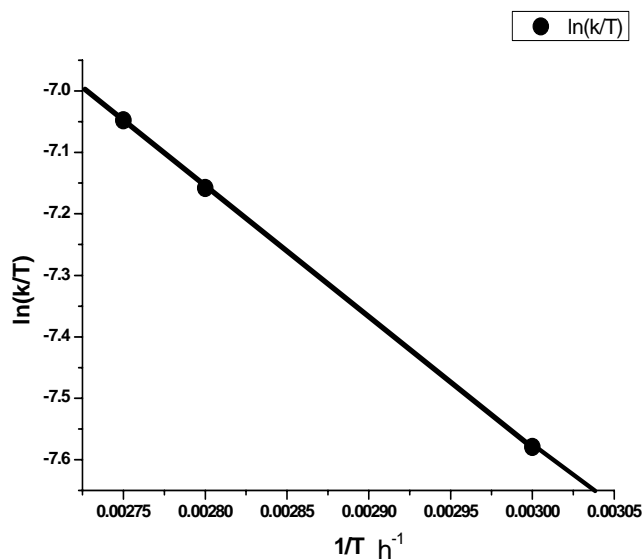


Fig.6.8 Eyrings plot with CeCr (10%) as the catalyst

Table 6.5 Values of different kinetic parameters

Kinetic parameters	Values
Activation energy $E_a$	21.37 kJ/mol
Frequency factor A	$15.3 \times 10^8 \text{ (kg of catalyst)}^{-1} \text{ h}^{-1}$
Enthalpy of activation $\Delta H^\ddagger$	18.52 kJ /mol
Entropy of activation $\Delta S^\ddagger$	- 206.4 J/Mol /K

## 6.6 Conclusions

The present study on liquid phase oxidation of ethyl benzene can be summarized as given below.

- 1) Ethyl benzene can be oxidized effectively using mesoporous ceria modified catalyst using TBHP in liquid phase to get acetophenone selectively as the major product.

- 2) Reaction variables like temperature, weight of catalyst, time, solvent and volume of the solvent have predominant effect on the % conversion and selectivity to acetophenone.
- 3) Chromium, manganese and copper doped catalysts have more activity in the reaction and product selectivity. For the effective catalyst Cr doped ceria, the metal loading has pronounced influence on % conversion and selectivity.
- 4) These catalysts can replace the more hazardous, stoichiometric catalysts as these are regenerable and reusable.
- 5) Transition metal-incorporated mesoporous materials have proved to be potential catalysts in the oxidation of alkyl arenes to carbonyl compounds. The reactions were found to be extremely sensitive to the oxidant and solvents used. Mesoporous ceria materials appeared to be promising acid and redox catalysts and were also successfully applied as supports for active sites.
- 6) The reaction is proved to be following first order kinetics with ethyl benzene conversion with the frequency factor  $A$  and the activation energy  $E_a$  evaluated as  $15.3 \times 10^8 \text{ (kg of catalyst)}^{-1} \text{ h}^{-1}$  and  $21.37 \text{ kJ/ mol}$  respectively for (CeCr10%). catalyst. The kinetic parameters like  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$  of activation for the reaction are calculated.



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