

Selective Oxidation of Ethylbenzene Using Hydrotalcite-like Compounds as Catalysts

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Received: April 19, 2026

Published: October 08, 2026

ABSTRACT

Oxidation of ethylbenzene in a liquid-phase was tested with unique hydrotalcite-type materials serving as catalysts, the reaction proceeds without the need for an acid, with tert-butyl hydroperoxide (TBHP) acting as the oxidizing agent. Hydrotalcite (HTLc) versions with cobalt have demonstrated significant catalytic activity and remarkable selectivity for producing acetophenone. The effects of key reaction parameters, including temperature, catalyst loading, ethylbenzene concentration, and TBHP amount, on the conversion and product distribution were systematically investigated. The catalytic activity and product selectivity were strongly influenced by the metal composition and relative abundance of metal ions within the HTLc structure, as well as by the solvent and reaction conditions. Among the investigated catalysts, Co-Al-HTLc exhibited the most favorable catalytic performance, affording acetophenone selectivity above 93% with reasonable ethylbenzene conversion under optimized conditions. The Co-Al-HTLc catalyst also demonstrated good structural stability and could be reused, while the cobalt species remained predominantly in the Co(II) oxidation state throughout the reaction. These results demonstrate the potential of Co-Al-HTLc as a robust heterogeneous catalyst for the selective oxidation of ethylbenzene to acetophenone using TBHP.

Keywords: Acetophenone, Cobalt, Catalyst, Ethylbenzene, Hydrotalcite, Oxidation, TBHP

INTRODUCTION

Aromatic ketones hold significant importance in synthetic chemistry, functioning as intermediates in the production of fragrances and pharmaceuticals [1,2]. Conventional pathways for the industrial synthesis of aromatic ketones are based on Friedel-Craft's acylation of aromatic compounds with acid halides or acid anhydrides, employing stoichiometric amounts

of anhydrous aluminum chloride or homogeneous acid catalysts. This process produces large volumes of extremely toxic and dangerous corrosive wastes and hard to dispose [3,4]. The synthesis of aromatic ketones through the oxidation of benzylic methyl groups has been extensively investigated using stoichiometric quantities of strong oxidants. The commonly used oxidants includes potassium permanganate, selenium dioxide, chromium trioxide supported on silica ($\text{CrO}_3\text{-SiO}_2$), and potassium permanganate supported on montmorillonite K ($\text{KMnO}_4/\text{Mont-K}$) [5-7]. These reactions generate substantial quantities of inorganic salt waste, and the separation and isolation of the desired products from the unreacted substrate present significant challenges. Recently, attention shifted toward in generating cheaper and environmentally friendly catalytic methods for the benzylic oxidation of alkylaromatics to produce most valuable compounds such as ketones [8-11].

Acetophenone (Acph) serves as a one of the key intermediates in the fragrance, pharmaceutical, and drug industries. This compound can be synthesized through the ethylbenzene air oxidation in a liquid-phase, utilizing soluble cobalt, copper, iron or manganese compounds as a catalyst in presence of acetic acid as the solvent [12]. Although only minimal quantities of metal compounds serve as catalysts, the process frequently requires stringent conditions. The selectivity for the ketone remains limited, in addition to the primary catalyst a corrosive promoters, including bromide ions, are required. The recovery and reapplication of the catalyst involve complicated and expensive steps, further hindered by the formation of viscous, sticky byproducts. In production contexts, the expenses related to metallic catalysts require approaches that allow for simpler extraction, purification, and repeated use. The high operational requirements frequently compromise efficiency, even with low catalyst loading. For that reason, a lot of study has been done on catalyst poisoning for ethylbenzene oxidation, catalyst recovery, and heterogenization of transition metal catalyst systems. Most studies focused on using tertiary butyl hydrogen peroxide (TBHP) to oxidize ethylbenzene in liquid form using soluble and supported metal catalysts of cobalt, copper, nickel, tin and vanadium [13-21].

Heterogenized cobalt catalysts, such as cobalt oxide supported on mesoporous carbon nitride is the most successful [14]. Surprisingly, when TBHP is used as the oxidant, chromium-doped aluminophosphate materials as catalyst to produce ketones from alkyl arenes with high selectivity [22]. It has also been demonstrated that manganese counterparts of similar

systems may accelerate the oxidation of alkanes using TBHP [18,23-24].

Metal oxides along with layered double hydroxides - also known as hydrotalcites - have drawn notable interest because they can act as full catalysts, supports for catalytic materials, or agents that exchange ions [25-32]. This growing interest is driven by three main factors: first, these materials composed by two- and three-charged cations, capable of isomorphic substitutions; second, those metals spread evenly at nearly atomic levels; third, when heated, they turn into stable blends of oxides boasting large surface areas. The initial two characteristics are attributed to the precursor, while the final characteristic seems to be associated with the decomposition mechanism [33]. Although the oxidation of ethylbenzene to value-added oxygenated products, is an important transformation many reported catalytic systems suffer from limitations such as moderate conversion, limited selectivity toward the desired product, use of expensive or environmentally less desirable catalysts, and difficulties associated with catalyst separation and reuse. Furthermore, the relationship between the composition, basicity, and catalytic performance of hydrotalcite-like compounds (HTLcs) in ethylbenzene oxidation has not been sufficiently explored.

This research provides an in-depth analysis of the synthesis, characterization, and evaluation of various transition metals containing HTLcs as catalysts like cobalt, copper, nickel, and iron - used for the ethylbenzene oxidation to acetophenone in the liquid phase with TBHP serving as the oxidant [34]. The study examined the impact of the concentrations of ethylbenzene, catalyst, and oxidant on both activity and selectivity at temperatures ranging from 303 to 353 K. Among tested catalysts, cobalt-aluminum hydrotalcites stood out during trials. This catalyst achieves a high conversion rate of ethylbenzene, over 80% of ethylbenzene transformed while more than 96% selectivity for acetophenone emerged when operating at just 333 K. This work could be instrumental in enhancing the understanding of HTLcs as catalysts for the oxidation of ethylbenzene using TBHP as an oxidizing agent. Performance stayed strong even without extreme conditions. Observations suggest structural features of these layered solids help drive selective oxygen transfer. Insights gathered here add clarity on why such catalysts behave the way they do during alkane activation processes. Understanding their behavior may guide future designs involving similar redox systems.

EXPERIMENTAL

Chemicals

Metal salts such as $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ were acquired from Merck India Ltd. From S.D. Fine Chemicals NaOH and Na_2CO_3 were purchased. Various solvents such as acetonitrile, ethanol, ethyl acetate, methanol, N-Methyl-2-Pyrrolidone, tert-butanol, and others were sourced from Merck India Limited. Ethylbenzene and alternative forms of ethylbenzene also arriving from the same source.

Synthesis of Hydrotalcite (HTlcs)

As documented in prior literature, HTlcs form through co-precipitation technique when pH and temperature stay constant, provided supersaturation remains low [30]. The assembly used involves a three-neck round-bottom flask submerged in an oil bath attached with mechanical stirrer and pressure-equalizing dropping funnel and thermometer. An aqueous solution containing metal nitrates, such as $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in the desired molar ratio ($x = \text{Al}^{3+}/(\text{Co}^{2+} + \text{Al}^{3+}) = 0.25$) with a total cation concentration of 1.5 M. This solution was gradually mixed at 25°C with vigorous agitation with an alkaline solution of $\text{Na}_2\text{CO}_3/\text{NaOH}$, maintaining a carbonate concentration in the molar $\text{CO}_3^{2-}/\text{Al}^{3+}$ ratio of two. The pH of the mixture was kept at 9.5 by adjusting the rate of addition of the alkaline solutions. After this addition, the slurry underwent aging at 338K for 18 hours with gentle stirring. A reflux condenser was positioned on the vessel top to prevent the evaporation of water. The material in the slurry form was cooled to room temperature, filtered, washed with hot (303K) deionized water to remove the Na^+ , and subsequently dried at 90°C for a period of 12 hours.

Experimental Procedure for Oxidation Reaction

A 100 ml jacketed stirred glass reactor was used for all liquid phase oxidation reactions. A thermowell, sample port, overhead stirrer, and heating arrangement were all included in the reactor. A thermostat was used to maintain the reaction temperature, and a separate controller was used to control the agitation speed. Typically, the reactor was charged with a set amount of ethylbenzene (0.69 kmol/m^3); alongside tert-butyl hydroperoxide (2.1 kmol/m^3), both in solution. In every experiment, the reaction mixture's total volume was maintained at 50 ml ($5 \times 10^{-5} \text{ m}^3$). Samples were taken out for GC analysis prior to the commencement of the reaction.

The reactor containing the reaction mixture was charged with a measured quantity of powdered HTlc as a catalyst (2.2 kg/m^3) at the appropriate temperature. The reaction commenced with the adjustment of the agitation to a predetermined value. Samples were gathered at consistent intervals and analyzed through gas chromatography. After a specific time, the reaction was stopped and the contents of the reactor were cooled to normal temperature.

Catalyst Recycle Procedure

Once the oxidation experiment ended the obtained reaction mixture was cooled to room temperature and permitted to stand for 30 minutes to facilitate settling of the catalyst. Once the fine catalyst had fully settled at the bottom of the reactor, the supernatant liquid was meticulously drained off. The recovered catalyst was then washed by soaking in methanol, which was subsequently removed by careful siphoning to avoid catalyst loss. This washing procedure was conducted two times. Thereafter, the catalyst was dried under reduced pressure at 313 K, followed by further drying in an oven at 363 K for 12 hours. The dried catalyst was subsequently utilized again in the recycling experiment. The methodology for the recycling experiments was kept the same as that used in the standard oxidation experiment.

Analytical Methods

Infrared spectra were obtained using a Bio-Rad FTS 175C spectrometer in transmission mode, employing KBr pellets and liquid cells. Meanwhile, gas chromatography-mass spectrometry analyses were conducted on an Agilent 6890N unit, which was coupled with a 5973N mass-selective analyzer for detailed output.

The analysis of liquid samples was conducted using a Hewlett-Packard 6890 Series gas chromatograph fitted with an autosampler. This setup runs on software called HP-ChemStation. Separation was performed on an HP-1 capillary column thirty meters long with a 0.32-millimeter inner diameter and 0.25 micrometers of film thickness of a polymethyl siloxane stationary phase. The oven temperature was set to increase from 333 to 573 K while maintaining a constant column pressure of 10 psi.

Calibration curves constructed over the relevant concentration ranges were used to perform quantitative analysis. The calculation of percentage conversion was based on the initial amount of liquid substrate charged. Total aldehyde selectivity was determined by summing the selectivities of both linear

and branched aldehyde products. Estimation of amount of ethylbenzene, acetophenone, and 1-phenylethanol (PE) was carried out using their respective calibration curves.

The performance of the catalyst was evaluated with respect to conversion, selectivity,

turnover number (TON), and turnover frequency (TOF) by using following equations (eq. 1-4).

$$\text{Conversion (\%)} = \frac{\text{Initial ethylbenzene concentration} - \text{Final ethylbenzene concentration}}{\text{Initial ethylbenzene concentration}} \times 100 \quad (\text{eq1})$$

$$\text{Selectivity}_{\text{acetophenone}} (\%) = \frac{\text{Number of moles of acetophenone formed}}{\text{Number of moles of ethylbenzene converted}} \times 100 \quad (\text{eq2})$$

$$\text{TON} = \frac{\text{Number of moles of oxidation products formed}}{\text{Number of moles of catalyst}} \quad (\text{eq3})$$

$$\text{TOF (h}^{-1}\text{)} = \frac{\text{Number of moles of oxidation products formed}}{\text{Number of moles of catalyst} \times \text{time in hours}} \quad (\text{eq4})$$

TBHP Consumption Analysis: The consumption of TBHP in a typical reaction was determined by estimating the amount of unreacted oxidant using an iodometric titration method. The procedure was adapted from a literature-reported method with minor modifications [25].

An aliquot (20 mL) of the reaction mixture was gradually introduced into a solution of KI, which had been prepared in 10 mL of 2 N sulfuric acid within a sealed conical flask. The resulting mixture was permitted to sit for 15 minutes to ensure complete liberation of iodine. Afterward, distilled water (100

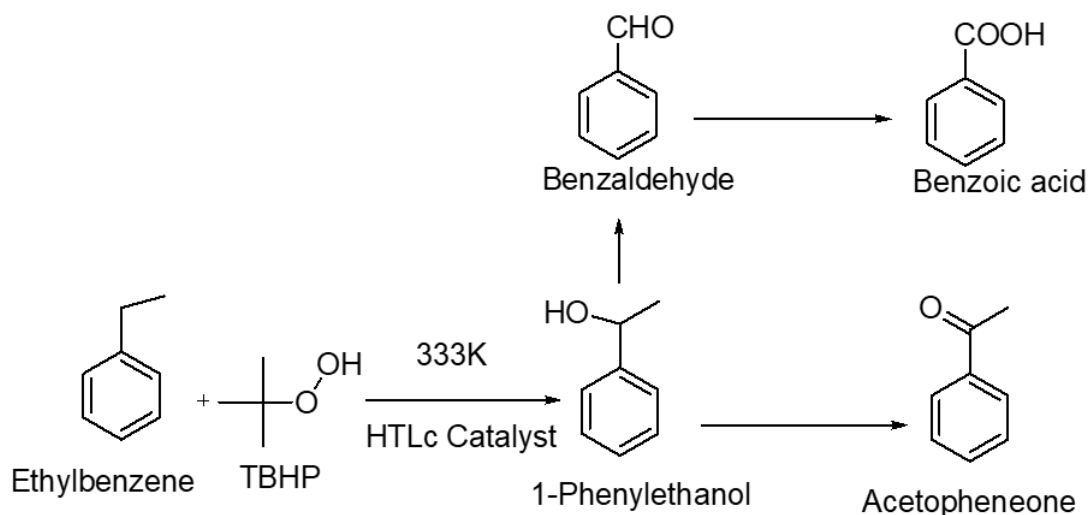
mL) was introduced, ensuring that the walls of the flask were thoroughly rinsed. The liberated iodine was subsequently titrated against a standard solution of 0.1 N sodium thiosulfate. Close to the endpoint, 2 mL of starch solution was introduced as an indicator, and the titration proceeded until the blue color vanished, signifying the endpoint. A blank experiment was carried out under equivalent conditions. In order to achieve accurate results, the volume of thiosulfate used in the blank was subtracted from the volume in the reaction mixture. The quantity of unreacted TBHP in the reaction mixture was determined using the following relationship (eq5):

$$1 \text{ mL of } 1 \text{ N Na}_2\text{S}_2\text{O}_3 \equiv 0.09 \text{ g of TBHP.} \quad (\text{eq5})$$

RESULTS AND DISCUSSION

Characterization tools like XRD, SEM, XPS, FTIR, TGA- DTA and surface analysis were applied to examine the synthesized hydrotalcite like materials. These findings support the formation of the hydrotalcite-like structure of the synthesized material. (see supporting information). Findings of these analyses were lined up well with similar studies noted previously in the literature [35-38]. In the liquid phase oxidation

of ethylbenzene, 1-phenyl ethanol (PE) is formed, which is further oxidized to yield acetophenone. The intermediate alcohol (PE) is subjected to additional oxidation, resulting in another product. For many known catalyst systems, the selective synthesis of acetophenone poses a significant challenge, as the generation of byproducts like benzaldehyde and benzoic acid compromises selectivity. Scheme 1 depicts the ethylbenzene oxidation in the liquid phase.



Scheme 1: Schematic representation of the ethylbenzene oxidation in the liquid phase.

The ethylbenzene oxidation in liquid phase was studied with 70% TBHP (aq) as the oxidant and non-noble metal containing HTLcs as catalysts. The important goals of the work are synthesis of HTLcs that contains non-noble transition metals along with their complete spectroscopic characterization and its further application for oxidation of ethylbenzene have been successfully met through experimentation, and the findings are presented for discussion.

Evaluation of Hydrotalcite (HTLcs)

The non-catalytic ethylbenzene oxidation with TBHP was first executed as a control experiment. A negligible amount of ethylbenzene conversion (0.9%) was recorded, with approximately 50% selectivity for acetophenone. Following this, an experiment was performed utilizing basic Mg-Al-HTlc as a catalyst. The hydrotalcite demonstrated slight catalytic activity, resulting in a merely 2.9% of ethylbenzene conversion and a selectivity of 69% for acetophenone. The reported selectivities are based on the quantified products, and that the difference from 100% is attributed to unidentified or unquantified products. Subsequently, evaluation of HTLcs featuring various M(II)-M(III) metal blends, for example cobalt, copper, iron, nickel, and zinc, was performed.

The outcomes of the catalyst screening were evaluated with regard to conversion of ethylbenzene and selectivity towards acetophenone as shown in Table 1. The results showed that Co-HTlc provided the maximum selectivity for acetophenone under identical reaction conditions. Apart from the all tested HTLcs the noticeable performance was obtained using Mg-Al-Fe giving 14.3% activity while Cr-Zn closely at 18.3% activity levels with reasonably lower acetophenone selectivity (around 80%) (Entry 7 and 8). It is believed that this reaction involves the development of acetophenone via a stepwise oxidation mechanism in which 1-phenylethanol (PE) is an intermediate. Furthermore, it has been noted that benzaldehyde is generated as a by-product in this reaction which might be subsequently oxidized to benzoic acid.

In this investigation, benzaldehyde and benzoic acid were produced as byproducts in the presence of nickel-containing HTLcs (Ni-Fe, Ni-Cr and Ni-Al), but in low amounts (Entry 3, 4 and 5). The introduction of cobalt into HTLcs improved both the activity and selectivity of ethylbenzene oxidation in the liquid phase (Entry 10, 11 and 12). The highest catalytic performance was achieved when the reaction was performed with Co-Al HTLcs, which gave rise to a high ethylbenzene conversion (43.9%) and a high selectivity 92.7% towards acetophenone.

Table 1: Evaluation of hydrotalcite for the ethylbenzene oxidation in the liquid phase

Entry	HTlcs	Conversion of Ethylbenzene, %	Selectivity, %			
			Acph	PE	BzH	BAc
1	Non-cat	0.9	50.0	35.0	8.0	3.0
2	Mg-Al	2.9	69.0	26.0	2.0	1.0
3	Ni-Fe	5.9	70.0	25.0	3.0	2.0
4	Ni-Cr	11.3	73.0	22.0	4.0	1.0
5	Ni-Al	12.4	84.0	10.0	2.0	1.0
6	Cu-Cr	11.2	80.2	12.3	4.0	1.5
7	Mg-Al-Fe	14.3	85.0	12.0	2.0	1.0
8	Cr-Zn	18.3	76.0	19.0	3.0	1.0
9	Mg-Al-Cu	13.8	74.0	18.0	5.0	3.0
10	Co-Cr	17.3	86.4	9.3	3.0	1.0
11	Co-Fe	27.6	88.0	9.0	2.0	1.0
12	Co-Al	43.9	92.7	6.9	0.6	0.0

Reaction Parameters: Ethylbenzene= 0.69 kmol/m³; TBHP= 2.1 kmol/m³; catalyst=2.2 kg/m³; Solvent= t-Butanol; T= 333K; time=3 h; Stirring speed= 16.7 Hz; Total volume =5 x 10⁻⁵ m³, Acph =Acetophenone, PE=1-phenylethanol, BzH=benzaldehyde, BAc= Benzoic acid.

Optimization of the Reaction Conditions

To optimize the concentrations of the reaction components, the effect of numerous reaction parameters on the behavior of the reaction was studied. To do this, the influence of catalyst concentration, Co-Al-HT (22% Co; Co:Al = 2), was primarily studied. The findings are outlined in Table 2. It was determined that the conversion of ethylbenzene increased linearly with the rise in Co-Al-HT concentration up to 3 kg/m³ (entries 1-4).

A significant selectivity of 92.5% for Acetophenone was noted at a conversion level of 24.4% for ethylbenzene (entry

2). Nevertheless, at increased catalyst concentrations, the selectivity towards acetophenone was negatively influenced, as evidenced by the formation of benzaldehyde and benzoic acid (entry 4). An increase in the reaction rate was detected with a higher concentration of ethylbenzene (entries 5, 6). Additionally, the production of 1-phenyl ethanol was higher with an increase in concentration of ethylbenzene. Multiple reactions were performed to streamline concentration of TBHP (entries 8-10), and an increase in conversion was noted up to 24.4 % at ethylbenzene: TBHP ratio of 1:3 (entry 2).

Table 2: Refinement of reaction parameters for ethylbenzene oxidation in liquid phase

Entry	Co-Al HTLc, kg/m ³	Ethylbenzene Conversion, %	Selectivity, %				Rate x 10 ⁵ , kmol/m ³ /s
			Acph	PE	BzH	BAc	
1	0.7	11.6	87.0	11.5	0.1	0.0	1.5
2	1.7	24.4	92.5	6.9	0.0	0.0	3.1
3	3.0	33.6	91.3	5.3	1.2	0.0	4.3
4	4.5	34.4	92.6	7.2	2.5	1.8	4.4
5 ^a	1.7	32.1	93.2	5.4	0.0	0.0	2.1
6 ^b	1.7	12.3	86.2	10.4	1.7	0.9	3.4
7 ^c	1.7	07.6	86.2	10.4	1.7	0.9	3.5
8 ^d	1.7	13.6	90.4	9.1	0.0	0.0	1.7
9 ^e	1.7	16.7	92.1	7.8	0.0	0.0	2.1
10 ^f	1.7	25.1	91.8	5.3	1.2	0.8	3.2

Reaction Parameters: Ethylbenzene=0.69 kmol/m³; TBHP=2.1 kmol/m³; Solvent= t-Butanol; T=, 333K; time= 1.5 h; Stirring speed= 16.6 Hz; Total volume = 5 x 10⁻⁵ m³; a ethylbenzene=0.5 kmol/m³; b ethylbenzene= 1.5 kmol/m³; c ethylbenzene=, 2.5 kmol/m³; d TBHP= 1 kmol/m³; e TBHP= 2 kmol/m³; f TBHP=4 kmol/m³.

Effect of Co: Al Ratio on Ethylbenzene Oxidation

Considering that Co-Al-HT operates as a bulk catalyst, it was anticipated that the quantity of cobalt and its distribution within the solid matrix would lead to differing catalytic activities for the TBHP-based oxidation. In order to investigate the influence of cobalt dispersion in hydrotalcite, several experiments were conducted with Co-Al-HTlcs featuring various Co:Al ratios (Table 3). The findings demonstrated that the ethylbenzene conversion increases with Co:Al ratio of 2, while a Co:Al ratio

of 3 did not show any significant improvement in catalytic activity. As a result, further investigations were undertaken precisely with a Co:Al ratio of 2 using Co-Al HTlc as catalyst. Further properties, including BET surface area, pH and basicity of Co-Al HTlcs, were also examined by the technique to those utilized by Jana and associates [40]. The findings from these studies are presented in Table 4. The surface areas of the hydrotalcites exhibited minor variations, with hydrotalcites having a lower Co:Al ratio displaying larger surface areas.

Table 3: Impact of Co-Al ratio on the oxidation of ethylbenzene

Entry	Co/Al	Ethylbenzene Conversion, %	Selectivity, %			
			Acph	PE	BzH	BAC
1	0.5	11.2	92.6	7.2	0.0	0.0
2	1	16.3	91.3	8.0	0.0	0.0
3	2	24.4	92.5	6.9	0.0	0.0
4	3	25.6	92.8	4.3	1.1	0.9

Reaction Parameters: Ethylbenzene= 0.69 kmol/m³; Cobalt=0.37 kg/m³; TBHP=2.1 kmol/m³; Solvent= t-Butanol; T=333K; time= 1.5 h; Stirring speed= 16.6 Hz; Total volume= 5 x 10⁻⁵ m³

Table 4: Characteristics of Co-Al Hydrotalcite (HTlc)

Entry	Co:Al	XRD phases	Surface area, m ² -gm ⁻¹	Pore volume, ml gm ⁻¹	pH of suspension in water ^a	μmol basic sites/ gm HTlc Basicity ^b
1	3	hydrotalcite	47.31	0.07	8.7	27.7
2	2	hydrotalcite	58.69	0.19	8.2	26.7
3	1	hydrotalcite	74.43	0.18	7.8	25.9

^a solution comprising 0.3 grams of hydrotalcite in 20 milliliters of deionized water

^b A suspension of 0.15 grams of hydrotalcite in 2 milliliters of phenolphthalein indicator solution was titrated using 0.01M benzoic acid.

Influence of Solvents

At 333K, the influence of various solvents was investigated in presence of Co-Al HTlc catalyst and the results are presented in Table 5. Results showed that there is strong correlation between experimental findings and the solvent polarity. The results indicated that solvents with lower polarities promoted

the ethylbenzene conversion. Among the solvents tested, ethyl acetate was identified as the most suitable solvent; however, it demonstrated reactivity under experimental conditions applied and hence excluded for further investigations. Tert-butyl alcohol was found to be the most efficient non-participating solvent, resulting in 24.4% ethylbenzene conversion with 92.3% selectivity for acetophenone.

Table 5. Evaluation of solvents for ethylbenzene oxidation the liquid phase

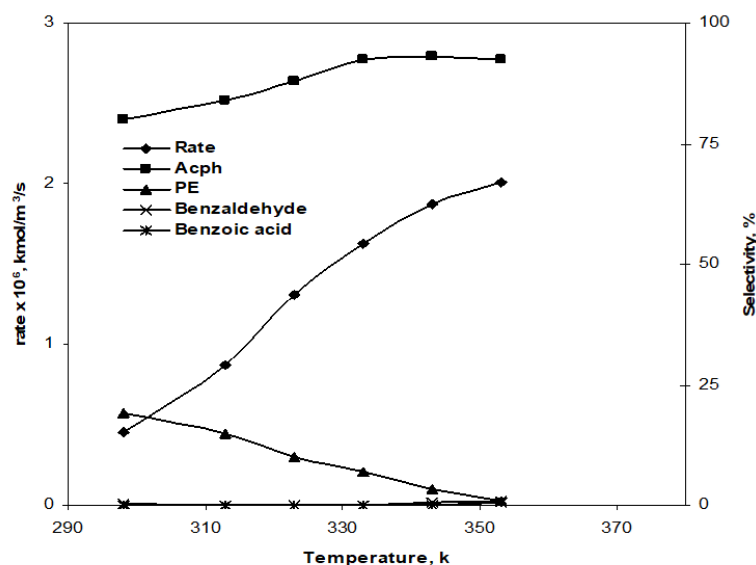
Entry	Solvents	Dielectric constant	Ethylbenzene Conversion, %	Selectivity, %				Rate x 10 ⁶ , kmol/m ³ /s
				Acph	PE	BzH	BAc	
1	EtOAc	6.02	26	92.8	6.9	0.0	0.0	1.73
2	t-BuOH	18	24.4	92.5	6.9	0.0	0.0	1.63
3	MeOH	33	15.3	89.2	7.9	0.5	0.1	1.02
4	NMP	32.4	11.9	88.0	8.3	0.3	0.0	0.79
5	EtOH	24.3	10	81.1	12.0	0.1	0.0	0.67

Reaction Parameters: Ethylbenzene=0.69 kmol/m³; TBHP= 2.1 kmol/m³; catalyst= 1.7 kg/m³; Solvent= t-Butanol; T=333K; time, 1.5 h; Stirring speed= 16.6 Hz; Total volume= 5 x 10⁻⁵ m³

Influence of Temperature

The temperature had a considerable impact on the Co–Al hydrotalcite-like compound (Co–Al HTlc) catalyzed oxidation of ethylbenzene in a liquid phase. A turnover frequency (TOF) of 82 h⁻¹ was noted at 303 K, with no indication of catalyst deactivation occurring. Increasing temperature in the range of 303 K to 343 K using Co–Al-HTlc catalyst system resulted in a substantial rise in conversion (illustrated in Figure 1).

Simultaneously, the rise in conversion levels improved the acetophenone selectivity while diminishing the PE selectivity. Temperature range was 303–333 K identified as the optimum for the reaction. A notable ethylbenzene conversion of 24.4% was achieved at 333 K, with a 92.5% selectivity towards acetophenone at this temperature. No significant enhancement in the conversion of ethylbenzene or the selectivity for acetophenone was noted beyond 333 K; therefore, additional investigation was carried out at 333 K.

**Figure 1:** Influence of temperature on oxidation of ethylbenzene.

Reaction Parameters: Ethylbenzene= 0.69 kmol/m³; TBHP= 2.1 kmol/m³; catalyst= 1.7 kg/m³; Solvent=t-Butanol; time, 1.5 h; Stirring speed=16.6 Hz; Total volume= 5 x 10⁻⁵ m³

Screening of Alkylbenzenes

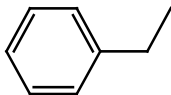
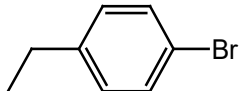
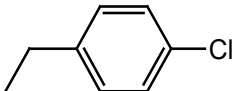
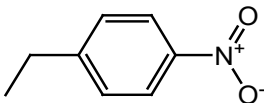
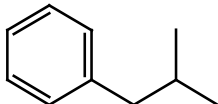
As illustrated in Table 6, the conversion of alkylbenzenes is predominantly high across various instances. In every scenario, the –CH₂– moiety of alkylaromatics is preferentially transformed into the –CO– group, which signifies a notable level of chemoselectivity during the oxidation process. The

properties of the substituent are essential in determining the oxidation product yield. It is evident that alkylbenzenes with electron-rich substituents on the ring enhance the oxidation process, whereas those with electron-withdrawing substituents lead to diminished conversions of the alkyl group into the respective ketone. For instance, the rates of conversion are favorable for ethylbenzene and isobutylbenzene; however,

ethylbenzenes that possess ring-deactivating substituents such as Br, Cl, or NO₂⁻ exhibit reduced conversion levels. These findings align with the research conducted by S. K. Jana and colleagues, [39] who have clearly noted the impact of substituent nature on the oxidation of alkylbenzenes in liquid-phase utilizing a heterogeneous Mn-containing hydrotalcite catalyst.

The findings of this study indicate that only the benzylic C–H bonds in alkylaromatics participate in oxidation, producing their respective ketones with a notable degree of selectivity, while minimal quantities of alcohols are also observed.

Table 6: Evaluation of alkylbenzene for liquid phase oxidation

Entry	Alkylbenzene	Conversion, %	Aryl ketone	Aryl alcohol	Rate x 10 ⁵ , kmol/m ³ /s
1		24.4	92.5	6.9	3.1
2		10.6	89.4	10.8	1.4
3		8.2	86.3	13.7	1.0
4		1.2	90.2	7.8	0.2
5		29.5	93.8	6.2	1.9

Reaction Parameters: Alkylbenzene= 0.69 kmol/m³; TBHP= 2.1 kmol/m³; catalyst= 1.7 kg/m³; Solvent= t-Butanol; T= 333K; time= 1.5 h; Stirring speed= 16.6 Hz; Total volume= 5 x 10⁻⁵ m³

Recycle Study for Catalyst

While Co-Al-HTlc showed remarkable effectiveness in the ethylbenzene oxidation and displayed significant selectivity for acetophenone, it was important to ensure that active catalyst component does not leach into the reaction solvent. A significant advantage of heterogeneous catalysts is their reusability, which would be compromised if cobalt were to leach from the hydrotalcite. Consequently, recycling experiments were conducted to assess the ability to reuse Co-Al-HTlc catalyst. The findings are illustrated in Figure 2.

It has been observed that the catalyst retains its effectiveness in the conversion of ethylbenzene and the selectivity for acetophenone for a minimum of four recycling cycles. Moreover, various spectroscopic evaluations of both the fresh and recovered Co-Al-HTlc indicate that the oxidation state of cobalt (Co²⁺) remains consistent, along with the crystallinity of the hydrotalcite material, as evidenced by the XRD and XPS spectral analyses of the catalysts. The SEM images further support this finding, showing no changes in the morphology or size of the crystallites of hydrotalcite.

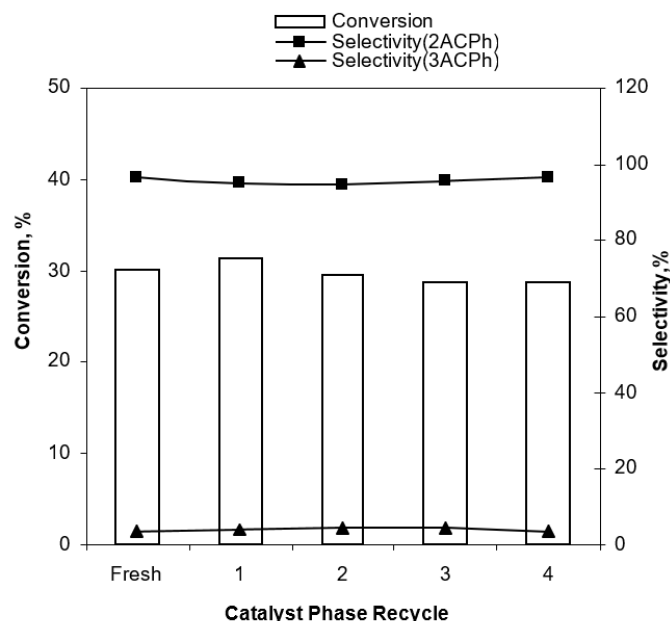


Figure 2: Investigation into the recycling of Co-Al-HTlc for the purpose of ethylbenzene oxidation.

Reaction Parameters: Ethylbenzene= 0.69 kmol/m³; catalyst=1.66 kg/m³; TBHP=2.1 kmol/m³; Solvent= t-Butanol; T= 333K; time= 1.5 h; Stirring speed= 16.6 Hz; Total volume= 5 x 10⁻⁵ m³

Although the recycling experiments provide insights into reusability, it was also vital to verify that the filtered liquid reaction mixture should not contain any soluble cobalt (through leaching), could potentially act as a catalyst for the oxidation process. This research was conducted for the ethylbenzene oxidation through two equivalent experiments, during which concentration-time profiles were generated by taking periodic samples and examining the liquid samples using GCMS. In one of the experiments, the reaction mixture was cooled after a reaction 2 hours of reaction time, followed by filtration through Whatman filter paper No. 1 to remove all hydrotalcite. Following this, fresh TBHP and ethylbenzene were introduced, and the reaction was continued under the same temperature and stirring speed.

Figure 3 illustrates the concentration-time profiles for both sets of experiments. It is evident that the ethylbenzene conversion entirely halted in the experiment where the catalyst was removed, coinciding with the moment the solid catalyst was extracted. To further validate this observation, the reaction mixture was concentrated and analyzed using atomic absorption spectroscopy (AAS) to detect the amount of cobalt. The analysis revealed minimal 2 ppm leaching of cobalt which is 0.1% of the initially charged amount of cobalt into the reaction mixture. These findings validate that there is no major cobalt leaching during the Co-Al-HT catalyzed ethylbenzene oxidation with TBHP as the oxidant, establishing itself as a robust, reusable, and effective catalyst.

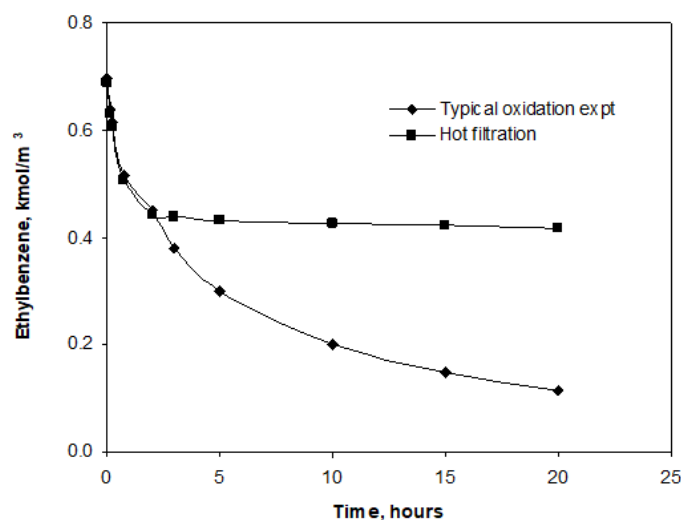


Figure 3: Hot filtration testing conducted to ascertain the reusability of the Co-Al-HT catalyst.

Reaction Parameters: Ethylbenzene= 0.69 kmol/m³; catalyst=1.66 kg/m³; TBHP=2.1 kmol/m³; Solvent= t-Butanol; T= 333K; time= 1.5 h; Stirring speed= 16.6 Hz; Total volume= 5 x 10⁻⁵ m³

CONCLUSIONS

Hydrotalcite-like compounds (HTLcs) that contain transition metals act as highly effective and recyclable heterogeneous catalysts for ethylbenzene oxidation to acetophenone, utilizing TBHP as the oxidizing agent in the liquid-phase. Characterization of these catalysts was performed through various spectroscopic and chemical methods to reveal their morphological and chemical characteristics both prior to and following the reaction.

The research further validated the thermal stability of the catalyst under the experimental conditions applied during the ethylbenzene oxidation. The produced HTLcs demonstrated varying catalytic efficiencies in the oxidation of ethylbenzene using TBHP as the oxidizing agent; Co-Al-HT was recognized as the most efficient catalyst in terms of conversion of ethylbenzene up to 24.4% under optimized experimental conditions and 92.4% selectivity towards acetophenone. The influence of substituent characteristics on the liquid-phase oxidation of various alkylbenzenes was examined. Catalyst recycling studies revealed that the Co-Al-HTlc catalyst retains its activity for ethylbenzene conversion and acetophenone selectivity through four cycles. This reveals that catalyst is robust and reusable and cobalt remains in 2⁺ oxidation state throughout as demonstrated by XPS analysis.

ACKNOWLEDGEMENTS

Kalpendra B. Rajurkar extends his appreciation to the Council of Scientific and Industrial Research (CSIR), India, for the provision of a research fellowship. This research constitutes a part of the doctoral dissertation of Kalpendra B. Rajurkar.

AI Statement

Artificial intelligence (AI) tools were exclusively employed for basic grammar corrections and language enhancement during the preparation of this manuscript.

Conflict of Interest Disclosure

The authors affirm that there are no financial conflicts of interest associated to this study.

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