

Selective Synthesis of *p*-Hydroxybenzaldehyde by Liquid-Phase Catalytic Oxidation of *p*-Cresol

Chandrashekhar V. Rode, Mahesh V. Sonar, Jayprakash M. Nadgeri, and Raghunath V. Chaudhari*

Homogeneous Catalysis Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune - 411008, India

Abstract:

Liquid-phase oxidation of *p*-cresol over insoluble cobalt oxide (Co₃O₄) catalyst under elevated pressure of air gave 95% selectivity to *p*-hydroxybenzaldehyde, an important flavoring intermediate. The selectivity to *p*-hydroxybenzaldehyde could be enhanced by manipulating the concentrations of *p*-cresol, sodium hydroxide, and catalyst and the partial pressure of oxygen in such a way that the byproducts normally encountered in this oxidation process were eliminated or minimized significantly.

Introduction

p-Hydroxybenzaldehyde (PHB) is an important intermediate for the manufacture of vanillin, a widely used flavoring agent, trimethoxybenzaldehyde, various agrochemicals, and pharmaceuticals such as semi-synthetic penicillin, amoxicillin, and the antiemetic drug trimethobenzamide.^{1–3} *p*-Hydroxybenzaldehyde is also used as an additive for metal-plating brighteners, electroplating, and in perfumes and in liquid crystals.³ Conventionally, *p*-hydroxybenzaldehyde is synthesized by the following methods:

(i) saligenin process in which base-catalyzed reaction of formaldehyde with phenol gives *p*-hydroxybenzyl alcohol which is oxidized over platinum or palladium to give *p*-hydroxybenzaldehyde;³

(ii) Reimer–Tiemann process in which phenol reacts with chloroform and aqueous sodium hydroxide to give benzal chlorides, which are rapidly hydrolyzed by the alkaline medium to give salicylaldehyde as a major product and PHB as a byproduct;

(iii) classical method of oxidation of alkyl benzenes by using chromic acid or potassium permanganate.⁴

From an industrial point of view such methods have several disadvantages such as use of relatively expensive reagents generating large amounts of inorganic salts which cause serious effluent problems and inefficiency of these processes due to lower yields of the desired product PHB.

The liquid-phase autocatalytic oxidation of *p*-cresol has major advantages in minimizing the effluent disposal problems and improvement of the overall process economics as

well as the product quality. The process reported by Nishizawa et al.⁵ involves oxidation of *p*-cresol using soluble as well as heterogeneous cobalt-based catalysts which gave 70–90% conversion of *p*-cresol with a selectivity to PHB in the range of 60–70%. Thereafter, several attempts were made to produce *p*-hydroxybenzaldehyde with high conversion of *p*-cresol using cobalt chloride as the main catalyst.^{6–8} Recently, catalysts containing cobalt and/or some other metal such as Cu or Mn supported on molecular sieves, carbon, or resins have been reported for *p*-cresol oxidation.^{9–11} The preparation of such catalysts is either a multistep procedure or the cobalt metal leaches out under reaction conditions. It is also important to note that in almost all reports, *p*-cresol oxidation has been carried out under atmospheric conditions with a longer reaction time (8–16 h) using large excesses of catalyst (up to 8 mol %) and solvent methanol. The selectivity of PHB is affected due to the formation of side products such as *p*-hydroxybenzyl alcohol, *p*-hydroxybenzyl methyl ether (PHBME), *p*-hydroxybenzoic acid and tarry material.⁸ We thought that the formation of side products could be eliminated by enhancing the rate of oxidation and conversion of *p*-cresol as well as the intermediate *p*-hydroxybenzaldehyde using particularly higher partial pressure of oxygen. Therefore, the objectives of this work were (i) to assess the suitability of the insoluble tricobalt tetraoxide as a catalyst rather than soluble cobaltous chloride and (ii) to optimize reaction conditions under elevated pressure of oxygen. In this contribution, we demonstrate that Co₃O₄ is an excellent heterogeneous catalyst for *p*-cresol oxidation, which can be very easily separated and reused for subsequent cycles. The effects of various reaction parameters such as catalyst loading, substrate concentration, temperature, partial pressure of oxygen, solvent and base concentrations on the conversion of *p*-cresol, and selectivity of *p*-hydroxybenzaldehyde were also investigated. It was found that increase in substrate concentration (up to 24%) caused increase in PHB selectivity, while increase in partial pressure of oxygen led to a decrease in PHB selectivity. The catalyst turnover number (TON) was found to be much higher than that reported in the literature.

* To whom correspondence should be addressed. Fax: 91 20 25893260. E-mail: rvc@ems.ncl.res.in.

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Experimental Section

Materials. *p*-Cresol was supplied by Loba Chemie, while sodium hydroxide was obtained from Merck. Analytical grade methanol and cobalt oxide (Co₃O₄) were supplied by M/s SD Fine chemicals, Pune (India).

Experimental Setup. The oxidation reactions were carried out in a 300 cm³ capacity high-pressure Hastelloy reactor supplied by Parr Instruments Co., U.S.A. The reactor was connected to an air reservoir held at a pressure higher than that of the reactor. The pressure drop in the reservoir vessel (monitored using a transducer) was equivalent to the oxygen consumed; hence, the reactor was cooled, inert gas (N₂) was vented out, and the reactor was again pressurized by air after attaining the temperature. This procedure was repeated until the reaction was over as indicated by absorption of stoichiometric amount of oxygen. The initial rate of reaction was calculated in the region where change in partial pressure of oxygen was <0.13 MPa.

A Hewlett-Packard model 1050 liquid chromatograph equipped with an ultraviolet detector was employed for the analysis. HPLC analysis was performed on a 25 cm RP-18 column supplied by Hewlett-Packard. The products and reactant were detected using a UV detector at $\lambda_{\text{max}} = 210$ nm using 30% methanol–water as mobile phase at a column temperature of 40 °C and flow rate of 1 mL/min. Samples of 10 μ L were injected into the column using an autosampler HP 1100.

Procedure. In a typical oxidation experiment, 50 cm³ of methanol, 17.777 gm of NaOH (mole ratio of *p*-cresol:NaOH = 4) was heated in a flask with a reflux condenser until most of the NaOH was dissolved; then 12 gm (2.2 kmol/m³) of *p*-cresol was added. This reaction mixture was charged to a 300 cm³ Parr autoclave provided with provisions such as gas inlet and vent, liquid sampling, safety rupture disk, cooling coil, stirrer, and thermowell. A weighed amount of catalyst (Co₃O₄) was added, and the reaction mixture was heated to 80–100 °C. When the desired temperature was attained, the reactor was pressurized with air up to 600 psig, and then the reaction was started by agitating at 900 rpm. When the pressure dropped to an extent of 20% corresponding to the O₂ content in air, the reaction mixture was cooled to 25 °C, and the rest of the gas (i.e., unabsorbed nitrogen) was vented out. Again the reactor was heated to the reaction temperature, and the reactor was pressurized with air to 600 psig. The same procedure was repeated until the stoichiometric amount of oxygen was absorbed. The progress of the reaction was monitored by the observed pressure drop in the reservoir vessel as a function of time. Liquid samples were also withdrawn from time to time and analyzed by HPLC for reactant and product concentration. After the reaction was over, the contents were cooled to room temperature and discharged.

Workup Procedure for the Recovery of Pure Product. A quantity of 80–100 cm³ of water was added to the reaction crude to make the sodium salt of phenolic products completely soluble, and then the catalyst could be separated quantitatively by filtration. Methanol was distilled off on a rotavap. After complete removal of methanol, the reaction

mixture was acidified by concentrated hydrochloric acid until the pH of the mixture became 1–2, so that the sodium salts of product and reactant were liberated. This aqueous reaction mixture was extracted with ethyl acetate. The ethyl acetate layer containing organic compounds was concentrated and then eluted on a 60–120-mesh silica gel column to recover the unreacted *p*-cresol, the product *p*-hydroxybenzaldehyde, and other side products such as *p*-hydroxybenzyl alcohol, *p*-hydroxybenzyl methyl ether, and the *p*-hydroxybenzoic acid.

Results and Discussion

Although a homogeneous CoCl₂·6H₂O catalyst has been widely used for *p*-cresol oxidation, we found that, after the oxidation reaction, cobaltous chloride gets converted to a solid-black residue which separates out from the reaction crude and it cannot be reused for subsequent reactions. Cobaltous chloride (CoCl₂) in the presence of O₂ and water gets oxidized to give a black residue of a mixture of cobalt oxide and hydroxide which cannot be reused again. Therefore, we used solid tricobalt tetraoxide as a catalyst for *p*-cresol oxidation. A few preliminary experiments showed that 0.1 g of catalyst was sufficient for complete conversion of *p*-cresol **1** to *p*-hydroxybenzaldehyde **3** (Scheme 1). In these experiments, the oxidation reaction was monitored by liquid-phase analysis as a function of time, and the various products formed were the following: *p*-hydroxybenzyl alcohol **2**, *p*-hydroxybenzaldehyde **3**, *p*-hydroxybenzyl methyl ether **4**, *p*-hydroxybenzoic acid **5**, and a coupling product of *p*-cresol. From the observed concentration–time profile (see Figure 1) it was clear that, initially, *p*-hydroxybenzyl alcohol is formed and, with the progress of the reaction, *p*-hydroxybenzaldehyde started building up. Also, the formation of *p*-hydroxybenzyl methyl ether is greater when a higher methanol concentration was used. Based on these observations and other data obtained at other reaction conditions, the reaction pathway of *p*-cresol oxidation is shown in Scheme 1. The results in the following sections are discussed on the basis of conversion of *p*-cresol, selectivity, yield, and turnover frequency which were calculated as follows.

$$\% \text{ conversion} = \frac{\text{initial concentration of } p\text{-cresol} - \text{final concentration of } p\text{-cresol}}{\text{initial concentration of } p\text{-cresol}} \times 100 \quad (1)$$

$$\% \text{ selectivity} = \frac{\text{concentration of product formed}}{\text{concentration of } p\text{-cresol consumed}} \times 100 \quad (2)$$

$$\% \text{ yield} = \frac{\text{concentration of product formed}}{\text{concentration of } p\text{-cresol charged to reaction}} \times 100 \quad (3)$$

$$\text{TON} = \frac{\text{concentration of } p\text{-cresol consumed}}{\text{concentration of catalyst (active metal)}} \quad (4)$$

Further work on the effects of various parameters were studied over Co₃O₄ catalyst in the presence of sodium hydroxide. In each experiment, a final sample was analyzed by HPLC to calculate the conversion of *p*-cresol and selectivity of *p*-hydroxybenzaldehyde, which agreed well with the oxygen absorption data and recovered *p*-hydroxy-

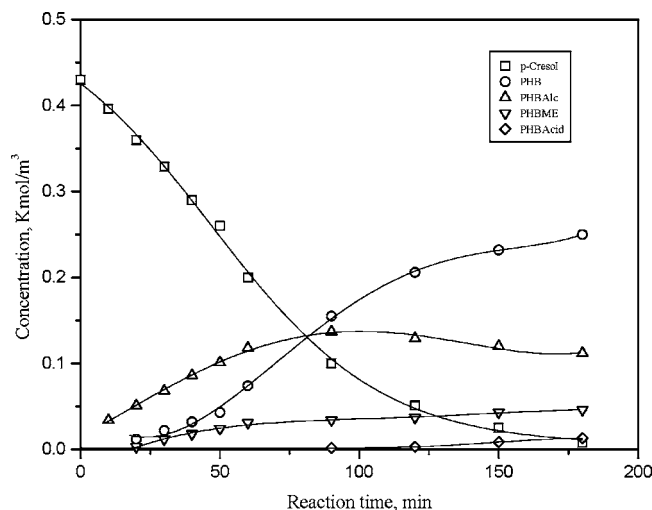


Figure 1. Concentration-time profile. Reaction conditions: temperature 373 K; mole ratio of NaOH to *p*-cresol 4; catalyst 1.5 kg/m³; agitation 900 rpm; total reaction volume 7.2×10^{-5} m³; p_{O_2} 0.1 MPa.

Scheme 1

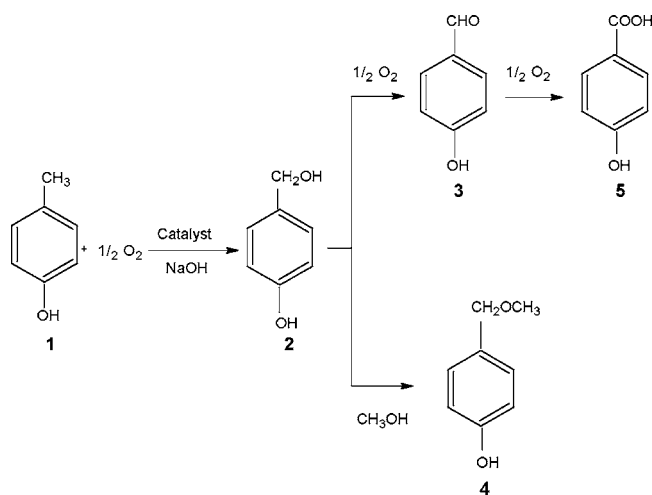


Table 1. Range of operating conditions

1	partial pressure of O ₂	0.1–1.5 MPa
2	temperature effect	333–393 K
3	substrate concentration	0.49–1.53 kmol/m ³
4	mole ratio of NaOH to <i>p</i> -cresol	1–5
5	catalyst loading	0.38–3.03 kg/m ³
6	substrate-to-solvent ratio	0.13–0.24
7	total reaction volume	7.2×10^{-5} m ³
8	agitation speed	900 rpm

benzaldehyde. In each experiment $\geq 98\%$ conversion was observed. Table 1 presents the range of various process parameters studied.

Effect of Oxygen Partial Pressure. Oxidation experiments carried out by varying the air pressure allowed to study the effect of oxygen partial pressure on the initial rate of oxidation as well as on the selectivity of *p*-hydroxybenzaldehyde. For this purpose, the partial pressure of oxygen was varied in the range of 0.1–1.5 MPa at 373 K. The initial rate increased linearly with increase in partial pressure of oxygen up to 0.8 MPa, beyond which the rate was found to remain constant as shown in Figure 2. Effect of oxygen

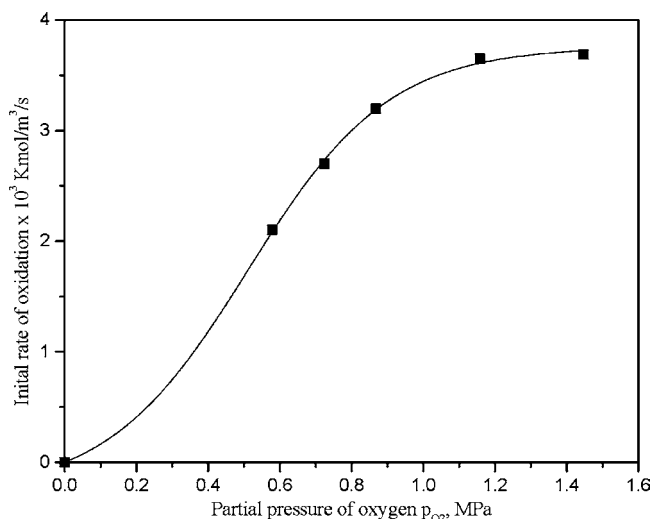


Figure 2. Effect of partial pressure of oxygen on initial rate of *p*-cresol oxidation. Reaction conditions: *p*-cresol concentration 1.5 kmol/m³; mole ratio of NaOH to *p*-cresol 4; catalyst 1.5 kg/m³; temperature 373 K; total reaction volume 7.2×10^{-5} m³.

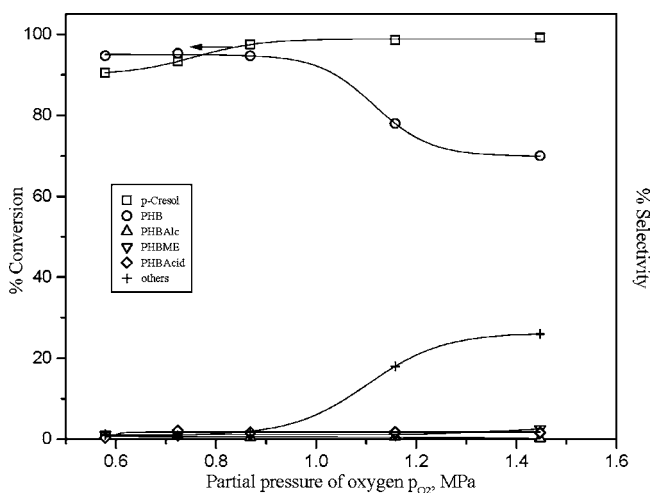


Figure 3. Effect of oxygen partial pressure on conversion and product selectivity. Reaction conditions: *p*-cresol concentration 1.5 kmole/m³; mole ratio of NaOH to *p*-cresol 4; catalyst 1.5 kg/m³; temperature 373 K; total reaction volume 7.2×10^{-5} m³; reaction time 3 h.

partial pressure on the conversion of *p*-cresol and selectivity of *p*-hydroxybenzaldehyde is shown in Figure 3. It was found that the conversion of *p*-cresol was in the range of 90–93% at lower oxygen partial pressure while, beyond 0.8 MPa as the partial pressure of O₂, conversion stabilized around 98%. The selectivity to *p*-hydroxybenzaldehyde was about 95% for oxygen partial pressure of 0.57–0.85 MPa, while beyond 0.85 MPa of p_{O_2} selectivity to PHB decreased drastically (to 70%) due to formation of side products, viz., *p*-hydroxybenzoic acid and a tarry product, in higher amount. The increase in oxygen partial pressure retards the desorption of *p*-hydroxybenzaldehyde from the catalyst surface, facilitating further oxidation of *p*-hydroxybenzaldehyde to *p*-hydroxybenzoic acid as well as formation of a tarry product due to a condensation type of reaction between the PHB and *p*-cresol, leading to a decrease in selectivity of *p*-hydroxybenzaldehyde.

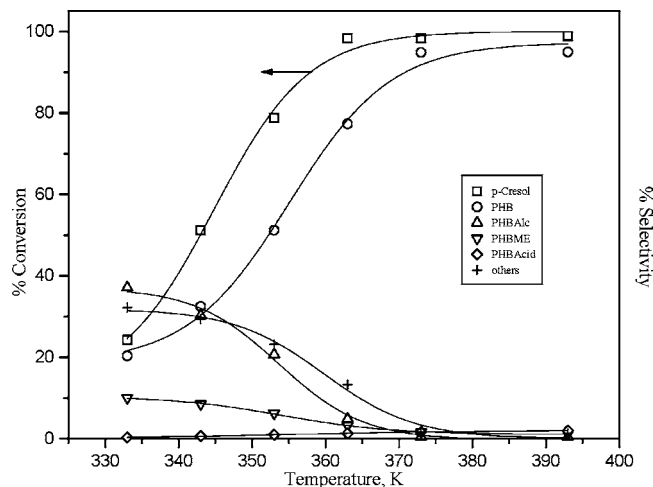


Figure 4. Effect of temperature on conversion and selectivity. Reaction conditions: *p*-cresol concentration 1.5 kmol/m³; mole ratio of NaOH to *p*-cresol 4; catalyst 1.5 kg/m³ gm; *p*O₂ 0.83 MPa; total reaction volume 7.2 × 10⁻⁵ m³; reaction time 3 h.

Effect of Temperature. The effect of temperature on both conversion of *p*-cresol and selectivity to PHB was studied in the temperature range of 333–393 K and results are presented in Figure 4. It was found that the conversion of *p*-cresol increased from 24% to 98% with increase in temperature from 333 to 363 K and remained almost constant at 98% with further increase in temperature up to 393 K. The selectivity to PHB increased from 17 to 95% with increase in temperature from 333 to 373 K, while it remained constant with further increase in temperature up to 393 K. The selectivity to *p*-hydroxybenzyl alcohol and that of other byproducts was high at lower temperature and decreased gradually with increase in temperature. The high concentration of *p*-hydroxybenzyl alcohol observed at lower temperatures clearly indicates that *p*-hydroxybenzyl alcohol is the first intermediate formed in *p*-cresol oxidation as shown in Scheme 1. The formation of *p*-hydroxybenzyl methyl ether is also substantial (8–10%) at lower temperatures (333 and 343 K), while it decreased to a minimum value of 1.2% at the highest temperature (393 K) studied. The considerable amount of formation of other byproducts at lower temperatures might be due to the fact that NaOH is not completely dissolved at lower temperatures; hence, complete conversion of *p*-cresol to its sodium salt does not take place. This leaves some free *p*-cresol available to form some other oxidation-coupling products under the reaction conditions. The initial rate of reaction increased with increase in temperature, and the activation energy evaluated from the Arrhenius plot (Figure 5) was found to be 22.6 kJ mol⁻¹, indicating that the reaction may be diffusion controlled under the conditions of the present study.

Effect of Substrate Concentration. Typical results on the effect of initial concentration of substrate in the range from 0.49 to 1.53 kmol/m³ at 373 K are shown in Figure 6. It was found that the initial rate of reaction decreased by about 36% with 4-fold increase in *p*-cresol concentration up to 1.53 kmol/m³. As can be seen from Figure 7, *p*-cresol conversion was almost constant for all concentrations of *p*-cresol studied in this work. However, the selectivity to PHB

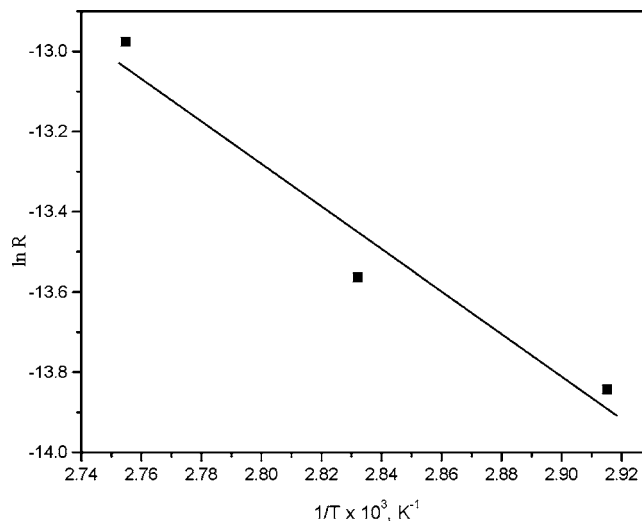


Figure 5. Effect of temperature on rate of oxidation of *p*-cresol. Reaction conditions: *p*-cresol concentration 1.5 kmol/m³; mole ratio of NaOH to *p*-cresol 4; catalyst 1.5 kg/m³; *p*O₂ 0.83 MPa; total reaction volume 7.2 × 10⁻⁵ m³.

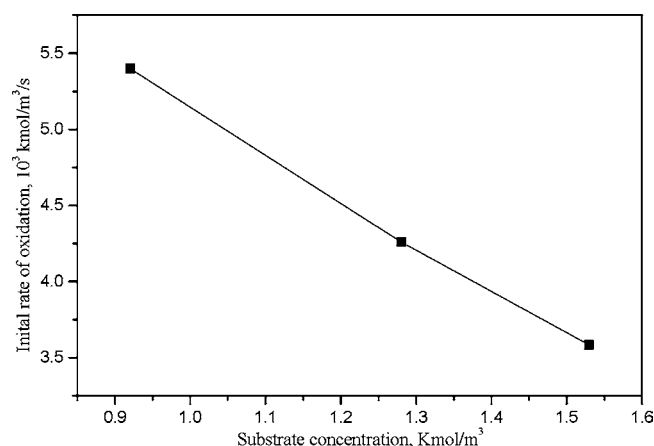


Figure 6. Effect of substrate concentration on rate of oxidation of *p*-cresol. Reaction conditions: mole ratio of NaOH to *p*-cresol 4; catalyst 1.5 kg/m³; temperature 373 K; *p*O₂ 0.83 MPa; total reaction volume 7.2 × 10⁻⁵ m³.

was found to increase from 54 to 95% with increase in *p*-cresol concentration from 0.49 to 1.53 kmol/m³. Initially, at lower concentration of *p*-cresol (0.49 kmol/m³), a substantial amount of *p*-hydroxybenzyl methyl ether (>20%) was observed which decreased gradually with an increase in substrate concentration. Since, the total reaction volume is kept constant at lower substrate concentration, solvent (methanol) concentration was high, causing a nucleophilic attack of CH₃O⁻ on the benzyl carbon of the intermediate *p*-hydroxybenzyl alcohol, leading to the formation of *p*-hydroxybenzyl methyl ether.

Effect of Sodium Hydroxide Concentration. Since the phenolic hydroxyl group of *p*-cresol interferes in the oxidation process, it is necessary to convert *p*-cresol into its sodium phenolate salt in the presence NaOH. Hence, it was important to study the effect of NaOH concentration in the *p*-cresol oxidation process. These experiments were carried out by varying the mole ratio of NaOH to *p*-cresol from 2 to 5 at a constant *p*-cresol concentration of 1.5 kmol/m³, and the results are shown in Figure 8. It was observed that the

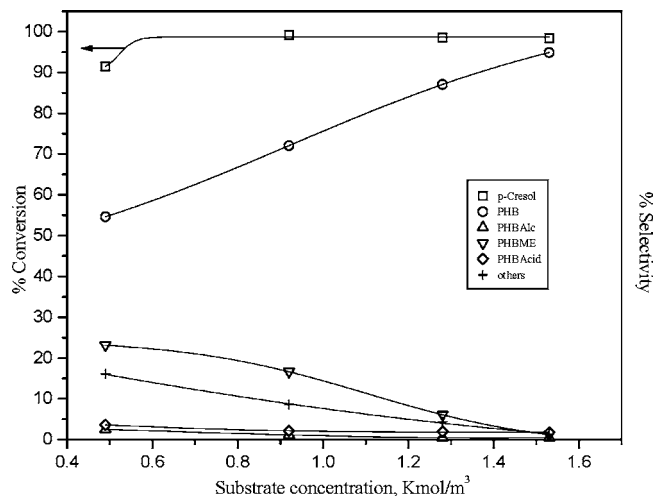


Figure 7. Effect of substrate concentration on conversion and selectivity. Reaction conditions: mole ratio of NaOH to *p*-cresol 4; catalyst 1.5 kg/m³; *p*O₂ 0.83 MPa; total reaction volume 7.2 × 10⁻⁵ m³; reaction time 3 h.

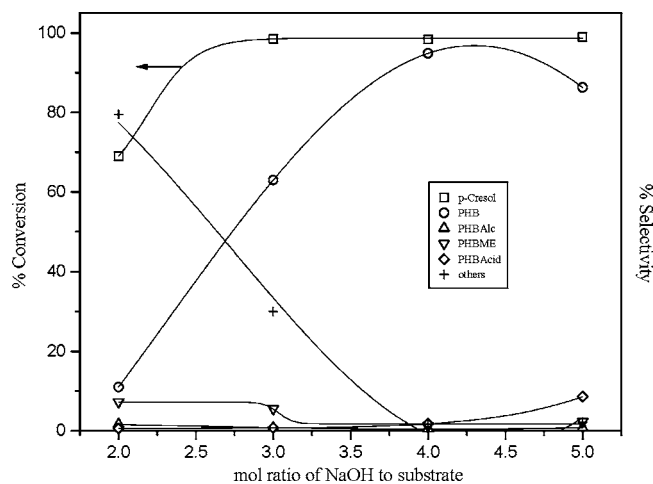


Figure 8. Effect of mole ratio of NaOH to substrate on conversion and selectivity. Reaction conditions: *p*-cresol concentration 1.5 kmol/m³; catalyst 1.5 kg/m³; temperature 373 K; *p*O₂ 0.83 MPa; total reaction volume 7.2 × 10⁻⁵ m³; reaction time 3 h.

conversion of *p*-cresol increased from 69 to 98.5% with increase in NaOH to *p*-cresol mole ratio from 2 to 4, and it remained constant with further increase in mole ratio to 5. At a lower value of NaOH to *p*-cresol mole ratio 2, selectivity to PHB was minimum (11%) while that of other byproduct was very high (>76%). Even when NaOH to *p*-cresol mole ratio was 3, byproduct formation was more than 28%. Lower selectivities of PHB under these conditions were due to the oxidative dimerization of *p*-cresol which appears to give dihydroxy diphenyl compound **6**¹² (Scheme 2), as evidenced by NMR analysis.¹²

Effect of Catalyst Loading. The effect of catalyst loading on the initial rate of reaction was studied in the range of 0.38–3.03 kg/m³ at 373 K and 0.83 MPa of oxygen partial pressure, and the results are presented in Figure 9. The initial rate was found to increase by about 3 times when the catalyst loading was increased from 0.38 to 1.5 kg/m³ beyond which

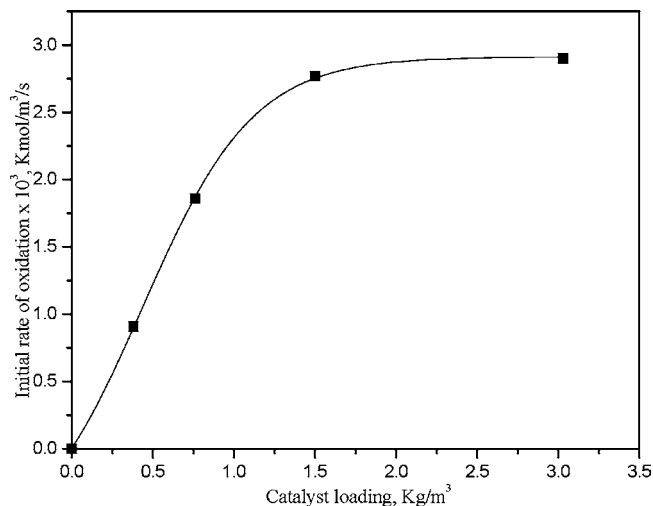
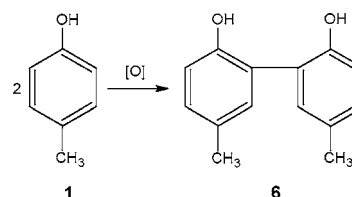


Figure 9. Effect of catalyst loading on rate of oxidation of *p*-cresol. Reaction conditions: mole ratio of NaOH to *p*-cresol 4; temperature 373 K; *p*O₂ 0.83 MPa; total reaction volume 7.2 × 10⁻⁵ m³.

Scheme 2



the rate of reaction was independent of catalyst loading, indicating that external gas–liquid mass-transfer resistance may be significant under these experimental conditions.¹³ Further experiments on effect of agitation speed and quantitative analysis of initial rate data for ascertaining the importance of mass-transfer resistance is in progress for kinetic studies. A plot of selectivity of *p*-hydroxybenzaldehyde vs catalyst loading for the same range of conditions is also shown Figure 10. At a very low catalyst loading (0.153 kg/m³), *p*-cresol conversion was 60% and increased with increase in catalyst loading. The selectivity to PHB was also low (58%) for lower catalyst loading and gradually increased to 95% with increase in catalyst loading to 1.53 kg/m³. Major formation of an intermediate (*p*-hydroxybenzyl alcohol) was observed for lower catalyst concentrations due to suppression of further oxidation of *p*-hydroxybenzyl alcohol to PHB. At a higher catalyst loading of 3.03 kg/m³, formation of *p*-hydroxybenzoic acid and other byproducts was observed in appreciable amounts due to further oxidation of PHB.

Effect of Solvent. To assess the suitability of a solvent for *p*-cresol oxidation, three common solvents were screened, viz., water, ethanol, and methanol. As can be seen from Figure 11, the conversion of *p*-cresol was marginally affected, while selectivity pattern was dramatically altered for water and ethanol as oxidation solvents. In case of water, PHB formation was only 2% with major amounts of other oxidation byproducts due to the fact that NaOH had very high solubility in water and it was not available for protecting

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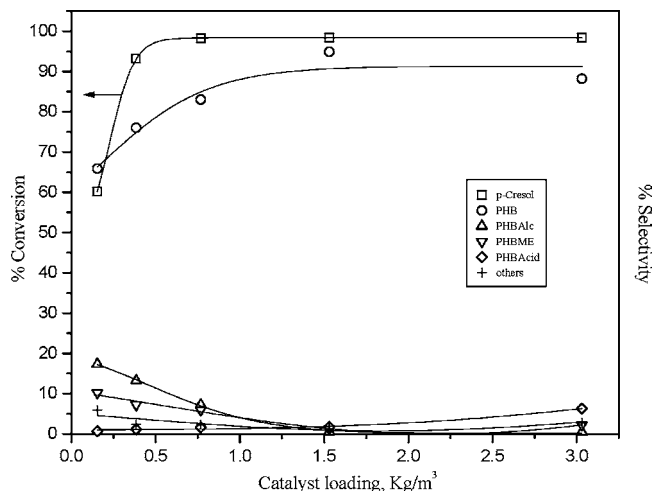


Figure 10. Effect of catalyst loading on conversion and selectivity. Reaction conditions: *p*-cresol concentration 1.5 kmol/m³; temperature 373 K; *p*_{O₂} 0.83 MPa; total reaction volume 7.2 × 10⁻⁵ m³; reaction time 3 h.

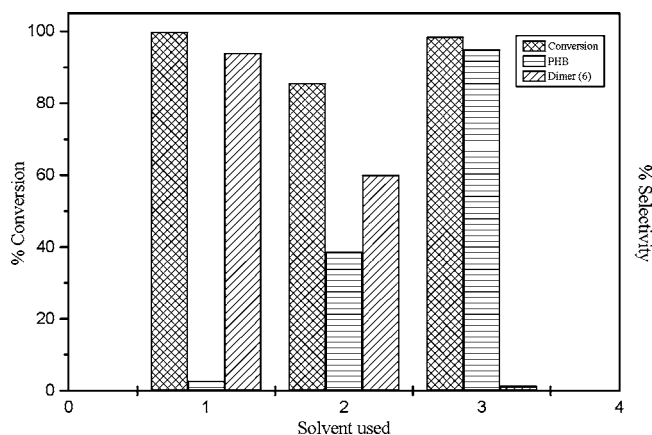


Figure 11. Effect of solvent on conversion and selectivity. Reaction conditions: *p*-cresol concentration 1.5 kmol/m³; temperature 373 K; catalyst loading 1.5 kg/m³ m.; *p*_{O₂} 0.83 MPa; total reaction volume 7.2 × 10⁻⁵ m³; reaction time 3 h; (1) water, (2) ethanol, (3) methanol.

the -OH group of *p*-cresol. For ethanol as a solvent, PHB selectivity was somewhat higher than that in water but still around 38%. The ethanol used was not in completely anhydrous form, and it may have contained water in appreciable amount; hence, free -OH of *p*-cresol is again available to form other oxidation byproducts. From this study, it was confirmed that methanol was the only suitable solvent that gave 95% selectivity to PHB with almost complete conversion of *p*-cresol.

Catalyst Recycle. The catalyst recycle experiments were carried out in the following way: after the first oxidation run with the fresh catalyst, it was filtered out and dried in an oven at 373 K for 3 h and was recharged to the reactor for the subsequent run. This procedure was followed for three subsequent oxidation experiments, and the results are shown

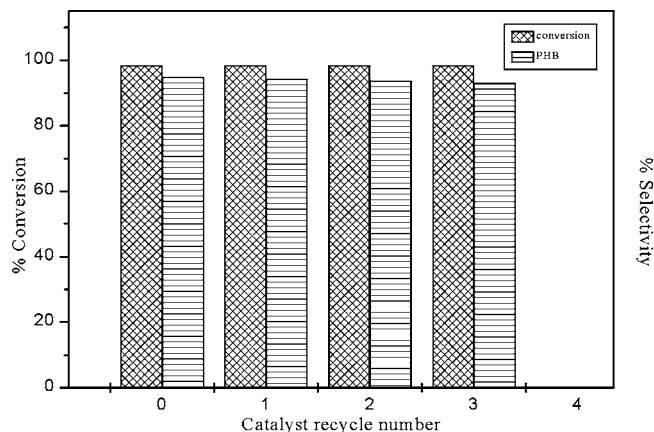


Figure 12. Catalyst recycle study. Reaction conditions: *p*-cresol concentration 1.5 kmol/m³; temperature 373 K; catalyst loading 1.5 kg/m³; *p*_{O₂} 0.83 MPa; total reaction volume 7.2 × 10⁻⁵ m³; reaction time 3 h.

in Figure 12. The catalyst was found to retain its activity even after the third recycle without affecting the conversion of *p*-cresol; however, selectivity for PHB was marginally decreased by 2–3%. This lowering of selectivity could be due to the handling of losses of catalyst in the subsequent recycle runs. The overall turnover number (TON) for the catalyst for our process was found to be 1 × 10³ which is higher than the literature value of 3.25 × 10² for a resin-supported cobalt oxide catalyst.¹⁴ The catalyst recycle studies also showed the absence of any leaching of cobalt in the solution under reaction conditions.

Conclusions

Liquid-phase oxidation of *p*-cresol under elevated pressure of air was carried out using Co₃O₄ as a catalyst in the presence of sodium hydroxide to give *p*-hydroxybenzaldehyde with selectivity as high as 95% and almost complete conversion of *p*-cresol. As compared to air oxidation of *p*-cresol under atmospheric conditions, elevated pressure of air completely converted the intermediate *p*-hydroxybenzyl alcohol to PHB. A systematic study on the effect of reaction conditions on conversion and selectivity to *p*-hydroxybenzaldehyde was carried out. The selectivity to PHB was strongly dependent on substrate concentration, temperature, oxygen partial pressure, mole ratio of NaOH to substrate, and catalyst loading. It was found that the high substrate concentration (24%) eliminated the formation of a byproduct, *p*-hydroxybenzyl methyl ether, while a mole ratio of NaOH to substrate concentration below 3 gave rise to formation of a dihydroxy diphenyl compound causing a decrease in selectivity to PHB. The catalyst was successfully used for three recycle experiments, giving a total TON of 1.023 × 10³, which is about 3 times higher than the literature value.

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