



SELECTIVE OXIDATION OF TOLUENE TO BENZALDEHYDE USING Cu/Sn/Br CATALYST SYSTEM

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ABSTRACT

Liquid phase oxidation of toluene to benzaldehyde using a bimetallic catalyst consisting salts of copper, stannous; and sodium bromide as a promoter in acetic acid medium in the presence of air as oxidant has been investigated. The effect of different reaction parameters like temperature, pressure, substrate concentration, catalyst concentration on the toluene conversion and selectivity to benzaldehyde, benzyl alcohol and benzoic acid were studied. The catalytic activity and selectivity was found to be strongly influenced by the temperature and catalyst concentration. Br was found to be an essential component to initiate the oxidation reaction. High selectivity to benzaldehyde (50-65%) with good conversion was achieved using Cu/Sn/Br catalyst system.

Key words: Liquid phase oxidation of toluene, Cu/SnCl₂/NaBr, Catalyst, Toluene conversion, Benzaldehyde selectivity.

INTRODUCTION

Benzaldehyde is the simplest and industrially the most important aromatic aldehyde. Benzaldehyde is widely used in food, pharmaceutical and perfume industry. Conventionally, benzaldehyde is produced by the hydrolysis of benzal chloride or the gas phase oxidation of toluene^{1,2}. Due to the industrial demand and the obligation to reduce chlorine-dependent chemical production, the oxidation of toluenes in gas and liquid phase is getting much more attention. The gas phase oxidation is usually carried out by passing a vaporized toluene–air mixture through a catalyst bed at a temperature of 300-600°C, which results into the formation of benzoic acid as main product and benzaldehyde as a co-product^{3,4}.

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In most of the reported literature on liquid phase toluene oxidation, air has been used as the oxidant and acetic acid as the solvent; in the presence of a transition metal catalyst and cobalt is the most active catalyst in terms of toluene conversion. Borgaonkar et al.⁵ have reported liquid phase oxidation of toluene with good yield of benzaldehyde (27-35%) with cobalt acetate as a catalyst, sodium bromide as a promoter and acetic acid as a solvent. Selective synthesis of benzaldehyde by transition metal catalyzed oxidation of toluene is challenging, as the aldehydes are better substrates for oxidation compared to their parent hydrocarbons and it is difficult to control the over-oxidation of benzaldehyde to benzoic acid. Recently, a catalyst system consisting of cobalt and manganese with zinc bromide as a promoter instead of sodium bromide has been reported to give good selectivity (62%)⁶.

We have reported herein a bimetallic catalysts system consisting of Cu (OAc)₂ and SnCl₂ in the presence of NaBr as the promoter, which gives a very high selectivity to benzaldehyde (64.2%), with moderate conversion of toluene (11.2%). The detailed parametric investigation has been carried out with Cu (OAc)₂-SnCl₂-NaBr catalyst system to understand the effect of catalyst system and reaction parameter on conversion of toluene and selectivity to benzaldehyde.

EXPERIMENTAL

Catalytic air oxidation of toluene: Oxidation of toluene was carried out in a stirred SS-316 autoclave of 300 mL capacity having a temperature and pressure controller. Predetermined quantities of copper acetate, SnCl₂, sodium bromide, toluene and acetic acid were charged in the reactor at room temperature. It was then pressurized with air and the contents heated to a desired temperature. The reaction was carried out for 4 hours.

Catalyst recycle experiment: After completion of the reaction, the reaction mixture was cooled to 283 K and the gas inside the autoclave was slowly vented off. The contents of the autoclave were concentrated at reduced pressure and at low temperature to distil off the volatiles. To the concentrate, about 20 mL toluene and equal volume of water were added and mixed vigorously in a separating funnel. The organic layer was then separated and then washed with water (3 × 25 mL) to extract completely the water-soluble catalyst components. The aqueous layers were mixed and concentrated on rotavapor to obtain the catalyst components, which were used for recycle experiments. The experimental procedure for recycle experiments were kept exactly the same as that of the typical oxidation procedure except that, the catalyst components recovered as above were used in recycle experiments.

The result of liquid phase oxidation toluene are discussed on the basis of conversion of toluene, selectivity, which were calculated as follows.

$$\text{Conversion (\%)} = \frac{\text{Initial concentration of toluene} - \text{Final concentration of toluene}}{\text{Initial concentration of toluene}} \times 100$$

$$\text{Selectivity (\%)} = \frac{\text{Number of moles a product formed}}{\text{Number of moles toluene converted}} \times 100$$

Analytical

Liquid samples were quantitatively analyzed for reaction products and unreacted toluene on a Hewlett-Packard 6890 series GC controlled by the HP-Chemstation software and equipped with an auto sampler unit, using an HP-FFAP capillary column (0.32 mm ID, 60 meters, 0.25 μm film thickness. The oven temperature was programmed between 303-484 K). The quantification of toluene, benzaldehyde, benzyl alcohol, benzyl acetate, benzoic acid was done based on the respective calibration curve.

RESULTS AND DISCUSSION

The aim of the present study was to investigate the liquid phase oxidation of toluene using a bimetallic catalyst system in the presence of a bromide promoter, copper (II) acetate being the principle catalyst. The screening of a few co-catalysts like CrCl_2 , NiCl_2 , SnCl_2 was carried out with $\text{Cu}(\text{OAc})_2$ and NaBr . The results on the catalytic activity and selectivity are presented in Table 1. The results show that when the reaction was conducted the absence of a co-catalyst, 7.8 % toluene conversion and 41.3 % selectivity to benzaldehyde was obtained, with formation of benzoic acid (termed byp-2) as the major byproduct and benzyl alcohol and benzyl acetate (termed cumulative as byp-1) as minor byproduct (entry 1). It was observed that high conversions were obtained using CrCl_2 as co-catalyst with poor selectivity to benzaldehyde (51.3 %). Slightly better selectivity was observed on using NiCl_2 as co-catalyst, but with low conversion of toluene (entry 3). A large enhancement in the benzaldehyde selectivity to 64.2% with a moderate 11.2% conversion of toluene was observed when the reaction was carried out using $\text{Cu}(\text{OAc})_2$ - SnCl_2 - NaBr catalyst system (entry 4). A similar experiment carried out in absence of NaBr showed no oxidation of toluene (entry 5), which clearly indicates that the presence of bromide is an essential requirement to initiate the reaction. Similarly there was increase in conversion, when NaBr concentration was increased, with decrease in benzaldehyde selectivity (entry 6).

Marginal decrease in the conversion of toluene with a good selectivity to benzaldehyde (64.5%) was observed when the reaction was carried out at lower partial pressure of air (entry 7, Table 1). This trend reversed exactly, with marginal increase in conversion of toluene with increase in total pressure of air, but with some decrease in

selectivity of benzaldehyde (entry 8). When the concentration of toluene was increased, there was decrease in the conversion of toluene with increase in the selectivity of benzaldehyde (entry 9, 10). However, there was no oxidation reaction observed in the absence of acetic acid as solvent (neat toluene) (entry 11).

Table 1: Effect of catalyst screening and reaction parameters

Entry	Catalyst, kmol/m ³			Toluene conversion (%)	Selectivity (%)		
	Copper	Co-catalyst	NaBr		Benzaldehyde	Alcohol + acetate (byp-1)	Benzoic acid (byp-2)
1	0.02	-	0.021	7.8	41.3	14.8	39.3
2	0.02	CrCl ₂	0.021	10.6	51.3	15.2	28.9
3	0.02	NiCl ₂	0.021	8.5	53.8	15.4	25.6
4	0.02	SnCl ₂	0.021	11.2	64.2	14.1	20.1
5	0.02	SnCl ₂	0.000	0	-	-	-
6	0.02	SnCl ₂	0.045	18.5	49.2	12.8	30.5
7 ^a	0.02	SnCl ₂	0.021	10.4	64.5	14.1	18.4
8 ^b	0.02	SnCl ₂	0.021	13.5	54.8	11.9	26.9
9 ^c	0.02	SnCl ₂	0.021	14.1	60.5	11.3	22.6
10 ^d	0.02	SnCl ₂	0.021	5.8	65.1	14.1	18.5
11 ^e	0.02	SnCl ₂	0.021	0	-	-	-

Reaction conditions: Toluene: 0.93 kmol/m³, co-catalyst: 0.020 kmol/m³ pAir: 3.45 MPa, Temperature: 120°C, Stirring speed : 1000 rpm, Time: 4 h, Solvent: Acetic acid, Total charge: 6 x 10⁻⁵ m³, a pAir : 2.1 MPa, b pAir : 4.5 MPa, c Toluene : 0.5 kmol/m³, d Toluene : 1.8 kmol/m³ e reaction in neat toluene.

These experiments showed the synergistic effect of SnCl₂ on the catalytic performance in oxidation of toluene. The optimization of copper acetate, tin (II) chloride, sodium bromide and the reaction parameters was carried out in view to achieve high selectivity to benzaldehyde with good conversion of toluene.

Effect of Cu (OAc)₂ concentration

To study the effect of copper acetate concentration on conversion of toluene and selectivity of benzaldehyde the range selected was 0.0 - 0.044 kmol/m³. It was observed that

the selectivity of benzaldehyde decreases (66.3 to 51.2%) with the increase in the conversion of toluene (1.1 to 16.9%) as shown in the Fig. 1. The higher levels of toluene conversion are found to be associated with a decrease in the selectivity towards benzaldehyde and simultaneous increase in the benzoic acid. The oxidation of toluene has been reported to proceed from toluene to benzoic acid via benzaldehyde and benzyl alcohol. These sequential oxidations are catalyzed by transition metals and hence are competitive.

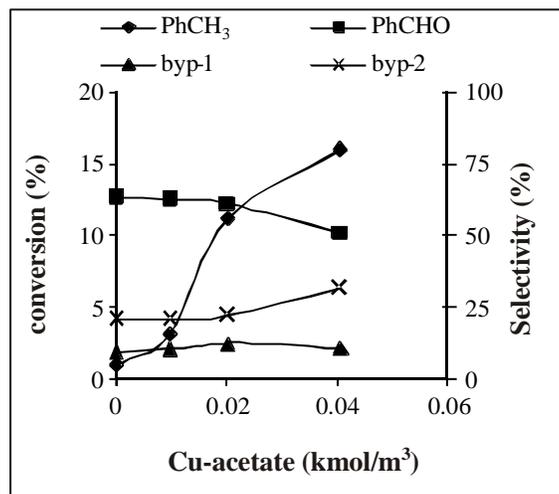


Fig. 1: Effect of copper acetate concentration on oxidation of toluene

Reaction conditions: Toluene: 0.93 kmol/m³, SnCl₂: 0.020 kmol/m³, NaBr: 0.020 kmol/m³, Temperature, 120°C, pAir: 3.45 MPa, Stirring speed: 1000 rpm, Time: 4 h, Solvent: Acetic acid, Total Charge: 6 x 10⁻⁵ m³

Effect of SnCl₂ concentration

To study the effect of SnCl₂ concentration on oxidation of toluene, the range used was 0.0095-0.038 kmol/m³. It was observed that the selectivity to benzaldehyde increases from 58.3 to 65.8 % with decrease in the conversion of toluene from 13.9 to 7.8% as shown in the Fig. 2.

Effect of temperature

To study the effect of temperature on oxidation of toluene the range used was 383 – 403 K. It was observed that the selectivity of benzaldehyde decreases from 63.8 to 50.3% with the increase in the conversion of toluene from 5.8 to 14.6% as shown in the Fig. 3. This result implies that the higher temperatures facilitate the air oxidation of benzaldehyde to benzoic acid.

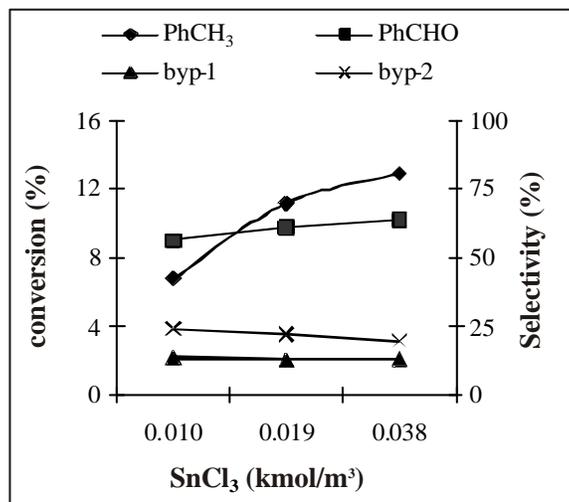


Fig. 2: Effect of SnCl₂ concentration on oxidation of toluene

Reaction conditions: Toluene: 0.93 kmol/m³, Cu (OAc)₂: 0.020 kmol/m³, NaBr: 0.020 kmol/m³, Temperature, 120°C, pAir: 3.45 MPa, Stirring speed: 1000 rpm, Time: 4 h, Solvent: Acetic acid, Total Charge: 6 x 10⁻⁵ m³

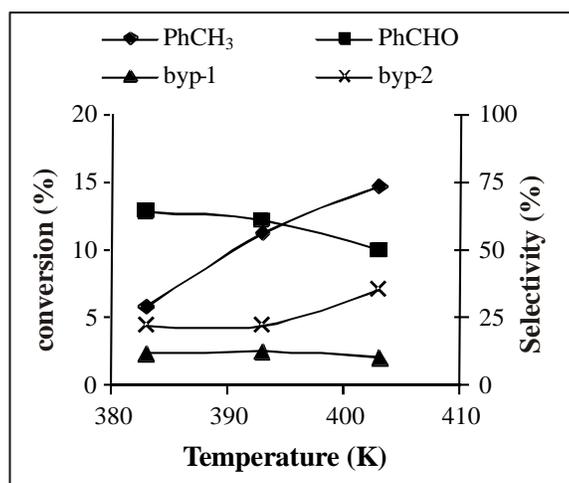


Fig. 3: Effect of temperature on oxidation of toluene

Reaction conditions: Toluene: 0.93 kmol/m³, Cu (OAc)₂: 0.020 kmol/m³, SnCl₂: 0.020 kmol/m³, NaBr: 0.020 kmol/m³, pAir: 3.45 MPa, Stirring speed: 1000 rpm, Time: 4 h, Solvent: Acetic acid, Total Charge: 6 x 10⁻⁵ m³

Catalyst recycle study

The recycle experiments were carried out as explained in the experimental procedure. Three recycle experiments were carried out. It was observed that the selectivity towards benzaldehyde was unaffected and conversion was decreased gradually from 11.2 to 7.5%.

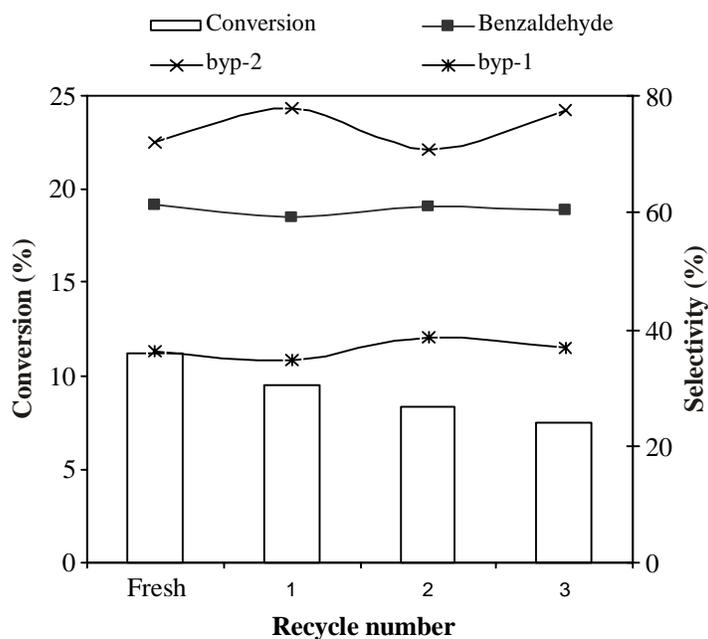


Fig. 4: Catalyst recycle study on oxidation of toluene

Reaction conditions: Toluene: 0.93 kmol/m³, Cu(OAc)₂: 0.020 kmol/m³, SnCl₂: 0.020 kmol/m³, NaBr: 0.020 kmol/m³, pAir: 3.45 MPa, Stirring speed: 1000 rpm, Time: 4 h, Solvent: Acetic acid, Total Charge: 6x10⁻⁵ m³

CONCLUSION

A catalyst system consisting salts of copper, tin and sodium bromide as a promoter showed a promising catalytic performance with high selectivity to benzaldehyde (50-65%) and good activity in the oxidation of toluene. Bromide is found to be an essential requirement to initiate the reaction. The reaction parameters like concentrations of toluene, catalyst components and the reaction conditions like reaction temperature and partial pressure of air have significant effect on the product profile and conversion levels. Stringent reaction conditions result in over oxidation of toluene, thus lowering the benzaldehyde selectivity. The catalyst system reported herein gives moderate conversion levels and

appreciable selectivity to benzaldehyde, with tailored reaction conditions and parameters. The water-soluble catalyst system is also found to be recyclable and retains its property of enhanced benzaldehyde selectivity upon recycle.

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