An improved process for selective liquid-phase air oxidation of toluene

Mannepalli Lakshmi Kantam *, Pentlavalli Sreekanth, Kottapalli Koteswara Rao,
Thella Prathap Kumar, Bhavnari Purna C. Rao, and Boyapati Manoranjan Choudary
Inorganic Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500 007, India

Received 10 December 2001; accepted 12 March 2002

An improved process for the oxidation of toluene to obtain benzaldehyde and benzyl alcohol with high selectivities using a Co/Mn/Br^- composite catalytic system in liquid phase is described. A protocol for recovery and reuse of the composite catalyst is developed. The use of low concentrations of composite catalytic systems aimed at minimizing corrosion of the reaction, and higher concentrations of toluene affording higher productivity and recyclability of the catalyst giving high turnover number, are the remarkable achievements of the present methodology. Investigation into the recycle, aging and spectroscopic studies of the catalytic system improves the understanding of the process, chemistry and mechanism of the reaction. As the market demand for each product fluctuates, the dynamic system developed here to meet changing demands is very important to obtain one of the products in excess quantities with a change of the ratio of Br^-/Cl^-.

KEY WORDS: partial oxidation of toluene; Co/Mn/Br^- catalyst; benzaldehyde; homogeneous catalysis; electronic spectroscopy.

1. Introduction

In bulk chemical manufacture, traditional environmentally unacceptable processes are largely being replaced by cleaner catalytic alternatives. Indeed, catalytic oxidation is the single most important technology for the conversion of hydrocarbon feedstocks (olefins, alkanes and aromatics) to industrially important oxygenated derivatives [1]. The fine-chemicals industry, in contrast, is the domain of synthetic organic chemists who, generally speaking, usually use stoichiometric quantities of classical inorganic oxidants such as potassium dichromate and potassium permanganate. As smaller volumes were involved, there was much less pressure in the past to replace such antiquated, environmentally unacceptable technologies. The stringent laws now laid down all over the world for the protection of the environment have prompted the development of eco-economic processes recently.

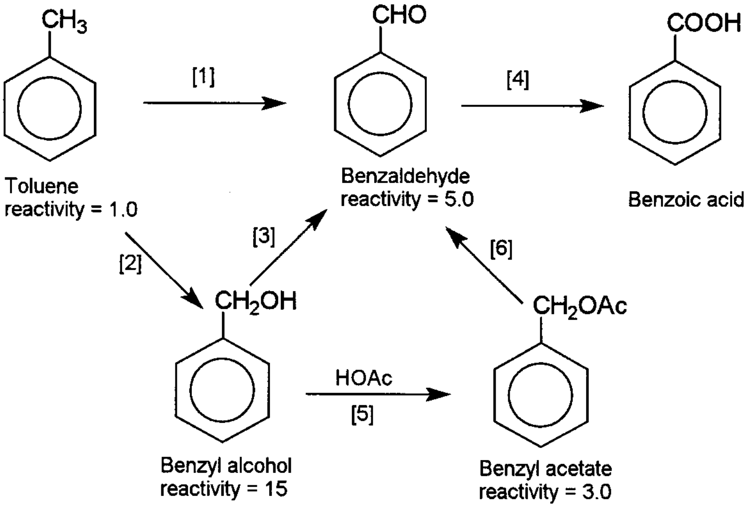
Selective oxidation of the C–H bonds in methylbenzenes is an attractive field as well as an unsolved problem in chemistry, as the intermediates such as alcohols and aldehydes are more susceptible to secondary oxidation reaction to the corresponding carboxylic acid which lowers the selectivity. Thus, the formation of alcohols or aldehydes with high selectivity is more difficult. The production of alcohols and aldehydes impacts high-value addition. For instance, benzaldehyde and substituted benzaldehydes are used as intermediates for the manufacture of odorants, flavors such as almond and cherry and in various fragrances for soap and toiletries. Benzaldehyde is an F.D.A.-approved synthetic flavoring substance generally recognized as safe in food. Technical grade benzaldehyde is a versatile chemical intermediate in the manufacture of pharmaceuticals, dyes, perfume and flavoring chemicals. Technical grade benzoic acid is used as an intermediate in the manufacture of chemicals, alkyd resins, polyesters, plasticizers, dyestuffs, preservatives, rubber activators and retardants. Industrial grade benzoic acid is used as a chemical intermediate and as a diverting agent in crude-oil recovery applications.

Presently, commercial production of benzyl alcohols and benzaldehydes is still resorted to *via* chlorination of methylbenzenes followed by hydrolysis/oxidative hydrolysis in some cases. The chlorination method suffers from serious disadvantages such as not conforming to F.C.C. quality, relatively high production cost, and large amounts of pollutant residues. However, the major demand for benzaldehyde is being met by the dedicated benzoic acid production plants wherein the benzaldehyde is formed as a by-product in small proportions in air oxidation of toluene at higher conversion. As the process of phenol from benzoic acid is currently uneconomical, the benzoic acid produced through this process is unable to find good markets. Hence, the interest in the development of efficient and selective catalytic systems for air oxidation of toluene to benzaldehyde is being rejuvenated.

The cobalt bromide is a highly efficient catalyst for the oxidation of methylbenzenes in acetic acid solvent [2,3], but most of the substrates are converted to the corresponding carboxylic acids, such as toluene to benzoic acid. Moreover, the higher the conversion of

---

* To whom correspondence should be addressed.
E-mail: mlakshmi@iict.ap.nic.in



Scheme 1. Products during autoxidation of toluene.

methylbenzenes, the lower will be the selectivity of aldehydes. Many spectrometric and mechanistic studies showed that the cobaltous-monobromide species is responsible for the oxidation of the C–H bonds in methylbenzenes [4–8]. Also, many improved methods of this catalytic system have been investigated to convert methylbenzenes to the intermediates selectively [8,9–12]. Recently Zn,Cu,Al-layered double hydroxides (LDHs) have been used for the low-temperature liquid-phase oxidation of toluene and *o*-, *m*- and *p*-xylene with hydrogen peroxide as an oxidant [13]. The catalytic reaction involves both the side-chain oxidation and the hydroxylation/oxidation of the aromatic ring. In a divergent approach, deoxygenation of benzoic acid to benzaldehyde has been reported recently using molecular hydrogen [14]. These processes are uneconomical due to the use of expensive hydrogen peroxide and molecular hydrogen.

In this paper, we report an improved process for the selective oxidation of toluene to obtain benzaldehyde conforming to F.C.C. quality with high selectivity using Co/Mn/Br$^-$ composite catalytic system in liquid phase. The use of low concentrations of composite catalytic systems aimed at minimizing corrosion of the reaction and higher concentrations of toluene affording higher productivity and recyclability of the catalyst giving high turnover number are the remarkable achievements in the present methodology. Investigation into the recycle, aging and spectroscopic studies on the catalytic system provides further understanding of the process, chemistry and mechanism of the reaction.

2. Experimental

2.1. Materials

Cobalt(II) acetate tetrahydrate (Aldrich) and manganese(II) acetate tetrahydrates (Fluka), sodium bromide, zinc bromide, hydrobromic acid (30% in acetic acid) and benzoic acid (s.d. fine-chem) were used as received. Toluene and acetic acid were distilled before use. Composite catalysts were prepared by dissolving the specified quantities in acetic acid as detailed in the text.

2.2. Spectroscopic measurements

The UV–vis spectra were recorded on a GBC Cintra 10e scanning spectrophotometer in the region of 200–800 nm. The liquid homogeneous samples containing specified amounts of composite catalyst in defined quantities, acetic acid or benzoic acid and toluene were analyzed in a quartz cell (10 ml).

2.3. Catalytic reactions

An all-glass Buchi autoclave (500 ml capacity) fitted with a hot-oil circulation facility, gas connecting tube, stirrer and pressure gauge was fitted with a water condenser, through which ice-cold water was circulated.

A composite mixture of a catalyst comprising $Co(OAc)_2{\cdot}4H_2O$, $Mn(OAc)_2{\cdot}4H_2O$ and sodium bromide or zinc bromide in specified quantities were charged in the autoclave containing defined quantities of toluene, acetic acid or benzoic acid. After the system attained the required temperature, it was pressurized with air to 10 kg/cm^2 with 2 l/min outflow. After a specified time, the reaction mixture was rapidly cooled to room temperature. The products and unreacted toluene were analyzed by gas chromatography (Schimadzu, GC-14B with a 1.83 m (6 ft) 10% SE-30 S.S. packed column, 3.2 mm ($\frac{1}{8}$ in.) o.d. and FID detector) and titrimetric analysis. The selectivity towards benzaldehyde (BA) and benzyl alcohol (BAl) in the reaction is calculated using the equation: (the selectivity of the BA or BAl) = (moles of BA or BAl formed)/(total moles of the product formed). **Caution**: The use of high pressures

Table 1
Effect of catalyst composition/concentration[a] on air oxidation of toluene

Experiment No.	Co/Ac (g mol/l)	Mn/Ac (g mol/l)	$ZnBr_2$[b]/NaBr[c] (g mol/l)	Time (h)	Overall conversion of toluene (%)	Yield (g)		
						BA	BAl	BAc
1	0.02	0.0012	0.08	2	16.46	11.84	1.24	6.82
2	0.02	0.0012	0.04	1.15	26.44	13.25	1.63	18.00
3	0.015	0.0008	0.03	1.15	18.70	9.29	1.07	12.91
4	0.01	0.0006	0.02	2	19.91	10.99	1.26	12.35
5	0.005	0.0003	0.01	2.30	9.73	5.70	0.85	5.41
6	0.005	0.0003	0.01	2.30	16.40	8.26	0.65	11.53
7	0.04	–	0.148	1.30	38.31	17.27	1.01	29.80
8	0.02	–	0.074	2	23.47	14.14	1.71	12.93
9	0.02	–	0.0148	1.15	18.79	10.70	1.50	10.94
10	0.02	0.0008	0.0148	1.15	26.87	13.67	1.73	17.96
11	0.02	0.0008	0.0022	1	27.92	12.05	0.86	22.21
12	0.02	0.0008	0.0016	1	21.03	10.57	1.45	14.10
13	0.02	0.0008	0.001	1	21.43	9.97	1.65	15.10

[a] Reaction volume: 300 ml; toluene: 64.32 w/v%; temperature: 110 °C; pressure: 10 kg/cm^2; airflow: 2 l/min.
[b] $ZnBr_2$ as promoter.
[c] NaBr as promoter.

and the use of dioxygen/nitrogen mixture is potentially explosive and dangerous. They should be performed only with adequate precautions.

2.4. *Recycling procedure*

After completion of the reaction, the reaction mixture was cooled to room temperature and washed with distilled water three times (3 × 30 ml) to extract the catalyst. The organic and aqueous layers were separated and the aqueous solution was evaporated to dryness to obtain the catalyst. 5% of Co/Mn salts were also added for each cycle to replenish the metal salts consumed in analysis and lost in recovery during extraction. A fresh amount of promoter, NaBr or HBr (100%), was added for each cycle, as all the promoter was consumed during the reaction. The catalyst was reused for 10 cycles.

3. Results and discussions

A composite catalytic system was developed for liquid-phase air oxidation of toluene employing cobalt and manganese as catalysts and bromide as promoter to obtain high selectivity towards benzaldehyde and near-zero emission of effluents, factors essential for the commercial process. We studied the effect of different parameters such as promoters (zinc bromide and sodium bromide), solvents (benzoic acid and acetic acid), toluene concentration, temperature and reaction time on the selective oxidation of toluene.

In the present studies, in an effort to optimize the catalyst concentration, we studied the effect of the different ratios of Co/Mn using zinc bromide or sodium bromide as a promoter on the conversion of toluene, and selectivities and yields towards primary products, benzaldehyde and benzyl alcohol in the air oxidation of toluene (table 1). The use of manganese acetate as an initiator improved the conversion of toluene and yields of benzaldehyde and benzoic acid, and thus recorded higher rates of productivity even at a low concentration of cobalt, as can be seen from the data (table 1, entries 9 and 10). This high productivity is very interesting, when compared with the results obtained using very high ratios of Br^-/Co [15]. However, the ideal system is the one that provides high selectivity of benzaldehyde that is possible at lower conversion. There is no reaction in a specified time (1–2 h) when the reaction is conducted without bromide [7]. However, after a prolonged time, the reaction occurs without the bromide promoter. Therefore, it is necessary to use the bromide promoter, as it reduces the induction period of the reaction. This result is in agreement with other studies in the air oxidation of toluene using a cobalt catalytic system. With increased concentration of $Co/Mn/Br^-$, the overall conversion of toluene and yield of benzaldehyde are enhanced without much affecting selectivity towards benzaldehyde. However, with prolonged reaction, the formation of benzoic acid is increased while the benzaldehyde concentration remains static. Air oxidation of methyl aromatic species, aromatic alcohols and benzaldehydes using metal/bromide catalysts generally operate *via* a free radical chain mechanism. The free radical chain mechanism gives the oxidizability of toluene, benzyl alcohol and benzaldehyde as 0.05, 0.85 and 290 respectively [1]. It is clear from these values that the steady-state concentration of benzaldehyde is *expected* to remain low in metal/bromide catalyzed systems. At low concentration of benzaldehyde, the reaction is first-order as the increased concentration of toluene increases the conversion of toluene. At higher concentration of benzaldehyde, the rate of disappearance of benzaldehyde is equal to the rate of formation of the benzaldehyde. At this juncture, the order of the reaction is shifted to second-order, as the reaction is dependent on concentrations of both toluene and benzaldehyde.

Even with the reduction of Br^- content by 5–50 times as NaBr replaces $ZnBr_2$ as the promoter in the experiments, it is observed that the conversion of the toluene and selectivity and yields towards benzaldehyde are not much affected (table 1, entries 2 and 10–12) and it is ascribed to the availability of free Br^- to the reaction, which is higher in the case of NaBr than with $ZnBr_2$ due to the inherent highly ionic nature of the former. Based on these results, the optimized $Co/Mn/Br^-$ ratio is found to be 1 : 0.06 : 2 (table 1, entry 2) for zinc bromide and 1 : 0.04 : 0.08 (table 1, entry 12) for sodium bromide for the induction of high selectivity towards benzaldehyde. No traces of benzyl bromide are observed when zinc bromide or low concentration of NaBr (table 1, entries 12 and 13) is used as promoter. However, at high concentration of NaBr, less than 1% of benzyl bromide was formed.

3.1. *Effect of sodium bromide/sodium chloride ratio*

The effect of the use of Cl^- in conjunction with Br^- in the air oxidation of toluene on the selectivity and productivity towards benzaldehyde is studied (figure 1). By changing the molar ratio of sodium bromide and sodium chloride from 0.047 to 0.47, the overall conversion is increased. When this ratio is further increased to 2, the overall conversion and yields of benzoic acid are reduced. However, there is no reaction with sodium chloride without using sodium bromide. The yield of benzaldehyde is independent of the ratio of Br^-/Cl^- used in the air oxidation of toluene. On the other hand, the selectivity towards benzaldehyde is reduced with the increased conversion of toluene prompted by an increased Br^-/Cl^- ratio from 0.047 to 0.47. Since our studies are directed to obtain high selectivity towards benzaldehyde and benzyl alcohol, the low conversion of toluene is preferred. As the market demand for each product fluctuates, the dynamic system developed here as described to meet the changing demands is very important for obtaining the desired product in relatively excess quantities by the change of the Br^-/Cl^- ratio. As the cost of NaCl is very low, the use of NaBr/NaCl at a lower ratio to afford higher selectivity towards benzaldehyde and benzyl alcohol is the ultimate choice, since it reduces the process cost. In the experiments, it is observed that the composite mixture of $Co/Mn/Cl^-/Br^-$ shows higher activity than the $Co/Mn/Br^-$ system. Benzylic bromide, which is an inactive form of bromide, rapidly forms in metal/bromide autoxidation. The addition of chloride causes a displacement reaction, $PhCH_2Br + NaCl \longrightarrow PhCH_2Cl + HBr$, which releases the catalytically active bromide. A high ratio of Cl^-/Br^- facilitates the displacement reaction more rapidly [16]. Therefore, the admix of Cl^- to Br^- ions enhances the rate of air oxidation of toluene and ensures a product mix devoid of benzyl bromide, a nasty by-product, since the inert bromide is converted into facile benzyl chloride.

3.2. *Effect of concentration of toluene in the reaction mixture*

3.2.1. *With sodium bromide*

When the concentration of toluene was increased from 28.56 to 64.32 (w/v% of the reaction mixture) in the air oxidation of toluene, the conversion of toluene and productivity with respect to all the products was enhanced twofold. However, the selectivity towards benzaldehyde and benzyl alcohol, desired products in terms of value addition, is almost the same, while yields with respective products are enhanced (figure 2). When the concentration of toluene is further increased to 80.27 w/v%, the overall conversion of toluene and productivity in terms of all the products decreases significantly, because at this concentration the catalyst

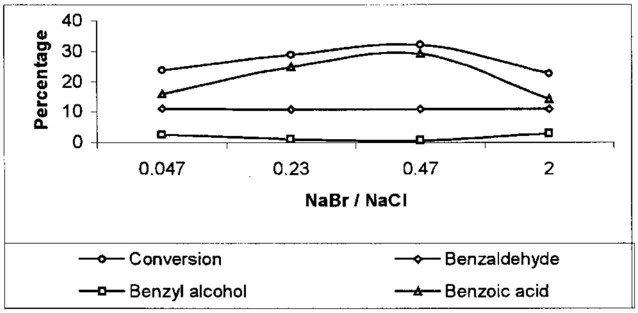


Figure 1. Effect of the ratio of NaBr/Cl on the selective air oxidation of toluene. Reaction volume: 300 ml; toluene: 64.32 w/v%; cobalt acetate: 0.0012 g mol/l; manganese acetate: 0.0008 g mol/l; time: 1.15 h; temperature: 120 °C; pressure: 10 kg/cm^2; airflow: 2 l/min.

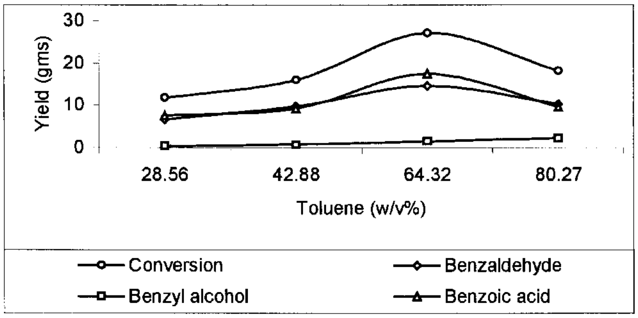


Figure 2. Effect of toluene concentration using NaBr as promoter in air oxidation of toluene. Reaction volume: 300 ml; cobalt acetate: 0.02 g mol/l; sodium bromide: 0.16 g mol/l; time: 2.15 h; temperature: 110 °C; pressure: 10 kg/cm^2; airflow: 2 l/min.

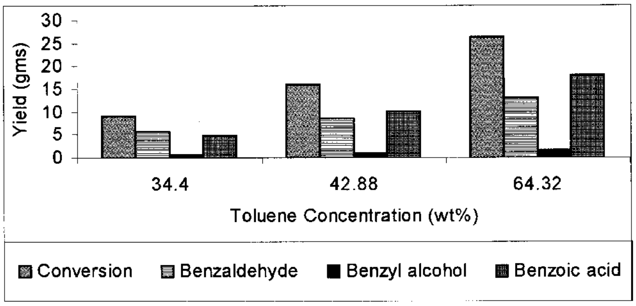


Figure 3. Effect of toluene concentration using $ZnBr_2$ as promoter in air oxidation of toluene. Reaction volume: 300 ml; cobalt acetate: 0.02 g mol/l; manganese acetate: 0.0012 g mol/l; zinc bromide: 0.04 g mol/l; pressure: 10 kg/cm^2; airflow: 2 l/min.

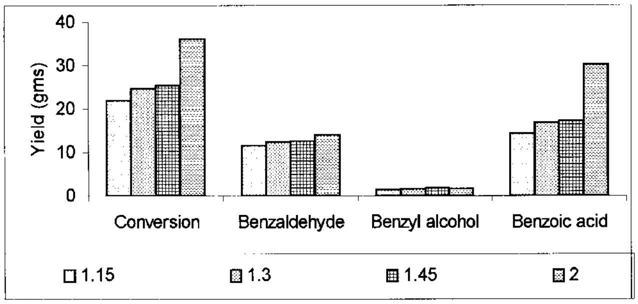


Figure 5. Effect of the reaction using zinc bromide as promoter in air oxidation of toluene. Reaction volume: 300 ml; toluene: 64.32 w/v%; cobalt acetate: 0.02 g mol/l; manganese acetate: 0.0012 g mol/l; sodium bromide: 0.04 g mol/l; temperature: 110 °C; pressure: 10 kg/cm^2; airflow: 2 l/min.

mixture is not completely soluble in the reaction mixture. The enhanced productivity towards products as obtained in the use of increased concentration of toluene is the significant achievement, when compared with an earlier report [14].

3.2.2. *With zinc bromide*

In this case also, with the increased concentration of toluene from 34.4 to 64.32 w/v% in reaction mixture, the overall conversion of toluene and yield of benzaldehyde and benzyl alcohol increased significantly (figure 3).

With the increased concentration either of the catalyst or toluene it is observed that the rate of the chemical reaction is enhanced, as reflected in the higher conversion of toluene to indicate the reaction is first-order. Low concentration of acetic acid in our reaction, designed to effect the controlled release of the adequate free Br^- to the initiation and sustenance of the reaction, is employed to minimize the loss of expensive bromine in the form of volatile HBr.

3.3. *Benzoic acid as solvent*

When the oxidation of toluene is carried out with benzoic acid as a solvent with a view to simplifying the product separation, it is found that an almost quantitative yield of benzaldehyde was obtained up to 10% level of conversion. At higher conversions, the yield of benzaldehyde decreased markedly.

We studied different concentrations of benzoic acid and found that, as the concentration increases from 0.34 to 1.25 g mol/l, the increase in the overall conversion of toluene was noticeable. When distilled water is added (3 ml) to the reaction mixture, the overall conversion increases significantly but the selectivity towards benzaldehyde is reduced phenomenally (figure 4).

3.4. *Effect of reaction time*

When varying the reaction time from 1.15 to 2 h, the conversion of toluene increases significantly, but the concentration of benzaldehyde more or less remains almost the same (figure 5). This indicates that during this time interval, the rate of formation of benzaldehyde from toluene is almost equal to its rate of disappearance to form benzoic acid. Thus, the selectivity towards benzaldehyde decreased markedly with the increase in the overall conversion of toluene.

3.5. *Recycle experiments*

Since the use of benzoic acid eases the separation of the products during downstream operation, the recycle of the composite catalytic system was studied. As can be

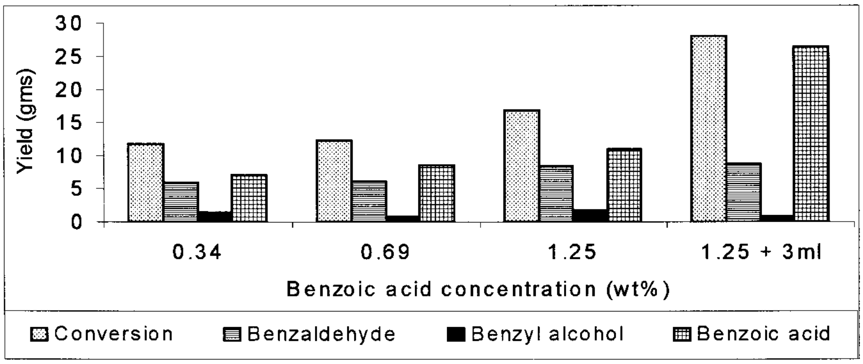


Figure 4. Results of benzoic acid concentration in air oxidation of toluene. Reaction volume: 300 ml; toluene: 80.20 w/v%; cobalt acetate: 0.02 g mol/l; manganese acetate: 0.0012 g mol/l; sodium bromide: 0.0016 g mol/l; time: 1.30 h; temperature: 130 °C; pressure: 10 kg/cm^2; airflow: 2 l/min; distilled water: 3 ml.

Table 2
Recycle experiment results using benzoic acid as solvent without replenishment[a]

Experiment No.	Conversion (%)	Selectivity		
		BA	BAl	BAc
1	9.94	33.6	27.96	38.44
2	5.68	29.0	38.5	32.5
3	3.8	38.9	16.58	44.52
4	3.42	36.5	19.60	43.90

[a] Toluene: 90 w/w%; cobalt acetate: 0.016 g mol/l; manganese acetate: 0.0008 g mol/l; zinc bromide: 0.03 g mol/l; time: 1 h; temperature: 120 °C; pressure: 10 kg/cm^2; airflow: 2 l/min.

seen in the recycle experiments summarized in table 2, conversion of toluene is reduced in each cycle. As the catalyst is recovered by aqueous extraction and reused, it is found that a large amount of catalyst is found in the organic phase. During the reaction, metal acetates are converted to benzoates on reaction with benzoic acid. As the partial coefficient of these metal benzoates is higher in toluene than their analogues, metal acetates, it is natural that a large amount of metal benzoates could not be extracted with aqueous extraction from the toluene and remain in the organic phase, and depleted amounts of catalyst are responsible for the rapid decrease of conversion for each cycle. When the losses of the composite mixture, Co/Mn/Br$^-$, are replenished and recycle studies are conducted, the conversion of toluene remains constant but the selectivity towards benzaldehyde is drastically reduced. This is because metal benzoates are not as active as metal acetates in induction of the selectivities towards primary products (figure 6).

In the reusability of the catalyst in the air oxidation of toluene using acetic acid as solvent, almost all the Co and Mn salts are recovered. However, a significant amount of bromide loss is noticed as it is consumed during the reaction. Two sets of recycle experiment were conducted replenishing with NaBr on each cycle or with 30% HBr in AcOH in each cycle for 10 cycles, and consistent results have been obtained (figures 7 and 8). 5% of Co/Mn salts were also added for each cycle to replenish the metal salts consumed in analysis and lost in recovery during extraction. In the case of NaBr (100% replenishment) used as a promoter throughout the cycles, the conversion of the toluene and composition of the products remain almost unchanged for 10 cycles. In the second set of experiments, in which NaBr was used as a promoter and HBr as a replenishment, a slight decrease in the conversion after the ninth cycle is observed.

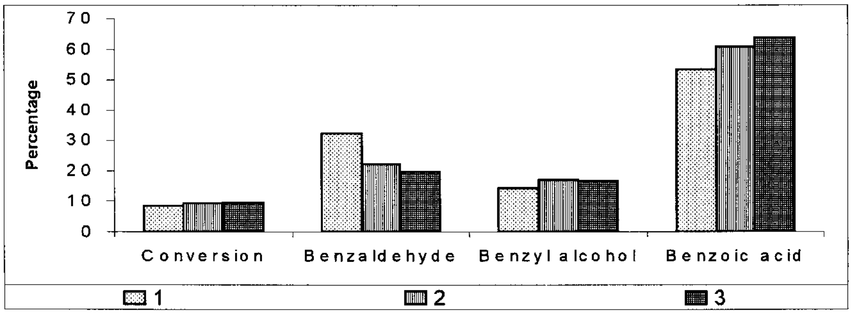


Figure 6. Results of recycle experiments using benzoic acid as solvent in air oxidation of toluene. Toluene: 90 w/w%; cobalt acetate: 0.016 g mol/l; manganese acetate: 0.0008 g mol/l; zinc bromide: 0.03 g mol/l; time: 1 h; temperature: 120 °C; pressure: 10 kg/cm^2; airflow: 2 l/min.

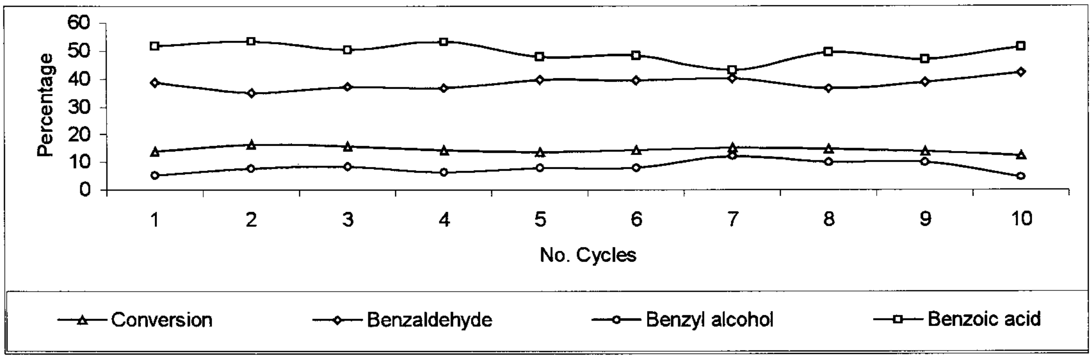


Figure 7. Results of recycle experiments using acetic acid as solvent and replenishing NaBr in each cycle. Reaction volume: 200 ml; toluene: 64.32 w/v%; cobalt acetate: 0.0012 g mol/l; manganese acetate: 0.0008 g mol/l; sodium bromide: 0.0036 g mol/l; time: 1 h; temperature: 120 °C; pressure: 10 kg/cm^2; airflow: 2 l/min. For each recycle 0.0036 g mol/l of sodium bromide is added.

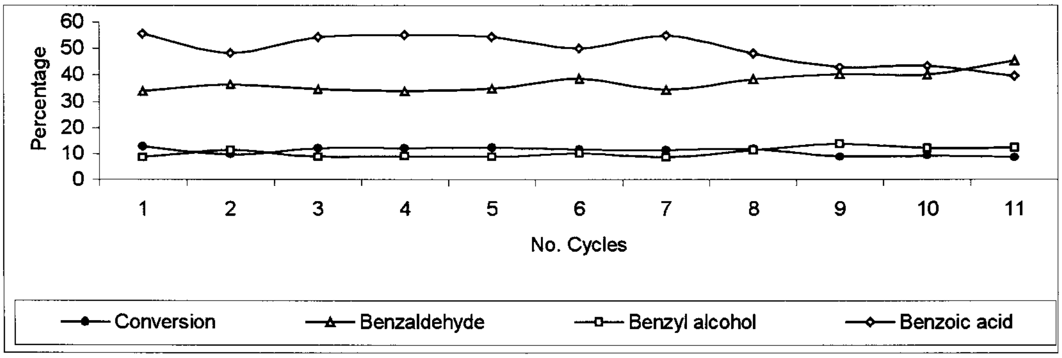


Figure 8. Results of recycle experiments using acetic acid as solvent and replenishing with HBr in each cycle. Reaction volume: 200 ml; toluene: 64.32 w/v%; cobalt acetate: 0.0012 g mol/l; manganese acetate: 0.0008 g mol/l; sodium bromide: 0.0036 g mol/l; time: 1 h; temperature: 120 °C; pressure: 10 kg/cm^2; airflow: 2 l/min. For each recycle 0.2 ml of 30% HBr in AcOH is added.

3.6. Aging studies

Here two sets of recycle experiments were conducted using the same ratio of Co/Mn/Br$^-$ for air oxidation of toluene under similar conditions. The aqueous extraction to recovery of the catalyst was reported within 2 h and the other after 6 h. When the reaction mixture is aged more than 6 h before the catalyst is extracted, it is noticed that the activity is reduced considerably for each cycle, while in the second set of experiments in which the catalyst is recovered within 2 h, the activity is consistent for all the recycles (figure 9). The deterioration of the catalyst in the first set of experiments is due to the hydrolysis of Co/Mn salts to hydoxides, caused and accelerated by the NaOAc formed in each cycle. Indeed, formation of colloidal metal hydroxides intensified with the time of aging is visibly noticed. When HBr was used for replenishment of Br$^-$ ion to avoid the formation of NaOAc, the hydrolysis of metal salts is minimized and deactivation is controlled.

3.7. Corrosion studies

The reaction was carried out in an acetic acid medium using a composite catalytic system consisting of cobalt acetate, manganese acetate and sodium bromide or zinc bromide. The presence of sodium bromide in the reaction mixture in high concentrations was known to cause severe corrosion, and stainless steel (SS316) could not be used as a material of construction [15]. Although the low concentration of bromide used in this system minimized the rate of corrosion, we studied the effect of various constituents of SS316 on the rate of air oxidation and selectivity towards primary products to meet any eventuality. The results are summarized in table 3. As can be seen in the results, the rate of conversion of toluene and selectivity remain unaffected even when 3 mg of metal constituents are deliberately added.

3.8. Electronic spectroscopy

In UV–DRS, a homogeneous solution reaction mixture composed of $Co(OAc)_2 4H_2O$ (2 mmol)/$Mn(OAc)_2 4H_2O$ (0.16 mmol) in acetic acid (75 ml) and toluene (225 ml) shows a characteristic band centered at 540 nm, and the shoulder at 490 nm is assigned to the Co(II) octahedral complex of $Co(OAc)_2(H_2O)_{4-n}(AcOH)_n$. The addition of NaBr (0.72 mmol) to the homogeneous solution causes a marked change in electronic spectra with the appearance of three new bands at 470, 630 and 670 nm, weaker than the original band centered at 540 nm (figure 10). The band at 470 nm corresponds to the *d–d* transitions, characteristic of the Mn(III)–acetato complex, and bands at 630 and 670 nm assigned to the $Co(III)(OAc)_2Br$

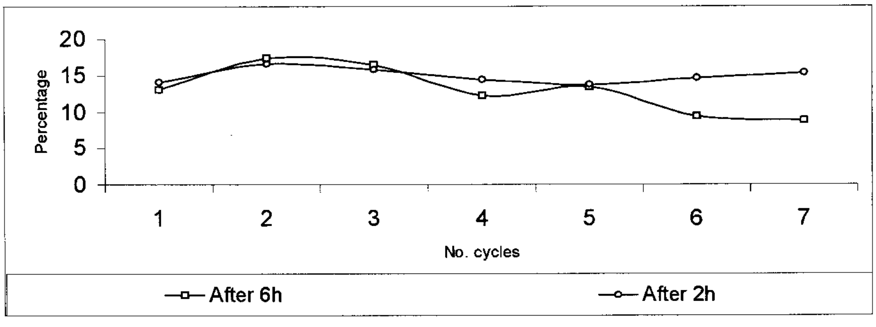


Figure 9. Effect of aging of the aqueous extract of composite catalyst system on recycles. Reaction volume: 300 ml; toluene: 64.32 w/v%; cobalt acetate: 0.02 g mol/l; manganese acetate: 0.0012 g mol/l; sodium bromide: 0.04 g mol/l; temperature: 110 °C; pressure: 10 kg/cm^2; airflow: 2 l/min.

Table 3
Effect of different metal additives[a] on air oxidation of toluene

Experiment No.	Metal salts (mg)	Conversion of toluene (%)	Selectivity (%)		
			Benzaldehyde	Benzyl alcohol	Benzoic acid
1	$Fe(NO_3)\cdot 9H_2O$ (40)	7.47	46.18	13.56	36.89
2	$Fe(NO_3)\cdot 9H_2O$ (10)	10.28	35.56	11.20	49.24
3	$Fe(NO_3)\cdot 9H_2O$ (3)	11.02	41.54	9.50	46.0
4	$Cr(NO_3)\cdot 9H_2O$ (3)	11.68	44.34	9.68	43.87
5	$Ni(NO_3)\cdot 9H_2O$ (3)	11.26	31.8	6.1	58.5
6	$MoCl_5$	13.06	37.93	9.39	50.30

[a] Reaction volume: 30 ml; toluene: 80.20 w/v%; cobalt acetate: 0.02 g mol/l; manganese acetate: 0.0012 g mol/l; sodium bromide: 0.0016 g mol/l; time: 1 h; temperature: 120 °C; pressure: 10 kg/cm^2; airflow: 2 l/min.

and Co(III)(OAc)Br_2 complexes [8]. On bubbling of the air into the solution, the electronic spectrum of the reacting solution is not changed. However, a sample of the solution drawn at the end of the reaction conducted at 110 °C and 10 kg/cm^2, as defined in the experimental section, composed of the used catalyst, shows bands at 470, 490 and 540 nm assigned to the Mn(III)–acetato complex, and $Co(OAc)_2(H_2O)_{4-n}(AcOH)_n$. When the promoter (NaBr or HBr) is added the bands at 630 and 670 nm reappeared, indicating the formation of Co(III)$(OAc)_2$Br and Co(III)$(OAc)_2$Br. The absence of the Co(III) complex and the continued presence of Mn(III) in the product mixture at the end of the reaction provide evidence that the half-life period of Mn(III) is longer than Co(III). This is inconsistent with the earlier observation [8]. The electronic spectra results which indicate the formation of mononuclear Co(III) and Mn(III) complexes failed to notice the formation of homo- and heterocluster complexes. This is further confirmed by the selective formation of toluic acid in an experiment separately carried out for air oxidation of *p*-xylene using the composite Co/Mn/Br$^-$ catalytic system. It is known that the mononuclear complexes can abstract the hydrogen of the methyl of *p*-xylene, whereas the cluster complexes of Co and Mn can even abstract the hydrogen of the methyl of *p*-toluic acid, a resilient one to form terephthalic acid in the air oxidation of *p*-xylene [8].

3.9. Plausible mechanism

The aerobic oxidation of toluene by the Co/Mn/Br$^-$ catalyst system proceeds *via* a free radical chain mechanism [16]. Co(III) is the radical initiating species formed from $Co(OAc)_2$ on reaction with NaBr [17]. The Co(III) then reacts rapidly with $Mn(OAc)_2$, generating Mn(III) and Co(II) in this process. The Mn(III) ion

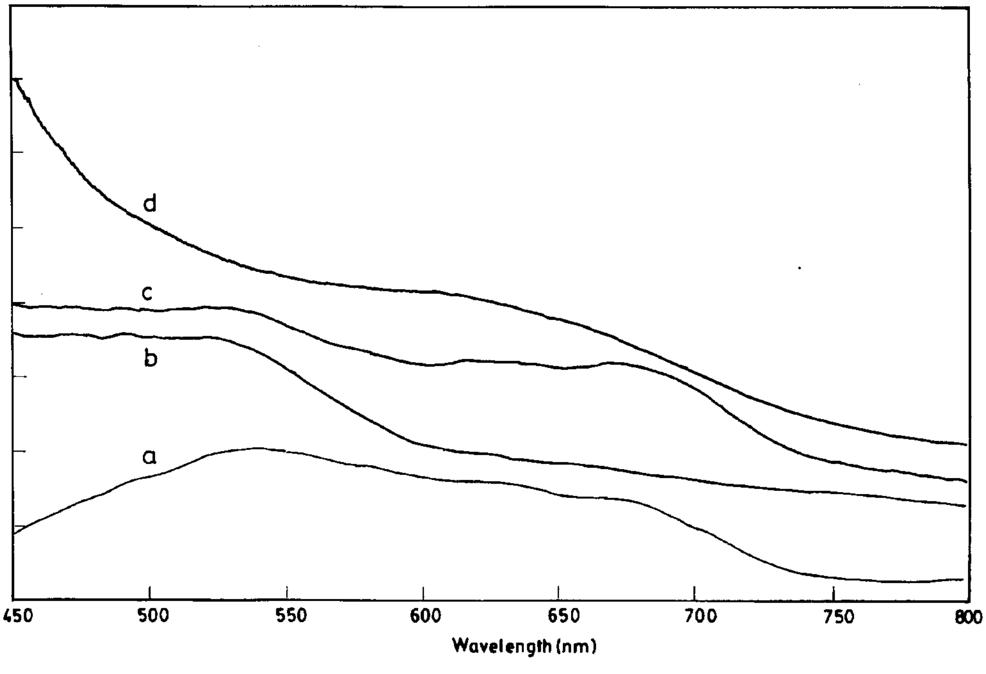
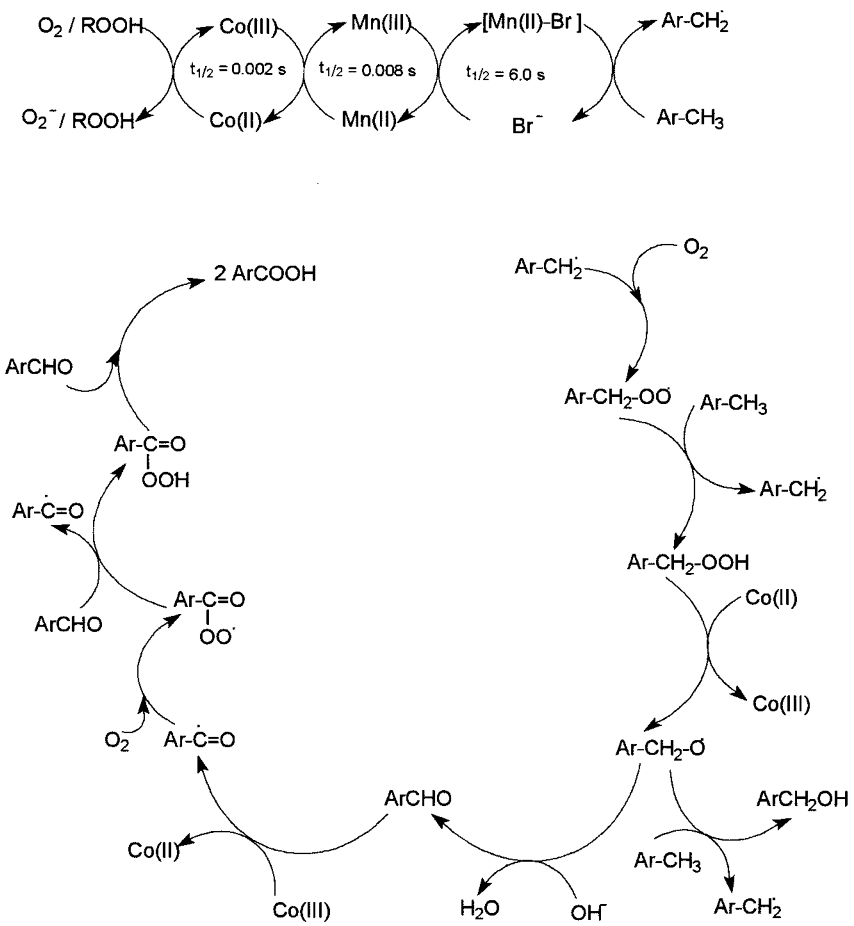


Figure 10. UV–DRS spectrum of composite catalytic system (a) before reaction, (b) after reaction, (c) after replenishment, (d) before reaction in benzoic acid as solvent.



Scheme 2. Plausible reaction pathways.

then abstracts an electron from Br^- to give a bromine radical, $Br^\bullet$, which in turn abstracts a hydrogen atom from a methyl group of toluene to initiate the oxidation of toluene as described in scheme 2.

4. Conclusions

The novelty of the present method is the realization of the high productivity of benzaldehyde and benzyl alcohol in the air oxidation of toluene, with a high turnover number. The use of manganese acetate as an initiator improved the conversion of toluene and yields of benzaldehyde and benzoic acid, and thus recorded a higher rate of productivity even at a low concentration of cobalt and high concentration of toluene. Even with the reduction of Br^- content by 5–50 times as NaBr replaces $ZnBr_2$, it is observed that the conversion of the toluene and selectivity and yields towards benzaldehyde are not much affected. Low concentration of solvent, carboxylic acids in our reaction, designed to release adequate free Br^- which gives *in situ* free radical $Br^\bullet$ on interaction with Mn(III) to the initiation of the reaction, is employed to minimize the loss of expensive bromine in the form of volatile HBr and to minimize the corrosion problem. Use of NaBr/NaCl at lower ratios to accelerate the rate of the reaction and to afford higher selectivity towards benzaldehyde and benzyl alcohol is the ultimate choice, since it reduces the process cost. As the market demand for each product fluctuates, the dynamic system developed here as described is very important to enable one to choose the required composition of Br^-/Cl^- to obtain the desired product in excess quantities to meet changing demands. A protocol for recovery and reuse of the composite catalyst is developed. Recycle and aging studies described here allow evolution of the strategy for commercial production of benzaldehyde in high selectivities. UV–vis studies identified mononuclear Co and Mn complexes as active species for selective oxidation of toluene to benzaldehyde. The process is environmentally safer since there is no effluent disposal problem as encountered in chlorination of toluene followed by oxidation.

Acknowledgments

We gratefully acknowledge CSIR, New Delhi, India, for the award of SRF to P.S.K. and JRF to B.P.C.R. and Dr. K.V. Raghavan, Director, IICT, India, for useful discussions.

References

[1] R.A. Sheldon and J.K. Kochi, in: *Metal-Catalyzed Oxidations of Organic Compounds* (Academic Press, New York, 1981).

[2] P.J.A.C. Camerman and J.D.V. Hanotier, UK Patent 1,275,699 (1972).

[3] T.F. Blackburn and J. Schwartz, J. Chem. Soc., Chem. Commun. (1972) 157.

[4] A.S. Hay and H.S. Blanchard, Can. J. Chem. 43 (1965) 1306.

[5] Y. Kamaya, J. Catal. 33 (1974) 480.

[6] C. Guoying and X. Xi Zuwei, Chinese J. Catal. 3 (1983) 218.

[7] T. Morimoto and Y. Ogata, J. Chem. Soc. B (1967) 1353.

[8] S.A. Chavan, S.B. Halligudi, D. Srinivas and P. Ratnasamy, J. Mol. Catal. 161 (2000) 49; S.A. Chavan, D. Srinivas and P. Ratnasamy, Chem. Commun. (2001) 1124.

[9] E.I. Heiba, R.M. Dessau and W.J. Koehl, J. Am. Chem. Soc. 91 (1969) 6831.

[10] C.L. Jenkins and J.K. Kochi, J. Am. Chem. Soc. 94 (1972) 856.

[11] T. Okada and Y. Kamiya, Bull. Chem. Soc. Jpn. 54 (1981) 2724.

[12] V.A. Adamyan, Y.V. Geletii and M. Hronec, Kinet. Catal. 34 (1993) 573.

[13] K. Bahranowski, R. Dula, M. Labanowska, A. Michalik, L.A. Vartikian and E.M. Serwicka, Appl. Clay Sci. 18 (2001) 93.

[14] M.W. de Lange, J.G. van Ommen and L. Lefferts, Appl. Catal. A: General 220 (2001) 41.

[15] H.V. Borgaonkar, S.R. Raverkar and S.B. Chandalla, Ind. Eng. Chem. Prod. Res. Dev. 23 (1984) 455.

[16] W. Partenheimer, Catal. Today 23 (1995) 69.

[17] W. Partenheimer, J. Mol. Catal. 67 (1991) 35.