



A new approach to electrochemical production of benzaldehyde from toluene in an undivided cell in the presence of the couple V^{5+}/V^{4+}

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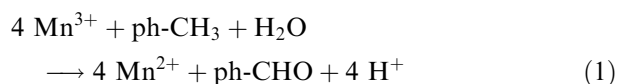
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Abstract

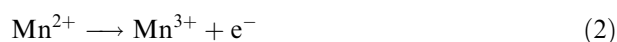
Oxidation of toluene to benzaldehyde in the presence of the redox couple V^{5+}/V^{4+} was carried out in an undivided cell where oxygen gas was continuously bubbled over the cathodic surface and the electrolyte was a mixture of aqueous H_2SO_4 solution containing V^{5+} and toluene. Some experimental conditions affecting the current efficiency for benzaldehyde production, such as H_2SO_4 concentration, current density, V^{5+} concentration and surfactants, were determined. The maximum current efficiency for benzaldehyde production at ambient temperature was 156.3% under the conditions of 11 M H_2SO_4 , 2.7×10^{-4} M CTAB, current density 1.25 mA cm^{-2} and 0.0128 M V^{5+} .

1. Introduction

Indirect electrochemical production of benzaldehyde from toluene is carried out by mediator couples such as Mn^{3+}/Mn^{2+} , Ce^{4+}/Ce^{3+} , Co^{3+}/Co^{2+} and V^{5+}/V^{4+} . Besides being used in indirect electrosynthesis of benzaldehyde [1–4], the couple Mn^{3+}/Mn^{2+} is also used in indirect electrosynthesis of other organic compounds, such as *p*-methylbenzaldehyde [5]. In addition, redox couples have been used in the treatment of waste water containing benzene, aniline and phenol [6–8]. Wendt et al. [9, 10] reported the direct anodic oxidation of toluenes to benzaldehyde or methyl substituted benzaldehydes in nonaqueous solutions. Electrochemical studies on the Ce^{4+}/Ce^{3+} couple have been well-researched [11–14]. Generally, the oxidized species of the couple M_{OX}/M_{RE} is electrochemically regenerated from its reduced species in a divided cell by an ion-selective membrane. For example, in sulfuric acid solution toluene is chemically oxidized to benzaldehyde by Mn^{3+} ion, as shown in Reaction 1:



The Mn^{2+} ion is then separated from the mixture and transferred to the anodic compartment of a cell where Mn^{3+} is electrogenerated by the anodic oxidation of Mn^{2+} :



Therefore, Mn^{3+} can be used repeatedly. However, these two Reactions 1 and 2 are generally carried out in two separated reactors, resulting in an increase of experimental steps. The present authors previously studied the chemical oxidation of toluene to benzaldehyde by V^{5+} ion in sulfuric solution and the yield for benzaldehyde production was 73.2% [4].

In addition, Tomat [15] reported that benzaldehyde is also produced with electrochemically generated Fenton reagent. Fenton's reagent can be prepared by the simultaneous cathodic reduction of molecular oxygen and Fe^{3+} , V^{5+} , V^{4+} or Cu^{2+} [15]. Jiin et al. [16] reported the oxidation of toluene to benzaldehyde by Mn^{3+} and $\cdot OH$ free radicals, generated in the anodic and cathodic reactions, respectively. Electrolysis was carried out in a divided cell with anodic and cathodic chambers separated by an anion exchange membrane. The maximum total current efficiency for benzaldehyde production in the paired electro-oxidation was 171%. For Tomat's experimental procedures [15], the cathodic and anodic compartments were separated by a salt bridge where the salt concentration would decrease with the proceeding of electrolysis.

Because of its wide application in production of hydrogen peroxide, treatment of wastewater and synthesis of organic or inorganic species, electroreduction of oxygen in cathodes has been well-studied [17]. Many methods, including surface modification of cathodes, application of different cathodic materials and addition of surfactants, have been applied in order to increase the current efficiency of oxygen electroreduction [17–20].

In this work V^{5+}/V^{4+} was chosen as the redox couple because a higher yield was obtained with the system V^{5+}/V^{4+} than with those based on indirect toluene oxidation using such inorganic redox couples such as Mn^{3+}/Mn^{2+} , Ce^{4+}/Ce^{3+} and Ag^{2+}/Ag^+ [15]. Oxygen gas was continuously bubbled over the cathodic surface and electrochemically reduced to H_2O_2 . A cationic surfactant CTAB, cetyltrimethylammonium bromide, was added to the reaction mixture to increase the cathodic electroreduction rate of oxygen on the basis of Gyenge's work [20]. Both anodic and cathodic reactions were carried out in an undivided cell where the electrolyte was a mixture of aqueous sulfuric solution containing V^{5+} and toluene.

2. Experimental details

All chemicals used were analytical grade products; water was deionized. Both the anode and cathode were graphite plates (surface area $\sim 40 \text{ cm}^2$). Before each run, electrodes were pretreated by polishing with emery paper, then washing with acetone and deionized water. Finally they were air-dried. The reference electrode was a saturated calomel electrode (SCE). The cell was filled with 60 cm^3 of toluene to which 200 cm^3 of aqueous sulfuric acid solution containing NH_4VO_3 and surfactants were added. This mixture was stirred at a constant rate to obtain a fine suspension with O_2 saturation maintained by a slow stream of high purity oxygen [15]. The electrolysis was carried out at constant temperature $25 \pm 0.5 \text{ }^\circ\text{C}$, monitored and maintained by a temperature regulator. The electrochemical cell is shown in Figure 1.

After electrolysis, the organic phase was separated from the reaction mixture. The benzaldehyde remaining in the aqueous solution was then extracted three times, using 100 ml toluene each time. The benzaldehyde content in the total organic phase was used to calculate the current efficiency for benzaldehyde production. The remaining benzaldehyde in the aqueous phase, after extraction, was not included in the benzaldehyde current efficiency. This is an approximate treatment according to the distribution coefficient for benzaldehyde between the aqueous H_2SO_4 solution and toluene, as shown in Table 1. Although the solubility of benzaldehyde in the aqueous H_2SO_4 solution would decrease considerably if the reaction mixture was neutralized by $NaHCO_3$ [15], this made it impossible for the aqueous solution to be recycled for the next electrolysis.

After electrolysis, the organic phase was separated from the reaction mixture and washed with dilute $NaHCO_3$ solution and then water. The content of benzaldehyde in the organic layer, together with the benzaldehyde in the extraction agent, was analysed by both chromatography and $NaHSO_3$ titration method. These two methods gave the same result. For example, the benzaldehyde concentration in the toluene phase was 0.09 M under the conditions of 11 M H_2SO_4 , 2.7×10^{-4} M CTAB, current density 1.25 mA cm^{-2} ,

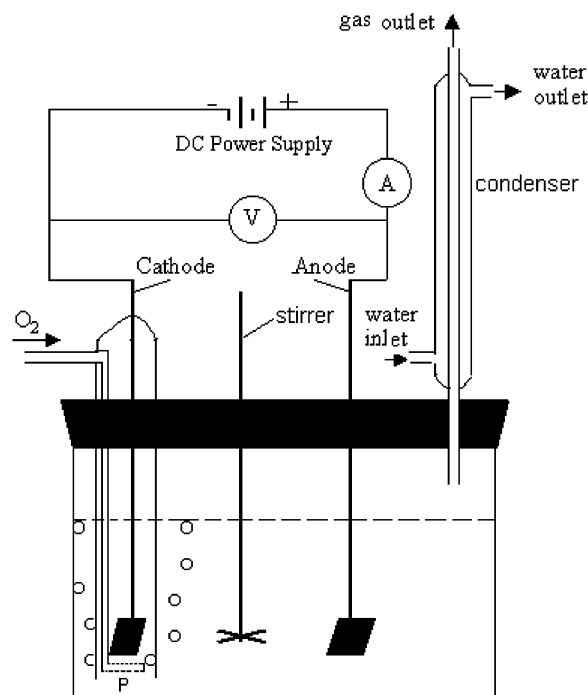


Fig. 1. Electrochemical cell. P is a hollow glass pipe ducting oxygen.

Table 1. Distribution coefficient for benzaldehyde between toluene (org.) and 11 M H_2SO_4 aqueous solution (aq.) at $25 \text{ }^\circ\text{C}$

Volume ratio ($V_{org.}/V_{aq.}$)	$C_{org.}/\text{mol dm}^{-3}$	$C_{aq.}/\text{mol dm}^{-3}$	D
0.08	0.1123	0.03335	3.367
0.4	0.098	0.0290	3.379
1.9	0.127	0.0369	3.442
2.0	0.135	0.0408	3.309
3.5	0.157	0.047	3.341
6.5	0.162	0.049	3.306

Note: C_{org} and C_{aq} are concentrations of benzaldehyde in toluene and aqueous phases, respectively. Distribution coefficient $D = C_{org}/C_{aq}$ on the supposition that the activity coefficient of benzaldehyde in both toluene and aqueous phases is 1.

electrolysis time 11 h and $0.0128 \text{ M } V^{5+}$. Benzoic alcohol or benzoic acid was not detected by chromatography.

3. Results and discussion

3.1. Effect of surfactants

Being a phase-transfer catalyst (PTC), CTAB enhances the reaction between the salt dissolved in the aqueous solution, such as V^{5+} , and the organic species. The effect of the CTAB on the current efficiency for benzaldehyde production involves two aspects: (i) CTAB acts as a phase-transfer catalyst in order to enhance the reaction between the oxidizing agent dissolved in the aqueous phase and the organic species; (ii) CTAB speeds up the electroreduction rate of oxygen. Being a PTC, CTAB

was used to increase the oxidation rate of toluene to benzaldehyde in the presence of the redox couple $\text{Mn}^{3+}/\text{Mn}^{2+}$ [21–23]. CTAB was also applied in the oxidation of $p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_3$ to $p\text{-CH}_3\text{C}_6\text{H}_4\text{CHO}$ in the presence of $\text{Mn}^{3+}/\text{Mn}^{2+}$ [24]. Liu et al. reported the indirect electrosynthesis of *o*-chlorobenzaldehyde from *o*-chlorotoluene by using $\text{Ce}^{4+}/\text{Ce}^{3+}$ in sulfuric acid as an oxidative mediator and CTAB as a phase-transfer catalyst [25]. The presence of CTAB increased the reaction rate between the mediators and the organic species and also increased the current efficiency.

According to Gyenge [20], the electroreduction rate of oxygen at the cathodes was influenced by the addition of surfactants. Three types of surfactant were tested to obtain the maximum rate: anionic, cationic and non-ionic. Gyenge's study showed that the cationic surfactant (Aliquai 336[®], tricaprilmethylammonium chloride), at mM levels, increased the standard rate constant of O_2 electroreduction to H_2O_2 15 times in Na_2CO_3 and 1900 times in H_2SO_4 , to $1.8 \times 10^{-6} \text{ m s}^{-1}$ and $9.9 \times 10^{-10} \text{ m s}^{-1}$, respectively. On the basis of this reference three types of surfactants were also tested: polyethylene glycol (nonionic, PEG), dodecyl phenylsulfonate (anionic, DDPS), and cetyltrimethylammonium bromide (anionic, CTAB). It was found that both PEG and DDPS had little effect on current efficiency for benzaldehyde production. However, CTAB, a cationic surfactant, was able to increase the reaction rate. For example, under the conditions of 11 M H_2SO_4 , 60 ml toluene, and 0.0128 M V^{5+} at 25 °C, it needed about one minute for the reaction mixture to change its colour in the presence of $2.7 \times 10^{-4} \text{ M}$ CTAB. Three minutes were needed in the absence of CTAB. Dependence of current efficiency for benzaldehyde production on CTAB is shown in Figure 2.

3.2. Concentrations of V^{5+} ion

Dependence of V^{5+} concentration on the current efficiency for benzaldehyde production is shown in Figure 3. When either V^{5+} is present in the solution at higher concentration levels or V^{5+} ion is absent, the

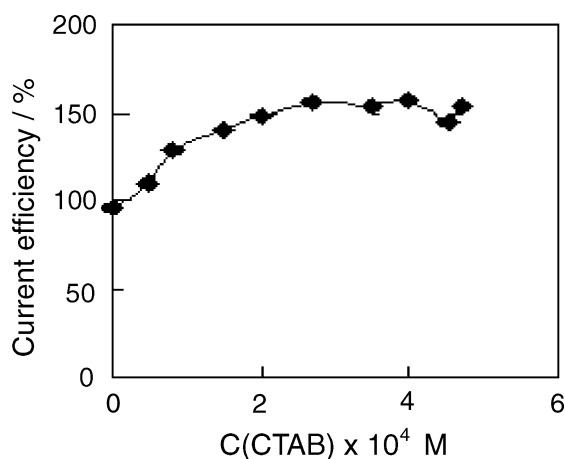


Fig. 2. Effect of CTAB concentration on current efficiency. H_2SO_4 11 M; electrolysis time 11 h; $C(\text{V}^{5+}) = 0.0128 \text{ M}$; $i = 1.25 \text{ mA cm}^{-2}$.

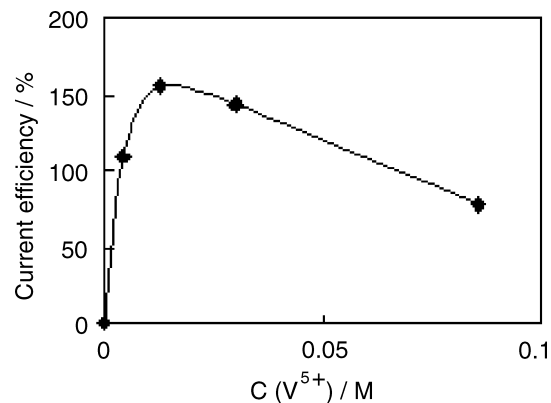
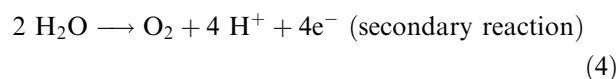


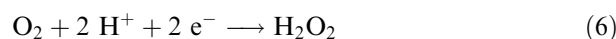
Fig. 3. Effect of V^{5+} ion on current efficiency. H_2SO_4 11 M; electrolysis time 11 h; $C(\text{CTAB}) = 2.7 \times 10^{-4} \text{ M}$; $i = 1.25 \text{ mA cm}^{-2}$.

current efficiency for benzaldehyde production is lower. According to the reaction mechanism [15, 16], the main reactions in this system can be expressed as follows: Anodic reaction:

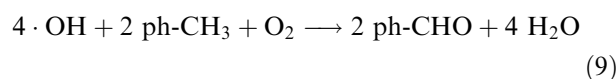
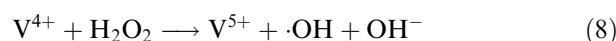
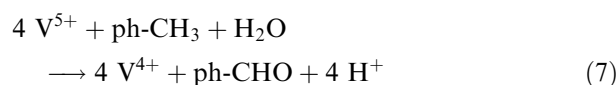


The potential range of the electrode Reaction 3 is 0.85–0.90 V vs SCE. The overpotential to generate oxygen is higher in a strong acid solution than in a weak acid solution or alkaline solution [26, 27]. Therefore, generation of oxygen on the anode can be inhibited in concentrated sulfuric acid aqueous solution.

Cathodic reactions:



Chemical reactions in bulk solution:



If concentrations of V^{5+} ion are higher (Reaction 5), then the reduction of V^{5+} to V^{4+} at the cathodes will be predominant. This is supported by our experimental observation, an example of which is the rapid change of the solution color from initial orange yellow to blue green if the V^{5+} concentration is 0.03 M. In addition, the absence of V^{5+} ion in the solution also results in a low current efficiency. This phenomenon indicates that the V^{5+} ion plays a key role in electrosynthesis of benzaldehyde, as shown in Reactions 7–9. In other words,

benzaldehyde can be produced both by Reaction 7 between toluene and V^{5+} ion and by Reaction 9 between toluene and OH radicals formed with Reaction 8 between H_2O_2 and V^{4+} ion which is the reduced species of V^{5+} ion in Reaction 7. Increasing V^{5+} concentration increases the possibility of reduction of V^{5+} on the cathode to form V^{4+} , hence the V^{4+} concentration also increases. Furthermore, the $\cdot OH$ free radical may be consumed by the V^{4+} ion [27]:

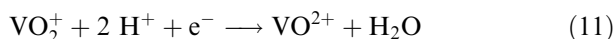


The rate constant of Reaction 10 is also much larger than the rate constant for generation of $\cdot OH$ free radicals, i.e. Reaction 8. Therefore, the increase in V^{4+} concentration increases the rate of Reaction 10, resulting in decreasing current efficiency for benzaldehyde production.

Therefore, it is necessary for the initial V^{5+} concentration in the electrolyte to be kept at an appropriate value. According to Figure 3 this appropriate concentration was 0.0128 M under our experimental conditions.

3.3. Concentration of H_2SO_4

H_2SO_4 concentrations had a considerable effect on the current efficiency for benzaldehyde production [4]. The current efficiency increased with H_2SO_4 concentration, as shown in Figure 4. The effect of H_2SO_4 may be mainly associated with conductance of the electrolyte, the increasing oxidation potential of V^{5+} ion and the electroreduction rate of oxygen at the cathodes. It is known that the V^{5+} ion is actually a simplified form of the VO_2^+ ion, even in strong acidic solutions. Therefore, oxidation potentials of VO_2^+ are dependent on pH values:



where VO^{2+} is generally expressed with the form of V^{4+} . The dependence of potentials $E(VO_2^+/VO^{2+})$ on pH is shown in Equation 12:

$$E(VO_2^+/VO^{2+}) = E^0(VO_2^+/VO^{2+}) - 0.118 \text{ pH} + 0.05917 \log \frac{[VO_2^+]}{[VO^{2+}]} \quad (12)$$

From Reaction 7 and Equation 12, it is found that the stronger acidity of the solution is favourable for the formation of benzaldehyde. The appropriate H_2SO_4 concentration was 11 M on the basis of our experimental conditions, since a H_2SO_4 concentration which exceeds 11 M may lead to some undesired reactions.

Another effect of higher concentrations of H_2SO_4 is to increase the rate of oxygen electroreduction. The tendency for production of H_2O_2 increases with decrease of pH [28], as in Reaction 6. Subsequently, the current

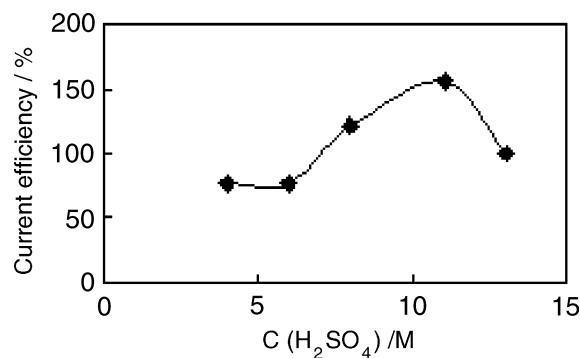


Fig. 4. Effect of H_2SO_4 concentration on current efficiency. $C(V^{5+}) = 0.0128$ M; electrolysis time 11 h; $C(CTAB) = 2.7 \times 10^{-4}$ M; $i = 1.25$ mA cm⁻².

efficiency for benzaldehyde production increases with H_2O_2 concentration, as in Reactions 8 and 9.

3.4. Cathodic current density

The electrolysis was carried out at a constant current density controlled with a d.c. power supply (Figure 1). The effect of current density on the current efficiency for benzaldehyde production is indicated in Figure 5. Under the conditions of 11 M H_2SO_4 , 2.7×10^{-4} M CTAB, electrolysis time 11 h, 60 ml toluene and 0.0128 M V^{5+} , both low and high current densities lead to low current efficiencies. For low current densities it takes a long time to carry out oxidation of toluene to benzaldehyde. When the current density increases from 0.25 mA cm⁻² to 1.25 mA cm⁻², the current efficiency increases dramatically. The maximum current efficiency is 156.3%, corresponding to the current density 1.25 mA cm⁻². The current efficiency decreases for a current densities higher than 1.25 mA cm⁻². Higher current densities result in an increase in cathodic overpotential and secondary reactions, resulting in a decrease in current efficiency. When the cathodic current density is about 1.25 mA cm⁻², the cell voltage is between 1.5 to 2.0 V, depending on the electrolysis time and the electrolyte concentration change. Appropriate elevation of electrolysis temperature and a specially designed cell may be helpful in

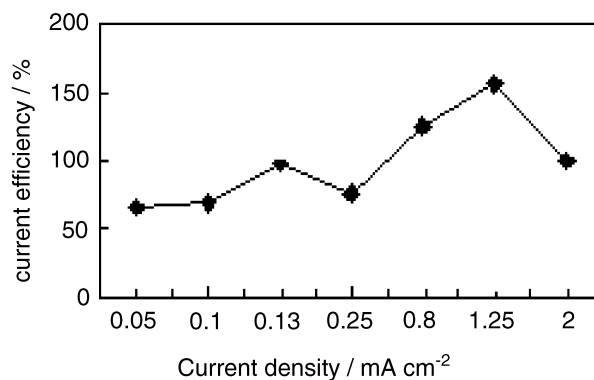


Fig. 5. Effect of current density on current efficiency. $C(V^{5+}) = 0.0128$ M; electrolysis time 11 h; $C(CTAB) = 2.7 \times 10^{-4}$ M; H_2SO_4 11 M.

increasing the cathodic current density. This is currently under investigation.

4. Conclusions

In an undivided cell, toluene was oxidized to benzaldehyde by V^{5+} ions and $\cdot OH$ radicals produced by electroreduction of oxygen at a graphite electrode. Effects of surfactants, H_2SO_4 concentration, V^{5+} concentration and cathodic current density on the current efficiency for benzaldehyde production were investigated. The effect of cationic surfactant CTAB on the current efficiency for benzaldehyde production may be attributed to its function as a phase-transferred catalyst, and an increase in electroreduction rate of oxygen to hydrogen peroxide, or both. A reasonably high concentration of H_2SO_4 is necessary to obtain a higher oxidation potential of V^{5+} . The effect of V^{5+} includes two aspects: directly oxidizing toluene to benzaldehyde and reacting with hydrogen peroxide to produce OH radicals which, in turn, oxidize toluene to benzaldehyde. The dual effect makes it possible for the current efficiency of oxidation of toluene to benzaldehyde to exceed 100%.

Although there are such disadvantages as low current density and possible electrode fouling by organic polymers from secondary reactions, the electro-oxidation of toluene to benzaldehyde in an undivided cell in the presence of the couple V^{5+}/V^{4+} still has a high current efficiency since both $\cdot OH$ free radicals and V^{5+} take part in the oxidation. In addition, this process is simple. Therefore, the process is attractive and, on the basis of further work, may become a commercial process for the production of benzaldehyde. Studies on other experimental conditions affecting current efficiencies for benzaldehyde production, such as reaction temperature, electrolysis time and electrode materials, are under way.

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