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Synthesis of chloroanilines at a Ti/ceramic TiO_2-cathode

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Electroreduction of 2-, 3- and 4-chloronitrobenzenes (2-CNB, 3-CNB and 4-CNB) to the corresponding chloroanilines has been carried out under galvanostatic conditions in aqueous H_2SO_4 at a Ti/ceramic TiO_2-cathode. A comparison of the yield and current efficiency (CE) for the amine formation at a Ti/ceramic TiO_2-cathode with that at a copper cathode indicates the electrocatalytic nature of the former electrode. The results on the cyclic voltammetric behaviour of 2-CNB, 3-CNB and 4-CNB at a Ti/ceramic TiO_2-cathode are also reported, and indicate a mechanism involving heterogeneous redox catalysis by Ti^{4+}/Ti^{3+}.

1. Introduction

The electrochemical reduction of nitro compounds involving their direct reduction at the electrode surface has been well studied [1, 2] in acid medium. However, the method suffers from the disadvantages of low yield and CE for amine formation. This was overcome by employing indirect electroreduction involving redox electron carriers such as Sn^{4+}/Sn^{2+} and Ti^{4+}/Ti^{3+} [3, 4], which involves homogeneous reduction of the nitro compound by the Sn^{2+} or Ti^{3+} formed at the electrode surface. This method was further improved upon by incorporating the redox species at the electrode surface itself. Beck and coworkers developed a titanium cathode with a ceramic TiO_2 layer [5, 6] whose surface behaves as a stable redox electron carrier and reduction occurs through heterogeneous redox catalysis [7].

In this paper the results on the galvanostatic reduction of chloronitrobenzenes in aqueous H_2SO_4 at a Ti/ceramic TiO_2-cathode are reported. These results are compared with those obtained at a conventional copper cathode. The results on the cyclic voltammetric behaviour of the chloronitrobenzenes at a Ti/ceramic TiO_2-cathode in aqueous H_2SO_4 medium are also reported.

It may be mentioned that the chloroanilines are prepared chemically by reducing the corresponding chloronitrobenzenes with Fe and HCl [8]. This method suffers from the point of view of environmental pollution. The chloroanilines find applications as intermediates for rubber, chemicals, pigments, pesticides, pharmaceuticals and dyes [9].

2. Experimental details

2.1. *Galvanostatic electrolysis*

The Ti/ceramic TiO_2-cathode was prepared at 550° C by the method employed in the production of ceramics [5]. The cell assembly is similar to that employed earlier [10]. The Ti/ceramic TiO_2-cathode (area 0.84 dm^2) served as cathode and a lead strip (placed inside the porous pot) served as the anode. The catholyte consisted of 400 ml of H_2SO_4 of different concentrations (1–6 M with the nitro compound added (12 g) and the anolyte consisted of 25 ml of H_2SO_4 of the same concentration as that used for the catholyte. The catholyte was stirred mechanically using a glass stirrer. The temperature of the electrolyte was adjusted manually using a water bath. The quantity of current consumed was 6 F mol^{-1}. The yield and CE for amine formation were calculated for different values of temperature, current density at the working electrode and acid strength. The amine content in the electrolysis product was estimated by diazotisation [11].

Studies involving the re-use of the electrolyte have also been carried out in order to isolate the amine as the amine sulphate. It was later neutralised to give the amine. The chloroanilines so synthesized were identified by their melting points and i.r. spectra which were compared with those of the authentic samples. The LR grade compounds, 2-, 3- and 4-chloronitrobenzenes were purified by repeated recrystallisation from ethanol and then used.

2.2. *Cyclic voltammetric studies*

The details regarding the instrumentation, cell and electrodes employed for cyclic voltammetric studies are the same as reported earlier [10]. The depolarizer solution in the concentration range 1–25 mM in 1 M H_2SO_4 was used. The experimental solution was deaerated using pure nitrogen gas.

3. Results and discussion

3.1. *Galvanostatic electrolysis*

The results on the galvanostatic reduction of 2-CNB at the Ti/ceramic TiO_2-cathode under varying conditions of temperature, current density and acid strength are reported in Table 1. Due to the poor solubility of 2-CNB in the solid form or the liquid

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Table 1. Galvanostatic reduction of 2-CNB at a Ti/ceramic TiO_2-cathode in aqueous H_2SO_4 containing 0.01% CTAB

Sl. No.	*Weight of 2-CNB* /g	*Acid strength* (H_2SO_4) /M	*Current density* /A dm^{-2}	*T* /°C	*Recovered unreduced 2-CNB* /g	*Weight of 2-CA estimated* /g	*Estimated yield of 2-CA* /%	*Current efficiency* /%
1*	12	5	5.0	40–50	12.0	–	–	–
2	12	5	5.0	30–40	4.0	4.4	68.0	65.0
3	12	5	5.0	40–50	–	8.7	89.1	97.2
4	12	5	5.0	50–60	–	8.2	84.2	90.8
5	12	5	2.5	40–50	6.0	2.3	48.1	45.0
6	12	5	7.5	40–50	–	8.0	83.0	78.7
7	12	3	5.0	40–50	2.2	5.2	66.2	50.9
8	12	4	5.0	40–50	1.0	6.0	67.4	48.7
9	12	6	5.0	40–50	0.4	8.3	88.2	96.5
10†	12	5	5.0	40–50	5.0	3.1	54.7	44.4

* Without CTAB.
† At copper cathode.

form (in which it exists under the present experimental conditions, m.p. 33–36° C), no reduction occurs (Experiment 1). Addition of 0.01% cetyl trimethylammonium bromide (CTAB) to the catholyte effected complete emulsification of 2-CNB in the given medium, and hence had a marked effect on the yield and CE for amine formation (Experiments 2–9).

The effect of temperature (*T*) (Experiments 2–4) is found to have a marked influence on the yield and CE for amine formation. Increase of *T* from 30–40° C to 40–50° C increases the yield and CE appreciably due to increased solubility of 2-CNB as well as 2-chloroaniline. A slight reduction in the yield and CE observed on further increase of *T* is attributed to the side reaction involving resin formation.

Experiments 3, 5 and 6 show that a current density of 5 A dm^{-2} produces the best yield and CE. At higher current density, competitive hydrogen evolution occurs, thereby decreasing the yield and CE.

The effect of acid strength (Experiments 3, 7–9) has been studied under best conditions of *T* and current density. The yield and CE were found to increase considerably on increasing the acid strength from 3 M to 5 M due to the improved solubility of 3-CNB as well as that of the product, 3-chloroaniline. On further increasing the acid strength, a slight reduction observed in the yield and CE is due to the side reaction involving resin formation.

From Table 1 it is also seen that the yield and CE for amine formation are very much higher at a Ti/ceramic TiO_2-cathode than at a conventional copper cathode (Experiments 3 and 10), under identical experimental conditions, thus indicating the electrocatalytic nature of the former.

Similar runs were performed for the galvanostatic reduction of 3-CNB and 4-CNB but both in the absence of any CTAB. The best conditions for the galvanostatic reduction of the isomeric chloronitrobenzenes in aqueous sulphuric acid at Ti/ceramic TiO_2-cathode are given in Table 2.

For the galvanostatic reduction of 3-CNB and 4-CNB, the yield and CE for amine formation was very much higher at a Ti/ceramic TiO_2-cathode than at a conventional copper cathode under identical experimental conditions.

Studies on the reuse of the electrolyte for building up the concentration of the product to saturated solubility were carried out for the isomeric chloronitrobenzenes choosing the best experimental conditions from Table 2 and the results of these studies are shown in Table 3.

A comparison of Table 2 with Table 3 shows that the yield of the corresponding chloroaniline is considerably reduced under conditions of electrolyte reuse. This behaviour may be attributed to the fact that the isomeric CNBs which exist in the liquid form under the given experimental conditions, as well as their reduction products, the isomeric chloroanilines, are volatile in steam and this effect becomes pronounced under conditions of reuse.

The prepared 2- and 3-chloroanilines boiled at 208–210° C (208–210° C) and at 232° C (230–231° C) and 4-chloroaniline melted at 72.5° C (72.5° C) with the corresponding values of an authentic sample [12]

Table 2. Optimum conditions for the galvanostatic reduction of the isomeric chloronitrobenzenes in aqueous sulphuric acid at Ti/ceramic TiO_2-cathode

Educt	*Additive 0.01% CTAB*	*Current density* /A dm^{-2}	*T* °C	$C_{H_2SO_4}$ /M	*Estimated yield of CA* /%	*CE* /%
2-CNB	+	5	40–50	5	89.1	97.2
3-CNB	–	5	50–60	4	82.9	83.0
4-CNB	–	5	80–85	2	85.9	95.4

Table 3. Galvanostatic reduction of the isomeric chloronitrobenzenes at a Ti/ceramic TiO_2-cathode at a current density of 5 A dm^{-2} showing reuse of electrolyte

Educt	*Weight of nitro-compound /g*	*T °C*	*Acid strength /M*	*Weight of CA obtained on neutralisation /g*	*Weight of CA in solution /g*	*Yield of CA /%*
2-CNB	84	40–50	5	49.9	0.6	74.3
	92			47.0	0.4	63.6
	100			51.3	1.8	65.6
3-CNB	76	50–60	4	44.8	0.5	73.7
	81			37.6	1.2	59.2
	80			36.8	0.8	58.1
4-CNB	32	80–85	2	18.8	0.5	74.5
	40			19.5	0.7	62.4
	48			23.1	1.4	63.0

given in parentheses. Also, the corresponding anilide derivatives were prepared which melted at 74° C (74° C), 78° C (79° C) and 178–179° C (178.4° C) respectively with the corresponding values of the authentic sample [13] in parentheses. Further, the i.r. spectra of the isomeric chloroanilines, prepared as above, exactly matched those of the authentic samples [14].

3.2. *Cyclic voltammetry*

The cyclic voltammetric behaviour of the Ti/ceramic TiO_2-cathode (T = 550° C) in 1 M H_2SO_4 at a sweep rate of 0.2 V s^{-1} in the absence and presence of 0.033% CTAB are shown in Fig. 1. The two redox peaks observed under each condition are due to the reversible reduction of $Ti(OH)_4$ and TiO_2, respectively [15]. The two basic curves almost coincide. This is to be expected for an intrinsic redox process. In the presence of 0.033% CTAB, however, the cathodic and anodic peak currents increased considerably.

Figure 2a shows the cyclic voltammetric behaviour for the Ti/ceramic TiO_2-cathode (T = 550° C) in 1 M H_2SO_4 in the presence of 2-CNB without CTAB and 2-CNB with 0.033% CTAB. It is clearly seen from

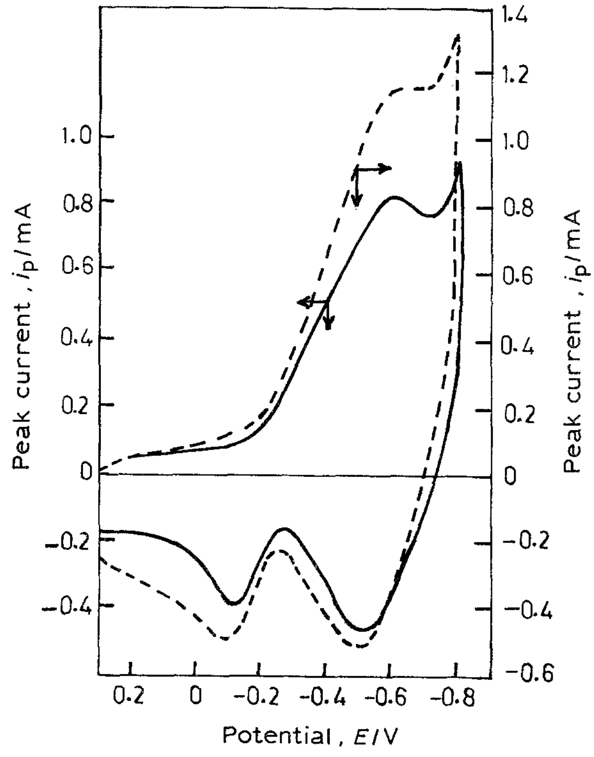

Fig. 1. Cyclic voltammetric behaviour of Ti/ceramic TiO_2-cathode (T = 550° C) in 1 M H_2SO_4 at a sweep rate of 0.2 V s^{-1} in the absence of CTAB (——) and in the presence of 0.033% CTAB (– – –).

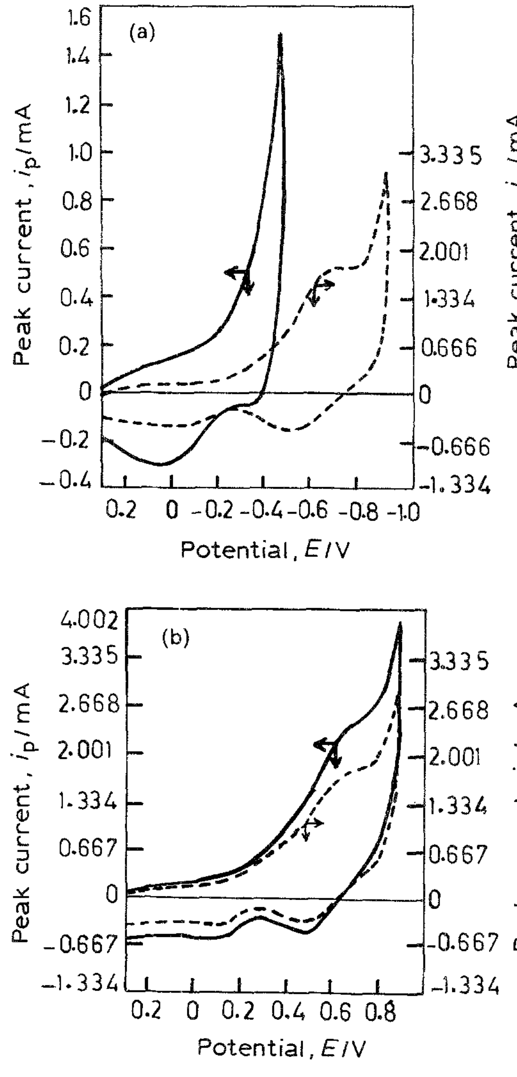

Fig. 2. Cyclic voltammetric behaviour of Ti/ceramic TiO_2-cathode (T = 550° C) in 1 M H_2SO_4 in the presence of: (a) 2-CNB without CTAB (——) and 2-CNB with 0.033% CTAB (– – –); (b) 3-CNB (——) and 4-CNB (– – –) at a sweep rate of 0.2 V s^{-1}.

Fig. 2a that the reduction of 2-CNB is observed only in the presence of CTAB, as was seen for the galvanostatic reduction of 2-CNB.

Figure 2b shows the cyclic voltammetric behaviour of 3-CNB and 4-CNB under identical experimental conditions (without CTAB). It is clearly seen from Fig. 2a (in the presence of CTAB) and 2b that the addition of the corresponding CNB resulted in an increase in the cathodic peak height with simultaneous decrease in the anodic peak height, thereby indicating heterogeneous redox catalysis by the Ti^{4+}/Ti^{3+} redox system.

In the time scales of low sweep rates, in the range 0.005–0.01 $V s^{-1}$, the anodic peak as seen above was not clearly visible. This indicates that the reaction between the CNB and the Ti^{3+} generated at the electrode surface is slow on the time scale of the higher sweep rates such as 0.2 $V s^{-1}$ but is sufficiently fast on the time scale of lower sweep rates, such as the range 0.005–0.01 $V s^{-1}$.

4. Conclusion

The galvanostatic reduction of isomeric chloronitrobenzenes to the respective chloroanilines can be conveniently carried out at a Ti/ceramic TiO_2-cathode in aqueous H_2SO_4 medium. The yield and CE for amine formation are higher at a Ti/ceramic TiO_2-cathode than at the conventional copper cathode, indicating the favourable electrocatalytic nature of the former. CV studies show a mechanism involving heterogeneous redox catalysis by the Ti^{4+}/Ti^{3+} redox system.

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