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Electroreduction of cyclohexanone oxime

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An electrochemical method for preparing cyclohexylamine from cyclohexanone oxime has been developed. Cyclohexanone oxime underwent smooth reduction in an aqueous ethanolic ammonium sulphate medium on nickel black deposited on graphite. The oxime is not reducible at ordinary copper or nickel electrodes. Nickel black deposited on copper or nickel was also found to be ineffective due to poor adhesion of the nickel black.

1. Introduction

Cyclohexylamine, a corrosion inhibitor is prepared mainly by catalytic reduction of aniline [1–3] and reduction of cyclohexanone oxime [4]. No literature is available on the electroreduction of cyclohexanone oxime to yield the amine, though electroreduction of other oximes [5–6] are known to give poor yields of amine.

Following the successful electroreduction of organic cyanides to amines [6–10] the electroreduction of oxime was carried out. This involves the conversion of

$$>C{=}NOH \text{ to } -CH_2-NH_2.$$

In this paper, the successful electroreduction of cyclohexanone oxime to cyclohexylamine at a nickel black cathode is discussed. The behaviour of other cathodes, copper, nickel and nickel black deposited on copper and nickel are also reported.

2. Experimental details

2.1. *Deposition of nickel black on to graphite plate*

An aqueous solution (1.8 dm^3) of $NiSO_4 \cdot 6H_2O$ (5g) and $(NH_4)_2SO_4$ (10 g) was the plating bath. A graphite plate of effective area 2.0 dm^2 was the substrate for deposition. This was flanked on either side by two ceramic diaphragms containing a lead plate and 10% aqueous H_2SO_4 as anode and anolyte, respectively. The deposition was effected at a current density of 5.0 A dm^{-2} (the cell voltage was 12.0 V), keeping the temperature and pH of the bath at 20 ± 5° C and 5.5, respectively.

A similar procedure was adopted to deposit nickel black onto copper and nickel substrates.

2.2. *Electroreduction of cyclohexanone oxime to cyclohexylamine*

A solution of oxime (20 g) in aqueous $(NH_4)_2SO_4$ solution (3%, 1.21 dm^3) was the catholyte. Deposited nickel black on graphite was the cathode. The arrangement of diaphragms, anode and anolyte were the same as given in Section 2.1. During reduction the catholyte was continuously stirred, its pH was maintained around 8.0 by addition of NH_3 and its temperature at 25 ± 1° C. As the theoretical charge was found to be inadequate, excess current was passed to increase the yield of amine. After the electrolysis, the catholyte was concentrated by distillation under reduced pressure. To liberate the amine, NaOH was added to the concentrate with sufficient cooling to get a pH of 10. The liberated amine was repeatedly extracted with benzene, the benzene extract after drying over anhydrous Na_2SO_4 was distilled to recover the amine which is further purified by distillation, bp 135° C.

Employing similar conditions, the above experiments were repeated at cathodes of copper, nickel and nickel black deposited onto copper and nickel.

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Table 1. Influence of current density on the reduction of cyclohexanone oxime

Current density (A dm^{-2})	Cell voltage (V)	Yield of amine (%)	Current efficiency (%)
1.0	6.5	76.42	50.91
2.0	7.0	72.36	48.24
4.0	9.5	64.46	42.94
6.0	11.0	58.38	38.92

3. Results and conclusion

The results of the electroreduction experiments carried out on nickel black on graphite cathode at several current densities are presented in Table 1 and the amine yield is observed to be maximum at low current densities.

The above reduction was repeated at temperatures in the range of 20 to 50° C, and several total charges and concentrations of $(NH_4)_2SO_4$. Temperature variation did not affect the amine yield. 20 to 30% excess charge over theoretical was found to be adequate. Anything beyond this requirement failed to improve the yield. A change in the concentration of $(NH_4)_2SO_4$ in the catholyte did not affect the final result. No improvement in the yield of amine was seen even on doubling the concentration of $(NH_4)_2SO_4$.

The electroreduction of cyclohexanone oxime at copper and nickel cathodes gave no isolable yield of amine suggesting their insensitivity and unsuitability for oxime reduction.

The experiments of nickel black on nickel and copper substrate, however, produced the amine in very poor yield which may be ascribed to poor adherence of nickel black over smooth copper or nickel.

In contrast, the high reduction efficiency observed at nickel black on graphite may be ascribed to good adherence of the deposit to porous graphite. Besides in many catalytic reduction carbon serves as a base to the catalyst. It may be possible that graphite substrate may be

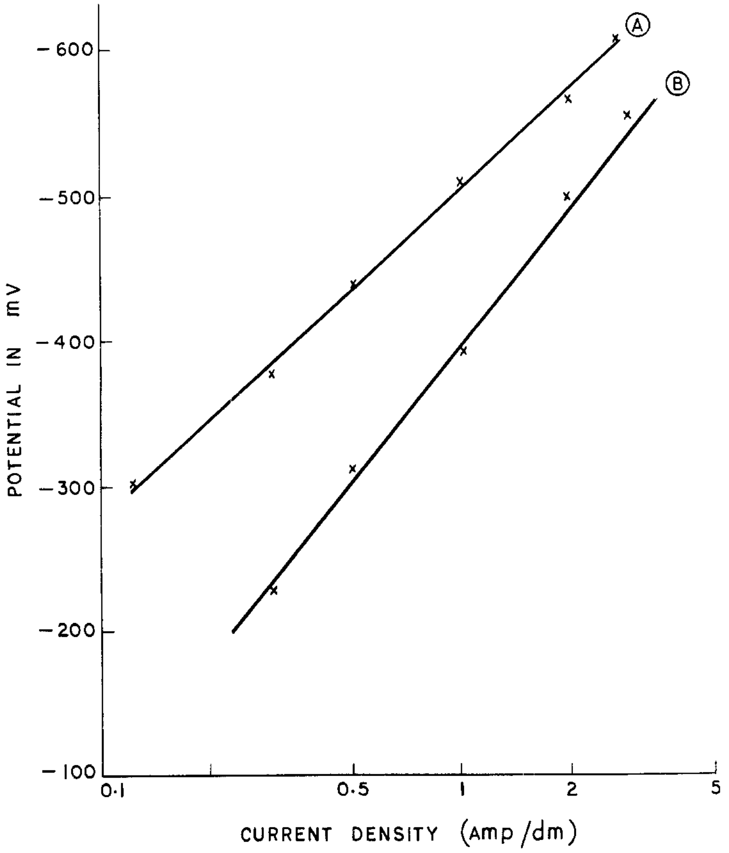

Fig. 1. Galvanostatic polarization using nickel black cathode (A) without cyclohexanone oxime and (B) with cyclohexanone oxime.

playing a similar role in electrochemical reduction too.

3.1. *Galvanostatic polarization measurement*

In a supporting electrolyte of aqueous ammonium sulphate, cathodic potentials were measured using a nickel black on graphite cathode with a Philips VTVM. Cathode potentials were noted both in the presence and absence of cyclohexanone oxime. Fig. 1 gives a plot of cathodic potentials against current density in a semilogarithmic form. The figure indicates considerable depolarization at low current densities. At higher current densities there is less depolarization leading to more hydrogen evolution.

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