Bulletin of Electrochemistry 7 (9) Sept 1991, pp 410–411

0256-1654/91/$ 3-50

ELECTROCATALYTIC REDUCTION OF NITRILES ON RANEY NICKEL

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[Received: 1991 August; Accepted: 1991 September]

An electrochemical method for the preparation of primary amines from organic nitriles using a Raney nickel cathode is reported. It has been observed that it is possible to reduce benzyl cyanide to β-phenylethyl amine with an yield efficiency of 85% and to reduce benzonitrile to benzylamine with an yield efficiency of 20%.

Key words: Electroreduction, Raney nickel, β-phenylethyl amine, benzylamine

INTRODUCTION

Raney nickel alloy catalysts either as powder or lumps have characteristics which make them superior catalysts for hydrogenation or organic compounds [1]. The powder is extremely active and has a high settling rate and hence the catalyst can be reused. It is used as a cathode in fuel cells [2] and in water electrolysis [3]. Only in a few cases, it is used as a cathode for the reduction of organic compounds. Chiba et al [4] used Raney nickel as a catalytic cathode for the reduction of various unsaturated compounds. Park et al [5] have studied the conversion of glucose to sorbitol and gluconic acid with a Raney nickel cathode and a graphite anode. In view of the catalytic nature of Raney nickel, an attempt has been made to use it as a cathode for the reduction of nitriles to primary amines. It has already been established that it is possible to prepare primary amines from nitriles using deposited nickel black cathodes [6-14]. In the present work, the reduction of benzonitrile and benzyl cyanide with a Raney nickel cathode has been studied.

EXPERIMENTAL

The electrolysis was carried in a 600ml beaker containing 30g of Raney nickel cathode (powder) prepared as per the procedure described elsewhere [15]. A nickel plate placed below the Raney nickel powder was used as the current collector. A lead sheet was used as the anode and it was placed in a glass vessel having a frit at the bottom which served as anode compartment. The catholyte was 10% ammonium sulphate dissolved in 1:1 alcohol-water mixture in which the corresponding nitrile was also dissolved. The anolyte was 10% aqueous sulphuric acid.The temperature of the cell was maintained at 298 ± 5K. The pH of the electrolyte was maintained around 8.5 by adding ammonia. The hydrogen evolved during the reaction itself was a good agitator for the reaction. The current density employed for the electrolysis was 2 to 3 $A \cdot dm^{-2}$ and the cell voltage was arround 12V. As the theoretical current was insufficient, 50% excess current was passed. After the completion of the reaction, Raney nickel powder was allowed to settle and the electrolyte was decanted. The catholyte was processed for the product while the settled catalyst powder was taken up for use in subsequent reactions.

RESULTS AND DISCUSSION

In the chemical route for the preparation of amines from nitriles, alkyl nitriles and very pure hydrogen (under pressure) are passed over Raney metals [16]. In the present electrochemical method, the same effect is brought out by electrolysis of aqueous alcoholic solution of the nitrile using a Raney nickel cathode and ammonium sulphate electrolyte. Benzonitrile and benzyl cyanide are reduced to benzyl amine and β-phenylethyl amine respectively. The yield of benzyl amine is 20% while that of β-phenylethyl amine is 85%.

Raney nickel is known to absorb hydrogen when the latter is passed over it. In the electrochemical method, hydrogen discharged on the cathode during electrolysis is adsorbed on the surface of Raney nickel. This chemisorbed hydrogen brings about the reduction of the nitrile which can be represented as

$$\underset{\text{I}}{RC \equiv N} \xrightarrow{[H]} \underset{\text{II}}{RCH = NH} \xrightarrow{[H]} \underset{\text{III}}{RCH_2 - NH_2}$$

In addition to the formation of primary amines,a small quantity (3 to 5%) of the secondary amines is formed during the electrolysis. This may be due to the reaction of the intermediate (II) with (III)

$$RCH_2 - NH_2 + RCH = NH \longrightarrow RCH_2NHCH_2R + NH_3$$

In our earlier studies [7] on the reduction of benzyl cyanide over deposited nickel black, iron black and cobalt black cathodes, the yield of β-phenyl amine was found to be in the range 55% to 80%. However, with the Raney nickel cathode, the efficiency increases to 85%.

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