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Electro-oxidation of benzyl alcohol on ruthenium oxide coated titanium anode

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Electro-oxidation of benzyl alcohol in 0.5 mol.dm^{-3} sulphuric acid at ruthenium oxide coated titanium anodes was studied using preparative electrolysis, galvanostatic polarisation, linear sweep voltammetry and chronopotentiometric techniques. Based on the data collected,a mechanism is proposed for the electro-oxidation.

Key words: Electro-oxidation, benzyl alcohol, ruthenium oxide coated Ti

EXPERIMENTAL & RESULTS

Electrode preparation

Ruthenium oxide was deposited over pretreated titanium by the thermal decomposition of a thin ruthenium-trichloride film applied over the substrate.

Preparative electrolysis

Constant current as well as constant potential electrolyses were carried out using 0.1 mol.dm^{-3} benzyl alcohol in 0.5 mol.dm^{-3} sulphuric acid. At potentials below 1.8V, benzaldehyde was the only oxidation product. Product of oxidation was estimated by analysis and isolated.

Galvanostatic polarisation studies

Steady state galvanostatic polarisation studies were carried out in 0.5 mol.dm^{-3} sulphuric acid at different benzyl alcohol concentrations and temperature. At potentials below 1.4V, Tafel slopes ranged from 230 to 260 mV. decade^{-1} and above 1.4V, Tafel slopes vary from 210 to 340 mV. decade^{-1}. Higher Tafel slope indicated that the electrode process was not charge transfer controlled. Order of reaction with respect to alcohol concentration was fractional. Apparent energy of activation was found to be 4.76 k cal.mol^{-1} in the potential range 1.4 – 1.6V. Fractional reaction order and low energy of activation implied adsorption controlled electrode process.

Voltammetric experiments

Linear sweep as well as cyclic voltammograms recorded in 0.2 mol.dm^{-3} benzyl alcohol in 0.5 mol.dm^{-3} sulphuric acid were featureless. No kinetic information could be obtained from the voltammograms.

Chronopotentiometric experiments

These studies were conducted in 0.2 mol.dm^{-3} benzyl alcohol in 0.5 mol.dm^{-3} sulphuric acid. Benzyl alcohol was allowed to adsorb on the electrode surface at open circuit potential. The adsorbed alcohol was oxidised by applying a constant current pulse across this electrode and a large surface area platinum electrode. The time (t) required for the oxidation of adsorbed alcohol was determined for different current densities (i).

The quantity "it$^{1/2}$" was not constant and it increased with increase in current density. This indicated that the electrode process was not diffusion controlled. Further the quantity "it" was constant. This controlled the electrode process to be adsorption controlled.

MECHANISM

Based on the above, a mechanism is proposed for the electro-oxidation of benzyl alcohol, wherein the chemical reaction between the surface species and benzyl alcohol is rate determining. Up to a potential of 1.5V, OH$_{ads}$ is the surface species and above 1.5V, perruthenate is the surface species. The surface reaction yields benzaldehyde according to the following reaction scheme:

Up to potentials of 1.5V

$$H_2O \rightleftharpoons OH_{ads} + H^+ + e$$

$$C_6H_5CH_2OH + OH_{ads} \xrightarrow{rds} (C_6H_5CH_2OH \cdots OH)_{ads}$$

$$(C_6H_5CH_2OH \cdots OH)_{ads} \longrightarrow C_6H_5CHO + H_3O^+ + e$$

At potentials above 1.5V

$$RuO_2 + 2H_2O \rightleftharpoons RuO_4^- + 4H^+ + 3e$$

$$C_6H_5CH_2OH + RuO_4^- \xrightarrow{rds} (C_6H_5CH_2OH \cdots RuO_4^-)_{ads}$$

$$(C_6H_5CH_2OH \cdots RuO_4^-)_{ads} \longrightarrow C_6H_5CHO + RuO_4^{--} + 2H^+ + e$$

$$RuO_4^{--} \rightleftharpoons RuO_4^- + e$$

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