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Indirect electrooxidation of crotyl and cinnamyl alcohol using a $Ni(OH)_2$ electrode

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Abstract

The heterogeneous catalytic redox behaviour of the nickel oxyhydroxide electrode surface was investigated with and without crotyl and cinnamyl alcohols using cyclic voltammetry. A comparison of the cyclic voltammograms recorded in the absence and presence of these alcohols confirmed the catalytic oxidation of the alcohols by the surface Ni^{3+}/Ni^{2+} redox system at the electrode surface. Preparative scale experiments were also carried out using $Ni(OH)_2$ electrodes of large surface area and the redox behaviour of the electrode was confirmed by the isolation of crotonic and cinnamic acids with high yield efficiency. The influence of molecular size on the catalytic oxidation process is examined.

1. Introduction

Indirect electroorganic synthetic methods have been developed in which metal ionic redox couples such as Ni^{3+}/Ni^{2+}, Ti^{4+}/Ti^{3+} and Sn^{4+}/Sn^{2+} have been used as mediators or electron carriers. Homogeneous as well as heterogeneous redox catalysts of this type improve selectivity and yield. They also make product recovery and electrolyte reuse possible. The Ni^{3+}/Ni^{2+} redox couple has been used for the oxidation of alcohols and amines [1–3].

Since direct electrooxidation of alcohols at platinum or carbon anodes is of only limited preparative value due to the high oxidation potentials required [4], indirect electrochemical oxidation at a nickel hydroxide electrode has been studied by many workers [5–7]. Although the reactions are very selective, the current densities that may be achieved with smooth nickel are rather low and this restricts their applications. This has motivated the preparation of stable, high area nickel oxide electrodes [8, 9]; indeed, such electrodes have been used in a large pilot plant for the oxidation of a sugar derivative [10, 11]. A black surface layer nickel(III) hydroxide, similar to the well-known oxidant nickel peroxide [12], is continuously electrogenerated from nickel(II) hydroxide deposited on a nickel sheet.

The oxidation of benzylic type alcohols and alkenols with the double bond more than three carbon atoms distant from the hydroxyl group leads to unsaturated carboxylic acids in good yields [3]. A neutral electrolyte improves the aldehyde yield [13]. Electrochemical oxidation of allylic type alcohols has also been carried out in alkaline *t*-butanol/water mixtures of various proportions. The surface redox process in this medium and also in alkaline medium have been discussed by several workers [14–16]. In the present work, crotyl and cinnamyl alcohols are oxidized to crotonic and cinnamic acids on a cathodicaly deposited, adherent, high surface area nickel hydroxide electrode.

2. Experimental details

$Ni(OH)_2$ electrodes were prepared according to the method of Corrigan [17]. The sand blasted nickel sheet was electrochemically cleaned in 5.5 M KOH anodically and cathodically for 90 s at a current density of 7 mA cm^{-2}. This pretreated nickel sheet was used as cathode for electrodeposition of $Ni(OH)_2$ from a bath containing nickel nitrate with trace amounts of cobalt and cadmium for 2 h at 25 mA cm^{-2} [18, 19]. It was aged in 5.5 M KOH solution containing 250 mg ZnO, for an hour at 70 °C for the conversion of α-$Ni(OH)_2$ to β-$Ni(OH)_2$. The presence of zinc reduces electrode swelling and increases oxygen overvoltage [20]. Then the electrode was anodically treated in 5.5 M KOH solution containing 15 g l^{-1}LiOH at 40 mA cm^{-2} for an hour. The addition of lithium is to increase the oxygen overvoltage and to eliminate the poisoning effect of iron [21].

The cyclic voltammetric experiments were carried out in an undivided glass cell provided with ground joints. The $Ni(OH)_2$ strip (geometric surface area 0.196 cm^2) used as working electrode and Hg/HgO and a platinum foil served as reference and counter electrodes, respectively.

Preparative experiments were carried in a 0.25 dm^3 (250 ml) glass cell. The cell cover was equipped with openings for introducing the porous diaphragm, thermometer, condenser and electrodes. About 0.2 dm^3 (200 ml) of 1 M KOH was used as electrolyte and a nickel hydroxide electrode of area 22 cm^2 and a stainless steel sheet of the same size were used as anode and cathode, respectively. The glass cell was placed in a water bath to maintain the required temperature.

Analar grade crotyl alcohol and cinnamyl alcohol were used for cyclic voltammetric and preparative electrolysis experiments. Very high purity nickel, cobalt and cadmium nitrate obtained from E-Merck (India) was used. Triple distilled water was used as a solvent for both experiments. After electrolysis, the electrolyte was ether extracted to remove the unreacted alcohol and acidified to obtain the crotonic and cinnamic acids. The products were dried and their melting points were verified.

3. Results

3.1. *Cyclic voltammetric studies*

The cyclic voltammogram obtained for $Ni(OH)_2$ in 1 M KOH (Figure 1) shows the well defined reversible surface redox process of the electrode due to the $Ni(OH)_2/NiOOH$ redox couple. The effect of sweep rate on the voltammetric behaviour of the $Ni(OH)_2$ electrode in 106.7 mM crotyl alcohol is presented in Figure 2. At slow sweep rates, the anodic peak is not sharp due to competitive oxygen evolution. In the reverse cathodic direction, the peak current is decreased slightly. Cyclic voltammograms obtained for the oxidation of 106.7 mM cinnamyl alcohol on $Ni(OH)_2$ in 1 M KOH are presented in Figure 3. The anodic peak current increase is high at slow sweep rates and small at higher sweep rates.

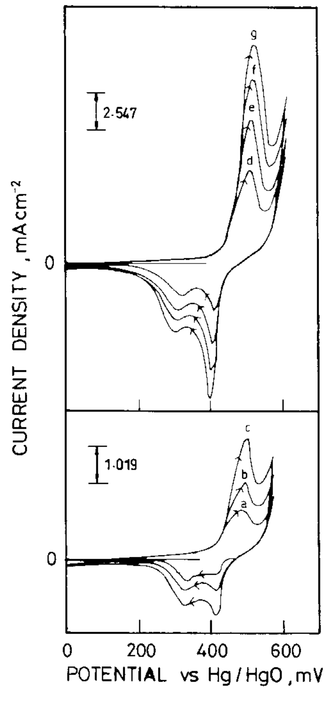

Fig. 1. Cyclic voltammetric behaviour of $Ni(OH)_2$ in 1 M KOH at different sweep rates: (a) 5, (b) 10, (c) 50, (d) 50, (e) 100, (f) 150 and (g) 200 mV s^{-1}.

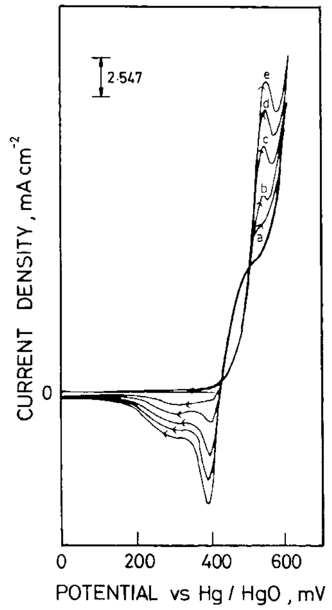

Fig. 2. Effect of sweep rate on the cyclic voltammograms for the oxidation of 106.7 mM crotyl alcohol on $Ni(OH)_2$ in 1 M KOH. sweep rate: (a) 20, (b) 50, (c) 100, (d) 150 and (e) 200 mV s^{-1}.

Cyclic voltammograms obtained for crotyl and cinnamyl alcohols at 10 mV s^{-1} and at two concentrations on $Ni(OH)_2$ in 1 M KOH are presented in Figure 4 for comparison. On increasing the alcohol concentration, the anodic peak current increases with a slight potential shift. At low alcohol concentrations the anodic peak is sharp and at high concentration the peak widens and tends to join that of dioxygen evolution. At the same concentration of the two alcohols, the anodic peak current increase is slightly higher for crotyl alcohol.

3.2. *Galvanostatic electrolysis*

A number of preparative scale experiments were carried out under galvanostatic conditions to optimize the yield conditions for acids. These experiments were carried out at various current densities, ranging from 1.0 to 7.5 A dm^{-2}. At lower current densities, preferably at 3.0 A dm^{-2}, maximum yield is obtained. At higher current densities, the percentage yield of the product is lower probably due to competitive oxygen evolution.

Preparative scale experiments were also carried out at temperatures between 30 and 70 °C. On increasing the temperature of the electrolyte, the product yield is reduced. For comparative studies, a pure nickel sheet without $Ni(OH)_2$ coating was also used as anode. These results are summarized in Table 1.

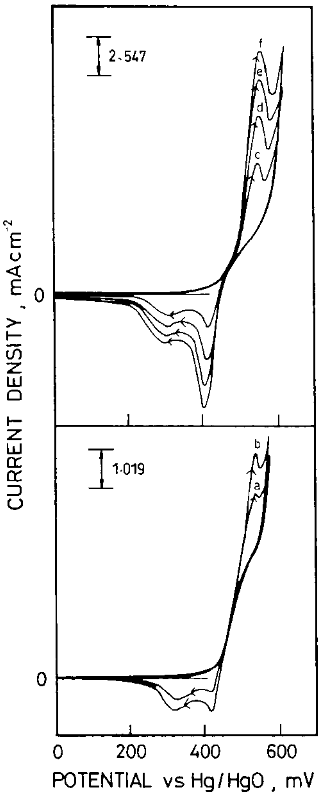

Fig. 3. Effect of sweep rate on the cyclic voltammograms for the oxidation of 106.7 mM cinnamyl alcohol on $Ni(OH)_2$ in 1 M KOH. sweep rate: (a) 10, (b) 20, (c) 50, (d) 100, (e) 150 and (f) 200 mV s^{-1}.

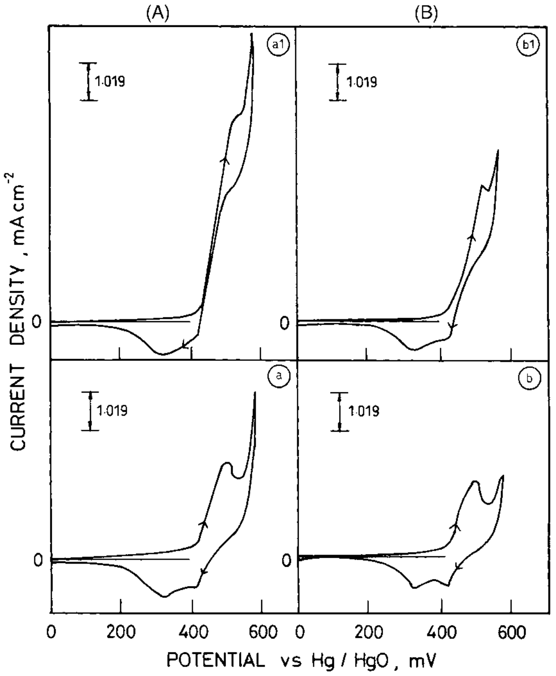

Fig. 4. Effect of concentration on the cyclic voltammograms for the oxidation of crotyl alcohol (A) and cinnamyl alcohol (B) on $Ni(OH)_2$ in 1 M KOH of 10 mV s^{-1}. Concentration: (a, b) 1.7 and (a_1, b_1) 53.3 mM.

4. Discussion

Cyclic voltammetric results show that at all concentrations studied, the oxidation peak potential of the two alcohols are very close to the heterogeneous redox oxidation potential of the nickel hydroxide electrode in 1 M KOH. The Ni^{3+} species formed on the $Ni(OH)_2$ electrode surface during anodic polarization does not completely react with the oxidizable organic compound (i.e., alcohol), as indicated by the presence of the reverse cathodic peak. Only at high alcohol concentrations does the cathodic peak current decrease to a small level. The catalytic oxidation current in the presence of the alcohols is always higher than the oxidation current in their absence. The heterogeneous redox catalytic process of the $Ni(OH)_2$ electrode with these alcohols is thus evident [22]. From the voltammograms, the occurrence of a chemical reaction between the alcohol and electrogenerated oxidizing agent, namely, surface bound Ni^{3+} species, may be confirmed.

Figure 5 shows the plots obtained for crotyl and cinnamyl alcohols at two concentrations and their corresponding anodic peak currents obtained are compared. At slow sweep rate, the anodic peak current increases linearly with alcohol concentration. The

Table 1. Galvanostatic oxidation of crotyl alcohol to crotonic acid and cinnamyl alcohol to cinnamic acid at $Ni(OH)_2$ in KOH

Current density /mA cm^{-1}	Temperature /°C	Crotyl alcohol (4.5 g) to crotonic acid		Cinnamyl alcohol (7.0 g) to cinnamic acid	
		Yield of product /g	Yield /%	Yield of product /g	Yield /%
10	30	4.1	76	7.3	79
20	30	4.7	87	7.9	86
30	30	5.1	96	8.3	90
40	30	4.3	80	8.0	87
50	30	3.8	71	7.1	77
75	30	3.2	59	6.5	71
30	50	4.4	82	7.6	85
30	70	3.3	61	7.5	82
30*nickel anode	30	4.6	86	7.8	85
30† 1 M NaOH	30	5.0	93	8.1	89

* Pure nickel anode.

† Electrolyte 1 M NaOH.

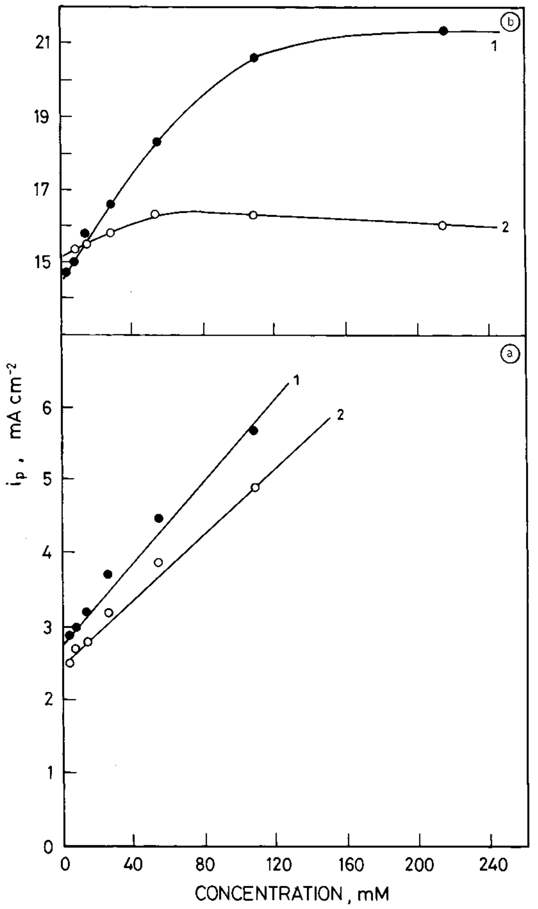

Fig. 5. Effect of concentrations of crotyl (●) and cinnamyl alcohol (○) on peak current with different sweep rates: (a) 10 and (b) 200 mV s^{-1}.

anodic peak current values for crotyl alcohol are higher than those for cinnamyl alcohol at the same concentration. Even at high concentration of crotyl alcohol, the anodic peak current increases to a smaller extent but for cinnamyl alcohol after a concentration of 60 mM the peak current value starts to decrease, which is mainly due to the adsorption or blocking effect of the alcohol molecules on the electrode surface [22, 23]. From these observations it is evident that the oxidation of crotyl and cinnamyl alcohols takes place on Ni(OH)$_2$ in 1 M KOH, strictly according to the mechanism proposed by Robertson [7]. On increasing the temperature the product yield is reduced. This may be due to desorption of the alcohol at high temperatures which leads to slower chemical reactions between the oxide/hydroxide layer, NiOOH, and reactant.

In galvanostatic electrolysis, on increasing the current density the yield efficiency decreases. Only at low current density is the maximum yield obtained. Crotyl alcohol is oxidized to crotonic acid with much higher efficiency than cinnamyl alcohol to cinnamic acid. This fact is also supported by the cyclic voltammetric results.

5. Conclusion

The galvanostatic oxidation of crotyl and cinnamyl alcohols to the corresponding acids can be carried out at cathodically deposited Ni(OH)$_2$ in KOH. The yields of acids at a Ni(OH)$_2$ anode are higher than at a smooth nickel anode, indicating the electrocatalytic nature of the former. CV studies show a mechanism involving heterogeneous redox catalysis by the Ni^{3+}/Ni^{2+} redox system. Low molecular size alcohols are oxidized more readily than high molecular size alcohols on Ni(OH)$_2$.

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References

1. H.J. Schafer, *Topics in Current Chemistry* **142** (1986) 101.
2. G. Vertes, G. Horanyi and F. Nagy, *Tetrahedron* **28** (1972) 37.
3. J. Kaulen and H.J. Schafer, *Tetrahedron* **38** (1982) 3299.
4. N.L. Weinberg (Ed.), 'Technique of Electroorganic Synthesis', Part I, (Wiley, New York, 1974) p. 435.
5. M. Fleischmann, K. Korinek and D. Pletcher, *J. Chem. Soc., Perkin II.* (1972) 1396.
6. M. Fleischmann, K. Korinek and D. Pletcher, *J. Electroanal. Chem.* **31** (1971) 39.
7. P.M. Robertson, *J. Electroanal. Chem.* **111** (1980) 97.
8. C.W. Briggs, E. Jones and W.F.K. Wynne-Jones, *Trans. Faraday Soc.* **51** (1955) 1433.
9. K. Manandhar and D. Pletcher, *J. Appl. Electrochem.* **9** (1979) 707.
10. P. Seiler and P.M. Robertson, *Chimia* **36** (1982) 305.
11. P.M. Robertson, P. Berg, H. Reimenn, K. Schleich and P. Seiler, *J. Electrochem. Soc.* **130** (1983) 591.
12. M.V. George and K.S. Balachandran, *Chem. Rev.* **75** (1975) 491.
13. R. Schneider, Diploma thesis, Munster (1987).
14. M.A. Sattar and B.E. Conway, *Electrochim. Acta* **14** (1969) 695.
15. B.E. Conway and M.A. Sattar, *J. Electroanal. Chem.* **19** (1968) 351.
16. D.M. MacArthur, *J. Electrochem. Soc.* **117** (1970) 422.
17. D.A. Corrigan, *J. Electrochem. Soc.* **134** (1987) 377.
18. R.L. Beauchamp and D.W.Maurer, Electrochemical society meeting (Oct. 1971).
19. G. Halpert, 'The Effect of Cadmium on the Nickel Hydroxide Electrode', Dissertation, Catholic University, (1983).
20. M.E. Unates, M.E. Folquer, J.R. Vilche and A.J. Arivia, *J. Electrochem. Soc.* **135** (1988) 25.
21. R.D. Armstrong, G.W.D. Briggs and M.A. Moore, *J. Electrochim. Acta.* **31** (1986) 25.
22. M. Noel and K.I. Vasu, 'Cyclic Voltammetry and the Frontiers of Electrochemistry' (Oxford and IBH, New Delhi, 1990).
23. C. Ravichandran, M. Noel and P.N. Anantharaman, *J. Appl. Electrochem.* **26** (1996) 195.