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Electrooxidation of benzyl alcohol at high surface area nickel (NiS_x) electrodes in alkaline solution

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The heterogeneous catalytic redox behaviour of NiS_x deposited electrodes was investigated with and without benzyl alcohol in KOH solution using cyclic voltammetry and linear sweep voltammetry. The limiting current density for benzyl alcohol oxidation on a NiS_x electrode was 22 times larger than that on a polished nickel electrode. The experimental results in galvanostatic electrolysis using fractional factorial design showed that the main and interaction effects of benzyl alcohol concentration, temperature, and OH^- concentration are the key variables influencing the selectivity of benzaldehyde formation during electrolysis.

1. Introduction

Electrooxidation of many organic compounds at nickel has been proved to be an indirect, heterogeneous anodic dehydrogenation [1–3]. The rate determining step was a chemical reaction, for example, abstracting hydrogen from the α-carbon of the alcohol by a nickel hydroxide (NiOOH), which is continuously regenerated on the electrode surface. Indeed, the application of nickel (more exactly, NiOOH) for the oxidation of alcohols, aldehydes, amines and related compounds has been extensively reviewed [4]. Unfortunately, however, many reactions only give an acceptable current efficiency at a very low current density (about $< 1\,\mathrm{mA\,cm^{-2}}$) [1–3]. In order to overcome this problem, many modified nickel electrodes have been developed, all of which possess either high surface area or special properties, in order to increase the reaction rate between the organic compounds and nickel hydroxide [5–10].

Cox and Pletcher [5, 6], studying the electrochemical oxidation of alcohols and amines on spinel electrodes (i.e. $NiCo_2O_4$ etc.), found that the mechanism for organic compound oxidation on spinel electrodes was similar to that on nickel, and reported that the chemical reaction rate between nickel hydroxide and the organic was considerably enhanced by use of spinel electrodes and current efficiency reached 100% for ethanol oxidation at the high current density of $120\,\mathrm{mA\,cm^{-2}}$ in a flow cell system. Budniok and Kozlowska [7] compared the rate of propanol oxidation on nickel and Ni–Ni_5P_2 modified electrodes in alkaline solution and found that the oxide layers formed on Ni–P alloys for propanol oxidation are more active than those on a nickel electrode. Kunugi *et al.* [8–10] studied the electrooxidation of various organic compounds on nickel/poly(tetrafluoroethylene) composite-plated anodes and reported that the current efficiencies for the corresponding products were considerably improved, due to the hydrophobicity of the anode. However, Wen *et al.* [11] recently reported that the high electrocatalytic activity of the Ni/PTFE electrode is due to the fact that the presence of PTFE in a nickel electrode alters the formation pathway of the γ-phase nickel hydrous oxide and is not caused by the enhanced surface area of the Ni/PTFE electrode.

Among modified nickel electrodes, NiS_x deposited electrodes have been shown to be suitable cathodes for hydrogen evolution, due to the high surface area exposed after long term polarization [12, 13]. In this work, the application of NiS_x deposits to the oxidation of benzyl alcohol in alkaline solution was examined. The cyclic voltammetric behaviour of nickel and NiS_x electrodes in alkaline solution were first compared and the effect of prolonged polarization on the activity for benzyl alcohol oxidation was also presented. In addition, fractional factorial design [14] was employed in planning the experiments for studying the effects of the electrolysis variables on benzyl alcohol oxidation current efficiency and benzaldehyde production yield.

2. Experimental details

2.1. NiS_x *deposit preparation*

NiS_x deposited electrodes were prepared in a manner similar to that reported in previous work [13]. In order to prevent the electrode from pitting corrosion during anodic electrolysis, the substrate, low carbon steel, was first plated with a compact nickel deposit using a typical Watts bath, containing mainly $NiSO_4 \cdot 6H_2O$ ($250\,\mathrm{g\,dm^{-3}}$), $NiCl_2 \cdot 6H_2O$ ($40\,\mathrm{g\,dm^{-3}}$), and H_3BO_3 ($35\,\mathrm{g\,dm^{-3}}$), at current density of $30\,\mathrm{mA\,cm^{-2}}$ for 30 min, at 55° C. The plated cathode was then further plated in the above mentioned Watts bath with the

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addition of 55 g dm^{-3} thiourea, at a current density of 4 mA cm^{-2} for 225 min, at 55° C.

The prepared NiS_x electrode, before anodic electrolysis, was first cathodically polarized at a current density of 700 mA cm^{-2} for 0, 25, 50, 100 and 200 h. The 1 M KOH solution employed for cathodic polarization, was pre-electrolyzed under a cathodic current density of 10 mA cm^{-2} using titanium and IrO_2/Ti electrodes as the cathode and anode, respectively.

Nickel rod (99.9945%, Johnson Matthey), used for comparison with the NiS_x electrode, was polished with a 1 μm diamond polish slurry, then rinsed with distilled water, before use.

2.2. *Electrochemical characterization*

Electrochemical experiments were carried out in a BAS-100B potentiostat/galvanostat system (Bioanalytic System, Inc., USA). An Ag/AgCl electrode (Argenthal, 3 M KCl, 0.207 V vs NHE at 25° C) was used as the reference, while a platinum wire was employed as the counter electrode. A Luggin capillary, whose tip was set at a distance of about 1 mm from the surface of the working electrode, was used in minimizing errors due to *iR* drop in the electrolytes. There was no *iR* compensation during the potentiodynamic measurements. Voltammetry was carried out at a scan rate of 20 mV s^{-1} in 1 M KOH solution at 25° C. Steady state *I/E* curves were obtained at a scan rate of 1 mV s^{-1} in 0.5 M KOH solution containing 20% *t*-butanol before and after addition of 0.1 M benzyl alcohol, at 25° C.

2.3. *Galvanostatic electrolysis*

Galvanostatic electrolysis was carried out in a divided cell with Nafion 435®, a platinum wire, and a NiS_x electrode (after 50 h cathodic polarization) as separator, cathode and anode, respectively. The anolyte was agitated by a motorized stirrer (Labo stirrer, Model LR-41B, Japan). The d.c. power was supplied by a HA-301 potentiostat/galvanostat system (Hokuto Denko Company, Japan) and the amount of electricity passed was 0.5 F mol^{-1}. The organic vapour was condensed by a reflux condenser and the reactor was immersed in a water bath controlled at a desired temperature with an accuracy of 0.05° C by means of a water thermostat (HAAKE D8 and G).

Table 1. EDAX-determined element content (wt %) in NiS_x electrode

Time /h	*Element content/wt %*		
	S	*Fe*	*Ni*
0	10.68	0.37	88.95
25	5.77	0.58	93.66
50	5.12	1.03	93.86
100	4.13	1.20	94.70
200	3.87	1.12	95.08

Table 2. Factors and levels for the 2_V^{5-1} fractional factorial design

Factors	*Levels*	
	−	+
A, BA Concentration/M	0.2	0.6
B, Agitation rate/r.p.m.	500	800
C, Temperature/° C	25	60
D, Current density/mA cm^{-2}	20	40
E, OH^- Concentration/M	0.5	1.0

The effects of the following electrolysis parameters on current efficiency and benzaldehyde selectivity were investigated: (A) benzyl alcohol concentration, (B) agitation rate, (C) temperature, (D) current density, and (E) OH^- concentration. Fixed levels of these five parameters are given in Table 2, with the design levels being given in Table 3.

After electrolysis, samples taken from the anodic compartment were acidified with hydrochloric acid prior to analysis by high performance liquid chromatography (LC-10A, SPD-10A, Shimazu, Japan).

3. Results and discussion

3.1. *Electrochemical studies*

Typical cyclic voltammograms of nickel and NiS_x electrodes in 1 M KOH solution are shown in Fig. 1. The shapes show important differences. The polished nickel electrode exhibits a sharp anodic peak at about 400 mV corresponding to the Ni(II)/Ni(III) redox transition and oxygen evolution commences at about 500 mV. In comparison to the polished nickel electrode, the NiS_x electrode, after first being cathodically polarized for 50 h, shows a very broad peak between 370 and 500 mV, and possesses 40 times larger peak current corresponding to the Ni(II)/Ni(III) redox transition (30 as compared to 0.75 mA cm^{-2} for the polished nickel electrode). The

Table 3. Design matrix and experimental data from the 2_V^{5-1} fractional factorial design

Run	*Factors*					*Current efficiency* /%	*Aldehyde selectivity* /%
	A	*B*	*C*	*D*	*E*		
1	−	−	−	−	+	94.54	46.57
2	+	−	−	−	−	96.48	42.40
3	−	+	−	−	−	91.71	41.76
4	+	+	−	−	+	84.50	50.89
5	−	−	+	−	−	96.89	54.56
6	+	−	+	−	+	97.05	52.28
7	−	+	+	−	+	90.78	33.08
8	+	+	+	−	−	97.55	66.32
9	−	−	−	+	−	89.79	38.05
10	+	−	−	+	+	80.79	32.68
11	−	+	−	+	+	54.75	53.12
12	+	+	−	+	−	80.04	62.12
13	−	−	+	+	+	92.58	36.04
14	+	−	+	+	−	82.91	69.45
15	−	+	+	+	−	92.55	41.46
16	+	+	+	+	+	77.42	46.88

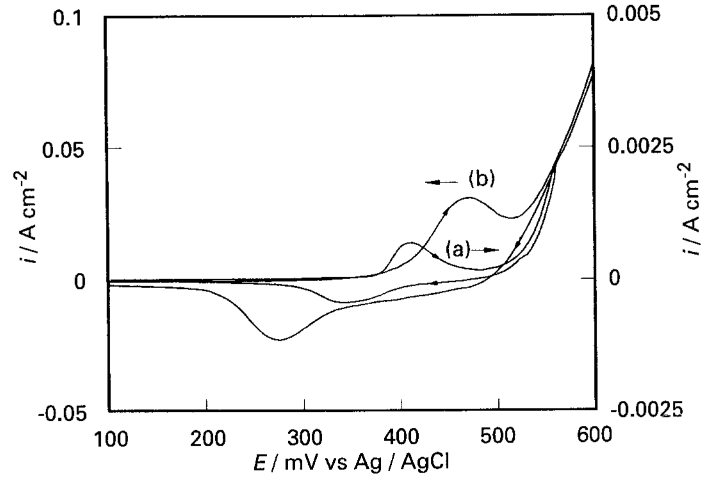

Fig. 1. The voltammetric behaviour of nickel and NiS_x electrodes in 1 M KOH solution at a scan rate of 20 mV s^{-1}. (a) Ni electrode; (b) NiS_x electrode after cathodic polarization for 50 h.

former result suggests that the NiS_x electrode possesses more 'inner' (less accessible) active sites than the nickel electrode. These 'inner' active sites may result from the cracks and porosity of the NiS_x deposits [12, 13]. The higher Ni(II)/Ni(III) redox transition peak current in the NiS_x electrode indicates that the active surface area on the NiS_x electrode is higher than that on the nickel electrode.

Cyclic voltammograms of the NiS_x electrode in 0.5 M KOH containing 0.1 M benzyl alcohol at a scan rate of 20 mV s^{-1} are presented in Fig. 2. In comparison to curve (a) in Fig. 2, the currents of curve (b) in the 400–500 mV potential range for both the anodic and cathodic sweeps are positive and much larger, indicating that the nickel hydroxide (NiOOH) formed here is an active species for the catalytic oxidation of benzyl alcohol. This result indicates that benzyl alcohol oxidation on the NiS_x electrode is similar to that on the nickel electrode, that is, a chemical reaction between the nickel hydroxide and the benzyl alcohol, and does not involve direct electron transfer from the organic compound to the anode [1–3].

The I/E curves recorded for a very slow scan rate of 1 mV s^{-1} for a NiS_x electrode in 0.5 M KOH solution containing 20% *t*-butanol without and with the addition of 0.1 M benzyl alcohol are shown in curves (a) and (b), respectively (Fig. 3). In 0.5 M KOH solution only one peak at about 400 mV was observed prior to the commencement of oxygen evolution at about 500 mV; while in the presence of benzyl alcohol in the solution, the anodic current increased considerably and reached a rising plateau at about 470 mV. The limiting current density for benzyl alcohol oxidation on the NiS_x electrode is 22 times larger than that on the polished nickel electrode (57 as compared to 2.6 mA cm^{-2} for the polished nickel electrode); thus the rate of chemical reaction between nickel hydroxide and benzyl alcohol is considerably enhanced on the NiS_x electrode.

3.2. *Effect of polarization time*

In previous papers [12, 13], the hydrogen overpotential of a NiS_x electrode was decreased and stabilized after long-term (about 200 h) cathodic polarization at relatively high current densities (about 500–800 mA cm^{-2}) due to the washing-out of adsorbed residues of thiourea or reduction of sulfur, which resulted in the exposure of a larger active

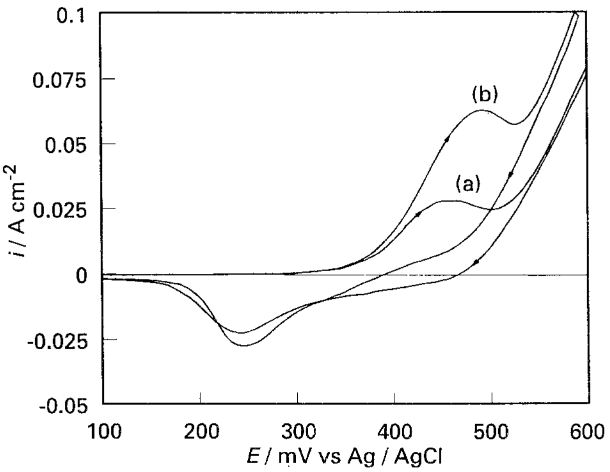

Fig. 2. Cyclic voltammograms of NiS_x electrode. (a) 0.5 M KOH containing 20% *t*-butanol; (b) 0.5 M KOH containing 20% *t*-butanol + 0.1M benzyl alcohol.

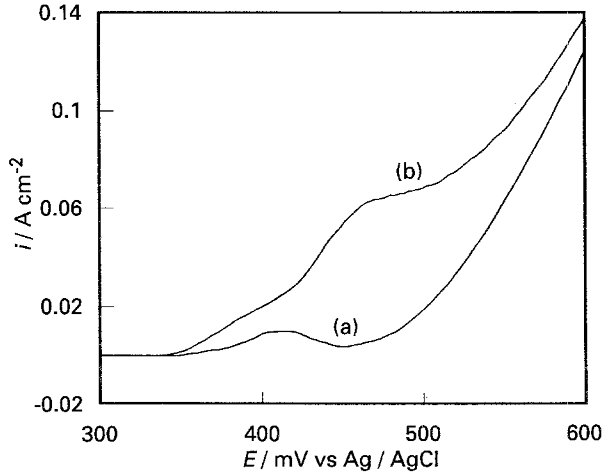

Fig. 3. I/E curves for NiS_x electrode in (a) 0.5 M KOH containing 20% *t*-butanol; (b) 0.5 M KOH containing 20% *t*-butanol + 0.1 M benzyl alcohol.

surface area for hydrogen evolution. In this study, the effect of cathodic polarization time on limiting current density for benzyl alcohol oxidation was examined.

Limiting current densities for benzyl alcohol oxidation on the NiS_x electrode against cathodic polarization time are plotted in Fig. 4, which reveals that the limiting current density increases substantially after 25 h (from 28 to 52 mA cm^{-2}) and reaches a maximum value at 50 h. In order to understand the above results, the elemental content of the NiS_x electrodes was analysed by EDAX and the surface morphological changes were examined by SEM. The results are shown in Table 1 and Fig. 5, respectively.

An examination of Table 1 reveals that the sulphur content substantially decreases (from 10.68 to 5.77 wt %) after 25 h polarization and then gradually decreases from 5.77 to 3.87 wt %. The nickel content increases from 89 to 95 wt % and also a small amount of iron is observed. Figure 5(a) for the surface morphology of as deposited NiS_x shows a smooth structure with small cracks, on which granular particles deposit. While after being cathodically polarized, the cracks become more obvious and the number of the deposited granular particles decreases (Fig. 5(b) and (c)). The former result was ascribable to hydride formation at the active nickel surface [15], which induced hydrogen embrittlement during cathodic polarization; while the latter result was thought to arise from the washing out of adsorbed residues of thiourea or the reduction of sulphur during polarization. H_2S could be detected on the NiS_x electrode after long-term cathodic polarization; suggesting that the sulphur content was removed from the sulphur reduction which was also evidenced by EDAX data. Based on the above SEM and EDAX results, it can be stated that the increase in limiting current density for benzyl alcohol oxidation after cathodic polarization is due to crack formation and sulphur reduction, resulting in the exposure of a larger active surface area for benzyl alcohol oxidation. The 'mud-crack' and porous morphology of the NiS_x electrode after cathodic polarization also support our previous supposition on the cyclic voltammetric result that the $Ni(OH)_2$/NiOOH transition charge from the 'inner' (less accessible) region is due to diffusion, through cracks and pores, of OH^- ions and water during anodic scans giving the observed broad and more irreversible redox transition peak in Fig. 1.

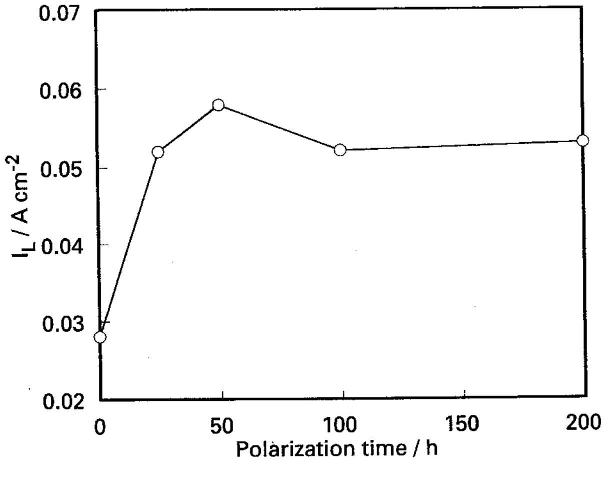

Fig. 4. Dependence of limiting current density for benzyl alcohol oxidation on cathodic polarization time.

3.3. *Galvanostatic electrolysis*

Products of benzyl alcohol oxidation on the nickel electrode in alkaline solution containing organic solvent (*t*-butanol) were reported to be benzaldehyde and benzoic acid, and the yield of aldehyde was strongly affected by electrolysis conditions [3, 4, 6]. In this study, the fractional factorial design method [14] was established in order to identify the key variables influencing the current efficiency and aldehyde yield from the following variables: (A) benzyl alcohol concentration, (B) agitation rate, (C) temperature, (D) current density, and (E) OH^- concentration. This experimental design allows the influence on each process variable to be observed at a variety of other variable levels, as well as allowing observations of the interaction effects among the variables.

The design factors and levels for the 2_V^{5-1} fractional

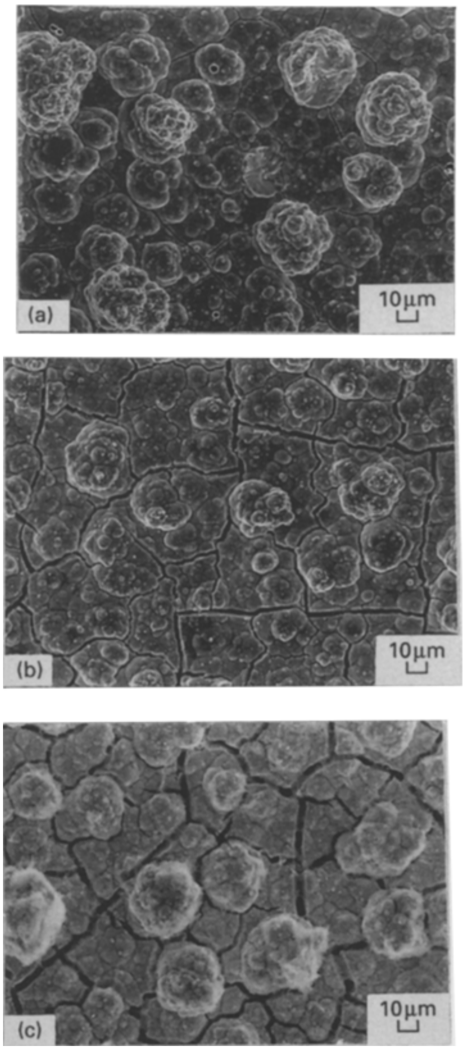

Fig. 5. SEM photographs of NiS_x electrode: (a) as deposited; (b) after 25 h polarization; (c) after 200 h polarization.

factorial experiments are listed in Table 2 and the results of these experiments are given in Table 3. The level of each variable during a run is indicated in columns 2 to 6 of Table 3, with the current efficiency and aldehyde selectivity corresponding to each set of conditions, being shown in columns 7 and 8, respectively.

Estimates of the experimental variable effects were algebraically calculated following the procedure recommended by Box *et al.* [14] and are given in Table 4. Table 4 reveals that the current efficiency increases with decreasing agitation rate, current density, OH^- concentration, and with increasing temperature. The latter result can be explained by the fact that the rate of chemical reaction between nickel hydroxide and organic compounds increases with increasing electrolysis temperature [3]. At higher current density, competitive oxygen evolution occurs, thereby decreasing the current efficiency. Moreover, the current efficiency decreases with increasing OH^- concentration. This result is thought to arise from the fact that phase separation occurs at high OH^- concentration. Under such circumstance, benzyl alcohol is dispersed in the solvent phase, and consequently decreases the possibility of benzyl alcohol in contact with the electrode, resulting in the observed low current efficiency at high OH^- concentration.

Table 4 also reveals that the effects of benzyl alcohol concentration (A), temperature (C), and OH^- concentration (E) are the key variables influencing the aldehyde selectivity, and that the two factor interactions on aldehyde selectivity of benzyl alcohol concentration and temperature (AC), of agitation rate and temperature (BC), of benzyl alcohol concentration and OH^- concentration (AE), and of temperature and OH^- concentration (CE) are significant. These effects are indicated with an asterisk in Table 4, and represent the relatively larger positive and negative estimated values.

The effects of benzyl alcohol concentration (A), temperature (C), and OH^- concentration (E) cannot be discussed separately due to the significant interactions on aldehyde selectivity between benzyl alcohol concentration and temperature (AC) and benzyl alcohol concentration and OH^- concentration (AE), as well as temperature and OH^- concentration (CE). Hence, the aldehyde selectivity is depicted as a function of benzyl alcohol concentration (A), temperature (C), and OH^- concentration (E) in Fig. 6. An examination of Fig. 6 reveals that the average aldehyde selectivity increases with decreasing OH^- concentration. This result was consistent with that obtained previously by Pletcher *et al.* [3]. They reported that the dependence of the formation of aldehyde or acid on the OH^- concentration was attributable to the change in the nickel oxide surface with pH, which changes the stability to desorption of surface species with intermediate degrees of oxidation. The result of high aldehyde yield at low pH indicates that the desorption of intermediate (aldehyde) for benzyl alcohol oxidation to benzoic acid on the nickel hydroxide surface formed at low pH must be easier than that formed at high pH value.

Table 4. Estimates of the effects from the 2_V^{5-1} fractional factorial design

Effects	*Estimate*	
	Current efficiency/%	*Aldehyde selectivity*/%
A	−1.14	−9.79*
B	−7.32	2.94
C	6.61	4.05*
D	−12.06	−1.00
E	−6.55	−8.06*
AB	2.89	4.39
AC	−3.33	7.64*
AD	−1.55	0.83
AE	2.24	−6.31*
BC	4.54	−9.11*
BD	−2.22	3.90
BE	−6.38	1.16
CD	2.85	−2.08
CE	3.53	−7.80*
DE	−2.55	−2.53

In alkaline solution, the oxidation of primary alcohol to acid on nickel has been formulated as [1–4]:

$$OH^- + Ni(OH)_2 \xrightarrow{\text{fast}} Ni(OOH) + H_2O + e^- \quad (1)$$

$$RCH_2OH_{sol} \longrightarrow RCH_2OH_{ads} \quad (2)$$

$$RCH_2OH_{ads} + NiOOH \xrightarrow{\text{r.d.s.}} R\dot{C}HOH + Ni(OH)_2 \quad (3)$$

$$R\dot{C}HOH + H_2O \longrightarrow RCO_2H + 3e^- + 3H^+ \quad (4)$$

Accordingly, in an aqueous solution, the major product of benzyl alcohol oxidation was benzoic acid. Conversely, in mixed organic solvents, or in an emulsion electrolysis, alcohol can be converted to aldehyde as main product in the following manner:

$$R\dot{C}HOH \longrightarrow RCOH + H^+ + e^- \quad (5)$$

In the present results, the aldehyde selectivity increase with increasing benzyl alcohol concentration and temperature, in 0.5 M KOH solution can be explained by

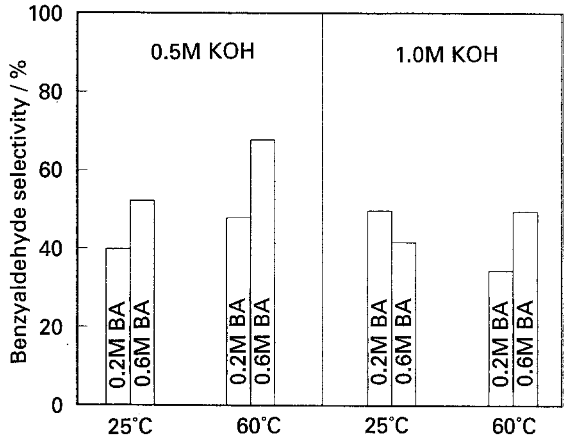

Fig. 6. Estimated values for the average benzaldehyde selectivity as a function of benzyl alcohol concentration, temperature, and OH^- concentration.

the fact that an emulsion solution easily forms at the relatively high benzyl alcohol concentration and temperature. In emulsion electrolysis, it is conceivable that the intermediate aldehyde is extracted into the organic phase and thus prevented from further oxidation to acid.

Based on the above results and discussion, it is concluded that the benzyl alcohol oxidation current efficiency and aldehyde selectivity can be increased with increasing benzyl alcohol concentration, temperature, and with decreasing agitation rate, current density and OH^- concentration. To confirm the validity of the statistical experimental strategy, an additional confirmatory experiment was performed under the following conditions: 0.4 M KOH solution containing 20% *t*-butanol and 0.9 M benzyl alcohol, current density 20 mA cm^{-2}, electrolysis temperature 60° C and agitation rate 500 r.p.m. The resulting current efficiency and aldehyde selectivity were 95.4 and 76.2%, respectively, which lends further support to the previous conclusion.

4. Conclusions

The $Ni(OH)_2/NiOOH$ redox transition formed anodically on a NiS_x electrode was found to be a suitable electrocatalyst for benzyl alcohol oxidation. Long-term cathodic polarization exposed a large active surface area for benzyl alcohol oxidation, resulting in a high limiting current density for benzyl alcohol oxidation. The effects of the following electrolysis parameters: benzyl alcohol concentration, agitation rate, temperature, current density, and OH^- concentration on the benzyl alcohol oxidation current efficiency and benzaldehyde selectivity were experimentally investigated. The experimental results from fractional factorial design showed that the benzyl alcohol oxidation current efficiency and aldehyde selectivity increased with increasing benzyl alcohol concentration, temperature, and with decreasing agitation rate, current density and OH^- concentration.

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