Electrocatalytic hydrogenation of phenol on various electrode materials

Anna Martel, Behzad Mahdavi, Jean Lessard, Louis Brossard, and Hugues Ménard

Abstract: The electrocatalytic hydrogenation (ECH) of phenol was investigated at room temperature under galvanostatic control in aqueous sulfuric acid solutions on platinized platinum (Pt/Pt) electrodes and on composite Rh/Ni and Ru/Ni electrodes consisting of rhodium or ruthenium chemically deposited on nickel particles dispersed in a lanthanum polyphosphate matrix. The order of electrocatalytic activity at a current density (based on the geometric area) of 1 mA/cm^2 was found to be Ru/Ni > Pt/Pt > Rh/Ni. The efficiency decreased with increased current density. For the Ru/Ni electrodes, the efficiency increased with the percentage of Ru (2.3 to 5%). On Ru 5%/Ni electrodes and at a current density of 5 mA/cm^2, cyclohexanol was obtained with a high selectivity of 91% and a current efficiency of 23% after 94% conversion. In neutral aqueous boric acid containing sodium chloride as supporting electrolyte, the Rh/Ni and Ru/Ni electrodes showed very low activity. The influence of the supporting electrolyte, periodic current control, and temperature was studied in the neutral medium with composite Raney nickel (RaNi) electrodes consisting of Raney nickel particles dispersed in a nickel matrix. At 60°C and a current density of 10 mA/cm^2, the selectivity of cyclohexanol formation was 100% with a 11% current efficiency after 92% conversion with sodium chloride as supporting electrolyte.

Key words: electrocatalytic hydrogenation, phenol, ruthenium on nickel cathodes, rhodium on nickel cathodes, Raney nickel cathodes.

Résumé : L'hydrogénation électrocatalytique (HEC) du phénol a été étudiée à la température ambiante en solution aqueuse d'acide sulfurique sur des électrodes de platine platinisé (Pt/Pt) et sur des électrodes composites de Rh/Ni et Ru/Ni, consistant en rhodium ou ruthénium métallique déposé chimiquement sur des particules de nickel dispersées dans une matrice de polyphosphate de lanthane. On a trouvé une activité décroissante dans l'ordre Ru/Ni, Pt/Pt et Rh/Ni à une densité de courant de 1 mA/cm^2 (basée sur la surface géométrique) et une diminution de l'activité des électrodes avec l'augmentation de la densité de courant. Avec les électrodes de Ru/Ni, une augmentation de l'efficacité de l'HEC a été observée avec le pourcentage de Ru de 2.3 à 5%. Sur les électrodes de Ru 5%/Ni, on a obtenu le cyclohexanol avec une très bonne sélectivité de 91% et une efficacité de courant de 23% après 94% de conversion. En solution neutre d'acide borique contenant du chlorure de sodium comme électrolyte support, les électrodes Ru/Ni et Rh/Ni se sont avérées pratiquement inactives. L'influence de l'électrolyte support, d'un courant pulsé et de la température a été étudiée en solution neutre avec des électrodes de RaNi faites de particules de nickel de Raney dispersées dans une matrice de nickel. Le phénol a été électrohydrogéné en cyclohexanol avec une sélectivité de 100% et une efficacité de courant de 11% après 92% de conversion, en effectuant l'électrolyse à 60°C et à une densité de courant de 10 mA/cm^2 en présence de chlorure de sodium comme électrolyte support.

Mots clés : hydrogénation électrocatalytique, phénol, cathodes de ruthénium sur nickel, cathodes de rhodium sur nickel, cathodes de nickel de Raney.

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Introduction

The electrocatalytic hydrogenation (ECH) of organic compounds constitutes a mild and efficient method for hydrogenating a variety of organic substrates (for a recent review, see ref. 1). The mechanism is described by reactions [1]–[4] where M represents the metallic surface. Chemisorbed hydrogen, (H)M, generated in situ by electroreduction of water (or the hydronium ion) (reaction [1]), reacts with the adsorbed organic substrate, (Y = Z)M, (reactions [2]–[4]). Hydrogenation (reaction [3]) competes with hydrogen desorption (reactions [5] and (or) [6]) (2, 3). The efficiency of ECH depends on the relative rates of these two processes, which are influenced by a number of factors such as the substrate and its concentration (2, 4), the electrode material and surface (5, 6), the reaction medium (organic cosolvent (2), pH (2, 4), buffer (2, 4), supporting electrolyte (2), surfactants (7)), the temperature (2), the current density (2, 4, 8) and current pulsation (8).

$$[1] \quad 2H_2O\ (H_3O^+) + 2e^- + M \rightarrow 2(H)M + OH^-\ (H_2O)$$

$$[2] \quad Y = Z + M \rightarrow (Y = Z)M$$

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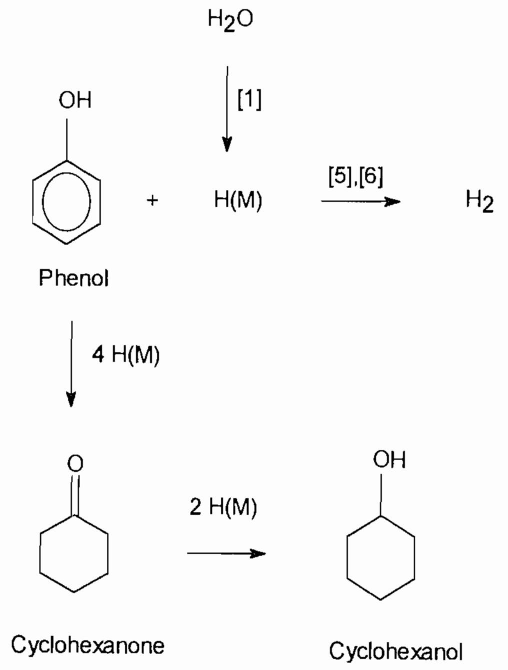
Scheme 1.



[3] $(Y = Z)M + 2(H)M \rightarrow (YH - ZH)M$

[4] $(YH - ZH)M \rightarrow YH - ZH + M$

[5] $(H)M + H_2O + e^- \rightarrow H_2 + M + OH^-$

[6] $(H)M + (H)M \rightarrow H_2 + M$

This paper reports the results of a study on the effect of current density, current pulsation, pH (acidic and neutral), and electrode material on the efficiency of the ECH of phenol to cyclohexanol in aqueous solutions. Scheme 1 shows the conversion of phenol to cyclohexanol via cyclohexanone as intermediate. The electrode materials investigated in acidic medium were: platinized platinum (Pt/Pt), rhodium on nickel (Rh/Ni) (9), ruthenium on nickel (Ru/Ni) (10), and ruthenium on stainless steel (Ru/Inox). The electrodes consisted of rhodium or ruthenium metal chemically deposited on nickel or stainless steel particles dispersed in a lanthanum polyphosphate matrix (lanthanum phosphate-bonded electrodes) (9, 10). In neutral medium, the electrodes studied were made of Rh/Ni, Ru/Ni, or RaNi particles dispersed in a nickel matrix (2). The ECH of phenol to cyclohexanol has been reported before in aqueous acid solutions on platinum (11–14), Pd/C (12), and Rh/C (12) electrodes. Cyclohexanol is an important industrial product as a starting material for preparing adipic acid used in the production of nylon 6 and nylon 6–6 (15).

Experimental

Electrolysis

Electrolysis was carried out at room temperature with an Electrosynthesis (ESC) 410 potentiostat coupled to an ESC 640 digital coulometer and an ESC 2830 digital multimeter or with an EG&G Princeton Applied Research (PAR) 173 potentiostat coupled to a PAR 179 digital coulometer. For the pulse current electrolysis, the PAR 173 potentiostat coupled to a PAR 175 universal programmer was used. A two-compartment glass H-cell with a jacketed cathodic compartment (volume of each compartment 25 mL) with a Nafion-324 (E.I. du Pont de Nemours & Co.) membrane (1.8 cm^2) was used. For the electrolysis at 60°C, it was connected to a Haake D8 constant-temperature circulating bath filled with water – ethylene glycol. The counter electrode was a glassy carbon plate (~12 cm^2) or a platinum grid cylinder (4 cm long and 6 cm in diameter). The neutral electrolyte consisted of a solution of boric acid (0.5 M) (ACS from BDH) and sodium chloride (0.005 to 0.05 M) (ACS from Anachemia) in distilled water. To ensure a high concentration of protons, the concentration of boric acid in the anolyte was sometimes increased to saturation. The pH was measured at the beginning (pH = 4) and at the end (pH = 6) of the electrolysis with a pHydrion Vivid 6–8 (Micro Essential Laboratory) or a Spezialindikator pH 2.5–4.5 (Merck) paper indicator. The acid electrolyte consisted of a solution of sulfuric acid (0.1 M) (ACS from Fisher Scientific) in distilled water. The anodic and cathodic compartments were filled with one of the above solutions. Phenol (ACS from BDH) was dissolved in the cathodic compartment (20 mg, 8.5×10^{-3} M solution), the anode and cathode were immersed, and the catholyte stirred with a magnetic bar and stirrer. The progress of the electrolysis was followed by gas–liquid chromatography (glc) on a Hewlett Packard (HP) 5790a chromatograph equipped with a FID detector and an HP integrator using a 30 m long DB-5 fused silica capillary column heated at 78°C. Aliquots (0.5 mL) from the catholyte were added to a saturated NaCl solution (1 mL), acidified (pH ≈ 1) with concentrated HCl, and extracted with ether. The products were identified by comparing their retention time with that of an authentic sample. The mass balance (92–100%) was determined by the internal standard method.

Electrodes

The Raney nickel (RaNi) electrodes were prepared as already described (2) by codeposition on a stainless steel grid (1.6 cm × 2.2 cm) of nickel and of particles of Raney alloy suspended in a nickel-plating bath, followed by leaching the aluminum in 30% aqueous NaOH at 70°C for 7 h. The composite rhodium–nickel (Rh/Ni) (9) and ruthenium–nickel (Ru/Ni) (10) electrodes consisted of metal/Ni particles (98% by weight) dispersed in a lanthanum polyphosphate matrix (2% by weight). They were prepared as previously described: chemical deposition of Rh or Ru from $RhCl_3$ or $RuCl_3$ on Ni (Rh 3.5%/Ni; Ru 2.3, 3.5, and 4.4%/Ni); thorough mixing of Rh/Ni or Ru/Ni powder and an homogeneous mixture of $La(H_2PO_4)_3$ and $La(OH)_3$; pressing of the resulting mixture under vacuum at room temperature at 1000 lbs/in^2 ($1\ lb/in^2 = 7.03 \times 10^2\ kg/m^2$) in a stainless steel cylindrical mould (diameter: 1.33 cm); polymerization by heating the pellet at 300°C for 3–4 h under a flow of argon. The pellet was coated on one side and along the edge with Epoxyfix resin (Struers) after a Ni foil had been introduced (to ensure electrical contact) to obtain a 1.33 cm^2 geometric area. The Ru 4.4%/Inox electrode was prepared in the same way with stainless steel particles 316-L (100 mesh, Consolidated Astronautics) and 90% Ru/Inox in 10% lantha-

Table 1. ECH of phenol (8.5×10^{-3} M) in a 0.1 M H_2SO_4 aqueous solution on Pt/Pt, Rh/Ni, and Ru/Ni electrodes at $J = 1$ mA/cm^2[a] and at room temperature.

Entry	Cathode[b]	F/mol	Unreacted phenol[c] (%)	Yield of products[c] Cyclohexanone (%)	Yield of products[c] Cyclohexanol (%)	Current efficiency (%)
1	Pt/Pt	2	77	23	1	44
2		4	58	41	1	43
3		12	—	38	62	42
4	Rh 3.5%/Ni	2	61	29	10	~87[d]
5		6	39	38	23	~46[d]
6		14	—	51	49	~36[d]
7	Ru 3.5%/Ni	2	32	7	60	—[e]
8		12	—	—	100	—[e]

[a] Based on the geometric area.
[b] See the experimental section.
[c] Determined by glc (mass balance = 92–100%).
[d] Some dissolution of nickel was observed, so the true current efficiencies are probably lower.
[e] Could not be determined due to dissolution of nickel (see text).

num polyphosphate. The composite electrodes were activated by cathodic polarization curves obtained by decreasing the applied current galvanostatically from 250 to 0.01 mA/cm^2 after applying a current density of 250 mA/cm^2 for 30 min and repeating the cycle until superimposable Tafel curves were obtained. The platinized platinum electrodes (16) were prepared by electrodeposition of platinum from a 2% platinic chloride solution in hydrochloric acid (2 N) for 10–20 min at 10–20 mA/cm^2 on a platinum plate (1.2 cm × 1.1 cm). This electrode was activated by cathodic and anodic polarization (5 cycles of 15 s in each direction) in sulfuric acid (0.01 M) at 0.5 mA/cm^2 just before electrolysis.

Results and discussion

Electrolysis in an acid medium

Previous studies on the ECH of phenol (11–14) were carried out in aqueous sulfuric (0.05 to 0.2 M) and aqueous perchloric (1 M) acid solutions at different current densities (0.02–12.7 mA/cm^2 based on the geometric area) and different phenol concentrations (0.001–0.2 M).The latter two factors influence the competition between hydrogenation (reactions [2]–[4]) and hydrogen desorption (reactions [5] and (or) [6]) and, hence, the efficiency (current efficiency and conversion rate) of ECH: higher current densities usually favor hydrogen evolution over ECH (2, 4, 8, 13) and higher substrate concentrations favor ECH over hydrogen evolution (4, 13). Thus, it is not possible to make a strict comparison between the various results presented in the literature. Our studies in an acidic medium were carried out in aqueous sulfuric acid (0.1 M) with a 8.5 mM phenol concentration. The results are summarized in Tables 1 and 2.

Table 1 reports the results of a comparison of Pt/Pt, Rh/Ni, and Ru/Ni electrodes at a relatively low current density ($J = 1$ mA/cm^2). Both cyclohexanone and cyclohexanol were identified as products, cyclohexanone being formed first and then hydrogenated to cyclohexanol (Scheme 1), as already reported by Miller and Christensen (12) and Amouzegar and Savadogo (14). As the charge increased (theoretical charge = 6 F/mol), more cyclohexanol was formed and the current efficiency decreased due to a decrease in substrate concentration that causes a decrease of the rate of hydrogenation (reaction [3]). It was not possible to determine the current efficiency for the ECH on Ru 3.5%/Ni electrodes (entries 7 and 8) because of electrons provided by the dissolution of nickel during the electrolysis as evidenced by the green coloration of the catholyte. An open-circuit experiment under the same conditions confirmed that the dissolution of nickel did lead to the formation of chemisorbed hydrogen, (H)M, and then to the hydrogenation of phenol: after a period of time corresponding to the end of the electrolysis of entries 7 and 8, 95% of phenol had been converted to 3% cyclohexanone and 92% cyclohexanol. This experiment shows that the Ru/Ni electrode is very active for the hydrogenation of phenol in dilute aqueous sulfuric acid. The Pt/Pt and Rh/Ni electrodes are less active. After 12–14 F/mol, the yield of cyclohexanol was slightly higher with the Pt/Pt electrode (62%, 12 F/mol, entry 3) than with the Rh/Ni electrode (49%, 14 F/mol, entry 6), which suggests that the former electrode is more active. On a Pt/Pt electrode, Miller and Christensen (12) reported the following results in 0.2 M H_2SO_4, after a charge corresponding to 6 F/mol, at a current density of 1.45 mA/cm^2 and a phenol concentration of 0.2 M: 50% conversion, 7% cyclohexanone, 17% cyclohexanol, 22% current efficiency.

Since ruthenium was shown to be an active metal in such composite catalysts in aqueous sulfuric acid, we investigated the Ru/Ni electrodes further, looking at how their activity was affected by current density, the percentage of ruthenium on nickel, and the replacement of nickel with stainless steel. The results are recorded in Table 2 and those of entries 1–10 show that, as reported in the literature with other electrode materials (2, 4, 8, 13), an increase of current density (from 3 to 15 mA/cm^2) led to a decrease in ECH efficiency due to an increase in the rate of hydrogen desorption as already mentioned. There was no dissolution of nickel at current densities of 3 mA/cm^2 and greater so the current efficiencies of entries 1–16 repre-

Table 2. ECH of phenol (8.5×10^{-3} M) in a 0.1 M H_2SO_4 solution on ruthenium electrodes at room temperature: effect of %Ru, metal support, and current density.

Entry	Cathode	J[a] (mA/cm^2)	F/mol	Unreacted phenol[b] (%)	Yield of products[b]		Current efficiency (%)
					Cyclohexanone (%)	Cyclohexanol (%)	
1	Ru 2.3%/Ni	3	2	94	2	4	15
2			6	75	5	20	23
3			13	50	6	45	23
4			24	23	7	70	20
5	Ru 2.3%/Ni	10	2	98	1	1	4
6			4	97	1	2	4
7			42	48	8	44	7
8	Ru 2.3%/Ni	15	2	98	1	2	6
9			6	92	2	6	7
10			13	82	5	14	8
11	Ru 4.4%/Ni	10	3	89	1	10	22
12			6	75	3	22	23
13			12	60	4	37	20
14	Ru 5%/Ni	5	3	69	4	27	66
15			6	41	6	52	56
16			25	6	3	91	23
17	Ru 4.4%/Inox[c]	1	2	96	2	3	11
18			6	92	3	6	7
19			12	88	5	7	5

[a] Based on the geometric area.
[b] Determined by glc.
[c] Ruthenium deposited on stainless steel particles (see the experimental section).

sent true current efficiencies. An increase in the percentage of ruthenium did lead to an increase in efficiency as shown by a comparison of entries 5 and 6 (Ru 2.3%/Ni, J = 10 mA/cm^2) with entries 11 and 12 (Ru 4.4%/Ni, J = 10 mA/cm^2) and a comparison of entries 1 and 2 (Ru 2.3%/Ni, J = 3 mA/cm^2) with entries 14 and 15 (Ru 5%/Ni, J = 5 mA/cm^2): the conversion rate, yield of cyclohexanol and current efficiency are higher in entries 11 and 12 as well as in entries 14 and 15 (despite the fact that the current density was larger in the electrolysis of entries 14 and 15 than in that of entries 1 and 2). As revealed by a comparison of entries 7 and 8 of Table 1 with entries 17–19 of Table 2, replacing nickel with stainless steel led to a notable decrease in electrode activity. This shows that the metal supporting ruthenium does have an influence on the competition (relative rates) between hydrogenation (reaction [3]) and hydrogen desorption (reactions [5] and (or) [6]). This is not surprising since the supporting metal is not completely covered with ruthenium at percentages of ruthenium lower than 10%, as previously shown by X-ray (EDX) mapping (10).

The Ru 5%/Ni electrode appears the most interesting for the ECH of phenol in an aqueous acidic medium with a 94% conversion rate, a 91% yield of cyclohexanol, and a 23% current efficiency at a current density of 5 mA/cm^2 after a charge corresponding to 25 F/mol (Table 2, entry 16). After 6 F/mol (entry 15), the conversion rate was 59%, the yield of cyclohexanol 52%, and the current efficiency 56%. These results can be compared with those of Amouzegar and Savadogo (14) in 0.05 M H_2SO_4 on a Pt/C/Teflon electrode: 100% conversion, 5% cyclohexanone, 95% cyclohexanol, and 85% current efficiency at 6 F/mol. However, they used a much lower current density (0.02 mA/cm^2) and larger phenol concentration (0.05 M), both of which strongly favor the ECH process over hydrogen evolution as pointed out above. On the other hand, the results of entry 12 (Ru 4.4%/Ni electrode, J = 10 mA/cm^2, 6 F/mol, 25% conversion, 3% cyclohexanone, 22% cyclohexanol, 23% current efficiency), could be compared to those obtained by Miller and Christensen (12) for their most active electrode (Rh/C) (J = 11 mA/cm^2, 6 F/mol, 100% conversion, 15% cyclohexanone, 74% cyclohexanol, 84% current efficiency), bearing in mind, however, that they used a much larger concentration of phenol (0.2 M), which again markedly favors the ECH process over hydrogen evolution.

Electrolysis in a neutral medium

For the ECH of phenanthrene in ethylene glycol – water solutions, we reported earlier that the presence of boric acid at concentrations between 0.1 to 0.5 M was beneficial in favoring hydrogenation over hydrogen desorption and thus improving the efficiency of the ECH process (2). It also served as a buffer to maintain the pH between 3.5 and 6.5 during electrolysis (14 F/mol) since hydoxide ions are produced (see eq. [1]) (2). We thus investigated the ECH of phenol on the various electrodes used in the above section as well as on Raney nickel (RaNi) electrodes in an aqueous solution of boric acid (0.5 M) containing sodium chloride (0.05 M) as supporting electrolyte. The pH varied from 4 to 6 during the electrolysis. The

Table 3. ECH of phenol (8.5×10^{-3} M) at room temperature in an aqueous solution containing H_3BO_3 (0.5 M) and NaCl (0.05 M) on Pt/Pt, Rh/Ni, Ru/Ni, and RaNi electrodes.[a]

Entry	Cathode	J^b (mA/cm^2)	F/mol	Unreacted phenol[c] (%)	Yield of products[c]		Current efficiency (%)
					Cyclohexanone (%)	Cyclohexanol (%)	
1	Pt/Pt	1	12	41	36	23	23
2		10	12	91	9	—	3
3		30	12	97	2	1	1
4	Rh 3.5%/Ni	1	13	100	—	—	0
5		10	13	100	—	—	0
6		30	10	100	—	—	0
7	Ru 3.5%/Ni	1	6	98	2	—	1
8			12	96	4	—	1
9		10	6	100	—	—	0
10			12	>99	<1	<1	<1
11		30	6	99	<1	6	6
12			11	89	<1	11	6
13	Ru 2.3%/Ni	30	6	98	<1	2	2
14			15	95	1	4	2
15	Ru 4.4%/Ni	30	6	90	1	8	10
16			16	79	2	19	8
17	RaNi 56%	1	6	100	—	—	0
18			27	83	—	17	4
19	RaNi 58%	10	6	95	—	5	5
20			27	59	—	41	9
21			56	25	—	75	8
22	RaNi 60%	30	6	96	—	4	4
23			12	91	—	9	5
24			21	82	—	18	5

[a] pH before starting the electrolysis: 4.5; pH after the electrolysis: 6.4–8.0.
[b] Based on the geometric area.
[c] Determined by glc (mass balance = 98–100%).

results of the studies carried out at room temperature are recorded in Table 3. It is clear from the current efficiencies and the yield of cyclohexanol that the ECH of phenol on Pt/Pt, Rh/Ni, and Ru/Ni electrodes under those conditions was much less efficient than in aqueous sulfuric acid: compare entry 1 of Table 3 with entry 3 of Table 1 for the Pt/Pt electrodes; no hydrogenation occurred on the Rh/Ni electrodes (entries 4–6) and little hydrogenation occurred on the Ru/Ni electrodes (entries 7–18), which were the most active electrodes in the aqueous acid medium. The RaNi electrodes (entries 17–24) appear somewhat more active than the Ru/Ni electrodes. Thus, under these neutral electrolysis conditions, desorption of chemisorbed hydrogen (reactions [5] and (or) [6]) was much faster than hydrogenation of phenol (reaction [3]). Increasing the current density caused a decrease in ECH efficiency in the case of the Pt/Pt electrodes (entries 1–3) as usually observed (see previous section), had little effect on the low efficiencies of ECH on RaNi electrodes (entries 17–24), but caused a small increase in ECH efficiency on the Ru/Ni electrodes (entries 7–18). However, the reproducibility of these experiments was not assessed since the current efficiencies were very low. The charge had also little effect on the low current efficiency (compare entries 19–21), so it was possible to reach 75% conversion with the quantitative formation of cyclohexanol at a charge corresponding to 56 F/mol (see entry 21). It is noteworthy that no cyclohexanone was detected during the electrolysis on RaNi electrodes, which strongly suggests that its hydrogenation is much faster on these electrodes than that of phenol under the conditions used.

We had previously reported for the ECH of phenanthrene in ethylene glycol — water on RaNi electrodes that replacing sodium chloride as supporting electrolyte by sodium sulfate caused some decrease in efficiency (2) and that pulsating the current (8) and increasing the temperature (2) improved efficiency. We looked at the influence of these factors on the efficiency of the ECH of phenol in a neutral medium. The results of Table 4 show that the ECH of phenol was similarly less efficient when using sodium sulfate as supporting electrolyte (entries 3–5) and that the efficiency was also significantly improved when carrying out the electrolysis at 60°C instead of at room temperature (entries 9–11: 92% conversion, quantitative formation of cyclohexanol, 11% current efficiency in entry 11). However, the ECH of phenol was significantly less efficient when pulsating the current (entries 6–8), contrary to the ECH of phenanthrene. We have no satisfactory explanation for this difference in behavior.

Table 4. ECH of phenol (8.5×10^{-3} M) in an aqueous H_3BO_3 (0.5 M) solution on RaNi: effect of supporting electrolyte, periodic current control, or temperature.

Entry	Supporting electrolyte	T (°C)	Current density[a] (mA/cm^2)	F/mol	Unreacted phenol[b] (%)	Yield of cyclohexanol[b] (%)	Current efficiency (%)
1[c]	NaCl 0.05 M	R.T.	10	6	95	5	5
2[c]				56	25	75	8
3	Na_2SO_4 0.5 M	R.T.	10	6	98	2	2
4				12	95	5	2
5				57	68	32	3
6	NaCl 0.05 M	R.T.	10	6	99	1	1
7			Periodic current control[d]	12	96	4	2
8				41	86	14	2
9	NaCl 0.05 M	60	10	6	79	20	20
10				12	60	40	19
11				51	8	92	11

[a] Based on the geometric area.
[b] Determined by glc (mass balance = 98–100%).
[c] Taken from Table 3 (entries 19 and 21).
[d] T_1 = 100 ms at 0.05 mA/cm^2; T_2 = 200 ms at 10 mA/cm^2.

Conclusions

We have shown that composite electrocatalysts consisting of a small amount of rhodium or ruthenium metal chemically deposited on nickel particles (2–4% Rh or Ru/Ni) dispersed in a polyphosphate matrix were active for the ECH of phenol *in aqueous sulfuric acid*. Ruthenium supported on stainless steel was much less active, which shows that nickel has an influence on electrocatalytic activity. At a relatively low current efficiency of 1 mA/cm^2, dissolution of nickel generating active chemisorbed hydrogen occurred but no dissolution was observed at J = 3–15 mA/cm^2. The order of activity of the electrodes was Ru/Ni > Pt/Pt > Rh/Ni. The best results were obtained with a Ru 5%/Ni electrode, which gave, at a current density of 5 mA/cm^2, a conversion rate of 94%, a 91% yield of cyclohexanol, and a current efficiency of 23%. A meaningful comparison with literature data on other electrocatalysts could not be made because of the widely different electrolysis conditions used which have an influence on the competition between the reaction of phenol with chemisorbed hydrogen and desorption of chemisorbed hydrogen and thus the efficiency of ECH. *In aqueous boric acid* (*neutral medium*), the Rh/Ni and Ru/Ni electrodes were found to be practically inactive, whereas a composite Raney nickel electrocatalyst consisting of Raney nickel particles dispersed in a nickel matrix did quantitatively electrohydrogenate phenol to cyclohexanol (no cyclohexanone detected) at 60°C although with low current efficiencies (≈17%).

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