Electrochemical hydrogenation of citral
5.* The use of a nickel electrode in the electrocatalytic process

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The conditions for preparative electrocatalytic hydrogenation of citral to citronellol were found. Changes in the electrocatalytic properties of the nickel cathode depend on the method of pretreatment of the electrode (mechanical surface cleaning, thermal treatment, cathode-anode activation, and electrodeposition). The use of the nickel cathode with the surface covered with dispersed nickel in electrocatalytic hydrogenation was recommended.

Key words: citral, electrocatalytic hydrogenation, nickel cathode, modification of electrode, electrodeposition of nickel.

Nickel is a promising metal as the cathode material in electrosynthesis due to its accessibility and catalytic properties. However, electrocatalytic activity of nickel depends to a considerable extent on a method of pretreatment of the electrode. For example, it was shown for the ketone series[2] that the reduction on the polished nickel electrode occurred *via* the electron mechanism, whereas this process on the Raney nickel was electrocatalytic. Electrocatalytic hydrogenation (ECH) of several α,β-unsaturated ketones on the Raney nickel, which is fixed on the cathode by a magnet, made it possible[3] to perform selective hydrogenation of the conjugated C=C bond with retention of the carbonyl group and to obtain the corresponding saturated ketones in high yields.

The authors of the reviews[4,5] devoted to structural factors in electrocatalysis report that the adsorption and electrocatalytic properties of high-dispersed metals differ from those of bulky metals, and the influence of crystallographic orientation and defectiveness of the surface of a metallic electrocatalysts on the electrocatalytic parameters is smaller than the influence of their dispersity. Electrodeposition of metals on their surface is a traditional method for increasing the catalytic activity of electrodes. Unlike skeleton catalysts, electrolytic precipitates can be prepared prior to use, which allows labor-consuming preliminary stages to be avoided.[6] The type of an electrolytic precipitate depends on conditions of its preparation;[5] evidently, the precipitates should differ in electrocatalytic activity as well. Despite many works on ECH of unsaturated organic compounds on different catalysts,[7] the electrode material and conditions of the electrochemical process are still selected empirically in each particular case.

The purpose of this work is to monitor the change in the catalytic properties of the nickel electrode when different methods (those most often used in electrosynthesis) of cathode activation are applied (depending on the change in the type of its surface). The model reaction of ECH of citral was used as an example.

Experimental

A P-5848 potentiostat and a cell with a glass diaphragm were used for preparative electrolysis. A cylindrical Ni plate (S_{work} = 0.88 dm^2) was used as the cathode (the methods of preparation are described below). A Pt wire gauze served as the anode, and a saturated calomel electrode was the reference electrode.

Citral (0.16 g, 0.024 mol L^{-1}) was electrocatalytically hydrogenated in a 0.1 *M* solution of KCl in the presence of acetic acid (0.096 mol L^{-1}) using 40% DMF in H_2O as the solvent. The volume of the catholyte was 50 mL, and I_{start} was 70—80 μA. The electrolysis course was monitored by TLC (ether—hexane, 1 : 1) and GLC (an LKhM-80 chromatograph with a column 3 m×3 mm filled with 5% XE-60 on Chromaton N-AW-DMCS). The electrolysis was stopped either after the disappearance of citral or after passing an excess quantity of electricity (Q) compared to that necessary for the complete hydrogenation of citral to citronellol (Q_{calc} = 0.128 A h). After electrolysis, the solution was extracted with ether, washed with water, and dried with $MgSO_4$. Yields of the products in the mixture were determined by GLC using *p*-nitrochlorobenzene as the internal standard. All products after isolation were identified by comparing them to authentic samples (commercial preparations from Aldrich and Sigma) using GLC, TLC, and ^{1}H NMR spectroscopy (a Bruker WM-250 instrument).

Preliminary preparation of the nickel cathode (see Table 1).

Polished nickel (entry *1*) — to remove oxide, the cathode was washed with dilute HNO_3 (1 : 10) and water prior to electrolysis. A polished nickel electrode was stored during annealing in the flame of a glass-blowing burner (entry *2*) for

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* For Part 4, see Ref. 1.

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Table 1. Results of electrocatalytic hydrogenation of citral on the Ni cathode

Entry	Type of cathode, pretreatment	E/V	Q_{cons} /A h	Residue of citral (%)	Yield of products (%)		
					1	2	3
1	Polished Ni	−1.7	0.27	15	5	29	17
2a	Polished Ni, annealing in flame	−1.9	0.32	10	2	22	18
2b	Polished Ni, repeated annealing	−1.9	0.59	20	—	—	—
3	Polished Ni, calcination in a muffle furnace	−2.0	0.50	9	—	—	—
4a	Polycrystalline Ni/Ni (i = 1 A dm^{-2})	−1.6	0.31	—	—	—	77
4b	The same precipitate washed	−1.2	0.23	—	—	11	67
4c	The same precipitate washed	−1.3	0.23	—	—	11	54
5	Поликристаллический Ni/Ni (i = 1 A dm^{-2})	−1.4	0.26	—	—	9	53
6	Polycrystalline Ni/Ni (i = 0.1 A dm^{-2})	−1.1	0.23	—	—	18	70
7a	Dispersed Ni/Ni, deposition for 2 h	−1.3	0.28	—	—	—	90
7b	The same	−1.1	0.20	—	—	—	95
7c	The same	−1.0	0.16	—	—	—	90
8a	Dispersed Ni/Ni, deposition for 1 h	1.0	0.17	—	—	—	85
8b	Dispersed Ni/Ni, deposition for 0.5 h	−1.0	0.18	—	—	—	80
9	Cathode-anode activation	−1.0	0.27	16	17	17	51

Note. [Citral] = 0.024 mol L^{-1}, [AcOH] = 0.096 mol L^{-1}; background is 0.1 *M* KCl, solvent is 40% DMF in H_2O.

4 min (the temperature on the surface was not higher than 300 °C according to the thermocouple indications) and washed with dilute HNO_3 and water. Thermal treatment in a muffle furnace (entry *3*) was carried out at 700 °C for 15 min, and then the cathode was washed with dilute HNO_3 and water.

Polycrystalline nickel (entries *4*—*6*) was obtained by electrodeposition on the cleaned cathode surface from a bath of 1 *M* $NiCl_2 \cdot 6 H_2O$ + 0.5 *M* H_3BO_3 [8] for 2 h at a cathode current densities of 1 A dm^{-2} or 0.1 A dm^{-2}. The electrode was washed with water, and its surface, was gray, mat-finish.

Dispersed nickel (entries *7* and *8*) was obtained by electrodeposition on the cleaned cathode surface from a solution of 0.5 *M* $NiCl_2 \cdot 6 H_2O$ for 2 h at a cathode current density of 0.1 A dm^{-2}. The electrode was washed with water, and its surface was uniform, covered with a powder-like black precipitate (black enamel).

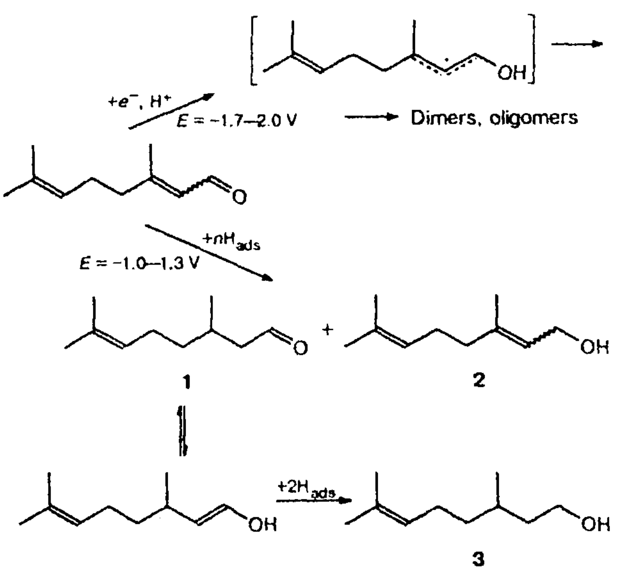
Cathode-anode activation of the cathode (entry *9*) was carried out for 4 min in a solution of 0.05 *M* $NiSO_4$ + 0.1 *M* CH_3COONa + 0.005 *M* NaOH (stainless steel was used as the anode) at a cathode current density of 0.001 A dm^{-2} with multiple (5—10 times) polarity inversion (period 10 s).[9]

Results and Discussion

Previously,[1,10] in studying ECH of citral on the annealed copper cathode, we found an efficient method for pretreatment of the copper cathode and optimum conditions for the electrochemical process. However, it remained unclear whether the composition of the medium found would be optimum for another solid electrode. In this work, we used a nickel electrode with obvious catalytic activity. The yields of products of ECH of citral obtained on the nickel cathode are presented in Table 1.

It is noteworthy that the direct electroreduction of α,β-unsaturated carbonyl compounds *via* the radical mechanism results in either the formation of a mixture of dimers or resinification (Scheme 1), and the formation of aldehyde **1** and alcohols **2** and **3** is possible only *via* the ECH mechanism. Therefore, the existence of dimeric products (after ECH of citral) and the low yield of alcohols and noticeable resinification indicate the contribution of direct electron transfer to the citral molecule to the overall electrochemical process.

Scheme 1



Dimeric and oligomeric products, the signals of which are observed on the chromatogram (GLC) of the mixture at high temperatures of the column, are formed on the polished Ni electrode (see Table 1, entry *1*) along with the products of ECH of citral: citronellal (**1**), isomeric nerol and geraniol (**2**), and citronellol (**3**), whose overall yield is 51%. The great hydrogen overvoltage on the polished Ni electrode requires an increase in the working potential to $E = -1.7$ V at which the direct electron transfer to the citral molecule becomes possible. The low efficiency of ECH is a consequence of the parallel occurrence of the process *via* these two directions: even at expenditures of more than double the quantity of electricity (compared to that theoretically required for the complete hydrogenation of the system of conjugated bonds), a noticeable amount of the starting reagent remains unreacted.

We have previously observed[10] that annealing of copper in the flame of a glass-blowing burner results in a decrease in the overvoltage of hydrogen release and a considerable enhancement of the catalytic activity of the Cu cathode in the reaction of ECH of citral. By contrast, after a similar treatment of nickel, the hydrogen overvoltage increases (entry *2a*), and the yield of the hydrogenation products decreases. The repeated annealing procedure leads to the almost complete disappearance of the hydrogenation products (entry *2b*). After calcination in the muffle furnace, the hydrogen overvoltage increases further (entry *3*); no hydrogen is evolved at $E = -2.0$ V. Two different regimes of thermal treatment are used because of different changes in the metal:[8] elimination of internal strains at 300 °C and grain growth in the metal at 700 °C. Thus, unlike copper, the thermal treatment of nickel results in the retardation of hydrogen release and a decrease in the electrocatalytic activity during ECH of citral. Perhaps, this extends the possibilities of using nickel for direct electroreduction, because the working potential is shifted to the cathodic region.

The evolution and activation of hydrogen is the key stage of ECH. It is known[2] that the hydrogen overvoltage on the loosened nickel surface is lower than on the polished surface. Metal electrodeposition is mostly often used to obtain electrodes with developed surfaces. Evidently, the structure of the precipitate can change strongly under different electrodeposition conditions:[5,8,11] the composition of the medium, the presence of additives, the concentration of the components, temperature, current density, support material, *etc.* Although the comprehensive literature on electrocrystallization of metals is mainly devoted to the development of smooth solid coverings with anticorrosive and decorative properties, the procedures developed make it possible to obtain simultaneously surfaces with the structures known beforehand. For example, the precipitate formed during the electrodeposition of nickel from the chloride—borate bath[8] is characterized as polycrystalline and flat, with pronounced grains. Under these conditions,[8] we performed the electrodeposition of nickel on the electrode subjected previously to the thermal treatment. The ECH of citral on this electrode gave one product: alcohol **3** in a high yield (entry *4a*). However, repeated electrolysis on the same electrode but treated with an organic solvent and water gave alcohol **2** along with alcohol **3**, *i.e.*, the selectivity of ECH decreases, and the overall yield of alcohols decreases as well (entries *4b,c*).

The phenomenon of electrode "aging" during electrosynthesis is well known.[12] The comparison of the results of entries *4a—c* shows a pronounced decrease in the electrocatalytic activity of the polycrystalline residue. Evidently, this is related to a change in the structure of the polycrystalline surface during electrocatalysis due to its "etching out," *i.e.*, insertion of an alkali metal in the crystal lattice of nickel.[13] Renewal of the polycrystalline electrode covering by the electrodeposition of nickel on the cleaned surface under the same conditions does not increase the selectivity of ECH of citral: a mixture of alcohols (entry *5*) was obtained in an overall yield of 62%.

The current density has a substantial effect on the precipitate structure during electrodeposition (the higher the current density, the smaller the crystals[8,11]); therefore, a decrease in the current density during electrodeposition should result in the formation of a precipitate with larger crystals. The nickel electrodeposited at a low current density ($i = 0.1$ A dm^{-2}) exhibits a substantial decrease in the hydrogen overvoltage, and the overall yield of products of ECH of citral reaches 88% (entry *6*); however, the selectivity of the process does not increase (the ratio of alcohols **3** : **2** = 4).

Thus, in the series of experiments on the polycrystalline Ni cathode, it is impossible to reproduce the result of selective ECH of citral primarily obtained in entry *4a*. The structure of the polycrystalline precipitate, as known,[11] is determined to a great extent by the state of the metal surface of the support. It is most likely that the nickel surface structure (with enlarged grains, flattened defects) formed as the result of multiple thermal treatments in different regimes determines the character of the covering during electrocrystallization of nickel in entry *4a*. Therefore, to obtain the catalytically active and well-reproducible electrode surface by electrocrystallization from bath, not only the electrodeposition regime should be rigidly maintained, but the state of the support should be controlled as well.

The use of the Ni electrode modified by dispersed nickel is more reasonable for ECH. Only one product, alcohol **3**, was obtained in a high yield in a series of experiments (entries *7a—c*) on this electrode with the surface renewed prior to each electrolysis (products **1** and **2** were observed only in trace amounts). A gradual decrease in the hydrogen overvoltage and quantity of electricity consumed in ECH of citral (an increase in the current efficiency) was observed from test to test. The corresponding structurization of the metal surface most likely occurs due to multiple electrodeposition of dispersed nickel. The decrease in the time of nickel deposition in the next experiments (entries *8a,b*) only insignificantly decreases the yield of alcohol **3** in ECH of citral. This effect is similar to the "memory effect" described,[14] *i.e.*, the results of ECH are improved by performing a series of electrolyses with the same object (with the same pretreatment of the electrode).

The cathode-anode activation with periodic alternation of the electrode polarity is another often recommended method for the preparation of the electrode surface.[12] In addition to cleaning the surface from contaminators, this activation leads to a change in the surface structure: loosening due to the formation of oxides and their subsequent reduction.[14] This method of activation is inefficient for ECH of citral (entry *9*). Although the hydrogen overvoltage is decreased ($E = -1.0$ V), the selectivity of the process is low: the mixture contains the whole set of hydrogenation products and a considerable amount of the starting unreacted citral. The quantity of electricity transmitted is more than twofold higher than that theoretically necessary. However, it is known[14] that either the strongly loosened or crystallographically oriented surface can be obtained at different forms of pulses, their frequencies, and current values. Probably, a detailed study of the influence of this method of treatment can reveal conditions of the cathode-anode activation of the Ni electrode favoring ECH.

Thus, the modification of the Ni cathode with dispersed nickel is the most efficient method for its activation. A simple preliminary procedure of nickel electrodeposition under the conditions determined provides a good reproducibility of the results of ECH of citral and makes it possible to obtain citronellol in high yield and with high current efficiency. It should be specially mentioned that the ECH process on this electrode is selective. The conjugated system of bonds C=C—C=O in the citral molecule is completely hydrogenated, and the isolated C=C bond is not touched, which was unambiguously confirmed by the ^{1}H NMR spectrum of the ECH product. The results obtained indicate that conditions on the medium composition, which have been previously determined for ECH on the Cu cathode, are also appropriate for ECH on the Ni cathode.

Using the model reaction of ECH of citral as an example, we showed that the efficiency, selectivity, and even the direction of the process can change substantially at different types of the cathode surface (*i.e.*, due to different pretreatments of the cathode).

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