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ELECTROCATALYTIC HYDROGENATION OF ORGANIC COMPOUNDS ON DEVARDA COPPER AND RANEY NICKEL ELECTRODES IN BASIC MEDIA

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Using Devarda copper and Raney nickel electrodes, nitrobenzene, nitrocyclohexane, p-nitroacetophenone, N-methyl-p-anisaldehyde imine, benzophenone, and phenanthrene have been electrocatalytically hydrogenated with high chemical and current efficiency.

Electrocatalytic hydrogenation has been extensively studied on platinum or platinized platinum electrodes. Mechanistic and theoretical aspects were thoroughly investigated in the case of ethylene (1 and 2, and references cited therein).

With electrodes having catalytic properties towards hydrogenation, such as Raney nickel or Devarda copper, the hydrogen overvoltage should be low and the hydrogen generated at the surface of the catalyst is expected to be very active and react readily. Therefore it can be anticipated that electrocatalytic hydrogenation on these electrodes could be a powerful, versatile, and inexpensive hydrogenation method.

In this paper we report on the efficient and mild (low applied potentials) electrocatalytic hydrogenation of nitro compounds, an imine, a ketone, and a polycyclic aromatic hydrocarbon in a basic medium. So far, very little attention has been paid to the use of Raney nickel electrodes (3-7) and none to the use of Devarda copper electrodes for electrohydrogenation. **The latter electrodes appear to hydrogenate specifically nitrocompounds to the amines;** ketones, imines, oximes, hydroxylamines, and aromatic hydrocarbons are totally inerts.

$$2H_2O + 2e^- \rightarrow H_{2ads} + 2HO^-$$

$$ArX{=}Y + H_{2ads} \rightarrow ArHX{-}YH$$

The electrodes are prepared in the following way: unleached powdered Raney or Devarda alloy (200-325 mesh) is dispersed into a nickel bath (8). Using a nickel plate as anode and a stainless steel screen as cathode, electroplating is then carried out. The composition of the coating (tiny particles of alloy embedded in deposited nickel) depends widely on such factors as composition of the plating bath, temperature, size of the particles, etc. The average content of alloy is 20%. The electrode is activated by leaching the deposited alloy in a 20% aqueous solution of NaOH or KOH according to procedures drawn from the different preparations of Raney nickel (9). The activity of the electrode depends both on its composition and activation process. The electrode is then transferred to the cathodic compartment of an H shape three compartment electrochemical cell. The "electrolysis" can be carried out either under potentiostatic or intensiostatic conditions. A typical experimental procedure is described below.

Six relevant examples of electrocatalytic hydrogenation are presented in the table.

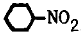
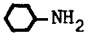
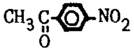
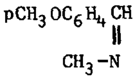
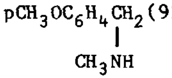
On a Devarda copper electrode, nitrobenzene and nitrocyclohexane (entries 1 and 2) are electrohydrogenated to aniline and cyclohexylamine respectively with high current and chemical yields and at low applied potentials. On a copper electrode, other conditions being the same, the reduction of nitrobenzene is very inefficient giving 14% of azobenzene and traces of aniline besides 50% of starting material. Treated according to the conditions of entry 2, nitrocyclohexane is not reduced on a copper electrode. Entry 3 shows that a nitrogroup can be reduced selectively in the presence of a carbonyl group. Attempts to hydrogenate benzophenone, N-methyl-p-anisaldehyde imine, cyclohexanone oxime, and phenanthrene were unsuccesful; the starting materials were recovered unchanged.

On a Raney nickel electrode, and at a low applied potential, the electrohydrogenation of N-methyl-p-anisaldehyde imine to N-methyl-p-anisidine (entry 4) and of benzophenone to benzhydrol (entry 5) are very efficient. Phenanthrene (entry 6) is electrohydrogenated, to a mixture of 9,10-dihydrophenanthrene and two other more hydrogenated compounds: a tetrahydro derivative (40%) and an octahydro derivative (6%) according to gas chromatography - mass spectrometry (GC-MS) analysis. On a nickel plated electrode (8), other conditions being the same, no reduction occurs in these cases.

The electrocatalytic hydrogenation of an aromatic system under such mild conditions (room temperature and ordinary pressure) clearly demonstrates the potential and future possible developments of this method. Thus the catalytic hydrogenation of phenanthrene to 9,10-dihydrophenanthrene on Raney nickel requires both an elevated temperature (110°C) and a high pressure of hydrogen (125 bar) (10).

We are currently studying the electrocatalytic activity of Raney type electrodes based on various transition metals. We are also investigating the use of composite electrodes doped by the introduction of additional components in order to increase the activity.

TABLE. Electrohydrogenation on Raney nickel and Devarda copper electrodes in basic media

Entry	Substrate[a]	Electrode	Supporting electrolyte; solvent	Conditions	Products (Yield)[b]	Current efficiency	Hydrogen evolution
1	$PhNO_2$	Devarda copper	KOH 0.28M; MeOH (1.5% H_2O)	Potentiostatic E=-0.800V (SCE)	$PhNH_2$ (92%) PhN=NPh (4%)	91%	None
2		Devarda copper	KOH 0.28M; MeOH (1.5% H_2O)	Potentiostatic E=-0.760V(SCE)	 (100%)	99%	None
3		Devarda copper	KOH 0.28M; MeOH(1.5% H_2O)	Potentiostatic E=-0.724V(SCE)	 (79%)	85%	None
4	 $pCH_3OC_6H_4CH{=}N{-}CH_3$	Raney nickel	KOH 0.28M MeOH(1.5% H_2O)	Potentiostatic E=-0.850V(SCE)	 $pCH_3OC_6H_4CH_2{-}NHCH_3$ (92%)	95%	None
5	$(Ph)_2C=O$	Raney nickel	NaOH 0.5M; EtOH 70%,H_2O 30%	Potentiostatic E=-1.08V (SCE)	$(Ph)_2CHOH$ (97%) unreacted benzophenone (3%)	100%	None
6	Phenanthrene	Raney nickel	$(n\text{-}Bu)_4NOH$ 0.5M EtOH 67%,H_2O 33%	Intensiostatic 10mA/dm^2[c]	9,10-dihydrophenanthrene (36%) more hydrogenated compounds (50%) unreacted phenanthrene (6%)	46%	Evolution

[a] The concentration ranged between 15 and 40 x 10^{-3} mol/l.

[b] In entries 1 and 4, the yields refer to products isolated by preparative layer chromatography and in entries 2,3 and 5 they were determined by gas liquid chromatography (OV 101 glass capillary column).

[c] The potential of the electrode was close to -1.00V *vs* SCE.

Experimental procedure: **Electrocatalytic hydrogenation of nitrocyclohexane** (entry 2). The activated Devarda copper electrode is placed in the cell containing the previously deaerated (N_2) electrolysis medium; its potential is lowered (-1.2v/SCE) in order to generate hydrogen at the surface of the electrode for at least 20 minutes, this brings the electrode active surface to saturation. Then the potential is slowly varied in order to get the zero current point (-0.760 v/SCE) and the substrate is added in one portion; this addition causes the reduction current to increase suddenly and stabilize (j = 160 mA/dm^2) while the hydrogenation proceeds. A significant drop of the current occurs at the end of the "electrolysis" when the substrate is almost completly consummed.

The catholyte is then neutralized, extracted with methylene chloride and dried. The quantitative analysis is performed on the crude product by GC with addition of known standards.

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REFERENCES AND NOTES

1. L.D. Burke, C. Kemball and F.A. Lewis. Trans. Faraday Soc., 1964 60, 913-918.

2. A.T. Hubbard, M.A. Young and J.A. Schoeffel. J. Electroanal. Chem., 1980, 114, 273-281.

3. B. Sakurai and T. Arai. Bull. Chem. Soc. Jpn., 1955, 28, 93-99.

4. X. De Hemptinne and J.C. Jungers, Z. Physik. Chem., 1958, 15, 137-148.

5. M. Fujihira, A. Yokozawa, H. Konoshita and T. Osa. Chemistry Letters, 1982, 7, 1089-1092.

6. Asahi Chem. Ind. Co. Ltd. Patent J.P. 57,174,478 [82,174,478] 27 Oct., 1982; C.A. 98, P 80592 f.

7. T. Chiba, M. Okimoto, H. Nagai and Y. Takata. Bull. Chem. Soc. Jpn., 1983, 56, 719-723.

8. $NiSO_4 . 6H_2O$ (120 g/l); NH_4Cl (15 g/l); H_3BO_3 (15 g/l); room temperature, 1 A/dm^2.

9. R.L. Augustine. "Catalytic Hydrogenation", M. Dekker Inc., New York, 1965, p. 27.

10. J.R. Durland and H. Adkins. J. Am. Chem. Soc., 1938, 60, 1501.

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