

Electrochemical production of heterogeneous nickel catalysts for organic hydrogenations

G. FILARDO, F. LA ROSA*, G. ALFEO†, S. GAMBINO, G. SILVESTRI

Istituto di Ingegneria Chimica, Facoltà di Ingegneria, Viale delle Scienze, Palermo, Italy

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The electrochemical deposition of nickel on copper, tin, aluminium or nickel in N,N-dimethylformamide is described. The cathodic surface becomes catalytically active towards the addition of molecular hydrogen onto unsaturated organic compounds. The activity of the catalyst is influenced by the nature of the cathode: copper gives the highest reactivity, then, in order of decreasing activity, aluminium, tin and nickel. The behaviour of the catalytic surfaces obtained with copper cathodes is comparable to that of the group of Raney nickel catalysts.

1. Introduction

Electrochemical techniques for the production of a catalyst inside a chemical reactor have been applied in various synthetic fields. Homogeneous catalysts have been produced for polymerization [1], oxidation [2], hydrogenation [3], and cyclo-dimerization [4, 5]. With heterogeneous systems, the surface activity of solid electrodes [6, 7] and those modified by foreign metal adatoms [8] has been widely investigated, but in all these cases the catalytic properties are shown only during the electrolysis. Even in the intriguing class of reactions, those "electrochemically triggered" by an electrode, the catalytic activity is due to the potential at which the electrode itself is maintained during the evolution of some chemical reactions [9, 10].

In this communication we report the first examples of the electrochemical *in situ* production of a solid heterogeneous catalyst, chemically active towards the addition of molecular hydrogen onto unsaturated compounds.

The electrochemical system we have employed consists of a metal cathode, on which small amounts of nickel are deposited from an organic electrolyte containing both the substrate and hydrogen, and a nickel sacrificial anode. The cathodic surface becomes catalytically active for some organic hydrogenations when copper, tin, aluminium or nickel are employed as cathodes.

2. Experimental procedure

2.1. Reagents and apparatus

The hydrogenations were performed in high pressure electrochemical reactors already described [11]. The nickel anodes and the metals employed as cathodes were 99.99% pure, they were mechanically polished, washed with benzene and then dried under vacuum. Pure grade solvents were rectified at reduced pressure and stored over 4 Å molecular sieves. Solid reagents and supporting electrolytes were recrystallized from suitable solvents.

Direct X-ray diffraction patterns of the cathodic deposits were made using a Philips model 1130 generator and a PW 1050 goniometer. CuK radiation was used at a scanning rate of $2\theta = 1^\circ \text{ min}^{-1}$. The d-spacings were measured and compared with the ASTM index values. Scanning electron micrography was carried out with a SEM Philips model 505, and X-ray energy dispersion microanalyses with an EDAX model PV 9100.

2.2. Synthetic procedure

A typical synthetic experiment, in which acenaphtylene was employed as substrate, is described here. The electrochemical cell, having an internal volume of 250 cm³, was equipped with a copper beaker as the cathode (apparent working

* Present address: SNAM PROGETTI, Milano, Italy.

† Part of the content of the dissertation of G.A. is published here.

surface 48 cm^2), and an internal nickel cylinder working as the anode (apparent working surface 10 cm^2). The cell was charged with *N,N*-dimethylformamide (30 cm^3), tetrabutylammonium bromide (1.0 g), and acenaphthylene (4.0 g), then closed, purged several times with hydrogen, and charged with the same gas until a pressure of 130 atm^* was reached. The cell was put into a thermostat bath at a temperature of 80° C , and, once it had reached the equilibrium pressure (147 atm), a constant current of 5 mA was imposed, until 19 C passed. After 4.5 C , the pressure started to decrease, and continued at about the same rate even after the interruption of the current until about 90% of the theoretical amount of hydrogen had reacted. The residual 10% reacted at a progressively decreasing rate (see Fig. 1, curve *c*). The cell was then cooled, the gas vented and the solution effluent was poured into water (200 cm^3). The white solid precipitate of acenaphthene was filtered, washed with water and dried. IR, NMR, and chromatographic analyses confirmed the high purity of the product. The conversion was 100% and the yield 99% with respect to the acenaphthylene introduced.

3. Results

3.1. Catalytic properties of the cathodic surfaces

The catalytic activity of the cathodic surfaces, after the deposition of $1.10\text{--}1.20 \cdot 10^{-4} \text{ g cm}^{-2}$ of nickel, is strongly influenced by the nature of the

cathode; with lead there is no activity at all, and over nickel the hydrogenation takes place at a lower rate in comparison with copper, tin and aluminium. Among these last metals, copper gives the highest reactivity, and aluminium and tin behave essentially in the same way (see Fig. 1).

The catalytic activity is not dependent on the presence of the components of the electrolytic system other than the cathode, i.e., the solvent, supporting electrolyte and nickel anode. In fact, it has been verified that the cathodic surfaces maintain their activity when, after the first hydrogenation cycle, they are washed several times with methanol and used again but without electrolysis, for the hydrogenation of other unsaturated compounds.

Cathodic current densities ranging from $0.1\text{--}0.5 \text{ mA cm}^{-2}$ were tested with positive results, employing copper cathodes. The current density has a marked influence on the macroscopic morphology of the cathodic deposit: at lower values a coherent layer adherent to the metallic support is obtained, whereas at higher currents nickel particles are found suspended in the electrolyte solution.

3.1.1. Behaviour of systems with copper cathodes.

The cathodic deposits on copper are active towards the addition of molecular hydrogen onto organic compounds containing olefinic or nitrile groups. Table 1 shows the results obtained, in simi-

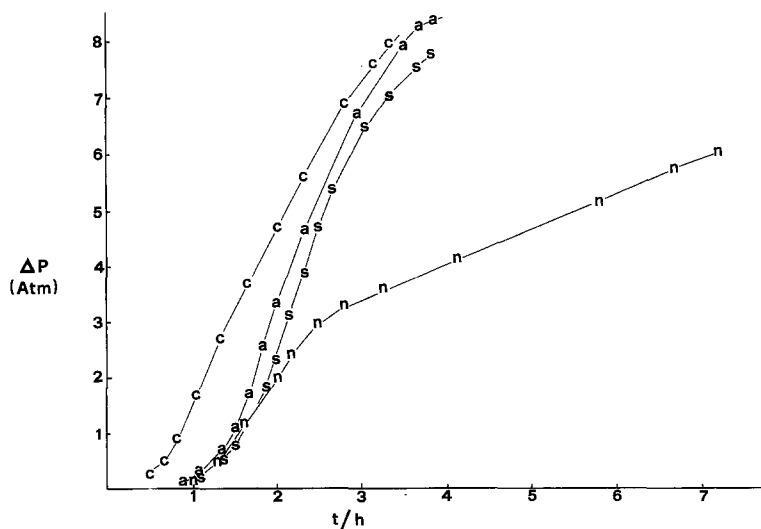


Fig. 1. Hydrogenation of acenaphthylene catalyzed by nickel electrodeposited over different cathodes. Cathodes: c = copper; a = aluminium; s = tin; n = nickel. DMF 26.5 g ; acenaphthylene 4.0 g ; tetrabutylammonium bromide 1 g . Temperature 80° C ; initial hydrogen pressure 118 Atm .

* $1 \text{ atm} = 1.013 \times 10^5 \text{ Pa}$.

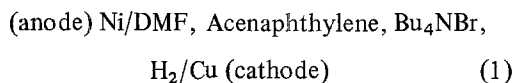
Table 1. Hydrogenation of different organic substrates with nickel catalysts electrodeposited over copper cathodes. The electrochemical system is described in detail in the experimental part. The hydrogen pressure values quoted here correspond to the initial value at 80° C

Substrate	Solvent	Hydrogen pressure (Atm)	Products	Product yields (%)
butan-2-one	DMF	176	butan-2-ol	5
acenaphthylene	DMF	180	acenaphthene	99
benzophenone	DMF	173	benzopinacol	13
			isopropanol	
acetone	acetone	172	pinacol	2 (overall)
			diacetonolcohol	
acetonitrile	acetone	177	ethylamine	90
cyclohexene	DMF	154	cyclohexane	99
buta-1,3-diene	DMF	150	butane	99
diethylmaleate	DMF	154	diethylsuccinate	99
diethylfumarate	DMF	154	diethylsuccinate	99
benzene	DMF	150	—	—
pyridine	DMF	152	—	—

lar conditions, with a series of unsaturated compounds. The kinetics of the reaction involving acetone is so slow that this compound can be used as solvent for the hydrogenation of other unsaturated substrates. Very high hydrogenation rates are obtained when conjugated olefins, such as dimethylmaleate, dimethylfumarate, butadiene or acenaphthylene are tested as substrates.

The hydrogenation of butadiene takes place in two steps; during the first just one of the double bonds is saturated, and in the second, butane is obtained in quantitative yields (see Fig. 2). When the experiment was interrupted after the first stage, but-1-ene (75%), *cis* but-2-ene (24%) and *trans* but-2-ene (1%) were found amongst the product.

3.1.2. Influence of physical parameters on the catalytic activity. The influence of temperature, hydrogen pressure, and substrate concentration on the kinetics of the hydrogenation has been tested with a catalyst prepared *in situ* by means of the following electrochemical system:



with a cathodic current density of 0.208 mA cm⁻².

A substantial increase in the kinetics of hydrogenation with the temperature (see Fig. 3) and

with increase of the pressure of the system (see Fig. 4) was observed. In a set of runs performed at 80° C and at an initial pressure of 92 ± 1 atm, the initial concentrations of acenaphthylene were 0.46 mol dm⁻³, 0.92 mol dm⁻³ and 1.38 mol dm⁻³, no appreciable differences in the hydrogenation kinetics were observed.

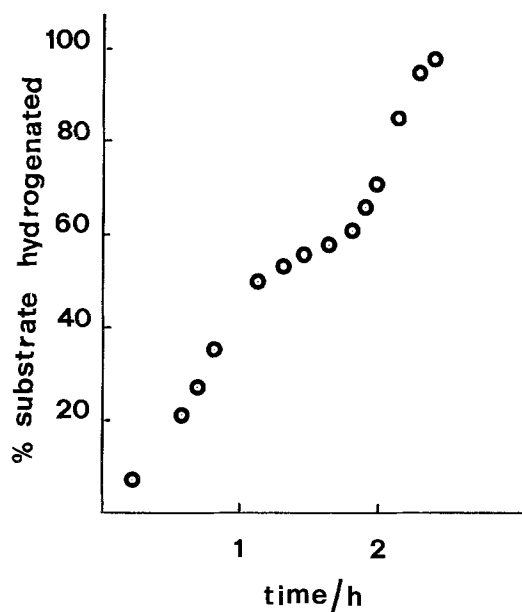


Fig. 2. Hydrogenation of 1,3-butadiene catalyzed by nickel electrodeposited over copper. DMF 26 g; 1,3-butadiene 2.0 g; tetrabutylammonium bromide 1 g. Temperature 80° C; initial hydrogen pressure 120 Atm.

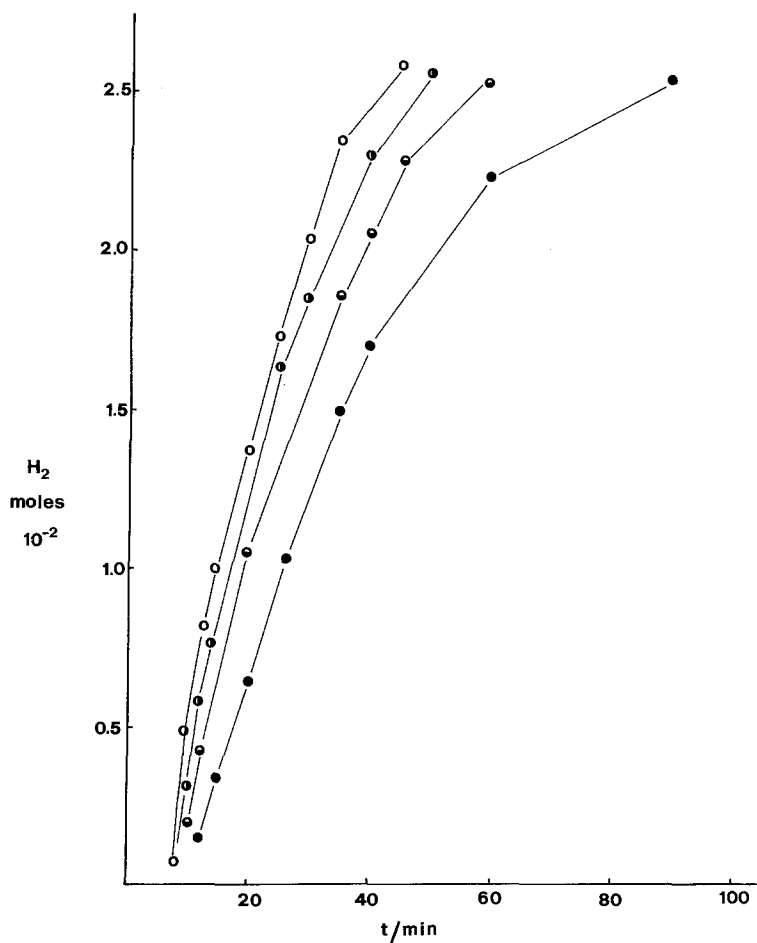


Fig. 3. Hydrogenation of acenaphthylene catalyzed by nickel electrodeposited over copper. Influence of the temperature on the kinetics of the reaction. DMF 26.5 g; acenaphthylene 4.0 g; tetrabutylammonium bromide 1 g. Initial hydrogen pressure 120 Atm. Temperatures: ● 25° C; ○ 40° C; ◐ 60° C; ○ 80° C.

The empirical relation (2), describing the rate of reaction

$$-dP_{H_2}/dt = 3.54 \times 10^{-3} P_{H_2} \quad (2)$$

proved to be valid at a temperature of 80° C and in a pressure range from 130–10 atm.

3.2. Structure of the cathodic surfaces

Some investigations were made on the surface structure of the copper cathodes after the deposition of nickel. Medium magnification ($\times 5,000$) electron micrographs of the cathode after the electrolysis show a smooth surface, without any significant morphologic modification compared with the surface before electrolysis. At higher degrees of magnification ($\times 30,000$) it was possible to show that the original copper surface was modified by the presence of crystallites whose shape is shown in Fig. 5.

Qualitative X-ray energy dispersive microanalyses indicated that both copper and nickel are present on the surface. X-ray diffractions gave angles intermediate between those of pure copper and nickel, in a range already reported by the ASTM values [12] as characteristic of the copper-nickel alloys (see Table 2).

4. Discussion

The results reported above indicate that copper, aluminium, and tin surfaces acquire, after deposition of not more than $1.20 \times 10^{-4} \text{ g cm}^{-2}$ of nickel, a good catalytic activity for the hydrogenation of olefins, a less enhanced reactivity for nitriles, even lower for carbonyl compounds, and no activity at all for the aromatic rings. In the many examples of hydrogenations catalyzed by the different types of Raney nickel, it is possible to find a rather similar reactivity; good or accept-

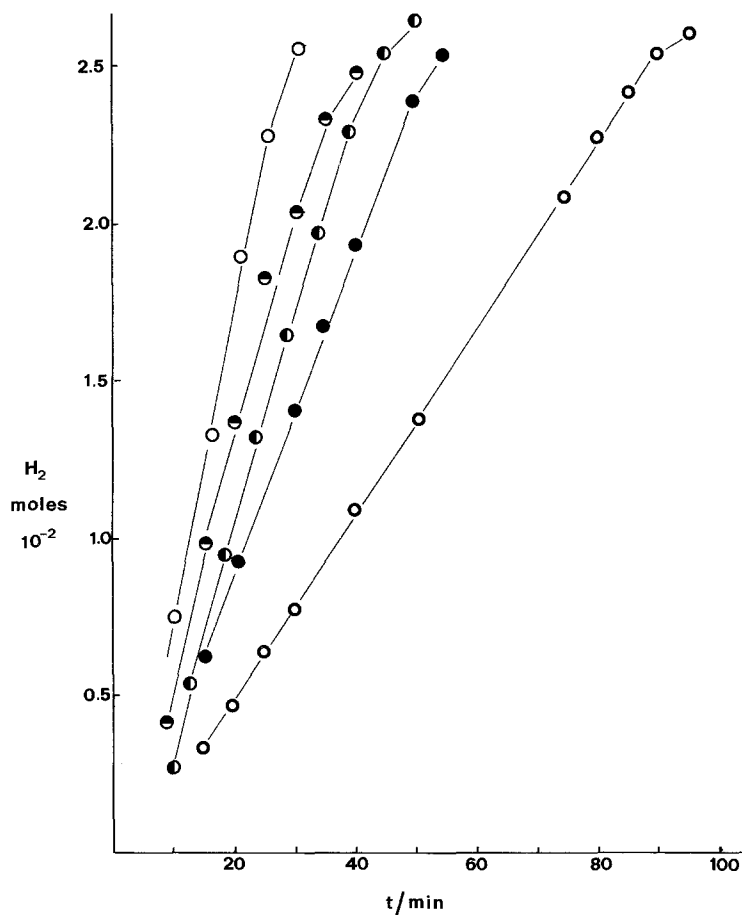


Fig. 4. Hydrogenation of acenaphthylene catalyzed by nickel electrodeposited over copper. Influence of the hydrogen pressure on the kinetics of the reaction. DMF 26.5 g; acenaphthylene 4.0 g; tetrabutylammonium bromide 1 g. Temperature 80° C. Initial pressure (Atm): ○ 23.5; ● 43.8; ◐ 69.7; ◑ 92.1; ○ 115.6.

able kinetics for olefins and nitriles, lower reactivity towards the carbonyl compounds, and, in comparable conditions, quite slow kinetics for the

aromatic compounds [13]. A similar reaction pathway for our hydrogenation system could therefore be expected, remembering that, when the Raney

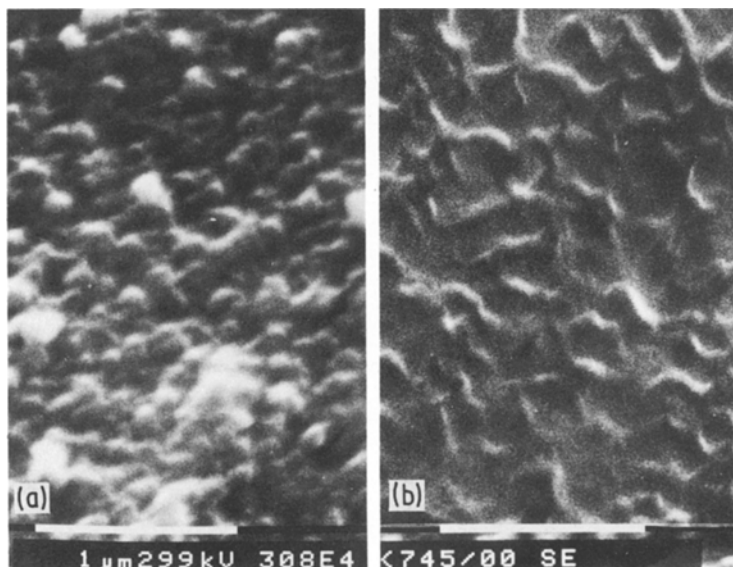


Fig. 5. Electron micrographs of the copper surface. (a) After the deposition of nickel; (b) before the electrolysis.

Table 2. Electrodeposition of nickel on copper cathodes from DMF solutions. Comparison of the X-ray diffraction patterns with the literature data (see [12])

	Copper			Nickel			Cu-Ni 79% Cu			Cu-Ni*		
2θ	43.34	50.46	74.20	44.54	51.90	76.46	43.51	50.82	74.82	43.55	50.70	74.33
d	2.088	1.808	1.278	2.034	1.762	1.246	2.08	1.797	1.269	2.078	1.801	1.276
i/i_1 †100		46	20	100	42	21	100	80	80	4	4	100

* Data obtained with a cathode sample after the circulation of 19 C in the electrolysis conditions described in the experimental section.

† Relative intensity of diffraction peaks.

catalysts are prepared from the Ni-Al alloys, the resulting nickel powder contains about 10–15% of unreacted aluminium, and that the main differences amongst the eight types of those catalysts are strictly connected to the procedure followed in the alkaline treatment of the alloy and the subsequent washings.

The results obtained with our catalysts appear rather encouraging, as the high reactivity observed for the olefins was due to a smooth surface, as shown by the electron micrograph, and not to the spongy, highly dispersed conventional catalysts.

The way in which the Cu-Ni alloy is formed during the electrolysis is currently under investigation and the results will be subject of a separate communication.

A previous study on similar systems, in which the hydrogenation of carbonylic substrates took place during the transfer of copper from the anode to a cathode, led to completely different conclusions about the nature of the catalytic species and the mechanism of the reaction [3]. In that system, the catalysis was due to copper compounds, acting homogeneously in the electrolytic solution. These species are very sensitive towards the presence of water, and any reutilization after the first run was forbidden, due to the fast deactivation in the presence of moisture and oxygen.

Looking at the synthetic applications of the process presented here, the following positive aspects should be stressed:

(a) specificity towards the olefin groups more enhanced than with the Raney catalysts;

(b) easy and precise dosage of the quantity of nickel to be deposited onto the cathodic support;

(c) good durability after exposure to moisture, air, and possible use of the same sample in several subsequent hydrogenation runs.

The problems related to the electrolytic production of a catalyst inside a chemical reactor lie essentially in the need for a polar solvent and a supporting electrolyte added to the chemical system. The presence of these components might in some cases interfere with the desired hydrogenation process. These problems are easily overcome when the electrolytic method is applied for the *ex situ* production of the catalyst. Quite obviously, in any case, in the hypothesis of large scale applications of these catalysts, copper cathodes of suitable properties (spongy, expanded, powdered) should be adopted.

Acknowledgements

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