- Communication -

Selective Catalytic Hydrogenation of 2-Cyclohexen-1-one to Cyclohexanone on Hydrogen Active Powder Electrodes

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1 Introduction

One of the most important aspects in electrochemical as well as in organic synthesis is the achievement of "selectivity". The aim of our present research is to obtain selectively a monomeric hydrogenation product of a carbon-carbon double bond from an unsaturated carbonyl compound by electrocatalytic hydrogenation. In the present case, 2-cyclohexen-1-one was the substrate to be hydrogenated to cyclohexanone. Raney-nickel (R-Ni), palladium carbon (Pd-C) and platinum carbon (Pt-C) were employed as the catalytic powder electrodes. Although such powders have been widely used as catalysts for hydrogenation, their electronic properties allow their use as cathodic materials (1).

Electrocatalytic hydrogenation of organic compounds with hydrogen-active powder electrodes has several intrinsic advantages over direct, uncatalyzed electroreductions: (i) The electrochemical route is the discharge of proton to form hydrogen which can be accomplished at mild potentials due to the low overvoltages of these catalytic metal electrodes; (ii) The large surface area and the high hydrogen adsorbability of the catalysts enhance the hydrogenation rate; (iii) The rate of hydrogenation can be controlled by the applied cathodic potential or the current density; and (iv) The formation of dimers is avoided in contrast with the use of EC or ECEC mechanisms of the direct reduction (2). Also, the electrochemical catalysis produces hydrogen in situ and avoids the need to introduce hydrogen from an external source. Thus, this in-situ generation of hydrogen makes the reaction easier to handle and the electrodes can be varied to enhance the selectivity.

2 Experimental

All chemicals, Ni-Al alloy (Ni:Al=1:1), Pd-C (5 % content) and Pt-C (5 % content) were purchased commercially. The R-Ni was prepared by the following method: The alloy (1.0 g) was first treated with 10 cm³ of 20 % NaOH aqueous solution at 100 °C for one hour. After removal of the solution by decantation, the R-Ni catalyst was washed with water. The powder was then treated with pentenes to remove the hydrogen adsorbed on the catalyst surface. The R-Ni (ca. 0.5 g), Pd-C (ca. 0.3 g), or Pt-C (ca. 0.3 g) catalyst was dispersed onto a Ni plate (13 cm²) which served as the electrical contact. The electrolysis was carried out in a conventional divided cell with the catalyst cathode and a Pt gauze anode under a constant current density (7.7 mA/cm²). The electrolyte consisted of 2-cyclohexen-1-one (3.1 mmol) and a proton source (25 mmol chloroacetic acid, pivalic acid, or phenol) dissolved in a THF:H₂O (9:1 in volume) solution (40 cm³) with 1.0 mol/dm³ NaClO₄. The products were determined by gas chromatography with tetralin as an internal standard.

3 Results and Discussion

The electrocatalytic hydrogenation of 2-cyclohexen-1-one yielded cyclohexanone as the major product with 2-cyclohexen-1-ol and cyclohexanol as minor products. No dimeric by-products were detected. Table 1 summarizes the results of the present electrocatalytic hydrogenation after the passage of 2x96,485 C/mol of electrical charge (theoretical charge required to produce

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cyclohexanone). The selectivity for the desired formation of cyclohexanone was very high on Pd-C (96-100 %) and R-Ni (91-100 %), whereas the selectivity on Pt-C was found in the 63-85 % range. Although four different proton sources with varying pKa values were examined, there appeared to be no correlation of the selectivity with the pKa value on Pt-C. On R-Ni and Pd-C, weak acids gave high selectivity. In general, Pd-C has higher selectivity toward olefinic compounds in ordinary catalytic hydrogenation at high pressures than Pt-C (3). The electrocatalytic results reported herein show a similar selectivity. Also, it can be concluded from the results that the end product of the reduction, cyclohexanol, is formed primarily via cyclohexanone as an intermediate.

Prior to electrolysis, attempts were made to pretreat the R-Ni to remove the adsorbed hydrogen. Similar pretreatment was not performed on Pd-C or Pt-C since these electrodes showed only limited amounts of hydrogenation (less than 5 % conversion) prior to electrolysis.

The current efficiency was somewhat dependent on the type of proton source and catalyst. The value of the efficiency was nonetheless quite high except on R-Ni, particularly with water as the proton source. The efficiency was also time-dependent with hydrogen bubble formation evident at the end of electrolysis. The higher than 100 % current efficiencies observed on Pt-C may be, in part, due to the presence of adsorbed hydrogen prior to electrolysis.

We have further carried out additional experiments on Pt-C with phenol as the proton source. When the electrolysis was exhaustive so that 100 % conversion resulted, the selectivity was 100 % although the current efficiency was 34 %.

Similar results were obtained with mesityl oxide and cinnamaldehyde as the substrate. Details of further studies of this electrocatalytic hydrogenation will be reported later.

Table 1 Electrocatalytic hydrogenation of 2-cyclohexen-1-one^{a)}

Cathode	Proton source	Conv ^{b)} /%	Selec ^{c)} /%	CE ^{d)} /%
R-Ni	ClCH ₂ COOH	51	91	55
	(CH ₃) ₃ CCOOH	66	91	71
	C ₆ H ₅ OH	53	100	53
	none(H ₂ O) ^{e)}	8	100	8
Pd-C	ClCH ₂ COOH	77	98	78
	(CH ₃) ₃ CCOOH	87	96	88
	C ₆ H ₅ OH	64	100	64
	none(H ₂ O) ^{e)}	88	100	88
Pt-C	ClCH ₂ COOH	93	82	107
	(CH ₃) ₃ CCOOH	93	85	107
	C ₆ H ₅ OH	81	63	111
	none(H ₂ O) ^{e)}	57	85	65

^{a)} Results after the passage of 2x96,485 C/mol of charge. Error limit for the conversion, selectivity and current efficiency is 2 %. ^{b)} Conversion. ^{c)} Selectivity for cyclohexanone formation. ^{d)} Total current efficiency for the products.

^{e)} Water is considered as the proton source.

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