Electrocatalytic Hydrogenation of Acetylenes on Palladium Incorporating Poly [*N*-(5-Hydroxypentyl) Pyrrole] Film-Coated Electrode

Nobuhiro Takano,* Yutaka Kawakami, and Noboru Takeno
Department of Applied Chemistry, Muroran Institute of Technology, Mizumoto-cho, Muroran 050

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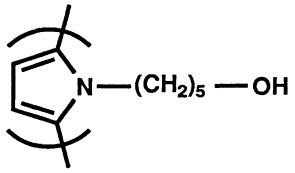
The catalytic polymer film electrode which was coated with poly [*N*-(5-hydroxypentyl) pyrrole] film on carbon materials and incorporated palladium metal microparticles in films was prepared. By use of the electrode the electrocatalytic hydrogenation of acetylenes in organic solvent-HCl buffer solution led to the efficient formation of ethanes in high current efficiencies.

Recently, catalytic metal particles incorporated in the polymer-modified electrodes have been recognized to have potential applications in electrocatalytic reactions.[1] On the other hand, the electrically-conducting polymers have been paid much attention for a development of new electro-active materials.[2] Moutet and his co-workers[3] have reported the preparation of catalytic electrodes modified by poly(viologen-linked pyrrole) film containing precious metal microparticles and the catalytic hydrogenation of organic compounds by those. We have also reported a new type of catalytic polymer film electrode in the previous paper.[4] This electrode is coated with a simple polypyrrole film (P5HPy) which is substituted by 5-hydroxypentyl group at *N*-position of pyrrole ring and incorporated palladium catalysts. This electrode possessing linear alkyl chains and hydroxyl groups in the polymer has exhibited a high catalytic ability and a strong stability with respect to hydrogen evolution. These results suggest an efficient hydrogenation for unsaturated organic compounds. In this paper we report some results of synthetic study for the hydrogenation of acetylenes using the catalytic polymer film electrode which was coated with the P5HPy on a grassy carbon or a carbon fiber and incorporated palladium metal microparticles in the films.

The catalytic polymer film electrodes, P5HPy(Pd)GC and CFi were prepared according to previously reported techniques.[4] The grassy carbon plate (GC), (Tokai Carbon Co., Ltd., GC-30, Surface area: 6.55 cm^2) and the bundle of carbon fiber (CFi),



P5HPy

(Asahi Kasei Carbon Fiber Co., Ltd., Hi-Carbolon-3KS, Surface area: 37 cm^2) electrode coated with the P5HPy by the controlled-potential electrolysis (CP) method at 1.10 V vs. SCE in acetonitlile of 10 mM (mmol dm^{-3}) monomer containing 0.1 M Bu_4NBF_4. The passed electricity for the electrochemical polymeization on the grassy carbon and the carbon fiber were 0.14 C cm^{-2} and 0.05 C cm^{-2}, respectively. After the P5HPy film coated electrode was dipped into a 50 mM Na_2PdCl_4 aqueous solution for 30 minute and washed with water, palladium metals were deposited by an electrochemical reduction technique at -0.3 V in a 0.1 M KCl solution. The current-potential curve of electrodes was measured by a linear sweep potential method. The controlled-potential electrolysis and the controlled-current electrolysis (CC) were performed in a divided cell equipped with a platinum plate anode (2×3 cm), the catalytic polymer film cathode, an SCE reference electrode, and a glass filter diaphragm. After deaeration by argon the electrochemical hydrogenation of acetylenes was carried out in a 50% organic solvent-0.1 M HCl buffer solution (10 ml) at room temperature under argon atmosphere. When the substrate and/or products were of low-boiling points, the electrochemical hydrogenation was carried out in a sealed-cell. After the reaction came to an end, the reaction mixture was extracted with ether. After the extract was washed with water and dried over Na_2SO_4, it was analyzed by GC (GL Sciences, Capillary Column, TC-1, Length = 15 m, Inner

Table 1. Electrocatalytic hydrogenation of acetylenes on catalytic polymer film electrodes in a 50 % ethanol-HCl buffer solution[a]

Entry	Acetylenes	Molecularity (μmol)	Catalytic Polymer Film Electrode[b]	W_{Pd} (μmol)	Electrolysis Method[c]	E / I (V vs.SCE)/(mA)	Time (min)	Yield of Ethanes[d] (%)	Current Efficiency (%)
1	PhC≡CPh	25	P5HPy(Pd)GC	0.5	CP	-0.4	450	93	89
2		25	P5HPy(Pd)CFi	6.6	CP	-0.4	60	97	91
3		25	P5HPy(Pd)CFi	6.6	CC	2.0	100	99	93
4		25	P5HPy(Pd)CFi	2.3	CC	2.0	110	98	95
5		250[e]	P5HPy(Pd)CFi	2.3	CC	4.0	660	100	96
6	$MeO_2CC{\equiv}CCO_2Me$	25	P5HPy(Pd)GC	0.5	CP	-0.4	420	94	87
7		25	P5HPy(Pd)CFi	2.3	CC	2.0	120	98	93
8		250	P5HPy(Pd)CFi	2.3	CC	4.0	440	100	99
9	PhC≡CH	25	P5HPy(Pd)CFi	2.3	CC	2.0	110	96	91
10		250	P5HPy(Pd)CFi	2.3	CC	4.0	420	98	97

[a] Electrolyses were carried out as described in the text. [b] GC : Glassy carbon plate, CFi : Carbon fiber. [c] CP : controlled-potential electrolysis, CC : controlled-current electrolysis. [d] Yields were based on the acetylenes and were determined by gas chromatography. [e] This reaction was run in a 50 % THF-HCl buffer solution.

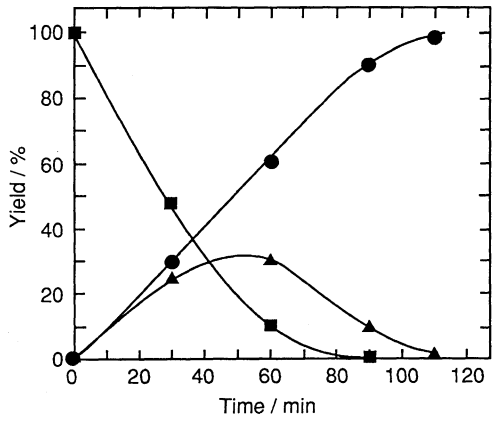


Figure 1. Time course for the electrocatalytic hydrogenation of diphenylacetylene on the catalytic polymer film electrode in a 50 % ethanol-HCl buffer solution (pH = 1).
Electrode: P5HPy(Pd)CFi (surface area = 37 cm^2, W_{pd} = 2.3 mol). Passed current = 2.0 mA ; (■) : diphenylacetylene (25 μmol) ; (▲) : *cis*-stilbene ; (●) : 1,2-diphenylethane.

diameter = 0.53 mm, Df = 1.5 μm).

The electrocatalytic hydrogenation of three acetylenes was carried out in organic solvent-HCl buffer solution (pH = 1) in a divided cell at room temperature. The results are summarized in Table 1. Using the P5HPy(Pd)GC electrode containing 0.5 μmol palladium metal (= W_{pd}), the electrohydrogenation of diphenylacetylene (25 μmol) by CP method at -0.4 V vs. SCE provided 1,2-diphenylethane in good yield and in high current efficiency (Entry 1). Further, the use of the P5HPy(Pd)CFi electrode in which the film was coated on a carbon fiber resulted in not only the shortening of required time for the hydrogenation but also the improvement of the yield and current efficiency (Entry 2). Employing of CC method (I = 2.0 mA) which is a more simple technique, an almost quantitative yield of 1,2-diphenylethane was obtained (Entry 3). The decrease in the amount of palladium incorporated in films almost unaltered the efficiency of reaction (Entry 4).

As shown in Figure 1, the electrohydrogenation of diphenylacetylene provided 1,2-diphenylethane *via* the formation of *cis*-stilbene under the same conditions with Entry 4. In the latter half of the reaction course, the acetylene had been consumed almost completely and the hydrogenation of formed stilbene proceeded. This is because the reactivity of stilbenes is lower than that of acetylenes. The lower reactivity of stilbene resulted in the lowering of current efficiency by wasting passed current for the generation of hydrogen.

When the amount of the substrate increased up to ten times (250 μmol), 1,2-diphenylethane was obtained in quantitative yield and in high current efficiency (Entry 5). In this case, THF as organic solvent was used due to poor solubility of the substrate in ethanol. The ratio of the amount of product, 1,2-diphenylethane, to the incorporated catalyst palladium metal was larger than 100. On the carbon-felt electrode modified by palladium microparticles in redox active polymer film, the large scale electrohydrogenation of diphenylacetylene (3 mmol) has produced 1,2-diphenylethane in 98 % yield and in 98 % current efficiency.[3] Although the experimental scale is small at this stage, the present system may expand to a large scale reaction by increasing the surface area of basic electrodes.

Dimethyl acetylenedicarboxylate possessing elector-attracting group was also transformed to dimethyl succinate *via* the formation of maleic derivative (Entries 6, 7, and 8). In the electrocatalytic hydrogenation of phenylacetylene, styrene was first produced and the formation of ethylbenzene as the final product took place in good yields and in high current efficiency (Entries 9 and 10). These two results were similar to that in the case of diphenylacetylene and the hydrogenation was not greatly affected by substituents on acetylenes.

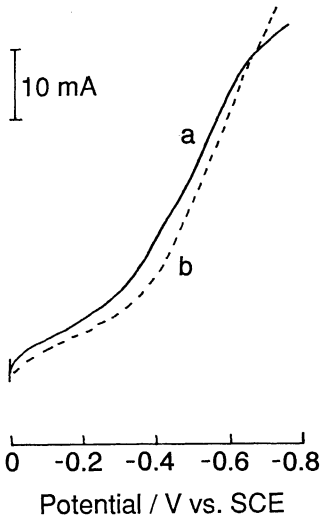


Figure 2. Cathodic current-potential curves on the P5HPy(Pd)CFi electrode before (a) and after (b) the hydrogenation of diphenylacetylene (250 μmol) in a 50 % ethanol-HCl buffer solution (pH = 1).

The cathodic current-potential curves on the P5HPy(Pd)CFi electrode before and after the hydrogenation of diphenylacetylene are shown in Figure 2a and 2b. This behavior showed that the catalytic activity of the P5HPy(Pd)CFi electrode almost unchanged after the catalytic hydrogenation. Further, the repeated hydrogenations with the P5HPy(Pd)CFi electrode for the several times were successful. The catalytic activity and the mechanical stability of the P5HPy(Pd)CFi electrode are probably due to the electrostatic holding of palladium particles in the P5HPy film and the strong adherence of hydroxyl groups with carbon fiber surface.

Further studies on the application of electrocatalytic hydrogenation for other organic compounds using this catalytic polymer film electrode are now in progress.

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References

1 W.-H. Kao and T. Kuwana, *J. Am. Chem. Soc.*, **106**, 473 (1984); D. E. Bartak, B. Kazee, K. Shimazu, and T. Kuwana *And. Chem.*, **58**, 2756 (1986); T. Yamada, T. Osa, and T. Matsue, *Chem. Lett.*, **1987**, 1611.

2 F. Garnier, *Angew. Chem. Int. Ed. Engl.*, **28**, 513 (1989); G. Tourillon and F. Garnier, *J. Phys. Chem.*, **88**, 5281 (1984); K. M. Kost, D. E. Bartak, B. Kazee, and T. Kuwana, *Anal. Chem.*, **60**, 2379 (1988); G. Arai, K. Matsumoto, T. Murofushi, and I. Yasumori, *Bull. Chem. Soc. Jpn.*, **63**, 121 (1990).

3 L. Coche and J.-C. Moutet , *J. Am. Chem. Soc.*, **109**, 6887 (1987); L. Coche, B. Ehui, D. Limosin, and J.-C. Moutet , *J. Org. Chem.*, **55**, 5905 (1990).

4 N. Takano, M. Nakabayashi, and N. Takeno, *Chem. Lett.*, **1995**, 219.