Electrochemical Catalytic Dechlorination of Chlorobenzene on the Polypyrrole (Pd) Coated Electrode

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Received May 27, 2004 ; Accepted August 20, 2004

The catalytic polymer film electrode which was coated with a poly [*N*-(6-aminohexyl) pyrrole] film on carbon-fiber and incorporated palladium microparticles in the film was prepared. By use of the electrode the electrochemical catalytic dechlorination of chlorobenzene in 50% alcoholic solutions led to the formation of benzene in good yields.

Key Words : Electrochemical Dechlorination, Chlorobenzene, Catalytic Polymer Film Electrode, *N*-(6-Aminoethyl) Pyrrole

1 Introduction

Recently chemicals are great cause of environmentally problems. The treatment of organic halides is especially important and a matter of great urgency. The various treatment methods have been investigated. It is worth noting that an electrochemically reducing method is superior in view of the reactivity of dehalogenation and the reusing of the product as source in syntheses.

On the other hand we have demonstrated the preparation of some catalytic polymer film electrodes and the application to the hydrogenation of organic compounds using its electrodes in previous papers.¹⁻⁴⁾ The electrochemical debromination of bromobenzene have been achieved in high yield on the catalytic polymer film electrode in a 50% ethanol-1/15 M (mol dm⁻³) phosphate buffer solution (pH = 7.0).²⁾

In this work, a poly [*N*-(6-aminoethyl) pyrrole] film (Pd) coated electrode, PAPy(Pd) electrode was developed for a mild treatment of organic chloride. This electrode exhibited catalytic activity for the dechlorination of chlorobenzene (Scheme 1).

Scheme 1 The polypyrrole (Pd) coated electrode for electrochemical catalytic dechlorination.

2 Experimental

The *N*-(6-aminoethyl) pyrrole monomer¹⁾ and the polypyrrole coated on a bundle of a carbon-fiber (S = 37 cm²) electrode²⁾ were prepared according to previous reports.

The electrolysis of chlorobenzene was carried out by controlled-current electrolysis method in a cylindrical two-compartment cell equipped with a platinum plate anode (2 × 3 cm), a catalytic polypyrrole coated cathode (37 cm²), and a glass filter diaphragm at room temperature. The electrolysis products were analyzed by a high-performance liquid chromatography (ODS, ϕ = 2.1 mm, L = 250 mm) after extracted with ether.

3 Results and Discussion

The PAPy(Pd) electrode was prepared by an electropolymerization ($Q = 0.05 \text{ C cm}^{-2}$) in acetonitrile and elec-

Fig. 1 Cathodic current-potential curves for hydrogen evolution on the polypyrrole (Pd) coated electrode in a 50% ethanol-hydrochloric acid buffer solution (pH = 1) (A) and in a 50% ethanol solution containing 0.1 M potassium acetate (B).

Fig. 2 Plots of cathodic current for hydrogen evolution vs. electrolysis time of the polypyrrole (Pd) coated electrode at -0.3 V vs. SCE in a 50% ethanol-hydrochloric acid buffer solution (pH = 1).

trochemical deposition of palladium micro particles in potassium chloride solution. The deposition amount of palladium in film was $1.5 \mu\text{mol}$.

An increase of in the cathodic current, based on hydrogen evolution, was clearly observed, when the resulting PAPy(Pd) electrode was subjected to potentiostatic sweeping in an ethanol-hydrochloric acid buffer solution (pH = 1) (Fig. 1, A). In a 50% ethanol solution containing 0.1 M potassium acetate, any cathodic current on the PAPy(Pd) electrode was also showed between 0 to -1.3 V (Fig. 1, B).

The PAPy(Pd) electrode showed remarkable stability for electrochemical hydrogenation experiments without peeling of the coated film from the carbon fiber surface. As shown in Fig. 2, although the current for hydrogen evolution in the controlled-potential electrolysis at -0.3 V decreased to *ca.* 13 mA after 50 h, this electrode preserved sufficient catalytic activity in hydrogenation experiments. In the cyclic voltammetry of this PAPy(Pd) electrode in an anodic potential region, the shape of the reversible redox couple which based on the doping-dedoping of anion was also similar to that before the above-mentioned hydrogen evolution experiment. The physical stability of this electrode was probably due to the strong interaction of substituted amino groups in the

polypyrrole film with the carbon-fiber surface.

The electrochemical catalytic dechlorination of chlorobenzene was performed by controlled-current electrolysis as a simpler electrolysis technique. Using the polypyrrole coated electrode without incorporating of palladium metal, the electroreduction of chlorobenzene did not take place, indicating that they were not hydrogenated directly on the polypyrrole coated electrode in a 50% ethanol solution containing potassium acetate.

As shown in Table 1, when the PAPy(Pd) electrode containing palladium metal was applied to the electrochemical catalytic dechlorination of $50 \mu\text{mol}$ (5 mM) chlorobenzene in various electrolytic solutions containing supporting electrolyte provided benzene in good yield. The current efficiency was in 30 to 46% region in electrolysis for 190 min. In the electrolysis in an ethanol solution containing potassium acetate, chlorobenzene was almost completely dechlorinated and benzene was produced (Entry 1). The electrolysis using the electrode, which was prepared on the condition of lower current density in the deposition of palladium was resulted in decline of yield (Entry 2). Using potassium chloride, sodium sulfate, and disodium hydrogen phosphate as a supporting electrolyte, chlorobenzene in an ethanol solution was dechlorinated to the benzene in good yields (Entries 3-5). In a 50% ethanol-acetic acid buffer (pH = 5.5) solution the yield of benzene lowered (Entry 6). The basic solution in the dechlorination is preferable to acidic it. Using 2-propanol instead ethanol as a cosolvent, the yield of benzene lowered in 73% (Entry 8). The solvent effect in the electrolysis is obscure. It is necessary to investigate the effect to the electrolysis of various supporting electrolytes.

4 Conclusion

Under mild conditions electrochemical catalytic dechlorination of chlorobenzene was efficiently accomplished by employing the poly [*N*-(6-aminoethyl) pyrrole] film incorporated palladium electrode.

Acknowledgement

We thank Dr. T. Kobayashi and Dr. I. Shimono (Hokkaido Industrial Technology Center) for valuable suggestions about the preparation and the estimation of catalytic

Table 1 Electrochemical catalytic dechlorination of chlorobenzene on the polypyrrole (Pd) coated electrode.^{a)}

Entry No.	0.1 M Supporting electrolyte	50% Cosolvent	Current density for Pd deposition	Yield of benzene	Current efficiency
			$\mu\text{A cm}^{-2}$	%	%
1	Potassium acetate	Ethanol	270	100	46
2	Potassium acetate	Ethanol	27	85	39
3	Potassium chloride	Ethanol	270	97	44
4	Sodium sulfate	Ethanol	270	99	45
5	Disodium hydrogen phosphate	Ethanol	270	82	37
6	Potassium acetate-Acetic acid ^{b)}	Ethanol	270	66	30
7	Potassium acetate	Methanol	270	89	41
8	Potassium acetate	2-Propanol	270	73	33

^{a)}Chlorobenzene = $50 \mu\text{mol}$, amount of electricity for polymerization = 0.05 C cm^{-2} , deposition amount of Pd = $1.5 \mu\text{mol}$, passed current for electrolysis = $50 \mu\text{A cm}^{-2}$, reaction time = 190 min. ^{b)}pH = 5.5.

polymer film electrode.

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