Successive hydrogenation of styrene at a palladium sheet electrode combined with electrochemical supply of hydrogen

Hiroshi Inoue, Toshiyuki Abe and Chiaki Iwakura*

Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 593, Japan

Electrochemically-formed hydrogen atoms diffused into a Pd sheet electrode are effectively used for successive hydrogenation of styrene on the reverse side.

Palladium is an effective catalyst for hydrogenation of various unsaturated organic compounds.[1] The electrocatalytic hydrogenation of several organic molecules has been investigated at a Pd-black electrode with high surface area,[2,3] and shown that the current efficiency for the hydrogenation is low. Recently, it has been reported that Pd, Ni and Rh microparticles dispersed in poly(pyrrole–alkylammonium) films were electrochemically active for the hydrogenation of some functional group in organic compounds.[4,5] In such chemical and electrochemical hydrogenation systems using Pd, chemcially adsorbed (activated) hydrogen is formed, leading to moderate reaction conditions because the kinetic barriers for dissociation and mass transfer of poorly soluble hydrogen molecules are no longer problems.

Since it is known that Pd reversibly absorbs and desorbs hydrogen, it is possible that hydrogen-absorbed Pd could operate not only as a catalyst but also as a source of hydrogen for hydrogenation. However, the limited amount of absorbed hydrogen will be used up by the hydrogenation process, resulting in the termination of the reaction. In the present study, a successive hydrogenation system without termination is proposed. In this system, both sides of a Pd sheet are utilized, each with a different function. At one side activated hydrogen is formed and absorbed in the Pd sheet, while at the other side, hydrogenation of styrene proceeds.

A glass cell separated into two compartments by a Pd sheet (contact area with electrolytic solution or styrene = 0.28 cm^2, thickness = 0.1 mm) was used in this study. KOH solution (6 mol dm^{-3}) as an electrolyte and neat styrene as a substrate for hydrogenation were put in each compartment. A Luggin capillary connected to a Hg–HgO–KOH (6 mol dm^{-3}) reference electrode and a Pt counter electrode were placed in the compartment containing the KOH solution. Qualitative and quantitative analyses of the hydrogenation products were carried out by GC.

In the galvanostatic reduction of water, one-electron reduction of water occurs at the Pd sheet in KOH solution, resulting in the adsorption of a hydrogen atom on the Pd sheet (H_{ad}), eqn. (1).

$$H_2O + e^- \rightarrow H_{ad} + OH^- \qquad (1)$$

Then the adsorbed hydrogen diffuses through the Pd sheet. Permeated hydrogen atoms can react with styrene molecules on the reverse side of the Pd sheet in the compartment containing styrene. In this study, ethylbenzene was the sole product for the hydrogenation of styrene.

Time courses of ethylbenzene production in the galvanostatic electrolyses at varous currents are shown in Fig. 1. The amount of ethylbenzene produced increased linearly with electrolysis time after an induction period which is dependent on the magnitude of applied current. The rate of ethylbenzene production increased with increasing applied current, suggesting strongly that the successive hydrogenation system of styrene illustrated in Scheme 1 was successfully demonstrated and kinetics of the hydrogenation was controlled by the magnitude of the applied current. Ethylbenzene was not produced by the introduction of hydrogen gas into styrene in place of the electrochemical supply of hydrogen, indicating that activated hydrogen atoms permeating through the Pd sheet participate in

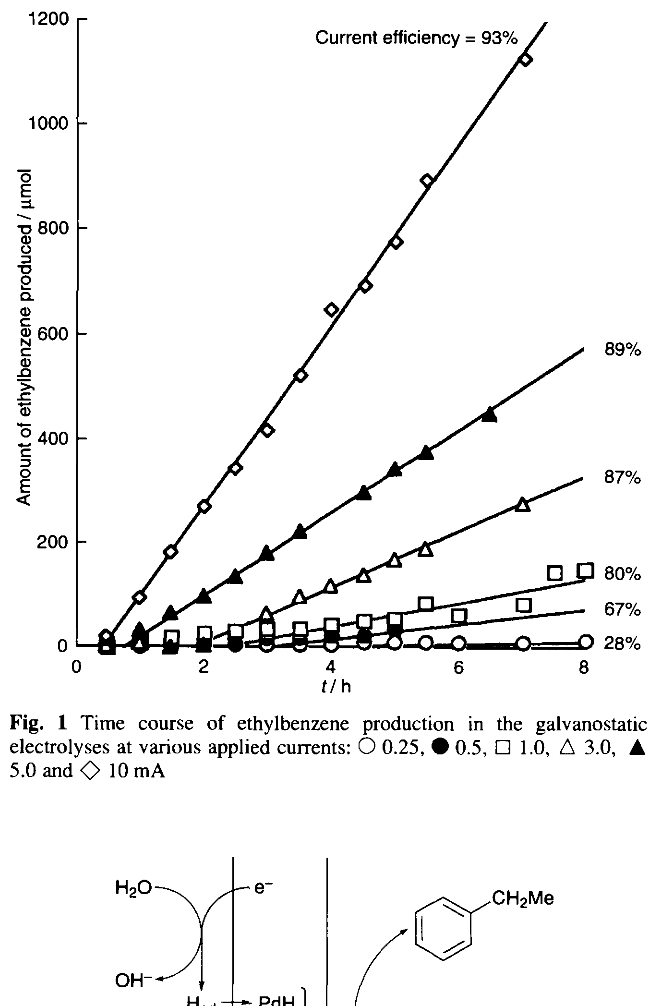
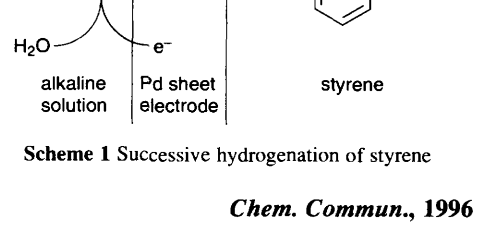


Fig. 1 Time course of ethylbenzene production in the galvanostatic electrolyses at various applied currents: ○ 0.25, ● 0.5, □ 1.0, △ 3.0, ▲ 5.0 and ◇ 10 mA



Scheme 1 Successive hydrogenation of styrene

the hydrogenation of styrene. The decrease of induction period with an increase of applied current seems to be ascribable to the increase of permeation rate of hydrogen through the Pd sheet. The current efficiency for the production of ethylbenzene was determined from the slope of the straight line after the induction period shown in Fig. 1. As a result, it was found that the electrochemical supply of hydrogen for the hydrogenation of styrene works with high efficiency, $>93\%$ in the galvanostatic electrolysis at 10 mA.

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