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Using a hydrogen-permeable palladium membrane electrode to produce hydrogen from water and hydrogenate toluene

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ABSTRACT

Hydrogen production and toluene hydrogenation were performed with a hydrogen-permeable Pd–Ag membrane as a cathode by using permeated pure hydrogen produced from the electrolysis of aqueous potassium hydroxide. For hydrogen production, the hydrogen flow rate on the permeation side increased with temperature because of the increased hydrogen permeability of the palladium membrane. The increase in pressure applied to the electrolysis side from 0.1 MPa to 0.8 MPa enhanced hydrogen production and hydrogen permeation through the membrane by reducing the effects of bubble formation, and achieved a high hydrogen permeation yield of 93% at 373 K regardless of the amount of hydrogen produced. Hydrogenation of toluene with 5 wt% Pt/Al_2O_3 and with 0.8 MPa of pressure applied to the electrolysis side yielded methylcyclohexane as a product, and the conversion increased to 95% at 393 K with increasing contact time. This electrolysis system is effective for producing pure hydrogen and for hydrogenating aromatics to synthesize chemical hydrides.

Introduction

Hydrogen production and storage technology is important for developing a hydrogen energy society [1]. Chemical hydrides such as methylcyclohexane and cyclohexane constitute a class of promising hydrogen carriers because of their high hydrogen density and ability to transport hydrogen as a liquid at ambient conditions [2]. Moreover, chemical hydrides can be produced by hydrogenating dehydrogenated aromatic compounds, and this process also serves to recycle chemicals.

Hydrogen production and hydrogenation using water as the source of hydrogen and solar power as the source of energy is a promising technology that utilizes renewable resources. When using a solar cell, only a relatively small potential of a few voltages is needed for the electrolysis of water to produce hydrogen, whereas thermochemical water decomposition requires a temperature of several hundred degrees Celsius [3]. The hydrogenation of aromatics following the production of hydrogen from the electrolysis of water can be a useful method for synthesizing chemical hydrides, because this process does not require high-pressure hydrogen gas and enables the construction of a compact system by combining hydrogen production and hydrogenation processes in the same apparatus. A compact system is convenient when using distributed energy to obtain the chemical

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hydride and for storing the chemical hydride in a small volume.

The electrolysis of water and the separation of the resulting hydrogen and oxygen using a membrane has been a widely used process [4]. Alkaline water electrolysis with a diaphragm is operated on a commercial level worldwide. In this process, the diaphragm separates product gas, but a little bit of cross-diffusion occurs [4,5], and such mixing of oxygen and hydrogen reduces the efficiency of the hydrogen production and poses safety concerns. The use of a polymer electrode membrane with water electrolysis is a general method for producing hydrogen, but product gas can cross through the membrane in this case, too [6]. The properties of metal particles on the membrane are important for determining the performance of the electrolysis system [7–9].

Hydrogenation using an organic membrane and hydrogen produced by electrolysis of water has been studied. Itoh et al. [10] conducted hydrogenation of benzene with a perfluorosulfonic-acid based membrane and used supported Rh–Pt as a cathode. Yang et al. [11] hydrogechlorinated 4-chlorobiphenyl with a Pd/Ni cathode on a cation exchange membrane. Other researchers were able to reduce nitrates with a palladium alloy supported on a Nafion membrane [12,13]. However, polymer membranes such as the Nafion membrane need to be moistened and are chemically and thermally less stable than inorganic membranes.

The palladium-based metal membrane, being selectively permeable to hydrogen and hence able to collect pure hydrogen, has been used to separate hydrogen from various mixtures [14]; this membrane is also more stable than organic membranes. In addition, having a metal that can conduct an electric current, the palladium membrane can be used as a cathode to produce hydrogen by decomposition of water, with some of the hydrogen produced able to permeate through the membrane. The electrolysis of water with a palladium-based membrane has been used to analyze the kinetics of hydrogen diffusion through the membrane and to obtain pure hydrogen [15–21]. Darling [16] revealed that the ratio of the amount of hydrogen that permeate through the membrane to the amount of hydrogen produced increases with temperature. Pozio et al. [19] conducted the electrolysis of a KOH aq. solution with a hollow tube of Pd–Ag as the cathode and nickel foil as the anode. They evaluated the effect of several parameters to reveal basic properties of a prototype alkaline electrolyzer on the laboratory scale. Furthermore, the kinetics of hydrogen permeation through a Pd–Ag membrane electrode following electrolysis of water was analyzed [20,21]. The structure of the Pd–Ag metal was found to change during electrolysis [20] with the formation of a surface oxide preventing hydrogen permeation [21]. The palladium-based metal membrane is considered as a unique electrode, whereas the deactivation of electrode side during long electrolysis is one of the problems of this membrane [21].

During electrolysis of water, bubbles form at both the cathode and anode, and such bubble formation is a critical factor in the efficiency of hydrogen production [22]. The coverage of bubbles on the electrode surface prevents the reaction on the electrode from proceeding and disturbs the current, thus increasing the electrical resistance and suppressing hydrogen formation. Pressurization of the electrolysis side is expected to reduce the electrical resistance related to bubble formation because high pressure makes the bubbles smaller.

The electrolysis of water on a Pd-based metal membrane hydrogenates various chemical compounds. Yoshida et al. [23] hydrogenated 4-methylstylene to 4-ethyltoluene with a metal-supporting Pd sheet membrane as a cathode and found that Au and Pt were effective when deposited on the membrane. The hydrogenation of carbon–carbon double bonds of benzalacetone and benzalacetophenone also proceeds on Pd and palladized sheets, with the latter sheet being more effective [24]. The regeneration of anti-oxidants in lubrication oil can be achieved by hydrogenation on a Pd–Ag membrane electrode [25]. It was found that the hydrogenation can proceed without any support metal on the membrane, but does so very slowly, as a 90% conversion of the reactant was found to take about 4 days. It is necessary to improve the reaction rate of hydrogenation with a Pd-based metal membrane system.

In this study, the electrolysis of water on a Pd–Ag membrane electrode for hydrogen production was examined, and positive effects of pressure on hydrogen production and permeation were revealed. This electrolysis system was then applied to the hydrogenation of toluene in the presence of a catalyst on the permeation side of the membrane and the effect of contact time on the hydrogenation was evaluated. We were able to synthesize a chemical hydride using a hydrogen-permeable Pd–Ag membrane electrode simply by adding a solid catalyst and using the hydrogen derived from the water.

Materials and methods

A KOH aq. solution was prepared by diluting 8 mol/L potassium hydroxide purchased from Wako Pure Chemical Industries Ltd. with distilled water obtained from a water distillation apparatus (WG-222, Yamato Co.). Toluene (>99.5%), benzyl alcohol (>99.0%) and 5 wt% Pt/Al_2O_3 were also purchased from Wako Pure Chemical Industries Ltd.

Fig. 1(a) shows the experimental apparatus for the hydrogen production experiment. The cell was separated into an electrolysis side containing the anode and a permeation side by a membrane. The cathode of the cell was a 75 wt% Pd–25 wt% Ag membrane (diameter: 18.0 mm; thickness: 0.1 mm) in the membrane unit and the anode was a platinum 99.98% wire (outside diameter (o.d.) 0.4 mm). The platinum wire and lead wire were covered with PEEK tube, except at their ends. The cell was constructed with high-pressure fittings (Swagelok), and PTFE tubes (inside diameter (i.d.): 7 mm) were inserted and glued into most of the interior of the cell on the electrolysis side with a silicone rubber compound (KE-3495, Shin-Etsu Chemical Co., Ltd.). A thermocouple was inserted close to the membrane and heating tape was wrapped around the membrane unit.

The KOH aq. electrolyte was supplied from an HPLC pump (PU-2086, JASCO Cooperation) through PEEK tubes (o.d. 1/16 in.) to a location near the membrane. The effluent was discharged through a back-pressure regulator (Swagelok) controlling the pressure of the electrolysis side. On the permeation side, argon was supplied via a PEEK tube (o.d. 1/16