Electrochemistry Communications 64 (2016) 5–8

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Short communication

Direct electrochemical hydrogenation of toluene at Pt electrodes in a microemulsion electrolyte solution

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ARTICLE INFO

Article history:
Received 8 December 2015
Received in revised form 24 December 2015
Accepted 7 January 2016
Available online 13 January 2016

Keywords:
Organic hydride
Hydrogenation
Microemulsion
Pt electrode
Surface-sensitive reaction
Hydrogenolysis

ABSTRACT

In the present study, we demonstrated a new concept for the direct electrochemical hydrogenation of toluene using an acidic microemulsion electrolyte with active Pt electrodes to pave the way for efficient methylcyclohexane mass production. We have achieved a Faradaic efficiency of 80% for the toluene/methylcyclohexane conversion at a Pt black electrode, under galvanostatic conditions and in a one-compartment cell. The reaction rate and selectivity of the toluene reduction were found to depend strongly on the surface structure of the Pt electrodes.

1. Introduction

To build a hydrogen-based society, it is imperative to establish a large-scale hydrogen supply system. Organic chemical hydrides have been attracting considerable attention as hydrogen carriers because they are liquid at ambient temperature and pressure [1]. Recently, the Chiyoda Corporation has demonstrated a large-scale hydrogen storage and transportation system making use of organic chemical hydride technology involving the catalytic hydrogenation of toluene, forming methylcyclohexane (MCH), and the dehydrogenation of MCH [2].

From the viewpoints of the effective use of electricity from renewable sources such as photovoltaics and wind power, and the total energy conversion efficiency, the direct electrochemical hydrogenation of toluene is preferable to the conventional multistep reaction process consisting of water electrolysis and gas–solid catalytic toluene hydrogenation with the produced hydrogen. So far, there have been several studies of the direct electrochemical hydrogenation of toluene by employing a membrane electrode assembly (MEA) that consisted of a polymer electrolyte, Pt-based nanoparticle electrodes containing an ionomeric binder and carbon paper [3–5]. However, it is questionable whether the MEA approach is best suited to the electrochemical hydrogenation of liquid aromatic organics because MEAs have been developed for fuel cells and water electrolyzers in which the reactants or products are gaseous.

Toluene is an organic that has very low solubility in aqueous solution. The question arises—how can toluene be supplied to a catalyst in a facile manner in an aqueous solution to react with protons? One of the possible strategies is to use a microemulsion, which is a thermodynamically stable system that consists of organic and aqueous phases plus surfactants. In a microemulsion, the electrochemical contact between the electrode and both micro-aqueous and organic phases can be simultaneously achieved by controlling the hydrophilicity and lipophilicity of the electrode surface [6–10]. So far, Rusling and coworkers have investigated the direct electrochemical reduction of arenes such as naphthalene and biphenyl at a non-catalyzed carbon electrode in neutral microemulsion media where the substrates were diluted with an organic solvent such as hexane [11,12]. However, these workers reported that only partial hydrogenation of aromatic rings and low Faraday efficiencies were achieved [11,12].

In the present study, we demonstrated the direct electrochemical hydrogenation of toluene using an acidic microemulsion electrolyte with active Pt electrodes. We achieved a Faradaic efficiency of 80% for

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http://dx.doi.org/10.1016/j.elecom.2016.01.001
1388-2481/

the toluene/methylcyclohexane conversion at a Pt black electrode. Furthermore, we found that the reaction rate and selectivity of the toluene reduction depend strongly on the surface structure of the Pt electrodes.

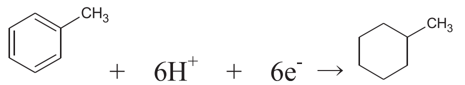
2. Material and methods

2.1. Microemulsion

The microemulsion electrolyte for the direct toluene hydrogenation was prepared from undiluted toluene (6 mL; 99.7% Cica-reagent for spectroscopy, Kanto Chemical Co., Inc., Japan) with sodium 1-dodecanesulfonate (0.75 g; >98% hygroscopic, Tokyo Chemical Industry Co., Ltd., Japan), *t*-butyl alcohol (1 mL; 99.0% Cica-reagent, Kanto Chemical Co., Inc., Japan) and 6 mL of 1 M H_2SO_4 aqueous solution. The 1 M H_2SO_4 solution was prepared by diluting 96% H_2SO_4 (Suprapur, Merck KGaA, Germany) with Milli-Q water. The chemical mixture was sonicated for 40 min and then left at least for a day to achieve equilibrium at room temperature. Fig. 1a shows a photo of the prepared microemulsion electrolyte, which separated into three phases (Winsor III type), i.e., organic phase, surfactant-rich middle phase and aqueous (1 M H_2SO_4) phase. The surfactant-rich middle phase exhibited a blue color due to Rayleigh scattering. The average diameter of the micelles in the middle phase was estimated to be 11 nm via a small-angle X-ray scattering (SAXS, Nano-STAR, Bruker AXS) measurement.

2.2. Cell configuration

Fig. 1b shows a schematic diagram of the three-electrode, single-compartment cell filled with the microemulsion electrolyte for the direct electrochemical hydrogenation of toluene. The working electrode (WE) is placed in the middle phase, at which the toluene hydrogenation occurs via the following half-cell reaction:

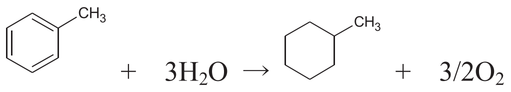


(1)

The produced MCH can be obtained from the organic phase, because the MCH molecules can diffuse through the middle phase. On the other hand, the counter electrode (CE) is placed in the aqueous phase, at which the oxygen evolution reaction takes place as follows:

$$H_2O \rightarrow 1/2O_2 + 2\,H^+ + 2e^- \qquad (2)$$

Thus, protons can be continuously supplied from the aqueous phase to the middle phase. Consequently, the overall cell reaction can be expressed as follows:



(3)

On the basis of the standard reaction Gibbs free energy, the standard cell voltage U^o for the overall reaction (3) can be calculated to be 1.07 V. Thus, the standard electrode potential E^o for the half-cell reaction of (1) is 0.16 V vs. the standard hydrogen electrode (SHE) [3–5]. In the present study, a reversible hydrogen electrode (RHE) in aqueous 1 M H_2SO_4 was employed as the reference electrode. Hereinafter, all of the electrode potentials are reported vs. RHE.

Unlike MEA-type cells, various forms of working electrodes can be examined in the microemulsion electrolysis cell. In the present study, we tested two types of Pt working electrodes, i.e. a mirror-finished Pt disk electrode (3 mm in diameter) purchased from ALS Co., Ltd., and a Pt-black grid electrode prepared by platinization of an 80 mesh/in. Pt grid (0.5 cm × 0.5 cm; Nilaco Corporation, Japan) in a chloroplatinic acid solution at 10 mA for 5 min. Prior to electrochemical measurements, each Pt working electrode was subjected to 10 potential cycles between 0.05 and 1.30 V in pure 1 M H_2SO_4 solution in order to clean the electrode surface. Electrochemically active areas of the Pt electrodes were calculated from measured hydrogen adsorption charge densities on the basis of the theoretical value of 210 $\mu C cm^{-2}$.

3. Results and discussion

3.1. Cyclic voltammetry and chronoamperometry

Fig. 2a shows cyclic voltammograms (CVs) at a mirror-finished Pt disk electrode in 1 M H_2SO_4 solution, 1 M H_2SO_4 solution containing

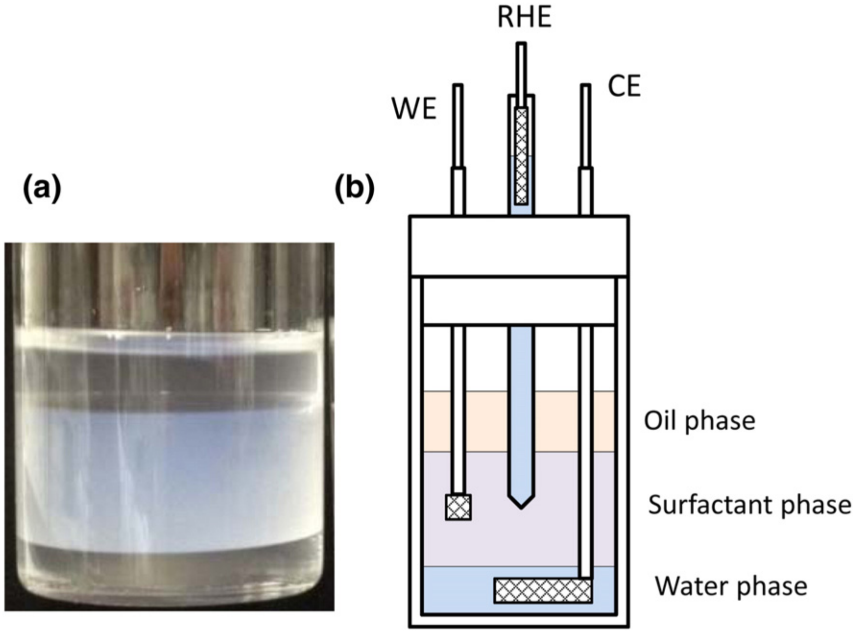


Fig. 1. (a) Photo of the prepared toluene microemulsion. (b) Schematic diagram of the electrochemical cell for the direct electrochemical hydrogenation of toluene.