Selective heating of Pd/AC catalyst in heterogeneous systems for the microwave-assisted continuous hydrogen evolution from organic hydrides: Temperature distribution in the fixed-bed reactor

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Satoshi Horikoshi [a,*], Momoko Kamata [a], Takuya Sumi [a], Nick Serpone [b]

[a] Department of Materials and Life Sciences, Faculty of Science and Technology, Sophia University, 7-1 Kioicho, Chiyodaku, Tokyo 102-8554, Japan
[b] PhotoGreen Laboratory, Dipartimento di Chimica, Universita di Pavia, Via Taramelli 12, Pavia 27100, Italy

ABSTRACT

Continuous hydrogen evolution occurred in near-quantitative yields from the dehydrogenation of an organic hydride (methylcyclohexane; MCH) through a microwave-assisted catalyzed process taking place in a fixed-bed reactor in the presence of Pd catalyst particles supported on activated carbon particulates (Pd/AC). Unlike conventional heating, the microwave heating method displayed a large temperature distribution experimentally observed along the vertical catalyst fixed-bed reactor attributed to the distribution of the microwave electric field, among other factors. A principal feature of the microwave-assisted method was the rapid heating response of the catalyst at low microwave power with considerable energy saving relative to conventional heating with a ceramics heater (2 min versus ca. 35–40 min; 33 W versus 139 W). A more uniform distribution of the microwave-generated heat and introduction of warmer liquid organic hydride (greater than ambient) should lead to significant improvement in process efficiency.

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Introduction

Building a sustainable energy society has been one of mankind's long-standing objectives, with hydrogen expected to provide a significant contribution as a clean energy carrier to any upcoming sustainable development [1]. Hydrogen is a regenerative and an environmentally friendly energy vector, which reacts cleanly with oxygen in a highly exothermic reaction to produce pure water as the unique exhaust by-product, as might occur when used as the fuel in a fuel cell device. The energy density per weight of hydrogen gas is high (142 MJ kg^{-1}) compared with other fuels (e.g., gasoline, 49 MJ kg^{-1}), whereas the energy density per volume is rather low (11.9 MJ m^{-3} versus 34.6 MJ m^{-3} for gasoline) [2]. Relative to liquefied natural gas (39.0 MJ m^{-3}), the volume energy density of hydrogen is about a quarter, whereas when compared on a weight basis (55 MJ kg^{-1}) it is about threefold greater.

Drawbacks of hydrogen as an energy vector are its storage, its transport, and energy costs because its energy density per volume is quite low relative to other commonly used fuels.

As one of its major objectives, Japan proposes to reduce the emission of the greenhouse gas CO_2 by 50% by the year 2050 [3]. Reduction of greenhouse gases is also an objective of several other countries. The introduction of renewable energy sources is indispensable to achieve such goals, and not least the hydrogen-based fuel cell technology can also contribute considerably to these efforts. Although fuel cell technology has made rapid progress, storage and transport of hydrogen gas remains at the developmental stage [4–6]. Our recent efforts have been expended mostly on the organic hydride methodology (no need for low temperatures and high pressures), which can make use of the infrastructure currently available for storage of gasoline (reservoir tanks) and for transport (e.g., Lorries and ships). After storing the hydrogen gas in organic hydrides, the hydrocarbons can be collected by known techniques and the hydrogen subsequently released through catalyzed dehydrogenation processes. The hydrocarbons can also be used as fuels in times of need as might be the case during natural disasters.

Improvements in energy conversion efficiency and decreased costs of fuel cell devices in recent years have led to a reconsideration of the use of hydrogen-based fuel cells [7], which require catalyst heating to drive the dehydrogenation process. Accordingly, to use hydrogen as the energy carrier to advantage, it is desirable to use as little energy as possible to produce it.

A number of studies have been carried out in the last decade on the dehydrogenation of organic hydrides using various catalysts (e.g. Ni, Pd, Pt, Sn) loaded onto various supports (e.g., activated carbon and γ-alumina) at high temperatures using conventional heat sources, and factors limiting efficiency have been described [8–20]. For instance, Tien and coworkers [18] have shown that hydrogen evolution from tetrahydronaphthalene proceeds smoothly under normal liquid-phase conditions in the presence of supported Pd catalysts on activated carbon fibers that possess high specific surface areas, and although the co-produced naphthalene retarded the reaction, it could be easily removed by a simple process.

In previous studies we reported a relatively efficient dehydrogenation reaction of a hydrocarbon by selectively heating the catalyst with microwave radiation as the source of heat [21,22]. In particular, adsorption and desorption of the organic hydride carrier onto and from the catalyst surface, respectively, proceeded efficiently under these conditions. The dispersal of heat was suppressed by packing the catalyst in a suitable reactor [23].

As part of our continued interest to seek and improve on the dehydrogenation of an organic hydride, we herein report a study on the methylcyclohexane ↔ toluene cycle with Pd particles as the catalysts supported on activated carbon particulates (Pd/AC) that were then activated by microwave heating. Energy saving of the power consumption was achieved using a semiconductor microwave generator and a resonator. For comparison, conventional heating was also examined using a ceramics heater to heat the reactor insulated from the surroundings to suppress loss of eat. The

developmental features examined for the microwave method were the yields of hydrogen gas generated (through the yield of toluene; Eq. (1)), the rate of temperature increase, and the distribution of temperature (heat) within the reactor in the presence of the Pd/AC catalyst and with or without the organic hydride presence.

$$(1)$$
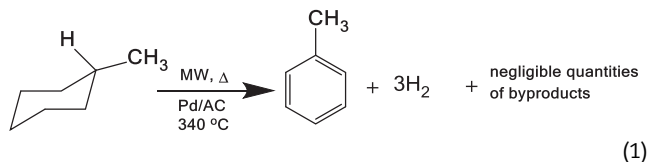
Experimental

The microwave irradiation setup consisted of a single-mode cavity TEM_{103} (transverse electric mode 103) and used to irradiate the reactor contents (Fig. 1a). It also included a short plunger, an electric field monitor, a power monitor, an E/H tuner and an air-cooling isolator. Continuous microwave radiation was generated from a microwave generator using a GaN semiconductor within a very narrow frequency (2.45000 GHz) that caused the microwaves to be suitably amplified by the resonator [24]. The resonance of the microwaves was adjusted with the E-field monitor and the plunger at various wavelength cycles. The wavelength of propagation of the microwaves in the TEM_{103} mode within the waveguide was 14.78 cm (Eq. (2) [25]):

$$\lambda = \frac{\lambda_o}{\sqrt{1 - (\lambda_o/2b)^2}} \qquad (2)$$

where λ is the wavelength in the waveguide; λ_o $_{(2.45GHz)} = 12.24$ cm is the wavelength in vacuum given by c/f, {c being the speed of light, 2.9979×10^{10} cm s^{-1}, and f being the microwave frequency 2.45×10^9 s^{-1}, i.e. 2.45 GHz}; and b is the height of the waveguide (10.92 cm; Fig. 1b). The maximal position of the E-field from the iris was located at 3/4 the wavelength of the standing wave in the waveguide, namely at 11.09 cm [26].

The Pd catalyst on the activated carbon support Pd/AC particulates (particle diameter: ~45 μm; Wako Pure Chem. Ind., Ltd.) was loaded (2.5 g) into a single-pass quartz fixed-bed tubular reactor (diameter: 1.7 mm; length: 55 mm), and then placed in the single-mode microwave apparatus of Fig. 1a at positions of maximal electric field (E-field) density within the waveguide. The upper and bottom parts of the reactor were closed with glass fiber wool to prevent loss of the Pd/AC catalyst powder introduced into the vertical reactor at the upper part of the tube. The quantity of Pd/AC catalyst powder used (2.5 g) filled a height of 5 cm in the reactor. Temperatures were measured with an Inconel thermometer whose tip was fixed at the center (diameter) and half-way up the reactor. A more precise optical fiber thermometer (FL-2000, Anritsu Meter Co. Ltd.) was used to register the distribution of heat (temperature). The maximal temperature that could be recorded with this was limited to 220 °C; temperatures above 220 °C were measured with the Inconel thermocouple. The temperature difference between the Inconel thermocouple