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Hydrogen production through the fuel processing of liquefied natural gas with silicon-based micro-reactors

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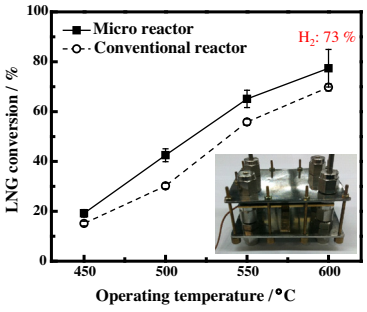
HIGHLIGHTS

- Silicon-based micro-reactors were fabricated for LNG fuel processor.
- A micro-LNG steam reformer achieved a LNG conversion of 77.4% at 600 °C.
- Carbon monoxide composition was 0.7% in product gas.
- Micro-reactors with an optimized catalyst can generate high-quality hydrogen.

GRAPHICAL ABSTRACT



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ABSTRACT

Silicon-based micro-reactors for the fuel processing of liquefied natural gas (LNG) were fabricated using silicon technologies. The micro-LNG steam reformer achieves a LNG conversion of 77.4%, and the hydrogen composition of the product was 73.3% at 600 °C. The product gas was supplied to consecutive micro-reactors to carry out carbon monoxide removal through a high-temperature water–gas shift (HTS) reaction and a low-temperature water–gas shift (LTS) reaction. Under operating conditions we investigated, the micro-HTS and LTS reactors demonstrated the highest carbon monoxide conversion of 61.5% at 450 °C and 77.5% at 300 °C, respectively. The final product gas of the micro-fuel processor was composed of 75.7% hydrogen and 0.7% carbon monoxide.

1. Introduction

Hydrogen has been considered as an attractive energy source owing to its high energy efficiency and environmentally friendly characteristics [1,2]. Therefore, several hydrogen production technologies, such as hydrocarbon steam reforming, coal gasification, enzymatic hydrogen generation and electrolysis (*e.g.*, photocatalytic, photobiological and biocatalysed), have been studied to prepare for the high demand for hydrogen in the near future [3,4]. Among the various hydrogen production methods which have been developed, hydrocarbon steam reforming is considered as a highly feasible method because it shows the highest energy efficiency in generating hydrogen, despite the fact that it produces greenhouse gases during the reforming process [5,6]. In particular, LNG consisting of high methane (~92%) has been recognized as a suitable hydrocarbon to produce hydrogen with a low level of energy consumption because methane has a high hydrogen-to-carbon ratio (CH_4) compared to other hydrocarbons [7–9]. The

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LNG infrastructure is also well established, thus facilitating the production of hydrogen from LNG with a residential reformer [10]. In addition, the LNG is a clean energy source because it does not contain dust, sulfur or nitrogen, which are main causes of environmental pollution.

In order to achieve reasonable conversion via the steam reforming of methane (SRM), it was originally considered that SRM requires a high operating temperature of over 700 °C, a high steam-to-carbon (*S*/*C*) ratio close to 3.0, and a highly pressurized reactant at over 20 bar [11–13]. These severe conditions limited the SRM process as a hydrogen production method for several decades. However, with the advances in catalyst technology and the optimization of operating conditions, recent studies have reported that SRM can be carried out at a relatively low operating temperature (~600 °C), at a low *S*/*C* ratio around 2.0, and under atmospheric pressure [14–16].

To obtain high-quality hydrogen through LNG steam reforming, the content of carbon monoxide in the product gas should be reduced or eliminated because low-quality hydrogen limits its application. For example, the performance of especially fuel cells drops when used with hydrogen containing carbon monoxide. The platinum catalyst in the fuel cell is poisoned by the strong adsorption of carbon monoxide [17,18]. To lower the carbon monoxide concentration, the water–gas shift (WGS) reaction ($CO + H_2O \leftrightarrow H_2 + CO_2$), which not only removes carbon monoxide in the product gas from LNG steam reformers but also produces additional hydrogen, has been investigated by many researchers [19,20], though it has reached a technical plateau.

Many studies have reported fuel processors with micro-reactor operation due to their high efficiency, fast heat transfer rates, high surface-to-volume ratios, and simple scale up processes [21–34]. We also reported a methanol fuel processor based on a silicon-based micro-reactor composed of a methanol steam reformer and a preferential oxidation reactor (PrO_x) [35–39]. In that study, the methanol steam reformer achieved 95% methanol conversion with a carbon monoxide concentration of 2100 ppm at 320 °C. The PrO_x reactor decreased the carbon monoxide concentration in the product gas such that it was lower than the detection limit of our gas chromatograph (GC) at 220 °C. However, research on LNG steam reforming during the operation of a micro-reactor is relatively rare because the operating temperatures required during the LNG steam reforming process are much higher than those needed during methanol and ethanol steam reforming, although the commercialization of the process has the advantages due to the well-established infrastructure, as mentioned above [30–32].

In this study, the application of a silicon-based micro-reactor is broadened to the operation of a LNG fuel processor consisting of a LNG steam reformer for hydrogen production and HTS/LTS reactors for carbon monoxide removal. After the fabrication processes, the performance of the micro-LNG steam reformer was tested under various operating conditions and then compared with the result of a conventional continuous flow fixed-bed reactor. The product gas from the micro-LNG steam reformer was passed through the micro-HTS and LTS reactors in sequence, and the composition of the exhaust gas was then compared with that exhausted from conventional HTS and LTS reactors.

2. Experimental

The detailed fabrication process of micro-reactor is described in our previous work [35]. Thus, the fabrication process is briefly introduced in this study. It is also summarized in Fig. 1. The steps were the preparation of a Si (1 1 0) wafer (Fig. 1a), the formation of a micro-channel with photolithography and chemical wet etching (Fig. 1b), the isolation of the micro-channel using anodic bonding followed by a hole fabrication step (Fig. 1c), the deposition of a Ta/TaN_x thin film heater. In this experiment, an improvement on

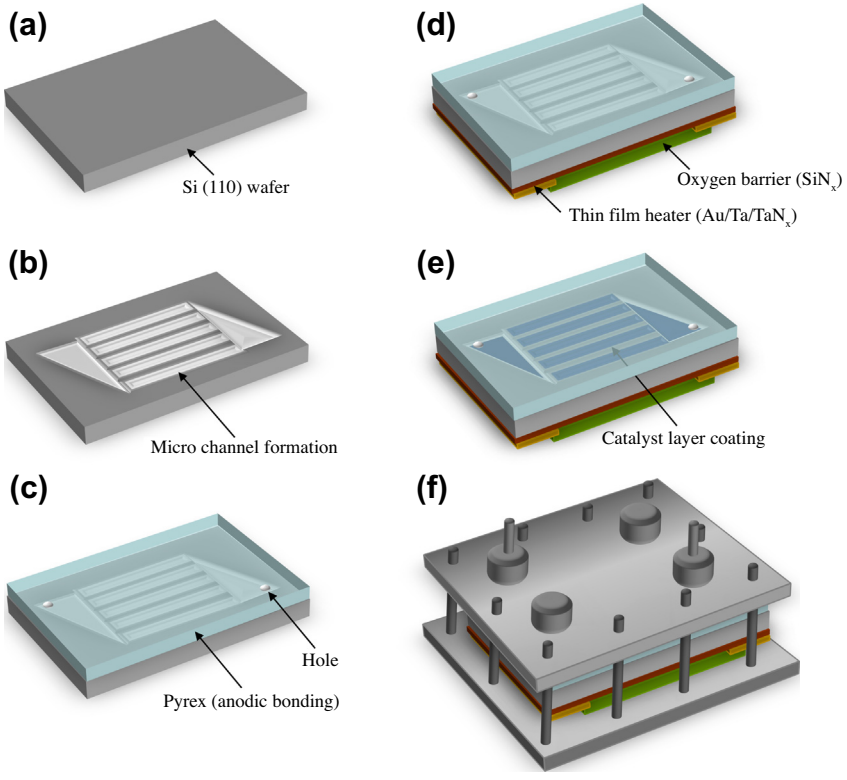

Fig. 1. Schematic diagram of the micro-reactor fabrication process: (a) preparation of the Si (1 1 0) wafer, (b) formation of the micro-channel, (c) isolation of the micro-channel, (d) deposition of the thin film heater including the oxygen barrier, and (e) coating of the catalyst layer and (f) packaging of the micro-reactor.