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Hydrogen production from a DME reforming-membrane reactor using stainless steel-supported Knudsen membranes with high permeability

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ABSTRACT

Stainless steel-supported composite membranes with the Knudsen-dominated permeation behavior were synthesized via the dipping–rolling–freezing–fast drying (DRFF) and soaking–rolling–freezing–fast drying (SRFF) method. A dimethyl ether (DME) steam reforming was performed in a membrane reactor using the stainless steel-supported Knudsen membrane (SKM) with remarkably high permeability. The Knudsen membrane with high permeability was used to improve DME conversion and hydrogen recovery. Compared to a conventional reactor, the DME conversion was improved up to 48% and the hydrogen recovery was 37–38% in the temperature range of 250–450 °C. Moreover, the DME steam reforming-membrane reactor was combined with water–gas shift (WGS) reaction in the permeate side of the membrane reactor to obtain high CO removal efficiency. As a result, the CO concentrations was significantly reduced to below 20 ppm in the permeate side of the membrane reactor via the WGS reaction in the temperature range of 300–450 °C.

1. Introduction

Hydrogen as a clean and carbon free energy carrier has attracted ever-increasing attention around the world in recent years, mainly due to developments in fuel cells and environmental pressures including climate change issues. It can be extracted from water, biomass, or hydrocarbons such as coal or natural gas. Its use in the vehicles powered by polymer electrolyte membrane (PEM) fuel cells can offer the non-toxic emissions and high overall efficiency compared to conventional internal combustion engines [1–6]. However, the on-board storage of hydrogen with high energy density is facing some technical problems. One promising solution to this can be an on-board production of hydrogen using liquid hydrocarbons like methanol, ethanol, dimethyl ether (DME), etc. [5–9]. Recently, many researchers offer several advantages of DME for the hydrogen production compared to other liquid organics [8,9]. DME is the simplest ether, with a chemical formula of CH_3OCH_3. The physical properties of DME are similar to those of liquefied petroleum gases (i.e., propane and butane) so that it can be handled and transported through the same LPG devices. DME burns with a visible blue flame and is non-peroxide forming in the pure state or in aerosol formulations. Unlike methane, DME does not require an odorant because it has a sweet ether-like odor. Moreover, DME is a volatile organic compound, but is non-carcinogenic, non-teratogenic, non-mutagenic, and non-toxic.

In this study, the DME steam reforming was carried out in a membrane reactor system. If the membrane reactor system is employed for the DME reforming as a hydrogen carrier of PEMFC, there are three important aims which have to be achieved from the DME reforming membrane reactor system. The first one is the improvement in the DME conversion, which is a basic objective in the membrane reactor field. The second one is high hydrogen recovery. From a viewpoint of its practical application in PEMFC system, the high hydrogen recovery is considered to be the most important aim, because the hydrogen recovery is directly associated with the capacity of the DME reforming membrane reactor. The last one is CO removal for prevention of the CO poisoning on the Pt anode catalysts in the PEMFC. If dense and microporous membranes such as Pd and microporous silica membranes are used in the DME reforming membrane reactor, CO can be efficiently eliminated. However, the dense and microporous membranes give considerably low hydrogen recovery. In other words, dense and microporous membranes are attractive for not hydrogen recovery, but hydrogen purification [10]. The hydrogen recovery is defined as a ratio of a molar flow rate of permeated hydrogen to a molar flow rate of total produced hydrogen from the steam reforming.

In contrast, utilization of mesoporous membranes leads to high hydrogen recovery combined with a significant falloff in CO removal efficiency. That is, in the case of mesoporous membrane reactors,

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although the permeated hydrogen flow includes other products such as CO, CO_2 and CH_4, the hydrogen recovery is much higher than the dense and microporous membranes. For the membrane reactor system which does not require the generation of high-purity hydrogen, the use of membranes with high hydrogen permselectivity such as Pd-based and microporous silica membranes could lead to a significant falloff in performance of the membrane reactor as proven in our previous report [10], because the trial to improve membrane permselectivity usually results in a decrease in its permeance [11–20]. Therefore, we used Knudsen membranes with high permeance by simple modification of porous stainless steel (PSS) substrates with only colloidal silica sol of 100 nm in particle diameter as our previous publication [18], and introduced additional CO elimination processes such as water–gas shift (WGS) reaction. Our aims of this study are to improve a DME conversion and to obtain high hydrogen recovery through using the Knudsen membrane. We also used the WGS reaction system to eliminate CO in the permeate side of the membrane reactor.

2. Experimental

2.1. Preparation of colloidal silica sol

Colloidal silica sol was synthesized under base-catalyzed condition via hydrolysis of tetraethyl orthosilicate (TEOS) and condensation reaction. A TEOS:ammonia:water:ethanol molar ratio was 1:0.64:53.6:40.1. Prior to addition of an ammonia/water mixture, a TEOS/ethanol mixture was stirred vigorously at 50 °C. The addition of the ammonia/water mixture was carried out dropwise, followed by refluxing the final mixture for 3 h, resulting in stable colloidal silica sol including silica spheres with about 100 nm in diameter.

2.2. Preparation and characterization of composite membranes

Disks of 316L porous stainless steel used as a substrate were purchased from Matt Metallurgical. The PSS disk has a thickness of 1 mm and surface area of 5 cm^2. Stainless steel-supported Knudsen membranes (SKMs) were synthesized using the colloidal silica sol (100 nm in diameter) by means of a dipping–rolling–freezing–fast drying (DRFF) and soaking–rolling–freezing–fast drying (SRFF) method. The PSS substrate was dipped into the colloidal silica sol including 100 nm-sized silica spheres for 30 s. The colloidal silica sol on the substrate surface was rolled out with a urethane rolling pin in order to eliminate a silica cake layer formed on the substrate. Subsequently, the substrate was frozen in liquid nitrogen for 10 s, followed by fast drying of the substrate for 10 s on a hot plate heated to 250 °C. The DRFF process was repeated 7 times. After calcination of the substrate at 650 °C for 2 h, we obtained a composite membrane.

To minimize defects on the membrane surface, we conducted additional infiltration of the colloidal silica spheres into the composite membrane by means of the SRFF process. A back side of the composite membrane loaded on the o-ring sealed-cell was vacuumed by a rotary vacuum pump. The colloidal silica sol was poured onto a front side of the composite membrane, and then the vacuum was maintained for 3 min so that the silica sol penetrates into defects of the composite membrane. After the soaking process, the colloidal silica sol on the substrate surface was rolled out with a urethane rolling pin. Subsequently, the substrate was frozen in liquid nitrogen for 10 s, followed by fast drying of the substrate for 10 s on a hot plate heated to 250 °C. The SRFF process was repeated 3 times. After calcination of the substrate at 650 °C for 2 h, a Knudsen-dominated membrane with high permeability was successfully synthesized. The morphology of the composite membranes was observed using a scanning electron microscopy (SEM; XL 30S FEG, Philips).

2.3. Permeation measurement

Permeation measurements for a single gas were made with pure nitrogen and hydrogen between 25 and 450 °C. The permeation area was 4.52 cm^2. A single gas test was conducted by means of the pressure drop method. A feed side of the membrane was pressurized by pure hydrogen or nitrogen while a permeate side of the membrane was under atmospheric pressure without a sweeping gas. The transmembrane pressure was 0.042 MPa and the flux of permeated gases was measured by a soap film flow meter. The permselectivity for the single gas permeation test is defined as a ratio of hydrogen permeance to nitrogen permeance measured at the same transmembrane pressure and temperature.

2.4. Membrane reactor tests

An apparatus for the DME steam reforming membrane reactor test is schematically shown in Fig. 1. For the DME reforming membrane reactor, 3 g of Cu-Al_2O_3 catalysts purchased from NIKKI Chemical Co. was used in a whole experiment of the DME steam reforming. The DME steam reforming experiments were carried out in the range of reaction temperature from 250 to 500 °C. Water was fed with a liquid feed flow rate of 0.02 ml/min, and was evaporated in a preheating line. Subsequently, the water vapor was mixed with DME of 5 ml/min and argon carrier gas of 100 ml/min. A flow rate

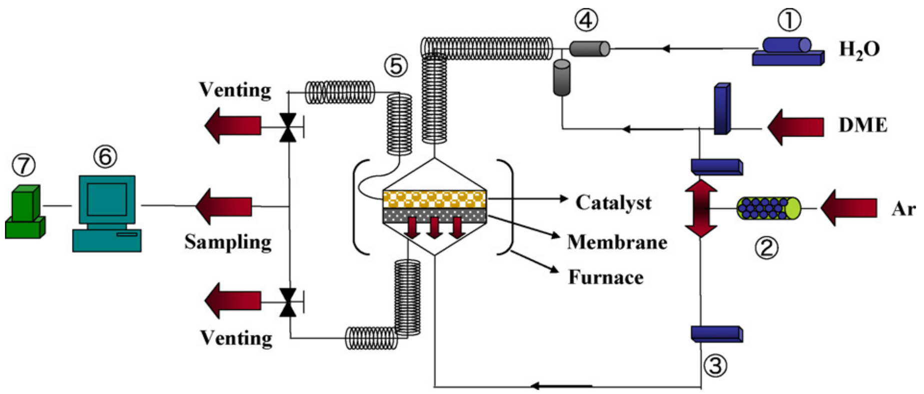

Fig. 1. Schematic diagram of the DME steam reforming membrane reactor test apparatus. (1) Micro pump; (2) silica gel; (3) mass flow controller; (4) check valve; (5) heating line; (6) gas chromatograph; (7) mass flow meter.