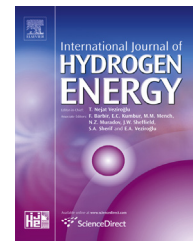




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Short Communication

Effect of palladium addition on catalytic activity in steam methane reforming over Ni-YSZ porous membrane

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ARTICLE INFO

Article history:

Received 15 July 2014

Received in revised form

7 October 2014

Accepted 13 October 2014

Available online xxx

Keywords:

Palladium

Ni-YSZ

Porous membrane

Steam methane reforming

ABSTRACT

This study investigated the additive effects of palladium, and the deposition method of palladium on Ni-YSZ porous membrane in steam methane reforming. Pd–Ni-YSZ porous membrane prepared by the wet impregnation method showed superior catalytic activity, where the methane conversion reached 94.6% at 650 °C, with H₂ yield above 3.9. The palladium particles were well dispersed, and the Pd–Ni-YSZ porous membrane exhibited high adsorption capacity for water. The addition of palladium and the deposition method of palladium are very important for the steam methane reforming reaction.

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Introduction

Steam methane reforming (SMR) is a well-established technology to produce hydrogen for fuel cells. The SMR reaction is a highly energy intensive process, due to its severe endothermic reaction. Thus, the SMR process is usually maintained at approximately 800–850 °C, with a catalyst. Among the SMR catalysts, the nickel-based catalysts are commercially preferred, due to their thermal stability, and low cost of nickel. However, the problem with nickel-based catalysts is coke formation, which causes catalyst deactivation. To overcome the problems, many efforts have been reported on

the development of Ni catalysts with high resistance to coking [1–4]. Some noble metal-based catalysts have been investigated for the SMR reaction, including Pd/NiO–MgO [5], Ru/Ni/Al₂O₃ [6], Pd–Rh/metal foam [7], Ru/ZrO₂–La₂O₃ [8], and Pd/La₂O₃–Al₂O₃ [9]. Among the noble metal-based catalysts, Palladium is known to be one of the best materials for C–H bond activation [10], which catalysts can exhibit higher activity and stability in methane reforming reactions, compared to that of Ni catalysts, due to their higher resistance to carbon deposition [7,11]. However there are also limited in their methane conversion rate, due to the thermodynamic equilibrium of SMR reactions [12]. In recent years, a number of studies have investigated the use of

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<http://dx.doi.org/10.1016/j.ijhydene.2014.10.054>

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catalytic membrane reactors to overcome the equilibrium limitation [13–15]. Oyama et al. [16] reported that membrane reactors improve the methane conversion and the product formation yields, for steam reforming using Ni/MgAl₂O₄ catalyst, with silica-based membrane. Tsuru et al. [17] reported that catalytic membrane reactors, consisting of a microporous Ni-doped SiO₂ top layer and a catalytic support, were prepared and applied experimentally for the steam reforming of methane at 500 °C. Ryi et al. [18] reported that the catalytic Ni–Al membrane promoted the steam reforming reaction due to the shift of the equilibrium caused by the difference in the permeation rates between hydrogen and the other reformate gases, i.e. carbon monoxide and carbon dioxide. And the catalytic nickel membrane exhibited good heat and mass transfer properties, providing the reactor with compactness. Their research group is also applied for preparing Ni based porous membrane such as methanation, mixed reforming and water gas shift reaction [19–21]. In this communication, we investigated the deposition method of palladium, and the effect of Pd addition as a catalytic function on Ni-YSZ porous membrane, in steam methane reforming. Pd combined Ni-YSZ catalytic porous membranes were prepared by a wet impregnation and attrition milling method, and their catalytic activity and surface properties were examined.

Experimental

Catalytic porous membrane preparation

Porous membranes were prepared by mechanically mixing Ni (Sigma–Aldrich, <5 μm), and 0.5 wt% nano-sized YSZ (Sigma–Aldrich, <10 nm). The Ni-YSZ mixed powder was compressed without binder, in a metal cylindrical mould, using a hydraulic press under specific pressure (558–980 MPa). The compressed Ni-YSZ porous membrane was further treated at 950 °C under hydrogen for 2 h [13], and is denoted as Ni-YSZ. Pd–Ni-YSZ catalytic porous membrane was prepared by the wet impregnation method. The calculated (0.5 wt% Pd w/w) of palladium (II) nitrate [Pd(NO₃)₂: Aldrich Chemical Co.] was dissolved in distilled water at 80 °C. After impregnation with Ni-YSZ mixed powder, the moisture was evaporated at 70 °C using a rotary vacuum evaporator, and then dried at 110 °C overnight. The Pd–Ni-YSZ porous membrane was prepared in accordance with the same procedure given above for Ni-YSZ porous membrane, and is denoted as Pd–Ni-YSZ (WI). In comparison, Pd–Ni-YSZ catalytic porous membrane was prepared by the wet attrition milling method, to maintain consistency in the sample. Wet attrition milling was performed, using a calculated amount of 0.5 wt% Pd solution and Ni-YSZ mixed powder, at 360 rpm for 3 h. The obtained sample was dried at 110 °C overnight. The Pd–Ni-YSZ porous membrane was also prepared in accordance with the same procedure given above for Ni-YSZ porous membrane, and is denoted as Pd–Ni-YSZ (WA). The CH₄ conversion and H₂ yield were calculated using the following equations:

$$\text{CH}_4 \text{ conversion (\%)} = \left[1 - \frac{[(\text{CH}_4)_{\text{area}}/(\text{N}_2)_{\text{area}}]}{[(\text{CH}_4)_{\text{in}}/(\text{N}_2)_{\text{in}}]} \right] \times 100 \quad (1)$$

$$\text{H}_2 \text{ yield(\%)} = \text{H}_{2\text{out}}/\text{CH}_{4\text{out}} \text{ (molar ratio)} \quad (2)$$

Characterizations

SEM/Mapping (JEOL, JSM-6500F) was used, to characterize the surface and cross-section of the samples. The temperature-programmed desorption (TPD) of CH₄ was measured using 5% CH₄/Ar and 0.3 g of the catalytic membrane, at a total flow rate of 50 cc/min. Before the CH₄ TPD measurement, the catalytic membrane was pretreated in a flow of 10% H₂/Ar at 650 °C for 0.5 h, and 5% CH₄/Ar adsorbed for 60 min at 650 °C. After CH₄ adsorption, the catalytic membrane was cooled to 50 °C by none gas. Before starting the TPD experiments, Ar was fed for at least 1.5 h at 50 °C. During the CH₄ TPD experiments, CH₄ (16) and C (12) products were continuously monitored using a quadrupole mass spectrometer (QMS 422), by increasing the temperature to 800 °C, at a rate of 10 °C/min. Fourier-transform infrared spectroscopy experiments were conducted in a diffuse reflection cell equipped with a CaF₂ window, using a 660 plus FT-IR spectrometer (JASCO). The spectra included 30 accumulated scans at a resolution of 4 cm⁻¹, using a mercury–cadmium–telluride (MCT) detector. Prior to the measurements, the catalyst samples were pretreated in Ar at 400 °C for 1 h. Then, a gas mixture comprising 3% CH₄/Ar was passed through the sample. Moisture was added to the reactor, by injecting Ar containing water vapor through the bubbler. After a steady state was reached, the FT-IR spectra were recorded.

Catalytic activity tests

Methane steam reforming activity tests were carried out with a steam-to-methane (S/C) ratio of 3, and a gas hourly space velocity of 3800 h⁻¹. The feed steam gas mixture consisted of CH₄, H₂O and N₂, with a vol. % ratio CH₄:H₂O:N₂ = 1:3:1. The schematic of the catalytic membrane reactor system is shown in Fig. 1. The experimental apparatus consisted of a catalytic membrane assembly, a pressure indicator, mass flow controllers, and a digital bubble flow meter. The gases supplied to the reactor were CH₄ and steam; and their flow rates were controlled, using mass flow controllers (MKS, Mass Flow Controller), and micro liquid pump (JASCO, MINICHEMI PUMP). The entire gas supply pipe was made of stainless steel (1/4' sus), and was wrapped with a heating band at 200 °C for preheated CH₄ gas; and the steam supply pipe was made of stainless steel (1/16' sus) in stainless steel (1/4' sus), and was wrapped with a quartz tube coiled by nichrome wire, at 450 °C, for vapor production. The temperature of the reactor was controlled using a PID controller, and a K-type thermocouple fixed on the bottom of the bed. The product gases were analyzed by gas chromatograph (Agilent 6890N), equipped with 6 Å molecular sieves and porapak-Q columns, and

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