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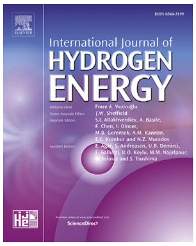

Ni-loaded (Ce,Zr)$O_{2-\delta}$-dispersed paper-structured catalyst for dry reforming of methane

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ABSTRACT

A paper-structured catalyst (PSC) for biogas reforming was prepared with the aim of improving coking tolerance. During the paper-making process using inorganic fibers, Ni-loaded (Ce,Zr)$O_{2-\delta}$ particles were synthesized via co-precipitation and subsequent chemical reduction (on-paper synthesis). The effects of the CeO_2/ZrO_2 weight ratio during preparation and the Ni loading amount on the catalytic activity for dry reforming of CH_4 were investigated at 750 °C. A Ni loading of 6 wt% with $CeO_2/ZrO_2 \geq 1$ led to stable CH_4 conversion of 85% without coking under a gas hourly space velocity of 3800 h^{-1}. The oxygen storage capacity of the (Ce,Zr)$O_{2-\delta}$ particles dispersed in the inorganic fiber network may contribute to the oxidation of carbonaceous species deposited on the catalyst surface.

Introduction

Fuel cell systems for household use have gradually become ubiquitous in Japan because of their high electrical efficiency (40–50%) [1,2]. Among the different types of fuel cells, solid oxide fuel cells (SOFCs) are typically operated at a high temperature (usually between 600 and 900 °C), at which ceramic electrolytes can exert satisfactory ionic conductivity for power generation, have the highest efficiency, and also demonstrate the highest fuel flexibility. This behavior is unlike that of low-temperature fuel cells, which accept only pure H_2 [3–5]. At present, a hydrogen energy-based society may not be the optimum choice, especially in developing countries, because of the associated high cost. However, as these countries have abundant biomass resources, the direct conversion of biofuel such as biogas, which is obtained from the anaerobic fermentation of organic wastes and mainly composed of 50–60% CH_4 and 40–50% CO_2 in volume [6], into electricity using a SOFC system is highly promising in terms of social acceptability as well as reduction of CO_2 emissions. By adopting the direct internal reforming (DIR) operation, system downsizing and enhancement of energy conversion efficiency can be expected

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[7,8]. When biogas is directly fed to the SOFC anode, dry reforming of CH_4 (Reaction (1)) takes place within the Ni-based anode material to produce syngas (mixture of H_2 and CO) that is subsequently oxidized to generate electricity [9].

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO \ (\Delta H^{\circ}_{298} = 247 \text{ kJ/mol}) \quad (1)$$

However, inhomogeneous temperature distribution in a cell and carbon deposition within the porous anode are the major problems leading to significant degradation of cell performance [10–14]. To eliminate these problems, the application of additional catalyst layers on the SOFC anode is very effective [15,16]. Recently, Shiratori et al. utilized paper-structured catalysts (PSCs) and considerably improved the electrochemical performance of DIR-SOFCs fueled by biogas [17,18] and biodiesel fuels [19,20]. These authors applied the Ni-loaded hydrotalcite (HT)-dispersed PSC (Ni/HT-PSC) on the Ni-stabilized zirconia cermet anode. The unique structure of the PSC based on the inorganic fiber network, in which fine Ni particles and support oxides were well-dispersed, was geometrically suitable for hydrocarbon reforming.

Despite their intolerance to coking, Ni-based catalysts are often used for methane reforming to produce hydrogen because of their lower cost in comparison to noble metal (Ru, Rh, Pd, Ir, Pt) catalysts [21–23]. Promoters with oxygen storage capacity (OSC) such as CeO_2 or CeO_2-based solid solutions with other metal oxides are often utilized to suppress coking on Ni [24–26]. Carbon formed on the CeO_2 surface can react with lattice oxygen to form non-stoichiometric $CeO_{2-\delta}$ (Reaction (2)). Subsequently, CeO_2 can be recovered by interacting with oxygen-containing gas such as CO_2, charging oxygen into the lattice (Reaction (3)). Through the oxygen exchange, reverse Boudouard reaction (Reaction (4)) is promoted and carbonaceous species deposited on the Ni surface can be removed [26].

$$CeO_2 + \delta C \rightarrow CeO_{2-\delta} + \delta CO \quad (2)$$

$$CeO_{2-\delta} + \delta CO_2 \leftrightarrow CeO_2 + \delta CO \quad (3)$$

$$CO_2 + C \leftrightarrow 2CO \quad (4)$$

In general, the impregnation method is applied to load metal catalyst particles in the inorganic fiber network [15,17]. In this study, Ni-loaded $(Ce,Zr)O_{2-\delta}$ (Ni/CZ) particles were synthesized by co-precipitation in the paper-making process and subsequent heat treatment led to the formation of Ni/CZ-dispersed PSCs (Ni/CZ-PSCs). By adopting this process, PSC preparation could be simplified. Catalytic activity of the prepared PSCs for dry reforming of CH_4 was investigated at 750 °C. The effects of the CeO_2/ZrO_2 weight ratio and the Ni loading amount on the catalytic activity are discussed.

Experimental

Preparation of Ni/CZ-PSCs

For the preparation of Ni/CZ-PSCs, 5 g of ceramic fiber (52 wt% SiO_2 and 48% Al_2O_3), and Cf (Ibiden Ltd., Japan) with an average length of approximately 500 μm and width of 2 μm, were mixed with 2.5 g of polyvinylpyrrolidone (PVP) in 250 mL of deionized water (DI). This was followed by the addition of designated amounts of the precursors $Ni(NO_3)_2 \cdot 6H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, and $ZrO(NO_3)_2$ (Chameleon Reagent, 98%) to the suspension. Next, 1 g of NaOH was added and the suspension was stirred vigorously to form Ni, Ce, and Zr hydroxide precipitates. Subsequently, 40 mL of an aqueous solution containing 2.5 g of $NaBH_4$ (reducing agent) was added dropwise into the stirred slurry at room temperature for 1 h and the paper-making process was initiated by using cationic and anionic polymers to form flocculates including inorganic materials to achieve 100% retention of them [15]. In this process, 15 g of a solution of 0.2 wt% of the cationic polymer poly diallyldimethylammonium chloride (PDADMAC) (Sigma-Aldrich LCC, USA), 16.3 g of a solution of 0.2 wt% of the anionic polymer acrylamide-*co*-acrylic acid (Fujikasui Engineering Co., Ltd., Japan), and 2.5 g of the organic pulp fiber suspension were poured into the slurry in that order with 3 min stirring for each addition. The resulting slurry was solidified by a filtration process using a 200-mesh filter to form a wet-state paper sheet with a diameter of 16 cm, which was subsequently pressed at 350 kPa for 3 min and dried at 105 °C for 5 h to obtain raw paper. Finally, Ni/CZ-PSC was obtained by heat treatment at 600 °C (ramp rate of 5 °C min^{-1}) in air for 1 h. The average porosity of the prepared PSCs was measured by the mercury intrusion method and found to be 85%. The five types of Ni/CZ-PSCs fabricated with different Ni loading amounts and weight ratios of CeO_2/ZrO_2 and $Ni/(Ce,Zr)O_{2-\delta}$ are listed in Table 1.

For XRD analysis of CeO_2 powder, $Ce(NO_3)_3 \cdot 6H_2O$ and PVP were mixed in DI water with a weight ratio of Ce^{3+}:PVP = 1:1. This suspension was stirred for 2 h on a hot plate at 80 °C and pH 11. The resulting precipitate was dried overnight in the oven, then heat treated at 600 °C in air for 1 h to obtain CeO_2 powder.

Characterizations and analyses

The structures of the prepared PSCs were analyzed by an X-ray diffractometer (Rint-Ultima III; Rigaku, Japan) with CuKα radiation at 40 kV and 40 mA with 0.02°/step for scanning. The crystallite size of Ni was calculated using Scherrer's equation. Microstructures of the PSCs were investigated using a field emission scanning electron microscope (FE-SEM-S5200; Hitachi High Technologies, Japan) with an energy-dispersive X-ray spectrometer (EDX) and a scanning transmission electron microscope (STEM-HD2300A; Hitachi High Technology, Japan). The specific surface area of the samples, S_{BET}, was measured by the nitrogen adsorption method using a Belsorp-mini II analyzer (MicrotracBEL Corp., Japan). Ni loading in the PSCs was quantified by inductively coupled plasma (ICP) spectrometry (Shimadzu ICPE-9000 plasma atomic emission spectrometer (AES)).

The reducibility of the prepared PSCs was evaluated by temperature-programmed reduction (H_2-TPR) using a BELCAT-A analyzer (MicrotracBEL Corp.) with a thermal conductivity detector (TCD). The sample (200 mg) was placed in a glass U-tube and heated from room temperature to 800 °C in increments of 2 °C min^{-1} under a 5% H_2/Ar flow (30 mL min^{-1}).

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