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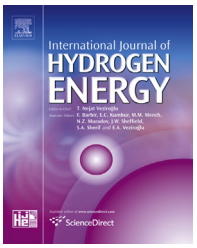

Hydrotalcite-dispersed paper-structured catalyst for the dry reforming of methane

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ABSTRACT

A paper-structured catalyst (PSC) is a flexible planar catalyst that can be stacked on the anode of SOFCs and exhibits excellent catalytic activity for the reforming of hydrocarbon fuels at the operating temperature of the SOFC. Although our final goal is the realization of direct internal reforming (DIR) SOFCs fueled by biogas by applying a PSC, the tolerance of PSCs to sulfur impurities in biogas (H_2S) must be improved for the practical application of PSCs to DIR-SOFCs operated by biogas. In this study, an inorganic fiber network in which a layered double hydroxide (Mg/Al-hydrotalcite denoted as HT) is dispersed was prepared by a paper-making process, and Ni was then loaded in this paper matrix via an impregnation process. This Ni-loaded HT-dispersed PSC exhibited considerably higher tolerance to H_2S than that of HT-free PSC.

Introduction

Solid oxide fuel cells (SOFCs) that operate at high temperatures between 873 and 1173 K have the highest energy conversion efficiency of all fuel cells [1]. High-temperature SOFCs allow us to not use precious metal catalysts, such as Pt and Ru, for the anode. In principle, SOFCs can accept the direct feed of a hydrocarbon fuel, and they are therefore expected to penetrate the market of distributed power generation as a compact and highly efficient energy conversion device. SOFCs operated by the direct feed of a hydrocarbon fuel without an external reforming system are called direct internal reforming (DIR) SOFCs, and the performance enhancement of the anode has been addressed by many research groups to enable the realization of DIR-SOFCs [2–6]. From the viewpoint of the reduction of greenhouse gas emissions, it is effective to run a DIR-SOFC using a biofuel. Biogas, which can be obtained by the anaerobic digestion process of organic matter such as garbage, agricultural residue and manure of livestock, is expected to

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spread as an alternative fuel, especially in the distributed power generation sector, and several groups have reported the power generation characteristics of biogas-fueled SOFCs [6–14]. Using an anode-supported single cell based on a Ni-ScSZ (scandia-stabilized zirconia) anode material, the long-term stability of a DIR-SOFC fueled by practical biogas has been demonstrated [10]. Biogas is a mixture of methane and carbon dioxide that contains hydrogen sulfide (H_2S), ammonia, nitrogen, oxygen, and water as minor constituents [10,14]. The major drawbacks of DIR-SOFCs fueled by biogas are the deactivation of the anode, which is attributed to carbon deposition on the Ni catalyst, and sulfur poisoning, which hinders methane reforming, as well as electrochemical reactions, which induce further carbon formation.

Kitaoka et al. developed a flexible planar catalyst called a "paper-structured catalyst (PSC)" for methanol steam reforming that proceeds at the low temperature of 473–573 K [15,16]. The PSC based on a metal catalyst loaded in an inorganic fiber network can be prepared by a simple paper-making process. They have found a distinctive advantage for PSC in the improved contact efficiency of the reactant gas with the surface of the catalyst particles widely spread through the inorganic fiber network.

Recently, PSCs for application in DIR-SOFCs have been developed [17,18]. This PSC, which can be stacked on the anode of the SOFC, exhibits high catalytic activity for the reforming of bio-fuels, such as biogas and biodiesel fuels, at the operating temperature of the SOFC (approximately 1073 K). However, in this high-temperature reducing atmosphere, the agglomeration and coarsening of the Ni catalyst particles easily occur, especially for the particles loaded on inorganic fibers with a smooth surface. Because the Ni coarsening will degrade the catalytic activity, the improvement of the PSC structure is indispensable for the practical application of PSC in an SOFC system operated by biofuels.

Takehira et al. reported that a Ni-loaded catalyst prepared by solid phase crystallization using a layered double hydroxide (Mg/Al-hydrotalcite denoted as HT) precursor containing nickel is very effective for methane reforming because fine Ni particles can be formed on a Mg/Al composite oxide derived from HT [19,20]. Moreover, because the Mg^{2+} in HT can easily be exchanged for Ni^{2+} in aqueous solution, highly dispersed Ni can be obtained on the support oxide by a simple impregnation process [20].

In this study, aiming at the performance enhancement of PSC, the preparation process of PSC was improved by making use of the unique nature of HT mentioned above. By the dispersion of HT particles in the paper matrix, Ni can be selectively loaded on the HT in the impregnation process to suppress Ni loading on the inorganic fibers, where Ni agglomeration is more promoted under the reducing atmosphere. The catalytic activities of the prepared PSCs for the dry reforming of methane were compared with that of the conventional HT-free PSC under 5 ppm H_2S poisoning.

Experimental

In this study, HT powder purchased from Wako Pure Chemical Industries, Ltd. was applied to the preparation of PSC. The particle size and specific surface area of the HT are listed in Table 1.

Table 1 – Hydrotalcite (HT) powder used in this study.

Molecular formula	Particle size/nm	BET specific surface area/m^2g^{-1}	
		After drying at 378 K	After heat treatment at 1073 K
$[Mg_6Al_2(OH)_{16}CO_3]$ $4H_2O$	100	72	159

PSCs were prepared by an established papermaking technique through a dual polyelectrolyte retention system [15,17]. 5 g of ceramic fiber (SiO_2: 52 wt%, Al_2O_3: 48 wt%), Cf, (IBIDEN Ltd., Japan) with 500 μm average length and 2 μm average width was added to ca. 600 ml of distilled water, and the fiber was then crushed by an electric mixer. 1 or 2 g of HT and distilled water were added to the slurry, and the resulting 1 L water suspension was mixed with a designated amount of cationic polyelectrolyte (polydiallyldimethylammonium chloride) (PDADMAC, Sigma–Aldrich LCC, USA) and stirred for 3 min. Subsequently, 0.5 g (solid base) of yttria-stabilized zirconia sol (Zs) (Nissan Chemical Industries Ltd., Japan), which serves as an inorganic binder through high-temperature heat treatment, was added, followed by the addition of an anionic polyelectrolyte (acrylamide-co-acrylic acid) (FA-405S, Fujikasui Engineering Co., Ltd., Japan) and stirring for 3 min. Then, 0.25 g (solid base) of an organic pulp fiber suspension was poured into the mixture and solidified by dewatering using a 200-mesh with a diameter of 16 cm. The wet-state paper sheet was pressed at 350 kPa for 3 min and dried at 105 °C for 2 h to form raw paper (RP). The three types of RP prepared in this study are listed in Table 2. RP-1 is HT-free paper, and RP-2 and -3 are HT-dispersed papers with HT(wt)/Cf(wt) ratios of 0.2 and 0.4, respectively. Finally, RP-1 and -2 were heat-treated at 1073 K, and RP-3 was heat-treated at 873 or 1073 K for 5 h to improve the physical strength by binder welding, while the pulp fibers as a temporary matrix were thoroughly burned up to leave porous structures. The obtained paper composite was cut into donut-shaped pieces (20 mm outer diameter, 6 mm inner diameter and 1.1 mm thickness), and the pieces of the paper were immersed in 0.1 or 0.5 M $Ni(NO_3)_2$ aqueous solution. After the impregnation process, the samples were oven-dried at 378 K for 3 h, followed by heat treatment to burn out the nitrate at 1073 K for 5 h.

6 types of PSCs (PSC-A, -B, -C, -D, -E and -F listed in Table 3) were prepared in this study. The weight ratio of HT to Cf was set to 0 (PSC-A), 0.2 (PSC-B) or 0.4 (PSC-C, -D, -E and -F). Only PSC-A is an HT-free PSC. Although the raw paper was

Table 2 – Composition of raw papers (RPs) prepared in this study.

Name of raw paper	HT/wt%	Cf/wt%	Zs/wt%	Cationic polymer/wt%	Anionic polymer/wt%	Pulp/wt%
RP-1	0	86.1	8.6	0.5	0.5	4.3
RP-2	14.7	73.3	7.3	0.5	0.5	3.7
RP-3	25.5	63.9	6.4	0.5	0.5	3.2

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