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Paper-structured catalyst for the steam reforming of biodiesel fuel

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ABSTRACT

Architectonics of the paper-structured catalyst for the application to the biofuel reformer or direct internal reforming SOFC (DIRSOFC) was studied. Inorganic fiber network, "paper", composed of yttria-stabilized zirconia (YSZ) fiber (Zf), alumina fiber (Af) and inorganic binder (Al_2O_3 sol (As) or ZrO_2 sol (Zs) or CeO_2 sol (Cs)) was prepared by a simple paper-making process. Then, the catalytic activities of the Ni and Ni–MgO loaded papers called "paper-structured catalysts (PSCs)" for the steam reforming of biodiesel fuels (BDFs) were evaluated. Ni–MgO loaded PSC using Cs as an inorganic binder, Ni–MgO/ZfAfCs, exhibited excellent performance over $Ru/\gamma Al_2O_3$ catalyst beads. Formation of light hydrocarbons, especially C_2H_4, was eliminated and water–gas shift reaction was more promoted compared to the catalyst beads.

1. Introduction

In principle, high temperature solid oxide fuel cells (SOFCs) can be operated by direct internal reforming (DIR) mode, that is, direct feed of hydrocarbon fuels, such as city gas, propane gas, and coke oven gas, biogas and biodiesel fuel (BDF) is possible. BDF is an oxygenated fuel produced from biomass resources such as animal fat, plants, and waste-cooking oils, and their high flash point, non-toxicity and biodegradability make their handling and storage safer compared to petro-diesel fuels [1]. BDF is a promising feedstock for SOFCs, and steam reforming of BDFs for the production of renewable-hydrogen has been previously reported [2–4]. However, in the DIR operation of SOFC with practical BDFs containing mono-, di- and tri-unsaturated fatty acid methyl esters (FAMEs) with high carbon number over 17 and trace impurities such as sulfur, carbon deposition on the anode material will become severe problem because of the insufficient catalytic activity of the conventional anode material for the steam reforming of BDFs. Moreover, strong endothermicity of the steam reforming of BDFs will cause destruction of the cell due to the rigid structure of the conventional anode material.

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Recently, development of structured catalysts with micrometer-scale pores has much attention in terms of highly effective diffusion of heat and reactants [5,6]. Various types of structured supports, such as string [7], honeycomb [8] and foam [9], have been reported. In practical application, honeycomb-structured supports with arranged parallel channels have been popularized, especially in environmental applications such as elimination of nitrogen oxide and unburnt hydrocarbons in exhaust gas emissions of the transportation vehicles. However, this type of support material has certain drawbacks as the results of getting heavy and lacking three-dimensional diffusion of reactants. Consequently, the structural design of the porous catalyst supports is still being intensively investigated for the practical applications. Development of paper-structured catalysts (PSCs) has been reported by Kitaoka et al. [10–12]. Their PSCs based on the network of SiC or SiO_2–Al_2O_3 fibers exhibited efficient hydrogen production through methanol steam reforming at low temperature between 250 and 300 °C using Cu–ZnO powders as catalyst [11,12].

The goal of this study is the creation of flexible reaction field to realize direct internal reforming SOFC (DIRSOFC) running on biofuels by the application of PSC technology which can suppress carbon deposition and thermal shock problems caused by endothermic steam reforming reaction. Through the course of this study, novel PSCs consisting of YSZ and alumina fibers, which exhibit high catalytic activity for the steam reforming of BDFs under SOFC operating condition, were developed. The significant advantages of the PSCs are their high mechanical flexibility and material workability. PSCs can be easily assembled or integrated with SOFC, creating new concept DIRSOFC.

2. Experimental

2.1. Preparation of YSZ fiber containing paper-structured catalysts

Paper-structured catalysts (PSCs) were prepared by an established paper-making technique through a dual polyelectrolyte retention system [11,12] and a subsequent on-paper synthesis. The procedure of this process was shown in Fig. 1. A water suspension of YSZ fiber, Zf, (Zircar Inc., USA) and alumina fiber, Af, (Denki Kagaku Kogyo, Japan) was mixed with a designated amount of cationic polyelectrolyte, (polydiallyldimethylammonium chloride) (PDADMAC; molecular weight *ca.* 3×10^5 g mol^{-1}; charge density 5.5 meq g^{-1}, Sigma–Aldrich LCC, USA). PDADMAC with positive charge density is adsorbed in the excess onto suspended inorganic fibers with a weak negative charge in an aqueous system. Subsequently, either alumina sol (As), zirconia sol (Zs) or ceria sol (Cs) (Nissan Chemical Industries Ltd., Japan), which serves as an inorganic binder after thermal treatment at high temperature, was added, followed by the addition of anionic polyelectrolyte (acrylamide-co-acrylic acid) (A-PAM, HH-351; molecular weight *ca.* 4×10^6 g mol^{-1}; charge density 0.64 meq g^{-1}, Kurita Ltd., Japan). The negatively charged stretched A-PAM adsorbs on inorganic materials via interaction with preadsorbed PDADMAC on inorganic fibers and sol, and provided bridging between positively overcharged inorganic materials. The mixture was poured into an organic pulp fiber suspension, and solidified by dewatering using a 200-mesh wire. The wet-state paper sheets were pressed at 350 kPa for 3 min, and dried at 105 °C for 1 h. The retention of fibers and other components reached *ca.* 100%. Finally, the paper matrix was thermally treated at 1300 °C for 10 h to improve the physical strength by binder welding, while pulp fibers as a temporary matrix were thoroughly burned up to make porous structures. The obtained Zf containing paper composites (ZfAfAs, ZfAfZs and ZfAfCs) were cut into disc-shaped pieces (16 mm in diameter and 1.0 mm in thickness), and the discs were immersed in an aqueous solution of 1 M $Ni(NO_3)_2$ or 1 M mixture of $Ni(NO_3)_2$ and $Mg(NO_3)_2$. The treated discs were oven-dried at 105 °C for 3 h, followed by thermal treatment to burn out the nitrate at 800 and 400 °C for 5 h for the PSCs with and without Mg, respectively. Constituents of the prepared papers and types of PSC are summarized in Tables 1 and 2, respectively.

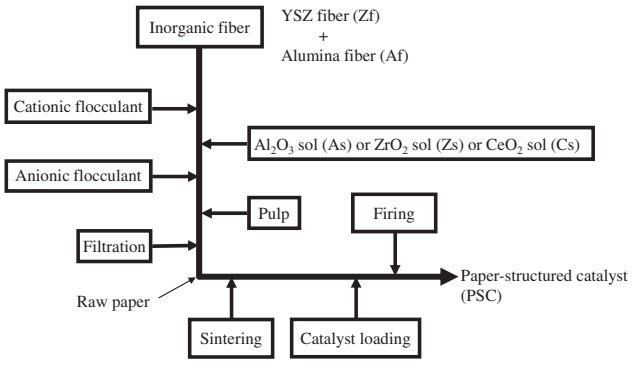

Fig. 1 – Process flow of paper-structured catalysts.

2.2. Characterizations

Morphologies of the prepared PSCs were investigated with a field emission scanning electron microscope (FESEM-S5200, Hitachi High-Technologies, Japan) equipped with an energy-dispersive X-ray spectrometer (EDS) for microstructural and chemical characterizations. Crystal structures of the samples were analyzed by using an X-ray diffractometer (Rint-Ultima III diffractometer, Rigaku, Japan) with CuKα radiation at 40 kV and 40 mA, 0.02°/step for scanning. The Scherrer formula was used to estimate the Ni crystallite size on the basis of the full width at half maximum of Ni (111) reflection ($2\theta = 44.3°$). The surface of the PSC was observed by a scanning probe microscopy (SPM) (Nanocute, SII NanoTechnology Inc., Japan).

Table 1 – Constituents of the YSZ fiber (Zf) containing paper.

Components	Materials
Inorganic fiber	YSZ fiber (Zf) + Al_2O_3 fiber (Af)
Inorganic binder	Al_2O_3 sol (As) or ZrO_2 sol (Zs) or CeO_2 sol (Cs)
Organic binder	Pulp (Bleached chemical pulp)
Flocculants	Cationic polyelectrolyte (PDADMAC) + Anionic polyelectrolyte (A-PAM)