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Characteristics of alkali-resistant Ni/MgAl₂O₄ catalyst for direct internal reforming molten carbonate fuel cell

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ABSTRACT

Direct internal reforming – molten carbonate fuel cell (DIR–MCFC) has advantages of higher efficiency and smaller size. However, deactivation of the catalyst by alkali carbonate electrolytes poses a significant problem in MCFC. To solve this problem, Ni/MgO and Ni/MgAl₂O₄ catalysts were compulsively mixed with a eutectic mixture of Li₂CO₃ and Na₂CO₃ prior to a methane steam reforming activity test. Activity of Ni/MgO rapidly decreased, while that of Ni/MgAl₂O₄ remained steady due to good alkali resistance. To analyze the effects of alkali addition, N₂ adsorption-desorption, X-ray diffraction, temperature-programmed reduction and oxidation, scanning electron microscopy, and X-ray photoelectron spectroscopy experiments were carried out. Both Ni/MgO and Ni/MgAl₂O₄ showed sintering of Ni and blocking of pores, which reduced the catalytic activity. However, Ni/MgAl₂O₄ showed other positive effects such as stronger metal–support interaction and increased dissociative adsorption.

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1. Introduction

Molten carbonate fuel cell (MCFC) is a high temperature fuel cell that produces electricity through an electrochemical reaction with carbonate ions as electrolytes. It does not require precious metal electrodes since it can operate with inexpensive transition metal electrodes at a relatively high temperature (650 °C). Thus MCFC has an economical advantage over other types of fuel cells when it comes to commercialization. MCFC uses hydrogen as fuel, which is obtained from various hydrocarbons (methane, ethanol etc.) through reforming reactions. MCFC is classified into three types according to the location of the reformer; external reforming MCFC, indirect internal reforming MCFC, and direct internal reforming MCFC. Direct internal reforming MCFC (DIR–MCFC) utilizes the exothermic heat of electrochemical reaction at the stacks for the endothermic reforming reaction. Therefore it

has an intrinsically high reforming efficiency. In addition, hydrogen produced at the reformer is consumed in situ by the electrochemical reaction, adding to the high reforming efficiency [1]. On the other hand, main disadvantage of DIR–MCFC is that it is more prone to poisoning of the reforming catalyst by alkali metal electrolytes.

Among various reforming catalysts, Ni/MgO has been widely used for DIR–MCFC since its basicity prevents coking [2–5]. However, the catalytic activity of Ni/MgO is known to decrease drastically due to severe poisoning by electrolytes [3]. Therefore considerable effort has been put into elucidating the effect of alkali metals and the mechanism of their poisoning process, especially Li and K [6–9]. Recently, many researchers have developed alkali-resistant catalysts for application to DIR–MCFC. Zhou et al. [10] prepared core-shell nickel catalysts by encapsulating Ni/SiO₂ and Ni/Al₂O₃ within zeolite shells. These catalysts showed good (Li/K)₂CO₃-

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resistance in an out-of-cell test for 60 h. Roh et al. [11] prepared Ni/Al₂O₃ using urea as a precipitation agent. Prepared Ni/Al₂O₃ catalyst exhibited strong stability against KOH compared to commercial reforming catalysts. Devianto et al. [12] suggested MgO–PbO support for low-wettability of the catalyst against electrolytes as a reason for the alkali resistance.

In this study, we tried to develop a reforming catalyst resistant to the electrolyte mixture with eutectic composition of Li₂CO₃ and Na₂CO₃. The electrolyte consisting of (Li/Na)₂CO₃ has better ionic conductivity than (Li/K)₂CO₃, therefore it can generate higher output voltage. It also shows smaller electrolyte loss and NiO dissolution than any other electrolytes. When compared to (Li/K)₂CO₃, however, it causes the SUS material to corrode more easily. MC Power, Hitachi, IHI, and MELCO, frontrunners in MCFC technology, have recently employed (Li/Na)₂CO₃ as the electrolyte of MCFC [13].

Moon et al. [4,5] reported that Ni/MgO is deactivated by reaction with alkali metals. In this paper, we studied the effect of the electrolyte on Ni/MgAl₂O₄, a modified form of Ni/MgO. The MgAl₂O₄ spinel structure displays high resistance to most acids and alkalis, good chemical stability, and high mechanical strength [14–16].

2. Experimental

2.1. Preparation of the catalysts

The magnesium aluminate (MgAl₂O₄) spinel was made by co-precipitation method using Mg(NO₃)₂·6H₂O (Kokusai) and Al(NO₃)₃·9H₂O (Aldrich) as precursors. Al/Mg molar ratio was set to 2, and NH₄OH reagent was used as the precipitant. The gel was filtered and washed with distilled water. After drying at 110 °C for 24 h, calcination was performed at 800 °C for 4 h [17]. Commercial (Yakuri) MgO powder was used as a reference. 20 wt% nickel was loaded on two supports, MgAl₂O₄ and MgO, by precipitation method using Ni(NO₃)₂·6H₂O and NaOH as the Ni precursor and the precipitant, respectively. The catalysts were calcined at 700 °C for 1 h and activated in situ at 650 °C for 0.5 h in H₂ just before the reforming reaction. Nickel supported on MgO and MgAl₂O₄ were denominated NM and NMA, respectively [18].

2.2. Compulsory alkali poisoning and catalytic activity test

To confirm the effects of mixed alkali carbonate electrolytes in MCFC, the catalysts were treated with a eutectic mixture of Li₂CO₃ and Na₂CO₃. The preparation procedure for the eutectic mixture is as follows. Lithium carbonate (Kanto) and sodium carbonate (Kanto) were physically mixed with a ratio corresponding (Li/Na: 52/48) to the eutectic point. Then, the mixture was heated to 530 °C, above the eutectic temperature (501 °C), in order to be liquefied. Prepared molten carbonate salt was then cooled down to room temperature and shattered. To confirm alkali poisoning, deactivation catalytic test was performed with a physical mixture of the catalyst and the prepared molten carbonate salt. Electrolyte-added catalyst was heat-treated at 730 °C for 3 h in H₂/N₂ for fast aging of the

catalyst. Amounts of added electrolytes were 5.7 wt% Li₂CO₃ and 6.5 wt% Na₂CO₃. Fast deactivation mode was also simulated by Matsumura [19] and Choi [20], and Choi [20] verified that catalysts were fully affected by adding alkali metal components through the above simulated poisoning method. The added amount of electrolyte was equivalent to the amount after operation for 20,000 h in a real MCFC system. To elucidate the individual effects of each alkali metal, Li and Na were exclusively added to different catalysts. Electrolyte-, lithium-, and sodium-added NMA were denominated e-NMA, L-NMA, and N-NMA, respectively. L-NMA and N-NMA were prepared using lithium carbonate and sodium carbonate, respectively. The amounts of added lithium and sodium were 5.7 wt% and 6.5 wt%, respectively, identical to the amounts of added electrolytes, for comparison with the electrolyte-added NMA. Treatment process of lithium-added NMA was same as the simulated deactivation process of electrolyte-added catalysts. Lithium carbonate powder was mechanically mixed with NMA, and was then heat-treated at 730 °C for 3 h in H₂/N₂. We could not carry out the same deactivation process for the sodium-added NMA, because melting point (805 °C) of sodium carbonate is higher than 730 °C, our treatment temperature. Therefore, we prepared the poisoned catalyst by impregnation method using the aqueous carbonate solution. Subsequently we carried out the heat treatment at 730 °C for 3 h [21].

The catalytic activity test was performed in quartz reactor at 650 °C under 1 bar to simulate the real MCFC reformer system. The flow rate of methane and the molar ratio of H₂O and CH₄ (S/C ratio) were set to 30 sccm and 2.5, respectively. Product gases were analyzed by on-line gas chromatography (DS6200, Donam) using a TCD detector.

2.3. Characterization

For the analysis of the bulk property of materials, powder X-ray diffraction (XRD) experiment was carried out on a high power X-ray diffractometer (Rigaku, D-MAX2500-PC) using Cu K_α as the radiation source at 40 mA and 200 kV. The average crystalline size of nickel was measured using the Scherrer equation.

Through the N₂ adsorption-desorption experiment, BET surface area and the pore size distribution were determined using a porosimetry analyzer (ASAP 2010, Micromeritics Corp.).

Temperature-programmed reduction, desorption and oxidation (TPR, TPD and TPO) of the catalysts were carried out in a quartz TPR tube reactor using a BEL-CAT (BEL Japan) instrument. In the case of CO-TPD experiment, CO was adsorbed on the catalyst at 50 °C for 2 h and the catalyst was preheated for 30 min at 650 °C in H₂/N₂ before CO adsorption. To quantify-check the dissociative adsorption of methane, TPO analysis was carried out after the adsorption of methane at 200 °C for 2 min from room temperature to 1000 °C.

For the analysis of catalyst morphology, scanning electron microscope (SEM) images were taken. Electron microscopic images were obtained using an SEM (FEI XL-30 FEG) at 200 kV. Powder samples were ground and vacuum treated for half an hour before analysis.

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