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# The effect of Ni content on a highly active Ni–Al<sub>2</sub>O<sub>3</sub> catalyst prepared by the homogeneous precipitation method

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## ARTICLE INFO

### Article history:

Received 3 August 2010

Received in revised form

20 September 2010

Accepted 24 September 2010

Available online 16 October 2010

### Keywords:

Ni–Al<sub>2</sub>O<sub>3</sub>,

Ni content

Homogeneous precipitation

Molten carbonate fuel cell (MCFC)

Internal reforming

## ABSTRACT

Highly active Ni–Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by the homogeneous precipitation method with a variety of high nickel contents ranging from 30 to 70 wt.%. The effects of nickel content on the physicochemical properties and catalytic activities of the Ni–Al<sub>2</sub>O<sub>3</sub> catalysts were investigated. XRD measurements showed that the catalyst with 30 Ni wt.% only had a diffraction peak corresponding to NiAl<sub>2</sub>O<sub>4</sub>, whereas the catalysts of 50, 60 and 70 Ni wt.% had diffraction peaks corresponding to NiO and NiAl<sub>2</sub>O<sub>4</sub>. Hydrogen chemisorption results showed that the nickel surface area increased with increasing nickel content in the order: 30 < 40 < 50 < 60 < 70 Ni wt.%. Specifically, the nickel surface area increased steadily from 11 to 22 m<sup>2</sup>/g with increasing the nickel content from 30 to 50 wt.%, after which it stayed nearly constant at 22 m<sup>2</sup>/g despite the increase in nickel content from 50 to 70 wt.%. TEM images of the reduced Ni–Al<sub>2</sub>O<sub>3</sub> catalysts revealed that the average sizes of the Ni particles were 12, 13 and 16 nm for the catalysts with 30, 50 and 70 Ni wt.%, respectively, suggesting that a higher nickel content yielded a larger Ni particle. The catalytic performance of methane steam reforming showed that the catalytic reaction rate increased steadily with increasing nickel content from 30 to 50 wt.%, after which it stayed nearly constant despite that the nickel content increased to over 50 wt.%. As a result, about 50 wt.% of nickel was found to be a reasonable nickel content to obtain the maximum catalytic activity.

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## 1. Introduction

The molten carbonate fuel cell (MCFC) is attracting worldwide attention for use in distributed electric power supply systems [1–3]. Hydrogen is supplied to the MCFC via steam reforming of methane, and Ni-based catalysts are usually used in the reformation process [4–6]. MCFCs can be classified by the type of method used in the reforming reaction as external reforming (ER-MCFC), direct internal reforming (DIR-MCFC), or indirect internal reforming (IIR-MCFC) [7,8]. In the ER-MCFC, hydrogen is synthesized out of a stack system and is supplied to an anode electrode. In the DIR-MCFC, however, reforming

catalysts are placed in the anode current collector of a stack cell, and hydrogen is synthesized within the stack cell. The cell structure of the DIR-MCFC can be more complex than the ER-MCFC. The DIR-MCFC has advantages with respect to the thermal management of the cell. The methane steam reforming reaction and electrochemical reaction occur simultaneously at the anode of the cell. Because the reaction is endothermic, it is sustained by the heat released in the electrochemical reaction [6–8].

DIR-MCFCs still have problems that should be improved. One such problem is the deactivation of the reforming catalysts loaded in the anode current collector. The reforming catalysts

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can be deactivated by either the vapor or liquid of the molten carbonate electrolyte ( $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$  or  $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3$ ). Extensive studies have been conducted to overcome this problem [9–13]. The deactivation of reforming catalysts by the liquid phase of the electrolyte can be prevented by choosing a proper material for the anode current collector, but the deactivation by the vapor phase cannot be prevented [14]. Accordingly, reforming catalysts that are durable toward deactivation by the vapor phase of the electrolyte have been developed extensively. Although nickel catalysts supported on alumina or alkaline earth metal oxides are the most often used as reforming catalysts for DIR-MCFC, there is a need to develop more reliable catalysts that are not deactivated by the electrolyte. Furthermore, the internal reforming catalyst for DIR-MCFC is operated at 550–650 °C, which is a somewhat low temperature by comparison to the conventional operating temperature (700–900 °C) of steam reforming, therefore requiring a highly active catalyst to provide sufficient catalytic activity.

Numerous nickel catalysts supported on  $\text{Al}_2\text{O}_3$  have been prepared by various manufacturing methods, including the sol–gel method [15], the impregnation method [16,17], the co-precipitation method [17,18] and the homogeneous precipitation method [19–22]. Among these methods, the homogeneous precipitation method can provide catalysts with highly dispersed active particles [23,24] and can be favorable for internal reforming catalysts in DIR-MCFCs. Moreover, this method is suitable for preparing Ni– $\text{Al}_2\text{O}_3$  catalysts with a high Ni content of 30–60 wt.% to raise the catalytic activity to a high level.

In our previous work [5,25], Ni– $\text{Al}_2\text{O}_3$  catalysts were prepared by the homogeneous precipitation, and they exhibited good catalytic performance as well as strong resistance to poisoning by KOH. However, studies on the specific parameters of this method, such as synthesis temperature, nickel content and aging time are still needed to develop better catalysts for internal reforming in DIR-MCFCs.

The aim of the present study is to examine the effects of Ni content on the Ni– $\text{Al}_2\text{O}_3$  catalyst prepared by the homogeneous precipitation method using urea. The Ni– $\text{Al}_2\text{O}_3$  catalysts were prepared at high Ni contents ranging from 30 to 70 wt.% and their physicochemical properties and catalytic activities were investigated.

## 2. Experimental

### 2.1. Preparation of the catalysts

The Ni– $\text{Al}_2\text{O}_3$  catalysts were prepared by the homogeneous precipitation method using urea as the precipitant. The metal solutions of nickel nitrate and aluminum nitrate were prepared by dissolving  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in distilled water. The nickel nitrate concentration was varied between 0.051 and 0.119 mol  $\text{L}^{-1}$  and the aluminum nitrate concentration was varied between 0.137 and 0.059 mol  $\text{L}^{-1}$ . The precipitant solution was prepared by dissolving urea ( $(\text{NH}_2)_2\text{CO}$ ) in distilled water to form a 6 mol  $\text{L}^{-1}$  solution regardless of the nickel nitrate and aluminum nitrate concentrations used. The metal solutions and precipitant solution were mixed in a 2 L batch type reactor. A thermometer was located at the center of the reactor. The mixed

solution was reacted at 85 °C for 10 h. After this time, the precipitates were filtered, washed and dried at 110 °C overnight. The dried precipitates were calcined at 650 °C or higher for 6 h. The Ni– $\text{Al}_2\text{O}_3$  catalysts prepared by homogeneous precipitation were named KX (X = 30, 40, 50, 60 and 70), where X represents the Ni content, defined as Ni weight percentage in Ni– $\text{Al}_2\text{O}_3$  catalysts.

### 2.2. Characterization

Nitrogen adsorption–desorption isotherms of the catalysts were obtained with a BELsorp (BEL Japan) instrument. BET surface areas of the catalysts were determined by the Brunauer–Emmett–Teller (BET) method. The crystalline structures of the catalysts were investigated by XRD (D-Max2500, Rigaku) measurements. To investigate the metal–support interaction in the catalysts, temperature-programmed reduction (TPR) measurements (BELCAT-B, BEL Japan) were performed at temperatures ranging from room temperature to 1000 °C with a rate of increase of 5 °C  $\text{min}^{-1}$ . For the TPR measurements, 10%  $\text{H}_2$  in Ar (50 mL  $\text{min}^{-1}$ ) was used for 0.1 g of catalyst samples.

Hydrogen chemisorptions (BEL-METAL-3, BEL Japan) were measured to investigate the nickel dispersion and nickel surface area of the catalysts. Before measuring the chemisorption, 30 mg of the catalyst was reduced with pure  $\text{H}_2$  (50 mL  $\text{min}^{-1}$ ) at 700 °C for 1 h. The amount of hydrogen uptake was determined by injecting mixed gas (20%  $\text{H}_2$  in Ar) periodically into the reduced catalyst. The nickel dispersion and nickel surface area were calculated by assuming that one hydrogen atom occupies one surface nickel atom and that the cross-sectional area of atomic nickel is  $6.49 \times 10^{-20}$  m<sup>2</sup> Ni-atom<sup>-1</sup>.

A transmission electron microscope (FE-TEM, Tecnai G2 F30, FEI Company) operating at 300 kV was used to investigate the crystal sizes and properties in both the fresh and reduced Ni– $\text{Al}_2\text{O}_3$  catalysts.

### 2.3. Steam reforming of methane

The steam reforming of methane was carried out at reaction temperatures ranging from 420 to 650 °C under atmospheric pressure. The fresh catalyst (5 mg, 60–100 mesh-sized granules) was diluted with  $\text{Al}_2\text{O}_3$  granules (100 mg, 60–100 mesh) in a fixed-bed quartz reactor (I.D. = 4 mm). Before starting the methane reforming reaction, the catalyst was reduced at 700 °C for 1 h under a mixture of 10%  $\text{H}_2$  in  $\text{N}_2$  (100 mL  $\text{min}^{-1}$ ). The  $\text{H}_2\text{O}$ ,  $\text{CH}_4$  and  $\text{N}_2$  reactants were supplied at flow rates of 75 (vapor), 37.5 and 75 mL  $\text{min}^{-1}$ , respectively. The ratio of  $\text{H}_2\text{O}$  and  $\text{CH}_4$  was fixed at 2.0. The reforming reaction was stabilized at 650 °C for 1 h, and then the reaction temperature was decreasing from 650 to 420 °C at a rate of 1 °C  $\text{min}^{-1}$ . Reaction products were sampled periodically and analyzed using an on-line micro gas chromatograph (Agilent 3000) equipped with a TCD.

## 3. Results and discussion

### 3.1. Characterization of the catalysts

Precipitates prepared by the homogeneous precipitation method are composed of a layered double hydroxide (LDH)

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