Low temperature steam reforming of methane using metal oxide promoted Ni-Ce$_{0.8}$Zr$_{0.2}$O$_2$ catalysts in a compact reformer

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ABSTRACT

Metal oxide (MgO, CaO, and La$_2$O$_3$) promoted Ni-Ce$_{0.8}$Zr$_{0.2}$O$_2$ catalysts have been applied for low-temperature steam reforming of methane (SRM), and the promoter effect was investigated. The addition of the metal oxides improved the basicity which enhances the resistance coke formation and catalytic activity. Among the prepared catalysts, the Ni-La$_2$O$_3$-Ce$_{0.8}$Zr$_{0.2}$O$_2$ catalyst exhibited high activity and stability at a very high gas hourly space velocity of 621,704 h^{-1}. This was mainly due to high dispersion of Ni, strong basicity of La$_2$O$_3$, and strong interaction between Ni and La$_2$O$_3$.

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Introduction

Recently, hydrogen production has received much attention as a clean energy carrier for the future [1]. Because methane has the highest H/C ratio among the hydrocarbons, it is an ideal source of hydrogen [2]. Moreover, utilization of existing natural gas pipeline infrastructure makes methane a convenient feedstock for hydrogen production [3]. The transference and storage of hydrogen are difficult because of its low density, but these problems can be solved by the production of hydrogen on site and on demand by small-scale reformers [4]. Large-scale hydrogen plants do not have constraint of size, but on site hydrogen generation systems by using small-scale reformers are limited by the size, volume, weight, and several technical limitations [5]. Consequently, small-scale reformers

should be compact with high hydrogen production efficiency per unit hour. To achieve this, it is necessary to develop highly active and stable catalysts.

Steam reforming of methane (SRM) is one of significant step for the production of pure hydrogen from methane [6,7]. Ni based catalysts are the most attractive because these are economical and the most active among non-precious metal based catalysts [8,9]. However, Ni-based catalysts are prone to carbon formation. It has been reported that the CH_4 decomposition (1) and the Boudouard reaction (2) are main routes of coke formation on SRM catalysts [5,10,11].

$$CH_4 \ (g) \rightarrow 2H_2 \ (g) + C \ (s) \tag{1}$$

$$2CO \ (g) \rightarrow 2CO_2 \ (g) + C \ (s) \tag{2}$$

The Boudouard reaction is about 3—10 times faster than methane decomposition and is favorable at relatively lower temperatures [12]. The temperature of catalyst bed decreases as the SRM reaction proceeds because it is a highly endothermic reaction. Moreover, the temperature gradient between the inlet and outlet expedites the Boudouard reaction [5,13,14]. Thus, Ni-based catalysts for low temperature steam reforming are easily deactivated by coke formation. Therefore, it is necessary to develop a catalyst with high resistance to coke formation at low temperatures.

In our previous work, to develop highly active and stable Ni-CeZrO$_2$ catalysts for low temperature SRM, the CeO$_2$/ZrO$_2$ ratio was optimized [5]. Ni-Ce$_{0.8}$Zr$_{0.2}$O$_2$ catalysts exhibited the highest CH_4 conversion due to the synergistic effect of the Ce$_{0.8}$Zr$_{0.2}$O$_2$ solid solution, resulting from high Ni dispersion and enhanced reducibility. However, the stability problem associated with coke formation of the Ni-Ce$_{0.8}$Zr$_{0.2}$O$_2$ catalyst was not fully addressed.

Researchers have attempted to improve catalytic performance and resistance against coke formation by the addition of promoters [15—28]. Dan et al. reported that the addition of La$_2$O$_3$ or CeO$_2$ on Ni/Al$_2$O$_3$ catalysts improves the SRM catalytic activity through the enhancement of Ni dispersion [15]. Nieva et al. discovered that Mg or Zn enhances the interaction between Ni and support/promoter on the Ni/Al$_2$O$_3$ catalysts for SRM [16]. Likewise, it has been widely reported that strong interaction between Ni and a support/promoter prevents coke formation. MgO and CaO are also known to improve the resistance of carbon formation by increasing the steam-carbon reaction and the neutralizing the acidity of the support [17—20]. In this study, MgO, CaO, and La$_2$O$_3$ are added on Ni-Ce$_{0.8}$Zr$_{0.2}$O$_2$ catalyst as promoters. These metal oxides have been known to improve the catalytic performance for the reforming reactions by enhancing the several properties. Because MgO has almost the same lattice parameter as NiO, two oxides can easily form a solid solution. NiO-MgO forming a solid solution is expected to enhance resistance against sintering and coke formation [21—23]. The coke deposition is diminished with the addition of CaO, which is attributed to the formation of carbonate species on Ca [24—26]. The addition of La$_2$O$_3$ on the Ni-based catalysts leads to the formation of a homogeneous NiLaO$_3$ solid solution. This is reported to

play an important role in the enhancement of Ni dispersion [27—32]. Our group developed a Ni-MgO-CeZrO$_2$ catalyst for the carbon dioxide reforming of methane with high resistance to coke formation [33]. However, according to our previous study for the thermodynamics analysis of the reforming reaction, coke formation strongly depends on the reaction conditions (reaction temperature, and pressure) and the type of oxidizing agent (CO$_2$, H$_2$O) even when the ratio between the oxidizing agent and CH$_4$ is same [14]. The coke formation originates from both the CH$_4$ decomposition and Boudouard reactions, but it is mainly affected by the Boudouard reaction in low temperature region. The coke formation is efficiently suppressed in higher ratio of oxidizing agent/CH$_4$. However, it is difficult to supply enough oxidizing agent in compact reformer due to the limitation of size and volume. Therefore, this study focuses on the performance of catalysts for the SRM at low temperatures and H$_2$O/CH$_4$ ratio.

The objectives of this study were the enhancement of the catalytic performance of the Ni-Ce$_{0.8}$Zr$_{0.2}$O$_2$ catalyst by the addition of metal oxides (La$_2$O$_3$, CaO, and MgO) as a promoter and the investigation of the promoter effect on the Ni-Ce$_{0.8}$Zr$_{0.2}$O$_2$ catalyst for the low-temperature reforming reaction. To understand the promoter effect for the catalytic performance on a Ni-Ce$_{0.8}$Zr$_{0.2}$O$_2$ catalyst, the catalysts were characterized with Brunauer—Emmett—Teller (BET), H$_2$-chemisorption, X-ray diffraction (XRD), temperature-programmed reduction (TPR), CO$_2$-temperature programmed desorption (CO$_2$-TPD), and thermogravimetric analyses (TGA).

Experimental

Catalyst preparation

Ni-Ce$_{0.8}$Zr$_{0.2}$O$_2$ (Marked as NCZO), Ni-MgO-Ce$_{0.8}$Zr$_{0.2}$O$_2$ (Marked as Mg-NCZO), Ni-CaO-Ce$_{0.8}$Zr$_{0.2}$O$_2$ (Marked as Ca-NCZO), and Ni-La$_2$O$_3$-Ce$_{0.8}$Zr$_{0.2}$O$_2$ (Marked as La-NCZO) catalysts were prepared by a co-precipitation method [34,35]. The Ni and metal oxide loading were fixed at 15 and 10 wt%, respectively. Stoichiometric quantities of Ni(NO$_3$)$_2$·6H$_2$O (97%, Junsei Chemical Co., Tokyo, Japan), Ce(NO$_3$)$_3$·6H$_2$O (99%, Sigma—Aldrich, St. Louis, MO, USA), zirconyl nitrate solution (20 wt% ZrO$_2$ basis, MEL Chemicals, Manchester, UK), Mg(NO$_3$)$_2$·6H$_2$O (99%, Sigma—Aldrich), Ca(NO$_3$)$_2$·4H$_2$O (99% Sigma—Aldrich), and La(NO$_3$)$_3$·H$_2$O (99.9%, Sigma—Aldrich) were combined in distilled water. To this solution, a 15% KOH solution was added drop-wise at 80 °C with constant stirring to attain a pH of 10.5. After digestion for 72 h, the catalysts were thoroughly washed with distilled water several times to remove any potassium impurities, then air-dried for 24 h followed by drying at 110 °C for 6 h. The catalysts were calcined at 500 °C for 6 h in air.

Characterization

The BET surface areas of catalysts were measured using a nitrogen physisorption technique on an ASAP 2010 (Micromeritics Instrument Corp., Norcross, GA, USA) accelerated surface area and porosimetry instrument [36]. Before analysis, the samples were degassed for 12 h at 110 °C under a vacuum