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Cyclic production of syngas and hydrogen through methane-reforming and water-splitting by using ceria–zirconia solid solutions in a solar volumetric receiver–reactor

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Abstract

For cyclic production of syngas and hydrogen by methane reforming (reduction) and water splitting (re-oxidation) under simulated solar-light irradiation, foam devices coated with ceria–zirconia ($Ce_xZr_{1-x}O_2$, where $x = 0.3$, 0.5 and 0.8) solid solutions and CeO_2 were used. Reduction characteristics of the foam devices were investigated in the temperature range from 873 to 1173 K. The solid solutions were found to be reduced more easily than pure CeO_2 especially at low temperatures. The gas yields by the solid solutions increased with increasing Ce content. Depending on temperature and composition of the solid solutions, the optimum operating times for methane reforming, during which carbon deposition was negligible, were determined. Among the solid solutions, $Ce_{0.8}Zr_{0.2}O_2$ showed the best stability and gas yields during repeated operations of the redox cycle at 1173 K, and it was confirmed from the XRD analysis that sintering of $Ce_{0.8}Zr_{0.2}O_2$ was the least. To find the effect of metallic foams on the gas productivity, a Ni foam coated with $Ce_{0.8}Zr_{0.2}O_2$ was investigated, and it rendered significantly higher gas yields than the SiC foam device; however, its long-term stability was assessed to be inferior to the latter.

Keywords: Ceria–zirconia; Foam device; Syngas; Hydrogen; Methane reforming-water splitting; Solar simulator

1. Introduction

Conversion of concentrated solar heat into chemical energy is increasingly recognized as an important technology for sustainable energy (Gokon et al., 2008, 2009, 2011; Kodama et al., 2009). For this purpose, many metal oxides have been investigated for stepwise production of syngas and hydrogen by performing cyclic redox operations consisting of methane reforming (MR: reduction) and water splitting (WS: re-oxidation) (Kodama et al., 2002, 2003; Kang et al., 2008, 2010; Jeong et al., 2011; Kwak et al., 2013, 2014; Jang et al., 2014a,b). The redox operations can be achieved under high temperatures obtained from concentrated solar heat, and the syngas and H_2 produced can be used for synthesis of other chemicals such as methanol and synthetic fuels and for fuel cells. One advantage of the use of CH_4 as a reducing agent is that reduction can be achieved below 1273 K, while direct thermal reduction of metal oxides requires temperatures higher than 1673 K (Steinfeld et al., 1993, 1998; Otsuka et al., 1999; Kodama et al., 2000; Shomizu et al., 2001; Go et al., 2008). For example, Abanades and Flamant (2006) studied a solar redox process for H_2 production based on

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CeO_2. The reduction of CeO_2 was carried out thermally at a very high temperature (2273 K) and the melting and vaporization of Ce_2O_3 were observed. Nevertheless, the redox system of CeO_2 is considered a promising candidate for the cyclic process if MR and WS are performed at lower temperatures (Jeong et al., 2011).

Various metal oxides have been investigated for cyclic production of syngas and hydrogen production by MR and WS:Fe_3O_4 (Steinfeld et al., 1993), ZnO (Steinfeld et al., 1998), Ni-, Co-, Zn-, Mn- and Cu ferrites (Kodama et al., 2002; Go et al., 2008; Kang et al., 2008, 2010), CeO_2 (Jeong et al., 2011; Jang et al., 2014a, 2014b), and WO_3 (Kodama et al., 2000, 2003; Kwak et al., 2013, 2014). Among these, CeO_2 is interesting because it has been reported that CeO_2 has unique redox properties and high oxygen storage capacity compared with other metal oxides such as Fe_3O_4, ZnO, and WO_3 (Jeong et al., 2011). In addition, it has been reported that CeO_2 can decrease carbon deposition during MR when used as the support. For example, Kang et al. (2010) investigated the redox cycling of $CuFe_2O_4$ supported on ZrO_2 and CeO_2 for a two-step syngas and hydrogen production process. They reported that using the supports improved the reactivity, and CeO_2 was revealed to be a better support than ZrO_2 in the aspect of reactivity, suppression of carbon deposition and CO selectivity during repeated cyclic reactions.

CeO_2/ZrO_2 systems have been investigated in our laboratory. Jeong et al. (2011) found that ZrO_2-supported CeO_2 systems exhibited good performance and reproducibility during repeated cyclic operations of MR and WS in a tube furnace. It was also found that carbon deposition was inevitable and became more serious at higher temperatures and/or with longer operation times. Hence, the optimum operating temperature and reaction time were determined for minimization of the carbon deposition. Jang et al. (2014a) investigated the effect of foam devices on the syngas and hydrogen production employing SiC, Ni and Cu foams coated with ZrO_2-supported CeO_2 powders; the foams were installed in a volumetric receiver–reactor equipped with a solar simulator. During ten repeated cyclic operations on the foam devices, the Ni and Cu foams showed better gas yields than the SiC foam, primarily due to the high thermal conductivity of the metals which could attain more uniform temperature throughout the foams. In addition, partial reduction and re-oxidation of the metallic foams considerably contributed the increase in the gas yields.

Studies on CeO_2–ZrO_2 mixed oxide solid solutions ($Ce_xZr_{1-x}O_2$) as well as ZrO_2-suppoted CeO_2 reported that addition of ZrO_2 to CeO_2 led to improvements in oxygen storage capacity, redox properties and thermal resistance (Hori et al., 1998; Pengpanich et al., 2002, 2004). A primary cause for the improvements is known to be partial replacement of Ce cations in the crystal lattice with Zr cations. It was also demonstrated that $Ce_xZr_{1-x}O_2$ solid solutions produced syngas with a H_2/CO ratio of 2.0 and the production rates of H_2 and CO were increased. In addition, Sim et al. (2010) reported that a $Ce_xZr_{1-x}O_2$ solid solution stabilized non-stoichiometric tungsten oxide during the redox reactions by methane and water, by which reduction of WO_3 did not proceed beyond WO_2 at 1023 K and the redox cycle could be repeated many times without loss of hydrogen production efficiency. However, the H_2/CO ratio in the syngas was close to unity due to formation of H_2O, which is a characteristic involved with tungsten oxides.

Even though $Ce_xZr_{1-x}O_2$ solid solution has high thermal stability and higher potential for oxidizing methane (or in itself higher reducibility by methane) due to better oxygen storage capacity than CeO_2 (Hori et al., 1998; Pengpanich et al., 2002, 2004), it has rarely been used as the metal oxide for the redox process. On the other hand, a solar volumetric receiver–reactor requires a foam device by which the energy in concentrated solar radiation can directly be absorbed (Do et al., 2012). In this study, a SiC foam device coated with $Ce_xZr_{1-x}O_2$ ($x = 0.3$, 0.5, 0.8 and 1) was employed for the cyclic production of syngas and hydrogen by MR and WS under simulated solar-light irradiation. The role of the SiC foam device was the receiver with high thermal and chemical stability for absorbing concentrated solar radiation as well as the reactor with the coated solid solutions for the redox reactions. In addition, a Ni foam was also investigated to confirm its effects suggested in our previous study (Jang et al., 2014a). The objectives were to investigate the yields of syngas and hydrogen with respect to temperature and time, to find the optimum MR times for negligible carbon deposition, to evaluate the long-term stability of the solid solutions during repeated cyclic operations, and to determine the optimum composition of the solid solution.

2. Experimental

2.1. Synthesis of $Ce_xZr_{1-x}O_2$ powder

$Ce_xZr_{1-x}O_2$ solid solutions were prepared by a precipitation method. An aqueous solution of cerium nitrate was prepared by dissolving $Ce(NO_3)_3 \cdot 6H_2O$ (from Kanto Chemical, 99.99% purity) in deionized water, and to this solution $ZrOCl_2 \cdot 6H_2O$ (Sigma–Aldrich, 98% purity) as the precursor of zirconia was added, and then the pH of the solution was adjusted to 9.5 by adding ammonia water while stirring. After 2 h, the precipitate in the mixture was filtered by using an aspirator (Joie-Tech., VE-11), washed with distilled water, and then dried at 343 K for 12 h. The dried solid was calcined at 1173 K for 6 h in a muffle furnace (DeaHeung Science, DF-ZC) and then crushed into powder with particles smaller than 90 μm. The Ce/Zr ratio was adjusted using the corresponding amounts of the precursors to obtain $Ce_xZr_{1-x}O_2$, where $x = 0.3$, 0.5, 0.8 and 1; the prepared samples were named CeZrX ($X = 3$, 5 and 8) and CeO_2, respectively.

2.2. Foam devices as the radiation absorber

The foam devices were prepared by following the procedure described in our previous study (Jang et al., 2014a), as