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The effect of Zn addition into $NiFe_2O_4$ catalyst for high-temperature shift reaction of natural gas reformate assuming no external steam addition

Myung Suk Lee [a,1], *Joon Yeob Lee* [a,1], *Dae-Won Lee* [b,*], *Dong Ju Moon* [c,d], *Kwan-Young Lee* [a,d,**]

[a] *Department of Chemical and Biological Engineering, Korea University, 5-1, Anam-dong, Seongbuk-gu, Seoul 136-713, Republic of Korea*
[b] *Research Institute of Clean Chemical Engineering Systems, Korea University, 5-1, Anam-dong, Seogbuk-gu, Seoul 136-713, Republic of Korea*
[c] *Clean Energy Center, Korea Institute of Science and Technology (KIST), 39-1, Hawolgokdong, Seongbuk-gu, Seoul 136-130, Republic of Korea*
[d] *GREEN SCHOOL, Korea University, Anam-dong, Seongbuk-gu, Seoul 136-713, Republic of Korea*

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ABSTRACT

In this study, the effect of the addition of Zn to a $NiFe_2O_4$ catalyst was investigated for a high-temperature shift (HTS) of the natural gas reformate under the assumption that no external steam was added. In our previous study, $NiFe_2O_4$ proved to be a notable HTS catalyst, but it produced methane as a by-product in the presence of such a highly reductive reformate. In this study, we found that the addition of Zn to $NiFe_2O_4$ was effective in suppressing methanation as well as in promoting HTS activity. Such improvements were expected to be related to the enhanced redox property of the inverse-spinel species included in the catalyst. To elucidate the effects of Zn addition, inductively coupled plasma spectroscopy (ICP), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), thermo-gravimetric analysis under a CO gas atmosphere (CO-TGA), and temperature-programmed reduction of H_2 (H_2-TPR) were performed.
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1. Introduction

Hydrogen is considered the most promising alternative energy source to petroleum because, among the chemical fuels available, it not only exhibits the high heating value (122 kJ/g) but is also the most environmentally clean alternative [1]. Hydrogen is generally (and commercially) produced through the steam reforming of hydrocarbons. Among the hydrocarbon feedstocks available, natural gas (methane) has great potential because methane exhibits the highest in H/C ratio among hydrocarbon resources [2]. However, when natural gas is used as a hydrogen resource for polymer electrolyte membrane fuel cells (PEMFC), the carbon monoxide in the reformate gas should be reduced to less than 10 ppm because it poisons the Pt electrodes of PEMFCs [3,4].

* *Corresponding author*. Research Institute of Clean Chemical Engineering Systems, Korea University, 5-1, Anam-dong, Seogbuk-gu, Seoul 136-713, Republic of Korea. Tel.: +82 2 3290 3727; fax: +82 2 926 6102.
** *Corresponding author*. Department of Chemical and Biological Engineering, Korea University, 5-1, Anam-dong, Seongbuk-gu, Seoul 136-713, Republic of Korea. Tel.: +82 2 3290 3299; fax: +82 2 926 6102.
E-mail addresses: stayheavy@korea.ac.kr (D.-W. Lee), kylee@korea.ac.kr (K.-Y. Lee).
[1] These authors contributed equally to the manuscript.
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The water–gas shift reaction (WGSR) has been adopted in most steam reforming processes to reduce carbon monoxide in the steam-reformate. It is also advantageous in that extra hydrogen is produced during the reaction (Eq. (1)) [5,6].

$$CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g), \quad \Delta H^{o}_{298} = -41.1\ kJ/mol \qquad (1)$$

Due to the exothermic, reversible nature of the reaction, the WGSR is usually performed in two stages: a high-temperature shift (HTS) reaction conducted at 350–450 °C for the rapid conversion of CO, which leads to a low-temperature shift (LTS) reaction at 200–250 °C in which further CO conversion is performed under relaxed equilibrium conditions. In commercial applications, Fe-based (*e.g.,* Fe/Cr/Cu) and Cu-based (*e.g.,* Cu/Zn/Al) catalysts have generally been used for the HTS and LTS reactions, respectively [7–12].

Most of the Fe-based catalysts applied in the HTS processes consist of inverse-spinel (ferric) oxides. The spinel structure is basically defined as $A^{2+}_{(1-x)}B^{3+}_{x}[A^{2+}_{x}B^{3+}_{(2-x)}]O_4$, where x is the degree of inversion, which implies the stoichiometric fraction of A^{2+} ions that occupy octahedral sites. Spinel structures are classified into three types according to x: normal spinels ($A^{2+}[B^{3+}]_2O_4$, $x = 0$), inverse-spinels ($B^{3+}[A^{2+}B^{3+}]O_4$, $x = 1$) and mixed spinels ($0 < x < 1$). The inverse and mixed spinels are known to have catalytic activity that originates from a change in the oxidation state of the B-site ion (+2 and +3) [13].

In the HTS reaction, the most well-known inverse-spinel oxide, Fe_3O_4 (*magnetite*), is known to be catalytically active but easily deactivated through thermal agglomeration [14]. Chromium oxide (Cr_2O_3) is usually introduced to retard the thermal sintering of Fe_3O_4; consequently, some commercialized HTS catalysts are structured on the basis of Cr/Fe entities [15]. However, the level of ~1 wt.% Cr^{6+} in commercial HTS catalysts should be decreased or replaced with another element because of its toxicity to humans and other organisms [16]. Hence, many researchers have investigated catalysts that maintain (or improve) the WGSR activity of Fe/Cr-based catalysts by replacing Cr with transition metals such as Ni, Mo, Cu, V, Mn, Co or Zn [13,14,17–29].

The *R* factor (reduction factor; Eq. (2)) is used to estimate the degree of a catalyst to undergo reduction in a given steam-reformate in the HTS operation:

$$R = \frac{P_{CO} + P_{H_2}}{P_{CO_2} + P_{H_2O}} \qquad (2)$$

Operations conducted with iron oxide catalysts in a high *R* factor ($R > 1.6$) result in the over-reduction of Fe_3O_4 species, which yields FeO and/or metallic iron [15]. Consequently, the *R* factor has been decreased to approximately 1 by the addition of a large amount of extra steam [13,15,19,22]. However, the addition of extra stream should be minimized or eliminated due to the corresponding increase in operational costs [19,20]. Therefore, the development of a robust catalyst for HTS processes under highly reductive, natural gas reformates with no external stream addition is necessary. Under the assumption of a no-additional-steam WGSR operation, a natural gas reformate, which this study deals with, is more reductive than those of any other hydrocarbon reformates because, with no-additional-steam added, the *R* factor reaches $R = 2$ when the steam reforming progresses with 100% CH_4 conversion at a H_2O/CH_4 ratio of 3 [14].

In our previous studies, a Ni/Fe catalyst exhibited high HTS activity at 400 °C under natural gas reformate conditions, which was comparable to those achieved with magnetite and commercial catalysts. However, as the catalyst contained nickel oxide as a component, it showed a drawback that methanation occurred during its HTS catalysis [14]. In this study, Zn was added to a Ni/Fe catalyst to restrain methanation and increase HTS activity. This approach was based on literature reports that the addition of Zn to Ni-containing catalysts is effective in suppressing methanation in various reactions [30–33]. Moreover, Zn was selected because it was basically one of the most widely known, WGSR-active elements along with Pt, Cu, Fe [34,35]. Also, Zn is well known to have high affinity for spinel structure and increase the stability of spinels [36]. The HTS activity of the Zn/Ni/Fe catalyst was measured under natural gas reformate conditions under the assumption that no extra stream was added ($R = 2$). The catalysts were characterized using X-ray diffraction (XRD), inductively coupled plasma spectroscopy (ICP), N_2-adsorption analysis (Brunauer–Emmett–Teller (BET) method), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis under a CO atmosphere (CO-TGA) and temperature-programmed reduction of H_2 (H_2-TPR).

2. Experimental

2.1. Preparation of catalysts

All of the catalysts were prepared using the co-precipitation method. Initially, the metal precursors (nitrate hydrate forms, Aldrich) were dissolved together in deionized water. An aqueous solution of sodium hydroxide (2.5 M) was dropped slowly into the precursor solution under vigorous stirring until the pH reached 8.5. The precipitates were aged overnight. After being collected by filtration, the precipitates were washed several times with sufficient amounts of deionized water. The washed cakes were dried at 110 °C for 24 h and calcined at 500 °C for 5 h. The notations, elemental compositions and BET surface areas of the prepared catalysts are listed in Table 1.

2.2. Characterization of catalysts

The BET properties were measured using the N_2-adsorption method with a Micromeritics ASAP 2010 apparatus. The XRD

Table 1 – The notations, BET areas and elemental compositions of the prepared catalysts.

Notation of catalyst	Elemental composition		BET area [m^2/g] [b]
	Intended weight ratio	Weight ratio from ICP analysis	
F	Fe [100 wt.%]	N.M.[a]	40
ZF	Zn [5 wt.%]/Fe	Zn [4.2 wt.%]/Fe	11
NF	Ni [34 wt.%]/Fe	Ni [33.9 wt.%]/Fe	79
ZNF	Zn [5 wt.%]/Ni [32 wt.%]/Fe	Zn [5.7 wt.%]/Ni [31.8 wt.%]/Fe	55

a Not measured.
b Measured for a sample in the fresh state.

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