



Performance of spinel ferrite catalysts integrated with mesoporous Al_2O_3 in the high temperature water–gas shift reaction



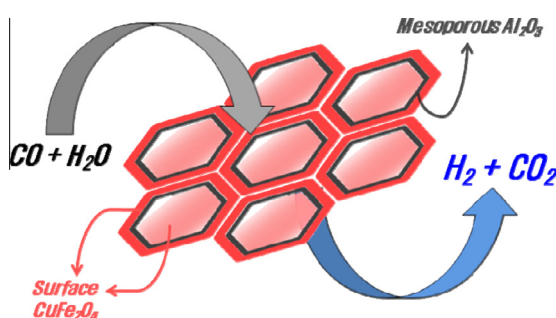
Dae-Woon Jeong, Ajay Jha, Won-Jun Jang, Won-Bi Han, Hyun-Seog Roh*

Department of Environmental Engineering, Yonsei University, 1 Yonseidae-gil, Wonju, Gangwon 220-710, South Korea

HIGHLIGHTS

- Spinel ferrite catalysts supported on mesoporous Al_2O_3 have been applied for WGS.
- Cu-modified Fe_3O_4 -MA showed the highest CO conversion.
- The Cu/Fe ratio was systematically varied to optimize $\text{Cu}_x\text{Fe}_{(3-x)}\text{O}_4$ -MA catalysts.
- The $\text{Cu}_{1.5}\text{Fe}_{1.5}\text{O}_4$ -MA exhibited stable activity with TOS even at a very high GHSV.
- The improved performance of the catalyst is correlated with easier reducibility.

GRAPHICAL ABSTRACT



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ABSTRACT

The present study focuses on the use of spinel ferrite (MFe_2O_4) catalysts ($\text{M} = \text{Ni}, \text{Co}, \text{Fe}, \text{or Cu}$) integrated with mesoporous alumina for the high temperature water–gas shift (WGS) reaction. Among these catalysts, copper ferrite integrated with mesoporous alumina exhibits outstanding performance. To optimize the Cu/Fe ratio in the copper ferrite catalyst, we prepared different $\text{Cu}_x\text{Fe}_{(3-x)}\text{O}_4$ -MA catalysts ($x = 0.5, 1.0, 1.5, 2.0, \text{or } 2.5$) by varying the Cu/Fe mole ratio. Of the various Cu/Fe catalysts, the 1:1 mole ratio of Cu/Fe exhibited the highest CO conversion (84%) and 100% selectivity to CO_2 at a very high GHSV of $42,000 \text{ h}^{-1}$. The improved performance of the catalyst is correlated with its easier reducibility.

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1. Introduction

In the current era, the high temperature water–gas shift (WGS; $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{CO}_2$) reaction has gained new interest in relation to the production of pure hydrogen from waste-derived synthesis gas [1]. Waste-derived synthesis gas consists of a wide range of gaseous products, including H_2 , CO, CO_2 , CH_4 , N_2 , and possesses a higher concentration of CO than the synthesis gas produced from

the steam reforming of hydrocarbons. Because of the high concentration of CO in the waste-derived synthesis gas, which can make the conditions severe for the reaction, it is necessary to develop a novel high temperature WGS catalyst to withstand these severe conditions.

The WGS reaction offers the ability to produce clean H_2 for many technological applications, such as the synthesis of NH_3 and the removal of CO contamination in feed streams for fuel cells [2]. Industrially, the WGS reaction occurs in two stages: a high temperature shift (HTS) at $350\text{--}500^\circ\text{C}$ and a low temperature shift (LTS) at $180\text{--}250^\circ\text{C}$ [3–5]. The commercial catalysts used for the HTS and the LTS are $\text{Fe}_2\text{O}_3\text{--Cr}_2\text{O}_3$ and Cu–Zn–Al oxide, respectively

* Corresponding author. Tel.: +82 33 760 2834; fax: +82 33 760 2571.

E-mail address: hsroh@yonsei.ac.kr (H.-S. Roh).

[6–8]. These oxide catalysts are pyrophoric and normally require lengthy and complex activation steps prior to the WGS reaction [9]. The catalytically active phase of iron oxide for the WGS is Fe_3O_4 (magnetite), which is produced by the partial reduction of Fe_2O_3 (hematite) [10]. Extreme care is required during the reduction process to avoid the formation of metallic iron via over reduction, which may lead to undesirable side reactions. In addition, pure magnetite catalysts rapidly lose activity at higher temperatures because of the reduction in surface area caused by sintering. To solve this problem, Cr_2O_3 was incorporated into the commercial catalyst ($\text{Fe}_2\text{O}_3\text{--Cr}_2\text{O}_3$), in which chromium is recognized as a stabilizer to prevent the thermal sintering of Fe_3O_4 and subsequent loss of catalyst surface area [11]. However, during the WGS reaction, Cr^{3+} is oxidized to Cr^{6+} , which is soluble in water and considered to be a very toxic for the living organisms [12]. Therefore, extensive attention has been paid to develop a Cr-free Fe based catalyst for the WGS reaction [13–17].

Researchers first attempted to replace Cr using an element capable of forming a spinel structure with iron oxide [13–15]. The replacement for Cr was selected according to ionic radius and oxidation number. Fe/Zn [13,14], Fe/Mg [13], Fe/Ca [15], and Fe/Zr [15] catalysts were used for the WGS reaction, but the activities of these modified catalysts were lower than that of magnetite. The promising results for a Cr-free Fe based catalyst were reported by Araújo et al. [16] and Liu et al. [17] who replaced the Fe/Cr catalyst with a Fe/Al based catalyst. Al_2O_3 has been reported to be a viable replacement of the toxic Cr_2O_3 support, which may improve catalytic stability in the HT-WGS reaction [1]. Moreover, the incorporation of Al into the iron oxide system is more facile because of the similarity in the ionic radius of Al^{3+} (0.675 Å) and Fe^{3+} (0.690 Å). Thus, Al is expected to be easily incorporated into the iron oxide lattice. In addition to the potential environmental concerns over Cr based catalysts, the activation of Fe_2O_3 to catalytically active Fe_3O_4 is also a crucial factor. Therefore, researchers have studied a Fe–Al–Cu catalyst for use in the WGS reaction because Cu selectively promotes the reduction of hematite to magnetite in ferrite catalysts by hydrogen spillover effect [10,18,19]. In addition, Cu is well known as a structural promoter that provides new active sites in the WGS reaction [20,21].

In our previous study, we designed a CuFe_2O_4 catalyst integrated with mesoporous alumina ($\text{CuFe}_2\text{O}_4\text{--MA}$) for the high temperature WGS reaction [22]. The $\text{CuFe}_2\text{O}_4\text{--MA}$ catalyst exhibited stable CO conversion (80%) with high selectivity for CO_2 and H_2 at 500 °C for 10 days under realistic conditions without any pre-activation. Integration of CuFe_2O_4 with mesoporous alumina was found to play a key role in determining the performance of the $\text{CuFe}_2\text{O}_4\text{--MA}$ catalyst in the HT-WGS reaction. The $\text{CuFe}_2\text{O}_4\text{--MA}$ catalyst clearly showed higher catalytic performance than bare CuFe_2O_4 catalyst and CuFe_2O_4 catalyst integrated with conventional alumina. Integration of CuFe_2O_4 with mesoporous alumina in a honeycomb-like nano-architecture ensures an uninterrupted diffusion of molecules to and from the active sites of the catalysts [23,24]. In the $\text{CuFe}_2\text{O}_4\text{--MA}$ catalyst, alumina acts as a texture promoter and aids in the fine dispersion of copper ferrite, whereas the role of CuO is to accelerate the WGS reaction by promoting the $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ reduction at a lower temperature. CuFe_2O_4 is an inverse spinel consisting of Cu^{2+} in the octahedral site and Fe^{3+} ions equally distributed in the tetrahedral and octahedral sites. The substitution of Cu^{2+} for Fe^{2+} in the octahedral site can increase the electron hopping between $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$, subsequently leading to an increase in the catalytic activity via the formation of $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Cu}^{2+}/\text{Cu}^+$ redox couples. Ni has been considered unsuitable as a catalyst for the WGS reaction due to its high methanation activity. However, Ni based catalysts have a higher CO adsorption efficiency than Cu based catalysts [12,25]. In addition, Ni is capable of forming a solid solution with iron oxide,

producing a Fe/Ni catalyst that exhibits reasonable WGS activity [12,25]. Cobalt oxide catalysts have also attracted much attention due to their unique activity for ambient CO oxidation [26].

In light of this, different Fe-substituted metal ferrite catalysts ($\text{M} = \text{Co}, \text{Ni}, \text{or Cu}$) integrated with mesoporous alumina were prepared by the sol–gel method using a non-ionic triblock copolymer template, $(\text{EO})_{20}(\text{PO})_{70}(\text{EO})_{20}$. The purpose of the use of template is to give mesoporous structure to the catalysts. The performances of these catalysts toward the high temperature WGS reaction were compared within the reaction temperature range of 350–550 °C. Among the screened metal ferrite catalysts, CuFe_2O_4 integrated with mesoporous alumina exhibited superior performance in the high temperature WGS reaction. The objective of the present study is to determine the optimum ratio of Cu/Fe for incorporation into the mesoporous alumina to promote maximum WGS activity. The chosen atomic ratios for the Cu/Fe catalysts were 0.2, 0.5, 1, 2, and 5. The effect of the Cu/Fe ratio on the structure and physicochemical properties of the $\text{Cu}_x\text{Fe}_{(3-x)}\text{O}_4\text{--MA}$ catalysts were examined by the X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), BET, hydrogen-temperature programmed reduction ($\text{H}_2\text{--TPR}$), and ultraviolet–visible spectroscopy (UV–vis) techniques. In particular, we attempted to explain the relationship between the addition of Cu and reduction patterns of Fe species using $\text{H}_2\text{--TPR}$, XPS, and UV–vis techniques. These reduction patterns strongly affect the catalytic performance in the WGS reaction.

2. Experimental

2.1. Catalyst preparation

The spinel ferrite (MFe_2O_4) catalysts ($\text{M} = \text{Ni}, \text{Co}, \text{Fe}, \text{or Cu}$) integrated with mesoporous alumina were prepared by the sol–gel method using a non-ionic template (P123). The loadings of spinel ferrite and mesoporous alumina were fixed at 30 wt% and 70 wt%, respectively. The M:Fe ratio of 1:2 was maintained in the total quantity of 10 mmol. In a typical synthesis, solution ‘A’ was prepared by dissolving 1.0 g of $(\text{EO})_{20}(\text{PO})_{70}(\text{EO})_{20}$. Triblock copolymer (Pluronic P123, molecular weight = 5800, Sigma–Aldrich) into 10 ml of anhydrous *iso*-butanol. Similarly, solution ‘B’ was made with the combination of 10 ml of anhydrous *iso*-butanol, 1.0 g P123 and corresponding nitrates precursors of different metals ($\text{M} = \text{Ni}, \text{Co}, \text{Fe}, \text{or Cu}$). Both solution A and B were allowed to stir separately for 1 h. Meanwhile, 10 mmol of aluminum *iso*-propoxide was dissolved into 10 ml of anhydrous *iso*-butanol and 1.6 ml of 67 wt% HNO_3 . Once dissolved, it was added to solution A, and then solution B was also mixed drop by drop with solution A. To obtain a homogeneous solution, the entire mixture solution was stirred for 5 h. Next, the formed gel was kept at 120 °C for 48 h in an oven for solvent evaporation. The final catalyst, $\text{MFe}_2\text{O}_4\text{--MA}$, was obtained after calcination at 400 °C for 5 h. A series of copper ferrite catalysts integrated with mesoporous alumina were also prepared by varying the molar ratio of Cu/Fe in the range of 0.2–5. The amount of Al_2O_3 was fixed to 10 mmol in all the catalysts. The catalysts prepared are henceforth denoted as $\text{Cu}_{0.5}\text{Fe}_{2.5}\text{O}_4\text{--MA}$, $\text{Cu}_{1.0}\text{Fe}_{2.0}\text{O}_4\text{--MA}$, $\text{Cu}_{1.5}\text{Fe}_{1.5}\text{O}_4\text{--MA}$, $\text{Cu}_{2.0}\text{Fe}_{1.0}\text{O}_4\text{--MA}$, and $\text{Cu}_{2.5}\text{Fe}_{0.5}\text{O}_4\text{--MA}$.

2.2. Characterization

The BET surface area was measured by nitrogen adsorption at -196 °C using an ASAP 2010 (Micromeritics). XRD patterns were recorded using a Rigaku D/MAX-IIIC diffractometer (Ni filtered Cu K α radiation, 40 kV, 100 mA). The crystallite size was estimated using the Debye–Scherrer equation [27–29]. $\text{H}_2\text{--TPR}$ experiments

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