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Revisiting magnesium oxide to boost hydrogen production via water-gas shift reaction: Mechanistic study to economic evaluation

Seongmin Jin^a, Yongha Park^{a,b}, Gina Bang^a, Nguyen Dat Vo^a, Chang-Ha Lee^{a,*}^a Department of Chemical and Biomolecular Engineering, Yonsei University, Seoul, Republic of Korea^b Center for Hydrogen Fuel Cell Research, Korea Institute of Science and Technology, Seoul, Republic of Korea

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ABSTRACT

Herein, we report the use of a MgCeO_x-supported Cu (MgCuCe) catalyst with a unique bead structure to augment the water-gas shift (WGS) reaction. The MgCuCe catalyst exhibited an exceptionally high reaction rate of 83 μmol g⁻¹ s⁻¹ at 300 °C, compared with that without MgO (30 μmol g⁻¹ s⁻¹). Very few studies have focused on MgO-supported catalysts owing to the reports on the inferior activity of MgO. However, this paper reports unprecedented enhancements by introducing MgO and illustrates the WGS reaction mechanism: (1) numerous defects promoted water dissociation and subsequent associative mechanism; (2) the labile oxygen in MgO participated in redox mechanisms. The hydrogen production cost realized due to the use of the MgCuCe was 0.63 USD/kg H₂, which is lower than that achieved by using commercial and CeO₂-supported catalysts. This study paves the way for exploiting earth-abundant MgO in developing efficient catalysts and contributes to reducing H₂ production costs.

1. Introduction

The water-gas shift (WGS) reaction is an important industrial process in the production of H₂, which is widely considered as an attractive energy carrier. Since the WGS reaction causes high exergy destruction [1], oxide-supported Cu catalysts have been extensively studied to enhance the reaction because of the high activity and low price of Cu. In this regard, the roles of the support and the interaction between the metal and oxide have been investigated in attempts to enhance the catalyst performance [2,3]. Among the many advanced catalysts, Cu/CeO₂ catalysts have shown potential owing to their prominent reducibility and oxygen storage capacity [4,5].

The structure-activity relationship derived via different synthesis methods [6], design of inverse catalysts [7], direct observation of the atomic structure [4], and *in situ* techniques [8] have been thoroughly examined to comprehend the catalytic active sites in Cu/CeO₂ catalysts. The general consensus is that the roles of the metal and metal oxide phase are the adsorption of CO and the adsorption and dissociation of water, respectively [2]. In the redox mechanism underlying the WGS reaction, CO adsorbed on the metal is oxidised by an oxygen atom of CeO₂ at the metal/oxide interface, followed by re-oxidation of Ce₂O₃ by H₂O [9]. In the associative mechanism, CO adsorbed on Cu reacts with

surface OH groups on ceria to produce intermediates, such as carboxyl, formate, or carbonates [2,10], which eventually decompose to generate the products, H₂ and CO₂.

It is widely known that the interface between copper and ceria is an active site where the important step in both reaction mechanisms occurs [4]. Specifically, it was reported that the strongly bound Cu-[O_x]-Ce species, plausibly associated with the oxygen vacancies of ceria, have a significant impact on the catalyst activity during the WGS reaction [4, 11]. However, the use of highly dispersed Cu nanoparticles to increase the interface between Cu and CeO₂ is limited by the susceptibility of these species to thermal sintering [12], which leads to deactivation of the catalysts [13]. Therefore, it is highly important to design alternative routes for achieving high activity while preventing the sintering of the Cu species.

A few studies were conducted about the activity of MgO-supported noble metal catalysts for the WGS reaction, but the results of these studies indicated that the activity was much inferior than that of the ceria-supported catalysts [10,14]. However, it was reported that water is preferentially dissociated at the edge or corner sites on the MgO surface, and the isolated OH groups are responsible for producing the surface formate by reacting with adsorbed CO [15]. Although the importance of OH groups in MgO has been emphasised, research on MgO-supported

* Corresponding author.

E-mail address: leech@yonsei.ac.kr (C.-H. Lee).<https://doi.org/10.1016/j.apcatb.2020.119701>

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