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journal homepage: www.elsevier.com/locate/jiecEffective hydrogen production from ethanol steam reforming using CoMg co-doped $\text{SiO}_2@\text{Co}_{1-x}\text{Mg}_x\text{O}$ catalystKang Min Kim^a, Byeong Sub Kwak^a, Younghwan Im^a, No-Kuk Park^b, Tae Jin Lee^b, Sang Tae Lee^c, Misook Kang^{a,*}^a Department of Chemistry, College of Natural Science, Yeungnam University, Gyeongsan, Gyeongbuk 38541, Republic of Korea^b School of Chemical Engineering, Yeungnam University, Gyeongsan, Gyeongbuk 38541, Republic of Korea^c Wooshin Com., Gyeongsan, Gyeongbuk 38470, Republic of Korea

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ABSTRACT

In this study, the activities of core@shell-structured $\text{SiO}_2@\text{Co}_{1-x}\text{Mg}_x\text{O}$ catalysts in ethanol steam reforming (ESR) were investigated, and the promotion effect of Mg upon H_2 production was assessed. The loading of $\text{SiO}_2@\text{CoO}$ with Mg resulted in an increase in ethanol conversion and H_2 yield with the concomitant suppression of carbon coke deposition and CO emission. Oxygen transfer from the MgO supporter (or improver) to the main cobalt catalytic species during ESR might play a role in maintaining the partially oxidized Co state. In longevity tests, the $\text{SiO}_2@\text{Co}_{1-x}\text{Mg}_x\text{O}$ core@shell material, despite being reused three times, exhibited superior H_2 production for 100 h without structural collapse or coke formation.

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Introduction

Much research effort has been dedicated to the use of non-noble metals, such as Ni or Co, as potential catalytic species in ethanol steam reforming (ESR) because of their high dehydrogenation activity and low cost [1,2]. However, catalytic deactivation is a serious problem with monometallic catalysts that contain only Ni or Co, due mainly to the deposition of various types of carbon on their surfaces, and cobalt or nickel sintering [3,4]. In general, the addition of small amounts of promoter elements to a catalyst material significantly improves its steam reforming activity and stability [5,6], as indicated by the partial oxidation of the metallic sites observed after exposure to the reaction medium. For example, lanthanides enhance the sintering resistance, leading to smaller nickel or cobalt crystallites in Ni- or Co-based catalysts [7,8]. Cerium promotion effectively inhibits coking by increasing the number of active oxygen species on the nickel or cobalt surface owing to its enhancement of water adsorption and gasification [9,10]. The incorporation of cerium also decreases the dissolution and diffusion of carbon through nickel and cobalt particles, thereby preventing the formation of carbon filaments. Recently, the use of

ceria has become more common because it improves catalytic stability and activity, due primarily to its higher oxygen mobility.

Despite these advantages, the catalytic species mentioned above are too expensive for general use in industry. Therefore, alkaline earth metal species have been developed as relatively inexpensive promoter elements [11]. Ca and Mg are used most commonly because of their appropriate basicity [12,13]. In recent years, the use of MgO has increased rapidly. The presence of Mg in the support decreases Ni^{2+} reducibility and increases basicity and specific surface area, allowing higher dispersion of metallic particles and improved resistance to carbon deposition during the ESR reaction [14,15]. Generally, Ni/MgO catalysts exhibit higher activity and selectivity for H_2 production than Co/MgO catalysts because of the lower tendency of Ni to oxidize during the reaction and thus promote the carbon monoxide methanation and ethanol decomposition reactions [16]. Nevertheless, coke formation is strongly suppressed through the use of the basic carrier MgO. Therefore, Ni or Co/MgO catalysts possess appropriate characteristics for application as an efficient catalytic system for the production of H_2 .

Core@shell materials, however, have enormous potential as catalytic materials, as their porous shells act as selective barriers against impurities, poisons, and byproducts, resulting in enhanced catalyst activity, selectivity, and lifetime. For example, Zhang et al. [17], who conducted an out-of-cell test simulating the operating

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