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Synergies between Ni, Co, and Mn ions in trimetallic $Ni_{1-x}Co_xMnO_4$ catalysts for effective hydrogen production from propane steam reforming

Seung Won Jo [a], Younghwan Im [a], Jeong Yeon Do [a], No-Kuk Park [b], Tae Jin Lee [b], Sang Tae Lee [c], Moon Soon Cha [d], Min-Kyu Jeon [d], 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
[d] ORDEG Co., Ltd., 331 Songdogukje-daero, Yeonsu-gu, Inchon, 21990, Republic of Korea

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ABSTRACT

To suppress the rapid degradation of Ni-based catalysts, Co along with Ni was used as a catalytic active species with a Mn oxide promoter that has excellent oxygen transfer ability. This study examines the optimal ratios between Ni and Co in the synthesized catalyst $Ni_{1-x}Co_xMnO_4$ for high hydrogen production in the propane reforming reaction. The synthesized catalysts were characterized by XRD, TEM, XPS, and TPD of CO, C_3H_8, and H_2O, and TPR of H_2. In addition, the reaction mechanism of propane reforming and the behaviors of the gases adsorbed on the catalyst were investigated by NMR analysis. The results confirmed that the reduction of Ni mainly occurs before that of Co, which means that Ni acts as the main active species. In addition, gas adsorption increases over catalysts that contain both Ni and Co; the synthesized catalysts also showed improved catalytic activities. The optimum ratio of Ni:Co is 0.6:0.4, with high hydrogen evolution of >80%; complete propane conversion was obtained for the $30Ni0_{0.6}Co_{0.4}MnO_4/Al_2O_3$ catalyst over 10 h.

1. Introduction

Hydrogen does not affect the environment adversely, unlike fossil fuels and nuclear power, and thus is considered a clean next-generation energy source with great potential for commercialization. When calculating the energy efficiency compared with the amount of hydrogen that can be produced economically, the most efficient method is reforming using fossil fuels as a hydrogen source, and almost half of the total hydrogen produced globally has been prepared in this way. Some significant types of reforming methods include steam reforming [1], partial oxidation reforming [2], dry-reforming [3], and auto-thermal reforming [4]. In particular, steam reforming is an environmentally friendly process that discharges the least amount of carbon monoxide. The propane steam reforming reaction used in this study follows equations (1)–(3), and 7–10 mol of hydrogen are generated per mole of propane [5].

$$C_3H_8 + 3H_2O \rightarrow 3CO + 7H_2, \Delta H = +118.8\,\text{kcal/mol} \quad (1)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2, \Delta H = -9.8\,\text{kcal/mol} \quad (2)$$

$$C_3H_8 + 6H_2O \rightarrow 3CO_2 + 10H_2, \Delta H = +89.6\,\text{kcal/mol} \quad (3)$$

The reforming reaction being used currently includes the main reforming reaction (1) and the water gas shift (2) as a side reaction. Although the propane reforming reaction requires higher thermal energy than methane reforming because it is a strongly endothermic reaction, more hydrogen is generated. Moreover, this reaction has a low cost and a wide range of applications, and can be carried out using the existing infrastructure.

* Corresponding author.
E-mail address: mskang@ynu.ac.kr (M. Kang).

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