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journal homepage: www.elsevier.com/locate/apcataReduced perovskite LaNiO_3 catalysts modified with Co and Mn for low coke formation in dry reforming of methaneWon Yong Kim^a, Jum Suk Jang^b, Eun Cheol Ra^c, Kwang Young Kim^c, Eun Hyup Kim^c, Jae Sung Lee^{c,*}^a Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH), Pohang, 790-784, South Korea^b Division of Biotechnology, Advanced Institute of Environmental and Bioscience, College of Environmental and Bioresource Sciences, Chonbuk National University, Iksan, 570-752, South Korea^c School of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan, 44919, South Korea

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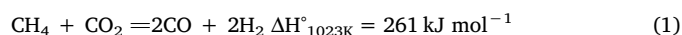
ABSTRACT

In dry reforming of methane (DRM), coke deposition on the Ni-based catalyst is the main cause of instability of the process. Perovskite LaNiO_3 is a well-known highly active catalyst precursor for DRM, but the La-Ni catalyst derived from it is susceptible to severe coke deposition and thus difficult for practical applications. To improve its stability and activity, Co and Mn are introduced to develop a tri-metallic $\text{LaNi}_{0.34}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_3$ catalyst precursor. The role of Mn is to improve the stability of the catalyst, whereas Co is an additional active component to increase the reaction rates. A strong metal and support interaction mediated by MnO is noted in the tri-metallic catalyst, which contributes to a synergistic effect of the tri-metals to sustain the high activity and stability under the harsh conditions of DRM.

1. Introduction

Mitigation of carbon dioxide emission is an urgent global issue today to slow down the pace of climate change [1]. There have been immense research efforts worldwide to develop technologies for CO_2 capture and storage (CCS) last three decades [2]. Yet, those past years have observed that storage of CO_2 in a geological reservoir has significant drawbacks of the possible leakage, long-term liability, and unavailability of enough storage capacity. Hence, interest has been shifting from CCS to carbon capture and utilization (CCU) that can convert the captured CO_2 into useful products such as fuels, chemicals, plastics, and alternative building materials. Some of these measures represent only a CO_2 -neutral path because fuels or chemicals turn to CO_2 again upon combustion. Yet, to the extent that they replace fossil fuels and petrochemicals, they result in net reduction in CO_2 emission to the atmosphere by reducing the consumption of the fossil fuels.

Dry reforming of methane (DRM) is a promising route of CCU that converts carbon dioxide and methane into a synthesis gas ($\text{CO} + \text{H}_2$), which is a versatile raw material to synthesize useful chemicals, fuels, and polymers [3]. The syngas is also used as a reducing gas of iron ores in steel-making industry [4,5] and a fuel for fuel cells [6].



Nickel-based catalysts are most commonly used for DRM mainly for economic reason, but they have a serious stability problem, which poses the most critical barrier to industrial realization of the process. There are two major causes of instability of the DRM catalysts - metal sintering and coke formation [7]. Both causes are related with the high reaction temperatures ($> 1000 \text{ K}$) of this highly endothermic reaction. Sintering of metal is thermodynamically favorable under the reaction conditions and results in loss of active metal surface areas. Carbon deposition (or coking) also reduces the activity by covering the active metal surface and alters product selectivity. More importantly, operation of DRM could be interrupted by reactor plugging by excessive coke formation [7–10]. Thus, reactants cannot penetrate into the catalyst bed and instead are accumulated at the inlet side of catalyst bed causing additional pressure drop on the reactor, leading to eventual reactor plugging. Several approaches have been tried to minimize the deactivation of Ni-based reforming catalysts by sintering and coking. For example, bimetallic Ni-Co [11] or Ni-Mn [12] catalysts were reported to suppress the metal sintering. Small Ni particles exhibited better resistance against coke formation [13], and thus it is important to maintain small metal particles for stable DRM operation.

Perovskite LaNiO_3 was introduced as a highly promising active catalyst precursor for DRM because of their high initial activity [14]. However, the reduced LaNiO_3 catalyst by hydrogen has a critical

* Corresponding author.

E-mail address: jlee1234@unist.ac.kr (J.S. Lee).<https://doi.org/10.1016/j.apcata.2019.02.029>

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