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Syngas Production via Ethanol Dry Reforming: Effect of Promoter Type on Al_2O_3-supported Co Catalysts

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Abstract. Lanthanide-promoted (ceria and lanthana) and unpromoted 10%Co/Al_2O_3 catalysts were synthesized via co-impregnation technique and evaluated for ethanol dry reforming in a quartz fixed-bed reactor at P_{CO2} = P_{C2H5OH} = 20 kPa and reaction temperature of 973 K under atmospheric pressure. Both Co_3O_4 and $CoAl_2O_4$ phases were formed on the surface of promoted and unpromoted catalysts. The reduction of Co_3O_4 to CoO phase was facilitated by CeO_2 or La_2O_3 addition. C_2H_5OH conversion improved significantly up to about 1.2 and 1.9 times with the addition of CeO_2 and La_2O_3 promoters, respectively. La-promoted catalyst appeared to be the best catalyst in terms of H_2 and CO yields as well as C_2H_5OH conversion followed by Ce-promoted and unpromoted catalysts.

Keywords: Ethanol dry reforming, Co-based catalysts, Hydrogen, Syngas

1. Introduction

The growing concerns about the depletion of fossil fuels and increasing greenhouse gas emissions have resulted in the urgent exploration of alternative and green energy sources which can contribute to reduce the significant dependence on conventional fuels and utilize efficiently the undesirable greenhouse gasses. Syngas (referring to CO and H_2 mixture) has been considered as a potential source for the production of environmentally friendly synthetic fuels. Conventionally, syngas is produced via partial oxidation, steam or dry reforming of methane (Usman *et al*., 2015). However, methane is also a nonrenewable fossil fuel diminishing in the near future. Thus, there is a requirement for a sustainable and green process for generating syngas. Ethanol dry reforming (EDR) seems to be a promising method for syngas production and receives significant attention from both academic and industrial research since this process not only use a renewable reactant, *viz.*, ethanol to generate syngas employed as feedstock for downstream methanol production and Fischer-Tropsch synthesis, FTS (Vo and Adesina, 2012) but also mitigate undesirable CO_2 greenhouse gas. Additionally, ethanol, which is rich of hydrogen content, readily available, and easily stored, can be simply produced via fermentation of biomass such as lignocellulose, sugar cane or starch-rich materials (Ni *et al*., 2007; Vicente *et al*., 2014).

Like other catalytic reforming processes of methane, EDR reaction is commonly carried out using Ni-based catalysts in order to aid the cleavage of C-C and C-O bonds in ethanol (Hu and Lu, 2009; Bellido *et al.*, 2009). However, Ni-based catalysts were easily deactivated during EDR process due to carbon formation through the Boudouard, methane cracking and ethylene polymerization reactions (Zawadzki *et al.*, 2014; Bellido *et al.*, 2009). Lanthanide metals (including La_2O_3 and CeO_2) have been recently employed as dopants or supports for Ni-based catalysts to improve carbon resilience during EDR reaction owing to their strong basic properties, high CO_2 adsorption capacity, great oxygen storage capacity and hence excellent coke resistance (Srisiriwat *et al.*, 2009; Mazumder and de Lasa, 2014). In fact, Zawadzki *et al.* (2014) investigated the influence of different types of supports (such as CeO_2, Al_2O_3, ZrO_2 and MgO) on Ni-based catalysts