



Synthesis gas production to desired hydrogen to carbon monoxide ratios by tri-reforming of methane using Ni–MgO–(Ce,Zr)O₂ catalysts

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ABSTRACT

This paper highlights the performance of Ni–MgO–(Ce,Zr)O₂ tri-reforming catalysts under various reaction conditions and explains results using catalyst characterization. Testing under controlled reaction conditions and the use of several catalyst characterization techniques (BET, XRD, TPR, SEM-EDS, and XPS) were employed to better explain the effects of the synthesis parameters on the reaction performances. The support Ce:Zr ratio, metal loading techniques, metal wt%, and Ni:Mg ratios all had a pronounced influence on the catalyst performance. An even ratio of Ce:Zr for the support and an even ratio of Ni:Mg gave the best performance. The wet impregnation method consistently showed more resistance to coke formation when compared to the deposition precipitation method, but the difference was attributed to a better ability to load Mg by wet impregnation. Lower than previously reported H₂O concentrations in the feed gas composition also led to desired H₂:CO ratios needed for FT synthesis while maintaining high conversions of CO₂ and resistance to coke formation. High GHSV (61,000 h⁻¹) yielded significantly higher H₂:CO ratios when compared to reactions run at lower GHSV (25,000 h⁻¹). These results suggest that steam reforming reactions are kept further from equilibrium at higher GHSV and result in higher H₂ production. The tested tri-reforming catalyst produced desired H₂:CO ratios with minimal deactivation, high reactant conversions, and extended catalyst lifetime.

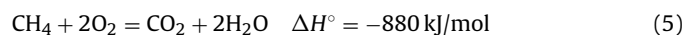
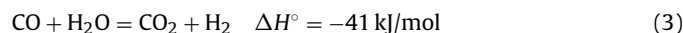
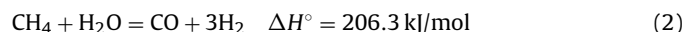
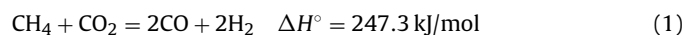
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1. Introduction

In today's environmentally conscious world, a recent shift towards using fuels produced from renewable resources has been seen. The US military has taken a strong stance towards the use of renewable fuels. Both the Air Force and Navy have stated goals of reducing their petroleum consumption 50% by 2016 and 2020 respectively [1–3]. Biomass found in municipal solid waste (MSW) provides an excellent opportunity as a major, near-term, carbon-neutral energy resource. Currently, less than 15% of the over 243 million tons of MSW produced per year is used to generate energy with the majority accumulating in landfills [4]. This MSW naturally biodegrades producing landfill gas composed mainly of methane and carbon dioxide, two major greenhouse gases. Gasification of the biomass in MSW also proves to be a promising and environmentally friendly technology for thermal conversion of biomass to energy. Gasification produces synthesis gas (syngas) for the production of high value chemicals, electricity, and clean burning hydrocarbon fuels. The work presented here concentrates on upgrading landfill gas, produced via biodegradation, through the use of a tri-reforming

catalyst to syngas containing a H₂:CO ratio of 2:1 needed for Fischer Tropsch (FT) synthesis of hydrocarbon fuels, in particular jet fuel and diesel.

The tri-reforming process has recently received attention for its ability to consume greenhouse gases like methane and CO₂ to produce syngas with a higher H₂:CO ratio desired for FT synthesis. Tri-reforming involves a combination of CO₂ reforming (Eq. (1)), steam reforming (Eq. (2)), water-gas shift (Eq. (3)) and methane oxidation (Eqs. (4) and (5)) in a single reactor.



Use of the tri-reforming process eliminates the serious problem of carbon formation and high energy consumption commonly seen in CO₂ reforming by incorporating H₂O and O₂ (see Eqs. (6)–(10)). Heat is generated in situ that can be used to increase energy efficiency and achieve a thermo neutral balance of reactions [5–7]. H₂ and CO selectivity can also be adjusted by controlling the amount of steam and CO₂ added to the reaction [7–13]. This provides an

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