



# Synthesis gas production to desired hydrogen to carbon monoxide ratios by tri-reforming of methane using Ni–MgO–(Ce,Zr)O<sub>2</sub> catalysts

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## ARTICLE INFO

### Article history:

Received 3 May 2012

Received in revised form 3 August 2012

Accepted 8 August 2012

Available online 24 August 2012

### Keywords:

Gas-to-liquid

Fischer Tropsch synthesis

Energy

Biofuel

Hydrogen production

## ABSTRACT

This paper highlights the performance of Ni–MgO–(Ce,Zr)O<sub>2</sub> 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 H<sub>2</sub>O concentrations in the feed gas composition also led to desired H<sub>2</sub>:CO ratios needed for FT synthesis while maintaining high conversions of CO<sub>2</sub> and resistance to coke formation. High GHSV (61,000 h<sup>−1</sup>) yielded significantly higher H<sub>2</sub>:CO ratios when compared to reactions run at lower GHSV (25,000 h<sup>−1</sup>). These results suggest that steam reforming reactions are kept further from equilibrium at higher GHSV and result in higher H<sub>2</sub> production. The tested tri-reforming catalyst produced desired H<sub>2</sub>:CO ratios with minimal deactivation, high reactant conversions, and extended catalyst lifetime.

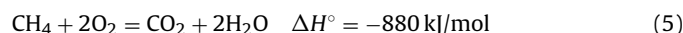
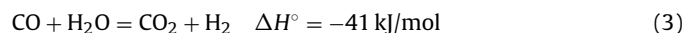
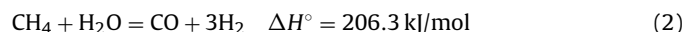
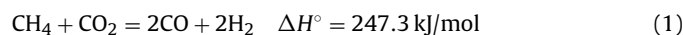
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## 1. Introduction

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 H<sub>2</sub>: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 CO<sub>2</sub> to produce syngas with a higher H<sub>2</sub>:CO ratio desired for FT synthesis. Tri-reforming involves a combination of CO<sub>2</sub> reforming (Eq. (1)), steam reforming (Eq. (2)), water-gas shift (Eq. (3)) and methane oxidation (Eqs. (4) and (5)) in a single reactor.



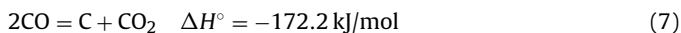
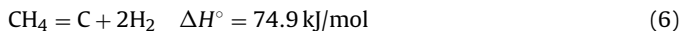
Use of the tri-reforming process eliminates the serious problem of carbon formation and high energy consumption commonly seen in CO<sub>2</sub> reforming by incorporating H<sub>2</sub>O and O<sub>2</sub> (see Eqs. (6)–(10)). Heat is generated in situ that can be used to increase energy efficiency and achieve a thermo neutral balance of reactions [5–7]. H<sub>2</sub> and CO selectivity can also be adjusted by controlling the amount of steam and CO<sub>2</sub> added to the reaction [7–13]. This provides an

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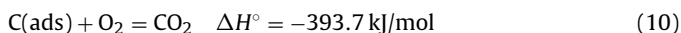
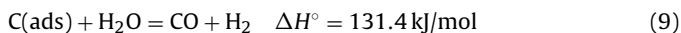
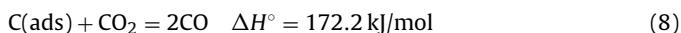
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important role in both industrial and environmental applications allowing production of high value chemicals via oxo-synthesis, electricity via solid oxide fuel cells or molten carbonate fuel cells, and clean burning hydrocarbon fuels via FT synthesis (FTS) [14–18].

#### Coke formation



#### Coke destruction



Tri-reforming catalyst must be thermally stable, have a high surface area, high oxygen storage capacity (OSC), good redox properties, provide resistance to coke formation, and be economically advantageous in order to be feasible as a renewable energy alternative. Ni-based catalysts have shown good potential for reforming methane and provide a more economically friendly option over noble metals. However, Ni has the disadvantage of being susceptible to coke formation [5,19]. Deactivation is directly related to catalyst structure and composition and, therefore, research is aimed at producing a suitable catalyst in the upgrading of MSW syngas.  $\text{CeO}_2$  is reported to have a high oxygen storage capacity (OSC) and is often used as a promoter with Ni for methane conversion to syngas [20–22]. Addition of  $\text{ZrO}_2$  to  $\text{CeO}_2$  has shown to improve OSC, redox property, thermal stability, metal dispersion, selectivity, and catalytic activity [23–28]. These improved characteristics are attributed to the formation of a  $(\text{Ce,Zr})\text{O}_2$  solid solution [25,26,29–33]. Zhuang et al. has attributed the increase OSC from modifying the local oxygen environment around Ce and Zr generating active oxygen [34]. This result may be explained by the introduction of undersized Zr ions into the Ce framework that helps compensate for the volume increase associated with the valence change of  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$ , easing the transition [35,36]. Research has shown that the Ce/Zr mixed oxides consistently perform with higher activity compared to the pure oxide supports and  $\text{Al}_2\text{O}_3$  due to its ability to promote POM and steam reforming reactions [22,25,37–42]. Because of this,  $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$  support materials have received much attention with  $0.6 < x < 0.8$  being preferred for catalytic applications [5].

Basic oxides, such as magnesia and zirconia, have shown to catalyze the gasification of coke with steam and prove to help prevent deposition of carbon in dry reforming [43–46]. This phenomenon may be attributed to the low concentration of Lewis sites and increase of oxygen vacancies by introducing  $\text{ZrO}_2$  and  $\text{MgO}$  into the catalyst composition. By coupling these basic oxides with Ni, catalysts promote  $\text{CO}_2$  and  $\text{H}_2\text{O}$  adsorption leading to enhanced  $\text{CO}_2$  conversion and  $\text{H}_2$  production [7,14]. Song and Pan also attribute the enhanced  $\text{CO}_2$  conversion to a higher interface between Ni,  $\text{MgO}$ , and  $\text{ZrO}_2$  resulting from  $\text{NiO/MgO}$  and  $\text{ZrO}_2/\text{MgO}$  solid solutions [13]. This work highlights the effects of  $\text{ZrO}_2$ ,  $\text{CeO}_2$ , and  $\text{MgO}$  in Ni based tri-reforming catalyst and examines reaction selectivity due to variations in structure/composition and feed gas composition respectively.

## 2. Experimental

### 2.1. Catalyst synthesis

Ce/Zr oxide supports were prepared using the co-precipitation method reported by Rossignol et al. using  $\text{Ce}(\text{NO}_3)_3 \times 6\text{H}_2\text{O}$  and  $\text{ZrO}(\text{NO}_3)_2 \times \text{H}_2\text{O}$  as precursors [47]. Pure ceria and zirconia oxides as well as the mixed oxides with Ce:Zr molar ratios of 0.16:0.84,

0.6:0.4, and 0.8:0.2 were all prepared using the same method. Appropriate quantities of the precursor salts were dissolved in deionized (DI) water and precipitated by the addition of  $\text{NH}_4\text{OH}$  to form hydrous zirconia, ceria, or Ce/Zr solution. This precipitate was vacuum-filtered and re-dispersed into a 0.25 M  $\text{NH}_4\text{OH}$  solution. This dilute, basic solution was again vacuum filtered and dried in an oven at  $120^\circ\text{C}$  overnight. The dried powder was then calcined at  $800^\circ\text{C}$  for 4 h.

The loading of Ni and Mg to the oxide support was carried out using two different loading procedures: wet impregnation (WI) and deposition precipitation (DP). All metals were loaded on a mass basis to achieve desired wt% of metal on the catalyst. For the WI method, appropriate amounts of  $\text{Mg}(\text{NO}_3)_2 \times \text{H}_2\text{O}$  and  $\text{Ni}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$  were dissolved in deionized water to form a homogeneous solution. This solution was then added drop-wise to the support until incipient wetness and dried at  $120^\circ\text{C}$  for 2 h. This step was repeated until all of the metal nitrate solution had been added to the support. Following the final drying step, the catalyst was calcined at  $500^\circ\text{C}$  for 4 h. DP was done using a modified method adapted from Li et al. [48]. Appropriate amounts of  $\text{Mg}(\text{NO}_3)_2 \times \text{H}_2\text{O}$  and  $\text{Ni}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$  were added to a volumetric flask and dissolved in 25 ml DI water. The powder support was added to the metal salt solution and mixed with a stir plate to form a slurry. In a separate beaker,  $\text{CO}(\text{NH}_2)_2$  (urea) was added in excess to 10 ml of DI water to achieve a 1:4 ratio of total metal nitrates:urea. The urea solution was added drop-wise to the metal salt solution while stirring. The top of the volumetric flask was sealed to prevent evaporation of the solution and heated to  $115^\circ\text{C}$  while stirring at 600 rpm on a heated stir plate. Urea hydrolyzes slowly at temperature allowing hydroxyl groups to react as rapidly as they form maintaining a constant pH and allowing precipitation on surface and interior of pores [49]. The solution was aged for 24 h and then cooled to room temperature before vacuum filtering with a Buchner funnel. Cold DI water was used to wash any remaining precursors and impurities from the filtered catalyst. The catalyst was then dried at  $120^\circ\text{C}$  for 4 h followed by calcination at  $500^\circ\text{C}$  for 4 h.

### 2.2. Characterization methods

BET SA, XRD, TPR, SEM-EDS, and XPS were used to characterize catalysts. The combination of these techniques provides valuable data helping to aid in the rational of the catalyst design by providing insights into physical and chemical structure. Physisorption experiments were performed using a Quantachrome Autosorb-iQ. The BET surface area was calculated using data in the  $P/P_0$  range of 0.05–0.3, where a linear relationship for the BET isotherm is maintained.

X-ray diffraction (XRD) analysis was carried out with a Philips X'pert XRD using a powder X-ray diffraction technique. The machine was operated in a Bragg angle ( $2\theta$ ) range of  $15\text{--}80^\circ$ . The step size was  $0.06^\circ$  and set at a dwell time of 1 s for each step. X'pert Highscore software was used to assist in data analysis.

Temperature-programmed reduction (TPR) was carried out using the Quantachrome Autosorb-iQ, mentioned above, using 50 mg of catalyst loaded into a quartz sample cell. Each sample was pretreated with helium while ramping the temperature  $10^\circ\text{C}/\text{min}$  from  $25^\circ\text{C}$  to  $110^\circ\text{C}$  and holding at temperature for 30 min. The sample was then cooled to  $50^\circ\text{C}$ . Following pretreatment, the carrier gas was switched to 5%  $\text{H}_2/\text{N}_2$  and the temperature ramped to  $1100^\circ\text{C}$  at  $10^\circ\text{C}/\text{min}$ . Gas analysis was performed using a thermal conductivity detector (TCD) measuring the conversion of  $\text{H}_2$  under the temperature-programmed conditions.

A Hitachi S-800 SEM coupled to an Ametek EDAX was utilized to conduct SEM-EDS experiments. An excitation energy of 10 keV, a magnification of 1010, and a tilt angle of  $30^\circ$  was used in this analysis.

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