Applied Catalysis A: General 445–446 (2012) 61–68

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Synthesis gas production to desired hydrogen to carbon monoxide ratios by tri-reforming of methane using Ni–MgO–(Ce,Zr)O_2 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_2 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_2O concentrations in the feed gas composition also led to desired H_2:CO ratios needed for FT synthesis while maintaining high conversions of CO_2 and resistance to coke formation. High GHSV (61,000 h^{-1}) yielded significantly higher H_2: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 H_2 production. The tested tri-reforming catalyst produced desired H_2:CO ratios with minimal deactivation, high reactant conversions, and extended catalyst lifetime.

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_2: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_2 to produce syngas with a higher H_2:CO ratio desired for FT synthesis. Tri-reforming involves a combination of CO_2 reforming (Eq. (1)), steam reforming (Eq. (2)), water-gas shift (Eq. (3)) and methane oxidation (Eqs. (4) and (5)) in a single reactor.

$$CH_4 + CO_2 = 2CO + 2H_2 \quad \Delta H^\circ = 247.3\,\text{kJ/mol} \tag{1}$$

$$CH_4 + H_2O = CO + 3H_2 \quad \Delta H^\circ = 206.3\,\text{kJ/mol} \tag{2}$$

$$CO + H_2O = CO_2 + H_2 \quad \Delta H^\circ = -41\,\text{kJ/mol} \tag{3}$$

$$CH_4 + (1/2)O_2 = CO + 2H_2 \quad \Delta H^\circ = -35.6\,\text{kJ/mol} \tag{4}$$

$$CH_4 + 2O_2 = CO_2 + 2H_2O \quad \Delta H^\circ = -880\,\text{kJ/mol} \tag{5}$$

Use of the tri-reforming process eliminates the serious problem of carbon formation and high energy consumption commonly seen in CO_2 reforming by incorporating H_2O and O_2 (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_2 and CO selectivity can also be adjusted by controlling the amount of steam and CO_2 added to the reaction [7–13]. This provides an

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http://dx.doi.org/10.1016/j.apcata.2012.08.015

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

$$CH_4 = C + 2H_2 \quad \Delta H^\circ = 74.9\,\text{kJ/mol} \tag{6}$$

$$2CO = C + CO_2 \quad \Delta H^\circ = -172.2\,\text{kJ/mol} \tag{7}$$

Coke destruction

$$C(ads) + CO_2 = 2CO \quad \Delta H^\circ = 172.2\,\text{kJ/mol} \tag{8}$$

$$C(ads) + H_2O = CO + H_2 \quad \Delta H^\circ = 131.4\,\text{kJ/mol} \tag{9}$$

$$C(ads) + O_2 = CO_2 \quad \Delta H^\circ = -393.7\,\text{kJ/mol} \tag{10}$$

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. 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 ZrO_2 to 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 $(Ce,Zr)O_2$ 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 Ce^{4+} to 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 Al_2O_3 due to its ability to promote POM and steam reforming reactions [22,25,37–42]. Because of this, $Ce_{1-x}Zr_xO_2$ 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 ZrO_2 and MgO into the catalyst composition. By coupling these basic oxides with Ni, catalysts promote CO_2 and H_2O adsorption leading to enhanced CO_2 conversion and H_2 production [7,14]. Song and Pan also attribute the enhanced CO_2 conversion to a higher interface between Ni, MgO, and ZrO_2 resulting from NiO/MgO and ZrO_2/MgO solid solutions [13]. This work highlights the effects of ZrO_2, CeO_2, and MgO in Ni based trireforming 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 $Ce(NO_3)_3 \times 6H_2O$ and $ZrO(NO_3)_2 \times H_2O$ 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 NH_4OH to form hydrous zirconia, ceria, or Ce/Zr solution. This precipitate was vacuum-filtered and re-dispersed into a 0.25 M NH_4OH solution. This dilute, basic solution was again vacuum filtered and dried in an oven at 120 °C overnight. The dried powder was then calcined at 800 °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 $Mg(NO_3)_2 \times H_2O$ and $Ni(NO_3)_2 \times 6H_2O$ 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 °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 °C for 4 h. DP was done using a modified method adapted from Li et al. [48]. Appropriate amounts of $Mg(NO_3)_2 \times H_2O$ and $Ni(NO_3)_2 \times 6H_2O$ where 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, $CO(NH_2)_2$ (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 °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 °C for 4 h followed by calcination at 500 °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 (2θ) range of 15–80°. The step size was 0.06° 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 °C/min from 25 °C to 110 °C and holding at temperature for 30 min. The sample was then cooled to 50 °C. Following pretreatment, the carrier gas was switched to 5% H_2/N_2 and the temperature ramped to 1100 °C at 10 °C/min. Gas analysis was performed using a thermal conductivity detector (TCD) measuring the conversion of 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° was used in this analysis.