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Kinetic and process study for ethanol reforming using a Rh/Pt washcoated monolith catalyst

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ABSTRACT

The reforming of pure ethanol was studied over a bi-metallic precious metal (Rh/Pt) catalyst deposited on a ceramic monolith in order to analyze reforming process conditions. High ethanol conversion tests performed at low space velocities (<20,000 h^{-1}) confirmed that the catalyst could achieve 100% ethanol conversion to equilibrium concentrations of H_2, CO, CO_2 and CH_4. Low conversion tests at high space velocities ($\geq$50,000 h^{-1}) were conducted to produce an overall rate expression with an activation energy of 85 kJ $mole^{-1}$. The reaction was found to have a 1.2 reaction order for ethanol and zero order for water for stoichiometric ethanol and water ratios. In addition, the impact of non-catalytic reactions was studied. The results showed that the catalyst was capable of reforming ethanol as well as the by-products from non-catalytic reactions at 500–700 °C.

This work is part 1 of a series to develop a process for steam reforming E85 (85% ethanol + 15% gasoline) to generate hydrogen for a fuel cell.

1. Introduction

Ethanol has recently been considered as a potential fuel for generating hydrogen for use in fuel cells because it is produced from renewable sources. As the world begins to focus on more environmentally benign ways to replace fossil fuels, more alcohol and bio-derived fuels will likely be produced. Bio-derived fuels such as ethanol will be used in traditional combustion engine vehicles and will have an associated infrastructure for production and delivery. Ethanol, however, has a low vapor pressure relative to gasoline and therefore it is likely that traditional combustion vehicles will use an ethanol/gasoline blend rather than pure ethanol. Therefore, the next step in examining ethanol steam reforming is to consider the steam reforming of ethanol/gasoline blends (i.e. E85 composed of 85% ethanol and 15% gasoline), since the production and delivery system will be in place for service stations to reform this transportation fuel to hydrogen for fuel cell vehicles. Since gasoline present in E85 contains sulfur we elected to use a non-sulfating carrier in the current study as a baseline for future comparisons with E85.

The steam reforming of pure ethanol produces H_2 according to the following endothermic reaction:

$$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2, \quad \Delta H^\circ_{298} = 174\,\mathrm{kJ\,mole^{-1}}, \quad \Delta G^\circ_{298} = 66\,\mathrm{kJ\,mole^{-1}} \tag{1}$$

The catalytic steam reforming of ethanol has been reported primarily for Ni-containing catalysts [1–4] and noble metals including Rh [5–11]. These studies have focused on maximizing catalyst activity and hydrogen production and, particularly for the nickel catalysts, have also focused on preventing carbon build-up and deactivation. To date most studies have used powders to investigate fundamental reaction data yet a field process will likely be based on a more structured support. Monolithic ceramic or metal supports washcoated with an active catalyst, allow for low pressure drop and an efficient mechanism for enhanced heat transfer for the endothermic reforming reactions [12]. In order to ensure low pressure drops monolith structures use thin washcoats with high activity catalysts. This study investigates a high activity Rh/Pt catalyst that is less susceptible to coke formation than nickel and can be easily regenerated if coking does occur. This catalyst is also sulfur tolerant which will be important for reforming ethanol/gasoline blends that will contain sulfur.

Recently, bi-metallic catalysts were proposed that would simultaneously promote ethanol steam reforming as well as the forward water gas shift (WGS) reaction to increase H_2 and decrease CO [13]. Several authors have used high water/ethanol ratios to

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