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Steam reforming of ethanol/gasoline mixtures: Deactivation, regeneration and stable performance

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ABSTRACT

The steam reforming of 85% pure ethanol, 15% gasoline (E85) with and without sulfur was studied over a bimetallic precious metal (Rh/Pt) catalyst deposited on a ceramic monolith. Tests performed at low space velocities (22,000 h^{-1}) confirmed that the catalyst could achieve 100% ethanol and gasoline conversion to equilibrium concentrations of H_2, CO, CO_2 and CH_4 with no signs of deactivation for at least 110 h reforming a sulfur-free E85 fuel. In the presence of 5 ppm sulfur the catalyst maintained 100% ethanol and 100% gasoline conversion for approximately 22 h before rapid deactivation resulted in ethanol conversion values below 21%. TPO analysis established large carbon deposits had formed on the catalyst surface demonstrating that sulfur promoted carbon formation. Following such extensive deactivation full activity was recovered after treating the catalyst with air; however subsequent deactivation occurred more rapidly indicating that some amount of permanent damage had occurred. A process with preemptive regeneration via air treatment was studied and it was found to extend the period of stable activity.
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1. Introduction

Increasing concerns about the environmental impact of vehicles with gasoline powered combustion engines have increased efforts to find technologies to reduce emissions and reduce fossil fuel consumption. Recently there has been an increased focus on generating transportation fuels from renewable resources, in particular on efforts to convert cellulosic feedstock into ethanol via conventional fermentation routes and next generation genomic modification routes. Ethanol has a lower vapor pressure relative to gasoline and therefore ethanol/gasoline blends such as E85 (85% ethanol) or E15 (15% ethanol) are more likely to be available then 100% ethanol within the current infrastructure. If hydrogen fuel cell vehicles or hydrogen powered combustion engines are transitioned into the transportation sector hydrogen will initially be produced from fuels available at local service stations. Thus it is important to understand the reforming capabilities of these mixed transportation fuels for hydrogen production.

Previously we reported on steam reforming of pure ethanol with a Rh/Pt catalyst on a zirconia containing carrier [1]. In this previous study both non-catalytic and catalytic performance were investigated and two kinetic regimes were identified [1]. The current work focuses on studying the reforming of ethanol/gasoline blends.

There has been extensive research on the reforming of conventional transportation fuels of gasoline, diesel, or jet fuel and additionally there are many published studies on the reforming of pure ethanol, however, literature on ethanol–gasoline blends is limited. Swartz et al. reported on auto-thermal reforming of E85 at 800 °C and steam/carbon ratio's of 5:1 and 6:1 [2]. Assuming gasoline is represented by iso-octane the E85 reforming reaction normalized to 1 mol of fuel is:

$$0.94C_2H_5OH_{(g)} + 0.06C_8H_{18(g)} + 3.78H_2O_{(g)} \rightarrow 7.14H_2 + 2.36CO_2 \quad \Delta H^0_{298} = 207 \ \text{kJ/mol} \qquad (1)$$

A major challenge in steam reforming liquid transportation fuels is catalyst deactivation. It has been found that the presence of higher hydrocarbons in a fuel, specifically aromatics, increase deactivation due to carbon deposition [3]. In addition, sulfur, which is also present in many transportation fuels is a known catalyst poison and typically has a detrimental effect on catalyst stability [4]. The impact of sulfur on catalyst performance for autothermal reforming transportation fuels has been studied for both synthetic fuels [5–9] and commercial fuels [6,8,10–14]. Steam reforming for transportation fuels has mostly been studied for synthetic fuels [7–9,15–20] however, papers by both Wang et al. and Strohm et al. researched the catalytic steam reforming of commercial grade JP8 [15,21].

Noble metal catalysts have been found to be more sulfur tolerant than Ni-based catalysts [15]. Several papers that have investigated sulfur tolerance studied the effect of using bimetallic catalysts

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