

Catalytic reforming of ethanol/gasoline blends for fuel cell vehicles

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Introduction

Ethanol has recently been considered as a potential fuel to generate hydrogen for use in fuel cells because it is produced from renewable sources such as municipal solid waste¹. There have been studies of pure ethanol steam reforming reported in the literature² using mostly Ni-based catalysts. The key issue appears to be coking and subsequent catalyst deactivation. Rhodium appears to be an effective catalyst with greatly reduced coking tendency³. Pure ethanol, however, is not available within the current fuel infrastructure and instead ethanol/gasoline blends such as E85 (85% ethanol, 15% gasoline) are available and used in traditional combustion engines. Therefore, the next step in examining ethanol reforming is to examine the reforming of ethanol/gasoline blends since the production and delivery system will be in place for service stations to reform this transportation fuel to hydrogen for fuel cell vehicles. In this study, the reforming of both pure ethanol and E85 is studied over a bimetallic precious metal (Rh/Pt) catalyst.

Materials and Methods

Experiments were performed using a 0.75 inch ID quartz flow-through reactor and a Rh/Pt catalyst washcoated monolith (400 cps) obtained from BASF Catalysts. Since gasoline, present in E85, contains sulfur a non-sulfating catalyst support was used. 100% pure ethanol was obtained from Sigma Aldrich and E85 was obtained from a local service station. The fuel and water delivery system utilized two HPLC pumps. Results were measured using an on-line Agilent Micro GC.

Results and Discussion

The first sets of tests were done using pure ethanol to understand the performance of the monolith reactor. Thus far, the monolithic catalyst has proven capable of 100% conversion of pure ethanol to H₂, CO₂, CO and CH₄. Additionally, the catalyst was found active for reforming byproducts produced from ethanol decomposition reactions to H₂, CO₂, CO and CH₄ with minimal deactivation. CH₄ was found to be both an intermediate that is reformed and a product that is produced via methanation.

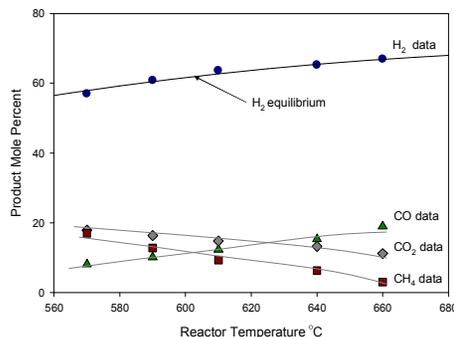


Figure 1: Results for GHSV=16,900 h⁻¹, 3:1 water/ethanol, washcoat loading = 0.12 g cm⁻³

Further results investigating catalyst selectivity have found that the catalyst may show a preference for reforming acetaldehyde (and therefore may compete with the ethanol for active sites).

Kinetic parameters were collected to develop a rate expression for a process using the Rh/Pt washcoated monolith. Initial tests performed on pure ethanol have shown that both the dependence on ethanol and the dependence on water (reaction orders) varied significantly with water/ethanol ratio. This effect was investigated as it pertained to a monolith for which water/ethanol ratio would vary along the catalyst bed (increasing with increasing conversion). The effective reaction orders for water and ethanol are noted in the rate expressions at left for near stoichiometric water/ethanol ratios (3:1-6:1) and for high water/ethanol ratios (6:1-15:1).

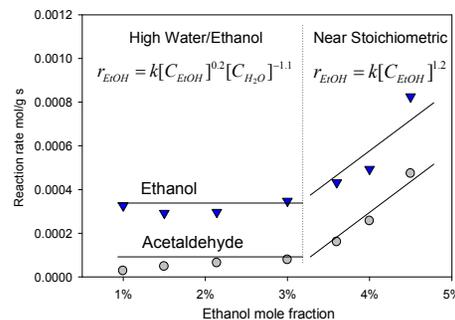


Figure 2: Effect of ethanol concentration on production/consumption rates for GHSV = 100,000 h⁻¹, washcoat loading = 0.03 g cm⁻³, for ethanol (▼), acetaldehyde (●).

Based on the reaction orders a full rate expression with activation energy was determined for near stoichiometric conditions. Due to the process oriented nature of the experiments, there was a temperature gradient in the monolith during the tests. In order to best extract overall kinetic parameters for the monolith, the temperature difference across the monolith was included in the estimation:

$$\int \frac{d[C_{EtOH}]}{[C_{EtOH}]^{1.2}} = A \int e^{\frac{-E_{app}}{R(a+bt)}} dt$$

Integrating across the monolith considering the temperature differential led to an activation energy of 85 kJ/mole for near stoichiometric conditions. Current work investigates the effects of adding gasoline to the ethanol mixture on product selectivity, rate parameters and deactivation.

Significance

It is likely that pure ethanol will not be reformed for hydrogen fuel cell vehicles but rather an ethanol/gasoline mix (which will be available at service stations), however, reforming of ethanol/gasoline blends has not been reported in the ethanol reforming literature. This research will explore the capability of a robust, non-sulfating catalyst for reforming ethanol and gasoline blends for hydrogen production.

References

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