Developing a process for ethanol reforming using a Rh/Pt catalyst.

Amanda Simson, Earl Waterman, Bob Farrauto and Marco J. Castaldi*

Earth & Environmental Engineering (HKSM), Columbia University, New York, NY 10027

aes2171@columbia.edu

Abstract

The reforming of ethanol was studied over a bimetallic precious metal (Rh/Pt) catalyst deposited on a ceramic monolith. High conversion tests performed at low space velocities (<20,000 h^{-1}) confirmed that the catalyst could achieve 100% ethanol conversion to H_2, CO_2, CO and CH_4. Low conversion tests at high space velocities (>50,000 h^{-1}) were conducted to produce an overall rate expression with an activation energy of 45.2 kJ/mol. In addition, the catalyst was found active for reforming the byproducts produced from non-catalytic reactions. This work was meant to provide a baseline for future work studying the reforming of E85 (an 85% ethanol/15% gasoline blend).

Motivation

Ethanol reforming has been studied to evaluate its ability for hydrogen generation for fuel cell applications. Numerous studies have shown that between 600-800°C 100% ethanol conversion to H_2, CO, CO_2 and CH_4 can be achieved with base metal or precious metal catalysts [1, 2]. However:

- Previous studies have generally reported on powder catalysts in quartz reactors, yet an industrial process will use a catalyst deposited on a monolith.
- Few studies have reported the impacts of non-catalytic reactions.
- Few studies have reported rate parameters and activation energies.
- It is likely that pure ethanol will not be reformed but a gasoline/ethanol mix available at service stations. Ethanol/gasoline blends such as E85 have not been studied for their ability to be reformed for hydrogen production.

Experimental

Test Conditions

- SR10D Rh/Pt catalyst (BASF) on a non-sulfating carrier deposited on a ceramic monolith
- GHSV varied using flow rates for constant monolith size (½" long, ½" diameter)
- Washcoat loading was 2.0 g/in³ for high conversion tests; 0.5 g/in³ for low conversion tests. Precious metal content on the carrier was 4%.
- Non-catalytic tests were performed with a blank monolith in reactor tube.

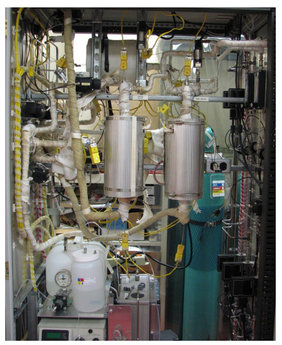
Investigated Parameters

- Conversion and selectivity at high and low conversion conditions
- Activation energy and rate dependence on water and ethanol concentrations.
- Impact of non-catalytic reactions on overall rate and selectivity

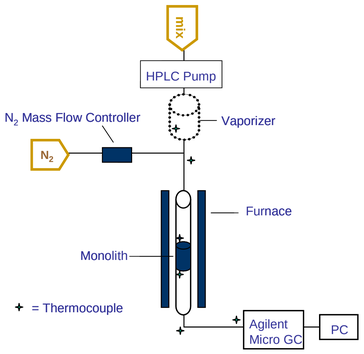
The overall stoichiometry is shown below:

$$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2 \qquad (1)$$

Experimental Set-up



Major Components



Results and discussion

Non-catalytic and Catalytic Reactions

- Passivating the stainless steel reactor reduced ethanol decomposition and coking.
- On the passivated reactor ethanol decomposed thermally via reactions (2), (3) and (4).

Thermal Reactions:

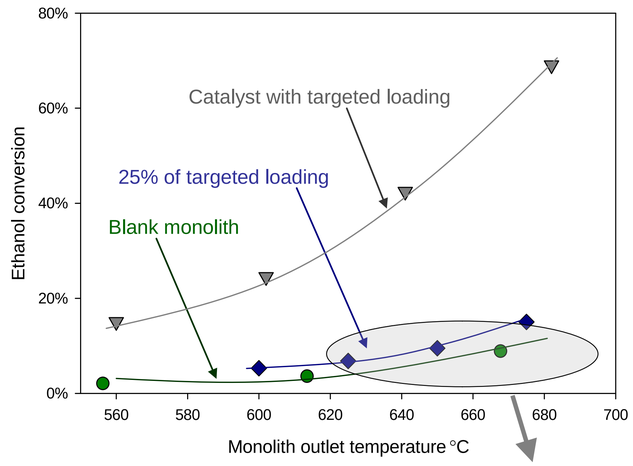
$< 650\ ^\circ C$ $\quad C_2H_5OH \rightarrow C_2H_4O + H_2 \qquad (2)$

$\quad C_2H_5OH \rightarrow C_2H_4 + H_2O \qquad (3)$

$> 650\ ^\circ C$ $\quad C_2H_4O \rightarrow CH_4 + CO \qquad (4)$

- At low loading, high GHSV, the catalyst and blank monolith had the same conversion.
- At this condition, the catalyst produced less acetaldehyde and more H_2, CO and CO_2 indicating it may preferentially reform the acetaldehyde.

At low washcoat loading, ethanol conversion was similar to that on the blank monolith.



Comparison of product distribution for blank monolith and catalyst with 25% loading at approximately equal ethanol conversion.

Mole of product/mole ethanol consumed							
	Temperature	*H2*	*C2H4O*	*CO*	*CO2*	*CH4*	*C2H4*
Blank	670C	0.81	0.81	0.06	0.00	0.06	0.12
Catalyst	650C	1.65	0.51	0.35	0.16	0.12	0.11

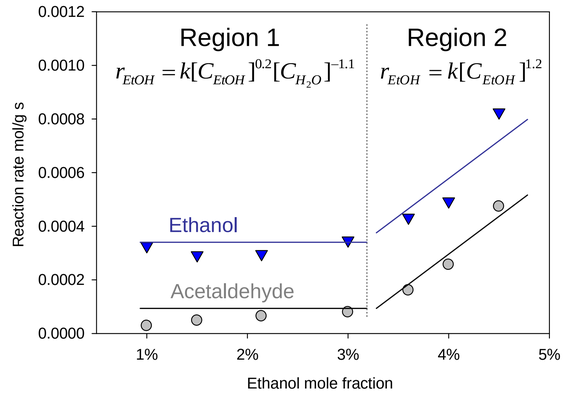
At the condition of similar ethanol conversion, the catalyst was active for acetaldehyde reforming, increasing H_2, CO, CO_2 concentrations. The catalyst showed it could not only reform byproducts of thermal decomposition, but could preferentially reform acetaldehyde.

Catalytic reactions:

Ethanol + Thermal decomposition products: Ethylene, Acetaldehyde $\rightarrow$ *CO, CO_2, H_2* (5)

Reaction Order Calculations

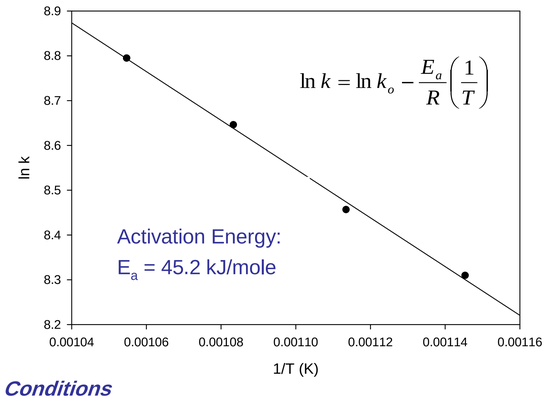
Ethanol, acetaldehyde's rate dependence on ethanol indicated two separate regions.



Overall Rate Expression Calculations

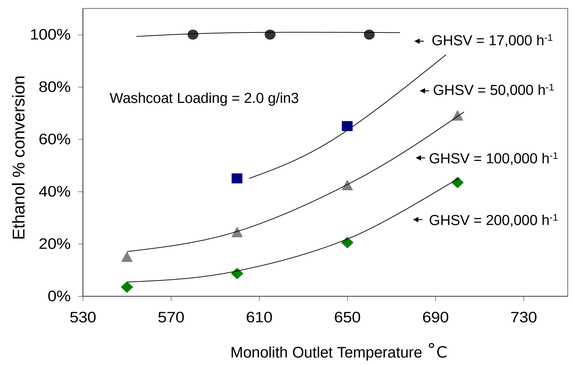
As a baseline for a process, a rate expression was developed for near stoichiometric conditions.

From calculated k values, an activation energy of 45.2 kJ/mol was found.



Process Conditions

At low space velocities, 100% ethanol conversion was achieved between 600-700˚C



Conclusions:

- *Ethanol thermal decomposition occurs, however, the catalyst is active for reforming its products and can still achieve 100% conversion to H_2, CO, CO_2, CH_4.*
- *This work will provide a baseline for future work studying the reforming of E85 (an 85% ethanol 15% gasoline blend).*

[1] M. Ni, Y. Leung, M. Leung., A review on reforming bio-ethanol for hydrogen production. Int. J. Hydrogen Energy, 32 (2007) 3238-3247; [2] A. Haryanto, S. Fernando, N. Murali, S. Adhikari, Current Status of Hydrogen Production Techniques by Steam Reforming of Ethanol: A review M. Energy & Fuels, 19 (2005) 2098-2106