Catalyst deactivation and regeneration studies reforming ethanol/gasoline blends.

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Abstract

The reforming of E85 (an 85% ethanol/15% gasoline blend) was studied over a bimetallic precious metal (Rh/Pt) catalyst deposited on a ceramic monolith. High conversion tests (<20,000 h^{-1}) confirmed that the catalyst could achieve 100% conversion of E85 to only H_2, CO_2, CO and CH_4 at 650°C. A 110 hour aging test was run with a 1.1 Water/E85 ratio which showed deactivation after approximately 14 hours at 650°C. Catalyst aging tests reforming E85 without sulfur demonstrated no signs of deactivation over a 110 hour run indicating that the primary cause of deactivation was the sulfur present in the E85. Catalyst regeneration with air returned the catalyst to full activity. A preemptive regeneration process was developed whereby the catalyst could maintain initial activity with periodic air treatments prior to deactivation.

Motivation

Ethanol has been considered as a potential fuel to generate hydrogen for fuel cells because it is produced from renewable sources and its catalytic reforming capability has been well documented. However:

- Pure ethanol is not available within the current fuel infrastructure; instead ethanol/gasoline blends are available.
- Aging and deactivation for E85 reforming (which contains sulfur) has not been studied, nor have methods for regenerating catalysts.
- Sulfur is a common cause of catalyst deactivation, however, the deactivation mechanisms are not well understood.

Experimental

Investigated Parameters

- Reactant dependencies and activation energy for reforming pure ethanol (kinetic results not shown)
- Conversion and selectivity for E85 reforming at typical process conditions
- Aging and regeneration studies at process and experimental conditions with pure ethanol, ethanol/isooctane and both sulfur containing and sulfur free E85 (only E85 results shown).
- Aging runs with preemptive air treatments reforming E85 containing sulfur

Pure ethanol reforming is shown below:

$$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2$$

E85 reforming (15% vol. gasoline as iso-octane):

$$94C_2H_5OH + 6C_8H_{18} + 378H_2O \rightarrow 236CO_2 + 1428H_2$$

Catalyst Information

- Rh/Pt catalyst (BASF) on non-sulfating carrier on ceramic monolith
- Precious metal content 4%

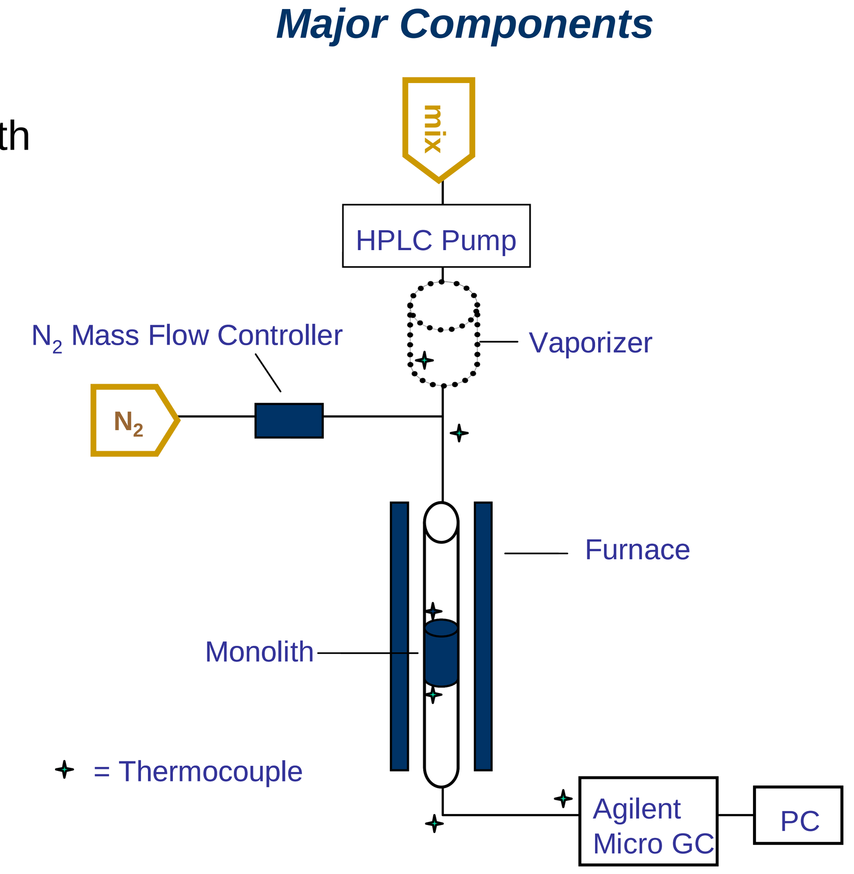
Process Conditions

- O/C ratio = 2.2
- Washcoat loading 2.0 g/in^3
- GHSV < 22,000 h^{-1}

Experimental Conditions

- O/C ratio = 2.0 – 2.6
- Washcoat loading 0.25 g/in^3
- GHSV > 40,000 h^{-1}

Major Components

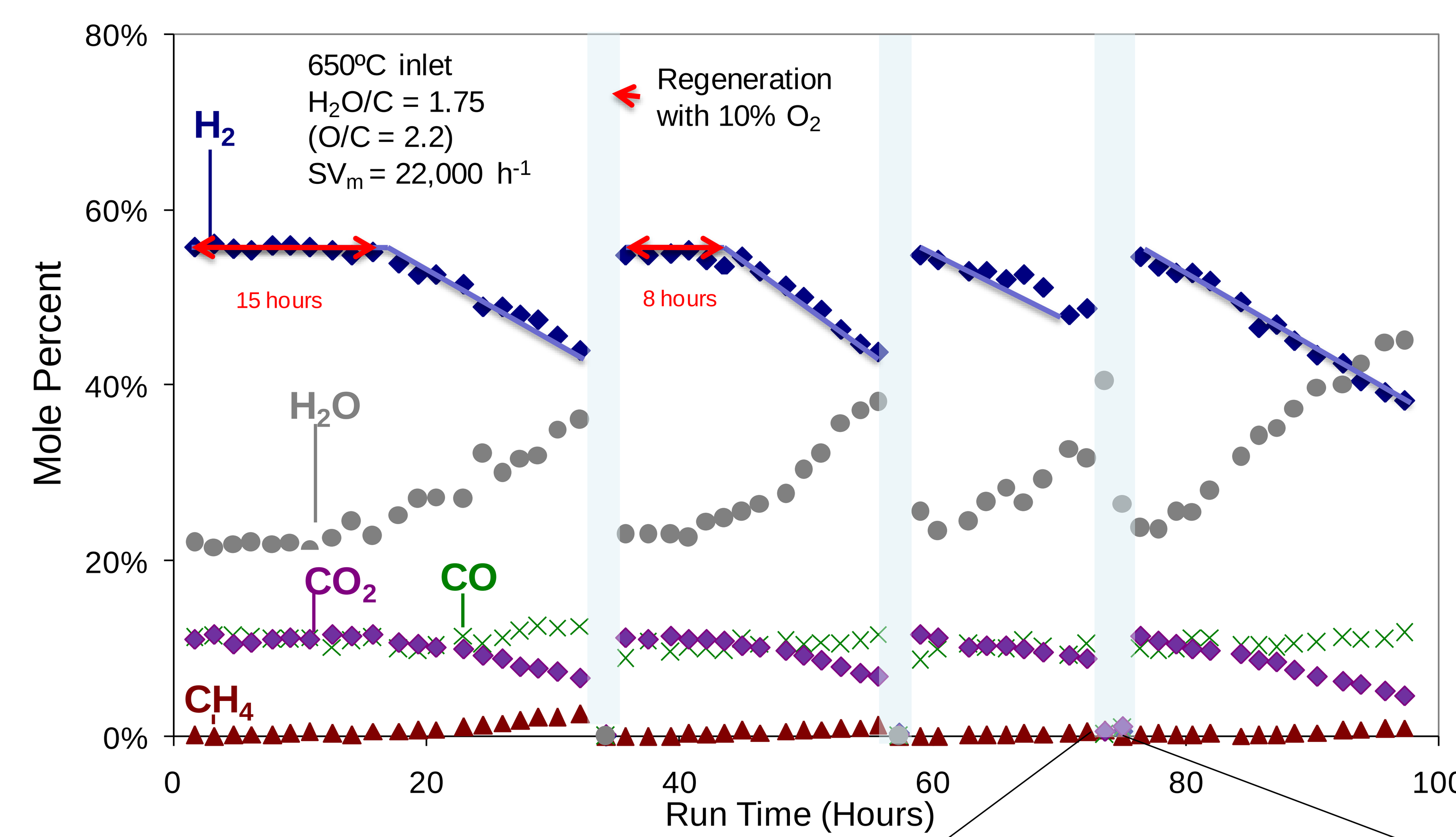


1.S. Swartz, P. Matter, G. Arkenberg, F. Holcomb, N. Josefik, Journal of Power Sources 188 (2009) 515-520

Results and discussion

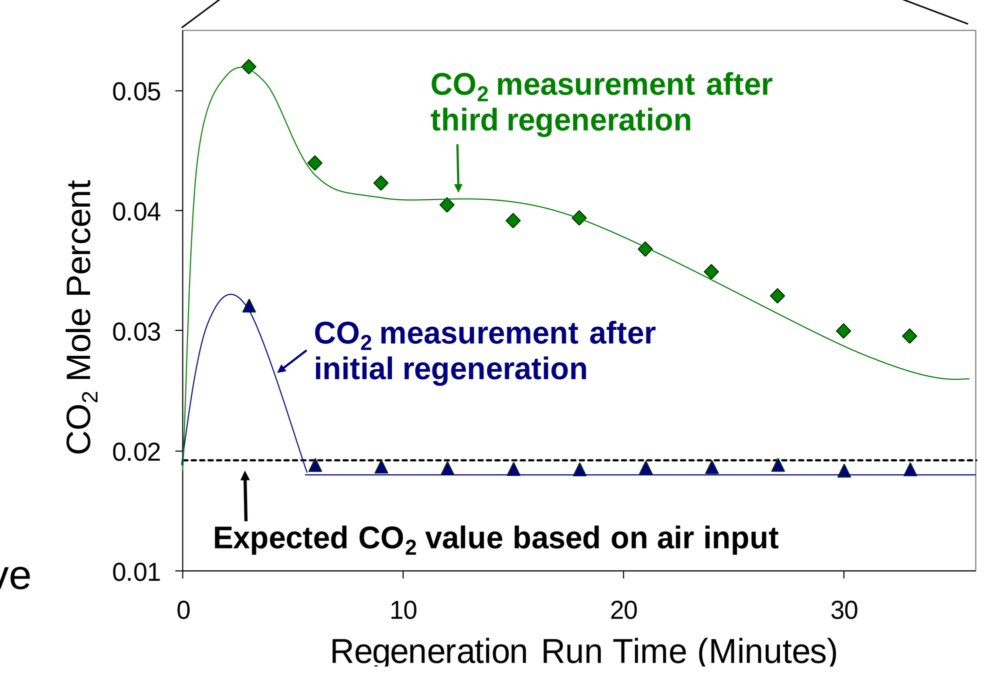
Aging Tests: Reforming of E85 with and without sulfur

Catalyst deactivated after 14 hours reforming E85 (28 ppm sulfur). No deactivation was seen using pure ethanol or E85 without sulfur for at least 110 hours.



E85 Aging Test Results:

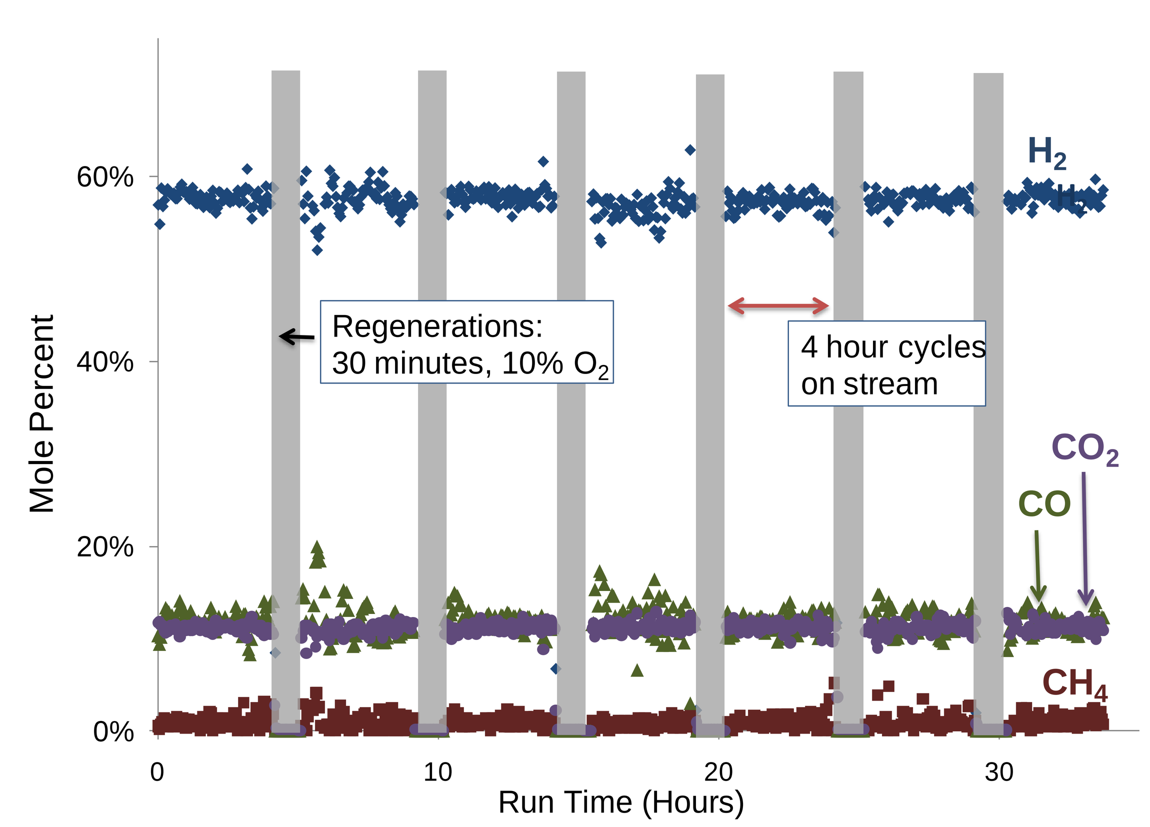
- Catalyst regenerated to initial activity but period of stable activity decreased with each regeneration.
- Selectivity changed after 14 hours, conversion was maintained.
- C_2 species measured after 20 hours on stream, had an earlier onset after each regeneration.
- Increasing CO_2 and increasing exotherms measured during successive regenerations.



Pre-emptive regeneration process maintains activity despite sulfur.

- Under the same reforming conditions the catalyst was periodically exposed to one hour without reformate and 10% oxygen.

Stable period of activity extended by frequent regenerations with air. Four hour cycles with 30 minute pre-emptive regeneration allowed for 35 hours of consistent on-stream activity despite deactivation previously seen after 14 hours.



E85 Cyclic Test Results:

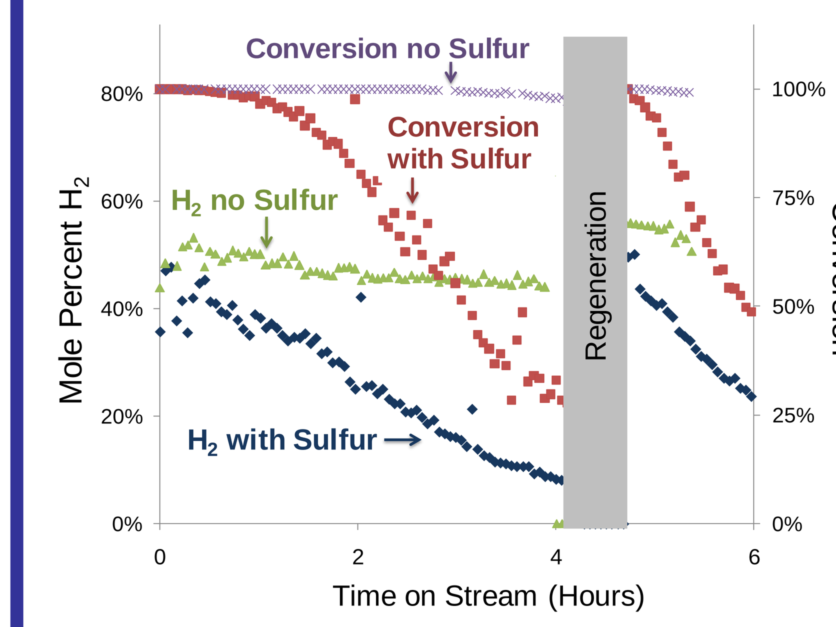
- No change in conversion during 35 hours on stream
- No change in product distribution during 35 hours
- No C_2 species measured during 35 hours
- During air treatments exotherms produced and CO_2 measured in effluent.

The success of preemptive regenerations indicated there might be a time dependent nature of deactivation.

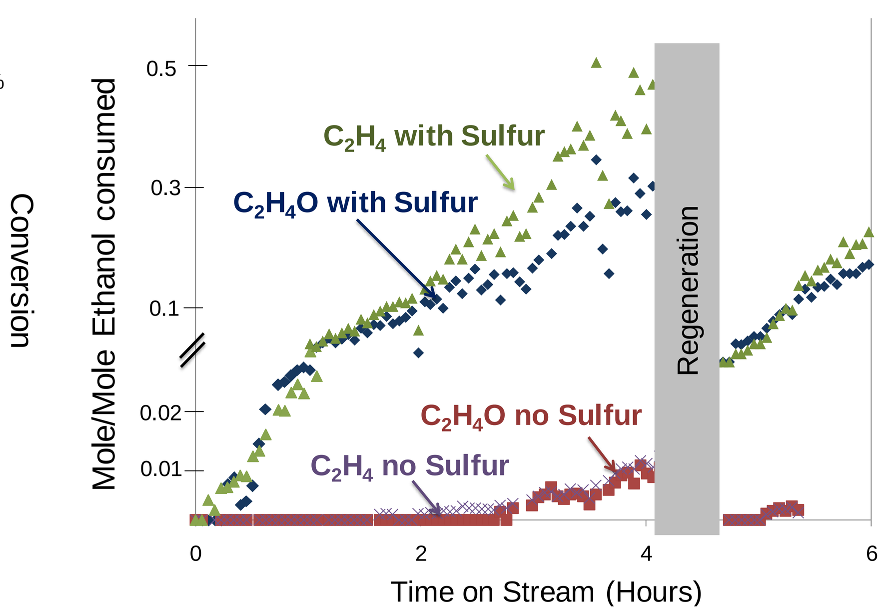
The role of intermediate species:

- Catalyst deactivated reforming pure ethanol at high space velocities.
- Intermediates of acetaldehyde and ethylene present during high space velocity tests hypothesized to result in carbon formation or have fouling effect.

Sulfur had significant effect on conversion, H_2 selectivity.

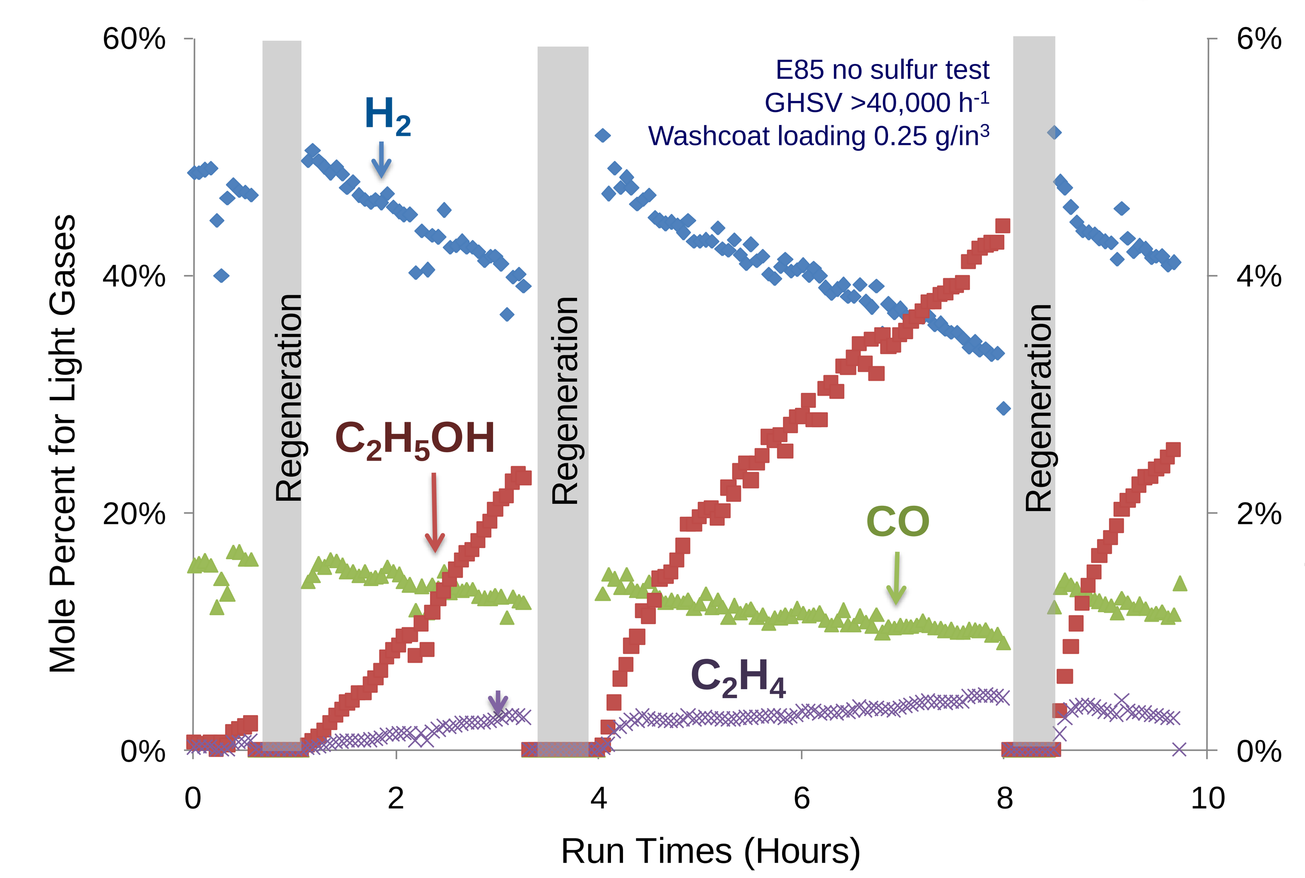


Sulfur increased production of ethylene, acetaldehyde by order of magnitude.



Regeneration Methods:

- Regeneration with water or pure nitrogen did not return activity.
- Exposing the catalyst to 10% air mix burned carbon off the surface and returned catalyst activity.
- The onset of intermediates occurred earlier with successive regenerations



Deactivation profile changed after regeneration even in the absence of sulfur indicating regeneration affected catalyst or permanent deactivation occured.

Conclusions and Future Work

Current Observations:

- Sulfur is primary cause for deactivation even when present in < 30 ppm levels.
- Carbon deposition plays a role in catalyst deactivation and may be the result of C_2 intermediates such as ethylene or acetaldehyde.
- Sulfur increases the production rates of these C_2 species likely contributing to additional deactivation.
- Air treatments increased time of stable activity. May indicate ability for process of maintaining activity despite sulfur.

Current and future work will attempt to answer:

- Does regeneration impact the catalyst and subsequent deactivation profile?
- Is there a time dependent aspect to deactivation specific to sulfur?
- What is the mechanism for sulfur deactivation?
- What is the most effective regeneration method for prolonging stable activity?