Trace contaminant removal via enhanced mass transfer selective catalytic reaction

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Abstract

The paper describes the research activities carried out in the Combustion and Catalysis Lab at Columbia University, aimed to develop, assemble and test a CO cleanup train for a PEM Fuel Cell. The experimental apparatus and associated instrumentation were set up to incorporate a single WGS (Water Gas Shift) reactor (operating at about 300°C) and a two-stage PROX (Preferential Oxidation) reactor (operating in the 130-240°C range) with integrated interstage cooling. Prior to testing the integrated system, the individual reactors were studied separately. A closer look into the PROX reactors lead to the observation of peculiar behavior (multiple steady states).

On the PROX reactors, the effect of steam-to-carbon (S:C) and oxygen-to-carbon (O:C) ratios was also investigated. A broad range of conversions was achieved (from 20% to 99.99%) for PROX-1 exit temperatures between 180°C and 375°C. A selectivity vs. conversion plot was generated, showing a maximum selectivity to be achieved (~50%) for various conversions. Operating at high S/C yields high selectivity and conversion at low Oxygen-to-Carbon (O/C) whereas a lower S/C causes high selectivity and conversion to occur at high O/C.

Introduction

A highly active catalytic material is always required to meet the conversion requirements under the expected reaction conditions but often the lowest level of contaminant that is achievable can not be reduced due to bulk mass transfer limitations at these low levels of reactants.

We are proposing that new short contact time supports, with:

- High geometric area,
- Low pressure drop and
- High structural stability
- High thermal conductivity of the substrate
- enhanced mass transfer capabilities

SCT catalyst support

Experimental

The feed to the WGS simulates the effluent concentration of a liquid fueled (JP-8) ATR (Autothermal Reforming Reactor). A resulting H_2 stream of 35% outlet concentration was generated, with a 0.21kW system. Precious metal coated Short Contact Time (SCT) catalyst elements were used for all units, allowing ultra-compact and lightweight reactor design.

The H_2/CO/CO_2/N_2/H_2O mixture of composition 26.7/8.3/8.5/31.2/25.2 (for S:C=2 and O/C=1) was provided via mass flow controllers for a total flowrate of 2.15 SLPM. The two PROX reactors were operated with a combined Lambda value of 2.5. The achieved WGS effluent CO concentration is 1% at 27,000hr-1, and for the PROX it is less than 10ppm at a combined space-velocity (PROX-1 and PROX-2 together) of 90,000 hr-1.

- five mass flow controllers (Aalborg),
- water fed with syringe pump
- steam generator (custom made)
- five temperature probes (E-type)
- reactor/tube furnace assembly
- ice-water-cooled condenser
- micro gas-chromatograph (Agilent Micro GC 3000)

Process variables

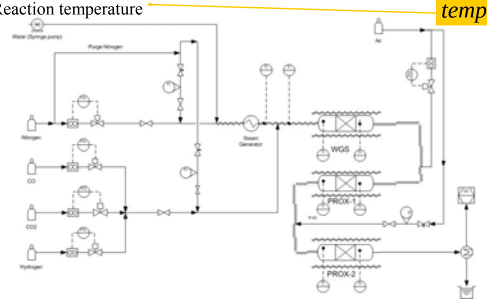
Simulated ATR inlet

Total flowrate &Catalyst bed volume

Furnace temperature

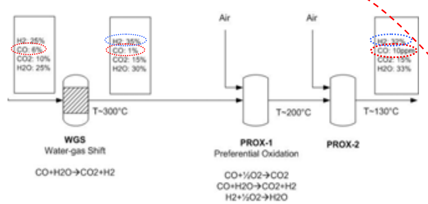
Investigated Parameters:

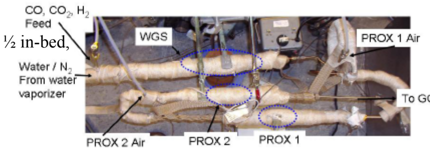
- •Steam-to-Carbon ratio –S:C (1.0-2.0)
- •Oxygen-to-carbon ratio –O:C (0.8-1.2)
- •Space velocity –GHSV (20000-180000 h-1)
- •Reaction temperature



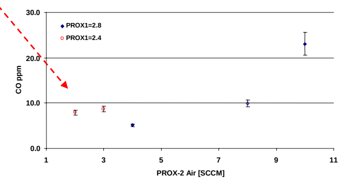
Integrated H_2 cleanup train for PEM Fuel cells

- System consists of **WGS, 2-stage PROX**
- WGS: promoted Pt catalyst on ɣ-Alumina, 60 screens, ½ in-bed,
- Final CO less than 10 ppm





Condition	H_2	CO_2	H_2O	N_2	CO (ppm)
A	25	13.8	28	33.2	8
B	25	13.9	28	33.1	9



WGS-PROX 1+2 performance: CO effluent concentration in ppm

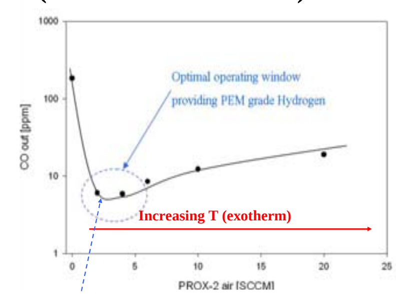
Selective catalytic reactions allow a contaminant, at ppm concentrations, dispersed within a complex mixture of inert and reactive components, to be completely neutralized in one step.

Preferential Oxidation investigation (PROX-1 and PROX-2)

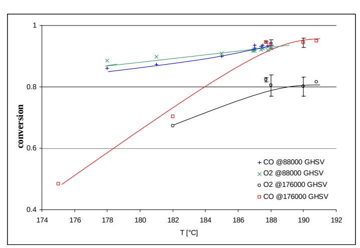
The preferential catalytic oxidation of CO to CO2 with oxygen is the simplest and most cost effective technique available for CO removal.

- •high CO oxidation activity,
- •high selectivity with respect to the CO oxidation,
- •minimal combustion of H_2
- •Mild temperatures, btw WGS (250-300 °C) and PEFC stack (70-80 °C).

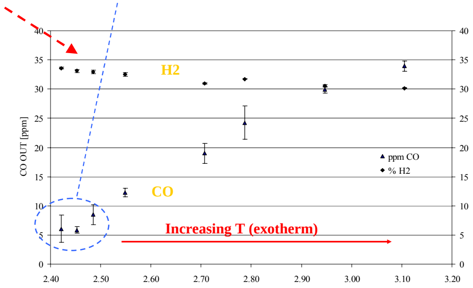
reduction in exothermic heat generated → improvement in selectivity for CO oxidation



Stainless steel ¾in reactor



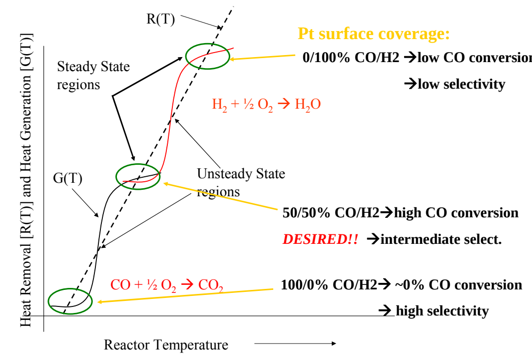
CO and Oxygen conversion; PROX 1 with 1/8th in bed. S/C=2, O/C=1, λ =2.4



PROX-1+2 CO and H2 exit concentration. λ (1) =2.4, . λ (2) =2.4-3.2

•Ideally, the catalyst must selectively oxidize up to about 1% (10,000 ppm) CO to less than 5 ppm, while oxidizing as little of the ~30-40% H_2 as possible.
•Observed Multiple steady states!

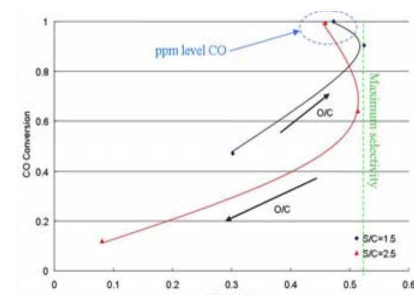
Multiple Steady States for PROX:



$CO + \frac{1}{2}O_2 \Rightarrow CO_2$	Desired reaction:
$H_2 + \frac{1}{2}O_2 \Rightarrow H_2O$	Undesired reaction:

O_2 stoichiometry $\lambda = \frac{2C_{O_2}}{C_{CO}}$ If λ=1 → stoichiometric feed

CO Selectivity $S = \frac{\frac{1}{2}\Delta C_{CO}}{\Delta C_{O_2}}$ If S=0.5 and λ=2 → 100% O2 conversion



Conversion-Selectivity Plot: Parametric study for PROX train, Parameters: Steam-to-Carbon and Oxygen-to-Carbon ratio

Results & Conclusions

- •Target CO concentration <10ppm can be achieved in a wide operation window (Lambda and S/C&O/C ratios)
- •CO conversion and selectivity is function of CO surface coverage and H_2 lightoff reaction
- •Maximum Selectivity to CO~50% for different conversions
- •Multiple steady states need to be understood and managed