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Hydrogen Recombiners for Non-Nuclear Hydrogen Safety Applications

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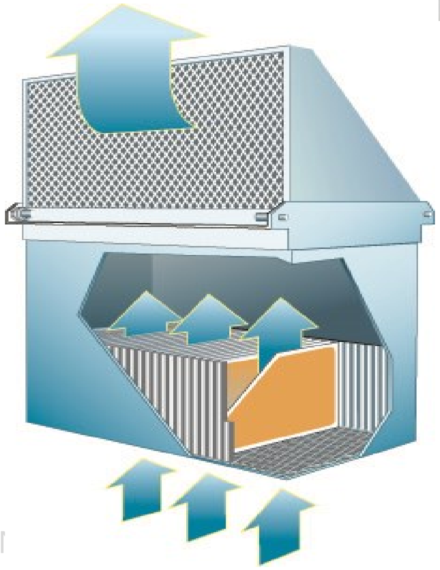


Outline

- Background and Motivation
- Facilities and Experimental Set-up
- Results and Discussion
  - H_2 Recombination Rate and CO Tolerance
  - Low Temperature Performance
- Conclusions

Motivation

- H_2 accumulation in confined and semi-confined H_2 applications is a concern
  - Sufficient ventilation
  - Alternative mitigation strategies (H_2 recombiners)
- Very likely to have facilities with combined H_2 and hydrocarbon fuels
- Hydrocarbon engine exhaust can contain catalyst poisons
  - e.g., CO or NO_x
  - A range of CO concentrations up to 1000 ppm was selected - Grenier[1] reported that up to 500 ppm CO may be present in maintenance garages
- Such applications may also experience temperatures below 0 °C

1. Grenier, M., Measurement of carbon monoxide in diesel engine exhaust, CANMET Mining and Mineral Sciences Laboratories Report No. R-436, 2005.

Hydrogen Recombiners

Self-Start Threshold

- Minimum H_2 concentration required to develop self-sustained convective flow through the PAR at a given temperature
- Largely dependant on catalyst activity/reaction kinetics

Recombination Rate

- Amount of H_2 that a PAR recombines per unit of time (i.e., kg/h)
- Largely dependant on fluid dynamics and convective flow

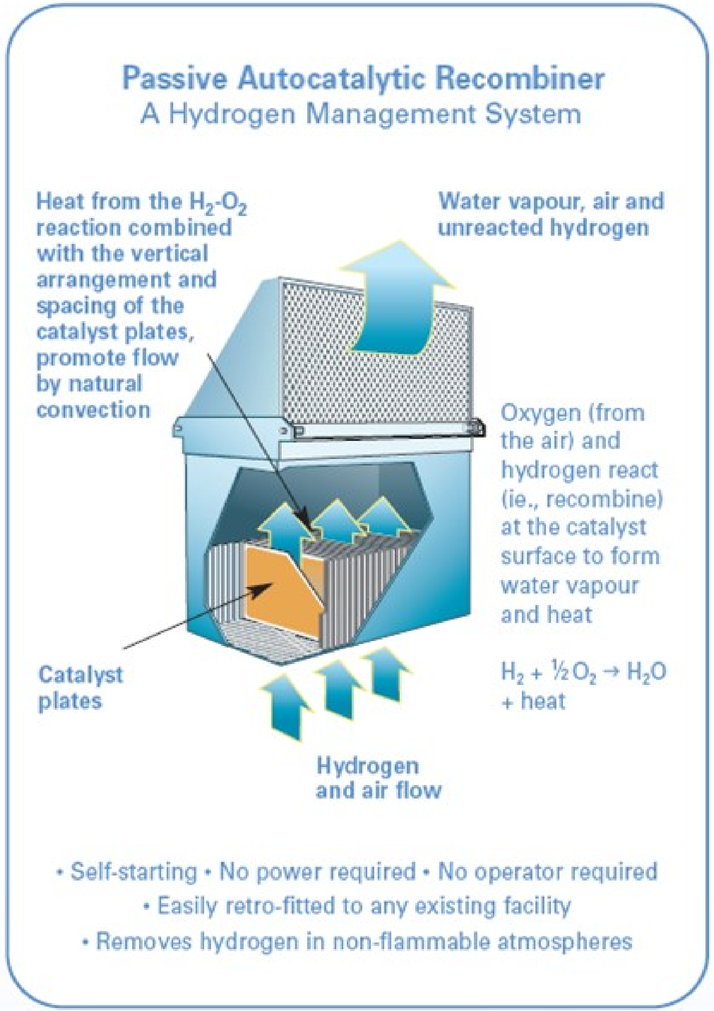
Catalyst Poisoning

- Platinum catalysts can adsorb CO molecules and hinder the catalytic reaction with H_2 by consuming active sites

Low Temperature

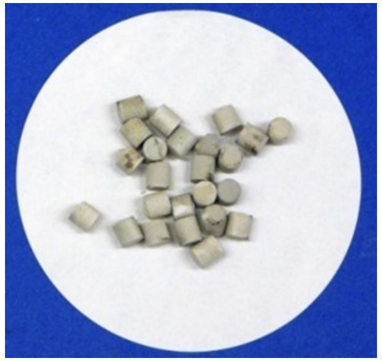
- Lower temperatures reduce the reaction kinetics/rate by increasing the activation energy

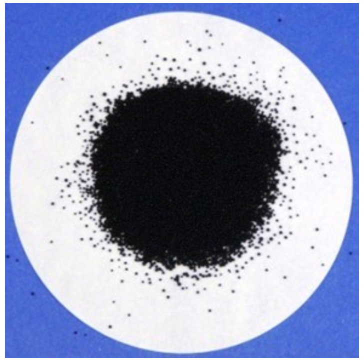
$$H_2 + \frac{1}{2}O_2 \leftrightarrows H_2O + heat$$



Catalyst Development

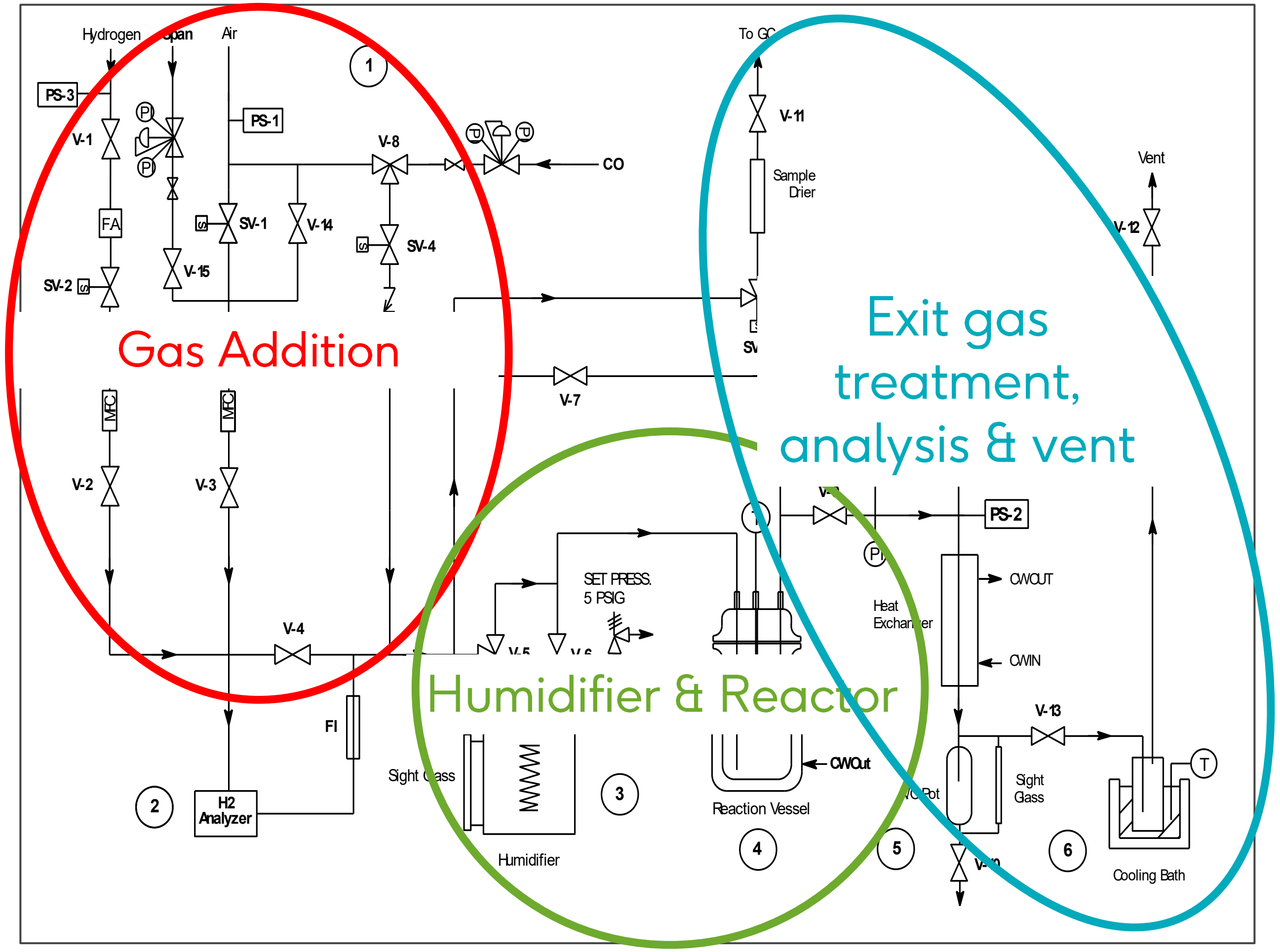
- Type 99-11 (used as baseline) is the standard Pt-based recombiner catalyst used in the PAR and GPR
- New catalyst formulations containing Pt + Ir as active metals and different catalyst preparation techniques were explored to improve the recombiner performance in combined H_2 and hydrocarbon applications
- All catalyst discussed have the same Pt loading as Type 99-11
- New catalyst formulations have varying Ir loadings:
  - CO-CAT01 = CO-CAT02 < CO-CAT03 < CO-CAT04
  - CO-CAT01 and CO-CAT02 were made using different catalyst preparation techniques





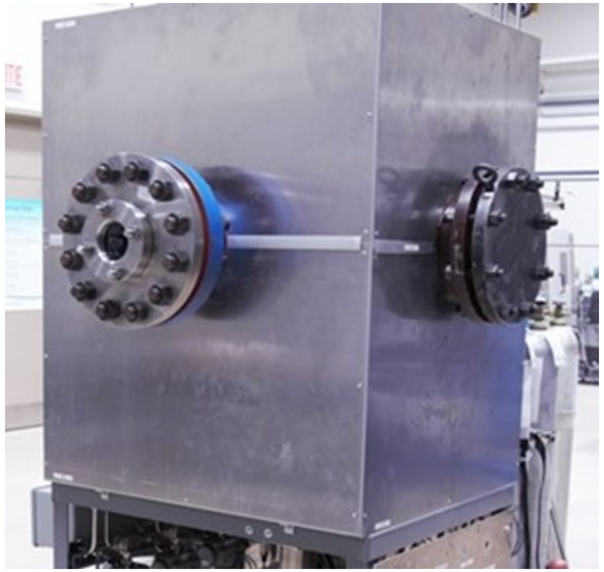
Facility and Experimental Set-Up: Catalyst Activity Bench Scale (CABS)

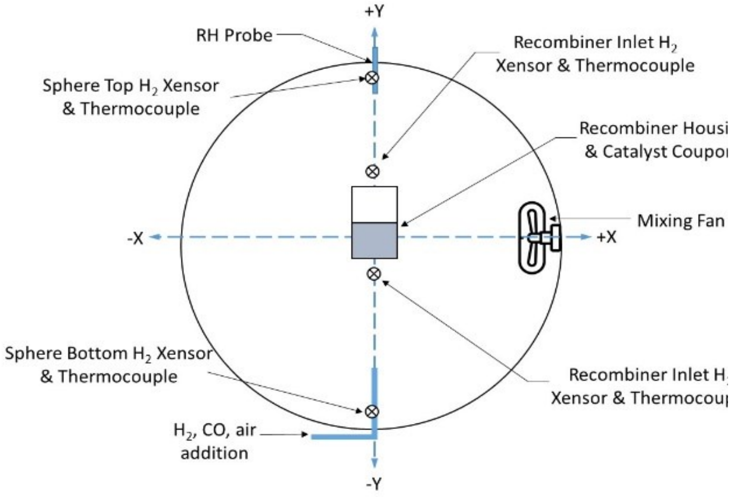
- CABS system developed for bench scale testing recombiner catalysts with potential poisons
- Used to assess the new catalyst formulations self-start behavior with CO and at low temperature
- 6 L glass jacket vessel
- Flow-through system controlled at 3 L/min
- Various H_2 and CO concentrations tested at 20 °C and atmospheric pressure
- Tests performed with H_2 and reactor temperatures -10 to 20 °C



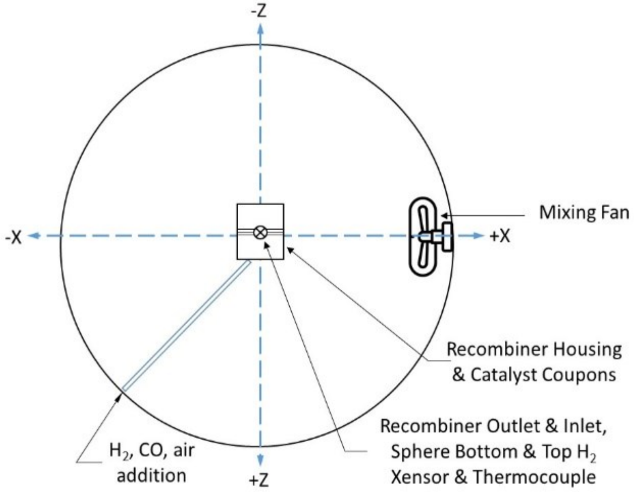
Facility and Experimental Set-Up: Hydrogen Safety Test Facility (HSTF)

- Self-start tests to investigate the CO tolerance of recombiner catalysts in a geometry that approximates a confined or semi-confined H_2 installation
- 30 inch ID, ~250 L
- 1.72 MPa and 100 °C
- Systems for controlled addition of H_2, CO, and air
- Vacuum and vent systems
- Gas analysis: H_2 (multiple) and CO
- Mixing fan
- Static pressure measurement
- Temperature measurement (6 thermocouples)





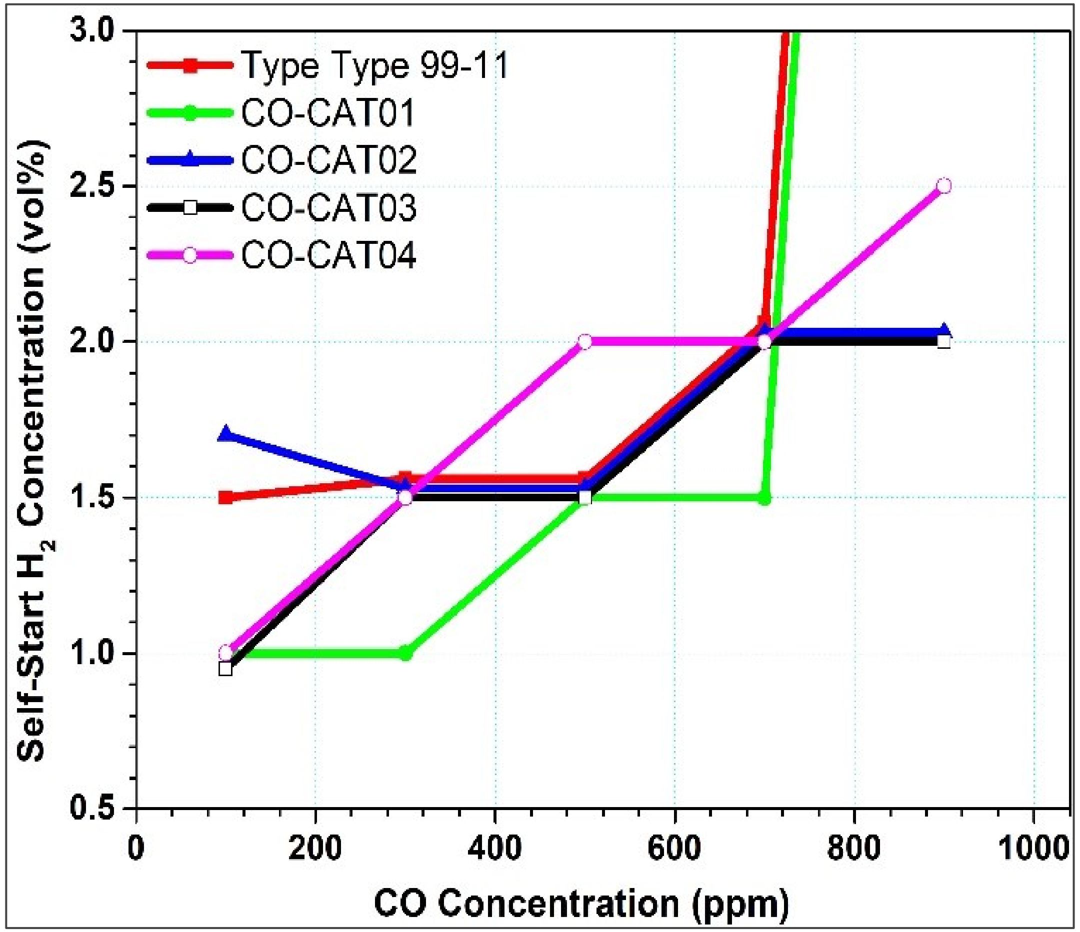
Side View



Top View

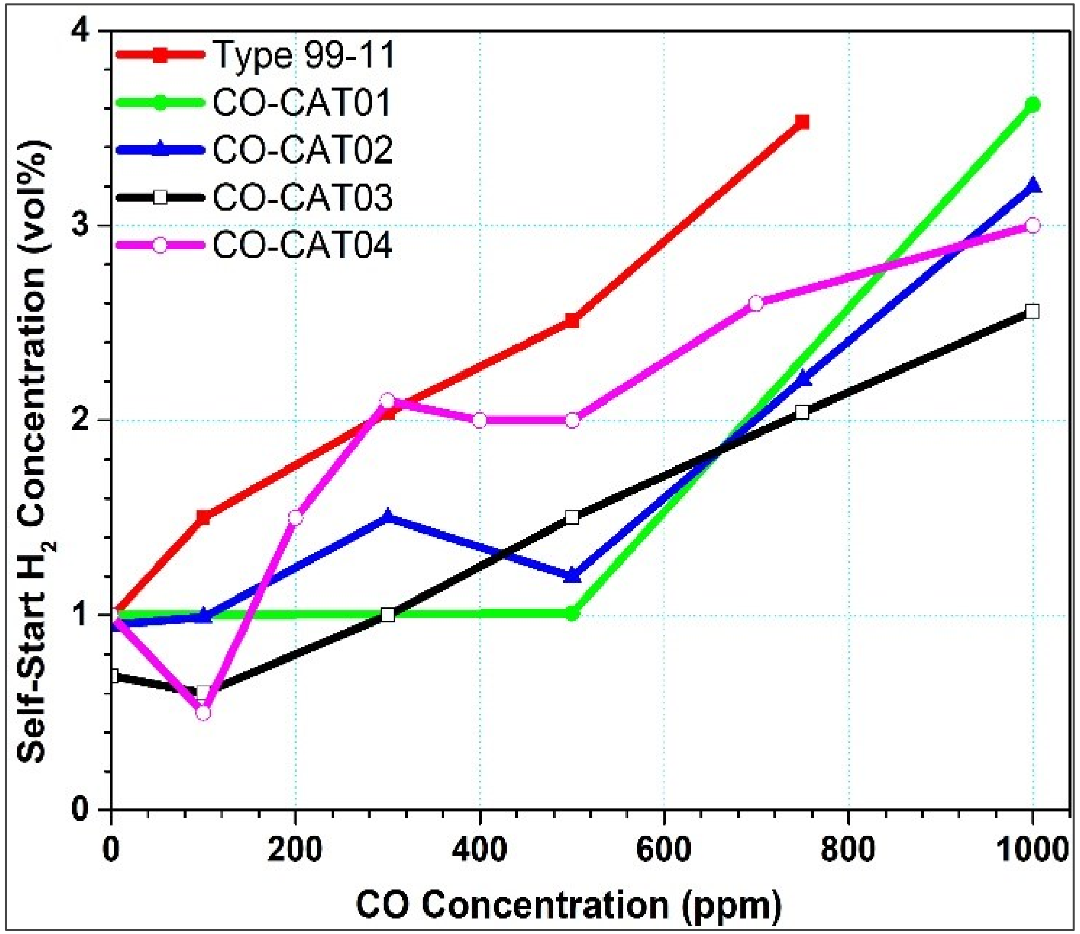
Results – CO Tolerance: CABS

- Results from the experiments to investigate the minimum H_2 concentration to generate a self-start at a given CO concentration
- Similar to the HSTF tests, H_2 was added in stepped increments of 0.5 vol.% at each CO concentration tested
- CO-CAT01 responds the best, but fails to start at 900 ppm CO with less than 3 vol.% H_2
- As found in the HSTF test results, the catalyst formulations CO-CAT02 and CO-CAT03 performed the best over the full range of CO concentrations
- Based on the H_2 conversion data (not shown), the Pt-Ir catalyst formulations consistently demonstrated higher H_2 conversion in the presence of CO than Type 99-11



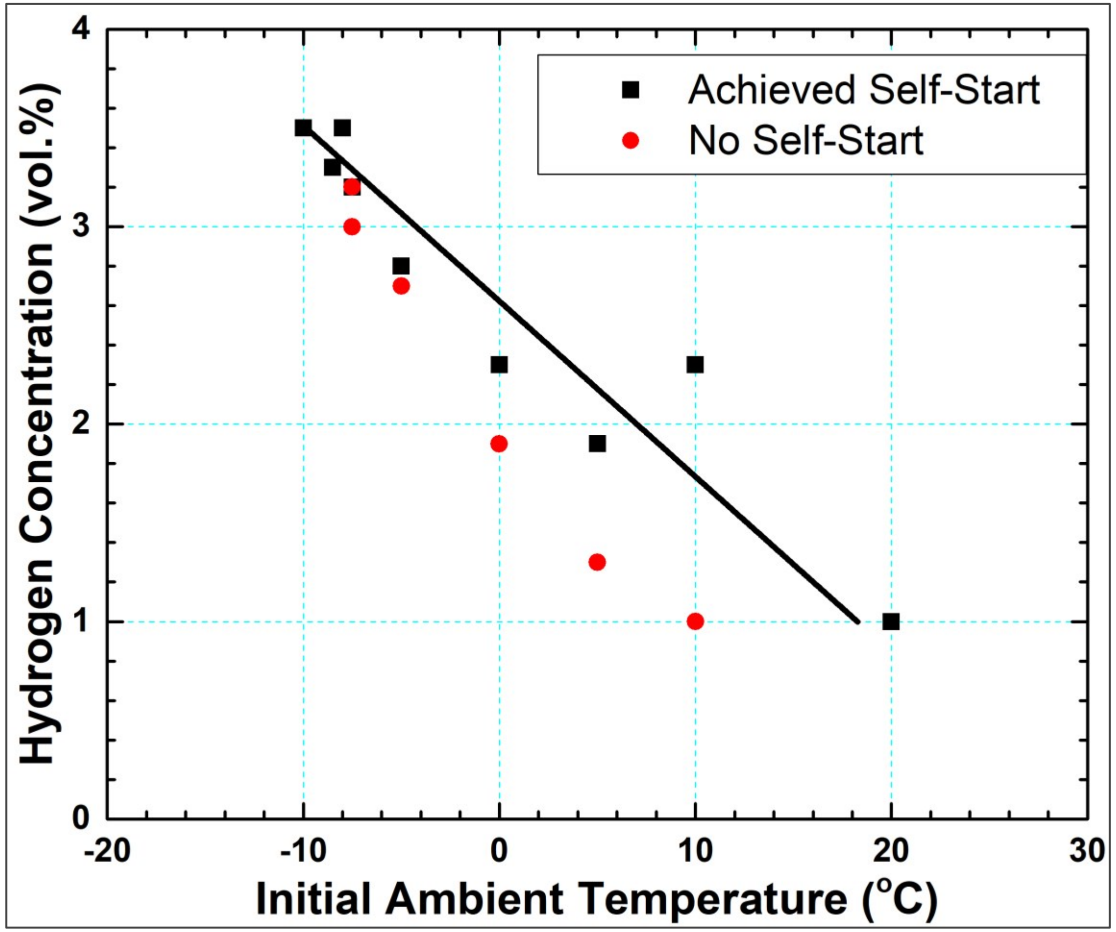
Results – CO Tolerance: HSTF

- Results from the experiments to investigate the minimum H_2 concentration to generate a self-start at a given CO concentration
- H_2 was added in stepped increments of 0.5 vol.% at each CO concentration tested
- Newly developed Pt-Ir catalysts respond similarly to H_2 as the reference catalyst, but have greater CO tolerance
- Overall, catalyst formulations CO-CAT02 and CO-CAT03 performed the best over the full range of CO concentrations
- Recombination rate of the new Pt-Ir catalyst formulations was verified with the new catalyst formulations



Results – Low Temperature: CABS

- Low temperature (below room temperature) experiments to understand the self-start performance of H_2 recombiner catalysts
- Experimental conditions: atmospheric pressure and flow of 3 L/min
- Only Type 99-11 catalyst tested
- Self-start achieved at the lowest temperature tested (-10 °C)
- Results demonstrate that higher H_2 concentration is required at lower temperatures
    - Linear trend found



Conclusions

- The addition of Ir to the H_2 recombiner catalyst successfully increases the catalyst H_2 recombination activity in the presence of low CO concentrations (<1000 ppm)
- New Pt-Ir catalyst formulations CO-CAT02 and CO-CAT03 performed better than the others
- Results from the HSTF and CABS were consistent between each other
- Addition of Ir to the catalyst did not affect the recombination rate
- The standard AECL/CNL recombiner catalyst self-starts below the H_2 LFL at temperatures as low as -10 °C
- Next steps:
  - NO_X on the recombiner catalyst performance
  - Assess the economics of H_2 recombiners versus mechanical ventilation
  - Other recombiner catalyst formulations at low temperatures

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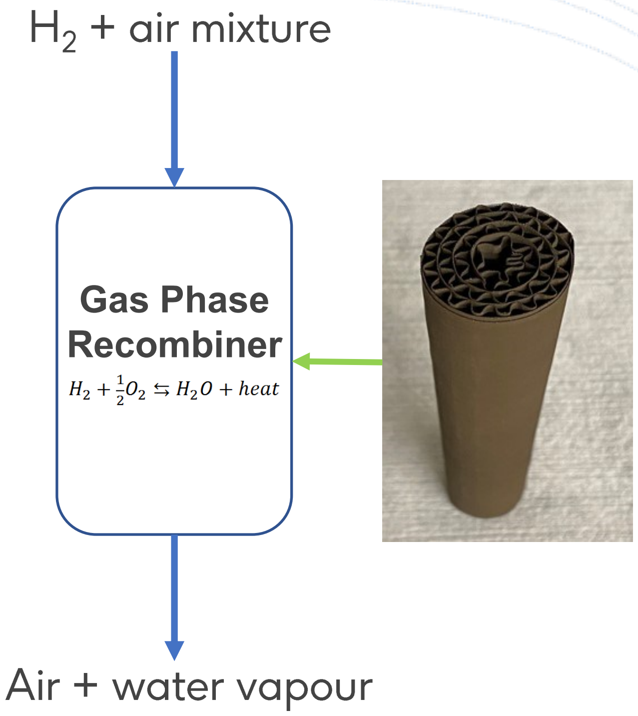
Hydrogen Recombiner Technologies

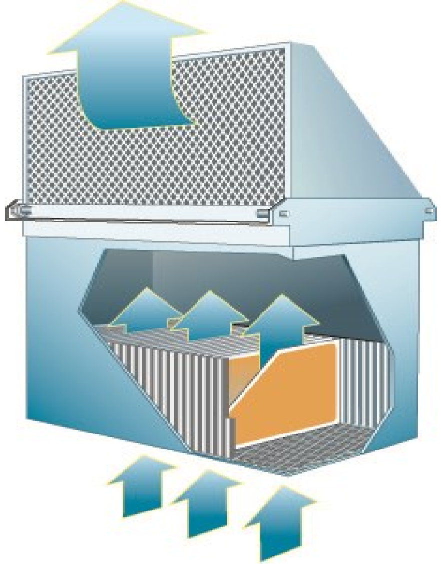
$$H_2 + \frac{1}{2}O_2 \leftrightarrows H_2O + heat$$

- Passive Autocatalytic Recombiner (PAR), Gas Phase Recombiner (GPR), Trickle-Bed Recombiner (TBR)
- Passive/convective or forced flow
- Most common form (PARs) utilized in nuclear reactor containment buildings
- Technology has been used in battery rooms or for gas clean up systems, deoxo catalyst for electrolyser product purification
- Manufacturers of PARs: Canada, Germany, France, Korea, China, Japan (in development), Russia

CNL developed wetproofed catalyst materials

- Recombines H_2 at ppm level
- Different catalyst materials and catalyst forms available to suit applications (spheres, rings, pellets, granules, screens, monoliths)





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