Dry Reforming of Landfill Gas Using Precious Metal Catalysts

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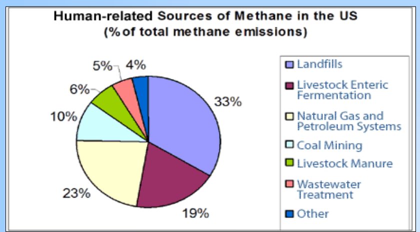
Landfill Gas – Production and Composition



Composition

About 50% CH4 and 50% CO2

Other important components: 21 ppmv Hydrogen Sulfides

Previous Reforming Work

- Steam Reforming
  - $CH_4 + H_2O \rightarrow CO + 3\,H_2$ $\Delta H = +\,226$ kJ/mol
  - Most important industrial process to make syn gas
  - Problems:
    - Superheated steam is expensive
    - Water-gas shift reaction produces CO_2
    - H_2-to-CO ratio too high for some downstream processes
- Partial Oxidation of Methane
  - $CH_4 + \frac{1}{2}\,O_2 \rightarrow CO + 2\,H_2$ $\Delta H = -\,44$ kJ/mol
  - Problem: At the stoichiometric CH_4-to-O_2 ratio there is significant carbon formation on catalysts other than noble metal catalysts
- Dry Reforming

  $CH_4 + CO_2 \rightarrow 2\,CO + 2\,H_2$ $\Delta H = +\,261$ kJ/mol
- Combinations of the above

Dry Reforming

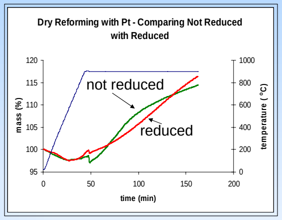
Order of reactivity for precious metal catalysts:
Ru, Rh, Ni, Re>> Ir > Pt > Pd
Other catalysts that have been investigated: Fe, Co, Ca, Mn
Reaction is thermodynamically favored above 913 K
Problems:

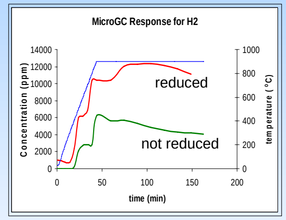
Carbon deposition

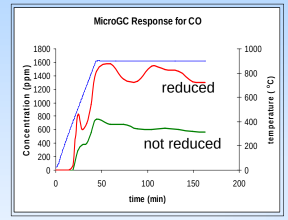
Energy intensive (more endothermic than steam reforming)

Platinum – 5%Pt/Al_2O_3

Reduced vs. Not Reduced







Rate of Deactivation:
Not Reduced = -1.279 %/min
Reduced = -0.519 %/min

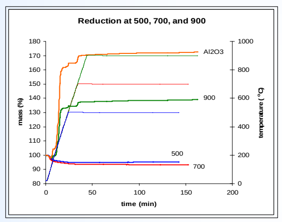
More H_2 production for the reduced state

More CO production for the reduced state

Therefore, higher activity for the reduced state

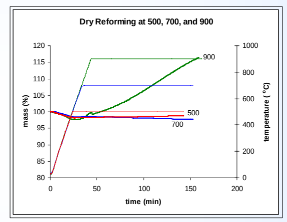
Reforming at 500, 700, and 900˚C

Reduction:



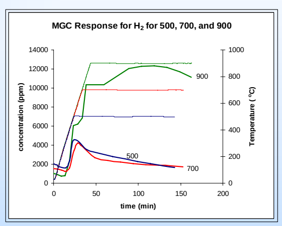
Unexpected weight increase for 900˚C reduction

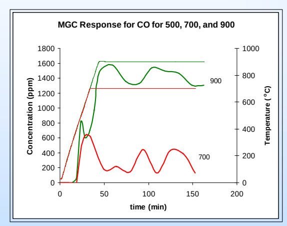
Dry Reforming:



900˚C shows weight increase due to carbon deposition (see EDX results)

MicroGC Results from 500, 700, and 900˚C



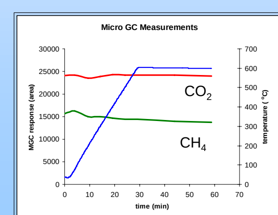


900˚C shows highest activity even though there is carbon deposition

Gold - Au/TiO_2

- Relatively new catalyst
- Inert in most reaction but very active when deposited in small particles (< 20 nm)

CO and H2 were **not** detected on the MicroGC



EDX Results:

Run Description	Species	Weight %
DR Temp = 900 No Reduction Industrial Grade gases	C	24.1
	O	Not measured
	Al	71.7
	Pt	4
DR Temp = 900 No Reduction UHP gases	C	18.86
	O	7.80
	Al	66.04
	Pt	7.30
DR Temp = 900 Reduction Temp = 1000 Industrial Grade gases	C	16.60
	O	12.06
	Al	66.89
	Pt	4.45
DR Temp = 900 Reduction Temp = 900 Industrial Grade gases	C	22.46
	O	11.81
	Al	61.19
	Pt	4.53
DR Temp = 900 Reduction Temp = 900 Industrial Grade gases	C	27.82
	O	13.05
	Al	57.31
	Pt	4.16
DR Temp = 700 Reduction Temp = 700 Industrial Grade gases	C	9.94
	O	13.66
	Al	72.81
	Pt	3.59
DR Temp = 500 Reduction Temp = 500 Industrial Grade gases	C	3.82
	O	14.32
	Al	74.03
	Pt	7.83

Conclusions:

Platinum

- Reduction enhances the production of syn gas and decreases the rate of deactivation
- The higher the reduction temperature, the more syn gas produced
- There is a period of interesting weight change followed by a drastic weight increase for the 900˚C tests
- The weight increase on the catalyst reformed at 900 is due to deactivation by carbon deposition
- The support itself has some sort of catalytic properties at high temperatures

Gold

- Sinters at 400 before reforming reaction can begin

Current Work:

BET analysis
Kinetic Analysis
Increasing CO2 flow to see effects on Carbon deposition
Catalyst regeneration through Carbon burn-off

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