Effect of Methyl Chloride on Catalytic Landfill Gas Reforming

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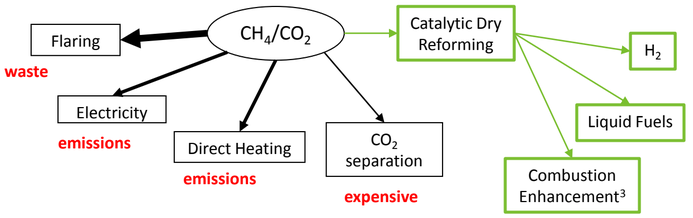
Motivation

• CH_4/CO_2 mixtures such as landfill gas, biogas, and wastewater digester gas are relatively small scale but local and cheap sources of energy
•They are most often flared due to the low energy content[1], but dry reforming can make use of the entire mixture[2]:

Dry Reforming: $CH_4 + CO_2 \rightarrow 2H_2 + 2CO$ ΔH=247 kJ/mole

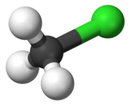


•These CH_4/CO_2 mixtures may contain poisons that could deactivate a catalyst:

Class	Examples	Amount (PPMV)
Chlorinated	Vinyl Chloride, Chlorocarbons	10-50
Sulfur	Hydrogen Sulfide, Methyl Sulfide	30
Aromatic	Toluene, Benzene	100
C2s	Ethane, Ethanol	70
C3s	Propane, Acetone	30

Typical poisons in a landfill gas[1]

Chlorocarbons originate from natural presence of chlorinated compounds in biological material.

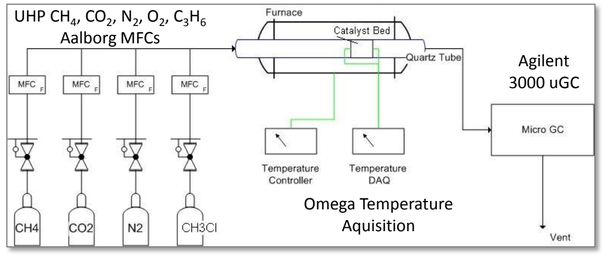


•Aromatics and hydrocarbons result in carbon formation that can be countered with additional oxidant
•Sulfur is extensively studied

•No studies to our knowledge on effect of chlorocarbon on dry reforming
•As use of bio-derived fuels becomes more widespread, effect of chlorocarbons on reforming catalysts will become more important

Experimental Setup

Flow through Reactor



Catalyst: 4% Rh/γ-Al_2O_3 powder, 10 μ obtained from BASF catalysts. Prepared with Rh Nitrate solution

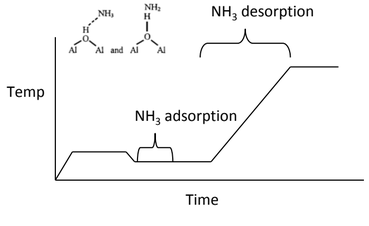
FTR used to pulse 10-50 ppm CH_3Cl into dry reforming feed

Characterization

Samples prepared for characterization:

Name	Reforming Feed	$[CH_3Cl]$	Temp °C	Reaction Time
400°C, 10hr	5% CH_4, 6% CO_2	0	400	10 hours
400°C, 10hr, w/Cl	5% CH_4, 6% CO_2	50 ppm	400	10 hours
700°C, 10hr	5% CH_4, 6% CO_2	0	700	10 hours
700°C, 10hr, w/Cl	5% CH_4, 6% CO_2	50 ppm	700	10 hours

NH_3 Temperature Programmed Desorption (TPD)



XPS: Thermo Fisher K Alpha XPS equipped with an Al K(alpha) monochromatic source. Binding energies referenced to C1s=285.0 eV

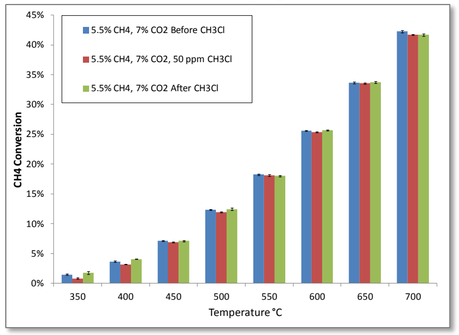
CO_2 chemisorption: TGA (Netzsch, STA 409 PC Luxx) used to measure weight gain during CO_2 adsorption to measure surface basicity

CO chemisorption: TGA used to measure weight gain during CO adsorption to measure available metal sites

BET: Quantachrome Nova 2200e

Effect of CH_3Cl on Activity, Selectivity

CH_3Cl poisons CH_4 reforming activity



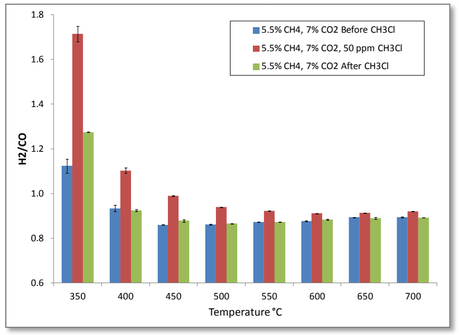
•1 hour 50 ppm pulse of CH_3Cl into dry reforming feed reversibly decreases dry reforming activity:
$CH_4 + CO_2 \rightarrow 2H_2 + 2CO$
with CH_3Cl

ΔH=247 kJ/mole

•Syngas production drops commensurately with loss of CH_4 reforming

•Poisoning is greatest at low temperatures (350-500°C)

CH_3Cl increases selectivity to H_2



•Change in selectivity indicative of reverse water-gas shift poisoning:
$H_2 + CO_2 \leftrightarrow H_2O + CO$
with CH_3Cl

ΔH=42 kJ/mole

•During CH_3Cl pulse, CO_2 and H_2 increase, H_2O and CO decrease

•HCl pulse gives same change in selectivity as CH_3Cl, indicating chloride is key species

CH_3Cl introduction reversibly poisons dry reforming and reverse water-gas shift reactions, especially at low temperatures

Surface Characterization

XPS shows surface chloride deposition is highest at low temperatures

Known Binding Energies from NIST[4] and Literature [5,6]		
Orbital	**B.E. eV**	**Species Name**
Rh3d5	309.4	rhodium oxide
	310.0	diffuse rhodium oxide
	310.1	rhodium chloride
Cl2p	198.0, 198.4	alumina hydroxi-chloride[6]
	198.3	Al-Cl[5]
	198.6	rhodium chloride
	199.1	alumina oxi-chloride[6]
	199.3	rhodium chloride

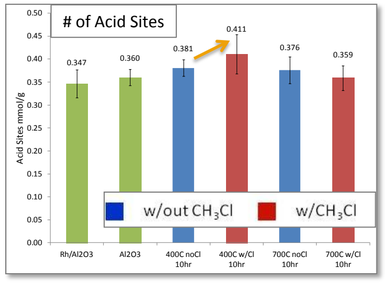
•Location of chloride is not definitive because binding energies for related species are similar

•Chloride deposition decreases with temperature; little effect of time on stream

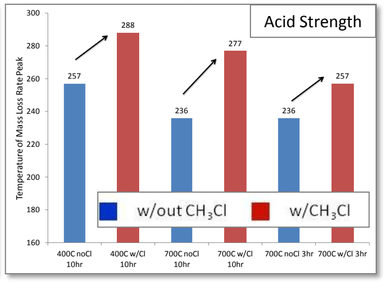
Sample	Chloride Wt %
400°C, 10 hr, w/Cl	1.25
700°C, 3 hr, w/Cl	0.72
700°C, 10 hr, w/Cl	0.65

NH_3 TPD shows CH_3Cl increases acidity of catalyst surface

CH_3Cl exposure increases number of acid sites at 400°C



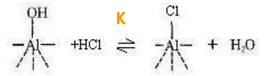
CH_3Cl exposure increases strength of acid sites at all temperatures



Mechanism and Model

Alumina chlorination model developed for Pt/γAl_2O_3 can be applied here

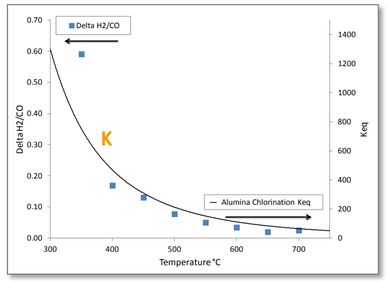
Alumina Chlorination Reaction[7]:



$$R = \frac{[H_2O]}{[HCl]} \qquad L = [Cl] + [OH]$$

K=equilibrium constant of chlorination reaction

L=chloride retention capacity



Expression for Adsorbed Chloride:

$$[Cl^*] = \frac{KL(1/R)}{1 + K(1/R)}$$

•K decreases with temperature, meaning chlorination is not favored at high temp

•K function correlates with experimentally observed selectivity change; means that alumina chlorination reaction could be valid on Rh/γAl_2O_3

If alumina OH removal by chloride is a reasonable poisoning mechanism, change in selectivity can be explained, because forward and reverse water-gas shift reactions rely on OH groups:

Reverse Water-Gas Shift [8]
$H_2 + CO_2 \rightarrow H_2O + CO$ ΔH=42 kJ/mole

Water-Gas Shift [8]
$H_2O + CO \rightarrow H_2 + CO_2$ ΔH=-42 kJ/mole

•OH groups are likely intermediates in forward and reverse water-gas shift reactions
•Chloride replaces OH groups, so poisons water gas shift
•Mechanism for CO_2 activation in RWGS also important for dry reforming activity; could be cause for dry reforming activity loss as well

Conclusions and Recommendations

Effect of CH_3Cl:

CH_3Cl → *CH_3 → Not unique to CH_3Cl, also present from CH_4
CH_3Cl → *Cl → Replaces OH on Al_2O_3
- Increases surface acidity
- Poisons water-gas shift reaction
- Poisons dry reforming reaction

•Co-feeding biogas with O_2 or H_2O decreases chloride poisoning

•Operating the reactor at a higher temperature decreases chloride poisoning

•Auto-thermal reforming is a good reforming option for LFG with chlorocarbons because it supplies H_2O to remove chloride deposition from alumina and O_2 to keep surface free of carbon

Acknowledgements

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Doctoral thesis based on this work: Catalytic Reforming of Biogas for Syngas Production, McKenzie Kohn, Columbia University, 2012

1. Tchobanoglous, G., H. Theisen, and S. Vigil, *Integrated Solid Waste Management*, McGraw-Hill, 1993
2. Kohn, M.P.; Castaldi, M.J.; Farrauto R.J., (2010) *Applied Catalysis B:Environmental*. 94:125-133
3. Kohn, M. P., Lee, J., Basinger, M. L., & Castaldi, M. J. (2011) *I&ECR, 50*(6): 3570-3579.
4. NIST Standard Reference Database 20, Version 4.1 ; Alexander V. Naumkin, Anna Kraut-Vass, Stephen W. Gaarenstroom, and Cedric J. Powell (2012)
5. H. Karhu, A. Kalantar, I.J. Vayrynen, T. Salmi, D.Y. Murzin, (2003) *Applied Catalysis A: General*, 247: 283-294
6. I. Bennour, V. Maurice, P. Marcus, (2010) *Surface and Interface Analysis*, 42: 581-587
7. Castro, A. A., Scelza, O. A., Benvenuto, E. R., Baronetti, G. T., & Parera, J. M. (1981). *J. Catalysis, 69*(1):222-226
8. Adapted from: F.C. Meunier, D. Tibiletti, A. Goguet, R. Burch, (2006) *Oil Gas Sci. Technol.*, 61: 497-502