Survey of Catalysts for Oxidation of Mercury in Flue Gas

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Mercury in Flue Gas

- **Elemental mercury (Hg₀)**
  - Emitted from high-temperature coal combustion
  - Insoluble in water
  - Can be removed with activated carbon injection (ACI)

- **Oxidized mercury (Hg²⁺)**
  - Typically assume HgCl₂
  - Water soluble, sorbs to AC

- **Particle-bound mercury (Hg(p))**
  - Both Hg₀ and Hg²⁺
  - Typically a small fraction of total mercury

- **Ratio of Hg₀/Hg²⁺ depends on a number of factors (coal-Cl, LOI, time-temperature history, etc.)**
Mercury Removal Technologies

• Activated carbon injection (ACI)
  – Inefficient mixing/contact: Requires C/Hg mass ratios >1000:1
  – AC is a general sorbent
  – Potentially makes fly ash unusable as cement additive
  – Low cost: AC costs < $1/lb
  – Current ‘best bet’

• Catalytic mercury oxidation
  – Use catalyst to convert Hg$^0$ to Hg$^{2+}$
  – Removal of Hg$^{2+}$ with wet FGD (>90% efficient)
  – Proposed catalysts: SCR catalysts, carbon-based materials, metals and metal oxides

There is no “magic bullet” – mercury control will involve multiple technologies/products
Major Uncertainty: Reaction Mechanism

- Assumption: Chlorine (HCl or Cl₂) is the oxidizer for mercury in flue gas
- Hg⁰(g) + HCl(g)/Cl₂(g) is too slow to explain observed extents of oxidation
  - Hg⁰(g) + Cl(g) is fast, but Cl(g) concentrations are low
  - Cl₂ could be catalytically generated from HCl (Deacon process), but Cl₂ concentrations are generally low
- Likely oxidation mechanism is heterogeneous
Heterogeneous Reaction Mechanisms

- **Langmuir-Hinshelwood**

  \[
  A(g) \leftrightarrow A(ads) \\
  B(g) \leftrightarrow B(ads) \\
  A(ads) + B(ads) \xrightarrow{k_{surf}} AB(ads) \\
  AB(ads) \rightarrow AB(g)
  \]

- **Reaction between adsorbed Hg^0 and HCl**
  - Both Hg^0 and HCl can adsorb to carbon sorbents
Heterogeneous Reaction Mechanisms

- **Eley-Rideal**
  - Reaction between an adsorbed species and a gas-phase species
  - Either Hg$^0$ or HCl can be the adsorbed species

\[
A(g) \leftrightarrow A(ads) \\
A(ads) + B(g) \overset{k}{\longrightarrow} AB(g)
\]
Heterogeneous Reaction Mechanisms

- **Mars-Maessen**
  - Hg⁰ reacts with lattice oxidant (O or Cl)
  - Oxidant is replenished from gas-phase

\[
A(g) \leftrightarrow A(ads) \\
A(ads) + M_x O_y \rightarrow AO(ads) + M_x O_{y-1} \\
M_x O_{y-1} + \frac{1}{2} O_2 \rightarrow M_x O_y \\
AO(ads) \rightarrow AO(g)
\]

- This mechanism may explain effectiveness of halogenated sorbents
  - Lattice halide could serve as the oxidant
Other Major Questions

- Is Hg\(^0\) physically or chemically adsorbed to sorbent surfaces?
- What are the intermediate products, if any?
- Is the final oxidized species HgCl\(_2\)?
- What are the effects of co-reactants such as SO\(_2\) and NO\(_x\)?

Big picture: We lack predictive ability!
**SCR Catalysts**

- Used for reduction of NO to N\textsubscript{2}
  - V\textsubscript{2}O\textsubscript{5}/WO\textsubscript{3} on TiO\textsubscript{2} support
  - T > 300\textdegree\ C

Flue gas:
- NO, NO\textsubscript{2}
- HCl
- SO\textsubscript{2}
- Hg\textsuperscript{0}, Hg\textsuperscript{2+}
- N\textsubscript{2}
- O\textsubscript{2}

NH\textsubscript{3}

Less NO, more Hg\textsuperscript{2+}

NH\textsubscript{3}-rich zone
- NO reduction
- NH\textsubscript{3} adsorbs to V\textsubscript{2}O\textsubscript{5} sites

NH\textsubscript{3}-poor zone
- Hg\textsuperscript{0} oxidation
- HCl, Hg\textsuperscript{0}, or both adsorb
SCR Catalysts: Reaction

- **Mechanism could be:**
  - Langmuir-Hinshelwood
  - Eley-Rideal
    - Either HCl or Hg⁰ adsorbed to surface

- **Likely competitive adsorption between NH₃ and HCl and/or Hg⁰**
  - Size of NH₃-rich and NH₃-poor zones determined by NH₃/NO ratio
  - Increasing NH₃/NO reduces the extent of Hg⁰ oxidation, and may force Hg⁰ from the surface
SCR Catalysts: Results

- **Laboratory scale**
  - >95% oxidation of Hg\(^0\) in simulated flue gas

- **Slipstream of subbituminous/bituminous flue gas**
  - 60-80% oxidation over 6 days

- **Pilot scale test (bituminous coal)**
  - SCR was placed downstream of ESP (T ~ 150° C)
  - Efficiency fell from 70% to 30% during 10-month test
  - Ash plugging may have been a problem

- **Full scale test**
  - Essentially no oxidation for lignite flue gas
  - Ash plugged/blocked catalyst and limited both NO and Hg\(^0\) conversion
SCR Catalysts: Outlook

- Installing SCR for NO\textsubscript{x} reduction may provide co-benefit Hg\textsuperscript{0} oxidation
  - Greatest benefit for bituminous coals (high Cl)
  - Long-term conversion is uncertain

- Installing SCR catalyst specifically for Hg\textsuperscript{0} oxidation may not be economical
  - Other materials are cheaper and give higher conversion to Hg\textsuperscript{2+}
Carbon-based Catalysts

- Carbon catalysts, activated carbons, fly ash, or Thief™ carbon
- Mercury adsorbs to carbon sites on fly ash particles
  - Hg(ads) is oxidized (chemisorbed) on carbon surfaces
  - Correlation between extent of oxidation and UBC in ash
  - Increased oxidation across baghouses
Carbon-based Catalysts: Reaction

- **HCl adsorbs to carbon sorbents**
  - Langmuir-Hinshelwood mechanism
    - Adsorbed Hg\(^0\) and HCl
  - Eley-Rideal mechanism
    - Either HCl or Hg\(^0\) as adsorbed species

- **NO appears to inhibit oxidation**

- **Role of SO\(_2\) is unclear**
  - SO\(_2\) can oxidize to H\(_2\)SO\(_4\) on activated carbon
Carbon-based Catalysts: Results

- **Carbon catalyst** maintained >80% oxidation (pilot-scale) for two months
  - Effectiveness reduced by extended exposure to fly ash

- **Fly ash**
  - Performance depends on source – high (>50%) conversion for bituminous ash, very low (<10%) for unpromoted lignite ash

- **Thief carbon**
  - Achieved >70% oxidation in short-term tests
  - No long-term tests
Carbon-based Catalysts: Outlook

- Fly ash and Thief carbon may be economical
  - Inexpensive
  - Can be promoted with halogens
  - Regenerable
- Commercial carbon catalysts have shown good performance in pilot-scale tests
- These materials may be more cost-effective than metal or metal oxide catalysts
Metal and Metal Oxide Catalysts

- Iron/Iron oxides
- Noble metals – Cu, Pd, Au, Ag
- Ir and Ir/Pt
- MnO₂
Metal catalysts: Iron

- Fe and Fe/Cr catalysts showed poor conversion
  - Studies suggest that stainless steel may catalyze oxidation
- Fe$_2$O$_3$ may enhance Hg$^0$ oxidation on fly ash particles
  - Fe$_2$O$_3$ in model fly ash (fixed bed) catalyzed oxidation
  - $\alpha$-Fe$_2$O$_3$ injected into flue gas had little catalytic ability
  - $\gamma$-Fe$_2$O$_3$ coated onto fabric filters enhanced oxidation
  - Catalytic effect of Fe$_2$O$_3$ in fly ash may result from mix of species
Metal Catalysts: Noble Metals

• Palladium
  – Most exhaustively tested noble metal catalyst
  – Pilot-scale test using Pd deposited onto commercial forms
  – >80% oxidation for ten months
    • Sonic horns required to remove ash particles
  – Preliminary economics
    • 62% savings over ACI for 80% Hg removal
    • 9% savings over ACI for 90% Hg removal
Metal Catalysts: Noble Metals

- Expect similar performance for Cu, Au, Ag as Pd
  - Lack of mechanistic understanding is a hindrance!
  - Example: Au catalyst
    - Meischen and Van Pelt: Hg$^0$ + HCl
    - Zhao et al: Hg$^0$ + Cl$_2$; HCl reduced oxidation relative to Cl$_2$ alone

- Cu is an interesting case
  - CuO in a model fly ash oxidized >90% of Hg$^0$ from simulated flue gas
  - CuCl can catalyze Hg$^0$ even without HCl (Mars-Maessen reaction?)
Metal Catalysts: Outlook

- Noble metals (Pd) have promise
  - Possibly more cost-effective than ACI/COHPAC
  - Catalyst loading as little as 1 wt.%
- More work is required to better understand reaction dynamics
Recommendations for Future Research

• Understanding reaction mechanism and kinetics is paramount!
  – Predictive ability
  – Requires lab-scale tests using simulated flue gas
    • Downside: Differences between simulated and real flue gas

• Novel catalysts and catalyst supports
  – Cost effectiveness, regeneration

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