Survey of Catalysts for Oxidation of Mercury in Flue Gas

Albert A. Presto and Evan J. Granite
National Energy Technology Laboratory

DOE/NETL Mercury Control Technology Conference
Pittsburgh, PA
December 2006

Mercury in Flue Gas

- **Elemental mercury (Hg^0)**
  - Emitted from high-temperature coal combustion
  - Insoluble in water
  - Can be removed with activated carbon injection (ACI)
- **Oxidized mercury (Hg^{2+})**
  - Typically assume $HgCl_2$
  - Water soluble, sorbs to AC
- **Particle-bound mercury (Hg(p))**
  - Both Hg^0 and Hg^{2+}
  - Typically a small fraction of total mercury
- **Ratio of Hg^0/Hg^{2+} depends on a number of factors (coal-Cl, LOI, time-temperature history, etc.)**

NETL

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

NETL

Major Uncertainty: Reaction Mechanism

- **Assumption: Chlorine (HCl or Cl_2) is the oxidizer for mercury in flue gas**
- **Hg^0(g) + HCl(g)/Cl_2(g) is too slow to explain observed extents of oxidation**
  - Hg^0(g) + Cl(g) is fast, but Cl(g) concentrations are low
  - Cl_2 could be catalytically generated from HCl (Deacon process), but Cl_2 concentrations are generally low
- **Likely oxidation mechanism is heterogeneous**

NETL

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

$$A(g) \leftrightarrow A(ads)$$

$$A(ads) + B(g) \xrightarrow{k} AB(g)$$

Heterogeneous Reaction Mechanisms

- **Mars-Maessen**
  - Hg^0 reacts with lattice oxidant (O or Cl)
  - Oxidant is replenished from gas-phase

$$A(g) \leftrightarrow A(ads)$$

$$A(ads) + M_xO_y \rightarrow AO(ads) + M_xO_{y-1}$$

$$M_xO_{y-1} + \frac{1}{2}O_2 \rightarrow M_xO_y$$

$$AO(ads) \rightarrow AO(g)$$

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

Other Major Questions

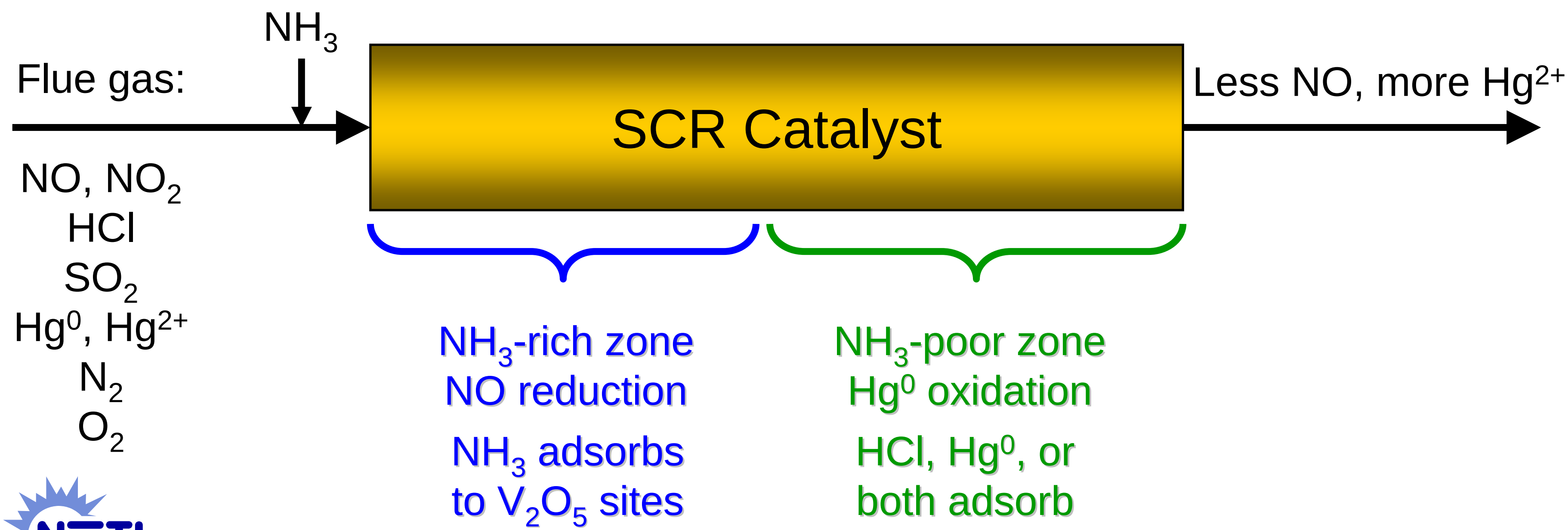
- Is Hg^0 physically or chemically adsorbed to sorbent surfaces?
- What are the intermediate products, if any?
- Is the final oxidized species $HgCl_2$?
- What are the effects of co-reactants such as SO_2 and NO_x?

Big picture: We lack predictive ability!

NETL

SCR Catalysts

- **Used for reduction of NO to N_2**
  - V_2O_5/WO_3 on TiO_2 support
  - T > 300º C



SCR Catalysts: Reaction

- **Mechanism could be:**
  - Langmuir-Hinshelwood
  - Eley-Rideal
    - Either HCl or Hg^0 adsorbed to surface
- **Likely competitive adsorption between NH_3 and HCl and/or Hg^0**
  - Size of NH_3-rich and NH_3-poor zones determined by NH_3/NO ratio
  - Increasing NH_3/NO reduces the extent of Hg^0 oxidation, and may force Hg^0 from the surface

NETL

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^o 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

NETL

SCR Catalysts: Outlook

- **Installing SCR for NO_x reduction may provide co-benefit Hg^0 oxidation**
  - Greatest benefit for bituminous coals (high Cl)
  - Long-term conversion is uncertain
- **Installing SCR catalyst specifically for Hg^0 oxidation may not be economical**
  - Other materials are cheaper and give higher conversion to Hg^{2+}

NETL

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

NETL

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_2SO_4 on activated carbon

NETL

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
- MnO_2

Metal catalysts: Iron

- **Fe and Fe/Cr catalysts showed poor conversion**
  - Studies suggest that stainless steel may catalyze oxidation
- **Fe_2O_3 may enhance Hg^0 oxidation on fly ash particles**
  - Fe_2O_3 in model fly ash (fixed bed) catalyzed oxidation
  - α- Fe_2O_3 injected into flue gas had little catalytic ability
  - γ- Fe_2O_3 coated onto fabric filters enhanced oxidation
  - Catalytic effect of Fe_2O_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

NETL

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

Acknowledgments

ORISE, IEP Program

NETL