Removal of Elemental Mercury from Flue Gas by V$_2$O$_5$/TiO$_2$ Catalysts Dispersed on Mesoporous Silica

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Anthropogenic Mercury Emissions

Global Mercury Emissions: 2,382 metric tons

- Coal/Fuel combustion: 1470 (62%)
- Non-ferrous metal production: 170 (7%)
- Pig iron and steel production: 30 (1%)
- Cement production: 130 (5%)
- Waste disposal: 110 (5%)
- Artisanal gold mining: 300 (13%)
- Chlor-alkali: 172 (7%)

Mercury Emissions in China by Sectors, 2003

- Coal combustion: 39%
- Petroleum combustion: 1%
- Zinc smelting: 31%
- Lead smelting: 11%
- Copper smelting: 3%
- Gold smelting: 7%
- Steel smelting: 1%
- Cement industry: 5%
- Household Garbage Incineration: 2%
- Other sources: 39%

Mercury Emissions in the U.S. – 33% from coal-fired power plants

Coal combustion is the major source of mercury emissions!

Source: UNEP Global Mercury Assessment, UNEP, Geneva, December 2002
Elemental mercury (Hg$^0$): volatile, not soluble in water
Oxidized mercury (Hg$^{2+}$): water soluble $\rightarrow$ Wet Scrubber
Particulate mercury (Hg$_p$): bound on fly ash $\rightarrow$ ESP

Solutions
- Adsorption of Hg$^0$ and Hg$^{2+}$ on sorbents
- Oxidation of Hg$^0$ to Hg$^{2+}$
Mercury Control Technologies: Sorbent Injection

- Injection of activated carbon upstream of an ESP or FF showed effectiveness in mercury capture, but the resultant carbon content in the fly ash makes the combustion by-products unsellable → cost increase!

Source of Figure: http://www.dnr.state.wi.us/air/toxics/mercury/rule.htm
Elemental mercury is oxidized by injected bromine or bromide species, and the oxidized mercury is removed by wet scrubber.

**Balance-of-plant impacts of bromine/bromide injection**
Elemental mercury is oxidized by SCR or metal oxides catalysts, and the oxidized mercury is removed by wet scrubber – $\text{V}_2\text{O}_5$ is the active site for Hg oxidation.

- Suitable for multipollutant control option if installed with SCR and/or Wet FGD.
- Efficiency of Hg oxidation by SCR catalyst varies.
- Mechanism of Hg–SCR catalyst interaction is not clear.

Source of Figure: http://www.dnr.state.wi.us/air/toxics/mercury/rule.htm
Previously we have developed novel SiO$_2$/TiO$_2$/V$_2$O$_5$ catalysts and tested them in simulated flue gas downstream of an ESP (T = 135 °C) – The results showed high efficiencies of Hg oxidation (90%) and Hg capture (40%) due to high surface area support and optimized V$_2$O$_5$ content (Li, Wu, et al. *Environ. Sci. Tech.* 2008, 42, 5304-5309)

- The SiO$_2$/TiO$_2$/V$_2$O$_5$ catalysts have not been tested at SCR temperatures (300 ~ 400 °C).
- It is hypothesized that temperature will affect the catalytic performance.

Source of Figure: [http://www.dnr.state.wi.us/air/toxics/mercury/rule.htm](http://www.dnr.state.wi.us/air/toxics/mercury/rule.htm)
Research Objectives

• To investigate the temperature effect on Hg$^0$ oxidation and capture using SiO$_2$/TiO$_2$/V$_2$O$_5$ catalysts

• To study the mechanism of Hg$^0$ catalytic oxidation over SiO$_2$/TiO$_2$/V$_2$O$_5$ catalysts and the effects of flue gas components

• To recommend the best strategy to apply the SiO$_2$/TiO$_2$/V$_2$O$_5$ catalysts as an alternative technology for Hg removal in coal-fired power plants
Catalyst Synthesis and Characterization

**Synthesis of SiO$_2$/TiO$_2$/V$_2$O$_5$: Sol-Gel method**

**Chemicals:** D/I water, ethanol, TEOS (SiO$_2$ precursor), TiO$_2$ nanoparticles (Degussa, P25), VTPO ($V_2$O$_5$ precursor), 1M HNO$_3$, 3% HF

**Procedures:** Mix chemicals → stir for 2 h → pipette the solution to assay plate → gelation → age at room temperature for 2 days → heat in oven at 65 °C for 2 days → rinse with D/I water → dry at 103 °C for 18 h → dry at 180 °C for 6 h


Cylindrical Pellets: 3 mm × 5 mm
BET Surface Area: 260–320 m$^2$/g
Pore Size: ~14 nm

(a) SEM image, (b) Si mapping, (c) Ti mapping
## Catalyst Characterization

### BET Surface Area

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET specific surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>341.8</td>
</tr>
<tr>
<td>SV2</td>
<td>263.4</td>
</tr>
<tr>
<td>SV5</td>
<td>283.2</td>
</tr>
<tr>
<td>SV8</td>
<td>273.8</td>
</tr>
<tr>
<td>SV10</td>
<td>262.9</td>
</tr>
<tr>
<td>ST12</td>
<td>319.4</td>
</tr>
<tr>
<td>ST12V2</td>
<td>258.0</td>
</tr>
<tr>
<td>ST12V5</td>
<td>262.5</td>
</tr>
</tbody>
</table>

### X-Ray Diffraction (XRD) Analysis

- **SiO₂**: amorphous
- **TiO₂**: mixture of anatase and rutile
- **V₂O₅**: amorphous vanadate species; crystalline phase appears when **V₂O₅** > 8 wt%
Experimental Setup – Packed-Bed Reactor
## Experimental Plan

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Carrier gas</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set 1</td>
<td>ST18V5</td>
<td>N₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N₂ + 4% O₂</td>
</tr>
<tr>
<td>Set 2</td>
<td>SV5</td>
<td>Simulated flue gas(SFG)</td>
</tr>
<tr>
<td></td>
<td>ST6V5</td>
<td>4%O₂, 8%H₂O, 12%CO₂,</td>
</tr>
<tr>
<td></td>
<td>ST12V5</td>
<td>10ppm HCl, 300ppmNO,</td>
</tr>
<tr>
<td></td>
<td>ST18V5</td>
<td>400ppm SO₂, balanced</td>
</tr>
<tr>
<td></td>
<td></td>
<td>with N₂</td>
</tr>
<tr>
<td>Set 3</td>
<td>ST18V5</td>
<td>N₂ + 4% O₂ + individual flue gas components</td>
</tr>
</tbody>
</table>

- The feeding Hg⁰ concentration was 65 ~ 75 µg m⁻³
- In each test 200 mg catalyst was used
O₂ enhanced the Hg⁰ oxidation ability of ST18V5 catalyst at both 135 °C and 350 °C

\[
\begin{align*}
V_2O_5 + Hg & \rightarrow V_2O_4 + HgO \\
V_2O_4 + \frac{1}{2} O_2 & \rightarrow V_2O_5
\end{align*}
\]

Overall Reaction \[Hg + \frac{1}{2} O_2 \rightarrow HgO\]
• STV catalysts have better Hg oxidation ability than SV catalyst in the range of 135 to 400 °C.
• Catalytic activity increases as TiO₂ content of the STV catalysts increases from 0 ~ 18%.
• Hg⁰ oxidation by STV catalysts decreases as temperature increases from 135 to 350 °C and levels off from 350 to 400 °C.
Set 3: Effect of Individual Flue Gas Components for ST18V5 in the range of 135 ~ 350 °C

- 400 ppm SO₂ has insignificant effect
- 300 ppm NO increases Hg⁰ oxidation to some extent
- 5 ppm HCl increases Hg⁰ oxidation dramatically
Set 3: Effect of Moisture at Different Temperatures

Moisture significantly inhibits mercury oxidation, particularly at higher temperatures

- Eley-Rideal reaction mechanism, where adsorbed Cl reacts with gas-phase (or weakly adsorbed) Hg\(^0\).

- Competitive adsorption on the active sites by water vapor lowers Hg\(^0\) oxidation rate
Conclusions

- SiO$_2$/TiO$_2$/V$_2$O$_5$ (STV) catalysts have been synthesized and tested for Hg$^0$ removal from simulated coal-combustion flue gas in the temperature range of 135 to 400 °C.
- STV catalysts with higher TiO$_2$ content show higher Hg$^0$ oxidation ability.
- Hg$^0$ oxidation efficiency decreases as temperature increases from 135 to 400 °C.
- O$_2$, NO, and HCl are the flue gas components that promote Hg$^0$ oxidation, with HCl having the most important effect.
- Water vapor significantly inhibits Hg$^0$ oxidation, probably due to its competitive adsorption on the active sites.

It is recommended that the SiO$_2$/TiO$_2$/V$_2$O$_5$ (STV) catalysts be applied in the lower temperature region (i.e. in between ESP and FGD) for best performance on Hg removal from flue gas.
Future Studies

• More systematic experimental studies to investigate the effects of flue gas components at different concentrations corresponding to burning different types of coals
• Further understanding of the mechanism of Hg$^0$ oxidation and adsorption on SiO$_2$/TiO$_2$/V$_2$O$_5$ catalysts
• Optimize the composition and nanostructures of SiO$_2$/TiO$_2$/V$_2$O$_5$ catalysts
• Compare the Hg removal efficiency of SiO$_2$/TiO$_2$/V$_2$O$_5$ catalysts with commercial SCR catalysts under flue gas conditions
THANK YOU!

Questions?
Effect of individual flue gas component at 350 °C

Hg Oxidation Efficiency:

\[
E_{\text{oxi}}(\%) = \frac{\Delta H_g^0}{H_g^0_{\text{in}}} = \frac{H_g^0_{\text{in}} - H_g^0_{\text{out}}}{H_g^0_{\text{in}}} \times 100\%
\]

Hg Capture Efficiency:

\[
E_{\text{cap}}(\%) = \frac{\Delta H_g^T}{H_g^T_{\text{in}}} = \frac{H_g^T_{\text{in}} - H_g^T_{\text{out}}}{H_g^T_{\text{in}}} \times 100\%
\]