Development of Silica/Vanadia/Titania Catalysts for Removal of Elemental Mercury from Coal-Combustion Flue Gas

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Received January 11, 2008. Revised manuscript received March 26, 2008. Accepted May 5, 2008.

SiO2/V2O5/TiO2 catalysts were synthesized for removing elemental mercury (Hg0) from simulated coal-combustion flue gas. Experiments were carried out in fixed-bed reactors using both pelleted and powder catalysts. In contrast to the SiO2–TiO2 composites developed in previous studies, the V2O5 based catalysts do not need ultraviolet light activation and have higher Hg0 oxidation efficiencies. For Hg0 removal by SiO2–V2O5 catalysts, the optimal V2O5 loading was found between 5 and 8%, which may correspond to a maximum coverage of polymeric vanadates on the catalyst surface. Hg0 oxidation follows an Eley–Rideal mechanism where HCl, NO, and NO2 are first adsorbed on the V2O5 active sites and then react with gas-phase Hg0. HCl, NO, and NO2 promote Hg oxidation, while SO3 has an insignificant effect and water vapor inhibits Hg0 oxidation. The SiO2–TiO2–V2O5 catalysts exhibit greater Hg0 oxidation efficiencies than SiO2–V2O5 may be because the V–O–Ti bonds are more active than the V–O–Si bonds. This superior oxidation capability is advantageous to power plants equipped with wet-scrubbers where oxidized Hg can be easily captured. The findings in this work revealed the importance of optimizing the composition and microstructures of SCR (selective catalytic reduction) catalysts for Hg0 oxidation in coal-combustion flue gas.

Introduction

Coal-fired utility boilers are currently the largest single-known source of anthropogenic mercury (Hg) emissions in the United States, accounting for one-third of the 150 tons of Hg emitted annually. In 2005 the U.S. EPA issued the Clean Air Mercury Rule (CAMR) to cap and reduce Hg emissions from coal-fired power plants; meanwhile, it reversed its December 2000 finding that it was “appropriate and necessary” to regulate coal- and oil-fired power plants for Hg emissions (2). In February 2008, the U.S. Court of Appeals for the District of Columbia vacated both the reversal and the CAMR (3). While it takes time for the U.S. EPA to establish new rules, a significant number of U.S. states have enacted their own Hg emissions regulations, which are generally more stringent than the CAMR.

In the coal-derived flue gas, there are three basic forms of Hg: elemental Hg (Hg0), oxidized Hg (Hg+2) and particle-bound Hg (Hg+) (4). Hg0 can be collected in electrostatic precipitators (ESPs) and/or baghouses. Hg+2 is soluble in water and is readily captured by wet flue gas desulfurization (FGD) equipment. Hg+2 is volatile and insoluble in water, and thus, it is poorly captured using conventional control technologies. Unfortunately, Hg speciation studies showed that Hg+2 is the dominant species in flue gas when burning low rank (subbituminous or lignite) coals. Therefore, need exists for a low cost Hg oxidation/capturing process.

Activated carbon injection (ACI) is one of the major commercially available technologies for Hg control from coal-fired power plants. However, the incremental cost of Hg control via ACI is estimated to range from $3810 to $166 000/lb Hg removed (5). A variety of noncarbon based Hg0 oxidation catalysts have also been studied, which fall into two groups: SCR catalysts (typically composed of V2O5/WO3 supported on TiO2), and metals and metal oxides (6). SCR catalysts were found to oxidize Hg0 at their typical operating temperatures (300–400 °C), particularly in the presence of NO (7,8). Lee et al. (8) reported that Hg0 oxidation across a pilot-scale SCR facility reached ~90% burning three Illinois bituminous coals (HCl > 100 ppm in flue gas) but was less than 20% burning a Powder River Basin (PRB) subbituminous coal (HCl = 7.9 ppm). Blythe et al. (11) demonstrated that SCR catalysts can also oxidize Hg0 at low temperatures (~130 °C) upstream of pilot-scale wet FGD systems; however, their activities (~67% Hg0 oxidation for fresh catalysts) were lower than those of palladium and certain carbon-based catalysts (~95% Hg0 oxidation) when burning North Dakota lignite. Although the mechanisms of Hg0 oxidation over SCR catalysts are not clear to date, V2O5 species supported on TiO2 is believed to be the active phase of SCR catalysts for the reduction of NO by NH3 (12–14). The amount of V2O5, in commercial SCR catalysts is generally less than 1 wt% (14), but it was reported that 8 wt% V2O5 loading corresponded to the highest SCR activity for NO reduction at low temperatures (~250 °C) (15). Similarly, V2O5 loading may play a significant role in low-temperature SCR activity for Hg oxidation. On the other hand, the nature of the support for V2O5 is also an important factor for SCR catalytic activity (13). TiO2 as a support normally has drawbacks such as low surface area; hence, a common practice is to use a SiO2 support coated with TiO2 (16).

As a novel metal oxide catalyst for Hg0 oxidation, TiO2-based nanomaterials (in situ generated TiO2 nanoparticles and SiO2–TiO2 nanocomposites) under UV irradiation have demonstrated greater than 90% Hg0 removal under room conditions (17,18). Follow-up studies by Li et al. (19–21) indicated that flue gas components significantly affect Hg capture on SiO2–TiO2 composites (12 wt% TiO2), with HCl and SO2 enhancing Hg0 oxidation while water vapor and NOx having inhibitory effects. The detrimental effect of NO that only 50 ppm NO reduced Hg0 oxidation to 10% (using 8 g SiO2–TiO2) necessitates adding more active species to the composite (19).

Since both commercial SCR catalysts and the SiO2–TiO2 composites have their limitations on Hg0 oxidation in coal-combustion flue gas, this study aimed to enhance the catalytic activity by incorporating V2O5 into the SiO2–TiO2 composites. The synthesized SiO2/V2O5/TiO2 catalysts take the advantage of high surface area SiO2 support over the SCR catalysts. The optimal V2O5 loading of the synthesized catalysts was
explored. The effects of individual flue gas components on the catalytic performance were investigated as well. While commercial SCR catalysts are usually tested “as received” with little information reported on their chemical composition and microstructures, findings in this study would contribute to fabrication of more effective SCR catalysts for Hg\(^\circ\) oxidation through optimization of catalyst properties.

Materials and Methods

Catalyst Preparation. The procedure of synthesizing the SiO\(_2\)–TiO\(_2\) composite using a sol–gel method was reported in detail in our previous studies \((19–22)\). When synthesizing the SiO\(_2\)–TiO\(_2\)–V\(_2\)O\(_5\) composite, vanadium triisopropoxide oxide (VTPO) (Alfa Aesar) was added as the precursor of V\(_2\)O\(_5\). A known amount of VTPO was first dissolved in well stirred ethanol to form an orange-brown solution. It was then added dropwise to the prepared silica sol under vigorous stirring. TiO\(_2\) nanoparticles (P25, Degussa) were finally added to the mixture before it started to gel. When synthesizing the SiO\(_2\)–V\(_2\)O\(_5\) composite, the step of adding TiO\(_2\) nanoparticles was skipped. The composites were originally made in the pellet form (3 mm in diameter and 5 mm in length). A powder was skipped. The composites were originally made in the pellet form (3 mm in diameter and 5 mm in length). A powder form of the composites was also obtained by grinding the pellet form (3 mm in diameter and 5 mm in length). A powder form of the composites was also obtained by grinding the pellets and sieving through 40/100 meshes (425/150 \(\mu\)m). The catalysts are abbreviated by way of ST\(_x\)Vy, where S represents SiO\(_2\), T represents TiO\(_2\), V represents V\(_2\)O\(_5\), and \(x\) and \(y\) represent the weight percentages of the TiO\(_2\) and V\(_2\)O\(_5\), respectively.

Powder Characterization. The BET surface areas of the powder catalysts were measured using a Quantachrome NOVA1200 gas sorption analyzer (Boynton Beach, FL). It is assumed that the pellets and powder have equivalent specific surface areas due to their highly porous structure. X-ray diffraction (XRD) patterns of the powders were recorded with a Philips APD 3720 diffractometer using Cu Ka radiation (\(\lambda = 0.1542 \text{ nm}\)) in the range of 15–40° \((2\theta)\) with a step size of 0.02°. X-ray photoelectron spectroscopy (XPS) analysis of the samples was carried out by a Perkin-Elmer PHI 5100 ESCA system using Mg Ka (\(h\nu = 1253.6\text{ eV}\)) radiation to excite photoelectrons.

Catalyst Activity Measurement. As reported in our previous studies \((19–22)\), the SiO\(_2\)–TiO\(_2\) composite needs activation by UV light. Thus, the dependence of UV light activation for V\(_2\)O\(_5\) based composites was first investigated. Pellet form of the catalysts was used because the space contribution to fabrication of more effective SCR catalysts for Hg\(^\circ\) oxidation through optimization of catalyst properties.

Table 1 summarizes the experimental conditions for activity measurement of the catalysts.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>form</th>
<th>reactor</th>
<th>mass (g)</th>
<th>carrier gas*</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ST12</td>
<td>pellet</td>
<td>UV</td>
<td>8.0</td>
<td>FG1(^b), FG2(^c)</td>
</tr>
<tr>
<td>SV2</td>
<td>pellet</td>
<td>UV</td>
<td>8.0</td>
<td>FG1, FG2</td>
</tr>
<tr>
<td>ST12V2</td>
<td>pellet</td>
<td>UV</td>
<td>8.0</td>
<td>FG1, FG2</td>
</tr>
<tr>
<td>set II</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SV2</td>
<td>powder</td>
<td>non-UV</td>
<td>0.50</td>
<td>FG3(^d)</td>
</tr>
<tr>
<td>SV5</td>
<td>powder</td>
<td>non-UV</td>
<td>0.50</td>
<td>FG3</td>
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<td>non-UV</td>
<td>0.50</td>
<td>FG3</td>
</tr>
<tr>
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<td>powder</td>
<td>non-UV</td>
<td>0.50</td>
<td>FG3</td>
</tr>
<tr>
<td>ST12V5</td>
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<td>non-UV</td>
<td>0.50</td>
<td>FG3</td>
</tr>
<tr>
<td>ST12V2</td>
<td>powder</td>
<td>non-UV</td>
<td>0.50</td>
<td>FG3</td>
</tr>
<tr>
<td>ST6V5</td>
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<td>non-UV</td>
<td>0.50</td>
<td>FG3</td>
</tr>
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<td>non-UV</td>
<td>0.50</td>
<td>FG3</td>
</tr>
<tr>
<td>set III</td>
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</tr>
<tr>
<td>SV6</td>
<td>powder</td>
<td>non-UV</td>
<td>0.25</td>
<td>individual gas (O(_2), HCl, NO, NO(_2), SO(_2), or H(_2)O) at varied conc.</td>
</tr>
</tbody>
</table>

* Containing 15–16.5 ppb Hg\(^\circ\) balanced with N\(_2\) in all tests; total flow rate = 1.5 lpm. \(^a\) FG1 = 4% O\(_2\), 12% CO\(_2\), 8% H\(_2\)O, 30 ppm HCl, 1200 ppm SO\(_2\), 300 ppm NO, 10 ppm NO\(_2\). \(^b\) FG2 = 4% O\(_2\), 12% CO\(_2\), 12% H\(_2\)O, 10 ppm HCl, 400 ppm SO\(_2\), 300 ppm NO, 10 ppm NO\(_2\). \(^c\) FG3 = 3% O\(_2\), 12% CO\(_2\), 8% H\(_2\)O, 10 ppm HCl, 400 ppm SO\(_2\), 300 ppm NO, 10 ppm NO\(_2\).

Figure 1. The U-tube quartz reactor was immersed in an oil bath heated by a hotplate to a constant temperature of 135 °C (±0.5 °C). The catalyst powders were packed in between glass wools in the reactor. FG3 was used as the simulated flue gas which is also in the range of those burning low rank coals but has a lower water vapor concentration than FG2.

Finally, to explore the reaction mechanisms and the roles of the flue gas components in the catalytic reactions, the catalytic activity of a fixed amount of catalyst (SV5) was examined with introduction of individual flue gas components (set III).

It is generally agreed that the decrease in Hg\(^\circ\) concentration across the catalysts is due to Hg\(^\circ\) oxidation, and thus, the oxidation efficiency (\(E_{\text{ox}}\)) is defined as \((7, 9)\)

\[
E_{\text{ox}}(\%) = \frac{\Delta Hg^0_{\text{in}} - \Delta Hg^0_{\text{out}}}{\Delta Hg^0_{\text{in}}} \times 100\% \tag{1}
\]

where \(Hg^0_{\text{in}}\) and \(Hg^0_{\text{out}}\) represent Hg\(^\circ\) at the inlet and outlet of the reactor, respectively. All or part of the \(\Delta Hg^0\) is captured on the catalysts as solid phase and the rest escapes to the gas phase. Thus, the Hg capture efficiency (\(E_{\text{cap}}\)) is always less than or equal to \(E_{\text{ox}}\), with \(E_{\text{cap}}\) calculated as

\[
E_{\text{cap}}(\%) = \frac{\Delta Hg^0_{\text{in}} - Hg_{\text{out}}^T}{Hg^0_{\text{in}}} \times 100\% \text{ or } E_{\text{cap}}(\%) \tag{2}
\]

where \(Hg^0_{\text{in}}\) and \(Hg_{\text{out}}^T\) represent Hg\(^\circ\) at the inlet and outlet of the reactor, respectively. Note that in this study Hg\(^T_\text{out}\) = Hg\(^T_\text{in}\) and Hg\(^T_\text{out} \geq Hg^\circ_\text{out}\).

Results and Discussion

Characterization of the Catalysts. The BET specific surface areas of the catalysts are listed in Table 2. All the catalysts

VOL. 42, NO. 14, 2008 / ENVIRONMENTAL SCIENCE & TECHNOLOGY ■ 5305
exhibit high surface areas (>250 m²/g). Without any doping, the pure silica gel had the highest surface area. The inclusion of 12% TiO₂ to the silica gel (ST12) slightly reduced the surface area. The doping of V₂O₅ (2–10%) to the silica gel moderately reduced the surface area, but all the SiO₂–V₂O₅ catalysts had a similar level of surface areas. It is not clear why there is no apparent trend between the surface area and V₂O₅ loading. The surface areas of the SiO₂–TiO₂–V₂O₅ catalysts were close to those of the SiO₂–V₂O₅ catalysts.

The XRD patterns of the catalysts are shown in Figure 2. No discernible crystal phase of V₂O₅ (peak at 2θ 26.1°) was detected for SV2 and SV5, which indicated that the vanadium contents were highly dispersed on these catalysts (15). A very small peak of crystalline V₂O₅ was detected for SV8, whereas SV10 showed a relatively broader and more prominent peak of crystalline V₂O₅. Molecular structures of vanadium oxides at different surface loadings have been reported in literature. As surface vanadia concentration increases, monomeric vandyl (V⁴⁺) species, polymeric vanadates, and aggregated amorphous/crystalline V₂O₅ clusters are subsequently formed (12, 13, 23). The XRD results in this study indicated that crystalline V₂O₅, which was detected for SV8, whereas SV10 showed a relatively broader and more prominent peak of crystalline V₂O₅. Molecular structures of vanadium oxides at different surface loadings have been reported in literature. As surface vanadia concentration increases, monomeric vandyl (V⁴⁺) species, polymeric vanadates, and aggregated amorphous/crystalline V₂O₅ clusters are subsequently formed (12, 13, 23).

The oxidation states of vanadium species (V⁵⁺ and/or V⁴⁺) in the catalysts were identified by XPS analysis as shown in Table 2. For SV5, SV8, and SV10, V⁵⁺ dominates (~90%) the vanadium content. Combining with the XRD results, it may imply that monomeric vandyl (V⁴⁺) species transformed to polymeric vanadates (V⁵⁺) as V₂O₅ loading increased to over 5%. For ST12V5, the fraction of V⁵⁺ was a little less than that in SV5. However, there could be errors involved in the quantitative analysis due to the overlap of binding energies (peaks) of V⁵⁺ and V⁴⁺ species as well as the interference from nearby O1s satellite peak (23).

**Mercury Removal Using Pellet Catalysts.** Tests were first performed and showed that pure silica pellets were inert to Hg removal and that homogeneous oxidation of Hg in the gas-phase was negligible under the experimental conditions. Figure 3 demonstrates Hg oxidation and capture efficiencies (Eoxi and Ecap) using different pellet catalysts (set I). For ST12 in FG1, there was negligible removal of Hg without UV light. With UV, Eoxi and Ecap were around 50%. In contrast, the activities of SV2 and ST12V2 on Hg removal were almost the same with or without UV irradiation. Thus, only the results without UV are shown for SV2 and ST12V2. Both SV2 and ST12V2 demonstrated very high efficiencies of Hg oxidation and capture (~90%), although their specific surface areas are lower than ST12 (Table 2). Apparently, the addition of V₂O₅ is advantageous due to the enhancement in chemisorption of Hg⁶⁺. It also simplifies the system by eliminating

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**TABLE 2. Catalysts Characterization and Their Activities on Hg Removal**

<table>
<thead>
<tr>
<th>sample</th>
<th>BET specific surface area (m²/g)</th>
<th>surface V⁵⁺/V (mol %)</th>
<th>surface V⁴⁺/V (mol %)</th>
<th>V₂O₅/TiO₂ mass ratio</th>
<th>Hg oxi. rate (µg/g-hr)</th>
<th>Hg cap. rate (µg/g-hr)</th>
<th>Eoxi (%)</th>
<th>Ecap (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica gel</td>
<td>341.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ST12</td>
<td>319.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SV2</td>
<td>263.4</td>
<td>91.7</td>
<td>8.3</td>
<td></td>
<td>3.8</td>
<td>3.8</td>
<td>11</td>
<td>11</td>
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<tr>
<td>SV5</td>
<td>283.2</td>
<td>91.7</td>
<td>8.3</td>
<td></td>
<td>12.7</td>
<td>12.5</td>
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<td>SV8</td>
<td>273.8</td>
<td>90.1</td>
<td>9.9</td>
<td></td>
<td>17.7</td>
<td>14.0</td>
<td>77</td>
<td>68</td>
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<tr>
<td>SV10</td>
<td>262.9</td>
<td>87.2</td>
<td>12.8</td>
<td></td>
<td>14.4</td>
<td>10.5</td>
<td>69</td>
<td>50</td>
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<td>ST12V2</td>
<td>259.0</td>
<td>0.17</td>
<td></td>
<td></td>
<td>19.8</td>
<td>12.6</td>
<td>87</td>
<td>65</td>
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<td></td>
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<td>13.5</td>
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<td>0.42</td>
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<td></td>
<td>19.6</td>
<td>8.7</td>
<td>85</td>
<td>35</td>
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<td>ST6V5</td>
<td>268.2</td>
<td>0.83</td>
<td></td>
<td></td>
<td>21.7</td>
<td>9.7</td>
<td>99</td>
<td>43</td>
</tr>
</tbody>
</table>

*From tests in set II where 0.50 g of powder catalysts were used. Recorded at the end of the 6-h test in set II.*
the UV devices and reduces the cost by saving the energy of UV irradiation.

In FG2, the catalysts behaved in a similar pattern as in FG1, i.e., \(E_{\text{oxi}}\) of both SV2 and ST12V2 were much higher than ST12. Generally, \(E_{\text{oxi}}\) and \(E_{\text{cap}}\) in FG2 are less than in FG1, most likely due to the lower HCl and higher H\(_2\)O concentrations in FG2. It should be noted that for ST12V2, \(E_{\text{cap}}\) was much lower than \(E_{\text{oxi}}\) in FG2. This may be because that a larger fraction of certain volatile Hg compounds (such as mercuric nitrate, Hg(NO\(_3\))\(_2\)) were produced.

**Mercury Removal Using Powder Catalysts.** No UV light was used for the study of powder catalysts since vanadia based catalysts do not need UV light activation. Tests were also performed to verify that the glass wools (used as the support of powders) and pure silica powders were inert to Hg removal. Then, experiments (set II) were carried out in FG3 using 500 mg of each catalyst (corresponding to a bed height of 17 mm) in a 6 h test. The profiles of normalized Hg concentration as a function of time for selected catalysts, SV8 and ST12V5, are shown in Figure 4. At the beginning Hg\(_{\text{in}}\) and Hg\(_{\text{in}}^0\) were measured and they were very close to each other. Then the flue gas passed through the reactor and Hg\(_{\text{out}}\) and Hg\(_{\text{out}}^0\) were measured. Hg\(_{\text{out}}\) and Hg\(_{\text{out}}^0\) were rechecked after a 6 h period. For SV8, Hg\(_{\text{out}}^0\) initially dropped to a very low level (\(E_{\text{cap}} = 93\%\)), and then it increased and maintained relatively stable at around 32% of Hg\(_{\text{in}}\) (\(E_{\text{cap}} = 68\%\)). Hg\(_{\text{out}}\) was found to be slightly lower than Hg\(_{\text{out}}^0\), indicating that a small portion of the oxidized Hg penetrated the reactor. \(E_{\text{oxi}}\) was around 77% at the end of the 6 h test for SV8. Results for other SiO\(_2\)–V\(_2\)O\(_5\) catalysts are summarized in Table 2. The Hg oxidation and capture rates averaged in the 6 h period increased as the V\(_2\)O\(_5\) loading increased from 2 to 8% but decreased as the V\(_2\)O\(_5\) loading further increased to 10%. \(E_{\text{oxi}}\) and \(E_{\text{cap}}\) measured at the end of the test followed the same trend. This suggested that the V\(_2\)O\(_5\) loading for an optimal catalytic activity is somewhere near 8%. Combining the XRD and XPS results, it is inferred that the optimal V\(_2\)O\(_5\) loading may be coincident with the maximum coverage of polymeric vanadates on the catalyst surface (5–8% V\(_2\)O\(_5\)). This is inline with the literature that the SCR activity of polymeric vanadates was much higher than that of monomeric vanadyl species, particularly at low temperatures (12, 15). While little literature has compared the activity of polymeric vanadates with crystalline V\(_2\)O\(_5\), results in this study suggested that crystalline V\(_2\)O\(_5\) is not superior to polymeric vanadates for Hg\(_0\) oxidation.

For ST12V5 (Figure 4), Hg\(_{\text{out}}^0\) remained almost constantly low at 15% of Hg\(_{\text{in}}\) (\(E_{\text{oxi}} = 85\%\)). Hg\(_{\text{out}}\) initially dropped to 11% of Hg\(_{\text{in}}\) but quickly increased and stabilized around 65% (\(E_{\text{cap}} = 35\%\)). Comparing the four SiO\(_2\)–TiO\(_2\)–V\(_2\)O\(_5\) catalysts (Table 2), the rates of Hg oxidation and capture are not an apparent function of the mass ratio of V\(_2\)O\(_5\)/TiO\(_2\). All the SiO\(_2\)–TiO\(_2\)–V\(_2\)O\(_5\) catalysts exhibited high oxidation efficiencies (\(E_{\text{oxi}}\)
Mercury Removal Mechanisms. To explore the Hg removal mechanisms on the SiO2−V2O5 catalysts, experiments (set III) were conducted by mixing Hg with individual flue gas components and/or in combination with O2, balanced with N2. 250 mg of fresh SV5 was used in each test since it was found in set II that 5% V2O5 is close to the optimal loading. The results are summarized in Figure 5.

Role of O2. Using high purity N2 (>99.995%, Airgas) as the carrier gas without O2, very little Hg removal was detected. This indicated that Hg is not physically adsorbed on the SiO2−V2O5 catalyst in pure N2. E\text{rem} increased to about 15% when 4% O2 was introduced, and E\text{rem} further increased to 26% as O2 increased to 20%. Granite et al. (25) studied various metal oxides for catalytic Hg removal and proposed that lattice oxygen of the metal oxides can serve as the oxidant of Hg, forming mercuric oxide (HgO). It has also been reported that lattice oxygen is the most abundant reactive intermediates that are responsible for oxidative dehydrogenation of alkanes over V2O5-based catalysts (26). Gas-phase O2 on the other hand, reoxidizes the reduced metal oxides, replenishing the lattice oxygen (25, 26). The redox cycle can be summarized as follows:

\[ V_2O_5 + Hg \rightarrow V_2O_4 + HgO \] (3)

\[ V_2O_4 + \frac{1}{2}O_2 \rightarrow V_2O_5 \] (4)

The overall reaction then becomes

\[ Hg + \frac{1}{2}O_2 \rightarrow HgO \] (5)

Role of HCl. HCl was found to enhance HgO oxidation over the SiO2−V2O5 catalyst. Ten ppm HCl resulted in 15% HgO oxidation, whereas 50 ppm HCl increased E\text{rem} to 25%.

The combination of 50 ppm HCl with 20% O2 further improved E\text{rem} to 39%. Parfitt et al. (27) found that HCl can adsorb on rutile surface generating hydroxy (OH) groups on the surface which further react with excess HCl to form Cl ions and water. It has also been reported that Hg oxidation on unburned carbon or SCR catalysts occurs via an Eley−Rideal mechanism, where adsorbed HCl reacts with gas-phase (or weakly adsorbed) HgO (9, 28). Following the Eley−Rideal mechanism, the reaction of HCl with the V2O5 surface occurs via

\[ V−O−V + HCl \rightarrow V−OH−V−Cl \] (6)

\[ V−OH + HCl \rightarrow V−Cl + H_2O \] (7)

Actually, the V−OH structures are one type of the active sites readily present on the surface of vanadia based catalysts (12, 14, 29). Thus, the reaction with HCl can directly start from Reaction 7. The chemically adsorbed Cl species then react with gas-phase HgO to generate an intermediate HgCl species, which then further reacts with chloride species to form a more stable mercuric chloride, HgCl2. The overall reaction can be written as follows:

\[ \frac{1}{2}O_2 + 2HCl + Hg \xrightarrow{V_2O_5} HgCl_2 + H_2O \] (8)

It should be noted that chlorination of Hg may take place without the presence of O2, as shown in Figure 5. In this case, V2O5 is consumed to form V2O4. The addition of 20% O2 to 50 ppm HCl enhanced the total oxidation of HgO, very likely due to the oxidation of V2O5 to V2O4, i.e., the regeneration of the catalyst.

Role of NO2. The effect of NO2 was also found to be promotional. In the presence of 10 ppm NO2, 57% of Hg was oxidized, whereas 50% was captured. When 20% O2 was added, E\text{rem} remained at a similar level. Increasing NO2 concentration to 30 ppm (with 20% O2) increased E\text{rem} to 68% and E\text{rem} to 57%. It has been reported that NO2 significantly improves heterogeneous oxidation of HgO on fly ash (30) and on activated carbon based sorbents (31). Other researchers have reported that adsorption of NO2 on TiO2 supported V2O5 catalysts was the first step in the process of selective catalytic reduction of NO (12, 29). Kantcheva et al. (29) indicated two pathways for the NO2 adsorption on V2O5 involving V=O and V−OH sites:

\[ V^5+O + N^+O_2 \rightarrow V^4+NO_3 \] (9)

\[ 2V^5+OH + 3NO_2 \rightarrow 2V^4+NO_3 + H_2O + NO \] (10)

In this work, NO2 is first adsorbed on V2O5 via Reactions 9 and 10 and then transformed to adsorbed nitrate species, which react with gaseous HgO to form Hg(NO3)2 via the Eley−Rideal mechanism. The overall reaction can be written as follows:

\[ O_2 + 2NO_2 + Hg \rightarrow Hg(NO_3)_2 \] (11)

Considering the low melting point of Hg(NO3)2, 79 °C, it is likely that the product is volatile at the reactor temperature (135 °C) and thus part of it may be released from the reactor in the gas-phase. This formation of volatile Hg(NO3)2 initiates NO2 in agreement with the findings by other researchers. Using a carbon-based sorbent to remove Hg6, Miller et al. (31) observed nearly 100% breakthrough of a volatile oxidized Hg species in a gas mixture of SO2 and NO2. This volatile Hg species was identified to be Hg(NO3)2 in a follow-up study conducted by Olson et al. (32). Considering the much higher melting/decomposing point of HgCl2 (277 °C) and HgO (500 °C), the penetration of these two less volatile Hg species is less likely.

Role of NO. As illustrated in Figure 5, E\text{rem} was 29% in the presence of 300 ppm NO, and an addition of 20% O2 further
increased to 48%. 

Role of SO2. Figure 5 shows that the effect of SO2 on Hg removal was insignificant at 400–1200 ppm. When combining 20% O2 with 400 ppm SO2, Ew and Ead were very close to that without SO2. In the literature, the effect of SO2 on Hg capture in flue gas is not conclusive; either promotional or inhibitory effects over activated carbon or fly ash have been reported (30, 33). Hence, further studies combining SO2 with other flue gas components would warrant a better understanding of the role of SO2 for Hg removal on the SiO2-V2O5 catalyst.

Role of H2O. H2O was found to inhibit Hg removal over SiO2-V2O5 catalysts. As shown in Figure 5, under flue gas conditions (FG3) using 250 mg SV5, Ew decreased from 66 to 20% when the gas was switched from dry to humid (8% H2O). Results of other two tests (not shown in Figure 5) indicated that the inhibitory effect of H2O at very low concentration 0.6% is also observable. For a gas with 10 ppm HCl and 20% O2, switching the gas from dry to 6.6% H2O caused a decrease in Ead from 30 to 19%. For another gas with 10 ppm NO2 and 20% O2, the introduction of 0.6% H2O caused a decrease in Ead from 43 to 24%. The competitive adsorption of water vapor on active catalysts, as demonstrated in set II experiments (Table 2). In addition, in a full flue gas, the promotional effects of HCl, NO, and NO2 on Hg0 oxidation, as previously demonstrated, may outweigh the adverse effect of H2O.

Acknowledgments

We thank VICI Metronics, Inc. for supplying the Hg permeation device, and Sameer Matta, Jie Gao, and Qi Zhang for assisting with the experiments and chemical analysis.

Literature Cited


(2) U.S. EPA. Clean Air Mercury Rule, 40 CFR Parts 60, 63, 72, and 75; U.S. EPA: Washington, DC, 2005.


