Mercury oxidation over SCR catalysts

Mercury oxidation over selective catalytic reduction (SCR) catalysts

by
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Abstract
The vanadium-based SCR catalyst used for NOx-control promotes the oxidation of elemental mercury Hg⁰ to Hg²⁺ in flue gases from coal-fired power plants. Hg²⁺ is water soluble and can effectively be captured in a wet scrubber. This means that the combination of an SCR with a wet FGD can offer an effective control option for mercury.

Laboratory experiments have been carried out to elucidate and quantify the inhibition by the DeNOx reaction on the Hg⁰ oxidation by HCl over commercial SCR catalysts at different operating temperatures. In the presence of NO and NH₃, the following three net reactions have been identified as relevant for the mercury chemistry over the SCR:

R₁: 2 HCl + Hg⁰ + 1/2 O₂ ↔ HgCl₂ + H₂O
R₂: 2 NH₃ + 3 HgCl₂ ↔ N₂ + 3 Hg⁰ + 6 HCl
R₃: 2 NO + 2 NH₃ + ½ O₂ ↔ 2 N₂ + 3 H₂O

Reaction R₁ is the oxidation of Hg⁰ by O₂ and HCl, reaction R₂ is the reduction of HgCl₂ with NH₃ and reaction R₃ is the DeNOx reaction.

The importance of the different reactions on the Hg⁰ oxidation depends on the SCR operating temperature. At T>325°C, reduction of HgCl₂ with NH₃ will take place. The observed Hg⁰ oxidation will reflect the relative rate of the Hg⁰ oxidation via reaction R₁ and the HgCl₂ reduction via reaction R₂. For T=250-375°C, the DeNOx reaction will inhibit the kinetics of reaction R₁ by consuming active vanadia-sites that must be oxidized to regain activity for Hg⁰ oxidation.
Model predictions suggest that the Hg⁰ oxidation over high dust SCR reactors is limited by external mass transport, when the HCl concentration in the flue gas exceeds 13 ppmv. This means that existing commercial SCR catalysts are sufficiently active for the Hg⁰ oxidation for many applications.

For T>350ºC and low HCl, the surface reactivity will be limiting for the overall Hg⁰ oxidation. A high Hg⁰ oxidation can be achieved just the same by installing an additional catalyst layer, so a catalyst volume with negligible concentrations of NO and NH₃ is available for the catalytic oxidation.

Introduction

The worldwide anthropogenic emission of mercury was in 2005 estimated to be 1,930 tons per year. 45% of this comes from the combustion of fossil fuels¹.

The emitted mercury will deposit on land or water, where it can transform into methyl mercury and thereby enter the food chain. Humans are most likely exposed to methyl mercury through the consumption of fish. The primary health effect of methyl mercury is an impaired neurological development for fetuses, infants and children.

Mercury is present in coal in the order of 0.1 ppmw, which yields concentrations in combustion gases at power plants in the range 1-20 μg/Nm³. The amount of mercury emitted to the atmosphere will depend on the fuel, the operating conditions and the air pollution control devices (APCDs) installed.

Existing APCDs for control of other pollutants is found to remove some mercury. The approach of integrating mercury control with other regulatory actions, such as NOx, particulate and/or SO₂-removal offers a reduced compliance cost compared to introduction of dedicated mercury control options.

Three mercury species are normally considered in flue gases from coal-fired power plant: Elemental (Hg⁰), oxidized (Hg²⁺), and particulate bound mercury (Hgp). This mercury speciation will determine the capture in existing APCDs:

- Hg⁰ is very volatile and difficult to capture
- Hg²⁺ is water soluble and can effectively be captured in a wet desulphurization device.
- Hgp can effectively be removed in a particulate control device.
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Based on measurements at over 80 coal-fired power plants in the US\textsuperscript{a}, it was shown that mercury removals for plants burning bituminous coals generally were higher than those burning subbituminous and lignite coals. The lower removals were in turn an effect of a larger fraction of mercury being on the elemental form Hg\textsuperscript{0}.

**Mercury control by the combination SCR + wFGD**

A wet flue gas desulphurization (FGD) will capture oxidized mercury Hg\textsuperscript{2+} in the flue gas with efficiency around 90\%, whereas almost no Hg\textsuperscript{0} will be captured\textsuperscript{iii}. An increased fraction of Hg\textsuperscript{2+} will therefore enhance the mercury removals in a wet FGD.

The selective catalytic reduction (SCR) catalyst used for NOx-control has been shown to promote the oxidation of Hg\textsuperscript{0} to Hg\textsuperscript{2+} in flue gases from coal-fired power plants. For bituminous coals, the combination of an SCR with a wet FGD have been shown to give superior mercury removals compared to systems without the SCR. **Table 1** shows the range of mercury capture for the two configurations.

<table>
<thead>
<tr>
<th>Control configuration</th>
<th>Wet FGD</th>
<th>SCR + wet FGD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercury removals</td>
<td>43-87%</td>
<td>56-97%</td>
</tr>
</tbody>
</table>

**Table 1.** Mercury removals according to references\textsuperscript{vii, viii}

The combination with an SCR poses an option for mercury capture by a wet FGD for flue gases that would otherwise primarily contain elemental Hg\textsuperscript{0}.

**Mercury oxidation over SCR reactors**

The oxidation of Hg\textsuperscript{0} over full-scale SCR reactors has been reported in the range of 4-98\% depending on coal rank/type, operating conditions and catalyst type/geometry\textsuperscript{xiii}.

Hg\textsuperscript{0} is oxidized by halogens (via O\textsubscript{2}) in the flue gas. Chlorine is primarily responsible for the oxidations, since this halogen is typically present in the highest concentrations in coal.

The net oxidation takes the form:

$$\text{Hg}^0 + 2 \text{HCl} + \frac{1}{2} \text{O}_2 \leftrightarrow \text{HgCl}_2 + \text{H}_2\text{O}$$

The concentration of chlorine in the coal appears to be the major determining factor for the observed Hg\textsuperscript{0} oxidation across different SCR applications, where an increasing oxidation is seen for increasing HCl. There is a tendency of lower oxidation achieved over
SCR reactors for subbituminous coal combustion compared to bituminous coals, which in part is due to a typically lower concentration of chlorine in lower rank coals\textsuperscript{viii}.

In the SCR reaction, NO\textsubscript{x} is reduced by reacting with NH\textsubscript{3} over a vanadium catalyst according to the reaction stoichiometry:

\[
4 \text{ NO} + 4 \text{ NH}_3 + \text{ O}_2 \leftrightarrow 4 \text{ N}_2 + 6 \text{ H}_2\text{O}
\]

This will be referred to as the \textit{DeNOx-reaction}. The oxidation of Hg\textsuperscript{0} is a beneficial side reaction over commercial SCR reactors that are optimized for NO\textsubscript{x} reduction. An interesting controversy is posed for the now two feasible reactions over the SCR, because it turns out the DeNO\textsubscript{x} reaction inhibits the Hg\textsuperscript{0} oxidation\textsuperscript{ix,x}. The inhibition is typically explained by a competitive adsorption between NH\textsubscript{3} and Hg\textsuperscript{0}, but (as will be shown here) the explanation is not as simple.

The fundamental understanding of the catalytic Hg\textsuperscript{0} oxidation and the relevant chemistry over the SCR is in its early stage. Furthermore, the available experimental investigations on the effect of the two pivotal parameters, HCl and the DeNO\textsubscript{x}-reaction, only seem to cover a narrow range of conditions for each individual study. Combined this makes the means to optimize the Hg\textsuperscript{0} oxidation over SCR catalysts for different applications unclear.

This study serves to elucidate and quantify the effect of the DeNO\textsubscript{x} reaction on the Hg\textsuperscript{0} oxidation by HCl over commercial SCR catalysts at different temperatures.

**Experimental**

**Catalyst**

Commercial corrugated-type monoliths obtained from Haldor Topsoe A/S are applied in this study. The catalysts are based on V\textsubscript{2}O\textsubscript{5} and WO\textsubscript{3} dispersed on a fiber reinforced TiO\textsubscript{2} carrier.

**Laboratory setup**

The mercury chemistry over SCR catalysts is studied in a laboratory setup at Haldor Topsoe A/S. Here a simulated flue gas containing Hg\textsuperscript{0} is passed through a SCR reactor and the change in mercury speciation is measured for different operating temperatures and gas compositions. A schematic drawing of the setup is given in Figure 1. The setup consists of a mixing module, where all gases are mixed and preheated, a SCR reactor, a reduction unit (to reduce all HgCl\textsubscript{2} to Hg\textsuperscript{0}) and a mercury (Hg\textsuperscript{0})-analyzer.
All tubing in contact with mercury consists of Pyrex glass, which is heated to 140ºC to avoid precipitates and adsorption on the surfaces. Hg⁰ is introduced into the gas via VICI Metronics Dynacal® Permeation devices. H₂O is added by passing part of the gas through a bubble-flask with H₂O at 37ºC. The remaining gas components HCl, NO, NH₃, O₂ and N₂ are added from gas bottles. The simulated flue gas in this study contains the concentrations given in Table 2.

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg⁰</td>
<td>2.5-25 μg/Nm³</td>
</tr>
<tr>
<td>O₂</td>
<td>4 %(vol)</td>
</tr>
<tr>
<td>H₂O</td>
<td>5 %(vol)</td>
</tr>
<tr>
<td>HCl</td>
<td>2.5-55 ppm</td>
</tr>
<tr>
<td>NH₃</td>
<td>0-100 ppm</td>
</tr>
<tr>
<td>NO</td>
<td>0-100 ppm</td>
</tr>
</tbody>
</table>

Table 2 Composition of the simulated flue gas

The reactor consists of Pyrex glass and contains a single monolithic SCR channel. Experiments across the channel are run isothermally with a temperature profile of +/- 2ºC.

Mercury is analyzed in the Lumex RA-915+ analyzer, which uses cold vapor atomic absorption spectrometry to measure gaseous elemental mercury Hg⁰ continuously. The reduction unit serves the purpose of reducing all HgCl₂ in the gas stream to Hg⁰, which enables a total mercury measurement (Hgᵀ) with the analyzer that only detects Hg⁰.
Testing procedure

Fresh SCR catalysts are initially preconditioned over night at $T=350^\circ$C in a gas flow containing $20 \ \mu g/Nm^3 \ Hg^0$, 4 ppm HCl, 5% $O_2$, 2% $H_2O$, 50 ppm NO and $NH_3$ in balance $N_2$. SCR catalysts have a capacity for mercury adsorption in an amount that is very dependent on the gas composition and temperature. The preconditioning serves the purpose of saturating the catalyst with adsorbed mercury under conditions that are similar to the experiments.

The conversion ($X$) of $Hg^0$ to $Hg^{2+}$ over the SCR is measured for different temperatures and gas compositions. The steady-state conversion over the SCR is calculated as

$$X = \frac{[Hg^0]_{in} - [Hg^0]_{out}}{[Hg^0]_{in}}$$

The calculation presupposes that all $Hg^0$ disappearing over the SCR has been oxidized to $Hg^{2+}$, which only will be true at steady-state, where no sorption phenomena are occurring. Various measures have been carried out to ensure this: The initial preconditioning of the catalyst minimizes sorption transients between experiments and each set of testing conditions have stabilized for minimum 1 hour before the measurement. Experiments where larger changes are imposed on the test conditions were left over night to stabilize.

The repeatability of the measurements has been validated across three different test days and two different catalysts, where the standard deviation of the measurements is $\sigma=1.2\%$.

The testing conditions are given in Table 3. The presented experiments are run at a very high linear flow rate in order to minimize the effect of external mass transfer. In this way, the variation in surface reactivity across testing conditions is enhanced, which is feasible for the purpose of a greater mechanistic understanding of the catalytic reaction. Notice, however, that the experimental data do not represent typical full-scale conversions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Vanadia content (Typical)</th>
</tr>
</thead>
</table>
| **Operating conditions** | \(
| Linear flow rate [Nm/s] | 10.3 |
| Temperature [°C] | 250-450 |

Table 3 Range of operating conditions.
Results

Effect of temperature

Figure 2 shows the steady-state Hg⁰ oxidation over the SCR reactor across temperature in the absence of the DeNOx-reaction. The experiments have been performed for two different HCl concentrations: HCl= 4 and 46 ppm.

The experimental data shows that the Hg⁰ oxidation is independent of both temperature and HCl in the range T=250-350ºC. The Hg⁰ oxidation only starts to decrease, when the thermodynamic equilibrium is approached for HCl=4 ppm at T>400ºC.

The intuitive first explanation for the low temperature dependency is that the catalytic reaction is controlled by external mass transfer. This is not the case for this experiment, which has been verified by running the same tests on a catalyst with a higher loading of vanadia. Here, the Hg⁰ oxidation increases from 80 to ~100%.

The low temperature dependency of the catalytic reaction then suggests that adsorption of reactant on the catalyst surface is limiting the reaction rate. Since the reaction is independent of the HCl concentration (HCl=4-46 ppm), it must be adsorption of Hg⁰ that is limiting.

![Figure 2](image_url)

Figure 2 The conversion of Hg⁰ over the SCR at v=10.3 Nm/s as function of temperature. The gas contains 4-12.5 μg/Nm³ Hg⁰, 4.2/46 ppm HCl, 4% O₂ and 5% H₂O in balance N₂. The thermodynamic equilibrium for HCl=4.2 ppm is shown in full line. Notice that the test is run at a very high linear velocity to minimize the effect of external mass transport. The conversions do, therefore, not represent typical full-scale SCR installations.
Effect of temperature with DeNOx

Figure 3 shows the steady-state Hg\(^0\) oxidation over the SCR reactor across temperature for three different gas compositions:

A) 4 ppm HCl, B) 4 ppm HCl and 100 ppm NH\(_3\) and C) 4 ppm HCl and 100 ppm NH\(_3\) and NO.

![Figure 3](image_url)

The conversion of Hg\(^0\) over the SCR at \(v=10.3\) Nm/s as function of temperature. The gas contains 4-12.5 \(\mu\)g/Nm\(^3\) Hg\(^0\), 4.2 ppm HCl, 4% O\(_2\) and 5% H\(_2\)O in balance N\(_2\). The thermodynamic equilibrium for HCl=4.2 ppm is shown in full line. Notice that the test is run at a very high linear velocity to minimize the effect of external mass transport. The conversions do, therefore, not represent typical full-scale SCR installations.

The experimental data shows that the presence of NH\(_3\) inhibits the Hg\(^0\) oxidation at both low and high temperature, but no inhibition is seen for the middle temperature range \(T=300-325^\circ\text{C}\). Furthermore, a synergistic inhibition between NO and NH\(_3\) appears to take place in the entire SCR operating temperature range.

Previous studies in the same experimental scheme\(^{xi, xii}\) has identified that a HgCl\(_2\)-reducing reaction taking place in the presence of NH\(_3\) for \(T>325^\circ\text{C}\):

\[
2\text{NH}_3 + 3\text{HgCl}_2 \leftrightarrow \text{N}_2 + 3\text{Hg}^0 + 6\text{HCl}
\]
This reaction explains the effect seen by NH₃ alone at higher temperature. In the given studies, the rate of the HgCl₂ reduction is seen to increase with increasing NH₃ and decreasing HCl. Also, an increasing vanadia-load on the SCR is seen to minimize the HgCl₂ reduction.

The current experimental investigation identifies that different mechanisms are responsible for the inhibition by the DeNOx reaction on the Hg⁰ oxidation at different temperatures.

1. For T<300ºC, NH₃ alone inhibits the Hg⁰ oxidation. The effect is hypothesized to be caused by a competitive adsorption on active vanadia-sites between Hg⁰ and NH₃.
2. For T>325ºC, a reduction of HgCl₂ by NH₃ takes place.
3. For T=250-375ºC, a synergistic inhibition takes place by NO and NH₃. The effect is hypothesized to be caused by the DeNOx-reaction consuming active vanadia-sites that must be reoxidized to regain activity for both Hg⁰ oxidation and DeNOx-reaction.

The following three reactions are, therefore, proposed to be relevant for the mercury chemistry taking place over the SCR:

\[
R1: 2 \text{HCl} + \text{Hg}^0 + \frac{1}{2} \text{O}_2 \leftrightarrow \text{HgCl}_2 + \text{H}_2\text{O} \\
R2: 2 \text{NH}_3 + 3 \text{HgCl}_2 \leftrightarrow \text{N}_2 + 3 \text{Hg}^0 + 6 \text{HCl} \\
R3: 2 \text{NO} + 2 \text{NH}_3 + \frac{1}{2} \text{O}_2 \leftrightarrow 2 \text{N}_2 + 3 \text{H}_2\text{O}
\]

Reaction R1 is the oxidation of Hg⁰ with HCl, reaction R2 is the reduction of HgCl₂ with NH₃, and reaction R3 is the DeNOx-reaction. The importance of the different reactions on the Hg⁰ oxidation depends on the SCR operating temperature:

At T<300ºC, the rate of R1 is reduced in the presence of NH₃ due to competitive adsorption. At T>325ºC, the observed Hg⁰ oxidation will reflect the relative rate of the Hg⁰ oxidation via reaction R1 and the HgCl₂ reduction via reaction R2. In the entire range of operating temperatures, the DeNOx-reaction R3 will inhibit the rate of reaction R1.
Effect of HCl with DeNOx

It has just been established that different mechanistic regimes exist within each of the temperatures ranges: T<300ºC and T>325ºC. This means that the effect of changing a variable may not be the same at different temperatures.

Figure 4 shows the steady-state Hg⁰ oxidation over the SCR reactor as function of HCl at T=250ºC and T=350ºC. The experiments are carried out in the presence of 100 ppm NO and NH₃.

![Figure 4](image)

**Figure 4** The conversion of Hg⁰ over the SCR at v=10.3 Nm/s as function of HCl. The gas contains 4.2-12.2 μg/Nm³ Hg⁰, 100 ppm NO and NH₃, 4% O₂ and 5% H₂O in balance N₂. The experimentally measured conversion of Hg⁰ in the absence of DeNOx is ~82% in the range: T=250-350ºC and HCl=4.2-46 ppm. This is shown in full line. Notice that the test is run at a very high linear velocity to minimize the effect of external mass transport. The conversions do, therefore, not represent typical full-scale SCR installations.

For T=350ºC, the Hg⁰ oxidation increases with increasing HCl up to 17 ppm. The maximum Hg⁰ oxidation is just slightly below the level seen in the absence of NO and NH₃. The overall Hg⁰ oxidation at this temperature reflects the relative rate of the Hg⁰ oxidation via reaction R1 and the HgCl₂ reduction via reaction R2.

It has previously been demonstrated[XI,XII] that the HgCl₂ reduction by NH₃ (reaction R2) is minimized by increasing HCl. This explains that the overall Hg⁰ oxidation increases at this temperature.
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For T=250ºC, only a minor promotion by increasing HCl is seen. The Hg⁰ oxidation continues to be at a much lower level than in the absence of NO and NH₃. In this study, Hg⁰ adsorption has been suggested to limit the rate of the catalytic Hg⁰ oxidation via reaction R1. At T<300ºC, the Hg⁰ adsorption is further limited by both competitive adsorption with NH₃ and by the DeNOx reaction consuming the active vanadia-sites. Since Hg⁰ adsorption is rate limiting for the oxidation, there is no effect of increasing the HCl-concentration at this temperature.

Discussion

The experimental work has investigated the Hg⁰ oxidation over a commercial SCR reactor under conditions where external mass transfer is minimized. This has enhanced the variations in the surface reaction rate across different gas compositions and temperatures. In this way, a greater mechanistic insight is achieved.

The experimental investigation points at the following means to maximize the surface reactivity towards Hg⁰ oxidation:

- Increasing the vanadia-content of catalyst. This should be done while still keeping the SO₃ production low.
- Add additional halogens for T≥350ºC for low chlorine coals (HCl in flue gas < 13ppmv).
- Add an additional catalyst layer. The concentrations of NO and NH₃ will be negligible at the final catalyst layer and the inhibition on the Hg⁰ oxidation is eliminated.

It is important to note that under operating conditions relevant to full-scale SCR installations, mass transfer will be also be limiting the overall rate of Hg⁰ oxidation over the SCR reactor.

A kinetic model has been built that predicts the Hg⁰ oxidation over entire SCR reactors, where both mass transfer and the rates of the three reactions R1-R3 are taken into account. The conclusions for a typical high-dust SCR installation operating at a relevant linear velocity (v~2Nm/s) are:
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For $T<325^\circ C$: The $Hg^0$ oxidation will be greatly limited by external mass transport for $HCl>4$ ppm.

For $T \geq 325^\circ C$: The overall $Hg^0$ oxidation will be governed by the $HgCl_2$ reduction by $NH_3$ at low $HCl$ concentrations. Means for maximizing the surface reactivity towards $Hg^0$ oxidation are listed above. At high $HCl$ concentrations ($HCl>13$ ppmv) and/or low $NH_3$ concentration, the $HgCl_2$ reduction is unimportant and external mass transfer will mainly limit the overall $Hg^0$ oxidation over the SCR.

External mass transfer is the diffusion of reactants from the bulk gas to the catalyst surface. Under conditions where external mass transfer is greatly limiting for the catalytic $Hg^0$ oxidation, there will only be a minor benefit from enhancing the surface reactivity by e.g. optimizing the catalyst formulation. This study shows that existing commercial SCR catalysts have sufficient activity for $Hg^0$ oxidation for the many applications, where the catalytic reaction is greatly governed by external mass transport.

Conclusions

The $Hg^0$ oxidation over commercial SCR catalysts in the presence of the DeNOx reaction has been studied via laboratory experiments.

The inhibition by the DeNOx reaction on the $Hg0$ oxidation is complex. Different effects by NO and $NH_3$ on the overall $Hg^0$ oxidation have been shown to be of importance in the range of SCR operating temperatures.

- At $T<300^\circ C$, $NH_3$ alone inhibits the $Hg^0$ oxidation – probably due to competitive adsorption between $Hg^0$ and $NH_3$.
- For $T>325^\circ C$, a reduction of $HgCl_2$ by $NH_3$ takes place.
- For $T=250-375^\circ C$, a synergistic inhibition takes place by NO and $NH_3$ – probably due to the DeNOx-reaction consuming active vanadia-sites on the catalyst surface.

The study demonstrates that different mechanistic regimes exist for the kinetics of the $Hg^0$ oxidation at relevant SCR operating temperatures. This means that the effect of increasing $HCl$ is different, when operating at low ($T<300^\circ C$) and high temperatures ($T>325^\circ C$).
At high HCl (>13ppmv), it is found that the overall Hg⁰ oxidation over high-dust SCR reactors is primarily limited by external mass transfer. This means that the surface reactivity of existing commercial SCR catalysts for Hg⁰ oxidation is sufficiently high for most applications.

Acknowledgements
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