**XANES Study of Elemental Mercury Oxidation over RuO₂/TiO₂ and Selective
Catalytic Reduction Catalysts for Mercury Emissions Control**

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Abstract

Linear combination fitting of the X-ray Absorption Near Edge Spectroscopy (XANES) was used to quantify oxidized mercury species over RuO₂/TiO₂ and Selective Catalytic Reduction (SCR) catalysts under different simulated flue gas conditions. Halogen gases play a major role in mercury oxidation. In the absence of halogen gas, elemental mercury can react with sulfur that is contained in both the RuO₂/TiO₂ and SCR catalysts to form HgS and HgSO₄. In the presence of HCl or HBr gas, HgCl₂ or HgBr₂ is the main oxidized mercury species. When both HCl and HBr gases are present, HgBr₂ is the preferred oxidation product and no HgCl₂ can be found. The formation of HgO and HgS cannot be neglected with or without halogen gas. Other simulated flue gas components such as NO, NH₃, SO₂ and CO₂ do not have significant effect on oxidized mercury speciation when halogen gas is present.

Keywords:

XANES, mercury oxidation, SCR, ruthenium oxide, linear combination fitting

1. Introduction

Mercury is a highly toxic and persistent pollutant, and it is estimated that around 44 tons of mercury is emitted from coal-fired power plants each year in the United States, accounting for more than 30% of emissions from all anthropogenic mercury sources.[1]When mercury from the air enters water systems, it can be converted into methylmercury during biological processes and accumulate through food chains. Methylmercury is highly toxic and is especially harmful to fetuses, infants and children by causing damage to the development of the nervous system.The U.S. EPA estimated that due to *in utero* exposure to methylmercury, more than 300,000 newborns each year are at increased risk of learning disabilities.[2]In 2012, the U.S. EPA finalized the air toxics standards for coal and oil fired electric generating units also known as the Mercury Air Toxics Standards (MATS). Prior to the MATS in 2011, EPA finalized the Cross-State Air Pollution Rule (CSAPR), replacing the EPA's earlier Clean Air Interstate Rule (CAIR) from 2005.[3]CSAPR further reduces NO_x and SO₂ emissions from power plants in 28 states, and as a result, additional installations of flue gas desulfurization (FGD) and NO_x control systems (e.g. SCR unit) are expected.

Currently, sorbent injection, calcium bromide (CaBr₂) injection and SCR optimization are commercially available mercury emissions control technologies.[4]Due to different coal properties and power plant configurations, there is no universal mercury control solution that fits all scenarios, and combinations of control methods are often needed. The U.S. Department of Energy estimates that the costs for sorbent injection (at 90 percent mercury removal) are estimated to be between \$25,000 and \$70,000 per pound of mercury removed.[5]**Due to the high cost of sorbent injection and increasing number of FGD units, oxidizing elemental mercury using SCR or other catalysts, followed by oxidized mercury capture in FGD is a viable option, and**

several papers review catalysts for the oxidation of mercury.[6-8] For bituminous coal with high chlorine (HCl in a range of 50 to 200 ppmv in flue gas), SCR catalyst can oxidize most elemental mercury. For low rank sub-bituminous and lignite coals with low chlorine (HCl <10 ppmv in flue gas), additional halogen is needed to achieve satisfactory mercury oxidation, and CaBr₂ injection to the boiler is one of the most widely accepted methods.[9, 10] Little has been reported about heterogeneous Hg(0) oxidation over RuO₂ catalyst.[11] Its chemical and physical properties including structure, oxidation state, and surface area were characterized and the Hg(0) oxidation were tested under different conditions. SCR catalyst has also been found to be able to oxidize Hg(0), making SCR optimization a viable solution for mercury removal.[12-14] Modified SCR catalysts have also been studied by adding other metals such as Fe₂O₃, CeO₂, and MoO₃. [15-17] In our preliminary tests, RuO₂ catalyst showed superior Hg(0) oxidation performances and was selected for further studies. Some mechanisms of Hg(0) oxidation over SCR catalyst were proposed.[18, 19] However, in general, there is a lack of experimental evidence and thus the mechanisms are not clear.

Several studies have been conducted using X-ray Absorption Spectroscopy (XAS) to investigate the speciation and binding of mercury on various activated carbon sorbents.[20-23] However, the speciation of oxidized mercury from heterogeneous oxidation by SCR or other catalysts under coal combustion flue gas conditions has not been reported in the literature. Due to the complexity of coal combustion flue gases (containing NO_x, SO₂, NH₃, HCl, etc.), different oxidized mercury species could be formed. Currently the knowledge of heterogeneous elemental mercury oxidation is very limited, and obtaining the oxidized mercury speciation information will help understand oxidation mechanism and design mercury separation systems. In this study,

linear combination fitting of the mercury L_{III} edge XANES was conducted to quantify oxidized mercury species over RuO_2/TiO_2 and SCR catalysts under different simulated flue gas conditions.

2. Experimental

2.1 Catalyst preparation, treatment and characterization

RuO_2/TiO_2 catalyst with 1% (wt) metal loading was synthesized by following the procedure below: 16 g of TiO_2 powder (STR-100W, Sakai Chemical), 0.4 g of methylcellulose (Sigma-Aldrich) and 0.32 g of glass fiber (FibreGlast) were dry mixed for 10 minutes. 0.416 g of $RuCl_3$ hydrates (Yurui Chemical) dissolved in 16 ml of deionized water was added to the above powders and the dough was kneaded for 10 minutes to achieve uniform mixing. Then the catalyst was extruded into 1 mm $\times$ 5 mm (D $\times$ L) cylindrical pellets, dried in air at room temperature, followed by calcination at 400 °C in air for 3 hours. SCR catalyst was synthesized by following a procedure below: 12 g of TiO_2 powder (DT-58, Cristal, containing 9.1% (wt) tungsten and 10.5% (wt) silica), 0.3 g of methylcellulose (Sigma-Aldrich) and 0.24 g of glass fiber (FibreGlast) were dry mixed for 10 minutes. 0.138 g of NH_4VO_3 (Sigma-Aldrich) dissolved in 11 ml of 1 M oxalic acid (Sigma-Aldrich) was added to the above powders and the dough was kneaded for 10 minutes to achieve uniform mixing. Then the catalyst was extruded into 1 mm $\times$ 5 mm (D $\times$ L) cylindrical pellets, dried in air at room temperature, followed by calcination at 500 °C in air for 3 hours.

Oxidized mercury from RuO_2/TiO_2 and SCR catalysts was collected using a fixed-bed reactor system. A schematic of the apparatus is shown in Figure 1. Elemental mercury ($Hg(0)$) vapor was generated using a permeation oven (Dynacalibrator, VICI Metronics) held at 70°C and

using N₂ as a carrier gas. The catalysts (1.7 g of RuO₂/TiO₂ catalyst or 1.6 g of SCR catalyst) were placed inside a quartz reactor and the temperature was maintained at 350 °C in a tube furnace. The temperature was chosen to approximate the temperature at the tail end of the SCR unit. The total flow of the simulated flue gas was 1 L/min with a gas hourly space velocity 40,000 h⁻¹ (about 10 times higher than typical SCR units). The elemental mercury concentration (15 ppb) used in this study was higher than that of a typical coal combustion flue gas to ensure sufficient loadings of oxidized mercury onto the activated carbon sorbent bed located after the fixed-bed reactor and to accommodate the sensitivity of the mercury measurements. All the simulated flue gas components were generated from compressed gas cylinders (Wright Brothers, Inc.) and the concentrations were controlled by mass flow controllers. The Hg(0) vapor concentrations at the inlet and outlet of the reactor were measured by collecting it in a wet impinger system following the Ontario Hydro method. Then the Hg(0) vapor captured in a 4%(w/v) KMnO₄/10%(v/v) H₂SO₄ impinger solution was analyzed with a cold vapor atomic absorption spectrophotometer (Model 400A, Buck Scientific Inc.). The Hg(0) oxidation efficiency was calculated by measuring the concentrations across the reactor bed using the following equation (1):

$$Hg(0)oxidation = \frac{Hg(0)_{in} - Hg(0)_{out}}{Hg(0)_{in}} \times 100\% \quad (1)$$

A total of 6 different gas conditions was used for both catalysts and the gas compositions are listed in Table 1. Case 5 is to simulate coal combustion flue gas with high HCl concentration, and Case 6 is for that with low HCl concentration and bromine addition. Both Cases assumed that the catalysts are located at the tail end of a SCR unit. Hg(0) oxidation under these gas conditions was negligible in the absence of the catalysts. For each Case, 100 mg raw activated carbon (DARCO-HG, Norit Americas, Inc.) at the outlet of the fixed-bed reactor was used to

capture the oxidized mercury generated from the catalysts for 24 hours, resulting in 1,000 to 2,000 ppmw mercury in the activated carbon sorbent based on mercury mass balance. The sulfur contents in the RuO₂/TiO₂ catalyst and SCR catalyst were measured using a CHNS elemental analyzer (Vario MICRO cube, Elementar Americas, Inc.).

2.2 Mercury XANES

Hg L_{III} edge (12,284 eV) XANES spectra were collected using the 20-BM-B beamline (sector 20) at the Advanced Photon Source (APS) at Argonne National Laboratory (ANL, Chicago, IL). A Si (111) monochromator was used, with energy resolution ($\Delta E/E$) of approximately 1.4×10^{-4} . Energy calibration was performed using Au metal foil (Au L_{III} edge is 11,919 eV). A series of reference mercury compounds including HgO, HgSO₄, HgS, HgCl₂, and HgBr₂ (all obtained from Sigma-Aldrich except for HgBr₂, which was obtained from Alfa Aesar) were dispersed on Kapton (polyimide) tape for XAS measurements. The activated carbon samples were loaded into thin Teflon sample holders between the layers of Kapton tape. For reference mercury compounds, the transmission data were used for data processing. A 13-element germanium detector was used to collect fluorescence spectra from the activated carbon samples which were much lower in mercury content than the reference compounds. The step size in the near edge region was 0.2 eV. At least five scans were collected for each sample in order to improve the signal-to-noise ratio. During the measurements, neither X-ray induced redox reaction nor sample damage was observed.

3.Results and Discussion

3.1 Hg(0) oxidation over RuO₂/TiO₂ and SCR catalysts

In our preliminary studies, RuO₂ supported on rutile TiO₂ was found to be an excellent catalyst for Hg(0) oxidation. Prior to collecting the oxidized mercury generated from the catalytic reaction for speciation, the mercury oxidation performances of RuO₂/TiO₂ catalyst and SCR catalyst with respect to HCl and HBr concentrations were evaluated. The simulated flue gas conditions used were close to those at the tail end of a SCR unit where NO_x and NH₃ concentrations are low. Elemental mercury at the outlet of the fixed-bed reactor was measured to calculate the percentage of Hg(0) oxidation and the results are shown in Figure 2. The RuO₂/TiO₂ catalyst shows better mercury oxidation capability at all HCl and HBr concentrations compared to the SCR catalyst. When a HCl concentration was increased to 25 ppmv, ~90% and ~80% of Hg(0) oxidation could be achieved for the RuO₂/TiO₂ and SCR catalysts, respectively. Further improvement in Hg(0) oxidation at higher HCl concentrations was not significant. Considering bituminous coal combustion flue gas usually contains 50 to 200 ppmv of HCl, RuO₂/TiO₂ is an excellent mercury oxidation catalyst candidate. HBr is much more effective for Hg(0) oxidation than HCl in terms of halogen gas concentration requirements. With only 1 ppmv HBr, the Hg(0) oxidation performance was comparable to that with 25 ppmv of HCl. Further Hg(0) oxidation at HBr higher than 1 ppmv was limited. These results confirm the effectiveness of bromine injection for improved Hg(0) oxidation when catalysts are present.

3.2 XANES data analysis

XANES data were processed by following a standard procedure using Athena interface to the IFFEFIT program.[24] Multiple scans were aligned and merged as $\mu(E)$ with each dataset

weighted the same. Mercury XANES data were analyzed by taking the first derivative of the $\mu(E)$ with respect to energy. The inflections of the pre-edge of mercury XANES has two distinct peaks in the first derivative, and the inflection point difference (IPD) can be used to determine mercury species.[20, 21, 23] The IPD of mercury XANES is related to mercury bonding nature with nearest neighboring atoms and coordination number, making it a suitable indicator of oxidized mercury species. The mercury L_{III}-edge XANES spectra and the first derivative of the spectra for the reference mercury compounds measured are shown in Figure 3. These spectra are similar to those reported in other studies.[21, 22]

However, the IPD determined from the oxidized mercury compounds captured in the activated carbon sorbent samples is the average information derived from multiple mercury compounds captured in the samples. Therefore, the sole use of IPD for oxidized mercury speciation is suitable only for the samples with simple compositions or with one dominant species, and is less useful for complex samples such as current study samples. In a typical coal combustion flue gas, there are many other gas compositions including SO₂, NH₃, NO_x, HCl and HBr (when bromine addition is used). The oxidized mercury species such as HgO, HgS, HgCl₂, HgSO₄ and HgBr₂ are all stable mercury species that could exist as oxidation products. By fitting a linear combination of the spectra for reference mercury compounds to an unknown spectrum, the speciation and quantification of individual mercury compounds in a complex activated carbon sample can be determined. Linear combination fitting of XANES spectra has been used for the quantitative speciation of inorganic compounds in many environmental samples and metal speciation for catalysis studies.[25-31] In this study, linear combination fitting of L_{III}-edge XANES in the first derivative of $\mu(E)$ in a range of -15 and +15 eV ($E_0=12,284$ eV) using up to 5 reference mercury compounds including HgO, HgS, HgCl₂,

HgSO₄ and HgBr₂ was used to quantify the oxidized mercury species generated from RuO₂/TiO₂ and SCR catalysts under different gas conditions.

3.3 Oxidized mercury speciation from RuO₂/TiO₂ catalyst

All commercial TiO₂ and SCR catalysts contain some amount of sulfur added from their manufacturing processes. The sulfur content of the RuO₂/TiO₂ catalyst and SCR catalyst used in this study was measured using a CHNS analyzer, and the sulfur content was found to be 0.1% (wt) and 0.2% (wt), respectively. The sulfur content on these catalysts cannot be neglected, considering that a typical gas-phase Hg(0) concentration in a coal combustion flue gas is at a ppbv level. The XANES spectra and linear combination fittings of Hg(0) oxidation products from RuO₂/TiO₂ catalyst are shown in Figure 4, and the quantitative speciation results obtained are listed in Table 2. XANES of spent catalysts were also measured, but the mercury signal was too low to be detected, indicating the adsorption of oxidized mercury on the catalysts is negligible.

For RuO₂/TiO₂ catalyst with only N₂ and O₂ gases (Case 1), the oxidized mercury species are mainly HgS and HgSO₄, with <20% HgO. Our result also indicated that the TiO₂ support itself has very little Hg(0) oxidation capability. The sulfur-containing oxidized mercury should come from the sulfur on the TiO₂ surface and the catalytic effect of RuO₂. It is why both RuO₂/TiO₂ and SCR catalysts showed ~40 and ~30% Hg(0) oxidation performance, respectively, in Figure 2 even when HCl or HBr is not introduced to the fixed-bed reactor. When 1 ppmv HBr gas is added (Case 2), HgBr₂ becomes the major species, accounting for ~65% of all oxidized mercury. While the percentage of HgO slightly decreased, HgS and HgSO₄ both significantly decreased. For the case with 50 ppmv HCl gas (Case 3), the trend is similar to that of HBr. HgCl₂ is a main species and sulfur-containing oxidized mercury species significantly decreased.

When the low concentrations of 5 ppmv HCl and 1 ppmv HBr were both added (Case 4), it is interesting to note that no HgCl_2 was found and HgBr_2 was found to be a main oxidized mercury species. These results indicate that when halogen gas is absent, HgS is a main oxidized mercury species with sulfur coming from the TiO_2 support. When HCl or HBr is present, HgCl_2 or HgBr_2 prefers to be formed as a result of the catalytic reaction, respectively. If both HCl and HBr are present, although HCl concentration is 5 times higher than HBr concentration, elemental mercury still prefers to react with bromine. Comparing Cases 3 and 4 to Cases 5 and 6, NH_3 , NO, and SO_2 do not have any significant effect on oxidized mercury speciation.

3.4 Oxidized mercury speciation from SCR Catalyst

The XANES spectra and linear combination fittings of mercury oxidation products from SCR catalyst are shown in Figure 5, and the quantitative speciation analysis results obtained are listed in Table 3. For SCR catalyst under only N_2 and O_2 gases (Case 1), less than 10% of oxidized mercury species is HgO , while HgS portion is ~80%. Considering the SCR catalyst has 2 times greater sulfur content than the $\text{RuO}_2/\text{TiO}_2$ catalyst, more HgS formation should be expected. For a medium size (500 MW) coal-fired power plant, the mercury emissions are ~200 kg per year.[1] A typical SCR unit uses 20 tonnes of commercial SCR catalysts, which contain 0.1 to 0.5% (wt) sulfur and are replaced every 12 to 24 months. Based on these calculations, the sulfur in the SCR catalysts will not be depleted during the catalyst lifetime. When HCl and/or HBr gases are present, oxidized mercury speciation is similar to that of the $\text{RuO}_2/\text{TiO}_2$ catalyst. HgCl_2 is a main oxidized mercury species when HCl is the only halogen gas, and HgBr_2 is a preferred mercury oxidation product when bromine injection is used. NH_3 (up to 5 ppmv), NO (up to 5 ppmv), and SO_2 (up to 200 ppmv) gases at the tail end of a typical SCR unit still do not give a significant effect on oxidized mercury speciation. Sulfur trioxide is known to have a

profound impact on the capture of mercury by activated carbons, and the impact of SO_3 on the catalysts can be an area of future research.[32, 33] For both $\text{RuO}_2/\text{TiO}_2$ and SCR catalysts, it needs to be pointed out that even in the presence of HCl and/or HBr gases, ~30-50% of oxidized mercury can exist still in the forms of HgO and HgS. While HgCl_2 and HgBr_2 are soluble in water and thus can be readily captured in wet FGD, it may not be able to effectively remove HgO and HgS due to their low solubility. According to previous field mercury measurements in coal-fired power plants with SCR and FGD, ~18-54% of oxidized mercury could not be removed by FGD.[34] Some of this could be attributed to the insolubility of the compounds of mercury, and the rest is due to re-emission of mercury from the wet scrubber. This is possibly due to HgO and HgS with very low solubility identified in this study. More studies on oxidized mercury speciation and separation performances across wet FGD will be required to understand the fate of various oxidized mercury species.

3.5 Proposed Hg(0) oxidation mechanism over RuO_2 catalyst

The XANES results confirmed that Hg(0) is oxidized to HgCl_2 and/or HgBr_2 in the presence of HCl and HBr. Also, between the two oxidized species, HgBr_2 is a preferred oxidized species when HCl and HBr are both present in a simulated flue gas. This may be attributed to a fact that the bond dissociation energy of HBr is lower than that of HCl (366.3 kJ/mol vs. 431.6 kJ/mol).[35] This could make HBr easier to dissociate on the active catalyst sites. Then Hg(0) in the gas phase may react with surface molecular halogen to form $\text{HgX}_2(\text{ad})$ and be desorbed to the gas phase. This proposed Hg(0) oxidation mechanism following the Deacon reaction is summarized in Figure 6.[36, 37]

4. Conclusions

In this study, the speciation of oxidized mercury from RuO₂ and SCR catalysts was conducted under different simulated flue gas conditions. The XANES spectra were analyzed using linear combination fitting for the identification and quantification of the oxidized mercury species captured in activated carbon. In the absence of HCl and HBr gases, Hg(0) was found to react with sulfur contained in the TiO₂ support to form HgS and HgSO₄. When HCl and/or HBr are/is present, HgCl₂ and/or HgBr₂ are/is the main oxidized mercury species. HBr is much more active for Hg(0) oxidation. When both HCl and HBr gases are present, HgBr₂ is the main mercury oxidation species. Furthermore, even in the presence of halogen gases, the formation of HgO and HgS should not be neglected. These oxidized mercury species may not be effectively removed in wet FGD systems due to their low solubility. These results warrant additional studies on the fate of oxidized mercury species in order to improve mercury removal performances in wet FGD systems.

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Figure Captions:

Figure 1. Experimental set-up for catalytic reactor and subsequent oxidized mercury capture in activated carbon sorbent.

Figure 2. Mercury oxidation over $\text{RuO}_2/\text{TiO}_2$ and SCR catalysts. Gas conditions: 15 ppbv $\text{Hg}(0)$, 5 ppmv NH_3 , 5 ppmv NO , 200 ppmv SO_2 , 3%(v) O_2 , 12%(v) CO_2 balanced in N_2 .

Figure 3. The XANES spectra (left) and the first derivative of the spectra (right) for reference oxidized mercury compounds.

Figure 4. Linear combination fitting of oxidized mercury generated from $\text{RuO}_2/\text{TiO}_2$ catalyst. Cases 1 to 6 are denoted by Ru_1 to Ru_6.

Figure 5. Linear combination fitting of oxidized mercury generated from SCR catalyst. Cases 1 to 6 are denoted by SCR_1 to SCR_6.

Figure 6. Proposed $\text{Hg}(0)$ oxidation mechanism over RuO_2 catalyst in the presence of HCl or HBr .

Table 1. Simulated flue gas conditions used for oxidized mercury speciation

Case	Gas Conditions
1	N ₂ + 3%(v) O ₂
2	N ₂ + 3%(v) O ₂ + 1 ppmv HBr
3	N ₂ + 3%(v) O ₂ + 50 ppmv HCl
4	N ₂ + 3%(v) O ₂ + 1 ppmv HBr + 5 ppmv HCl
5	N ₂ + 3%(v) O ₂ + 50 ppmv HCl + 5 ppmv NO + 5 ppmv NH ₃ + 200 ppmv SO ₂ + 12%(v) CO ₂
6	N ₂ + 3%(v) O ₂ + 1 ppmv HBr + 5 ppmv HCl + 5 ppmv NO + 5 ppmv NH ₃ + 200 ppmv SO ₂ + 12%(v) CO ₂

Note: All gas concentrations are based on volume.

Table 2. Linear combination fitting results for oxidized mercury species generated from RuO₂/TiO₂ catalyst.

Case	HgO (%)	HgS (%)	HgSO ₄ (%)	HgCl ₂ (%)	HgBr ₂ (%)
Ru_1	17±2	55±3	28±2	--	--
Ru_2	14±1	20±7	1±3	--	65±5
Ru_3	17±4	31±2	0	51±1	--
Ru_4	16±2	20±6	0	0	64±4
Ru_5	17±2	25±4	0	58±6	--
Ru_6	14±3	26±4	0	0	60±10

Table 3. Linear combination fitting results for oxidized mercury species generated from SCR catalyst.

Case	HgO (%)	HgS (%)	HgSO ₄ (%)	HgCl ₂ (%)	HgBr ₂ (%)
SCR_1	6±2	79±4	15±5	--	--
SCR_2	14±1	25±4	0	--	61±7
SCR_3	19±3	34±5	0	47±2	--
SCR_4	19±1	15±5	1±2	0	65±6
SCR_5	21±2	24±5	0	55±2	--
SCR_6	11±2	36±8	0	0	53±14

Figure1

Figure2

Figure3

Figure4

Figure5

Figure6