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It is entitled:
Heterogeneous Catalytic Elemental Mercury Oxidation in Coal Combustion Flue Gas

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Heterogeneous Catalytic Elemental Mercury Oxidation in Coal Combustion Flue Gas

A dissertation submitted to the
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By

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Abstract

The new Mercury and Air Toxics Standards issued by US EPA require the reduction of mercury emissions from coal-fired power plants by 90% starting from 2016. Oxidizing elemental mercury using the HCl that exists in the flue gas or additional halogen and catalysts, followed by oxidized mercury capture in the wet Flue Gas Desulfurizer (FGD), is a viable option for mercury removal in coal-fired power plants. The aim of this study is to develop effective and reliable mercury oxidation catalysts, advance the mechanistic understandings of heterogeneous mercury oxidation, and obtain information on heterogeneous mercury oxidation kinetics.

CuCl$_2$ supported on $\gamma$-Al$_2$O$_3$ showed excellent Hg(0) oxidation performance and SO$_2$ resistance at 140 °C. After extensive characterizations of the CuCl$_2$/$\gamma$-Al$_2$O$_3$ catalyst, the existence of multiple copper species was identified. It was found that CuCl$_2$ forms inert copper aluminate on the surface of $\gamma$-Al$_2$O$_3$ at lower loadings. At higher loadings, CuCl$_2$ exists in a highly dispersed amorphous form that is active for Hg(0) oxidation by working as a redox catalyst. The CuCl$_2$/$\gamma$-Al$_2$O$_3$ catalyst with high loadings has the potential to be used as a low temperature Hg(0) oxidation catalyst.

RuO$_2$ catalyst was found to be an excellent Hg(0) oxidation catalyst. When rutile TiO$_2$ was used as the catalyst support, RuO$_2$ formed well dispersed nano-layers due to the very similar crystal structures of RuO$_2$ and rutile TiO$_2$, giving higher Hg(0) oxidation activity over anatase TiO$_2$ support. The RuO$_2$/rutile TiO$_2$ catalyst showed good Hg(0) oxidation performance under sub-bituminous and lignite coal simulated flue gas conditions with low concentration of HCl or HBr gas. It also showed excellent resistance to SO$_2$. The RuO$_2$/rutile TiO$_2$ catalyst can be used at the tail end section of the SCR unit for Hg(0) oxidation.
Linear combination fitting of the X-ray Absorption Near Edge Spectroscopy (XANES) was used to quantify oxidized mercury species over RuO$_2$/TiO$_2$ and SCR catalysts under different simulated flue gas conditions. In the absence of halogen gas, elemental mercury can react with sulfur that is contained in both the RuO$_2$/TiO$_2$ and SCR catalysts to form HgS and HgSO$_4$. In the presence of HCl or HBr gas, HgCl$_2$ or HgBr$_2$ is the main oxidized mercury species. When both HCl and HBr gases are present, HgBr$_2$ is the preferred oxidation product and no HgCl$_2$ can be found. Other simulated flue gas components such as NO, NH$_3$, SO$_2$ and CO$_2$ do not have significant effect on oxidized mercury speciation when halogen gas is present.

Mechanistic and kinetic studies of the heterogeneous oxidation of Hg(0) by HCl gas over a RuO$_2$/rutile TiO$_2$ catalyst were conducted. The experimental evidence of HCl adsorption was obtained using in-situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). Based on this result, a steady-state kinetic study was conducted to determine an intrinsic reaction kinetic expression for Hg(0) oxidation over the catalyst under HCl, NH$_3$ and SO$_2$ gases for the first time. The kinetic expression obtained could reasonably predict the Hg(0) oxidation performance under the competitive adsorption of NH$_3$ and SO$_2$ gases.
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Finally, I would like to thank my parents, my wife Patcha Huntra and our cat Cinderella for their support and company during the most difficult days of my life. And for that I am forever grateful.
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Nomenclatures

\(C_{\text{HCl}}\): gas-phase HCl concentration (gmol/m\(^3\))

\(C_{\text{Hg,B}}\): Hg(0) concentration in the bulk gas phase (gmol Hg(0)/m\(^3\))

\(C_{\text{Hg,S}}\): Hg(0) concentration at the catalyst surface (gmol Hg(0)/m\(^3\))

\(C_{\text{NH3}}\): gas-phase NH\(_3\) concentration (gmol/m\(^3\))

\(C_{\text{SO2}}\): gas-phase SO\(_2\) concentration (gmol/m\(^3\))

\(E_a\): activation energy (kJ/gmol)

\(k'\): reaction rate constant (m\(^3\)/(g catalyst·s))

\(k_g\): mass-transfer coefficient (m/s)

\(K_{\text{HCl}}\): HCl adsorption equilibrium constant (m\(^3\)/gmol)

\(K_{\text{NH3}}\): NH\(_3\) adsorption equilibrium constant (m\(^3\)/gmol)

\(K_{\text{SO2}}\): SO\(_2\) adsorption equilibrium constant (m\(^3\)/gmol)

\(L\): length of the catalyst bed (m)

\(N\): number of the catalyst particles

\(-r'_{\text{Hg,int}}\): intrinsic Hg(0) reaction rate (gmol Hg(0)/(g catalyst·s))

\(-r'_{\text{Hg,obs}}\): observed Hg(0) reaction rate (gmol Hg(0)/(g catalyst·s))

\(R_p\): radius of the catalyst particle (m)

\(Re_p\): Reynolds number

\(S\): external surface area of the catalyst (m\(^2\))

\(Sc\): Schmidt number

\(T\): temperature (K)

\(u_z\): superficial gas velocity (m/s)

\(W\): mass of the catalyst (g)
z: axial distance from the fixed-bed inlet (m)

$\Delta H_{\text{ad,HCl}}$: adsorption enthalpy of HCl (J/gmol)

$\Delta H_{\text{ad,NH}_3}$: adsorption enthalpy of NH$_3$ (J/gmol)

$\Delta H_{\text{ad,SO}_2}$: adsorption enthalpy of SO$_2$ (J/gmol)

$\varepsilon_b$: bed porosity

$\theta_{\text{Cl}}$: fractional surface coverage for Cl

$\theta_{\text{H}}$: fractional surface coverage for H

$\theta_{\text{V}}$: fractional surface coverage for vacant site

$\rho_c$: density of the catalyst (g/m$^3$)
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>Activated Carbon</td>
</tr>
<tr>
<td>ACI</td>
<td>Activated Carbon Injection</td>
</tr>
<tr>
<td>APCD</td>
<td>Air Pollution Control Devices</td>
</tr>
<tr>
<td>APS</td>
<td>Advanced Photon Source</td>
</tr>
<tr>
<td>BC</td>
<td>Boundary Condition</td>
</tr>
<tr>
<td>CAA</td>
<td>Clean Air Act</td>
</tr>
<tr>
<td>CAIR</td>
<td>Clean Air Interstate Rule</td>
</tr>
<tr>
<td>CAMR</td>
<td>Clean Air Mercury Rule</td>
</tr>
<tr>
<td>CSAPR</td>
<td>Cross-State Air Pollution Rule</td>
</tr>
<tr>
<td>CVAA</td>
<td>Cold Vapor Atomic Absorption</td>
</tr>
<tr>
<td>DP</td>
<td>Deposition Precipitation</td>
</tr>
<tr>
<td>DRIFTS</td>
<td>Diffuse Reflectance Infrared Fourier Transform Spectroscopy</td>
</tr>
<tr>
<td>ESP</td>
<td>Electrostatic Precipitation</td>
</tr>
<tr>
<td>FF</td>
<td>Fabric Filter</td>
</tr>
<tr>
<td>FGD</td>
<td>Flue Gas Desulfurization</td>
</tr>
<tr>
<td>ID</td>
<td>Inner Diameter</td>
</tr>
<tr>
<td>IPD</td>
<td>Inflection point difference</td>
</tr>
<tr>
<td>LCF</td>
<td>Linear Combination Fitting</td>
</tr>
<tr>
<td>MATS</td>
<td>Mercury and Air Toxics Standards</td>
</tr>
<tr>
<td>SCR</td>
<td>Selective Catalytic Reduction</td>
</tr>
<tr>
<td>SEA</td>
<td>Sorbent Enhancement Additive</td>
</tr>
<tr>
<td>SEM-EDS</td>
<td>Scanning Electric Microscopy-Energy Dispersive Spectroscopy</td>
</tr>
<tr>
<td>TCD</td>
<td>Thermal Conductive Detector</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TGA-MS</td>
<td>Thermal Gravity Analyser-Mass Spectroscopy</td>
</tr>
<tr>
<td>TPR</td>
<td>Temperature Program Reduction</td>
</tr>
<tr>
<td>WI</td>
<td>Wetness Incipient</td>
</tr>
<tr>
<td>XAFS</td>
<td>X-ray Absorption Fine-structure Spectroscopy</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray Absorption Near-Edge Structure</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray Adsorption Spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
</tbody>
</table>
Chapter 1 Introduction

1.1 Mercury emissions from coal-fired power plants and health effects

In the United States, more than 30% of the electricity generated is from coal-fired power plants currently.[1] Although the electricity generation from coal has been decreasing in the past a few years due to more stringent regulations and low natural gas prices, coal will continue to play a major role in power industry because of its abundant reserve in the U.S. and the advancements of pollution control technologies. All coals naturally contain a small amount of mercury at a level of 0.1-0.2 ppm by weight and it will be released into the atmosphere after combustion.[2] Depending on the types of coal, operating conditions, and the configuration of the power plants, the amount of mercury in the coal combustion flue gas ranges from 1 to 20 μg/m³.[3] Due to the extremely high flue gas flow rate of power plants (several million m³ per hour), coal-fired power plants are the major anthropogenic mercury emissions sources. U.S. Environmental Protection Agency (EPA) identified power plants as the dominant emitters of mercury, contributing to ~50% of all mercury emissions in the U.S.[4] Mercury emissions from coal-fired power plants exist in three forms: elemental mercury (Hg(0)), particulate mercury (Hg(p)), and oxidized mercury (Hg(2+)).[5] These different forms of mercury can cause both local and global scale pollutions. While particulate and oxidized mercury tend to deposit near the power plants because of particulate settling and high solubility, elemental mercury can remain in the atmosphere for up to a year and travel thousands of miles due to its inert nature.[5-7]

When mercury from the atmosphere reaches soil or water, it can be converted into methylmercury, which is highly toxic form that can build up in the environment through food chains. Human exposure to mercury is mainly through the consumption of fish especially the
ones at a higher level of the food chain with a much higher mercury accumulation. Methylmercury has significant neurological health impacts especially to women of childbearing age, fetuses and young children by causing damages to the developing nervous system.[4] EPA estimated that due to in utero exposure to methylmercury, over 300,000 newborns each year are having increased risk of learning disabilities.[6] The National Research Council (NRC) reassessed the toxicological effects of mercury and concluded that the 0.1 μg/(day·body weight) exposure limit set by EPA was justifiable for the protection of public health against the neurologic effects of mercury.

1.2 Mercury emission legislations

The 1990 Amendments to the Clean Air Act listed mercury as one of the most toxic pollutants among 188 hazardous air pollutants. In December 2000, EPA announced that it was appropriate and necessary to regulate air toxics including mercury from coal- and oil-fired power plants under section 112 of the Clean Air Act. On March 15th, 2005, EPA issued the final Clean Air Mercury Rule (CAMR). The CAMR limited mercury emissions from new and existing utility boilers and created a market-based cap-and-trade program to reduce nationwide utility emissions of mercury in two phases. The first phase was to cap mercury emissions from utilities at 38 tons/year, and followed by further reduction to 15 tons/year in 2018. On February 8th, 2008, the D.C. Circuit Court vacated the CAMR, removing power plants from the Clean Air Act list of sources of hazardous air pollutants. EPA then announced plans to propose new air toxics standards including mercury for coal- and oil-fired electric generating units.
After reviewing public comments on the proposed rule, EPA finalized the Mercury and Air Toxics Standards (MATS) for power plants on Feb 16th, 2012.[8] This final rule adopted a Maximum Achievable Control Technology (MACT) approach instead of a cap-and-trade approach for mercury emissions. On June 29th, 2015, the U.S. Supreme Court ruled that the EPA erred when the agency failed to considered the cost of the MATS to the industry. After providing supplemental findings that a consideration of the cost does not alter EPA’s previous determination that it is appropriate and necessary to regulate air toxic emissions from coal- and oil-fired power plants, the MATS has remained in place.

The MATS set standards for air toxics emitted from all new and existing coal- or oil-fired electricity generating units 25 megawatts or greater. The rule will result in reducing 90% of mercury emissions from coal-fired power plants, 88% of acid gas emissions from power plants, and 42% of sulfur dioxide emissions from power plants beyond the Cross State Air Pollution Rule. The MATS require power plants to meet the emissions limit in 2015, and one additional year can be requested from the state permitting authorities. EPA is also providing up to an additional year to achieve compliance for some utilities. The mercury emission limits of coal-fired power plants required by the MATS are listed in Table 1.1.

Table 1.1 Summary of the mercury emission limits for coal-fired power plants required by the MATS.

<table>
<thead>
<tr>
<th>Category</th>
<th>Mercury emission limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Existing unit not low rank coal</td>
<td>1.2 lb/TBtu or 1.3E-2 lb/GWh</td>
</tr>
<tr>
<td>Existing unit low rank coal</td>
<td>4 lb/TBtu or 4E-2 lb/GWh</td>
</tr>
</tbody>
</table>
New unit not low rank coal 2E-4 lb/GWh
New unit low rank coal 4E-2 lb/GWh

Notes: lb/TBtu = pounds of mercury per trillion British thermal units.
lb/GWh = pounds of mercury per gigawatt-hour electric output (gross).

1.3 Current mercury control technologies in coal-fired power plants

With the increasing number of environmental regulations, modern coal-fired power plants are equipped with a series of air pollution control devices (APCDs) for mitigating pollutants such as fly ash, NOx, and SO₂. Although not designed to remove mercury from the flue gas, these systems have impacts on mercury emissions. For a typical coal-fired power plant, the flue gas first enters a Selective Catalytic Reduction (SCR) unit where NOx reacts with NH₃ over V₂O₅ based catalysts. Then the fly ash is removed by an Electro-Static Precipitator (ESP) or Fabric Filter (FF). Finally, a wet Flue Gas Desulfurization unit is used to capture SO₂ by spraying limestone slurries. A schematic of typical APCDs in a coal-fired power plant is shown in Figure 1.1 below.

Figure 1.1 Schematic of typical APCDs in a coal-fired power plant.
These APCDs have some co-benefits for mercury removal under some conditions. The SCR can convert some Hg(0) into Hg(2+) which has high solubility and can be captured in wet FGD. Mercury bound to particles can be removed together with the fly ash in ESP or FF.[3, 5, 9] Although these co-benefits help with mercury removal, most coal-fired power plants need to take additional measures to meet the MATS.

Currently there are several commercially available mercury control technologies for coal-fired power plants. Depending on individual conditions such as configurations, types of coal being used, and existing APCDs, power plants will choose to use one or a combination of these options:

1) Activated carbon injection (ACI) + ESP or FF: Raw AC or modified AC (mainly chlorinated or brominated AC) is injected in the flue gas stream to adsorb mercury, and the injected AC can be removed from the flue gas together with fly ash in ESP or FF.[10-13] ACI sets the benchmark for mercury removal performances.

2) Halogen addition + wet FGD: Fuel additives such as CaCl$_2$ and CaBr$_2$ can be added into the boiler to boost the halogen contents in the flue gas and increase mercury oxidation.[14-17] Oxidized mercury can be captured subsequently in the wet FGD.

3) SCR optimization + wet FGD: V$_2$O$_5$ based SCR catalysts can also oxidize Hg(0) into Hg(2+) by using HCl in the flue gas. By optimizing the operating conditions and compositions of the SCR catalysts, mercury oxidation performance can be improved especially for coals with higher halogen contents such as the bituminous coal.[18-21]
1.4 Problem statement

Utilities always look for technologies with the highest compliance certainty at the lowest cost. EPA estimated that the annual cost for achieving the MATS compliance will be around 3% of annual electricity sales. The main drawback of ACI is its high capital and operating cost. The U.S. Department of Energy estimates that the costs for ACI to achieve 90 percent removal are estimated to be between $25,000 and $70,000 per pound of mercury removed.[22] Also, activated carbon sorption capacity is significantly reduced under high sulfur coal conditions.[11] Although the SCR catalysts help mercury removal by oxidizing it into more soluble forms (Hg(2+)) to promote removal in the wet FGD, most power plants cannot solely rely on it to meet the MATS, especially for plants burning lignite and bituminous coals with low chlorine contents.[18, 23] The mercury oxidation performance of SCR catalysts can also be significantly reduced by high SO₂.[24] Halogen additions to the boiler are often used together with SCR catalysts to improve mercury oxidation under low chlorine coal conditions. However, high injection rate of halogen salts (CaCl₂ and CaBr₂) could cause other problems and it was reported to cause corrosions especially in the air-preheater.[15, 25]

1.5 Objective of this Research

Due to the increasing number of FGD units resulted from recent EPA rules, oxidizing elemental mercury using SCR or other catalysts, followed by oxidized mercury capture in wet FGD is a viable option. A catalyst specific for mercury oxidation can overcome the limitations of SCR catalysts mentioned above. Due to the complexity and extremely high cost
of APCDs in power plants, it is important that new systems are compatible with and can be incorporated into existing ones. A mercury specific catalyst can be installed using the following options as illustrated in Figure 1.2:

1) For power plants with SCR catalysts, a high temperature mercury oxidation catalyst (working temperature in the range of 300 to 400 °C) can be installed inside the SCR unit at the front end before the NH₃ injection point. In this scenario, the effect of NH₃ can be avoided.

2) A high temperature mercury oxidation catalyst can also be installed at the tail end of the SCR unit where the NH₃ concentration is low. Since most SCR units have extra space for catalysts management and engineering margin, this option should be widely available.

3) For power plants without SCR catalysts, a high temperature mercury oxidation catalyst can be inside a stand-alone unit.

4) A low temperature mercury oxidation catalyst can be installed between the fly ash removal system and the wet FGD where the temperature is around 150 °C.
This research aims to develop catalysts for heterogeneous mercury oxidation under coal-fired power plants flue gas conditions, and to advance the fundamental mechanistic understandings in heterogeneous catalytic oxidation reaction using CuCl$_2$ and RuO$_2$ based catalysts. This dissertation is arranged following the specific research objectives below:

1) Develop low temperature mercury oxidation catalyst based on CuCl$_2$ with porous alumina support. Conduct performance tests and characterizations of the catalysts using techniques including Thermo-Gravimetric Analysis-Mass Spectroscopy (TGA-MS), X-ray Adsorption Fine Structure (XAFS), Temperature Programming Reduction (TPR), X-ray Diffraction (XRD), and X-ray Photoelectron Spectroscopy (XPS).

2) Synthesize high temperature mercury oxidation catalyst based on RuO$_2$ with different TiO$_2$ supports. Evaluate the mercury oxidation performance of the
catalysts under different simulated flue gas conditions and compare the results with the SCR catalysts. Performance catalyst characterizations using techniques including Transmission Electron Microscopy (TEM), XAFS, BET, and XRD.

3) Identify the oxidized mercury species formed from the SCR and RuO$_2$ catalysts under simulated flue gas conditions using characterization techniques such as X-ray Absorption Near-Edge Structure (XANES) to give information on reaction mechanisms.

4) Conduct mechanistic and kinetic studies of mercury oxidation over the RuO$_2$/TiO$_2$ catalyst using in-situ Four Transform Infrared spectroscopy (FTIR) and fixed bed steady state experiments. Provide experimental evidences for a better understanding of heterogeneous oxidation of mercury and obtain kinetic parameters for predicting mercury oxidation.

The work in this study is expected to provide useful information on catalytic heterogeneous mercury oxidation in the flue gas, advance the understandings of its reaction mechanisms, and help developing cost effective mercury control technologies in coal-fired power plants.

1.6 References


Chapter 2  Oxidation of Elemental Mercury Vapor over γ-Al₂O₃

Supported CuCl₂ Catalyst for Mercury Emissions Control *

2.1 Introduction

The new Mercury and Air Toxics Standards (MATS) rule that was effective on April 16, 2012 limits the emissions of mercury, acid gases, and other toxic heavy metals from coal-fired utility, industrial and commercial boilers.[1] Starting from 2016, most coal-fired power plants will need to reduce mercury emissions by >~90%. In addition, the new Transport Rule issued in 2010 regulates sulfur dioxide (SO₂) from power plants in 28 states from 2012. The U.S. EPA estimates a total 272.2 GW of flue gas desulfurization (FGD) units to be installed by 2020 in order to meet the Transport Rule requirements.[2, 3] In this context, the oxidation of elemental mercury (Hg(0)) vapor into a more soluble form (such as HgCl₂) followed by its capture in the subsequent wet FGD system is a viable solution for mercury emissions control in coal-fired power plants. In our previous studies of CuCl₂-impregnated sorbent and catalyst, CuCl₂ was proven to be effective in Hg(0) oxidation.[4-7] When CuCl₂ was impregnated onto non-carbonaceous substrates (such as alumina), the resultant oxidized mercury was not adsorbed onto the substrate surface. When CuCl₂ was dispersed over α-Al₂O₃, it consistently and reliably showed >90% Hg(0) oxidation performances in the presence of 10 ppmv HCl and 6%(v) O₂ with good resistance to SO₂ at 140 °C. While α-Al₂O₃ substrate did not react with CuCl₂ and thus was effective in demonstrating the Hg(0) reaction mechanisms for our previous study, a substrate with a high surface area is usually preferred for industrial

applications. Therefore, in this study, the Hg(0) oxidation over CuCl₂/γ-Al₂O₃ with different loadings has been studied.

A CuCl₂/γ-Al₂O₃ catalyst with KCl as a promoter was previously studied for the oxychlorination reaction of hydrocarbons.[8-13] However, no general agreement has been reported on the structure and nature of copper species formed onto CuCl₂/γ-Al₂O₃ catalysts other than the existence of multiple phases of copper species. In addition, the active species and mechanisms responsible for the oxychlorination by CuCl₂ are still under study. It is difficult to find other applications of CuCl₂/γ-Al₂O₃ as a catalyst from the literature. Therefore, the objective of this study is to investigate the copper speciation of CuCl₂/γ-Al₂O₃ catalyst responsible for the Hg(0) oxidation under different gas conditions at 140 °C, which is a typical flue gas temperature after the air preheater. Several characterization techniques, including BET, SEM, TGA-MS, TPR, XRD, and XPS, have been used to examine the copper speciation from fresh and spent CuCl₂/γ-Al₂O₃ catalysts and to understand the Hg(0) oxidation mechanism.

2.2 Experiment

2.2.1 Catalyst preparation

γ-Al₂O₃ substrate was obtained from Alfa Aesar (aluminum oxide-43855, φ1/8” pellets). γ-Al₂O₃ pellets were activated at 400 °C for 2 hours and then ground and passed through a 40-μm sieve. CuCl₂/γ-Al₂O₃ catalyst was impregnated by wetness incipient method with an aqueous solution of CuCl₂ (Sigma-Aldrich, >98% purity). Different catalyst loadings ranging from 1 to 15%(wt) in terms of CuCl₂ were achieved by controlling the concentration
of CuCl₂ in the aqueous solution. After impregnation, the catalyst with different CuCl₂ loadings was dried in a vacuum oven at 105 °C for 2 hours.

### 2.2.2 Performance Evaluation of CuCl₂/γ-Al₂O₃ Catalyst

The Hg(0) oxidation performance of the CuCl₂/γ-Al₂O₃ catalyst was evaluated using a lab-scale fixed-bed quartz reactor with simulated flue gases. 25 mg of the catalyst was mixed with 4 g silica sand and the volume of the fixed bed was ~2.25 mL. Three different simulated flue gas conditions were used in this study: (1) N₂ (99.999% UHP, Wright Brothers, Inc.); (2) 10 ppmv HCl and 6%(v) O₂ (balanced with N₂); and (3) 2,000 ppmv SO₂, 10 ppmv HCl, and 6%(v) O₂ (balanced with N₂). Mercury vapor was generated from a mercury permeation tube (Dynacal, VICI Metronics) and the inlet Hg(0) vapor concentration was 250 µg/Nm³ (= 30 ppbv) in 1 L/min of a carrier gas flow. The reactor was placed in an oven maintained at 140 °C, targeting an installation of the Hg(0) catalytic reactor after the air preheater. When a spent catalyst was prepared for characterization, silica sand was not used and the inlet Hg(0) vapor concentration was increased to ~2 mg/Nm³ (= 240 ppbv) to saturate the catalyst in a short period of time. Elemental and oxidized mercury concentrations were measured at the outlet of the reactor using the Ontario Hydro method with a cold vapor atomic absorption mercury analyzer (Model 400A, Buck Scientific) or an online mercury analyzer (VM3000, Mercury Instruments). A schematic of the system set-up is shown in Figure 2.1 below.
2.2.3 Catalyst characterization

Surface areas were calculated by using the BET equation for N\textsubscript{2} adsorption isotherms measured at 77 K with a Micrometrics ASAP 2020 system (Micromeritics Instrument Company, Norcross, GA). Thermal Gravimetric Analysis-Mass Spectrometry (TGA, TA Instruments Q5000IR, and MS, Pfeiffer-Vacuum Thermostar) was used to evaluate the thermal stability of pure CuCl\textsubscript{2} and CuCl\textsubscript{2}/γ-Al\textsubscript{2}O\textsubscript{3} catalysts. Samples were heated up to 800 °C at a ramp rate of 5 °C/min under nitrogen flow (99.999% UHP). The H\textsubscript{2}-Temperature Programmed Reduction (TPR) experiments were performed using a Micromeritics Autochem 2910 automated catalyst characterization system. The samples were pretreated at 300 °C for 1 hr in ultra pure argon gas at a flow rate of 30 mL/min. After the furnace temperature decreased to ~50 °C, the feed gas (10%(v) H\textsubscript{2} balanced with Ar) was fed into the system at a
flow rate of 30 mL/min. H$_2$-TPR runs were performed by heating the sample up to 600 °C at a linear heating rate of 6.5 °C/min. The amount of hydrogen gas consumed during the TPR experiment was measured by a built-in thermal conductive detector (TCD). The X-ray diffraction (XRD) measurement was carried out with an X’Pert Pro MPD X-ray diffractometer under Cu Kα radiation (wavelength=1.5406 Å). The samples were loaded in an aluminum holder with a depth of 1 mm. The scanning range was from 10 to 60° (2θ) with a step size of 0.02° and a step time of 0.5 s. XPS (Kratos Axis Ultra, with a monochromated Al Kα source (1486.6 eV)) measurements were used to examine copper speciation with a concentric hemispherical analyzer. The power applied to the X-ray gun was 130 W (I=10 mA, V=13 kV), and the base vacuum pressure was 1×10$^{-7}$ Torr, and the pass energy of the analyzer was set to 20 eV. The resolution of the spectra was ~0.2 eV with a step size of 0.1 eV. The carbon 1s peak at 284.5 eV was used for calibration. Cu K edge X-ray Absorption Fine Structure (XAFS) spectroscopy measurement was performed using the 9-BM-C beamline of the Advanced Photon Source (APS) at the Argonne National Laboratory (ANL, Argonne, IL). All samples and standards (CuCl$_2$ and CuO) were pressed into pellets and measured in both transmission and fluorescence modes. XAFS data collected were analyzed using the Athena software.[14]

2.3 Results and Discussion

2.3.1 Hg(0) Oxidation Performance

The Hg(0) oxidation performances of CuCl$_2$/γ-Al$_2$O$_3$ catalyst with different CuCl$_2$ loadings under N$_2$ gas are shown in Figure 2.2. With 1%(wt) and 3.5%(wt) loadings, CuCl$_2$/γ-Al$_2$O$_3$ showed almost no Hg(0) oxidation capability. When the CuCl$_2$ loading
increased to 10% (wt), CuCl$_2$/γ-Al$_2$O$_3$ could oxidize >95% Hg(0) during the first 20 hours in N$_2$ flow and lost its oxidation capability after ~80 hours. As shown in our previous study, CuCl$_2$ is the active species responsible for Hg(0) oxidation when doped onto α-Al$_2$O$_3$.[7] The Hg(0) oxidation performances under different CuCl$_2$ loadings indicate that at low loadings (i.e. 1 and 3.5%), Cu species on γ-Al$_2$O$_3$ may not be CuCl$_2$ and thus is inactive for Hg(0) oxidation. This inactive Cu species may result from other copper species formed from CuCl$_2$ and γ-Al$_2$O$_3$. At 10% (wt) CuCl$_2$ loading, extra CuCl$_2$ covers the surface of inactive Cu species and has Hg(0) oxidation capability. The presence of multiple Cu species on high loading CuCl$_2$/γ-Al$_2$O$_3$ catalyst is studied and discussed in the following sections.

![Figure 2.2](image)

Figure 2.2 Catalytic performance of CuCl$_2$/γ-Al$_2$O$_3$ catalysts with different CuCl$_2$ loadings under different gas conditions with 30 ppbv inlet Hg(0) vapor in 1 L/min of a carrier gas flow at 140 °C.
The Hg(0) oxidation performances of 10% (wt) CuCl$_2$/γ-Al$_2$O$_3$ catalyst under different simulated flue gas conditions are also shown in Figure 2.2. Regardless of a gas condition, the catalyst could oxidize >95% Hg(0) for the first 20 hours. Under N$_2$, the catalyst gradually lost its Hg(0) oxidation activity after 20 hours and becomes completely inactive after 80 hours. However, in the presence of both 6%(v) O$_2$ and 10 ppmv HCl, CuCl$_2$/γ-Al$_2$O$_3$ catalyst continues to oxidize Hg(0) vapor during the entire evaluation period (~140 hours). Also, an addition of 2,000 ppmv SO$_2$ gas did not show any negative effect on Hg(0) oxidation. These performance results of 10%(wt) CuCl$_2$ loading onto γ-Al$_2$O$_3$ support were similar to those of CuCl$_2$/α-Al$_2$O$_3$ obtained from our previous study.[7] The different Hg(0) oxidation performance of CuCl$_2$/γ-Al$_2$O$_3$ catalysts with respect to different CuCl$_2$ loadings and gas conditions led us to conducting the following characterization studies of the fresh and spent catalysts to gain a better understanding of the CuCl$_2$ speciation and Hg(0) oxidation mechanisms.

2.3.2 BET and SEM

γ-Al$_2$O$_3$ used as a catalyst support in this study has a high surface area (220 m$^2$/g) with mesopores (medium pore diameter ~7 nm, average pore volume 0.62 cm$^3$/g). In comparison, α-Al$_2$O$_3$ has a very small surface area (0.25 m$^2$/g). The SEM images of 10%(wt) CuCl$_2$/γ-Al$_2$O$_3$ and raw γ-Al$_2$O$_3$ are shown in Figure 2.3. No visible CuCl$_2$ crystal can be observed from the γ-Al$_2$O$_3$ surface, indicating that CuCl$_2$ is in a highly dispersed amorphous phase.
Figure 2.3 SEM images of (a) raw $\gamma$-Al$_2$O$_3$ and (b) 10% (wt) CuCl$_2$/γ-Al$_2$O$_3$. 
2.3.3 TGA-MS

The thermal stability of unsupported CuCl₂·2H₂O, CuCl, raw γ-Al₂O₃, and CuCl₂/γ-Al₂O₃ with different loadings was examined by TGA-MS as shown in Figure 2.4.

![TGA-MS results](image)

Figure 2.4 TGA-MS results for CuCl₂·2H₂O, CuCl and CuCl₂/γ-Al₂O₃ catalyst with different loadings.

Unsupported CuCl₂·2H₂O lost ~21% of its weight at 100 °C, corresponding to the vaporization of the dihydrate, and then all CuCl₂ evaporated between 350 °C and 550 °C where chlorine evolution was detected by MS. Unsupported CuCl lost most of the weight between ~410 and 560 °C, but chlorine release was not detected by MS. Pure CuCl melts and vaporizes at ~420 °C, and the CuCl vapor is too heavy to reach the MS capillary tube inlet. These results indicate that dehydrated CuCl₂ loses additional 21% by releasing chlorine and...
turns into CuCl at 438 °C and then the remaining CuCl starts to evaporate without any chlorine release. It should be noted that the 3.5%(wt) CuCl₂/γ-Al₂O₃ and raw γ-Al₂O₃ samples showed very similar weight loss curves, indicating that there are strong interactions between CuCl₂ and γ-Al₂O₃ surface at the loading, and the copper species formed appears to be thermally stable. As demonstrated in the Hg(0) oxidation performance section, the copper species formed onto γ-Al₂O₃ at 1 and 3.5%(wt) loadings did not exhibit any significant catalytic activities. In contrast, 10%(wt) CuCl₂/γ-Al₂O₃ lost 5.7% more weight and this additional weight loss is derived from H₂O and the thermal decomposition of CuCl₂. The results from TGA analysis indicate that CuCl₂ forms thermally stable species with γ-Al₂O₃ first, then extra CuCl₂ is deposited on the surface. For 10%(wt) CuCl₂/γ-Al₂O₃, 4.3%(wt) of CuCl₂ is converted into nonreactive forms, and the rest 5.7% appears to be in the form of CuCl₂. Previous studies reported that the threshold concentration of copper in copper aluminate formation between CuCl₂ and γ-Al₂O₃ is 0.95% (wt) Cu per 100 m² surface area.[9, 10] According to the estimate, the copper aluminate content formed with the γ-Al₂O₃ used in this study (with a surface area of 220 m²/g) is estimated to be 4.42%(wt) in terms of CuCl₂ loading, and this is consistent with our TGA result. For 10%(wt) CuCl₂/γ-Al₂O₃, the release of water was similar to that of unsupported CuCl₂·2H₂O. However, the release of chlorine had a different pattern. Chlorine started to be released at a lower temperature ~200 °C (compared to ~350 °C for unsupported CuCl₂) and continued to be released slowly up to higher temperatures. This is also in agreement with the formation of copper aluminate. Since copper aluminate does not contain chlorine, the chlorine left from the reaction between CuCl₂ and γ-Al₂O₃ was weakly bonded to the surface and was released at lower temperatures.
2.3.4 TPR

H$_2$-TPR was used for 3.5%(wt) CuCl$_2$/γ-Al$_2$O$_3$, 10%(wt) CuCl$_2$/γ-Al$_2$O$_3$ and 10%(wt) CuCl$_2$/α-Al$_2$O$_3$ to measure the redox activity of the supported CuCl$_2$ in terms of temperature as shown in Figure 2.5. The H$_2$-TPR profile of 3.5%(wt) CuCl$_2$/γ-Al$_2$O$_3$ did not show any peak below 600 °C, indicating that the Cu species formed at the loading on γ-Al$_2$O$_3$ was inactive or Cu was in a reduced state. This is in consistent with the TGA result. This Cu species (presumably copper aluminate) formed at this CuCl$_2$ loading appears to have strong interactions with the γ-Al$_2$O$_3$ surface, resulting in high thermal stability and no redox activity.

Figure 2.5 H$_2$-TPR profiles of 3.5%, 10%(wt) CuCl$_2$/γ-Al$_2$O$_3$, and 10%(wt) CuCl$_2$/α-Al$_2$O$_3$.

For the cases of 10%(wt) CuCl$_2$ loading, the 10%(wt) CuCl$_2$/γ-Al$_2$O$_3$ catalyst had two H$_2$-TPR peaks at 200 °C and 375 °C. As previously reported, these peaks were assigned to the two-step reduction of Cu(II) to Cu(I) and Cu(I) to Cu(0), respectively.[15] The 10%(wt)
CuCl₂/α-Al₂O₃ catalyst also showed two peaks at 340 °C and 400 °C. The higher reduction temperature was possibly due to the larger CuCl₂ particle size on α-Al₂O₃ and poor dispersion. [16] The H₂-TPR profile showed that 10%(wt) CuCl₂/γ-Al₂O₃ had higher redox activity at lower temperature than 10%(wt) CuCl₂/α-Al₂O₃. It should be beneficial to CuCl₂ working as a redox catalyst.

2.3.5 XRD

The XRD patterns of raw γ-Al₂O₃ and CuCl₂/γ-Al₂O₃ with different loadings (1%, 3.5% and 10%) are shown in Figure 2.6. No CuCl₂·2H₂O or CuCl₂ peaks were detected from all the samples, indicating the highly dispersed amorphous phase of CuCl₂ on the γ-Al₂O₃ surface. At 1 and 3.5% loadings, no additional peak was detected. At 10%(wt) loading, two peaks at 32.5° and 39.9° appeared and these peaks can be assigned to Cu₂(OH)₃Cl (paratacamite). Paratacamite can be formed from the hydrolysis of CuCl₂·2H₂O, and it is not stable at elevated temperatures, changing into CuCl₂ by losing hydroxyl groups.[9, 10, 17] In order to confirm this, a 10%(wt) CuCl₂/γ-Al₂O₃ sample was heated at 140 °C under a vacuum for 2 hours before XRD measurement. The paratacamite peaks disappeared after the heat treatment, indicating that at the reaction temperature (140 °C), Cu does not exist in the form of paratacamite. In our previous studies, paratacamite peaks were never detected on CuCl₂/α-Al₂O₃, due to a lack of active hydroxyl groups on α-Al₂O₃ surface.[7] The XRD patterns of a spent 10%(wt) CuCl₂/γ-Al₂O₃ sample under different gas conditions including (1) 30 ppbv Hg(0) + N₂; (2) 30 ppbv Hg(0) + 6%(v) O₂ + 10 ppmv HCl + N₂; and (3) 30 ppbv Hg(0) + 6%(v) O₂ + 10 ppmv HCl + 2,000 ppmv SO₂ + N₂ were also examined. All the spent samples showed similar patterns to that of raw γ-Al₂O₃ and no new noticeable peaks were
observed (10% (wt) CuCl$_2$/γ-Al$_2$O$_3$ spent in N$_2$ is shown in Figure 2.6). It should be noted that no CuCl peaks were detected by XRD characterization, which were expected to appear from the spent samples as an intermediate compound of CuCl$_2$ derivatives from the reaction of Hg(0) and CuCl$_2$.[7] In this regard, the amorphous nature of copper species on γ-Al$_2$O$_3$ requires the use of other surface characterization techniques.

2.3.6 Solvent Extraction

The copper species in 10% (wt) CuCl$_2$/γ-Al$_2$O$_3$ identified by the above characterization techniques were further quantified by solvent extraction experiment. Among all potential copper species that can be formed on the γ-Al$_2$O$_3$ surface including copper chlorides, oxychlorides, hydroxychlorides, and oxides, CuCl$_2$ is the only copper compound that is

![Figure 2.6 XRD patterns of CuCl$_2$/γ-Al$_2$O$_3$ catalysts with different CuCl$_2$ loadings.](image-url)
soluble in ethanol.[18] Solvent extraction of 100 mg of 10%(wt) CuCl$_2$/γ-Al$_2$O$_3$ catalyst was performed in 100 mL of ethanol for 4 hours and the extracted Cu was measured by UV-vis spectroscopy. It was determined that 60.8%(wt) of all the Cu was able to be extracted, indicating that it was in the form of CuCl$_2$ (i.e. ~6.1%(wt) CuCl$_2$/γ-Al$_2$O$_3$). This result was in agreement with the result obtained from TGA analysis (i.e. ~4.4%(wt) copper aluminate in 10%(wt)). For 3.5%(wt) CuCl$_2$/γ-Al$_2$O$_3$, no Cu was extracted using ethanol, suggesting that the Cu species is not CuCl$_2$.

2.3.7 XPS

The 3.5%(wt) CuCl$_2$/γ-Al$_2$O$_3$, 10%(wt) CuCl$_2$/γ-Al$_2$O$_3$, unsupported CuCl$_2$ and CuCl standards measured by XPS are shown in Figure 2.7. The standards show the Cu 2p$_{3/2}$ binding energies of 934.5 eV for Cu(II) in CuCl$_2$ and 932.0 eV for Cu(I) in CuCl. The results obtained from the low CuCl$_2$ loading sample (i.e. 3.5%(wt) CuCl$_2$/γ-Al$_2$O$_3$) showed only one major peak at a binding energy of 932.0 eV, which can be assigned to Cu(0) or Cu(I) species. At this stage, the Cu species formed over the 3.5%(wt) CuCl$_2$/γ-Al$_2$O$_3$ sample is not determined. According to previous studies, it could be either atomically dispersed Cu species interacting via oxygen bonds with the support,[19] or surface copper aluminates through isolated copper ions occupying the octahedral vacancies of the alumina surface.[10] The presence of the surface copper aluminate on the γ-Al$_2$O$_3$ surface requires the formation of a Cu-O-Al bond with the elimination of Cl, while the Cl released from CuCl$_2$ is bound to alumina, which was suggested by multiple characterization techniques.[9, 10]
Figure 2.7 Cu 2p$_{3/2}$ high resolution XPS results for fresh CuCl$_2$ /γ-Al$_2$O$_3$ samples and standards.

For fresh 10%(wt) CuCl$_2$ /γ-Al$_2$O$_3$, one additional peak at a binding energy 934.5 eV was observed. This peak position matched that of Cu(II) in CuCl$_2$, supporting our hypothesis that at higher CuCl$_2$ loadings, extra CuCl$_2$ is deposited on the surface and exists in the form of amorphous CuCl$_2$. Spent 10%(wt) CuCl$_2$ /γ-Al$_2$O$_3$ sample under different gas conditions including (1) 30 ppbv Hg(0) + N$_2$ and (2) 30 ppbv Hg(0) + 6%(v) O$_2$ + 10 ppmv HCl + N$_2$ were also measured and the high resolution Cu 2p$_{3/2}$ spectra were obtained as shown in Figure 2.8. As discussed in the Hg(0) oxidation performance section, the reaction could proceed for a certain period of time even without the presence of HCl. The XPS spectra of the sample spent in Hg(0)+N$_2$ showed an increased intensity of the Cu(I) peak, and the Cu(II) peak
corresponding to CuCl$_2$ significantly decreased. In the presence of 10 ppmv HCl, the CuCl$_2$ peak was much stronger, indicating that HCl can help regenerate CuCl to CuCl$_2$ to attain the Hg(0) oxidation capability. It was also observed from survey XPS spectra (data not shown) that the peak intensities for Al and O did not significantly change from the CuCl$_2$/$\gamma$-Al$_2$O$_3$ samples before and after Hg(0) oxidation.

Figure 2.8 Cu 2p$_{3/2}$ high resolution XPS results of spent 10% (wt) CuCl$_2$/$\gamma$-Al$_2$O$_3$ samples under different gas conditions.
2.3.8 Extended X-ray Absorption Fine Structure (EXAFS)

The $k^2$-weighted and Fourier transformed EXAFS spectra ($|\chi(R)|$) for 3.5% (wt) CuCl$_2$/γ-Al$_2$O$_3$, 15% (wt) CuCl$_2$/γ-Al$_2$O$_3$, and two standards (CuCl$_2$ and CuO) are shown in Figure 2.9. CuO showed a single peak at 1.55 Å corresponding to the Cu-O bond (position marked by the solid vertical line in Figure 2.9). CuCl$_2$ showed one major peak at 1.86 Å derived from the Cu-Cl bond (position marked by the dashed vertical line) and a minor shoulder peak at a lower R region representing the Cu-O bond due to the interaction between Cu and the dihydrate.[20] The 3% (wt) CuCl$_2$/γ-Al$_2$O$_3$ sample had only one peak indicating the Cu-O bond and no Cu-Cl bond was detected. This further suggests the formation of copper aluminate when low CuCl$_2$ loading such as 3.5% (wt) was doped onto γ-Al$_2$O$_3$. Since no Cu-Cl bond was found to exist from the 3.5% (wt) sample, the catalysts with such low CuCl$_2$ loadings did not show mercury oxidation capability. On the other hand, the 15% (wt) CuCl$_2$/γ-Al$_2$O$_3$ sample showed a broad peak that shifts to higher R region, indicating the co-existence of both of the Cu-O and Cu-Cl bonds. These results are in agreement with the other characterization results and corroborate the co-existence of multiple copper species on the CuCl$_2$/γ-Al$_2$O$_3$ catalysts at high CuCl$_2$ loadings.
Figure 2.9 $k^2$-weighted and Fourier transformed Cu EXAFS signals ($|\chi(R)|$) for CuO, CuCl$_2$, 3.5\%(wt) CuCl$_2$ /\(\gamma\)-Al$_2$O$_3$ and 15\%(wt) CuCl$_2$ /\(\gamma\)-Al$_2$O$_3$. The vertical lines indicate the Cu-O and Cu-Cl bonding distances.

### 2.3.9 Hg(0) Oxidation over CuCl$_2$ /\(\gamma\)-Al$_2$O$_3$

From the above characterization results obtained from the CuCl$_2$ /\(\gamma\)-Al$_2$O$_3$ catalyst and the results reported in the literature with different CuCl$_2$ loadings, the following findings are summarized: (1) at low CuCl$_2$ loadings, copper aluminate is the only species and it is inactive for Hg(0) oxidation; (2) as CuCl$_2$ loading increases, the extra Cu will exist in the form of paratacamite and amorphous CuCl$_2$; and (3) at the reaction temperature of 140 °C, paratacamite will be converted back into CuCl$_2$ by losing hydroxyl groups and CuCl$_2$ is
believed to be the active species for Hg(0) oxidation. Leofanti et al. reported that in low CuCl₂ loading samples, Cu occupies the octahedral vacancies of the alumina surface with the formation of diluted surface aluminate and the chloride anions released upon the dissociation of CuCl₂ molecules do not contribute to the first coordination shell of Cu.[9, 10] The reaction between CuCl₂ and hydroxylated alumina surface can be represented by Eqs. (2-1)-(2-3).

\[
\begin{align*}
\text{CuCl}_2 + 4\text{Al-OH} & \rightarrow \text{AlO-Cu-OAl} + 2\text{Al-Cl} + 2\text{H}_2\text{O} \quad (2-1) \\
\text{Al-O-Al} + \text{HCl} & \rightarrow \text{Al-OH} + \text{Al-Cl} \quad (2-2) \\
\text{Al-OH} + \text{HCl} & \rightarrow \text{Al-Cl} + \text{H}_2\text{O} \quad (2-3)
\end{align*}
\]

In this study, the γ-Al₂O₃ support was used to provide a high surface area for the Hg(0) oxidation. Although highly dispersed CuCl₂ provides more active sites for Hg(0) adsorption and oxidation, some of CuCl₂ is used to form copper aluminate and paratacamite phases. In the absence of HCl and O₂ gases, CuCl₂/γ-Al₂O₃ can still oxidize Hg(0) by consuming lattice Cl atoms and CuCl₂ is reduced to CuCl. This suggests that Hg(0) oxidation over CuCl₂/γ-Al₂O₃ via a Mars-Maessen mechanism.[21, 22] In the presence of HCl and O₂ gases, CuCl can be converted back into CuCl₂ and the catalyst is regenerated. In this context, CuCl₂/γ-Al₂O₃ works as a redox catalyst for Hg(0) oxidation. It has been proposed that the conversion from CuCl to CuCl₂ involves two steps: CuCl forms Cu₂OCl₂ by oxidation with O₂ gas and is subsequently converted into CuCl₂ with HCl gas.[23, 24] In our previous study on Hg(0) oxidation over CuCl₂/α-Al₂O₃ [7], all Cu species are in crystalline form and the intermediate Cu₂OCl₂ was detected by XRD. However, for CuCl₂/γ-Al₂O₃, Cu₂OCl₂ was not detected due to the amorphous nature of Cu species formed onto γ-Al₂O₃ and its formation is not clear. Despite that, the reactions involved in the Hg(0) oxidation over CuCl₂/γ-Al₂O₃ can be summarized as follows:
Hg(g) → Hg(ad) \hspace{1cm} (2-4)

Hg(ad) + 2CuCl₂ → HgCl₂(ad) + 2CuCl \hspace{1cm} (2-5)

HgCl₂(ad) → HgCl₂(g) \hspace{1cm} (2-6)

2CuCl + 1/2O₂ + 2HCl → 2CuCl₂ + H₂O \hspace{1cm} (2-7)

Overall: Hg(g) + 2HCl + 1/2O₂ → CuCl₂ → HgCl₂(g) + H₂O \hspace{1cm} (2-8)

Compared with Hg(0) oxidation over CuCl₂/α-Al₂O₃, the CuCl₂/γ-Al₂O₃ catalyst also forms the Cu₂(OH)₃Cl phase. It involves a transfer of Cl atoms between CuCl₂ and the surface alumina. Cu₂(OH)₃Cl is not thermally stable as shown from the XRD result. At the reaction temperature of 140 °C, it will be completely converted into CuCl₂ and catalyze the oxidation of adsorbed Hg(0) via Eq. (5). It should be noted that for the regeneration of CuCl₂, both HCl and O₂ gases are required.

2.4 Conclusion

When CuCl₂ is impregnated onto γ-Al₂O₃ support using wet incipient method, multiple Cu species were found to be formed. This is different from the impregnation onto α-Al₂O₃, as only a single CuCl₂ phase was formed. At low CuCl₂ loadings (e.g. <4.3%(wt)), strong interactions were found between CuCl₂ and γ-Al₂O₃ to form copper aluminate (CuAlO₂). It is thermally stable and chemically inert for Hg(0) oxidation. As the loading increases, additional CuCl₂ dopant will cover the copper aluminate surface to form paratacamite (Cu₂(OH)₃Cl) and highly dispersed amorphous CuCl₂. At the reaction temperature of 140 °C, paratacamite will lose hydroxyl groups to be converted into CuCl₂, and the latter is the active species responsible for the Hg(0) oxidation reaction. CuCl₂ works
as a redox catalyst and oxidizes Hg(0) by reducing itself to CuCl, following a re-chlorination back to CuCl₂ under O₂ and HCl gases. High loadings of CuCl₂ onto the γ-Al₂O₃ support showed excellent Hg(0) oxidation performance and SO₂ resistance under 10 ppmv HCl. The CuCl₂/γ-Al₂O₃ catalyst has the potential to be used as a low temperature Hg(0) oxidation catalyst in coal-fired power plants for mercury emissions control.

2.5 References


Chapter 3  Heterogeneous Oxidation of Elemental Mercury Vapor over RuO$_2$/rutile TiO$_2$ Catalyst for Mercury Emissions Control*

3.1 Introduction

Coal naturally contains small amounts of mercury (around 0.1~0.2 ppm by weight) and they will be released into the flue gas after the combustion.[1, 2] It is estimated that around 53 tons of mercury are emitted from coal-fired power plants each year in the United States, accounting for around 50% of emissions from all anthropogenic mercury sources.[3] Mercury has long been recognized as a highly toxic and persistent pollutant. The 1990 Amendments to the Clean Air Act listed mercury as one of the most toxic pollutants among 188 hazardous air pollutants. 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).[4] Prior to the MATS rule in 2011, EPA finalized the Cross-State Air Pollution Rule (CSAPR), replacing the EPA's earlier Clean Air Interstate Rule (CAIR) from 2005.[5] CSAPR further reduces NO$_x$ and SO$_2$ emissions from power plants in 28 states, and as a result, additional installations of flue gas desulfurization (FGD) and NO$_x$ control systems such as a selective catalytic reduction (SCR) unit are expected.

After combustion, mercury is released and exists in three forms in coal-fired power plants flue gas: oxidized mercury (Hg(2+)), particulate mercury (Hg(p)), and elementary mercury (Hg(0)). The first two forms are readily removed with existing air pollution control

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systems such as fabric filter (FF), electrostatic precipitators (ESP), and wet FGD.[6-8] Hg(0) is most difficult to remove due to its high volatility, low reactivity and low solubility. Currently, sorbent injection (raw or modified activated carbon), halogen salt (e.g. CaBr₂) addition to the boiler and SCR optimization are commercially available mercury emissions control technologies.[9] Because of the vastly 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. Activated carbon injection is the most well-studied and mature technology, but the cost is high. The U.S. Department of Energy estimates that the costs for sorbent injection to achieve 90 percent removal are estimated to be between $25,000 and $70,000 per pound of mercury removed.[10] Also, activated carbon sorption capacity is significantly reduced under high sulfur coal conditions.[11] Due to the increasing number of FGD units resulted from recent EPA rules, oxidizing elemental mercury using SCR or other catalysts, followed by oxidized mercury capture in wet FGD is a viable option. Noble metal-based catalysts such as gold, platinum and palladium have been studied as Hg(0) oxidation catalysts.[12, 13] Various metal oxide-based Hg(0) oxidation catalysts, SCR and modified SCR catalysts have also been studied for Hg(0) oxidation.[14-22] Due to the oxygen storing and releasing property of CeO₂, its application in Hg(0) oxidation and adsorption in flue gas has been studied in recent years. Nanostructured CeO₂-MnOₓ catalyst and CeO₂-based solid solutions showed good Hg(0) removal performance from increased oxygen vacancies and catalytic activity.[23, 24] CeO₂-TiO₂ and CeO₂ modified MnOₓ-TiO₂ were reported to have Hg(0) adsorption capability.[25, 26] CeO₂ was also reported to have a promotional effect for Hg(0) oxidation in a modified SCR catalyst.[27] But, most of them only showed limited Hg(0) oxidation performances at low HCl concentrations of typical flue
gases from lignite and sub-bituminous coals. Also, these catalysts are susceptible to SO₂ and NH₃ inhibition and showed degraded performances under high sulfur bituminous coal flue gas conditions (e.g., 2,000 ppmv SO₂). For low rank sub-bituminous and lignite coals with low chlorine (typically with HCl <10 ppmv in the flue gas), additional halogen is usually needed to achieve satisfactory Hg(0) oxidation. Currently, halogen salts such as CaCl₂ or CaBr₂ injection to the boiler to enhance Hg(0) oxidation is one of the most widely used methods.[28]

In the absence of any catalyst (either SCR or Hg(0) oxidation catalyst), high injection rate of the halogen salts is required, and it was reported to cause corrosion problems especially in the air-preheater.[29, 30] A combination of halogen salts addition and Hg(0) oxidation catalysts could be an economical and feasible solution.[31]

Recently, RuO₂-based catalysts were developed for the Deacon reaction for the oxidation of HCl by O₂ to produce Cl₂.[32, 33] It was also found that many Deacon reaction catalysts can also catalyze the Hg(0) oxidation reaction by utilizing HCl gas.[17] In our previous study, oxidized mercury species obtained from the RuO₂/rutile TiO₂ catalyst were analyzed using X-ray Absorption Near-Edge Structure (XANES) spectroscopy.[34] A major focus of the study was to identify and quantify the oxidized mercury species generated as a result of the reaction of Hg(0) vapor over the catalyst under different simulated flue gas conditions. In the presence of HCl or HBr gas with O₂ gas, HgCl₂ or HgBr₂ was found to be a major oxidized mercury species. HgCl₂ and HgBr₂ have high solubility in water, and can be easily scrubbed by wet FGD scrubbers in coal-fired power plants. In this study, the performances of the RuO₂/rutile TiO₂ catalyst were investigated in terms of different TiO₂ phases, synthesis methods and gas and temperature conditions.
3.2 Experimental

3.2.1 Catalyst synthesis

RuO$_2$/TiO$_2$ catalysts were synthesized using RuCl$_3$ (Sigma-Aldrich) as the precursor. Commercial anatase- and rutile-phase TiO$_2$ were obtained from Cristal Co. and Sakai Chemical, respectively. Three synthesis methods were used for RuO$_2$/TiO$_2$ catalysts, and the procedures are summarized below.

Wetness incipient (WI) method: RuCl$_3$ was dissolved in a small amount of water (around 0.9 mL per gram of TiO$_2$) and the solution was added to dry TiO$_2$ powder. After thorough mixing, the catalyst was dried at room temperature for 12 hours and calcined at 400 °C in air for 3 hours.

Deposition-precipitation (DP) method: TiO$_2$ powder was added to water (25 mL water per gram of TiO$_2$ powder) under vigorous stirring. Then RuCl$_3$ was added and the slurry was heated to 45 °C. A 1 M Na$_2$CO$_3$ solution was added dropwise until pH>10 to precipitate all RuCl$_3$. The catalyst was then filtered, washed thoroughly, dried at room temperature for 12 hours and calcined at 400 °C in air for 3 hours.

Strong electrostatic adsorption (SEA) method: TiO$_2$ powder was added to water (25 mL water per gram of TiO$_2$ powder) under vigorous stirring and an ammonium hydroxide solution was added until pH reached 11.5. RuCl$_3$ was then added and stirred for 3 hours. This method utilizes electrostatic charges for adsorption of active metals onto substrate. The point of zero charge (PZC) for TiO$_2$ in the aqueous phase is around 6. When the pH of a solution is greater than that the PZC (i.e. ~6), TiO$_2$ surface is negatively charged. Ru(NH$_3$)$_6^{3+}$ formed from RuCl$_3$ and ammonium hydroxide is positively charged and adsorbs onto the TiO$_2$
surface. The catalyst was then filtered, washed thoroughly, dried at room temperature for 12 hours and calcined at 400 °C in air for 3 hours.

SCR catalyst with 1 wt.% V\textsubscript{2}O\textsubscript{5} loading was synthesized by following a procedure below: 12 g of anatase TiO\textsubscript{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 (Fibre Glast) were dry mixed for 10 minutes. 0.138 g of NH\textsubscript{4}VO\textsubscript{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 for uniform mixing. All the catalysts were extruded into 1 mm (diameter) × 5 mm (length) cylindrical pellets, and were dried in air at room temperature, followed by calcination at 500 °C in air for 3 hours.

3.2.2 Characterization

The BET surface area, pore volume and pore diameter were measured by an accelerated surface area and porosimetry system (ASAP 2020, Micromeritics). The high-resolution transmission electron microscopy (HR-TEM) experiments were conducted using JEOL 2010F equipped with a field emission gun operating at 200 keV with a point-to-point resolution of 0.19 nm. Energy-dispersive X-ray spectroscopy was conducted using the same instrument with an Oxford INCA EDX detector. The X-ray diffraction (XRD) measurement was carried out with an X'Pert Pro MPD X-ray diffractometer under Cu K\textalpha radiation (wavelength=1.5406 Å). The powdered samples were loaded in an aluminum holder with a depth of 1 mm. The scanning range was from 10 to 60° (2\theta) with a step size of 0.02° and a time step of 0.5 s. Ruthenium K edge (22,117 eV) X-ray absorption fine structure (XAFS) spectra were collected using the 9-BM-B beamline (Sector 9) 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 $1.4 \times 10^{-4}$. Energy calibration was monitored by measuring the absorption through a reference ruthenium foil simultaneously with the absorption through the samples. Samples were loaded onto Teflon holder between two layers of Kapton tapes and measured in transmission mode. A RuO$_2$ standard was obtained from Sigma-Aldrich. A spent RuO$_2$/rutile TiO$_2$ catalyst sample treated after 48 hours of Hg(0) oxidation under a simulated flue gas (containing 15 ppbv Hg(0), 10 ppmv HCl, 5 ppmv NH$_3$, 5 ppmv NO, 200 ppmv SO$_2$, 3%(v) O$_2$, 10%(v) H$_2$O, 12%(v) CO$_2$ balanced with N$_2$) at 350 °C was also examined for XRD and XAFS analyses. At least five scans were collected for each sample in order to improve the signal-to-noise ratio. XAFS data collected were analyzed using the Athena software package.[38]

3.2.3 Performance tests

The performances of RuO$_2$/TiO$_2$ catalysts were tested using a fixed-bed reactor system. A schematic of the apparatus is shown in Figure 3.1. Elemental mercury (Hg(0)) vapor was generated using a permeation oven (Dynacalibrator, VICI Metronics) using N$_2$ as a carrier gas and the inlet Hg(0) vapor concentration was 10-15 ppbv. Water vapor was generated using a bubbler. All the other simulated flue gas components were prepared from compressed gas cylinders (Wright Brothers, Inc.) and the concentrations were controlled by mass flow controllers. The catalysts with ruthenium metal loading of 0.2-1 wt.% (in terms of Ru) were used for the performance tests. The catalysts in the form of extruded pellets (1 mm $\times$ 5 mm (D $\times$ L)) were placed inside a vertically mounted quartz reactor with a diameter of 16 mm and the temperature was maintained at 350 °C in a tubular furnace. For performance tests under
simulated flue gas conditions, 1.7 grams of catalysts were used and the catalyst bed height was around 15 mm. The temperature was chosen to approximate the temperature at the tail end of the SCR unit at coal-fired power plants. The total flow rate 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 commercial SCR units). It was confirmed that Hg(0) oxidation under the simulated flue gas conditions was negligible in the absence of the catalysts. Each performance test was conducted for 6 to 24 hours after making sure that the system was stabilized. The Hg(0) oxidation efficiency and oxidation rate were calculated by measuring the concentrations across the reactor bed using the following equations (3-1) and (3-2):

\[
\text{Hg(0) oxidation efficiency} = \frac{Hg(0)_{\text{out}} - Hg(0)_{\text{in}}}{Hg(0)_{\text{in}}} \times 100\% \tag{3-1}
\]

\[
\text{Hg(0) oxidation rate} = \frac{Hg(0)_{\text{in}} - Hg(0)_{\text{out}}}{\text{time}} \tag{3-2}
\]

Figure 3.1 A schematic of the experimental set-up for the catalysts performance test.
SO$_3$ generated from the catalyst under a simulated flue gas containing high SO$_2$ concentration was measured using U.S. EPA Method 8.[39] Two impinger solutions containing 80%(v) isopropanol in water and 3%(v) H$_2$O$_2$ in water in series were used to capture SO$_3$ and SO$_2$, respectively. Then both fractions were measured separately by the barium-thorin titration method.

### 3.3 Results and Discussion

#### 3.3.1 Catalysts characterization

##### 3.3.1.1 TEM

In this study, two types of TiO$_2$ support (anatase and rutile) and three synthesis methods (WI, DP, SEA) were used. The TEM images of these RuO$_2$/TiO$_2$ catalysts with 1%(wt) Ru loading were taken to obtain the information on the morphology of the metal oxides. When anatase TiO$_2$ was used, RuO$_2$ formed large aggregates ranging from 50 to 100 nm for all three synthesis methods as shown in Figure 3.2-b, 3.2-c and 3.2-d. RuO$_2$ particles were much bigger than anatase TiO$_2$ particles and the metal dispersion was poor. EDX indicated that RuO$_2$ mainly existed as large aggregates and there was only a very small amount present on the anatase TiO$_2$ surface. The morphology of RuO$_2$ changed significantly when rutile TiO$_2$ was used as a support. Under low resolution TEM, no RuO$_2$ particle could be found from all the three different synthesis methods. However, EDX proved that RuO$_2$ was present on the surface. Figure 3.2-e and 3.2-f are rutile TiO$_2$ and RuO$_2$/rutile TiO$_2$ (prepared by WI) samples, respectively. The lighter spots on the TiO$_2$ surface are holes and pores. In order to confirm the morphology of RuO$_2$, the catalysts were also examined by high resolution TEM. Rutile TiO$_2$ itself had clean surfaces (Figure 3.2-g). After doping with
ruthenium, it was found that RuO$_2$ formed a thin uniform coating on rutile TiO$_2$ surface with a thickness of 1~2 nm as shown in Figure 3.2-h. No noticeable difference on RuO$_2$ morphology was observed among the three different synthesis methods.
Figure 3.2 TEM images of the RuO$_2$/TiO$_2$ catalysts with different supports and synthesis methods.  a: anatase TiO$_2$; b: RuO$_2$/anatase TiO$_2$WI; c: RuO$_2$/anatase TiO$_2$DP; d: RuO$_2$/anatase TiO$_2$SEA; e: rutile TiO$_2$; f: RuO$_2$/rutile TiO$_2$WI; g: HR-TEM of rutile TiO$_2$; h: HR-TEM of RuO$_2$/rutile TiO$_2$WI.  
Scale bars: a~d=50 nm; e~f=20 nm; g~h=2 nm

For RuO$_2$ as a Deacon catalyst, Seki also reported the formation of a nano-sized layer of RuO$_2$ crystals on rutile TiO$_2$.[32] Xiang et al. observed the transformation from RuO$_2$ particles to epitaxial layer during Deacon reaction.[40] Both RuO$_2$ and rutile TiO$_2$ have the same body-centered tetragonal structure with very similar lattice constants: RuO$_2$ with a=b=0.46 nm, c=0.30 nm and rutile TiO$_2$ with a=b=0.45 nm, c=0.31 nm. This similarity makes it easier for RuO$_2$ to deposit onto rutile TiO$_2$ surface and to form highly dispersed nano-layers.[40, 41] These results suggest that lattice matching between RuO$_2$ and rutile TiO$_2$ be a stronger driving force for the dispersion of RuO$_2$ than the effects of different catalyst synthesis methods.

4.3.1.2 BET

The BET surface area, pore volume and average pore diameter of RuO$_2$/rutile TiO$_2$WI catalysts with different metal loadings and synthesized SCR catalyst were measured and listed in Table 3.1. The BET surface area, pore volume and average pore diameter decreased from 72 to 64 m$^2$/g, 0.38 to 0.28 cm$^3$/g and 202 to 186 Å, respectively, as the ruthenium loading increased to 1 wt.%. The impregnation of ruthenium onto rutile TiO$_2$ did not significantly decrease surface area or block the pores. For the synthesized SCR catalyst, the anatase TiO$_2$ support had a higher BET surface area than rutile TiO$_2$, and the values measured were within a range of typical commercial SCR catalysts.[42-45]
Table 3.1 BET surface area, pore volume and average pore diameter measurements for synthesized RuO$_2$/rutile TiO$_2$ and SCR catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET surface area (m$^2$/g)</th>
<th>Pore volume (cm$^3$/g)</th>
<th>Average pore diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rutile TiO$_2$</td>
<td>72</td>
<td>0.38</td>
<td>202</td>
</tr>
<tr>
<td>0.2% Ru loading</td>
<td>69</td>
<td>0.31</td>
<td>194</td>
</tr>
<tr>
<td>0.5% Ru loading</td>
<td>66</td>
<td>0.28</td>
<td>184</td>
</tr>
<tr>
<td>1% Ru loading</td>
<td>64</td>
<td>0.28</td>
<td>186</td>
</tr>
<tr>
<td>Synthesized SCR</td>
<td>95</td>
<td>0.29</td>
<td>126</td>
</tr>
<tr>
<td>Commercial SCR [36-39]</td>
<td>61-120</td>
<td>0.17-0.29</td>
<td>103-151</td>
</tr>
</tbody>
</table>

4.3.1.3 XRD

Both RuO$_2$/anatase TiO$_2$ WI and RuO$_2$/rutile TiO$_2$ WI catalysts were examined by XRD and the patterns are shown in Figure 3.3. Other synthesis methods (DP and SEA) showed the same results as the WI method. The RuO$_2$/anatase TiO$_2$ catalyst showed two additional RuO$_2$ peaks at $2\theta$=28.0° and 35.1° compared to pristine anatase TiO$_2$. However, when rutile TiO$_2$ was used as a support, no RuO$_2$ could be detected. This result was consistent with the information obtained from the TEM results. On anatase TiO$_2$, the RuO$_2$ crystal formation could be easily detected by XRD, while the nano-layers of RuO$_2$ were formed on rutile TiO$_2$. For nano-structures, the local atom arrangements lack long-range 3-D periodicity that typical crystals have, making XRD nonideal for analyzing nanomaterials.[46] Therefore, an alternative characterization technique was needed to identify the ruthenium species on rutile TiO$_2$. 
4.3.1.4 XAFS

XAFS can give structural information of materials not affected by the state or morphology of the sample. Since XRD was unable to detect the RuO$_2$ nano-layers formed on rutile TiO$_2$, XAFS was used to confirm the speciation of ruthenium. RuO$_2$ catalysts supported on rutile TiO$_2$ were used for the analysis. Ruthenium K edge (22,117 eV) XAFS spectra for the RuO$_2$/rutile TiO$_2$ catalyst were collected. Since XAFS is an element-specific characterization technique, TiO$_2$ in the catalyst does not interfere with the ruthenium measurement. The Fourier transformed spectra $\chi(R)$ are shown in Figure 3.4. RuO$_2$/rutile TiO$_2$ catalysts with different synthesis methods showed the same result and only the result obtained from WI is shown here. Compared with a RuO$_2$ standard, a fresh RuO$_2$/rutile TiO$_2$ catalyst showed the same structure. The first major peak at around 1.5 Å is from a ruthenium
atom and the neighboring oxygen atoms, and the second major peak at around 3.1 Å is from a center ruthenium atom and the neighboring ruthenium atoms. The spectra are similar to those reported in other studies.[47, 48] The spectrum of the spent catalyst did not show any change, indicating that RuO₂ was structurally stable under the simulated flue gas conditions.

Figure 3.4 Fourier transformed Ru XAFS spectra (|χ(R)|) for fresh RuO₂/rutile TiO₂ WI, spent RuO₂/rutile TiO₂ WI and RuO₂ standard.

3.3.2 Hg(0) oxidation performances

3.3.2.1 Effects of TiO₂ support and metal loading

The above catalyst characterization results showed major differences in morphology and dispersion of RuO₂ on anatase and rutile TiO₂ supports. Therefore, Hg(0) oxidation
performances of 1 wt.% RuO\textsubscript{2} catalysts with different TiO\textsubscript{2} supports and synthesis methods were evaluated and the results are shown in Figure 3.5. Although the surface area of rutile TiO\textsubscript{2} is slightly lower than anatase TiO\textsubscript{2} under the same conditions, the Hg(0) oxidation performances of RuO\textsubscript{2}/rutile TiO\textsubscript{2} catalysts were around 70\% higher than those of RuO\textsubscript{2}/anatase TiO\textsubscript{2} catalysts on average. When RuO\textsubscript{2} was used as a Deacon catalyst for HCl oxidation, higher catalytic activity of RuO\textsubscript{2} was reported over rutile TiO\textsubscript{2}.\cite{32} However, it is important to note that the different synthesis methods did not result in significant performance differences. These results are consistent with TEM images. The higher dispersion of RuO\textsubscript{2} over rutile TiO\textsubscript{2} due to lattice matching of these two very similar structures very likely leads to higher catalytic activity. Therefore, rutile TiO\textsubscript{2} was chosen as a preferred substrate in this study, and WI was also selected as a preferred synthesis method because of its simplicity.

![Graph showing Hg(0) oxidation rates for different catalysts](image)

Figure 3.5 Hg(0) oxidation activities of 1 wt.% RuO\textsubscript{2}/TiO\textsubscript{2} catalysts with different TiO\textsubscript{2} supports and synthesis methods. Conditions: 10 ppbv Hg(0), 10 ppmv HCl, 3\%(v) O\textsubscript{2}, and balance N\textsubscript{2} at T=350 °C.
As a precious metal, a ruthenium loading on catalyst support should be optimized for the maximum utilization of the active metal. Therefore, the RuO\textsubscript{2}/rutile TiO\textsubscript{2} catalyst with different ruthenium loadings (0.2, 0.5 and 1 wt.%) were compared (Figure 3.6). In terms of the reaction rate of Hg(0) oxidized per mole of ruthenium used (i.e. turnover frequency), 0.5 wt.% Ru loading gave the highest ruthenium utilization efficiency. The determination of RuO\textsubscript{2} on TiO\textsubscript{2} support using a chemisorption method has an inherent difficulty. It is well reported in the literature that the reduced form of RuO\textsubscript{2} (i.e. Ru) becomes mobile and agglomerates on the TiO\textsubscript{2} surface during the reduction step in chemisorption. This phenomena was reported by Komaya et al., and the attempts to eliminate the agglomeration by using different reduction conditions were not successful.[49] In this study, the determination of RuO\textsubscript{2} dispersion over rutile the TiO\textsubscript{2} phase was also attempted, but was not successful. Therefore, mass was used as a basis for the Ru loading instead of dispersion.

![Figure 3.6 Effect of metal loadings on the utilization efficiency of ruthenium on rutile TiO\textsubscript{2} (WI method). Conditions: 10 ppbv Hg(0), 10 ppmv HCl, 3%(v) O\textsubscript{2}, and balance N\textsubscript{2} at T=350 °C.](image-url)
3.3.2.2 Effects of temperature

When RuO$_2$ was used as a Deacon catalyst, the activity was reported to be highest at around 400 °C.[41] This RuO$_2$/rutile TiO$_2$ Hg(0) oxidation catalyst can be located between the economizer and air preheater at coal-fired power plants. For power plants with a SCR unit, the catalyst can be located inside the SCR unit, or it can be a stand-alone unit before or after the SCR unit. 300~400 °C is an optimal temperature window for typical SCR catalysts when the boilers are at a full load.[50] The RuO$_2$/rutile TiO$_2$ Hg(0) oxidation catalyst can also utilize the same temperature window. The Hg(0) oxidation performances of RuO$_2$/rutile TiO$_2$ catalyst at temperatures between 300 and 400 °C were evaluated as shown in Figure 3.7. The results indicated that RuO$_2$/rutile TiO$_2$ catalyst prefers higher temperature within the temperature window for Hg(0) oxidation.

![Figure 3.7 Effect of temperature on the 1 wt.% RuO$_2$/rutile TiO$_2$ WI catalyst activity. Conditions: 10 ppbv Hg(0), 5 ppmv HCl, 3%(v) O$_2$, and balance N$_2$.](image)

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3.3.2.3 Hg(0) oxidation under simulated flue gases

For coal-fired power plants with SCR units for NO\textsubscript{x} removal, NH\textsubscript{3} as a reductant is injected into the front end of the SCR units. As the de-NO\textsubscript{x} reaction proceeds, NH\textsubscript{3} concentration decreases along the SCR unit, and an NH\textsubscript{3} slip at the tail end is usually controlled at \(<\ 2\ \text{ppmv}\) for commercial SCR catalysts.[51] The effect of NH\textsubscript{3} gas on Hg(0) oxidation is shown in Figure 3.8. NH\textsubscript{3} has a strong inhibition effect on Hg(0) oxidation over RuO\textsubscript{2}/rutile TiO\textsubscript{2} catalyst. The catalyst lost almost all its Hg(0) oxidation capability when NH\textsubscript{3} concentration was increased to 50 ppmv. When the 50 ppmv NH\textsubscript{3} was lowered back to 5 ppmv, Hg(0) oxidation was fully recovered. This corroborates that the adverse effect of NH\textsubscript{3} is most likely derived from competitive adsorption with HCl onto active catalytic sites and not catalyst poisoning. Due to this limitation, the RuO\textsubscript{2}/rutile TiO\textsubscript{2} catalyst is not suitable for being located at the front end of a SCR unit. Installing at the tail end of a SCR unit, after the SCR unit, or for power plants without the SCR unit are possible options.

![Figure 3.8](image)

Figure 3.8 Effect NH\textsubscript{3} concentrations on Hg(0) oxidation performances of 1 wt.% RuO\textsubscript{2}/rutile TiO\textsubscript{2}_WI catalyst under simulated flue gas. Conditions: 15 ppbv Hg(0), 10 ppmv HCl, 5 ppmv NO, 200 ppmv SO\textsubscript{2}, 3%(v) O\textsubscript{2}, 10%(v) H\textsubscript{2}O, 12%(v) CO\textsubscript{2} balanced with N\textsubscript{2} at 350 °C.
A SO$_2$ concentration in a coal combustion flue gas greatly varies in terms of different types of coals with different sulfur contents. Generally, lignite and sub-bituminous coals have low SO$_2$ (a few hundred ppmv in the flue gases) while bituminous coal has high SO$_2$ (up to ~2,000 ppmv in the flue gas). The Hg(0) oxidation performances under different SO$_2$ concentrations are shown in Figure 3.9. It should be noted that these tests were carried out with only 10 ppmv HCl just to demonstrate the effect of SO$_2$ under extreme conditions. For bituminous coal flue gas with high SO$_2$ concentration, the HCl concentration is also much higher (e.g., ~50-200 ppmv). Under such high HCl concentrations, the resistance of Hg(0) oxidation to SO$_2$ is much lower as reported in our previous study.[34] In general, the RuO$_2$/rutile TiO$_2$ catalyst has higher resistance to SO$_2$ compared with other metal oxides-based catalysts such as MnO$_2$ and CeO$_2$.[52, 53] The Hg(0) oxidation performance was recovered when SO$_2$ was lowered back to 200 ppmv, also indicating the competitive adsorption of SO$_2$ with HCl. XRD analysis for the spent catalyst can be used to identify possible sulfates formation.[54] As shown in Figure 3.10, the XRD diffraction pattern was consistent with that for the fresh RuO$_2$/rutile TiO$_2$ catalyst (Figure 3.3), and the peaks for sulfate species were not observed. The XAFS analysis for the spent RuO$_2$/rutile TiO$_2$ catalyst (Figure 3.4) did not detect a formation of any potential bonding between ruthenium and sulfur. These results indicated that the catalyst was not poisoned by SO$_2$ during the reaction. Other flue gas components such as CO$_2$, water vapor, and NO did not show any noticeable effect on Hg(0) oxidation over RuO$_2$/rutile TiO$_2$ catalyst.
Figure 3.9 Effect of SO₂ concentrations on Hg(0) oxidation performances of 1 wt.% RuO₂/rutile TiO₂-WI catalyst under simulated flue gas. Conditions: 15 ppbv Hg(0), 10 ppmv HCl, 5 ppmv NH₃, 5 ppmv NO, 3%(v) O₂, 10%(v) H₂O, 12%(v) CO₂ balanced with N₂ at 350 °C.
Figure 3.10 XRD pattern of the spent RuO$_2$/rutile TiO$_2$ catalyst. Conditions: 15 ppbv Hg(0), 10 ppmv HCl, 5 ppmv NH$_3$, 5 ppmv NO, 200 ppmv SO$_2$, 3%(v) O$_2$, 10%(v) H$_2$O, 12%(v) CO$_2$ balanced with N$_2$ at 350 °C for 48 hours.

The Hg(0) oxidation performances of RuO$_2$/rutile TiO$_2$ catalyst under simulated flue gas of sub-bituminous or lignite coal at the tail end of a SCR unit can be found in our previous paper.[34] The RuO$_2$/rutile TiO$_2$ catalyst showed better Hg(0) oxidation performances than the SCR catalyst under all HCl concentrations. With only 10 ppmv HCl, the oxidation was > 85%, and > 90% could be achieved at 25 ppmv HCl under a typical simulated flue gas condition of low rank coal. For the scenario of bromine addition, HBr is at least 10 times more effective than HCl and > 90% Hg(0) oxidation performance could be achieved with < 1 ppmv HBr. Again, the RuO$_2$/rutile TiO$_2$ catalyst performed better than the SCR catalyst under all HBr concentrations.

Bituminous coal usually has high sulfur and chlorine contents with typical concentrations of ~1,000-2,000 ppmv SO$_2$ and ~50-200 ppmv HCl. Such high SO$_2$ concentrations usually significantly decrease the Hg(0) oxidation performances of most metal oxide-based catalysts.[53, 55, 56] The performance of the RuO$_2$/rutile TiO$_2$ catalyst with a simulated flue gas containing 2,000 ppmv SO$_2$ is shown in Figure 3.11. Although the Hg(0) oxidation performance at low HCl concentrations (e.g. < 10 ppmv) decreased, > 90% Hg(0) oxidation performances were obtained at a typical HCl concentration range (e.g. > 50 ppmv) of bituminous coal. Overall, the RuO$_2$/rutile TiO$_2$ catalyst has excellent Hg(0) oxidation performance and superior resistance to high SO$_2$. One drawback of typical vanadium-based SCR catalysts is that V$_2$O$_5$ can also oxidize SO$_2$ to SO$_3$. The SO$_3$/H$_2$SO$_4$ emissions can cause
corrosion problems and plume opacity especially when high sulfur coals are used. Therefore, the vanadium loading on SCR catalysts is limited by SO$_3$ generation and typical commercial SCR catalysts try to keep the SO$_2$ conversion below 1%.[50] The conversion was measured for the RuO$_2$/rutile TiO$_2$ catalyst under the above simulated flue gas containing 2,000 ppmv SO$_2$. It was found that only 0.17% of the SO$_2$ was oxidized to SO$_3$, demonstrating another advantage of the RuO$_2$/rutile TiO$_2$ catalyst under high sulfur conditions.

![Figure 3.11 Hg(0) oxidation performances of 1 wt.% RuO$_2$/rutile TiO$_2$-WI catalyst with respect to different HCl concentration under a simulated flue gas condition of high sulfur bituminous coal. Conditions: 15 ppbv Hg(0), 5 ppmv NH$_3$, 5 ppmv NO, 2,000 ppmv SO$_2$, 3%(v) O$_2$, 10%(v) H$_2$O, 12%(v) CO$_2$ balanced with N$_2$ at 350 °C.](image)

In our previous study, oxidized mercury species obtained from the RuO$_2$/rutile TiO$_2$ catalyst were analyzed using XAFS.[34] In the presence of HCl or HBr gas, HgCl$_2$ or HgBr$_2$ was found to be the major oxidized mercury species. HgCl$_2$ and HgBr$_2$ have high solubility in water, and can be easily scrubbed by wet FGD scrubbers in coal-fired power plants.
3.4 Conclusions

In this study, the RuO$_2$/rutile TiO$_2$ catalyst for Hg(0) vapor oxidation was systematically studied in terms of different TiO$_2$ phases and synthesis methods for the first time. A combination of the two structurally similar components of RuO$_2$ as the active component and rutile TiO$_2$ as the support resulted in excellent RuO$_2$ dispersion over the rutile TiO$_2$ phase as opposed to anatase TiO$_2$ and thus high catalytic activity. The RuO$_2$ catalyst supported on rutile TiO$_2$ showed much higher Hg(0) oxidation activity than that on anatase TiO$_2$. Among 0.2, 0.5, and 1 wt.% Ru loadings, 0.5 wt.% Ru loading onto rutile TiO$_2$ gave the highest turnover frequency for Hg(0) oxidation. Different synthesis methods (WI, DP and SEA) did not show noticeable differences in the morphology or the activity of the RuO$_2$/rutile TiO$_2$ catalyst. The RuO$_2$/rutile TiO$_2$ catalyst performed well in a typical SCR temperature window of 350-400 °C and preferred higher temperature. NH$_3$ and SO$_2$ gases had negative effects on Hg(0) oxidation performances due to competitive adsorption with HCl. Between the two gases, the RuO$_2$/rutile TiO$_2$ catalyst was more prone to NH$_3$. However, the catalyst showed very good Hg(0) oxidation performances under typical simulated flue gas conditions of sub-bituminous and lignite coals with low concentrations of HCl or HBr. It also showed excellent resistance to SO$_2$ in comparison with a SCR catalyst under typical simulated flue gas conditions of high sulfur bituminous coal with up to 2,000 ppmv SO$_2$. It has potential for Hg(0) oxidation at the tail end section of the SCR unit in coal-fired power plants especially for high sulfur conditions where the catalytic activities of most metal oxide- or noble metal-based catalysts are significantly inhibited.
3.5 References


Chapter 4  XANES Study of Elemental Mercury Oxidation over 
RuO$_2$/TiO$_2$ and Selective Catalytic Reduction Catalysts for Mercury 
Emissions Control

4.1 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 SO$_2$ 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 (CaBr$_2$) 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 $70,000 per pound of mercury removed.[5] Due to the high cost of sorbent injection and increasing number of FGD units, oxidizing elemental mercury using SCR or other catalysts, followed by oxidized mercury capture in FGD is a viable option, and several papers review catalysts for the oxidation of mercury.[6-8] For bituminous coal with high chlorine (HCl in a range of 50 to 200 ppmv in flue gas), SCR catalyst can oxidize most elemental mercury. For low rank sub-bituminous and lignite coals with low chlorine (HCl <10 ppmv in flue gas), additional halogen is needed to achieve satisfactory mercury oxidation, and CaBr$_2$ injection to the boiler is one of the most widely accepted methods.[9, 10] Little has been reported about heterogeneous Hg(0) oxidation over RuO$_2$ 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 Fe$_2$O$_3$, CeO$_2$, and MoO$_3$.[15-17] Generally these SCR based catalysts do not work well enough under low halogen or high sulfur conditions. In our preliminary tests, RuO$_2$ catalyst showed superior Hg(0) oxidation performance 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\textsubscript{x}, SO\textsubscript{2}, NH\textsubscript{3}, 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\textsubscript{III} edge XANES was conducted to quantify oxidized mercury species over RuO\textsubscript{2}/TiO\textsubscript{2} and SCR catalysts under different simulated flue gas conditions.

4.2 Experimental

4.2.1 Catalyst preparation, treatment and characterization

RuO\textsubscript{2}/TiO\textsubscript{2} catalyst with 1% (wt) metal loading was synthesized by following the procedure below: 16 g of TiO\textsubscript{2} powder (STR-100W, Sakai Chemical), 0.4 g of methylcellulose (Sigma-Aldrich) and 0.32 g of glass fiber (Fibre Glast) were dry mixed for 10 minutes. 0.416 g of RuCl\textsubscript{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 × 5 mm (D × 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 (Fibre Glast) were dry mixed for 10 minutes. 0.138 g of NH$_4$VO$_3$ (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 4.1. Elemental mercury (Hg(0)) vapor was generated using a permeation oven (Dynacalibrator, VICI Metronics) held at 70 °C and using N$_2$ as a carrier gas. The catalysts (1.7 g of RuO$_2$/TiO$_2$ 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) KMnO$_4$/10%(v/v) H$_2$SO$_4$ 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:

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

Figure 4.1. Experimental set-up for catalytic reactor and subsequent oxidized mercury capture in activated carbon sorbent.

A total of 6 different gas conditions was used for both catalysts and the gas compositions are listed in Table 4.1. 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 RuO$_2$/TiO$_2$ catalyst and SCR catalyst were measured using a CHNS elemental analyzer (Vario MICRO cube, Elementar Americas, Inc.).

Table 4.1 Simulated flue gas conditions used for oxidized mercury speciation

<table>
<thead>
<tr>
<th></th>
<th>Gas Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N2 + 3%(v) O2</td>
</tr>
<tr>
<td>2</td>
<td>N2 + 3%(v) O2 + 1 ppmv HBr</td>
</tr>
<tr>
<td>3</td>
<td>N2 + 3%(v) O2 + 50 ppmv HCl</td>
</tr>
<tr>
<td>4</td>
<td>N2 + 3%(v) O2 + 1 ppmv HBr + 5 ppmv HCl</td>
</tr>
<tr>
<td>5</td>
<td>N2 + 3%(v) O2 + 50 ppmv HCl + 5 ppmv NO + 5 ppmv NH3 + 200 ppmv SO2 + 12%(v) CO$_2$</td>
</tr>
<tr>
<td>6</td>
<td>N2 + 3%(v) O2 + 1 ppmv HBr + 5 ppmv HCl + 5 ppmv NO + 5 ppmv NH3 + 200 ppmv SO2 + 12%(v) CO$_2$</td>
</tr>
</tbody>
</table>

4.2.2 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 $1.4 \times 10^{-4}$. Energy calibration was performed using Au metal foil (Au L$_{III}$ edge is 11,919 eV). A series of reference mercury compounds including HgO, HgSO$_4$, HgS, HgCl$_2$, and HgBr$_2$ (all obtained from Sigma-Aldrich except for HgBr$_2$, 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.

4.3 Results and Discussion

4.3.1 Hg(0) oxidation over RuO$_2$/TiO$_2$ and SCR catalysts

In our preliminary studies, RuO$_2$ supported on rutile TiO$_2$ 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 RuO$_2$/TiO$_2$ 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 NH$_3$ 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 4.2. The RuO$_2$/TiO$_2$ 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 RuO$_2$/TiO$_2$ 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, RuO$_2$/TiO$_2$ 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.

![Figure 4.2 Mercury oxidation over RuO$_2$/TiO$_2$ and SCR catalysts. Gas conditions: 15 ppbv Hg(0), 5 ppmv NH$_3$, 5 ppmv NO, 200 ppmv SO$_2$, 3%($v$) O$_2$, 12%($v$) CO$_2$ balanced in N$_2$.](chart)

**4.3.2 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 4.3. These spectra are similar to those reported in other studies.[21, 22]

Figure 4.3 The XANES spectra (left) and the first derivative of the spectra (right) for reference oxidized mercury compounds.

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 SO\textsubscript{2}, NH\textsubscript{3}, NO\textsubscript{x}, HCl and HBr (when bromine addition is used). The oxidized mercury species such as HgO, HgS, HgCl\textsubscript{2}, HgSO\textsubscript{4} and HgBr\textsubscript{2} 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, HgCl$_2$, HgSO$_4$ and HgBr$_2$ was used to quantify the oxidized mercury species generated from RuO$_2$/TiO$_2$ and SCR catalysts under different gas conditions.

### 3.3.3 Oxidized mercury speciation from RuO$_2$/TiO$_2$ catalyst

All commercial TiO$_2$ and SCR catalysts contain some amount of sulfur added from their manufacturing processes. The sulfur content of the RuO$_2$/TiO$_2$ 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 RuO$_2$/TiO$_2$ catalyst are shown in Figure 4.4, and the quantitative speciation results obtained are listed in Table 4.2. 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.
Figure 4.4 Linear combination fitting of oxidized mercury generated from RuO$_2$/TiO$_2$ catalyst.

Cases 1 to 6 are denoted by Ru_1 to Ru_6.
Table 4.2 Linear combination fitting results for oxidized mercury species generated from RuO$_2$/TiO$_2$ catalyst.

<table>
<thead>
<tr>
<th>Gas condition</th>
<th>HgO (%)</th>
<th>HgS (%)</th>
<th>HgSO$_4$ (%)</th>
<th>HgCl$_2$ (%)</th>
<th>HgBr$_2$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17±2</td>
<td>55±3</td>
<td>28±2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>14±1</td>
<td>20±7</td>
<td>1±3</td>
<td>65±5</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>17±4</td>
<td>31±2</td>
<td>0</td>
<td>51±1</td>
<td>64±4</td>
</tr>
<tr>
<td>4</td>
<td>16±2</td>
<td>20±6</td>
<td>0</td>
<td>0</td>
<td>58±6</td>
</tr>
<tr>
<td>5</td>
<td>17±2</td>
<td>25±4</td>
<td>0</td>
<td>0</td>
<td>60±10</td>
</tr>
<tr>
<td>6</td>
<td>14±3</td>
<td>26±4</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

For RuO$_2$/TiO$_2$ catalyst with only N$_2$ and O$_2$ gases (Case 1), the oxidized mercury species are mainly HgS and HgSO$_4$, with <20% HgO. Our result also indicated that the TiO$_2$ support itself has very little Hg(0) oxidation capability. The sulfur containing oxidized mercury should come from the sulfur on the TiO$_2$ surface and the catalytic effect of RuO$_2$. It is why both RuO$_2$/TiO$_2$ and SCR catalysts showed ~40 and ~30% Hg(0) oxidation performance, respectively, in Figure 4.2 even when HCl or HBr is not introduced to the fixed-bed reactor. When 1 ppmv HBr gas is added (Case 2), HgBr$_2$ becomes the major species, accounting for ~65% of all oxidized mercury. While the percentage of HgO slightly decreased, HgS and HgSO$_4$ both significantly decreased. For the case with 50 ppmv HCl gas (Case 3), the trend is similar to that of HBr. HgCl$_2$ 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.

### 4.3.4 Oxidized mercury speciation from SCR Catalyst

The XANES spectra and linear combination fittings of mercury oxidation products from SCR catalyst are shown in Figure 4.5, and the quantitative speciation analysis results obtained are listed in Table 4.3. 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 RuO$_2$/TiO$_2$ catalyst, more HgS formation should be expected.
Figure 4.5 Linear combination fitting of oxidized mercury generated from SCR catalyst.

Cases 1 to 6 are denoted by SCR_1 to SCR_6.
Table 4.3 Linear combination fitting results for oxidized mercury species generated from SCR catalyst.

<table>
<thead>
<tr>
<th>Gas condition</th>
<th>HgO (%)</th>
<th>HgS (%)</th>
<th>HgSO4 (%)</th>
<th>HgCl2 (%)</th>
<th>HgBr2 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6±2</td>
<td>79±4</td>
<td>15±5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>14±1</td>
<td>25±4</td>
<td>0</td>
<td>61±7</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>19±3</td>
<td>34±5</td>
<td>0</td>
<td>47±2</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>19±1</td>
<td>15±5</td>
<td>1±2</td>
<td>0</td>
<td>65±6</td>
</tr>
<tr>
<td>5</td>
<td>21±2</td>
<td>24±5</td>
<td>0</td>
<td>55±2</td>
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</tr>
<tr>
<td>6</td>
<td>11±2</td>
<td>36±8</td>
<td>0</td>
<td>0</td>
<td>53±14</td>
</tr>
</tbody>
</table>

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 RuO2/TiO2 catalyst. HgCl2 is a main oxidized mercury species when HCl is the only halogen gas, and HgBr2 is a preferred mercury oxidation product when bromine injection is used. NH3 (up to 5 ppmv), NO (up to 5 ppmv), and SO2 (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 SO3 on the catalysts can be an area of future research.[32, 33] For both RuO2/TiO2 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 HgCl2 and HgBr2 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. 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.

4.5 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). 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 HgX\(_2\)(ad) and be desorbed to the gas phase. This proposed Hg(0) oxidation mechanism following the Deacon reaction is summarized in Figure 4.6.

![Figure 4.6 Proposed Hg(0) oxidation mechanism over RuO\(_2\) catalyst with the presence of HCl or HBr.](image)

Figure 4.6 Proposed Hg(0) oxidation mechanism over RuO\(_2\) catalyst with the presence of HCl or HBr.
4.4 Conclusion

In this study, the speciation of oxidized mercury from RuO$_2$ 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 TiO$_2$ support to form HgS and HgSO$_4$. When HCl and/or HBr are/is present, HgCl$_2$ and/or HgBr$_2$ are/is the main oxidized mercury species. HBr is much more active for Hg(0) oxidation. When both HCl and HBr gases are present, HgBr$_2$ 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.

4.5 References


5.1 Introduction

Mercury has long been recognized as a toxic and persistent pollutant and the 1990 Amendments to the Clean Air Act listed mercury as one of the most toxic pollutants among 188 hazardous air pollutants. Mercury that naturally exists in coal will be released into the flue gas after combustion, and it is estimated that mercury emitted from coal-fired power plants accounts for > 30% of emissions from all anthropogenic sources in the United States (U.S.).[1] The growing public concern over the long-term environmental impacts and health effects of mercury has led to more stringent regulations of mercury emissions. In 2011, the U.S. Environmental Protection Agency (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 rule, U.S. EPA finalized the Cross-State Air Pollution Rule (CSAPR), replacing the U.S. EPA's earlier Clean Air Interstate Rule (CAIR) from 2005. The CSAPR further reduces NO\textsubscript{x} and SO\textsubscript{2} emissions from coal-fired power plants. It is expected that the installations of flue gas desulfurization (FGD) and NO\textsubscript{x} control systems (such as selective catalytic reduction (SCR) unit) will continue to increase in the coming years. In this context, the oxidation of elemental mercury (Hg(0)) using catalysts or oxidants followed by the separation of oxidized mercury in FGD system is a viable option for mercury removal.

* Part of the content in this chapter has been published in Liu, Z., Sriram, V., & Lee, J. Y. (2017). Mechanistic and Kinetic Studies of Elemental Mercury Oxidation over RuO\textsubscript{2}/rutile TiO\textsubscript{2} Catalyst. Catalysis Science and Technology.
Under typical coal combustion conditions, the homogeneous mercury oxidation is kinetically limited.[2] At temperature < 400 °C, oxidized mercury should be a dominant species at equilibrium.[2] However, full-scale field measurements report that oxidized mercury fractions can greatly vary from 30% to 90%, indicating that the heterogeneous oxidation of Hg(0) plays a critical role in meeting mercury emissions in coal combustion flue gases for the MATS rule.[3] It is generally accepted that HCl content in the flue gas plays the most important role in Hg(0) oxidation. A correlation between the amount of halogen in the flue gas and the extent of Hg(0) oxidation was observed in most studies.[4-6] However, the homogeneous reaction between Hg(0) and HCl cannot be considered a major pathway due to very high energy barrier.[7] It was found that Cl\textsubscript{2} is more active for Hg(0) oxidation than HCl and thus promotes Hg(0) oxidation, but the homogeneous reaction between Hg(0) and Cl\textsubscript{2} is still too slow to account for the Hg(0) conversion observed in the field.[8-11] Homogeneous mercury oxidation kinetics for the reactions involving mercury and chlorine species was also studied using quantum chemical methods.[12, 13]

Therefore, heterogeneous Hg(0) oxidation plays a more important role in controlling mercury emissions. Although the heterogeneous oxidation of Hg(0) over noble metals, metal oxides, and SCR catalysts has been previously reported, most of these studies have focused on synthesis, characterization and performance evaluations under different conditions.[14-20] On the other hand, studies on heterogeneous Hg(0) oxidation mechanisms and kinetics have been far less conducted. Although different mechanisms including Mars-Maessen, Langmuir-Hinshelwood and Eley-Rideal have been proposed for various catalysts, in general, there is a lack of experimental evidence to support these proposed mechanisms.[16, 19, 21-25] In addition, most heterogeneous Hg(0) oxidation kinetic studies have been limited to
global observed kinetic expressions without taking into account the effects of flue gas constituents, and determined the reaction rate constant and order using finite approximation.[26-29]

In this context, Deacon catalysts used for HCl oxidation to Cl\(_2\) can be good candidates for heterogeneous Hg(0) oxidation, and RuO\(_2\) is currently the most active Deacon catalyst.[30-32] In our previous studies, RuO\(_2\) supported on rutile TiO\(_2\) showed excellent Hg(0) oxidation performances and resistance to SO\(_2\). The Hg(0) oxidation performances of RuO\(_2\) were higher than other metal oxide catalysts including the SCR catalyst especially under high SO\(_2\) conditions.[33] Therefore, the RuO\(_2\)/rutile TiO\(_2\) catalyst was selected in this study. The primary objective of this study is to investigate the reaction mechanisms and kinetics for the heterogeneous Hg(0) oxidation over RuO\(_2\)/rutile TiO\(_2\) catalyst. In-situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) can provide useful information on a change of surface-adsorbed species during the catalytic reactions. It has been used to investigate various heterogeneous catalytic reaction mechanisms such as SCR of nitrogen oxides by ammonia.[34, 35] In this study, in-situ DRIFTS was used to probe the Hg(0) oxidation mechanism over RuO\(_2\)/rutile TiO\(_2\) catalyst under different simulated gas conditions. Then the information obtained from the mechanistic study was used to develop an intrinsic kinetic expression for the heterogeneous Hg(0) oxidation under O\(_2\), HCl, SO\(_2\) and NH\(_3\) gases. To the best of our knowledge, these approaches have not been used for heterogeneous Hg(0) oxidation, and a kinetic expression for Hg(0) oxidation containing the competitive adsorption of HCl, NH\(_3\) and SO\(_2\) was reported for the first time.
5.2 Experimental Section

5.2.1 Catalyst preparation

A RuO$_2$/rutile TiO$_2$ catalyst with 0.2 wt.% and 1 wt.% Ru metal loadings was synthesized using RuCl$_3$ (Sigma-Aldrich) as a precursor. The 1 wt.% loading catalyst was used for DRIFTS study, and the 0.2 wt.% catalyst was used for the kinetic study. The high activity of RuO$_2$ resulted in high Hg(0) oxidation conversion with 1% RuO$_2$ loading even under different experimental conditions of gas conditions and temperatures. Therefore, low 0.2% RuO$_2$ loading was used for this kinetic study. Commercial rutile TiO$_2$ (STR-100w) was purchased from Sakai Chemical. In our previous study, wetness incipient method showed excellent RuO$_2$ dispersion on rutile TiO$_2$.[33] Therefore, it was used for the catalyst synthesis: RuCl$_3$ was dissolved in a small amount of water (0.9 mL per gram of TiO$_2$) and the solution was added to the dry rutile TiO$_2$ powders. After thorough mixing, the catalyst was dried at room temperature for 12 hours and calcined at 400 °C in air for 3 hours.

5.2.2 In-situ DRIFTS

FTIR (Shimadzu IR Prestige21) equipped with a DRIFTS environment chamber (DiffusIR, Pike Technologies) was used for this study. A powdered RuO$_2$/TiO$_2$ catalyst was loaded into a porous ceramic cup sample holder and placed inside the environment chamber with a KBr window that allowed the infrared light to reach the sample surface. Gas flowed downwards through the catalyst. A schematic for the DRIFT system is shown in Figure 5.1. Nitrogen gas at a flow rate of 100 mL/min was used as a carrier gas. The temperature was electronically controlled by a computer. The catalyst was first heated to 350 °C under N$_2$ gas (ultra-high purity, 99.999%) for 2 hours to remove all moisture and a background spectrum was collected. Then HCl gas was added to the N$_2$ gas stream and the spectra were collected.
The infrared features originating from the structural vibrations of the catalyst itself were eliminated from the sample spectra. For each sample, at least 100 scans at a spectral resolution of 4 cm\(^{-1}\) were collected to achieve a better signal-to-noise ratio. Diffuse reflectance spectra were collected in transmission mode and a Kubelka-Munk conversion was applied. \(\text{N}_2\) (ultra-high purity, 99.999\%), \(\text{O}_2\) (99.99% purity), HCl (certified standard), \(\text{CO}_2\) (technical grade), \(\text{NH}_3\) (certified standard), NO (certified standard), and \(\text{SO}_2\) (certified standard) gases were supplied from compressed gas cylinders (Wright Brothers, Inc.), and the individual gas flows were controlled using mass flow controllers.

Figure 5.1 Schematic of in-situ DRIFTS system.

### 5.2.3 Fixed-bed system

For the kinetic study of Hg(0) oxidation, 5 mg of the RuO\(_2\)/TiO\(_2\) catalyst with 0.2 wt.% Ru loading mixed with 4 g of silica sand was placed inside a quartz reactor and the temperature was controlled in a tube furnace between 300 and 400 °C. The silica sand was found to be inert toward the oxidation or adsorption of Hg(0). The powdered catalyst was used to minimize the pore diffusional mass-transfer resistance in the interparticle phase. The
dimensions of the catalyst bed were approximately 15 mm × 16 mm (height × diameter). The information on the fixed-bed system can be found in our previous paper.[33] Hg(0) vapor was generated from a permeation oven (Dynacalibrator, VICI Metronics) using N₂ as a carrier gas and the inlet Hg(0) vapor concentration was in a range of 5 to 20 ppbv. 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 total flow of the simulated flue gas was 1 L/min with a gas hourly space velocity of 40,000 h⁻¹. The Hg(0) vapor concentrations at the inlet and outlet of the reactor were measured by following the Ontario Hydro method in a wet impinger system and/or an online mercury analyser (VM 3000, Mercury Instruments).[36] 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 (CVAAS, Model 400A, Buck Scientific Inc.). The detailed description is given in our previous study.[37, 38]

5.3 Results and Discussion

5.3.1 Hg(0) oxidation over RuO₂ under different gas conditions

In our previous X-ray Adsorption Near Edge Spectroscopy (XANES) study, HgCl₂ was identified as a major oxidized mercury species generated over the RuO₂/rutile TiO₂ catalyst in the presence of HCl.[39] The heterogeneous oxidation of Hg(0) over metal oxide catalysts with HCl and O₂ has been reported to follow the reaction below.[16, 40]

\[ Hg(0) + 2HCl + 1/2O₂ → HgCl₂ + H₂O \]  \hspace{1cm} (5-1)

To acquire a better mechanistic understanding of the heterogeneous Hg(0) oxidation over the RuO₂ catalyst, the roles of HCl and O₂ gases were examined. Before conducting catalytic Hg(0) oxidation, homogeneous Hg(0) oxidation inside the quartz reactor in the
absence of the catalyst was found to be negligible as shown in Fig. 5.2(a). The RuO$_2$ catalyst prepared by following the procedure in the previous section was used in the fixed-bed reactor system and the results are shown in Figure 5.2(b & c). When 3%(v) O$_2$ gas was added to Ultra High Purity (UHP, purity >99.999%) N$_2$, only less than 10% of the Hg(0) was oxidized. When additional 10 ppmv HCl was added, outlet Hg(0) concentration started to decrease and >95% Hg(0) oxidation conversion was achieved (Fig. 5.2(b)). Then the order of an addition of O$_2$ and HCl gases was reversed (Fig. 5.2(c)). In the absence of O$_2$, Hg(0) oxidation was insignificant with 10 ppmv HCl only. After adding 3%(v) O$_2$ again, significant Hg(0) oxidation started to re-occur. These results indicate that both O$_2$ and HCl gases are required for Hg(0) oxidation over RuO$_2$. This also suggests that the lattice oxygen of RuO$_2$ cannot be used to oxidize Hg(0), and thus excludes the possibility of a Mars-Maessen mechanism, which involves the re-oxidation of catalytic metal oxide by gaseous oxygen.

A gas detector tube (Gastec Corp., detection limit: 0.05 ppm) was also used at the outlet of the reactor to detect possible Cl$_2$ formation. Under the experimental conditions used in this study (i.e. low 0.2% RuO$_2$ loading, high 40,000 hr$^{-1}$ space velocity, < 100 ppmv HCl, and at 300-400 °C), Cl$_2$ was never detected. Typical operating conditions for the Deacon process using RuO$_2$/TiO$_2$ catalyst comprise <3,000 h$^{-1}$ space velocity, 10-20%(v) HCl, 20-80%(v) O$_2$, and 300 °C. This indicates that the conditions used in this study warranted good Hg(0) oxidation performance, but did not merit HCl oxidation to Cl$_2$.[41]
Figure 5.2 (a) homogeneous Hg(0) oxidation inside the quartz reactor in the absence of the catalyst; Hg(0) oxidation over RuO$_2$ under different gas conditions: (b) addition of O$_2$
followed by HCl; and (c) addition of HCl followed by O₂ and cut-off O₂. Inlet Hg(0)=15 ppbv, T= 350 °C, catalyst: RuO₂/TiO₂ with 1 wt.% Ru loading.

5.3.2 In-situ DRIFTS study

5.3.2.1 HCl adsorption on RuO₂ surface

Currently there is a limited understanding of heterogeneous Hg(0) oxidation mechanism in the presence of HCl, and there is no consensus on the reaction mechanism. Although the Langmuir-Hinshelwood mechanism, which treats both Hg(0) and HCl as adsorbed species that react on the catalyst surface, was proposed by a few researchers, most studies found that the adsorption of Hg(0) on metal oxide catalysts was insignificant particularly in the presence of HCl.[19, 42-44] Therefore, the Eley-Rideal mechanism may provide more reasonable description for the heterogeneous Hg(0) oxidation over metal oxide-based catalyst surfaces, where HCl is adsorbed on the surface and Hg(0) in the gas phase directly reacts with the adsorbed surface chlorine species. Many metal oxides including V₂O₅ and RuO₂ can also catalyze the Deacon reaction[30, 45], which is the oxidation of HCl by O₂ to produce Cl₂:

\[
2HCl + \frac{1}{2}O₂ → H₂O + Cl₂ \quad (5-2)
\]

The active chlorine species formed on the catalyst surfaces during the Deacon reaction could be responsible for Hg(0) oxidation. The mechanisms of the Deacon reaction over metal oxide catalysts including RuO₂ have not been well studied so far. The limited mechanistic studies are available based on density function theory calculations, and the experimental evidence of the active intermediate species is very limited.[30, 46]
The vibrational frequencies of most metal-halide bonds are in a range of far infrared region. For ruthenium, the Ru-Cl vibration is in a range of 300 to 400 cm\(^{-1}\), which is well within the far infrared range.\[^{[47]}\] However, far infrared is in an energy-starved region, and the weak signal strength limits its use in catalysis studies. In particular, it is difficult to apply the far infrared technique to in-situ experiments to detect active intermediate species required for this study. In our preliminary tests, the detection of the Ru-Cl vibration on our RuO\(_2\) catalyst surface under in-situ and ex-situ conditions using FTIR was not successful due to the aforementioned limitations of far infrared. However, HCl should dissociate on the catalyst surface. After the dissociation of adsorbed HCl, the formation of Ru-Cl bond should be accompanied by the formation of Ru-H bond. Due to a 1:1 atomic ratio of H to Cl in HCl, the Ru-H bond detectable in the mid infrared region can be used as an indirect indicator of the surface Ru-Cl bond.

After exposing the RuO\(_2\)/TiO\(_2\) catalyst to 200 ppmv HCl in nitrogen at different temperatures, the infrared spectra were collected. O\(_2\) was not introduced so that the Ru-H bond can remain on the surface. As shown in Figure 5.3, when temperature was higher than 300 °C, a distinct sharp peak at around 1,898 cm\(^{-1}\) was observed. It should also be noted that when only TiO\(_2\) sample was measured under the same conditions, this peak was not detectable, indicating that it was associated with RuO\(_2\) only. According to the previous FTIR studies of H\(_2\) adsorption on RuO\(_2\) and the characterizations of hydrogen-containing ruthenium complexes, this peak was identified as the Ru-H asymmetric vibration.\[^{[48-51]}\] Undissociated free HCl (2,886 cm\(^{-1}\)) or undissociated HCl attached to metal atoms (typically shown at a few hundred wavenumbers lower than free HCl in a range of 2,160–2,755 cm\(^{-1}\)) were not observed.\[^{[52-54]}\] The formation of OH groups (3,200–3,640 cm\(^{-1}\)) was not observed,
either.[55] This indicates that the dissociation reaction of HCl on the RuO$_2$ surface is fast. It should be noted that the hydrogen in the Ru-H bond can result from HCl only. When a NaOH dry scrubber was placed before the DRIFTS chamber to remove HCl in the gas stream, the Ru-H peak was not detectable. This ruled out a possibility of other hydrogen sources such as water vapor that may exist in the gas cylinders, and confirmed that the only source of hydrogen for the Ru-H bond is HCl.

Figure 5.3 In-situ DRIFTS spectra of the RuO$_2$/TiO$_2$ catalyst after HCl adsorption: effects of temperature on Ru-H stretching.

Based on the above Hg(0) oxidation results from a fixed-bed reactor, DRIFTS observations and the findings reported in the literature, it is hypothesized that HCl gas molecules adsorb onto RuO$_2$ and dissociate.[31, 46] Hg(0) in the gas phase will react with adsorbed Cl to form HgCl$_2$(ad), and the dissociated H from HCl will combine the adsorbed O from O$_2$ to form H$_2$O(ad). Then HgCl$_2$ and H$_2$O will be released to the gas phase to complete
the catalytic reaction cycle as previously reported.[39] A schematic of the proposed mechanism of Hg(0) oxidation over RuO₂ catalyst is shown in Figure 5.4.

Figure 5.4 Proposed mechanism of Hg(0) oxidation over RuO₂ catalyst.

5.3.2.2 Effects of other flue gas components

Other gases in the flue gas such as CO₂, NO, NH₃ and SO₂ may have impacts on HCl adsorption and influence Hg(0) oxidation. The effects of these flue gas components on HCl adsorption were studied by a change in the intensity of the Ru-H vibration. As presented in our previous study, other flue gas components such as NO, CO₂ and H₂O vapor do not have noticeable promotional or adverse effect on the Hg(0) oxidation performance of the RuO₂/TiO₂ catalyst.[33] After exposing the RuO₂/TiO₂ catalyst to 200 ppmv HCl at 350 °C, 12%(v) CO₂ or 200 ppmv NO was added to the flow. The resultant DRIFTS spectra are shown in Figure 5.5. Both CO₂ and NO gases did not give any noticeable effect on the intensity of the Ru-H peak. This is consistent with the observation in our previous study that CO₂ and NO had no effect on Hg(0) oxidation performance.[33] Unlike the V₂O₅-based SCR catalyst which can preferentially adsorb NO, noticeable NO adsorption was not observed on the RuO₂ surface.[35] It was not possible to keep the entire the DRIFTS chamber at high
temperature to prevent potential flooding. Thus water vapor was not introduced to the chamber to examine the effect.

Figure 5.5 In-situ DRIFTS spectra of the RuO$_2$/TiO$_2$ catalyst after HCl adsorption: effects of (a) CO$_2$ and (b) NO on Ru-H stretching.

NH$_3$ had an inhibition effect on Hg(0) oxidation due to its competitive adsorption as identified in our previous study.[33] After exposing the RuO$_2$/TiO$_2$ catalyst to 200 ppmv HCl
at 350 °C, 200 ppmv NH$_3$ was added to the flow, and the DRIFTS spectra results are shown in Figure 5.6. After an addition of NH$_3$, two IR peaks appeared at 3,047 cm$^{-1}$ and 3,141 cm$^{-1}$ corresponding to N-H stretching, indicating the adsorption of NH$_3$ on the catalyst surface.[55] At the same time, the intensity of Ru-H peak corresponding to HCl adsorption significantly decreased. This is consistent with the degraded Hg(0) oxidation performance of RuO$_2$/TiO$_2$ catalyst in the presence of NH$_3$ in the fixed-bed reactor.[33]
Figure 5.6 In-situ DRIFTS spectra of the RuO$_2$/TiO$_2$ catalyst after HCl adsorption: the effects of NH$_3$ on (a) N-H stretching and (b) Ru-H stretching.

SO$_2$ also showed a negative impact on the Hg(0) oxidation performance of RuO$_2$/TiO$_2$ catalyst by competitive adsorption with HCl in our previous study.[33] The effect of SO$_2$ gas was also examined using in-situ DRIFTS. However, when 200 ppmv SO$_2$ alone was present in the gas stream without HCl, the Ru-H peak (1,898 cm$^{-1}$) as well as the strong asymmetric stretching IR peak for adsorbed SO$_2$ (~1,380 cm$^{-1}$) appeared (Figure 5.7).[55] This may be attributed to sulfuric acid impurities in the SO$_2$ gas cylinder or sulfuric acid generated from SO$_2$ and hydroxyls on the catalyst surface. Nafion tubing and desiccant scrubbers were added to remove any potential water vapor in the gas cylinders, but no noticeable effect was observed. Due to this interference, DRIFTS is not suitable for studying the competitive adsorption of SO$_2$ and HCl on the RuO$_2$/TiO$_2$ catalyst.

Figure 5.7 In-situ DRIFTS spectra of the RuO$_2$/TiO$_2$ catalyst after SO$_2$ adsorption.
5.3.3 Steady-state kinetic study

Kinetic studies on heterogeneous Hg(0) oxidation reactions are very limited in the literature. Gao et al. reported that an Hg(0) oxidation reaction order with respect to Hg(0) concentration is close to 1 over a commercial SCR catalyst.[56] Li et al. also found that Hg(0) oxidation reaction kinetics with HCl gas over their Mn/α-Al2O3 catalyst is first order in terms of Hg(0) concentration.[26] These kinetic studies used a finite approximation approach without considering a change in Hg(0) concentrations along the reactor length. However, as the reaction proceeds along the reactor length, Hg(0) concentration gradually decreases and thus the reaction rate also decreases.

5.3.3.1 Hg(0) reaction kinetic model

A spent RuO2/TiO2 catalyst was treated under a simulated flue gas containing 15 ppbv Hg(0), 5 ppmv NH3, 5 ppmv NO, 200 ppmv SO2, 3%(v) O2, 10%(v) H2O, and 12%(v) CO2 at 350 °C for 12 hours. After digesting the spent catalyst by following the procedure in the Ontario Hydro method, it was found that of all the Hg(0) introduced, only 1.05% was adsorbed on the catalyst. It is also equivalent to 0.6 µg Hg/g catalyst (=0.6 ppmw), which is much lower than Hg determined from a spent SCR catalyst reported in the literature.[42] This result indicates that different catalyst surfaces follow different Hg(0) oxidation mechanisms. Therefore, Hg(0) adsorption onto the RuO2/TiO2 catalyst was assumed to be negligible and Hg(0) vapor is most likely to react with surface chlorine formed as a result of dissociative HCl adsorption, supporting an Eley-Rideal mechanism.

A steady-state kinetic study was conducted using the fixed-bed system described above at different temperatures, Hg(0), and HCl concentrations. The effects of the
competitive adsorption of NH\textsubscript{3} and SO\textsubscript{2} on Hg(0) oxidation kinetics was also studied. Assumptions made in the kinetic model include:

1) The gas travels in plug flow in the fixed-bed system;
2) RuO\textsubscript{2}/rutile TiO\textsubscript{2} catalyst particles are spherical, and all the particles have the same size and are uniformly dispersed in the fixed bed;
3) RuO\textsubscript{2} is uniformly dispersed over the rutile TiO\textsubscript{2} phase as shown in our previous study;[27]
4) The heat effect associated with the oxidation of Hg(0) is negligible due to its low concentration. The temperature of the fixed bed is constant and uniform;
5) A combined Eley-Rideal followed by Langmuir–Hinshelwood mechanism is assumed, where HCl is strongly adsorbed onto the catalyst surface to form Cl(ad) through dissociation and Hg(0) in the gas phase reacts with Cl(ad) to form HgCl(ad), and HgCl(ad) reacts with another Cl(ad) to form HgCl\textsubscript{2}(ad). In this case, the reaction is first order with respect to Hg(0).

Our in-situ FTIR experimental results provide the evidence of HCl adsorption and dissociation on the RuO\textsubscript{2}/TiO\textsubscript{2} catalyst surface. From the Langmuir adsorption theory with dissociative diatomic molecular species, the adsorption of HCl on the catalyst surface can be represented as follows:

\[ HCl + 2S \leftrightarrow Cl \cdot S + H \cdot S \]  \hspace{1cm} (5-3)

where HCl, S, Cl·S, and H·S are gas-phase HCl, surface site, adsorbed Cl, and adsorbed H, respectively. The equilibrium constant $K_{HCl}$ (m\textsuperscript{3}/gmol) is given by:

\[ K_{HCl} = \frac{\theta_H \theta_{Cl}}{c_{HCl} \theta_Y^2} \]  \hspace{1cm} (5-4)
where the surface coverages of H ($\theta_H$) and Cl ($\theta_{Cl}$) are defined as the fractions of the adsorption site occupied by H and Cl after the dissociation of HCl, respectively; $\theta_V$ is the surface coverage of vacant sites; and $C_{HCl}$ is the gas-phase HCl concentration (gmol/m$^3$).

These surface coverage terms have the following relations:

$$\theta_H + \theta_{Cl} + \theta_V = 1 \quad (5-5)$$

$$\theta_H = \theta_{Cl} \quad (5-6)$$

By combining equation (5-4), (5-5) and (5-6), the fractional surface coverage of Cl can be expressed as

$$\theta_{Cl} = \frac{\sqrt{K_{HCl}C_{HCl}}}{1 + 2\sqrt{K_{HCl}C_{HCl}}} \quad (5-7)$$

The above in-situ DRIFTS results support an Eley-Rideal followed by Langmuir–Hinshelwood mechanism where Hg(0) in the gas phase reacts with surface Cl from dissociated HCl. The intrinsic Hg(0) reaction rate is

$$-r'_{Hg,\text{int}} = -\frac{1}{W} \frac{dN_{Hg}}{dt} = k' C_{Hg,S} \theta_{Cl}^2 \quad (5-8)$$

where $-r'_{Hg,\text{int}}$ is the intrinsic reaction rate in gmol Hg(0)/(g catalyst·s); W is the mass of the catalyst in g; $k'$ is the reaction rate constant in m$^3$/ (g catalyst·s); and $C_{Hg,S}$ is Hg(0) concentration at the catalyst surface (gmol Hg(0)/m$^3$). Our previous mercury speciation study indicates that HgCl$_2$ is the main oxidation product, which will require two surface Cl atoms for Hg(0) atom.[39] Therefore, the fractional surface coverage for Cl ($\theta_{Cl}$) should be squared. Both HCl and O$_2$ were found to be required for Hg(0) oxidation, and 100 ppmv HCl could fully cover the catalyst surface (discussed in the next section).

A shell mole balance for Hg(0) vapor in the fixed bed was taken to describe a change in Hg(0) concentrations along the reactor ($C_{Hg,R}$).
\[ 0 = u_z \frac{dC_{Hg,B}}{dz} + (1 - \varepsilon_b) \rho_c (-r'_{Hg,obs} = k'_{obs} C_{Hg,B}) \]  

(5-9)

where \( z \) is the axial distance from the fixed-bed inlet in m; \( C_{Hg,B} \) is Hg(0) concentration in the bulk gas phase in gmol Hg(0)/m\(^3\); \( \varepsilon_b \) is the bed porosity; \( \rho_c \) is the density of the catalyst in g catalyst/m\(^3\) catalyst; \( u_z \) is the superficial gas velocity in m/s; \((-r'_{Hg,obs})\) is the observed reaction rate using the bulk Hg(0) concentration \( (C_{Hg,B}) \) in gmol Hg(0)/(g catalyst\cdot s). Since the external mass transfer of Hg(0) from the bulk gas phase to the catalyst surface and the surface reaction take place in series, these two reaction and mass-transfer rates are equal as shown in eq. (5-10).

\[ (-r'_{Hg,int}) W = k' C_{Hg,S} \theta_{Cl}^2 W = k_g S \left( = 4\pi R_p^2 N_p \right) (C_{Hg,B} - C_{Hg,S}) \]  

(5-10)

where \( S \) is the external surface area of the catalyst in m\(^2\); \( R_p \) is the radius of the catalyst in m; and \( N_p \) is the number of the catalyst particles. Then the surface concentration \( (C_{Hg,S}) \) can be expressed as a function of the bulk phase concentration \( (C_{Hg,B}) \).

\[ C_{Hg,S} = \frac{4\pi R_p^2 N_p k_g}{4\pi R_p^2 N_p k_g + k' \theta_{Cl}^2 W} C_{Hg,B} \]  

(5-11)

Since the observed and intrinsic rates are the same, the observed rate constant is a function of both the intrinsic rate constant \( (k') \) and the mass-transfer coefficient \( (k_g) \) shown in eq. (5-12).

\[ -r_{Hg,obs} = k'_{obs} C_{Hg,B} = -r_{Hg,int} = k' C_{Hg,S} \theta_{Cl}^2 = \frac{4\pi R_p^2 N_p k_g k'}{4\pi R_p^2 N_p k_g + k' \theta_{Cl}^2 W} C_{Hg,B} \theta_{Cl}^2 = \]

\[ \frac{1}{k' + \frac{4\pi R_p^2 N_p k_g}{\theta_{Cl}^2 W}} C_{Hg,B} \theta_{Cl}^2 \]

\[ k'_{obs} = \frac{1}{k' + \frac{4\pi R_p^2 N_p k_g}{\theta_{Cl}^2 W}} \theta_{Cl}^2 \]  

(5-12)

Here the mass-transfer coefficient \( (k_g, \text{ m/s}) \) was calculated by using the Ranz-Marshall correlation given in eq. (5-13):
\[ S h = \frac{2 R_p k_g}{D_m} = 2 + 0.6 Re_p^{1/2} Sc^{1/3} \] (5-13)

where \( Re_p \) and \( Sc \) are Reynolds and Schmidt numbers, respectively. The governing equation in eq. (5-9) requires the following boundary condition:

\[ C_{Hg,B}(z = 0) = C_{Hg,B0} \] (5-14)

Then the coupled eqs. (5-9) and (5-12) were solved for the intrinsic rate constant \( (k') \) that minimizes the difference between the experimental Hg(0) concentration and the model prediction at the outlet of the reactor as defined in eq. (5-15). When the intrinsic rate constant \( (k') \) was determined, 100 ppmv HCl was used to warrant the full surface coverage with HCl (i.e. \( \theta_{Cl} = 0.5 \)). This parameter estimation was performed using COMSOL Multiphysics software.

\[ \text{Min} \underbrace{\sum_{z=0}^{L} (C_{Hg,B}^{cal}(z = L) - C_{Hg,B}^{exp}(z = L))^2}_{(5-15)} \]

The parameters used in the model are listed in Table 5.1. In this study, 5 mg of the catalyst was mixed with 4 g of silica sand. The bed porosity \( (\varepsilon_b) \) filled with 4 g of quartz sand was determined to be 0.38. However, since the quartz sand is inert, the bed porosity should include both the sand volume and the void volume between the sand particles. Then the modified bed porosity excluding 5 mg of the catalyst in the fixed bed was found to be 0.998.

<table>
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<th>Parameter</th>
<th>Value</th>
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<td>Catalyst density, ( \rho_c ) (g/cm(^3))</td>
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</tr>
<tr>
<td>Catalyst diameter, ( R_p ) (nm)</td>
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</tr>
<tr>
<td>Superficial velocity, ( u_z ) (m/s)</td>
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</tr>
<tr>
<td>Mass-transfer coefficient, ( k_g ) (m/s)</td>
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</tr>
<tr>
<td>Bed porosity, ( \varepsilon_b^* )</td>
<td>0.998</td>
</tr>
</tbody>
</table>

(Note) \( \varepsilon_b^* \): This is a bed porosity determined by taking into account the volume of inert sand toward Hg(0) adsorption in the fixed bed.
5.3.3.2 Effects of O\textsubscript{2} on Hg(0) oxidation

Coal-fired power plants always use excess air to ensure the complete combustion of coal, and as a result, the flue gas usually contains 2-6\%(v) O\textsubscript{2}.[57] The Hg(0) and HCl concentrations in coal combustion flue gas are on the orders of ppbv and ppmv levels, respectively. O\textsubscript{2} is always several orders in excess for Hg(0) oxidation. The effects of O\textsubscript{2} concentrations in the range of 2-6\%(v) on Hg(0) oxidation over the RuO\textsubscript{2}/TiO\textsubscript{2} catalyst are shown in Figure 5.8. In a temperature range of 300-400 °C, the Hg(0) oxidation rate is close to zeroth order with respect to O\textsubscript{2} concentration. Therefore, the effects of O\textsubscript{2} were neglected, and O\textsubscript{2} concentration was kept constant at 3\%(v) in the following kinetic study.

Figure 5.8 Effects of temperature and O\textsubscript{2} concentration on observed Hg(0) oxidation rate. Conditions: 10 ppbv Hg(0) and 10 ppmv HCl.
5.3.3.3 Reaction kinetics for Hg(0) oxidation

For the determination of the intrinsic rate constant ($k'$), the Hg(0) oxidation rates at 5, 10, and 20 ppbv Hg(0) concentrations with 100 ppmv HCl and 3%(v) O$_2$ were measured between 300 and 400 °C (Figure 5.9). The high dust configuration in which the SCR unit is located before fly ash removal and between the economizer and the air pre-heater is the most common one in coal-fired power plants in the U.S. because the flue gas temperature (300–400 °C) is optimal for the catalyst activity. The RuO$_2$/TiO$_2$ catalyst was found to be suitable for Hg(0) oxidation in this same temperature window in our previous study.[33] Therefore, the kinetic experiments were conducted at 300, 350 and 400 °C.
As a result of the parameter estimation, the intrinsic rate constant \( (k') \) with respect to temperature are summarized in Table 5.2. With a high HCl concentration of 100 ppmv, the catalyst surface is to be fully covered with adsorbed HCl as shown in Figure 5.10, and the value of \( \theta_{Cl} \) in eq. (5-12) is 0.5. The mass-transfer resistance in eq. (5-12) \[
\left(\frac{\theta_{Cl}^2 W}{4\pi R_p^2 N_p k_g}\right)
\] was found to be \(<2\) orders of magnitude smaller than the reaction resistance \((1/k')\). Therefore, the observed and intrinsic rate constants as well as the surface and bulk Hg(0) concentrations were almost equal under the experimental conditions used in this study. The activation energy of Hg(0) oxidation over V_2O_5-based SCR catalyst and noble metals (Au and Ir) have been reported to be in a range of 20 to 120 kJ/gmol.[14, 27, 29, 56, 58]
Table 5.2 Intrinsic reaction rate constant for 1st order Hg(0) reaction.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>k' (m³/(g catalyst·s))</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>15.92±2.64</td>
</tr>
<tr>
<td>350</td>
<td>22.02±0.03</td>
</tr>
<tr>
<td>400</td>
<td>29.36±1.69</td>
</tr>
</tbody>
</table>

Figure 5.10 Effects of temperature and HCl concentration on Hg(0) oxidation rate.

To determine the HCl adsorption kinetics, experiments were conducted at different HCl concentrations and temperatures as shown in Figure 5.10. The HCl adsorption equilibrium constant (K_{HCl}) for each temperature was determined using parameter estimation that can best fit the Hg(0) conversion values under different HCl concentrations from coupled eqs. (7), (9) and (12) used in the kinetic model. The HCl adsorption equilibrium constant values (K_{HCl}) are summarized in Table 3. The model predictions were in good agreement with the experimental data as shown in Figure 10. The HCl adsorption equilibrium constant
(K\textsubscript{HCl}) increased with temperature within a 300-400 °C range, implying a chemisorption that requires activation for HCl dissociation.

5.3.3.4 Competitive adsorption of NH\textsubscript{3} and SO\textsubscript{2}

As shown in our previous study, NH\textsubscript{3} has a negative effect on Hg(0) oxidation over the RuO\textsubscript{2}/TiO\textsubscript{2} catalyst through competitive adsorption.[33] Based on our DRIFT results for NH\textsubscript{3} and HCl, a diatomic molecule HCl is dissociated after its adsorption onto the RuO\textsubscript{2} sites for the reaction with Hg(0) vapor, and these two gases compete for the same RuO\textsubscript{2} sites. Then the fractional surface coverage for HCl with the competitive adsorption of NH\textsubscript{3} following Langmuir adsorption can be expressed as:

$$\theta_{Cl} = \frac{\sqrt{K_{HCl}C_{HCl}}}{1+2\sqrt{K_{HCl}C_{HCl}+K_{NH3}C_{NH3}}}$$

(5-16)

where $K_{NH3}$ is the NH\textsubscript{3} adsorption equilibrium constant (m\textsuperscript{3}/gmol) and $C_{NH3}$ is the gas-phase NH\textsubscript{3} concentration (gmol/m\textsuperscript{3}). Experiments were conducted at 10 ppbv Hg(0), 10 ppmv HCl, 10-100 ppmv NH\textsubscript{3}, 3%(v) O\textsubscript{2} and temperatures between 300 and 400 °C. By applying the updated $\theta_{Cl}$ in eq. (16) to the rate constant in eq. (12) for the kinetic model in eq. (9), the NH\textsubscript{3} adsorption equilibrium constants at different temperatures were determined as listed in Table 3. The experimental data and model results are shown in Figure 5.11. As temperature increases, the adsorption of NH\textsubscript{3} decreases and that of HCl increases, promoting high Hg(0) conversion and thus reaction rate.

Table 5.3 Adsorption equilibrium constants for HCl, NH\textsubscript{3} and SO\textsubscript{2}.
<table>
<thead>
<tr>
<th></th>
<th>300 °C</th>
<th>350 °C</th>
<th>400 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{HCl}$ (m$^3$/gmol)</td>
<td>1,221±149</td>
<td>4,062±129</td>
<td>8,106±1,029</td>
</tr>
<tr>
<td>$K_{NH_3}$ (m$^3$/gmol)</td>
<td>743±94</td>
<td>614±60</td>
<td>578±37</td>
</tr>
<tr>
<td>$K_{SO_2}$ (m$^3$/gmol)</td>
<td>70±9</td>
<td>103±7</td>
<td>176±10</td>
</tr>
</tbody>
</table>

Figure 5.11 Effects of temperature and NH$_3$ concentration on Hg(0) oxidation rate.

Similar to NH$_3$, SO$_2$ also has a negative effect on Hg(0) oxidation through the competitive adsorption:

$$\theta_{Cl} = \frac{\sqrt{K_{HCl}C_{HCl}}}{1+2\sqrt{K_{HCl}C_{HCl}}+K_{SO_2}C_{SO_2}}$$  \hspace{1cm} (5-17)

where $K_{SO_2}$ is the SO$_2$ adsorption equilibrium constant (m$^3$/gmol) and $C_{SO_2}$ is the gas-phase SO$_2$ concentration (gmol/m$^3$). By using the same method, the adsorption equilibrium constant ($K_{SO_2}$) was obtained. The experiments were conducted in a concentration range of 200 to 2,000 ppmv SO$_2$ while keeping the other conditions the same as above. The results are shown in Figure 5.12 and Table 5.3. Similar to HCl, SO$_2$ adsorption onto the RuO$_2$/TiO$_2$ catalyst is
also chemisorption that requires activation as indicated by an increase in adsorption equilibrium with temperature.

![Graph](image)

**Figure 5.12** Effects of temperature and SO\(_2\) concentration on Hg(0) oxidation rate.

Finally, by combining the effects of the competitive adsorption for both NH\(_3\) and SO\(_2\), the intrinsic Hg(0) oxidation rate expression in terms of bulk gas-phase Hg(0) concentration can be obtained:

\[-r'_{Hg,int} = \frac{1}{\theta_{Cl}^2 W} \frac{1}{k^2} + \frac{C_{Hg,B} \theta_{Cl}^2}{4\pi R_p^2 N_p k_g} \]

where \(\theta_{Cl} = \frac{\sqrt{K_{HCl}C_{HCl}}}{1 + 2\sqrt{K_{HCl}C_{HCl} + K_{NH3}C_{NH3} + K_{SO2}C_{SO2}}} \) \((5-18)\)

As discussed in our previous study, other flue gas components such as NO, CO\(_2\) and H\(_2\)O vapor do not have noticeable effect on the Hg(0) oxidation performance of the RuO\(_2\)/TiO\(_2\) catalyst.[33] There is always excessive O\(_2\) in the flue gas and all the kinetic tests were conducted in the presence of 3%(v) O\(_2\). Therefore, its effect is incorporated into the rate constant \(k'\). Experiments were conducted to validate the combined kinetic expression in eq.
(18) when both NH₃ and SO₂ were present. An optimal location of the RuO₂/TiO₂ catalyst is at the tail end of the SCR unit where NH₃ concentration is low. Therefore, 25 mg of the RuO₂/rutile TiO₂ catalyst was tested under 5 ppmv NH₃, 5 ppmv NO and 3%(v) O₂ at 350 °C with different concentrations of HCl (10 to 100 ppmv) and SO₂ (200 to 2000 ppmv) simulating the combustion flue gas conditions of lignite and bituminous coals with low to high sulfur content. The experimental data and model predictions are shown in Figure 5.13. Higher HCl concentration could alleviate the negative effect of SO₂ on Hg(0) oxidation even with 0.2 wt.% Ru loading used in this study. The modeling results and measurements are in good agreement over a wide range of HCl concentrations.

Figure 5.13 Comparisons of model predictions and experimental data. Conditions: 10 ppbv Hg(0), 5 ppmv NH₃, 5 ppmv NO, and 3%(v) O₂ at 350 °C.
5.4 Conclusion

In this study, in-situ DRIFTS and steady-state kinetic studies of the heterogeneous oxidation of Hg(0) vapor by HCl gas over the RuO$_2$/TiO$_2$ catalyst were conducted. After exposing the RuO$_2$/TiO$_2$ catalyst to 200 ppmv HCl in nitrogen between 300 and 400 °C, the asymmetric vibration of Ru-H bond was observed as a result of the dissociation of adsorbed HCl, indicating chemisorption of HCl onto the RuO$_2$ surface. Due to the 1:1 ratio of H and Cl atoms in HCl, the intensity of the Ru-H peak should be proportional to the concentration of surface chlorine species responsible for Hg(0) oxidation. These results substantiates an Eley-Rideal followed by a Langmuir–Hinshelwood mechanism where HCl is an adsorbed species and Hg(0) in the gas phase directly reacts with Cl(ad) to form HgCl(ad), and then HgCl(ad) reacts with another Cl(ad) to form HgCl$_2$(ad). Based on the mechanistic study, a kinetic model was formulated to determine the reaction rate constants, activation energy, and adsorption equilibrium constants of HCl, NH$_3$ and SO$_2$ over the RuO$_2$/TiO$_2$ catalyst. The activation energy value determined for the reaction was a low end value for the heterogeneous Hg(0) oxidation reaction using HCl gas reported in the literature. The intrinsic kinetic expression obtained for the RuO$_2$/rutile TiO$_2$ catalyst is expected to be applicable to the design of an Hg(0) catalyst that can be installed at the tail end of a typical SCR unit.

5.5 References


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Chapter 6  Summary

6.1 Summary

The work in this study aims to develop effective and reliable mercury oxidation catalysts, advance the mechanistic understandings of heterogeneous mercury oxidation, and obtain information on heterogeneous mercury oxidation kinetics. The outcome of this research work includes:

(1) The CuCl\(^2\)/\(\gamma\)-Al\(_2\)O\(_3\) catalyst for low temperature Hg(0) oxidation. The properties and performances of CuCl\(_2\) supported onto \(\gamma\)-Al\(_2\)O\(_3\) with high surface area were investigated. From various characterization techniques using XPS, XAFS, XRD, TPR, SEM and TGA, the existence of multiple copper species was identified. At low CuCl\(_2\) loadings, CuCl\(_2\) forms copper aluminate species with \(\gamma\)-Al\(_2\)O\(_3\) and is inactive for Hg(0) oxidation. At high loadings, amorphous CuCl\(_2\) forms onto the \(\gamma\)-Al\(_2\)O\(_3\) surface, working as a redox catalyst for Hg(0) oxidation by consuming Cl to be converted into CuCl and then being regenerated back into CuCl\(_2\) in the presence of O\(_2\) and HCl gases. The 10%(wt) CuCl\(_2\)/\(\gamma\)-Al\(_2\)O\(_3\) catalyst showed excellent Hg(0) oxidation performance and SO\(_2\) resistance at 140 °C under simulated flue gas conditions containing 6%(v) O\(_2\) and 10 ppmv HCl. The oxidized Hg(0) in the form of HgCl\(_2\) has a high solubility in water and can be easily captured by other air pollution control systems such as wet scrubbers in coal-fired power plants. The CuCl\(_2\)/\(\gamma\)-Al\(_2\)O\(_3\) catalyst can be used as a low temperature Hg(0) oxidation catalyst.

(2) The RuO\(_2\)/rutile TiO\(_2\) catalyst for high temperature Hg(0) oxidation. RuO\(_2\) catalyst was found to be an excellent Hg(0) oxidation catalyst. When rutile TiO\(_2\) was used as the catalyst support, RuO\(_2\) formed well dispersed nano-layers due to the very similar crystal
structures of RuO$_2$ and rutile TiO$_2$, giving higher Hg(0) oxidation activity over anatase TiO$_2$ support. The RuO$_2$/rutile TiO$_2$ catalyst can be used at the tail end section of the SCR unit for Hg(0) oxidation. It showed good Hg(0) oxidation performance under sub-bituminous and lignite coal simulated flue gas conditions with low concentration of HCl or HBr gas. The RuO$_2$/rutile TiO$_2$ catalyst also showed excellent resistance to SO$_2$ under bituminous coal simulated flue gas, maintaining higher than 90% Hg(0) oxidation with up to 2,000 ppmv SO$_2$ present. The oxidized mercury in a form of HgCl$_2$ has a high solubility in water and can be easily captured by other air pollution control systems such as wet scrubbers in coal-fired power plants.

(3) Identification of oxidized mercury species from heterogeneous catalysis under simulated flue gas conditions. Linear combination fitting of the XANES was used to quantify oxidized mercury species over RuO$_2$/TiO$_2$ and 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 RuO$_2$/TiO$_2$ and SCR catalysts to form HgS and HgSO$_4$. In the presence of HCl or HBr gas, HgCl$_2$ or HgBr$_2$ is the main oxidized mercury species. When both HCl and HBr gases are present, HgBr$_2$ is the preferred oxidation product and no HgCl$_2$ 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, NH$_3$, SO$_2$ and CO$_2$ do not have significant effect on oxidized mercury speciation when halogen gas is present.

(4) Mechanistic and kinetic studies of the heterogeneous oxidation of Hg(0) vapor by HCl gas over a RuO$_2$/rutile TiO$_2$ catalyst. It was found that under reaction conditions, chemically adsorbed HCl was dissociated on the catalyst surface, and the formation of Ru-H
bond was observed by in-situ FTIR. The active chlorine species on the surface generated from HCl was found to be responsible for the Hg(0) oxidation. The intensity of the Ru-H IR signal could be used as an indicator of the available surface chlorine. Based on the in-situ FTIR and performance results, Hg(0) oxidation over the RuO$_2$/TiO$_2$ catalyst was proposed to follow Eley-Rideal followed by Langmuir–Hinshelwood mechanisms where HCl is an adsorbed species and reacts with gas-phase Hg(0) to form HgCl(ad), then HgCl(ad) reacts with another Cl(ad) to form HgCl$_2$(ad). A steady-state kinetic study were also conducted to determine an intrinsic reaction kinetic expression for Hg(0) oxidation over the catalyst under HCl, NH$_3$ and SO$_2$ gases for the first time. The kinetic expression could reasonably predict the Hg(0) oxidation performance under the competitive adsorption of NH$_3$ and SO$_2$ gases. The methodology used in this study can be applied to other Hg(0) oxidation catalysts for a better mechanistic understanding and the design of a catalytic reactor.

6.2 Suggested future studies

(1) This study focused on developing Hg(0) oxidation specific catalysts. Due to the recent EPA rules on NOx, more coal-fired power plants will be equipped with SCR units. Under this context, a catalyst for simultaneous NOx reduction and Hg(0) oxidation will have additional benefits for some power plants. Further investigations can be conducted on modified RuO$_2$ or SCR catalyst using other active metals to achieve better NH$_3$ resistance and simultaneous NOx reduction and Hg(0) oxidation.

(2) All the tests in this study were conducted using a lab scale fixed bed system under simulated flue gas conditions. For coal-fired power plants, catalysts have to be in the form of honeycomb or plate type due to the extremely high flue gas flow rate. Further tests at larger
scale (bench or pilot scale) using structured catalysts, real combustion flue gas, or slip-stream will give more information on the performances of these catalysts.

(3) Further investigation on more in-depth heterogeneous Hg(0) oxidation mechanisms can be conducted using molecular simulation and advanced in-situ spectroscopy such as Density Function Theory (DFT) and in-situ XAFS. Kinetic studies using structured catalysts can also be conducted to give additional information to help with the designing of the catalytic systems.
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Education

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Patent


Journal Articles


Selected Presentations


