Mercury Oxidation during Coal Combustion by Injection of Vanadium Pentoxide (V_2O_5)

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Abstract

Although there are many commercially available methods to capture Hg emission from coal combustion, it is still difficult to use a single method that can control Hg emission both efficiently and economically from coal combustors due to the varying coal seams, operating conditions and downstream control devices. One methodology is the use of sorbent injection at elevated temperatures; and is examined in this study. V_2O_5 was tested as the sorbent and was found to effectively oxidize elemental mercury (Hg^0). Ultrafine V_2O_5 particles are formed during the combustion process resulting in a high surface area aerosol that can effectively catalyze the oxidation of Hg^0 . The effect of varying chlorine (Cl) concentration in coal on Hg^0 oxidation was also examined. The result shows that Cl can enhance Hg^0 oxidation on the V_2O_5 surface.

Keywords: Mercury, sorbent, coal combustion, V_2O_5

1. Introduction

Coal combustion in the United States emits approximately 50 tons of mercury per year into the atmosphere (Houyoux and Strum, 2011). The US Environmental Protection Agency (EPA) has implemented the strict regulation of emissions of Hg and other pollutants from coal combustion by promulgating the Mercury and Air Toxics Standard (MATS). For example, according to the standard, if a new coal-fired power plant uses coal with the following characteristics — Hg content: 50 ppb, Heating value: 28 MJ/kg, assumed thermal efficiency for electrical generators is 30% — then at least 91.5% of Hg needs to be captured. During combustion, trace amounts of mercury in coal is released in its elemental form, $\text{Hg}^0(\text{g})$. (Pavlish et al., 2003) In the post combustion environment where the temperature is decreasing, some of $\text{Hg}^0(\text{g})$ may be oxidized to Hg^{2+} compounds. HCl and Cl_2 are important oxidants of these reactions. Hg^{2+} compounds can adsorb onto particulate matter in flue gas and form particulate mercury, $\text{Hg}(\text{p})$ (Galbreath and Zygarlicke, 2000; Senior et al., 2000a; Senior et al., 2000b). Thus, there are 3 forms of Hg in the exhaust gas of coal combustion: 1) $\text{Hg}^0(\text{g})$; 2) $\text{Hg}^{2+}(\text{g})$; and 3) $\text{Hg}(\text{p})$. $\text{Hg}^{2+}(\text{g})$ is water-soluble and can be readily removed by wet flue gas desulfurization (WFGD) systems (Zhuang et al., 2004). $\text{Hg}(\text{p})$ can also be easily removed by particulate matter control devices such as in baghouse fabric filters (FF) and electrostatic precipitators (ESP). However, $\text{Hg}^0(\text{g})$ is relatively difficult to capture and it is reported that the elemental form is the main form of Hg emission from coal combustion systems (Pavlish et al., 2003; Presto and Granite, 2006; Wang et al., 2010).

Several technologies have been proposed to capture Hg in combustion exhaust. The most established method in the United States is activated carbon injection (ACI). Powdered activated carbon is injected into flue gas ductwork and absorbs Hg^0 . Then particulate control device can remove it with fly ash. It is a simple and efficient method. However, there are some

disadvantages. The cost is significant (Jones et al., 2007); activated carbon (AC) will mix with fly ash and affect its flammability and salability (Pflughoeft-Hassett et al., 2009). Noticeably, there are some concrete-friendly AC sorbents that have been developed and are available on market. However, their costs are higher than traditional AC sorbents. Thus, a low cost non-carbon technology is still desired for mercury capture from coal combustion.

One general approach for a non-carbon method is promoting the oxidation of Hg^0 to Hg^{2+} , a mercury form that can be more easily captured. Many halogen species are oxidizers of $\text{Hg}^0(\text{g})$. Chlorine is major halogen specie in coal and plays key roles in Hg oxidation (Senior et al., 2000b). It is reported that addition of Br_2 or HBr can greatly enhance $\text{Hg}^0(\text{g})$ oxidation (Liu et al. 2007; Cao et al., 2007b). Li et al. (2009) also showed that KI has the capability to oxidize $\text{Hg}^0(\text{g})$, and demonstrated effective capture in a pilot scale study. Many metals/metal oxides can catalyze $\text{Hg}^0(\text{g})$ oxidation, such as Fe_2O_3 , CuO , and some precious metals (Au , Ag and Pd) (Galbreath et al., 2005; Ghorishi et al., 2005; Zhao et al., 2006). Besides these metals/metal oxides, selective catalytic reduction (SCR) catalysts have been studied extensively, because they have been already widely installed for NO_x reduction and are also shown to have the capability of oxidation of Hg^0 (Cao et al., 2007a; Cao et al., 2008; Presto and Granite, 2006). SCR catalysts are typically consist of V_2O_5 , WO_3 or zeolite supported on various carriers such as TiO_2 . It can help reduce NO_x with NH_3 to N_2 . Many studies have reported that SCR catalysts can also oxidize $\text{Hg}^0(\text{g})$, particularly in the presence of halogen species (Cao et al., 2007a). There are several factors that can affect the performance of SCR catalysts, such as concentrations of HCl and sulfur oxides in flue gas (Cao et al., 2007a; Eswaran and Stenger, 2005; Senior, 2006).

Another general approach is sorbent injection into the combustion zone (high temperature sorbent) (Biswas and Wu, 1998; Biswas and Zachariah, 1997; Gale and Wendt, 2002, 2003,

2005; Jeong et al., 2007; Lee et al., 2005; Lee et al., 2001; Suriyawong et al., 2010; Suriyawong et al., 2009; Wendt and Lee, 2010). In the high temperature combustion environment, metallic species are released to gas phase and form vapors. At the exit of combustor, when the temperature drops, these vapors will undergo homogeneous nucleation or heterogeneous condensation and form submicrometer aerosols. When sorbent particles are injected into the combustor, metallic vapors can be scavenged and these metallic species are associated with sorbent particles which usually can be designed to be in sizes that can be easily removed by the particulate matter control devices (Owens and Biswas, 1996). This methodology can be applied to Hg removal. For instance, TiO_2 is a well-studied photocatalyst which can help oxidize $\text{Hg}^0(\text{g})$ (Li et al., 2011; Li et al., 2012). Wu et al. reported a method using TiO_2 sorbent (Wu et al., 1998): the sorbent precursor was added into the combustor. Then the precursor was oxidized to form TiO_2 agglomerate with large surface area, which can efficiently capture $\text{Hg}^0(\text{g})$. They also showed that using UV radiation can further improve binding of Hg with TiO_2 sorbent particles, thereby enhancing Hg capture and preventing its leachability when disposed to the environment. Suriyawong et al. (2009) have demonstrated the effectiveness of this method on a pilot scale. In addition, calcium- and iron-based sorbents are shown to have similar capability of Hg removal (Pavlish et al., 2003; Zhuang et al., 2007).

Both SCR catalysts and sorbent injection into the combustion zone (high temperature sorbent) have good performance on Hg capture. The combination of these two technologies may be an effective methodology for Hg control. V_2O_5 , which is one of most active component in SCR catalysts and a relatively low-cost material, can be used as a sorbent to remove elemental Hg. This study examines the performance of this new method from pulverized coal combustion in a drop-tube furnace. Its effects on particulate matter formation have been investigated. In

addition, the effects of chlorine and sulfur contents in coal have also been studied, since they may have significant influences on this method.

2. Experimental Section

The experimental setup shown in Fig. 1 consists of a coal feeding system, a drop-tube furnace (Lindberg/Blue M, Model HTF55342C, ThermoElectron Corp., USA) with an alumina reactor tube (5.7 cm inner diameter, and 122 cm long), a cascade impactor, and various sampling and measuring systems. Pulverized Powder River Basin (PRB) sub-bituminous coal (coal particle diameter $\leq 50 \mu\text{m}$; supplied by Ameren UE, St. Louis, MO) was introduced into the electrically heated alumina tube in the drop-tube furnace by a self-made coal feeder (design of the feeder can be found in the literature (Quann et al., 1982)) at 1.5 g/h. For all experiments, a total gas flow rate of 1.0 liter-per-minute (LPM) was fixed. At the exit of the combustor, 7 LPM particle-free air was added as primary dilution, and then a six-stage cascade impactor (Mark III, Pollution Control System Corp., Seattle, WA) was used to remove particles with diameter larger than 600 nm in the diluted exhaust gas. A slip stream from downstream of the impactor was then drawn to a real time scanning mobility particle sizer (SMPS, TSI Inc., Shoreview, MN) to determine the particle size distribution ranging from 9 to 425 nm. The submicrometer particles were also collected on Teflon filters for elemental analysis by an X-ray fluorescence spectroscopy (XRF, Panalytical Epsilon 5 energy dispersive XRF spectrometer, Almelo, Netherlands), crystal determination by X-ray diffraction (XRD, Rigaku Geigerflex D-MAX/A diffractometer) and morphology examination using an FEI Nova NanoSEM 230 Scanning Electron Microscope (SEM).

Figure 1. Schematic diagram of the experimental set-up

For mercury concentration measurements, a 0.47 LPM flue gas was drawn from the exhaust gas (before the primary dilution) and passed through a mercury sampling train to determine oxidized and elemental mercury concentrations (the dilution gas was turned off during Hg sampling). The sampling train and technique used for gaseous mercury collection and measurement are based on the method developed by Hedrick et al. (2001). The sampling train consists of five impingers.

The following solutions were used to collect gaseous mercury: two impingers of 1.0 M tris-buffer and EDTA for oxidized mercury capture, one impinger of 10% hydrogen peroxide and 2% nitric acid for oxidizing and capturing of elemental mercury, and two impingers of 0.05 M potassium iodide and 2% hydrochloric acid for elemental mercury capture. The impinger solutions with captured mercury content were then analyzed by a direct mercury analyzer (DMA-80, Milestone S.r.l., Italy) to determine the elemental and oxidized fractions of mercury in the exhaust gas.

The overall test plan is summarized in Table 1. First, the baseline elemental mercury concentration from PRB coal combustion was determined. Set I experiments were then carried out to compare elemental mercury removal efficiency of using V_2O_5 (purity $\geq 98\%$, particle size: 325 mesh) with CuO and Fe_2O_3 as sorbent at same mixing ratio (100 part-per-million based on mass, ppm). Set II experiments were designed to study the effects of varying mixing ratio of V_2O_5 on mercury removal efficiency. V_2O_5 concentrations of 50, 100, 300, and 500 ppm were tested. The objects of Set III experiments were to determine the effects of chlorine content in coal on mercury capture efficiency.

Table 1. Experimental test plan for this study

Set	#	Sorbent Material	Mixing Ratio of Sorbent (PPM)	NaCl Addition (PPM)	Objectives
Baseline	1	N/A	N/A	0	To determine baseline Hg^0 concentration from PRB combustion
	2	N/A	N/A	500	
I	1	V_2O_5	100	0	To determine Hg^0 removal efficiency for each sorbent
	2	CuO	100	0	
	3	Fe_2O_3	100	0	
II	1	V_2O_5	50	0	To determine the effect of V_2O_5 mixing ratio on Hg^0 removal
	2		100	20	
	3		300	40	
	4		500	60	
III	1	V_2O_5	100	100	To determine the effect of chlorine concentration on Hg^0 removal
	2			300	
	3			500	

3. Results and Discussion

The overall study examined the performance of injecting V_2O_5 as a sorbent on elemental Hg oxidation from pulverized coal combustion in a drop-tube furnace at various conditions. Particulate matter formation and the effects of chlorine and sulfur contents in coal on Hg oxidation were also studied.

3.1 Oxidation Hg^0 by mixing V_2O_5 with coal

As shown in Fig. 2a, V_2O_5 particles were mixed with PRB coal at different ratios (Set 1, Table 1). Without adding V_2O_5 , the Hg^0 concentration (the baseline concentration) in the flue gas was $2.25 \mu\text{g}/\text{m}^3$. The Hg content in PRB coal was about 0.08 ppm. The coal burning rate was fixed at 1.5 gram/hour. The input air flow rate is 1 LPM. Thus, assuming all Hg from coal is released to the flue gas after burning, the total Hg concentration in flue gas should be $\sim 2 \mu\text{g}/\text{m}^3$, which was close to the measured baseline Hg concentration, $\sim 2.3 \mu\text{g}/\text{m}^3$. The Hg^{2+} concentration was only $\sim 0.05 \mu\text{g}/\text{m}^3$, which was much less than the Hg^0 concentration, suggesting that there were insufficient oxidants in the combustion system, due to the low coal Cl concentrations in the PRB coal. When V_2O_5 was mixed with coal, the Hg^0 concentration decreased significantly. For example, when the mixing ratio was 50 ppm, the Hg^0 concentration was $1.09 \mu\text{g}/\text{m}^3$, and the Hg^0 removal efficiency ($= 1 - \frac{Hg^0 \text{ Concentration}}{\text{Baseline } Hg^0 \text{ Concentration}}$) was about 51.2%. Experimental results show that Hg^0 concentration decreased with increased V_2O_5 mixing ratio with coal, and the highest removal efficiency, 64.4%, was achieved when the mixing ratio was 500 ppm. These results demonstrate that V_2O_5 is effective in the capture of Hg^0 . In our previous study (Li et al., 2009), potassium iodine (KI) was used as a sorbent. The Hg^0 removal efficiencies were 30%, 53% and 61%, when KI mixing ratios were 235, 389 and 777 ppm, respectively, lower than the

performance of V_2O_5 . Beside V_2O_5 and KI, CuO and Fe_2O_3 were also tested, since previous studies report that they also remove Hg^0 (Galbreath et al., 2005; Granite et al., 2000; Presto and Granite, 2006). The results revealed that their Hg^0 removal efficiencies were 44.4% and 28.3%, respectively. Therefore, V_2O_5 has a superior performance as a sorbent.

Figure 2. Combustion of PRB coal mixed with V_2O_5 at different ratios: (a) Mercury concentrations in the flue gas; (b) Fine particle size distribution; and (c) Elemental compositions of fine particulate matter

Figure 2a shows that the Hg^0 removal efficiency did not increase significantly on increasing the V_2O_5 mixing ratio above 100 ppm. This finding suggests that V_2O_5 was not the limiting factor in the mercury removal process. The mechanism of Hg^0 oxidation by V_2O_5 is the catalytic oxidation of Hg^0 on the V_2O_5 particle surface (Cao et al., 2007a; Li et al., 2011; Presto and Granite, 2006). Hg^{2+} is the product formed after this process. Thus, when V_2O_5 was added, a significant fraction of Hg^0 should be converted to Hg^{2+} in the flue gas. However, Fig. 2a shows that Hg^{2+} concentrations were very low for all experiments. This can be explained by the fact that Hg^{2+} (such as HgO and HgCl_2) has much lower vapor pressure than Hg^0 (Johnson et al., 1966; Lamoreaux et al., 1987). The temperature of flue gas dropped to the room temperature very quickly in our system. This resulted in the conversion to the particulate phase or condensation of Hg^{2+} on existing particles or tubing surfaces. Our previous research also showed a similar result (Li et al., 2009). In the bench-scale system used in this study, fine particles did not provide significant surface area ($\sim 1 \times 10^{-4} \text{ cm}^2/\text{cm}^3$, calculated from particle size distribution showed in Fig. 2b), and is comparable to the surface area of the tubing. Therefore, most of Hg^{2+} may condense on the inside surface of the tubing, rather than on the particle surface. The low Hg concentrations found in particulate matter (shown in Fig. 2a) also confirms this pathway. In a full scale coal fired power plant, if V_2O_5 injection is used, an additional wet scrubber needs to be installed to remove Hg^{2+} , because most of Hg^{2+} may not be adsorbed by fly ash particles and removed by particulate capture device, such as ESP and filter baghouse.

V_2O_5 addition could also impact particulate matter (fly ash) formation: adding sorbent particles could provide extra surface for condensation of metallic species during coal combustion, thereby shifting the particle size distribution to larger sizes that can be more effectively captured in devices such as the ESP (Biswas and Wu, 1998). Figure 2b shows the size distributions of fine

particles from the experiment set 1. However there is no significant difference among those size distributions, indicating that a low V_2O_5 mixing ratio does not have significant influence on fly ash particle formation. Generally, all size distributions peak at about 60 nm. Elemental compositions for those particles are shown in Fig. 2c. Again, no significant difference was observed. Calcium (Ca) is one of the dominant species in particulate matter, since PRB coal has high calcium content (Wang et al., 2013). Other major species include silicon (Si), iron (Fe), sulfur (S), titanium (Ti) and potassium (K). It is interesting to note that sulfur concentration in particulate matter slightly increased when more V_2O_5 was mixed with coal. The increase may be due to the oxidation of SO_2 to SO_3 on V_2O_5 surface, because V_2O_5 is an efficient catalyst of SO_2 oxidation (Kamata et al., 2001). SO_3 is a strong acidic gas. It may react with water vapor and form sulfuric acid which can easily condense on surface and enter the particle phase.

3.2 Transformation of V_2O_5 during coal combustion

The previous section results demonstrated that adding V_2O_5 to coal can efficiently reduce Hg^0 concentration in the exhaust gas. The role that V_2O_5 plays in Hg^0 removal needs to be further investigated. Pristine V_2O_5 particles were inlet into the drop-tube furnace. Particle size distribution has been measured at the outlet of the drop-tube furnace (Fig. 3a), which shows the presence of high concentration of ultrafine particles. In the SEM image (Fig. 3b) of the pure V_2O_5 particle that was collected on a Teflon filter from the outlet of the drop-tube furnace, there are some micrometer size particles and large amount of nanoparticles, which are attached to the fibers of the filter. Almost all particles have spherical shape. Figure 3c shows the original shape of V_2O_5 particles, most of which are rod; and their sizes are much larger (~ 100 to $200\ \mu m$ in length). The change of size and shape strongly indicates a gas-to-particle conversion process that the V_2O_5 particles were undergoing in the furnace (Widiyastuti et al., 2009). The melting

point of V_2O_5 is 963 K. And the temperature inside the drop-tube furnace was around 1376 K. Therefore, V_2O_5 particles would quickly become liquid droplet in the furnace. Some liquid may be evaporated and form V_2O_5 vapor. When the gas is leaving from the furnace and its temperature drops below 963 K. V_2O_5 vapor would start nucleation process, which produce high concentration of V_2O_5 ultrafine particles. The ultrafine V_2O_5 particles provide large surface area, which can greatly facilitate the oxidation of Hg^0 . Fine V_2O_5 particles had been also collected for the analysis of X-ray Diffraction (XRD) (Fig. 3d). No significant peak has been found in the spectrum, suggesting that ultrafine V_2O_5 particles are in amorphous phase. Figure 4 summarizes this whole process.

Figure 3. (a) Particle size distribution from pure V_2O_5 experiment; (b) SEM image of V_2O_5 particles collected from the outlet of the drop-tube furnace; (c) SEM image of original V_2O_5

particles; and (d) X-ray Diffraction (XRD) spectrum of the collected particles from pure V₂O₅ experiment

Figure 4. Illustration of ultrafine V₂O₅ particles formation

3.3 Effect of chlorine (Cl) concentration in coal on Hg⁰ oxidation

During coal combustion, the trace amounts of chlorine in coal are released into the gas phase, which is the main oxidizer for Hg^0 oxidation (Senior et al., 2000b; Zhuang et al., 2007). By adding different mixing ratio of NaCl into the mixture of PRB coal and 100ppm V_2O_5 , Cl concentrations were changed (shown in Experiment Set 2 in Table 1); and its effect on Hg^0 removal has been investigated. Figure 5a shows that Hg^0 concentration decreased when Cl was added to coal, suggesting that Cl did help oxidize Hg^0 . This result is consistent with previous studies, which report that adding Cl into coal can promote the oxidations of Hg^0 in both gas phase and particle surface (Galbreath et al., 2005; Zhuang et al., 2007). Moreover, Fig. 5a also shows that adding 500ppm NaCl and 100ppm V_2O_5 has higher Hg^0 oxidation efficiency than adding 500ppm NaCl alone (without adding V_2O_5), which indicates adding Cl probably enhanced Hg^0 's oxidation on V_2O_5 surface. Thus adding Cl is an effective way to enhance Hg^0 oxidation. However in practice, although the halogen injection method can efficiently remove elemental Hg from flue gas, it could have some undesired effects, such as causing serious corrosion in power plant (Zhuang et al., 2009). Noticeably, V_2O_5 can catalyze the oxidation of SO_2 to SO_3 , which react with water vapor to form sulfuric acid and also cause the corrosion. Thus, using the V_2O_5 injection method in power plant may have the similar undesired effect.

Figure 5. Effect of chlorine content in coal on mercury concentrations in the flue gas

Particulate formation was also studied. The size distribution of fine particles shifted to larger particle sizes when more NaCl was added (Fig. 5b). During coal combustion, NaCl is evaporated into gas phase readily as it is volatile at the high temperatures. At the exit of the drop-tube furnace, the temperature drops and the sodium vapor may condense on particles, thereby increasing particle sizes. This process may affect Hg removal by V₂O₅, since it can block some active sites on V₂O₅ particles. Thus the process may account for the decreased performance of V₂O₅ when 500 ppm NaCl was added. Elemental compositions for the fine particles are shown in Fig. 5c. No significant difference is found.

3.4 Potential environmental impact

It is important to notice that V_2O_5 is also a modest toxic substance to human. The lethal dose (LD_{50}) for inhalation of V_2O_5 dust is 4–11 mg/kg (Bauer et al., 2000). Efficient particulate control device is required for removal V_2O_5 particles in flue gas. The fly ash management needs to be carefully treated, because V_2O_5 could leach to groundwater. Moreover, dry fly ash particles can be easily carried away by air flow. The resuspension of fly ash during handling, transporting and reusing or landfilling processes could also introduce V_2O_5 into the ambient air and cause some health concerns.

4. Conclusions

This study examined the performance of injecting V_2O_5 as sorbent on Hg^0 oxidation during pulverized coal combustion in a drop-tube furnace. It shows significant performance on Hg^0 oxidation with about 60 to 70% of elemental mercury conversion rate at a range of 100 to 500 ppm of V_2O_5 addition. It is proposed that the injected V_2O_5 particles catalyzed Hg^0 oxidation to Hg^{2+} , and this species condenses onto fly ash and other surfaces. In full scale coal fired boiler, an additional scrubber may be required to remove Hg^{2+} from flue gas. On injection into the combustor, high concentrations of ultrafine V_2O_5 particles were formed. By comparing morphology of V_2O_5 particles at the inlet and outlet, the formation pathway was elucidated. The solid V_2O_5 particles are quickly converted to liquid droplets in the combustor that rapidly evaporate at the high temperatures. As the temperature drops at the exit of the combustor, V_2O_5 vapor starts nucleating to form high concentrations of ultrafine particles. These ultrafine V_2O_5 particles provide large surface areas, which can greatly facilitate the oxidation of Hg^0 . Particulate matter (fly ash) formation was not significantly affected by V_2O_5 injection, in terms

of particle size distributions and chemical compositions. In addition, the experimental results show that chlorine content in coal can enhance Hg^0 oxidation on V_2O_5 surface.

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Figure Captions

Figure 1. Schematic diagram of the experimental set-up

Figure 2. Combustion of PRB coal mixed with V_2O_5 at different ratios: (a) Mercury concentrations in the flue gas; (b) Fine particle size distribution; and (c) Elemental compositions of fine particulate matter

Figure 3. (a) Particle size distribution from pure V_2O_5 experiment; (b) SEM image of V_2O_5 particles collected from the outlet of the drop-tube furnace; and (c) SEM image of original V_2O_5 particles.

Figure 4. Illustration of ultrafine V_2O_5 particles formation

Figure 5. Effect of chlorine content in coal on mercury concentrations in the flue gas: (a) Mercury concentrations in the flue gas; (b) Fine particle size distribution; and (c) Elemental compositions of fine particulate matter