Chemistry of Mercury Species and Their Control in Coal Combustion

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OBJECTIVES

The objectives for this reporting period are:

- 1) The study of characteristics of sorbent agglomerate generated for Hg capture
- 2) The study of particle formation mechanisms of submicron particles generated from pulverized coal combustion.

SUMMARY OF TECHNICAL PROGRESS

Structural Studies of the SiO₂ Agglomerates

Silica aggregates produced in a tubular aerosol reactor were classified according to the electrical mobility equivalent radius (R_E) by differential mobility analyzer (DMA). Then the classified aerosol was further analyzed by 1) *in situ* light scattering measurement, 2) TEM micrograph analysis to evaluate the properties of agglomerates, such as the radius of gyration (R_g), fractal dimension (D_f), primary particle diameter (d_m) and number of primary particles (N). Based on the properties measured by the experiments, the actual surface area of the silica sorbent particles can be calculated.

The schematic diagram of the system is shown in Figure 1. Two sets of experiments were performed. In set 1, the wave length of the laser light was set at 488 nm and in set 2, it was set at 514 nm. The conditions for the SiO₂ agglomerates generation were 1) furnace temperature of 1000 °C, 2) silica precursor feed rate of 25 cc/min, and 3) silica precursor feed temperature of 20 °C. The DMA rod voltages were set at 1.7739 V, 2.4524 V, 3.3403 V, 4.7072 V, 5.9521 V, which classified the SiO₂ agglomerates according to the electrical mobility equivalent diameters of 184 nm, 228 nm, 283 nm, 365 nm, 437 nm, respectively. The measured signal S in arbitrary unit vs. wave factor q are plotted in Figure 2 and 3.

Hg Capture in Presence of Simulated Flue Gas Coal Combustion Experiment

Experiments were conducted in simulated flue gas environments to determine Hg capture. The details are provided in Appendix I.

Coal Combustion Experiment

To study the submicrometer particle distribution from pulverized coal combustion, a laboratory scale drop-tube reactor was set up. The schematic diagram of the system is shown in Figure 4. The present experiment system allows for combustion of very small amounts of coal under well-controlled condition. The emphasis in this work has been on the ultra-fine particle formation mechanism in the flue gas. The pulverized coal powders (around 40-60 μm) flow into the vertical tubular reactor. Combustion products then pass through a MARK-III cascade impactor (last stage cutoff diameter = 0.46 μm) to separate the large particle from the flue gas. The CPC (Condensed Particle Counter) was used to measure the total number concentration of ultra-fine particles (in the range between 30 nm and 800 nm), and DMA (Differential Mobility Analyzer) was used for the measurement of particle size distribution. A filter assembly was also installed after the impactor to capture all the submicron particles smaller than 0.5 μm for chemical analysis.

The effects of reactor temperature and residence time of coal particle on the particle characteristics were examined by means of changing the reactor temperature and air flow rate through the reactor. Total number concentrations of submicron particles (smaller than 0.5 μm), and the particle size distributions, were measured under different working condition. The results are plotted in Figure 5 and 6. It can be found that the shorter the residence time of coal particles in the reactor, the lower the total number concentrations. It is also noted that, with the increase of temperature, the total number concentration first significantly increased. Then, after reaching certain temperature, the total number concentration reduced a little. Particle size distributions under different temperature are shown in Figure 7. Peak value could be observed around 100 nm particle diameter. It is found that with the rise of temperature, the peak value shifts to the smaller particle size.

PUBLICATIONS

- 1) Yang G. and Biswas P.: "Study of the Sintering of Nanosized Titania Agglomerates in Flames Using In Situ Light Scattering Measurements", *Aerosol Science and Technology*, vol. 27(4), 507-521, 1997.
- 2) Wu C.Y. and Biswas P.: "Particle Growth by Condensation in a System with Limited Vapor", *Aerosol Science and Technology*, vol. 28(1), 1-20, 1998.
- 3) Biswas P. and Wu C.Y.: "Control of Toxic Metal Emissions from Combustors Using Sorbents: A Review", *J. Air and Waste Management Associn.*, vol 48, 113-127, 1998.

- 4) C.Y.Wu, T.G.Lee, E.Arar, G.Tyree, P.Biswas, "Capture of Hg from Combustion System By In-Situ Generated Titania Particle with UV-Irradiation", to appear, Combustion Science & Technology, 1998.

WORK TO BE PERFORMED OVER NEXT REPORTING PERIOD

During the next period, the following experiments will be performed:

- 1) Results of mercury capture with other sorbent will be reported. In addition, a detailed kinetic examination of TiO_2 -Hg complexation is being carried out.
- 2) Effective capture of the toxic species on combustion of coal in electrical fields will be discussed.

Appendix I

KINETICS OF MERCURY CAPTURE USING TITANIA SORBENTS

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KEYWORDS

Air toxics, Metals, Sorbent capture, Photocatalyst

A novel sorbent methodology wherein a vapor phase sorbent precursor is injected into the combustor has been developed for control of toxic metals emissions from high temperature environments (Owens and Biswas, 1996). This methodology was further developed using in situ generated titania sorbents with uv irradiation for the effective capture of mercury from high temperature gas streams (Biswas and Wu, 1998; Wu et al., 1998). In this work, we examine the kinetics of mercury capture using titania sorbents in simulated combustion environments.

A schematic diagram of the flow reactor with its associated components is shown in Figure 1. Mercury vapors are introduced in precisely controlled amounts using a temperature controlled impinger, titanium isopropoxide vapors are introduced by bubbling argon through a solution of the precursor, and a combustion exhaust was simulated by adding varying amounts of sulfur dioxide. The photochemical reaction cell at the exit of the reactor tube is used to photocatalyze the mercury - titania reactions for better binding of the mercury to the sorbent particle surface. An on line Hg analyzer (Shimadzu, uv absorption spectrophotometer, 253.7 nm absorption) was used to monitor the elemental Hg concentration in the gas phase as indicated in Figure 1.

Figure 1. Schematic diagram of experimental system for Hg capture experiments.

Previous tests (Wu et al., 1998) illustrated capture efficiencies of mercury as high as 98.6%. The capture efficiency is defined as the mass of Hg on the filter (Figure 1) to the total mass of mercury on the filter and impingers (gas phase). Initial tests were carried out to determine the effectiveness of the titania particles to capture mercury in a simulated flue gas environment. On addition of increasing amounts of sulfur dioxide, the capture efficiency drops (Table 1), probably due to the occupation of some of the active sites on the titania particles. On increasing the feed rate of the titanium precursor, and thus the concentration of titania particles (and the available surface area), the efficiency increases to 81.5% (Table 1), confirming that sulfur dioxide occupies some of the active sites on titania.

Table 1. List of Preliminary Simulation Conditions and Results

	Total Flow Rate (lpm)	Flow Rate of Ar through Ti bubbler (lpm) / TiO ₂ conc. (#/cc)	SO ₂ Conc. (ppm)	η (%)
Air + Hg + Ti	1.12	0.1 / (4.40*10 ⁷)	0	0
Air + Hg + Ti + UV	1.12	0.1 / (4.40*10 ⁷)	0	98.6
Air + Hg + SO ₂ + Ti + UV - (I)	1.12	0.1 / (5.28*10 ⁷)	300	64.36
Air + Hg + SO ₂ + Ti + UV - (II)	1.12	0.1 / (5.50*10 ⁷)	600	55.56
Air + Hg + SO ₂ + Ti + UV - (III)	1.17	0.15 / (> 10 ⁸)	300	81.68
Air + Hg + SO ₂ + Ti + UV - (IV)	1.17	0.15 / (>10 ⁸)	600	81.48

Furnace Temperature : 1000 °C; Air Flow Rate : 1.0 lpm; Hg Inlet Condition : 30 °C, 20 cc/min
Hg Inlet Concentration (measured): 27.22 ~ 28.43 µg / m³ ; Ti Precursor Inlet Temperature : 75 °C

Results of detailed experiments on kinetics of Hg capture will also be presented. This will be done by examining capture at different residence times in the reactor. In addition, the role of inhibiting the Hg capture will be firmly established by developing a mechanistic interpretation of the Hg capture process. Preliminary results indicate that reasonably low ratios of Ti:Hg can be used in realistic flue gas environments for cost effective capture of Hg.

ACKNOWLEDGMENTS

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Wu C.Y., Lee T.G., Tyree G., Arar E. and Biswas P. (1998) Capture of Mercury in Combustion Systems By In Situ Generated Titania Particles with uv Irradiation, *to appear, Combust. Sci. & Technol.*.

Figure 1 The schematic of the modified system for the structural studies of the agglomerates.

Figure 2 Measured signal (S) vs. wave factor (q)
Signal Inversion: wave length=514 nm

Figure 3. Measured signal (S) vs. wave factor (q)
Signal Inversion: wave length=488 nm

Fig.4 Schematic Diagram of the Coal Combustor

Fig.5 **The Variation of Total Number Conc. of Sub-micrometer Particle ($dp_{50} < 0.53 \mu\text{m}$) with Time**

Fig.6 Effect of flow rate of air on total number concentration

Fig.7 Effect of temperature on particle size distribution