ELEGANT ELUSIVE OXIDATION MECHANISM OF MERCURY

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Introduction

Although the levels of mercury in coal generally are small (0.1-1.0 parts per million by weight (ppmw)), the United States alone currently burns about 900 million tons/year. The problem with combustion or incineration of any material containing traces of mercury is that all the mercury volatizes as atomic elemental mercury and none is retained in any bottom ash. This applies even to crematoria. The behavior stems from its unusual chemistry. Mercury has no condensed phase molecules that are stable above about 600-700 ^{o}C. This is partly why liquid mercury, quicksilver, was discovered in ancient times and is documented by the Phoenicians and Carthaginians. It is easily obtained from its ore cinnabar, HgS, solely by heating in air. Also, the thermal instability of mercuric oxide, HgO, helped Priestley discover oxygen. Even in the gas phase, the only molecule of mercury with significant stability is mercuric dichloride. As a result, what is observed in combustion or other high temperature systems is that the majority of the mercury in the exhaust is atomic. Because of this, and the fact that liquid mercury is very volatile, it is difficult to capture mercury with conventional type ab- or adsorption techniques[1]. Although the formation of the dichloride is thermodynamically favored, there are no direct kinetic channels for its production. Even so, in practice a small and unpredictable fraction of the mercury is exhausted as the dichloride, the two constituting the mass balance of mercury in the system. This partial conversion or oxidation as it is generally referred to, is extremely intriguing and has never been understood. Its important practical significance stems from the fact that whereas atomic mercury is very difficult to capture, the dichloride is readily soluble in water and so can be removed and processed by the already present water scrubbers. Consequently the more mercury present as the dichloride in an exhaust, the less is emitted to the atmosphere.

Extensive gas phase kinetic modeling studies over many years have failed to adequately describe this formation of the dichloride[2] . The dilemma is that its formation has to occur via the monohalide, HgCl. This is chemically weakly bound and will be very short-lived at temperatures much above 400 ^{o}C. Consequently, there are very restrictive constraints imposed on the gas phase chemistry. The temperatures can not be too high or molecular formation is not possible and when they fall low enough the kinetic reaction rates are beginning to freeze because of activation energy barriers. The temperature, time and concentration limitations prove to be very severe in practical combustion systems and the modeling is clearly inadequate in predicting the fractional distribution of mercury between the element and the dichloride. The majority of gas kineticists now acknowledge this fact[3] and conclude that the system is "complex" [4]. In reality, the value of these modeling studies has been two-fold. Firstly, they have established that the gas phase chemistry can only be marginally involved, if at all, in the conversion of atomic mercury to its dichloride. Secondly, they provide a useful reminder to all of us not to hold too firmly to preconceived ideas.

Full-scale combustor observations have never been able to correlate the observed fractional conversion to the dichloride with any operational parameter. Recently, however, it has been increasingly clear that blowing fly ash or particles into the flue gases does enhance the production of the dichloride[5].

A very recent review assesses the current status of all the control options currently being tested by the coal industry[1]. However, the conclusion remains that no method has yet proven to be generally successful or economically attractive.

In previous studies in this laboratory it was found if sodium and sulfur are present in flame gases at very low levels (ppmv) that sodium sulfate forms very efficiently not in the burned gases but on any cooler surface intercepting the flow[6,7]. The reduced dimensionality of the surface, 2-D instead of that of the 3-D gas phase, appears to be very important in facilitating the process as well as changing the chemistry from the gas phase to the condensed phase regime. It was also noted in that work that concepts such as dew point lose all meaning. Because of this experience, and having the experimental system available, it was decided to run test experiments with mercury. These introduced low levels of mercury (ppmv), sulfur and chlorine into flames, the burned gases of which were then intercepted by a cooled probe at various temperatures.

Experimental

Deposition Methods

Cylindrical propane or hydrogen, oxygen, nitrogen flames have been burned on a well-characterised flat flame burner. Mercury was introduced as a fine aqueous aerosol of either its nitrate or acetate solution from an ultrasonic nebulizer such that its flame concentration was in the range of 5-30 ppmv[6-8]. Small quantities of SO_2, HCl or Cl_2 could be added from certified gas mixtures, or alternately via the nebulizer in the form of their appropriate salt solutions. Several cylindrical collection probes were used of either Inconel-600 stainless steel or tightly clad with platinum foil. Air or water internally cooled these and a thermocouple was built into their wall thickness.

Two types of experiments have been accomplished. Those in the hotter burned gases used cooled probes. Such studies are highly quantitative and have resolved the nature of mercury's heterogeneous chemistry and its dependence on the variables in the system. Important additional experiments that relate to cooler downstream flue gas temperatures and industry also were undertaken to simulate the mercury behavior in practical systems. In these cases the probe was located downstream where the burned gas temperature has decayed to about 200 ^{o}C or less. In such experiments an electrically internally heated collection probe was used to maintain a desired probe surface temperature.

Characterization Methods

Four powerful modern analytical systems have helped to fully characterize these observed deposits. These are a Nicolet Fourier Transform Raman Spectrometer, a Bruker High Temperature Powder x-ray Diffractometer, a Thermo Jarrell Ash Inductively Coupled Plasma/Atomic Emission Spectrometer (ICP/AES), and a Mettler Thermogravimetric Analyser. By this means the chemical composition of deposits and their quantitative rates of deposition have been accurately measured. In all, over two hundred experiments now have been studied involving mercury deposition.

Results

From the very first experiment, it was apparent that mercury has a significant propensity for heterogeneous deposition. Provided that the probe temperatures are within a desirable temperature window, deposits are obtained with a formation efficiency that is essentially the same as with alkali metals. The deposits are molecular in nature. Figure 1 illustrates the Raman spectrum of such a deposit. It is immediately apparent that mercuric sulfate deposition is dominant if sulfur is present in the flame. However, the exact nature of the sulfate depends on the amount of sulfur in the flame. A ratio of sulfur

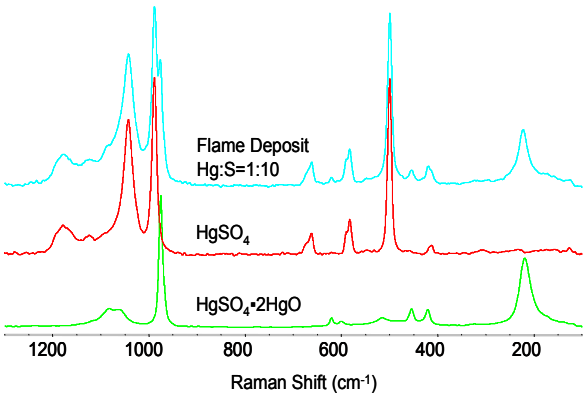

Figure 1. Raman spectrum of a deposit from the burned gases of a propane flame containing traces of mercury (25 ppmv) and sulfur. Compared to spectra of pure samples of mercuric sulfate and its basic sulfate, Schuetteite, $HgSO_4.2HgO$.

to mercury of above 10-fold produces predominantly mercuric sulfate with the basic Schuetteite, $HgSO_4.2HgO$, increasing as the ratio decreases. With no sulfur in the flame a brown deposit results that is pure HgO. These results are validated by auxiliary x-ray analyses of the deposits. As was seen with alkali deposition, the mercury illustrates a preferential ranking that appears to reflect thermodynamic stabilities. On reaching the surface it will make its favored molecule if possible but whether it be sulfate or oxide the rate of deposition remains the same. As indicated in Fig. 2, deposits of sulfate can be obtained in the hot burned gases of a flame over an extended range of temperatures.

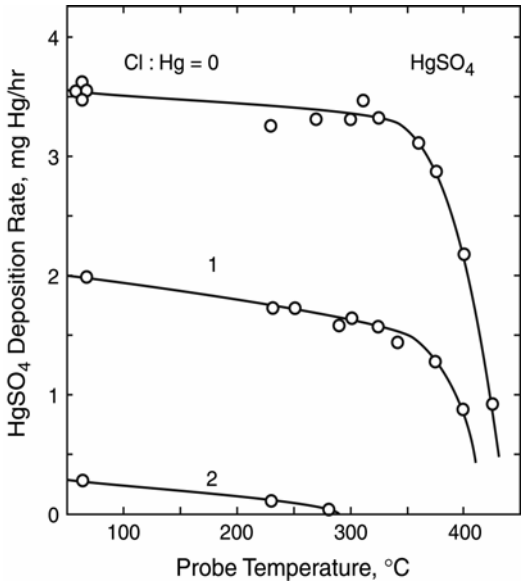

Figure 2. Rates of deposition of $HgSO_4$ as a function of probe temperature and flame chlorine content. Measurements in a fuel lean $C_3H_8/O_2/N_2$; 0.9/5/20 flame 12 ms downstream.

Precise additions of chlorine together with the mercury and sulfur indicate a quantitative reduction of the deposit. Experiments indicate that the chlorine in the flame as HCl vigorously attacks the sulfate deposit converting it to volatile $HgCl_2(g)$ that sublimes back into the gas flows. In normal coal combusters, the levels of impurities generally are S>>Cl>>Hg. As a result, under the right conditions, this heterogeneous conversion will occur naturally. It represents the elusive chemical mechanism missing from models and explains the variability of the amount of $HgCl_2(g)$ observed. Recent analyses

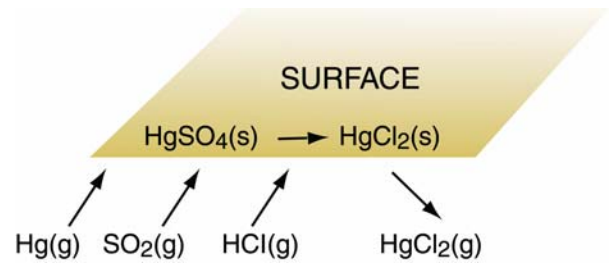

Figure 3. Heterogeneous mechanism whereby gaseous atomic mercury is efficiently converted to gaseous $HgCl_2$.

suggest that the HCl directly ablates $HgCl_2(g)$ from the sulfate and the step through the less stable $HgCl_2(s)$ as indicated does not occur. In this way, the mercury uses the surface as a catalytic means whereby it can satisfy its thermodynamic desire to convert to the stable dihalide.

Flue Gas Measurements and Mercury Control

To confirm the generality of this heterogeneous formation of $HgSO_4$ an internally heated stainless steel probe was positioned downstream in burned gases where mixing had cooled the flows to 200 ^oC or less. Deposits again were obtained however their formation window was narrowed. Temperatures in the range 150-250 ^oC were optimal. Moreover such deposits disappear if chlorine is present in the system. Additionally it is clear that these deposits once formed are stable and are only removed by HCl. They can be converted though to more stable mercury compounds. In other words if a sulfur free system is initially used the deposit is HgO. If a small amount of sulfur is added, this all changes to the basic sulfate and with more sulfur becomes the sulfate. Changes occur up the chain of preferential ranking but once converted the process is irreversible. It is clear that this is a dominant channel and an explanation of the role of fly ash or particle additions. A control method of solely providing adequate surface in the flue gases at the optimal surface temperature and ensuring adequate gas/surface collisions now is recommended[9].

References

(1) Pavlish, J. H.; Sondreal, E. A.; Mann, M. D.; Olson, E. S.; Galbreath, K. C.; Laudal, D. L.; Benson, S. A., *Fuel Process. Technol.* **2003,** 82, 89-165.
(2) Xu, M.; Qiao, Y.; Zheng, C.; Li, L.; Liu, J., *Combust. Flame* **2003**, 132, 208-218.
(3) Fujiwara, N.; Fujita,Y.; Tomura, K.; Moritomi, H.; Tuji, T.; Takasu, S.; Niksa, S., *Fuel* **2002**, 81, 2045-2052.
(4) Laudal, D. L.; Brown, T. D.; Nott, B. R., *Fuel Process. Technol.* **2000**, 65/66, 157-165.
(5) Dunham, G. E.; DeWall, R. A.; Senior, C. L., *Fuel Process. Technol*. **2003**, 82, 197-213.
(6) Steinberg, M.; Schofield, K., *Proc. Combust. Inst.* **1996**, 26, 1835-1843.
(7) Schofield, K., *Combust Flame* **2003**, 133, 147-156.
(8) Steinberg, M.; Schofield, K., *Combust Flame* **2002**, 129, 453-470.
(9) Schofield, K., *U.S. Patent Application No*. 10/429,114, **2003**, May 1.