THE MECHANISM FOR CHEMISORPTION OF ELEMENTAL MERCURY ON ACTIVATED CARBONS IN FLUE GAS

E.S. Olson, J.D. Laumb, S.A. Benson, G.E. Dunham, R.K. Sharma, B.A. Mibeck, S.J. Miller, M.J. Holmes, J.H. Pavlish

Energy & Environmental Research Center, University of North Dakota, Box 9018, Grand Forks, ND 58202-9018

Introduction

Control of mercury emissions from coal-burning power plants has been extensively investigated over the last decade at the Energy & Environmental Research Center (EERC). Injection of fine-powdered activated carbon (AC) into the hot flue gas stream has been successful in removing a large portion of the mercury in the flue gas, even when the mercury is mainly elemental. But high heterogeneous reaction rates of the gas-phase elemental mercury on the carbon sorbent surface may be needed to capture the mercury in the short contact time demanded when the sorbent is quickly removed from the gas stream, such as with electrostatic precipitation of ash and carbon particulates. Elucidating the nature of the interactions between the mercury and the flue gas components on AC surfaces is crucial to the design of carbons with faster kinetics and greater capacities.

Summary of Initial Capacity Test and XPS Results

Initial studies included a large factorial series of tests using powdered ACs that were conducted in a bench-scale system consisting of a thin fixed-bed reactor in gas streams (100° to 150°C) containing 11 to 15 $\mu g/m^3$ of Hg^0 in various simulated flue gas compositions consisting of acidic SO_2, NO_2, and HCl gases plus a base mixture of N_2, O_2, NO, CO_2, and H_2O [1,2]. As a result of these experiments, a number facts emerged that were important to understanding the activating and poisoning effects exhibited by flue gas components and their mixtures on mercury capture. These are summarized in the following brief statements:
1. Either NO_2 or HCl–O_2 is required for effective Hg^0 capture from the gas phase at temperatures of 100° to 150°C.
2. Very little breakthrough occurred when SO_2 was omitted.
3. Increasing SO_2 concentration gives shorter breakthrough times.
4. H_2O is required for breakthrough to occur.
5. Increasing NO_2 concentration gives shorter breakthrough times.
6. Nearly all the Hg emitted after breakthrough is oxidized.
7. Emitted Hg(II) at breakthrough can exceed 100% of inlet Hg.
8. There is a negative temperature effect on capacity.

Thus the chemisorption of Hg is seriously affected by flue component concentrations, especially SO_2.

Based on these capacity data, an initial model was presented [3] that described the chemisorption of Hg^0 in flue gas. Oxidation of Hg^0 to form a bound Hg(II) species occurs with the electrons donated to the carbon and eventually to NO_2 or O_2. The binding site for Hg(II) must be basic in nature, since the Hg(II) is a Lewis acid. Sulfuric acid forms

from SO_2 and requires H_2O and NO_2. At breakthrough, the basic binding sites are completely occupied by acidic S(VI) species, and Hg(II) salts are displaced from the binding sites. Although binding sites are poisoned at breakthrough, the oxidation reaction is unaffected, since nearly 100% oxidation occurs even after complete breakthrough. This fact argues against any explanation for loss of capacity based on pore plugging by species resulting from acid gases, since this would inhibit both reactions. The Hg(II) species that forms or is released after breakthrough is volatilized as $HgCl_2$ or $Hg(NO_3)_2$ [4].

The nature of the mercury–flue gas–sorbent interactions was further elucidated in x-ray photoelectron spectroscopy (XPS) experiments performed with two AC sorbents, Norit FGD and the EERC lignite-derived AC, exposed to various simulated flue gas compositions containing Hg^0 with various levels of SO_2, NO_2, HCl, and H_2O for time periods before and after breakthrough of mercury [5]. Because of the interference caused by silicon, XPS data could not be obtained for the mercury species present in the exposed sorbents. These studies verified that sulfur(VI) (sulfate, bisulfate, sulfonate, or sulfuric acid) is the major sulfur species and increases with exposure time. When NO_2 or H_2O was omitted from the flue gas, less sulfate was accumulated. The XPS data also indicate that two types of chlorine are present: ionic and covalent, and that both chlorine forms disappeared from the sample at breakthrough. That chlorine is present as both chloride ion and covalent (organic) chlorine indicates that the HCl in the flue gas can donate a hydrogen ion to a basic site, as well as add both hydrogen and chlorine to a basic site to form the organochlorine product. The accumulation of chlorine in the absence of SO_2 as well as the disappearance of chlorine after continued exposure in SO_2 is explained by competition of HCl with S(VI) acids. As more S(VI) is generated from SO_2 at the carbon surface, it displaces the HCl, owing to the high volatility of HCl. The competition for the basic carbon site amongst the acids present on the surface implies that Hg(II) also competes, but is eventually displaced by the S(VI), resulting in breakthrough of Hg(II).

The Hg(II) Binding Site Model
A refinement of the binding site model was proposed [6] that offers more detail on the nature of the carbon site and its interaction with flue gases and Hg. This model used the concept of zigzag carbene structures recently proposed for states at the edges of the carbon graphene layers [7]. In the carbene model, the zigzag carbon atom positioned between aromatic rings is hypothesized to be the Lewis base site The zigzag Lewis basic carbene reacts with the Hg(II) species and also with HCl, H_2SO_4, and SO_2 to form carbenium ions that can combine to form the observed organochlorine forms. Sulfinate functionality could also form from SO_2.

The Role of HCl
In tests conducted at relatively high HCl concentrations (50 ppm), the capture of mercury at the start was always very high (less than 5% of inlet concentration), but in very low HCl concentrations such as those obtained when low-Cl coals are burned (1 ppm), an initial breakthrough was observed at about 50%–60% of inlet [8], followed by an increase in capture efficiency to the 5%–10% level. The higher HCl concentration thus eliminated this induction period where poor capture is obtained. It is clear that HCl

is not an oxidizing reagent, since it already is in the most reduced state. This is, therefore, a promotional effect of the HCl on the activity of the carbon in catalyzing the oxidation of mercury. A similar promotional effect of adding aqueous HCl to the sorbent was reported recently by Ghorishi et al. [9].

Oxidation Site Models and Tests
The previously described carbene model for the acid gas interactions, while consistent with breakthrough capacity and spectroscopic data, also sets the basis for the Hg^0 oxidation reaction(s). A variation of this scheme, as shown in Figure 1, explains the promotional effect of HCl. In this oxidation mechanism, the carbenium ion intermediate, formed when protonic acids add to the carbene as described above, is actually the oxidation site for the adsorbed Hg^0. Donation of electrons from the Hg^0 to the carbene forms an organomercury species. A subsequent oxidation step with NO_2 or O_2 will generate the organomercury carbenium ion. Thus HCl or other protonic acids promote the oxidation step by generating the positive carbenium ion oxidation sites, but the reaction site eventually becomes cluttered with sulfuric acid molecules. Thus, at breakthrough, there are still carbenium ions for oxidation of Hg^0, but the reaction is driven toward loss of the more volatile species, $HgCl_2$ and HCl.
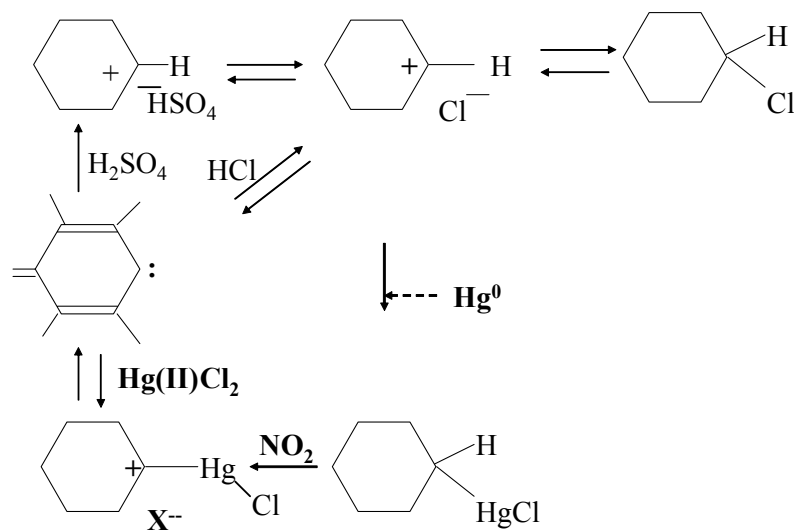

Figure 1. Oxidation Mechanism – Carbenium Ion Oxidant

In an alternative mechanism, a radical carbon chlorine pair is formed either from a radical addition of HCl to a triplet state of the carbene or by homolytic cleavage of the organochlorine intermediate. The chlorine atom could oxidize the Hg^0 to form Hg(I)Cl that could combine with the carbon edge radical to form the organomercury species identical to that formed via carbenium addition. This chlorine atom hypothesis was rejected because radical scavengers fail to prevent Hg oxidation from occurring.

Conclusions
The refinement of the mechanistic model for Hg^0 oxidation and binding is now proposed that offers more detail on the nature of the carbon site and its interaction with flue gases and Hg. This model uses a zigzag carbene edge structure model to explain how the

carbon graphene surface can provide a basic site for which acid gas components compete and how a reactive oxidation site is generated as a result of the acid addition. An alternative mechanism for oxidation involving generation of a chlorine radical was not consistent with the result from addition of a radical scavenger that would have depleted the chlorine atoms.

Acknowledgments

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