THE MECHANISTIC MODEL FOR FLUE GAS–MERCURY INTERACTIONS ON ACTIVATED CARBONS: THE OXIDATION SITE

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Introduction

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 flue gas from coal combustion, even when the mercury is mainly elemental. To minimize the amount of sorbent used, 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. Part of our work has focused elucidating the nature of the interactions between the mercury and the flue gas components on AC surfaces, particularly the ACs derived from Texas (Norit FGD) and from Fort Union lignites (prepared at the Energy & Environmental Research Center [EERC]). This understanding is crucial to developing a model for mercury chemisorption and subsequent design of carbons with faster kinetics and greater capacities.

AC is an effective chemisorbent for mercury in combustion flue gas. 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 μg/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). The results of these experiments showed that NO_2 or HCl–O_2 is required for effective Hg^0 capacity, no breakthrough occurred when SO_2 was omitted, and increasing SO_2 concentration gave shorter breakthrough times. H_2O is also required for breakthrough to occur. Increasing NO_2 concentration gave shorter breakthrough times. The Hg emitted after breakthrough is mostly oxidized and can exceed inlet Hg concentration. Related work showed that Hg emitted after breakthrough in the absence of HCl was $Hg(NO_3)_2$ (3). Thus the chemisorption of Hg is seriously affected by flue gas component concentrations, especially SO_2.

Based on these capacity data, an initial model was presented (4) that described the chemisorption events following adsorption of Hg^0. 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. But following oxidation, the binding site for Hg(II) must be basic in nature, since the Hg(II) is a Lewis acid. At breakthrough, the basic binding sites are completely occupied by acidic species derived from the flue gas, especially those derived from SO_2, and then Hg(II) salts are displaced from the binding sites. As breakthrough occurs, the oxidation reaction decouples from the binding reaction(s), since nearly 100% oxidation occurs even after complete breakthrough, when the binding sites are completely occupied. 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 $Hg(NO_3)_2$.

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 on all the exposed sorbent samples, and the longer the exposure to SO_2, the more sulfate is found in the sample. When NO_2 or H_2O was omitted from the flue gas, less sulfate was accumulated.

Thus adsorbed SO_2 is clearly oxidized on the sorbent surface to sulfur(VI) species in a process facilitated by NO_2 and H_2O, and the sulfur(VI) is the main poison for the basic sites. 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 bisulfate or sulfuric acid. As more bisulfate is generated from SO_2 at the carbon surface, it displaces the HCl, owing to the high volatility of HCl.

Refined Model for the Hg(II) Binding Site

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 (Figure 1). This model uses the concept of zigzag carbene structures recently proposed for states at the edges of the carbon graphene layers (7) rather than oxygen functional groups suggested by other authors. 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 as shown in Figure 1 to form an organomercury carbenium ion and also with HCl, H_2SO_4, and SO_2 to form carbenium ions with associated chloride and sulfate, that can combine to form the observed organochlorine and possibly also ester moieties. Sulfinate functionality could also form from SO_2.

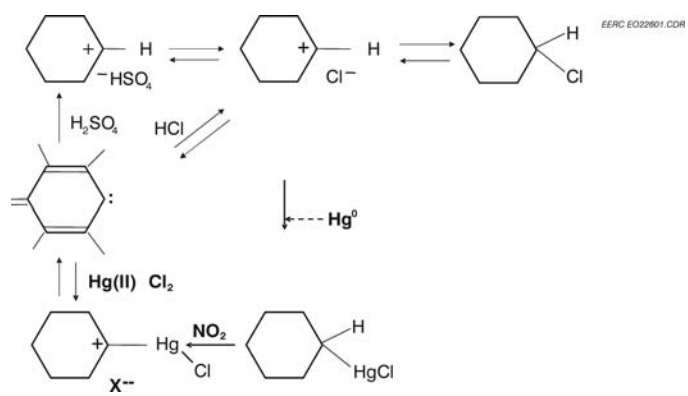

Figure 1. Oxidation mechanism – carbenium ion oxidant.

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 is already 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 the breakthrough capacity and spectroscopic data, also secures the foundation 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 exactly 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, mercury and HCl.

An alternative mechanism involving the same carbene site is depicted in Figure 2. In this model, 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. It should be noted, however, that Hg oxidation occurs perfectly well without HCl, once the sorbent is active.

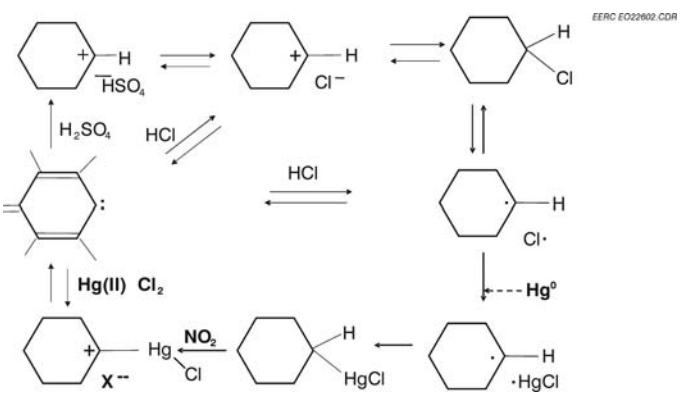

Figure 2. Oxidation mechanism – chlorine atom oxidant.

An experiment was performed to test the hypothesis that chlorine atoms are generated on the carbon surface and are responsible for the accelerated oxidation. An FGD carbon sorbent was pretreated with HCl and then with radical scavengers which should reduce reactivity. The mercury capture results showed that this sorbent oxidized Hg^0 equally as well as a sorbent untreated with radical scavenger.

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.

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