

Survey of Catalysts for Oxidation of Mercury in Flue Gas

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Methods for removing mercury from flue gas have received increased attention because of recent limitations placed on mercury emissions from coal-fired utility boilers by the U. S. Environmental Protection Agency and various states. A promising method for mercury removal is catalytic oxidation of elemental mercury (Hg^0) to oxidized mercury (Hg^{2+}), followed by wet flue gas desulfurization (FGD). FGD cannot remove Hg^0 , but easily removes Hg^{2+} because of its solubility in water. To date, research has focused on three broad catalyst areas: selective catalytic reduction catalysts, carbon-based materials, and metals and metal oxides. We review published results for each type of catalyst and also present a discussion on the possible reaction mechanisms in each case. One of the major sources of uncertainty in understanding catalytic mercury oxidation is a lack of knowledge of the reaction mechanisms and kinetics. Thus, we propose that future research in this area should focus on two major aspects: determining the reaction mechanism and kinetics and searching for more cost-effective catalyst and support materials.

1. Introduction

Coal-fired utility boilers are the largest anthropogenic emitters of mercury in the United States, accounting for approximately one-third of the 150 tons of mercury emitted annually (1, 2). In 2005, the U. S. Environmental Protection Agency (EPA) announced the Clean Air Mercury Rule (CAMR), which permanently caps mercury emissions from coal-fired utility boilers and establishes a mercury cap-and-trade program. CAMR will be implemented in two phases, with a first phase cap of 38 tons in 2010 followed by a final cap of 15 tons in 2018 (3). The final cap requires an approximately 70% reduction from 1999 emission levels. Mercury exists in three forms in coal-derived flue gas: elemental (Hg^0), oxidized (Hg^{2+}), and particle-bound ($\text{Hg}(\text{p})$) (4, 5). During combustion, mercury is liberated from coal as Hg^0 . As the flue gas cools, some of the Hg^0 is oxidized, presumably to HgCl_2 because of the large excess of chlorine present in coal. The extent of mercury oxidation depends upon a number of factors, including combustion characteristics, coal composition (including chlorine content) (6–8), concentrations of other species (i.e., NO_x and SO_2) (9, 10) in the flue gas, and the time–temperature history (11, 12). Both Hg^0 and Hg^{2+} can enter the particulate phase by adsorption onto fly ash particles (13–16).

Hg^{2+} and $\text{Hg}(\text{p})$ are relatively easy to remove from flue gas using typical air pollution control devices (APCD). $\text{Hg}(\text{p})$ is captured, along with fly ash particles, in electrostatic precipitators (ESPs) and/or baghouses. Hg^{2+} is soluble in

water and is therefore removed with high efficiency by wet flue gas desulfurization (FGD) equipment (17). Hg^0 , however, is difficult to capture. It is insoluble in water and is therefore not removed by FGD. Activated carbon injection (ACI) will remove both Hg^0 and Hg^{2+} , and currently this is the best method for removing Hg^0 from flue gas (18).

In addition to the CAMR, the U. S. EPA also enacted the Clean Air Interstate Rule (CAIR), which requires reductions in NO_x and SO_2 emissions in 28 states (19). An expected consequence of CAIR is increased use of wet FGD for SO_2 removal (20). Among the technologies being considered for mercury reduction in coal-fired boilers is thus the combination of a catalyst and a wet scrubber; the catalyst oxidizes Hg^0 to Hg^{2+} , and the oxidized mercury is subsequently absorbed by the scrubber solution. Catalysts capable of significant conversion (>80%) of Hg^0 to Hg^{2+} would have tremendous value because the oxidized mercury can be removed concurrently with acid gases during FGD. Several materials have been proposed as catalysts for oxidation of mercury. These materials include palladium, gold, iridium, platinum, iron, selective catalytic reduction (SCR) catalysts, fly ash, activated carbons, and Thief carbons.

A variety of potential mercury oxidation catalysts have been tested under experimental conditions ranging from laboratory-scale packed beds using simulated flue gas to full-scale tests; the experimental time scales span a similarly large range, with laboratory tests often lasting a few hours and some pilot-scale tests conducted over the course of several months. The testing to date has identified a number of potential catalysts that can be classified among three groups: SCR catalysts, carbon-based catalysts, and metals and metal oxides. Each of these groups of materials has its relative merits and shortcomings, and none has emerged as a clear favorite in terms of either mercury conversion efficiency or economic viability. Thus, research into each of the three catalyst groups remains active.

A near-term goal is to develop mercury control technologies that can achieve 50–70% mercury capture at costs 25–50% less than baseline estimates of \$50 000–\$70 000 per pound of mercury removed (\$/lb Hg removed) (21). Thus, future studies of mercury oxidation catalysts will likely include efforts to identify the most cost-effective catalyst and support materials as well as to optimize operating conditions for each catalyst. We feel that the task of identifying catalysts and supports therefore requires two important aspects: (1) extensive testing of novel materials and supports, including both the continued study of previously identified catalysts and the identification of new catalysts, and (2) a more complete understanding of the reaction mechanism and kinetics. Understanding the surface-catalyzed mercury oxidation mechanism will aid in identifying candidate catalyst materials; knowledge of the reaction kinetics will offer a degree of predictability that will aid in scaling up laboratory experiments to pilot or larger scale.

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We feel it is prudent to review the available catalyst data and discuss the potential reaction mechanisms. Herein, we review previous results for each of the three classes of catalysts: SCR, carbon-based, and metals and metal oxides. Additionally, several mechanisms of mercury oxidation are proposed; where appropriate, these mechanisms are discussed in relation to the available catalyst data.

2. Mercury Oxidation Mechanisms

Elemental mercury can undergo homogeneous or heterogeneous oxidation. Proposed catalyst materials are believed to facilitate heterogeneous oxidation, which is typically faster than homogeneous oxidation. Regardless of the dominant mechanism for mercury oxidation, it is well-known that the transformation from Hg^0 to Hg^{2+} in flue gas is kinetically limited. For temperatures below ~ 450 °C, at equilibrium, nearly all mercury should exist as Hg^{2+} (11, 12). Due to the excess of chlorine-containing species (HCl and Cl_2), HgCl_2 is assumed to be the dominant form of Hg^{2+} . However, mercuric oxide (22), nitrate (23–25), and sulfate (22, 26) may also be formed.

In real flue gas, the fraction of oxidized mercury ranges from nearly 0% to 100%, depending upon a number of factors, including coal type and the time–temperature history of the flue gas. It is therefore obvious that flue gas does not reach thermodynamic equilibrium; thus understanding the kinetics and mechanism of mercury oxidation are of tremendous importance. Significant uncertainty exists for both methods of oxidation; the following sections discuss proposed reaction mechanisms for both homogeneous and heterogeneous oxidation.

2.1. Homogeneous Oxidation. Gas-phase Hg^0 can react with several gas-phase oxidants, including Cl_2 (27, 28), HCl (28), chlorine radicals (29), and ozone (30). Sliger et al. (29) proposed that Hg^0 oxidation occurs primarily via reaction with chlorine radicals between 400 and 700 °C. In this temperature range there is an abundance, though not necessarily a large excess, of chlorine radicals. The $\text{Hg} + \text{Cl}$ reaction has a low energy barrier and occurs near the collision limit at room temperature; reaction with Cl is therefore much faster than $\text{Hg} + \text{HCl}$, which has a high energy barrier (31) and is unfavorable at typical operating temperatures. The reaction proceeds through an intermediate product, HgCl .

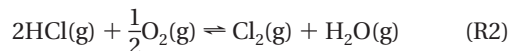


HgCl is subsequently oxidized by HCl, Cl_2 , or chlorine radicals. The results of Sliger et al. (29) agree with observations that the extent of mercury oxidation (expressed as the fraction of Hg^{2+}) increases with HCl concentration and coal-Cl content. (6–8)

The Sliger et al. (29) mechanism, however, cannot explain the extent of mercury oxidation in all cases. Notably, Niksa and Fujiwara (32) observed that coal-Cl is not the determining factor in the extent of mercury oxidation for pilot-scale coal combustion data. Thus, other oxidation pathways must be available.

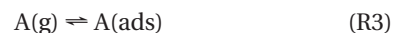
Wang and Anthony (33) considered the reaction of Hg^0 with Cl_2 , comparing data from two previous studies (27, 28). Their analysis revealed that the homogeneous reaction $\text{Hg} + \text{Cl}_2$ is too slow to generate significant Hg^0 conversion and that the large discrepancies between published rate constants for the reaction were in fact the result of heterogeneous mercury oxidation occurring on the reactor walls. At typical flue gas temperatures, the heterogeneous oxidation of mercury dominates; this assertion is consistent with observations that, in addition to coal-Cl, the extent of mercury oxidation is affected by loss on ignition (34) and the presence of a baghouse or fabric filter (6, 35).

2.2. Heterogeneous Reaction. Several mechanisms have been proposed for heterogeneous mercury oxidation. The Deacon process (36) for generating Cl_2 from HCl is known to be catalyzed by metal oxides, which are present in flue gas, at high temperatures (300–400 °C).



In the presence of an appropriate catalyst, the Deacon process could convert the large concentrations of HCl in flue gas to Cl_2 , thereby enhancing mercury oxidation. However, the equilibrium concentration of Cl_2 is small ($\sim 1\%$ of the HCl concentration) (37), and as noted above, the reaction between Cl_2 and Hg^0 is slow. A modeling study by Niksa and Fujiwara (38) indicated that gas-phase reactions alone are not enough to account for observed extents of mercury oxidation. Therefore, another mechanism is likely responsible for heterogeneous mercury oxidation.

The bimolecular reaction between two species adsorbed to a surface can be described by a Langmuir–Hinshelwood mechanism (39).



For the case of mercury oxidation, A is Hg^0 and B is a chlorine species, likely HCl. For this mechanism, the rate of reaction is dependent on the concentrations (or partial pressures, p_i) of reactants A and B, the adsorption equilibrium constant (K_i), and the rate constant for the surface reaction (k_{surf}).

Elemental mercury adsorbs to activated carbon and other sorbents (40) and is believed to adsorb to carbon in fly ash (13, 14, 16, 34, 41). HCl can also adsorb to carbon sites (42, 43). Thus, the Langmuir–Hinshelwood mechanism is plausible for catalyzing HgCl_2 formation in the presence of substrates that can adsorb both Hg^0 and HCl. However, there is only indirect evidence with which to test this mechanism. Several studies have noted a correlation between HCl concentration and the extent of mercury oxidation, even for large excesses of HCl. (6–9, 29) Additionally, the presence of HCl sorbents, such as CaO, reduces the extent of oxidation (44, 45).

SO_2 competes with HCl for carbon sites on activated carbon and fly ash sorbents (43). High concentrations of SO_2 have been observed to inhibit mercury oxidation in simulated flue gases (9) perhaps because of this competition for sites. However, in some cases, SO_2 appears to enhance oxidation (46) or have no effect (45, 47).

Schofield proposed a mechanism for the oxidation of Hg^0 to HgSO_4 (48, 49). In a simulated flue gas containing SO_2 and Hg^0 , HgSO_4 was observed to spontaneously deposit on stainless steel or platinum surfaces. The reaction was observed to be first-order in mercury and zero-order in SO_2 . In the absence of SO_2 , HgO was observed to deposit. Adding HCl to the flame after deposit formation led to the removal of the deposit via reaction to HgCl_2 followed by sublimation. The work asserts that in flue gases HgCl_2 formation is preceded by surface reaction to form either HgO or HgSO_4 , both of which are efficiently removed from the surface via reaction with HCl. Additionally, Granite and Pennline observed deposition of mercuric oxide and mercurous sulfate during photochemical oxidation of mercury in the absence of HCl (22).

Olson et al. (23) and Dunham et al. (24) proposed a mechanism to describe the effects of SO_2 and NO_2 . Mercury

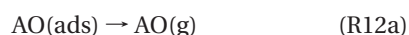
and NO₂ can react on a carbon surface to form mercuric nitrate (Hg(NO₃)₂). In this reaction, NO₂ acts as an electron sink. In the presence of SO₂, some of the carbon surface is converted to a sulfate form, and direct formation of Hg(NO₃)₂ does not occur. Instead, mercury bisulfate (Hg(HSO₄)₂) forms on the surface, with NO₂ still acting as the electron sink. The mercury bisulfate can react with NO₃⁻ to form mercuric nitrate, which has been tentatively identified in simulated flue gas exposed to a MnO₂ sorbent (25).

Niksa et al. (32, 38) assert that while HCl adsorbs to surfaces, Hg⁰ does not (or is only weakly adsorbed). The researchers propose that mercury oxidation occurs via an Eley–Rideal mechanism, where adsorbed HCl reacts with gas-phase (or weakly adsorbed) Hg⁰ (R7–R8). However, it is known that Hg⁰ adsorbs to various sorbents. Because HCl often has high gas-phase concentrations in flue gas, an Eley–Rideal reaction between adsorbed Hg⁰ and gas-phase HCl is also a logical possibility (i.e., species A in R7 could be either Hg⁰ or HCl).



Eley–Rideal and Langmuir–Hinshelwood mechanisms can be inferred by surface analysis of used catalysts to confirm adsorption of specific reactants such as mercury and HCl. Additionally, pre-exposure of the catalyst to an oxidant such as HCl, followed by mercury oxidation in the absence of gas-phase HCl, would suggest either a Langmuir–Hinshelwood reaction or an Eley–Rideal reaction with HCl as the adsorbed species. A Langmuir–Hinshelwood mechanism can also be identified via chemical kinetics, though the relative adsorption behavior of the reacting species may complicate analysis. In some cases, a Langmuir–Hinshelwood mechanism is characterized by a reaction that is first-order in each of the reactants (i.e., Hg⁰ and HCl). However, if one species saturates the surface, then the reaction order with respect to the saturating species can be -1 (39).

Granite et al. (40) proposed that mercury oxidation could occur via a Mars–Maessen mechanism. In this mechanism, adsorbed Hg⁰ would react with a lattice oxidant (either O or Cl) that is replenished from the gas phase. This mechanism may be consistent with the observation of enhanced Hg⁰ sorption to halogen-promoted sorbents and fly ashes (40, 50). Reactions R9–R12 show the Mars–Maessen mechanism for the reaction of an adsorbed species (Hg⁰) with lattice oxygen. The Mars–Maessen mechanism can be confirmed by the observation of mercury oxidation in the absence of gas-phase oxygen or chlorine, respectively (through variations of R10).



To date, none of the above mechanisms has been verified as the dominant mechanism for catalytic mercury oxidation. Significantly, this shortcoming hinders the ability to predict the extent of mercury oxidation affected by various catalysts. Other significant areas of uncertainty include:

1. Is Hg⁰ chemically (51) or physically adsorbed to sorbent and catalyst surfaces?

2. What are the intermediate products, if any? Homogeneous mechanisms assume that Hg⁰ oxidation proceeds via HgCl, (29) but is this true for heterogeneous oxidation (48, 49)?

3. What is the nature of the final Hg²⁺ species? HgCl₂ is assumed, but many current measurement techniques can only differentiate between oxidized and elemental mercury.

4. What are the effects of other gaseous components such as CO, NO_x, and SO₂? Specifically, how do these species affect the reaction mechanism?

Further research, especially research focusing on the fundamental aspects of heterogeneous Hg⁰ oxidation, is required to answer these questions and improve our understanding of this reaction.

3. Proposed Catalysts: Previous Studies

Oxidation catalysts studied to date fall into one of three groups: SCR catalysts, carbon-based catalysts, and metals and metal oxides. The following sections discuss results obtained with each group of catalysts. The results presented here include laboratory investigations using simulated flue gas as well as pilot-scale and full-scale tests using real flue gas.

3.1. Selective Catalytic Reduction Catalysts. Selective catalytic reduction (SCR) catalysts are employed to reduce NO_x concentration in flue gas. The catalyst is typically composed of vanadium pentoxide (V₂O₅)/tungsten trioxide (WO₃) supported on titanium dioxide (TiO₂). During operation, NO is reduced by NH₃, which is injected upstream of the SCR, at temperatures above 300 °C. NH₃ strongly adsorbs to the V₂O₅ sites, and NO reacts either from the gas phase or as a weakly adsorbed species (Eley–Rideal mechanism) (38). The efficacy of SCR for oxidizing mercury has been tested at the laboratory (52–57), pilot (58–60), and full scale (61–64) for a variety of different HCl concentrations, NO concentrations, NH₃/NO ratios, temperatures, and coal types.

Laboratory-scale tests verified that SCR catalysts oxidize Hg⁰ to Hg²⁺, particularly in the presence of HCl. Several studies observed a direct link between HCl concentration in a simulated flue gas and the extent of mercury oxidation (53–57). Eswaran and Stenger (57) also observed mercury oxidation in the presence of H₂SO₄, presumably to HgSO₄. Significant conversion of Hg⁰ to Hg²⁺, as high as 95% (53), was observed in simulated flue gas containing HCl for temperatures above 300 °C.

In a pilot-scale study, Laudal et al. (58) observed a negative correlation between the Hg⁰ concentration at the SCR outlet and the concentrations of chlorine (i.e., HCl) and sulfur (i.e., SO₂) in the flue gas at approximately 340 °C, consistent with laboratory results. In a separate pilot-scale study using bituminous coal, the extent of mercury oxidation over a cold-side SCR catalyst fell from ~70% to <30% during a 10 month test, presumably because of ash buildup on the catalyst surface (60).

Several studies (61–64) have investigated the effect of SCR catalysts on mercury oxidation in full-scale power plants. Machalek et al. (62) observed that the extent of mercury oxidation was reduced from 40% down to 5% as the gas space velocity increased from 3000 to 7800 h⁻¹ for subbituminous-derived flue gas. The study also observed that increasing the NH₃ concentration reduced the extent of mercury oxidation and seemed to deactivate the catalyst.

Senior (63) reported the effectiveness of several commercial SCR catalysts for mercury oxidation in a power plant burning a mixture of subbituminous (87%) and bituminous (13%) coals. The SCR was placed downstream of the economizer and was therefore exposed to fly ash, which is typically not included in laboratory-generated simulated flue gases. Under typical operating conditions (315–345 °C), Hg⁰ conversions as high as 60–80% were observed. Consistent

with Machalek et al. (62), increasing the NH₃/NO ratio (higher NH₃ concentration) decreased the extent of mercury oxidation; the extent of Hg⁰ oxidation also decreased when the HCl concentration decreased, consistent with laboratory results. (53–57)

Benson et al. (64) tested SCR performance at power plants burning subbituminous and lignite coals. The study observed that alkali and alkaline species can reduce the effectiveness of SCR catalysts for mercury oxidation by depositing on the catalyst and reacting with acidic sites on the catalyst surface. SCR catalysts were tested at three plants; in all three cases, ash blocked both the entrance and the pores of the catalyst, thereby severely reducing both Hg⁰ and NO conversion.

The mechanism for mercury oxidation on SCR catalysts is unknown, but we can propose several possibilities. According to the mechanism presented by Niksa and Fujiwara (38), the oxidation of Hg⁰ across an SCR catalyst occurs via a similar reaction as NO reduction—HCl present in the flue gas adsorbs to the V₂O₅ sites and reacts with either gas-phase or weakly bound Hg⁰. NH₃ and HCl compete for sites on the catalyst surface, though when both are present NH₃ is the dominant adsorbed species. The SCR catalyst can therefore be envisioned as having two distinct “zones”. In the first zone (near the entrance to the SCR) NH₃ is present; it is adsorbed to the catalyst surface and reduces NO. When the NH₃ is exhausted, HCl becomes the dominant adsorbed species, and mercury oxidation takes place.

The Niksa and Fujiwara (38) mechanism can explain the observation that the extent of mercury oxidation decreases for larger NH₃/NO ratios (62, 63); however, it does not account for the adsorption of Hg⁰ to the catalyst surface. Hocquel (55) observed that Hg⁰ adsorbs to the catalyst; this phenomenon was also observed by Eswaran and Stenger (57). Additionally, both laboratory- and full-scale studies noted that increasing the NH₃ concentration caused Hg⁰ to desorb from the catalyst surface (53, 63). Senior recently proposed a model for Hg⁰ oxidation across SCR catalysts (65). The model assumes an Eley–Rideal reaction between adsorbed Hg⁰ and gas-phase HCl and that mercury adsorption is in competition with NH₃ adsorption. The model accurately predicts results from both laboratory-scale experiments using a simulated flue gas and pilot-scale experiments using slipstreams of real flue gas and accounts for the effects of temperature, space velocity, HCl concentration, and catalyst design (plate or monolith). The model also reproduces the expected inverse relationship between the NH₃/NO ratio and the extent of Hg⁰ oxidation.

Hocquel proposed that NH₃, HCl, and Hg⁰ compete for active sites on the catalyst surface. Mercury oxidation therefore could occur between adsorbed Hg⁰ and HCl adsorbed at an adjacent site via a Langmuir–Hinshelwood mechanism. In this case, the competitive adsorption between NH₃, Hg⁰, and HCl could explain both the decrease in mercury conversion and the desorption of Hg⁰ from the catalyst surface when the NH₃ concentration increases.

Gutberlet et al. (52) observed the production of Cl₂ across SCR catalysts; thus, the Deacon process exists as a third possible reaction mechanism for mercury oxidation. At this point, it is impossible, given the available data, to determine the reaction mechanism. Further research is required to probe the fundamental nature of this reaction.

3.2. Carbon-Based Catalysts. Activated carbon injection (ACI) is an established method for removing both Hg⁰ and Hg²⁺ from combustion flue gas (40, 41, 66, 67). Activated carbons are general sorbents and can remove a number of different species from flue gas. For example, in addition to removing mercury, carbon sorbents can adsorb NO (68, 69), SO₂ (68–72), and HCl (42, 43). The presence of adsorbed Hg⁰ and/or HCl opens the possibility for the heterogeneous oxidation of mercury and therefore the use of carbon-

containing materials as mercury oxidation catalysts. In fact, a number of studies have shown that Hg⁰ will also adsorb to the carbon content of fly ash (13, 14, 16, 34, 41) and that the extent of mercury oxidation in flue gas depends upon the amount of unburned carbon (UBC) present in fly ash (32, 34, 73).

To date, most of the research in carbon-based catalysts has focused on fly ash, and this bias is likely coincidental. To remove 90% of Hg⁰ from a flue gas stream containing 10 μg m⁻³ Hg⁰ with ACI, carbon to mercury (C/Hg) mass ratios of 3000:1 and 18 000:1, respectively, are required for 4 and 10 μm particles (18). Thus, experiments testing the adsorption capacity and characteristics of activated carbons typically use very large C/Hg ratios. Mercury oxidation may occur in these experiments, but (1) measuring mercury oxidation is not the goal, and (2) the large excess of activated carbon can also adsorb HgCl₂, making determining the extent of oxidation difficult.

Mercury oxidation on fly ash particles is believed to take place at carbon sites (51) in the ash, hence the relationship between UBC—sometimes noted as loss on ignition (LOI), which is analogous but often overestimates the carbon content of fly ash (74–76)—and the extent of mercury oxidation (32, 34, 73). While the basic premise of the catalytic effect of fly ash seems simple—surface reaction to form HgCl₂—there are many competing factors in play. Galbreath and Zygarlicke (7) observed that in the presence of fly ash increasing the concentration of HCl in simulated flue gas caused an increase in Hg²⁺. Kellie et al. (77) observed that higher coal-Cl, which generates higher HCl concentrations in flue gas, favors greater formation of Hg²⁺.

Laudal et al. (9) observed a significant interaction between fly ash and NO_x, perhaps controlled by the NO/NO₂ ratio. NO₂ can heterogeneously oxidize Hg⁰ (10), though this reaction is often considered of minor importance compared to chlorination. Norton et al. (46) observed that, in the presence of fly ash, NO₂ enhances the extent of mercury oxidation, while NO inhibits oxidation. At this time the mechanisms describing the NO and NO₂ effects are unknown.

The role of SO₂ is unclear. Laudal et al. (9) noted that SO₂ can inhibit Hg⁰ oxidation. Serre and Silcox (14) observed that SO₂ can inhibit Hg⁰ uptake by fly ash particles; less mercury uptake may lead to less oxidation. Norton et al. (46) made a contradicting observation, reporting that SO₂ increases the extent of mercury oxidation. Kellie et al. (77) observed that higher coal-S (which manifests itself as SO₂) correlates with a greater fraction of Hg²⁺ in flue gas. Certainly, more research is required to fully understand the impact of NO_x and SO₂ on Hg⁰ oxidation in flue gas.

Hargrove et al. (6) tested several fly ashes in a fixed bed at ~150 °C. Several bituminous and subbituminous fly ashes converted 20–50% of the Hg⁰ in a simulated flue gas to Hg²⁺. Lignite-derived fly ashes exhibited less catalytic ability, and two out of the three lignite ashes tested oxidized less than 10% of the incident Hg⁰.

Several different fly ashes and carbon catalysts were exposed to flue gas from lignite (78), subbituminous (79), and bituminous (80) coals at ~150 °C with variable results. In the presence of lignite-derived flue gas, fly ash and carbon catalyst mercury conversion fell from 100% to 0% after 18 weeks of exposure (78). In the presence of subbituminous-derived flue gas, one carbon catalyst deactivated completely within 2000 h (83 days) of operation. Another carbon catalyst fell from converting 100% of the incident Hg⁰ to ~80% (79); during another test in the presence of bituminous flue gas, the same catalyst maintained >80% mercury oxidation over the course of 2 months (60).

An alternative to fly ash is Thief carbon. Thief carbon is partially combusted coal drawn from the furnace after a short residence time. It has a high percentage of carbon (30–50

wt %) and is an effective Hg⁰ sorbent (81). The high content of UBC also gives Thief carbon catalytic properties; testing of Thief carbon in a packed bed showed that it oxidized 75% of the Hg⁰ in a bench-scale slipstream of flue gas at ~140 °C (82).

The reaction mechanism for mercury oxidation on fly ash is unknown. Because Hg⁰ is known to adsorb to the UBC in fly ash (13, 14, 16, 34, 41), logical possibilities include a Langmuir–Hinshelwood reaction between adsorbed Hg⁰ and HCl or an Eley–Rideal reaction between adsorbed Hg⁰ and gas-phase HCl. Fly ash also contains a wide array of metal oxides and chlorides. Therefore, a Mars–Maessen reaction is also possible. The adsorption of Hg⁰ to fly ash is highly temperature-dependent (13); it is therefore likely that the Hg⁰ is physically adsorbed to the surface. However, Olson et al. (51) propose that Hg⁰ is chemically adsorbed to the fly ash and that the observed temperature dependence is the result of a physisorbed pre-equilibrium step for binding Hg⁰ to the surface. Regardless of whether the mercury is physically or chemically bound to the surface, evidence suggests that the oxidation reaction includes adsorbed Hg⁰.

3.3. Metal and Metal Oxide Catalysts. In addition to V₂O₅ present in SCR catalysts, a number of other metals and metal oxides have been investigated as potential mercury oxidation catalysts. As with the SCR and carbon-based catalysts presented above, the reaction mechanisms for the metal and metal oxide catalysts presented here are unknown; often the mechanism is not even postulated. A simple and logical assumption is that the possible reaction mechanisms noted above—Langmuir–Hinshelwood, Eley–Rideal (with either Hg⁰ or HCl as the adsorbed species), Mars–Maessen, and the Deacon process—exist as possibilities for these catalysts as well.

Iron and its oxides may catalyze Hg⁰ oxidation (18). Dunham et al. (15) observed that the extent of mercury oxidation in the presence of fly ash increased with the magnetite (Fe₃O₄) content of the ash at 120 and 180 °C. Ghorishi et al. (45) exposed simulated flue gas containing HCl to model fly ashes in a fixed bed reactor and found that ash containing Fe₂O₃ achieved 90% oxidation of the incident Hg⁰ at 250 °C. Removing Fe₂O₃ from the model ash resulted in only a 10% conversion of Hg⁰ to Hg²⁺, suggesting that Fe₂O₃ catalyzed Hg⁰ oxidation in the Fe-containing ash. Galbreath et al. (10) injected α-Fe₂O₃ and γ-Fe₂O₃ into flue gas containing fly ash. Injection of α-Fe₂O₃ did not change mercury speciation in the flue gas. Upon being coated onto baghouse filters, γ-Fe₂O₃ increased the extent of mercury oxidation. These results suggest either that the catalytic effect of Fe₂O₃ is limited to γ-Fe₂O₃ or that the catalytic effect observed by Dunham et al. (15) results from the mixture of species present in fly ash. Simply injecting Fe₂O₃ into flue gas may not mimic the complexity, and therefore the catalytic effect, of Fe₂O₃ present in fly ash.

Iron catalysts have been tested at both laboratory and pilot scale. Hargrove et al. (6) observed less than 50% Hg⁰ oxidation in lab tests of an iron catalyst held in a fixed bed at ~150 °C. Injection of the same catalyst into a pilot-scale flue gas stream (injection occurred between an ESP and baghouse at ~150 °C) achieved 10–60% oxidation. A cold-side iron catalyst tested by URS Corporation achieved ~30% mercury oxidation in subbituminous-derived (79) flue gas and 90% oxidation in bituminous-derived (80) flue gas during short-term (3–9 days) testing. The catalyst lost activity rapidly, however, and Hg⁰ conversion dropped to ~40% after 2000 h (~83 days) of use. Two other sources (82, 83) note that iron and iron compounds present in stainless steel might make it an effective catalyst. The use of stainless steel is intriguing because of its high corrosion resistance; however, laboratory-scale testing of an Fe/Cr catalyst proved it ineffective at oxidizing mercury in simulated flue gas at ~150 °C (78).

Noble metals, including copper, gold, silver, and palladium, have been tested as potential mercury oxidation catalysts. Ghorishi et al. (45) prepared a model fly ash containing CuO that oxidized >90% of the Hg⁰ present in simulated flue gas containing HCl at 250 °C; removing the CuO resulted in only 10% oxidation. The same study found that CuCl, present in a model fly ash, was reactive enough to oxidize Hg⁰ even in the absence of gas-phase HCl; this may suggest a Mars–Maessen reaction. Meischen and Van Pelt (83) proposed gold, silver, platinum, copper, and mixtures of these metals as potential catalysts; a 46 h test of a gold catalyst achieved >95% oxidation of the Hg⁰ present in a simulated flue gas at low temperature (70 °C). Zhao et al. recently reported 40–60% Hg⁰ oxidation across a gold catalyst in the presence of Cl₂ at 175–225 °C (47). In contrast to the results of Meischen and Van Pelt (83), Zhao et al. observed that the presence of HCl reduced Hg⁰ oxidation relative to Cl₂ alone (47).

Initial studies of palladium catalysts showed less than 30% mercury oxidation at ~150 °C (6). Several tests of cold-side palladium catalysts at sites burning lignite (78), subbituminous (79), and bituminous (80) coals have shown >90% conversion of Hg⁰ to Hg²⁺ for short (3–9 day) tests. During a 10 month test, the palladium catalyst maintained a high extent of mercury oxidation, falling from an initial value of >90% to approximately 80% at the end of the test (60). Even though the catalyst was located downstream of an ESP, fly ash buildup on the catalyst was a problem. Initial tests showed a sharp decline in catalyst activity due to ash buildup on the surface; the problem was alleviated by installing sonic horns (60). The palladium catalyst can also be regenerated to nearly new performance by purging with either N₂ or CO₂ (80). Because of its high activity over long times and its ability to be regenerated, palladium is a very promising catalyst candidate.

Other proposed catalyst species include iridium and manganese. MnO₂ may be useful as a mercury catalyst (18). Tests with iridium and iridium/platinum catalysts also show promise (82).

A novel catalytic method involves the use of TiO₂ and UV radiation (84–88). Under dark conditions, Hg⁰ does not adsorb to the inorganic fraction of fly ash, including TiO₂ (13). In the presence of UV light, Hg⁰ and water react on the surface to form a TiO₂·HgO complex (87, 88). This reaction is first-order in Hg⁰ concentration and is capable of removing 99% of Hg⁰ at low temperature (<80 °C) (85). However, at temperatures above 110 °C, the extent of oxidation begins to decrease because of mercury desorption from the catalyst surface (87).

4. Potential Application and Effectiveness of Proposed Catalysts

4.1. SCR Catalysts. Mercury oxidation across existing SCR catalysts (or SCR newly installed as a NO_x control measure), followed by FGD removal, is an example of co-benefit mercury reduction resulting from NO_x and SO₂ controls imposed by the CAIR (19). SCR catalysts are mostly placed upstream of particulate control devices and are therefore exposed to high concentrations of fly ash; this was the case in the lignite-fired power plant studied by Benson et al. (64) SCR catalysts typically operate at temperatures above 300 °C; the high temperature may limit the extent of mercury oxidation because of increased desorption of certain adsorbed species from the catalyst surface. In one test an SCR catalyst was installed specifically for mercury removal; the catalyst was placed downstream of the particulate control device and operated at lower temperatures (~150 °C) than the upstream SCR for NO_x removal (60).

The extent of mercury conversion across SCR catalysts appears to be highly variable. At the laboratory scale, SCR

catalysts oxidized >95% of Hg⁰ from a simulated flue gas (53). SCR performance in the presence of real flue gas, however, was severely reduced. Benson et al. (64) observed essentially no Hg⁰ oxidation in the presence of lignite-derived flue gas at 350–360 °C. Short-term tests in the presence of a mixed subbituminous/bituminous flue gas showed a relatively high extent of mercury oxidation (60–80%) across an SCR catalyst over a period of several days at 315–345 °C (63); however the catalyst rapidly lost activity during a 10 month test at ~150 °C, with the extent of mercury oxidation falling from an initial 70% to <30% (60). A factor in the long-term test may have been ash buildup on the catalyst surface; Benson et al. (64) observed significant catalyst plugging by ash, which led to reduced conversion of both NO_x and Hg⁰.

The current evidence suggests that SCR catalysts, if kept clean from ash plugging, can provide additional mercury oxidation, especially for bituminous coals. The extent of oxidation is uncertain and may change temporally, as shown during the 10 month test (60). Installation of an SCR catalyst specifically for the purpose of mercury oxidation (i.e., downstream of the particulate control device) does not appear to be an economical choice, as better mercury conversion can be achieved with cheaper carbon-based catalysts (60).

4.2. Carbon-Based Catalysts. Many laboratory studies of different catalysts, including carbon-based catalysts and fly ash, have relied on packed beds. At full scale, these catalysts are likely to take commercial forms—for example, fly ash can be deposited onto commercially available inert (i.e., alumina) supports (60). Additionally, fly ash (6) and Thief carbons (81) can be injected into ductwork either upstream of the particulate control device or in an Electric Power Research Institute (EPRI) COHPAC configuration, between an ESP and a baghouse. The COHPAC configuration achieves high extents of mercury removal when used for ACI because (1) there is greater contact between the sorbent and the gas-phase mercury downstream of the ESP, which removes 99% of the fly ash, and (2) the carbon that builds up on the baghouse filters increases the contact time between the mercury and carbon, thereby enhancing Hg⁰ oxidation (6, 35). The COHPAC configuration also allows the fly ash and injected catalyst or sorbent to be treated separately; fly ash is primarily collected by the ESP, and the injected species is primarily collected in the baghouse.

Fly ash and Thief carbon may offer an inexpensive alternative to metal or metal oxide catalysts; each can be drawn directly from the existing process and used without pretreatment. Fixed bed studies using a subbituminous fly ash showed >80% conversion of Hg⁰ to Hg²⁺ for over 3000 h of exposure (79). The same catalyst, however, lost roughly half of its effectiveness over the course of 7 months (60). The Thief technology is in its infancy. Thief carbons have not been subjected to long-term testing at this time, and therefore their long-term effectiveness remains unknown. Both fly ash and Thief carbons can also be regenerated by heating in the presence of N₂ or CO₂ (79, 80, 82); regeneration of fly ash can return catalytic activity to near-new levels (79, 80).

Carbon catalysts can also achieve high conversion (>80%) of Hg⁰ over extended periods of time (2 months) (60). These catalysts can also be regenerated to near-new performance by heating and purging with N₂ or CO₂.

Detailed economic analyses for carbon-based catalysts have not been conducted. Given the relatively inexpensive nature of the catalyst materials, carbon-based catalysts may be a cheaper option for mercury removal than ACI/COHPAC (60). However, more long-term tests are required to determine if carbon-based catalysts offer significant savings over ACI.

4.3. Metal and Metal Oxide Catalysts. Full-scale implementation of metal or metal oxide catalysts will likely involve depositing the catalytic material on a commercially available substrate, such as an alumina honeycomb (60, 80). Unlike

the SCR catalyst, which is already optimized for NO_x removal, using commercial materials will allow for the development of catalysts optimized for mercury removal. The catalyst bed could be placed downstream of the particulate control device ($T \approx 150$ °C) to limit exposure to fly ash, which can plug and/or deactivate the catalyst. Palladium has received the most extensive testing of the metal and metal oxide catalysts (6, 60, 79, 80) and has performed well (>80% oxidation) over periods as long as 10 months. Similar long-term behavior may be expected from other metal catalysts, including gold, silver, copper, and iridium, but further testing is required to verify this assumption.

The cost of precious metals should not prove prohibitive for their use in mercury oxidation for two reasons. First, metal catalysts can be effective even at low mass loading. A mass loading of 1% iridium catalyst (99% alumina) was sufficient to oxidize 75% of Hg⁰ from a simulated flue gas at ~140 °C (82). Second, the catalyst can be regenerated by heating to high temperature (370 °C) and purging with either N₂ or CO₂ (60, 79, 80, 82). Due to their high conversion of Hg⁰ to Hg²⁺ and their ability to be regenerated, metal catalysts, notably palladium, offer a cost-effective method to catalytic mercury oxidation. Preliminary economic analysis shows that palladium catalysts (coupled with FGD) offer a 62% cost savings over ACI/COHPAC for an overall Hg removal of 80% and a 9% savings for Hg removal of 90% (80). Certainly, catalysts other than those noted here may also be of value, but determining their potential usefulness will require extensive testing.

5. Avenues for Future Research

5.1. Reaction Mechanism. As detailed above, the mechanism and kinetics for mercury oxidation are highly uncertain. This lack of understanding presents a severe limitation in predicting the extent of oxidation achieved over different catalysts. In fact, many of the longer-term pilot- and full-scale studies referenced above treat the catalyst as a “black box”; this is due in large part to the lack of knowledge concerning the reaction mechanism and kinetics. Elucidating the oxidation pathway will allow for at least a limited ability to predict the extent of oxidation for a given inlet Hg⁰ concentration, catalyst mass and surface area, flow conditions, and concentrations of co-reactants such as NO_x and SO₂.

Mechanistic investigations will most likely require laboratory-scale testing using a simulated flue gas. Past studies (including many of the references in this article) have shown that the complexity of real flue gas often produces results that are significantly different from experiments using a simulated flue gas. Future researchers must be aware of this fact; however, the complexity of real flue gas may prevent elucidation of the reaction mechanism. The use of simulated flue gas allows for the investigation of the effects of specific species (i.e., HCl); subtleties of individual constituent effects may be obscured by the complex mixture present in real flue gas.

A potential complication in the study of the reaction mechanism is the difficulty in reaching steady-state conditions in small-scale laboratory or pilot-scale experiments. Recent experiments at the National Energy Technology Laboratory (NETL) using carbon-based catalysts have illustrated the difficulty in reaching steady state in laboratory-scale packed bed reactors when the catalyst strongly adsorbs mercury (82). Laboratory experiments must also be designed to separate the effects of mass transfer and chemical reaction. In some cases, the adsorption of mercury onto the catalyst surface may be mass-transfer-controlled (65).

Surface chlorine is likely to be involved in the oxidation of elemental mercury; therefore the rate of catalytic oxidation may be correlated with the free energy of formation of the

catalyst chloride (for example, in a Mars–Maessen reaction). Recent work has focused on the use of sorbents impregnated with other halogens, notably bromine and to a lesser extent iodine. Less is known about the heterogeneous mechanism by which bromine oxidizes mercury, and the products, perhaps including mercuric bromide, are unknown.

It is known that carbons and the precious metals can act as catalysts for the formation of carbonyl chloride (89), sulfur chloride (90), and nitrosyl chloride (91). Gas-phase carbon monoxide, sulfur dioxide, and nitrogen oxide can react with surface chlorine to form carbonyl chloride, sulfur chloride, and nitrosyl chloride respectively. Therefore, CO, SO₂, and NO could strip surface chlorine from the catalyst, reducing the rate of mercury oxidation to mercuric chloride. It is suggested that the impacts of CO, SO₂, and NO be investigated in more detail to confirm this potential effect. Additionally, the deactivation of catalysts, whether from fly ash exposure or poisoning by gas-phase species, should be investigated.

We also recommend a change in the way that mercury oxidation results are reported. Many of the studies cited here report the fraction of mercury oxidized by a certain catalyst. Applying the results of these catalyst studies—for the purpose of sizing a catalyst bed, for example—is therefore difficult. Reporting results in terms of traditional kinetic quantities, including an effective rate constant for mercury conversion, would allow for results to be translated from the laboratory scale to larger scales. One possibility would be to report reaction rates as mol Hg⁰ converted/(s × g catalyst), though other formulations are certainly available. This would allow for at least qualitative prediction of mercury conversion across different catalysts.

Further investigation into the fundamental nature of mercury oxidation is critical to the advancement of particular catalysts. Ultimately, catalysts will need to treat gas streams significantly larger than the slipstreams sampled for pilot-scale tests, and installing such equipment carries significant capital cost. Obtaining a degree of predictability in the performance of different catalysts will be needed to make the jump from pilot-scale to full-scale implementation; understanding the reaction mechanism and kinetics offers the most rigorous method for making these predictions.

5.2. Novel Catalysts and Supports. Inexpensive catalysts such as Thief carbons, halogenated carbons, and halogen salts merit further investigation for promoting the formation of water-soluble mercuric chloride. These materials have recently shown promise during short-duration tests using slipstreams from the NETL 500 lb/h coal combustion facility (82). Precious metal catalysts such as palladium, gold, and iridium also merit further investigation. Iridium has shown potential as an oxidation catalyst during recent bench-scale slipstream tests at the NETL (82).

The optimum reactor configuration for contacting the catalyst with the flue gas needs to be determined. Precious metal catalysts can contact the flue gas through a packed bed, monolith, or parallel plate configuration (6, 60, 80, 82). Each of these configurations has certain advantages with respect to particulate blinding and pressure drop. Inexpensive catalysts could be disposable and injected upstream of the electrostatic precipitator or fabric filter baghouse (6).

Methods for regenerating precious metal catalysts merit further examination. Sulfur, selenium, and arsenic are well-known poisons for precious metal catalysts that are also present within coal-derived flue gas. Surface analysis of the used precious metal catalysts can point toward agents within the flue gas that lead to deactivation.

The supports employed for the noble metal catalysts can include aluminas, silica, aluminosilicates, zirconias, cerates, stainless steels, titanias, carbons, and zeolites (60, 82). The purpose of the support is to maximize the number of collisions between mercury, halogen species, and the catalyst

surface. The potential for beneficial catalyst–support interactions, such as spillover of adsorbed halogen species, merits further study.

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