

A Kinetic Approach to the Catalytic Oxidation of Mercury in Flue Gas[†]

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Four mercury oxidation catalysts were tested in a packed bed reactor in the presence of flue gas generated by the NETL 500 lb/h coal combustor. The four catalysts tested were Ir, Ir/HCl, Darco FGD activated carbon, and Thief/HCl. The Thief/HCl and Darco converted the highest percentage of the inlet mercury; however, the high conversion in these experiments was aided by larger catalyst loadings than in the Ir and Ir/HCl experiments. We propose a method for analyzing mercury oxidation catalyst results in a kinetic framework using the bulk reaction rate for oxidized mercury formation normalized by either the catalyst mass or surface area. Results reported for fractional mercury oxidation are strongly influenced by the specific experimental conditions and are therefore difficult to translate from experiment to experiment. The catalyst-normalized results allow for more quantitative analysis of mercury oxidation catalyst data and are the first step in creating a predictive model that will allow for efficient scaling up from laboratory-scale to larger-scale studies.

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 emitted annually.^{1,2} Mercury exists in three forms in coal-derived flue gas: elemental (Hg^0), oxidized (Hg^{2+}), and particle-bound ($\text{Hg}(\text{p})$).³ 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 Cl present in coal. The extent of mercury oxidation depends on a number of factors, including combustion characteristics, coal composition (including chlorine content),^{4–6} concentrations of other species (i.e., NO_x and SO_2)^{7,8} in the flue gas, and the time–temperature history.⁹ Both Hg^0 and Hg^{2+} can enter the particulate phase by adsorption onto fly ash

particles.¹⁰ $\text{Hg}(\text{p})$ is captured, along with fly ash particles, in ESPs (electrostatic precipitators), baghouses, or both. 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.¹¹

The EPA recently announced the Clean Air Mercury Rule (CAMR)¹² and the Clean Air Interstate Rule (CAIR).¹³ CAMR calls for reductions in mercury emissions from coal-fired utility boilers of approximately 70% from 1999 levels by 2018. In addition, several states have proposed more stringent mercury emissions requirements. CAIR requires reductions in NO_x and SO_2 emissions in twenty-eight states. An expected consequence of CAIR is increased use of wet flue gas desulfurization (FGD) for SO_2 control.¹⁴ Hg^{2+} is soluble in water and is therefore removed with high efficiency (>90%) by FGD equipment.¹⁵ Hg^0 , on the other hand, is insoluble in water and is therefore not removed by FGD. Thus, the study of catalysts that enhance mercury oxidation and offer a possible cost-effective alternative to ACI has received increased attention in recent years.¹⁶

A significant shortcoming is present in nearly all of the available catalyst data. Results are typically reported as “percent

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(1) *Mercury Study Report to Congress*; U.S. Government Printing Office: Washington, D. C., 1997.

(2) *A Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units: Final Report to Congress*; U.S. Government Printing Office: Washington, D. C., 1998.

(3) Galbreath, K.; Zygarićke, C. Mercury speciation in coal combustion and gasification flue gases. *Environ. Sci. Technol.* **1996**, *30*, 2421.

(4) Hargrove, O.; Carey, T.; Richardson, C.; Skarupa, R.; Meserole, F.; Rhudy, R.; Brown, T. *Enhanced Control of Mercury and Other HAPs by Innovative Modifications to Wet FGD Processes*; Report to DOE/NETL, U.S. DOE Agreement No. DE-AC22-95PC95260; Radian International, LLC: Austin, TX, 1997.

(5) Galbreath, K.; Zygarićke, C. Mercury transformations in coal combustion flue gas. *Fuel Proc. Technol.* **2000**, *65–66*, 289.

(6) Senior, C.; Sarofim, A.; Zeng, T.; Helble, J.; Mamani-Paco, R. Gas-phase transformations of mercury in coal-fired power plants. *Fuel Proc. Technol.* **2000**, *63*, 197.

(7) Laudal, D.; Brown, T.; Nott, B. Effects of flue gas constituents on mercury speciation. *Fuel Proc. Technol.* **2000**, *65–66*, 157.

(8) Galbreath, K.; Zygarićke, C.; Tibbetts, J.; Schultz, R.; Dunham, G. Effects of NO_x , $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$, and HCl on mercury transformations in a 7-kW coal combustion system. *Fuel Proc. Technol.* **2004**, *86*, 429.

(9) Wang, J.; Clements, B.; Zanganeh, K. An interpretation of flue-gas mercury speciation data from a kinetic point of view. *Fuel* **2003**, *82*, 1009.

(10) Serre, S.; Silcox, G. Adsorption of elemental mercury on the residual carbon in coal fly ash. *Ind. Eng. Chem. Res.* **2000**, *39*, 1723.

(11) Pavlish, J.; Sondreal, E.; Mann, M.; Olson, E.; Galbreath, K.; Laudal, D.; Benson, S. Status review of mercury control options for coal-fired power plants. *Fuel Proc. Technol.* **2003**, *82*, 89.

(12) U. S. EPA Clean Air Mercury Rule. <http://www.epa.gov> (accessed 2005).

(13) U. S. EPA Clean Air Interstate Rule. <http://www.epa.gov> (accessed 2005).

(14) Srivastava, R.; Hutson, N.; Martin, B.; Princiotta, F.; Staudt, J. Control of mercury emissions from coal-fired electric utility boilers. *Environ. Sci. Technol.* **2006**, *40*, 1385.

(15) Carey, T. Effect of mercury speciation on removal across wet FGD processes, Presented at the AWMA 92nd Annual Meeting, St. Louis, MO, June 1999.

(16) Presto, A.; Granite, E. Survey of catalysts for oxidation of mercury in flue gas, *Environ. Sci. Technol.* in press.

mercury oxidized.” While qualitatively useful, presenting results in this manner makes the comparison of different experiments and experimental conditions difficult. The fractional conversion of Hg^0 to Hg^{2+} is a function of a number of factors, possibly including the temperature, the concentrations of Hg^0 and other flue gas constituents, and the amount (mass or surface area) of catalyst. Percent mercury oxidized combines all of these effects into a single number. Herein, we propose a method for describing mercury oxidation catalyst results in a kinetic framework using nomenclature (reaction rates, rate constants, etc.) that is both familiar and allows for comparison between different experiments and conditions.

Significant advantages of considering catalyst results in terms of chemical kinetics come in predictability and scaling. With the currently available data, predicting the change in the extent of mercury oxidation resulting from a change in a process parameter (i.e., HCl concentration) is difficult at best; appropriately scaling a laboratory experiment to pilot or full scale is nearly impossible and may lead to costly overdesign. With kinetic data, specifically, reaction orders, rate constants, and apparent activation energies, we can begin to have some predictability. Furthermore, it is known that mercury conversions in flue gas are kinetically, and not thermodynamically, controlled.⁹ Thus, detailed knowledge of heterogeneous mercury oxidation kinetics can be used to supplement existing homogeneous kinetic models¹⁷ and hopefully facilitate predictions of the effectiveness of different mercury control measures and strategies.

In this article, we present a method for analyzing mercury oxidation catalyst data from a kinetic point of view and apply the method to data collected at NETL. We present results for four catalysts: Iridium (Ir), Ir/HCl, Norit Darco FGD activated carbon, and Thief/HCl. The data provide a telling example of how presenting results as percent mercury oxidized can be misleading, and introduce a catalyst material (iridium) that has not been previously reported in the literature.

2. Experimental Section

Flue gas was generated in NETL's 500 lb/h coal combustor,^{18,19} which consists of a pulverized coal wall-fired furnace equipped with a water-cooled convection section, a recuperative air heater, spray dryer, baghouse, and associated ancillary equipment (fin-fan coolers, surge tanks, coal hoppers, blowers, pumps, etc.). The 500 lb/h combustor is an indirect-fired unit. Coal is first pulverized off-line in a Williams roller mill, and then it is transported through a series of hoppers before being fed by an Acrison weight-loss differential feeder to the combustor. The wall-fired dry-bottom-type combustor is capable of firing both coal and natural gas. The combustor's four wall-fired burners are equipped with secondary air registers that can be adjusted to improve combustion. On-line temperature readings, flow measurements, and four separate banks of continuous gas analyzers (O_2 , NO_x , CO , SO_2 and CO_2) characterize the overall system operating performance.

A wide range of flue gas temperatures can be obtained at the duct test section, baghouse, and stack. The options for altering the flue gas temperature include indirect cooling by adjusting system operating conditions, direct cooling by humidification, or both. Also,

Table 1. Typical Flue Gas Conditions Downstream of the Baghouse for the Two Coal Types Used in This Study^a

	90/10	PRB
O_2 (%)	8.3–9.6	8.7–9.4
SO_2 (ppm)	225–260	210–230
NO_x (ppm)	320–430	330–340
CO_2 (%)	10–11	10–11
HCl (ppm)	6.5	1.6

^a The upper and lower limits shown for O_2 , SO_2 , NO_x , and CO_2 indicate the full range of concentrations observed. The HCl concentrations are calculated from the mean concentrations for the given coal type.

sorbent can be injected at one location selected from numerous ports along the duct test section, allowing for a wide range of sorbent in-duct residence times relative to the baghouse and gas-sampling locations.

Two different coals were used in the combustor for these experiments. In several experiments, pure Powder River Basin subbituminous coal (PRB) was burned. In other experiments, a mixture of 90% PRB and 10% eastern bituminous (referred to here as 90/10) was burned. The bituminous coal was used to increase the chlorine ($\text{Cl}_2 + \text{HCl}$) concentration in the flue gas. Table 1 gives approximate flue gas compositions, measured downstream of the baghouse, for the two coals used in these experiments. There was significant in-leakage of air in the baghouse; outside air constitutes approximately 10% of the total flue gas downstream of the baghouse and is the reason for the relatively high O_2 concentrations noted in Table 1. The CO concentration is not listed in Table 1; the CO concentration was typically below the detection limit, however, occasional periods of poor combustion produced spikes as large as several hundred parts per million. The spikes in CO concentration generally lasted for only a few minutes and did not appear to have any effect on the catalyst performance. The primary difference between the two flue gases is the HCl concentration, which is roughly a factor of 4 larger in the 90/10 experiments. The Cl_2 concentration was typically less than 0.1 ppm. Both the HCl and Cl_2 concentrations were determined using EPA Method 26A.

An 8 ± 1 lpm slip stream of flue gas was extracted downstream of the baghouse and passed through a chiller to remove water. The dehumidified particle-free flue gas was then passed through a packed bed of catalyst. The packed-bed reactor was constructed of a vertically oriented 0.5 in. o.d. by 12 in. long quartz tube.¹⁹ The catalyst material was held in place by glass wool packed into the tube; tests revealed that the glass wool was inert toward mercury. The quartz tube was surrounded by a clam shell furnace, and the temperature was held at 280 °F (411 K) for most experiments.

Table 1 does not include mercury concentrations or speciation. The mercury concentration in the flue gas was typically $5\text{--}10 \mu\text{g Nm}^{-3}$ and 80 to >90% of the mercury was elemental. For some experiments, a mercury spiking system was used to increase the elemental mercury concentration entering the packed bed. The spiking system consisted of a dimpled glass vessel containing a pool of mercury. A controlled flow of nitrogen gas was passed over the mercury, and an oven was used to control the temperature of the mercury pool. The temperature of the mercury pool determined the vapor pressure of mercury, thereby setting the mercury concentration that exited in the nitrogen sweep gas. The use of the spiking system increased the inlet total mercury concentration to as much as $50 \mu\text{g Nm}^{-3}$. The mercury concentration was monitored using a PS Analytical Sir Galahad CEM (continuous emission monitor). Inlet total ($[\text{Hg}^{\text{TOT}}]_{\text{inlet}}$) and elemental ($[\text{Hg}^0]_{\text{inlet}}$) mercury concentrations were measured by bypassing the packed bed; outlet concentrations were measured at the exit of the packed-bed reactor. The oxidized mercury concentration was calculated as the difference between the total and elemental mercury concentrations.

Four catalysts were tested: Iridium (Ir), Ir/HCl, Norit Darco FGD activated carbon, and Thief/HCl. The Ir catalyst consisted of 1 wt % Ir deposited on 4 mm $\gamma\text{-Al}_2\text{O}_3$ beads and was used as received from Alfa Aesar. Ir/HCl was prepared by soaking the Ir catalyst in 37% trace-metal grade HCl and drying it on a hot plate.

(17) Xu, M.; Qiao, Y.; Zheng, C.; Li, L.; Liu, J. Modeling of homogeneous mercury speciation using detailed chemical kinetics. *Combust. Flame* **2003**, *132*, 208.

(18) O'Dowd, W.; Hargis, R.; Granite, E.; Pennline, H. Recent advances in mercury removal technology at the National Energy Technology Laboratory. *Fuel Proc. Technol.* **2004**, *85*, 533.

(19) Granite, E.; Freeman, M.; Hargis, R.; O'Dowd, W.; Pennline, H. The Thief process for mercury removal from flue gas. In *Proceedings of the 22nd Annual International Pittsburgh Coal Conference*; September 15–18, 2005, Pittsburgh, PA; University of Pittsburgh: Pittsburgh, PA, 2005.

Table 2. Experimental Conditions for Each of the Catalysts Tested in This Study

catalyst	coal	<i>T</i> (K)	[Hg ⁰] _{inlet} (μg Nm ⁻³)	[Hg ^{TOT}] _{inlet} (μg Nm ⁻³)	active catalyst mass (mg)
Ir	PRB	411	9.6	12.0	20
		411	14.8	17.0	20
Ir/HCl	PRB	411	9.5	10.0	30
		444	9.5	10.0	30
		90/10	4.0	5.3	20
Darco	90/10	424	28.6	42.9	100
Thief/HCl	90/10	411	26.3	34.8	100
		411	49.6	57.9	100

The goal of the HCl treatment was to increase the surface Cl concentration,²⁰ as surface-bound chlorine may participate in mercury oxidation. Darco activated carbon was used as received. Thief carbon is partially combusted coal drawn from the furnace after a short residence time. It has a high percentage of unburned carbon (30–50 wt %) and is an effective Hg⁰ sorbent.^{19,21,22} Thief/HCl was generated from Thief carbon by the same procedure used to chlorinate the Ir catalyst. Table 2 details the experiments conducted with each catalyst.

3. Theory

From the CEM data, we can calculate a bulk reaction rate for Hg²⁺ formation across the catalyst bed.

$$R_{\text{gas}} = \frac{\Delta[\text{Hg}^{2+}]}{\Delta t} \quad (1)$$

$\Delta[\text{Hg}^{2+}]$ is the change in oxidized mercury concentration across the catalyst, and Δt is the contact time between the flue gas and the catalyst, assuming plug flow. For the conditions used in the experiments presented here, Δt was less than 0.1 s. In the limit of small changes in Hg²⁺ concentration and short contact times, the right-hand side of equation 1 reduces to the derivative $d[\text{Hg}^{2+}]/dt$.

The bulk reaction rate defined in eq 1 can be expressed as an apparent gas-phase reaction.

$$R_{\text{gas}} = k_{\text{gas}}[\text{Hg}^0]^\alpha[\text{Oxidant}]^\beta \quad (2)$$

Here, k_{gas} is the apparent gas-phase rate constant. It is important to note that while eq 2 looks like the rate equation for a homogeneous gas-phase reaction, the measured rate is dependent upon the amount and type of catalyst. The oxidant is often assumed to be HCl,^{23–25} and eq 2 assumes a single oxidant; however, flue gas contains several species, including Cl₂,^{23,26} SO₂,²⁷ and NO_x⁸ that may also oxidize Hg⁰. We assume a single oxidant, likely HCl, as a first approximation.

(20) Granite, E.; Pennline, H.; Hargis, R. Novel sorbents for mercury removal from flue gas. *Ind. Eng. Chem. Res.* **2000**, *39*, 1020.

(21) Pennline, H.; Granite, E.; Freeman, M.; Hargis, R.; O'Dowd, W. Thief process for the removal of mercury from flue gas. U.S. Patent 6,521,021, 2003.

(22) Granite, E.; Pennline, H. Catalysts for oxidation of mercury in flue gas. US Patent Application, 2005.

(23) Hall, B.; Schager, P.; Lindqvist, O. Chemical reactions of mercury in combustion flue-gases. *Water, Air, Soil Pollut.* **1991**, *56*, 3.

(24) Niksa, S.; Fujiwara, N. A predictive mechanism for mercury oxidation on selective catalytic reduction catalysts under coal-derived flue gas. *J. Air Waste Manage. Assoc.* **2005**, *55*, 1866.

(25) Niksa, S.; Fujiwara, N. Predicting extents of mercury oxidation in coal-derived flue gases. *J. Air Waste Manage. Assoc.* **2005**, *55*, 930.

(26) Menke, R.; Wallis, G. Detection of mercury in air in the presence of chlorine and water-vapor. *Am. Ind. Hyg. Assoc.* **1980**, *41*, 120.

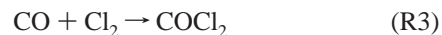
(27) Schofield, K. Mercury emission chemistry: The similarities or are they generalities of mercury and alkali combustion deposition processes? *Proc. Comb. Inst.* **2005**, *30*, 1263.

R_{gas} and k_{gas} both obscure the role of the catalyst in mercury oxidation; neither quantity expresses any dependence on the amount (mass or surface area) of catalyst, and therefore, the calculated values for R_{gas} and k_{gas} are experiment dependent. We treat this by normalizing the rate constant by the catalyst mass.

$$R_{\text{cat}} = R_{\text{gas}} \left(\frac{V_{\text{cat}}}{m_{\text{cat}}} \right) = k_{\text{cat}}[\text{Hg}^0]^\alpha[\text{Oxidant}]^\beta \quad (3)$$

V_{cat} is the catalyst volume (bulk), and m_{cat} is the catalyst mass; thus, R_{cat} has units of moles of Hg²⁺ per gram of catalyst per second. k_{cat} is the catalyst-normalized rate constant: $k_{\text{cat}} = k_{\text{gas}} \cdot (V_{\text{cat}}/m_{\text{cat}})$. R_{gas} and k_{gas} could alternatively be scaled by the total catalyst surface area. In this case, the catalyst surface area would replace m_{cat} in eq 3.

The catalyst-normalized rate constant (k_{cat}) allows for direct comparison of different catalysts; however, there are several shortcomings to this approach. First, as noted above, the nature of the oxidant is unclear. While HCl is often assumed because it is typically present in excess relative to Hg⁰, other species may also oxidize mercury. Second, the reaction mechanism and reaction order (α , β) are unknown. Equation 2 presents the simplest case, binary reaction between Hg⁰ and a single oxidant, but it is unknown how other flue gas species such as CO, SO₂, and NO_x factor into the mercury oxidation mechanism. For example, it is known that precious metals and carbon can catalyze the formation of the halides SO₂Cl₂,²⁸ NOCl,²⁹ and COCl₂³⁰ through the following reactions



Reactions R1–R3 may impact the oxidation of mercury through either depletion of surface chlorine or blocking of sites for mercury adsorption.

One simple set of assumptions sets HCl as the oxidant and the reaction order for both HCl and Hg⁰ equal to one. This is consistent with the results of Yan et al.,³¹ who observed that the kinetics of the reaction of mercury with Cl₂ on a quartz surface can be described by $R = k_{\text{surf}}[\text{Cl}_2][\text{Hg}^0]_{\text{surf}}$. The data presented in this article are treated according to these assumptions to determine an initial estimate of k_{cat} for the catalysts tested here; ultimately, however, widespread application of kinetic nomenclature to mercury oxidation catalyst data requires a more thorough understanding of the reaction mechanism.

4. Results and Discussion

Figure 1 shows a time series of a typical experiment using the Ir/HCl catalyst. The inlet concentrations of total and elemental mercury are measured both at the start and end of the experiment to verify that the inlet composition is approximately constant throughout the experiment. Inlet concen-

(28) Cicha, W.; Manzer, L. Process for producing oxochlorides of sulfur. U.S. Patent 5,879,652, 1999.

(29) Nottingham, W.; Sutter, J. Kinetics of the oxidation of nitric oxide by chlorine and oxygen in nonaqueous environments. *Int. J. Chem. Kinet.* **1986**, *18*, 1986.

(30) Babad, H.; Zeiler, A. The chemistry of phosgene. *Chem. Rev.* **1973**, *73*, 75.

(31) Yan, N.-Q.; Liu, S.-H.; Chang, S.-G.; Miller, C. Method for the study of gaseous oxidants for the oxidation of mercury gas. *Ind. Eng. Chem. Res.* **2005**, *44*, 5567.

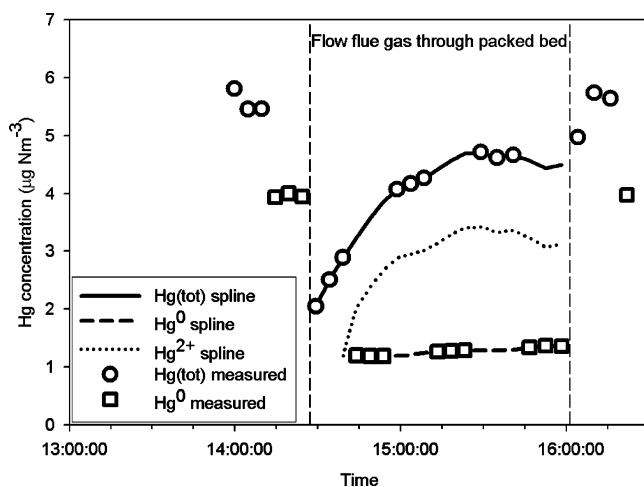


Figure 1. Time series of a typical experiment. The inlet elemental ($[\text{Hg}^0]_{\text{inlet}}$) and total ($[\text{Hg}^{\text{TOT}}]_{\text{inlet}}$) mercury concentrations are measured at the start and end of the experiment and are constant. The catalyst material initially acts as a sorbent and adsorbs both Hg^0 and Hg^{2+} ; the outlet total mercury concentration reaches equilibrium approximately 1 h after initial exposure of the catalyst to flue gas. Catalytic activity is confirmed by the increase in outlet Hg^{2+} concentration, which is determined as the difference between the total and elemental mercury concentrations. The lines are cubic spline interpolations to the CEM data.

trations are measured by bypassing the packed bed and sending the slip stream directly to the CEM. Mercury concentrations exiting the packed bed (the data between the vertical dashed lines in Figure 1) are measured at the outlet from the packed-bed reactor. Several tests were conducted to verify that neither the quartz tube nor the glass wool used as a catalyst support sorb or oxidize a significant amount of the inlet mercury. The alumina beads used to support the Ir and Ir/HCl catalysts were also tested and found to be essentially inert in the flue gas.

All of the catalyst materials initially act as sorbents, as shown by the low concentration of Hg^{TOT} exiting the packed bed at 14:30. The outlet concentration of Hg^{TOT} rises to a near-equilibrium value over the course of the experiment. The initial sorbent activity, the time to equilibrium, and the equilibrium sorption are functions of the different catalyst materials. For example, the Ir and Ir/HCl catalysts initially adsorb approximately 60% of the total mercury and reach an equilibrium adsorption of 10–20% within 1 h. Darco activated carbon, on the other hand, is a more effective sorbent that initially removes >90% of the total mercury; mercury sorption only decreases to approximately 50% in 2.5 h.

The behavior of each material as a sorbent has a significant impact on the catalyst results. Mercury conversion data (i.e., the oxidation rate) is measured during the equilibrium period. Ideally, kinetic data would be collected at conditions approaching true equilibrium, with less than 10% sorption. In practice, we are limited by time constraints and the actual near-equilibrium achieved during each experiment. Several experiments using Thief/HCl and Darco had to be discarded because of high-equilibrium adsorption. In these experiments, the outlet concentration of oxidized mercury was lower than the inlet concentration. This does not imply mercury reduction across the catalyst bed; indeed, the fraction of oxidized mercury in the outlet was larger than the fraction of oxidized mercury entering the packed bed, indicating catalytic oxidation. In these experiments, the large extent of mercury adsorption is the reason for the apparent negative $\Delta[\text{Hg}^{2+}]$.

Table 3 details the results for each catalyst. The data are

Table 3. Comparison of Percent Oxidation versus Kinetic Quantities (R_{cat} and k_{cat}) for the Tested Catalysts

catalyst	% oxidation	R_{cat}^a ($\times 10^{11}$) (mol of Hg^{2+}) (g of catalyst) $^{-1}$ s $^{-1}$	k_{cat} (411 K) b (m 3 mol $^{-1}$ s $^{-1}$) (m 3 of catalyst) (g catalyst) $^{-1}$
Ir	40	3.8 ± 0.9	25 ± 6
Ir/HCl	30	2.3 ± 0.6	12 ± 3
Darco	50	2.2 ± 0.6	3.6 ± 0.9
Thief/HCl	60–70	2.1 ± 0.5	3.3 ± 0.8

^a R_{cat} measured at the following conditions: $[\text{Hg}^0]_{\text{inlet}} = 10 \mu\text{g Nm}^{-3}$, $T = 411 \text{ K}$, 90/10 coal ($[\text{HCl}] = 6.5 \text{ ppm}$). ^b k_{cat} calculated assuming $R_{\text{cat}} = k_{\text{cat}}[\text{Hg}^0]_{\text{inlet}}[\text{HCl}]$.

presented using three metrics: percent oxidation across the catalyst bed; R_{cat} , as determined for an inlet elemental mercury concentration of $10 \mu\text{g Nm}^{-3}$, temperature of 411 K, and 90/10 (high HCl) coal; and k_{cat} , calculated assuming a reaction first order in both $[\text{Hg}^0]$ and $[\text{HCl}]$ (α and β from eq 2 equal to one) at 411 K. The Thief/HCl catalyst oxidized the largest fraction of the inlet mercury; however, the rate of oxidation across this catalyst was the lowest. The Ir catalyst had a significantly larger k_{cat} than any of the other catalysts.

The data in Table 3 illustrate how results presented as percent mercury oxidized can be misleading. The Thief/HCl and Darco converted a higher percentage of the inlet mercury than the Ir catalyst, but as shown in Table 2, this high conversion was aided by larger catalyst mass. According to eq 3, the apparent gas-phase reaction rate and, therefore, the fractional extent of mercury oxidation, is dependent upon the catalyst mass. Thus, large differences in catalyst mass between different experiments, as is the case here, can skew the results to artificially favor the experiments that use larger amounts of catalyst. It is important to note that, while the Darco and Thief/HCl experiments used significantly more catalyst (a factor of 3–5) than the Ir and Ir/HCl experiments, all of the experiments used milligram amounts of catalyst. Mercury oxidation will increase with catalyst loading; however, the maximum mass of catalyst practical for industrial applications is limited by other considerations such as pressure drop and catalyst cost.

In addition, the experiments using Darco and Thief/HCl used the 90/10 coal blend, which has a higher chlorine content than the PRB used in most of the Ir and Ir/HCl experiments. According to eq 3 and our assumption that mercury oxidation occurs during the reaction with HCl, the higher HCl concentration in the Darco and Thief/HCl experiments will also increase the fractional mercury conversion.

Normalization via the catalyst mass removes the dependence on this variable and facilitates the comparison between differing experimental conditions. The kinetic parameters R_{cat} and k_{cat} show that, when normalized for catalyst mass, the Thief/HCl catalyst is actually the worst of the four catalysts tested. If we were to simply report these results as percent mercury oxidized, we would be overlooking a significant result: the Ir catalyst converted Hg^0 to Hg^{2+} nearly twice as fast per gram of catalyst than any of the other materials tested here.

The Ir catalyst performed better than Ir/HCl. The purpose of the HCl treatment was to increase the surface Cl concentration, as surface-bound Cl may participate in mercury oxidation. One possible conclusion from the decreased activity of Ir/HCl relative to Ir is that the HCl treatment saturated the catalyst surface with Cl and prevented Hg adsorption. However, previous experiments with halogenated sorbents showed enhanced mercury sorption to HCl-treated materials.²⁰ The poor performance of the Ir/HCl catalyst may alternatively indicate that the oxidation reaction does not include adsorbed Cl and that adding Cl to the surface

inhibits oxidation by reducing the number of sites available for mercury reaction. The BET surface areas of the Ir and Ir/HCl catalysts were not measured. Thus, a simple explanation for the performance of the Ir/HCl catalyst may be that HCl treatment reduced the available surface area.

Darco activated carbon was a better catalyst than Thief/HCl, and this result was expected. It is believed that mercury oxidation occurs at carbon sites in fly ash and other carbon-containing materials. While the Thief carbon has a higher carbon content (30–50 wt %) than typical fly ash, the surface of the Darco activated carbon is composed almost entirely of carbon sites. Thus, the surface of the Darco should be more amenable to mercury oxidation than the Thief/HCl and should exhibit a larger oxidation rate. The Thief/HCl catalyst remains an intriguing material; k_{cat} for Thief/HCl was only 10% lower than for Darco, and Thief has a significantly lower cost than activated carbon.¹⁹

The different concentrations of Hg^0 and HCl allowed for a preliminary investigation into the reaction order for each of these species. For the Ir and Thief/HCl catalysts, the reaction appears to be first-order in Hg^0 ; this is consistent with the assumption used to calculate k_{cat} . This is also consistent with Yan et al.,³¹ who observed a first-order dependence on $[\text{Hg}^0]$ during heterogeneous oxidation by Cl_2 . For the Ir/HCl catalyst, the reaction order for Hg^0 may be negative. The Thief/HCl catalyst shows a positive reaction order for HCl.

We can use the preliminary reaction order results to gain some mechanistic insight. Several heterogeneous mechanisms have been proposed for catalytic mercury oxidation. The Langmuir–Hinshelwood mechanism for the reaction between two adsorbed species, perhaps Hg^0 and HCl, can exhibit either a +1 or –1 order for individual reactants.³² A reaction order of –1 is consistent with the saturation of the surface by one reactant at the expense of the other. The negative reaction order for Hg^0 on the Ir/HCl catalyst may be an indication of saturation of the surface with Cl and Langmuir–Hinshelwood kinetics, but the data presented here is certainly not conclusive. The Eley–Rideal mechanism describes the reaction between an adsorbed species and a gas-phase species; this reaction can be first-order in each of the reactants. Previous research has proposed that either Hg^0 or HCl could be the adsorbed species.^{10,25} The preliminary results obtained here cannot preclude or confirm either the Eley–Rideal mechanism or the Langmuir–Hinshelwood mechanism. Further investigation is required to elucidate the reaction mechanism.

Assuming an Arrhenius form to k_{cat} (i.e., $k = A \exp(-E_a/RT)$), we were able to estimate an apparent activation energy of $\sim 20 \text{ kJ mol}^{-1}$ for the Ir/HCl catalyst. This is consistent with the apparent activation energy of $\sim 30 \text{ kJ mol}^{-1}$ measured by Zhao et al.³³ for mercury oxidation across a gold catalyst. This may indicate that the mechanism for mercury oxidation across gold and Ir/HCl catalysts is the same, although Zhao et al. used

Cl_2 as the oxidant. Zheng et al. used an ab initio quantum mechanical model to calculate the activation energy for the gas-phase reaction between Hg^0 and HCl and determined a value of 256 kJ mol^{-1} .³⁴ The large reduction in activation energy for this reaction in the presence of a catalyst lends further evidence that the oxidation of Hg^0 proceeds via reaction with HCl.

5. Conclusions

Ir, Ir/HCl, Darco FGD activated carbon, and Thief/HCl were all observed to catalyze mercury oxidation in real flue gas generated in the NETL 500 lb/h coal combustor. Data were analyzed in terms of typical kinetics parameters, reaction rates and rate constants, rather than as percent mercury oxidized. When normalized for catalyst mass, the rate of mercury oxidation for the four catalysts was $\text{Ir} > \text{Ir/HCl} > \text{Darco} > \text{Thief/HCl}$. These data illustrate the importance of considering mercury catalyst results in terms of reaction kinetics because the traditional metric of percent mercury oxidized gave the erroneous conclusion that Thief/HCl was the most effective catalyst. The important implication is that fractional conversion is a result of specific conditions of a potentially large array of variables: concentrations, residence times, catalyst mass, and others. Kinetic data, specifically, rate constants and apparent activation energies, allow for the prediction of the extent of conversion for a given reaction. While conversion is ultimately the desired quantity, knowledge of the kinetics can allow for accurate prediction of conversion in a variety of different operating conditions.

Further research is required to resolve the uncertainties surrounding catalytic mercury oxidation. In this article, we calculated k_{cat} assuming a reaction first-order in both Hg^0 and HCl; future work must substantiate this assumption and investigate the effects of other flue gas constituents such as CO , SO_2 , and NO_x . The kinetic analysis presented here was also simplified by assuming a bulk reaction rate. While the short contact time ($< 0.1 \text{ s}$) in the packed-bed experiments presented here facilitates this approach, application of this analysis method to other experiments should proceed with care. Specifically, the bulk rate assumption may break down in cases with long residence times or large changes in Hg^0 concentration. For the experiments presented here, however, the bulk rate approximation provided consistent results for each of the catalysts tested and appears to be an appropriate method for handling the data.

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Supporting Information Available: Figures showing a schematic of the NETL 500 lb/h coal combustor and the laboratory-scale packed bed reactor used to test the mercury sorbents and catalysts. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(32) Pillig, M.; Seakins, P. *Reaction Kinetics*; Oxford Science Publications: Oxford, U.K., 1995.

(33) Zhao, Y.; Mann, M.; Pavlish, J.; Mibeck, B.; Dunham, G.; Olson, E. Application of gold catalyst for mercury oxidation by chlorine. *Environ. Sci. Technol.* **2006**, *40*, 1603.

(34) Zheng, C.; Liu, J.; Liu, Z.; Xu, M.; Liu, Y. Kinetic mechanism studies on reactions of mercury and oxidizing species in coal combustion. *Fuel* **2005**, *84*, 1215.