Catalyst Additives to Enhance Mercury Oxidation and Capture

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Abstract

Preliminary research has shown that SCR catalysts employed for nitrogen-oxide reduction can effectively oxidize mercury. This report discusses initial results from fundamental investigations into the behavior of mercury species in the presence of SCR catalysts at Southern Research Institute. Three different SCR catalysts are being studied. These are honeycomb-type, plate-type, and a hybrid-type catalyst. The catalysts are manufactured and supplied by Cormetech Inc., Hitachi America Ltd., and Haldor-Topsoe Inc., respectively. A parametric test matrix was developed for current and future testing. Methods and procedures for experimentally performing this matrix were developed in the previous quarter. The methods and procedures equalize factors influencing mercury adsorption and oxidation (surface area, catalyst activity, and pore structure) that normally differ for each catalyst type. The major effort will be to examine the kinetics of mercury oxidation across the SCR catalysts with respect to changes in mercury concentration and with respect to HCl concentration. Other gases present in SCR systems (NH_3 and SO_3) will also be investigated for their effects on mercury oxidation.

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Introduction

The objective of this project proposed by Southern Research Institute (Southern Research) is to investigate the enhancement of elemental-mercury oxidation in coal-fired flue gas through catalysis. In addition to testing various catalyst materials, fundamental mechanisms associated with enhanced Hg-oxidation on SCR catalysts are being investigated. Data obtained in this work will be provided to Niksa Energy Associates (NES) and Reaction Engineering International (REI) to develop and improve models to predict mercury speciation in full-scale boilers, burning different coal types, ranging from sub-bituminous to high-volatile bituminous coals. Where necessary, Southern Research will develop semi-empirical mechanistic model(s) describing the mechanisms associated with catalysis enhanced mercury oxidation. Results from the project will contribute to a greater understanding of mercury oxidation in flue gas.

Executive Summary

Southern Research Institute continues bench-scale reactor studies to evaluate the behavior of vapor-phase mercury in the presence of Selective Catalytic Reduction (SCR) catalysts. SCR catalysts are employed in coal-fired power plants for the reduction of nitrogen oxide (NO_x) emissions, but SCR catalysts also affect the speciation of other gases, such as mercury. Mercury primarily exists in two-different forms in coal-derived flue gas, HgCl_2 and the elemental form, and each type behaves somewhat differently in the “back end” pollution control equipment of power plants. Oxidized mercury is readily captured in some of the commonly employed pollution control devices, such as wet scrubbers, while elemental mercury is much harder to capture. Therefore, a low-cost mercury-oxidation technology is desired for coal-fired power plants. The best option would be a multi-pollutant solution, such as SCR catalysts for NO_x reduction and mercury oxidation.

The Catalyst Test Facility (CTF) continues to be used to derive fundamental kinetic information about each catalyst and catalyst material investigated for mercury oxidation and capture. The CTF is described and illustrated in this quarterly report. At the core of the CTF is an extensive flue-gas simulation, gas flow, and metering system. Catalyst samples are supported in a 1-1/2” square (for honeycomb-type and hybrid catalysts) or 1-1/4” x 2” rectangular (for plate-type) Pyrex reactor, through which the entire gas flow must pass. The CTF simulates clean (no particles) flue gas with all the major flue-gas species present, including CO , CO_2 , H_2O , O_2 , N_2 , HCl , NO , SO_2 , SO_3 , and Hg^0 , in concentrations representative of that found in flue gases of existing power plants, burning specific coal types.

The simulated flue gas originates from compressed-gas cylinders. The gases from the cylinders are then mixed to known concentrations by use of precision mass-flow controllers. The appropriate moisture content is generated through precise control of water evaporation. Mercury is added to the system via a mercury-soaked porous-ceramic tube within an excess-volume chamber. The simulated flue-gas stream is well mixed and preheated before entering the reaction chamber. A 3”-diameter by 3’-long tube furnace heats the reactor, which allows the simulated flue gas to pass through the furnace while holding the catalyst samples in place.

Bench-scale SCR catalyst tests were conducted to elucidate the relationship between the SCR catalysts and mercury speciation under particular flue-gas environments. The procedure and

basis for normalizing mercury adsorption and oxidation, in order for all three catalyst types to be compared on an equal basis, was performed in the last quarter of 2004. These procedures were described in the January 2005 Quarterly Report. The procedures described in that report were adjusted from discoveries made in the current quarter. It was found that it was not possible to return the catalyst samples to their “as delivered” state. That is, the residual mercury contained in each sample after testing could not be entirely removed by heating and flowing gases through them, in a reasonable amount of time (many hours or even several days). Therefore, the remaining experiments under this test program will use catalyst samples that have been previously exposed to gaseous mercury species, and only partial regeneration of the catalysts will be performed between test conditions using the same catalyst sample.

Next quarter, experiments will continue to progress through the test matrix described in this report. The kinetic rate of mercury adsorption by each catalyst will be determined. Also, the impact of varied partial pressures of ammonia will be investigated. Fundamental rates and mechanisms of mercury oxidation on SCR catalysts will be elucidated from the results of these experiments.

Experimental

Figures 1-3 show pictures of the CTF’s quartz furnace (micro-reactor), gas-conditioning bubblers for mercury speciation and stabilization prior to mercury monitoring, flue-gas continuous emission monitors (CEMs), and gas-flow control systems. Both elemental and total mercury are measured at the outlet of the CTF.

Figure 1. CTF quartz furnace at ~1000 °C (left) and outside of furnace (right).

Figure 2. From left to right, honeycomb, plate, and hybrid SCR catalysts.

The CTF simulates clean (no particles) flue gas with all the major flue-gas species present, including CO , CO_2 , H_2O , O_2 , N_2 , HCl , NO_x , SO_2 , SO_3 , and Hg° , in concentrations that exist in the flue gases of existing power plants, burning specific coal types. The simulated flue gas is originated from compressed-gas cylinders. The gases from the cylinders are then mixed to known concentrations by use of mass flow controllers. The appropriate moisture content is generated through precise control of water evaporation. Mercury is added to the system via a mercury-soaked porous-ceramic tube within an excess-volume chamber. The simulated flue-gas stream is well mixed and preheated before entering the reaction chamber. A 3''-diameter by 3'-long tube furnace heats the reactor, which allows the simulated flue gas to pass through the furnace while holding the catalyst samples in place. The three different catalyst samples are shown in Figure 2.

The majority (i.e., over 95%) of NO_x in the flue gas of coal-fired boiler systems is in the forms of NO . Hence, NO is generally used in this work to simulate the NO_x in the flue gas, except for experiments specifically conducted to observe the effect of NO_2 . In such case, mixed NO/NO_2 gas bottles will be used to simulate the NO_x in the flue gas. With only NO in the flue gas, the NO_x reduction reaction is simplified to the following:

All heated sections of the micro-reactor within the CTF system are made of quartz glass to limit side reactions that might occur as a result of wall effects. A semi-continuous emission monitor (SCEM) is employed to detect the mercury levels exiting the reaction chamber. A gas-conditioning system is used to convert all Hg into the elemental form, for detection using a combined gold-trap and atomic fluorescence monitor. A Tekran Model 2573A Mercury Vapor Analyzer is used to detect the elemental mercury. Along with mercury, simultaneous measurements of oxygen, carbon dioxide, nitrogen oxides, and sulfur dioxide are made using continuous emission monitors. Figure 4 shows a schematic of the CTF system layout.

Figure 3. Catalyst Test Facility.

Figure 4. CTF gas-flow system.

For details concerning the validation and operation of the catalyst test facility, refer to the March 04 DOE Quarterly Report for the Calcium-Based Hg-Sorbents project conducted at Southern Research Institute [1] and a previous Quarterly Report on this project [2].

Results and Discussion

Sorption Testing

The adsorption of mercury onto the surface of SCR catalysts is an important step in the mercury-oxidation process. In the previous quarter (October 1st – December 31st, 2004), experiments were performed to build an understanding of the mechanisms governing mercury adsorption on each of the three catalyst types. A total of twelve tests were intended, comprising four inlet mercury concentration values and three-different catalyst types. The time required for each sample to reach a steady-state mercury oxidation was measured for each catalyst type.

Initial testing showed that the state of the catalyst sample could affect the adsorption of mercury onto the catalyst. If the catalyst had been exposed to mercury prior to the beginning of the experiment, then a steady-state concentration was achieved much faster than experiments using a sample that had not been exposed to mercury. Because of this phenomenon, the experiments performed during this stage of the project were required to use unexposed (fresh) catalyst samples. Also, it was thought that the samples could be returned to their fresh state by placing the samples in a clean nitrogen stream and heating them to reaction temperatures to purge the desorbed mercury. Through testing these regenerated samples it was shown that all of the adsorbed mercury was not removed in a reasonable amount of time (< 24 hrs). Thus, the experiments for the remainder of the program will use samples that have previously been exposed to gaseous mercury species and subsequently subject to only partial regeneration.

During the initial test with each catalyst, the variability in the total mercury measurement was too great to determine a steady-state concentration value. In the last report, this was attributed to acid condensation in the mercury sampling system. The sampling system was retrofit with a circulation pump to continuously wash the walls of the total-mercury impinger preventing the acid from concentrating on the walls of the impinger. This removed the majority of the concentration data variability. Figure 5 displays the improvements in total mercury concentration measurements. It also shows a comparison of the equilibrium times associated with fresh versus regenerated samples. Negative Time-axis values (see Fig. 5) were taken with a blank reactor. At time zero, a catalyst was quickly loaded into the reactor, and data collection resumed.

Figure 5. Transition to steady state, for fresh and regenerated catalyst samples.

Kinetics Testing

The remainder of the test program will be used to study and quantify the effects of catalyst type, gas concentrations, and temperatures on mercury oxidation across SCR catalysts. A test matrix has been developed to use for these tests, which will commence in the second quarter of 2005. Two tables have been provided to show each test condition to be performed. Table 1 offers conditions and terminology for Table 2, which displays the test matrix. A total of 27 test conditions have been identified, though some of these will be expanded to look at effects of HCl, NH₃, and SO₃ on mercury oxidation. Preliminary testing has shown that two to three conditions can be completed per test day; therefore the test matrix should take approximately 5 – 6 weeks of actual testing.

Table 1. Test Parameters and Notations for Table 2.

Catalyst Type	Temperature (°F)
1. Plate 2. Honey Comb 3. Hybrid	1. 600 2. 675 3. 750
Simulated Flue Gas Type (SFGT)	Measurements
1. PRB Coal 2. Low-sulfur & chlorine bituminous 3. High-sulfur & chlorine bituminous 4. Isolation of HCl, NH ₃ , and SO ₃	1. SO ₂ /SO ₃ Conversion 2. NO/NO ₂ outlet concentrations 3. Mercury Removal 4. Mercury Oxidation 5. Complete gas composition, flows, etc.

Table 2. Bench-scale Experimental Test Matrix.

Condition Number	Catalyst Type	Temp.	SFGT	Meas.
1	1	1	1, 4	1 – 5
2	1	2	1, 4	1 – 5
3	1	3	1, 4	1 – 5
4	1	1	2, 4	1 – 5
5	1	2	2, 4	1 – 5
6	1	3	2, 4	1 – 5
7	1	1	3, 4	1 – 5
8	1	2	3, 4	1 – 5
9	1	3	3, 4	1 – 5
10	2	1	1, 4	1 – 5
11	2	2	1, 4	1 – 5
12	2	3	1, 4	1 – 5
13	2	1	2, 4	1 – 5
14	2	2	2, 4	1 – 5
15	2	3	2, 4	1 – 5
16	2	1	3, 4	1 – 5
17	2	2	3, 4	1 – 5
18	2	3	3, 4	1 – 5
19	3	1	1, 4	1 – 5
20	3	2	1, 4	1 – 5
21	3	3	1, 4	1 – 5
22	3	1	2, 4	1 – 5
23	3	2	2, 4	1 – 5
24	3	3	2, 4	1 – 5
25	3	1	3, 4	1 – 5
26	3	2	3, 4	1 – 5
27	3	3	3, 4	1 – 5

Conclusions

Initial tests have demonstrated the ability of SCR catalysts to promote mercury oxidation in coal-derived flue-gas environments. In addition, a test matrix was developed for current and future experiments, to aid in determining the mechanisms governing mercury oxidation across SCR catalysts. Initial mercury-sorption testing has been performed on the three-different catalyst types. The adsorption experiments discussed in the January 2005 Quarterly Report have been discontinued due to the inability to return the samples to their original state. The transient spikes, variability, and loss of oxidized mercury during the initial tests were partially resolved with a retrofit of the mercury sampling system. Experiments will progress towards the completion of the identified test matrix.

Future Work

Testing of mercury oxidation across SCR catalysts will continue during the next quarter. The effects of different mercury and ammonia concentrations will be investigated, and the data will be used to elucidate the mechanisms governing the adsorption of mercury onto SCR catalysts. Also, each catalyst's potential to oxidize mercury and generate SO_3 will be investigated. Further, experiments will be conducted using different flue gases for specific coal types, varied levels of individual gas components (HCl , Hg , SO_3 , and NH_3), and multiple gas temperatures. The data generated from these experiments will be used to develop a clear understanding of mercury oxidation across SCR catalysts relative to full-scale coal-fired power plants.

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