STUDY OF MERCURY TRANSFORMATION WITH CHLORINATED SPECIES UNDER HOMOGENEOUS AND HETEROGENEOUS CONDITIONS

Bhargavi Busireddy*
University of Dayton
*Corresponding author: Email id: busireddy.bhargavi@gmail.com

ABSTRACT

Coal-fired utility boilers are presently the largest significant source of mercury emissions in the U.S. The US-EPA ICR for the coal burning utilities indicated there were 70 tons of mercury in the 900 million tons of coal burned in U.S. power plants during 1999. The estimated total Hg emissions from coal-fired plants ranged from 40 to 50 tons. On average, 40% of Hg entering power plant is captured and 60% is emitted. Hg emissions continue to be a significant air pollution problem globally.

Mercury (Hg) transformation under homogeneous and heterogeneous environments were investigated. Gas Phase experiments were performed in the presence of chlorine source such as Cl_2 and HCl. A large body of literature studies indicates that during combustion in the coal-fired power plants coal mineral matter components play a major role in Hg transformation. Surface activity of these components with respect to Hg adsorption and overall Hg removal were evaluated, fixed bed flow reactor where initial Hg concentration, temperature, residence time, gas composition, and the metal oxide surface were carefully controlled. The metal oxides of interest were γ–Fe_2O_3, TiO_2, Al_2O_3, and CaO. These catalytic materials were immobilized between quartz wool in a quartz flow reactor.

Homogeneous experiments with different gas compositions, different chlorine sources (HCl or Cl_2), and gas-phase residence times of 1 and 2 sec showed no measurable difference in Hg oxidation except at 100_0C. Hg removal (oxidation) efficiencies ranged from 2 to 15%. Heterogeneous studies in the presence of metal oxides (with Cl_2 and HCl as the chlorine source) indicated γ–Fe_2O_3 showed the highest Hg removal efficiency at 1 sec residence time, compared to other metal oxides under the same experimental conditions. TiO_2, used in the presence of Cl_2 at 100_0C, resulted in a 60% Hg removal efficiency which decreased with increasing temperature. TiO_2 used in the presence of HCl resulted in a 55% Hg removal efficiency at 400_0C. Al_2O_3 and CaO were ineffective with regard to Hg oxidation in the presence of Cl_2 or HCl compared to –iron oxide and TiO_2. Adsorption and Overall Hg removal efficiencies showed the following trend γ-Fe_2O_3>TiO_2>Al_2O_3>CaO.

Key words: adsorption, emission, TiO_2

INTRODUCTION

Mercury (Hg), commonly referred to as quicksilver (during ancient times), is a heavy, odorless metal belonging to group (IIB) of the Periodic Table. Unlike the other IIB group elements, Hg exhibits two oxidation states: mercurous, Hg^+ and mercuric, Hg^{2+}. Hg metal is widely distributed in nature; however, it is usually found in low concentrations. The occurrence of Hg ranges from 50 ppb (parts per billion) in terrestrial abundance to 100 ppb in soils, and 10 to 20,000 ppb in rocks.

The properties of Hg include uniform volume expansion over its entire liquid range, as well as high surface tension; i.e., inability to wet and cling to make glass. These properties make Hg essential for barometers, manometers, thermometers and many other measuring devices. Because of its low electrical resistivity, Hg is rated as one of the best electric conductors among the metals. Hg also has the ability to form alloys known as amalgams.

Mercury occurs in different chemical forms in the environment, which vary depending on the source type and other factors. There are three primary categories of Hg: elemental, organic and inorganic compounds. Elemental Hg, a shiny and silver-white metal which is liquid at room temperature, is considered as the main form of mercury that is released into air as vapor. Hg has a vapor pressure of 0.5426 Pascal (Pa) at 30^oC^2, and exhibits a significant vapor-phase concentration at ambient temperatures. Elemental Hg is considered to be soluble in lipids and nitric acid, and is insoluble in hydrochloric acid and water. Inorganic mercury enters the air from mining ore deposits, burning coal and waste.[3]

Coal-fired utility boilers are presently the largest significant source of mercury emissions in the U.S. The US-EPA Information Collection Request (EPA-ICR) for coal burning utilities indicated there were 70 tons of mercury in the 900 million tons of coal burned in U.S. power plants during 1999. Based on the EPA-ICR, the estimated total Hg emissions from coal-fired plants ranged from 40 to 52 tons. On average, 40% of Hg entering a coal-fired power plant is captured and 60% is emitted. On March 15, 2005, the US-EPA decided that Hg emissions should be reduced to 31.3 tons in 2010, 27.9 tons in 2015, and 24.3 tons in 2020.[7]

Understanding the transformation of Hg during the coal combustion process is an important part of controlling mercury emissions because there are different forms of mercury in flue gases, formed either by oxidation or by reduction reactions. Homogenous and heterogeneous reactions help to understand the behavior of Hg and Hg flue gas chemistry in the combustion zone,[14,9] depending on the coal characteristics, flue gas chemistry and combustion conditions. Chlorine sources are believed to affect Hg speciation in flue gas through homogeneous and heterogeneous reactions. Using reactive chlorine sources such as atomic chlorine (Cl) and molecular chlorine (Cl_2), homogeneous elemental Hg-chlorine reactions occur effectively when compared to HCl, as HCl in its reduction state cannot oxidize elemental Hg directly.[15] According to Niksa, heterogeneous Hg and chlorine reactions follow two mechanisms; the first is the bonding of Hg directly by a chlorinated site on solid surface. The second mechanism is the indirect Hg oxidation reaction that occurs by transforming of atomic chlorine (Cl) to molecular (Cl_2).[16]

Gas phase Hg speciation:

Transformation of Hg is mainly influenced by temperature, flue gas composition, and residence time.[17] Gas phase oxidation reactions are mainly considered to involve potential chlorine sources in the flue gas. Atomic chlorine in flue gas is considered to be the dominant sources in oxidation of elemental Hg.[18,19] Kinetic studies have reported large rate constants for both k_1 and k_2 ($k_2 = 1.95 \pm 1.05 \times 10^{13}$ cm^3/mol-s) for the following reactions of Hg with Cl:

$$Hg^o + Cl \longrightarrow HgCl \qquad\qquad (1)$$
$$HgCl + Cl \longrightarrow HgCl_2 \qquad\qquad (2)$$

These studies found that the higher the chlorine atom concentration, the higher will be the Hg oxidation in the gas phase.

Chlorine improved the vaporization of Hg, and Hg reacted with flue gases at higher temperatures to form $HgCl_2$ (g), HgO (g), and Hg^o (g). Among these three forms of Hg, $HgCl_2$ (g) is dominant at temperatures below 450^oC.[17] Figure 2.2 explains the sub-mechanism for the Cl atom recycle involving in Hg oxidation proposed by Niksa. The diagram shows that the partial oxidation between Hg^o and Cl atom forms HgCl, producing $HgCl_2$ by further reaction with Cl_2.[20]
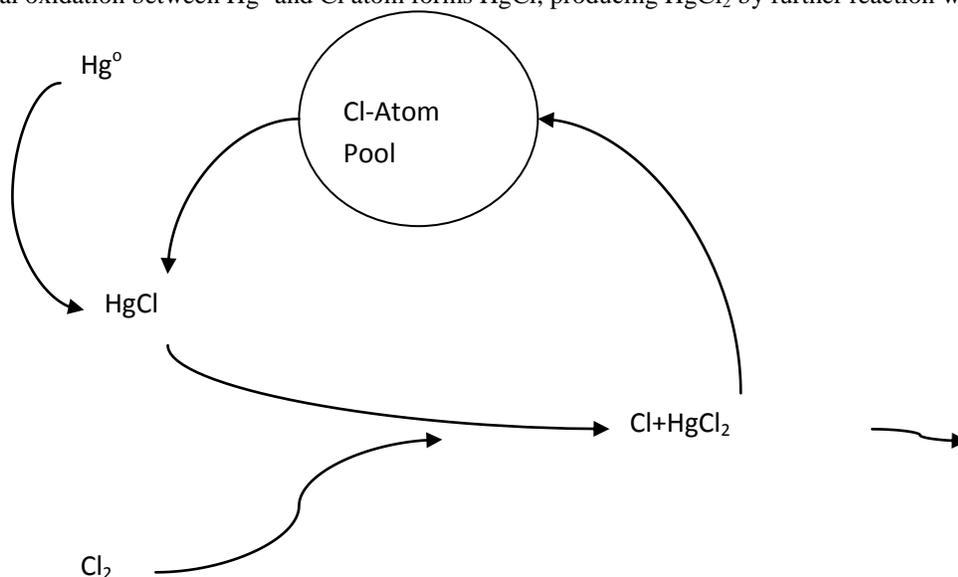

Figure: Cl-atom recycle during homogeneous Hg oxidation

Hall proposed reactions for elemental Hg and acid gases such as Cl_2 and HCl and determined a rate constant from kinetic data.[21] The data indicated that the reaction of Hg (g) with Cl_2 is greater than the reaction of Hg (g) with HCl by about three orders of magnitude. Rate constants were presented as 4.1×10^{-16} cm^3/molecule-sec for reactions with Hg + Cl_2, and $< 1.0 \times 10^{-19}$ cm^3/molecule-sec for reactions with Hg + HCl at temperatures ranging from 20 to 900^oC.

$$Hg (g) + Cl_2 (g) \longrightarrow HgCl_2 (s, g) \qquad\qquad (3)$$
$$2Hg (g) + Cl_2 (g) \longrightarrow Hg_2Cl_2 (s) \qquad\qquad (4)$$
$$Hg (g) + 2HCl (g) \longrightarrow HgCl_2 (s, g) + H_2 (g) \qquad\qquad (5)$$

Kramlich[22] proposed sub-mechanisms involving Hg, Cl_2 and HCl. In this report, he suggested that Hg + Cl   HgCl is the fastest reaction to occur during Hg oxidation at room temperature. The rate constants for reactions (6), (7) and (8) were presented as $k = 1.95 \pm 1.05 \times 10^{13}$ cm^3/mol-s. This work also presented several additional pathways involving oxidation of HgCl to $HgCl_2$:

$$HgCl + HCl \longrightarrow HgCl_2 + H \qquad\qquad (6)$$
$$HgCl + Cl_2 \longrightarrow HgCl_2 + Cl \qquad\qquad (7)$$
$$HgCl + Cl \longrightarrow HgCl_2 \qquad\qquad (8)$$

Kramlich and Niksa proposed the same kind of reaction pathways for the oxidation of Hg with Cl.[22,20] Both authors discussed the mechanism, but Niksa demonstrated the oxidation of Hg with atomic chlorine using the chlorine atom recycle mechanism detailed in Figure 2.2.[20] This explains the partial oxidation of Hg and Cl to form HgCl and the further formation of $HgCl_2$ with Cl_2.

The gas phase study by Ghorishi indicated that the oxidation of elemental mercury is slow in the presence of HCl, but effective at temperatures greater than 700^oC for concentrations of HCl in the range 100-200 ppm.[23] The studies of Hall and Schager showed that the reaction between elemental mercury and HCl was temperature sensitive and proceeded faster at temperature $> 500^oC$. HCl was shown to be a very good oxidizing agent, especially in the presence of metal oxides. In this process, it follows the deacon reaction mechanism and converts into chlorine, which is also a very good oxidizing agent.[24,21] It can be concluded that the reaction for Hg and Cl, Hg and Cl_2 is fast compared to the reaction for Hg and HCl. While the reaction for Hg and HCl can be effective at temperatures greater than 500^oC and $HgCl_2$, it is considered to be the dominant product at temperatures less than 450^oC.

Effect of O_2 with Hg:

Hall indicated an increase in the reaction rate of Hg and O_2 with increases in temperature until it reaches the decomposition temperature. [21]

$$Hg\ (ads) + O_2\ (g) \longrightarrow HgO\ (s,\ g) \hspace{3cm} (9)$$

Galbreath reported that adsorbed Hg^o or O_2 on the surface could lead to heterogeneous reactions, resulting in HgO (g). [25]

$$Hg^o\ (g,\ ads) + 1/2O_2\ (g,\ ads) \longrightarrow HgO\ (g) \hspace{2cm} (10)$$
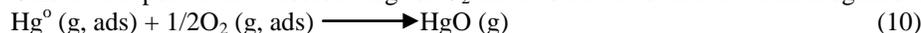
Heterogeneous Hg Speciation:

In the combustion zone, chemical reactions proceed at high temperatures rather than under post-combustion conditions. It is believed that Hg transformations are controlled by heterogeneous reactions which occur in the post-combustion zone. Gas-phase reactions alone are not sufficient to describe the Hg transformation in flue gas. Metallic oxides of fly ash are found to promote Hg oxidation, especially in the presence of HCl. Hg capture increased when flue gas temperature was reduced to below 400^oC.[26]

HgO (g) formation involves heterogeneous reactions of Hg^o (ads) with O_2 adsorbed on a catalyst surface. Initially, mercury oxidation studies were conducted in the presence of fly ash, which was shown to enhance the Hg oxidation reactions in the post-combustion zone. This study provided strong evidence that catalytic surfaces play an important role in explaining the surface catalytic mechanism in the post-combustion zone. It is very important to explain the role of fly ash constituents, such as Fe_2O_3, Al_2O_3, TiO_2, and CaO in the transformation of Hg to HgO and $HgCl_2$ under the influence of flue gas compositions.[9]

Effect of Hg Speciation with Fe_2O_3:

As mentioned earlier, metallic oxides showed to be more effective than activated carbon in enhancing Hg oxidation. Iron oxide, one of the metallic constituents of fly ash, tested to be a better catalyst in improving the oxidation of Hg. Zhuang study demonstrated that iron oxide promoted Hg oxidation in the presence of HCl.[15] This has also been shown by Ghorishi, who conducted Hg speciation experiments using a fixed bed reactor with HCl concentration ranging from 100-200 ppm in the presence of metal oxides, such as iron oxide, alumina, silica, calcium oxide and copper oxide.[23]

α-Iron oxide was ineffective when injected into fly ash in the presence of HCl, but α-Iron oxide and γ-iron oxide were effective in enhancing the Hg oxidation in the presence of HCl and NO_x. In his study, Galbreath concluded that γ-iron oxide readily captures Hg^o. The availability of Hg^{2+}, HCl and γ-iron oxide in excess in the Blacksville coal combustion flue gas suggested that γ-iron oxide catalyzes Hg^{2+} formation in the presence of HCl and elemental Hg. The experimental conditions maintained at 150^oC in the fabric filter containing 65 g/m^2 of γ-iron oxide with combustion flue gases flowing through fabric filter resulted in 30% of elemental Hg being converted to Hg^{2+} and Hg (p) with 100 ppmv of HCl injection. The addition of more HCl and γ-iron oxide did not have any effect on elemental mercury oxidation.[27]

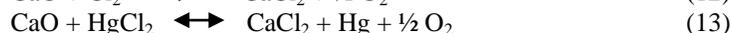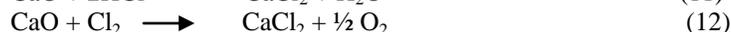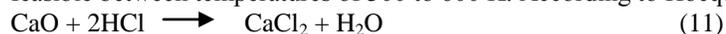**Effect of Hg Speciation with Al_2O_3:**

Hg transformations using an aluminum oxide catalyst show no significant differences. The various studies gave the same results, proving that aluminum oxide is inactive in the capture of mercury. Mercury speciation in the presence of alumina using 100 ppm of HCl concentration in a fixed bed reactor was ineffective. The results obtained by Galbreath demonstrated that using 50-100 ppm of HCl for speciation of mercury in the presence of alumina were also ineffective.

Effect of Hg Speciation with TiO_2:

Galbreath's results demonstrated the inability of titanium dioxide to promote Hg oxidation. The reasons for this inability were not clear, but Galbreath proved that either the chemically complex flue gas might catalytically affect TiO_2 or the catalyst itself is not a good oxidizing agent. The experiments were conducted in a cylinder containing working standard grade HCl (g) (10290 ± 510 ppmv in N_2) with a permeation tube used as source of Hg^o, which was connected to an inline mercury analyzer at flue gas temperatures 970, 620 and 250^oC.

Effect of Hg Speciation with CaO:

Calcium oxide was found to be sensitive to the formation of Hg and flue gas composition in an experiment performed to find the role of calcium in the presence of HCl for Hg oxidation and adsorption. Calcium oxide was not effective in capturing Hg. This study also showed that calcium-rich adsorbents adsorb oxidized Hg. When acid gases were introduced, the adsorption of acid gases prevailed and oxidation decreased. Investigations by Hocquel explained the role of CaO in the presence of HCl for Hg speciation as a function of temperature. A continuous emission monitor was used for analyzing Hg. CaO played a key role in the transformation of ionic $HgCl_2$ (g) into Hg^o (g). In the combustion process, the reactions were feasible between temperatures of 300 to 600 K. According to Hocquel's experiments, the following reactions were possible:

$$CaO + 2HCl \longrightarrow CaCl_2 + H_2O \hspace{3cm} (11)$$
$$CaO + Cl_2 \longrightarrow CaCl_2 + 1/2\ O_2 \hspace{3cm} (12)$$
$$CaO + HgCl_2 \longleftrightarrow CaCl_2 + Hg + 1/2\ O_2 \hspace{2.5cm} (13)$$

Hocquel concluded that under influence of different temperatures and HCl concentrations, CaO improves the adsorption of Hg.

This research was performed in an effort to systematically study the oxidation and adsorption of Hg using both a gas phase and gas-surface reaction system. From the literature review, it is known that in the combustor the Hg present in coal is converted to gaseous elemental Hg. Elemental Hg is subsequently oxidized in the post-combustion zone, where the temperature is much lower than average temperatures in the combustor. Gas-phase Hg oxidation reactions are mainly those involving different chlorine sources such as Cl_2 or HCl, whereas heterogeneous Hg oxidation reactions also involve various surfaces including metal oxides associated with fly ash generated from the high-temperature transformation of the mineral matter

originally present in the coal. In the presence of chlorine and surfaces, Hg oxidation occurs under both homogeneous and heterogeneous oxidation conditions.[11] In addition, it has been shown that the heterogeneous oxidation of Hg is influenced by the post-combustion flue gas composition, including constituents such as NO_x, SO_x, O_2, and water vapor. This thesis will focus on the effects of acid gases on the oxidation of Hg in the presence of different metal oxide surfaces.

2. EXPERIMENTAL APPROACH

The experiments performed for this study were conducted with an assembly of instruments and a data acquisition procedure with flow reactor apparatus, trace level Hg analyzer, and data reduction method for homogeneous and heterogeneous chlorination of elemental mercury. A separate fused silica quartz tube was used for each experiment, and carrier gas with varied compositions was passed through the reactor which contained surface materials, where mercury chlorination reactions were performed.

2.1. Experimental Procedure: Homogenous and heterogeneous Hg adsorption and oxidation was performed as a function of residence time, gas composition, and temperature. Experimental conditions were maintained at gas-phase residence times of 1 or 2 sec; temperatures of 100, 200, 300 or 400°C; a chlorine source of Cl_2 or HCl, and gas compositions of N_2, N_2+CO_2, or $N_2+CO_2+O_2$.

For the heterogeneous studies, four different kinds of metal oxides were examined: Fe_2O_3, Al_2O_3, TiO_2, and CaO. In a given experiment, a bypass line was plumbed to the Hg analyzer, which in turn helped calculate the overall oxidation of Hg and the adsorption efficiency of metal oxides. The entire experimental setup is shown in Figure 4.1. Each set of experiments was repeated three times to examine the consistency of the results, and the measurements were averaged.

Residence time (s)	1	2
Hg gas flow rate (mL/min)	13.14	6.57
Carrier gas flow rate (N_2) mL/min	2668	1317
Flow rate of O_2 (mL/min)	98	49
Flow rate of CO_2 (mL/min)	488	244
Cl_2 flow rate (mL/hr)	19.5	9.8
HCl flow rate (mL/hr)	19.5	9.8

Table 1: Experimental Conditions at 100°C

Table 2: Experimental Conditions at 200°C

Residence time (s)	1	2
Hg gas flow rate (mL/min)	10.4	5.2
Carrier gas flow rate (N_2) mL/min	2077	1039
Flow rate of O_2 (mL/min)	77	38
Flow rate of CO_2 (mL/min)	385	192
Cl_2 flow rate (mL/min)	15.4	7.7
HCl flow rate (mL/min)	15.4	7.7

Table 3 : Experimental Conditions at 300°C

Table 4: Experimental Conditions at 400°C

Residence time (s)	1	2
Hg gas flow rate (mL/min)	8.5	4.3
Carrier gas flow rate (N_2) mL/min	1715	857
Flow rate of O_2 (mL/min)	64	32
Flow rate of CO_2 (mL/min)	318	159
Cl_2 flow rate (mL/min)	12.7	6.4
HCl flow rate (mL/min)	12.7	6.4

Residence Time (s)	1	2
Hg Gas Flow Rate (mL/min)	7.28	3.64
Carrier Gas Flow Rate (N_2) mL/min	1460	730
Flow Rate of O_2 (mL/min)	54	27
Flow Rate of CO_2 (mL/min)	270	135
Cl_2 Flow Rate (mL/min)	10.82	5.41
HCl Flow Rate (mL/min)	10.82	5.41

3. RESULTS AND DISCUSSION:

Figures 5.29 through 5.32 show a comparison of gas phase, adsorption, and overall Hg removal efficiency for all catalysts at residence times of 1 and 2 sec in the presence of Cl_2 and or HCl, and N_2. From Figures 5.29 and 5.30, it was observed that for γ-Fe_2O_3 and TiO_2, overall Hg removal efficiency was higher compared to gas phase and other catalysts (CaO and Al_2O_3) with Cl_2 injection. From Figures 5.31 and 5.32 with presence of HCl, the overall removal efficiency for γ-Fe_2O_3 and TiO_2 was higher and also adsorption for γ-Fe_2O_3 was higher than gas phase oxidation and other catalysts (CaO and Al_2O_3). Compared to gas phase results, the γ-Fe_2O_3 and TiO_2 showed surface oxidation. Although Al_2O_3 showed slightly higher overall Hg removal than adsorption efficiencies, the overall Hg removal efficiency is similar to gas phase oxidation. CaO was ineffective for the Hg transformation in presence of HCl and Cl_2. When compared to gas phase results, CaO did not show significant surface oxidation, which shows its ineffectiveness and played a major role as reducing agent.
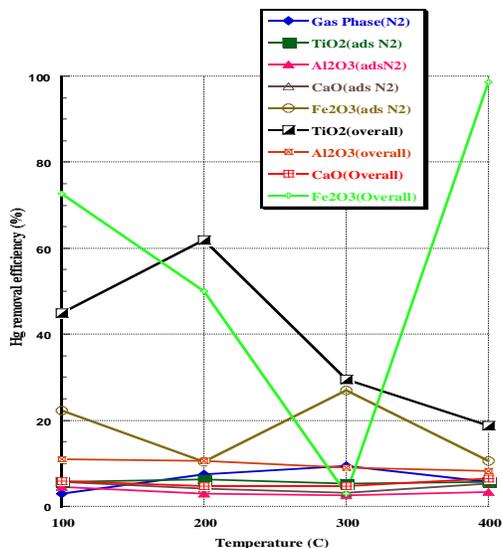
Figure 5.29: Hg removal efficiency as a function of temperature after 1 ppm Cl$_2$ injection in presence of N$_2$ gas with combination of all catalysts and gas phase, R.T. = 1 sec.
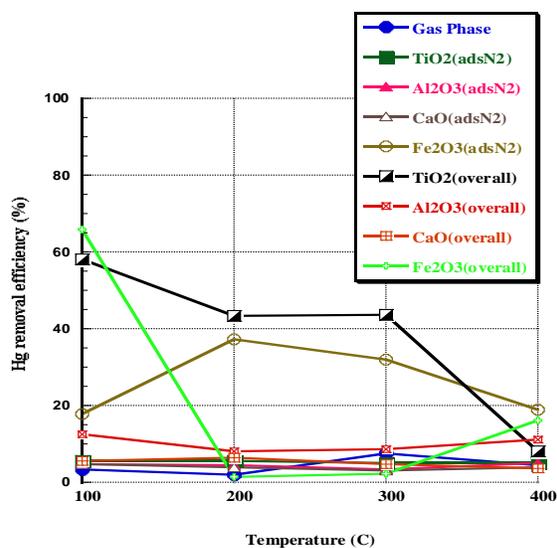

Figure 5.30: Hg removal efficiency as function of temperature after 1 ppm Cl$_2$ injection in presence of N$_2$ gas with combination of all catalysts and gas phase, R.T. 2 sec
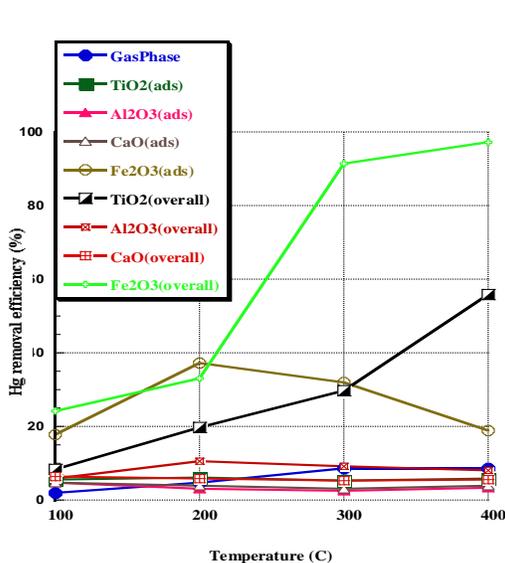

Figure 5.31: Hg removal efficiency as function of temperature after 100 ppm HCl injection in presence of N$_2$ gas with combination of all catalysts and gas phase, R.T. = 1 sec
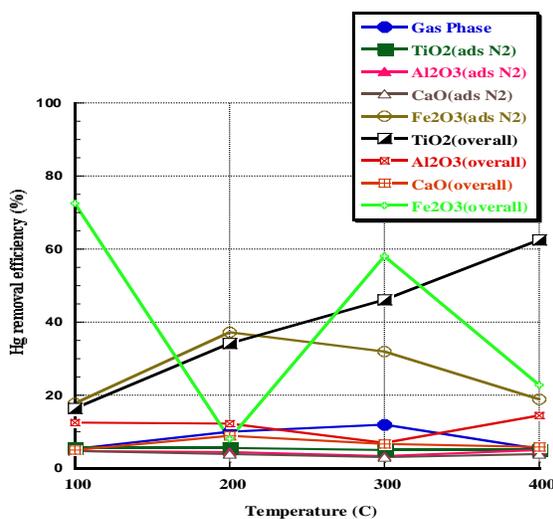

Figure 5.32: Hg removal efficiency as function of temperature after 100 ppm HCl injection in presence of N$_2$ gas with combination of all catalysts and gas phase: Residence time 2 sec

4. CONCLUSIONS

Experiments were designed to investigate Hg transformation under homogeneous (gas-phase) and heterogeneous (gas-surface) environments in presence of chlorine sources (Cl$_2$ and HCl). The following conclusions were drawn from the experimental studies:

- Gas phase results did not show any measurable difference for Hg oxidation at 1 and 2 sec residence time, for the various gas compositions in the presence of either HCl or Cl$_2$.
- Surface activity of catalysts, in terms of adsorption only, followed the following descending order of reactivity: Fe$_2$O$_3$ > TiO$_2$ > Al$_2$O$_3$ > CaO. The overall Hg removal efficiency in the presence of Cl$_2$ or HCl followed the same descending order of reactivity.

For iron oxide, the data was highly scattered and further investigation is needed to elucidate the Hg adsorption and oxidation mechanisms. TiO_2, in presence of Cl_2, showed high overall Hg removal efficiencies at low temperatures. TiO_2, in presence of HCl, showed high overall Hg removal at high temperature (400^oC).

6. REFERENCES:

1. Othermer, K. Encyclopedia of Chemical Technology. (2006), Ed. 5, Vol. 16.
2. Hill, F. C., Laboratory of Physics, Univ. of Illinois, Phys. Rev. (1922), 20, 259-266.
3. Characterization of products containing mercury in municipal solid waste in the United States, 1970-2000, OSW No.EPA530-R-92-013 (NTIS no.PB92-162 569), U. S. Environmental Protection Agency.
4. Global Mercury Assessment (www.chem.unep.ch/Mercury/Report/Key-findings.htm).
5. United States Department of Labor, Occupational Safety and Health Administration (http://www.osha.gov/SLTC/healthguidelines/mercuryvapor/recognition.html)
6. Mercury Study Report to Congress, December (1997), Volume 1, EPA-452/R-97-003.
7. Controlling Power Plant Emissions, US-EPA Report (http://epa.gov/mercury/control_emissions/emissions.htm).
8. Chemical and Engineering News, March 2, page 13, 2009 (WWW.CEN-ONLINE.ORG).
9. Dunham, G.E., Dewall R.A. and Senior, C.L., Fuel Process. Technol. (2003), 82,197-213.
10. Niksa, S. and Fujiwara, N. (2004) Predicting Complete Hg Speciation Along Coal-fired Utility Exhaust Systems, Combined Power Plant Air Pollution Control Mega Symposium, Washington, D.C.
11. Pavlish, J.H., Sondreal, E.A., Mann, M.D., Olson, E.S., Galbreath, K.C., Laudal, D.L., and Benson, S.A., Fuel Process. Technol. (2003), 82, 89-165.