



Heterogeneous catalytic reaction of elemental mercury vapor over cupric chloride for mercury emissions control

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ABSTRACT

In this study, the reaction mechanism of Hg(0) vapor oxidation over cupric chloride (CuCl_2) was investigated using 10% (wt) $\text{CuCl}_2/\alpha\text{-Al}_2\text{O}_3$ for mercury emissions control from coal-fired power plants. The $\text{CuCl}_2/\alpha\text{-Al}_2\text{O}_3$ sample showed >90% Hg(0) oxidation with excellent resistance to SO_2 at 140 °C in a simulated flue gas containing 10 ppmv HCl, 2000 ppmv SO_2 , and 6% O_2 gases balanced with N_2 gas. In the absence of HCl and O_2 gases, Hg(0) vapor was found to be oxidized by consuming atomic Cl of CuCl_2 and reducing it to CuCl, following a Mars–Maessen mechanism. The reduced CuCl could be re-chlorinated back to CuCl_2 by replenishing empty Cl atoms under 10 ppmv HCl and 6% O_2 gases readily present in coal combustion flue gases even under 2000 ppmv SO_2 concentration for continuous Hg(0) oxidation. Cl_2 gas generation was not observed over CuCl_2 at 140 °C, indicating a heterogeneous catalytic reaction. CuCl_2 shows potential that can be realized in a honeycomb or plate catalyst bed.

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1. Introduction

On December 21, 2011, the U.S. Environmental Protection Agency (EPA) announced the Mercury and Air Toxics Standards (MATS) rule that would limit mercury, acid gases, and other toxic heavy metal emissions from coal- and oil-fired utility, industrial, commercial, and institutional power plants [1]. The new rule, which was effective on April 16, 2012, will reduce mercury emissions by >90%. In July 2010 prior to the MATS, the U.S. EPA also issued a new proposed rule, the Transport Rule, which replaces the 2005 Clean Air Interstate Rule (CAIR) and will start to regulate sulfur dioxide (SO_2) and nitrogen oxide (NO_x) emissions from power plants in 28 states from 2012 [2,3]. The U.S. EPA estimates that a total 272.2 GW of flue gas desulfurization (FGD) and 217.6 GW of selective catalytic reduction (SCR) units of a total 373 GW to be generated from coal combustion would be operative by 2020 in order to meet the Transport Rule requirements (according to the TR SB Limited Trading model) [4].

The use of powder river basin (PRB) subbituminous coal, which generates higher percentages of elementary mercury ($\text{Hg}(0)$) vapor, is increasing [5], and the proposed Transport Rule is very likely to increase the installation of wet FGD systems (>95% for SO_2 control on a basis of total electricity generation) and SCR units for large coal-fired power plants. In this context, heterogeneous Hg(0) oxidation using catalysts or oxidants is highly expected to play a critical

role in future mercury emissions control in the U.S. [6–8]. Among these oxidized mercury species, HgCl_2 has high solubility in water (i.e. 7.37 g/100 g water at 25 °C) and other oxidized forms have very low solubility [9]. Therefore, HgCl_2 is the most desirable oxidized form for capture in wet FGD systems and is proven to be removable by activated carbon injection.

To date, noble metals and metal oxides have been primarily studied for heterogeneous catalytic Hg(0) oxidation. Noble metal-based catalysts have shown limited success in the absence of HCl or Cl_2 gas [7,10–12]. Au and Pd catalysts oxidize Hg(0) vapor primarily by Cl_2 gas, but Pt catalyst requires HCl and O_2 gases for Hg(0) oxidation, suggesting different mechanisms [10–12]. Recently, various metal oxide-based Hg(0) catalysts including V_2O_5 , MoO_3 , Cr_2O_3 , MnO_x , CeO_2 , Co_3O_4 and RuO_2 have been studied for the development of a Hg(0)-specific or modified SCR catalyst [13–19]. However, even in the presence of HCl gas, many of these metal oxide catalysts exhibited limited Hg(0) oxidation at a low HCl level typically found in subbituminous or lignite coal combustion flue gas (e.g. ≤ 10 ppm) due to the competitive adsorption of multiple gases including SO_2 , NH_3 , HCl, and Hg(0) onto metal oxide sites. The Deacon reaction shown in reaction (1) producing Cl_2 gas from HCl and O_2 gases over V_2O_5 , MnO_x , and RuO_2 was proposed to correlate with Hg(0) oxidation [14,16,20]. However, the homogeneous reaction between Cl_2 gas and Hg(0) vapor is known to be slow, and is not enough to explain the extent of observed Hg(0) oxidation [7,21,22]. The production of Cl_2 gas was also significantly inhibited by higher concentrations of SO_2 gas over metal oxides [14,23,24]. Recently, it was supposed that the Cl atom adsorbed onto coordinatively unsaturated ruthenium atoms might be enough and responsible

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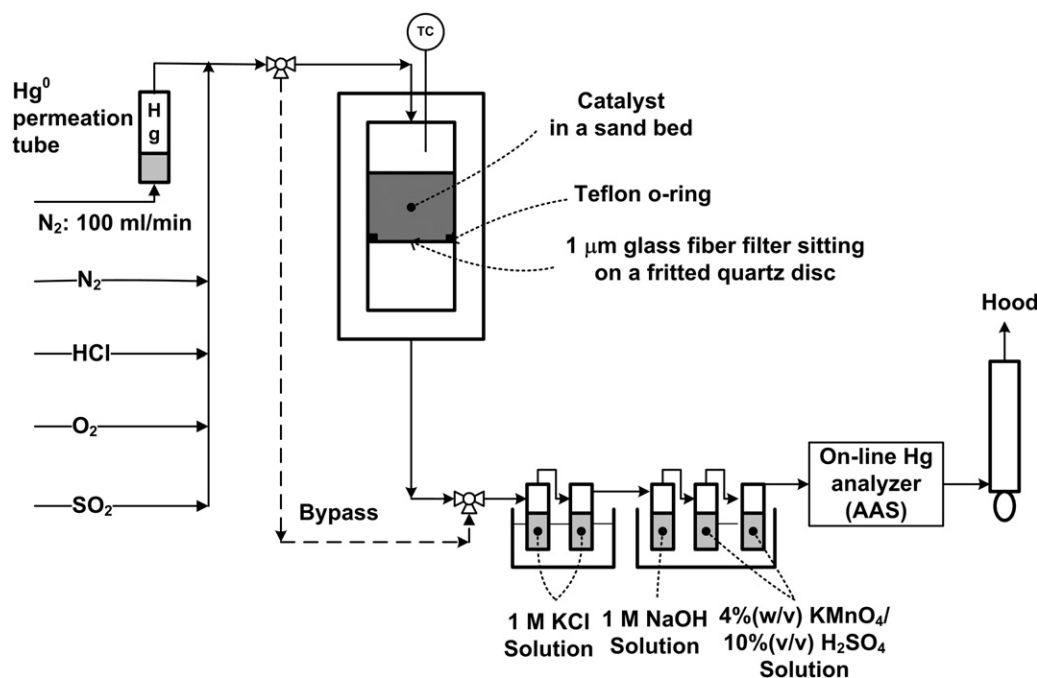


Fig. 1. A schematic of fixed-bed reactor.

for high Hg(0) conversion, suggesting a heterogeneous catalytic reaction [16]. The adsorption of HCl gas followed by the formation of Cl atoms onto metal oxide surfaces is thought to be the key to successful Hg(0) oxidation.

$2\text{HCl} + \frac{1}{2}\text{O}_2 \leftrightarrow \text{Cl}_2 + \text{H}_2\text{O}$ ·· Deacon reaction,

$$\Delta H^0 = -28.4 \text{ kJ/mol} \quad (1)$$

It was reported that $\text{CuCl}_2/\text{TiO}_2$ -based catalysts could simultaneously oxidize Hg(0) vapor and reduce NO gas but the NO reduction performance significantly decreased above 300–350 °C [25]. In our previous study, CuCl_2 was found to readily oxidize Hg(0) vapor but its resultant oxidized mercury is not easily adsorbed onto the non-carbonaceous substrate surface [26]. Carbon seems to be the only substrate that can effectively adsorb oxidized mercury. The resultant oxidized mercury species has recently been found to be primarily mercuric chloride (HgCl_2) using X-ray absorption fine structure (XAFS) spectroscopy [27]. Based on these findings, the primary objective of this study is to investigate the reaction mechanism of Hg(0) vapor oxidation over CuCl_2 under selected different gas conditions at 140 °C, targeting typical flue gas temperatures between the air preheater and electrostatic precipitator/fabric filter ranging between ~130 and ~180 °C [28].

2. Experimental

2.1. Catalyst preparation

There are many factors that can influence the performance of CuCl_2 -based catalyst on Hg(0) oxidation such as $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ loading, dispersion, copper speciation on different substrate, surface area, and pore volume. A $\text{CuCl}_2/\alpha\text{-Al}_2\text{O}_3$ catalyst was prepared by impregnating $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Sigma, 97% purity) onto $\alpha\text{-Al}_2\text{O}_3$ (Alfa Aesar aluminum oxide-43862, 1/8" pellets, BET surface area = 0.25 m^2/g) in the aqueous phase following the incipient wetness method. In this study, non-porous $\alpha\text{-Al}_2\text{O}_3$ was selected as a substrate, and 10% (wt) CuCl_2 (excluding the weight of $2\text{H}_2\text{O}$) was used throughout the study. $\alpha\text{-Al}_2\text{O}_3$ is found to be inert toward copper speciation and not to react with CuCl_2 and form other

copper compounds during CuCl_2 impregnation. In addition, while $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ forms an amorphous form of CuCl_2 , CuCl_2 formed onto $\alpha\text{-Al}_2\text{O}_3$ was found to be in a crystalline form, allowing for the surface reactions between CuCl_2 and Hg(0) using X-ray diffraction (XRD). After impregnation, the samples were dried at 100 °C for 8 h. The synthesized catalyst was ground and sieved to ~40 μm particles for the characterization and performance evaluation of Hg(0) oxidation.

2.2. Performance evaluation of $\text{CuCl}_2/\alpha\text{-Al}_2\text{O}_3$ catalyst

A lab-scale fixed-bed system was used for the performance evaluation of Hg(0) oxidation and preparation of a spent catalyst for X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) analysis. 25 mg of the catalyst was mixed with 4 g quartz sand and then was loaded into a fixed-bed reactor with an inner diameter of 12 mm. The length of reaction zone was ~20 mm. Before loading a catalyst, a blank test has been performed and showed negligible Hg(0) adsorption on the internal wall of either borosilicate reactor or Teflon tubing. The outlet mercury speciation was measured by the Ontario Hydro method. A 1 M KCl impinger solution was used to capture oxidized mercury. A 4% (w/v) $\text{KMnO}_4/10\%$ (v/v) H_2SO_4 impinger solution was used to capture Hg(0) vapor as shown in Fig. 1. Oxidized mercury and Hg(0) concentrations in the effluent gas stream were determined by analyzing those solutions using a cold vapor atomic absorption spectrophotometer (Model 400A, Buck Scientific Inc.). More detailed information on the system and experiments are described in our previous study [29]. The inlet Hg(0) concentration was 0.25 $\text{mg}/\text{N m}^3$ (=30 ppbv) in 1 L/min of a carrier gas flow, and the reactor was placed in an oven maintained at 140 °C. Four different gas conditions were used in this study: (1) N_2 (99.999% UHP, Wright Brothers, Inc.); (2) 6% O_2 (balanced with N_2); (3) 10 ppmv HCl and 6% O_2 (balanced with N_2); and (4) 2000 ppmv SO_2 , 10 ppmv HCl, and 6% O_2 (balanced with N_2). When 2000 ppmv SO_2 was added, a 1 M NaOH solution was used to capture SO_2 gas, which was found to interfere with Hg(0) vapor captured in a 4% (w/v) $\text{KMnO}_4/10\%$ (v/v) H_2SO_4 impinger solution. When spent catalysts were prepared for characterization, the catalysts were not mixed with quartz sand and an inlet Hg(0) vapor

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