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Microwave assisted catalytic removal of elemental mercury from flue gas using Mn/zeolite catalyst

Zaishan Wei, Yuwei Luo, Baoren Li, Zhouyang Cheng, Jianbin Wang, Qihong Ye

School of Environmental Science and Engineering, Sun Yat–Sen University, Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology, Guangzhou 510275, China

ABSTRACT

The integrated microwave with Mn/zeolite and ozone (MCO) and combined microwave with Mn/zeolite (MC) was employed to oxidize elemental mercury (Hg^0) in simulated flue gas. The results show that mercury removal efficiency attained 35.3% in the MC, over 92% of Hg^0 removal efficiency could be obtained in the MCO. The optimal microwave power and empty bed residence time (EBRT) in the microwave plasma catalytic oxidation were 264 W and 0.41 s, respectively. The effect of Hg^0 oxidation in the MCO was much higher than that in the MC. Microwave accentuated catalytic oxidation of mercury, and increased mercury removal efficiency. The additional use of ozone to the microwave–catalysis over Mn/zeolite led to the enhancement of mercury oxidation. Mn/zeolite catalyst was characterized by X–ray diffraction (XRD), X–ray photoelectron spectroscopy (XPS), Fourier transform infrared spectra (FT–IR), scanning electron microscopy (SEM) and the Brunauer Emmett Teller (BET) method. Microwave catalytic mercury over Mn/zeolite was dominated by a free radical oxidation route. Ozone molecules in air could enhance free radical formation. The coupling role between ozone and radicals on mercury oxidation in the MCO was formed. The MCO appears to be a promising method for emission control of elemental mercury.

Keywords: *Elemental mercury, flue gas, Mn/zeolite, microwave catalytic oxidation, characterization*

Corresponding Author:
Zaishan Wei
☎ : *+86-20-84037096*
℡ : *+86-20-39332690*
✉ : *weizaishan98@163.com*

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1. Introduction

Mercury is a pollutant of concern due to its toxicity, volatility, persistence, and bioaccumulation in the environment (Zheng et al., 2012). Mercury is generated in the off–gas from coal–fired electric utilities, municipal waste combustors, medical waste incinerators, chlor–alkali, metal and cement plants (Ci et al., 2011). Mercury emission from coal–fired flue gas often presents in three main forms: particulate–associated [Hg(p)], gaseous divalent (Hg^{2+}) and elemental (Hg^0) (Kim et al., 2010), in which elemental mercury is the most difficult to be captured with the existing air pollution control devices (Shetty et al., 2008; Wu et al., 2011). Due to the potential mercury pollutant, elemental mercury treatment has attracted significant attention.

Conversion of Hg^0 to Hg^{2+} can be accomplished by heterogeneous catalysis or homogeneous gas phase oxidation. Magnetic zeolite composites with supported silver nanoparticles were able to capture mercury from the flue gases of an operational, full–scale, coal–fired power plant (Dong et al., 2009). Bromine chloride (BrCl) was employed to oxidize Hg^0 to $HgCl_2$ (Qu et al., 2009). Several materials have been proposed as catalysts for mercury oxidation, these materials include palladium, gold, iridium, platinum, iron, selective catalytic reduction (SCR) catalysts, fly ash, activated carbons (AC), and thief carbons (Presto and Granite, 2006; Wilcox et al., 2012). A co–benefit of SCR implementation was that it was effective at oxidizing Hg^0 to Hg^{2+} (Li et al., 2012a). The MnO_X–CeO_2/TiO_2 catalyst was highly active for Hg^0 oxidation even under SCR condition, but NH_3 consumed surface oxygen and limited Hg^0 adsorption, hence inhibited Hg^0 oxidation (Li et al., 2012b). $CuCl_2$/TiO_2 catalysts revealed high activity for mercury oxidation, the activity for mercury oxidation was significantly increased with the increase of $CuCl_2$ loading and HCl concentration (Kim et al., 2010). Hg^0 was oxidized by a heterogeneous reaction with surface Cl atom of $CuCl_2$, while oxidizing Hg^0 to $HgCl_2$ and reducing itself to CuCl (Li et al., 2013). Au/TiO_2 and Pd/Al_2O_3 catalysts on fabric filters were effective, yielding mercury oxidation ranges of 40–60% and 50–80%, respectively (Hrdlicka et al., 2008). V_2O_5/AC showed a high capability for flue gas Hg^0 capture due to catalytic oxidation of Hg^0 to Hg^{2+} by V_2O_5 (Wang et al., 2010a). Hg^0 was likely to be oxidized and retained by the oxidative elements produced on an activated carbon using zinc chloride surface through chemical activation (Hu et al., 2009). Hg^0 capture by Mn–Fe spinel could be promoted by the incorporation of Ti, Fe–Ti–Mn spinel could be magnetically separated from the fly ash (Yang et al., 2011). Using ICl to oxidize elemental mercury in coal–fired flue gas could save the consumption of iodine (Qu et al., 2010). The Hg^0 removal efficiency of titania nanotubes could exceed 90% for 100 h reaction (Wang et al., 2011). Hg^0 could be oxidized by active oxygen atom on the surface of nano–Fe_2O_3 as well as lattice oxygen in nano–Fe_2O_3 (Kong et al., 2011). Catalytic oxidation of Hg^0 transformation into Hg^{2+} could be a determining step to promote the adsorption of Hg species onto the TiO_{2-X} surface (His and Tsai, 2012). The integrated membrane delivery with catalytic oxidation systems was used to convert Hg^0 to Hg^{2+}, the conversion efficiency of Hg^0 reached 95% with Mo–Ru–Mn catalyst (Guo et al., 2012).

Non–thermal plasma catalysis is a promising technology for flue gas treatment. Microwave irradiation was applied to a

pyrolytic carbon such as activated carbon and char, enhancing the reaction of sulfur dioxide (SO_2) and nitrogen oxides (NO) with carbon (Cha and Kim, 2001). NO, SO_2 and Hg^0 oxidation efficiencies depended primarily on the radicals (OH, HO_2, O) and the active species (O_3, H_2O_2, etc.) produced by the pulsed corona discharge (Xu et al., 2009). A dielectric barrier discharge (DBD) reactor could be used to oxidize up to 80% mercury, the presence of NO_X enhanced mercury oxidation in the DBD reactor (Chen et al., 2006). Negative DC discharge induced more ozone production and a higher Hg^0 oxidation efficiency than positive DC discharge and 12 kHz AC discharge (Wang et al., 2009). Hg^0 was oxidized by utilizing both DBD of a gas mixture of Hg^0 and the injection of O_3 into the gas mixture of Hg^0 at room temperature (Byun et al., 2008). The formation of HgO_3(s) species deposited on the DBD reactor surface using O_3 injection accelerates the removal rate of Hg^0 (Byun et al., 2011). Active radicals including O, O_3 and OH all contributed to the oxidation of elemental mercury in the DBD, Hydrogen chloride could promote the oxidation of mercury due to chlorine atoms produced in the plasma process. Both NO and SO_2 had inhibitory effects on mercury oxidation, which could be attributed to their competitive consumption of O_3 and O (Wang et al., 2010b).

This work aims to study the integrated microwave with Mn/zeolite and ozone (MCO) and combined microwave with Mn/zeolite (MC) for Hg^0 oxidation. The study evaluates the role of microwave and catalyst, the coupling role of ozone and microwave catalysis on elemental mercury oxidation. This study utilizes X–ray diffraction (XRD), X–ray photoelectron spectroscopy (XPS), Fourier transform infrared spectra (FT–IR), scanning electron microscopy (SEM) and the Brunauer Emmett Teller (BET) method toward the understanding of the formation of the intermediate products and their involvement in the reaction mechanism of microwave catalytic mercury oxidation.

2. Material and Methods

2.1. Catalyst preparation

The Mn/zeolite catalyst was prepared by an incipient wetness impregnation using $Mn(NO_3)_2$ as the metal precursor, $Mn(NO_3)_2$ concentration was 0.1 mol L^{-1}. After impregnation in Ca–5A zeolite for 24 h in room temperature, the catalyst samples were dried in the vacuum drying oven at 80 °C for 2 h, and placed in the middle of muffle furnace, calcinated at 550 °C for 120 min. After cooling to room temperature, the Mn/zeolite samples were taken out for further investigations.

2.2. Experimental setup

The experimental flow loop of a microwave catalytic reactor over Mn/zeolite was shown in Figure 1. The reactor consisted of a quartz tube (10 mm i.d. and 250 mm long) with Mn/zeolite (external diameter of 3 to 4.6 mm) 10 mm in diameter and 220 mm in working height using ozone as oxidizing agent, which was set up to study elemental mercury oxidation from stimulated flue gas. Hg^0 vapor was prepared from the Hg^0 permeation unit (placed in a water bath with a temperature of 333 K) and was blended with the gases before they entered the reactor, ozone supplied from the ozone generator, were flowed upwards through the microwave reactor. Gas flow rate was monitored by the rotameter and the mass flow controllers. A constant input microwave power of 136–440 W was used and the microwave frequency was 2 450 MHz.

2.3. Analytical methods

The inlet and outlet of the bubbler were sampled for gaseous mercury in accordance with Ontario Hydro Method of U.S. EPA Method 23 and U.S. DOE. The concentrations of mercury were quantified by atomic fluorescence spectrophotometry (AFS).Gas collection was made at a velocity of 1 L min^{-1} for 5 min. Fraction analysis of soluble and insoluble mercury was performed with a series of absorption bottles that contained distilled water and an aqueous acidic solution of potassium permanganate ($KMnO_4$). The outlet gas was absorbed for the trap for divalent mercury by a bottle containing saturated KCl solution. The soluble mercury was taken to be $HgCl_2$, and the insoluble mercury was taken to be Hg^0. Ozone concentration was measured by an electro–chemical gas analyzer (AIC–800–O_3, Shenzhen aopul Co. Ltd, CHINA). XRD, XPS, FT–IR, SEM and the BET method were employed to fully characterize the Mn/zeolite. The BET method, using ASIQC0V100.2 Quantachrome (USA) instrument was used to determine the total surface area of the prepared catalysts by physisorption of nitrogen at liquid nitrogen temperature (77 K) in static mode.

3. Results and Discussion

3.1. Characterization of the Mn/zeolite

The BET area was determined to be 280.793 $m^2 g^{-1}$ for the Mn/zeolite; the total pore volume and average pore diameter of the corresponding sample were 0.094 $cm^3 g^{-1}$ and 17.047 nm, respectively (Figure 2). The Mn/zeolite had rich pore structure, and the main aperture of them was mesoporous.

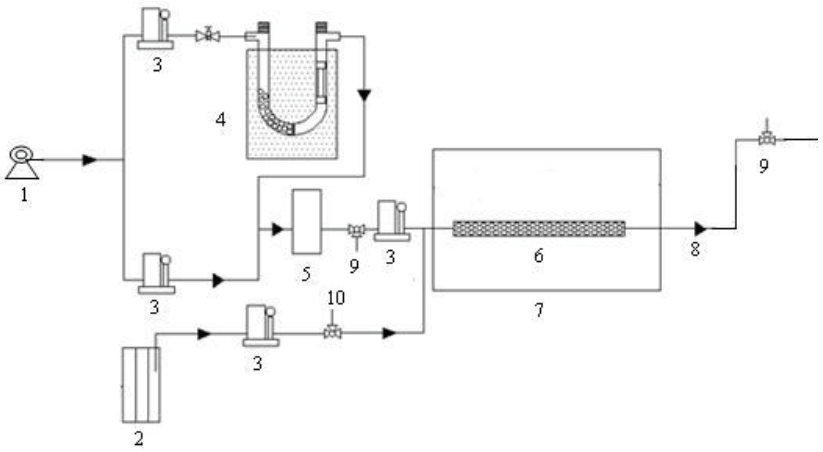

Figure 1. *Experimental flow loop of microwave catalytic elemental mercury removal over Mn/zeolite.* ***(1)*** *air compressor;* ***(2)*** *ozone generator;* ***(3)*** *flow meter;* ***(4)*** *the Hg^0 permeation unit;* ***(5)*** *the bottle of gas mixture;* ***(6)*** *catalyst bed;* ***(7)*** *microwave catalytic reactor;* ***(8)*** *outlet port;* ***(9)*** *gaseous elemental mercury sampling port;* ***(10)*** *ozone inlet sampling port.*