Chemical Engineering Journal 325 (2017) 708–714

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Non-thermal plasma injection-CeO_2-WO_3/TiO_2 catalytic method for high-efficiency oxidation of elemental mercury in coal-fired flue gas

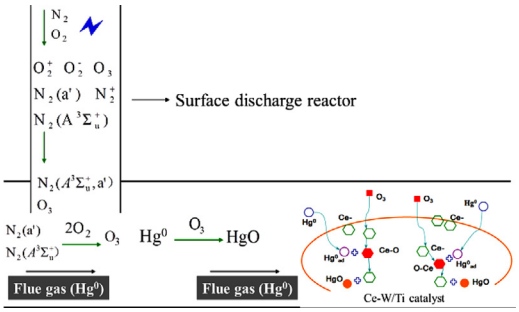
Jiutao An [a,*], Jing Lou [a], Qingmei Meng [a], Zijian Zhang [a], Xiaoxuan Ma [a], Jie Li [b]

[a] College of Resources and Environment Engineering, Shandong University of Technology, 266 Xincun West Road, Zibo, Shandong Province, PR China
[b] College of Electrical Engineering, Dalian University of Technology, Dalian, PR China

HIGHLIGHTS

- A non-thermal plasma and catalysis system based on CeO_2-WO_3/TiO_2 was developed to oxidize Hg^0 in the flue gas.
- Approximately 86.6% of the Hg^0 was oxidized and 32.9 μg kJ^{-1} of energy yield was obtained at 110 °C and 2.6 J L^{-1}.
- The NTPIC system widened the temperature windows of the catalyst (80–300 °C).
- The NTPIC system overcame the inhibitory effect of NO in the plasma alone system.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 24 November 2016
Received in revised form 28 April 2017
Accepted 2 May 2017
Available online 6 May 2017

Keywords:
CeO_2-WO_3/TiO_2
Non-thermal plasma
Hg^0 oxidation
Flue gas

ABSTRACT

The combined method of non-thermal plasma injection and 3%CeO_2-WO_3/TiO_2 catalysis system was proposed to enhance Hg^0 oxidation in flue gas. Compared with the plasma system, the combined system had excellent oxidation performance. Approximately 86.6% of Hg^0 was oxidized and energy yield reached 32.9 μg kJ^{-1} at 2.6 J L^{-1} and 110 °C . The combined system widened the temperature windows of CeO_2-WO_3/TiO_2 catalyst (80–300 °C), showed good resistance to H_2O and SO_2, and also overcame the inhibitory effect of NO on Hg^0 oxidation in the plasma system·NH_3 inhibited the Hg^0 oxidation; however, the coexistence of NO with NH_3 significantly mitigated the inhibition. In the combined system, the CeO_2-WO_3/TiO_2 catalyst could catalytically decompose the ozone generated by gas discharge, and increased the production of high adsorbed active oxygen, which was favorable for Hg^0 oxidation process. The Hg^0 oxidation process followed the homogeneous reaction mechanism and the Mars-Maessen mechanism in NTP injection system and CeO_2-WO_3/TiO_2 system, respectively.

1. Introduction

Coal combustion produces a large amount of flue gas pollutants [1], and mercury as one of flue gas pollutants is the high toxicity and bioaccumulation ability [2]. Hence, United States already mandated the emission standards of mercury to reduce its emissions for coal-fired power stations by November 2011, and China also issued the emission standards of mercury by July 2014 [3]. Mercury generally exits in flue gas: gaseous oxidized mercury (Hg^{2+}) compounds, elemental mercury (Hg^0) and particulate-bound mercury (Hg^p) [3,4]. Hg^p and Hg^{2+} are easily captured by bag-type dust collector/electrostatic precipitators (ESP) and wet flue gas desulfurization (WFGD), respectively [4]. However, it is

* Corresponding author.
E-mail address: anjiutao@163.com (J. An).

http://dx.doi.org/10.1016/j.cej.2017.05.010
1385-8947/

very hard to remove Hg^0 by ESP or WFGD due to its insolubility in water [3]. Hence, Hg^0 pollution control has attracted significant concerns.

Various technologies such as powder activated carbon injection [5], oxidant injection [6] and catalytic oxidation [7] have been investigated. Nowadays, installing selective catalytic reduction (SCR) systems is a trend to limit NOx emission, and how to take full advantage of SCR catalysts for Hg^0 oxidation has received great emphasis [8,9]. Among the SCR catalysts, V_2O_5-based catalysts as high-temperature SCR catalysts have been intensively investigated to oxidize Hg^0, and high concentration HCl was required to achieve high Hg^0 oxidation. In addition, the V_2O_5-based SCR catalysts require high operating temperature from 300 °C to 400 °C, and must be located upstream of the bag-type dust collector/ESP [8]. However, because the SCR catalysts are exposed to high particulate matter concentration, these catalysts are very susceptible to poisoning deactivation [9]. To avoid these limitations, the low-temperature SCR catalysts are developed at low temperatures from 100 to 250 °C, and should be installed downstream of WFGD. Hence, the low-temperature SCR catalysts for Hg^0 oxidation have become an important research scope.

Due to their excellent oxygen storage/release capacity, CeO_2 based catalysts have been proved to be very promising catalysts to oxidize Hg^0 at low temperature [10]. Nevertheless, the oxidation activity of CeO_2 based catalysts still needs to be improved at lower temperature (less than 200 °C). Less than 80% Hg^0 oxidation was observed over CeO_2/TiO_2 at 100–180 °C [10], and less than 65% Hg^0 oxidation was achieved over CeO_2/Al_2O_3 catalyst at low reaction temperature (150–270 °C) [11]. Therefore, the temperature window of the catalysts needs to be further broadened.

Non-thermal plasma (NTP), one of the advanced oxidation processes, has received great emphasis on flue gas treatment due to large amount of active species (especially ozone) [12], and was able to widen the temperature window for the SCR catalysts [13]. In our previous studies [14], NTP injection exhibited excellent oxidation performance for Hg^0 because of less investment cost and system size. Accordingly, the NTP injection-CeO_2 based catalysts (NTPIC) system was proposed to enhance the Hg^0 oxidation at low reaction temperature. In addition, pure CeO_2 was thermo-unstable [10]. Ti^{4+} was introduced into the CeO_2 lattice by forming CeO_2-TiO_2 mixed oxide, which enhanced the thermal stability, and WO_3 was suitable for this system because tungsten was a catalytic activity and structure promoter [15].

In this work, a NTPIC technique was proposed to enhance Hg^0 oxidation in flue gas. The primary objective of the study is to provide a novel approach of NTPIC technique for a cobenefit of Hg^0 oxidation at low temperature.

2. Experimental

2.1. The NTPIC system

Fig. 1 shows the experimental apparatus of the NTPIC system. AC voltage (50 Hz) with peak value varying from 8 to 12 kV was applied on the discharge reactor to produce the discharge plasma. Experiments were performed using a surface dielectric barrier discharge (SDBD) reactor, and the SDBD reactor was composed of a quartz tube, a stainless mesh and a spring. The quartz tube as barrier material was the inner diameter of 4 mm and the thickness of 1.5 mm. The stainless mesh (length 25 mm) as grounded electrode tightly wrapped the outside of the tube. The spring as high-voltage electrode consisted of stainless steel (diameter 0.5 mm), and fitted closely to the inner wall of the barrier material. The discharge reactor was plugged into the duct, and the duct consisted of quartz tube (outer diameter of 16 mm, inner diameter of 13 mm and length of 1000 mm). The catalysts (1.5 g) with the volume of 1.23 cm^3 were introduced at 50 mm after the discharge reactor.

The simulated gas flow rate was approximately 2.0 L min^{-1} for all experiments with space velocity approximately 57,500 h^{-1}, and the NTP injection gas flow rate was approximately 10 mL min^{-1}. Hg^0 initial concentration was approximately 100 μg m^{-3}. The desired Hg°Concentration and water vapor were produced by a mercury permeation device (Dynacal, VICI Metronic, Inc. USA) and an evaporator using N_2 as the carrier gas, respectively.

2.2. Catalysts

$M_xO_y(3)$-$WO_3(9)/TiO_2$ catalysts (M = Ce, Cu, Co and Mn) were prepared by a certain quality of TiO_2 (Degussa P25) into 150 ml 5 $(NH_4)_2O{\cdot}12WO_3{\cdot}5H_2O$ and nitrate hydrate solution, and about 3% of M_xO_y weight was set. A commercial $V_2O_5(3)$-$WO_3(9)/TiO_2$ catalyst, $WO_3(9)/TiO_2$ and $CeO_2(3)/TiO_2$ catalysts were used. The samples were firstly stirred for 24 h and following heated at 110 °C, and the catalysts were achieved through the calcination of the dried samples under air at 550 °C for 4 h.

2.3. Chemical analysis

The voltage-discharge (V-Q) Lissajous method was applied to test the discharge power. The Hg°Concentration and water vapor were tested by a mercury analyzer (RA-915 + Lumex, RU) and a humidity tester (Rotronic HC2-HK40 + HP22-A), respectively. Ozone was analyzed by the iodometry method [16].

Hg^0 oxidation efficiency (η), energy yield and specific energy density (SED) are defined as:

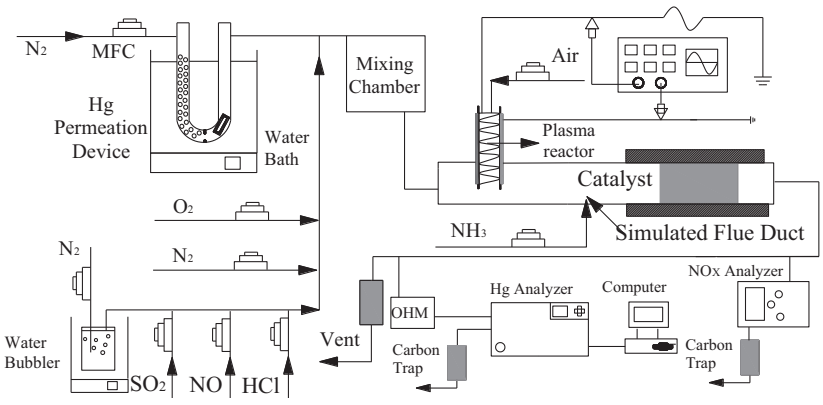


Fig. 1. Schematic diagram of the experimental setup.