



Full Length Article

Investigation on synergistic oxidation behavior of NO and Hg⁰ during the newly designed fast SCR processZijian Zhou^a, Xiaowei Liu^{a,*}, Yingchao Hu^a, Jie Xu^a, Xiangkun Elvis Cao^b, Zhiqiang Liao^a, Minghou Xu^{a,*}^a State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan 430074, China^b Sibley School of Mechanical and Aerospace Engineering, Cornell University, Ithaca, NY 14853, USA

ARTICLE INFO

Keywords:

NO
Elemental mercury
Catalytic oxidation
Interactions
Homogeneous oxidation

ABSTRACT

In the present study, elemental mercury (Hg⁰) oxidation behavior in the NO oxidation step of fast SCR process was investigated. The Mn doped CeO₂-ZrO₂ (CZM0.3) was selected as the catalyst, due to its superior oxygen storage capacity. The results showed that NO could be oxidized efficiently over the catalyst at around 250 °C under the atmosphere of NO/O₂/N₂. In the Hg⁰/NO/O₂/N₂ reaction system, NO oxidation reaction remarkably improved Hg⁰ oxidation efficiency. Two domination reaction pathways were proposed to interpret the influence of NO oxidation reaction on Hg⁰ oxidation: one through a heterogeneous oxidation process, and the other through a homogeneous reaction. In the heterogeneous oxidation process, NO was adsorbed on the active sites and activated by the surface oxygen to form more active intermediates for Hg⁰ oxidation. Hg⁰ was probably oxidized in its gaseous state, since the affinity between NO and the catalyst was stronger than that between Hg⁰ and the catalyst. The other reaction pathway was a homogeneous route, during which the gaseous NO₂ generated by NO oxidation could oxidize the gaseous Hg⁰ within the designed reaction conditions. According to the present research, synergistic oxidation of NO and Hg⁰ in the first step of fast SCR appears to be a promising way to remove Hg⁰ and NO_x in coal-fired power plants.

1. Introduction

Mercury (Hg) has been regarded as a hazardous pollutant to the atmosphere and human health [1]. Coal-fired power plants are the main sources of anthropogenic mercury emission to the environment [2,3]. In the coal-fired flue gas, three forms of Hg exist: elemental mercury (Hg⁰), divalent mercury (Hg²⁺) and particulate-bonded mercury (Hg^p) [4,5]. Hg²⁺ and Hg^p are easily removed by the existing air pollution control devices in coal-fired power plants, such as wet flue gas desulfurization (WFGD) scrubbers and the electrostatic precipitators (ESP) [6–9]. However, Hg⁰ is difficult to be controlled due to its high volatility and low solubility. The catalytic oxidation method is recognized as one of the most feasible ways to remove Hg⁰ by converting the insoluble Hg⁰ to soluble Hg²⁺ in the presence of catalyst. A number of studies have demonstrated that the selective catalytic reduction (NO-NH₃ SCR, denoted as “standard SCR”) DeNO_x unit in coal-fired power plants is obtained as co-benefit of Hg⁰ oxidation [10–15]. In this process, the gaseous Hg⁰ is adsorbed on the active sites of V₂O₅ based catalysts surface, and the lattice oxygen species are responsible for Hg⁰

oxidation [11,14,16,17]. Nevertheless, in the standard SCR reaction (NO + NH₃ + 1/4O₂ = N₂ + 3/2H₂O), NO adsorption on the commercial SCR catalyst is usually weak at the typical reaction temperature and atmosphere [18,19]. Accordingly, the effect of NO on Hg⁰ oxidation in the standard SCR reaction process is always negligible [14,17,20].

Recently, a newly designed process, the so-called fast SCR technology ((NO + NO₂)-NH₃ SCR), with higher NO_x removal efficiency has been developed [21]. In the fast SCR DeNO_x process, the reaction can be divided into two distinct steps, including NO catalytic oxidation reaction (NO + 1/2O₂ = NO₂) in one reactor and (NO + NO₂)-NH₃ selective catalytic reduction reaction (NO + NO₂ + 2NH₃ = 2N₂ + 3H₂O) in the other separate reactor. In the presence of NO₂, the (NO + NO₂)-NH₃ reduction reaction rate will be noticeably accelerated compared with the reaction rate of NO-NH₃. The higher reaction rate in the fast SCR process can be achieved by using an oxidative catalyst at upstream of the NO_x reduction unit to convert 50% of NO to NO₂, and this also enables the reduction of the SCR catalyst volume. Accordingly, NO oxidation to NO₂ is critical and it is also the rate-determining step of

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<https://doi.org/10.1016/j.fuel.2018.03.152>

Received 16 January 2018; Received in revised form 16 March 2018; Accepted 22 March 2018
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the whole fast SCR reaction [22]. In the fast SCR process, the catalysts used at different reaction steps are most likely to be different. In the NO oxidation process, the catalyst is always oxidative, and it perhaps also has the ability to oxidize Hg^0 simultaneously. However, few studies have focused on Hg^0 oxidation performance in the NO oxidation step of fast SCR reaction. The interactions between the two oxidation reactions are not clear as well.

There are some evident differences for Hg^0 oxidation behavior between the process of the standard SCR and the fast SCR reaction. In the fast SCR process, Hg^0 oxidation performance may be significantly affected by the NO oxidation process. Theoretically, there are two kinds of possible influences. On the one hand, NO oxidation reaction may have enhanced effects on Hg^0 oxidation. As reported, in the NO oxidation process of fast SCR reaction where reaction temperature is lower than that of the standard SCR reaction, NO will be strongly adsorbed on the catalyst and a number of intermediate species, like nitrite, will be generated [17,23,24]. Evidently, the intermediates and products of NO oxidation reaction are strongly oxidative species and are likely to oxidize Hg^0 simultaneously [20]. On the other hand, NO oxidation reaction may exert an inhibition effect on Hg^0 oxidation performance. From the proposed catalytic oxidation mechanisms for individual NO oxidation in the $\text{NO}/\text{O}_2/\text{N}_2$ system and single Hg^0 oxidation in the $\text{Hg}^0/\text{O}_2/\text{N}_2$ system [20,25], both NO and Hg^0 are adsorbed on the catalyst surface and oxidized by the adjacent chemical adsorbed oxygen species (O^*). This process implies that in the $\text{Hg}^0/\text{NO}/\text{O}_2/\text{N}_2$ reaction system, Hg^0 and NO are likely to be adsorbed on the same active sites and will compete for consuming the O^* on the catalyst surface. Practically, NO concentration in the coal-fired flue gas is constantly several orders of magnitude higher than that of Hg^0 , so the NO oxidation process may depress the Hg^0 oxidation behavior. Therefore, even though it seems possible to achieve effective Hg^0 oxidation in the NO oxidation step through fast SCR technology, some details of this process have not been fully understood yet. It is still unclear whether the Hg^0 oxidation reaction will be affected by the NO oxidation process. If so, what are the possible mechanisms for the influences or interactions? If the promotion and inhibition effects co-exist, which one will play a dominant role in Hg^0 oxidation process? These questions are still yet to be understood.

To clarify these issues, the Mn doped $\text{CeO}_2\text{-ZrO}_2$ based oxide was chosen in the present study, as the catalyst for NO oxidation reaction in the fast SCR, due to its large oxygen storage capacity. To achieve efficient oxidation of NO and Hg^0 simultaneously, we firstly investigated the NO oxidation performance over a series of catalysts at different temperatures to determine the optimal catalyst with the highest NO conversion rate. The individual Hg^0 catalytic oxidation activity over the selected catalyst was also studied, followed by the simultaneous oxidation of NO and Hg^0 . Most importantly, the effect of NO oxidation reaction on Hg^0 oxidation performance in the $\text{Hg}^0/\text{NO}/\text{O}_2/\text{N}_2$ system was examined, and two possible reaction pathways were proposed to interpret the influence of NO oxidation on Hg^0 oxidation behavior.

2. Experimental

2.1. Catalyst synthesis

The raw and Mn doped $\text{CeO}_2\text{-ZrO}_2$, $\text{Ce}_{2/3(1-x)}\text{Zr}_{1/3(1-x)}\text{Mn}_x\text{O}_2$ (CZM_x , $x = \text{Mn}/(\text{Mn} + \text{Ce} + \text{Zr})$ and $x = 0.1/0.2/0.3/0.4$), were prepared by the citric sol-gel method, which was described in our previous study [26]. Cerium nitrate, zirconium nitrate and manganese nitrate were used as precursors. Citric acid (CA) and ethylene diamine tetraacetic acid (EDTA) were added as complex agent. The nitrates, CA, EDTA and deionized water were mixed at a molar ratio of 1:1.5:1:100. The solution was stirred at 40 °C for 2 h and then heated at 80 °C for hours to form yellow gel. The gel was then dried, and calcined at 230 °C for 2 h and then at 500 °C for 4 h. For all the samples, the molar ratio of Ce/Zr remained the same value of 2:1.

2.2. Catalyst characterization

NO temperature-programmed desorption (NO-TPD) was carried out with an automated chemisorption analyzer (Chembet, Quantachrome). About 150 mg catalyst was first treated under N_2 flow (30 mL/min) at 200 °C for 1 h. After NO saturation for 1 h (200 mL/min), the gas was then switched to N_2 for 1 h. Subsequently, TPD was performed by ramping temperature to target temperature at 10 °C/min in N_2 (30 mL/min). The desorbed NO was detected by a thermal conductivity detector (TCD). NO_2 -TPD and O_2 -TPD were also similarly carried out by the automated chemisorption analyzer. For Hg -TPD, pure N_2 was used as the carrier gas to transport the desorbed mercury, at a flow rate of 1 L/min. 210 mg of the spent sample (60 mg of the catalyst and 150 mg of sands) was put in the fixed-bed reactor and heated from room temperature to 500 °C at a heating rate of 15 °C/min. The desorbed Hg^0 was recorded by the RA-915 M mercury analyzer.

2.3. Experimental method

NO and Hg^0 oxidation performance were separately tested on a fixed-bed quartz tubular reactor [27]. To evaluate NO oxidation efficiency, the simulated flue gas with 800 ppm NO + 6% O_2 (balanced with N_2) was fed into the reactor and the total flow rate was 400 mL/min. A mixture of 200 mg catalyst and 500 mg sand were used for NO oxidation efficiency test. An FT-IR gas analyzer (Gasmeter Dx-4000) was utilized to monitor flue gas composition. Activity data were collected when the reaction reached steady state conditions at different temperatures. NO oxidation efficiencies over all the five catalysts were obtained within the temperature range from 100 °C to 300 °C. Based on the NO oxidation efficiency result, CZM0.3 was selected as the optimal catalyst for the following investigations.

Hg^0 oxidation efficiency over CZM0.3 was obtained at the same fixed-bed reactor. The flue gas contained 120–150 $\mu\text{g}/\text{m}^3$ Hg^0 , 6% O_2 , balanced with N_2 , and the flow rate was 500 mL/min. 60 mg CZM0.3 catalyst and 150 mg sand were mixed for Hg^0 oxidation performance test. Hg^0 vapor was generated by the Hg^0 permeation device (VICI Metronics) and transported out by pure N_2 . An RA-915 M mercury analyzer (Lumex, Russia) was used to measure the Hg^0 concentration in the flue gas at upstream and downstream of the catalysts. Hg^0 concentrations in the effluent gas were obtained after the removal process had reached equilibrium state, during which Hg^0 concentration fluctuation was less than 5% for at least 1 h.

To investigate the effects of NO oxidation process on Hg^0 oxidation performance, Hg^0 oxidation behavior tests were carried out, under the atmosphere of $\text{Hg}^0/\text{NO}/\text{O}_2/\text{N}_2$. The flue gas contained 120–150 $\mu\text{g}/\text{m}^3$ Hg^0 , 6% O_2 and 0–800 ppm NO. The total flow rate was 500 mL/min and the mass of catalyst was 60 mg CZM0.3, blending with 150 mg sand. Furthermore, to understand the reaction process deeply, a homogeneous reaction between the reactants was also investigated. The Hg^0 oxidation behavior was studied in the presence of $\text{NO} + \text{O}_2$ and $\text{NO}_2 + \text{O}_2$ without catalyst at the selected temperature.

In order to verify whether these results can be applied to realistic conditions or not, the synergistic oxidation behavior of NO and Hg^0 over the catalyst was also tested under a typical coal-fired flue gas atmosphere with CO_2 , H_2O , SO_2 , etc. The simulated flue gas was prepared by mixing individual gas components: H_2O was fed by a high performance liquid chromatography (HPLC) pump (P600, LabTech), and the tube was heated to 250 °C to ensure all the liquid water turned into steam. Desired amounts of 15% CO_2 , 8% H_2O , 800 ppmv NO (when needed) and 1000 ppmv SO_2 (when needed) were mixed.

NO oxidation efficiency (E_{NO}) and Hg^0 oxidation efficiency (E_{Hg}) were calculated by Eqs. (1) and (2) [17]

$$E_{\text{NO}} = (\text{C}_{\text{in,NO}} - \text{C}_{\text{out,NO}}) / \text{C}_{\text{in,NO}} \quad (1)$$

$$E_{\text{Hg}} = (\text{C}_{\text{in,Hg}} - \text{C}_{\text{out,Hg}}) / \text{C}_{\text{in,Hg}} \quad (2)$$

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