



Elemental mercury oxidation over manganese-based perovskite-type catalyst at low temperature

Zijian Zhou, Xiaowei Liu^{*}, Bo Zhao, Haizhong Shao, Yishu Xu, Minghou Xu^{*}

State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, 1037 Luoyu Road, Wuhan 430074, China

HIGHLIGHTS

- $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ showed excellent performance on Hg^0 oxidation at 100–200 °C.
- $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ oxidized Hg^0 efficiently in flue gas with low HCl concentration.
- $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ had potential on low temperature SCR of NO with NH_3 .
- The adsorbed active surface oxygen species was significant for the Hg^0 oxidation.
- Good Hg^0 oxidation activity was gotten under the SCR atmosphere.

ARTICLE INFO

Article history:

Received 15 September 2015
Received in revised form 9 December 2015
Accepted 18 December 2015
Available online 21 December 2015

Keywords:

Hg^0 oxidation
Coal-fired flue gas
 $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$
Low temperature
Suprafacial process
Simultaneous removal of NO and Hg^0

ABSTRACT

$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LS_x , $x = 0/0.2/0.4/0.6$) perovskite-type oxides catalysts were synthesized for elemental mercury (Hg^0) oxidation in simulated coal-fired flue gas at low temperature. $\text{LS}_{0.4}$ exhibited superior catalytic behavior for Hg^0 oxidation at 100–200 °C. The superior performance was mainly due to the surface adsorbed oxygen species in the catalysts. Effects of different components in the flue gas including HCl, O_2 , SO_2 , H_2O , NO and NH_3 on Hg^0 oxidation efficiencies were studied. The results suggested that HCl significantly enhanced Hg^0 oxidation efficiency in the presence of O_2 and 10 ppmv HCl was sufficient for enhancing the oxidation process. As the catalyst had strong oxygen storage capacity, the Hg^0 oxidation activity was less dependent on O_2 concentration. As a result, the catalyst could be applied in the power plants burning low-chlorine coals. SO_2 , H_2O and NH_3 had inhibitory effect on Hg^0 oxidation, while NO enhanced it. SO_2 could deactivate the catalyst and the deactivation was irreversible. In terms of mechanism, Hg^0 oxidation with LS_x could be explained by the suprafacial process (Langmuir–Hinshelwood mechanism) whereby reactive species from adsorbed flue gas components reacted with adsorbed Hg^0 . The catalyst also had potential for selective catalytic reduction (SCR) of NO with NH_3 at low temperature, and the simultaneous removal of NO and Hg^0 over $\text{LS}_{0.4}$ was investigated. The NO and Hg^0 conversion were higher than 50% and 85% when the space velocity was $40,000 \text{ h}^{-1}$, respectively. The results indicated that the catalyst might be used to remove NO and Hg^0 simultaneously after the cold-side electrostatic precipitators in flue gas with low concentration of ash.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Coal combustion is one of the main sources of anthropogenic mercury emission around the world. Mercury and its compounds, especially methyl mercury species, are of high toxicity and bioaccumulation [1]. Three forms of mercury exist in coal combustion flue gas: elemental mercury (Hg^0), oxidized mercury (Hg^{2+}) and particle-bound mercury (Hg^p). Hg^{2+} can be easily removed by the

wet flue gas desulfurization (WFGD) due to its water solubility. Hg^p can be captured along with the fly ash by the electrostatic precipitators (ESP). However, Hg^0 is difficult to control because it is extremely volatile and water-insoluble [2]. Therefore, Hg^0 is the dominant form of mercury that released to the atmosphere. One of the feasible ways to remove Hg^0 is to use catalytic oxidation method to convert Hg^0 to Hg^{2+} .

The SCR catalyst was recognized as a promising catalyst for Hg^0 oxidation, as it can be used for NO reduction simultaneously. In particular, the V_2O_5 -based commercial SCR catalysts for NO removal have been reported as Hg^0 oxidation catalysts [3,4]. Since the activities of V_2O_5 -based commercial SCR catalysts are signifi-

^{*} Corresponding authors. Tel.: +86 27 87542417; fax: +86 27 87545526 (X. Liu).
Tel.: +86 27 87546631; fax: +86 27 87545526 (M. Xu).

E-mail addresses: xwliu@hust.edu.cn (X. Liu), mhxu@hust.edu.cn (M. Xu).

cantly affected by flue gas temperature, the catalytic activities are unstable due to the load variation of the boiler. Meanwhile, as the catalysts are placed before the ESP, they are deactivated easily due to the high concentration of dust in the flue gas [5,6]. It has been found that, relative to its effects on the efficiency of NO reduction, the catalyst deactivation could more significantly reduce Hg⁰ oxidation efficiency [7]. In this case, there is a need for a novel catalyst that could perform well for Hg⁰ oxidation at lower temperature, which can be located after the cold side ESP. Meanwhile, Huaneng group, a huge power generation company in China, has issued a strict NO_x emission standard (less than 50 µg/m³) for the coal-fired power plants. The existing commercial SCR catalysts cannot meet the emission standards. Therefore, to save the cost, the catalyst used for Hg⁰ oxidation at lower temperature was required to remove the NO escaped from upstream simultaneously.

Fortunately, the low toxic MnO_x catalysts have been proved to be the co-benefit catalysts for NO and Hg⁰ removal at lower temperature, and they exhibit excellent performance under certain conditions [8–10]. However, the Hg⁰ oxidation efficiencies of these catalysts strongly depended on HCl concentration in the flue gas, a factor that cannot be controlled in the power plants. The catalysts exhibited excellent mercury oxidation activities at ~250 °C, which were not the typical flue gas temperature after the cold-side ESP. Considering the above limitations, Mn-based oxides could be modified to be used for Hg oxidation at lower temperature subject to less influence of HCl concentration.

The Mn-based perovskite oxides seem an attractive candidate for Hg⁰ oxidation due to its excellent thermal stability, superior redox properties and great versatility [11,12]. The general formula of perovskite oxides is ABO₃. The A-site ions fitted into the dodecahedral interstices are always large rare-earth or alkaline-earth metal ions. The B-site ions are always the transition metal ions which occupy oxygen octahedrons and play a dominant role in the catalytic process. It is generally believed that the properties of the B-site ions, the concentration of oxygen species, and the existence of lattice defects are responsible for the good catalytic activities of the perovskite-type oxides [13]. A-site cations in the perovskite oxides play a role of structure-stabilizing and partial substitution of A-site cations can modify the physicochemical properties of perovskite oxides. The incorporation of a low valence cation in the A-site decreases the valence that is compensated by the creation of oxygen vacancies and generation of more higher valence B-site cations. The most common Mn-based perovskite catalyst is LaMnO₃, which has been investigated as a low temperature SCR catalyst recently [11].

Few researches investigated catalytic effects of LaMnO₃ for Hg⁰ oxidation. Hence, some tests need to be carried out to investigate whether LaMnO₃ can be served as an efficient catalyst for Hg⁰ oxidation. The abundant active oxygen species on the catalyst surface may be conducive for the formation of oxy-chloride or active chlorine species which are active for Hg⁰ oxidation. In addition, it has been reported that the perovskites exhibits better catalytic performance when the A-site ions La³⁺ are partially substituted by Sr²⁺ [14]. This is because partial substitution of La³⁺ with Sr²⁺ can generate mixed-valence manganese (Mn³⁺ and Mn⁴⁺) and more active oxygen species. The shift between Mn³⁺ and Mn⁴⁺ is beneficial for the generation of labile oxygen vacancies and bulk oxygen species [15]. The redox couple may also benefit the Hg⁰ oxidation due to the Mars-Maessen mechanism in the absence of HCl. It seems likely that the LaMnO₃ modified by partial substitution of La³⁺ by Sr²⁺ could oxidize Hg⁰ with low concentration of O₂ and HCl in the flue gas when low rank coals are burned.

Accordingly, we hypothesize that the La_{1-x}Sr_xMnO₃ (x = 0/0.2/0.4/0.6) perovskite catalysts could exhibit remarkable catalytic performance on Hg⁰ oxidation with low concentration of O₂ and HCl in the flue gas at low temperatures. In the present

work, the Mn-based perovskite oxides were synthesized and characterized to investigate the catalytic activity of the oxides on Hg⁰ oxidation. In order to improve the catalytic activity of the LaMnO₃, the La³⁺ ions were partially substituted by Sr²⁺ ions to increase the surface defects so as to generate more oxygen vacancies and active oxygen species. The catalytic performance of the oxides under conditions such as low concentration of O₂ and HCl at low temperature was also investigated, and the Hg⁰ oxidation mechanism was identified. The effects of SO₂, H₂O, NO and NH₃ on the Hg⁰ oxidation efficiency were studied. Hg⁰ oxidation efficiency under SCR atmosphere and the SCR activity of the selected catalysts (La_{0.6}Sr_{0.4}MnO₃) were considered as well. It is demonstrated that the synthesized perovskite oxides may serve as an environmentally friendly catalyst for simultaneous removal of NO and Hg⁰ from coal combustion flue gas at low temperature.

2. Experimental

2.1. Preparation of catalysts

The La_{1-x}Sr_xMnO₃ (x = 0/0.2/0.4/0.6) catalysts were prepared by complexation method using citric acid as a complexation agent [11]. They are denoted as LSx, where L is the raw LaMnO₃, S is the doped Sr, and x represents the mole ratio of Sr/(Sr + La). Stoichiometric amounts of lanthanum nitrate, strontium nitrate and manganese nitrate were dissolved in deionized water. Citric acid was separately dissolved in distilled water and added to the mixed solution. The amount of the citric acid was equal to the total number of moles of the metal ions. The solution was then stirred and heated up to 60 °C to form the sol, and then turned to dry gel at 105 °C overnight. After spontaneous combustion at 180 °C, the dry gel turned to a spongy mixture. The mixture was then ground and the resulted powder was calcined from room temperature to 500 °C, which was maintained for 2 h. The powder was then calcined from 500 °C to 800 °C, which was kept for another 4 h. All the heating processes were conducted at a rate of 3 °C/min.

2.2. Characterization of catalysts

The samples were investigated by X-ray powder diffraction (XRD) analysis (X'pert PRO, PANalytical, Holland) to understand the crystal phase structure. The surface property was analyzed by X-ray photoelectron spectroscopy (XPS) using VG Multilab 2000 X-ray photoelectron spectrometer. The pore size distribution and Brunauer-Emmett-Teller (BET) surface area were determined using a Micromeritics ASAP 2020 N₂ adsorption apparatus. Fourier transform infrared (FTIR) spectra were investigated with a Nicolet Protegé 460 spectrometer in KBr pellets.

2.3. Catalytic activity measurement

The mercury oxidation performance of LSx catalysts were evaluated on a fixed bed system, as shown in Fig. 1. The system consisted of a simulated flue gas system with an Hg⁰ permeation device (VICI Metronics), a quartz reactor (length 550 mm, inner diameter 10 mm) and a vertical furnace, an on line RA-915 M mercury analyzer (sensitivity: 0.1 µg/m³, Lumex-Marketing JSC, Russia) coupled with a mercury speciation conversion system and a carbon trap to purify the exhaust. The simulated flue gas was prepared by mixing individual gases. The total flow rate was 1 L/min. A flow of pure N₂ passed the permeation tube carrying the Hg⁰ vapor to provide a constant feed of mercury concentration (~60 µg/m³). The water vapor was fed by a high performance liquid chromatography (HPLC) pump (P600, LabTech). The tube was heated to 150 °C to ensure all the liquid water turns into steam.

Download English Version:

<https://daneshyari.com/en/article/6582213>

Download Persian Version:

<https://daneshyari.com/article/6582213>

[Daneshyari.com](https://daneshyari.com)