

Contents lists available at ScienceDirect

Chemical Engineering Journal



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

Elemental mercury oxidation over manganese oxide octahedral molecular sieve catalyst at low flue gas temperature



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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- OMS-2 was studied for the first time as a Hg⁰ oxidation catalyst.
 92% Hg⁰ oxidation efficiency was
- achieved even at a space velocity of $1,350,000 \text{ h}^{-1}$.
- SO₂ reduced the adsorbed HgO on the OMS-2 surface to Hg⁰.

ARTICLE INFO

Keywords: Mercury Catalytic oxidation OMS-2 Low temperature Flue gas



ABSTRACT

Manganese oxide octahedral molecular sieve (OMS-2) with cryptomelane structure synthesized by a solvent-free method was employed to oxidize gaseous elemental mercury (Hg⁰) in coal combustion flue gas for the first time. Brunauer-Emmett-Teller (BET) surface area analysis, X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectra, H₂ temperature-programmed reduction (H₂-TPR) and X-ray photoelectron spectroscopy (XPS) measurement were employed to characterize the catalyst. The OMS-2 with large surface area and abundant pores presented excellent Hg⁰ oxidation performance at a wide temperature range of 100-250 °C. At the optimal operating temperature of 150 °C, 93% Hg⁰ oxidation efficiency was obtained under a gas hourly space velocity as high as 1,350,000 h⁻¹. Hg⁰ oxidation on OMS-2 catalyst was supposed to follow the Mars-Maessen mechanism, where the gaseous Hg^0 was firstly adsorbed on the OMS-2 catalyst surface to form adsorbed Hg^0 , and then the adsorbed Hg⁰ was oxidized by the lattice oxygen over catalyst surface to form mercury oxide (HgO). Both HCl and NO in the flue gas promoted Hg⁰ oxidation mainly due to the formation of active species like Cl*, NO₂, which reacted with Hg⁰ to form volatile mercury species. SO₂ inhibited the Hg⁰ oxidation by reducing the adsorbed HgO into gaseous Hg⁰ or generating sulfate on the catalyst surface. Water vapor also played an inhibitive role in Hg^0 oxidation. However, the SO_2 and H_2O resistance of OMS-2 catalyst was much superior compared to other commercial catalysts, which makes it promising for industrial application. This knowledge is beneficial for developing economical and efficient Hg⁰ oxidation catalysts for coal-fired power plants.

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https://doi.org/10.1016/j.cej.2018.08.225 Received 29 May 2018; Received in revised form 1 August 2018; Accepted 31 August 2018 Available online 01 September 2018 1385-8947/ © 2018 Elsevier B.V. All rights reserved.

1. Introduction

On October 10th, 2013, the "Mercury Treaty Diplomatic Conference" sponsored by the United Nations Environment Program passed the "Minamata Convention on Mercury", which aims to control and reduce the global mercury emissions. The convention signed by 128 countries has entered into force in August 16th, 2017 [1]. Mercury emission from coal-fired power plant is one of the largest anthropogenic mercury emission sources [2]. Mercury exists mainly in three forms in coal-fired flue gas: particle-bound mercury (Hg^p), oxidized mercury (Hg²⁺), and elemental mercury (Hg⁰) [3]. Above 90% water-soluble Hg^{2+} can be removed by wet flue gas desulfurization (WFGD), and most of Hg^p is captured by particulate matter (PM) control devices. such as electrostatic precipitators (ESP) and fabric filters (FF) [4]. In contrast, Hg⁰ vapor, as the dominant mercury species in coal combustion flue gas, is difficult to be captured by existing air pollution control devices (APCD) due to its highly volatility and almost insoluble in water [5]. To limit the mercury emissions, efficient mercury control technologies are urgently needed.

A potential method for Hg⁰ control from coal-fired power plants is to catalytically oxidize Hg⁰ into Hg²⁺, and then co-beneficially captured by WFGD devices or PM control devices. MnOx-based catalysts have been widely researched for Hg⁰ oxidation [6,7] and selective catalytic reduction of NOx [8,9] because of their excellent catalytic activity and low cost. The large-span valence change of Mn from Mn⁴⁺ to Mn³⁺ and then to Mn²⁺ was responsible for the low-temperature Hg⁰ oxidation over Mn-based catalysts [10,11]. The relatively low operating temperature locates Mn-based catalysts downstream of the FF/ ESP systems, which would avoid the deactivation of catalysts by exposure to high PM concentrations [12]. However, pure MnO_x catalyst without any carriers could not efficiently catalytic oxidize Hg⁰, because of its poor structural performance, such as low specific surface area (less than $10 \text{ m}^2/\text{g}$) [13]. To overcome this deficiency, a commonly method is to load MnO_x on a support, such as TiO₂ or Al₂O₃. Nevertheless, this kind of methods do not change MnOx's poor crystal structure [14,15], which exposes a spot of MnO_x for catalytic processes, and hence resulted in a waste of manganese resources.

Doping other metals into the crystal structure of MnO_x is another effective method to improve its structure related catalytic performance. The addition of potassium into the crystal structure of MnO_x resulted in a one-dimensional tunnel structure composed of 2×2 [MnO₆] octahedral chains [16-18], namely manganese oxide octahedral molecular sieve (OMS-2), leading to a sharp increase in its specific surface area (about 10 times more than MnOx) [17] and a richer pore structure [19,20]. For the OMS-2, its Mn average valence is around 3.8 [21]. This means that majority of manganese in OMS-2 is present in Mn⁴⁺ species, which was suggested to be more beneficial for Hg⁰ oxidation than Mn^{2+} or Mn^{3+} [1,22]. Moreover, the preparation of OMS-2 is very simple [17] and takes much less time compared to many other traditional catalyst preparations [23-25]. Therefore, it is reasonable to believe that OMS-2 could be a promising candidate for Hg⁰ catalytic oxidation at low temperatures. However, no study regarding Hg⁰ oxidation over OMS-2 was reported to date.

In this work, OMS-2 catalyst was prepared and applied in Hg^0 oxidation. The prepared materials were characterized by Brunauer-Emmett-Teller (BET) surface area, X-ray diffraction (XRD) analysis, Xray photoelectron spectroscopy (XPS), hydrogen temperature programmed desorption (H₂-TPR) and Fourier transform infrared (FT-IR) spectroscopy. The Hg^0 oxidation performances of OMS-2 was studied under simulated coal combustion flue gas and compared with other reported catalysts. The influence of individual flue gas components on Hg^0 oxidation was studied and the mechanisms of Hg^0 oxidation were discussed.

2. Experimental

2.1. Catalysts preparation

The OMS-2 catalyst was prepared by a solvent-free method [17]. Firstly, 22.05 g $Mn(Ac)_2$ ·4H₂O and 9.48 g KMnO₄ powders, with molecular molar ratio of 3:2, were mixed and ground uniformly in a mortar. The mixed powder was heated at 80 °C for 4 h, and then the dark gummy product was washed with distilled water several time and dried at 80 °C overnight. Finally, the black solid particles were ground to 60–80 mesh. For comparison, MnO_x catalyst was synthesized by directly drying $Mn(NO)_3$ ·2H₂O at 110 °C overnight and calcining at 450 °C for 4 h in air.

2.2. Characterization

The specific surface area and pore parameter of catalyst was measured by a JW-BK132Z specific surface area analyzer (Beijing JWGB Sci & Tech Co., Ltd., China). The specific surface area and the pore volume and pore size of catalyst were determined through Brunauer-Emmett-Teller (BET) method and Barrett-Jioner-Halenda (BJH) method, respectively. The X-ray diffraction (XRD, D8, Bruker AXS, Germany) results were recorded at two theta from 10° to 80° with Cu_{α} $(\lambda = 0.15406 \text{ nm})$ to explore the crystal structure of catalysts. X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250Xi), with an Al Ka X-ray source and pass energy of 20 eV under ultrahigh vacuum, was used to analyze the surface characteristics of catalyst. The C 1s binding energy value of 284.8 eV was taken as the reference for all binding energy calibration. The H₂ temperature-programmed reduction (H₂-TPR) experiments were performed on a PCA-1200 thermal conductivity detector (Beijing Bi'aode Electronic Technology Co., Ltd., China). The catalyst pre-treated under Ar atmosphere at 200 °C for 3 h were heated from 50 to 750 °C with a heating rate of 10 °C/min, and the reducing gas mixture was 7% H₂/He. The fourier transform infrared (FT-IR) spectra ranging from 7800 to 350 cm⁻¹ was recorded to analyze the production of SO₂ and H₂O on OMS-2 catalyst. Before the FT-IR test, the spent OMS-2 catalysts were pre-treated under 500 ppm SO2 or 8% H2O for 1 h.

2.3. Catalytic activity measurement

The Hg⁰ oxidation activity of the catalyst was tested using a laboratory-scale experimental system, which was described in details in our pervious study [26]. Various flue gas components, such as HCl, NO, O2, SO2 and N2, were supplied from compressed cylinder gases and thoroughly mixed in a glass gas mixer. Water vapor was generated from a glass gas bottle filled with a certain amount of distilled water which placed in a thermostat water bath at a constant temperature of 80 °C, and then brought to the reactor by N₂. At the bottle outlet, soft silicone tube was wrapped around the heating tape to prevent condensation of water vapor on the tube wall. A continuous $75 \,\mu g/m^3 Hg^0$ vapor was generated from a Dynacal Mercury Infiltration Unit (VICI Metronics), which mounted in a sealed U-shaped glass tube into a thermostat water bath. The generated gas phase Hg⁰, with high purity N₂ as a carrier gas, was introduced into the glass gas mixer for mixing with other flue gases. The content of each gas was precisely controlled by mass flow controllers (MFC), and the total gas flow rate was kept at 1 L/min. Downstream of the glass gas mixer, a borosilicate glass reactor with an internal diameter of 10 mm was placed in a furnace equipped with a temperature control system to simulate the reaction temperature. The concentration of elemental mercury was monitored by a mercury analyzer (VM3000, Mercury Instruments Inc., Germany; Measurement accuracy: $0.1 \,\mu\text{g/m}^3$). A sodium hydroxide (NaOH) solution and a condenser were provided downstream of the reactor to remove acid gases and water vapor respectively, for avoiding their adverse effect on Hg⁰ concentration detection.

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