



Cobalt manganese oxides modified titania catalysts for oxidation of elemental mercury at low flue gas temperature



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HIGHLIGHTS

- The Co_xMn_yTi catalysts were synthesized by a deposition–precipitation method.
- CoO_x led to a better dispersion and more amorphous species of MnO_x over TiO₂.
- The Co₆Mn₃₀Ti catalyst was highly active for Hg⁰ catalytic oxidation.
- The adsorbed HgO on catalyst can be released at higher temperature.

ARTICLE INFO

Article history:

Received 11 June 2013

Received in revised form 11 September 2013

Accepted 14 September 2013

Available online 24 September 2013

Keywords:

Manganese oxide

Cobalt oxide

Elemental mercury

Catalytic oxidation

Low temperature

ABSTRACT

Cobalt manganese oxides modified titania (Co_xMn_yTi) catalysts synthesized by a deposition–precipitation method were employed to oxidize gas-phase elemental mercury (Hg⁰) without the aid of HCl at low temperature on a laboratory-scale fixed-bed reactor. The roles of O₂, NO, SO₂ and H₂O in Hg⁰ oxidation over the optimal catalyst were also evaluated. The catalysts were characterized by N₂ adsorption–desorption, SEM, TEM, XRD, XPS and TPR to determine the pore and surface chemistry structures. The results showed that with optimal loading of 6% Co species on Mn₃₀Ti, the Hg⁰ oxidation efficiency could reach around 98% at 150 °C. A great increase in Hg⁰ oxidation over Co₆Mn₃₀Ti catalyst with the assistance of O₂ occurred via the Mars–Maessen mechanism. In comparison with pure N₂ atmosphere, the presence of NO can slightly promote the oxidation of Hg⁰. The effects of SO₂ and H₂O with lower concentrations were insignificant. However, when SO₂ further increased above 1000 ppm, a seriously inhibitory influence on Hg⁰ oxidation was observed. The characterization results indicated that physical characteristics were not the main contributor for Hg⁰ oxidation. The presence of CoO_x led to a better dispersion and more amorphous species of MnO_x over TiO₂. Compared with those of Mn₃₀Ti and Co₃₀Ti catalysts, the chemisorbed oxygen of Co₆Mn₃₀Ti catalyst increased greatly, which played an important role in the promotion of Hg⁰ oxidation.

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1. Introduction

Coal-fired utility boilers and municipal waste incineration plants are major anthropogenic sources of mercury emissions [1–4]. In China, about 38% of the mercury emission comes from coal combustion [5]. It is well-known that mercury has an adverse effect on the central nervous system and can cause pulmonary and renal failure, severe respiratory damage, blindness, and chromosomal damage [6]. In recent decades, many countries, especially in the developed countries, have taken steps to reduce mercury uses and releases. On December 21, 2011, The US Environmental Protection Agency (EPA) announced standards to limit mercury, acid gases and other toxic pollution from power plants. On March

28, 2013, EPA updated emission limits for new power plants under the Mercury and Air Toxics Standards (MATS) [7]. Mercury in coal is released in three forms: elemental (Hg⁰), oxidized (Hg²⁺) and particulate-bound (Hg^p). Most of existing air pollution control technologies, such as electrostatic precipitators and baghouses, can remove effectively the Hg^p, but have a little effect on Hg⁰ removal. The oxidized form mercury, which is generally soluble in water, can be captured efficiently by a wet scrubber [8]. However, Hg⁰ is very difficult to control from the flue gas due to its high volatility and low solubility in water.

Activated carbons (ACs) are considered as “general purpose” material for Hg⁰ adsorption from flue gas due to their higher surface area and surface reactivity [9–11]. However, the capacity of raw AC is limited, especially at higher temperature [12]. For this reason, many investigations about chemically promoted carbonaceous sorbents such as the halogenated AC and metal oxides

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modified AC have been conducted to evaluate their behaviors on Hg^0 removal [6,13–15]. Nevertheless, these modified AC sorbents are expensive and they also will adversely affect the sales or disposal costs of fly ash [16].

In recent years, lots of researches involving transition metal oxide catalysts have been extensively conducted to develop effective Hg^0 oxidation technologies [17–24] due to they have been known to be very reactive and widely used for the oxidation of volatile organic compounds (VOCs) [25], selective catalytic reduction (SCR) or NO catalytic oxidation [26–28]; and other catalytic oxidation processes [29]. For higher Hg^0 oxidation efficiency, the presence of oxidant is normally essential for metal oxide catalysts. According to the literatures [17–24,30,31], the main oxidants involved in real flue gas are chlorine and oxygen. However, in China, it is reported that the chlorine content of feed-coal (63–318 mg/kg) is much lower than that of US coals (628 mg/kg) [18,30]. So catalytic oxidation of Hg^0 using gaseous O_2 in the flue gas as the oxidant is a simple and economical method for Hg^0 control. Furthermore, the oxidized mercury formed, such as HgO and Hg_2O , are in a solid state under lower reaction temperature (<300 °C) [18]. The oxidized mercury adsorbed on the catalyst/sorbent can be removed through the method of pyrolysis, and consequently, the used catalyst/sorbent can be regenerated many times. A sorption and desorption cycle based on a regenerable catalyst/sorbent may be a more ideal mercury control process [32]. Although the addition of a cold-side catalyst bed to remove Hg^0 also needs an additional unit operation for higher Hg^0 removal, in comparison with the traditional activated carbons and chemically treated ACs, the use of transition metal catalysts/sorbents will be inexpensive due to its regeneration performance and facile operation. Catalysts/sorbents are the core of the sorption and desorption processes for mercury removal from flue gas [32]. Therefore, finding a catalyst that can oxidize Hg^0 effectively without the aid of HCl at low or moderate temperature and can be regenerated at high temperature is of great significance.

Among the researched metal oxide catalysts [17–31], the manganese-based catalysts were found to be one of the best candidates for Hg^0 oxidation, owing to their excellent catalytic activity, easy manufacturing, and low cost compared to noble metal-based catalysts. Qiao et al. [22] found that $\text{MnO}_x/\text{Al}_2\text{O}_3$ had significant oxidation performance on capturing Hg^0 in the presence of HCl, and its favorable oxidation temperature was about 600 K. Ji et al. [23] reported that using CO as reductant, $\text{MnO}_x/\text{TiO}_2$ had been shown to be effective for both Hg^0 oxidation and low temperature NO-SCR. Furthermore, upon doping MnO_x -based catalysts with ceria, significant synergy for higher NO-SCR [33] and Hg^0 catalytic oxidation [21,31] efficiencies appeared. On the other hand, highly active for Hg^0 oxidation also had been investigated on cobalt-catalysts [20,34]. Liu et al. [20] found that the Co/TiO_2 catalyst showed higher Hg^0 oxidation activities within the temperature window of 120–330 °C and the oxygen performed a key role on Hg^0 oxidation process. Li et al. [35] studied the cobalt manganese oxides with different Co/Mn molar ratios on the catalytic combustion of methane and a great improvement of the catalytic activity was obtained over Co_5Mn_1 catalyst with a Co/Mn molar ratio of 5:1. Tian et al. [25] used $\text{Co}_{3-x}\text{Mn}_x\text{O}_4$ catalyst for acetylene and propene oxidation and found that the mixed oxide catalyst with $x = 0.34$ had a remarkable improvement in terms of the activity, selectivity and stability, which can possibly be a result of the increase of oxygen vacancies. To the authors' knowledge, the related research on cobalt manganese oxides modified titania (CoxMnyTi) catalysts for Hg^0 catalytic oxidation has rarely been reported in the literatures, especially at low temperature. Therefore, a better knowledge about the performance and mechanism of Hg^0 oxidation over CoxMnyTi catalyst is required.

Herein, the main objective of the present work is to perform an experimental study to investigate the performance of TiO_2 -supported Co–Mn mixed oxide catalysts for Hg^0 catalytic oxidation in the absence of HCl. First, series of CoxMyTi catalysts were synthesized by using deposition–precipitation method and a packed-bed reactor system was built to estimate their performance on Hg^0 oxidation. Second, the roles of flue gas components (such as O_2 , NO, SO_2 and H_2O) in Hg^0 oxidation over the optimal catalyst were surveyed, which is very important in evaluating the effectiveness of commercial catalyst on a real gas stream. Third, the catalysts were characterized by using N_2 adsorption-desorption isotherm, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and temperature programmed reduction (TPR).

2. Experimental section

2.1. Synthesis of catalysts

CoxMnyTi mixed oxide catalysts were prepared by a deposition–precipitation method [26] using commercial TiO_2 support (Degussa P25, Germany). The Mn/Ti molar ratio of the catalysts was fixed at 0.3, which was reported to be the optimal ratio of the $\text{MnO}_x/\text{TiO}_2$ catalyst for effective NO catalytic oxidation [26]. First, a mixed aqueous solution of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (AR) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (AR) with a fixed Co/Mn molar ratio was prepared, and then it was quickly added to a slurry solution (80 mL) containing 8 g of TiO_2 with vigorous stirring. In the mixing and continuous stirring step, a mixed solution of $\text{NH}_3 \cdot \text{H}_2\text{O}$ (15 wt%) and NH_4HCO_3 (15 wt%) was added dropwise to the above mixture until a constant pH = 10 was obtained. After that, the mother mixture solution was aged at 60 °C for 2 h, and the resulting precipitate was filtered and washed several times with distilled water. Finally, the solid was dried at 110 °C overnight and calcined at 450 °C for 4 h in flowing air. The obtained supports were ground and sieved to 60–80 mesh, and they were denominated as CoxMnyTi , where x represented the percentage of Co/Ti molar ratio ($x = 0, 6, 12, 18, \text{ and } 30$), and y stood for the percentage of Mn/Ti molar ratio ($y = 0, 30$).

2.2. Experimental apparatus and procedures

A laboratory-scale fixed-bed apparatus was constructed, as shown in Fig. 1, to explore the activity of the prepared catalysts on Hg^0 oxidation. The setup mainly consisted of a feed system, a vapor-phase Hg^0 generator, a fixed-bed reactor surrounded by a temperature-controlled oven, an on-line mercury analyzer, and a data acquisition system. A mercury permeation device (VICI Metronics Inc., Santa Clara, CA) was employed as the source of Hg^0 . The device, which designed to produce a constant release ratio of Hg^0 vapor at a specified temperature, was sealed in a U-type glass tube holder. High-purity grade of N_2 was supplied as carrier gas to transport the released Hg^0 vapor out of permeation tube holder. Water vapor (H_2O) was generated using a heated water bubbler and carried by N_2 gas. The content of H_2O was calibrated before starting all the tests. The fixed-bed reactor, a quartz reactor column with approximately 0.90 cm i.d. and 120 cm length, was placed in a temperature-controlled electric furnace, which can control the system temperature within ± 2 °C. The experiments were performed under atmospheric pressure at the temperature range of 50–250 °C. The inlet Hg^0 concentration (Hg_{in}^0) was 55 ± 2 $\mu\text{g}/\text{m}^3$, and about 200 mg catalyst was used if there was no special specification. The total gas flow rate passing through the fixed-bed reactor was 1000 mL/min with a gas hourly space velocity (GHSV)

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