



Research article

NH₃ inhibits mercury oxidation over low-temperature MnO_x/TiO₂ SCR catalyst

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ABSTRACT

Manganese oxide/titanium dioxide (MnO_x/TiO₂, or MnTi) catalyst prepared by an ultrasound-assisted impregnation method was employed for simultaneous nitrogen oxide (NO) reduction and elemental mercury (Hg⁰) oxidation under a simulated selective catalytic reduction (SCR) atmosphere. An NO reduction rate of 83% and Hg⁰ oxidation rate of 96% were simultaneously achieved at a relatively low temperature of 200 °C. Ammonia (NH₃) as a reducing agent in the NO-SCR process was systematically investigated for its effect on Hg⁰ oxidation. The results showed that NH₃ inhibited Hg⁰ oxidation over the low-temperature MnTi catalysis process. In the presence of NH₃, competitive adsorption between NH₃ and Hg⁰ on the MnTi catalyst was partly responsible for the weakening Hg⁰ oxidation. NH₃ consumed surface oxygen (O₂) on the MnTi catalyst, which also resulted in lower Hg⁰ oxidation rate, especially in the absence of gas phase O₂ in the flue gas. More importantly, oxidized mercury was reduced by NH₃ to form Hg⁰ with the aid of NO, i.e., the combined presence of NO and NH₃ induced the reduction of oxidized mercury, and hence partially offset Hg⁰ oxidation. The effects of individual SCR gases, such as O₂, NO, and the combinations, on Hg⁰ oxidation were also elaborated.

1. Introduction

Nitrogen oxide (NO_x) is a primary air pollutant emitted from most coal-fired power plants. It can lead to severe environmental issues, such as acid rain, photochemical smog, and stratosphere ozone depletion [1]. Besides NO_x, heavy metals emitted from coal-fired power plants [2] also posed seriously adverse impact on the environment [3,4]. Among these heavy metals, mercury (Hg) has drawn broad attention due to Hg's persistence, volatility, and severe toxic effects on human health [5–7]. In response to the recent global implementation of stringent emission standards on limiting NO_x and Hg emissions, various emission control technologies have been developed [8–11]. Among them, selective catalytic reduction (SCR) of NO_x with NH₃ and activated carbon injection (ACI) are considered the most effective means for removal of NO_x and Hg, respectively, from coal combustion flue gases [12,13]. However, the ACI for mercury removal has many drawbacks, such as high operating cost, low stability, and adverse effects on the usability of fly ash. All of these drawbacks impeded the application of ACI in industries [13,14]. In contrast, SCR catalysts can not only facilitate NO_x reduction to N₂, but can also oxidize elemental mercury (Hg⁰) to

oxidized mercury (Hg²⁺), which can then be removed in the widely-adopted wet flue gas desulfurization (WFGD) systems [15,16]. Therefore, utilization of the combination of SCR and WFGD is promising for simultaneous control of NO_x and Hg⁰, as well as other pollutants, such as sulfur dioxides (SO₂), from coal combustion.

To better combine SCR and WFGD, achieving efficient NO_x reduction and Hg⁰ oxidation with the same catalyst is crucial. Various types of SCR catalysts have been investigated for this purpose [11,17]. Among these catalysts, commercially-available vanadia (V₂O₅)-based SCR catalysts have been widely used in coal-fired power plants for several decades [18–20]. However, several problems remain to be solved. For instance, the optimal operating temperature for V₂O₅-based SCR catalyst is between 300 and 400 °C [17,21]. The operating temperatures require the SCR unit to be located upstream of particulate matter control device (PMCD) and WFGD systems, where high concentrations of fly ash and SO₂ accelerate the catalyst's deactivation [22]. In addition, V₂O₅-based SCR catalysts are not efficient for Hg⁰ oxidation when coal combustion flue gas lacks hydrogen chloride (HCl) [21]. Furthermore, V₂O₅ is harmful to human health and the environment [23]. Therefore, it is necessary to develop an environmentally-

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friendly SCR catalyst with excellent low-temperature (100–250 °C) SCR activity and superior Hg⁰ oxidation performance in flue gases with low concentrations of HCl, or even without HCl.

Manganese oxide (MnO_x)-based catalysts have been recognized as one of the most promising heterogeneous catalysts, due to their excellent low-temperature catalytic activity, abundant reserves on the earth, and environmental friendliness [24–26]. MnO_x-based catalysts are generally effective for NO_x reduction and Hg⁰ oxidation, due to the variable valance state of manganese and abundant surface oxygen [27]. However, these catalysts deactivate in the presence of SO₂ [28,29]. Titanium dioxide (TiO₂) is an excellent catalyst support with a high level of SO₂ resistance in SCR and Hg⁰ oxidation processes [30–32]. Moreover, the non-toxicity and low cost titania (TiO₂) has been demonstrated to be with high stability, great mechanical strength, and corrosion resistance in many other catalytic processes [33–36]. Therefore, the MnO_x supported by TiO₂ (MnO_x/TiO₂, or MnTi) catalyst was a potential candidate catalyst for simultaneous NO_x reduction and Hg⁰ oxidation [11,26,37]. Ammonia (NH₃) that is injected for SCR reactions usually plays an inhibitory role in Hg⁰ oxidation [38–40]. However, no systematic study was conducted to explore the mechanisms that were responsible for the inhibitory effect of NH₃ on Hg⁰ oxidation.

In the present study, a MnTi catalyst prepared by an ultrasound-assisted impregnation method was used for simultaneous NO reduction and Hg⁰ oxidation at a low temperature of 200 °C. Although the in-situ synthesized TiO₂ nanoparticle was widely used and found to be effective in many catalytic and electrochemical processes [41–44]. The commercial TiO₂ (P25, Evonik) was adopted as the support of the MnTi catalyst, as the focus of this study was the inhibitive effect of NH₃ on Hg⁰ oxidation over the MnTi catalyst rather than the catalytic performance of the MnTi catalyst. The effects of individual SCR gases (O₂, NO, and NH₃) and combinations of different SCR gases on Hg⁰ oxidation were systematically investigated. The involved inhibitory mechanisms of NH₃ on Hg⁰ oxidation over the MnTi catalyst were systematically identified. These new findings are of fundamental importance in developing effective technologies for simultaneous NO_x and Hg⁰ control in coal-fired power plants.

2. Experimental procedure

2.1. Material preparation

The MnTi catalyst was prepared by an ultrasound-assisted impregnation method. A manganese nitrate solution (AR, 50 wt% in H₂O, Aladdin) was diluted in deionized water to form the aqueous solution. TiO₂ nanoparticles (P25, Evonik) were then added to the solution. After vigorous stirring at room temperature for 1 h, the mixture was ultrasonically bathed for another 2 h. The mixture was then dried at 110 °C overnight and calcined at 400 °C for 4 h in air. Finally, the samples were extracted by grinding and sieving through 60–80 mesh for testing. The mass content of manganese oxide (calculated as MnO₂) in the MnTi catalyst was kept at 15%, which was the optimal ratio of MnTi for SCR of NO_x and oxidation of Hg⁰ [11].

2.2. Catalytic activity test

The catalytic performance of the MnTi catalyst was investigated through the fixed-bed system shown in Fig. 1. Simulated flue gases with different components, including nitrogen (N₂), O₂, NO, and NH₃, were acquired from compressed cylinder gases. Concentrations of individual gas were precisely controlled by mass flow controllers (MFC) using pure N₂ as the balance gas. The total inlet gas flow rate was 1 l per minute (L·min⁻¹). A Hg⁰ permeation device (VICI Metronics, Poulsbo, WA, USA) was placed in a U-shaped glass tube, in which a constant concentration (75 or 380 μg·m⁻³) of Hg⁰ vapor was generated by controlling the temperature of a thermostatic water bath. The catalyst was loaded into a quartz tube reactor with an inner diameter of 10 mm and

a length of 550 mm. The quartz tube reactor was then placed in a temperature-controlled tubular furnace. The reaction temperature was kept at 200 °C, at which temperature MnTi catalysts exhibit an optimal catalytic activity, reported in a previous study [32]. In each test, 0.1 or 0.8 g of catalyst was used, corresponding to a gas hourly space velocity (GHSV) of 380,000 h⁻¹ or 48,000 h⁻¹, respectively. The reactor inlet and outlet concentrations of NO were measured with a flue gas analyzer (OPTIMA7, MRU Emission Monitoring Systems, Germany). The inlet and outlet Hg⁰ concentrations were monitored by an online mercury analyzer (VM3000 Mercury Instruments, Inc., Germany). Before entering the mercury analyzer, the flue gas passed through a silica gel to remove the moisture. To avoid the influence of NH₃ on NO measurement, residual NH₃ was removed by an ammonia trap containing a phosphoric acid solution before entering the flue gas analyzer. Finally, the exhaust gas was treated with an activated carbon trap before exhausting.

2.3. Experiment matrix and procedure

Seven sets of experiments were conducted. The experimental conditions are summarized in Table 1. Set I experiments were conducted to evaluate the simultaneous NO reduction and Hg⁰ oxidation activity of MnTi catalyst at 200 °C. In Set II experiments, the role of individual SCR gases (O₂, NO, and NH₃) in Hg⁰ oxidation were investigated. In Set III experiments, the coexistence of NO and NH₃, with and without the aid of O₂, in Hg⁰ oxidation was examined. First, fresh MnTi catalyst was pretreated in Set IV experiments under a gas flow containing 380 μg·m⁻³ Hg⁰ balance in pure N₂ for 15 h. NH₃ then passed through the catalyst loaded with Hg⁰ to study the competition between NH₃ and Hg⁰ over the MnTi catalyst. Set V and VI experiments were designed to determine whether NH₃ consumed the surface oxygen that actively oxidized Hg⁰. Oxidized mercury (Hg²⁺) reduction, which may offset Hg⁰ oxidation, was identified in Set VII experiments with the coexistence of NO and NH₃. Prior to the Set VII experiments, fresh MnTi catalyst was pretreated in a gas flow containing 380 μg·m⁻³ Hg⁰ and 4% O₂ balanced with N₂ at 200 °C for 72 h to accumulate enough oxidized mercury.

Before each test, the concentrations of NO and Hg⁰, including the inlet NO concentration ([NO]_{inlet}), the inlet Hg⁰ concentration ([Hg⁰]_{inlet}), the outlet NO concentrations ([NO]_{outlet}), and the outlet Hg⁰ concentration ([Hg⁰]_{outlet}), were recorded after reaching equilibrium, which was defined as the variations in NO and/or Hg⁰ concentration at less than 5% for more than 30 min. The NO reduction efficiency (*E*_{red}) and Hg⁰ oxidation efficiency (*E*_{con}) values were calculated using Eqs. (1) and (2), respectively.

$$E_{\text{red}} = ([\text{NO}]_{\text{inlet}} - [\text{NO}]_{\text{outlet}}) / [\text{NO}]_{\text{inlet}} \times 100\% \quad (1)$$

$$E_{\text{con}} = ([\text{Hg}^0]_{\text{inlet}} - [\text{Hg}^0]_{\text{outlet}}) / [\text{Hg}^0]_{\text{inlet}} \times 100\% \quad (2)$$

3. Results and discussions

3.1. Simultaneous NO reduction and Hg⁰ oxidation over MnTi catalyst

The simultaneous NO reduction and Hg⁰ oxidation rates over the MnTi catalyst are shown in Fig. 2. More than 80% NO reduction and 90% Hg⁰ oxidation were simultaneously achieved at 200 °C. The results indicate that the low-temperature MnTi catalyst synthesized by ultrasound-assisted impregnation method was active for both NO reduction and Hg⁰ oxidation under normal NH₃-SCR atmosphere. The GHSV in this experiment was much higher than that of a real SCR operation (2000–4000 h⁻¹). Lower GHSV can facilitate both NO reduction and Hg⁰ oxidation [45]. In addition, HCl was absent in the simulated flue gas. The presence of HCl would greatly promote Hg⁰ oxidation over MnO_x-based SCR catalysts [46]. Therefore, it is reasonable to believe that the MnTi catalysts present great potential for simultaneous control

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