



Research article

Simultaneous removal of NO and Hg⁰ from oxy-fuel combustion flue gas over CeO₂-modified low-V₂O₅-based catalysts

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ABSTRACT

CeO₂-doped low-V₂O₅-based catalysts (V0.5WCe/Ti) were investigated and showed outstanding stability for the simultaneous removal of NO (92.5%) and Hg⁰ (75%) from oxy-fuel combustion flue gas in 50 h compared to a normal V1.0W/Ti catalyst. The good NH₃-SCR performance of the V0.5WCe/Ti catalyst was due to the enhancement in acidity that arose from the introduced vanadium oxide, the better redox capability and greater amount of surface adsorbed oxygen species (O₂⁻, O⁻ and O²⁻) by Ce-modification, which generated a large amount of NO₂, conducting the “fast SCR reaction”. Hg⁰ oxidation was strongly affected by surface adsorbed oxygen and C=O functional groups in the absence of HCl in CO₂-enriched flow conditions, while the reaction was mostly between Hg_(ad)⁰/HgO_(ad) and gaseous Cl^{*} or Cl₂ in the presence of both HCl and O₂. In addition, a high concentration of CO₂ inhibited NO conversion, because of the rate of diffusion, but promoted Hg⁰ removal. Furthermore, while a high concentration of HCl prohibited NO conversion due to the formation of V–Cl and Ce–Cl on the catalyst surface, Hg⁰ adsorption and catalytic oxidation were inhibited when SO₂ and H₂O co-existed in the flue gas.

1. Introduction

Oxy-combustion is a promising technology for performing coal combustion with high-efficiency CO₂ capture and storage (CCS) [1,2]. However, due to different combustion conditions, such as combustion atmosphere, recycle rate, residence time, thermal profile and emission control devices, the flue gas components such as NO_x, SO_x, H₂O, Hg and fly ash, arise in the oxy-combustion flue gas, compared with those in air-combustion flue gas [2–6]. Mercury, an element that is toxic to human health and ecosystems, has attracted great interest. Coal-fired power plants are among the greatest anthropogenic sources of mercury emissions. The mercury concentration in the flue gas is higher in flue gas under oxy-firing conditions than air-firing conditions because of recycling of the flue gas [4,7]. Elemental mercury (Hg⁰) in the oxy-combustion flue gas accumulates in the CO₂ compression units and damages the aluminum heat exchangers [8,9]. Therefore, based on the safety and corrosion issues, effective removal of elemental mercury from oxy-combustion flue gas is an urgent issue and the choice of control units ultimately affects the plant cost and environmental concerns [9,10].

Recently, the Hg⁰ removal behavior in oxy-fuel combustion flue gas has received more and more attention. Although some reports was published about mercury removal behavior for the oxy-combustion flue

gas [4,11–14], the simultaneous removal of NO and Hg⁰ from oxy-fuel combustion systems has been little studied, especially by catalytic oxidation removal [15,16]. Yang et al. [12] investigated the Hg⁰ removal behavior and reaction mechanism under oxy-fuel combustion conditions using cobalt oxide-loaded magnetosphere catalysts from fly ash (Co–MF catalyst). Lopez-Anton et al. [11] studied mercury capture capacity of activated carbon obtained from leather industry waste, and part of the Hg⁰ was oxidized to Hg²⁺ in an oxy-combustion atmosphere. Spörl et al. [4] studied the mercury emissions and removal behavior by ash in an oxy-fuel combustion system. These studies showed that mercury oxidation was enhanced in an oxy-combustion atmosphere. Fernández-Miranda et al. [16] evaluated the oxidation and capture of Hg⁰ by SCR catalysts (VW/TiO₂ and Fe/Zelite) under a simulated oxy-combustion flue gas. The results showed that NO_x conversion was lower, and Hg⁰ oxidation was higher in a CO₂-enriched atmosphere than in a N₂-enriched atmosphere. The results were almost identical to our previous study [15].

The catalytic oxidation of Hg⁰ into Hg²⁺ using metal oxide catalysts has been extensively examined recently because the converted Hg²⁺ is water-soluble and can be readily removed by a subsequent wet system such as flue gas desulfurization (FGD). It has been reported that the V₂O₅-based catalysts as a typical selective catalytic reduction (SCR) catalyst are responsible for converting Hg⁰ to Hg²⁺ efficiently in the

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presence of a halogen compound [17,18]. And the mercury oxidation activity over V_2O_5 -based catalysts increases with their V_2O_5 content [19]. In order to increase the oxidation rate of mercury, the amount of a catalyst in the reaction system or the V content in catalysts should be increased. However, the vanadium is a toxic composition existing in catalysts which can cause large harm to human and environment [20]. Hence, developing environmentally friendly catalyst with low or no vanadium but high catalytic performance is desirable. Recently, cerium has attracted considerable attention as an oxygen reservoir due to its prominent ability to store/release oxygen via the redox shift between Ce^{4+} and Ce^{3+} under oxidizing or reducing conditions, respectively [21]. A variety of cerium catalysts, such as CeO_2/TiO_2 [22,23], CeO_2-WO_3/TiO_2 [24], CeO_2-MoO_3/TiO_2 [25], MnO_x-CeO_2 [26,27] and $V_2O_5-CeO_2/TiO_2$ [28,29] have been synthesized and measured as SCR catalysts for the Hg^0 removal. These catalysts exhibited relatively high mercury removal performance. Consequently, a low cost option for control of mercury from coal combustion flue gas can be achieved by this co-benefit of SCR with Ce modified catalysts. Based on these findings, the performance and mechanism of a CeO_2 -modified low- $V_2O_5-WO_3/TiO_2$ catalyst for the simultaneous removal of NO and Hg^0 under air and oxy-fuel combustion flue gas were studied and the comparative advantage was attainable in competition with those of normal $V_2O_5-WO_3/TiO_2$ SCR catalyst in this study.

2. Experimental

2.1. Catalyst preparation

The catalysts employed in this study were prepared using an ammonium metavanadate (NH_4VO_3), ammonium tungstate ($N_2H_{37}W_6O_{24} \cdot H_2O$) and/or cerium nitrate ($Ce(NO_3)_3 \cdot 6H_2O$) aqueous solution as a precursor and P25 (TiO_2 , Degussa P25, Germany) as the support by an ultrasonic-assisted impregnation method. The details of the synthetic procedure were reported in a previous study [15]. The four catalysts used in this work were denoted, 6 wt.% CeO_2/TiO_2 , 8 wt.% WO_3-6 wt.% CeO_2/TiO_2 , 0.5 wt.% V_2O_5-8 wt.% WO_3-6 wt.% CeO_2/TiO_2 and 1.0 wt.% V_2O_5-8 wt.% WO_3/TiO_2 and were referred to as the Ce/Ti, WCe/Ti, V0.5WCe/Ti and V1.0W/Ti catalysts, respectively.

2.2. Catalytic characterization

The specific surface areas of the catalysts were calculated via the Brunauer-Emmett-Teller (BET) method, and the pore volumes and pore sizes were determined using the Barrett-Joyner-Halenda (BJH) method. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements were used to analyze the catalysts. H_2 -temperature programmed reduction (TPR), NH_3 -temperature programmed desorption (TPD) and O_2 -TPD experiments were also performed using a tp-5080 automated chemisorption analyzer (Xianquan Co. Ltd, China) using ~100 mg of sample. The details of the material characterization methods were described in previous studies [15,30].

2.3. Catalytic tests

Supplemental Files (SF) Figs. S1 and S2 showed a schematic diagram of the experimental setup. The catalytic activity measurement for the removal of NO and Hg^0 was carried out at atmospheric pressure in a fixed bed continuous flow quartz reactor with i.d. 10 mm. A 0.64 ml of catalyst sample was loaded in the quartz reactor. The simulated flue gas was introduced into the reactor with the inlet flow rate at 800 ml/min, corresponding to a gas hourly space velocity (GHSV) of approximately $75,000 h^{-1}$. The composition of simulated flue gas including 80 vol.% CO_2 , 5 vol.% O_2 and N_2 (as balance) were precisely controlled by mass flow controllers (MFC). SCR atmosphere was defined as 5 vol.% O_2 , 80 vol.% CO_2 , 300 ppm NO, and 50–350 ppm NH_3 balanced in N_2 . And NO at the inlet and outlet of the reactor was monitored by using NO

analyzer (KM9106). Hg^0 was generated by a Hg^0 permeation tube (VICI Metronics, USA). In order to avoid Hg^0 and water vapor (when used) condensation, all teflon tubes that Hg^0 and water vapor passed through were wrapped with a temperature-controlled heating tape and heated up to 120 °C. The elemental mercury (Hg^0) concentrations at the inlet and outlet of the reactor were measured by a continuous mercury analyzer (VM-3000, Mercury Instruments Inc., Germany) with a wet-chemistry conversion unit containing a 10% $SnCl_2$ aqueous solution or 10% KCl aqueous solution (SF Fig. S2), in which the Hg^{2+} could be reduced into Hg^0 . Hg^{2+} concentration was calculated from the difference between the two measurements, similar to the method used in our previous study [15]. In addition, sodium bicarbonate was used to remove the acid gas (e.g. SO_2 , HCl) before the sampling gas entered the flue gas analyzer. It was also used to remove SO_2 before the flue gas entered the $SnCl_2$ solution, as SO_2 can interfere with the reduction of Hg^{2+} by $SnCl_2$.

The NO removal efficiency (E_{NO}) was defined in Eq. (1). The physical adsorption mainly occurred at normal or low temperature, and the chemical adsorption or oxidation occurred at high temperature [22]. V_2O_5 -based catalysts, as medium-temperature catalyst, are generally used at 350–420 °C. The NO and Hg^0 removal activity was investigated at 350 °C in this study, so physical adsorption was negligible and was not considered, which was also proved in this study by the breakthrough of Hg^0 over the catalyst, as presented in SF Fig. S3.

The total Hg^0 removal efficiency (E_{Hg^T}) was defined in Eq. (2), including the catalytic oxidation efficiency ($E_{Hg^{ox}}$) and the Hg^0 adsorption efficiency ($E_{Hg^{ad}}$), which were defined in Eq. (3) and Eq. (4), respectively.

$$E_{NO} = \frac{NO_{in} - NO_{out}}{NO_{in}} \times 100\% \quad (1)$$

$$E_{Hg^T} = \frac{Hg_{in}^0 - Hg_{out}^0}{Hg_{in}^0} \times 100\% \quad (2)$$

$$E_{Hg^{ox}} = \frac{Hg_{out}^{2+}}{Hg_{in}^0} \times 100\% \quad (3)$$

$$E_{Hg^{ad}} = E_{Hg^T} - E_{Hg^{ox}} \quad (4)$$

The subscript of “in” and “out” represented the concentrations at inlet and outlet of the reactor, respectively.

Three sets of experiments (Sets A, B and C) were conducted in Table 1 in this study. The Set A experiments were conducted in a simple flue gas composition with only CO_2 , N_2 and O_2 . The aim was to investigate the effects of CO_2 on the removal of only NO or Hg^0 over the catalysts. The reaction temperature was 350 °C for the Set B and Set C experiments, which represents a typical SCR catalytic reactive temperature over V_2O_5 -based catalysts. In the Set B-I and B-II tests, the experiment aimed to observe the interaction between the NH_3 -SCR and Hg^0 removal reaction in a CO_2 -enriched atmosphere. In addition, the Set B-III tests were conducted to test the stability of V0.5WCe/ TiO_2 catalysts for the simultaneous removal of NO and Hg^0 for 50 h under simulated complicated oxy-fuel combustion flue gas (containing O_2 , HCl, NO, NH_3 , SO_2 , and H_2O simultaneously), which was compared with the common catalyst of V1.0W/ TiO_2 . In the Set C tests, the experimental investigation aimed to determine the effects mechanism of separate flue gases (SO_2 , H_2O , and HCl) on the simultaneous removal of NO and Hg^0 over the CeO_2 -modified low- V_2O_5 -based catalyst in a CO_2 -enriched atmosphere at 350 °C.

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