



Full Length Article

The catalytic performance and characterization of ZrO₂ support modification on CuO-CeO₂/TiO₂ catalyst for the simultaneous removal of Hg⁰ and NO



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ABSTRACT

The different addition amounts of ZrO₂ on CuO-CeO₂/TiO₂ catalyst synthesized by co-precipitation method were investigated to research the simultaneous removal of Hg⁰ and NO in simulated flue gas. Results indicated that the CuCe/TiZr_{0.15} catalyst exhibited the superior Hg⁰ removal efficiency (72.7%) and prominent NO conversion (83.3%). Hg⁰ slightly restrained the NO conversion. Except for the effect of the separate NH₃ and NO on Hg⁰ removal, significances of the increased NH₃/NO ratio on Hg⁰ removal and NO conversion were detected. The lower GHSV could give rise to the significant acceleration of Hg⁰ and NO removal. With the existence of SO₂ and H₂O, the slightly prohibitive effect on Hg⁰ and NO removal was displayed. BET, XRD, SEM, H₂-TPR, XPS, FTIR analysis were applied to characterize catalysts and the results revealed the ZrO₂ modified support on CuO-CeO₂/TiO₂ resulted in strong redox ability, great mobility of surface oxygen and growing total amount of chemisorbed oxygen and lattice oxygen, which favorably impacted on Hg⁰ and NO removal. The introduction of Zr benefited great surface area, weakened crystallinity of TiO₂ and then improved the dispersion of metal oxide species. More stable Lewis acid sites to form coordinated NH₃ were generated due to ZrO₂ additive. The synergetic effect through redox equilibrium of $Ce^{3+} + Cu^{2+} \leftrightarrow Ce^{4+} + Cu^{+}$ contributed to Hg⁰ removal and NO conversion. In addition, the simultaneous removal of Hg⁰ and NO on CuCe/TiZr_{0.15} in terms of detailed mechanism was discussed.

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1. Introduction

Coal-fired power plants have become one of the leading anthropogenic emission sources and produce various air pollutants. Among, elemental mercury (Hg⁰) and nitrogen oxides (NO_x) are central environmental issues, which have drawn great attention recently. It is generally known NO_x (NO, NO₂ and N₂O) generate plenty of problems, including photochemical smog, acid rain, greenhouse effects and ozone depletion [1,2]. Due to the volatility, persistence, and bioaccumulation of mercury in the environment, it is a major air toxic contaminant [3]. The US Environmental Protection Agency (USEPA) on December 16, 2011 finalized the first ever national standards and controlled the discharge of mercury

and other harmful air contaminants [1,4]. Hence, mercury and NO_x emission need to be constrained nowadays.

Selective catalytic reduction (SCR) is proven to be the widely-applied technique for NO_x removal [5,6]. Various technologies have been investigated for controlling Hg⁰ [1,7], among which SCR is of great interest for development. In consequence, the SCR catalysts for simultaneous removal of mercury and NO_x might be an effective approach to be investigated. The valuable process of the SCR catalysts for reducing Hg⁰ and NO was suggested by some recent data. For example, CeO₂ modified V₂O₅-WO₃/TiO₂ catalysts were studied for Hg⁰ oxidation under different flue gas components (NO, SO₂, NH₃) [8]. Yan et al. [9] researched Hg⁰ oxidation on SCR catalysts modified by RuO₂ in lower level HCl. Li et al. [4] studied mercury conversion under SCR atmosphere (SCRA), that is, NO, NH₃ and O₂, over CuO-CeO₂/TiO₂ catalyst. Besides, a series of Ce-doped V₂O₅/TiO₂ catalysts was employed to remove Hg⁰ and NO simultaneously in bench scale tests [10]. Though, the traditional commercial SCR catalysts still suffer from severe problems, such as limited active temperature window and catalyst deactivation

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by SO₂ and H₂O [11–13]. TiO₂, as one significant and conventional support, is confined for its low resistance to sintering and surface area [14]. Our object is aimed to achieve the ideal titania-based support with optimizing thermal stability and high surface area for simultaneous removal of Hg⁰ and NO_x. Although the binary support, such as Al₂O₃-TiO₂ [15], TiO₂-SnO₂ [16] CeO₂-TiO₂ [8], was found to present the improved catalytic properties, ZrO₂-doped TiO₂ support might be a better alternative to replace TiO₂ [17]. The zirconia support was reported to supply the superior dispersion of active sites and better oxidation abilities than pure TiO₂ [18]. The strong thermostability, redox properties and surface acidity on the TiO₂-ZrO₂ binary oxides were displayed [14,17,19]. The surface area of catalysts could be increased by the addition of ZrO₂ [14]. The addition of Zr can inhibit the growth of TiO₂ crystallite size [17]. Marcotte et al. [20] proved multi constituent zirconia-titania oxides exhibited unprecedented catalytic properties of NH₃-SCR after aging test. The SO₂ tolerance could also be facilitated by the weak acidity and basic sites on ZrO₂ surface [21]. Furthermore, the CeO_x-based catalysts own its high catalytic oxidation on account of its large capacity storage and redox ability [13,14,22]. CuO has been explored because of its high activity at low temperature, non-toxic and relatively low price [23]. Yao et al. [23] studied the catalytic activities, structural performance and acidic property of CuO/Ti_{0.95}Ce_{0.05} for NH₃-SCR at low temperature. Cu²⁺ can enhance SCR performance at the low temperature on CeO₂-CuO catalyst [24]. Besides, there existed the interaction between Ce and Cu species, which could make for great Hg⁰ removal and SCR activities. However, little research on the roles of ZrO₂ doping CuO-CeO₂/TiO₂ catalyst for simultaneous removal of Hg⁰ and NO were conducted.

This study investigated the ZrO₂ modified support on CuO-CeO₂/TiO₂ catalysts prepared by co-precipitation method, which could accelerate simultaneous removal of Hg⁰ and NO in the simulated flue gas. The research proposed the efficiency of ZrO₂-doped catalyst on Hg⁰ removal and SCR reaction in simulated flue gas. Effects of simultaneous removal of Hg⁰ and NO with the changes of the adding quantity of ZrO₂ and reaction conditions (Hg⁰, NH₃/NO, GHSV, SO₂ and H₂O) of individual Hg⁰ and NO removal were investigated. The physicochemical characteristics and structure properties of catalysts with Zr additive were observed and characterized using the essential characterizations including BET, XRD, SEM, XPS, H₂-TPR, and FTIR. What is more, the catalytic properties and characterization results were operated to reveal the mechanisms of simultaneous removal of Hg⁰ and NO over CuO-CeO₂/TiO₂-ZrO₂ catalyst.

2. Experimental part

2.1. Preparation of catalyst

The co-precipitation method was applied to prepare TiO₂-ZrO₂ composite oxide carriers. The desired amount of Ti (SO₄)₂·ZrOCl₂·8H₂O were dissolved in the deionized water with continuous stirring for 1 h which was thoroughly dissolved and presented uniform mixing. After that, the ammonia solution was added dropwise into the obtained solution under vigorously whisking at room temperature until the pH of solution arrived at 10 and the solution was continued to be stirred for 3 h. The precipitate, after air aging for 24 h at room temperature, was collected by filtration subsequently and dried overnight at 80 °C. Then the product was calcined for 5 h at 400 °C in a muffle furnace. The TiO₂-ZrO₂ carriers were defined as TiZr_a (a=0, 0.05, 0.15, 0.25, 0.35), where a represented the molar ratio of ZrO₂/(TiO₂ + ZrO₂) (Zr/Ti + Zr). The support of TiO₂ or ZrO₂ was prepared likewise. The CuO-CeO₂/TiO₂-ZrO₂ (CuCe/TiZr) was prepared by the conventional impregnation method, which are detailed in supplemental materials (Part1). CuO-CeO₂/TiO₂

(CuCe/Ti), CuO-CeO₂/ZrO₂ (CuCe/Zr) catalyst was prepared with the same method.

2.2. Catalyst activity test

The simultaneous removal of Hg⁰ and NO in simulated flue gas was studied with a bench-scale experimental system. As showed in Fig. 1, the simulated flue gas (SFG) consisting of 100 ug/m³ Hg⁰, 6% O₂, 500 ppm NO, 500 ppmNH₃, N₂ as the balance, was controlled by mass flow controllers (MFCs). The total flow rate of 500 mL/min was commanded, which corresponded to a gas hourly space velocity (GHSV) of approximately 50000 h⁻¹. A Dynacal mercury permeation device (VICI Metronics, USA) generated 100 ug/m³ steady Hg⁰. The effects of different flue gas compositions on Hg⁰ removal and NO conversion were investigated, so 0–800 ppm SO₂ and 8 vol.% H₂O were also chosen when necessary. Among them, 0–800 ppm SO₂ was controlled by MFCs and H₂O was accurately controlled by peristaltic pump and carried out by 100 mL/min pure N₂ to the inlet of the SFG. The temperature-controlled heating tape wrapped all teflon tubes that Hg⁰ and water vapor got by and its temperature was maintained at 120 °C, which could prevent condensation of Hg⁰ and water vapor. Each test containing 500 mg catalyst was performed in a temperature controlled tubular furnace in the temperature window of 100–350 °C and the catalyst was packed into continuous flow quartz reactor with an inner diameter of 10 mm. The concentration of Hg⁰ and NO in the gas was respectively detected by an online RA-915 M mercury analyzer (LUMEX Ltd, Russia) and a flue gas analyzer (MGA5, Germany). The outlet Hg⁰ concentration was measured within the 2 h experiment, which was similar to NO concentration. Half an hour later, the relatively stable mercury concentration and NO concentration were obtained in the next tests (1.5 h). According to the average time interval (10 min) in the next 1.5 h experiment, the ten topic measured data were selected and then averaged. The error was also introduced to illustrate the credibility of data. To confirm mercury speciation, there was a mercury speciation conversion system when needed, which has been described in our previous study [25]. After this system, the flue gas ordinarily entered a 10 wt% NaOH solution where acid gases were caught and a condenser where H₂O can be eliminated. The Hg⁰ removal efficiency (η_{Hg}) and NO conversion efficiency (η_{NO}) were defined as the following equation, respectively:

$$\eta_{\text{Hg}} (\%) = \frac{Hg_{\text{in}}^0 - Hg_{\text{out}}^0}{Hg_{\text{in}}^0} \times 100\% \quad (1)$$

$$\eta_{\text{NO}} (\%) = \frac{NO_{\text{in}} - NO_{\text{out}}}{NO_{\text{in}}} \times 100\% \quad (2)$$

Where Hg_{in}⁰ and Hg_{out}⁰ represent the inlet and outlet Hg⁰ concentration (μg/m³) respectively, NO_{in} and NO_{out} represent the inlet and outlet NO concentration (ppm) respectively. Since the mercury including both Hg⁰ and Hg²⁺ went outside of reactor, partial Hg²⁺ might escape to the gas phase. The Hg⁰ capture efficiency (η_{HgT}) was introduced to be defined as the equation below:

$$\eta_{\text{HgT}} (\%) = \frac{Hg_{\text{in}}^0 - Hg_{\text{out}}^T}{Hg_{\text{in}}^0} \times 100\% \quad (3)$$

Where Hg_{out}^T represent the total concentration of mercury (Hg^T) (μg/m³) at the outlet of reactor. The details of Hg⁰ capture efficiency are described in supplemental materials (Part 2) (Fig. S1).

2.3. Catalyst characterization

The Brunauer-Emmett-Teller specific areas (BET) of catalysts were measured by N₂ adsorption isotherm on a Micromeritics Tris-

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