A sol-gel Ti-Al-Ce-nanoparticle catalyst for simultaneous removal of NO and Hg⁰ from simulated flue gas

Junyi Zhang, Caiting Li *, Lingkui Zhao, Teng Wang, Shanhong Li, Guangming Zeng

College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China
Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha 410082, PR China

HIGHLIGHTS

- $TiAl_{10}Ce_{20}$ showed superior activity for simultaneous removal of NO and Hg^0.
- The deactivation effects of H_2O and SO_2 were reduced by Al addition.
- The mechanisms for simultaneous removal of Hg^0 and NO were systematically studied.
- The connection between NH_3-SCR and Hg^0 removal was also obtained.

GRAPHICAL ABSTRACT
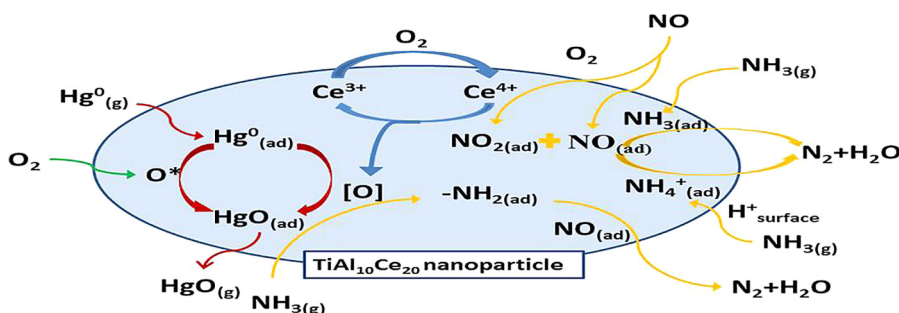
ARTICLE INFO

ABSTRACT

To optimize simultaneous control of NO and elemental mercury (Hg^0) and gain more insight into the mechanisms, nano-sized TiO_2-Al_2O_3-CeO_2 materials synthesized via sol-gel method were used for simultaneous removal of NO and Hg^0 from simulated flue gas. The physicochemical characteristics of catalysts were characterized by ICP-OES, BET, XRD, SEM, TEM, XPS, H_2-TPR and FT-IR. $TiAl_{10}Ce_{20}$ nanoparticle with the addition of 10 wt%Al_2O_3 showed superior NO removal efficiency (93.41%) and Hg^0 removal efficiency (80.54%) in the presence of SCR atmosphere at 300 °C. The deactivation effects of 8% H_2O and 400 ppm SO_2 were also reduced by Al addition. In the presence of SCR atmosphere, the capture of Hg^0 was inhibited by the existence of NH_3, while the presence of Hg^0 had little impact on NO removal. The characterization results showed that the excellent performance of $TiAl_{10}Ce_{20}$ nanoparticle might result from the stronger redox ability, lower crystallinity and better texture properties with highly dispersed Ce species, which were all attributed to Al addition. The mechanisms for simultaneous removal of NO and Hg^0 were also proposed on the basis of above results. $TiAl_{10}Ce_{20}$ nanoparticle developed in this work was considered to be a promising catalyst for simultaneous removal of NO and Hg^0.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Coal is one of the dominating fuel sources and will remain the primary one until 2030 according to the international energy agency (IEA) [1,2]. Various air pollutants are released during the combustion processes in coal-fired power plants, in which nitrogen oxides (NO_x) and elemental mercury (Hg^0) have received extensive attention as two atmospheric contaminants emitted from coal-fired boilers. NO_x emissions can cause high ground-level ozone concentration, photochemical smog and acid rain which can damage the environment [3]. Hg^0 is a global pollutant with toxicity, bio-accumulation and volatility that can result in lots of

---

* Corresponding author at: College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China. Tel.: +86 731 88649216; fax: +86 731 88649216.

E-mail addresses: ctli@hnu.edu.cn, ctli3@yahoo.com (C. Li).

environmental and health risks [4,5]. Accordingly, countries around the world set strict standards on NO_x and mercury control, such as standards of limiting mercury, acid gases and other toxic pollution from power plants enacted by the US Environmental Protection Agency (USEPA) on December 21, 2011 [6].

Several methods have been investigated to control NO and Hg^0 emissions respectively in coal-fired flue gas [5,7–9]. Among them, selection catalytic reduction of NO by NH_3 (NH_3-SCR) has been widely applied because of its high efficiency [10], and activated carbon injection (ACI) has become a common method for Hg^0 removal [9]. However, the large consumption of ACI due to adsorption saturation of carbon materials and the high cost of controlling the two emissions alone urged researchers to develop more cost-effective technologies to remove NO and Hg^0 [11–13]. According to researches in recent years [14,15], Hg^0 is difficult to remove by the existing air pollution control devices due to its high volatility and nearly insolubility in water. As oxidized mercury (Hg^{2+}) is soluble in water, Hg^0 could be oxidized to Hg^{2+} by SCR system and subsequently removed by wet flue gas desulfurization devices (WFGD), Hg^{2+} dissolved in desulfurization waste water was reported that could be removed by the conventional WFGD waste water treatment technology such as the addition of precipitating and agents or adsorption technology [16–18]. Hence, simultaneous removal of NO and Hg^0 with an already existing SCR system was considered to have higher efficiency of apparatus, lower operating costs and less investment than removing NO and Hg^0 separately [13,19,20]. Although some studies have been conducted to investigate simultaneous removal of NO and Hg^0 as well as the mechanisms of the process [21–23], the co-benefit of combining existing SCR system and WFGD inspired us to develop more novel materials which could control NO and Hg^0 emissions simultaneously.

Cerium oxide (CeO_2) has attracted much attention as an effective support, promoter, as well as active species for NH_3-SCR and Hg^0 oxidation respectively due to its high redox ability of Ce^{4+}/Ce^{3+} couple, large oxygen storage capacity, nontoxic and high efficiency [7,24,25]. Among various Ce-based catalysts, TiO_2-CeO_2 catalyst has been researched broadly for its excellent catalytic property. For example, Li et al. [26] found that TiO_2-CeO_2 catalyst possessed high Hg^0 oxidation activity; Gao et al. [27] indicated that TiO_2-CeO_2 catalyst showed superior activity for NH_3-SCR. However, a high concentration of SO_2 was proved to deactivate the activity of CeO_2/TiO_2 catalyst and restrict the application of it [28]. Alumina was widely applied as a support of catalyst due to its low cost and effective promotion effect on thermal stability as well as homogeneous mixing of components [29,30]. Al_2O_3 modified TiO_2 can significantly improve the structural stability and surface acidity of TiO_2 because of its interception effect on phase transition. Moreover, it is worth noting that Al modified catalyst was proved to possess stronger sulfur resistance [31,32]. The tolerance of catalyst to H_2O and sintering was also improved by Al modification [33]. For instance, Camposeco et al. [33] proved that the performance of V_2O_5/$NPTiO_2$ for NH_3-SCR was greatly enhanced by Al addition. On the basis of above states, it was deduced that the addition of Al to TiO_2-CeO_2 catalyst might result in higher catalytic activity in NH_3-SCR and Hg^0 removal. However, Al_2O_3 modified TiO_2-CeO_2 catalyst via sol-gel method has seldom been reported for simultaneous removal of NO and Hg^0.

Accordingly, a bench-scale test was conducted over TiO_2-Al_2O_3-CeO_2 nanoparticle synthesized by sol-gel method to study simultaneous removal of NO and Hg^0 from simulated flue gas. The focus of this work is to clarify the mechanism for simultaneous removal of NO and Hg^0 over TiO_2-Al_2O_3-CeO_2 nanoparticle and discuss the impacts brought by Al addition. The effects of various flue gas components including SO_2 and H_2O and the interaction between SCR process and Hg^0 removal were also investigated. Simultaneously,

crucial characterizations of catalysts were conducted to examine the physicochemical properties of catalysts and further reveal the mechanisms.

2. Experimental section

2.1. Preparation of the catalysts

A single step sol-gel method was applied to synthesize TiO_2, TiO_2-CeO_2 and TiO_2-Al_2O_3-CeO_2 catalysts. The preparation of catalysts consists of following steps. Butyl titanate (0.1 mol), an appropriate amount of Aluminium tri-sec-butoxide, anhydrous ethanol (2.6 mol) and acetic acid (0.02 mol) were mixed under continuous stirring. Subsequently, the mixture of an amount of cerium nitrate, nitric acid (0.05 mol) and deionized water (0.65 mol) was added dropwise into above solution. Then the mixed solution was maintained under constant and vigorous stirring at room temperature until the gel was formed. The obtained gels were aged at the synthesis temperature for 24 h and then dried at 80 °C for 24 h respectively. Finally, the dried gels were calcined at 400 °C for 6 h in air. All of the obtained catalysts were ground and sieved to 80–100 mesh for use and were labelled as $TiAl_xCe_y$, where x represented the mass percentage of Al_2O_3/(TiO_2 + Al_2O_3) (x = 5, 10, 15); y represented the mass percentage of CeO_2/(TiO_2 + Al_2O_3 + CeO_2) (y = 5, 10, 20, 40).

2.2. Catalytic activity tests

As shown in Fig. 1, the activity tests of catalysts for NH_3-SCR and Hg^0 removal were conducted in a fixed-bed system. A 0.5 g sample was loaded in a quartz reactor (i.d. 10 mm), the simulated flue gas (SFG) consisted of 500 ppm of NO, 500 ppm of NH_3, 5 vol% O_2, Hg^0 (80 μg/m³), 400 ppm SO_2(when used), 8 vol% H_2O(when used) and pure N_2 as balance. The gas-phase Hg^0 was generated by a mercury permeation tube (VICI Metronics, USA) and then transported into the reaction system with N_2. All the gas flows except H_2O were controlled by mass flow controllers (MFC). The water vapour was generated by injecting water into teflon tube wrapped with a temperature-controlling heating strip at 120 °C through peristaltic pump. For all experiments, a total gas flow of 500 mL/min (GHSV = about 50,000 h⁻¹) was introduced into the fixed-bed reactor at temperatures from 100 to 350 °C. The concentrations of NO and Hg^0 at inlet and outlet of the quartz reactor were analysed respectively using a flue gas analyser (MGA5, Germany) and an online RA-915 M mercury analyser (LUMEX Ltd, Russia). Sample tests and analyses were kept for 2 h after the catalytic process had reached equilibrium in each measurement. To reduce the experimental error, three or more replicates of sample tests were conducted. Besides, the error bars in each figure represent the standard deviation from the mean of the series of experiments at each condition.

The performance of simultaneous removal of NO and Hg^0 was expressed by NO removal efficiency (E_{NO}) and Hg^0 removal efficiency (E_{Hg}) according to Eq. (1) and Eq. (2) respectively:

$$E_{NO} = \left(1 - \frac{[NO]_{out}}{[NO]_{in}}\right) \times 100\% \tag{1}$$

$$E_{Hg} = \left(1 - \frac{[Hg]_{out}^0}{[Hg]_{in}^0}\right) \times 100\% \tag{2}$$

In which $[NO]_{in}$ and $[NO]_{out}$ denote the inlet NO concentration and outlet NO concentration; the inlet Hg^0 concentration and outlet Hg^0 concentration are defined as $[Hg]_{in}^0$ and $[Hg]_{out}^0$. An Hg speciation conversion system was applied in this study to recognize the