Chemical Engineering Journal 169 (2011) 186–193

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Oxidation and capture of elemental mercury over SiO_2–TiO_2–V_2O_5 catalysts in simulated low-rank coal combustion flue gas

Hailong Li[a,b], Ying Li[c], Chang-Yu Wu[b,*], Junying Zhang[a]

[a] State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China
[b] Department of Environmental Engineering Sciences, University of Florida, Gainesville, FL 32611, United States
[c] Department of Mechanical Engineering, University of Wisconsin-Milwaukee, Milwaukee, WI 53211, United States

ARTICLE INFO

Article history:
Received 6 December 2010
Received in revised form 1 March 2011
Accepted 2 March 2011

Keywords:
Mercury
Vanadia
SCR
Coal combustion
Flue gas

ABSTRACT

High surface area SiO_2–TiO_2–V_2O_5 (STV) catalysts of various titania loadings were synthesized by a sol–gel method. The STV catalysts were tested for oxidation of elemental mercury (Hg^0) and its capture in simulated coal combustion flue gas representing those from combustion of low-rank coals (sub-bituminous and lignite). Experiments were conducted in a fixed-bed reactor at temperatures ranging from 26 to 400 °C. In simulated flue gas, Hg^0 oxidation efficiency over the STV catalysts was found to decrease dramatically from 135 to 300 °C. At typical selective catalytic reduction (SCR) operating temperatures, the catalyst's oxidation activity increased as titania loading of the STV catalysts increased up to 18 wt%. The reaction mechanisms over the STV catalysts at SCR operating temperatures were investigated using individual flue gas components (HCl, NO, SO_2 and H_2O) with O_2 balanced in N_2. Hg^0 oxidation over STV catalysts follows the Eley–Rideal mechanism where active surface species generated from adsorbed flue gas components react with gas-phase or weakly adsorbed Hg^0. Fresh STV catalysts had some capability for adsorbing oxidized mercury (Hg^{2+}) at 350 °C, and no obvious effect of the adsorbed Hg^{2+} on subsequent Hg^0 oxidation was observed. The presence of HCl with O_2 had excellent oxidation and capture efficiency; however, without O_2 it remarkably inhibited Hg^0 adsorption on the STV catalysts. NO and SO_2 promoted Hg^0 oxidation and capture in the presence of O_2, but their promotional effects were insignificant in the absence of O_2. Water vapor showed prohibitive effects on Hg^0 oxidation due to its competition with reactive species such as HCl and NO for active adsorption sites. This study demonstrates the feasibility of using STV catalysts for Hg^0 removal at typical SCR operating temperatures. The identification of the reaction mechanism provides critical information for developing effective SCR catalysts for Hg^0 oxidation in coal combustion flue gas.

1. Introduction

With approximately 900 billion metric tons available that is sufficient to meet the current level of energy demand for nearly 200 years, coal is the most abundant fossil fuel on earth [1]. Currently, approximately 50% electricity in the United States is generated from coal-fired power plants [2]. Emitting approximately 48 tons of mercury (Hg) a year or one-third of the Hg emissions in the United States, coal-fired power plants are the largest single-known source of anthropogenic Hg emissions in the United States [3]. In recent years, concerns about Hg emissions have risen greatly because of the extreme toxicity, persistence, and bioaccumulation of methyl Hg transformed from emitted Hg [4]. By April 2010, more than 20 U.S. states had proposed or adopted rules that were more stringent than Clean Air Mercury Rule (CAMR) [5,6]. The U.S. Environmental Protection Agency (EPA) is also developing federal air toxics emission (include Hg) standards for power plants and intends to finalize the rules for coal-fired electricity generating units by November 2011 [7].

Hg in coal combustion derived flue gas is present in three forms: elemental Hg (Hg^0), oxidized Hg (Hg^{2+}) and particulate-bound Hg (Hg^p) [8]. Hg^p can be easily captured by particulate matter (PM) control devices. Hg^{2+} is readily adsorbed onto fly ash and subsequently collected along with ash in PM control devices. Hg^{2+} can also be effectively captured in a wet flue gas desulfurization (WFGD) system because it is water-soluble [8]. In contrast, it is very difficult for Hg^0 vapor to be collected by existing air pollution control devices (APCDs) [9] because it is highly volatile and nearly insoluble in water [10]. A promising method for the removal of Hg^0 from coal combustion flue gas is catalytic oxidation of Hg^0 to Hg^{2+} which can be subsequently captured by PM control devices or/and WFGD systems.

---

* Corresponding author. Tel.: +1 352 392 0845; fax: +1 352 392 3076.
E-mail address: cywu@ufl.edu (C.-Y. Wu).

1385-8947/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2011.03.003

Catalysts employed in the selective catalytic reduction (SCR) of nitrogen oxides, typically composed of vanadia supported on titania, have been proven in bench scale experiments [11–19], pilot scale tests [20–22] and coal-fired power plants field tests [23–28] to facilitate heterogeneous oxidation of Hg^0 to Hg^{2+}. This co-benefit of Hg reduction resulting from NO_x and SO_2 controls imposed by the Clean Air Interstate Rule (CAIR) [29] makes the cost of Hg control more economical than activated carbon injection (ACI) method, which currently is the best method for removing Hg^0 from flue gas [30]. However, Hg^0 oxidation efficiencies over SCR catalysts were found to depend on coal type, combustion condition and composition of flue gas. The flue gas Hg^0 oxidation across the SCR system in plants burning bituminous coal was reported to be higher than 90% [22], but in plants burning sub-bituminous coal less than 30% Hg^0 oxidation efficiency was observed [20]. HCl concentration in flue gas was considered to be one of the key factors that determine the Hg^0 oxidation efficiency [17,31]. However, the exact mechanisms for Hg^0 oxidation over SCR catalysts are still not clear to date, and only several possibilities have been proposed. Through Deacon process, HCl is heterogeneously oxidized by SCR catalysts to form Cl_2 [32], which then may be responsible for Hg^0 oxidation in the gas phase. However, Cao et al. [21] found that Cl_2 could not promote Hg^0 oxidation under real flue-gas atmosphere. He et al. [14] believed that Hg^0 oxidation over V_2O_5/TiO_2 catalyst occurred via Langmuir–Hinshelwood mechanism, because they found that the same vanadia site was responsible for the adsorption of both HCl and Hg^0. On the other hand, Straube et al. [33] observed that Hg^0 was no longer adsorbed on SCR catalysts in the presence of high concentration of HCl.

Conventional SCR catalysts have been successfully used in coal fired power plants to remove NO_x by NH_3 for more than 20 years. However, they still have some limitations where improvements can be made, such as low surface area relating to their titania supports [34]. To improve performance, high surface area SiO_2–TiO_2–V_2O_5 (STV) catalysts prepared by a co-precipitation method and a sol–gel method have been developed and reported to be suitable as SCR catalysts at temperature range from 250 to 400 °C [35–37]. Similar to SCR of nitrogen oxides, surface area of vanadia based SCR catalyst is also very important for Hg^0 removal. A nanosized aerogel V_2O_5/TiO_2 catalyst with relatively larger surface area has been demonstrated to be more effective for Hg^0 removal than that with smaller surface area and commercial SCR catalyst [38]. The STV catalysts with large surface area were also observed to have high Hg^0 removal efficiency in simulated coal combustion flue gas at 135 °C [39]. However, the operating temperatures of SCR are typically above 300 °C [27]. High temperature can limit the physical adsorption of Hg^0 [38,40] and active species such as HCl. Accordingly, the Hg^0 oxidation activity and reaction mechanisms would be different at higher temperatures. To evaluate the possibility of using STV catalysts for removing Hg^0, the temperature effect on Hg^0 oxidation activity as well as the reaction mechanisms should be studied. Hence, the objective of this work was to evaluate the catalytic activity of STV catalysts at a wide temperature range and to analyze the possible reaction mechanisms of Hg^0 oxidation. The effects of catalyst composition and individual flue gas components on Hg^0 oxidation and capture were investigated as well.

2. Materials and methods

2.1. Preparation and physical characterization of catalysts

The STV catalysts with different titania loadings were synthesized by a sol–gel method. Details are reported in our previous study [39], and therefore only a brief summary is provided here. First, a known amount of vanadium triisopropoxide (VTPO, Alfa Aesar), used as the precursor of vanadia was dissolved in well stirred ethanol and added dropwise to a prepared silica sol under vigorous stirring. TiO_2 nanoparticles (P25, Degussa) were then added to the mixture before it started to gel. The STV composites were originally made in a cylindrical pellet form (3 mm in diameter and 5 mm in length), which were grinded and sieved through 40/100 meshes (425/150 μm) to obtain the powder form. The weight fraction of vanadia in the catalyst powder was approximately 5%, which is close to the optimal vanadium loading in STV catalyst found in our previous work [39]. The catalysts are denoted as ST*x*V*y*, where S represents SiO_2, T represents TiO_2, V represents V_2O_5, and *x* and *y* represent the weight percentages of the TiO_2 and V_2O_5, respectively.

Brunauer–Emmett–Teller (BET) surface area analysis by N_2 adsorption was performed using a Quantachrome NOVA 1200 gas sorption analyzer (Boynton Beach, FL). X-ray diffraction (XRD) measurement was carried out on a Philips APD 3720 diffractometer using Cu Kα radiation ($\lambda = 0.1542$ nm) in the range of 15–40° (2θ) with a step size of 0.02°.

2.2. Catalytic activity measurement

A bench-scale system consisting of a Pyrex reactor, a temperature-controlled tubular furnace, a chemical Hg speciation conversion system, and a mercury analyzer was constructed for this study as shown in Fig. 1. All individual flue gas components were from cylinder gases and precisely controlled by mass flow controllers. Water vapor was generated using a heated water bubbler. A Dynacal Hg^0 permeation device (VICI Metronics) was used to provide a constant feed of Hg^0 concentration (~70 μg m^{-3}). In our experiments, the relatively high Hg^0 concentration was employed to reduce the experimental errors caused by the sensitivity of the mercury analyzer and to allow experiments to be completed in a reasonable time scale. An RA-915+ Hg analyzer (OhioLumex, essentially a portable Zeeman-modulated cold vapor atomic absorption apparatus) coupled with a wet chemistry Hg speciation conversion system were used to measure Hg^0 and total mercury (Hg^T) concentrations at both the inlet and outlet of the reactor. Details of the Hg speciation conversion system were reported in our previous study [41].

The experimental conditions are summarized in Table 1. In Set I, activity of STV catalysts for Hg^0 removal was first investigated using 200 mg STV catalysts with 5% vanadia loading and different titania contents to identify the optimal composition. Simulated flue gas representing those from combustion of low-rank coals (sub-bituminous and lignite) was introduced with a space velocity about 80,000 h^{-1} and at reaction temperature from 135 to 400 °C. Each experimental run consisted of two phases: heating and cooling. During the heating phase, temperature in the reactor rose from 135 to 250 °C then varied from 250 to 400 °C every 50 °C. In the subsequent cooling phase, temperature decreased from 400 °C down to 135 °C following the reverse steps of the heating phase. At each select temperature, Hg^0 and Hg^T concentrations downstream the catalysts were recorded after the process had reached equilibrium: fluctuation of Hg^0 concentration no more than 5% deviation for more than half an hour. Two values of outlet Hg concentration (both Hg^0 and Hg^T concentrations) were obtained from the heating and cooling phases, respectively. The mean values of these two Hg^0 and Hg^T concentrations were used to calculate Hg^0 oxidation and capture efficiencies, respectively.

In pure N_2 atmosphere, the loss of Hg^0 at room temperature is due to physical adsorption. However, Hg^0 may be oxidized by lattice oxygen over STV catalysts at typical SCR operating temperatures. Introduction of gas-phase O_2 has been reported to reoxidize the reduced metal oxides, replenishing the lattice oxygen [39,40]. In Set II, the breakthrough curves of ST18V5 were measured at room