



Full Length Article

Influences of water vapor and fly ash on elemental mercury removal over cerium-oxide-modified semi-coke

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ABSTRACT

A bench-scale fixed bed reactor was used to study the influences of water vapor and fly ash on Hg⁰ removal efficiency over CeO₂-modified semi-coke adsorbent (Ce/SC). Adsorption results showed that the mercury removal efficiency of Ce/SC decreased by 30% in the presence of 10% water vapor, and the introduction of 0.5 g fly ash had no significant effect on the Hg⁰ removal efficiency of Ce/SC. In the condition of water vapor and fly ash coexisted, the Hg⁰ removal efficiency of Ce/SC decreased by only 15%, indicated that the fly ash slowed down the inhibitory effects of water vapor on Hg⁰ removal efficiency over Ce/SC, which is mainly due to the interaction between water vapor and Fe₂O₃ in the fly ash to form Fe-OH groups, furthermore, γ-Fe₂O₃ exhibited higher Hg⁰ removal performance than α-Fe₂O₃. Hydrogen temperature-programmed reduction (H₂-TPR) revealed that the oxidation activity and capacity of α-Fe₂O₃ and γ-Fe₂O₃ increased significantly after water vapor treatment. X-ray photoelectron spectroscopy (XPS) results showed that the Fe-OH content of α-Fe₂O₃ and γ-Fe₂O₃ increased from 37.97% and 15.99% to 44.56% and 43.39%, while the lattice oxygen content decreased from 26.53% and 82.46% to 19.08% and 46.49%, respectively. Density functional theory (DFT) calculations revealed that H₂O molecules can be dissociated on both α-Fe₂O₃ (1 0 4) and γ-Fe₂O₃ (2 2 0) surfaces to form H atoms and OH fragments, the H atoms bound with O atoms in Fe-O groups of both α-Fe₂O₃ (1 0 4) and γ-Fe₂O₃ (2 2 0) surfaces, and the OH fragments associated with the adjacent iron atoms of α-Fe₂O₃ (1 0 4) surface or Fe-O groups of γ-Fe₂O₃ (2 2 0) surface to form Fe-OH. The formation of Fe-OH groups increased the oxidation activity and Hg⁰ removal efficiency of Fe₂O₃.

1. Introduction

Elemental mercury (Hg⁰) has attracted considerable worldwide attention as a hazardous atmospheric pollutant [1–4]. Coal-fired utility boilers accounts for 46% of total Hg emissions [5,6]. In recent years, cerium-oxide-modified adsorbents have been widely used for the catalytic oxidation and removal of Hg⁰ in coal-fired flue gas due to its large oxygen storage capacity and its redox reaction of Ce⁴⁺/Ce³⁺ [7–10]. Many studies have reported that CeO₂ loaded materials exhibit excellent Hg⁰ removal efficiencies in the temperature range of 100–300 °C [11,12].

As unavoidable components of coal-fired flue gas, the water vapor and fly ash have significant influences on the oxidization activities of cerium-oxide-modified adsorbents [13–15]. The inhibitory effect of water vapor on Hg⁰ removal performance over ceria-based adsorbents has been obtained by many researchers [16,17], our previous study revealed the inhibitory mechanism involves the chemisorption and subsequent dissociation of H₂O molecules on CeO₂ surface, which

hindered the capture and conversion of gaseous oxygen to high-activity lattice oxygen, thereby decreasing the Hg⁰ removal performance of Ce/SC adsorbent [18]. The chemical compositions of fly ash in flue gas mainly consist of SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO and a small amount of unburned carbon particles. To date, the influences of fly ash properties such as particle size, specific surface area, porosity and unburned carbon content on Hg⁰ adsorption were widely studied [19–21], but there is only a limited understanding about the underlying mechanism of inorganic components in fly ash on the Hg⁰ removal efficiency over ceria-based adsorbents. Bhardwaj et al. [22] found that Al₂O₃, MgO, SiO₂, CaO and TiO₂ did not contribute to the Hg⁰ oxidation and adsorption, but Fe₂O₃ and unburned carbon had higher Hg⁰ removal efficiencies. Galbreath et al. [23] revealed that α-Fe₂O₃ could not significantly alter the form of mercury, while γ-Fe₂O₃ could promote the oxidation and adsorption of Hg⁰. It can be seen that the effect of fly ash on Hg⁰ removal performance is closely related to its chemical composition, and conclusive mechanistic studies about the influences of fly ash chemical compositions on Hg⁰ removal are necessary.

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Table 1
The mass fraction of oxides in the simulated fly ash.

Metal oxide	SiO ₂	Al ₂ O ₃	α -Fe ₂ O ₃	CaO	MgO
w	55%	30%	8%	5%	2%

This paper aimed at studying the influences of different oxides in fly ash on Hg⁰ removal over CeO₂-modified semi-coke adsorbent (Ce/SC) in the conditions of with and without the presence of water vapor. The physical and chemical properties of samples were characterized, and the underlying mechanism was clarified through both adsorption experiments and numerical simulations.

2. Experimental section

2.1. Sample preparation

The semi-coke was prepared by the pyrolysis of lignite (Huolinhe City, Inner Mongolia Province, China) at 700 °C for 1 h under N₂ flow and referred to as SC. CeO₂-modified semi-coke (Ce/SC) was prepared by an impregnation method: 10.0 g SC was added to 100 mL cerium nitrate solution (0.02 mol/L) with stirring for 4 h at 90 °C. The mixture was filtered, washed, dried and finally subjected to thermal treatment at 500 °C for 4 h under N₂ to obtain the Ce/SC samples. The simulated fly ash was obtained by the mixture of typical oxides according to Table 1 and were named FA. The samples of pure α -Fe₂O₃ and γ -Fe₂O₃ were pretreated with water vapor for 4 h at 260 °C and were denoted as α -Fe₂O₃-H₂O and γ -Fe₂O₃-H₂O, respectively.

2.2. Characterization of samples

The power of the ICP spectrometer was performed in a plasma gas

(15.0 L/min) and auxiliary gas (1.50 L/min) mixture flow in Varian 710-ES. The CeO₂-modified semi-coke adsorbent was determined by X-ray diffraction (XRD) carried out on a Bruker D8-Advance X-ray diffraction using Cu K α radiation ($\lambda = 0.1542$ nm) and 2θ range from 5° to 80° at 5°/min. X-ray photoelectron spectroscopy (XPS) analysis on the CeO₂-modified semi-coke adsorbent was carried out using a thermo ESCALAB MARKII instrument equipped with a monochromatic Al K α radiation. Charging of the samples was corrected by setting the binding energy of the adventitious carbon (C1s) to 284.6 eV. The samples were outgassed in a vacuum oven overnight before analysis. Hydrogen temperature programmed reduction (H₂-TPR) was performed by heating the samples (50 mg) at 5 °C/min to 800 °C in a H₂-He mixture flow (75 mL/min) in Micromeritics Auto Chem II 2920.

2.3. First-principles calculations

First-principles calculations based on density functional theory (DFT) were performed using the Dmol 3 program package of Materials Studio 7.0 (Accelrys Software Inc). The exchange and correlation interactions were modeled using the Perdew-Burke-Ernzerhof (PBE) function within the generalized gradient approximation (GGA). A double-numerical basis set with a polarization function on all atoms (the DNP basis set) was used throughout the study. Monkhorst-Pack grid parameter for k-point sampling was $6 \times 6 \times 6$ with a convergence criterion of 10^{-6} eV. The α -Fe₂O₃ (1 0 4) and γ -Fe₂O₃ (2 2 0) models with 3 layers were used, and all layers were fully relaxed, the size of the vacuum regions being 15 Å.

2.4. Experimental set-up and test procedures

The adsorption experiment device and operation methods are referred to literature [18]. The activity of sorbents for Hg⁰ removal was carried out in a fixed bed reactor with simulated flue gas. The

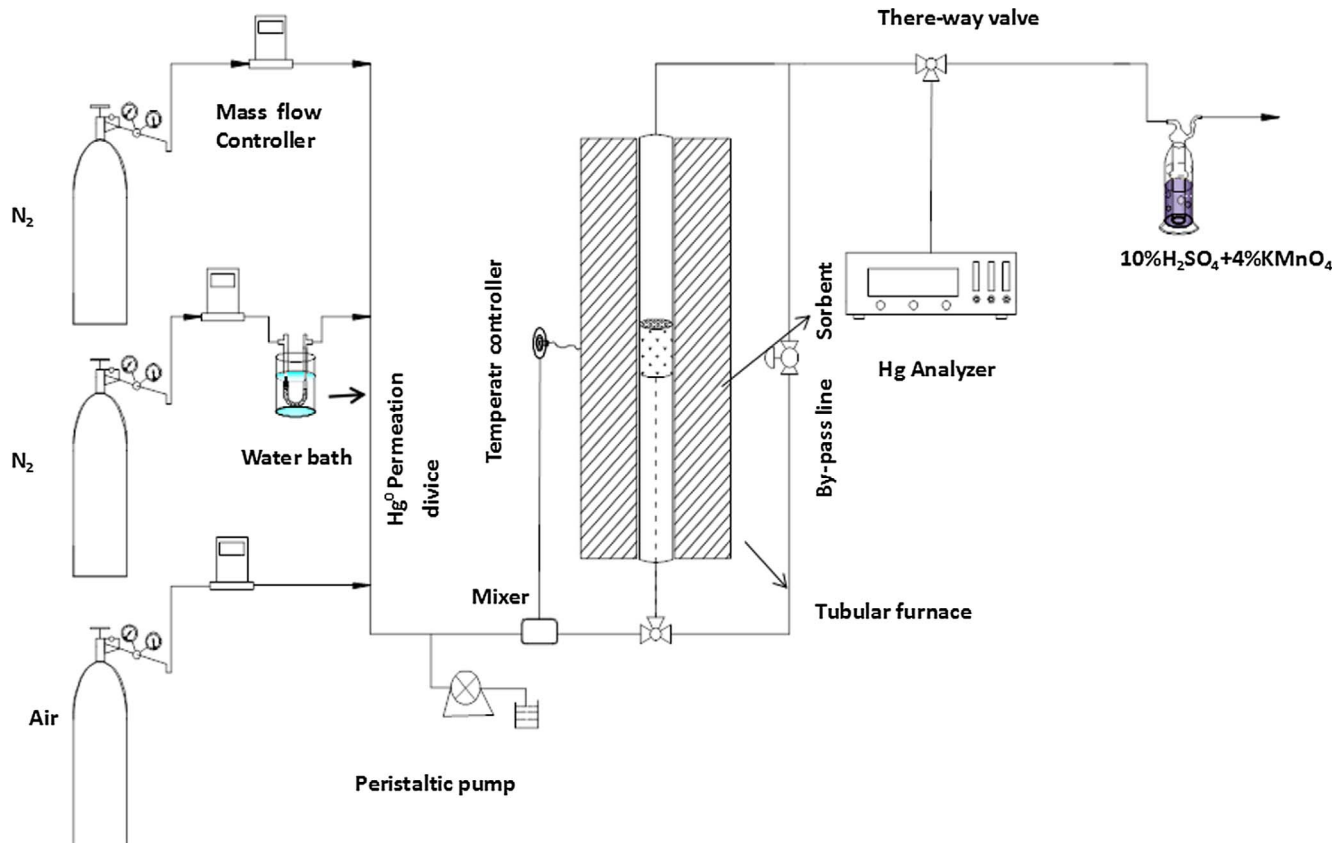


Fig. 1. Schematic of the fixed-bed reactor for removal of Hg⁰.

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