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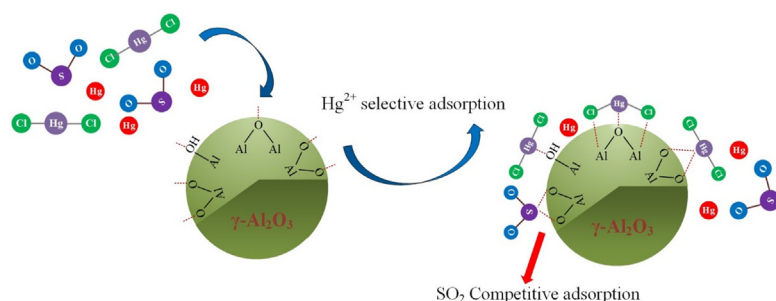
Experimental research on selective adsorption of gaseous mercury (II) over SiO₂, TiO₂ and γ -Al₂O₃



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GRAPHICAL ABSTRACT



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ABSTRACT

Solid selective adsorption to partition mercury speciation (Hg⁰, Hg²⁺) in flue gas is known as the innovative technology in developing solid agents application in online measurement of mercury speciation by continuous emission monitoring system (Hg-CEMS). Porous materials SiO₂, TiO₂ and γ -Al₂O₃ were chosen as the selective adsorbents and the systematical experiments were conducted in a fixed-bed reactor. Adsorption tests indicated that Hg⁰ was scarcely adsorbed by these three porous adsorbents while Hg²⁺ exhibited an apparent adsorption behavior. γ -Al₂O₃ was verified to be efficient in Hg²⁺/Hg⁰ separation because of its high HgCl₂ adsorption capacity and SO₂ anti-interference ability. The intrinsic mechanisms of HgCl₂ selective adsorption and SO₂ competition over γ -Al₂O₃ surface sites were further investigated. Temperature programmed desorption (TPD) analyses demonstrated that the weak interaction between Hg⁰ and γ -Al₂O₃ surface was ascribed to a physisorption manner while the adsorption of HgCl₂ was characterized chemical bonding. Hydroxyl (Al-OH), Lewis Alⁿ⁺-Bronsted Oⁿ⁻ pairs and the coordinatively unsaturated oxygen (O²⁻ ions) were deduced to be effective basic sites for the chemisorption of HgCl₂ on γ -Al₂O₃. Simultaneously, the competitive adsorption between SO₂ and HgCl₂ in O²⁻ ions was confirmed to be responsible for the increased breakthrough of HgCl₂ over γ -Al₂O₃ layer with the existence of SO₂.

1. Introduction

Mercury (Hg) and its compounds have been a global concerned pollutant due to its toxicity, volatility and persistence in the environment. Human health is greatly threatened by its biomagnification in

food chains at the same time, an excessive ingestion of Hg can cause an irretrievable damage of the brain, heart, lungs and immune system of human [1,2]. Coal combustion is widely known as the largest anthropogenic source of Hg emissions, accounting for 23% of the total anthropogenic Hg emission [3]. Generally, vapor phase Hg exists in the

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coal-fired flue gas mainly known as two forms, elemental mercury (Hg^0) and oxidized mercury (Hg^{2+}) [4,5]. Definitely, different chemical forms of Hg affect their properties and fates in the environment. Hg^0 is the predominate speciation of Hg emitted into the atmosphere, and it can undergo a long-range transport from source regions through atmospheric circulation. Hg^{2+} , mainly constituted by mercuric chloride (HgCl_2), has a high chemical reactivity and water solubility than that of Hg^0 , which contributes to its efficient removal by wet scrubbers [6]. Thus, quantification of individual Hg speciation from combustion sources is critical to the establishment of an emission inventory of Hg speciation and development of Hg control technology, correspondingly.

At present, several methods for sampling and quantifying Hg emitted from stationary sources are developed, including Ontario Hydro Method (OHM), Hg continuous emissions monitoring system (Hg-CEMS) and sorbent traps [7–9]. Among these methods, Hg-CEMS is hugely popular in coal-fired power plants because of its real-time online character. However, owing to the limitation of existing Hg detection techniques in Hg^{2+} recognition, a pretreatment/conversion unit designed for achieving a complete separation and conversion of Hg^{2+} to Hg^0 should be used prior to the analytical instrument to realize Hg speciation measurement by Hg-CEMS devices [10]. The conventional method for separation is applying the Hg^{2+} absorption solution, often KCl liquid, to react with Hg^{2+} and form a metal halomercurate [11]. Nevertheless, as a wet-chemistry method, the absorption solution requires to be replaced regularly and corrode the device seriously. Thus, a dry method for Hg speciation separation is urgently required with feature of economy, high-efficiency and long-term, especially, developing a solid sorbent which adsorb Hg^{2+} selectively and inert to Hg^0 has been a research emphasis [12,13].

Due to the inertness of Hg^0 , high quality Hg^0 adsorbents are mainly based on the chemical reaction or chemisorption via converting Hg^0 to Hg^{2+} , such as halogen or sulfur treated activated carbons [14,15] and transition metal oxides (Fe_2O_3 , MnO_2 , CeO_2 , $\text{V}_2\text{O}_5/\text{TiO}_2$, etc.) [16–19]. Therefore, those materials containing Hg^0 oxidation positions can't be used for Hg speciation separation. As a Lewis acidic molecule, HgCl_2 possesses a higher surface reactivity and is easier to be captured by particles than Hg^0 . Ca-based sorbents, particularly CaO, have been considered to be a potential material for HgCl_2 adsorption in coal-fired flue gas [20]. However, a poor gas-solid contact between its surface and adsorbate molecules has been found in the previous study owing to the limited specific areas and undeveloped pore structures of CaO [21]. Moreover, a 20% Hg^0 adsorption efficiency of CaO was reported by Ren et al. [22]. Unlike Ca-based sorbents, porous materials SiO_2 , TiO_2 and $\gamma\text{-Al}_2\text{O}_3$ have developed porous structures, large specific surface area and stable frameworks, which is beneficial for the diffusion of adsorbate in adsorbent pores and a further interaction with inner adsorption sites. Meanwhile, the poor adsorption performance of gaseous Hg^0 due to a lack of effective oxidation positions on these materials was confirmed by Bhardwaj et al. [23]. On the other hand, a large quantity of basic groups (hydroxyl) are found on SiO_2 , TiO_2 and $\gamma\text{-Al}_2\text{O}_3$ surfaces during hydrolysis preparation [24–26], which were reported to be essential for HgCl_2 capture. However, to date, few literatures comprehensively studied the gaseous Hg^0 and Hg^{2+} adsorption properties of these porous materials, and it is still uncertain whether HgCl_2 adsorption behaviors can be interfered by other acidic components in the flue gas such as SO_2 in high concentration or not.

In this work, porous materials SiO_2 , TiO_2 and $\gamma\text{-Al}_2\text{O}_3$ were chosen as the selective adsorbent to partition Hg speciation. The surface and pore structure features of adsorbents were investigated through N_2 adsorption/desorption characterization, and the basic sites of adsorbents were determined by the combination of CO_2 temperature programmed (CO_2 -TPD) method and Fourier transform infrared spectra (FTIR) characterization. Adsorption performances of gaseous Hg^0 and HgCl_2 over the adsorbents were studied in N_2 and $\text{N}_2 + \text{SO}_2$ atmosphere, respectively. Moreover, combined with mercury temperature programmed desorption ($\text{Hg}^0/\text{HgCl}_2$ -TPD) results, the selective

adsorption mechanism of Hg speciation on the adsorbent and the competitive manners between SO_2 and HgCl_2 were discussed in depth. The results of this work will offer a guiding significance to develop Hg speciation separation sorbents, which could be used in Hg-CEMS device for mercury speciation monitoring in coal-fired flue gas.

2. Materials and methods

2.1. Materials and analytical methods

The raw materials SiO_2 and TiO_2 were obtained from Sigma-Aldrich, America when $\gamma\text{-Al}_2\text{O}_3$ was received from Evonik Industries AG, German. All raw materials were sieved into particle with the size of 0.38–0.70 mm (24–40 mesh) and dried in a drying oven at 105 °C for 3 h before being used as adsorbents for Hg speciation adsorption experiments. Nitrogen (N_2 , purity $\geq 99.90\%$) and sulfur dioxide (SO_2 , purity 11.05%) used in this work were both provided by Nanjing Special Gas Co., Ltd, China.

The N_2 adsorption and desorption isotherms of the sorbents were determined at -196 °C on an automatic volumetric multipoint apparatus (ASAP 2020, Micromeritics, USA) and then the specific surface area and pore structure parameters were obtained on the basis of Brunauer-Emmett-Teller (BET) equation and Barrett-Joyner-Halenda (BJH) method. The basicity of sorbents was evaluated by temperature programmed desorption using CO_2 as the probe molecule in an AutoChem II 2920 chemical adsorption instrument (Microtrac, USA), samples was firstly purged at 40 °C for 30 min with He in order to eliminate weakly adsorbed CO_2 , and then heated from 40 °C to 800 °C under a helium flow (30 mL/min) with a pumping rate of 10 °C/min, CO_2 desorbed was finally detected by an on-line mass spectrometry. The IR spectra of sorbents was measured in a PerkinElmer 400 IR spectrometer (PerkinElmer, USA), and the data was recorded at a high resolution ratio of 1 cm^{-1} over the range of 4000–400 cm^{-1} .

2.2. Experimental apparatus

The gaseous Hg^0 and HgCl_2 adsorption experiments were carried out in a fixed-bed apparatus. As shown in Fig. 1, the apparatus consisted of $\text{Hg}^0/\text{HgCl}_2$ vapor generator, flue gas premixing and preheating system, fixed-bed adsorption reactor, Hg vapor online analyzer and tail gas treatment system. The $\text{Hg}^0/\text{HgCl}_2$ permeation device (VICI Electronics Inc, USA) was designed to produce persistent and constant Hg^0 or HgCl_2 vapor at a specified temperature, N_2 flow (200 mL/min) was used as the carrier gas in this work, carrying the volatilized $\text{Hg}^0/\text{HgCl}_2$ into the premixing and preheating system. Additionally, when investigated the effect of SO_2 , SO_2 concentration was set to 1000 ppm and the total flow rate of simulated flue gas was kept 2 L/min. After being preheated and well mixed, simulated flue gas then entered the adsorption reactor where each trap contained two separated sorbent sections loaded with 100 mg adsorbents respectively (front section for Hg collection and back section for Hg breakthrough). Adsorbents were insulated by Hg-free fiberglass and adsorbed $\text{Hg}^0/\text{HgCl}_2$ vapor at a constant temperature of 120 °C. Limited by the detection method of HgCl_2 , only the concentrations of Hg^0 in simulated flue gas from the inlet and outlet of the reactor could be detected continuously by an automatic Hg analyzer (VM3000, Mercury Instruments, GER).

In order to ascertain the adsorption structures of Hg^0 and HgCl_2 on sorbents surfaces, a series of desorption experiments were conducted on a temperature programmed desorption furnace as displayed in Fig. 2. Sorbents were placed on a quartz boat immediately after mercury adsorption experiments, and heated from 40 °C to 800 °C with a heating rate of 10 °C/min. Hg desorbed from sorbents was then carried by pure N_2 flow (2 L/min) into the automatic Hg analyzer (VM3000, Mercury Instruments, GER). According to the temperature of desorption peaks in $\text{Hg}^0/\text{HgCl}_2$ -TPD curves, $\text{Hg}^0/\text{HgCl}_2$ adsorption configurations and binding strength on adsorbent surfaces can be speculated.

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