Fuel 234 (2018) 384–391

Contents lists available at ScienceDirect

Fuel

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

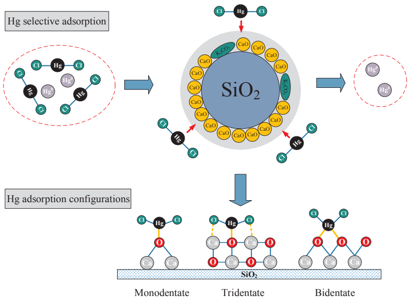
Full Length Article

Synthetic calcium-based adsorbents for gaseous mercury(II) adsorption from flue gas and study on their mercury adsorption mechanism

Chunfeng Li, Hongjian Tang, Yufeng Duan*, Chun Zhu, Yiwu Zheng, Tianfang Huang

Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, School of Energy and Environment, Southeast University, Nanjing, Jiangsu 210096, China

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Calcium-based sorbent
$HgCl_2$
Selective adsorption
Adsorption configuration

ABSTRACT

calcium-based sorbents are the potential materials for mercury chloride ($HgCl_2$) adsorption while inert to elemental mercury (Hg^0) due to their basic property. A series of calcium-based sorbents were chosen to evaluate the selective adsorption performance of mercury, these sorbents included a calcium oxide adsorbent, a KCl-doped calcium oxide adsorbent and a K_2CO_3-doped calcium oxide adsorbent which all supported by the mesoporous silica (C-SiO_2, CKL-SiO_2 and CKO-SiO_2) and were synthesized by an impregnation method. All sorbents were firstly characterized by Powder X-ray Diffraction (XRD), Brunauer-Emmett-Teller (BET) and Scanning Electron Microscope (SEM). Characterization results show that C-SiO_2 has the best surface structure while the doped KCl would evidently reduce the specific surface area and micropores volume of the sorbent, the doped K_2CO_3 also has an adverse effect on the surface structure of CaO sorbent but it can significantly improve the basicity of sorbent. Mercury adsorption performance of the sorbents was then evaluated in fixed bed apparatus, the results indicated that all sorbents exhibited a complete breakthrough for gaseous Hg^0. Due to the modification of K_2CO_3 to the CaO sorbent, $HgCl_2$ was fully adsorbed by CKO-SiO_2 no matter the SO_2 presented or not. CO_2-TPD combined with $HgCl_2$-TPD confirmed that diverse basic sites exist on the calcium-based sorbent surfaces and three $HgCl_2$ adsorption behaviors occurred during the adsorption process. Three $HgCl_2$ adsorption configurations were introduced to represent the different adsorption behaviors and the binding intensity of these configurations are in the successive order: monodentate $<$ tridentate $<$ bidentate. The monodentate adsorption configuration is the main $HgCl_2$ adsorption manner on the CaO surface while the bidentate adsorption configuration occurs on the defect surface of sorbent.

---

* Corresponding author.
E-mail address: yfduan@seu.edu.cn (Y. Duan).

https://doi.org/10.1016/j.fuel.2018.06.135
Received 1 April 2018; Received in revised form 23 May 2018; Accepted 30 June 2018

1. Introduction

Mercury and its compounds are considered as a dangerous heavy metal to both humans and the ecosystem because of the properties of high toxicity, bioaccumulation, and long-range transport [1]. Mercury pollution has attracted global attention since Hg emission had continuously increased with a certain annual rate [2,3]. Coal combustion is considered to be the largest anthropogenic mercury emission source, accounting for 23% global anthropogenic mercury emission to the atmosphere [4]. Gaseous mercury in coal-fired flue gas mainly exist in three forms: elemental (Hg^0), oxidized (Hg^{2+}) and particulate-bound mercury (Hg^p) [5]. Hg^0 with high volatility, chemical inertness and low water solubility [6], is recognized as the most abundant form in the atmosphere with the residence time of 0.5–2 years [7]. Due to its inertia, Hg^0 emission control by the conventional air pollution control devices (APCDs) is difficult. However, the reactivity of gaseous Hg^p and Hg^{2+} are higher than Hg^0 so that they can be easily captured by dust collectors and wet scrubbers in power plants [8]. Hence, effective control and prevention of mercury emission from coal-derived flue gas highly depend on mercury speciation in flue gas. However, the limitation of current mercury detection technique making mercury speciation measurement a hot spot [9].

Current mercury monitoring methods can be divided into two modes: the mercury continuous emission monitoring system (Hg-CEMS) and the manual field mercury sampling methods [10,11]. Hg-CEMS with high precision characteristic always focus on the Hg online monitoring, however, the high purchase and maintenance costs associated with real-time monitoring and the periodic calibration tests through additional equipment prohibit the widely use of this method [12,13]. The manual field mercury sampling methods mainly contain Ontario Hydro Method (OHM) and EPA Method 30B. OHM is considered to be the standard method for vapor phase mercury (Hg(g)) speciation measurement in coal-derived flue gas [14] and widely used in quantifying the gaseous mercury concentration of substantial power plants [1,5,6,15], however, EPA Method 30B based on solid sorbents is now highly recommended as a suitable alternative to complicated OHM due to its convenience and high precision [16,17]. For ensuring the measurement accuracy of Method 30B, high-efficiency Hg adsorption by solid sorbents is urgently required especially for the selective determination of the gaseous Hg^{2+}, which can also promote the development of mercury speciation adsorption method for coal-fired flue gas.

Calcium oxide as a common base material which is widely utilized into flue gas decarburization and desulfurization [18–20]. Adequate experimental [21,22] and simulation studies [23] were confirmed that CaO sorbents were potential for $HgCl_2$ adsorption since the $HgCl_2$ is identified as the dominant form of Hg^{2+} in the coal-fired flue gas. In our previous study [24], relatively higher HOMO energy level and lower Mulliken electronegativity has showed by CaO compared to other alkali metal materials such as MgO, KCl and NaCl, which makes it more efficient for $HgCl_2$ capture. Besides, alkali metal salts such as NaCl, KCl and Na_2CO_3 were often chosen to change the physical properties of calcium adsorbent in the decarburization and desulfurization process, the effect of these dopants on calcium adsorbent was believed to be associated with formation of a eutectic melt which enhanced ionic diffusion and accelerated molecular rearrangement of the adsorbent, it furthermore prevented or delayed degradation of the texture of those material, eventually enhancement of sulfur and carbon capture capacity of the modified limestones [25–27]. Particularly, some hydrotalcite-like compounds are also applied in decarburization studies, and the adsorption capacity of carbon dioxide onto them was enhanced greatly by the added K_2CO_3 [28].

In this study, calcium acetate and mesoporous silica which as the carrier were used to synthesize the supported CaO sorbents by hydration and impregnation method. Potassium chloride (KCl) and potassium carbonate (K_2CO_3) were chosen as dopants which purpose to modify the calcium-based sorbent, and then the KCl-doped CaO and K_2CO_3-doped CaO sorbent were prepared. The calcium-based sorbents in this paper were labeled as C-SiO_2, CKL-SiO_2 and CKO-SiO_2 which corresponds to CaO/SiO_2, CaO-KCl/SiO_2 and CaO-K_2CO_3/SiO_2 respectively. The morphological and crystal features of sorbents were investigated through sorbent characterizations. Surface basicity was estimated in virtue of CO_2 temperature programmed desorption (CO_2-TPD) method. The adsorption characteristics of gaseous Hg^0 and $HgCl_2$ over all the sorbents were evaluated under simulated flue gas respectively. Moreover, $HgCl_2$ adsorption configurations on surfaces of these calcium-based sorbents are further confirmed through $HgCl_2$ temperature programmed desorption ($HgCl_2$-TPD) analysis.

2. Materials and methods

2.1. Sorbents preparation

C-SiO_2 sorbents were synthesized through impregnation and hydration method by utilizing calcium acetate and mesoporous silica. 17.6 g of calcium acetate and 6 g of silica were added into a glass beaker with 200 mL of deionized water, the premixed solution was then continuous magnetic stirring for 4 h, and dried in an oven at 105 °C for 12 h. The dried solid sample were firstly calcined at 175 °C in a muffle for 1 h and subsequently heated up to 850 °C for 3 h, the heating rate in calcination process was set to 10 °C/min. The calcined product was then crushed and sieved into granule with an average diameter of 0.42–0.71 mm (24–40 mesh). Extra KCl and K_2CO_3 were added to the premixed solution and experience the same sample preparation process, then the CKL-SiO_2 and CKO-SiO_2 sorbents were obtained. The molar ratio of the active ingredients in each sorbent to SiO_2 was all guaranteed to be 1:1 (that is, the molar ratio of CaO to SiO_2 in C-SiO_2 sorbent, the molar ratio of (CaO + KCl) to SiO_2 in CKL-SiO_2 sorbent and the molar ratio of (CaO + K_2CO_3) to SiO_2 in CKO-SiO_2 sorbent, were all guaranteed to be 1:1), while the molar ratio between CaO and KCl (K_2CO_3) in CKL-SiO_2 (CKO-SiO_2) sorbent was 9:1.

2.2. Sorbents characterization

Nitrogen adsorption and desorption isotherms for all sorbent samples were tested at 77 K in a Tristar II 3020 nitrogen adsorption analyzer (Microtrac, USA). The specific surface area and pore volume were determined on the basis of the Brunauer-Emmett-Teller (BET) method. Powder X-ray diffractions (XRD) were measured on a D8-ADVANCE diffractometer (Bruker, USA) operating at 40 kV and 20 mA using Cu Kα radiation, the patterns were collected in the range from 10° to 80° with a path of 0.02°/s. The surface structure and morphology were characterized by the scanning electron microscope (SEM) measurement by using a SEM Quanta 400 FEG analyzer (FEI, USA) at 20 kV. CO_2 was used to probe the surface basic sites of the calcium-based sorbents. The samples were first pretreated at 500 °C under a helium stream and then cooled to 50 °C. CO_2 adsorption was performed under a flow of CO_2 (5% vol.) balanced by argon for 30 min and finally purged with helium at 40 °C for 1 h. CO_2 temperature programmed desorption (CO_2-TPD) was conducted in an AutoChem II 2920 chemical adsorption instrument (Microtrac, USA) under helium flow, and heated from room temperature to 800 °C at a 10 °C/min heating rate.

2.3. Mercury adsorption performance evaluation

Adsorption performance of Hg^0/$HgCl_2$ over all the calcium-based sorbents were evaluated in a fixed-bed reactor at 120 °C and the duration of each mercury adsorption experiment was 30 min. As shown in Fig. 1, persistent gaseous Hg^0/$HgCl_2$ was generated from the mercury permeation tube (VICI Metronics Inc; USA), and the thermostatic water bath guaranteed the constant permeability of mercury vapor. A N_2 flow (200 mL/min) carried the mercury vapor through the U-shaped quartz tube and was then mixed with a balance N_2 flow (800 mL/min) in a