

Removal of elemental mercury by iodine-modified rice husk ash sorbents

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Abstract

Iodine-modified calcium-based rice husk ash sorbents ($I_2/\text{CaO}/\text{RHA}$) were synthesized and characterized by X-ray diffraction, X-ray fluorescence, and N_2 isotherm adsorption/desorption. Adsorption experiments of vapor-phase elemental mercury (Hg^0) were performed in a laboratory-scale fixed-bed reactor. $I_2/\text{CaO}/\text{RHA}$ performances on Hg^0 adsorption were compared with those of modified Ca-based fly ash sorbents ($I_2/\text{CaO}/\text{FA}$) and modified fly ash sorbents (I_2/FA). Effects of oxidant loading, supports, pore size distribution, iodine impregnation modes, and temperature were investigated as well to understand the mechanism in capturing Hg^0 . The modified sorbents exhibited reasonable efficiency for Hg^0 removal under simulated flue gas. The surface area, pore size distribution, and iodine impregnation modes of the sorbents did not produce a strong effect on Hg^0 capture efficiency, while fair correlation was observed between Hg^0 uptake capacity and iodine concentration. Therefore, the content of I_2 impregnated on the sorbents was identified as the most important factor influencing the capacity of these sorbents for Hg^0 uptake. Increasing temperature in the range of 80–140°C caused a rise in Hg^0 removal. A reaction mechanism that may explain the experimental results was presumed based on the characterizations and adsorption study.

Key words: mercury; sorbents; fly ash; rice husk ash; iodine; impregnation

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Introduction

Mercury (Hg) ranks among the most harmful metals in the environment because of its toxicity, high volatility, and potential bioaccumulation. Coal-fired utility boilers represent the largest single-known source of anthropogenic Hg emissions (Presto and Granite, 2006). Hg emissions from coal combustion in China were estimated to climb from 202 tons in 1995 to 257 tons in 2003, with an average annual increase of 3.0% (Jiang et al., 2006; Wu et al., 2006). Increasing awareness on Hg emissions from coal-fired flue gas has resulted in significant efforts to develop strategies and technologies for Hg reduction (Zhang et al., 2009). On March 15, 2005, the United States Environmental Protection Agency (EPA) proposed to cap and reduce Hg emissions from power plants permanently; a first-phase cap of 38 tons/yr will be achieved in 2010, followed by a second cap of 15 tons/yr in 2018 (Qiao et al., 2009).

Hg occurs in the flue gas of coal-fired utility boilers as elemental mercury (Hg^0), oxidized mercury (Hg^{2+}), and particle-bound mercury (HgP) (Pavlish et al., 2003). Common knowledge dictates that Hg^{2+} and HgP can be removed with relative ease from flue gas using typical air pollution control devices (APCDs) (Granite et al., 2000). Nevertheless, Hg^0 is more difficult to capture due to its higher volatility, chemical inertness, and insolubility in

water (Presto and Granite 2006). In general, activated carbon (AC) is currently considered the most promising method of Hg removal in terms of efficiency and reliability. However, the high operating cost of this sorbent requires improvements in sorbent performance to facilitate full-scale applications (Pavlish et al., 2003).

Studies (Chi et al., 2009; Granite et al., 2000; Lee et al., 2004; Zhang et al., 2009) have proven that halogen-modified, especially iodine-impregnated carbon-based sorbents (containing I_2 or KI or both), exhibit superior capacity of Hg^0 capture. However, Hg control via carbon-based sorbents result in additional costs for by-product management and non-disposal (Jones et al., 2007). Instead of impregnating iodine on carbon-based sorbents, an alternative method involves impregnating on calcium (Ca)-based sorbents, which does not only potentially control multi-pollutants but also create environmentally benign ash product as well.

Reports (Fernandez et al., 2005; Ho and Shih, 1992; Jozewicz et al., 1988; Lin et al., 2003b) have revealed that when coal fly ash (FA) is mixed with calcium hydroxide ($\text{Ca}(\text{OH})_2$) in a hydration process, sorbents with high SO_2 capture capacity may be attained. If iodine was impregnated on these Ca-based sorbents, simultaneous SO_2 and Hg^0 would be captured in a single process unit. This is because Ca-based sorbents were effective in capturing Hg^{2+} (Ghorishi and Gullett, 1998) while it showed insignificant removal of Hg^0 (Ghorishi and Sedman, 1998).

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In parallel with efforts to synthesize Ca-based sorbents utilizing fly ash, a host of studies have focused on the development of Ca-based sorbents using various siliceous materials (Lin et al., 2003a; Zainudin et al., 2005). One potential siliceous material is rice husk ash (RHA), which draws on high silica content and is available in large quantities, especially in China (Feng et al., 2004). Moreover, in view of the green house issue (CO_2) and the need to conserve energy and resources, synthesizing Ca-based sorbents prepared from biomass (e.g., rice husk) may be more attractive compared with other materials. Further, RHA is industrial waste and can be disposed as landfill material. Synthesizing Ca-based sorbents prepared from these waste materials can not only further curb the cost of synthesizing process but likewise help to utilize these waste-derived siliceous materials, which otherwise offer no commercial value. Recently, CaO/RHA sorbents have been reported to exhibit better performance toward SO_2 adsorption compared with CaO/FA sorbents (Dahlan et al., 2006, 2008). Typically, the most common siliceous source for obtaining Ca-based sorbents is fly ash. However, to the best of the authors' knowledge, studies on Ca-based sorbents for capturing Hg^0 obtained from RHA are scarce. Adding iodine to Ca-based sorbents obtained from RHA may generate high-performance Hg^0 removal.

To investigate the effectiveness of Hg^0 removal by $\text{I}_2/\text{CaO/RHA}$ sorbents, a series of raw and modified Ca-based sorbents were synthesized in this study and characterization was performed. Adsorption experiments of Hg^0 were conducted in a laboratory-scale fixed-bed reactor using N_2 as carrier gas. Specifically, effects of I_2 concentration, supports, pore size distribution, impregnation manners of I_2 , and temperature were investigated, and the mechanism of these sorbents for Hg adsorption was discussed as well.

1 Materials and methods

1.1 Materials

Rice husk was sourced from a local rice mill in Wuhan City, China. FA was obtained from a coal-fired power plant in Guizhou province. Iodine, KI, CaO, $\text{Ca}(\text{OH})_2$, and anhydrous ethanol used were all analytical grade, and all solutions were prepared with deionized (DI) water or anhydrous ethanol.

1.2 Preparation of sorbents

A small quantity of RH powder was set on a porcelain dish and placed inside a muffle furnace. The furnace was heated in open atmospheric conditions at the rate of $10^\circ\text{C}/\text{min}$. The RH was combusted at 600°C for 4 hr (Krishnarao et al., 2001), after which the furnace was allowed to cool at room temperature. White ash was collected, stored at room temperature in a glass bottle, and used for further analysis.

Sorbents were synthesized in two separate steps. First, CaO/RHA and CaO/FA sorbents were prepared by water hydration method; optimum hydration conditions are out-

lined in related references (Dahlan et al., 2006; Ghorishi and Sedman, 1998). CaO/RHA sorbents were synthesized using the following steps: 2 g CaO was added to 90 mL of distilled water at 80°C . Upon stirring, the temperature of the slurry climbed to 90°C ; simultaneously, 5 g RHA was added into the slurry. The resulting slurry was heated at approximately 100°C for 16 hr with stirring.

The slurry was filtered and dried at 150°C for 2 hr. CaO/FA sorbents were prepared in a similar manner, although 2 g $\text{Ca}(\text{OH})_2$ instead of 2 g CaO and 6 g FA instead of 5 g RHA were used. Pore volume impregnation method (Tseng et al., 2003) was separately employed to obtain supports-impregnated iodine.

Two types of solvents-anhydrous ethanol and KI aqueous solution-were used to dissolve iodine. During impregnation, solutions were heated and constantly stirred until the liquid was fully eliminated. Impregnated sorbents were dried at 150°C for 2 hr. Through this procedure, samples of support CaO/RHA, CaO/FA, and FA were coated with different amounts of I_2 by varying the ratio of I_2 to supports. Obtained sorbents were called 5% $\text{I}_2/\text{CaO/RHA}$ or 10% $\text{KI/I}_2/\text{CaO/RHA}$ (all the ratios in this article are denoted as weight ratios). Here, I_2 and KI/I_2 indicate that impregnation employed anhydrous ethanol and KI aqueous solution, respectively; 5% and 10% signify the proportion of supports, and I_2 based on mass. I_2 sublimated at a relatively low temperature (113°C) (Jones et al., 2007), thus the real wt.% of I_2 impregnated onto sorbents was less than 5% or 10%. For convenience, 5% or 10%, instead of the real wt.%, was used. The mass of the iodine impregnated onto the sample was measured by directly weighing (Choi et al., 1996) sample cells before and after impregnation on an electronic balance (± 0.1 mg). The mass of the sample prior to impregnation was determined by weighting the bank test sample. All samples were ground and sieved into 150 mesh sizes.

1.3 Characterization

Textural characteristics of samples were determined by nitrogen adsorption-desorption method at -196°C on an accelerated surface area and porosimeter (ASAP 2020, Micromeritics Instrument Corporation, USA). Adsorption isotherm was employed to calculate the Brunauer-Emmett-Teller (BET) surface area and pore volume. Average pore diameter was calculated by four times the pore volume over the BET surface area.

Structural parameters of sorbents were determined by powder X-ray diffraction (XRD) using a Rigaku Rotaflex D/Max-C system with CuK_α radiation as X-ray source. Accelerating voltage and applied current were 35 kV and 30 mA, respectively.

Relative contents of RHA and FA wt.% (relative weight) in sorbents were determined by X-ray fluorescence (XRF) using the fluorimeter (Eagle III, EDAX Inc., USA).

1.4 Experimental apparatus and procedures

A laboratory-scale fixed-bed apparatus (Fig. 1) was constructed to explore the characteristics of sorbents during Hg^0 removal. The apparatus consisted mainly of a

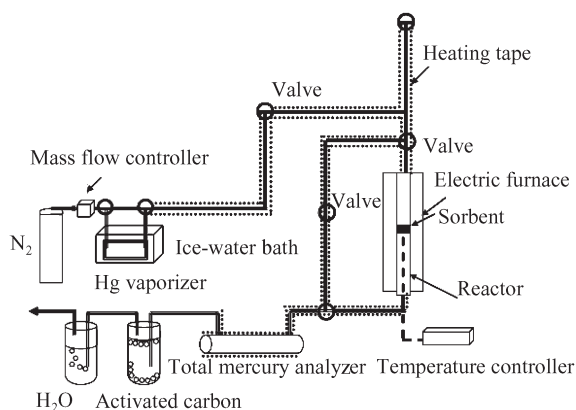


Fig. 1 Experimental setup for removal of Hg^0 .

vapor-phase Hg^0 generator, feed system, fixed-bed reactor surrounded by a temperature-controlled oven, and an on-line total Hg analyzer, which converts any Hg^{2+} vapor to Hg^0 by catalysts prior to analysis. An Hg permeation device (VICI Metronics Inc., USA) was used as Hg^0 source. The device was designed to produce constant release ratio of Hg^0 vapor at a specified temperature. High-purity grade nitrogen gas was supplied as carrier gas to transport Hg^0 vapor out of the permeation tube holder. The total gas flow rate of simulated gas passing through the fixed-bed reactor was 1.0 L/min, based on standard temperature and pressure. The fixed-bed reactor, a quartz adsorption column with 0.70 cm i.d. and 120 cm length, was placed in the temperature-controlled electric furnace, which could control system temperature within $\pm 1^\circ\text{C}$. These tests were all run at a temperature of 120°C , and inlet Hg concentration (C_0) was maintained within the range of $180 (\pm 0.2 \text{ ppb})$ in the absence of special specification. To provide sufficient bed length and reduce experimental time, approximately 60 mg of each prepared sorbent and 40 mg of silica with a similar size were sufficiently mixed and packed into the quartz column as sorbent. This type of silica is known to be inert to Hg during adsorption. Hg^0 concentrations were analyzed continuously using a total Hg online analyzer SM3 (Mercury Instruments Inc., Germany), a cold vapor atomic absorption spectrometer (CVAAS) that can analyze inlet or outlet total Hg concentration, including Hg^0 and Hg^{2+} , of the adsorption bed. During each test, measurements of inlet concentrations (C_0) and outlet concentrations (C) of Hg were performed. All experiments were duplicated or triplicated under the same experimental conditions. Dimensionless outlet Hg concentration (C/C_0) was employed to evaluate the performance of sorbents (Pitoniak et al., 2003). Thus, the removal of Hg^0 (η , %) was defined in the following Eq. (1) (Mendioroz et al., 1999):

$$\eta = (1 - C/C_0) \times 100\% \quad (1)$$

Mercury adsorption capacity was calculated by integrating the area above the removal curve within 30 min.

2 Results and discussion

2.1 Sorbent characteristics

Chemical compositions of rice husk ash are as follows (in wt.%): MgO 1.23; SiO_2 90.57; P_2O_5 1.24; SO_3 0.59; K_2O 2.05; CaO 1.00; MnO 0.21; Fe_2O_3 0.11; ignition loss 2.80. Meanwhile, chemical compositions of FA are as follows (in wt.%): Al_2O_3 30.66; SiO_2 51.75; SO_3 0.77; K_2O 1.50; CaO 1.99; TiO_2 1.02; V_2O_5 0.05; Fe_2O_3 2.42; ignition loss 11.20. Physical characteristics of adsorbents and XRD data are presented in Table 1 and Figs. 2 and 3, respectively. FA was mainly composed of quartz (SiO_2) and mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), while RHA (calcinations at 600°C) was mainly composed of amorphous silica with a broad diffraction of approximately 22° (Feng et al., 2004) in Fig. 2. These pozzolanic materials may react with $\text{Ca}(\text{OH})_2$ to form a small amount of tobermorite (JCPDS 00-029-0329) in the presence of water. Typically, these pozzolanic products were poorly crystallized and possessed relatively high surface areas (Lin et al., 2003b). Therefore, compared with FA and RHA, total surface area of CaO/FA and CaO/RHA both increased (Table 1). Further, CaO/RHA had eight times the surface area of CaO/FA because amorphous silica of RHA was more active than the crystalline quartz of FA in the pozzolanic reaction (Lin et al., 2003a). Incorporation of 5% I_2 on the CaO/RHA resulted in a decrease in specific surface area. Moreover, this sorbent displayed faint crystalline I_2 (JCPDS 00-005-0558). At the same time, when loading was 10%, no appreciable changes were observed in the shape and position of peaks. Based on these results, the success of the impregnation method in dispersing I_2 on CaO/RHA sorbents was implied.

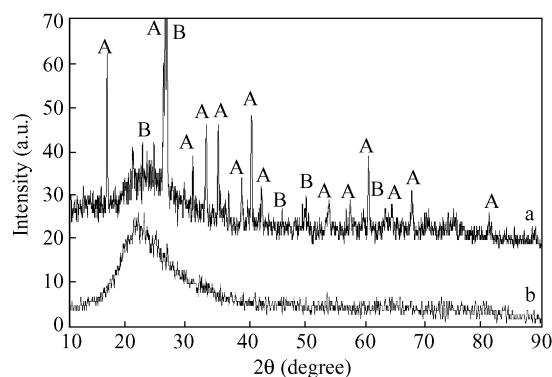


Fig. 2 XRD patterns of FA and RHA. Peak A: tobermorite; peak B: quartz. Line a: FA; line b: RHA.

Table 1 Physical characteristics of sorbents

Sample	Special surface area (m^2/g)	Pore diameter (nm)
FA	0.305	6.59
RHA	58.2	10.1
CaO/FA	14.7	18.9
CaO/RHA	124.5	15.8
5% I_2 /CaO/RHA	120.8	17.5
10% I_2 /CaO/RHA	115.2	19.2

2.2 Effect of I₂ concentration

Effect of I₂ loading on Hg⁰ removal by I₂/CaO/RHA was examined in a loading range of 5%–10%. As illustrated in Fig. 4, capture efficiency of Hg⁰ gradually climbed with the increase in I₂ content. At 10% loading, value of C/C₀ reached 0.2 in 30 min, indicating that over 80% of Hg⁰ was removed by adsorption on the surface of this sorbent. Surface area of these sorbents decreased as I₂ content increased from 5% to 10%; however, average pore diameter exhibited an opposite trend (Table 1).

Studies (Ghorishi et al., 1999, 2002) have revealed that impregnation of active phase over a support reduces surface area and increases average pore diameter at all times, which is agreement with results of the present study (Table 1). This observation was mainly due to the penetration of dispersed I₂ into pores of the support (Fig. 2). When increasing active phase (I₂) from 5% to 10%, despite the lower surface area and larger average pore diameter produced, higher efficiency may be obtained. Analogously, Ghorishi et al. (2002) observed that increasing the strength of oxidant solution increased Hg⁰ uptake, although the sorbents exhibited lower surface area and larger average pore diameter.

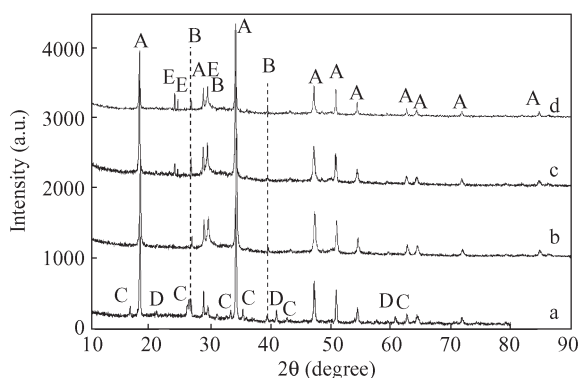


Fig. 3 XRD patterns of the sorbents. Peak A: Ca(OH)₂; Peak B: tobermorite; Peak C: mullite; Peak D: quartz; Peak E: I₂. Line a: CaO/FA; line b: CaO/RHA; line c: 5%I₂/CaO/RHA; line d: 10%I₂/CaO/RHA.

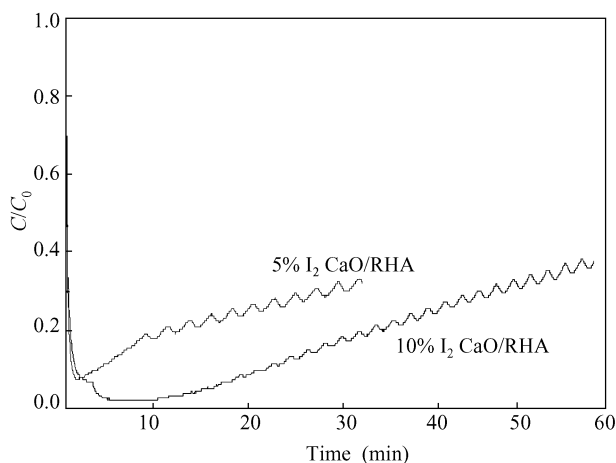


Fig. 4 Effect of I₂ loading on C/C₀ by CaO/RHA sorbent.

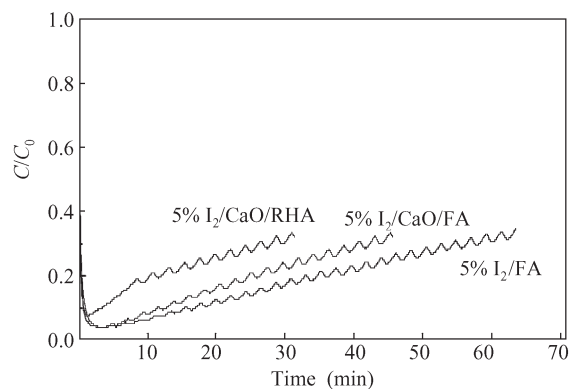


Fig. 5 Effect of supports on C/C₀ by modified sorbents.

2.3 Effect of supports

In this study, the purpose of support is to maximize the number of collisions between Hg, active species, and catalyst surface (Granite et al., 2000; Presto and Granite, 2006). Studies (Hsi et al., 2001; Tian et al., 2009; Vidic and Siler, 2001) have revealed that the surface area of supports is a key parameter affecting Hg⁰ adsorptive capacity. Therefore, Hg⁰ removal capacity was correlated with the surface area of supports. Three different supports (FA, CaO/FA, and CaO/RHA) impregnated with 5% I₂ were tested in this study. The performance of these sorbents is presented in Fig. 5, with results of surface area of three supports prior to impregnation given in Table 1. The C/C₀ for I₂-modified sorbents was different. Among the three supports, Hg⁰ capture efficiency decreased with the increase in surface area. This observation is inconsistent with previous results presented by Ghorishi et al. (2002), who observed that Hg⁰ capture efficiency increased as the surface area increased.

In broad terms, if sorbents had higher surface area, the number of collisions between Hg⁰, active species (I₂), and sorbent surface may be larger and more Hg⁰ should be adsorbed. Thus, with the increase in supports' surface area, Hg⁰ removal efficiency would increase. However, several exceptions have been observed especially with reference to FA. Lopez-Anton et al. (2006) reported that FA samples with greater surface area failed to retain higher Hg⁰ quantity. Li et al. (2007) likewise observed that Hg⁰ adsorption on the FA did not exhibit a strong correlation with specific surface area. These observations are similar to the results of the present study. Therefore, surface area was not identified as the key factor influencing the efficiency of these sorbents for Hg⁰ uptake.

2.4 Effect of pore size distribution

Ghorishi et al. (1999) evaluated the effect of pore size distribution on Hg⁰ uptake by Ca-based sorbents. Their results revealed that Hg⁰ capture required small pores, and pore volume. They speculated that modified Ca-based sorbents, having both fine pore structure and oxidizing species in the pore structure, could oxidize and sequester Hg⁰ from flue gas. In the present study, the role of pore size distribution on Hg⁰ uptake was examined as well, with the result illustrated in Fig. 6. Compared with FA

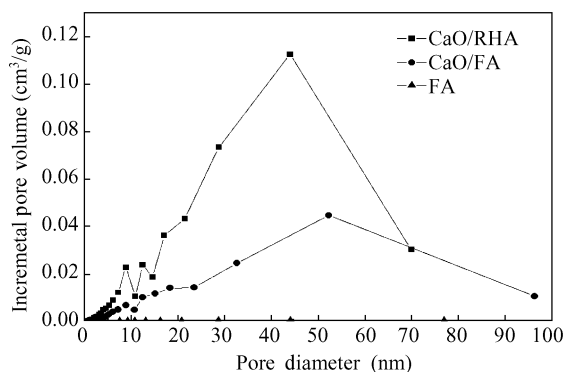


Fig. 6 Pore size distribution of sorbents.

and CaO/FA, the number of pores smaller than 10 nm was noticeably higher in CaO/RHA. However, as demonstrated in the Fig. 5, the I_2 /CaO/RHA sorbent exhibited poor Hg^0 performance while the I_2 /FA sorbent displayed the most effective Hg^0 capture, although this sorbent exhibited poor fine pore distribution. These results indicate that pore size distribution is not a key factor influencing the efficiency of these sorbents for Hg^0 uptake.

2.5 Effect of impregnation manners of I_2

Considerable effort has been exerted to investigate different manners of impregnating I_2 on Hg^0 oxidation. Chi et al. (2009) examined Hg^0 capture by iodine-impregnated FA and AC. Lee et al. (2004) likewise reported Hg^0 removal by KI-impregnated AC. Recently, Li et al. (2009) evaluated Hg^0 uptake by a powder composed of KI mixed with coal. However, the different manners of impregnating with iodine or iodine compounds were not compared on the same solid particles. Consequently, using iodine or iodine compounds as oxidants for impregnating or mixing on CaO/RHA sorbents is significant. Initial research revealed that KI-impregnated CaO/RHA sorbent exhibited no effect on Hg^0 removal. Subsequently, performance of KI/ I_2 -impregnated CaO/RHA sorbent was examined instead of KI-impregnated CaO/RHA sorbent. Hg^0 uptake using different manners of impregnation is illustrated in Fig. 7. Among the investigated sorbents, CaO/RHA sorbent impregnated with iodine using anhydrous ethanol was less effective than that with two other manners of impregnation. Moreover, CaO/RHA mixed with iodine exhibited relative-

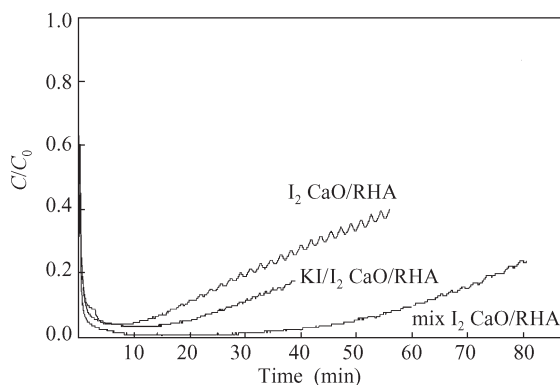


Fig. 7 Effect of impregnation manners of I_2 .

ly high Hg^0 uptake. Removal efficiency was as high as 98% in 30 min, approximately 12% higher than that for KI/ I_2 . When the sorbent was mixed with iodine, it exhibited the worst dispersion of active phase (I_2) than other two modes; however, it exhibited the most effective Hg^0 capture. These results indicate that iodine impregnation modes were not the key factor influencing the efficiency of these sorbents for Hg^0 uptake. Further, considering that mixing I_2 powder with CaO/RHA exhibits significant Hg^0 removal, the simple method of adding iodine to CaO/RHA sorbents may employ mechanical mixing.

2.6 Relationship between I_2 content and Hg^0 adsorptive capacity

Sorbent-special factors were noted to affect Hg adsorptive capacity. These include the physical characteristics of the support, modes of impregnated oxides, and content of oxides, which all influenced the Hg binding rate (Ghorishi et al., 1999, 2002). From the results, it could be inferred that the supports' physical characteristics (surface area and pore size distribution) and iodine impregnation modes did not produce a strong effect on Hg^0 adsorption efficiency. Thus, different Hg^0 adsorptive capacity only contributed to the different contents of oxides (I_2). Correlation between Hg^0 uptake capacity and real iodine content (excluding KI content) in the sorbent is presented in Fig. 8. Evidently, I_2 content on the finished sorbent was lower than that prior to drying. I_2 reportedly sublimated at a relatively low temperature of 113°C (Jones et al., 2007). Therefore, in the process of sample preparation, only a small number of I_2 was adsorbed. As illustrated in Fig. 8, Hg^0 removal capacity gradually climbed with the increase in iodine content. Moreover, fair correlation indicated the importance of iodine content in sorbent performance. These results may imply that for the content of I_2 impregnated on sorbents was the most important factor influencing the capacity of these sorbents for Hg^0 capture.

2.7 Effect of temperature

To identify temperature effects on Hg^0 removal performance, adsorption bed temperature was varied from 80 to 140°C with 10% I_2 /CaO/RHA; results are presented in Fig. 9. When temperature was at 80°C, Hg^0 removal efficiency was approximately 80%. A sharp increase in Hg^0 capture occurred at approximately 120°C and reached

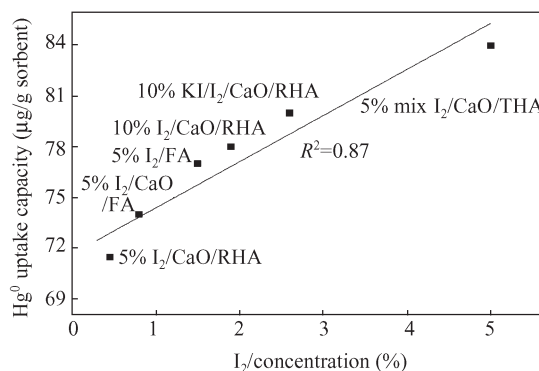


Fig. 8 Relationship between I_2 content and Hg^0 adsorptive capacity.

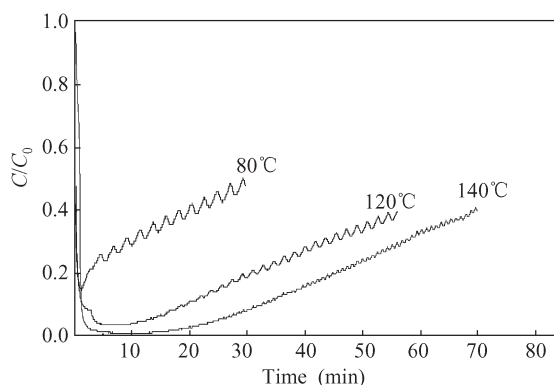


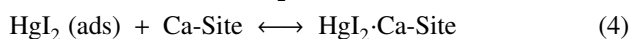
Fig. 9 Effect of temperature on C/C_0 by I_2 /CaO/RHA sorbent.

approximately 100% when the temperature exceeded 140°C. This positive temperature dependence suggested that Hg^0 removal was typical in a chemisorptions mechanism. Temperature dependence of Hg^0 removal by I_2 impregnation sorbents in this study is consistent with findings reported by other researchers (Lee et al., 2004; Li et al., 2009). This positive temperature dependence likewise indicated that this sorbent could inject into the low-temperature region of the boiler convective pass (e.g., prior to the electrostatic precipitators at 120–160°C) (Pavlish et al., 2003).

2.8 Possible mechanism of Hg removal for I_2 /CaO/RHA sorbent

Two mechanisms may explain the results. The first mechanism (Ghorishi et al., 1999) states that Hg^0 uptake by sorbents is a two-step reaction in which Hg^0 is oxidized at the surface (preferably in <10 nm pores) by oxides and further interacts with the alkaline sorbent. In this mechanism, the physical properties of sorbents, particularly total surface and pore size distribution, were observed to produce a significant effect on Hg^0 adsorptive capacity. However, as previously stated, surface area and pore size distribution did not strongly affect Hg^0 adsorption capacity. This deviation indicates that other mechanism may be plausible for the results presented here.

Recently, Chi et al. (2009) proposed a mechanism to describe Hg^0 oxidation by iodine. Both Hg^0 and I_2 are large atoms with 80 and 106 electrons moving around their nucleus, respectively. Further, London dispersion forces increase greatly as atom size increases. Thus, they are highly polarizable and the London dispersion forces play an important role in Hg^0 oxidation by iodine. This reaction mechanism for Hg capture by sorbents tested here may be written as follows:



The first step involves the London dispersion forces between Hg^0 and iodine, resulting in transient species (e.g., $Hg \cdots I_2^*$). This is assumed the initial step for further reaction. This step was initially proposed by Chi et al. (2009),

who observed that rate constant for the reaction between Hg^0 and iodine at 23°C was nearly three times larger compared with the reaction between Hg^0 and bromine. This trend may be explained by comparing the London dispersion forces between reactants. Similarly, the London dispersion forces likewise can be used for the iodine-impregnated sorbents tested in this study. This step is regarded as the most important because the increase of I_2 was significant in the Fig. 8.

The second step involves the collision of $Hg \cdots I_2^*$ with M; M can be any gaseous molecule or solid surface in the reaction system. It forms a stable product HgI_2 after shifting the extra energy to M. The sorbents' physical properties (total surface and pore size distribution) were not observed to affect Hg^0 adsorptive capacity. Therefore, in this step, sorbent surface is assumed to serve only as facilitator of the reaction, remaining unchanged and disguising its role. The effect of sorbent surface postulated here is not baseless. Recently, Schofield (2008) proposed a non-catalytic mechanism for Hg^0 oxidation. It was suggested that a receptive surface acted solely as an intermediary facilitating conversion while disguising its role.

The third step involves the reaction of adsorbed HgI_2 binding to the alkaline site of Ca-based sorbents (Ca-Site) to form the binary iodide. Ghorishi and Gullett (1998) have demonstrated that similar to HgI_2 , $HgCl_2$ can be controlled using any alkaline sorbent such as Ca-based ones. Moreover, Kim et al. (2009) reported that Hg^{2+} can adsorb on the alkaline site of CaO surface with higher binding energy (approximately 11.9 kcal/mol) compared with Hg^0 . Sites with higher binding energy are stable, and Hg is not released without any change in process conditions, such as heating. These sites are responsible for Hg capture by the sorbent.

The abundance of sites with high binding energy determines the Hg capacity of the sorbent (Granite and Karash, 2007). Ghorishi and Gullett (1998) have proved the abundance of $HgCl_2$ (Hg^{2+}) active sites in Ca-based sorbents. Therefore, high concentration of these sites is responsible for low outlet Hg concentration in Figs. 4 and 7. Further, Ghorishi and Gullett (1998) have demonstrated that surface area and pore structure were independent from $HgCl_2$ (similar to HgI_2) capacity by Ca-based sorbents. This may explain why the physical characteristics of sorbents (surface area and pore size distribution) have no evident effect on Hg capture in the present study.

3 Conclusions

The I_2 /CaO/RHA sorbents were synthesized for Hg^0 removal using a laboratory-scale fixed-bed reactor with an online total Hg analyzer. To understand clearly the mechanism of these sorbents in capturing Hg^0 , effects of oxidants loading, supports, pore size distribution, iodine impregnation modes, and temperature were investigated as well. These modified sorbents exhibited effective Hg^0 removal; even the lower loading (0.6% using anhydrous ethanol) sorbent revealed initial maximum Hg^0 removal ef-

iciency of 90% under simulated flue gas including only N_2 and Hg^0 . The physical characteristics of sorbents (surface area and pore size distribution) and iodine impregnation modes did not significantly affect Hg^0 capture efficiency, while fair correlation was observed between Hg uptake capacity and iodine content. Therefore, the content of I_2 impregnated on the sorbents is the most important factor influencing the capacity of these sorbents for Hg^0 capture.

The experiment under a wide range of temperature implied that chemisorptions played an important role in Hg^0 removal. The mechanisms of Hg^0 adsorption on $I_2/CaO/RHA$ sorbents were proposed as well. The synthetic optimization of lower I_2 loading and the effect of flue gas components, such as SO_2 , NO , and HCl , on Hg^0 removal efficiency will be evaluated in the future to obtain a type of promising and low-cost sorbent.

Acknowledgments

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