

Hg(0) Removal Using Se(0)-doped Montmorillonite from Selenite(IV)

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Potassium methylselenite ($\text{KSeO}_2(\text{OCH}_3)$) was reduced to elemental selenium, $\text{Se}(0)$, and then doped onto montmorillonite K 10 (MK10) clay to examine the interaction between elemental mercury ($\text{Hg}(0)$) vapor and $\text{Se}(0)$ in an effort to understand the possible heterogeneous reaction of $\text{Hg}(0)$ vapor and $\text{Se}(0)$ solid. The clay was used as a cost-effective support material for uniform dispersion of $\text{Se}(0)$. The $\text{Se}(0)$ -doped MK10 showed an excellent reaction performance with $\text{Hg}(0)$ under an inert nitrogen gas at 70 and 140 °C in our lab-scale fixed-bed system. However, the precursor, $\text{KSeO}_2(\text{OCH}_3)$ -doped MK10 showed a negligible reaction performance with $\text{Hg}(0)$, suggesting that the oxidation state of selenium plays a key role in the reaction of $\text{Hg}(0)$ vapor and selenium compounds.

Key Words : Mercury removal, Selenium species, Sorbent, Montmorillonite, Selenite

Introduction

Sulfur-impregnated activated carbon has been extensively studied for the control of elemental mercury ($\text{Hg}(0)$) emissions from coal-fired boilers.¹⁻⁴ It has been reported that it can capture both of the elemental and oxidized forms of mercury vapors by possible mercuric sulfide (HgS) formation.⁵ Among various sulfur functional groups generated from elemental sulfur on the activated carbon surface at a wide impregnation temperature window, the elemental sulfur functional group turned out to be the main sulfur form responsible for $\text{Hg}(0)$ adsorption onto sulfur-impregnated activated carbon.⁴ Although an effort was unsuccessful in identifying the thermally stable S-C bond using FTIR analysis due to high background noise in the overwhelming C-H and O-H vibrations stemming from the activated carbon surface, a previous study³ assumed that short linear-chain sulfur allotropes might be attributed to relatively thermally strong C-S bond which are formed at high impregnation temperatures and do not easily evaporate or decompose in a range of temperatures for sorbent injection.

In the meantime, studies^{5,6} have also been conducted to develop sulfur-impregnated noncarbonaceous mercury sorbents derived from elemental sulfur, which do not impact on fly ash sales and can capture $\text{Hg}(0)$ for sorbent injection. However, the sulfur-impregnated noncarbonaceous sorbents derived from elemental sulfur have shown very small $\text{Hg}(0)$ adsorption capacities probably due to the weak thermal/chemical bonding between impregnated-sulfur and the noncarbonaceous materials and/or weak molecular affinity between presumably formed HgS and the noncarbonaceous materials.

Selenium belongs to the same group number VIA in the periodic table as sulfur, and is believed to act similar manner

to sulfur and to have various oxidation state i.e., -2, 0, +2, +4, and +6, which affords broad window for facilitating chemical bonding to various Hg oxidation state in the vapor phase. Elemental selenium, $\text{Se}(0)$, in the crystalline form of Se_8 molecules, has relatively higher melting points (217 and 220 °C) than elemental sulfur in the form of S_8 molecules (113 and 119 °C),⁷ and is expected to be thermally more stable than elemental sulfur. Although selenium shows potential for reaction with $\text{Hg}(0)$ vapor, to date, its use as a dopant candidate for sorbents to remove mercury have been neither reported nor found in the literature. Thus the primary objective of this study is to investigate possible interaction between solid-phase selenium and $\text{Hg}(0)$ vapor, which may lead to a better sorption ability with $\text{Hg}(0)$.

Experimental

All of $\text{Hg}(0)$ adsorption tests were conducted using the lab-scale fixed-bed system as shown in Figure 1, and detailed descriptions about mercury measurement, lab-scale fixed-bed adsorption tests, and data analysis can be found in a previous study.⁶ The fixed-bed reactor was constructed to allow for a total flow of 1 L/min gas throughput at 23 °C. The 1.27 cm i.d. reactor made of borosilicate material was determined to meet a superficial velocity of 13 cm/s at 23 °C in the empty bed reactor. About 20-30 mg of each sorbent in 6 g of silica (SiO_2 , Fisher Scientific, fine granules, particle size: 149-420 μm) was used, and the bed material was supported by a fritted quartz disk with a TeflonTM o-ring and a glass fiber filter with a nominal 1 μm pore diameter in order to minimize channeling, and to prevent the escape of sorbent through the bed. An additional filter system with a glass fiber filter with a nominal 0.7 μm pore diameter was used at the outlet of the reactor to capture sorbent particles

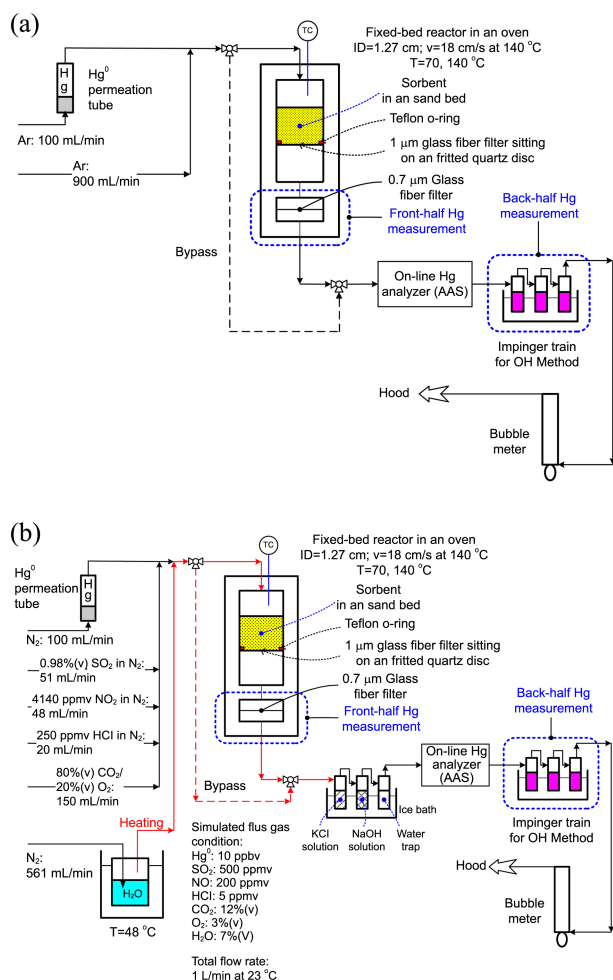


Figure 1. Schematic diagrams of a lab-scale fixed-bed system for Hg(0) adsorption test in (a) a N₂ gas and (b) a simulated flue gas.

potentially escaping from the bed.

During each test, the mercury-laden inlet gas bypassed the sorbent bed, and passed to the analytical system until the desired inlet mercury concentration was established. Then, the adsorption test was initiated by diverting the gas flow through the sorbent column in downflow mode to minimize the potential for fluidization of the bed. All of the tubing and valves in contact with Hg(0) were constructed from Teflon™, which has been demonstrated to have good chemical resistance and inertness toward Hg(0). The sorbent bed and filter system was placed in a temperature-controllable convection oven (Stabil-Therm® Electric Utility Oven, Model OV-500C-2, Blue M Electric Company, Blue Island, IL), which can maintain the system temperature within ± 0.5 °C. A Teflon™-coated thermocouple was installed inside the fixed-bed reactor to control the gas temperature at the inlet of the sorbent bed. Tests were first carried out in the system that was maintained at 70 and 140 °C under Hg(0)-laden nitrogen flow for screening purpose as shown in Figure 1-(a). When the tests were successfully completed at these temperatures, subsequent tests were carried out in a typical PRB subbituminous/lignite simulated flue gas (500 ppmv SO₂, 200 ppmv NO, 10 ppbv Hg(0), 7% H₂O, 3% O₂, 12%

CO₂ balanced with N₂) at 140 °C.

Synthesis of Selenium-Doped Montmorillonite K 10.

An array of Se(0)-doped montmorillonite K 10 (MK10) clay was synthesized from the liquid phase, and an example of the synthesis of 20%(w) Se(0)-MK10 clay is given below. The clay was used to uniformly disperse the selenium as a support material. The support material, MK10 clay, has a fairly high surface area in the order of 250 m²/g, and showed virtually no reactivity with Hg(0) in a wide temperatures range from 23 to 140 °C in the previous study.⁶ All chemicals were purchased from Sigma-Aldrich Co., St. Louis, MO and used without further purification. Selenium dioxide (SeO₂, 2.83 g, 25.7 mmol) in a methanol solution (30 mL) was treated with potassium carbonate (K₂CO₃, 1.76 g, 13.2 mmol) in a 100 mL round-bottom flask at room temperature for 1 h with vigorous agitation. As soon as K₂CO₃ was added, CO₂ started to evolve to afford a selenious compound, potassium methylselenite (KSeO₂(OCH₃)), in a colorless solution.^{8,9} Montmorillonite K 10 clay (8.0 g) was added to the resulting methanolic solution, followed by reflux for 24 h. After the methanol was driven off using a rotary evaporator (BÜCHI Rotavapor R-200, BÜCHI Laboratory Equipment, Switzerland), a beige solid was further dried at 80 °C overnight, and then calcined at 400 °C for 6 h, followed by reduction with a continuous flow of H₂ gas at 450 °C for 2 h, affording 20% of Se(0)-impregnated MK10 as a dark brown solid. Although 20%(w) of KSeO₂(OCH₃) was used for preparing 20%(w) Se(0)-doped MK10, after calcination, the actual Se content was found to be 8.8%(w) which was almost proportional to Se mole fraction out of KSeO₂(OCH₃). A 20%(w) KSeO₂(OCH₃)-doped MK10 sample was also prepared by omitting the H₂ reduction process for comparison purpose.

Results and Discussion

N₂-Flow Tests. It is reported that all elemental sulfur-containing sorbent (MK10, molecular sieve, and alumina) did not show any significant Hg(0) uptake capacities at either temperature (70 and 170 °C) whilst Na₂S doped MK10 showed an average adsorption capacity of Hg(0). The reason for better sorption ability of Na₂S is attribute to the formation of change from elemental sulfur to various amorphous sulfur functional groups, substantiating the formation of chemical bonding between sulfur and mercury.⁶ Since the selenium species having various oxidation state is expected show similar adsorption abilities an array of Se(0)-doped MK10 with four different selenium loadings (0.1, 0.5, 1, 20%(w)) and 20%(w) KSeO₂(OCH₃)-doped MK10 were tested in N₂ flow, and their breakthrough curves are shown in Figure 2.

Interestingly, only the Se(0)-doped MK10 reduced from its precursor, KSeO₂(OCH₃), showed excellent reactivity with Hg(0) at 70 and 140 °C, and the reactivity increased with the increasing amount of selenium, probably because the Se(0) interacts with the mercury to form mercuric selenide, HgSe. The exact reaction mechanism for the formation of active selenium species for adsorbing mercury is not clear at the moment, but it is assumed that the K₂Se₂O₅ generated from

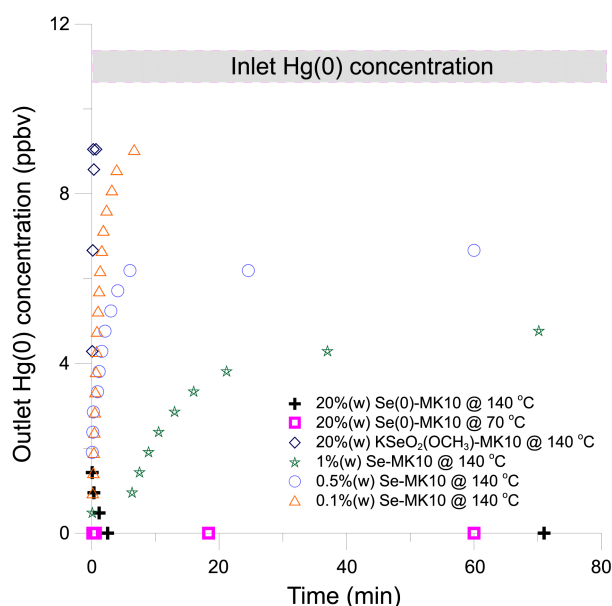
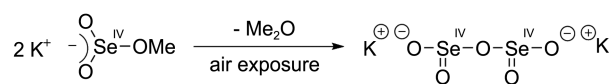


Figure 2. Breakthrough curves for selenium-doped MK10 in N_2 flow at 70 and 140 °C.



Scheme 1. Transformation of $KSeO_2(OCH_3)$ into $K_2Se_2O_5$.

the transformation of $KSeO_2(OCH_3)$ upon exposure to air can be further reduced to Se(0) at the atmosphere of hydrogen during calcination, which is responsible for capturing Hg(0).¹¹ However, $KSeO_2(OCH_3)$ -doped MK10 showed almost negligible reactivity with Hg(0) even at 140 °C, implying that high oxidation state of Se^{IV} has no ability to interact with Hg(0). The reason for negligible interaction of Se^{IV} with Hg(0) is likely attributed to the high valence state (+4) thus there is no room for interaction with Hg(0). While in the case of reduced form of Se(0), it is well recognized that mercury and sulfur bind together to form complexes and the interaction between mercury and selenium are of much higher affinity to form insoluble mercury selenides, $SeHg$.¹²

Simulated Flue Gas Tests. Three types of Se(0)-doped MK10 samples with different selenium loadings (1, 5, 10% (w)) were tested in the same fixed-bed column under a typical Powder River Basin (PRB)/lignite flue gas condition at 140 °C, and their breakthrough curves were obtained as shown in Figure 3.

The reactivity of Se(0) with Hg(0) increased with the amount of Se(0), however, these samples showed unusual concave breakthrough curves under the simulated flue gas condition. The outlet Hg(0) concentration monitored with an online mercury analyzer (UV-1201S with mercury analysis kit, Shimadzu Corp., Columbia, MD) did not initially drop to zero, but gradually decreased to the minimum and then increased to the inlet concentration. Other simulated flue gas components appear to interact with the Se(0) doped onto the

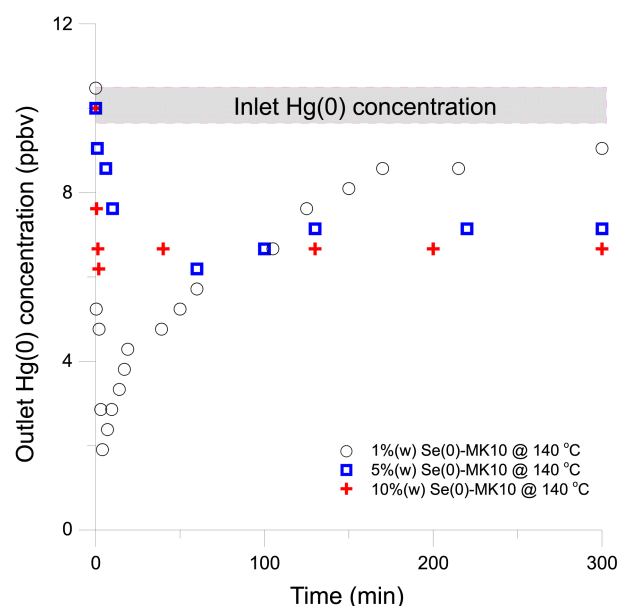


Figure 3. Breakthrough curves for Se(0)-doped MK10 in a typical PRB/lignite flue gas condition at 140 °C.

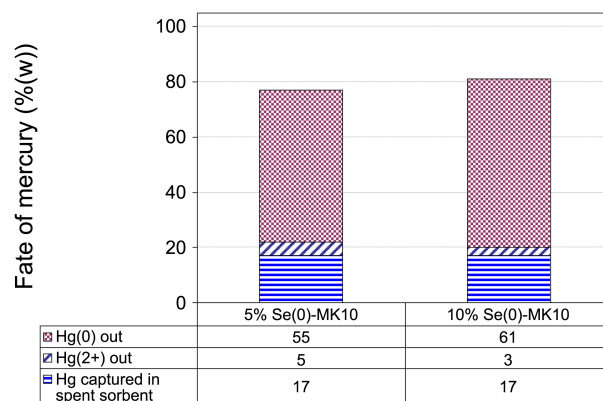


Figure 4. Fate of mercury obtained for Se(0)-doped MK10 after 5-h testing in a typical PRB/lignite simulated flue gas flow at 140 °C.

samples, however, at the current research stage, it is not clear about the interaction between individual flue gas constituents and Se(0).

The results of mercury speciation were also obtained for 5 and 10% (w) Se(0)-MK10 samples after 5-h testing, and two samples had almost the same mercury speciation results as shown in Figure 4. The mass balance closure for both of the samples was approximately 80%, and the amount of mercury adsorbed onto the spent sorbents was determined after performing the digestion procedures as described in the Ontario Hydro Method. ASTM Method D6784-02, "Standard Test Method for Elemental, Oxidized, Particle-bound and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario Hydro Method)".³ The amount of oxidized mercury vapor emitted from the fixed-bed system was relatively very small (5 and 3% for 5 and 10%, respectively), and 17% (w) of mercury was recovered from both of the spent sorbents, which suggests that most of mercury.

Conclusions

Elemental selenium was synthesized from a precursor selenium compound, $\text{KSeO}_2(\text{OCH}_3)$, and reductively impregnated onto montmorillonite K 10 in order to examine the reactivity with $\text{Hg}(0)$ vapor. $\text{Se}(0)$ -impregnated MK10 showed excellent reactivity with $\text{Hg}(0)$ in an inert N_2 gas flow at 70 and 140 °C, and the $\text{Hg}(0)$ adsorption capacities increased with the amount of selenium impregnated onto MK10. However, $\text{KSeO}_2(\text{OCH}_3)$ -impregnated MK10 did not show any noticeable reaction with $\text{Hg}(0)$, suggesting that the oxidation state of selenium does play a critical role. In addition, $\text{Se}(0)$ -impregnated MK10 showed unusual concave breakthrough curves and a decrease in their adsorption capacities under a PRB/lignite simulated flue gas condition in comparison with an inert N_2 gas flow, indicating possible interaction between $\text{Se}(0)$ and the individual flue gas constituents.

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