

SULFUR IMPREGNATION OF ACTIVATED CARBON THROUGH H₂S OXIDATION

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Introduction

Powdered sorbent injection is considered the most promising technology for the control of mercury emissions from coal-fired power plants. Our earlier studies revealed that the adsorptive capacity of activated carbon for elemental mercury vapors can be increased by several orders of magnitude by impregnating elemental sulfur on the carbon surface. Sulfur impregnation can be accomplished by exposure to elemental sulfur vapor or through catalytic oxidation of H₂S in the presence of oxygen [1-4]. Because H₂S is a waste product from a number of industrial processes, the latter approach could lead to the production of economical mercury sorbents through applied industrial ecology. The main objective of this study was to evaluate some of the key parameters of this reaction (e.g., reaction kinetics, impact of activated carbon surface chemistry, impact of oxygen partial pressure, etc.) that would result in high sulfur loading on activated carbon.

Experimental

The H₂S oxidation on activated carbon surface was conducted in a 3/4-inch diameter stainless steel reaction column. Carbon weight of 1 gram was used for all the runs. Bituminous coal-based activated carbon (BPL, Calgon Carbon Corporation, Pittsburgh, PA) with 4x10 (GAC) and 170x200 (PAC) particle sizes was used under the following impregnation conditions: temperature range from 20-200°C, reaction time range from 5-30 minutes, and the N₂/O₂/H₂S ratios in the influent gas of 0.75/0/0.25, 0.65/0.1/0.25, and 0.5/0.25/0.25 (the total flow rate was always maintained at 0.2 L/min). Sulfur content was determined by a sulfur analyzer (SC 132, Leco Corporation, St. Joseph, MI), while the thermal stability of impregnated sulfur was evaluated using a thermogravimetric analyzer (TGA-7, Perkin Elmer, Norwalk, CT).

Two pretreatment methods were performed to modify carbon surface characteristics: oxidation with 15N nitric acid for 24

hours (BPL-a) and reduction by heating in pure H₂ for 6 hours at temperature up to 950°C (BPL-h) [5]. Boehm titration [6] was used to classify and quantify oxygen-containing surface functional groups.

Results and Discussion

Impact of temperature on sulfur loading on GAC (BPL carbon) for different gas compositions is shown in Figure 1. It is clear that the presence of oxygen in the incoming gas has a dramatic impact on the ability of this activated carbon to promote oxidation of H₂S because the surface oxygen content of activated carbon is not sufficient to promote the reaction without an external source of electron acceptors. Sulfur loading on GAC sample also increased with the increase in temperature from room temperature to 100 °C. A slight decrease in sulfur loading at higher temperatures can be explained by the possibility of forming SO₂ or SO_x by the oxidation of H₂S at temperatures higher than 130°C, which may easily escape from the carbon bed.

Sulfur loading of close to 50 wt.% was obtained over a two-hour reaction period in our previous study [4]. However, the sorbents impregnated with such higher sulfur quantities showed considerably worse performance for mercury uptake in comparison with sorbents that contain only 10 wt.% sulfur. Such behavior is a result of the extensive plugging of activated carbon porous structure with extensive amounts of elemental sulfur deposited through H₂S oxidation. This study shows that shorter reaction times (up to 30 minutes) are sufficient for high sulfur loading (about 40 wt.%) if the reaction temperature is maintained at 100 °C. Figure 2 shows the impact of carbon particle size (GAC vs. PAC) on sulfur loading obtained at 100 °C for different reaction times. PAC sample tends to have less sulfur deposit, which can be attributed to reduced porosity and increased pressure drop across the carbon bed.

The weight loss profiles for sulfur-impregnated activated carbons prepared in this study were measured using TGA

and are shown in Figure 3. The weight loss obtained for each carbon sample was consistent with that of sulfur measurements, which indicates the sulfur deposited on the carbon surface can be recovered through thermal regeneration. Another important observation from the data presented in Figure 3 is that the observed sulfur loss was negligible until the ambient temperature reached about 200 °C. This is particularly important because typical flue gas temperatures at the point of sorbent injection would be between 120-180 °C. Therefore, sulfur deposits achieved through H₂S oxidation would remain on the carbon surface to facilitate chemisorption of elemental mercury from the flue gas.

Derivative weight loss profiles (derivative thermal analysis, DTA) obtained for pure sulfur and activated carbons impregnated through H₂S oxidation under different experimental conditions are compared in Figure 4. All the samples impregnated for 10 minutes exhibited initial weight loss at 250 °C and reach the maximum intensity at close to 400°C. This similarity in DTA profiles revealed that impregnation temperature has insignificant impact on thermal stability of impregnated carbon. The sample impregnated for 30 minutes started to lose sulfur at temperatures below 200 °C, which is similar to the behavior of pure sulfur. This difference in the temperature required to initiate sulfur loss may be due to the different locations of deposited sulfur on the carbon surface. Extended reaction times probably resulted in secondary sulfur deposition on top of already impregnated sulfur that is attached to carbon surface. This secondary sulfur may have much weaker bonding energy and can be volatilized easier than the primary sulfur deposits that are most likely embedded deeply into the pore structure of activated carbon particle.

Surface characteristics of the surface-modified activated carbons (BPL-a and BPL-h) determined using Boehm titration method are shown in Table 1. Clearly, acid treatment significantly increased the amount of acidic surface oxygen, while hydrogen reduction resulted in stable basic carbon. The ability of these carbons to promote H₂S oxidation (100°C for 10 minutes) is shown in Figure 5, while Figure 6 depicts DTA profiles for these sorbents before and after impregnation with sulfur. It is obvious that acidic carbon achieved higher sulfur loading than the basic counterpart, especially at temperature above 100°C. Such behavior suggests that surface functional groups may play an important role in improving catalytic properties of this carbon. However, the ability of BPL-a to promote H₂S

oxidation at room temperature was quite limited. One possible reason could be the presence of nitric acid treatment residuals or by-products (observed as weight loss at lower temperature in Figure 6) that hindered H₂S adsorption.

Conclusions

The findings of this study suggest that catalyzed H₂S oxidation that is performed for a period of 30 min at 100 °C results in significant sulfur deposition on the carbon surface (up to 40 wt.%). The presence of oxygen is critical to increase H₂S removal by activated carbon and higher oxygen content in the influent results in more effective H₂S conversion. Sulfur deposits resulting from this approach have high thermal stability, which extends their potentials for different applications (their performance for mercury is evaluated in the ongoing study). Oxygen-containing surface functional groups appear to enhance H₂S conversion and their role needs to be elucidated further.

References

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Table 1. Oxygen-containing functional groups, basicity, dissolvable PH, sulfur contents and TGA weight losses data

Sample	Surface Functional Groups ($\mu\text{eq/g}$)				Total Acidity ($\mu\text{eq/g}$)	Total Basicity ($\mu\text{eq/g}$)	Sulfur Content (wt.%)	TGA Weight Loss (%)
	Carboxyl	Lactonic	Phenolic	Carbonyl				
BPL-a	282	251	482	302	1317	141	0.52	4.1
BPL	8	25	125	9	249	456	0.52	2.2
BPL-h	0	0	20	34	54	507	0	0.48

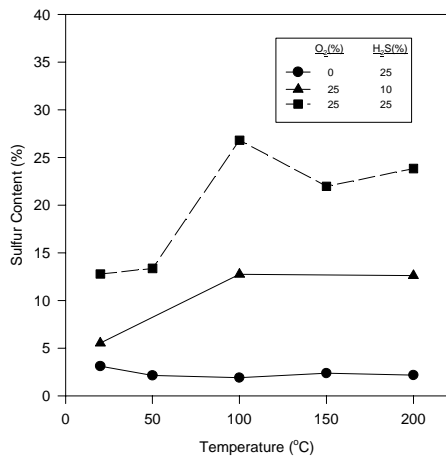


Figure 1. Impact of temperature on sulfur loading on GAC (BPL carbon)

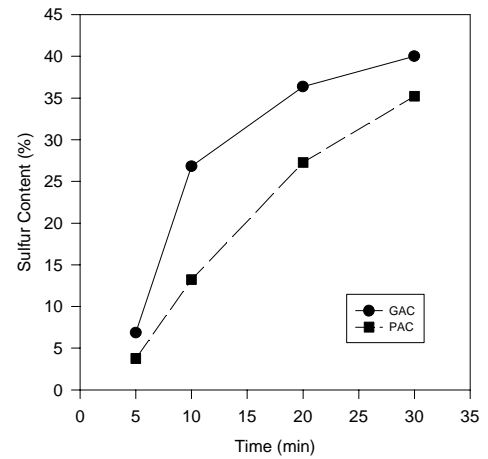


Figure 2. Impact of particle size on sulfur loading at 100 °C

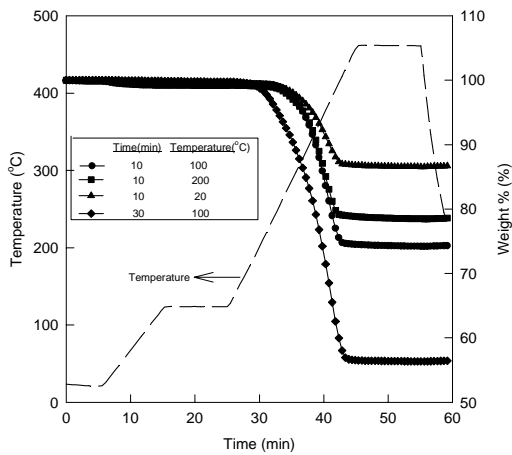


Figure 3. Weight loss profiles for GAC impregnated using 25% H_2S / 25% O_2

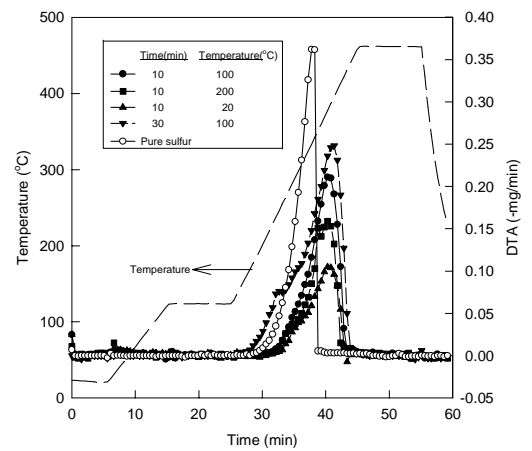


Figure 4. DTA profiles for GAC impregnated using 25% H_2S / 25% O_2

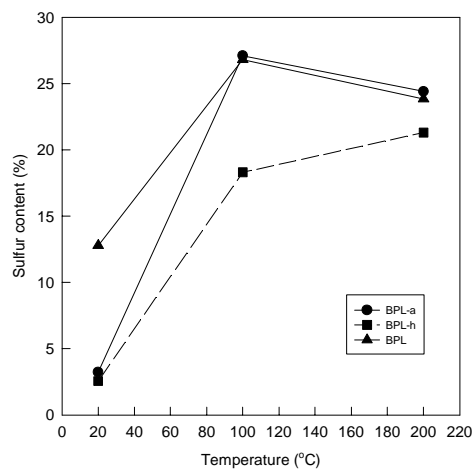


Figure 5. Impact of carbon treatment on sulfur loading

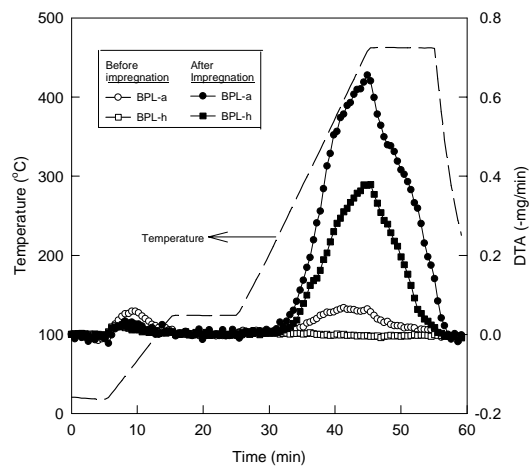


Figure 6. DTA profiles for treated carbons